CATALYSIS

VOLUME III

HYDROGENATION AND DEHYDROGENATION

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PREFACE

The basic ideas of homogeneous and heterogeneous catalysis have been the theme of Volumes I and II of the present series. It now remains to integrate these ideas with the factual matter and with the concepts and generalizations in the various fields of catalysis arranged according to the type of the over-all reaction involved. This, the third of a series of seven volumes, is concerned with a portion of the field of catalytic hydrogenation.

A logical subdivision of the subject of catalytic hydrogenation is difficult to make even if all contributed chapters were available at a given time. In a general way Volume III may be said to include a discussion of those reactions in which hydrogen is simply added to unsaturated bonds without the simultaneous ejection of such molecules as water vapor or hydrogen sulfide and without hydrocracking.

The study of the catalytic exchange of hydrogen and deuterium and of the interconversion of ortho-para hydrogen and ortho-para deuterium (Chapter 1) are basic to all catalytic hydrogenation. Ethylene hydrogenation (Chapter 2) is especially important as the most intensively studied hydrogenation of an organic compound. The hydrogenation of olefins, of carbon-carbon triple bonds, and of nitrocompounds represents a portion of the standard catalytic hydrogenation reactions (Chapters 3, 4 and 5); a discussion of the hydrogenation of other bonds will follow in Volumes IV and V.

Ammonia synthesis is one of the earliest and most important examples of catalytic hydrogenation. Chapters 6 and 7 combine to cover catalyst development and mechanism work on this subject from the start of the century up to the present time. Another example of an early and industrially important hydrogenation is the synthesis of methanol (Chapter 8).

Hydrogenation of oils to edible fats is one of the oldest but least publicized examples of the art of catalysis (Chapter 9). This chapter is followed by a discussion of what is probably our best illustration of the importance of catalytic dehydrogenation, viz., the production of butadiene from butene and butane (Chapter 10).

The editor has repeatedly expressed his thanks to the various contributing authors. In the present instance a special vote of thanks is due to the friendly international cooperation that has made possible contributions from outstanding authorities throughout the world. In this connection the author would also like to thank Dr. Umberto Colombo of the Montecatini Co. for translating from Italian to English the chapter by Professor Natta on methanol synthesis.

An attempt has been made in Volume III to emphasize the factual data on catalytic hydrogenation and the principal ideas as to the mechanism or mechanisms involved. Interspersed with these basic considerations will be found a wealth of practical information and experimental detail about the preparation of various hydrogenation catalysts and about the precautions essential to efficient operation of the various catalytic processes. It is hoped that the resulting blend of fundamental concepts and practical suggestions will make the present and following volumes valuable to those interested in the theory of catalysis as well as to the large group of workers now dealing with the more practical aspects of the subject.

PAUL H. EMMETT

Pittsburgh, Pa.
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CONTENTS

CHAPTER 1

THE PARAHYDROGEN AND ORTHODEUTERIUM CONVERSIONS AND THE HYDROGEN-DEUTERIUM EXCHANGE

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Introduction

Many of the problems in catalysis, such as those of reaction mechanisms, adsorption characteristics and the factors involved in catalytic specificity, can at present most usefully be attacked using relatively simple reactions on simple surfaces. The limiting factor in the subject, namely performing experiments permitting of almost unequivocal interpretation, seems to make the study of simple reactions most fruitful. This in turn means that the reactant molecules should be small, as largeness tends to confer complexity of reaction possibility.

Quantum theory led in 1927 to the assertions that the hydrogen molecule could exist in two distinct and stable forms, parahydrogen and orthohydrogen, having different optical and thermal properties, and that normal hydrogen was a mixture of the two forms. In 1929, parahydrogen was isolated[12, 13] and methods of analysis of mixtures were developed[14, 31, 34, 35], and the catalytic chemist then had available for study a reaction of ideal simplicity—the conversion of parahydrogen to normal hydrogen. When in 1931 the heavy hydrogen isotope, deuterium, was isolated, and later shown to exist as para- and orthodeuterium, two further reactions, the conversion of orthodeuterium to normal deuterium, and the exchange between normal hydrogen and normal deuterium to give hydrogen deuteride, became available.

Many surfaces, notably those of metals and of oxides, but also those of carbon, glass, and certain inorganic halides, have been found to be active catalysts for these reactions, and it is not surprising that a more complete knowledge is available concerning their mechanism than is available for any other catalytic reaction. For, not only are the possible surface complexes limited to a hydrogen atom, a hydrogen molecule, and possibly a transition complex, H_3, but in addition, the reactions have the considerable advantage that only one molecular species is under consideration. Where two or more reactants are involved, each may affect the mode and extent of adsorption of the others, and hence adsorption experiments on the isolated reactants cannot be related with any certainty to the actual catalytic system.

The kinetics and absolute rate of parahydrogen conversion and hydrogen deuterium exchange have been used as a convenient index of catalytic activity to study a wide variety of problems such as catalytic specificity, catalyst poisoning, and the heterogeneity of catalyst surfaces. Furthermore, the extent of conversion taking place during another catalytic reaction involving hydrogen has been used to elucidate the nature of the adsorbed layer during reaction and to identify the rate determining step.

HOMOGENEOUS CATALYSIS OF CONVERSION AND EXCHANGE

The Hydrogen Atom

The simplest of all catalysts for an ortho-para conversion or for exchange is the hydrogen atom, when reaction may take place according to the equations

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

$$H + D_2 \rightarrow HD + D$$

These reactions have been studied experimentally using hydrogen atoms produced thermally[14, 31, 32], photochemically[86], and from an electric discharge[56]. In all cases the dependence of velocity upon pressure was as expected, and the results of the various investigations agreed well with one another and quite well with those of theoretical treatments of the reaction by the London method. A summary of the results is shown in Table 1.

Paramagnetic Substances

The second means of catalyzing an ortho-para transition in hydrogen or deuterium, discovered by Farkas and Sachsse[47, 48], is by the inhomogeneous fields of paramagnetic substances. Such a catalysis can operate by a simple bimolecular mechanism in the gas phase, using oxygen or nitric oxide, or in solution, by dissolved oxygen, or by paramagnetic ions, such as those of copper, nickel, or the rare earths. In these cases, the perturbation due to the paramagnetic substance, which depends both on the electron spin and position of the nearby hydrogen molecule, gives rise to a finite possibility of an ortho-para transition.

It is, of course, to be emphasized that this type of catalysis operates for only ortho-para transitions and not for the exchange between hydrogen and deuterium, for which catalysts strong enough to break an H—H or a D—D bond are required.

The theoretical treatment of the paramagnetic conversion had been developed by Wigner[100], and refined by Kalckar and Teller[66]. In the Wigner treatment, the hydrogen molecule is brought with infinite velocity to the distance of closest approach to the paramagnetic, a_s, (which it must be noted is different from the gas kinetic collision distance) allowed to remain at this distance for the duration of the collision, and then withdrawn, again with infinite velocity. For a para to ortho transition with a change in rotational quantum number from 0 to 1, the probability of transition, W, is found to be

Table 1. The Conversion of Parahydrogen to Orthohydrogen by Hydrogen Atoms

Remarks	Temperature Range (°C)	Activation Energy (cal/mole)	Steric Factor in Arrhenius Equation
H atoms from discharge[56]	10–100	7,000 ± 500	0.13
H atoms produced thermally[14, 32]	600–750	5,000 ± 500	0.06
Theoretical treatment[35]	—	15,000	—
Theoretical treatment[74]	30	—	0.03
Theoretical treatment[74]	700	—	0.08

$$W = \frac{8\mu_A^2 \mu_p^2 I\pi^2}{3h^2 a_s^6 kT} \cdot e^{-E_1/kT}$$

where μ_A is the magnetic moment of the proton[55a] or deuteron, μ_p, of the paramagnetic molecule or ion; I is the moment of inertia of the hydrogen molecule, and E_1 is the energy difference between the para and ortho states.

Under experimental conditions, all hydrogen molecules will not be in the ground state, and the collision efficiency, $Z_{p\to 0}$ of the whole conversion is given by

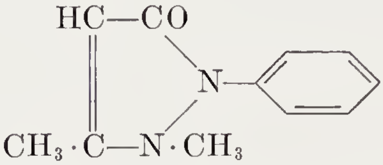
$$Z_{p\to 0} = \frac{8\mu_A^2 \mu_p^2 I\pi^2}{3h^2 a_s^6 kT} \left[\frac{e^{-E_1/kT} + 2e^{-E_2/kT} + 3e^{-E_3/kT} + \cdots}{1 + 5e^{-E_2/kT} + 9e^{-E_4/kT} + \cdots} \right]$$

where E_1, E_2 etc., represent the energies of transition among various possible rotation states. This equation explains most of the experimental data on the magnetic conversion. The following points may be noted:

(1) It is not possible to compare experimental and theoretical absolute rates accurately, as the latter depend on the inverse 6th power of a_s, and a_s is not known with any certainty. However, for $\mu_p = 1$ Bohr magneton, and for room temperatures, with $a_s = 1\text{Å}$, $Z_{p\to 0} \doteqdot 10^{-12}$, and for $a_s = 2\text{Å}$,

$Z_{p \to 0} \simeq 10^{-14}$. For most paramagnetics, a_s would be expected to lie between these limits, and for conversion by gaseous oxygen and nitric oxide at room temperatures,[47, 48], the values of $Z_{p \to 0}$ are respectively $5.1.10^{-13}$ and $1.9.10^{-12}$.

(2) The general dependence of rate upon distance of approach has been investigated by Wilmarth and Baes,[101] who measured the conversion rate by copper and chromium ions as access of hydrogen was progressively denied by coordination with larger and larger molecules, from ammonia to antipyrine, which has the formula



Coordination with antipyrine takes place at the oxygen atom. Their results indicated that the catalytic activity did not decrease regularly with increasing over-all size of the complexes. Thus, $Cr(CN)_6^{3-}$ was less active than $Cr(SCN)_6^{3-}$; and $Cr(NH_3)_6^{3+}$ was less active than the larger $Cr(antipyrine)_6^{3+}$. However, the distances of closest approach of a hydrogen molecule obtained from molecular models were in fair agreement with the a_s values calculated from the experimental results on the basis of the Wigner theory.

TABLE 2. THE CONVERSION OF PARAHYDROGEN TO ORTHOHYDROGEN BY RARE EARTH IONS[48]

Ion	k (mole^{-1} liter min^{-1})	μ_p (magnetons)	k/μ_p^2
Pr^{+++}	2.26	3.62	0.18
Nd^{+++}	2.37	3.68	0.17
Sm^{+++}	0.64	1.60	0.25
Gd^{+++}	17.50	7.94	0.28
Er^{+++}	38.20	9.70	0.42
Yb^{+++}	10.20	4.50	0.50

(3) The Wigner formula shows that for a constant value of a_s, the catalytic activity should be proportional to μ_p^2. The relationship was tested by Farkas and Sachsse[48], who measured the activities of some rare earth ions among which a_s should not vary very greatly; the results are shown in Table 2.

It is seen that although k/μ_p^2 is not quite constant, rising steadily with increasing atomic number, it varies throughout by a factor less than 3. Farkas and Sachsse attributed this to a small but progressive decrease in a_s. This decrease would amount to rather less than 15 per cent between Pr^{+++} and Yb^{+++}, a not unreasonable suggestion, and one in agreement with other data concerning these ions. Moreover the excellent constancy of

k/μ_{p^2} for Sm+++ and Gd+++, for example, where μ_p^2 varies by a factor of 25, seems to put the proportionality of transition probability to square of magnetic moment beyond doubt.

(4) The conversion velocity is also proportional to the square of the moment of the hydrogen nucleus. Thus in principle, by comparing the relative rates of conversion of parahydrogen and orthodeuterium, the ratio of the magnetic moment of the proton to that of the deuteron may be calculated. The Wigner formula suggests that the rates should be compared at the same temperature T; Kalckar and Teller[66] have however shown that greater reliability is obtained if the velocities at absolute teperatures $2T$ for parahydrogen and T for orthodeuterium, are used. In this way, with gaseous oxygen as the catalyst, Farkas and Farkas[37] found $\mu_H/\mu_D = 3.96$, in good agreement with values obtained by Frisch, Estermann and Stern[55] (3.6), and by Rabi, Kellogg and Zacharias[75] (4.3), who had used two different magnetic deflection methods.

TABLE 3. THE TEMPERATURE COEFFICIENT OF THE PARA-ORTHOHYDROGEN CONVERSION BY OXYGEN AND NITRIC OXIDE

Temperature (°K)	Z_{O_2} (exptl.)	Z_{O_2} (calc.)	Z_{NO} (exptl.)	Z_{NO} (calc)
77	$2.38.10^{-13}$	$1.9.10^{-13}$	—	—
143	—	—	$3.40.10^{-12}$	$3.5.10^{-12}$
193	$5.86.10^{-13}$	$6.1.10^{-13}$	$3.34.10^{-12}$	$3.3.10^{-12}$
293	$6.80.10^{-13}$	$6.8.10^{-13}$	$2.59.10^{-12}$	$2.6.10^{-12}$
373	$6.85.10^{-13}$	$7.4.10^{-13}$	$2.76.10^{-12}$	$2.5.10^{-12}$
493	$7.13.10^{-13}$	$6.8.10^{-13}$	$2.54.10^{-12}$	$2.3.10^{-12}$

TABLE 4. PARAHYDROGEN CONVERSIONS AT 85°K[96] OVER A FREE RADICAL OVER ZnO AND OVER A MIXTURE OF THE TWO*

Free Radical		Zinc Oxide		Radical Plus Oxide	
2 hr	13%	15 min	2%	15 min	84%
4 hr	25%	35 min	4%	30 min	100%
6 hr	69%	1 hr	11%		
		2 hr	20%		

* According to the article published by Turkevich and Selwood[96] the paramagnetic free radical was ground up with the ZnO in a motor and before testing. There is therefore a chance that part of the enhancement in activity might have been caused by an increase in surface area of the free radical on grinding.

(5) The temperature dependence of conversion velocity was also shown by Farkas and Sachsse[48] to be correctly expressed by the Wigner equation, as shown in Table 3 for catalysis by gaseous oxygen and nitric oxide. As it is not possible to determine a_s experimentally with any accuracy its

value was chosen so that the calculated and experimental rates agreed at 293°K; Table 3 shows that agreement at other temperatures is good.

(6) Turkevich and Selwood[96] have shown that the conversion velocity by paramagnetics is greatly increased if the number of molecules held by van der Waals forces in the neighborhood of the paramagnetic is increased. Thus, the paramagnetic free radical $\alpha\alpha$-diphenyl-β-picrylhydrazyl is a moderately good conversion agent at 85°K, but the efficiency is greatly increased, as shown in Table 4, on admixture with zinc oxide, a weak conversion agent but a strong van der Waals adsorbent.

Diamagnetics as Catalysts

In addition to conversion being catalyzed by paramagnetic molecules and ions, a slow conversion by certain diamagnetic liquids, notably hydrogen compounds, has been observed. This conversion is much slower than conversion by paramagnetics: it is a bimolecular process which may be represented by the equation

$$p\text{-H}_2 + \text{X} \rightleftharpoons o\text{-H}_2 + \text{X}$$

and is believed to be due primarily to the nuclear magnetism of the proton. The main evidence for this conclusion is that the ratio of the conversion rate constants by the paramagnetic gases oxygen or nitric oxide to that of water is about $5.2\ 10^6$, which is practically equal to the square of the ratio of the Bohr magneton to the nuclear magneton.

Early experiments on this type of conversion had been carried out by Bonhoeffer and Harteck[13], and by Keesom, Bijl and van der Horst[67], who had found a slow increase with time in the parahydrogen content of liquefied normal hydrogen (~0.5 per cent per hour). More refined work, which showed the process to be bimolecular with respect to orthohydrogen percentage, and which included some interesting experiments on the conversion in solid hydrogen, is due to Cremer and Polanyi[22]. The occurrence of conversions in condensed phases is due to nuclear magnetic forces being far more effective when the molecules are closely packed.

Later work by Farkas and Sandler[51] has to some extent modified the conclusion that inhomogeneous nuclear fields are the sole cause of conversions in diamagnetic liquids. First, it was found that there was an appreciable catalysis by CS_2, in which neither the carbon nor the sulfur atoms possess nuclear magnetic moments. Although slower than the conversion in water (half lives 1800 min and 183 min, respectively) this experiment nevertheless showed that inhomogeneous fields in liquids with no possible nuclear magnetism may be within an order of magnitude of those near the proton.

Measurement of the ratio of parahydrogen to orthodeuterium conversion rates in diamagnetics yielded further information. If nuclear magnetism of the solvent were solely responsible for catalysis, the ratio of rates at the same temperature should, according to the Wigner equation, be almost equal to the square of the ratio of the moment of the proton to that of the deuteron. The ratio of these rates had been previously measured for paramagnetics by Farkas and Farkas[37] who used oxygen, and subsequently by Farkas and Garbatski[50] who used nitric oxide, and found to be about 10 to 1, as shown in Tables 5 and 6.

The ratio of conversion rates is far lower than 10 for diamagnetic hydrogen compounds and other pure diamagnetic liquids. For water it is 2.6, for benzene, 4.2, for CS_2, 4.4 and for CCl_4, 5.2. This suggests that conversion by nuclear magnetism is not the sole effective cause even with hydrogen compounds, and Farkas and Sandler tentatively proposed that interaction between the nuclear quadrupole of deuterium and an inhomogeneous electric field provides an extra mechanism for ortho-para transitions in deuterium, which would not be available for hydrogen, with its electrically symmetrical nucleus.

TABLE 5. o-D_2 AND p-H_2 CONVERSIONS CATALYZED BY OXYGEN[37]

T (°K)	$k_{p\text{-}H_2}$ (mole^{-1} liter min^{-1})	$k_{o\text{-}D_2}$ (mole^{-1} liter min^{-1})	Ratio
293	8.34	0.828	10.1

TABLE 6. o-D_2 AND p-H_2 CONVERSIONS CATALYZED BY NITRIC OXIDE[50]

T (°K)	$k_{p\text{-}H_2}$ (mole^{-1} liter min^{-1})	$k_{o\text{-}D_2}$ (mole^{-1} liter min^{-1})	Ratio
193	10.1	0.98	10.3
290	12.0	1.28	9.9
600	14.1	1.34	10.5

HETEROGENEOUS CATALYSIS OF CONVERSION AND EXCHANGE

It was realized that surfaces active in catalyzing conversion and exchange of the hydrogen modifications could do so by one of two mechanisms. The first, formally equivalent to the para and diamagnetic mechanisms described above for homogeneous catalysts, is likely to operate only at liquid air temperatures, for only at low temperatures does the concentration of van der Waals adsorbed hydrogen at the surface become high enough to allow conversion at a sensible rate. The second mechanism, which has been observed at all temperatures from those of liquid air upward, may be compared with the homogeneous conversion by hydrogen atoms, inasmuch as the function of the catalyst is to provide hydrogen atoms on the surface by the act of chemisorption.

It is clear that as in the homogeneous case, the para and diamagnetic mechanisms are capable of catalyzing only conversions, whereas the second, or chemical mechanism, is capable of catalyzing both conversions and exchange. In theory, therefore, it should be possible to distinguish between the mechanisms by comparing the rates of parahydrogen conversion and hydrogen-deuterium exchange. However, this may not give an unequivocal result, for it is normally at low temperatures (e.g., 80–90°K) that an overlap of mechanisms may occur, and if a zero-point energy effect is operative, the H_2-D_2 exchange might proceed several orders of magnitude slower than the conversion at these temperatures even though the mechanism is chemical. A better method is to measure the velocities of parahydrogen conversion to orthodeuterium conversion, when the operation of a magnetic mechanism will be revealed by a ratio close to 10.

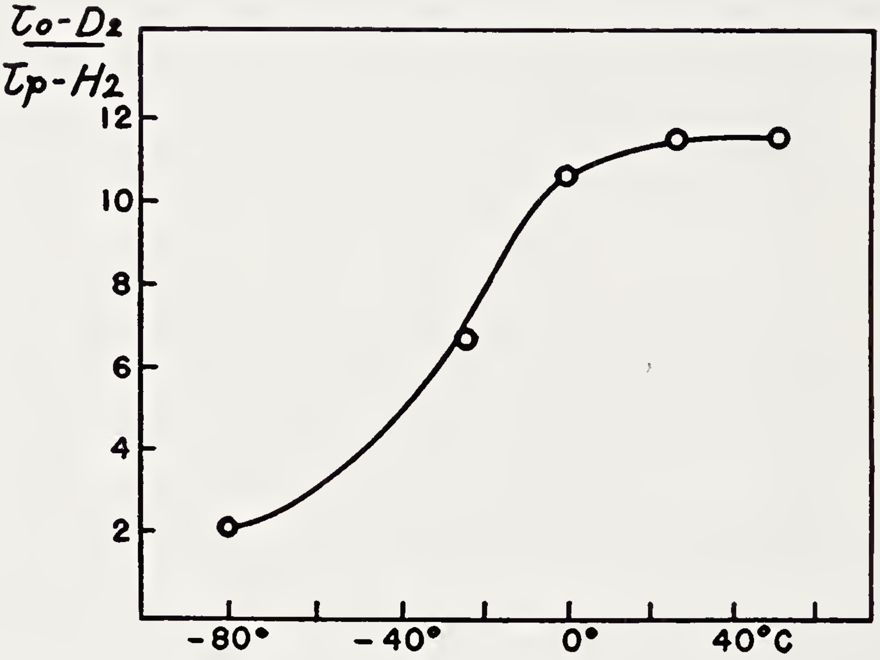


Figure 1. Temperature dependence of the ratio of the time of half conversion τ, for orthodeuterium to that for parahydrogen over neodymium oxalate.[52]

The ratio of the rate of parahydrogen to orthodeuterium conversion must, however, be measured under conditions where ortho-para transition is the rate determining step, for if the slower step is desorption and each absorbed molecule has such a long lifetime on the surface that it undergoes a transition, the conversion rates of parahydrogen and orthodeuterium will be almost the same and the mechanism appear to be chemical. Some experiments by Farkas and Sandler[52] on the magnetic conversion by neodymium oxalate, shown in Figure 1, indicate this effect. It is seen that the ratio of conversion rates only reaches the expected value above about 20°C. Below 20°C, where the ratio is low, desorption is rate determining; only above 20°C, where the actual transition is rate determining, does the ratio achieve the expected value 10.

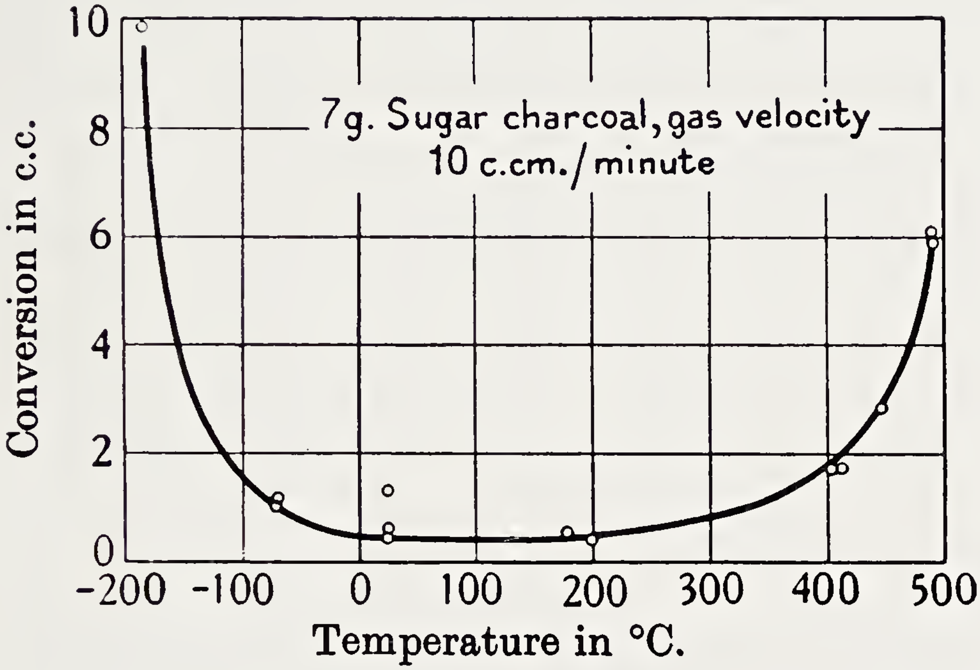


Figure 2. Temperature coefficient of the conversion of para to orthohydrogen over sugar charcoal.

The Magnetic Conversion

The early work of Bonhoeffer and Harteck[14], of Bonhoeffer and Farkas[15], and of Rummel[81], all of whom mainly used charcoal catalysts, is responsible for the isolation and elucidation of the magnetic conversion mechanism. First, it was found that the rate of conversion on charcoal passed through a definite minimum, as shown in Figure 2. This suggested that two mechanisms were operating, one increasingly effective as the temperature was lowered, and responsible for the negative temperature coefficient between liquid air and room temperatures, the other increasingly effective as the temperature was raised, and responsible for the positive temperature coefficient above about 20°C.

These mechanisms were compared with the two types of adsorption thought to occur in these temperature ranges[88], that is van der Waals adsorption as molecules at low temperatures, which decreases as the temperature is raised, and "activated" chemisorption as atoms above room temperatures, which increases with increase of temperature. The following results confirmed that as the adsorption at low temperatures did not involve breaking of the H—H bond, the conversion must be magnetic in origin.

(1) With a magnetic conversion, the rate would be increased by increasing the concentration of paramagnetic at the surface. Low temperature adsorption of oxygen as molecules should produce a very paramagnetic surface, and a strongly enhanced conversion was found under such conditions[15, 81] as shown in Table 7. Low temperature adsorption of the diamagnetic nitrogen gave no such effect.

The later work of Juza, Langheim and Hahn[64, 65], who measured the magnetic susceptibility of charcoals covered with oxygen at various temperatures and pressures, shows conclusively that the adsorbed oxygen in Rummel's experiments was present in paramagnetic, i.e. molecular, form. Furthermore, Rummel found that oxygen adsorbed at high temperatures, when Juza, Langheim and Hahn showed it to be diamagnetic (i.e., atomic), did not catalyze the conversion and in fact poisoned it, presumably by covering part of the active surface.

TABLE 7. THE CONVERSION ON CHARCOAL AT LIQUID AIR TEMPERATURES AS A FUNCTION OF OXYGEN ADSORPTION[15, 81]

Catalyst	Half Lifetime (secs)
Charcoal outgassed at 1000°C	1620
1 cc O_2 added	450
15 cc O_2 added	<180

(2) Gould, Bleakney and Taylor[58] later measured the rate of hydrogen-deuterium exchange on various surfaces, and were unable to detect any catalysis by outgassed charcoals at liquid air temperatures. This is suggestive of a magnetic mechanism.

When however we inquire a little further into the nature of the inhomogeneous magnetic fields causing the conversion, less definite answers may be given. First, it does not seem likely that the charcoal itself can be the catalyst, as it is a pure diamagetic, which would be incapable of giving such a high conversion velocity as that observed. Also, the suggestion that certain diamagnetic substances may possess a surface paramagnetism—which could be the cause of the catalysis—is really unsubstantiated at present, and the evidence advanced for its occurrence is tenuous to say the least. Two other possibilities seem more likely—either that a small amount of surface paramagnetic impurity is the cause of conversion, or that the reaction is similar to the conversion in liquid and solid hydrogen. Evidence is available that both of these possibilities may be operating. Thus, it is well known that even the purest carbons are likely to contain small amounts of iron as impurity, showing traces of ferromagnetism as a result and iron may be the effective catalyst in some experiments with carbon[18]. If the magnetic conversion by an impurity were operating, the rate should be proportional to the amount of adsorbed parahydrogen, and in dilute layers if the Langmuir isotherm is obeyed, to the parahydrogen pressure. Most of Rummel's conversion experiments did in fact follow a unimolecular law, but such behavior is by no means universal. Taylor and Sherman[90], for example, have reported bimolecular mechanisms, which must therefore be of the type operating in liquid and solid hydrogen.

TABLE 8. THE ACTIVITY OF PARAHYDROGEN CONVERSION CATALYSTS AT −187°C[91] AS A FUNCTION OF THEIR MAGNETIC PROPERTIES

Catalyst	Gram Susceptibility (at 20°C × 10^6)	Pressure of p-H_2 (mm)	Contact Time (min)	% Conversion
Gd_2O_3(20 g)	135	200	5	100
Nd_2O_3(20 g)	30	490	3	100
$MnCl_2$(14 g)	110	530	3	100
Fe_3O_4(22 g)	Ferromagnetic	640	5	56
			27	100
V_2O_3(80 g)	14	560	5	100
V_2O_5(10 g)	0.86	550	17	36
			147	100
CeO_2(16 g)	0.39	570	150	9
			430	19
ZnO(10 g)	−0.36	625	130	32
			360	58
La_2O_3(5 g)	−0.4	700	360	17
Ag(40 g)	−0.2	760	55	10
			320	50

Qualitative evidence that paramagnetic substances are better low temperature conversion catalysts than diamagnetics has been provided by Taylor and Diamond[91], as shown in Table 8.

Particularly significant in the table are the very high activities of the paramagnetics gadolinium and neodymium oxides and manganous chloride compared with the very low activities of the diamagnetics ceric, zinc, and lanthanum oxides and metallic silver; also the marked change in activity of vanadium on oxidation from the +3 to the +5 state.

Further points in connection with these experiments are as follows:

(1) Magnetite appears to possess a lower activity than might be ex-

pected—this was attributable to the sample possessing a very low surface area.

(2) The diamagnetics do show a measurable if very low conversion activity. This may be due to one of two causes:

(a) Some diamagnetics show an underlying paramagnetism which would cause a conversion. Haller and Selwood[59] have, for example, shown that the susceptibility of the purest lanthanum oxide does vary somewhat with temperature—behavior characteristic of paramagnetism though not of diamagnetism—as shown in Table 9. In view of the later result of Selwood and Trapnell[85] that a specimen of spectroscopically pure Eu_2O_3 was found by susceptibility measurements at 20°K to contain a trace of paramagnetic, removable by further purification, it seems that the La_2O_3 may not have been quite free of paramagnetic impurity.

(b) Although the mechanism of conversion operating through hydrogen chemisorption was originally called the high temperature mechanism, it is now known that many substances can chemisorb hydrogen at very low temperatures, and give a conversion or exchange by this mechanism. Smith and Taylor[87] subsequently showed that hydrogen-deuterium exchange takes place at the surface of zinc oxide at −133°C, and it is probable that the conversion activity of this substance recorded by Taylor and Diamond was operating through the "chemical" mechanism.

TABLE 9. SPECIFIC SUSCEPTIBILITIES OF La_2O_3 ($\times 10^6$)[59]

	Prepared from Sulfate	Prepared from Oxalate
χ_{20}	−0.1848	−0.1406
χ_{-150}	−0.1561	−0.1217

(3) Silver remains something of a mystery. It is normally in a high state of purity, is easy to clean, and would be expected to be free of paramagnetic. Conversion might therefore be thought to take place through the chemical mechanism but Trapnell has found[95] that evaporated silver films, shown to have clean surfaces by their ability to chemisorb oxygen at −183°C, do not chemisorb hydrogen even at room temperatures. Possibly conversion is due to a bimolecular process in a van der Waals layer; alternatively it is just conceivable that silver powders unlike films, do chemisorb hydrogen and cause conversion by the chemical mechanism. In the case of copper, evaporated films do not chemisorb hydrogen[1], whereas apparently pure powders do[99].

Similar evidence to that of Taylor and Diamond has been obtained by Eley[26], who measured the conversion activity at room temperatures of various porphyrin compounds. He found that the paramagnetic substances, haemin, haematin, and copper phthalocyanine catalyzed the conversion, whereas the diamagnetic haematoporphyrin and metal-free phthalocyanine were inactive.

The Temperature Coefficient of the Magnetic Conversion. Figure 2 showed that the temperature coefficient of the heterogeneous magnetic conversion was, in the case of a charcoal catalyst, strongly negative. A negative temperature coefficient is however by no means general, and Figure 3 shows the results obtained by Farkas and Sandler[52] on the magnetic conversion by neodymium oxalate.

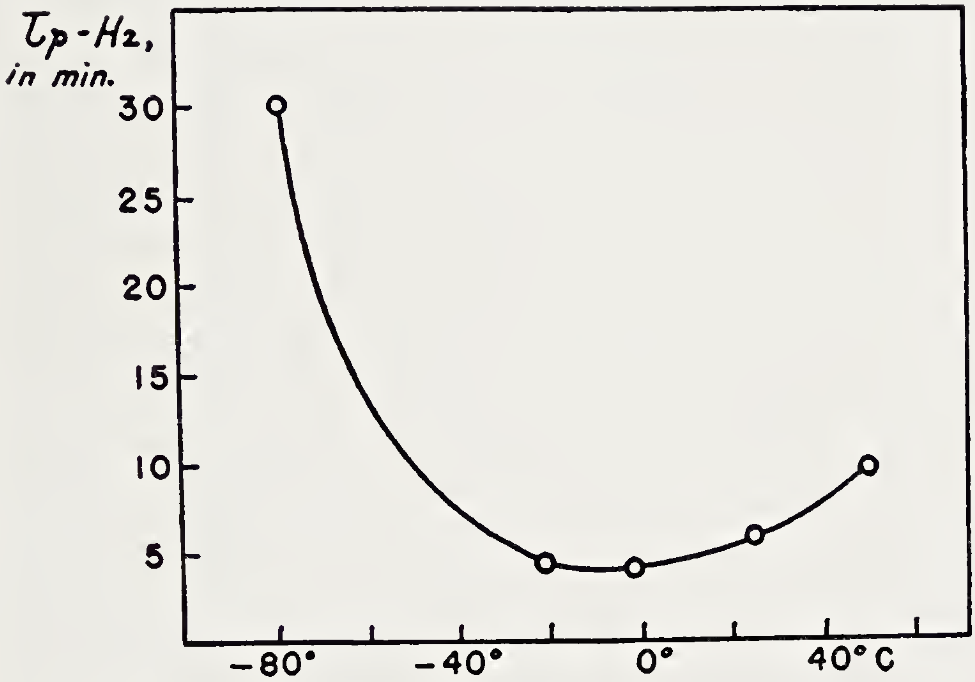


Figure 3. Time for half conversion of parahydrogen to orthohydrogen as a function of temperature[52] over neodymium oxalate.

The interpretation of these results can best be made in terms of the familiar Hinshelwood treatment of temperature coefficients of heterogeneous reactions. According to this treatment, when a surface is sparsely covered by a reactant, the temperature coefficient of velocity is:

$$\frac{d \ln K}{dT} = \frac{Q - \lambda}{RT^2}$$

where Q = true activation energy of reaction
λ = heat of adsorption of reactant.

However, when the surface layer is almost full

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

Thus, in concentrated layers, the temperature coefficient of velocity is bound to be positive, but in dilute layers it may be positive or negative according as $Q > \lambda$ or $Q < \lambda$. With the conversion on neodymium oxalate, it must be assumed that the activation energy of transition is very small so that $Q < \lambda$. Then, at temperatures between −80 and 0°C, we may conclude that the layer is still sufficiently concentrated for a positive coefficient, but that above 0°C, the change to a negative coefficient takes place.*

The Chemical Mechanism

The chemical mechanism of these reactions has been investigated at the surfaces of metal wires, powders and evaporated films, and on oxides, salts, and glass. Many features are shared by the reactions at all these surfaces, some of which differ from those of the conversion by magnetic mechanisms. First, it has been found that the kinetics and absolute rate of the ortho-para conversion for hydrogen and deuterium and the H_2/D_2 exchange usually lie very near to one another. Thus, Bonhoeffer, Bach and Fajans[17], using a nickel catalyst, found that parahydrogen conversion and HD formation showed the same dependence on temperature and pressure, and Fajans[30] later showed the absolute rates of the two reactions to be very close. On a platinized platinum catalyst Farkas and Farkas[43] found the ratio of the rate of conversion at 26°C of parahydrogen to the rate of conversion of orthodeuterium to the rate of the hydrogen-deuterium exchange to be 1:0.54:0.67; on an evaporated iron film, Farkas[38] found the relative rates to be 5:2:1. Later Eley[28] found parahydrogen and deuterium both exchanged at the same rate with hydrogen chemisorbed on an evaporated tungsten film. Farkas and Farkas[46] extended these experiments to other evaporated metal films, finding identity of rates with nickel at room temperature, although parahydrogen was converted five times faster than hydrogen and deuterium exchanged on platinum, and up to fifteen times faster on palladium.

With the magnetic conversion the ratio of the three rates is ordinarily 10:1:0.

These results, with emphasis on the exchange reaction, show that the chemical mechanism must involve dissociation (i.e., chemisorption) of hydrogen at the catalyst surface, a conclusion first stated for metal surfaces by Bonhoeffer and Farkas[15, 16, 33], and for oxide surfaces by Taylor

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* Additional work by Sandler[81a] has shown that the rate of the parahydrogen and orthodeuterium conversions is increased with a decrease in temperature below about −75°C. Furthermore the ratio of these rates rises both up to a value of 9 at −100°C as the temperature is dropped, and then decreases at lower temperatures to a value of 3 at −195°C. These added data seem to require the existence of two sets of paramagnetic centers; one set is active between −195 and about −75°, and the other, above −75°.

and Sherman[89, 90]. The conclusion of both workers has been confirmed by the result that chemisorption is always found when conversion and exchange take place.

As the chemical mechanism involves chemisorption it is not surprising to find that the activity of catalysts is very susceptible to poisoning. Typical catalyst poisons such as H_2S and tap grease greatly affect metallic catalysts for conversion and exchange: oxygen poisons tungsten very markedly[27, 33], as does ethylene, nitrogen and carbon monoxide[27]. Oxygen indeed poisons most metals by forming a stable chemisorbed layer. Only platinum is completely unaffected[15], although the activity of iron and nickel, which are strongly poisoned, may be restored by heating in hydrogen to moderate temperatures[33]. Salts such as NaCl and KI are also poisoned strongly by oxygen.

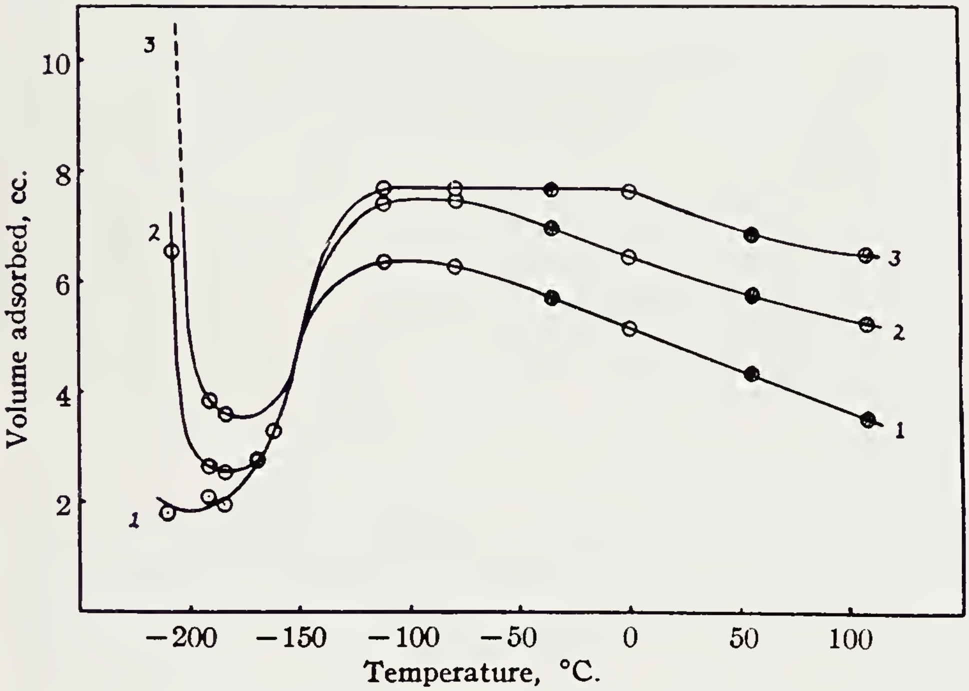

Figure 4. Isobars for hydrogen on nickel: Curve 1, at 2.5 cm pressure; Curve 2, 20 cm; Curve 3, 60 cm. (Benton and White[11])

A further feature of the chemical conversion is that it invariably has a positive temperature coefficient.

Two reaction mechanisms have been suggested. The original mechanism, proposed by Bonhoeffer and Farkas in 1931[15], may be represented by the equations

$$2M + p\text{-}H_2 \rightleftharpoons 2MH \rightleftharpoons 2M + o\text{-}H_2\,,$$

M being a catalyst atom.

According to this mechanism, chemisorbed atoms link up randomly in pairs and evaporate as molecules—reversal of nuclear spin, or formation of HD molecules is clearly possible in this process. According to the alternative mechanism, proposed in 1939 by Rideal[76] at a time when the experimental evidence seemed to preclude the original mechanism, interaction takes place between a chemisorbed atom and a van der Waals adsorbed molecule, according to the equation

$$MH + D_2 \rightleftharpoons MD + HD$$

Conversion and Exchange at Metal Surfaces. Soon after it was postulated, it became apparent that the Bonhoeffer-Farkas mechanism was not easily reconcilable with the adsorption data then available. For example, the work of Benton and White[11] on the adsorption of hydrogen by nickel powders, shown in Figure 4 as an isobar, seemed to show that chemisorption of hydrogen took place at a reasonable rate only above about −150°C so that desorption would require even higher temperatures. Now, desorption of chemisorbed hydrogen is, according to the Bonhoeffer-Farkas mechanism, the rate determining step in conversion, and this result, taken with that of Gould, Bleakney and Taylor[58], that H_2-D_2 exchange took place rapidly on nickel even at −187°C made the Bonhoeffer-Farkas mechanism seem unlikely.*

Similar, and more striking results were obtained with tungsten. Data on hydrogen chemisorption by tungsten powders by Frankenburger and Hodler[54] seemed to show that chemisorption only took place above 150°C, while Bonhoeffer and Farkas[15] had been able to detect chemical conversions of parahydrogen at tungsten filament surfaces even at −110°C, as shown in Table 10.

Equally, though, a mechanism involving molecules held in a van der Waals layer did not seem likely. On all metal surfaces studied at that time, the order of reaction had been very much lower than unity—results for tungsten and nickel[15] are shown in Tables 11 and 12.

Farkas stated[36] that if adsorbed hydrogen molecules had been involved in conversion at these surfaces, the order of reaction would have been at least unity and probably more for the following reason. Even at −100°C and certainly at 12°C, a van der Waals layer of hydrogen would be exceedingly dilute at the pressures of measurement. The fraction of the surface covered and hence the reaction rate would therefore be, according to the Langmuir

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* The smallness of the pressure coefficient at about −195° and the existence of a relatively large adsorption even at 2.5 cm pressure at that temperature suggest the existence of a low temperature form of activated adsorption of hydrogen on Ni at −195°C. This low temperature chemisorption of hydrogen is presumably responsible for the observed H_2-D_2 exchange at −187°C[58].

isotherm, proportional to the first power of the pressure. If the chemisorbed amount was also varying with pressure, this would increase the order of reaction beyond unity. The low orders definitely favored the Bonhoeffer-Farkas mechanism.

One thing which was clear, however, was that most of the adsorption experiments performed on very moderately outgassed and cleaned powders had been carried out under very unsatisfactory conditions. The work of Langmuir[70], executed as early as 1914, made this certain. Langmuir had used a filament, which has the clear advantage over a powder that it can be raised to a much higher temperature, with a far greater chance of cleaning the surface. Filament surface areas are however too small for adsorptions to be measured volumetrically with any accuracy, and it is necessary to measure some property of the surface which changes as adsorption proceeds. Langmuir had measured electron emissions from a tungsten filament, having found this to vary by up to 10,000 with change in surface state. Two of his results bear strongly on the problem under consideration. First, he found that an adsorbed oxygen layer on tungsten required many minutes to evaporate at 2,000°K, and extrapolation indicated that at 1,500°K several years would be required. Even in the presence of hydrogen to act as reducing agent, 24 minutes were required to free the surface of oxygen at 1,500°K. Second, Langmuir was able to show that with oxygen at least, chemisorption takes place on carefully flashed and cleaned tungsten surfaces with immeasurably great speed even at liquid air temperatures. These experiments showed very clearly that the ordinary powder adsorbent usually

Table 10. The Conversion of Parahydrogen on a Tungsten Filament[15]
Pressure = 50 mm

Temperature (°C)	−110	−100	−75	−50	−25	0
Half life (sec)	920	340	59	24	15	8

Table 11. Conversion of Parahydrogen on a Tungsten Filament at −100°C[15]

Pressure (mm)	25	50	100	200	400
Half life (sec)	150	240	510	720	1110

Apparent order of reaction is 0.3.

Table 12. Conversion of Parahydrogen on a Nickel Tube at 12°C[15]

Pressure (mm)	0.004	0.04	0.44	4.5
Half life (sec)	138	294	780	1980

Apparent order of reaction is 0.6.

outgassed and reduced in hydrogen at 900°K at most, was probably never freed of contamination, and that when precautions were taken to obtain a clean surface, the adsorbing properties were quite different from those usually observed. New methods of studying chemisorption would have to be developed before reaction mechanisms could be satisfactorily discussed. This was commenced by Roberts, working in Rideal's laboratory in Cambridge, England.

The filament was obviously to be preferred to the powder, and tungsten, which can be outgassed very thoroughly by virtue of its high melting point, was the obvious metal to use.

Roberts developed two new experimental methods[79]. In the first, adsorption was detected by its effect on the accommodation coefficient of neon, which is not adsorbed by tungsten. In the second, a very fine filament, having the maximum convenient surface/volume ratio was used as a calorimeter, and the rise in temperature of the filament when adsorption took place was measured. From this, heats of adsorption were derived. Furthermore, previous work having shown that the actual surface area of an aged tungsten filament is about 1.2 times its geometric area, approximate measurements of the very small adsorbed amounts were interpreted in terms of numbers of surface atoms covered.

(1) The Accommodation Coefficient Method. If gas molecules at a temperature T_1 strike a solid surface which is at a temperature T_2, and leave the surface at an average temperature T_2', the accommodation coefficient α is defined by

$$\alpha = \frac{T_2' - T_1}{T_2 - T_1}$$

Measurement of α resolves itself into measurement of the amount of heat, q, taken away from a heated filament in unit time by impinging gas. It is then possible to show that for a monatomic gas

$$q = 1.74 \cdot 10^{-4} \cdot \frac{\alpha p}{\sqrt{MT_1}} \cdot (T_2 - T_1)$$

and as all quantities except α in this equation are known, α may be determined. The apparatus used by Roberts is shown in Figure 5. Neon at a pressure of about 0.1 mm was continuously circulated over the tungsten filament, of length some 18 cm and diameter 0.066 mm, contained in the tube A, via the cooled charcoal traps B, which freed it from oxygen. A liquid air trap was also inserted between the apparatus and the MacLeod gauge.

After the neon had been circulating for some time, the filament, which was connected to a Wheatstone bridge, was flashed. When it had cooled a standard current was passed through it, sufficient to maintain it some 20° above the temperature of the bath in which the apparatus was immersed. Readings of the filament resistance at various intervals were taken: the temperature coefficient of the filament being known, these were sufficient to determine the accommodation coefficient as a function of time. The values are plotted in Figure 6 for room temperatures and liquid air temperatures. They are seen to show a slow drift with time, presumably owing to contamination by an impurity. Then, at the time indicated by the arrow, a small quantity of hydrogen, sufficient to produce a pressure of about 10^{-4} mm in the apparatus, was admitted to the filament via the charcoal tubes. The accommodation coefficient rose rapidly as the hydrogen was adsorbed.

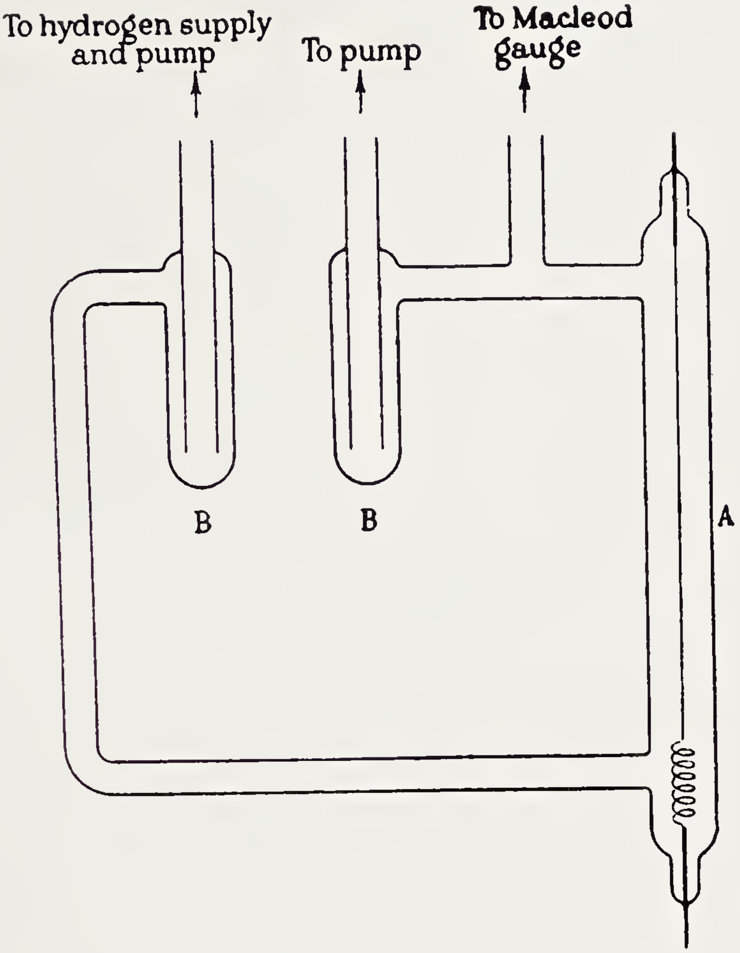

Figure 5. Apparatus for measuring accommodation coefficients.

(2) The Measurement of Heats of Adsorption. In the measurement of heats, the apparatus comprised a tube containing the tungsten filament

which was joined to MacLeod and Pirani gauges and a gas pipette. The filament was as before connected to a sensitive Wheatstone bridge, in which a Paschen galvanometer was used.

The filament was flashed, and switched into the bridge. After some 10 minutes, its rate of cooling was sufficiently slow for the drift of the galvanometer to be easily measured. The pumps were then cut off, and the known charge of hydrogen admitted to the filament. The galvanometer gave a rapid deflection, owing to the heat developed in the filament by adsorption of the hydrogen. A typical run is shown in Figure 7. The residual pressure of the hydrogen was measured on the Pirani gauge. From the galvanometer deflection the heat of adsorption was measured, and from the adsorbed amount, knowing the filament surface area, the corresponding fraction of the surface covered was derived.

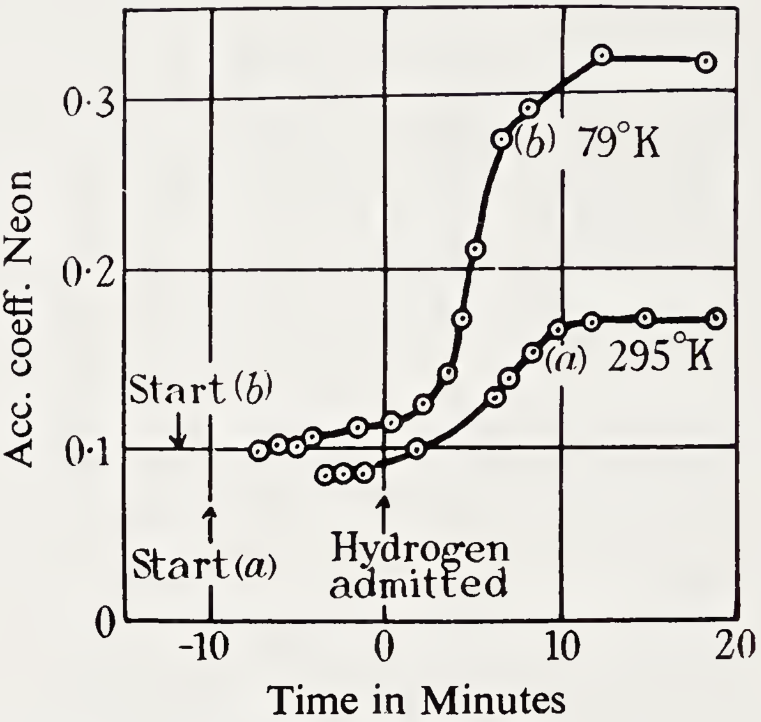

Figure 6. Influence of hydrogen on the accommodation coefficient for neon on tungsten[79].

The following of Roberts results are significant in relation to the para hydrogen conversion.

First, he showed that there was a rapid chemisorption of hydrogen even at liquid air temperatures, so that the activation energy of chemisorption is at most a few hundred calories. If the filament was deliberately dirtied, e.g., by oxygen, slow chemisorptions were then observed, suggesting that similar effects previously observed with powders were connected with surface contamination. This seems recently to have been proved in a conclusive manner by Schuit and de Boer[82], who found that the amount of hydrogen slowly adsorbed by a deliberately oxygenated catalyst was directly proportional to the extent of oxygenation.

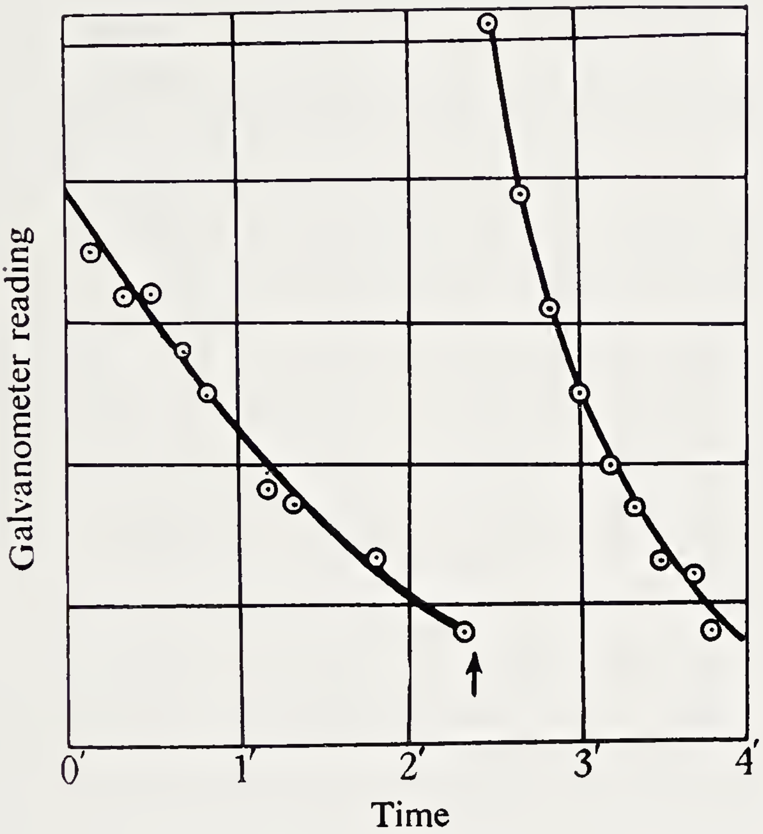

Figure 7. Typical curves obtained in measuring heat of adsorption of H_2 on tungsten filament[79].

Second, Roberts showed that fast chemisorption took place over the whole surface, the volume of gas taken up rapidly corresponding closely with the equation $2W + H_2 \rightarrow 2WH$.

Third, Roberts investigated the stability of chemisorbed hydrogen by heating the covered filament in vacuo with pumping to various temperatures for one minute, readmitting a small charge of hydrogen, and testing whether a heat evolution took place. His results are shown in Figure 8, where the readsorbed hydrogen is plotted against evaporation temperature. Roberts concluded from these results that chemisorbed hydrogen only commenced to be unstable above about 700°K.

Confirmation that this result was correct was reached in the following way. From his measurements of heats of adsorption, Roberts showed that although for very dilute layers the heat was 45,000 cal/mole, it fell to some 18,000 cal/mole for the last adsorption into the nearly complete layer. He then derived an equation for the rate of evaporation of the adsorbed layer[80] based on gas kinetic theory

$$t_f = -2.06 \cdot 10^{13} \log_{10} f \frac{\sqrt{MT}}{\phi} e^{\phi/RT}$$

where t_f is the time in seconds for a film to evaporate to such an extent that a fraction f of the initial adsorption remains, M is the molecular weight of the evaporating particle, and ϕ is the heat of desorption in cal/mole. Inserting for ϕ the value 59,000 cal/gram atom, the value of the heat of desorption of one gram atom from the complete layer as atoms according to the equation WH → W + H, Roberts showed that the film should become unstable for times of the order of one minute at about 700°K, in good agreement with the experimental result.

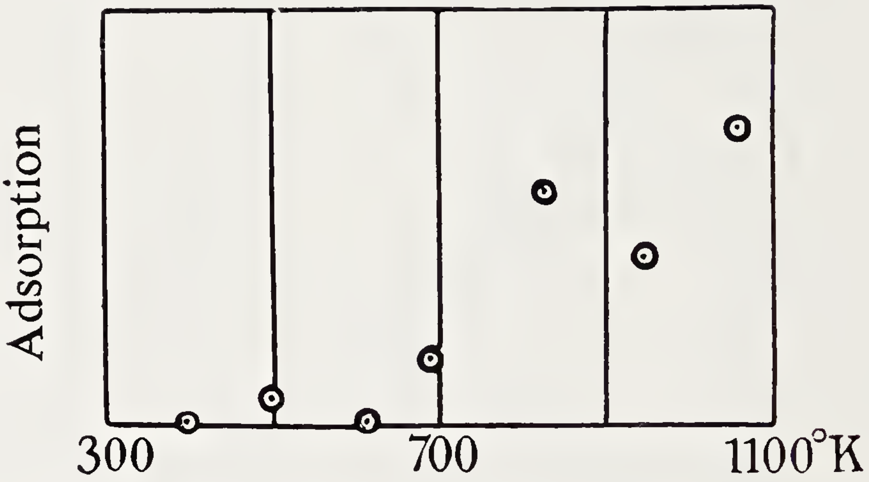

Figure 8. Temperature of pumping a tungsten filament coated with hydrogen plotted against the amount of hydrogen taken up at 25°C after pumping.[80]

Fourth, Roberts showed that at room temperatures, the neon accommodation coefficient showed no further change on increasing the hydrogen pressure beyond 3.10^{-4} mm. This suggested that the adsorption was complete under these conditions, and provided qualitative agreement with the experiments on the stability of chemisorbed hydrogen.

Turning now to the parahydrogen conversion, this work showed that although chemisorption over the whole surface took place far more readily than had hitherto been believed, nevertheless the stability of the chemisorbed hydrogen layer precluded the Bonhoeffer-Farkas mechanism. If evaporation cannot take place except above 400°C, and the conversion takes place on tungsten surfaces at −110°C (and later work has shown it to proceed even at liquid air temperatures[28]) the mechanism is impossible.

These results led Rideal to conclude[76] that the mechanism

$$\mathrm{WH} + \mathrm{D_2} \rightleftharpoons \mathrm{WD} + \mathrm{HD}$$

was the only other possible alternative. Farkas then suggested[45], however, that conversion might operate via the Bonhoeffer-Farkas mechanism, but on a relatively small number of weakly adsorbing sites. Roberts techniques would detect strong adsorption, which would certainly be inactive in the conversion, but the possibility of there being a few weakly adsorbing surface atoms, which might not be revealed by Roberts experiments, was not out of the question.

This possibility was soon shown to be untenable by Eley[28], by the following experiment. A clean evaporated tungsten film was prepared, covered with chemisorbed hydrogen at room temperature, and the system was then evacuated at room temperature for several minutes. If there were any sites present of the type postulated by Farkas, hydrogen would be removed from them—it is the essence of his mechanism that this evaporation should proceed as rapidly as the conversion, which in Eley's system had a half life of 10^{-2} min. Deuterium was then admitted to the surface and the rate of exchange measured. It was argued that the occurrence of exchange would then disprove Farkas's suggestion, and that nonoccurrence would prove it. In fact, Eley found a rapid exchange of the deuterium with the whole of the chemisorbed hydrogen well below room temperature, and concluded that the Rideal mechanism was correct. He has subsequently calculated[29] the conversion velocity according to the Rideal mechanism and found close agreement with the experimental value.

Further work has been carried out by Beeck[4, 6, 9], who has studied hydrogen adsorption on many metal films, and agrees with Roberts essential conclusions—that with tungsten, chemisorption is complete at very low pressures at room temperatures, and that the heat of adsorption under these conditions is about 15,000 cal/mole.

However, recent experimental work has shown that the evidence for the Rideal mechanism is by no means as conclusive as has been suggested.

First, however, it is to be noted that the essential link in the chain of evidence is Roberts claim that chemisorbed hydrogen is extremely stable. The evidence for this is in fact rather weak. It is doubtful whether in his evaporation experiments the possibility of recondensation of gas was really avoided: in addition his use of the evaporation formula is incorrect because it assumes preferential desorption according to the equation:

$$\mathrm{WH} \rightarrow \mathrm{W} + \mathrm{H} \qquad \text{with} \qquad \phi = 59{,}000 \text{ cal/gram atom}$$

whereas it seems clear that evaporation according to the equation

$$2\mathrm{WH} \rightarrow 2\mathrm{W} + \mathrm{H_2} \qquad \text{with} \qquad \phi = 18{,}000 \text{ cal/mole}$$

will actually take place first. Recalculation with the smaller value of ϕ indicates that some of Roberts chemisorbed hydrogen at least should evaporate quickly at room temperature, as would indeed be expected. It is usual for layers adsorbed with heats less than about 20,000 cal/mole to be reversibly adsorbed at room temperature.

Second, Roberts statement that chemisorption is only complete at the appreciable pressure 3.10^{-4} mm at room temperature in fact implies reversibility below this pressure, again indicating a rapid evaporation of chemisorbed hydrogen at room temperatures and possibly below.

Third, Eley's experiment is not conclusive, because if on admitting deuterium to the evacuated chemisorbed hydrogen layer, a small further chemisorption took place, and caused a fall in heat of chemisorption over the whole surface, chemisorption would become reversible and allow exchange according to the Bonhoeffer-Farkas mechanism.

Work by Frankenburg[53] reopened the crucial question of the stability of chemisorbed hydrogen layers. He used a powdered tungsten adsorbent, subjected to an unusually thorough outgassing and cleaning process. Considerable amounts of hydrogen were chemisorbed at very low pressures, but chemisorption was very incomplete at 10^{-4} mm at 0°C. Roberts claimed of course that under these conditions θ, the fraction of surface atoms covered by hydrogen atoms, was 100 per cent. Using the Brunauer-Emmett-Teller technique to measure the surface area, Frankenburg obtained values of θ given in Table 13.

TABLE 13. THE PERCENTAGE OF THE SURFACE OF TUNGSTEN COVERED BY HYDROGEN AT 0°C[53]

Pressure (mm)	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10
θ (%)	21.0	23.5	26.5	29.5	33.0	38.0

Chemisorption of hydrogen at 0°C was in fact believed to be incomplete until pressures of 3000 mm had been reached. Beyond 10^{-4} mm there is, according to Frankenburg, a region of weak chemisorption of low heat, extending to zero heat when $\theta = 1$. Roberts failed to detect these adsorptions because they are very slowly varying functions of the pressure, and the accommodation coefficient and heat techniques are too insensitive to detect them.

Finally, Frankenburg noted that his results could be reconciled with those of Roberts if the roughness factor of a tungsten filament is 4.5, and not 1.2, the value used by Roberts. In this case, Roberts coverages would be far smaller, and approximate those of Frankenburg. In spite of the general criticism of the use of powder adsorbents, Frankenburg's work did suggest that even on carefully cleaned surfaces there might be a region of weak hydrogen chemisorption of low heat, reversible at low temperatures, which would enable parahydrogen conversions to take place by the Bonhoeffer-Farkas mechanism.

Rideal and Trapnell[77, 78, 93] therefore investigated the chemisorption of hydrogen by clean evaporated tungsten films. The measurements are shown as linear isotherms in Figure 9, and as log-log isotherms in Figure 10. In Figure 10, A_0 is the adsorption irreversible to pumping at 0°C.

At each temperature a quantity of gas was chemisorbed with an immeasurably low equilibrium pressure, while subsequent adsorptions were reversible. The following evidence indicated that the reversible adsorptions were also chemisorption.

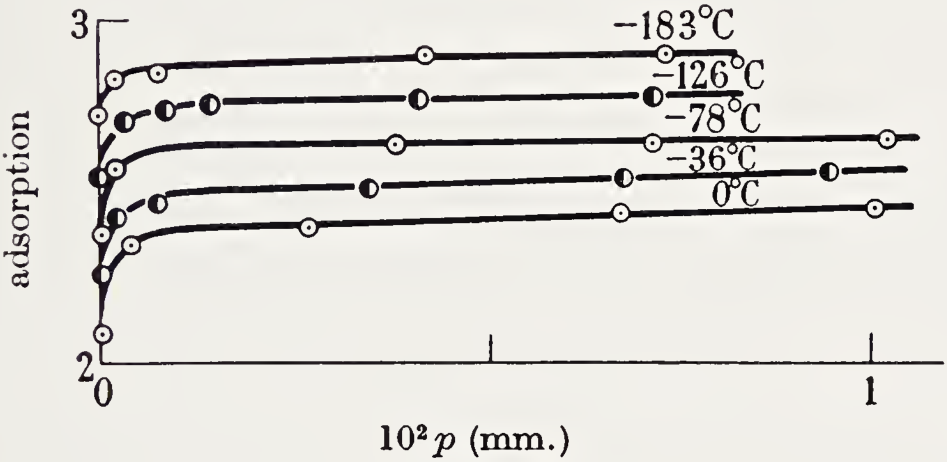

Figure 9. The isotherms for hydrogen adsorption on tungsten films[93].

1. Isothermal heats of the reversible adsorptions were obtained, and were found to fall continuously with increasing adsorbed amount from 15,000 cal/mole (when the temperature of adsorption was 0°C and the equilibrium pressure 10^{-4} mm) to 2,400 cal/mole (−183°C and 10^{-2} mm). Now heats of Van der Waals adsorption of hydrogen on a variety of surfaces are to be found in the literature and these never exceed 2,000 cal/mole. Thus at 2,400 cal/mole chemisorption and not van der Waals adsorption must still be taking place, that is, even at −183°C and 10^{-2} mm the reversible adsorptions are still chemisorption. The latter extends to a far lower heat than was believed by Roberts and by Beeck, and the layers that these workers believed to be complete were in fact only partly covered.

2. Film surface areas were reproducible to 20 per cent, and were determined by measurement of oxygen chemisorption, which takes place with one atom, covering one surface atom.

In Table 14 the chemisorption of oxygen and the adsorption of hydrogen at −183°C and 2.10^{-2} mm pressure on six films of roughly equal area are shown, the adsorptions being in the same arbitrary units.

It was then possible to convert the hydrogen adsorptions at various temperatures and pressures to θ values, to an estimated accuracy of 15 per cent. The results are shown in Table 15.

From these results it was possible to say that the surface coverage cannot exceed 100 per cent by more than a few per cent, even at the lowest temperatures and highest pressures (i.e., there is little or no van der Waals adsorption). Furthermore, allowing for experimental error, chemisorption could not have been complete at very low pressures until the temperature is as low as −78°C, so that on purely volumetric grounds much of the reversible adsorption must be chemisorption.

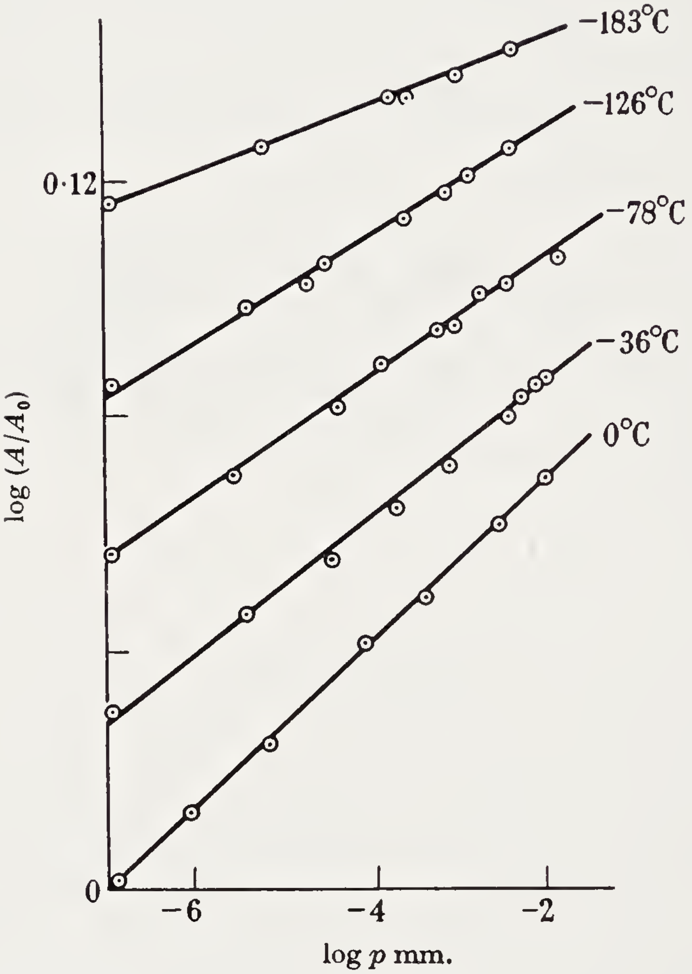

Figure 10. Log-log isotherms for hydrogen adsorption on tungsten films[93]. A is the amount adsorbed compared to A_0 the amount not removed by pumping at 0°C.

The heat of adsorption is given as a function of coverage in Table 16.

The work of Roberts was believed to be correct within the limits imposed by the use of a filament. These did not however enable him to detect adsorptions taking place beyond 3.10^{-4} mm, for it was calculated that an increase of pressure from 3.10^{-4} to 3.10^{-3} mm at 0°C, which changes the adsorption by 3 per cent, would only increase the accommodation coefficient from 0.190 to 0.192, a hardly detectable change. Equally, the change of adsorption with temperature is seen from Table 15 to be very slow, and it was suggested that this may have been at least a partial cause of Roberts' failure to detect evaporation below 400°C.

TABLE 14. RELATIVE ADSORPTIONS OF OXYGEN AND HYDROGEN ON TUNGSTEN FILMS

Oxygen Adsorption (1 atom per site)	H_2 Adsorption (− 183°C, 2.10^{-2} mm)
0.91	0.91
1.00	1.03
1.09	1.14
Mean values 1.00	1.03

TABLE 15. THE PERCENTAGE OF THE SURFACE ATOMS OF A TUNGSTEN FILM COVERED BY HYDROGEN[78, 93]

Pressure (mm)	Temp. (°C)				
	0	−36	−78	−126	−183
10^{-6}	76	80	86	92	97
10^{-4}	81	85	90	95	100
10^{-2}	86	90	94	99	103

TABLE 16. THE HEAT OF HYDROGEN ADSORPTION ON TUNGSTEN FILMS[93]

Isothermal heat (kcal/mole)	15.2	12.4	9.3	6.1	3.0
θ (%)	80	85	90	95	100

The work of Frankenburg probably does not refer to a clean surface, as has been indicated by Beeck[6], and this is almost certainly the reason why his results differ from those of Trapnell. But the qualitative similarity between the two is important, inasmuch as both show the weak chemisorption phenomenon.

The significance of Frankenburg's and Trapnell's results in relation to the parahydrogen conversion is clear. If chemisorption is reversible even at liquid air temperatures, there must be a rapid evaporation of chemisorbed hydrogen from the surface even at −183°C, and the main objection to the Bonhoeffer-Farkas mechanism, the apparent stability of chemisorbed hydrogen, vanishes. The further question then arises—is it possible to show that the kinetics of the conversion may be accounted for in terms of this mechanism. To this end, the rate expression for conversion according to the equations,

$$2W + p\text{-}H_2 \rightleftharpoons 2WH \rightleftharpoons 2W + o\text{-}H_2$$

which is the difference in rates of chemisorption and evaporation of parahydrogen, has been derived[93].

(a) The Rate of Chemisorption. If the adsorbed layer were immobile, the rate of condensation of hydrogen at a pressure p as atoms would be given by

$$R = \frac{\alpha p}{\sqrt{2\pi mkT}} \cdot (1 - \theta)^2 \qquad \text{mols/sq cm/sec}$$

where α is the condensation coefficient, and m the mass of the hydrogen molecule. However, the adsorbed layer is mobile, and in this case Peierls[73] gives for the condensation rate

$$R = \frac{\alpha p}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon} \qquad \text{mols/sq cm/sec}$$

where

$$\frac{\theta}{1 - \theta} = \frac{\epsilon(1 + \eta\epsilon)}{1 + \epsilon} \qquad \text{and} \qquad \eta = e^{-V/RT}$$

V being the repulsion energy between atoms adsorbed on adjacent sites. $1/(1 + \epsilon)$ is the chance that a site next to an unoccupied site is itself unoccupied. This term expresses the tendency of unoccupied sites to spread out in the mobile layer through repulsion forces.

(b) The Rate of the Parahydrogen Conversion. If a pressure, p, of parahydrogen is admitted to a tungsten surface

rate of conversion = rate of condensation − rate of evaporation

$$= \frac{\alpha p}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon} - f(\theta, \epsilon, \Delta H) \quad \text{mols/sq cm/sec}$$

where ΔH is the heat of adsorption.

But if at equilibrium, the pressure of parahydrogen is p',

$$\frac{\alpha p'}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon} = f(\theta, \epsilon, \Delta H)$$

and hence the rate of conversion under nonequilibrium conditions is

$$\frac{\alpha(p - p')}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon} \qquad \text{mols/sq cm/sec}$$

From this equation the absolute rate of conversion can be obtained, provided α and ϵ (or V) are known, and the reaction order and activation energy evaluated by comparing rates at different pressures and temperatures respectively.

With regard to α no reliable experimental value is available. However, a theoretical treatment of condensation has been made by Lennard-Jones and Devonshire[71], who give the condensation coefficient of hydrogen on metals as a function of the Debye characteristic temperature, Θ. Their values are shown in Table 17.

TABLE 17. CONDENSATION COEFFICIENTS OF HYDROGEN ON METALS[71]

θ (°K)	T (°K)			
	30	50	100	300
300	0.256	0.279	0.293	0.309
350	0.221	0.226	0.231	0.246
400	0.154	0.163	0.170	0.189
510	0.081	0.085	0.091	0.103

TABLE 18. CALCULATED[93] AND EXPERIMENTAL[27] KINETICS FOR THE PARAHYDROGEN CONVERSION

Kinetics	Experimental	Calculated	
		$V = 0$	$V = 400$ cal
Activation energy from temp. coefficient	1950 cal	1650	2150
Reaction order	0.1–0.5	0.6	0.59
Absolute rate at −100°C and 1 mm	$1.75 \cdot 10^{18}$ mol/sq cm/sec	$2.2 \cdot 10^{17}$	$7.8 \cdot 10^{16}$

Fortunately, α varies very little with temperature, and for tungsten, with $\Theta = 310$°K, α is taken as 0.30 throughout the range 80 to 300°K. With V we are on less satisfactory ground, as again no experimental value is available, and the absolute rate of reaction proves to be very dependent on V. V may however be made up of three terms, electrostatic dipole-dipole repulsions, shorter range attractions, and very short range repulsions arising from overlapping of electron clouds. The first term was calculable; the third term was suggested to be negligible as the diameter of the hydrogen atom is far less than that of the smallest lattice spacing on tungsten. The short range attractions will diminish V, but to an unknown extent. These considerations indicated that V must be between zero and 400 cal, the uncertainty being due to the attractive forces. The kinetics of conversion may then be calculated from the adsorption isotherms for the two extreme values of V, and compared with the experimental values of Eley and Rideal[27]. The results are shown in Table 18.

It is noted that the experimental reaction order was measured at a higher pressure than that which could be used in the calculation, and that at higher pressures the calculated order would be lower. Also, the absolute rate calculation is rather dependent on θ as $(1 - \theta)$ is very small, and an error of a few per cent in θ easily accounts for the divergence between calculation and experiment.

The low value of the calculated activation energy may seem surprising when it is remembered that according to the Bonhoeffer-Farkas mechanism the true activation energy is the sum of the heat and activation energy of chemisorption. The activation energy of chemisorption is at most a few hundred calories, but under the conditions used by Eley and Rideal the heat was between 7,000 and 11,000 cal/mole. However, the calculations from the Peierls equation showed that the temperature coefficient gives an *apparent* activation energy, which is far less than the true energy.

The reason for this is as follows. The ratio of evaporation rates at temperatures T_1 and T_2, may be written approximately as

$$\frac{\theta_1^2}{\theta_2^2} \cdot e^{(-\Delta H_1/RT_1 + \Delta H_2/RT_2)}$$

and this equals

$$e^{-E(1/RT_1 - 1/RT_2)}$$

where E is the activation energy derived from a temperature coefficient. Under experimental conditions, $\theta_1^2/\theta_2^2 \bumpeq 1$ even for large temperature intervals, and E is hence determined by the relative magnitudes of ΔH_1 and ΔH_2. Only if $\Delta H_1 = \Delta H_2$ (i.e., the heat of adsorption is independent of surface coverage) does $E = \Delta H_1$, i.e., do true and apparent activation energies become the same. But ΔH falls very sharply with increasing θ, and this causes the disparity between true and apparent activation energies.

The agreement between experiment and calculation for reaction order, activation energy and absolute rate showed that if, as suggested, V is low, the Bonhoeffer-Farkas mechanism is correct. Conversion by this mechanism is inevitable whenever chemisorption is reversible—the question is whether the *whole* velocity is accounted for by evaporation of chemisorbed hydrogen. If it can be, as in this case, the Rideal mechanism does not operate.

Equally, certain facts point against the Rideal mechanism. Thus, to account for the very low reaction orders found at −100°C and 1 mm pressure in terms of the Rideal mechanism, second layer coverages calculated from the Langmuir isotherm would be as shown in Table 19.

Not only is no case of a van der Waals adsorption of hydrogen at −100°C and 1 mm known as it would involve an impossibly high heat of 6,000 to 7,000 cal/mole, but in addition, Table 15 shows that even allowing for maximum experimental error the coverage of the second layer at this heat cannot exceed a few per cent, and can certainly not approach the values shown in Table 19.

It was, however, noted that if V is much higher than suggested, so that there are very few pairs of vacant sites, the conversion rate falls well below the experimental value, and the Rideal mechanism must become important. The correctness of the Bonhoeffer-Farkas mechanism has recently been queried by Couper and Eley[20] on this ground. They have repeated Trapnell's calculations, but with V = 4,400–4,800 cal. In this way they obtain an activation energy of 8,300 cal, and an absolute rate of $2.6 . 10^{12}$ mol/sq cm/sec, both in severe disagreement with experiment.

In using this value of V, Couper and Eley assume that the whole of the fall in heat with increasing surface coverage is due to repulsion forces. However, Trapnell's calculation suggests that V cannot exceed a few hundred calories, and no ordinary treatment of the interatomic forces can account for V = 4,400–4,800 cal. Also, it seems likely, as suggested by Halsey[61], that V will appear as an activation energy of chemisorption. In this case, the measurements of Roberts[79] and of Beeck, Givens and Ritchie[10] on the rate of hydrogen chemisorption at low temperatures precludes a value of V higher than a few hundred calories.*

TABLE 19. CALCULATED SECOND LAYER COVERAGES OF TUNGSTEN FILM BY HYDROGEN REQUIRED TO ACCOUNT BY RIDEAL MECHANISM FOR OBSERVED PARAHYDROGEN CONVERSION

Reaction order	0.5	0.4	0.3	0.2	0.1
Coverage (%)	41	52	63	74	87

Halsey[60] has also criticized the Bonhoeffer-Farkas mechanism on theoretical grounds, claiming that a Rideal mechanism is operating on a heterogeneous surface. The following criticisms may be made of his treatment.

First, his support of the Rideal mechanism is based on the assumption that the van der Waals energy of a site increases in direct proportion to the chemisorption energy, for which experimental justification is slender. Second, his calculations do not show that the absolute rate and order of reaction may be accounted for in terms of his mechanism; he simply shows that it gives a temperature coefficient in agreement with experiment.

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* A recent treatment of the velocity of adsorption by Laidler (*J. Phys. Chem.* **57**, 318 (1953)) using the method of absolute rates confirms that a low value of V must be used, and also shows that the whole velocity of conversion is due to the Bonhoeffer-Farkas mechanism.

Third, as pointed out to the author privately by Dr. C. Kemball, Halsey's main criticism of the Bonhoeffer-Farkas mechanism, namely that the calculated activation energy for this mechanism disagrees with the experimental, is based on incorrect mathematics. His equation (2.2) should in fact read

$$E_\tau = -R\,\frac{\partial[2 \ln (1 - \theta) + \ln T]}{\partial(1/T)}$$

This correction removes Halsey's principal objection to the Bonhoeffer-Farkas mechanism.

Experiments on Metals other than Tungsten. The properties of other metal surfaces in hydrogen chemisorption and the parahydrogen conversion have been studied far less intensively than those of tungsten, but the following results are relevant:

(1) Beebe and Stevens[3] working with a doubly-promoted iron catalyst (21 grams of catalyst 931), measured a calorimetric heat of adsorption of 5,300 cal/mole for 0.38 cc of H_2 adsorbed. This agrees with the result of Kummer and Emmett[69] who noted about 0.2 cc chemisorption of hydrogen use 12 grams of this catalyst at −195°C. However, these latter authors noted that the small amount of chemisorption occurring was not reversible and hence could not contribute to a chemical type parahydrogen conversion at this low temperature.

(2) Rideal and Trapnell[77] have reported qualitative experiments on hydrogen adsorption by nickel films at low temperatures, finding results very similar to those with tungsten. Here again a conversion through the Bonhoeffer-Farkas mechanism will take place*.

(3) Recent work by Kummer and Emmett[69] supports the Bonhoeffer-Farkas mechanism for the parahydrogen conversion on a singly promoted iron catalyst. In this work a marked difference was found between singly- and doubly-promoted catalysts, namely, that only the singly-promoted type was active in hydrogen-deuterium exchange at −195°C. It was also shown that whereas both catalysts chemisorbed hydrogen at these temperatures, only the hydrogen chemisorbed by the singly promoted catalyst was reversible to pumping at −195°. This suggests very strongly that hydrogen-deuterium exchange requires for its occurrence a reversible hydrogen chemisorption.

Summary and Conclusions. Data on hydrogen adsorption isotherms unfortunately allow only a qualitative conclusion about the conversion mechanism to be made, namely, that a conversion according to the Bonhoeffer-Farkas mechanism will operate to some extent whenever a reversible

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* Weak, reversible hydrogen chemisorptions have recently been reported on iron films by Porter and Tompkins (*Proc. Roy. Soc.* **A217,** 544 (1953)) and on iron and nickel films by Wahba and Kemball (*Trans. Faraday Soc.* **49,** 1351 (1953)).

hydrogen chemisorption is observed. In order to show that the whole velocity of conversion is or is not due to evaporation of chemisorbed hydrogen, we have at present to resort to calculation from the adsorption data. It is clear that before a final and unequivocal answer can be given to the question of the conversion mechanism, the velocity of chemisorption at catalytic coverages must be measured.

Finally, something should be said of the "solution theory" of conversion and exchange. It has from time to time been suggested that the catalytic reactions of hydrogen and also nitrogen may be due to dissolved atoms rather than chemisorbed atoms of these gases. Little evidence has been advanced to substantiate this suggestion, but it has recently been to some extent revived[8, 57] by the discovery by Beeck *et al.*[5] of a solution process of hydrogen in metals, which is activated but takes place with a low heat.

It seems likely that the idea of conversion through reversible solution of hydrogen can be discarded for the following reason. First, the fact that if a surface is covered by a foreign gas such as oxygen or ethylene, no solution takes place, indicates that solution must take place via chemisorption. Equally, if the principle of microscopic reversibility is not to be violated, so also must evolution of dissolved hydrogen occur via the chemisorbed state. Evaporation of chemisorbed hydrogen will then be more rapid than evolution of dissolved hydrogen, as the latter involves the extra activation energy of transfer from bulk to surface. This would appear to show that conversion by the Bonhoeffer-Farkas mechanism will always be more important than conversion by solution.

We may note that this result has been in essence found by Beeck, Givens and Ritchie[10] when they showed that in spite of the low heat of solution, it took a long time to remove dissolved gas by pumping.

The Chemical Conversion by Oxide Surfaces. Comparatively little work has been done on the chemical conversion by oxides. Early work by Taylor and Sherman[90] showed that activated adsorption of hydrogen by oxides took place in the temperature range in which the oxides were active in conversion. This might appear to favor the Rideal mechanism, as activated adsorption would take place too slowly to permit conversion according to the Bonhoeffer-Farkas mechanism at a sensible velocity, except at very high temperatures. However later work by Gould, Bleakney and Taylor[58] showed that hydrogen-deuterium exchange took place on chromia surfaces at −190°C, and at this temperature no activated chemisorption had been detectable. Also, Smith and Taylor[87] record that zinc oxide can catalyze the exchange at 140°K, when again adsorption work by Taylor and Strother[92] had failed to register an activated chemisorption until far higher temperatures had been reached. These results indicate that a *slow* high temperature chemisorption is not a necessary preliminary to conversion and exchange—rapid chemisorptions must have been taking place on these oxides at low temperatures.

Later work by Beebe and Dowden[2] is also pertinent. These workers found an instantaneous reversible adsorption of hydrogen by chromia at liquid air temperatures, which took place with a heat falling from 5,100 cal/mole for small adsorptions to 3,200 cal/mole for large adsorptions, as shown in Figure 11. These are too high to be van der Waals adsorption—it must be a weak chemisorption, and its rapidity of occurrence and reversible character indicate that the exchanges observed by Gould, Bleakney and Taylor[58] were in part if not entirely taking place through the Bonhoeffer-Farkas mechanism.

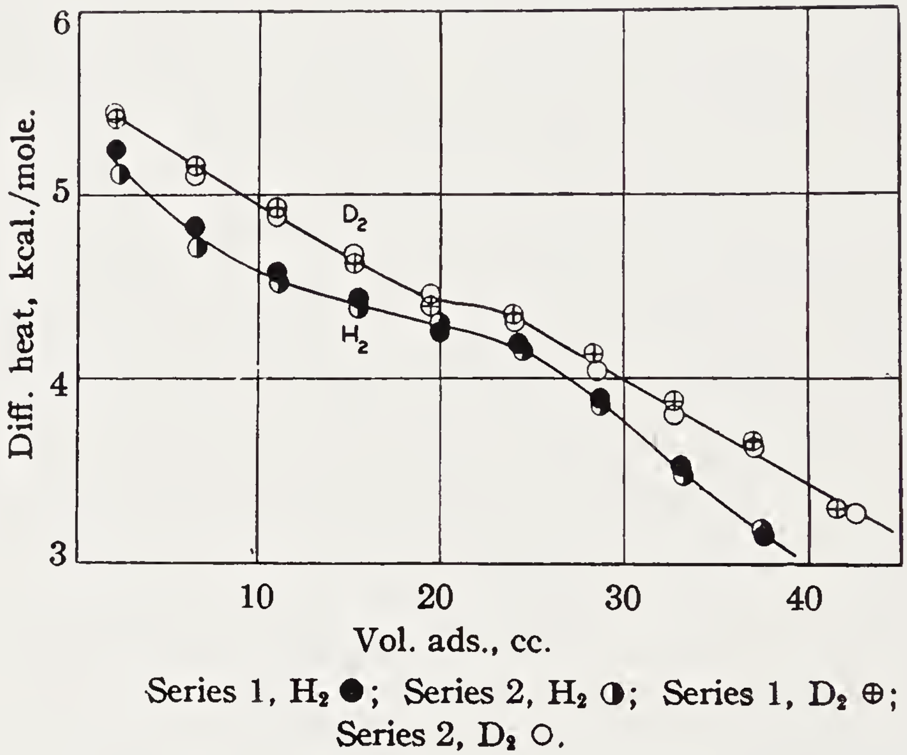


Figure 11. Heat of adsorption of H_2 and D_2 on chromium oxide gel[2].

The Poisoning of the Conversion

Most investigations of the poisoning of the conversion have been qualitative. Eley and Rideal[27] have however obtained quantitative data on the effect of adsorbed oxygen, ethylene, carbon monoxide and nitrogen on the conversion at the surface of a well cleaned tungsten filament. The technique was in most cases to measure the change in velocity constant after admitting a quantity of poison to the filament, and pumping out the excess.

With nitrogen and ethylene layers, it was found that the apparent activation energy of the parahydrogen conversion was markedly increased, although this was offset by an increase in the entropy of activation. With oxygen, the activity was measured as a function of surface potential, i.e., oxygen coverage, and although, as shown in Figure 12, the velocity fell sharply at first, the last adsorbed oxygen had little further poisoning effect.

At −73°C and 1.5 mm parahydrogen pressure, nitrogen layers reduced the activity by a factor of 340, ethylene layers by about 1000. Complete oxygen layers reduced the activity at −131°C by 750 fold.

Trapnell[94] has investigated the factors involved in the poisoning by studying on evaporated films first the adsorption of the poisons, and then the adsorption of hydrogen onto poisoned surfaces.

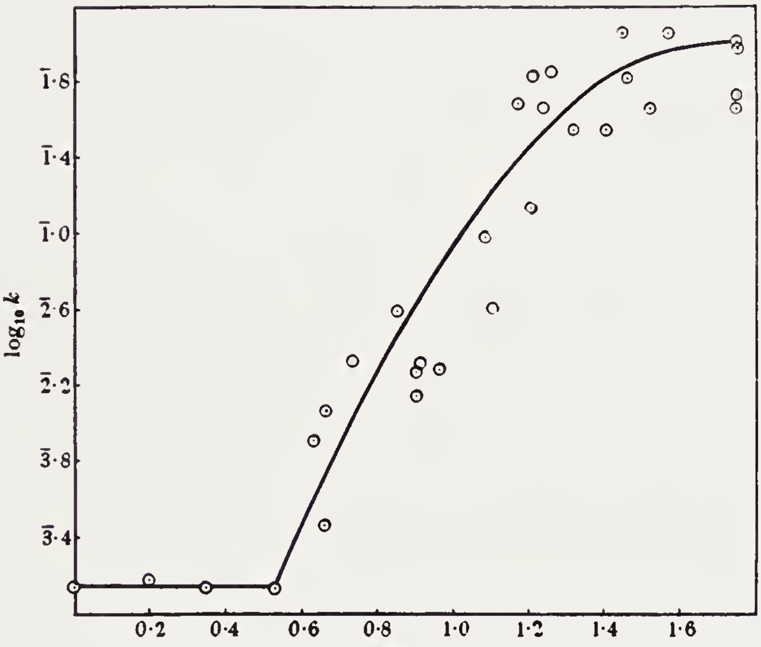


Figure 12. The parahydrogen conversion constant k as a function of the contact potential of a WO surface at constant wire temperature and hydrogen pressure[27].

It was found that oxygen and ethylene completely cover a tungsten surface and that no hydrogen is adsorbable into saturated oxygen layers. Poisoning is in other words due to nonavailability of any sites for hydrogen chemisorption.

Nitrogen was found to be irreversibly chemisorbed at room temperatures and below, but to cover only 50 per cent of the surface, i.e., in the saturated layer one nitrogen atom was present per 2 surface tungsten atoms. Hydrogen was chemisorbable into the bare sites of saturated nitrogen layers, and very similar isotherms to those with an unpoisoned surface were obtained. Reversible chemisorptions of low heat were observed between 0 and −183°C.

These results enabled three conclusions to be drawn:

(1) The velocity of conversion or exchange on a partly covered surface need not be directly proportional to the amount of surface available for hydrogen chemisorption. In this case, the conversion velocity is reduced 340 times by a loss of only half the surface.

(2) The poisoning cannot be due to surface heterogeneity. Preferential coverage by nitrogen of sites of high heat would take place on a heterogeneous surface, and whatever the reaction mechanism, it is sites of low heat which would be active in conversion.

(3) The poisoning cannot be due to simple blockage of surface sites, as with oxygen and ethylene. The effect did not seem explicable in terms of the Rideal mechanism, and the following mechanism of poisoning was suggested in terms of the Bonhoeffer-Farkas mechanism.

From the rate expression

$$R = \frac{\alpha(p - p')}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon} \qquad \text{mols/sq cm/sec}$$

the influence of a poison must be to alter α, θ or ϵ. Alteration of θ is impossible as experiment shows $(1 - \theta)$ to be larger for the poisoned than the unpoisoned layer. Also, poisoning did not seem ascribable to an alteration in ϵ, as it was shown that a larger number of adjacent pair sites would be expected for the poisoned than for the unpoisoned layer. Both these effects represent a catalysis of the conversion by the poison, and it was therefore concluded that the effect of the poison must be to reduce the condensation coefficient of the hydrogen molecule. Three possible mechanisms of this effect were noted, namely a greater shielding of a vacant site by a large adjacent chemisorbed nitrogen atom than a small adjacent hydrogen atom, a reduction in adsorbing power of bare sites adjacent to nitrogen-covered sites, and the possibility of condensation of hydrogen molecules on the nitrogen saturated surface having to take place on longer lattice spacings than is the case on the unpoisoned surface.

USE OF THE CONVERSION IN CATALYTIC PROBLEMS

In addition to the mechanistic studies of these reactions, much work has been carried out in which the conversion velocity has been used as an index of catalytic activity. Several main uses may be distinguished.

1. Comparison of rates of a catalytic reaction involving hydrogen and of the parahydrogen conversion under catalytic conditions has been used to give information concerning the rate determining step in these reactions. and the availability of the surface to hydrogen.

2. The variation of conversion velocity among certain metal surfaces has been used to give information on catalytic specificity.

3. The variation of velocity with temperature on zinc oxide has been claimed to show a very marked surface heterogeneity.

4. The magnetic conversion has been used to determine magnetic susceptibilities, and hence structures, of certain molecules.

The Mechanisms of Reactions involving Hydrogen

The method is due to Farkas and Farkas[39, 41], whose most detailed work was carried out on the exchange between deuterium and water, a reaction discovered by Horiuti and Polanyi[63]. Farkas and Farkas used a platinum wire catalyst, and first investigated the exchange in the vapor phase, obtaining the results shown in Table 20.

TABLE 20. PARAHYDROGEN CONVERSIONS AND DEUTERIUM-WATER EXCHANGE OVER A PLATINUM WIRE CATALYST[39, 41]

Temp. (°C)	Half Life (min)	Activation Energy (kcal)
(a) Parahydrogen conversions at 20 mm in the absence of water vapor		
142	9.5	6.4
182	4.8	
217	3.0	
(b) Parahydrogen conversions at 20 mm in the presence of 10 mm water		
186	45	10.8
252	10	
322	2.5	
(c) Exchange reaction, 20 mm D_2 plus 10 mm H_2O		
252	120	13.5
324	21	
410	5.2	
535	2.0	

Table 20 shows:

(1) That the presence of water vapor at the surface markedly inhibited the conversion (sections a and b).

(2) That the conversion proceeded much more rapidly than the exchange under identical conditions (sections b and c). In fact, the ratio of rates at the same temperature and pressure was between 8 and 10.

Other experiments then showed that the exchange was almost independent of water vapor pressure and roughly proportional to deuterium pressure.

With liquid water, different behavior was observed. With platinum black as a catalyst, conversion proceeded more slowly than the exchange, while with a suspension of *B. coli*, the conversion velocity was negligible in comparison with exchange.

These results were then interpreted as follows. With liquid water, chemisorption of hydrogen was the rate determining step. Any hydrogen which was chemisorbed had no chance to give a conversion by the mechanism

$$2MH \rightleftharpoons 2M + H_2$$

but immediately underwent the exchange process. Exchange velocity exceeded conversion velocity because the rate determining step was hydrogen chemisorption and not the exchange reaction. With water vapor, though, where conversion markedly exceeded exchange, the reverse was true. It was in fact suggested that in the higher temperature vapor phase experiments, a surface oxide was formed on the platinum, and that reduction of this oxide by the hydrogen was the slow step. Conversion was assumed to proceed on the part of the surface not covered by oxide, and to take place rapidly in comparison with exchange.

The work was extended to deuterium exchange with other substances[41]. Some results are shown in Table 21.

It is seen that in the cases of ether, benzene and acetone, conversion was very much faster than exchange, again suggesting the exchange step to be rate determining. With the alcohols, where the two processes took place at about the same speed, no clear decision on mechanism was possible, and furthermore, with ethyl alcohol, the relative concentrations of the reactants were shown to affect the conversion to exchange ratio very strongly, suggesting that the rate determining step might be changing. Results are given in Table 22.

Further work was carried out by Farkas[38] on the exchange between ammonia and deuterium at the surface of an evaporated iron film and it was claimed that the results could be explained in terms of the following steps, in which asterisks represent chemisorbed atoms or radicals:

$$D_2 \rightarrow 2\overset{*}{D} \qquad \text{(I)}$$

$$NH_3 \rightarrow \overset{*}{N}H_2 + \overset{*}{H} \qquad \text{(II)}$$

$$\overset{*}{N}H_2 + \overset{*}{D} \rightarrow NH_2D \qquad \text{(III)}$$

$$\overset{*}{H} + \overset{*}{D} \rightarrow HD \qquad \text{(IV)}$$

with $\overset{*}{N}H_2$ covering more of the surface than $\overset{*}{H}$ or $\overset{*}{D}$, and the rate determining step shown by the results on the parahydrogen conversion to be (III).

Other work by Farkas and Farkas[42] on the exchange between benzene and deuterium, and by Farkas[40] on the rate determining step in the diffusion of hydrogen through palladium are further examples of the same method. With benzene, little inhibition of the conversion by benzene was found at a platinum surface, and exchange proceeded at only 1 per cent of the rate of conversion. These results suggested relatively weak adsorption of benzene. However, the exchange depended on the 0.4th power of the benzene pressure, suggesting relatively strong benzene adsorption. The results were reconciled by suggesting that benzene and hydrogen were adsorbed on different parts of the surface. In more up-to-date terms, using concepts due to Herington and Rideal[62], we might suggest that although benzene adsorption is quite strong, the large size of the benzene molecule does not permit full coverage of the surface, relatively large numbers of interstitial sites being left free to chemisorb hydrogen and initiate conversion.

TABLE 21. EXCHANGE OF ALCOHOLS AND HYDROCARBONS WITH 25 MM D_2 ON Pt AT 17°C[41] VS RATE OF PARAHYDROGEN CONVERSION

Pressure of Exchange Partner	Half Life in Min (τ)		$\frac{\tau\text{ (exchange)}}{\tau\text{ (conversion)}}$
	Exchange	Conversion of parahydrogen	
17 mm ether	200	1	200
40 mm benzene	13	0.5	26
8 mm acetone	60	5	12
1 mm 2-ethyl hexanol	10	4	2.5
16 mm ethyl alcohol	8	4.5	1.8
3 mm *n*-butane	10	6	1.6

TABLE 22. DEPENDENCE OF DEUTERIUM EXCHANGE AND PARAHYDROGEN CONVERSION ON ALCOHOL PRESSURE[41]
Temperature 19°C Hydrogen Pressure 20–25 mm

Alcohol Pressure	Half Life in Min (τ)		$\frac{\tau\text{ (exchange)}}{\tau\text{ (conversion)}}$
	Exchange	Conversion	
0.01	200	3.5	57
0.5	11.5	3.3	3.5
3.5	9.5	5.0	1.9
24.0	12.5	9.4	1.3

For the diffusion of hydrogen through palladium, two characteristic types of behavior were noted between 20 and 320°C. In the first, conversion was only three to four times quicker than diffusion, and it was believed that the boundary reaction, i.e., dissociation of the hydrogen molecule, was rate determining. In the second, conversion was very much faster than diffusion, and the latter was believed to be determined by the actual transfer of hydrogen atoms through the bulk of the palladium.

The Farkas method is not, however, as has been implied in the presentation so far made, unequivocal. In fact, it necessitates the assumption[44] that exchange between a substance RH and deuterium proceeds by the mechanism

$$D_2 \rightarrow \overset{*}{D} + \overset{*}{D} \tag{I}$$

$$RH \rightarrow \overset{*}{R} + \overset{*}{H} \tag{II}$$

$$\overset{*}{R} + \overset{*}{D} \rightarrow RD \tag{III}$$

$$\overset{*}{H} + \overset{*}{D} \rightarrow HD \tag{IV}$$

If this is so, the method is valid—if conversion exceeds exchange (IV) is faster than (III), and the latter is rate determining. But the method does depend on this mechanism of exchange, and if for example, the exchange process were actually[68]

$$\overset{*}{R} + D_2 \rightarrow RD + \overset{*}{D} \tag{V}$$

i.e., a Rideal mechanism involving a van der Waals adsorbed hydrogen molecule, the rate of conversion might be very slow through the radical *R* being very strongly bound and covering nearly all the surface, while the rate of exchange represented by (V) might yet be rate determining.

Furthermore, care must be taken in accepting a claim that as a particular gas will reduce the conversion velocity to a small fraction of that observed at a clean surface, it must be occupying most of the surface. The example quoted where a tungsten surface only half covered by nitrogen has its conversion activity reduced by over 300 times shows clearly that the velocity of conversion is dependent on other factors than the amount of available surface for hydrogen chemisorption.

Two uses which have been made of the measurement of conversion velocity to obtain information about adsorbed layers are subject to possible criticism on this account. First, to test the idea that geometry may be a significant factor in determining structures of adsorbed layers, Twigg and Rideal[97] used a method involving hydrogen-deuterium exchange. Their calculations had indicated that although the ethylene molecule should be capable of covering a nickel surface completely, steric interference should preclude methyl substituted ethylenes from doing so. Their result that hydrogen-deuterium exchange took place in the presence of methyl substituted ethylenes but not in the presence of ethylene was claimed to confirm their calculations.

Second, Craxford[21] has used the occurrence or nonoccurrence of conversion during various conditions of Fischer-Tropsch synthesis to gain information about surface layers during reaction.

Catalytic Specificity

Much work had emphasized the importance of surface geometry in determining catalyst activity, but it was clear that many of the data on catalysis could not be explained solely in these terms. As long ago as 1931, for example, Wansbrough-Jones and Rideal[98] had obtained evidence that the ease of passage of an electron across a surface, as given by the work function, might determine its catalytic power.

Following work by Dilke, Eley and Maxted[23] on the change in magnetic susceptibility of a palladium powder on adsorption of dimethyl sulfide, it was suggested by Dowden[24, 25], and by Couper and Eley[19], that the extent of vacancies in a metal *d* band, in which there is a high density of energy states, might be important in determining catalyst activity. In terms of valence bond theory, catalyst activity would be said to be controlled by the number of atomic *d* orbitals. In pictorial terms, we might say that the covalent bonds between reactant and surface involve the metal *d* band, and that vacancies in the *d* band are required for catalysis to be possible.

Couper and Eley[19] measured the conversion activity of a series of carefully cleaned palladium-gold alloy filaments. In this system the lattice spacing does not change with composition, but the *d* band is progressively filled between 0 and 60 atomic per cent of gold, after which it remains complete for further increase in the gold content.

Their result was that the apparent activation energy of conversion varied very little between 0 and 60 atomic per cent gold, but subsequently increased very sharply with rising gold content; the frequency factor decreased steadily throughout.

Catalyst activities, plotted as $\log k - I/T$ lines are shown in Figure 13. It is probably wisest not to place too detailed an interpretation on Couper and Eley's results, both because the activation energies are only apparent, and are not significant properties of the reaction, and because the surface areas of the filaments were not measured, but must be assumed equal. But Figure 13 does show that at a particular temperature, the activity of filaments does not vary much between 0 and 60 atomic per cent gold, and that the subsequent decrease is rapid, amounting to several orders of magnitude in all—far more than could be due to surface area effects. The results indicate a strong correlation between *d* band character and catalytic power.

This conclusion was confirmed by the discovery that hydrogen dissolved in palladium, which is known to cause filling of the metal *d* band, reduced the converation activity very considerably—by a factor of 30 at room temperature in one experiment, shown in Figure 14.

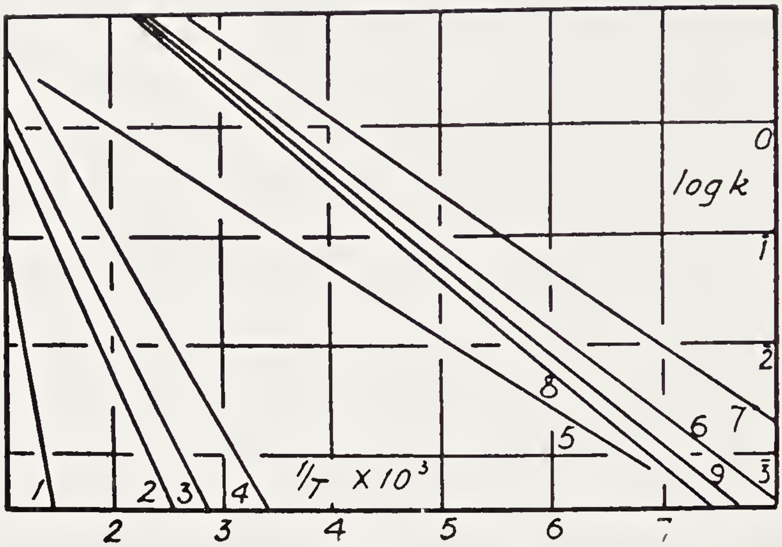


Figure 13. The parahydrogen conversion on the Pd/Au alloys (points omitted)[19].

1. Pure Au	*4.* 30 at. % Pd	*7.* 70 at. % Pd
2. 10 at. % Pd	*5.* 40 at. % Pd	*8.* 90 at. % Pd
3. 20 at. % Pd	*6.* 55.2 at. % Pd	*9.* Pure Pd

This view of catalytic specificity in the conversion may be discussed in terms of the rate equation

$$R = \frac{\alpha(p - p')}{\sqrt{2\pi mkT}} \cdot \frac{1 - \theta}{1 + \epsilon}$$

which shows that variation in activity is due to variation in α, θ or ϵ. For clean metal surfaces, Table 17 suggests that variation in α is unlikely to be a significant cause—at room temperatures α will not change by a factor of more than 3 from surface to surface. ϵ is determined, at constant θ, by V, and it has been suggested that V is largely made up of electrostatic forces as the adatoms are too far apart to allow short range repulsions to be effective. From such surface dipoles as are known from contact potential measurements, namely PtH and NiH, we may then conclude that V is low, as with tungsten, and in this case variation of ϵ is not large, a factor of 2 at most, at room temperatures.

Variation in $(1 - \theta)$ is then the most significant influence on specificity.

Low activity is to be associated with nonavailability of the surface for reversible hydrogen chemisorption, either because chemisorption is so strong that the entire surface is covered at the very lowest equilibrium pressures, or, because it is so weak that very little of the surface can participate in breaking the H—H bond and forming surface hydride. Strong catalysis requires a large surface fraction uncovered by hydrogen but participating in reversible chemisorption. This fraction will be determined mainly by the heat of chemisorption at zero coverage.

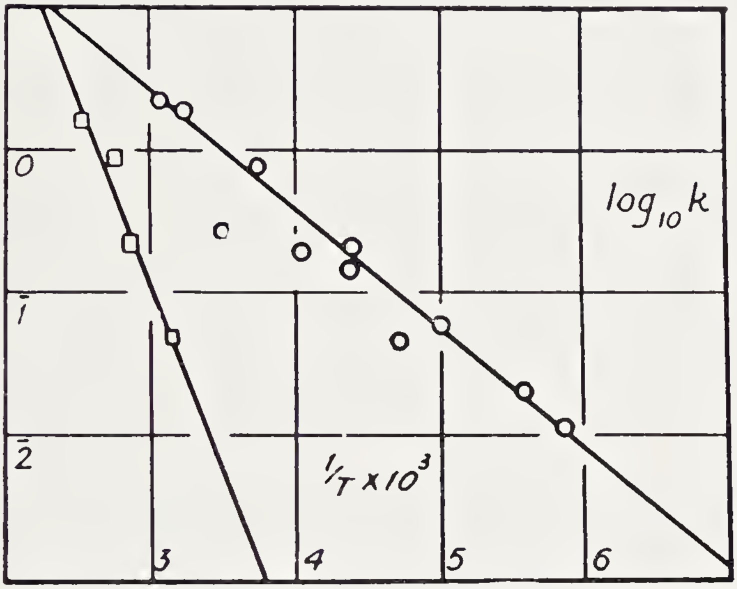


Figure 14. Effect of hydrogen dissolved in palladium upon the parahydrogen conversion[19].

○ Pd outgassed at 600°K *in vacuo*
□ Pd with dissolved hydrogen

It seems therefore that the alloy studies of Couper and Eley, and the mechanism studies of Trapnell, may be brought into line by suggesting that the *d* character of metals decides their initial heat of hydrogen chemisorption, and this result has actually been found by Beeck[7] to be the case. His results for the initial heats on evaporated metal films are shown in Figure 15. Except for tungsten the heat decreases uniformly with increasing *d* character of the metal bond.

In extension of Beeck's results, it would be interesting to know whether the heats of hydrogen chemisorption on the alloy surfaces follow the order of catalytic activity.

Catalyst Heterogeneity

Considerable complexity of behaviour of zinc oxide in hydrogen adsorption had been recorded by Taylor and Strother[92]—the isobar had two maxima between 80 and 700°K. Smith and Taylor[87] therefore studied the rate of hydrogen-deuterium exchange on the same oxide powder over part of the same temperature range used for adsorption studies. Their values for energies of activation are shown in Table 23 as a function of various temperature ranges.

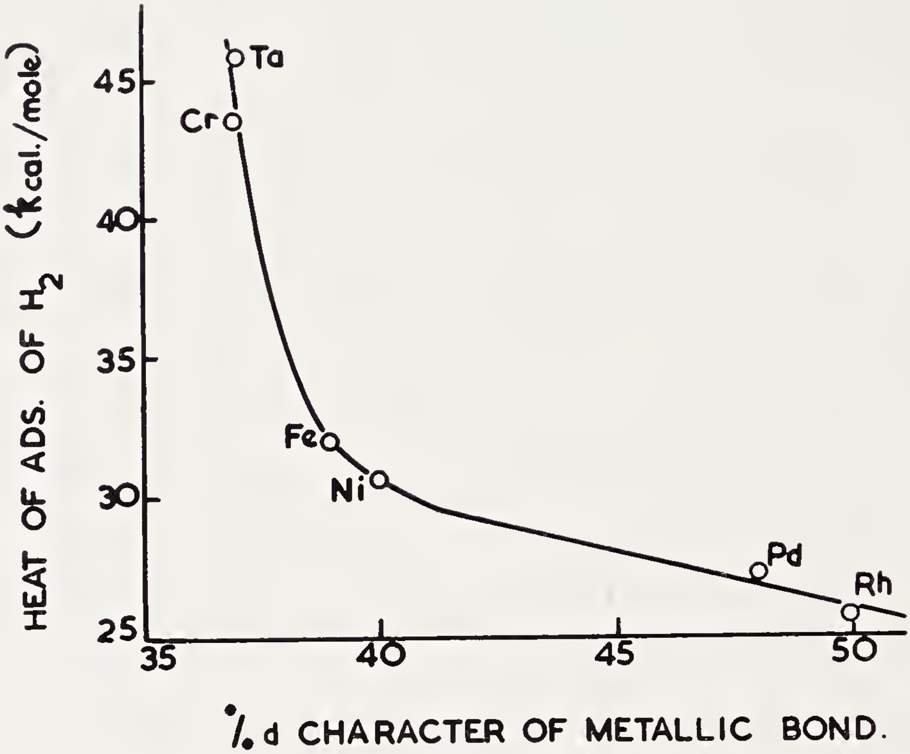


Figure 15. The initial heats of hydrogen chemisorption by metals[7].

Table 23. The Energy of Activation of Hydrogen-Deuterium Exchange on Zinc Oxide[87]

Temperature (°K)	143		178		195		227		255.5		273		298		
Activation energy (kcal)		0.6		4.4		7.8		7		8.8		7			
Temperature	329		353		373		383		405		430		457		491
Activation energy		9		6		12		11		0		7		13	

These fluctuations contrast with normal behaviour, which gives a single activation energy. In such cases Smith and Taylor suggest that there is a single type of adsorption site operating, so overwhelmingly active in comparison with others as to be responsible for effecting the entire catalysis. With zinc oxide, however, there must be a marked heterogeneity, with different types of sites able to contribute appreciably to the exchange velocity in different temperature ranges, so that no simple temperature dependence of velocity is possible. Only between 195 and 373°K, where the activation energy is roughly constant, may the active surface be regarded as uniform. Above and below these temperatures there is nonuniformity, and the fluctuating temperature rates could in fact be correlated with varying rates of adsorption observed by Strother and Taylor.

Their conclusions are subject to the criticism that the activation energies are only apparent and in fact determined by the rate of change of heat with surface coverage, a steep slope giving a low energy, and a gentle slope a high energy. In addition if, in the expression on page 30.

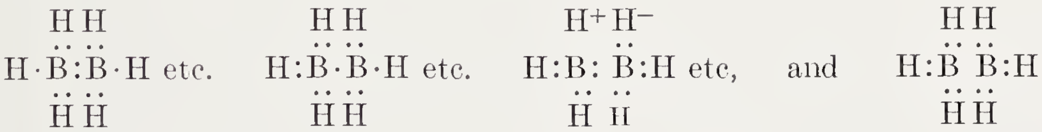
$$\Delta H_1/T_1 = \Delta H_2/T_2$$

the apparent activation energy is zero.

Magnetic Characteristics of Molecules

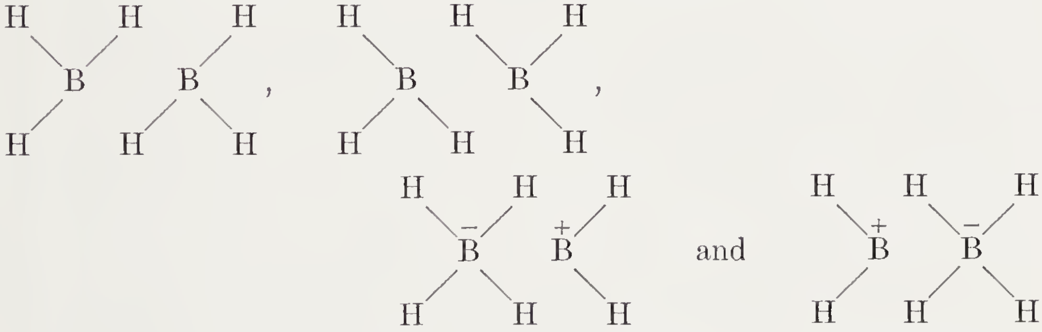
Determination of the susceptibility of weakly paramagnetic or of diamagnetic gases is not easy, and testing for the presence of a magnetic parahydrogen conversion can be a convenient approach to this problem.

Thus, Farkas and Sachsse[49] could detect no catalysis of conversion by diborane, and were therefore able to conclude that this substance is diamagnetic. Unfortunately, the result does not enable distinction to be made between the ethane type structures



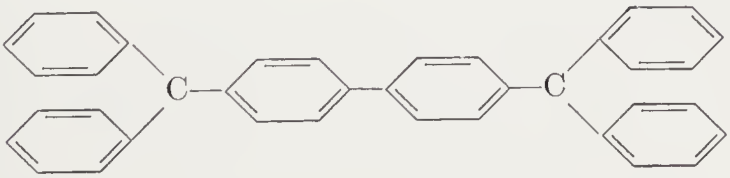
$$\begin{array}{c}\mathrm{H\,H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H\cdot B:B\cdot H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H\,H}\end{array}\ \text{etc.}\qquad \begin{array}{c}\mathrm{H\,H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H:B\cdot B\cdot H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H\,H}\end{array}\ \text{etc.}\qquad \begin{array}{c}\mathrm{H^{+}H^{-}}\\ \;\;\cdot\cdot\\ \mathrm{H:B:\;B:H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H\;\;H}\end{array}\ \text{etc,}\qquad \text{and}\qquad \begin{array}{c}\mathrm{H\,H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H:B\;\;B:H}\\ \cdot\cdot\;\cdot\cdot\\ \mathrm{H\,H}\end{array}$$

and the bridge type structures,

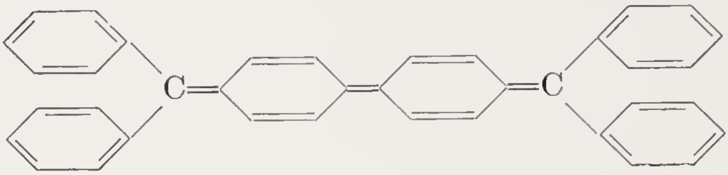


because in both cases, resonance requires pairing of the single electrons.

A more significant use of the magnetic conversion has however been recently developed by Schwab and Agliardi[83], who have used it to study the Chichibabin hydrocarbons. In particular, it had previously been found by the usual magnetic balance method that the compound

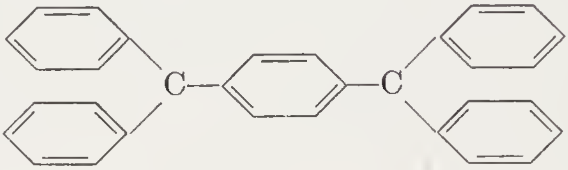


was diamagnetic[72]. This showed that either it existed in the quinonoid form



or that the odd electrons on the methyl carbons, though unpaired, had their spins opposed. In the latter case, the compound might, through the odd electrons being some distance apart, be able to catalyze conversions, behaving as if it had two centers of paramagnetism. It was in fact found that this hydrocarbon was an active catalyst for the conversion, the velocity corresponding to about 10 per cent of free radical form.

On the other hand, the similar compound,



again diamagnetic in a balance, is inactive in the conversion.

Further applications of the method are discussed by Schwab and Schwab-Agallidis[84].

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CHAPTER 2

THE CATALYTIC HYDROGENATION OF ETHYLENE

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This reaction was discovered by the two great French chemists, Sabatier and Senderens[64, 65], who favored the use of reduced nickel oxide as a catalyst. They considered the effect to involve "une combinaison directe et spécifique du nickel et de l'éthylène," and numerous investigations have been made in an attempt to put this statement on a more precise basis. The investigations of Langmuir[39] stimulated a good deal of kinetic work in the period 1920–1930, and the discovery by Farkas, Farkas and Rideal[54] that addition of deuterium to ethylene was accompanied by an atomic exchange

$$D_2 + C_2H_4 \rightleftharpoons C_2H_3D + HD$$

led to another outburst of activity. Finally, the investigations of Beeck and co-workers since 1940, using preadsorbed films of hydrogen and ethylene, bring us to the present day.

This chapter, then, deals with all the work concerned in the elucidation of the mechanism of hydrogen addition to ethylene. The greatest emphasis will be placed on kinetic studies, but it will also be essential to make some reference to the results of deuterium exchange. This latter subject is dealt with in Chapter 1, and so we shall not present it in detail. Also, the results on ethylene must be brought into relation with the results on other olefins and benzene.

In many ways ethylene is exceptional in its behavior, since it is easily decomposed on the catalyst surface, with a resultant poisoning effect absent with substrates such as benzene or cyclohexene. In fact, if one restricts the view to ethylene, one gets a somewhat one-sided picture of hydrogenation.

The Equilibrium

Reference to the equilibrium constant as a function of temperature[49], shows the forward reaction in

$$H_2 + C_2H_4 \rightleftharpoons C_2H_6$$

is favored for ordinary pressures up to 600°C, at which temperature at 1-atmosphere hydrogen pressure the yield of ethane is about 97 per cent. With larger olefins the back reaction sets in at lower temperatures (see, for example, Sabatier's[65] original observations, or the thermodynamic calculations of Taylor and Turkevich[77]). Dehydrogenation of cyclohexane to cyclohexene sets in at about 400°C and to benzene at about 200°C. Generally speaking, most of the kinetic studies on the hydrogenation of ethylene have been made in the range −80 to 200°C.

The Kinetics of Hydrogenation

A first discussion of the kinetic data may be made in terms of Langmuir kinetics[39, 70, 36], without reference to the finer details of the reaction path. A survey of the literature shows that three schemes are relevant to our considerations.

(1) Hydrogen and ethylene are reversibly adsorbed and complete for the same surface, regarded as uniform.

If p_H is the pressure of hydrogen and b_H its adsorption coefficient, and p_E and b_E similarly for ethylene, we have

$$v_H = k_H \cdot \frac{b_H p_H b_E p_E}{(1 + b_H p_H + b_E p_E)^2} \qquad \text{L (1a)}$$

where v_H indicates the velocity of hydrogenation and k_H its velocity constant.

Usually the surface is largely covered with ethylene and then $1 + b_H p_H \ll b_E p_E$ and

$$v_H = k_H \cdot \frac{b_H p_H}{b_E p_E} = k'_H \cdot \frac{p_H}{p_E} \qquad \text{L (1b)}$$

(2) Hydrogen and ethylene are reversibly adsorbed on two separate parts of the surface and interaction occurs at the "interline";

$$v_H = k_H \cdot \frac{b_H p_H}{(1 + b_H p_H)} \frac{b_E p_E}{(1 + b_E p_E)} \qquad \text{L (2a)}$$

and if the hydrogen adsorption is weak and the ethylene strong, $b_H p_H \ll 1 \ll b_E p_E$

$$v_H = k_H b_H p_H = k' p_H \qquad \text{L (2b)}$$

(3) Hydrogen is adsorbed on one set of sites which does not adsorb ethylene, while ethylene competes with hydrogen for a second set of sites.

$$v_H = k_H \cdot \frac{b_H p_H \cdot b_E p_E}{1 + b'_H p_H + b_E p_E} \qquad \text{L (3)}$$

The apparent activation energy is given by

$$E_{\text{app}} = RT^2 \frac{\partial \ln v_{\text{H}}}{\partial T}$$

Ethylene on Nickel

Most of the data have been obtained with this metal, in the earlier work on the reduced powder, and more recently on wires similarly activated by oxidation and reduction[57], and on the extremely active deposits formed by evaporation of a filament *in vacuo*[3]. Sabatier[65] noted that the metal in sheet form possessed only slight activity, but recent workers have obtained an active foil by heat treatment[72].

The authors concerned with this metal are Grassi[35], D. M. and W. G. Palmer[44], Rideal[53], Schuster[67] (nickel on charcoal), Zur Strassen[88] (nickel tape), Farkas, Farkas and Rideal[54], Toyama[79], Rideal and Tucholski[55] (wire), Schwab and Zorn[68, 69], Rienäcker and Bommer[52], Rideal and Twigg[57], Beeck, Smith and Wheeler[3], Beeck[4, 5], and Eucken[24, 25, 26]. Generally speaking, the reaction goes smoothly at 20°C and for a 1 hydrogen:1 ethylene mixture, if $p_{\text{H+E}}$ is the total pressure, $\log_{10} p_{\text{H+E}}$ is linear against time. An excess of ethylene, and especially pretreatment of the catalyst with ethylene, may give a decreased reaction velocity and, as was recently pointed out again by Schwab, the effect of excess ethylene is at least partly irreversible[71] and associated with a formation of poisoning polymerizates. The initial velocity v_{H} is proportional to $p_{\text{E}}^{0} p_{\text{H}}^{1}$, so long as excess ethylene is avoided, at temperatures up to 156°C[57]. Ethane added to the mixture acts as an inert diluent. These results were found in many of the investigations above, and especially in those by Rideal and Twigg, and Beeck, on which we place the greatest weight. Some authors[54, 55] have noted linear $p_{\text{H+E}}/t$ curves (zero order reaction), as first observed for solution hydrogenations by Armstrong and Hilditch[1], but they are not of frequent occurrence. One author only noted a negative order in p_{E}, in the range 0 to −78°C[79]. Most of these data, therefore, fit into Class L (2) kinetics.

Schwab and Zorn[68, 69] made a study of the "skeleton" catalysts, NiSi, NiSi_2, NiAl, NiAl_2, and found a complex order, the reaction following Eq. (3). Their interpretation was that the adsorbed amount of hydrogen was proportional to p_{H}, the suggested adsorption sites being just inside the metal, therefore not accessible to ethylene. They derived values of k_{H}, b_{E}, and b_{H}, by assuming $b'_{\text{H}} = b_{\text{H}}$.

As the temperature is raised the reaction accelerates, and in the neighborhood of room temperature the following values have been determined, 3.2 kcal/mole[53], 3.6[67], 4.6[55], 6.0[79], 8.2[57], and 10.7[4]. The last value, due to Beeck, is probably the most accurate since it was derived from a line, straight over the range −80 to 150°C. A value of Rienäcker's[52] of 5 kcal over 400 to 600°C may correspond to a much poisoned catalyst.

The log $v_H/\frac{1}{T}$ line often starts to fall off around 100°C[57], and the reaction velocity passes through a maximum, usually around 130 to 200°C, but a value of 60°C has been reported for the maximum by Zur Strassen[88] at low pressures. The last author, in fact, showed that the lower the partial pressure of ethylene, p_E, the lower the temperature optimum. Below the optimum he postulated a saturated layer of ethylene, and he supposed that the optimum was associated with desorption of ethylene. He wrote the apparent activation energy as

$$T < T_{\text{opt}} \; E_{\text{app}} = E_t - \lambda_H$$

$$T > T_{\text{opt}} \; E_{\text{app}} = E_t - \lambda_H - \lambda_E \,,$$

where E_t denotes a true activation energy for reaction of adjacently adsorbed molecules of ethylene and hydrogen, and λ_H and λ_E are the heats of adsorption of hydrogen and ethylene, respectively. He concluded from his data that $\lambda_H \sim 9$ kcal.

Schwab and Zorn[68, 69] examined the activation energy for their nickel skeleton contacts. These catalysts were porous, and reaction occurred in the pores. For the most active catalyst, as the temperature was raised the reaction velocity suddenly reached a constant value, limited by Knudsen diffusion of reactants into the pores. For the less active catalysts diffusion was adequate to maintain the surface reaction, and for these contacts E_{app} fell from 8.3 kcal at 100°C to 3.1 kcal at 180°C (a result closely similar to Twigg's values for nickel wire). The temperature optimum lay between 180 and 200°C. Assuming $b'_H = b_H$, Schwab and Zorn obtained temperature coefficients of k_t, b_H, b_E, hence

$$E_t = 18.7 \text{ kcal} \qquad \lambda_E = 13.7 \text{ kcal} \qquad \lambda_H = 12.5 \text{ kcal}.$$

Above the temperature optimum the reaction becomes second order, $v_H = k' p_H^1 p_E^1$, found by Grassi[35] at 200°C and Zur Strassen[88] at low pressures at 130°C.

Ethylene on Other Metals

There is some evidence for a negative order in ethylene, and therefore for competitive adsorption as exemplified in Class L (1) kinetics, for copper and platinum. Reduced copper oxide catalysts were investigated by Pease[46, 47], who found that $v_H = k p_H^1 p_E^{-1/2}$, very approximately, at 0°C, $v_H = k' p_H^1 p_E^0$ at 100°C; and $v_H = k' p_H^1 p_E^1$ at 200°C, with E_{app} falling from 13.2 kcal (0–100°C) to 10.8 kcal (150–200°C), and to 7.0 kcal (200–250°C). Constable[11] found that as the p_E/p_H ratio was increased the initial reaction velocity passed through a *maximum*, which was 18 per cent ethylene at 0°C, 42 per cent at 100°C, and 50 per cent at 200°C. Such results at first sight point to Class L (1) kinetics. Rienäcker and Bommer[52] found $E = 19.5$ kcal for a copper foil at 550 to 700°C. The value seems high for such a high temperature, and one either concludes that the catalysts were poisoned, or that reduced copper oxide is activated in some special way to give a lower E value, than is obtained with a foil.

A. and L. Farkas[30] used a platinized platinum foil, and found $p = p_0e^{-kt}$, a first order law, where p denotes the partial pressure of the gas not present in excess. This surely suggests L (1) kinetics, with the adsorption of ethylene not much stronger than that of hydrogen, i.e. $b_E \approx b_H$. The initial rate v_H increases as p_H increases, but increases as p_E decreases, at 0°C, again supporting the notion of competitive adsorption. The Arrhenius equation holds up to 150°C with $E = 10.0$ kcal, but above this temperature the reaction velocity falls off, as with nickel.

The apparent activation energy on a palladium catalyst has been reported as 10 kcal over -57 to 20°C[12].

O. Beeck[5] has briefly reported the results of a lengthy study of a range of metal catalysts, used in the form of evaporated films. He found, as for nickel, that $v_H = k'p_H^1p_E^0$, and a fall-off in activity by a factor 10^4 over the series Rh > Pd > Pt > Ni(110) > Ni(random) > Fe > Cr. In his earlier paper Beeck[3] laid stress on the five-fold larger activity of 110 oriented nickel over randomly oriented nickel. His first experiments merely demonstrated that the more active films possessed the 110 plane oriented to the backing[15], but later he used physical adsorption to demonstrate that they possessed an increased fraction of the total area as 110[6]. On all the above metals, $E_{app} = 10.7$ kcal, which would appear to be the best value for the metals concerned.

Beeck[5] stated that W and Ta films fall into a separate group of low activity, twenty times less than random nickel, but also with a low E_{app} of 2.4 kcal.

Beeck[4] makes the suggestion that the difference in activity of the transition metals resides in the "A factor" (frequency factor) of the Arrhenius equation.

Deuterogenation

The relative rates, v_H/v_D are: for copper at 0°C[48], 1.59; for nickel 1.5[55]; for platinum 1.2[30]; for iron 2.5 at 0°C, changing to 0.51 at 175°C[37]. For iron the optimum temperature for hydrogenation was 125°C, and for deuterogenation 150°C. Since we now know that the *exchange* reaction proceeds rapidly at higher temperatures, the exact significance of the results at 175°C is obscure. These effects are not very large (cf. the isotope effect found for double bond migration of butene-1[78]).

Stereochemistry of Hydrogenation

A. Farkas[32] summarized a number of experiments which favor the view that addition of hydrogen to triple or double bonds favors the "*cis*" isomer, although this may be thermodynamically less stable than *trans* addition. Linstead[40] *et al.* give a number of examples of cis addition of hydrogen to phenanthrene and diphenic acid derivatives on platinum black at room temperature. Reference should also be made to Weidlich[86]. Farkas's view was that *cis* addition necessarily implied addition of a hydrogen molecule or simultaneous addition of two atoms; but as pointed out by Polanyi and Greenhalgh addition of two hydrogen atoms successively, *via* the "half-hydrogenated state," will yield the same result[51].

Related Substrates

The kinetics of hydrogenation of benzene[51] and acetylene[73] are $p_{\mathrm{H}}^{1}p_{\mathrm{E}}^{0}$ (here p_{E} refers to benzene or acetylene). While the rates are much slower than for ethylene, the activation energies are not much different: acetylene on Ni, Pt, etc., 10.9 kcal[73], 6–7 kcal[5]; and benzene 7 kcal[51], 8.7 kcal[5], 7.4 kcal[74]. This emphasizes again that the frequency factor is important in determining the slow rate. The rate of hydrogenation on nickel decreases over ethylene > propylene > butene-2 > isobutene, but the apparent E also diminishes over the series, 8.2, 6.0, 3.3, 3.3 kcal[83]. Emmett and Gray[22c] found for an iron catalyst $E = 9.6$ kcal for ethylene, 7.4 for propylene, and 6.4 for butene-2. (These are corrected values since Emmett informs the author that his published E values should be multiplied by 2.303.) Schuster's results show the opposite trend of activation energy, and we regard diffusion as possibly playing a role with his catalyst, 1 per cent nickel on charcoal[67]. These last substituted ethylenes definitely give fractional orders, e.g., $v = k'p_{\mathrm{H}}^{1/2}p_{\mathrm{Bu}}^{1/2}$ where Bu signifies butene. Eucken[24, 25, 26] found that cyclohexene gave much less polymerization poisoning than ethylene on nickel, and $E_{\mathrm{app}} = 6$ kcal for hydrogenation.

Kinetic differences between acetylene, benzene and ethylene are more marked for the exchange reaction than for hydrogenation.

Summary of Above Results

Most of the evidence points to $v_{\mathrm{H}} = k'p_{\mathrm{H}}^{1}p_{\mathrm{E}}^{0}$ up to 100° or even higher, more especially for nickel, where many workers have obtained this result. This corresponds to L (2b) kinetics in general. However, a negative order in the ethylene pressure has been obtained for platinum and copper around 20°C, once even for nickel, and also for metallized silica gels[43b]. It is not clear how far in the latter case the irreversible poisoning effects which follow the formation of surface polymerizates have been eliminated, or how far the activity of the copper catalysts concerned may have been due to traces of other metals such as nickel, and further work is desirable because of the theoretical importance of distinguishing Class L (1) and Class L (2) kinetics. Class L (3) kinetics are really a development of Class L (1), and nickel-silicon contacts definitely fall into this class. The activation energy of 10.7 kcal (−80 to 100°C) falls off at higher temperatures, the reaction velocity passing through a maximum around 150 to 200°C, though possibly higher for copper. The effect of decreasing pressure suggests that the optimum temperature is associated with the desorption of ethylene. On this view for copper we should expect a lower temperature optimum than for nickel because of the weaker adsorption, so other factors may enter. At 200°C on transition metals $v = k' p_{\mathrm{H}}^{1} p_{\mathrm{E}}^{1}$ suggests that both gases were weakly adsorbed. The evidence is that the differences in activity over Rh to Cr are associated with "the *apparent* frequency factor." For benzene and acetylene, the kinetics and activation energies are very similar to those for ethylene, although the two hydrogenate much more slowly than ethylene, again emphasizing the frequency factor. Hydrogen usually adds (at least at low temperatures) to give *cis*-isomers.

Adsorbed Films

Hydrogen. Further development of the subject requires a consideration of modern knowledge of chemisorbed films. These stem from the researches of Irving Langmuir, who postulated a dissociation of hydrogen into atoms which were held by the free valencies of adjacent surface metal atoms.

$$H_2 + 2M \rightarrow 2M{-}H.$$

J. K. Roberts[62, 43] studied this process as it occurs on tungsten wire at room temperature. The gas was taken up instantaneously with negligible activation energy, and at saturation one H atom occupied one W site, calculating the W sites from the geometrical wire area times a roughness factor, 1.3. Figure 1 shows his results on the differential heat of adsorption, which fell from 45 kcal ($\theta = 0$) to 18 kcal per mole of hydrogen ($\theta = 1$). Beeck[3, 4, 7] has confirmed these results on a film of 10^4 times the area of Roberts' wire, and based his θ values on BET[22b] determinations with krypton. We have also indicated the results obtained by Frankenburg[34] on a tungsten powder, when the surface is probably partly poisoned[16], possibly by the 0.1 per cent silica initially present[7]. Trapnell[81] has further studied the hydrogen that is *reversibly* adsorbed on tungsten films in the neighborhood of $\theta = 1$. Rideal and Trapnell[60] base their area assignment on the assumption that irreversible saturation oxygen chemisorption is 1.08 atoms 0 per surface W atom (0.92 immobile atoms plus 0.08 molecules on the gaps). They obtain isosteric heats for hydrogen which fall as low as 2.4 kcal/mole at $\theta = 1.03$, i.e., only 3 atoms per cent in a second layer, or a nonstoichiometric monolayer. Trapnell would assign $\theta = 0.8$ to Beeck's lowest observed heat of 13 kcal (see Fig. 1).

We may summarize this discussion by saying that chemisorbed hydrogen is tightly bound on tungsten down to about $\theta = 0.8$ at least. Whether or not easily dissociable hydrogen goes into a stoichiometric primary monolayer, or into a nonstoichiometric primary monolayer[42] (the atoms moving from positions of equilibrium), or into a secondary monolayer is a matter which cannot be decided since none of the methods of surface area determination used can be accurate to better than 20 per cent. The contact potential of tightly bound hydrogen on tungsten is negative, but a positive value is to be associated with the weakly bound part, which Mignolet[42] believes points to the atoms entering a nonstoichiometrie primary layer.

On nickel films Beeck[4, 7] found that the heat fell from 31 kcal ($\theta = 0$) to 15 kcal ($\theta = 1$). For nickel-kieselguhr Schuit[66] found 24 to 9.6 kcal. For a reduced nickel powder Eucken and Hunsmann[23] found 22 kcal to 4 kcal. It may be that impurities tend to lower the curve in a more or less uniform fashion.

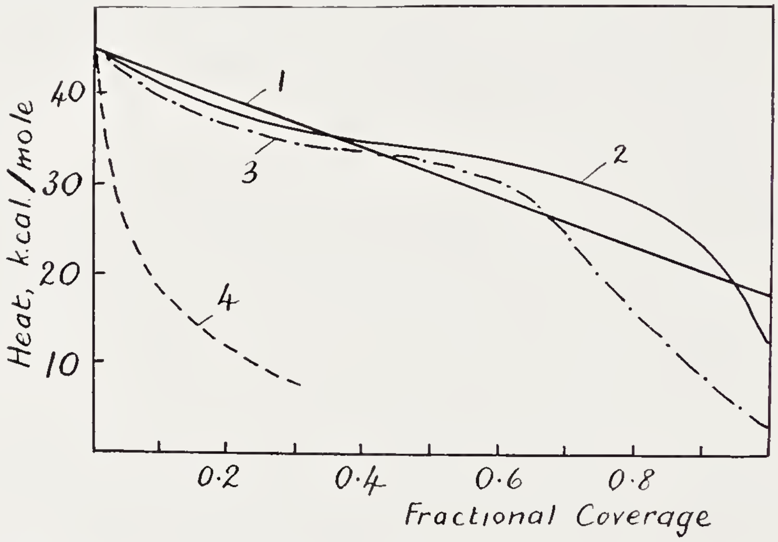

Figure 1. Heat of adsorption of hydrogen on tungsten according to (1) Roberts[43, 62], (2) Beeck[7], (3) Rideal and Trapnell[60] and (4) Frankenburg[34].

Ethylene. Our knowledge rests almost entirely on the work of Beeck. If ethylene is admitted to a nickel film very carefully so as never to build up an excess pressure, one ethylene molecule is adsorbed per four nickel sites; cf. the following ratios[3] for adsorbed amounts, at saturation,

CO	H_2	C_2H_4
1	½	¼

If an excess pressure of ethylene is admitted, ethane appears in the gas phase. These data Beeck explains by assuming that the initial act is a dissociation of ethylene into acetylene, occupying two sites, and two H atoms, each occupying one site. Excess ethylene immediately removes the H atoms to give ethane[2].

It had been established that admission of ethylene gas to a film of hydrogen preadsorbed on nickel gave an almost instantaneous formation of ethane[4].

Eventually all the hydrogen is removed and the adsorption ratio (relative to CO) for ethylene is ½, as found by Trapnell on tungsten films[82]. The surface is then completely covered by acetylenic complexes, so no hydrogen can be adsorbed, in agreement with earlier work on the poisoning of the parahydrogen conversion[58].

Beeck has examined the heats of adsorption of ethylene on Ni, Ta, W, Cr, Fe, Ni, and Rh[5, 6]. On nickel the heat falls from 58 kcal ($\theta = 0$) to a value of about 25 kcal at saturation, although the θ assignment here is uncertain owing to self hydrogenation.

The heat of adsorption at $\theta = 0$ for ethylene is generally about twice the value for hydrogen, and in both cases decreases over the series Ta > W,Cr > Fe > Ni > Rh. There is no evidence so far described that as $\theta \rightarrow 1$ the adsorption of ethylene can occur reversibly, which is surprising when one considers that ethylene is a product of acetylene hydrogenation on these metals. Beeck[5] has noted that the acetylenic residue produced from ethylene adsorption does not behave like acetylene itself. The completion of the process of self hydrogenation may yield a surface composition of $C_nH_{0.4n}$, and polymerization of the adsorbates. Presumably the eventual end product is graphite polymer on the surface, in accordance with the Sabatier observation[64, 65] that at 325°C on active nickel

$$3C_2H_4 = 2C + 2C_2H_6 .$$

Preadsorbed Ethylene and Gaseous Hydrogen

Beeck[5] has examined the slow reaction of gaseous hydrogen with preadsorbed ethylene, finding reaction rates and products identical for oriented and nonoriented films of nickel, 20 per cent of the adsorbed residues being removed in one hour at 23°C, the products being 10 per cent ethane and 90 per cent saturated C_4 polymers or higher*. On the other hand, rhodium reacts off 60 per cent adsorbate in one minute, the product being largely ethane. The effect of preadsorption of ethylene is to lower the initial rate of hydrogenation by only a few per cent on platinum and rhodium,

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* The product of a straight acetylene hydrogenation is ethylene, and so the process here is different. This difference may arise from the possibility that the reacting molecules in the stationary state of a straight hydrogenation are those with a low adsorption heat (in the stationary state the value of θ is near 1). In Beeck's experiment the chemisorbed ethylene is completely stripped off the surface by hydrogen.

60 per cent on nickel, 500 per cent on tungsten, and 1000 per cent on tantalum. In general, the higher the initial heat of chemisorption of ethylene on the metal, the greater the degree of dissociation into acetylenic residues and polymer, the greater the inhibition, and the longer the time required to clean the surface with hydrogen.

Reaction of Olefin with Chemisorbed Hydrogen

While the reaction of hydrogen with preadsorbed ethylene is very slow, at least on nickel, Beeck[5] found the reaction of ethylene with preadsorbed hydrogen to be very rapid. Eucken[25] has obtained the same results for cyclohexene and nickel.

Beeck has supposed that the reaction involves ethylene from a van der Waals layer, or gas phase, reacting with chemisorbed hydrogen. But, in the present author's opinion, it is not ruled out that the initial act is an ethylene *displacing* a hydrogen molecule from the surface and then reacting with two chemisorbed hydrogen atoms on neighboring sites.

The previous process, of hydrogen reacting with preadsorbed ethylene, might go the same way, but because of the greater heat of adsorption of ethylene, the initial act of a hydrogen molecule displacing an ethylene molecule would require an activation energy, and give a slow process.

The Theory of the Adsorbed Film

The contact potential of hydrogen on tungsten gives a dipole moment $\mu_{\theta=1}$, using the Helmholtz equation, of only -0.23 Debyes[9]. For hydrogen on nickel the value is -0.06 Debyes, for ethylene on nickel $+0.16$ Debyes[41]. These data, together with theoretical calculations for $\overline{W}\cdot\cdot H^+$, $\overline{W}\cdot\cdot H_2^+$, $W^+\cdot\cdot H^-$ [19], suggest that the adsorption link is essentially homopolar. It therefore seemed worth while to attempt a calculation of heats of adsorption, using Pauling's empirical equation for the bond energy[18]. Thus, in the case of hydrogen, for

$$H_2 + 2M \rightarrow 2(M—H)$$

we suppose that each surface metal atom possesses at least one free valency, of the transition octahedral metallic type[45] (d^2sp^3 or d^3sp^2). Thus we calculate the heat of adsorption for $\theta \rightarrow 0$ as

$$Q(\theta \rightarrow 0) = 2E(M—H) - E(H_2),$$

and obtain $E(M—H) = \frac{1}{2}\{E(M—M) + E(H—H)\} + 23.06(x_M - x_H)^2$.

$E(M—M)$ is taken as one-sixth of the heat of sublimation of the metal. The difference in electronegativities $x_M - x_H$ is equated to $\mu_{(\theta=0)}$, the dipole moment of the surface M—H bond, for the almost bare surface. In the revised version of the calculation[21] we obtain $\mu_{(\theta=1)}$ from the Helmholtz equation

$$\mu_{(\theta=1)} = \frac{V_{(\theta=1)}}{4\pi 300 c_s},$$

c_s being the average number of sites/cm^2 (the original paper used the factor 2π and thus included the electrical image in μ). $\mu_{(\theta=0)}$ is then obtained by Topping's formula

$$\mu_{(\theta=0)} = \mu_{(\theta=1)} \left\{1 + \frac{9\alpha}{a^3}\right\}$$

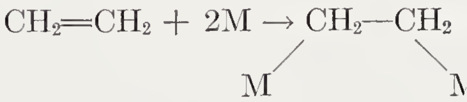
where a is the lattice constant, and α the polarizability of the surface bond which has to be estimated.

TABLE 1. HEATS OF CHEMISORPTION ($\theta = 0$) in kcal*/mole[21]

Gas	Metal					
	Ta	W	Cr	Fe	Ni	Rh
C_2H_4 (obs.)	138	102	102	68	58	50
C_2H_4 (calc.)	49	52	33	34	34	40
H_2 (obs.)	39	45	45	32	31	28
H_2 (calc.)	31	38	15	16	17	22
% *d*-character in hybrid bond	39	43	39	39.7	40	50

* The calculated values are derived for a lattice spacing $a_0 = 3$Å, whereas the values on pp. 23 to 30 of reference 21 in fact correspond to $a = 2$Å and not, as stated on page 23 of said reference, to 3Å.

The method has also been applied to calculate the heat of associative chemisorption of ethylene

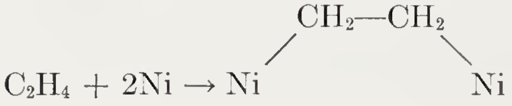


$$\mathrm{CH_2{=}CH_2 + 2M \rightarrow \underset{\displaystyle M}{CH_2}{-}\underset{\displaystyle M}{CH_2}}$$

It was necessary to assume for all metals the μ values established for nickel, since data are not available. Thus, all the variation in Table 1 arises solely from variations in $E(\mathrm{M{-}M})$, i.e., the sublimation energy of the metal. In a word, the higher the sublimation energy the higher the heat of adsorption, for this approximation, for both hydrogen and ethylene.

It is interesting that the deviations are largest for ethylene on those metals where we know most certainly that the primary adsorption is dissociative, with formation of acetylenic complexes, polymerization and the like. Beeck[5] suggested that the heat of adsorption correlated directly with the fraction of empty atomic *d*-orbitals, i.e., inversely with the percentage *d* in the hybrid bond. Beeck's correlation fails for W, while Eley's fails most conspicuously for Cr[20]. Beeck[5] suggested that tungsten films had a face-centered cubic structure, with a larger lattice constant and hence a smaller *d*-character for its bonding orbital. In this way he could reconcile tungsten with his theory, but the suggestion conflicts with the result that both film and wire give the same result, and the latter is certainly body-centered[20]. Recently tungsten films have been shown to be body-centered cubic by electron diffraction[36c]. The problem calls for further attention. However, the method of calculation has proved useful in several instances (cf. also the calculations of Winfield[87]).

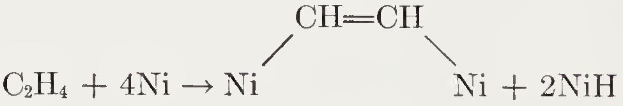
It is interesting to calculate the heats for various models of ethylene chemisorption, as below.

(1) 

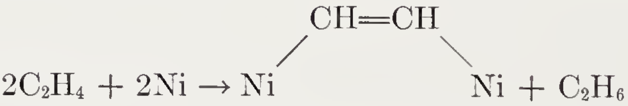
$$C_2H_4 + 2Ni \rightarrow Ni{-}CH_2{-}CH_2{-}Ni \qquad Q_{(\theta=0)} = 34\ \text{kcal}$$

(2) $C_2H_4 + Ni \rightarrow Ni{-}CH{=}CH_2 + \frac{1}{2}H_2$ $\qquad Q_{(\theta=0)} = 3$

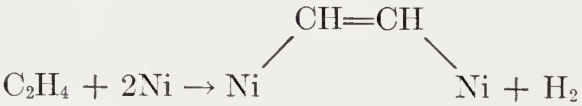
(3) $C_2H_4 + Ni \rightarrow Ni{=}CH{-}CH_3$ $\qquad Q_{(\theta=0)} = 26$

(4) 

$$C_2H_4 + 4Ni \rightarrow Ni{-}CH{=}CH{-}Ni + 2NiH \qquad Q_{(\theta=0)} = 23$$

(5) 

$$2C_2H_4 + 2Ni \rightarrow Ni{-}CH{=}CH{-}Ni + C_2H_6 \qquad Q_{(\theta=0)} = 17$$

(6) 

$$C_2H_4 + 2Ni \rightarrow Ni{-}CH{=}CH{-}Ni + H_2 \qquad Q_{(\theta=0)} = 6$$

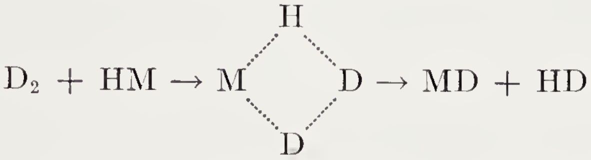
Model (1) is the associative model, Model (4) the Beeck dissociative model. Both give high heats. The onset of self-hydrogenation (Eq. 5) gives a low heat at $\theta = 0$. Model (2) is the Farkas dissociative model, which would seem to be energetically unfavorable at $\theta \rightarrow 0$. However, as $\theta \rightarrow 1$ we expect all the above heats to decrease by about 60 per cent. The single-site mechanisms, either (2) or (3), will tend to be favored, since the number of available double sites will be very small at high coverages. Model (3) has not so far been considered, but these calculations would suggest it as a favored mechanism as $\theta \rightarrow 1$.

The Parahydrogen Conversion

Work on this reaction and the related $H_2 + D_2$ reaction has been reviewed by A. Farkas[28] (up to 1935) and Eley[16] (up to 1948), and the subject is treated by Trapnell in the present volume. Here we briefly summarize the present author's view on this problem. Two mechanisms have been advanced for the chemical conversion (we may neglect the magnetic conversion at this time). The first, due to Bonhoeffer and Farkas[8], supposes a reversible dissociation of hydrogen molecules to give atoms in a loosely chemisorbed layer.

$$p\text{-H}_2 + 2\text{M} \rightarrow 2\text{MH} \rightarrow o\text{-H}_2 + 2\text{M} \tag{1}$$

The second, a three-atom mechanism suggested by Rideal[56] and developed by Eley[14], supposes an interchange between a molecule in a van der Waals layer and an atom in the underlying chemisorbed film.



$$\text{D}_2 + \text{HM} \rightarrow \text{M}\begin{array}{c}\text{H}\\ \diamond \\ \text{D}\end{array}\text{D} \rightarrow \text{MD} + \text{HD} \tag{2}$$

The Bonhoeffer-Farkas mechanism is almost certainly operative at higher temperatures, e.g., 300°C on transition metals. Until recently, following Roberts[63], it had been supposed that at lower temperatures, e.g., -180 to 20°C, the atomic layer was too firmly bound to take part in the recombination step of (1). Trapnell and Rideal[59, 81], however, have considered that the loosely bound hydrogen which is adsorbed on tungsten with a heat falling from 15 to 3 kcal enters the primary layer. They have considered that the process is fast enough to give the observed parahydrogen conversion, calculating the rate of dissociation into the almost full monolayer by the Peierls equation. An approximate form of this is

$$k_{\text{M}} = \alpha \frac{p}{\sqrt{2\pi mkT}} (1 - \theta)^2 e^{-V/kT}$$

where V is the repulsion potential between next neighbors. Trapnell[81] considers that $V \sim 0$ to 400 cals/mole, from a consideration of the electrostatic repulsion between the adsorbed dipoles. This value gives a calculated rate of the right order. Couper and Eley[22] have considered it more appropriate to take $V = 4{,}800$ cal/mole, which is required to fit the isotherm and heat of adsorption data, and this brings the calculated rate down to 10^6 times less than the observed rate of conversion. The effect of adsorbed nitrogen is not easily explained on the hypothesis that the loosely adsorbed hydrogen enters the chemisorbed layer and gives the conversion. Thus a nitrogen film on tungsten slows down the conversion 600-fold at -78°C, but leaves the *amount* of loosely adsorbed hydrogen apparently unaffected[22]. Trapnell[82] considers the effect of the nitrogen film is to lower the condensation coefficient α, and hence the *rate* of chemisorption, which, however, is still too fast to be measured. Unless a similar restriction is imposed on the rate of desorption, however, one would also expect a measurable change in the amount adsorbed.

Further work is in progress on the controversial points of mechanism, and in the present chapter the interchange mechanism (2) is taken as the operative process on the pure transition metals, at room temperature and below. The amount of tightly bound surface hydrogen may be determined by exchange with a low pressure of deuterium gas, and there is some evidence suggesting that the action of a poison is to cut down both the amount of strongly bound hydrogen, and the rate of conversion[14, 31b]. We therefore regard the poison as displacing hydrogen from the chemisorbed layer, but not necessarily affecting the loosely adsorbed hydrogen if this is in a second layer. However, the rate of conversion is not simply proportional to the amount of strongly bound hydrogen. Experiments[58] on oxygen as a poison for the conversion, in which the surface concentration of oxygen was measured by contact potential, led to the idea that an oxygen atom strongly lowered the reactivity of adjacently chemisorbed hydrogen. This would also seem to be so for nitrogen. Tungsten saturated with a 46 per cent nitrogen film will still chemisorb 30 per cent hydrogen, yet the conversion is lowered 600-fold[82]. On mechanism (2) the pressure dependency of the conversion depends on the concentration of molecular hydrogen in the van der Waals layer. On tungsten at −100°C the fractional order of the reaction indicates that this coverage must be 50 per cent or more, which is difficult to reconcile[33, 80] with a maximum value of 2 kcal for the heat of van der Waals adsorption of hydrogen. It is necessary to postulate the action of some additional force of the magnitude of the usual dispersion force, or else to assume a favorable entropy of adsorption.

Experiments[19] on a range of Pd-Au alloys has shown that the presence of some empty atomic *d*-orbitals ("holes" in the *d*-band) are essential for an efficient conversion catalyst. This criterion is supported by further unpublished work with other transition metals. It has been suggested that, in terms of mechanism (2), the initial M—H bond involves the d^2sp^3 orbital of the metal, while the additional orbital necessary to bond the activated complex is the atomic *d*-orbital of the metal.

The problems raised by promoted iron catalysts are brought out in the results of Kummer and Emmett[37b]. Only hydrogen chemisorbed at −195°C will exchange with deuterium, and hydrogen chemisorbed at higher temperatures will not (we refer here to the singly promoted catalyst). However the nature of much of the surface is in doubt, and on a basis of unit area these catalysts seem much less active than tungsten films. While these experiments allow us to infer that there are forms of chemisorbed hydrogen that will not exchange with deuterium at low temperatures, it is also quite possible that this hydrogen is associated with those parts of the surface covered by the promoter, and that no direct comparison with pure transition metals is possible, at the present stage.

Effect of Olefin on the Parahydrogen Conversion

The parahydrogen conversion, or the $H_2 + D_2$ reaction which has the same mechanism, is strongly[54], or even completely[57, 85] inhibited on nickel by an equal pressure of ethylene. On platinum ethylene inhibits the conversion by a factor 6[30]. The propenes and butenes, on the other hand, give very little inhibition on nickel[61], and a similar result is obtained for benzene vapor[51]. Acetylene completely inhibits the parahydrogen conversion on platinum[31]. One has the impression that the inhibiting effect decreases according to the series

$$\text{acetylene} > \text{ethylene} > \text{butenes} > \text{benzene}.$$

It is possible that this is the order of decreasing energy of adsorption, although quantitative measurements are not available. It is certain that the larger molecules cannot pack so well, and therefore spaces are left which may chemisorb hydrogen and thus give the conversion[61]. In addition, it is probably the order of decreasing tendency to give polymers blocking the surface. A careful comparison of rates of hydrogenation has not been made, but it would seem that, roughly, the rates decrease over the series

$$\text{ethylene} > \text{propene} > \text{butene} > \text{acetylene} > \text{benzene},$$

which does not correspond to the above series. In a mixture of ethylene and acetylene the acetylene is preferentially adsorbed on the catalyst and hydrogenated first[31]. Only when all the acetylene has been converted to ethylene does the latter gas start to add hydrogen.

Related Reactions

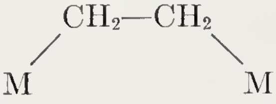
The reactions related to hydrogenation and investigated from the viewpoint of hydrogenation mechanisms are[50]:

1. Deuterium—ethylene exchange.
2. Ethylene—ethylene d_4 exchange.
3. Double-bond migration.
4. *Cis-trans* isomerization.

It is not the province of this Chapter to review this work in detail, but some reference must be made to it, since it is useless to advance hydrogenation mechanisms which conflict with exchange data.

Very briefly, with deuterium and ethylene on nickel[54, 57] the exchange is *slower* than hydrogenation below 60°C and faster above 60°C. The kinetics are identical, $v = kp_{H_2}^{1}p_E^{0}$, but the activation energy for exchange is much higher than for hydrogenation, $E_{ex} = 18.6$ kcal, falling off with an increase in temperature in the same way as for hydrogenation. A somewhat similar result holds for platinum[30]. For gaseous benzene on platinum[29, 51] and nickel[51], on the other hand $E_{ex} \sim E_H \sim 7$ kcal, but the kinetics may be different for hydrogenation and exchange (the two laboratories concerned obtained different results).

The associative theory links hydrogenation and exchange *via* the half hydrogenated state (underlined), the ethylene being adsorbed by opening of the double bond,



$M{-}CH_2{-}CH_2{-}M$, i.e., $*CH_2CH_2*$

$$H* + H* + *C_2H_4* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H* + \underline{*C_2H_5} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2H_6 \text{ (Polanyi}^{50}\text{)}.$$

or

$$H_2 + *C_2H_4* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H* + \underline{*C_2H_5} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_2H_6 \text{ (Twigg-Rideal}^{57}\text{)}$$

where k_{-1} in the presence of deuterium may lead to an exchange of atoms.

The *dissociative* theory regards the ethylene as adsorbed by rupture of a C—H bond,

$$C_2H_4 \rightleftharpoons C_2H_3* + H* \text{ (Farkas}^{32}\text{)}$$

$$D_2 \rightleftharpoons D* + D*$$

exchange occurring by recombination of $C_2H_3* + D*$ to give C_2H_3D.

There has been much controversy about the two modes of chemisorption of ethylene and the two mechanisms. The *dissociative* mechanism[32] regards the hydrogenation reaction as something quite separate from the exchange reaction, viz., simultaneous addition of 2H* to a (presumably physically) adsorbed ethylene,

$$C_2H_4 + H* + H* \rightarrow C_2H_6\,.$$

All authors regard ethane as not chemisorbed to any extent.

The present author's view is still substantially in accordance with the Twigg-Rideal view (cf. his earlier reviews[16, 17]). While the known exchange with saturated hydrocarbons must require some dissociation,

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n+1}* + H*$$

and therefore by analogy

$$C_2H_4 \rightleftharpoons C_2H_3* + H*$$

the very low rate of exchange of saturated hydrocarbons[75] with respect to ethylene[76] and the zero[10] or *relatively* low[13] rate of exchange between ethylene and ethylene-d_4

$$C_2H_4 + C_2D_4 \rightleftharpoons C_2H_3D + C_2HD_3\text{ , etc.}$$

suggest that the concentration of $C_2H_3{}^*$ radicals is *very low*. Here one may go back to early experiments which show that on nickel the D_2-C_6H_6 exchange is 10^7 times faster than the exchange of ethylene with partially deuterated benzene[50]. It has been objected that the interethylene exchange must be slow because of a low concentration of chemisorbed H* in the absence of gaseous hydrogen[32]. For ethylene-nickel the parahydrogen conversion shows a low concentration of H* even in the *presence* of gaseous hydrogen.*

We shall not go into questions of *cis-trans* isomerization and double-bond migration here, but note merely that these reactions have been discussed in terms of both associative and dissociative mechanisms.

The present author's view is that *in the reaction zone*, ethylene is probably predominantly adsorbed as $^*CH_2CH_2{}^*$, with opening of the double bond, rather than as $C_2H_3{}^*$, with fission of a C—H bond, although at no point has a really critical experiment been made. One must emphasize "in the reaction zone," since for nickel and some other metals Beeck has shown that most of the surface is covered by acetylenic and polymerized acetylenic radicals. We thus come to the following point of view for nickel. The admission of pure ethylene to a clean nickel surface gives $^*CH{=}CH^*$ complexes and chemisorbed H*, and as the surface fills up the heat of adsorption falls. In a second process pairs of chemisorbed H* atoms are removed by gaseous ethylene (self-hydrogenation), leaving pairs of empty sites. These may chemisorb ethylene by one or several of the mechanisms considered in the theoretical discussion, but possibly predominantly by the associative mechanism, $^*CH_2CH_2{}^*$. There is a very small amount of $C_2H_3{}^*$, which may arise from an equilibrium (Douglas and Rabinowitch[13]), which may well be established as $\theta \rightarrow 1$,

$$^*CH_2 \cdot {}^*CH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2{}^*CH + H^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CH^*CH^* + 2H^*$$

k_1 , k_2 and the reverse steps may be slow, but in any case the problem may be one of stationary states, involving further reactions. The point we

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* Bond, Sheridan and Whiffen [*Trans. Faraday Soc.*, **48,** 715 (1952)] have found an exchange of atoms between deuteroacetylene and acetylene, but none between deuteroethylene and ethylene, on nickel at 6°C. They postulate a reaction between chemisorbed acetylene and physically adsorbed acetylene or ethylene, which can only occur appreciably in the first case when the C—H link is sufficiently polar.

are making is that, as surface coverage increases and the heat of adsorption falls, owing to repulsive forces[62] and denudation of surface levels[17], we may expect the mode of chemisorption to change, both on ground of entropy (Beeck—number of available sites[5]) and energy.

It may well be that the situation is simpler for cases where the evidence suggests that dissociative adsorption is small, e.g., benzene-nickel, or ethylene-rhodium. The evidence available does not conflict with the theory that a large fraction of the surface is covered by substrate held by associative chemisorption.

Turkevich, Schissler and Irsa[83] have examined the interaction of deuterium and ethylene, C_2H_4, on a nickel catalyst at 90°C, where exchange proceeds more rapidly than by hydrogenation. In spite of pretreating the catalyst with deuterium, they find that the first ethane evolved is C_2H_6, and conclude that the hydrogen added must have come from another C_2H_4 molecule. The C_2H_6 concentration levels off at 30 per cent hydrogenation and is eventually surpassed by C_2H_5D, $C_2H_4D_2$, etc. In the exchange reaction C_2H_3D is the predominant product at first but $C_2H_2D_2$ and the others appear later, eventually all species being consumed by hydrogenation.

Twigg[85] has hydrogenated ethylene on nickel at −78°C, where exchange is negligible, with

(a) a mixture, 50 per cent H_2, 50 per cent D_2;
(b) an equilibrium mixture, H_2, D_2 and HD.

The products of both (a) and (b) have indistinguishable infrared spectra, which support the notion that hydrogenation occurs by the successive and independent addition of two chemisorbed H* atoms. Otherwise, if the mechanism were

$$H_2 + {}^*CH_2\text{—}{}^*CH_2 \rightarrow C_2H_6\,,$$

we should expect C_2H_6 and C_2D_6 only from (a), but in addition C_2H_5D from (b).

It is still, of course, possible that two H* atoms are added simultaneously by

$$H^* + H^* + C_2H_4 \rightarrow C_2H_6\,.$$

Wagner[85b] *et al.* have reacted *cis*-2-butene with D_2 on Ni at −78°C, where no exchange occurs between olefin or paraffin and D_2. They find a random distribution of D in the product of average composition $C_4H_8D_2$. They conclude that hydrogen transfer between two adjacent adsorbed species gives rise to butane plus an adsorbed "free radical," and that "diffusion" of the free radical over the surface gives rise to an equilibrium distribution of D in the adsorbed molecules. This process would give rise to the light ethane observed by Turkevich *et al.*[83] (cf. also Markham, Wall, and Laidler[38b]).

Quantitative Theories

Langmuir Adsorption. Laidler[38] and Eyring, Colburn and Zwolinski[27] apply the transition state theory to a calculation of the rate of reaction of hydrogen and ethylene adsorbed on adjacent sites on a uniform surface, i.e., the mechanism L(1a). We may consider the Laidler formulation, which is similar to the other treatment. For the equation

$$v = \frac{k_H b_H p_H b_E p_E}{(1 + b_E p_E)^2},$$

which is L(1a) with $b_H p_H \ll b_E p_E$, the maximum rate corresponds to a p_E value of $1/b_E$. Laidler then writes down a value for k_H in terms of activated complex theory.

$$v = \frac{sLp_H p_E}{(1 + b_E p_E)^2} \cdot \frac{kT}{h} \left(\frac{f_H f_E}{F_H F_E f_s^2} \right) \cdot \frac{f\ddagger}{f_{HE}} \cdot e^{\frac{-(\epsilon_0 - \epsilon_H - \epsilon_E)}{kT}}$$

L = number of sites/cm².
s = number of nearest neighbors to a site.
$f\ddagger$ = partition function of activated complex (partly desorbed ethane molecule).
$f_H f_E$ = partition function of adsorbed hydrogen and ethylene, respectively.
$F_H F_E$ = partition function of gaseous hydrogen and ethylene, respectively.
f_{HE} = partition function for an adsorbed pair of molecules.
ϵ_H, ϵ_E = energy of adsorption of hydrogen and ethylene, respectively, at 0°K.
ϵ_0 = energy of activation for reaction of adjacently adsorbed ethylene and hydrogen at 0°K.

Putting, for $v_{\max}$, $p_E = \frac{1}{b_E}$ when $b_E = \frac{f_E}{F_E f_s} \cdot e^{\epsilon_E/kT}$,

$$v_{\max} = \frac{sLp_H}{4} \cdot \frac{kT}{h} \cdot \frac{f_H}{F_H} \cdot \frac{f\ddagger}{f_s f_{HE}} \cdot e^{-((\epsilon_0 - \epsilon_H)/kT)}$$

Using explicit values for the partition functions a value of 10^{-6} may be calculated for the steric factor of ethylene hydrogenation on nickel. An experimental value of 10^{-6} was calculated by Beeck[4] from his results, and 4×10^{-5} by Eucken[26]. Thus the observed low steric factor may arise essentially from the loss of entropy on forming the adsorbed activated complex, and not necessarily from a small fraction of active surface, as postulated by Beeck, and this is probably the most useful result of this theory.

However, it is not possible to distinguish certain other mechanisms, e.g., gaseous ethylene plus adsorbed hydrogen, on the basis of this calculation.

Laidler also showed that at constant p_H and p_E one would expect as the temperature was raised that the activation energy would fall from $\epsilon_0 - \epsilon_H$ to $\epsilon_0 - \epsilon_E - \epsilon_H$. This is essentially the original Zur Strassen argument. This particular mechanism definitely requires that, as the ethylene pressure is increased, the hydrogenation velocity pass through a maximum and then begin to decrease. It is very doubtful if this behavior has ever been found for nickel. It may well be the state of affairs for copper*. Schwab's opinion is that when the hydrogenation velocity has been observed to decrease at high ethylene pressures, the process is largely due to irreversible effects of surface poisoning[71]. He has also noted that transition state calculations can be properly carried out only for cases where the extent of the active surface is known. To this we might add the comment that the whole kinetic situation is probably more complex than the idealized situation here, but that the result concerning the steric factor is a generally valuable one.

The Half-Hydrogenated State

There have been three treatments,† these will now be considered, in turn.

Polanyi and Greenhalgh Treatment[51]. This calculates the mechanism

$$*CH_2{-}*CH_2 + H* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{x}{*CH_2{-}CH_3} + H* \xrightarrow{k_2} CH_3CH_3$$

It assumes ideal adsorption of hydrogen and ethylene on a uniform surface and writes down the stationary state equation for the concentration of the intermediate species$*CH_2{-}CH_3$ (called x, for short). The adsorption assumptions are unrealistic for ethylene, but the treatment gives a useful discussion of the various effects of hydrogen pressure on hydrogenation and exchange with benzene.

Balandin Treatment[2]. This follows the kinetics of the Polanyi-Greenhalgh equation above, in addition allowing for k_{-2} (dehydrogenation). It

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* Ipatieff[36b] and others have attributed the activity of copper catalysts to the presence of nickel impurities, and as normally prepared the catalyst may therefore have a complex surface structure.

† J. Horiuti, of the Research Institute for Catalysis, Hokkaido University, Sapporo, Japan, has given an elaborate statistical mechanical theory of the hydrogenation of ethylene in articles entitled "Statistical Mechanical Research on the Heterogeneous Reaction," (Abstract), Parts I to IV, in the Journal *Catalyst* (reprint not dated).

assumes Langmuir adsorption of hydrogen on one set of sites (weak adsorption) and of ethylene on a second set of sites (strong adsorption). Presumably reaction occurs by a kind of adlineation (Schwab and Pietsch)[70] mechanism. The situation for hydrogenation is very similar to mechanism L (2b), and indeed, writing down the stationary state equation for the concentration of x, gives a reaction first order in hydrogen and zero order in ethylene, $v = k' p_{\mathrm{H}}^{1} p_{\mathrm{E}}^{0}$. This is so far satisfactory, but the rate of exchange, which is

$$v_{\mathrm{ex}} = k_{-1}\theta_x$$

where θ_x is the fraction of surface covered by —C_2H_5 radicals, comes out as proportional to $p_{\mathrm{H}}^{1/2}$. This may possibly be correct for benzene, but is certainly not so for ethylene-nickel.

Twigg Treatment[85]. Twigg supposes that the chemisorption of hydrogen or deuterium on ethylene-nickel can only occur by reaction with chemisorbed ethylene. This accords with the known poisoning of the parahydrogen conversion by ethylene,

$$\mathrm{C_2H_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\theta_{\mathrm{E}}}{\mathrm{{*}C_2H_4{*}}}$$

$$\mathrm{{*}C_2H_4{*}} + \mathrm{H_2} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\theta_x}{\mathrm{{*}CH_2CH_3}} + \underset{\theta_{\mathrm{H}}}{\mathrm{H{*}}} \xrightarrow{k_3} \mathrm{CH_3CH_3}$$

$$\mathrm{{*}CH_2CH_2{*}} + \mathrm{H{*}} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{{*}CH_2CH_3}$$

Reactions k_4 and k_{-4} are supposed to be very rapid, and this reaction was postulated[57, 84] to explain the fact that the hydrogen leaving the catalyst in the early stages of exchange between ethylene and deuterium is 80 per cent H_2. It will also (Twigg, private communication) lead to a random distribution of D atoms among the adsorbed species $*CH_2CH_2*$, H*, and $*CH_2CH_3$, as required by the experiments of Wagner *et al.*,[85b] and to an initial production of C_2H_6 on the addition of deuterium to ethylene, as found by Turkevich *et al.*[83]

Thus, suppose a deuterium molecule reacts with chemisorbed ethylene to give a $*CH_2CH_2D$ radical plus D* atom. The very rapid reaction 4 will immediately give a random distribution of D between the three chemisorbed species $*CH_2CH_2*$, $*CH_2CH_3$, and H*, and since there is so much more ethylene than deuterium on the catalyst the chances of D atoms in reacting $^*CH_2CH_3$ radicals and H* atoms will be small and the initial evolution of light ethane in the hydrogenation, and light hydrogen from the exchange reaction, very probable.

Steady state equations yield stationary values of θ_E, θ_x, and θ_H, the fractions of catalyst surface covered with the species indicated in the subscript, and hence the following expressions for velocity of hydrogenation and exchange:

$$v_H = k_3\theta_x\theta_H = \frac{k_2k_3}{k_{-2} + k_3}\cdot p_H\cdot\theta_E$$

and

$$v_E = k_{-2}\theta_x\theta_H = \frac{k_2k_{-2}}{k_{-2} + k_3}\cdot p_H\cdot\theta_E$$

These equations account for most of the ethylene-nickel data. Thus v_H and v_E have the same kinetic order (since $\theta_E \sim 1$, zero order in ethylene). Since $v_E/v_H = k_{-2}/k_3$, we expect a constant difference of activation energy of $E_{-2} - E_3$ over the entire temperature range, as found. Both activation energies may be shown to decline by a term $E_{-2} - E_3$ as the temperature is raised. Twigg's theory is that this term will be mainly responsible for the fall-off in apparent activation energy starting at 90°C, since in his view desorption of ethylene sets in only at 150°C. However, Beeck[4] has given the apparent activation energy as constant over $-80°C$ to $+150°C$, so there is some contradiction here. Twigg derives values of activation energy for individual steps,

$$E_2 = 11 \text{ kcal}$$

$$E_{-2} = 18\text{–}22 \text{ kcal}$$

$$E_3 = 9\text{–}13 \text{ kcal}$$

The method cannot be applied to the butenes, where direct chemisorption of hydrogen is occurring, i.e., $H_2 \rightleftharpoons 2H^*$.

This is the most satisfactory treatment of the ethylene-nickel system published to date. If we are to reconcile Twigg's view with Beeck's experiments we must postulate that the Twigg mechanism is occurring on a small fraction of the total surface which remains constant. In other words, that part of the surface covered by acetylenic complexes or polymers remains a constant independent of gas pressure and temperature. This assumption is different from that made by Beeck (see p. 71). However, it may be true, since the clean-up reaction of the poisoned surface with hydrogen, for nickel, requires hours and is apparently much slower than the ordinary hydrogenation reaction.

Beeck's Theory[4, 5]. This postulates that the metal surface is largely covered, to a fraction θ_A, by adsorbed acetylenic complexes only slowly removed by reaction with chemisorbed hydrogen which is adsorbed on the surface not covered by ethylene. Hydrogenation occurs by collision between ethylene from the gas phase and chemisorbed hydrogen, so

$$v_H = kp_E\theta_H .$$

Beeck now assumes that $\theta_H \sim p_H/p_E$, justifying this on a model of Langmuir's competitive adsorption, whence

$$v_H = k'p_H \frac{p_E}{p_E} = k'p_H .$$

The apparent activation energy of 10.7 kcal Beeck identifies with the activation energy of the clean-up reaction of chemisorbed hydrogen plus adsorbed acetylenic complex[5]. For tungsten and tantalum Beeck[5] believes that the poisoning action proceeds to the stage where four adjacent sites are no longer available to form acetylenic complexes. "Under these conditions the surface available becomes constant and the rate of removal of adsorbed ethylene is no longer rate-determining. The rate is now determined by the fast reaction of adsorbed hydrogen with ethylene from the gas phase. The low activation energy of the fast reaction should therefore prevail."

Let us follow out more exactly Beeck's statement of mechanism.

Acetylenic complexes are formed by reaction of ethylene with four bare sites (k_1) and removed by reaction with four atoms of chemisorbed hydrogen to give ethane (k_2). We neglect the formation of polymers, for simplicity.

$$\frac{d\theta_A}{dt} = k_1p_E(1 - \theta_A - \theta_H)^4 - k_2\theta_A\theta_H^4 = 0.$$

Since we may always assume θ_A is approaching unity, this gives

$$k_1p_E(1 - \theta_A - \theta_H)^4 \sim k_2\theta_H^4 .$$

Chemisorbed hydrogen is formed by dissociative adsorption of ethylene (k_1), by dissociation of hydrogen on two bare sites (k_3), and lost 2 molecules at a time by k_2, by reaction with ethylene from the gas phase (k_4) and by recombination and evaporation (k_5).

$$\frac{d\theta_H}{dt} = k_1p_E(1 - \theta_A - \theta_H)^4 + k_3p_H(1 - \theta_A - \theta_H)^2 - 2k_2\theta_A\theta_H^4 - k_4\theta_H^2p_E - k_5\theta_H^2 = 0.$$

Substituting for $(1 - \theta_A - \theta_H)^4$, one obtains, since, $\theta_A \sim 1$,

$$-k_2\theta_H^4 = \theta_H^2\left(k_4p_E + k_5 - \left(\frac{k_2k_3^2}{k_1}\right)^{1/2}\frac{p_H}{p_E^{1/2}}\right)$$

$$\therefore\ \theta_H^2 = \frac{1}{k_2}\left\{\left(\frac{k_2k_3^2}{k_1}\right)^{1/2}\frac{p_H}{p_E^{1/2}} - k_4p_E - k_5\right\}$$

and

$$\frac{d[C_2H_6]}{dt} = k_4p_E\theta_H^2$$

$$= k_4\left\{\left(\frac{k_3^2}{k_1k_2}\right)^{1/2}p_Hp_E^{1/2} - \frac{k_4}{k_2}\cdot p_E^2 - \frac{k_5}{k_2}\cdot p_E\right\}$$

The second and third terms are not expected to be negligible, and it does not seem that this equation can be put into the right form to explain the experimental results. In addition, the theory can lead only to an exchange reaction if we assume that in the stationary state, the clean up reaction does not give ethane ($k_2\theta_A\theta_H^4$), but rather ethylene ($k_2\theta_A\theta_H^2$). The reported speed of this reaction is, however, much too slow to account for the observed exchange.

The parahydrogen conversion on nickel and tungsten is completely inhibited by ethylene, and theories that postulate the presence of appreciable quantities of chemisorbed hydrogen, which would give a conversion reaction, are probably ruled out on these grounds. However, the conversion does go to some extent on platinum in the presence of ethylene. It has been mentioned that the observed kinetic order for hydrogenation on platinum may also point to a weaker adsorption of ethylene in the reaction zone.

The Energy Balance

Beeck[4] originally based his argument against the reaction of adjacently adsorbed ethylene and hydrogen on a consideration of the lack of energy balance for the postulated reaction. In fact, if one uses the appropriate values for the heats of adsorption (i.e., at $\theta \to 1$, not $\theta \to 0$), a good energy balance may be obtained[17]. In Figure 2 Q_E and Q_{H_2} denote the heats of chemisorption of ethylene and hydrogen into the almost full surface. E_G denotes activation energy of the hydrogenation in the gas phase, and E_s the *minimum* activation energy on the surface, which we equate to the heat of reaction on the surface. q denotes the heat of reaction of ethylene plus hydrogen to give ethane, 32.5 kcal/mole. We assume as a rough approximation that the heat of adsorption of ethane is zero, since this gas is only weakly adsorbed on the catalyst. The condition for an energy balance for the postulated reaction of adjacently chemisorbed molecules is that

$$Q_E + Q_{H_2} = q + E_s = 32.5 + E_s .$$

Since $Q_E \sim 25$ kcal/mole, $Q_{H_2} \sim 15$ kcal/mole, according to Beeck's calorimetric work, for an energy balance E_s is ~ 7.5 kcal. The value found is usually about this figure.

Before leaving Figure 2 there are two points which may require emphasis. The first is that, as previously mentioned, E_s is a minimum value, and this is because we neglect any energy hump over and above the heat of hydrogenation on the surface at the coverage concerned. However, we intend to deal with energy considerations only in the broad way raised by Beeck, at this time. It is probable that the observed activation energy involves a number of contributions and is more complex than implied by Figure 2. But if we used $\theta = 0$ for the heats of chemisorption the minimum values of E_s obtained are so large as quite to rule out the mechanism.

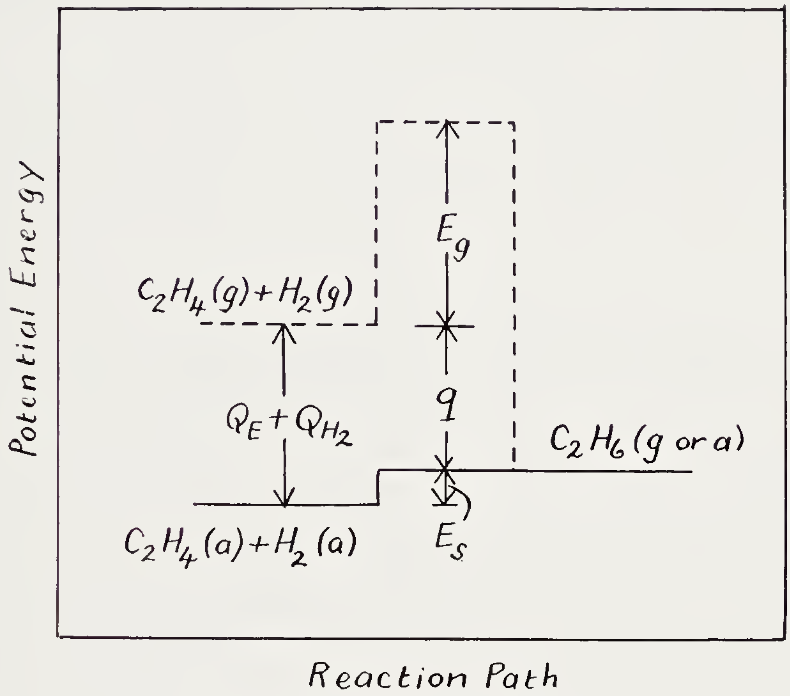

Figure 2. The energy balance for the hydrogenation of ethylene: (*a*) Full line, in the adsorbed phase on nickel; (*b*) broken line, in the gaseous phase.

Summary

It will be apparent from the foregoing that one cannot do more than weigh the evidence carefully relative to the mechanism of hydrogenation of ethylene since no really critical experiments for deciding this mechanism have as yet been made. Indeed, one may doubt whether a *qualitatively* critical experiment is possible. The mechanism for a given substrate-metal combination will eventually be derived from a consideration of quantitative data for all the hydrogenation, exchange and related reactions, determined on the same catalyst under similar conditions. The last condition is not easy to achieve in practice; for example, a mixture of ethylene-ethylene-d_4 in the absence of hydrogen will *favor* acetylenic chemisorption of ethylene, while a mixture of ethylene-hydrogen, especially if the pressure of hydrogen is high, will tend to oppose this type of adsorption, hydrogen coverage cutting down the concentration of 4-site groups necessary for the full dissociative process.

Ethylene-nickel is the most investigated case to date, but not necessarily the most favorable for academic investigation. Here, the balance of results seems to favor Twigg's development of the half-hydrogenated state mechanism,

$$H_2 + {}^*C_2H_4{}^* \rightleftharpoons {}^*C_2H_5 + H^* \rightarrow C_2H_6 ,$$

occurring on that part of the surface not already poisoned by chemisorbed acetylenic complexes. Dissociatively adsorbed ethylene $C_2H_3{}^*$ is also probably present, but in much lower concentration than the associative complexes ${}^*C_2H_4{}^*$.

An alternative view is that ethylene-hydrogenation is a separate reaction from the exchange reaction, e.g., as maintained by Farkas.

Wagner *et al.*[85b] mention two examples in which deuterogenation leads to a predominant formation of the d_2-ethane, which would favor his mechanism for these particular cases.

Generally speaking, the reaction path for ethylene hydrogenation has turned out to be too complex for the straightforward application of Langmuir kinetics in their simple form, as given earlier in this chapter. There is, however, still scope for experimental work in deciding how far the inhibiting effect of excess ethylene on classical copper catalysts is reversible, affected by impurities in the catalyst, pore size and so on, i.e., for extending the classical works of Grassi, Pease, Rideal and Schwab. The intrinsically complex nature of the system undoubtedly impedes a fuller interpretation of the important frequency factor, which has been shown to be "relatively low" and to determine differences in velocity for different metals and substrates. The complexity of the system would seem to be due especially to the possibilities for decomposition and polymerization of the substrate, and while modern techniques with wires and films are tending to reduce, at least, the complicating features of catalyst heterogeneity, the results of substrate decomposition are likely to be always with us, at least for metallic nickel.

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CHAPTER 3

CATALYTIC HYDROGENATION OF OLEFINIC HYDROCARBONS

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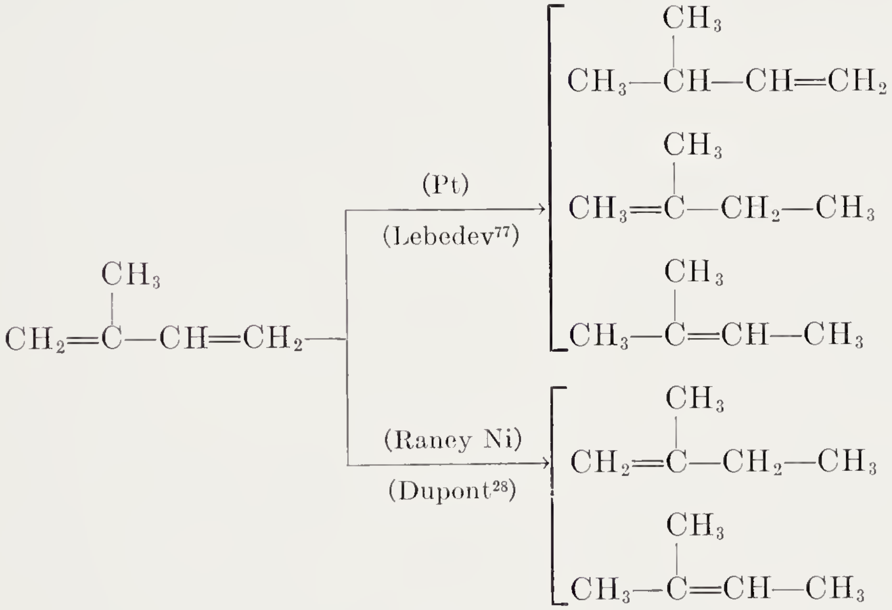
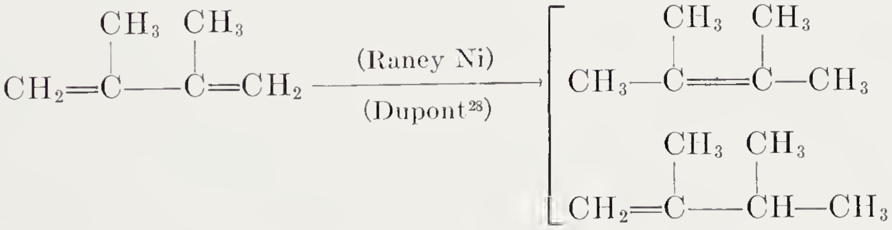
Selective Hydrogenation of Olefins

There are many examples of selective hydrogenation of hydrocarbons, some of which have achieved industrial application. The essence of selective hydrogenation lies in the possibility of preferentially adding hydrogen to one unsaturated bond rather than to another, although both unsaturations



$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \xrightarrow[\text{(Lebedev}^{77}\text{)}]{\text{(Pt)}} \left[\begin{array}{l} \mathrm{CH_3{-}\overset{CH_3}{\overset{|}{C}}H{-}CH{=}CH_2} \\ \mathrm{CH_3{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3} \\ \mathrm{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3} \end{array}\right]$$

$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2} \xrightarrow[\text{(Dupont}^{28}\text{)}]{\text{(Raney Ni)}} \left[\begin{array}{l} \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3} \\ \mathrm{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3} \end{array}\right]$$



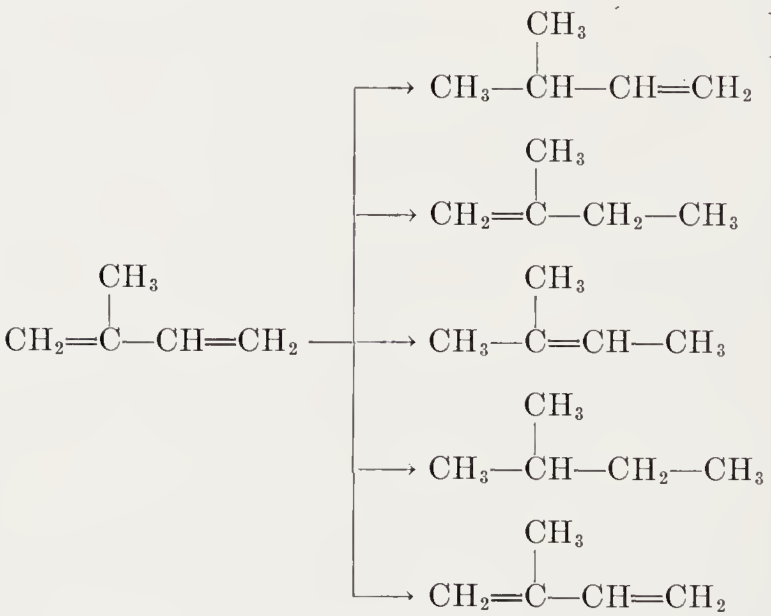
$$\mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2} \xrightarrow[\text{(Dupont}^{28}\text{)}]{\text{(Raney Ni)}} \left[\begin{array}{l} \mathrm{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3} \\ \mathrm{CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_3} \end{array}\right]$$

are capable of adding hydrogen. These unsaturated bonds may be located in the same molecule or in different molecules of a hydrocarbon mixture.

There is no catalyst or set of conditions which is specific for selective hydrogenation. The usual result is nonselective hydrogenation. It is only by the correct combination of catalyst and conditions that selective hydrogenation can be accomplished.

Lebedev *et al.*[77] report that the half-hydrogenation of butadiene, piperylene, and isoprene—i.e., the reaction of one mole of hydrogen with one mole of hydrocarbon—over platinum catalyst gives mixtures of all possible hydrogenation products. According to Dupont and Paquot[28] the half-hydrogenation of isoprene at 0°C in the presence of Raney nickel, which is more selective than platinum, yields equal amounts of 2-methyl-2-butene and 2-methyl-1-butene, whereas the reaction of one mole of hydrogen with one mole of 2,3-dimethyl-1,3-butadiene yields twice as much 1,4- as 1,2-addition product.

Kazanskii *et al.*[63] report the following data for the half-hydrogenation of isoprene in the presence of platinum, palladium, and Raney nickel:



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow$$

	Pt	Pd	Raney Ni
	mole %		
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH{=}CH_2$	7	25	16
$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2{-}CH_3$	26	30	40
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}CH_3$	15	41	40
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}H{-}CH_2{-}CH_3$	26	2	2
$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2$	26	2	2

An example of low degree selectivity is the hydrogenation of α,ω-diphenylpolyenes, in which the only selectivity thus far achieved is to produce either α,ω-diphenylparaffin or α,ω-dicyclohexylparaffin[71].

$$C_6H_5{-}(CH)_x{-}C_6H_5 \left\{ \begin{array}{l} \longrightarrow C_6H_5{-}(CH_2)_x{-}C_6H_5 \\ \longrightarrow C_6H_{11}{-}(CH_2)_x{-}C_6H_{11} \end{array} \right. \qquad (x = 2,4,6,8)$$

In the past there was some doubt that hydrogen could be added catalytically to the ends of conjugated unsaturation in hydrocarbons. Paal[89] in

1912 reported that partial hydrogenation of butadiene in the presence of platinum or palladium hydrosol produced a mixture of butane and non-reacted butadiene. Ingold[46] came to the same conclusion from other work. It is true that Lebedev[77] in 1928 reported the 1,4-addition of hydrogen to several conjugated hydrocarbons, but his evidence was not convincing[63] in that he did not isolate the dihydroproducts, but merely interpreted the hydrogen consumption curves. However, at present there is no doubt that catalytic hydrogenation can selectively produce dihydroproducts corresponding to 1,2-, 3,4-, and 1,4-addition of hydrogen to conjugated hydrocarbons.

The catalysts most often used for selective hydrogenation in the laboratory are palladium and Raney nickel. For large-scale operation[18, 108, 114], e.g., removal of olefins from cracked naphtha, various poisoned catalysts are recommended in the patent literature.

Mechanism of Selective Hydrogenation

The possibility of selectively hydrogenating certain components of a mixture of hydrocarbons cannot be predicted from the relative rates of hydrogenation of the individual components. For example, styrene hydrogenates faster than phenylacetylene[16, 125], but in admixture, it is the phenylacetylene which hydrogenates first. Also, the rates of hydrogenation of butadiene to butene, and of butene to butane, are approximately the same, but butadiene admixed with butene can be selectively hydrogenated to butene, with very little of the butene going to butane[123]. The apparent explanation is that the more highly unsaturated hydrocarbon monopolizes the catalyst surface because of its greater strength of chemisorption, and the less highly unsaturated hydrocarbon is unable to get onto the catalyst surface to be activated.

In the case of the acetylene-ethylene system, when the conditions are correct, ethylene does not start to hydrogenate until practically all of the acetylene has been hydrogenated. Ethane is very loosely held on the catalyst surface, compared with acetylene and ethylene, and the rate of hydrogen consumption speeds up as soon as all of the acetylene has been converted to ethylene, due to the ease with which ethane is desorbed from the catalyst to make room for fresh ethylene[36, 54].

Acetylene, methylacetylene, and allene, alone, can be selectively hydrogenated to monoolefins, although each of the monoolefins, alone, hydrogenates faster than the antecedent hydrocarbon[13].

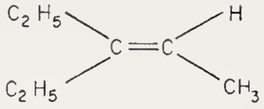
$$CH\equiv CH \rightarrow CH_2=CH_2$$

$$\left.\begin{array}{r} CH_3-C\equiv CH \\ CH_2=C=CH_2 \end{array}\right] \longrightarrow CH_3-CH=CH_2$$

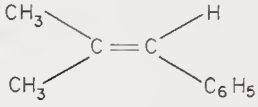
Acetylene, methylacetylene, and allene in admixture are hydrogenated simultaneously to the monoolefin stage. Presumably they are adsorbed with equal strength and share the active sites[13].

Selective Hydrogenation of Certain Tri- and Tetrasubstituted Ethylenes

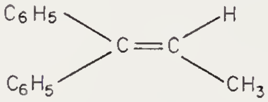
The following data illustrate the apparent unpredictability of competitive hydrogenation. The results are evidently closely dependent on the catalyst. These hydrogenations, made in ethanol solution at ordinary temperature and pressure, involved the hydrogenation of the aliphatic double bonds in the following tri- and tetrasubstituted ethylenes[60].



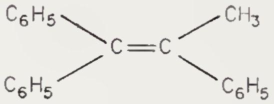
(I)



(II)



(III)



(IV)

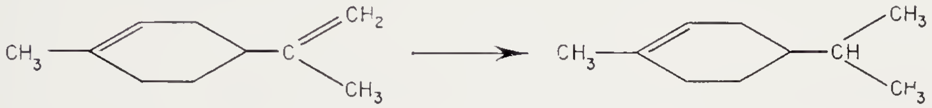
With Platinum. In the hydrogenation of 50–50 mixtures of (I) and (III) with sufficient hydrogen for only one of the components, the aliphatic-substituted olefin (I) consumed 85 per cent of the hydrogen. The order of activity was reported to be I > IV > II > III.

With Palladium or Raney Nickel. In the hydrogenation of similar mixtures in the presence of palladium or Raney nickel the situation was reversed, the phenyl-substituted olefins capturing 85 per cent or so of the hydrogen. In the hydrogenation of a 50–50 mixture of (III) and (IV), the triphenylated olefin consumed only 7 per cent of the hydrogen.

Selective Hydrogenation of Mixed Ethylenic-Aromatic Unsaturation

Aliphatic olefins can be hydrogenated to paraffins in the presence of aromatic hydrocarbons, without hydrogenating the latter. For example, the pentene component of a 50-50 pentene-toluene mixture can be quantitatively hydrogenated in the presence of a nickel catalyst in liquid phase at 40°C, or in vapor phase at 125 and 175°C[49], whereas the toluene remains unchanged.

Similar to the selective hydrogenation of aliphatic olefins in admixture with aromatic hydrocarbons is the selective hydrogenation of unsaturated aliphatic side chains attached to aromatic nuclei, e.g., the olefinic side chains in styrene, α-methylstyrene, allylbenzene, and vinylnaphthalene. There are many examples of this type of selective hydrogenation. In the case of limonene, the olefin bond in the isopropenyl group can be hydrogenated without affecting the olefin bond in the ring[47].



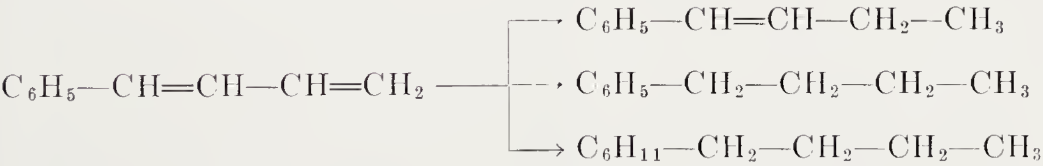
In the selective hydrogenation of indene to indan it is advisable to stop the hydrogenation before all of the indene has been hydrogenated, and wash out the nonhydrogenated indene with cold sulfuric acid. If the hydrogenation is continued until all the indene is hydrogenated, there is considerable production of octahydroindene[7, 72].

The olefins in cracked naphtha are selectively hydrogenated in large-scale operation to produce a liquid motor fuel with high octane number[114]. The high octane number of the product is due to the presence of isoparaffins and aromatics.

Selective Hydrogenation of Conjugated Unsaturation

As previously mentioned, the hydrogenation product of a 1,3-system of unsaturated bonds is apt to be a mixture of 1,4-, 1,2-, and 3,4-dihydro-, and 1,2,3,4-tetrahydroproducts. However, numerous selective hydrogenations have been reported. The following illustrative examples are given.

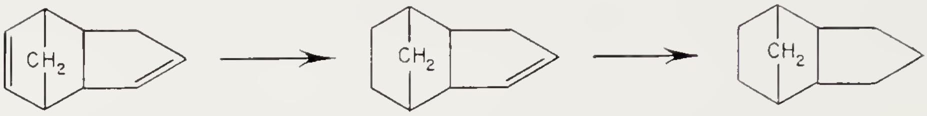
1-Phenyl-1,3-butadiene in acetic acid at room temperature in the presence of platinum adds hydrogen in the 3,4-position[87]. Under more drastic conditions, the 1,2-double bond is also saturated, and finally the benzene ring.



$$C_6H_5{-}CH{=}CH{-}CH{=}CH_2 \longrightarrow \begin{cases} \rightarrow C_6H_5{-}CH{=}CH{-}CH_2{-}CH_3 \\ \rightarrow C_6H_5{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \\ \rightarrow C_6H_{11}{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \end{cases}$$

Cyclopentadiene in cold ethanol solution in the presence of Raney nickel is hydrogenated to cyclopentene. There is a sharp fall in the rate of hydrogen consumption at the end of the first step. This selective hydrogenation offers an excellent preparative method for cyclopentene. Most of the reported hydrogenations of cyclopentadiene have yielded cyclopentane.

It is also relatively easy to hydrogenate dicyclopentadiene in steps—first to the dihydrocompound, then to the tetrahydrocompound[24].



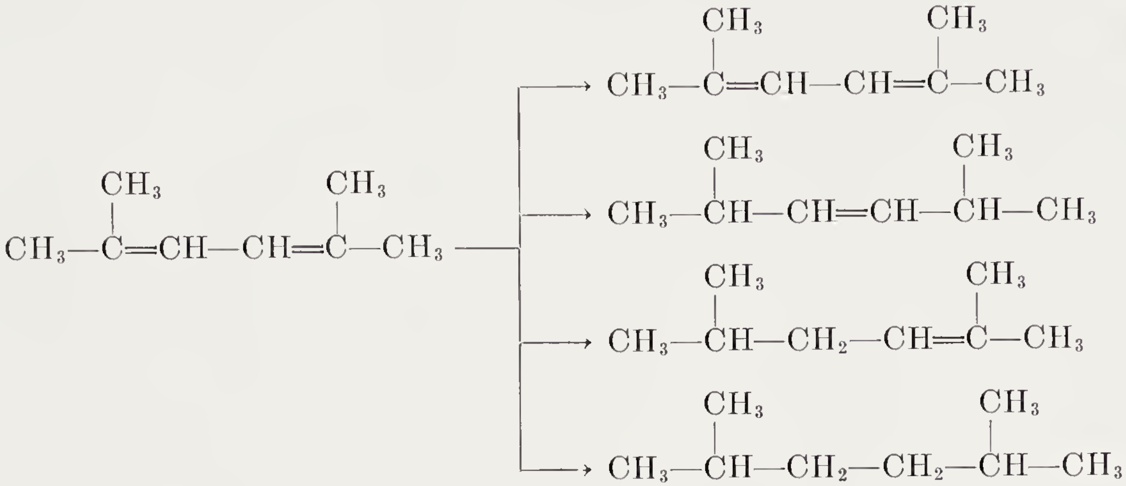
One mole of butadiene, hydrogenated in the presence of palladium at −12°C with 1.7 moles of hydrogen, gives a mixture containing 6 per cent of butane and 94 per cent of butene. The butene component contains 49 per cent of 1-butene, 11 per cent of *cis*-2-butene, and 40 per cent of *trans*-2-butene. The calculated thermodynamic equilibrium values for the butenes at −10°C are 2 per cent of 1-butene, 18 per cent of *cis*-2-butene, and 80 per cent of *trans*-2-butene. With other catalysts and conditions the 1-butene/*cis*-2-butene/*trans*-2-butene ratio varies widely[123].

The partial hydrogenation, however, of 1-butene or 2-butene at room temperature yields a mixture of butane and butenes in which the butene distribution approaches that of the thermodynamic equilibrium. It is interesting to note that this rearrangement does not take place in the absence of hydrogen (and partial hydrogenation)[123].

In view of the ease of interconversion of 1- and 2-butenes, it is evident that the respective yields of 1- and 2-butenes do not necessarily correspond to 1,2- and 1,4-addition of hydrogen, because subsequent to the addition of hydrogen, there may be rearrangement of the initially formed products before desorption from the catalyst. This possibility exists in the hydrogenation of other conjugated systems.

Another example of the effect of catalyst upon the type of product obtained is the hydrogenation of 2,5-dimethyl-2,4-hexadiene[61]. This hydrocarbon was hydrogenated in ethanol solution at room temperature and pressure in the presence of platinum, palladium, and Raney nickel, and the product was analyzed after the addition of one mole of hydrogen per mole of hydrocarbon. The product corresponding to 1,2-addition of hydrogen predominated. (see p. 85).

Vinylacetylene can be coverted to butadiene chemically, electrically, and catalytically, the yield depending upon the conditions. There is always a certain amount of butene and butane formed simultaneously. In methanol



$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 \longrightarrow$

	Pt	Pd	Ni
$CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$	11%	1%	0%
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3$	13	6	9
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$	62	86	90
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$	13	7	1

solution, at room temperature and pressure, in the presence of Raney nickel, the yield of butadiene is about 80 per cent[67].

$$CH{\equiv}C{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2$$

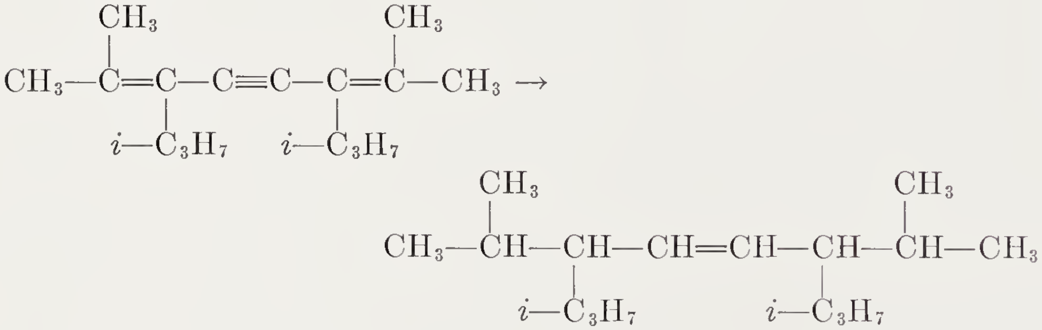
Divinylacetylene produces a mixture of 1,3,5-hexatriene, 2-hexene, and 3-hexene. 1,3-Hexadiene-5-yne, $CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH$, is also partially converted to 1,3,5-hexatriene on hydrogenation[66, 69, 70].

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \longrightarrow \left\{\begin{array}{l} \rightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \\ \rightarrow CH_3{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 \\ \rightarrow CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_3 \end{array}\right.$$

Sodium amalgam is reported to reduce divinylacetylene to 1,3,5-hexatriene in high yield. The initial reaction step is assumed to be 1,6-addition of sodium[66].

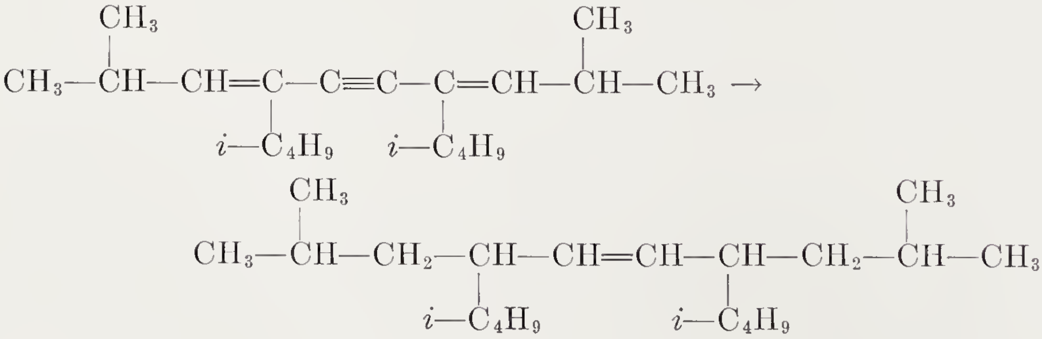
Certain C_8- and C_{12}-diene-yne conjugated hydrocarbons can be hydrogenated at ordinary temperature and pressure in four successive steps to give triolefin, diolefin, monoolefin, and paraffin[110]. Platinum usually hydrogenates the unsaturated hydrocarbons directly to paraffins, but with Raney nickel it is possible to halt the reaction at the stages corresponding to (1) partial hydrogenation of the triple bond, (2) 1,6-addition to the triene, and (3) 1,4-addition to the diene. (see p. 87).

In two hydrocarbons of this series, there is steric hindrance due to branching, and it is possible to stop the platinum-catalyzed hydrogenation at the monoolefin stage.



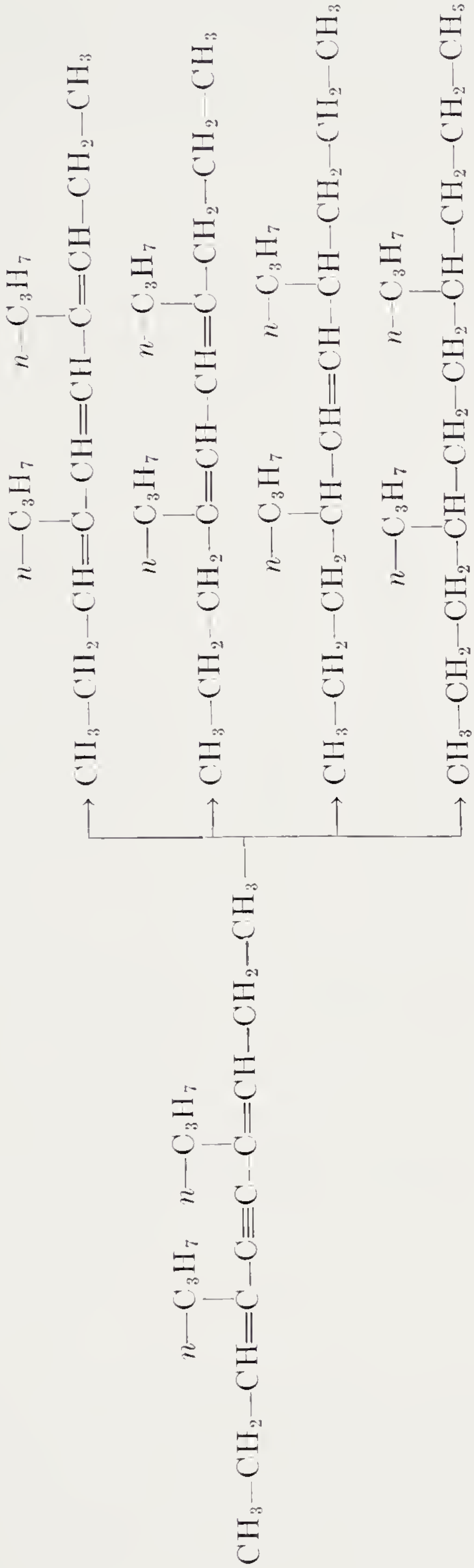
$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}\underset{\underset{i{-}C_3H_7}{|}}{C}{-}C{\equiv}C{-}\underset{\underset{i{-}C_3H_7}{|}}{C}{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3 \rightarrow$$

$$CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}\underset{\underset{i{-}C_3H_7}{|}}{CH}{-}CH{=}CH{-}\underset{\underset{i{-}C_3H_7}{|}}{CH}{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3$$



$$CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH{=}\underset{\underset{i{-}C_4H_9}{|}}{C}{-}C{\equiv}C{-}\underset{\underset{i{-}C_4H_9}{|}}{C}{=}CH{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3 \rightarrow$$

$$CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{i{-}C_4H_9}{|}}{CH}{-}CH{=}CH{-}\underset{\underset{i{-}C_4H_9}{|}}{CH}{-}CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3$$



$$CH_3—CH_2—CH{=}\underset{}{\overset{n—C_3H_7}{C}}—C{\equiv}C—\overset{n—C_3H_7}{C}{=}CH—CH_2—CH_3 \rightarrow$$

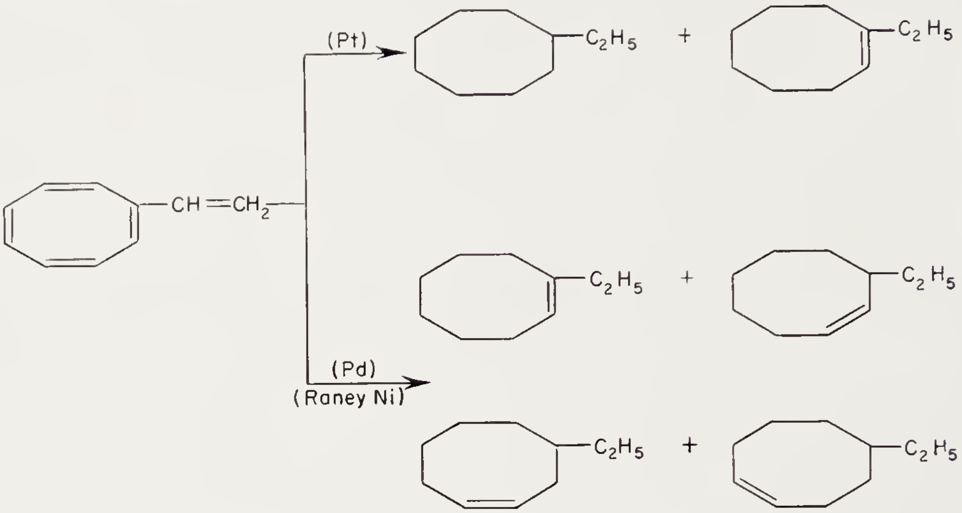
$$CH_3—CH_2—CH_2—CH{=}\overset{n—C_3H_7}{C}—CH{=}CH—\overset{n—C_3H_7}{C}{=}CH—CH_2—CH_3$$

$$CH_3—CH_2—CH_2—\overset{n—C_3H_7}{C}{=}CH—CH{=}\overset{n—C_3H_7}{C}—CH_2—CH_2—CH_3$$

$$CH_3—CH_2—CH_2—\overset{n—C_3H_7}{CH}—CH{=}CH—\overset{n—C_3H_7}{CH}—CH_2—CH_2—CH_3$$

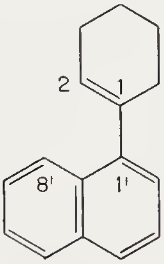
$$CH_3—CH_2—CH_2—\overset{n—C_3H_7}{CH}—CH_2—CH_2—\overset{n—C_3H_7}{CH}—CH_2—CH_2—CH_3$$

Vinylcyclooctatetraene is hydrogenated in the presence of platinum to a mixture of ethylcyclooctane and 1-ethylcyclooctene, whereas in the presence of palladium or Raney nickel, the product is a mixture of the four isomeric ethylcyclooctenes[75].

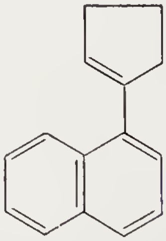


Electrolytic reduction of cyclooctatetraene at the mercury electrode in neutral or alkaline solution in the presence of tetramethylammonium ion gives a mixture containing 75 per cent of 1,3,6-cyclooctatriene and 25 per cent of 1,3,5-cyclooctatriene. It is believed that the 1,3,6-isomer is the primary product and that the 1,3,5-isomer results through isomerization. Sodium-alcohol converts cyclooctatetraene to a mixture of 1,4- and 1,5-cyclooctadienes[23].

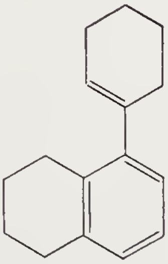
An interesting example of steric hindrance in catalytic hydrogenation is presented by hydrocarbons (I)–(V). 1-(1-Naphthyl)-1-cyclohexene (I) hydrogenates about half as fast as hydrocarbon (II), (III), (IV), or (V). Several explanations have been proposed. The latest is that hydrogenation is preceded by flatwise adsorption on the catalyst, and that (I) lacks coplanarity because of interference between the hydrogen atoms on carbons 2 and 8′ which hinders free rotation around the bond between carbons 1 and 1′[68].



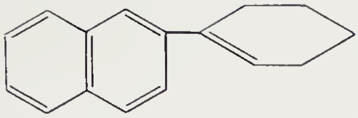
(I)



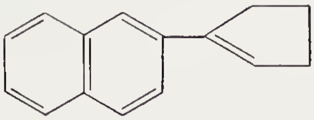
(II)



(III)



(IV)



(V)

Rate of Hydrogenation as Function of Hydrocarbon Structure

There is an abundance of discordant data disseminated throughout the literature concerning the rate of hydrogenation as a function of the hydrocarbon structure. The lack of agreement is not surprising in view of the lack of uniformity in the experimental conditions employed by the various investigators. The construction of an activity series is not a simple matter. The experimental conditions must be identical, and this is far from an easy requirement to satisfy, because of the multiplicity of variables which contribute to hydrogenation catalysis—amount of catalyst, catalyst activity, purity of solvent and hydrocarbon (catalyst poison), pressure, temperature, rate of agitation, etc. It is difficult to obtain the same activity in duplicate catalyst preparations, and even successive samples of the same batch of catalyst may not show the same activity[122]. Going still further, the observed rates of hydrogenation cannot rigorously be compared unless the concentrations of hydrogen and unsaturated hydrocarbon in the adsorption layer are comparable in different experiments[34]. Also an activity series which applies to catalyst A may not apply to catalyst B, e.g., platinum versus palladium.

In order to avoid confusion, only a few of the available data are discussed. These data were not selected on the basis of consistency. This would present a false picture. The inclusion of a certain number of contradictions serves to point out areas where constructive work is needed.

Hydrogenation at Superatmospheric Pressure and Elevated Temperature over Nickel Catalysts

The relative susceptibilities of various hydrocarbon classes to catalytic hydrogenation have been reported to be the following: open chain olefins $\geq$ cycloolefins > naphthalene > benzene > alkylbenzenes > arylbenzenes[81, 82]. The relative rates of hydrogenation of several olefins are listed in Table 1.

Hydrogenation at Atmospheric Pressure and Room Temperature

The following generalities apply to hydrogenation in ethanol and ether solution in the presence of Raney nickel, platinum, and palladium.

Monosubstituted double bonds hydrogenate faster than 1,1- and 1,2-disubstituted double bonds, and the rate of hydrogenation of monosubstituted double bonds remains constant throughout 85 per cent or so of the reaction, whereas the hydrogenation rates of di-, tri-, and tetrasubstituted double bonds show a gradual decline from start to finish, as well as being slower in proportion to the number of substituents[25, 27, 76].

If the olefins in a mixture are of the same degree of substitution, they are hydrogenated concurrently with no break in the hydrogen consumption curve, but if the olefins are of different degrees of substitution, they are hydrogenated consecutively as evidenced by breaks in the curve. By using an olefin of known structure as reference substance, it is said to be possible to determine the degree of substitution of an unknown olefin by inspection of the hydrogen consumption curve[76, 77].

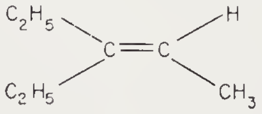
In the hydrogenation of certain monoalkylacetylenes, e.g., amyl- and phenylacetylenes, the rate remains constant throughout the hydrogenation of acetylene to paraffin, but with disubstituted acetylene, e.g., methylamylacetylene, the rate drops to 40 per cent or so of its initial value as soon as the acetylene has taken up two hydrogens. The hydrogenation product of methylamylacetylene at this stage is essentially pure *cis*-2-octene[27].

TABLE 1.[81, 82] RELATIVE RATES OF HYDROGENATION OF ALIPHATIC DOUBLE BONDS AT 75 TO 230°C AND 35 TO 200 ATMOSPHERES IN THE PRESENCE OF NICKEL-ALUMINA CATALYST

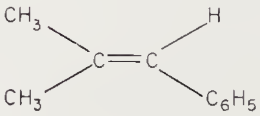
Hydrocarbon	Relative Rate
1-Methylcyclohexene	510
3-Methylcyclohexene	13,000
Cyclohexene	15,000
Cyclopentene	29,000
1-Hexene	31,000
Styrene	90,000

Platinum and palladium differ markedly with respect to the hydrogenation of the ethylenic double bond of phenyl-substituted olefins, platinum-catalyzed hydrogenation being retarded (poisoned) to a much greater extent than palladium-catalyzed hydrogenation—so much so that the order of the activity series is different for platinum than for palladium[60, 62, 124].

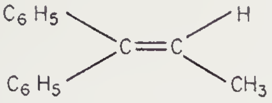
The hydrogenating activities of the following olefins, as measured by platinum-catalyzed hydrogenation, decrease in the order I > II > III > IV, but in the presence of palladium the order is III > II > IV > I. In the palladium-catalyzed hydrogenation of binary mixtures of (I) with (II), (III), or (IV), the phenyl-substituted ethylenes are selectively hydrogenated.



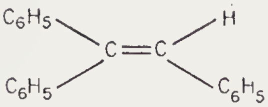
(I)



(II)



(III)



(IV)

Raney nickel is similar to palladium in that (II), (III), and (IV) hydrogenate much faster in its presence than in the presence of platinum. In fact, (II) hydrogenates as fast on Raney nickel as it does on palladium, but (III) and (IV) hydrogenate faster on palladium than on Raney nickel[60]. Tetraphenylethylene, which is not hydrogenated at all by platinum at ordinary temperature and pressure, is hydrogenated slowly in the presence of palladium[124].

Not only is the palladium-catalyzed hydrogenation of (I) retarded by phenyl-substitution, but also by admixture with phenyl derivatives such as isobutylbenzene, 1,1-diphenylpropane, and 1,1,2-triphenylethane. Similarly, benzene retards the palladium-catalyzed hydrogenation of 4-nonene[62].

The rate of hydrogenation of the double bond in monoolefins decreases roughly with an increase in the number and branching of the alkyl substituents. The data available on this subject consist in groups without intercomparison, and there is usually no information as to whether the *cis-*, *trans-*, or *cis-trans*-mixture is involved (Table 2)[73, 74, 99].

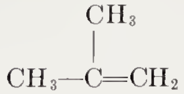
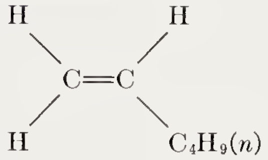
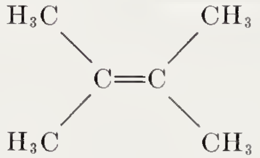
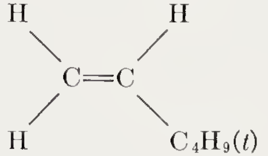
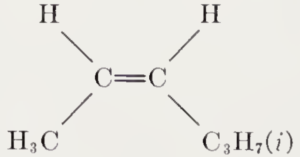
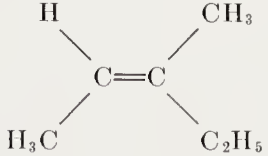
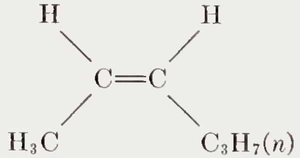
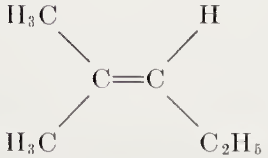
The relative ease of hydrogenation of 1-methylcyclopentene, unsymmethyl-*t*-butylethylene, 1-ethylcyclopentene, and 1-octene is qualitatively shown by the temperatures at which they are completely hydrogenated at constant contact time, viz., 110, 120, 140, and 140°C, respectively[86].

One method of obtaining relative rates of hydrogenation of a series of hydrocarbons is to hydrogenate each hydrocarbon competitively in the presence of a reference compound with insufficient hydrogen to satisfy both unknown and reference compounds[112]. The result is an activity series based upon a single reference substance, which is said to be independent of the amount and activity of the catalyst.

Competitive hydrogenation, however, except within a restricted series, cannot be relied upon to reflect the intrinsic activities of the separate components because other factors come into play such as preferential adsorption, catalyst type, and the reference compound. In the extreme case of the hydrogenation of mixtures of acetylenes and olefins, the results of competitive hydrogenation shows no relationship to the relative activities of the single components. Discordance has been observed in other systems[4].

The following olefins, competitively hydrogenated with α-pinene, consumed 96, 71, 70, and 65 per cent, respectively, of the hydrogen[112, 113]. When undecylenic acid was substituted for α-pinene, the amounts of hydrogen consumed by the olefins were 24, 14, 14, and 10 per cent, and 22, 22, 11, and 8 per cent, respectively, depending on the solvent.

TABLE 2. RELATIVE HYDROGENATION RATES OF CERTAIN OPEN CHAIN OLEFINS[a]

Group A[b]		Group B[c]		Group C[c]	
Hydrocarbon	Rate	Hydrocarbon	Rate	Hydrocarbon	Rate
 $CH_3-\underset{}{\overset{CH_3}{\overset{\vert}{C}}}=CH_2$	1		1		1.0
cis-$CH_3-CH=CH-CH_3$	2.3		2.1		1.1
trans-$CH_3-CH=CH-CH_3$	2.3				
$CH_2=CH-CH_2-CH_3$	4.8		4.4		1.2
$CH_3-CH=CH_2$	11		7.3		
$CH_2=CH_2$	138				

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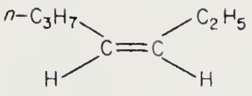
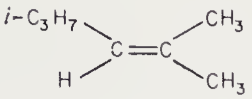
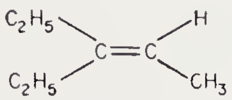
[a] There is no intercomparison between Groups A, B, and C.

[b] Nickel-charcoal and cobalt-charcoal catalysts.

[c] Platinum catalyst.







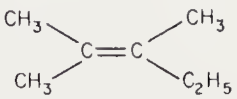


Table 3 compares the hydrogenation rates of benzene, cyclohexene, and cyclohexadienes in acetic acid solution at 30°C under 50 psig of hydrogen in the presence of a platinum catalyst[106]. Cyclohexene hydrogenates eight times as fast as benzene, and also faster than the cyclohexadienes. It is to be noted that the conjugated system of 1,3-cyclohexadiene hydrogenates faster than the nonconjugated system of 1,4-cyclohexadiene.

Usually the *cis*-olefin hydrogenates faster than the *trans*-olefin. *cis*-Stilbene is said to hydrogenate about five times as fast as *trans*-stilbene[91]. *cis*-1-Phenyl-2-butene[87] and *cis*-2-butene[123] hydrogenate somewhat faster than the corresponding *trans*-isomers. However, *cis*- and *trans*-dimethylstilbenes hydrogenate at the same rate[118].

TABLE 3. HYDROGENATION RATES OF CYCLOHEXADIENES AND CYCLOHEXENE COMPARED WITH THAT OF BENZENE

Hydrocarbon	Relative Hydrogenation Rate
Benzene	100
1,4-Cyclohexadiene	460
1,3-Cyclohexadiene	660
Cyclohexene	810

Bonner and Collins[14] report that the rate of hydrogenation of stilbene-α-C^{14} in the presence of Raney nickel is 98 per cent of that of unlabeled stilbene. It was shown that the isotopic fractionation was not due to the exchange of hydrogen between stilbene-α-C^{14} and bibenzyl. The extent of isotopic fractionation is much larger (12 per cent) in the hydrogenation of acetophenone-α-C^{14}.

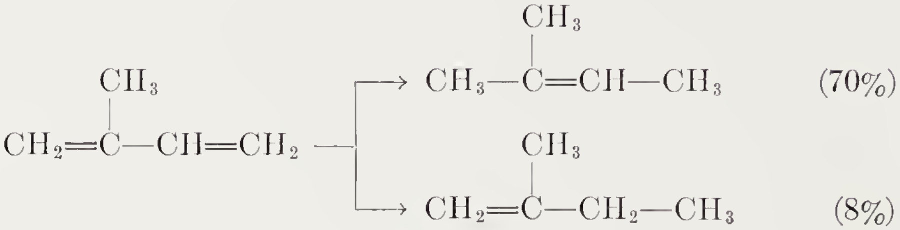
Wilson *et al.*[121] report that the product of reaction between *cis*-2-butene and deuterium in the presence of a nickel catalyst at −78°C contains all isotopic species from C_4H_{10} to C_4D_{10} in essentially random distribution of deuterium atoms among the hydrogen positions, even though the average composition of the product $C_4H_8D_2$. It is concluded from this work that an important reaction in olefin hydrogenation is the transfer of hydrogen atoms directly among chemisorbed hydrocarbon entities, resulting in hydrogen atom redistribution and finally alkane production.

REDUCTION OF OLEFINIC HYDROCARBONS BY CALCIUM-AMMONIA AND ALKALI METALS

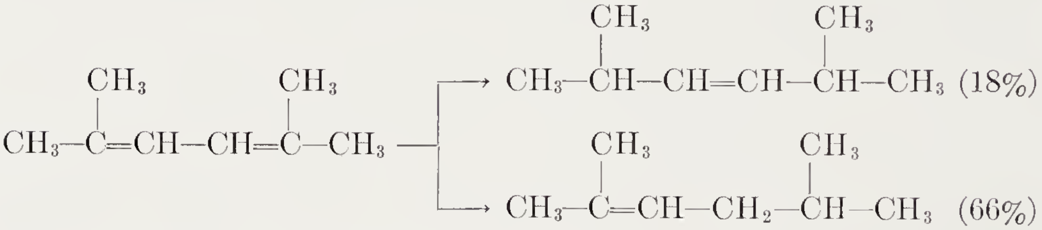
Reduction by calcium-ammonia, although presumably not a catalytic reaction, deserves mention as one of the methods of adding hydrogen to hydrocarbons.

Two experimental techniques have been employed: (1) passing dry ammonia into a mixture of calcium and hydrocarbon at room temperature; (2) preforming the calcium-ammonia complex and subsequently reacting it with hydrocarbon.

The following reductions of 1,3-conjugated systems by means of $Ca(NH_3)_6$ have been reported[58].

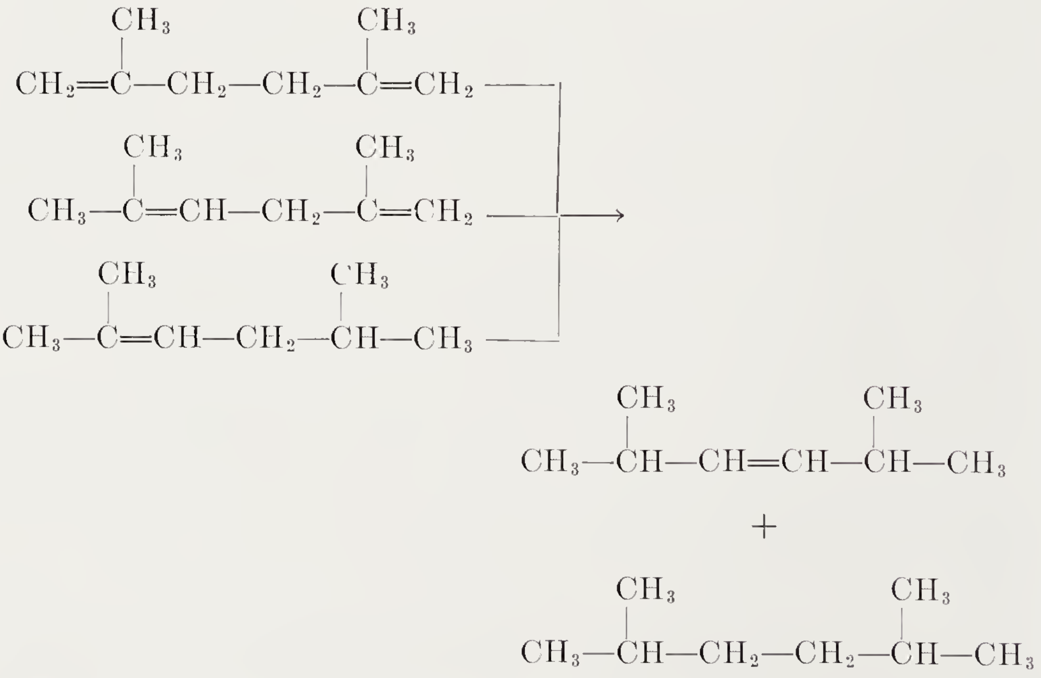


$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2 \longrightarrow \begin{cases} CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3 & (70\%) \\ CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_3 & (8\%) \end{cases}$$



$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3 \longrightarrow \begin{cases} CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH{=}CH{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3 & (18\%) \\ CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3 & (66\%) \end{cases}$$

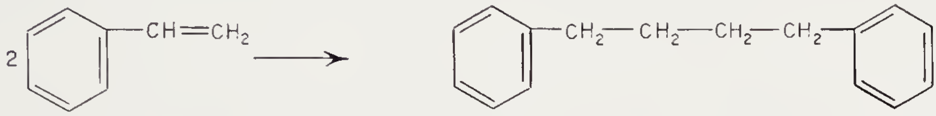
Hydrogenation-isomerization of nonconjugated double bonds by means of $Ca(NH_3)_6$ has also been described[59].

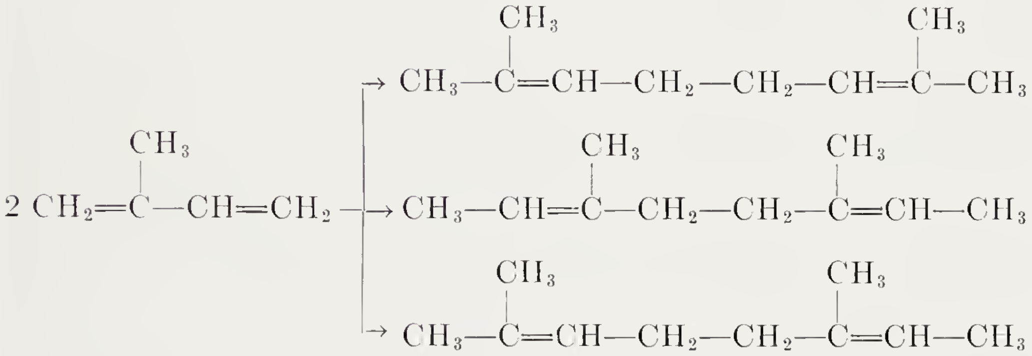


$$\left.\begin{array}{l} CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \\ CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \\ CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3 \end{array}\right] \longrightarrow$$

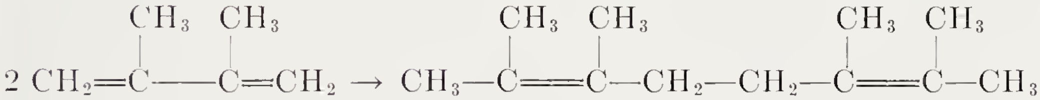
$$CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH{=}CH{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3 + CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3$$

Midgley's work on the hydrogenation of conjugated systems is of interest. Sodium-alcohol, potassium-alcohol, and sodium-ammonia were the reducing agents. Hydropolymerizates were produced, hydrogen adding to one end of the conjugated system, and coupling taking place at the other end. Besides hydropolymerizates there were also formed the usual monomolecular hydrogenated hydrocarbons, e.g., ethylbenzene from styrene[84, 85]. The hydrocarbons studied were styrene, isoprene, and 2,3-dimethyl-1,3-butadiene.





$$2\ \mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH{=}CH_2} \rightarrow \begin{cases} \mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3} \\ \mathrm{CH_3{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3} \\ \mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3} \end{cases}$$



$$2\ \mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2} \rightarrow \mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}{=}\overset{\overset{CH_3}{|}}{C}{-}CH_3}$$

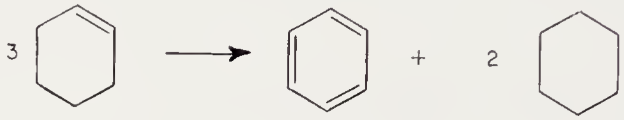
In similar manner, isobutene can be hydropolymerized to a mixture of octanes using a mixed hydrogenation-polymerization catalyst[51].

It is the general rule that isolated C—C double bonds are not reduced by metal combinations, e.g., by the metal-liquid ammonia system. There are two exceptions[39]: 1-hexene and 2-cyclopropyl-1-pentene are reduced by the action of sodium-methanol-liquid ammonia. 2-Hexene is not reduced by this combination.

Sodium, sodium hydride, sodium-potassium alloy, calcium, and lithium have been reported to function as hydrogenation catalysts. A possible advantage of sodium-potassium alloy is that it is a liquid catalyst and is therefore not deactivated by the usual trace amounts of poisons. It is to be noted that only those hydrocarbons which are capable of adding alkali metals can be hydrogenated by this method[41, 44, 45]. Most of the hydrocarbons hydrogenated by these catalysts have been polynuclear aromatics. However, stilbene has been converted to bibenzyl and 1,4-diphenylbutadiene to 1,4-diphenylbutane. Suitable conditions for this type of hydrogenation are 200 to 270°C and 1,000 to 2,000 psig of hydrogen.

HYDROGENATION OF OLEFINS BY HYDROGEN TRANSFER

A typical example of intermolecular hydrogen transfer is the conversion of cyclohexene to a mixture of one part benzene and two parts cyclohexane. This disproportionation takes place with extreme ease in the presence of a hydrogenation catalyst, in the absence of hydrogen. Cyclohexene acts both as donor and acceptor. The reaction takes place even in the presence of pure charcoal whose catalytic activity is so weak that it is unable to catalyze the hydrogenation of 1-nonene[127].



Although it is not certain that the disproportionation is third order, there is little doubt that it is a linked process, and that the rate-determining step involves both donor and acceptor[79]. It is not a two-step process consisting of independent, successive dehydrogenation and hydrogenation reactions. Cyclohexadiene is probably not intermediate in this reaction. Dehydrogenation in the absence of acceptor requires a higher temperature than disproportionation in the presence of acceptor[79].

In both liquid and vapor phase, in the presence of nickel-kieselguhr at 100°C, the yield of benzene-cyclohexane is quantitative[21]. In the absence of a catalyst, cyclohexene is unchanged by heating for 6 hours at 350°C[21]. This reaction of cyclohexene was discovered by Zelinskii in 1911. He reported that the product was a cyclohexene isomer[126].

Typical examples of this type of disproportionation are listed in Table 4.

Cyclohexene can also function as hydrogen donor to other acceptors than itself (Table 5).

Hydrogen transfer could become a useful preparative type of catalytic hydrogenation. The method is simple and requires no special apparatus. All that is required is to reflux the material to be hydrogenated with cyclohexene and catalyst. Cyclohexene may function as solvent as well as hydrogen donor, or the solvent may be methanol, ethanol, dioxane, or benzene. In the case of a compound containing several unsaturations, the hydrogen transfer method may be more selective than catalytic hydrogenation—*m*-dinitrobenzene is converted quantitatively to *m*-nitraniline[79].

Cyclohexene is one of the better-known hydrogen donors for this purpose, but there are probably others equally suitable. For example, several cinnamic acids have been hydrogenated by refluxing them in tetralin solution in the presence of palladium[65], and ethanol has been reported to hydrogenate toluene in the presence of nickel-alumina or platinum-asbestos, the dehydrogenated product being acetaldehyde[104].

Table 4.[79] Palladium-Catalyzed Disproportionation of Hydroaromatic Hydrocarbons in Tetrahydrofuran Solution at 65°C

Initial Hydrocarbon (1 mole)	Products	Reaction Half-Time (minutes)
Cyclohexene	⅓ mole benzene + ⅔ mole cyclohexane	20
1-Methylcyclohexene	⅓ mole toluene + ⅔ mole methylcyclohexane	40
4-Methylcyclohexene	⅓ mole toluene + ⅔ mole methylcyclohexane	25
1,3-Cyclohexadiene	⅔ mole benzene + ⅓ mole cyclohexane	10
1,4-Cyclohexadiene	⅔ mole benzene + ⅓ mole cyclohexane	8
1,2-Dihydronaphthalene	½ mole naphthalene + ½ mole tetralin	110
1,4-Dihydronaphthalene	½ mole naphthalene + ½ mole tetralin	50

Table 5.[79] Palladium-Catalyzed Hydrogen Transfer Between Cyclohexene and Unlike Acceptors

(At reflux temperature)

Unlike Acceptor	Hydrogenated Acceptor	Hours	% Yield (based on acceptor)
1-Octene	*n*-Octane	21	70
2-Octene	*n*-Octane	52	75
Allylbenzene	*n*-Propylbenzene	150	90
β-Methylstyrene	*n*-Propylbenzene	6	100
Indene	Indan	500	100
Tolane	*cis*-Stilbene	3	90
cis-Stilbene	Bibenzyl	20	100
trans-Stilbene	Bibenzyl	20	100
Acenaphthylene	Acenaphthene	15	100
1,1-Diphenylethylene	1,1-Diphenylethane	43	100

Stereochemistry of Hydrogenation of Olefins

It is assumed that catalytic hydrogenation involves *cis*-addition of hydrogen whereas chemical reduction (by metal combinations, etc.) operates through *trans*-addition[19, 35, 116, 119]. It is therefore a geometrical corollary that catalytic hydrogenation converts *cis*-tetrasubstituted ethylenes to meso compounds and *trans*-tetrasubstituted ethylenes to racemic mixtures (and vice versa for chemical reduction). There are, however, not many experimental data on this subject. Although the initial products of catalytic hydrogenation may correspond to *cis*-addition of hydrogen, the products actually isolated are often mixtures of stereoisomers, presumably due to subsequent rearrangement. Examples of *cis*-olefins hydrogenating to meso compounds, and *trans*-olefins to racemic mixtures are the hydrogenations of the dimethylmaleic and dimethylfumaric acids, and the isomeric dimethylstilbenes[88, 118].

GENERALITIES CONCERNING THE CATALYTIC HYDROGENATION OF HYDROCARBONS

Historical

The two great pioneers in catalytic hydrogenation and its companion field of dehydrogenation were Sabatier[97] in France and Ipatieff[48] in Russia. Sabatier studied vapor phase catalysis at ordinary pressure whereas Ipatieff chose the more difficult task of liquid phase catalysis at superatmospheric pressure. They started working at the turn of the century and they both lived to see great industries founded upon their discoveries. The practicality of Ipatieff's high-pressure technique was not appreciated for a generation. Operation at superatmospheric pressure was very new then. Sabatier said that it was dangerous and unnecessary[2], but the years have not borne out his dictum.

Catalysts and Catalyst Preparation

The most commonly used catalysts in the laboratory are Raney nickel, nickel-kieselguhr, platinum, palladium, copper chromite, and certain sulfided metals (nickel, molybdenum, cobalt, and tungsten).

Numerous sets of directions are available for preparing and using Raney nickel[105], nickel-kieselguhr[2, 49], platinum[19, 107], palladium[122], and copper chromite[2]. The preparative directions are empirical, but they must be followed if catalyst duplication is desired. Several types of hydrogenation catalysts can be purchased, and unless the object is a study of the fundamentals of catalysis, catalysts should be purchased rather than prepared.

The variables of catalyst preparation and hydrogenation are more complicated than ordinarily believed. The conflicting data in the literature furnish abundant evidence of this fact. Extreme care must be exercised if the objective is reliable data[55]. Even with successive portions of the same batch of catalyst for the hydrogenation of samples of the same substrate under apparently identical conditions, the degree of duplication is not as high as might be expected[122].

Nickel and cobalt probably possess about the same hydrogenating activity[53, 78, 80]. It may be that the high activity of Raney nickel is due to the promoting action of alumina. Raney nickel W-6[3], a highly active type, contains 70 per cent of nickel, 21 per cent of alumina, 1.4 per cent of metallic aluminum, and 7.6 per cent of sodium aluminate[52]. Raney nickel has been promoted by platinum[101].

Nickel boride (Ni_2B) and cobalt boride (Co_2B) are similar to Raney nickel in activity, and certain complex catalysts (Ni-B-Cr, Ni-B-W) of this series are said to be considerably more active than Raney nickel[92].

In the case of nickel-tungsten and nickel-molybdenum catalysts, the optimal ratios are 100 Ni/5W and 100 Ni/15 Mo[109]. Catalysts with these optimal ratios showed the highest densities, and x-ray photographs of the nickel-molybdenum catalysts revealed parallelism between hydrogenating activity and the amount of nickel in solid solution[96, 100].

Pure iron and promoted iron catalysts[32, 33, 42, 102] catalyze the hydrogenation of ethylene, propylene, and butylene. Ethylene is hydrogenated even at −100°C. The potassium oxide-aluminum oxide promoter, which enhances the activity of iron for the ammonia synthesis, decreases its activity for ethylene hydrogenation. It is the potassium oxide component of the promoter rather than the alumina which is responsible for this deactivation. Neither pure iron nor promoted iron catalyst is able to catalyze the hydrogenation of benzene,* although both of these catalysts possess as much surface area as certain other catalysts (e.g., cobalt catalysts) which are highly active for the hydrogenation of benzene. Other workers have reported the ability of iron to catalyze the hydrogenation of the lower olefins but not benzene[80].

It was originally believed that Raney iron[93] was specific for the hydrogenation of the triple bond to the double bond, and that it would not catalyze the hydrogenation of the latter, but it was recently reported that Raney iron catalyzes the hydrogenation of n-octadecene-9-yne to the corresponding alkane[31].

Copper is unable to catalyze the hydrogenation of benzene[33, 50, 80, 98], the findings of Pease and Purdum[94] notwithstanding. Emmett and Skau[33] have shown that the inactivity of copper for the hydrogenation of benzene is not due to lack of surface area. In fact, inactive copper catalysts possess several times as much surface area as cobalt catalysts which are quite active for the hydrogenation of benzene.

In a study of the hydrogenation of ethylene in the presence of copper-nickel alloys, Best and Russell[12] found no simple relationship between catalytic activity and alloy composition.† They report the most active copper-nickel alloy to be one containing 63 atom per cent of copper, this alloy being more active than either copper or nickel alone, the hydrogena-

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* There is one exception to this statement. Beeck and Ritchie (Beeck, O. and Ritchie, A. W., *Discussion Faraday Soc.*, **8**, 164 (1950), report the hydrogenation of benzene to cyclohexane over a thin iron film at 23°C.

† Dowden and Reynolds found, on the other hand, that the activity of a Ni-Cu alloy for the hydrogenation of styrene decreased steadily with increasing copper content, becoming zero when about 38 atom per cent copper was present (Dowden, D. A. and Reynolds, P. W., *Discussions Faraday Soc.*, **8**, 184 (1950).

tion velocity constant increasing more than 600-fold between copper and this copper-nickel alloy.

All six of the platinum group metals have been shown to be effective hydrogenation catalysts[15, 26, 103, 128], but platinum and palladium are the only ones in general use. The catalytic activity of certain alloys exceeds the additive effect of the two constituents. For example, copper-palladium alloys (Pd $\geq$ 47 per cent), and copper-platinum alloys (Pt $\geq$ 16 per cent) are as effective as the platinum group metals themselves[95].

It is known that Adams' platinum catalyst does not hydrogenate benzene in methanol solution at room temperature under 3 to 4 atmospheres of hydrogen, but that it will do so in acetic acid solution. Also, certain organic additives of the quaternary ammonium type will promote the hydrogenation of benzene. Adams' catalyst contains a certain amount of adsorbed sodium salt, and it seems that it is this sodium salt which deactivates the catalyst for the hydrogenation of benzene. When the catalyst is pre-reduced in acetic acid or methanol and subsequently thoroughly rinsed, it will then hydrogenate benzene either alone or in methanol[64].

The permutations of composition and methods of preparation of nickel catalysts are legion. Some carriers are better than others, but there is a wide choice. It may be that nickel and copper catalysts can be very simply prepared as follows[111]: precipitation of nickel or copper from aqueous solution by a more positive metal (e.g., zinc), followed by digestion with aqueous caustic. Adsorbed caustic is said to play an important role in producing catalytic activity. This type of catalyst has not yet been tested against olefins.

A highly satisfactory nickel-kieselguhr catalyst[49] is prepared by precipitating (with stirring) basic nickel carbonate from one mole of nickel sulfate (in 0.1 molal solution) in the presence of kieselguhr (e.g., "Filter Cel") by means of 1.7 moles of sodium carbonate (hot concentrated solution). The precipitate is washed free of sulfate, dried, decomposed (decarbonated), and finally reduced in a stream of hydrogen. The optimal temperature of reduction is 425°C. The reduced catalyst contains about 65 per cent of nickel and 35 per cent of kieselguhr. For vapor phase hydrogenation the dried precipitate (before decarbonation-reduction) is mixed with 4 per cent of die lubricant (e.g., powdered graphite) and tabletted in a pill machine. After being reduced, the pills are suitable for vapor phase hydrogenation, or they can be pulverized in a mortar with a few pieces of "Dry Ice" (to furnish an inert atmosphere) and used in liquid phase hydrogenation. The reduced pills are pyrophoric, but they can be rendered nonpyrophoric by superficial oxidation at room temperature in air. The superficial oxide layer is removable by hydrogen at 200°C. This catalyst shows essentially the same activity as Raney nickel, and has the advantage of cheapness and ease of preparation and handling.

Sensitivity of Hydrogenation Catalysis to Impurities

The extreme sensitivity of hydrogenation catalysis to impurities (promoters and poisons) is illustrated by Ipatieff's study[22, 50] of vapor phase hydrogenation at ordinary pressure over promoted copper catalysts. Copper, itself, is relatively inactive for hydrogenation, and therefore quite suitable for this type of study. With an active catalyst such as nickel, which when properly prepared is able to hydrogenate benzene quantitatively at 50°C at ordinary pressure in a contact time of one second, it is impossible to disentangle the many variables which contribute to hydrogenation catalysis.

Nickel is an extremely powerful activator for copper as shown by the fact that copper catalysts containing 0.002, 0.005, 0.05, 0.5, and 1 per cent of nickel hydrogenate benzene to the extent of 0, 0.5, 5.5, 42, and 79 per cent, respectively, at 225°C at ordinary pressure in a contact time of 12 seconds. At the contact time of 180 seconds copper catalyst activated by 0.005 per cent of nickel shows negligible hydrogenating activity with respect to benzene, but when activated by 0.007 per cent of nickel, it hydrogenates benzene to the extent of 8 per cent. Seven thousandths per cent of nickel corresponds to one nickel atom per 13,000 copper atoms. That this activation is the combined effect of copper and nickel, and not of nickel alone, is shown by replacing copper by alumina. There is no hydrogenation of benzene* at the above temperature and contact time, even with 5 per cent of nickel dispersed on alumina[22].

Lead, bismuth, and cadmium are poisons for nickel-activated copper catalyst; sodium chloride and sodium sulfate also poison it. Lead and bismuth show the highest toxicity. Cadmium and sodium chloride are next, and sodium sulfate is least toxic. Twenty-four hundredths per cent of sodium sulfate is required to lower the hydrogenating activity by 50 per cent, and 0.38 per cent to deactivate the catalyst completely. The corresponding amounts of lead are 0.02 and 0.09 per cent, respectively. Less than 0.02 per cent of lead impurity functions as a weak promoter[22].

The effect of a trace of chromium oxide as activator of copper is remarkable. Pure copper (containing about 0.001 per cent of nickel) requires 225°C at ordinary pressure to hydrogenate isopentene to the extent of 55 per cent in 10 seconds, whereas copper containing 0.1 per cent of chromium oxide shows the same activity at 75°C. Thus the presence of one molecule of chromium oxide in 2,500 atoms of copper lowers the temperature requirement 150°C, although chromium oxide alone has no hydrogenating ability

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* The variability of results on this system can be illustrated by the fact that at 125°C and a time of contact of about one second, 3 to 5 per cent conversion was obtained by Hill and Selwood on samples containing as little as 5 per cent NiO on Al_2O_3 (Hill, F. N. and Selwood, P. W., *J. Am. Chem. Soc.*, **71**, 2527 (1949)).

with respect to isopentene, even with long contact time at 350°C under 150 atmospheres of hydrogen[50].

The activity of a mixed catalyst depends upon the activator and its amount as illustrated by the activity-composition curves of mixed copper catalysts in Figure 1. Small additions of activator produce an abrupt rise in activity, but the shape of the remainder of the curve (beyond the 5 per cent point) depends upon the activator. In the case of the oxides of cerium, aluminum, thorium, and chromium the curve falls immediately after the 5 per cent point; with the oxides of uranium and manganese the curve remains horizontal from the 5 to the 80 per cent point and then drops; with the oxides of zinc and iron the curve gradually climbs from an initial peak at 5 per cent of activator to a much higher peak at 75 per cent of activator[22].

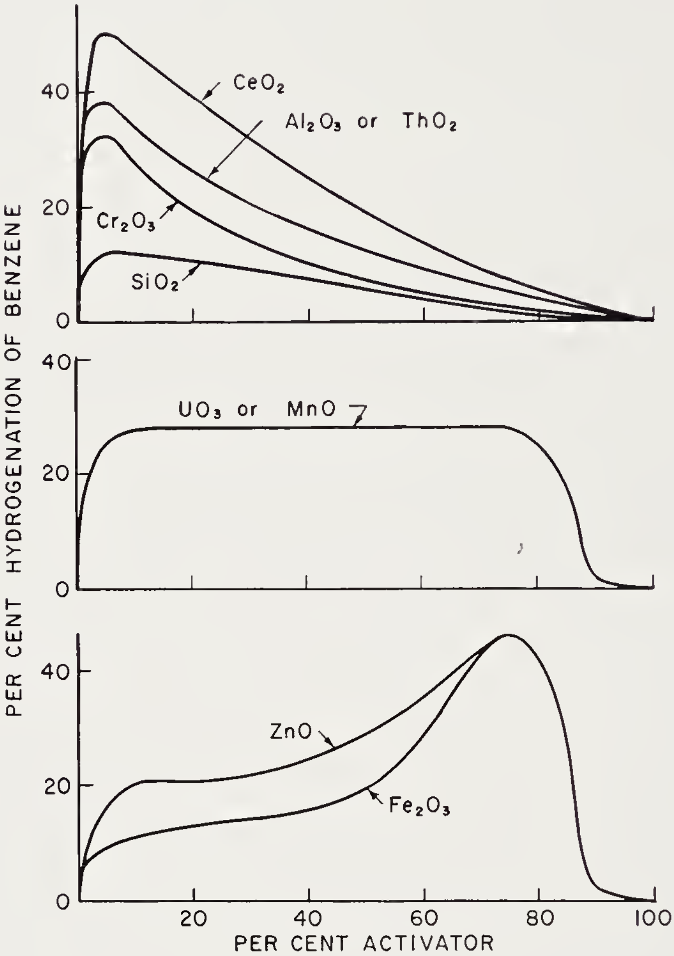


Figure 1. Activity of mixed copper catalysts.

These data emphasize the extreme delicacy of catalytic hydrogenation and the startling effect of minute amounts of impurities. The sensitivity of the benzene-hydrogen-copper-nickel system competes with the spectroscope in the detection of traces of nickel, bismuth and cadmium, and it goes beyond the range of the spectroscope in its sensitivity to lead. In the case of lead, spectroscopic purity is no guarantee of catalytic purity[22].

In the great majority of catalytic studies, little or no attention has been paid to trace impurities, or even to greater than trace impurities, which is one reason for the many discrepancies in the literature of catalysis. This situation is not too serious if it is realized that discrepancies are to be expected.

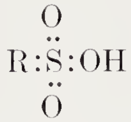
In passing, it should be mentioned that there is no certain relationship between the hydrogenating activity of a catalyst and its pyrophoricity. Many active catalysts are pyrophoric, and others are nonpyrophoric; also some relatively inactive catalysts are highly pyrophoric.

Catalyst Poisoning

There are two kinds of poisoning—deliberate and unintentional. In certain types of selective hydrogenation, the catalyst is deliberately poisoned in order to deactivate it to the desired level, e.g., the poisoning of nickel-kieselguhr for the selective hydrogenation of propylene in the presence of cyclopropane[20].

The following is a partial list of the poisons which have been proposed for the deactivation of nickel and the platinum group metals to make them suitable for the selective hydrogenation of hydrocarbons, especially the acetylenes: silver, copper, zinc, cadmium, mercury, aluminum, thallium, tin, lead, thorium, arsenic, antimony, bismuth, sulfur, selenium, tellurium, and iron (or their compounds)[56, 90].

Catalyst poisoning is usually unintentional, and it is the universal failing of hydrogenation catalysts that they become less effective with use—even on storage without use. Deterioration on use can be due to sulfidation, clogging of the catalyst pores with carbonaceous material, and a host of other causes. In general, groups V-b (N, P, As, Sb, Bi) and VI-b (O, S, Se, Te) are poisons for the hydrogenating metals of group VIII (Fe, Ni, Co, and the platinum metals)[83]. It is generally believed that poisoning is the result of the adsorptive blocking of the active centers of the catalyst, although other theories have been advanced. A recent theory is that hydrogenation catalysts function by virtue of promotion by dissolved hydrogen[5, 6, 37, 115] and that poisons (depromoters) are especially avid hydrogen acceptors.

According to Maxted[83], who subscribes to the adsorptive blocking of active centers as the mechanism of poisoning, it is the free electron pair of the poison which attaches the poison to the catalyst surface. He has shown that a poisoned catalyst can be reactivated by oxidation with certain peracids (pervanadic, pertungstic, permolybdic) in the presence of hydrogen peroxide. Oxidation converts the poison into a nontoxic compound with a "shielded structure" which no longer possesses the requisite free electron pair with which to attach itself to the catalyst. Thus, toxic R:S:H is converted to nontoxic  $R:\overset{O}{\overset{\cdot\cdot}{\underset{\underset{O}{\cdot\cdot}}{S}}}:OH$ and the latter can be washed off from the catalytic surface. Likewise, a poison in the hydrocarbon feed can be detoxified, prior to contacting with the catalyst, by oxidation to a nontoxic compound with a "shielded structure."

The usual method of detoxifying feed stock for hydrogenation is to contact it with a hydrogenation catalyst—preferably the one to be used for the actual hydrogenation—at a suitable temperature, in the presence or absence of hydrogen. The poisoned catalyst is subsequently removed and replaced by fresh catalyst for the hydrogenation proper. In vapor phase operation the poison-containing feed can be first passed over a "guard catalyst" before contacting the actual hydrogenation catalyst.

The patent literature proposes many methods of regenerating hydrogenation catalysts in situ. Whether or not an exhausted hydrogenation catalyst is reworked—dissolved and reprecipitated—depends upon its price, and it is usually only the platinum group metals which are so processed. Wichers[120] describes a method for the reworking of platinum residues.

Hydrogenation Technique and Scope

Excellent presentations are available on the technique[2, 40, 117], kinetics[8, 10, 43, 57], and scope of hydrogenation[2, 11, 17, 29, 30, 38, 97].

Practically any olefinic hydrocarbon, in the absence of poison, can be hydrogenated at 100 to 200°C under 100 atmospheres of hydrogen by means of nickel-kieselguhr or Raney nickel. Copper chromite hydrogenates olefins, but it requires a higher temperature than nickel[2]. The temperature employed in hydrogenation should be as low as compatible with the desired rate in order to avoid cleavage and isomerization reactions. Cycloolefins are hydrogenated to cycloparaffins, and the latter, at higher temperatures, cleave to open-chain paraffins, and they also rearrange, e.g., cyclohexane to methylcyclopentane, and vice versa. Similar rearrangements take place with cycloheptane and cyclooctane.

Large-Scale Hydrogenation of Olefinic Hydrocarbons

Octenes, prepared by the polymerization of butenes, have been hydrogenated industrially over a nickel-porcelain catalyst under 60 psig of hydrogen at about 180°C[108], and also over a sulfur-resistant catalyst[18] under more drastic conditions of pressure and temperature.

Olefin-containing cracked naphtha is selectively hydrogenated in large scale operation. The olefins, mainly of branched structure, are hydrogenated to isoparaffins of high octane number and the aromatics are not affected. The presence of sulfur in the feed requires the use of sulfur-resistant catalysts, and with naphtha of high sulfur content there is substantial elimination of sulfur as hydrogen sulfide[114].

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CHAPTER 4

THE ADDITION OF HYDROGEN TO CARBON-CARBON TRIPLE BONDS

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Introduction

Nomenclature

Hydrocarbons containing one or more carbon-carbon triple bonds will be referred to in this chapter by the interchangeable generic names acetylenes and acetylenic hydrocarbons, in place of the more rigorous term alkynes which the Geneva system recommends. The hydrocarbon C_2H_2 is acetylene, not ethyne, following the usual practice, and the hydrocarbon C_3H_4 will be called methylacetylene and not propyne; higher homologs are however conveniently described by the Geneva system. For the sake of brevity, the carbon-carbon triple bond will also be called the acetylenic bond, to avoid confusion with other triple bonds. The term hydrogen means the hydrogen molecule of mass 2, the isotopic species of mass 4 being referred as deuterium.

The Structure and Thermochemistry of the Acetylenic Bond

Interatomic distances in acetylenic hydrocarbons have been determined with great accuracy by a variety of modern physical methods[1], and the results are summarized in Table 1. These values are to be compared with normal carbon-carbon single and double bond distances of 1.54Å and 1.35Å, respectively.

In methylacetylene and the higher homologs of acetylene, hyperconjugation effects are thought to be operating[2]; this means that the π-electrons of the triple bond are less tightly bound (or are more delocalized) than they are in acetylene, and an increased stability results; the carbon-carbon single bonds therefore partake of some multiple character. Assuming a general relation between interatomic distance and bond-energy[3], the shortening of the formal single bond in methylacetylene (Table 1) means that it has a greater bond energy than has, say, the single bond in ethane. $CH_3—C\equiv$ bonds in dimethylacetylene and dimethyldiacetylene are similarly shortened, and in diacetylene and dimethyldiacetylene the central formal single bond is almost as short as the double bond in ethylene (1.353 Å). Hyperconjugation effects are also found in propylene and higher olefins, but are not as marked as in the acetylenes, due to the smaller number of mobile electrons[2].

The problem of the polarity of carbon-hydrogen bonds has recently been reviewed[4], and while it is well known that a carbon-hydrogen bond adjacent to an acetylenic bond has marked acidic properties (as witnessed for example by the ready formation of metal acetylides), the magnitude of the $\mathrm{C} \leftarrow\!\!\!+ \mathrm{H}$ dipole is not known. It is supposed that a carbon-hydrogen bond adjacent to an ethylenic bond is not markedly polar, and that in paraffins the direction of the dipole is reversed.

TABLE 1. INTERATOMIC DISTANCES IN ACETYLENIC HYDROCARBONS, IN Å

Molecule	$—C\equiv C—$	$\equiv C\text{-}C\equiv$	$H_3C—C\equiv$	$\equiv C—H$	$—CH_2—H$
$HC\equiv CH$	1.207	—	—	1.060	—
$CH_3—C\equiv CH$	1.207	—	1.460	1.056	1.097
$CH_3—C\equiv C—CH_3$	1.20	—	1.47	—	
$HC\equiv C—C\equiv CH$	1.19	1.36	—		—
$CH_3—C\equiv C—C\equiv C—CH_3$	1.20	1.38	1.46	—	

TABLE 2. HEATS OF FORMATION (Q_f) AND ATOMIC HEATS OF FORMATION (Q_a) OF SOME ACETYLENES, OLEFINS AND PARAFFINS IN KCALS PER MOLE

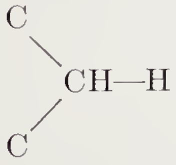
Molecule	Q_f	Q_a
Acetylene	−54.19	388.6
Ethylene	−12.50	533.7
Ethane	20.24	669.8
Methylacetylene	−44.32	671.6
Propylene	−4.88	814.4
Propane	24.82	947.5
Dimethylacetylene	−35.37	953.6
cis-Butene-2	1.36	1093.8
trans-Butene-2	2.04	1094.4
n-Butane	29.81	1225.6

The formation of acetylene from hydrogen and graphite is endothermic to the extent of about 54 kcals per mole and the heat evolved in its hydrogenation is correspondingly great. Values of the heats of formation (Q_f) at 25°C of acetylenes, olefins and paraffins have been obtained from their heats of combustion[5], and a selection of these is given in Table 2, together with the atomic heats of formation (Q_a), assuming the latent heat of sublimation of carbon to be 169.7 kcals per mole[6], and the dissociation energy of hydrogen to be 103.4 kcals per mole. From either of these sets of data, the heats of the various hydrogenation reactions can be readily computed, and such figures are given in Table 3, together with values found by direct experiment[7].

It is in theory possible to assign to each bond in a molecule a bond-energy (E), so defined that the sum of all the bond-energies in that molecule is equal to its atomic heat of formation. In practice however the task of distributing the available energy among the bonds of a molecule is never simple, and some assumptions have always to be made. It is probably safest to assume that the energy of a carbon-hydrogen bond is not greatly dependent on its environment[3]; it has been suggested[8] that the following values may be accepted:

TABLE 3. HEATS OF HYDROGENATION

Reaction	Heats of Hydrogenation (kcals per mole)	
	$-\Delta H_{298}$ (Derived from Q's)	$-\Delta H_{355}$ (Experimental)
Acetylene → ethylene	41.7	42.3
Ethylene → ethane	32.7	32.6
Methylacetylene → propylene	39.4	39.6
Propylene → propane	29.7	29.9
Dimethylacetylene → *cis*-butene-2	36.7	37.0
Dimethylacetylene → *trans*-butene-2	37.4	38.0
cis-Butene-2 → *n*-butane	28.4	28.6
trans-Butene-2 → *n*-butane	27.8	27.6



	=CH—H	≡C—H
98 kcals	99 kcals	100 kcals

With this assumption and knowing the heats of formation, it is possible to derive carbon-carbon bond-energies as defined above, but when two such bonds of differing multiplicities are present in the same molecule, only the sum of their energies and not their separate values may be found. However, in a case such as methylacetylene, where the interatomic distance is markedly different from that in a paraffin, it is possible to read off the bond-energy from a bond-energy—interatomic distance curve[9]. Some values for carbon-carbon bond-energies in various molecules obtained in this way are given in Table 4, where the last column shows the energy required to open the first π-bond of the multiple bond. These values are consistent with the known heats of formation, but their approximate nature must be stressed, although even so the qualitative trends which are shown will be of assistance in interpreting the results to be considered later.

The greater stability of methylacetylene over acetylene which was predicted on the grounds of hyperconjugation is shown by the fact that more energy is required to open the first π-bond in the former than in the latter, and by the necessary corollary that its heat of hydrogenation is about 3 kcals smaller than for acetylene (Table 3). A similar comparison may also be made between propylene and ethylene. Table 4 shows furthermore that it is easier to open a triple bond than a double bond, in agreement with the heats of hydrogenation results.

Table 4. Bond-Energies in Some Hydrocarbons, in kcals

Molecule	E_{C-C}	$E_{C=C}$	$E_{C\equiv C}$	E_{π}
Acetylene	—	—	190	50
Ethylene	—	140	—	57
Ethane	83	—	—	—
Methylacetylene	100	—	180	54
Propylene	89	137	—	60
Propane	83	—	—	—

Books and Reviews

The very rapid development of acetylene chemistry in the past decade has prompted the appearance of a number of books and reviews concerned principally with the organic chemistry of acetylene and its derivatives. The following books give accounts of progress in this field: "Acetylene Chemistry" by Bergman[10]; "Acetylene Homologs and Derivatives" by Piganiol[11]; "Acetylene and Carbon Monoxide Chemistry" by Copenhaver and Bigelow[12]; B.I.O.S. Report 30[13]; and "Chemistry of Acetylene" by Nieuwland and Vogt[14]. All have some mention of hydrogenation reactions, but their treatments are in general brief and incomplete. The review by Eley[15] deals briefly with the hydrogenation and exchange reactions of acetylene, and that by Campbell and Campbell[16] covers the whole field of the addition of hydrogen to multiple carbon-carbon bonds, including chemical as well as catalytic methods of reduction, up to 1942; but advances made since that date make desirable a more thorough treatment of the subject, which it is the object of this chapter to attempt.

The Hydrogenation of Acetylenic Bonds: A General Survey

The difficulties encountered in reviewing this field are many and varied; the subject has been approached from a number of different angles, and work reported in the literature is of very varying quality. No attempt will be made to produce a compendium of published work which might fall under the heading of this chapter, and the selection of material has been admittedly somewhat arbitrary; however, an honest effort has been made to give each piece of work the prominence it merits.

The industrialist's interest in the reactions to be reviewed is of quite long standing. For example, considerable effort has been devoted to the problem of obtaining high yields of ethylene from acetylene by hydrogenation; ethylene so obtained is, however, more costly than that produced from, for example, the cracking of natural gas, and so this method is only invoked when that and other sources of ethylene are not available[11, 13]. It has also been suggested that the polymers formed by side reactions during the hydrogenation of acetylene may be of potential value as motor fuels, although the relatively high cost of acetylene (when compared to the low cost of raw materials for the Fischer-Tropsch synthesis) makes this process uneconomical at the present time.

Turning to the more fundamental aspects of the subject, one finds that the study of the hydrogenation of acetylenic bonds has been greatly neglected in comparison with the very large volume of work concerning the problems of olefin hydrogenation[15]. This is the more to be deplored, since the hydrogenation of acetylenes also poses questions of great interest. It seems unprofitable to regard the mysteries of catalytic hydrogenation as being solely connected with olefins; comprehensive theories must take account of all known types of reaction, and the lack of knowledge which exists concerning the reactions of acetylenic compounds must necessarily retard the progress of such theories. Reasons for this want of balance are not however far to seek; the reactions are more complicated, and it is frequently found that acetylene acts as a strong catalyst poison[17, 18, 19]. Moreover, from a practical standpoint, the reactions are of rather less importance than the corresponding reactions of olefins.

There is, nevertheless, an impressive body of work to review, and it may be helpful at this time to draw attention to certain observations which in a general manner characterize the hydrogenation of acetylenes. Firstly, it has been widely found that in the gas phase the rate of reaction is roughly proportional to the hydrogen pressure, and independent of, or inhibited by increase of, acetylene pressure; these facts are interpreted to mean that acetylene is strongly adsorbed on the catalyst, to the effective exclusion of hydrogen. Much evidence also shows that acetylenes can successfully displace olefins from catalyst surfaces, with the result that the latter are often selectively produced. Secondly, the hydrogenation of acetylene gives rise to higher hydrocarbons under almost all conditions, and this occurs at temperatures far lower than those at which acetylene begins to polymerize by itself; this is a type of reaction not occurring with olefins, and so deserves special attention. The greater part of the work to be considered concerns the gas phase hydrogenation of acetylene itself, and each of the more important transition metals employed as catalysts is discussed separately.

The hydrogenation of higher acetylenic hydrocarbons and of organic molecules containing acetylenic bonds is usually accomplished in the liquid phase, and a variety of catalyst preparations is available and convenient for this type of work. Such reactions are however normally only preparative, and little fundamental work has been done on them; the main problems which arise are, firstly, how the reaction may be stopped at the olefin stage, and secondly, whether the olefin has a *cis* or *trans* configuration[16]. These points are of great importance in organic syntheses, and the present position of this subject is discussed on pages 142–145. The results are conveniently interpreted in terms of the ideas developed on pages 129–136.

THE GAS PHASE HYDROGENATION OF ACETYLENIC BONDS

The Hydrogenation of Acetylene

Nickel as Catalyst. The passage of hydrogen and acetylene over reduced nickel powder at room temperature was found by Sabatier and Senderens[20] to cause the catalyst to heat up. In addition to obtaining ethylene and ethane, they recorded the considerable formation of higher hydrocarbons containing aromatic and hydroaromatic materials, whose yield was increased by raising the acetylene concentration. The reaction is clearly one of some complexity, and any kinetic data obtained without full simultaneous analysis of the reaction products will therefore be of little value. This aspect of the problem has however been frequently neglected in the past.

It will be found convenient to classify the reactions which are taking place in the following manner:

$$C_2H_2 \xrightarrow{H_2} C_2H_4 \xrightarrow{H_2} C_2H_6 \tag{I}$$

$$C_2H_2 \xrightarrow{H_2} \text{higher hydrocarbons} \tag{II}$$

It is then possible to determine the relative extent of these two reactions under various conditions by defining the amount of ethylene and ethane found divided by the amount of acetylene removed, as the "percentage recovery" or "yield of C_2 hydrocarbons;" this then gives the ratio of the rates of the two reactions.

By the method of initial rates of pressure fall over a pumice-supported nickel catalyst at 79°C, orders of reaction were found by Sheridan[21] to be first with respect to hydrogen and zero or slightly negative with respect to acetylene; the reproducibility of the rates was hardly sufficient to make a clear-cut decision possible. Product analysis showed that both reactions had kinetics approximately of this type, differing only to the extent that changing the initial hydrogen:acetylene ratio from 1:8 to 8:1 increased the yield of C_2 hydrocarbons from about 40 to 67 per cent. In view of the wide range of partial pressures covered, this change is not of great significance. The detailed results are shown in Figure 1. It was also demonstrated that the kinetics were the same in the temprature range 0 to 91°C.

It is necessary to exercise the greatest caution when considering the kinetics of surface reactions; the orders of reaction, when placed in the form of an initial rate law may fail to predict the form of the pressure-time curve for a particular experiment. The hydrogenation of acetylene is such a case; the initial rate law

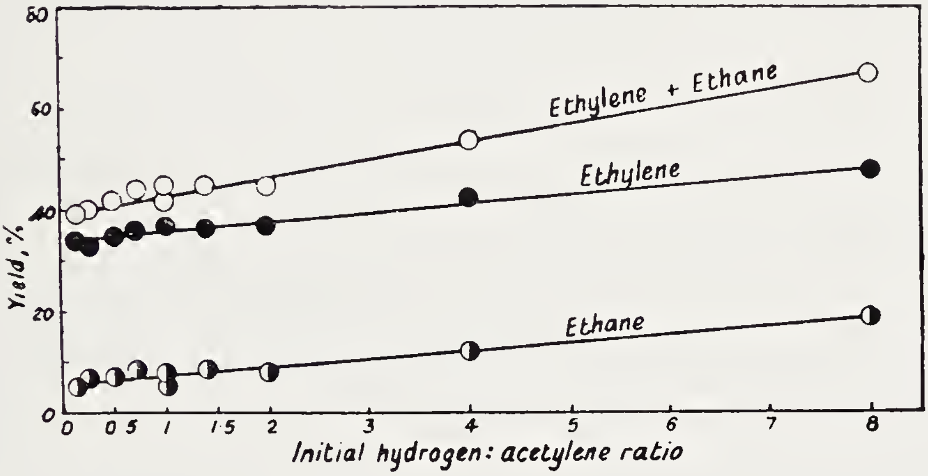


Figure 1. The effect of initial H_2/C_2H_2 ratio on yields at 83°C[21]. (Courtesy *J. Chem. Soc.*)

$$-\frac{dp}{dt} = kP_{H_2}P^0_{C_2H_2}$$

is valid only when applied to pressure-time curves if hydrogen is not in excess. When the hydrogen:acetylene ratio is equal to or greater than two, the rate of hydrogenation is constant until about 70 per cent of the acetylene is removed, at which point the hydrogenation of ethylene begins to predominate. This constancy of rate is clearly not in accord with the above expression. The rate, therefore, appears to be determined solely by the initial pressure of the reactants and no explanation of this has yet been published (see, however, Thon and Taylor[21a]). However the initial rate law suggests that acetylene is strongly chemisorbed on the surface, and that reaction is initiated when a gaseous hydrogen molecule strikes the layer of adsorbed acetylene with sufficient kinetic energy.

Kinetics of a somewhat different type were found by de Pauw and Jungers[22] over reduced nickel powder at 30°C. In experiments using a 3- to 20-fold excess of hydrogen, the rate of pressure fall was constant until an amount of hydrogen had been consumed equivalent to the initial pressure of acetylene, when a marked acceleration occurred. This was attributed to the more rapid hydrogenation of the ethylene formed in the first part of the reaction. The acceleration was not found at 52°C or at higher temperatures, which may explain why the phenomenon was not noticed by Sheridan, who performed no experiments under the necessary conditions.

Always using hydrogen in some excess, de Pauw and Jungers deduced the initial rate law

$$-\frac{dp}{dt} = kP_{\mathrm{H_2}} \cdot P_{\mathrm{C_2H_2}}^{-0.5} .$$

They interpreted this expression to mean that reaction occurs through the interaction of adjacently adsorbed acetylene molecules and hydrogen atoms, and by means of Langmuir isotherms for the adsorbed reactants, they were able to deduce coefficients of adsorption for both reactants and products. The strong inhibition by acetylene is somewhat surprising, and implies a weaker adsorption of acetylene than Sheridan's expression. It would therefore appear dangerous to attempt to generalize from the results obtained over any particular catalyst preparation.

Product analysis during the course of a static reaction yields information of great interest concerning its "selectivity," that is, the ratio of the rates of formation of ethylene and ethane. It is one of the most significant features of the hydrogenation of acetylenic bonds that frequently this ratio is constant until ethylene removal begins. Sheridan[21] has studied the courses of reaction of 1:1 and 2:1 hydrogen:acetylene mixtures at about 80°C and his results are reproduced in Figures 2 and 3. His catalyst Ni-2 had a nickel-pumice ratio of 1:5. In both cases, acetylene was removed rather more rapidly than hydrogen, and ethylene was formed about five times as fast as ethane; the yield of C_2 hydrocarbons was only 40 to 45 per cent. Higher olefins (presumably butenes) were detected in the gas, and the higher hydrocarbons had an empirical composition of C_4H_7 ; their formation ceased after the complete removal of the acetylene.

Sheridan[23] showed that although the kinetics of Reactions (I) and (II) are similar, their temperature dependences are quite different. By taking 1:1, 2:1 and 1:2 hydrogen:acetylene mixtures at various temperatures and analyzing the products formed afer a pressure fall equal to the initial pressure of whichever reactant was not in excess, he found that the yields of ethylene and ethane increased in every case as the temperature was lowered. For equimolar mixtures, the yield of C_2 hydrocarbons was 65 per cent at 0°C and 31 per cent at 126°C. From these figures, and knowing the effect of temperature on the initial rate of pressure fall, it was possible to deduce that the activation energy of Reaction (I) was 10.9 kcals (0–126°C) and of Reaction (II) was 12.7 kcals at 126°C, rising to 14.5 kcals at 0°C.

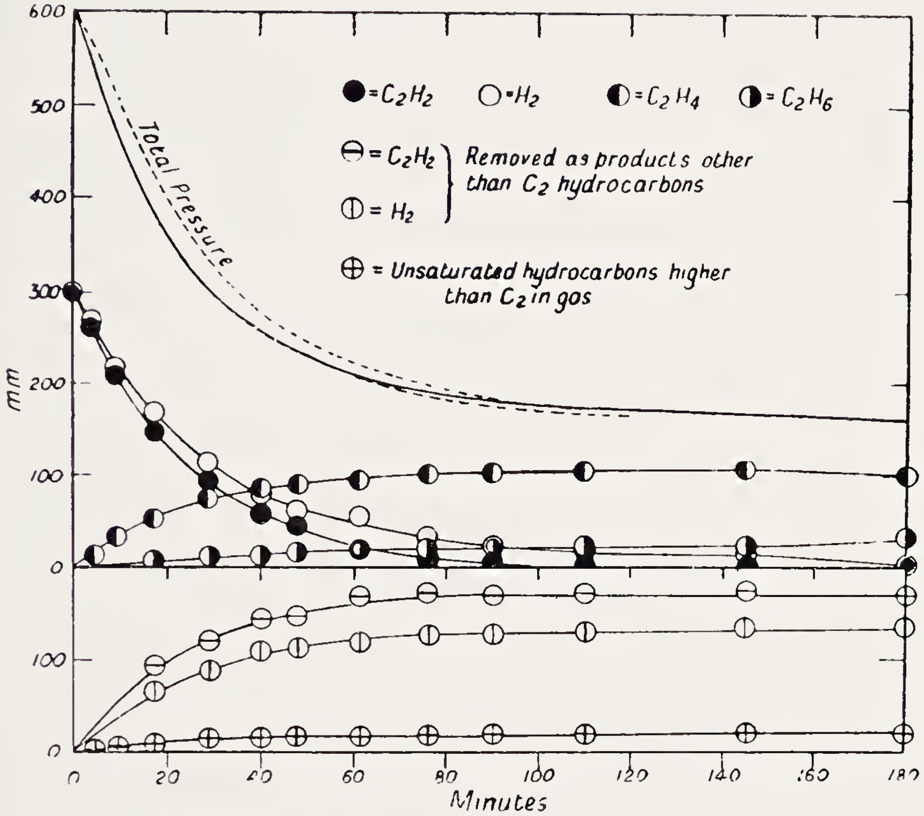


Figure 2. The course of reaction of a 1:1 H_2/C_2H_2 mixture at 79°C over catalyst Ni-2. The continuous total pressure curve is that for the experiment of 180 minutes duration. The dotted lines show the extremes of deviation of the total pressure curves from the continuous line[21]. (Courtesy *J. Chem. Soc.*)

It is, however, apparently not possible to extrapolate these data to higher and lower temperatures, and further investigation outside the temperature covered here is clearly needed. There is no evidence for an inversion of the temperature coefficient as is found in the case of ethylene[15].

The hydrocarbons higher than ethylene and ethane which are formed during the hydrogenation of acetylene over nickel have been the subject of several careful studies. With nickel on a zinc chloride base, Petrov and Antsus[24] reported the formation of butadiene and isobutene, together with mono- and diolefins having the carbon skeletons of *n*-hexane, 2- and 3-methylpentanes, 2,3-dimethylbutane, 3-ethylhexane and 2-, 3- and

4-methylheptanes. Traces of benzene were detected and n-C_8 hydrocarbons were thought to be present. It should be noted that zinc chloride is a highly active base, and may assist isomerization of the original products. On a kaolin base, which is much less active, they noted the formation of n-butane and isobutane structures.

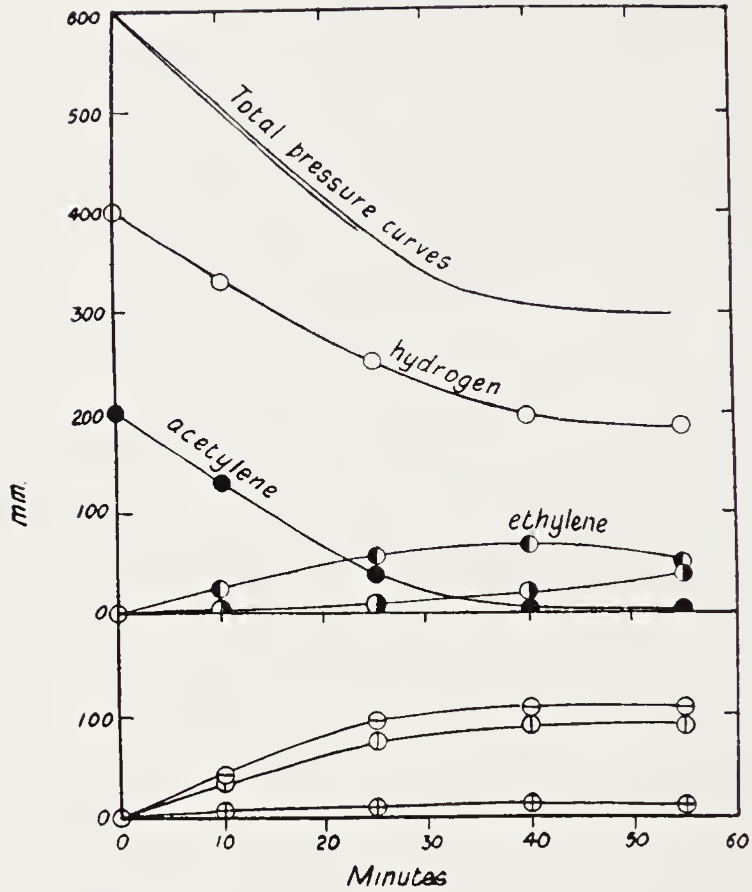


Figure 3. The course of reaction of a 2:1 H_2/C_2H_2 mixture at 72°C over catalyst Ni-2[21]. The significance of the various types of point are as in Figure 2. The two total-pressure curves shown are the extremes within which all the curves fall. (Courtesy *J. Chem. Soc.*)

The investigation of a quantity of higher hydrocarbons produced in a flow system at 200 to 250°C over a nickel-pumice catalyst has been described by Sheridan[23]. Distillation after complete hydrogenation showed that hydrocarbons containing from 4 to 8 carbon atoms were definitely present, and higher boiling material indicated that there were also present hydrocarbons of greater molecular weight. Refractive indices provided conclusive proof of the occurrence of pentanes. Infrared analysis gave further information on the type of carbon skeleton in these hydrocarbons; thus the C_6 fraction was mainly n-hexane and 3-methylpentane, and other skeletons positively located were *n*-pentane, 2-methyl-butane and 3-methylhexane. Table 5 gives approximate percentage yields for the various molecular weight ranges. Thus more than half of the polymers formed contain carbon skeletons which can be formed by the simple union of two or more C_2 units.

Vassiliev[25], using a nickel-alumina or nickel-kaolin catalyst, and temperatures in the range 210 to 280°C, found that saturated and nonsaturated aliphatic hydrocarbons formed the bulk of the products, but in addition by Raman spectroscopy he was able to demonstrate the presence of cyclohexane, cyclohexene and some of their methyl derivatives, which Sheridan did not detect. Vassiliev also found small amounts of benzene, toluene, xylene, trimethyl benzenes and isopropyl benzene.

The use of isotopic tracer methods greatly aids the understanding of the subtler points of catalytic hydrogenation mechanisms, but this technique has not yet been thoroughly applied to the hydrogenation of acetylene. However, in an interesting paper[26], Douglas and Rabinovitch report some qualitative experiments in which certain trends are apparent. In attempting to prepare *cis*-ethylene-d_2 from acetylene and deuterium by a flow method over a nickel-kieselguhr catalyst at room temperature, they found that all the possible deuterated ethylenes were formed, besides ethanes and "polymerized material." However, *cis* and *trans*-ethylene-d_2 were formed in excess of that expected from statistics, and together accounted for about half the total ethylenes. The early products contained 80 per cent ethylene and ethylene-d_1, and 0.4 per cent acetylene-d_1, whereas later products were deuterated ethylenes (unanalyzed) and 1 per cent acetylene-d_1. Also, in a flow system, acetylene-d_2 and hydrogen gave mixed ethylenes and 6 per cent acetylene-d_1. In a static system at −80°C, acetylene and deuterium gave 70 per cent ethylene-d_2, 15 per cent ethylene-d_1 and 10 per cent ethylene-d_3. Under similar conditions, the use of equilibrated and nonequilibrated hydrogen-deuterium mixtures showed very clearly that addi-

Table 5. Yields of Higher Hydrocarbons from Acetylene Hydrogenation Over Nickel at 200 to 250°C

Molecular Weight	Approximate Percentage Yield
C_4	25
C_5	2
C_6	25
C_7	2
C_8	5
C_9-C_{14}	7
C_{15}-C_{30}	17
C_{31}-C_x	17

tion proceeded atomically rather than molecularly. de Pauw and Jungers[22] reported that deuterium reacted with acetylene about 1.5 times faster than hydrogen. More detailed work is bound to give results of great interest.

The hydrogenation of acetylene has also been studied over evaporated nickel films, but since the results are apparently more characteristic of the method of preparing the catalyst than they are of the metal employed, they are more conveniently discussed on pages 128–129.

A certain amount of work has been done on the effect of the catalyst support, and on the effect of added substances on the reaction. Sheridan[27] investigated acetylene hydrogenation over nickel supported by pumice, kieselguhr-waterglass, commercial activated alumina, precipitated alumina, vanadium pentoxide-waterglass and chromium sesquioxide-waterglass. The temperature at which these preparations were active in a flow system varied somewhat, but all were active in the range 140 to 210°C. The yields of C_2 hydrocarbons were all in the range 29 to 52 per cent, showing that here the catalyst support had no major action.

It is generally agreed that added ethylene does not take part in the reaction, at least until most of the acetylene has been removed. Sheridan[21] and de Pauw and Jungers[22] both report results to this effect. Carbon dioxide and nitrogen both act as inert diluents[28]; however, more than 2 per cent of nitric oxide retards the rate of reaction, but does not greatly alter the yield of C_2 hydrocarbons[28]. Most of the nitric oxide apparently became incorporated in the polymers. Two per cent or more of carbon monoxide has been said to decrease the yield of C_2 hydrocarbons[29].

The hydrogenation of acetylenes is not nearly so much affected by the presence of oxygen as is the hydrogenation of olefins. In Sheridan's work[28], small amounts of oxygen retarded the rate of reaction, but no induction periods were found, and the catalyst regained its former activity after a few runs. The presence of oxygen increased the yield of C_2 hydrocarbons, and both this and the retardation were roughly proportional to the amount of oxygen present.

The introduction of steam into a flow system through which acetylene and hydrogen were being passed has been reported to raise the yield of C_2 hydrocarbons[30], but the probable effect here (as in the case of carbon dioxide, which has also been used for this purpose[31]) is that the diluent helps to dissipate the heat of reaction, and so cuts down the overheating of the catalyst which would result in greater polymer formation.

It is finally necessary to say something about the reactions of acetylene alone over the various nickel catalysts which have been used for hydrogenation purposes. At high temperatures acetylene undergoes decomposition, but only those reactions taking place below about 150°C will be considered here. The notable effect of the method of catalyst preparation on the form of the reaction has already been pointed out, and this is most likely to be due to variations in the manner of adsorption of the acetylene. In general it appears that acetylene is very strongly adsorbed on wires and films, with the result that the catalyst is poisoned for hydrogenation or other reactions, although on supported catalysts such action is often not detected. Further experimental evidence will now be given to elaborate on these generalizations.

It has been frequently noted that acetylene poisons a nickel wire so that it is subsequently not active for the hydrogenation of either acetylene or ethylene[17, 18]. Beeck reported that preadsorbed acetylene could not be hydrogenated off a nickel film at 23°C[32], but nothing is known of the state of adsorbed acetylene under these conditions. It has none the less been possible to measure the heat of adsorption of acetylene on an evaporated nickel film, at least up to about half surface coverage. For a bare surface the value is about 66 to 67 kcals[33], and this figure is not much dependent on the fraction of surface covered.

Douglas and Rabinovitch[26] state that on nickel-kieselguhr acetylene is adsorbed partly as a carbon complex, and that it self-hydrogenates to ethylene, but only to 20 per cent of the extent to which ethylene disproportionates under similar conditions. They also show that acetylene is able to exchange with hydrogen remaining from previous reduction. A nickel-pumice catalyst can be kept in acetylene without loss of activity, which suggests that in this case only reversible associative adsorption is taking place[8, 34]. The hydrogen atoms of acetylene thus adsorbed are easily exchangeable, as is witnessed by the occurrence of the reaction

$$C_2H_2 + C_2D_2 \rightleftharpoons 2C_2HD,$$

which has been the subject of a careful study[34]. This reaction to form C_2HD proceeds quite rapidly at 60°C, and exhibits first order kinetics, as is shown by Figure 4; the order of reaction with respect to total pressure of reactants is 0.65. Exprimental and theoretical determinations of the equilibrium constant gave a value of about 3.4, and between 40 and 100°C the activation energy was 10.7 kcals. The reaction

$$CH_3CCH + C_2D_2 \rightleftharpoons CH_3CCD + C_2HD$$

was also studied, and was found to be of 0.47 order with respect to total pressure, and to have an activation energy of 12.7 kcals. Neither of these reactions was accompanied by any polymerization, and excellent reproducibility of rates was found; however, if a hydrogenation experiment was made between two exchange runs, the rate of the second was less than the first, showing that hydrogenation had deposited polymers on the surface.

The absence of polymerization suggested that the exchange probably occurred without the formation of free hydrogen or deuterium atoms, and a mechanism invoking the reactivity of the strongly polar carbon-hydrogen bonds in acetylene was advanced to account for this.

It therefore appears that adsorbed acetylene behaves quite differently from gaseous acetylene, and that it is very strongly adsorbed on pure nickel. The varying results found with supported catalyst lend weight to the contention[35] that the normal nickel lattice is not in such cases present, but further investigation is required.

Iron as Catalyst. Very little work has been done using iron as a catalyst;

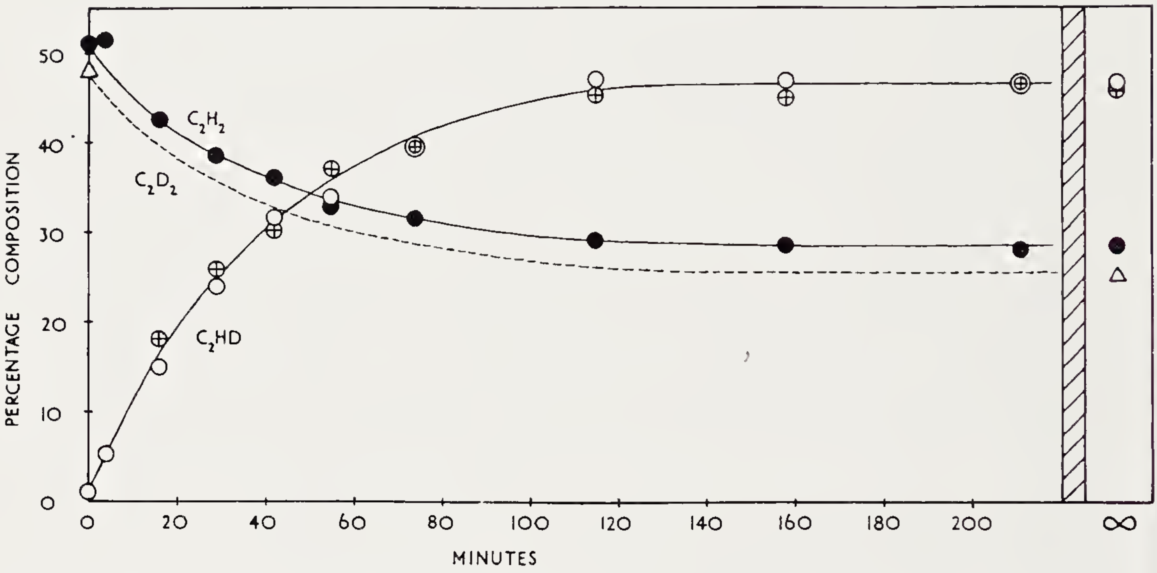


Figure 4. The course of the exchange[34] reaction between C_2H_2 and C_2D_2 at 119°C. ○ = C_2HD observed; ⊕ = C_2HD calculated from C_2H_2 removed (Courtesy *Trans. Faraday Soc.*)

Sabatier[36] stated that the hydrogenation did not occur below 180°C, and then always gave rise to the formation of large amounts of higher hydrocarbons, which were mainly unsaturated.

Sheridan[27] came to the conclusion that iron behaved very similarly to nickel; using iron supported on pumice, the reaction orders were as over nickel, and between 20 and 212°C the yields of C_2 hydrocarbons were 64 to 73 per cent. Increasing the hydrogen pressure only slightly increased the C_2 yield. Both reactions (I) and (II) therefore have similar pressure dependences and activation energies, the latter being estimated to be 15 to 16 kcals. Neither the addition of ethylene nor oxygen caused any alteration in the reaction, and in this last respect iron behaves very differently from nickel. It may also be noted in passing that oxygen has very little effect on the ethylene-hydrogen reaction over iron.

Cobalt as Catalyst. Cobalt has been even less thoroughly investigated than iron. Sabatier[37] found that cobalt was active for hydrogenation at 180°C, and that the chief product was ethane, with small amounts of higher hydrocarbons; their yield was however greater at 250°C. Using a cobalt-pumice catalyst, Sheridan[27] found that an equimolar mixture of hydrogen and acetylene gave about 50 per cent C_2 hydrocarbons at 200°C and 34 per cent at 250°C. At 200°C, reaction with a two-fold excess of hydrogen gave about 60 per cent C_2 hydrocarbons, and the indications were that reaction orders were similar to those for nickel and iron; however, rapid deactivation of the catalyst prevented systematic study.

Copper as Catalyst. Copper behaves very differently from those of the transition metals which have already been considered, inasmuch as it catalyzes the conversion of acetylene into a solid polymer cuprene, which Sabatier[38] said had the composition $(C_7H_6)_x$. This reaction also occurs in the presence of hydrogen provided that it is not in excess[38]. The specific action of copper in this respect is not well understood, but presumably may be associated with the geometric and electronic structure of the metal.

With excess of hydrogen, acetylene over copper gives rise to ethane and some liquid hydrocarbons[38]. Sheridan[27] found that with excess hydrogen over a copper-pumice catalyst at about 170°C the chief product was ethylene, with only a little ethane, and the total yield of C_2 hydrocarbons was 77 per cent. Owing to changes in the catalyst's activity, no systematic studies could be made.

Platinum as Catalyst. The metals most widely used for hydrogenation purposes are nickel, platinum and palladium; the last two have some features in common, but differ considerably from nickel. The results now to be presented show that the metal has at least an important modifying action on the form of the hydrogenation reaction, alhough it has not yet been possible to decide which parameters of the metal are responsible.

Sabatier[39] stated that with excess of hydrogen, acetylene gave pure ethane, and this result has been confirmed by Kistiakowsky and others[40], who used a platinum catalyst for their thermochemical studies. Sabatier added that with acetylene in excess, ethylene became the main product, but some ethane was also formed although unchanged acetylene still remained. Farkas and Farkas[41] stated that the rate of pressure fall over platinized platinum foil was accelerated by increasing the hydrogen pressure and retarded by increasing the acetylene pressure. Sheridan[42] reported that the order with respect to hydrogen was 1.2 and with respect to acetylene -0.7, over a platinum catalyst at 73°C. Over a similar catalyst at 162°C, the order was zero with respect to acetylene when the $H_2:C_2H_2$ ratio was less than unity, and negative when it was greater than unity, regardless of the total pressure employed.

This would suggest that the adsorption of acetylene over platinum is not as strong as over nickel, and that consequently hydrogen is able to displace acetylene from the surface when the former is present in sufficient excess. This would be in accordance with similar observations with olefins[43, 44]. In this case, the situation is similar to that found with nickel powder[22], and here also an adajcent-interaction mechanism may be operative.

According to Sheridan[42], when hydrogen was not in excess, pressure-time curves were of approximately first-order form, but when an excess of hydrogen was employed the rate of pressure change remained essentially constant until a point corresponding roughly to the complete removal of acetylene, when the rate accelerated. Other workers[41, 45] had also found a similar behavior, but had assumed that the formation was completely suppressed until the beginning of the acceleration, which they attributed to the more rapid hydrogenation of the ethylene.

By examining courses of reaction, Sheridan[42] came to the conclusion that this was only partly true; some of his results are shown in Figures 5 and 6. Over a platinum-pumice catalyst at 163°C, an equimolar mixture of reactants yielded about 70 per cent C_2 hydrocarbons, composed of roughly five parts of ethylene to one of ethane (Figure 5). With a 2-fold excess of hydrogen at 145°C, the yield of C_2 hydrocarbons was about 80 per cent, made up of about two parts of ethylene to one of ethane. The higher hydrocarbons formed were of relatively low molecular weight (not greater than C_8). At 57°C, the acceleration in the rate was much more marked than at 145°C (Figure 6), although ethylene formation was only twice as great as that of ethane in the early stages. The acceleration in general begins while a finite pressure (about 20 mm) of acetylene remains, the exact value in any particular case depending on the partial pressures of the other reactants present. This acceleration provides clear evidence that acetylene is more strongly adsorbed than ethylene, and the fact[42] that added ethylene acts merely as an inert diluent serves to confirm this. The ethane therefore probably arises from adsorbed ethylene which has not vacated the surface following the first addition process. At constant temperature, the yield of C_2 hydrocarbons was not markedly dependent on the hydrogen:acetylene ratio, and the kinetics of Reactions (I) and (II) are therefore similar, as in the case of nickel.

The effect of temperature has also been investigated; Sheridan[42] found that lowering the temperature increased the ethane yield relative to that of ethylene, affecting the total yield of C_2 hydrocarbons only slightly. The activation energies were expressed as, for Reaction (I), 12 kcals, and for Reaction (II), 13 to 14 kcals. Farkas and Farkas[41] gave the over-all activation as 12 to 17 kcals.

Farkas and Farkas also reported that deuterium reacts more slowly than hydrogen at 20°C, which is in contradistinction to its behavior over nickel[22]. During the reaction of acetylene with deuterium, the D content of the deuterium decreased by only 1 per cent while the acetylene was being hydrogenated, and after this it fell by 34 per cent during the hydrogenation of the ethylene. This indicates that the reaction

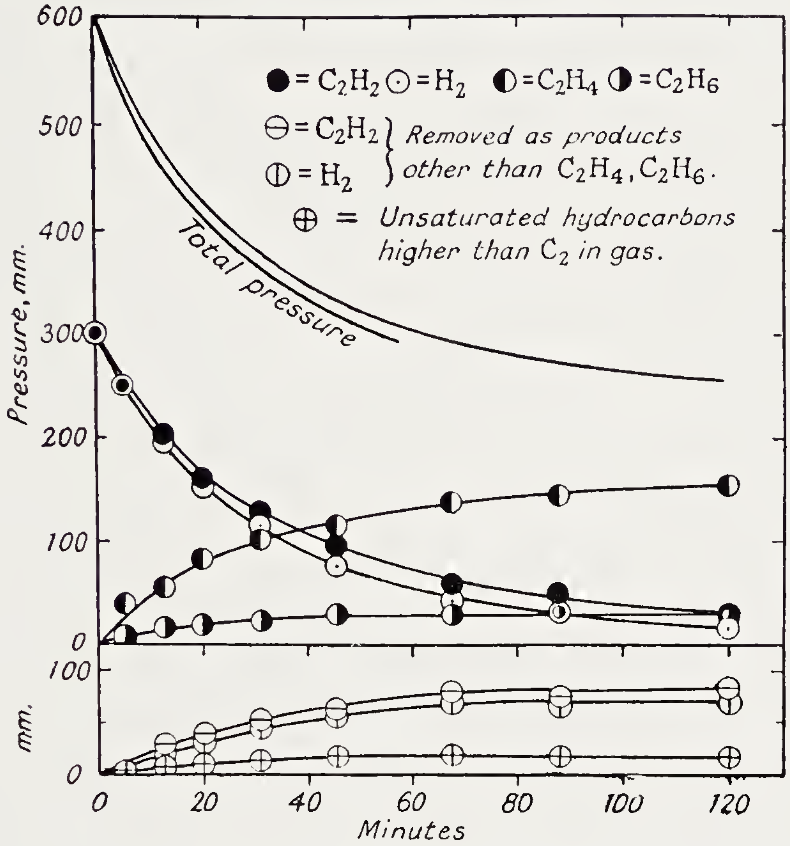


Figure 5. The course of reaction of a 1:1 H_2/C_2H_2 mixture over platinum at 160°C[42]. The limits of variation of total pressure curves are shown. (Courtesy *J. Chem. Soc.*)

$$C_2H_2 + D_2 \rightleftharpoons C_2HD + HD$$

was not proceeding readily, which is qualitatively in harmony with the results of Douglas and Rabinovitch over nickel[26]. The rate of parahydrogen conversion at 25°C, which was suppressed 3-fold by ethylene, was suppressed 15-fold by the presence of acetylene, indicating a very low concentration of free hydrogen atoms.

Palladium as Catalyst. Palladium shows very marked resemblances to platinum; thus at 24°C over a palladium-pumice catalyst, Sheridan[27] found that with a 3-fold excess of hydrogen, the pressure-time curve was initially linear, and that the rate began to increase when about 30 mm of acetylene remained. The initial rate of ethylene formation was about ten times that of ethane, and the total yield of C_2 hydrocarbons was about 75 per cent; the higher hydrocarbons were stated to have low molecular weights. The results are shown in Figure 7.

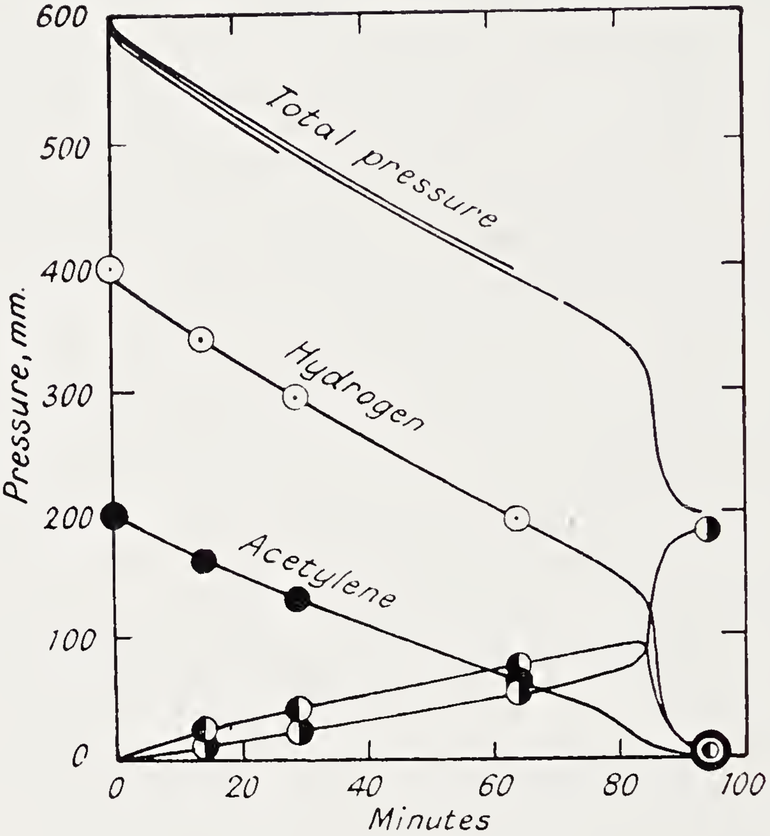


Figure 6. The course of reaction of a 2:1 H_2/C_2H_2 mixture over platinum at 57°C[42]. The significance of the various types of point is as in Figure 5, and the limits of variation of total pressure curves are shown. (Courtesy *J. Chem. Soc.*)

This system has also been examined by Cremer, Knorr and Plieninger[46], but their results were not supported by gas analyses. Tamaru[47], using a 1 per cent palladium-alumina catalyst at 30°C, stated that a rapid increase in rate occurred when all the acetylene was used up, and that no ethane was formed until that time. He also prepared[48] palladium-kieselguhr catalysts having metal:support ratios of from 1:50 to 1:750, and found that at 34°C the rate constant of ethylene formation decreased linearly with increasing palladium content, but that the rate constant of ethane formation went through a maximum when the metal:support ratio was 1:100. Thus more dispersed catalysts showed a higher selectivity. A similar catalyst (0.01 per cent palladium on silica) was employed in Germany in the last war for the large scale production of ethylene from acetylene[13].

Orders of reaction have been stated to be about first with respect to hydrogen and about −0.4 to −0.7 with respect to acetylene over palladium-

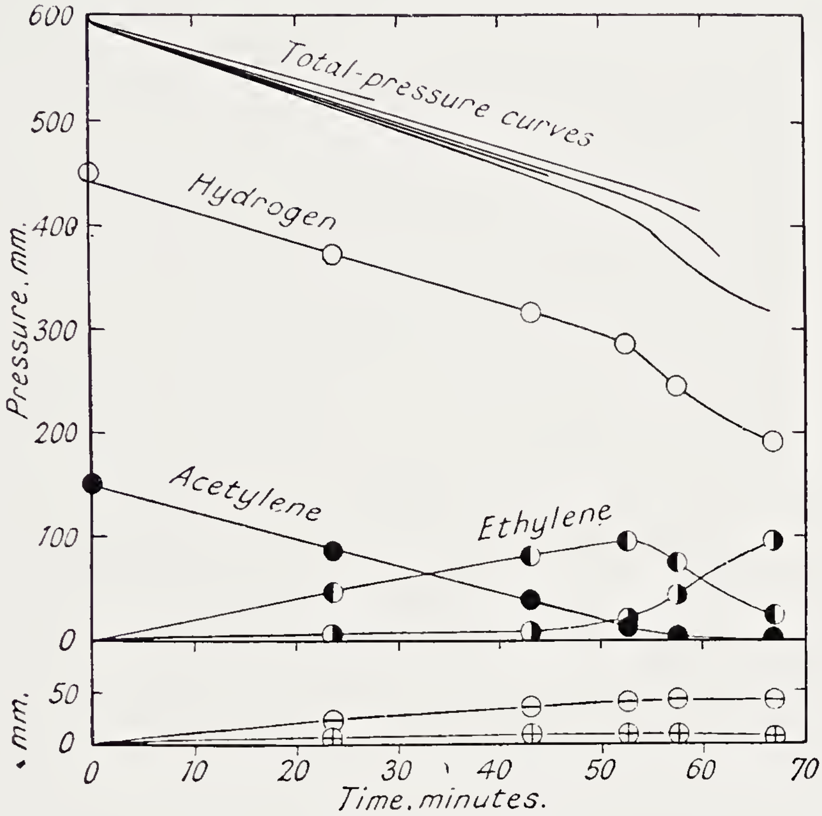


Figure 7. The course of reaction of a 3:1 H_2/C_2H_2 mixture over palladium at 24°C[27]. The significance of the points is as in Figure 5, and all total-pressure curves are shown. (Courtesy *J. Chem. Soc.*)

pumice catalyst at 49°C. Tamaru[47] expressed the kinetics in the form

$$-\frac{dp}{dt} = \frac{k_1 P_{H_2}}{1 + bP_{C_2H_2}},$$

and then attempted to correct this expression for retardation caused by the deposition of polymers on the surface[49], thus arriving at the rate equation

$$-\frac{dp}{dt} = \frac{k_1 P_{H_2}}{1 + b\sqrt{P_{C_2H_2}}},$$

but his methods are rather dubious. It is again, as in the case of platinum, possible that reaction occurs by the reaction of adjacently adsorbed atoms and molecules, which would be accommodated by a rate equation of the above type.

Sheridan[27] found that a 20-fold increase in the hydrogen:acetylene ratio increased the yield of C_2 hydrocarbons only from 62 to 80 per cent, from which he concluded that both Reactions I and II had similar kinetics. Tamaru[47] stated that no ethylene was produced when the initial acetylene was less than 41 per cent, and that no ethane was produced when it was greater than 51 per cent; he also reported greater polymer formation as the acetylene pressure was raised.

According to Tamaru[47], the difference between the rates of hydrogenation of ethylene and acetylene decreased as the temperature was raised, and the former became slower than the latter at about 74°C. The apparent activation energies which have been quoted are, for Reactions (I) and (II), 12 to 15 kcals[27], and for the over-all reaction, 12 kcals[47].

Ethylene acts primarily as diluent, confirming the stronger adsorption of acetylene which the previous results suggest; oxygen can considerably reduce the yield of C_2 hydrocarbons[27].

Other Transition Metals as Catalysts. Rhodium on pumice catalyzes the hydrogenation of acetylene at 80°C, and shows similar behavior to nickel; the usual orders of reaction are operative for both Reactions (I) and (II), and the yield of C_2 hydrocarbons is 70 to 80 per cent. The activation energy is 15.5 kcals[50]. It has been stated[32] that 40 per cent of a layer of preadsorbed acetylene can be hydrogenated off a rhodium film in one hour at 23°C, indicating that it is less strongly adsorbed than on nickel.

Iridium is not a very efficient catalyst, but it gives the normal orders of reaction, with yields of C_2 hydrocarbons of about 85 per cent. Ruthenium and osmium are scarcely active[50].

Mixed Transition Metals as Catalysts. Sheridan[27] has briefly examined the behavior of various combinations of nickel, cobalt and silver supported on pumice. He comments that nickel-cobalt was at least as active as nickel, but the yields of C_2 products (and especially of ethylene) were mostly rather greater than over nickel under like conditions. Nickel-silver resembled nickel in its action and nickel-cobalt-silver gave yields similar to those of nickel-cobalt; they were little affected by small amounts of nitrogen or nitric oxide.

Nickel, or preferably nickel combined with iron, cobalt or copper has been employed in the temperature range 125 to 250°C to remove acetylenes from cracking gases which may contain them[51].

Metallic Films as Catalysts. The use of evaporated metal films as catalysts has been urged in recent years, by reason of the high states of purity and reproducibility of surface area which can be attained by this technique; it is moreover possible to orient such films so that certain crystal faces are preferentially exposed[52]. There are however concomittant disadvantages[53]; such films are less active than supported catalysts, probably because the reactants are more strongly adsorbed on the former. They are also easily susceptible to poisoning for the same reason.

Experiments have been reported[19, 32] using films of iron, tungsten, nickel, rhodium, platinum and palladium; neither iron nor tungsten was active at 23°C. It was apparently possible to make certain generalizations concerning the reaction over all the other metals in the temperature range −20 to 100°C. "With all metals, in a given run in a static system, the rate increased as the reaction proceeded, due either to the surface being freed of a poisoning reversibly-adsorbed layer of acetylene, or to the decreasing partial pressure of acetylene; it passed through a maximum and then decreased to zero as all the acetylene and ethylene were hydrogenated. This maximum rate corresponded to a very small pressure of acetylene remaining, with mainly ethylene and ethane in the gas."

"On all metals, the hydrogenation of acetylene was slower by a large factor (10^2 to 10^3) than the hydrogenation of ethylene, due to the immediate and permanent poisoning of the catalyst, probably by acetylene polymers. This was in addition to the reversible poisoning referred to above. A fresh sample which had been exposed to even the lowest pressure of acetylene would never hydrogenate ethylene nearly as fast as a clean surface; it was therefore concluded that acetylene was a much more effective poison than ethylene."[19]

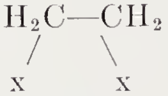
The order of activity (A) for the various films was as follows:

$$A_{\mathrm{Pd}} = 2A_{\mathrm{Pt}} = 2A_{\mathrm{Rh}} = 10A_{\mathrm{Ni}} .$$

The activation energies were in all cases 6 to 7 kcals, so that the variations in the rates must be associated with changes in the pre-exponential factor, as is the case with olefins[32].

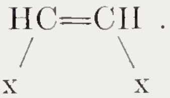
Reaction Mechanisms and Catalytic Activity. After this lengthy review of the experimental work which has been done on the gas-phase hydrogenation of acetylene over a variety of catalysts and under a variety of conditions, it may be profitable to consider what reaction mechanisms are operative. The task is much simplified by the fact that over all the catalysts employed (with the possible exception of evaporated films), the kinetics are of approximately the same form and particularly by the fact that in all cases the individual kinetics of the Reaction (I) and (II) (that is, the hydrogenation and the polymerization reactions) are closely similar. The detailed form of the kinetics, and probably also the activation energies, will be functions of the strength of adsorption of the reactants, and this in turn will be dependent upon the geometric and electronic structures of the catalyst (which are themselves inter-related).

The evidence shows that acetylene is strongly adsorbed on the catalyst, and this adsorption has been represented as associative chemisorption[21]. By analogy with ethylene, whose associative adsorption is generally shown as



$$\begin{array}{ccc} H_2C & — & CH_2 \\ / & & \backslash \\ X & & X \end{array}$$

adsorbed acetylene has been written as



$$\begin{array}{ccc} HC & = & CH \\ / & & \backslash \\ X & & X \end{array} .$$

Assuming that bond lengths and angles are the same in adsorbed ethylene as in ethane[54], and in adsorbed acetylene as in ethylene[55], one can calculate the X-X distances over which these molecules could be adsorbed with the least strain. The only unknown is the length of the C-X bond, and it has been supposed[21] that this is satisfactorily given by the sum of the covalent radii, as quoted by Pauling[9]. The C-Ni bond is therefore 2.0 Å, and the C-Pt and C-Pd bonds are both 2.1 Å. The optimum and the available X-X distances for adsorption are given in Table 6.

The (100) faces of each metal contain only the longer spacings, the (111) faces only the shorter spacings, while the (110) faces contain both. It is evident that ethylene will adsorb on the shorter distances, with greatest strain in the case of nickel, and that acetylene will adsorb on the longer distances, and will be strained in the opposite sense, least in the case of nickel. These considerations are of importance in treating the problem of selectivity in acetylene hydrogenation; it is possible that ethane is formed in the early stages of reaction, not by a second reaction before desorption, but by desorbing and then readsorbing on a crystal face (such as the (111) face) where none of the longer distances are available, and where it may be hydrogenated without further interference from the acetylene. Such an explanation is unlikely to hold good if the ethylene reacts faster than the acetylene, but in other cases it cannot be ruled out. It would be instructive to see whether oriented evaporated films showed different selctivity from unoriented films.

Ethylene is adsorbed on nickel films with a heat of adsorption of 58 kcals, at zero surface coverage[32]; if two-point associative adsorption is taking place, the energy of each C-Ni bond will be about 57 kcals. If acetylene is adsorbed in a similar way, and if the C-Ni bond has the same strength in this case also, it is possible to calculate the expected heat of adsorption from the bond-energy data presented in Table 4; the value obtained is 67 kcals, which is in excellent agreement with the value of 66 to 67 kcals given by Wilson[33]. This would seem to be evidence in favor of the associative mode of adsorption.

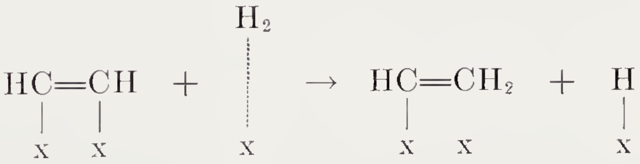
The heat of adsorption of ethylene is markedly dependent on the surface coverage, falling off to a value of 25 kcals when 5×10^{18} molecules per 100 mg of nickel have been adsorbed[32]; this corresponds to about half theoretical capacity for two-point adsorption. The heat of adsorption of acetylene is not however much dependent on surface coverage[33], and so at about half coverage the difference between the heats of adsorption of acetylene and ethylene is about 35 kcals.

The partially selective production of olefins which is almost always met with is most properly related to this fact. In the case of free competition for a uniform surface by acetylene and ethylene, the fraction covered by the latter under equilibrium conditions will be equal to exp $(-\delta\Delta G_a)$, where $\delta\Delta G_a$ is the difference in the free energies of adsorption of the two reactants under the experimental conditions[15]. The difference on a bare surface (about 6 kcals) is sufficient to produce a very marked selectivity; the appropriate value under hydrogenation conditions is however at present unknown. There is independent evidence[26] that acetylene monopolizes the surface, at least under nonreacting conditions, since the exchange of *trans*-ethylene-d_2 proceeds on a nickel surface only in the absence of acetylene.

TABLE 6. OPTIMUM AND AVAILABLE X-X DISTANCES (L_{xx}) FOR THE ADSORPTION OF ETHYLENE AND ACETYLENE, IN Å

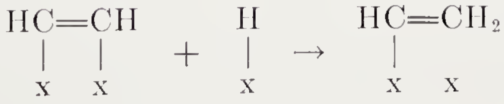
Metal	Optimum L_{xx} for C_2H_2	Optimum L_{xx} for C_2H_4	Available L_{xx}
Nickel	3.33	2.87	2.47, 3.50
Palladium	3.43	2.94	2.75, 3.91
Platinum	3.43	2.94	2.75, 3.88

Reaction between adsorbed acetylene and hydrogen could be initiated in one of two ways, either



$$\begin{array}{c}\mathrm{HC{=}CH}\\ |\quad\;\; |\\ \mathrm{X}\quad\;\mathrm{X}\end{array} + \begin{array}{c}\mathrm{H_2}\\ \vdots\\ \mathrm{X}\end{array} \rightarrow \begin{array}{c}\mathrm{HC{=}CH_2}\\ |\qquad\quad\\ \mathrm{X}\quad\;\mathrm{X}\qquad\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{X}\end{array} \qquad (1)$$

or



$$\begin{array}{c}\mathrm{HC{=}CH}\\ |\quad\;\; |\\ \mathrm{X}\quad\;\mathrm{X}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{X}\end{array} \rightarrow \begin{array}{c}\mathrm{HC{=}CH_2}\\ |\qquad\quad\\ \mathrm{X}\quad\;\mathrm{X}\qquad\end{array} \qquad (2)$$

The second mechanism requires the direct adsorption of hydrogen, as distinct from that produced by the first mechanism.

Due to the unequal zero-point energies of hydrogen and deuterium the activation energies for the addition reaction with each isotope may be expected to be different. Experiments to study this effect have been carried out with ethylene[56, 57, 58] and in one case[58] a difference was found which equals the estimated difference between the zero-point energies of Ni—H and Ni—D[59]. This argues in favor of the dissociation and adsorption of hydrogen before reaction. However, no similar experiments have been reported with acetylene. It is not sufficient merely to know whether one reacts faster than the other at any particular temperature, since if their activation energies vary, their relative rates will be temperature dependent.

It is not otherwise easy to distinguish between these mechanisms, for both are possible, although there are some indications[60] that the second may be somewhat more efficient than the first. It seems likely in cases where the reaction is inhibited by acetylene that the second type is operative; this will lead to a rate expression

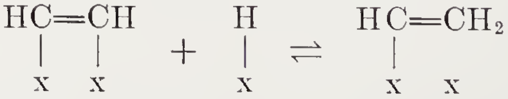
$$-\frac{dp}{dt} = k[C_2H_2]_{ads} \cdot [H_2]_{ads}$$

which reduces to direct dependence on $[H_2]_{ads}$, if the acetylene is much more strongly adsorbed. The area of surface covered by hydrogen is then proportional to the hydrogen pressure and inversely proportional to the acetylene pressure, and so

$$-\frac{dp}{dt} = kP_{H_2} \cdot P_{C_2H_2}^{-1} .$$

This expresses at least approximately the pressure dependences observed over platinum and palladium (and in certain conditions over nickel); a more rigorous treatment would consider the isotherms for competitively adsorbed reactants, and in this way the fractional exponents often observed could be accounted for. These methods have been tried by de Pauw and Jungers[22], by Cremer and others[46], and by Tamaru[47].

However, in such cases the stationary concentration of hydrogen atoms must be small[41], and so the initial reaction may be represented by the equilibrium



$$\begin{array}{c}HC{=}CH\\ |\qquad |\\ x\qquad x\end{array} + \begin{array}{c}H\\ |\\ x\end{array} \rightleftharpoons \begin{array}{l}HC{=}CH_2\\ |\\ x\qquad x\end{array} \qquad (3)$$

lying far to the right. In other words, as soon as a hydrogen atom adsorbs, it reacts very quickly with an adsorbed acetylene molecule, of which there are many, and forms the somewhat more stable half-hydrogenated state.

The rate equation over nickel, iron and other metals is more easily interpreted, and is quite in accord with the first type of mechanism; the rate is merely controlled by the rate of collision of gaseous hydrogen with as complete a layer as possible of chemisorbed acetylene, and so is proportional to the first power of the hydrogen pressure and independent of the acetylene pressure.

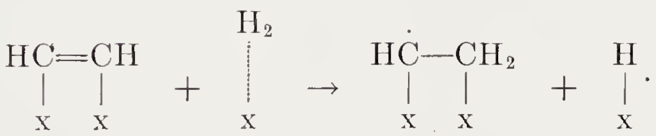
The fate of the half-hydrogenated species $\begin{array}{l}\mathrm{HC{=}CH_2}\\ \ \, | \\ \ \,\mathrm{X}\end{array}$ must now be examined; there are a number of possibilities for its further reaction.

(a) It may react with another hydrogen molecule, producing gaseous ethylene and a hydrogen atom, or with another hydrogen atom to produce gaseous ethylene. The work of Douglas and Rabinovitch[26] with deuterium shows that the half-hydrogenated state is unlikely to react with the hydrogen atom formed simultaneously with it, in the case that the first type of mechanism above is operative.

(b) It may isomerize into the free-radical form $\begin{array}{cc}\dot{\mathrm{H}\mathrm{C}}\!\!-\!\!&\mathrm{CH_2}\\ | & | \\ \mathrm{X} & \mathrm{X}\end{array}$ which may react with a hydrogen atom or molecule giving adsorbed ethylene; the formation of ethane in the early stages of reaction would be explained by the further addition of hydrogen to the ethylene so formed.

(c) The free-radical of the half-hydrogenated state may initiate a vinyl-type polymerization with other adsorbed acetylene molecules, yielding adsorbed polymers which are multiples of C_2 units[23]. The similarity of the kinetics of the hydrogenation and polymerization reactions, showing that the same intermediate is probably involved, lends weight to this argument.

It must also be noted that the free-radical form may also be produced directly from adsorbed acetylene without the intervention of the normal form:



$$\begin{array}{cc}\mathrm{HC}\!=\!&\mathrm{CH}\\ | & | \\ \mathrm{X} & \mathrm{X}\end{array} + \begin{array}{c}\mathrm{H_2}\\ \vdots \\ \mathrm{X}\end{array} \rightarrow \begin{array}{cc}\dot{\mathrm{H}\mathrm{C}}\!-\!&\mathrm{CH_2}\\ | & | \\ \mathrm{X} & \mathrm{X}\end{array} + \begin{array}{c}\mathrm{H}\\ | \\ \mathrm{X}\end{array}\cdot \qquad (4)$$

But the free-radical form has an ethane- rather than an ethylene-type structure, and can be accommodated only on the longer (3.50 Å in the case of nickel) spacing if it is twisted to reduce the strain. Figure 8 shows how this species can be adsorbed, and how it can react to give adsorbed polymers. Such a process can give rise to linear polymers containing only an even number of carbon atoms; it is not clear whether the branched molecules, and those containing an odd number of carbon atoms, reformed by isomerization and partial cracking of the primary products (which may occur to some extent above 200°C) or whether they are in fact themselves primary products of the reaction.

The reaction chains terminate by recombination, disproportionation or by addition of hydrogen; this last method is suggested by the fact that Reaction (II) is of slightly lower order with respect to hydrogen than is Reaction (I), that is, that hydrogen is involved in the chain termination. A great deal more practical work is needed before further advances can be made toward solution of the many interesting questions which arise; the problems are of great fundamental, as well as of potentially practical, interest, and as such merit attention.

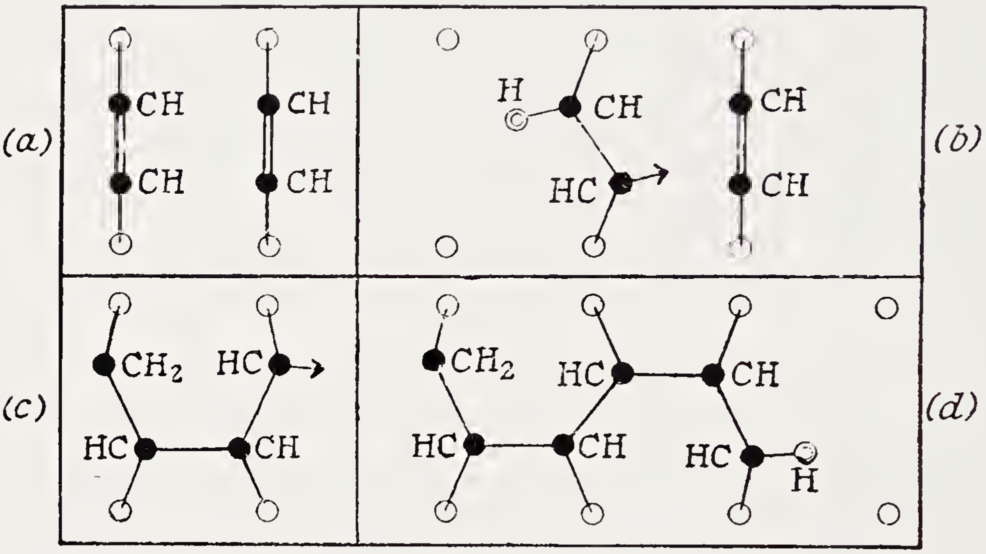
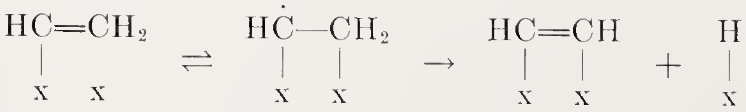


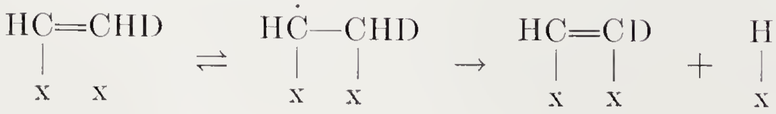
Figure 8. Approximate scale projection on the (110) face of nickel showing an example of a possible mode of polymerization without rupture of C—Ni bonds in associatively adsorbed acetylene[21]. ○, nickel atoms; ●, carbon atoms; ◎, hydrogen atoms. Carbon valencies not shown are taken up by other hydrogen atoms, except where arrows are shown, each of which indicates an unpaired electron. (Courtesy *J. Chem. Soc.*)

In treating the fate of the half-hydrogenated species, the exchange-type reaction



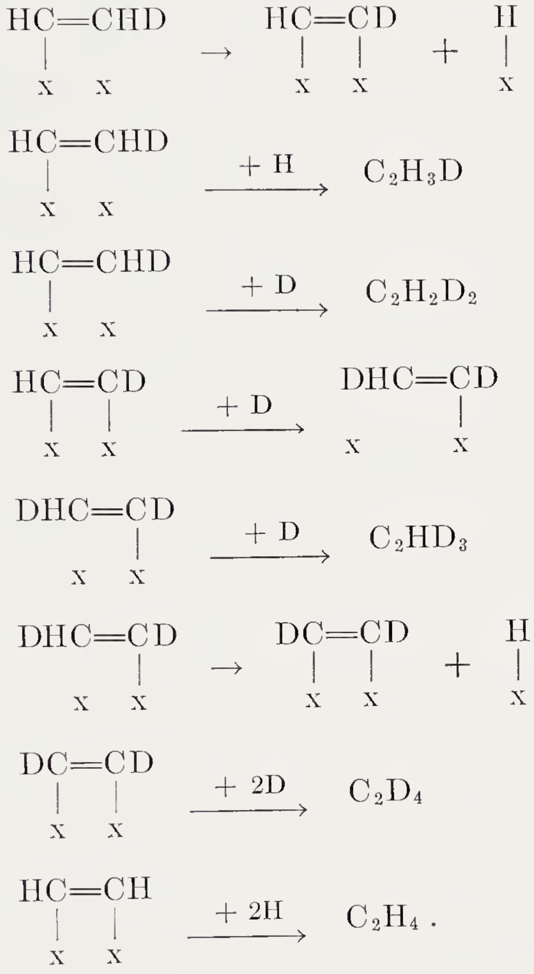
$$\begin{array}{l}\mathrm{HC{=}CH_2}\\ \;\,|\\ \;\mathrm{X}\quad\mathrm{X}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{H\dot{C}{-}CH_2}\\ \;\,|\qquad|\\ \;\mathrm{X}\quad\;\mathrm{X}\end{array} \rightarrow \begin{array}{l}\mathrm{HC{=}CH}\\ \;\,|\qquad|\\ \;\mathrm{X}\quad\;\mathrm{X}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{X}\end{array} \qquad (5)$$

was not considered. If the reaction is carried out with deuterium instead of hydrogen, the corresponding step would be



$$\begin{array}{l}\mathrm{HC{=}CHD}\\ \;\,|\\ \;\mathrm{X}\quad\mathrm{X}\end{array} \rightleftharpoons \begin{array}{l}\mathrm{H\dot{C}{-}CHD}\\ \;\,|\qquad|\\ \;\mathrm{X}\quad\;\mathrm{X}\end{array} \rightarrow \begin{array}{l}\mathrm{HC{=}CD}\\ \;\,|\qquad|\\ \;\mathrm{X}\quad\;\mathrm{X}\end{array} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{X}\end{array} \qquad (6)$$

Now the experimental evidence is that very little C_2HD is located in the gaseous products[26], and that very little hydrogen is returned to the gas phase[41]; this however does not necessarily preclude the existence of these species in the adsorbed state. The fact that acetylene and deuterium give rise to ethylenes containing from nought to four deuterium atoms means that some exchange process must be taking place[26], and the following steps are proposed to explain this:



(a) $$\underset{\underset{X}{|}}{HC}{=}\underset{X}{CHD} \rightarrow \underset{\underset{X}{|}}{HC}{=}\underset{\underset{X}{|}}{CD} + \underset{\underset{X}{|}}{H}$$

(b) $$\underset{\underset{X}{|}}{HC}{=}\underset{X}{CHD} \xrightarrow{+\,H} C_2H_3D$$

(c) $$\underset{\underset{X}{|}}{HC}{=}\underset{X}{CHD} \xrightarrow{+\,D} C_2H_2D_2$$

(d) $$\underset{\underset{X}{|}}{HC}{=}\underset{\underset{X}{|}}{CD} \xrightarrow{+\,D} \underset{X}{DHC}{=}\underset{\underset{X}{|}}{CD}$$

(e) $$\underset{X}{DHC}{=}\underset{\underset{X}{|}}{CD} \xrightarrow{+\,D} C_2HD_3$$

(f) $$\underset{X}{DHC}{=}\underset{\underset{X}{|}}{CD} \rightarrow \underset{\underset{X}{|}}{DC}{=}\underset{\underset{X}{|}}{CD} + \underset{\underset{X}{|}}{H}$$

(g) $$\underset{\underset{X}{|}}{DC}{=}\underset{\underset{X}{|}}{CD} \xrightarrow{+\,2D} C_2D_4$$

(h) $$\underset{\underset{X}{|}}{HC}{=}\underset{\underset{X}{|}}{CH} \xrightarrow{+\,2H} C_2H_4\,.$$

To reconcile the observations with this scheme, it is only necessary to postulate that an adsorbed acetylene molecule has very little chance of desorbing before suffering reaction, and that hydrogen atoms released in the exchange steps are very rapidly captured for addition purposes. If for a hydrogen atom to return to the gas, another adjacent hydrogen or deuterium atom is required, that is, if the process

$$\underset{\underset{X}{|}}{H} + \underset{\underset{X}{|}}{D} \rightarrow HD \qquad (7)$$

is the only one to be considered, this last postulate is quite plausible, since the surface concentration of hydrogen (or deuterium) atoms is known to be very low[41]. These reaction schemes are closely similar to ones recently proposed to account for the redistribution of hydrogen and deuterium atoms in the products of olefin hydrogenation[44].

The time is scarcely ripe to consider the detailed interpretation of the activity of the various metals used; activities should be correlatable with parameters of the metals, but a better understanding of the meaning of activation energies and pre-exponential factors in catalytic reactions is first desirable.

The Use of Other Types of Catalyst. It is finally necessary to record briefly that some other types of catalyst have been employed for the gas phase hydrogenation of acetylene; thus, Komarewsky and others[61] have found that a catalyst consisting of 35 per cent vanadium pentoxide and 65 per cent alumina, prepared by coprecipitation from sodium vanadate and aluminium nitrate, was active at 400°C, producing 93 per cent ethylene and 7 per cent ethane. This catalyst was said to be resistant to sulfur poisoning. In a patent to the DuPont de Nemours Company, Barry[62] stated that partially-sulfided nickel oxide was highly effective for carrying out selective hydrogenation in the presence of lower olefins.

In a Japanese patent[63], the Nippon Ceramic Material Company claimed that a catalyst consisting of a metal oxide (MgO, MnO_2, ZnO or Al_2O_3, either singly or in combination), loaded on an acid clay and mixed with $\frac{1}{40}$ to $\frac{1}{400}$ parts of barium chloride, hydrogenated equimolar mixtures of hydrogen and acetylene to ethylene in 90 to 93 per cent yields. Takahashi and Narimota[64] employed a catalyst of the composition: 2 parts nickel: 1 part metal oxide: 20 parts diatomaceous earth: 100 parts kaolin, and stated that zinc and calcium oxides increase the yield of ethylene, and tungsten and aluminium oxides suppress it.

Petrov and Antsus have used nickel supported on an inorganic salt, chiefly as a means of preparing higher olefins; thus with zinc chloride[24] they report high yields of butadiene and isobutene, and over cobaltous chloride[65] good yields of butene and isobutene, in a ratio which could be varied according to conditions.

The Hydrogenation of Methylacetylene

A study of the hydrogenation of methylacetylene has been carried out[66] in order to ascertain in what respects the molecular geometry of a system affects its behavior. The results, which are of interest inasmuch as they provide confirmation of the mechanisms proposed to explain the reactions of acetylene, will now be described.

Nickel as Catalyst. Over a nickel-pumice catalyst at 91°C the orders of reaction were the same as those found for acetylene at about 60°C. With hydrogen:methyl acetylene ratios of unity or less, pressure-time curves were of first order form, but with ratios of two or greater, the rate was constant until more than 80 per cent of the methylacetylene had been removed. For ratios between one and two the rate was constant for a fraction of the reaction proportional to the value of the ratio.

At the same temperature, an equimolar mixture of reactants yielded about 14 times as much propylene as propane, and a total yield of about 87 per cent C_3 hydrocarbons; this is significantly higher than the yield of C_2 hydrocarbons from acetylene under the same conditions. There was some evidence that the greater part of the polymers were formed in the early stages of the reaction. In the reaction with a two-fold excess of hydrogen, the selectivity was still high, and the hydrogenation of propylene, which became dominant when the pressure of methylacetylene had fallen to about 20 mm, was slower than the first stage of the reaction. Higher hydrocarbons had an empirical composition of $C_3H_{4.7}$ initially, but they were further hydrogenated during the reaction, and tended to a final composition of about C_3H_6; their formation ceased completely after all the methylacetylene had been removed. The results are shown graphically in Figure 9.

The yield of C_3 hydrocarbons did not depend on the initial hydrogen:acetylene ratio if this was in excess of unity. However, it was found that the selectivity was inversely proportional to the hydrogen pressure but independent of the methylacetylene pressure. The methylacetylene analogs of Reaction (I) and (II) are

$$C_3H_4 \xrightarrow{+\ H_2} C_3H_6 \xrightarrow{+\ H_2} C_3H_8 \qquad \text{(III)}$$

$$C_3H_4 \xrightarrow{+\ H_2} \text{higher hydrocarbons} \qquad \text{(IV)},$$

and these must therefore have the same pressure dependences.

Temperature variation had a slight but definite effect on the yield of C_3 hydrocarbons; the yield at 50°C was about 90 per cent and at 110°C about 80 per cent. Combined with the results on the effect of temperature on the initial rate of pressure fall, the activation energies were deduced to be, for Reaction (III), 13.8 kcals, and for Reaction (IV), 16.0 kcals.

The effect of a number of added substances on the hydrogenation of methylacetylene has been studied over the same type of catalyst[8,67]. The addition of propylene had no significant effect, but added acetylene was hydrogenated simultaneously with, and 1.25 times faster than, the methylacetylene. As judged by the yields of C_2 and C_3 hydrocarbons obtained, each reaction proceeded largely without interference from the other. Allene and methylacetylene were also hydrogenated together, and it appeared that the latter reacted about 1.2 times faster than the former. Taking account of the separate rates of reaction of these three hydrocarbons, it was possible to estimate fractional surface coverages of the hydrocarbon reactants in binary mixtures. Table 7 gives some of the results. The stronger adsorption of acetylene compared to methylacetylene has received independent confirmation[34].

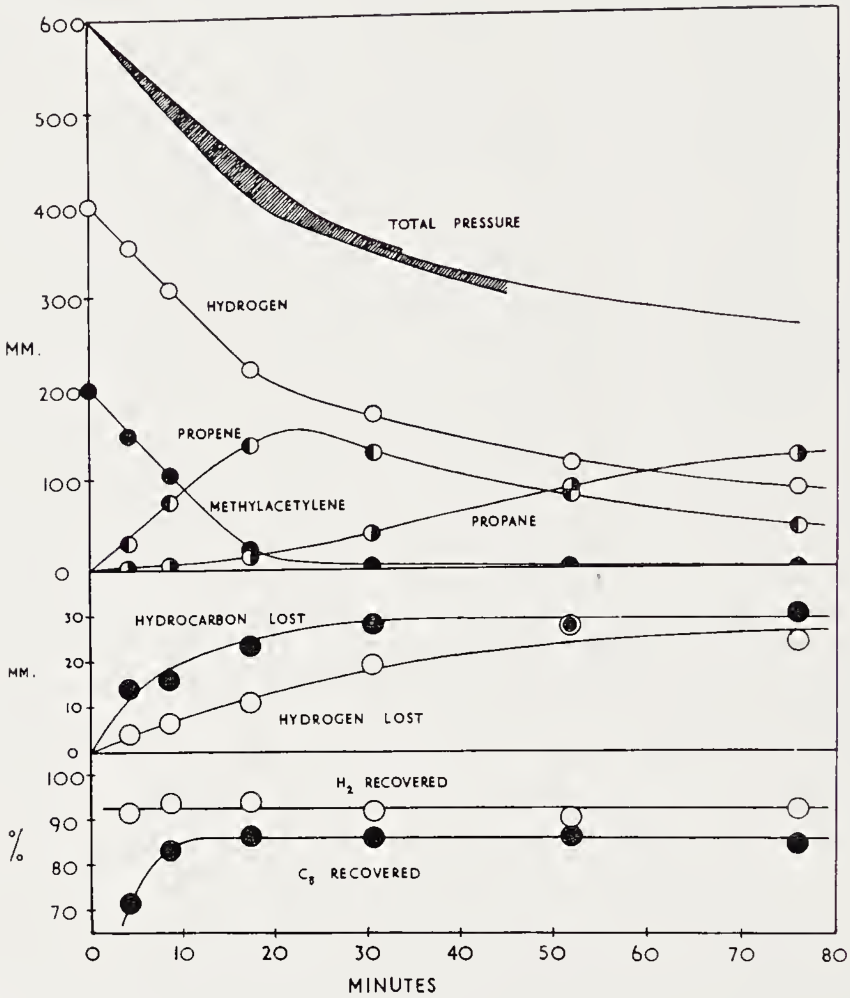


Figure 9. The course of reaction of a 2:1 H_2/C_3H_4 mixture over nickel at 90°C[66]. Total pressure curves lie within the shaded area. (Courtesy *Trans. Faraday Soc.*)

Platinum as Catalyst. The orders of reaction over a platinum-pumice catalyst were first with respect to hydrogen (at 47°C) and zero with respect to methylacetylene (at 68°C) with the latter in excess; however, as in the case of acetylene, the order in methylacetylene was negative when it was not in excess. With hydrogen in excess, pressure-time curves were linear, until the rate began to increase; this acceleration was hardly noticeable at 118°C. Again the similarity to acetylene is very striking.

At 75°C, an equimolar mixture of reactants gave eight times as much propylene as propane, and the total yield of C_3 hydrocarbons was 94 per cent, constant at all stages of the reaction. The higher hydrocarbons had an empirical composition of C_3H_5 throughout the reaction. With a 2-fold excess of hydrogen at 118°C, the selectivity was six in the initial stages, and the yield of C_3 hydrocarbons 88 per cent. The slight increase in the rate (referred to above) corresponded to the hydrogenation of propylene becoming the dominant reaction, and this started when the methylacetylene had fallen to about 25 mm. The effect of temperature on the yield of C_3 hydrocarbons was very slight, and it was concluded that both Reactions (III) and (IV) had an activation of about 17 kcals. Added propylene had no effect on the reaction. In mixtures of acetylene and methylacetylene, the former was hydrogenated about 1.5 times as fast as the latter. With due allowance for their separate rates of reaction, it was concluded that acetylene covered about 80 per cent of the active surface.

TABLE 7. FRACTIONAL SURFACE COVERAGES (θ) OF ACETYLENE, METHYLACETYLENE AND ALLENE IN BINARY MIXTURES

Mixture	$\theta_{C_2H_2}$	θ_{CH_3CCH}	$\theta_{H_2CCCH_2}$
Acetylene-methylacetylene	0.55	0.45	—
Acetylene-allene	0.82	—	0.18
Methylacetylene-allene	—	0.76	0.24

Palladium as Catalyst. Here once again the resemblance to acetylene is very marked; the order with respect to hydrogen over a palladium-pumice catalyst was 1.4 at 51°C, and with respect to methylacetylene at 89°C, slightly negative.

Experiments investigating the course of reaction showed a number of points of interest. Over a fresh catalyst, the yield of C_3 hydrocarbons was 93 per cent, the selectivity being about thirty; under these conditions the catalyst was only weakly active for the hydrogenation of propylene alone. However, over a well-used catalyst at 136°C, C_3 hydrocarbons were formed almost quantitatively in the later stages of reaction, the over-all yields rising from 70 per cent initially to 75 per cent finally. Propane formation was negligible, and the catalyst was not active for the hydrogenation of propylene alone. The empirical composition of the polymers was $C_3H_{4.7}$. Changing the initial hydrogen:methylacetylene ratio over a wide range had little effect on the products of the reaction.

Temperature variation in the range 76 to 198°C had no effect on the course of the reaction, and the activation energy derived from the temperature dependence of the initial rate of pressure fall was 16.5 kcals. The effect of added propylene on the reaction was quite negligible.

Reaction Mechanisms. The general similarity of the kinetics of methylacetylene to those found for acetylene is in itself significant, since it indicates that the same types of mechanism are operative. Statistical calculations[8, 66] based on molecular models have shown that it is not possible to adsorb as many methylacetylene molecules as acetylene molecules per unit surface area, due to the obstructing effect of the methyl group in the former; thus on a sample area of 400 sites on the (110) plane of nickel, 175 acetylene molecules could be adsorbed, but only 88 molecules of methylacetylene. Different kinetics might have been expected if this had led to the adsorption of appreciable amounts of hydrogen, but the same calculations showed that the number of vacant sites on which hydrogen atoms could be accommodated was only 50 per cent greater in the case of methylacetylene than in the case of acetylene, so the identity of the kinetics has a reasonable basis.

These considerations are also very helpful in interpreting the higher yields of C_3 hydrocarbons which are obtained (especially over nickel), compared to the yields of C_2 hydrocarbons obtained from acetylene. The temperature dependence of polymer formation over nickel suggests that at least part of it occurs by the same mechanism as was postulated for acetylene, and this mechanism involved the reaction of the free-radical form of the half-hydrogenated species with adjacently adsorbed acetylene molecules. In the case of methylacetylene, however, the molecules are less tightly packed, and so it is hardly surprising that the extent of the polymerization is less. The interpretation is only qualitative, and the procedure should be susceptible to further refinement.

It was believed[66] that in cases where the polymers had an empirical composition of $C_3H_{4.7}$, that the polymerization also involved physically-adsorbed methylacetylene. This would explain why the polymer yield was dependent on the methylacetylene pressure, and also why it was not dependent on temperature, since the concentration of physically-adsorbed methylacetylene (whose heat of adsorption is probably small) was unlikely to be very markedly affected by temperature. The fact that their composition indicated that on the average less than one hydrogen atom was removed per C_3 residue made it likely that the process was partially one of dimerization. Many details of this process remain to be elucidated.

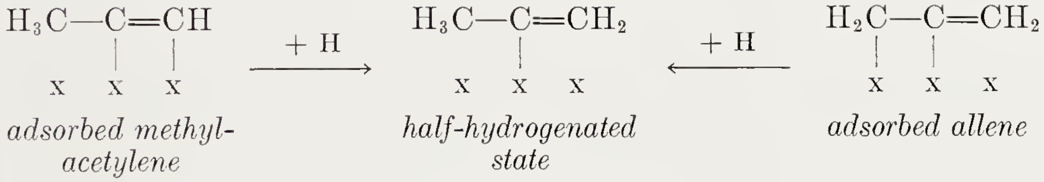
It is of interest to find that both acetylene and allene can be hydrogenated simultaneously with methylacetylene; this would mean that all can compete for the active surface on approximately equal terms. It has been possible to show that their heats of adsorption under experimental conditions therefore cannot vary by more than a kilocalorie or so, which is in rough accord with the conclusion arrived at by estimating the heats of adsorption from the bond-energy data.

It appears that in all cases, and especially over palladium, the selectivity is somewhat higher than in the corresponding reaction of acetylene. The results are summarized in Table 8. The same explanation is offered as was produced to explain the selectivity in the case of acetylene; although it is difficult to be precise because of many unknown factors, it is probable that methylacetylene will be very much more strongly adsorbed than propylene.

The hydrogenation of the hydrocarbon allene (1,2-propadiene) has also been the subject of study[68]; although this is strictly speaking not an acetylenic hydrocarbon, the adjacent position of the double bonds induces mutual strain, with the result that it possesses certain acetylenic properties. Thus, for example, its heat of hydrogenation to propylene is 41.4 kcals[69], which is only about 1 kcal. less than the corresponding reaction of methylacetylene, with which it is isomeric, and 10 kcals larger than the heat of hydrogenation of a "normal" double bond. Allene has been shown, not unexpectedly, to demonstrate a similar selectivity to acetylene and methylacetylene. It must be noted that allene may also give rise to the same half-hydrogenated state as methylacetylene. Thus:

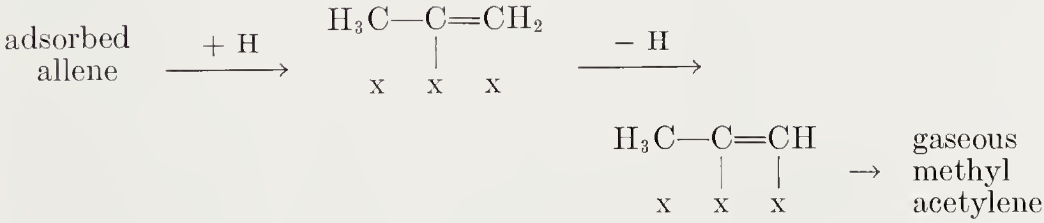
Table 8. Comparison of the Selective Actions of Nickel, Platinum and Palladium in the Hydrogenation of Acetylene and Methylacetylene (for Equimolar Mixtures of Reactants and a Three-Fold Excess of Hydrogen)

Metal	Ratio of C_2H_4/C_2H_6	Ratio of C_3H_6/C_3H_8
Nickel	5 at 79°C	14 at 91°C
Platinum	5 at 163°C	8 at 75°C
Palladium	11 at 24°C	30 at 82°C



$$\underset{\mathrm{x}\quad\mathrm{x}\quad\mathrm{x}}{\mathrm{H_3C{-}C{=}CH}} \xrightarrow{+\mathrm{H}} \underset{\mathrm{x}\quad\mathrm{x}\quad\mathrm{x}}{\mathrm{H_3C{-}C{=}CH_2}} \xleftarrow{+\mathrm{H}} \underset{\mathrm{x}\quad\mathrm{x}\quad\mathrm{x}}{\mathrm{H_2C{-}C{=}CH_2}}$$

However the isomerization of allene to methylacetylene, which is thermodynamically probable[70], was shown not to occur to any measurable extent under hydrogenation conditions, which would mean that the reaction



$$\text{adsorbed allene} \xrightarrow{+\mathrm{H}} \underset{\mathrm{x}\quad\mathrm{x}\quad\mathrm{x}}{\mathrm{H_3C{-}C{=}CH_2}} \xrightarrow{-\mathrm{H}} \underset{\mathrm{x}\quad\mathrm{x}\quad\mathrm{x}}{\mathrm{H_3C{-}C{=}CH}} \rightarrow \text{gaseous methyl acetylene}$$

cannot take place. This is quite in harmony with the schemes of reaction proposed to account for the reactions of acetylene; a molecule once adsorbed has only a very small chance of desorbing before undergoing reaction. No isotopic tracer studies of these reactions have yet been made, and it would be desirable to determine in a more thorough manner whether the proposed schemes are valid.

The Hydrogenation of Other Acetylenic Hydrocarbons

In addition to acetylene and methylacetylene, whose hydrogenations have been fairly fully investigated, a number of other acetylenic hydrocarbons have also been hydrogenated in the gas phase; such work as has been done on them is invariably of a qualitative nature, and no systematic studies have yet been undertaken. The employment of flow systems is largely responsible for this; the hydrocarbon is vaporized by one of a number of possible methods, and the vapor is passed with hydrogen over the catalyst at an elevated temperature.

Thus, for example, Sabatier and Senderens[71] hydrogenated 1-heptyne to *n*-heptane over a nickel catalyst at 170°C, but over a copper catalyst below 200°C heptene, "diheptene" and "triheptene" were produced in addition to some *n*-heptane. In this case, a polymerization similar to that undergone by acetylene must be taking place, and it is rather surprising that heptyne molecules may be adsorbed sufficiently close together to enable such a process to occur.

Over a nickel catalyst at 180°C, the same authors[72] found that phenylacetylene yielded ethyl-cyclohexane, but over copper between 190 and 250°C it gave ethyl benzene, styrene, and 50 per cent diphenylbutane, as well as a crystalline fluorescent solid, whose identity was not reported. These results emphasize the specific behavior of catalysts; in each case, nickel yields the completely saturated product with no by-products, whereas copper favors partial hydrogenation, dimerization and polymerization.

THE LIQUID PHASE HYDROGENATION OF ACETYLENIC BONDS

The Status of the Field

The same techniques are used to hydrogenate acetylenic bonds as are used for olefinic bonds, and these have been well described in a number of books[73, 74], and so will not be treated at length here. Of the many types of catalysts suitable for liquid phase work, metals in the form of finely divided powders, "blacks," and colloidal suspensions have been widely employed, and the Raney type of catalyst is of the greatest value. It is once again necessary to stress the specific behavior of the metals used; much more effort has been directed to finding selective catalysts, that is, those which will hydrogenate only acetylenic bonds, and different metals show very varying actions in this respect. The results leading to this conclusion will be presented shortly.

Another major problem is "the stereochemical course of the reaction"; di-substituted acetylenes generally give *cis*-olefins, and this requires careful explanation, which is partly to be found in terms of the reaction mechanisms previously given for acetylene.

It is difficult to carry out fundamental studies in the liquid phase, since the rate of reaction is likely to be controlled by the rate of diffusion of the hydrogen to the catalyst surface. For this reason, the kinetics, which should be regarded as the first target in any thorough study, cannot be rightly determined. Nevertheless, such information as is available on liquid phase hydrogenation is of great interest, and will now be briefly considered.

Addition of hydrogen to the acetylenic bond is conditional upon the adsorption of the molecule containing it to the catalyst surface, and if the steric hindrance by the substituted groups is such as to prevent this happening, no addition will take place. The findings of Wieland and Kloss[75], namely, that di-triphenylmethylacetylene is not attached by hydrogen in the presence of platinum or palladium, and that 1, 3, 3,3-tetraphenylmethylacetylene is hydrogenated only very slowly, are probably explained in this manner.

The Selective Action of Catalysts

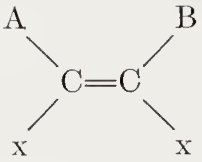
In general, with platinum catalysts such as "platinum black," reactions are not selective, and the olefin cannot be isolated; this is in harmony with the observations of Sheridan on acetylene. This property is of value when complete saturation is desired. "Palladium black" is similarly nonselective. Reactions over colloidal palladium, however, almost always stop at the olefin stage, as was found for methylacetylene; full references and many examples are quoted in reference 16. Raney nickel shows the same degree of selectivity, and mono- and di-substituted acetylenes can be easily reduced to the olefin over this catalyst. For mono-alkylacetylenes, phenylacetylene and phenylmethylacetylene, the pressure-time curves showed no break corresponding to the completion of the first stage of the reaction, although the olefins could be isolated in good yield; however, with dialkyl- and diaryl-acetylenes, the rate of hydrogenation of the olefin was much slower[76].

Raney iron shows an even more selective action[77], although it is less active than Raney nickel; it apparently catalyzes addition to the acetylenic bond without interfering with other points of unsaturation. 1-octyne, 1-heptyne and phenylacetylene yield the corresponding olefins, as does also 3-methoxy-1-phenylmethylacetylene. Palladium and Raney iron also show selectivity toward molecules containing both double and triple bonds; vinylacetylene can be reduced to butadiene over palladium, although butene and some polymers are formed[78]. 3-Methyl-butenyne has been reduced to isoprene by hydrogenation over Raney iron[79].

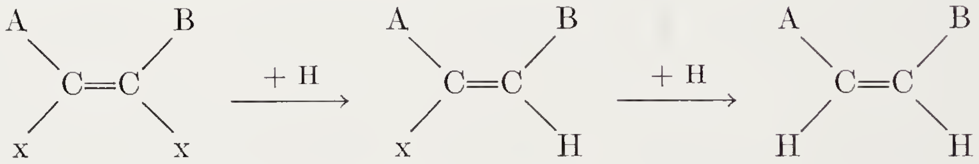
The phenomenon of selectivity in these cases is readily explained in the same terms as were employed to interpret the selectivity of gas phase reactions, namely that the acetylene is more strongly adsorbed than the olefin on the catalyst surface. Explanation in terms of different rates of reaction is clearly inadequate.

The Stereochemical Course of Reaction

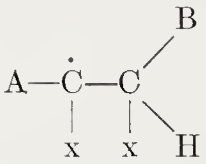
It is now well established that the primary product obtained from the hydrogenation of a di-substituted acetylene is generally the *cis*-olefin[16], although the *trans* isomer is produced by chemical methods of reduction, and is the more stable. This throws some light on the mechanism of the addition reaction: the acetylene will be adsorbed as a *cis*-ethylenic–catalyst complex



and the steps of the reaction may be written



Thus the *cis*-isomer is necessarily produced, since free rotation about the double bond in the half-hydrogenated state is not permissible. There is however the possibility that the half-hydrogenated state may isomerize into the free radical form



which has an ethane-like structure and in which the former stereochemical configuration may not be retained. If this were so, the addition of another hydrogen atom followed by desorption would produce a mixture of isomers. The fact that this does not usually occur may have one of two explanations: either, if the free radical species is formed, it does not give rise to the olefin, but only to polymers (due to its reactivity) or to saturated product (due to its remaining adsorbed), or that for some reason the free radical only exists in the reactions of the simpler acetylenic hydrocarbons. The observations of Arnett and Crawford[80] that over palladium acetylene and deuterium yield a mixture of *cis* and *trans* isomers of ethylene-d_2 would suggest that in this case the free radical form does exist, and does give rise to ethylene; but the formation of polymers from 1-heptyne and phenylacetylene over copper[71-72] would indicate that the larger molecules also are capable of forming the free radical half-hydrogenated state. It is therefore not yet possible to decide why di-substituted acetylenes yield usually *cis*-olefins, but sometimes *trans* products; further experimentation is clearly required.

Summary and Discussion

The hydrogenation of acetylenic bonds occurs readily over a number of the transition series metals, either in the gaseous or in the liquid phase, with the formation of olefins, saturation products and (especially in the case of acetylene itself) polymers. The number of times more quickly the olefin is formed than the saturated product is designated the selectivity of the reaction; this is frequently very high, and is determined by the adsorption characteristics of the reactants and the olefin. The reaction kinetics, where known, and the selectivity, indicate that the acetylene is more strongly adsorbed on the catalyst than is the hydrogen. The polymers arise through a surface free radical chain reaction.

The problems in this field still awaiting solution are to a certain extent also those of other catalytic reactions, and these may be enumerated as follows:

(a) The structure of the catalyst is a point of the greatest importance, since there is ample evidence that supporting a metal on a supposedly inactive base such as pumice or kieselguhr profoundly affects the reaction, apparently reducing the strength of adsorption of the hydrocarbon, and simultaneously causing a greater activity and a higher activation energy. Detailed knowledge of the state of surfaces responsible for catalytic reactions is still at an elementary stage.

(b) It unfortunately does not appear easy to devise an experiment which will prove beyond all doubt the mechanism by which catalytic hydrogenation reactions proceed; the best that can be done at present is to argue by logical inference from the available evidence. There is a distinct possibility that all the interpretation offered so far may have to be radically revised in the future; catalysis is not a subject on which it pays to be dogmatic, although it does seem that the reaction schemes which have been proposed account satisfactorily for the observations, as far as they are known.

There are, in addition, certain problems which are concerned more especially with the hydrogenation of acetylenic bonds, on which more work needs to be done. Firstly, there is the question of how the amount of acetylene removed as polymers is related to the catalyst structure; up to the present time, it has been impossible to relate it to any parameter of the catalyst, but clearly some connection must exist and should be capable of discovery. A necessary prerequisite is a much larger knowledge of the polymers, especially those formed at lower temperatures. The second problem peculiar to the hydrogenation of acetylenes is that of selectivity, and although the qualitative interpretation is probably sound, it is not possible to account with certainty for the difference in the selectivities shown by, for example, platinum and palladium. Further measurements on the heats of adsorption of the reactants on various surfaces would be of the greatest value, but this field has scarcely been touched.

In order to underline the great difference between the behavior of the various metal catalysts, Table 9 summarizes information concerning the yields of C_2 hydrocarbons obtained from equimolar mixtures of hydrogen and acetylene over pumice-supported catalysts at the temperatures named.

TABLE 9. YIELDS OF C_2 HYDROCARBONS FROM EQUIMOLAR MIXTURES OF HYDROGEN AND ACETYLENE

Metal	Temperature (°C)	Percentage Yield
Nickel	80	40–45
Iron	135	70
Cobalt	197	50
Copper	202	40
Platinum	163	70
Palladium	24	75
Rhodium	80	70–80
Iridium	—	85

The figures are rounded, and for more accurate values reference should be made to the appropriate paragraphs of the text, or to the original papers.

In conclusion it may be affirmed that the problem of catalysis is one of the major challenges to chemists and physicists, and that in particular the field which has been covered in this chapter eagerly awaits fresh attacks. The questions to be solved are of the greatest interest and importance, and no unified theory of catalysis will be acceptable until such time as a far greater knowledge of the hydrogenation of acetylenic bonds is aquired than is at present possessed.

Acknowledgment. Figures 4 and 9 are reproduced from the transactions of the Faraday Society and the remaining figures from the Journal of the Chemical Society, by kind permission of the respective societies.

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CHAPTER 5

THE CATALYTIC HYDROGENATION OF NITRO COMPOUNDS

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INTRODUCTION

Catalytic hydrogenation is often employed for the reduction of nitro groups because of the ease of hydrogenation, the absence of side reactions, and the facility of product recovery. The nitro group is reduced at moderate temperatures and pressures by hydrogen in the presence of Raney nickel or a platinum catalyst. Less active catalysts require more energetic conditions. Reductions are carried out with or without the presence of a solvent.

Commercially, nitro compounds are hydrogenated in both the liquid and vapor phase. Because of their longer life and smaller susceptibility to poisons, less active catalysts are generally employed, so that higher temperatures and pressures are required. In view of the large evolution of heat accompanying these reductions, temperature control is a major problem in large scale operations.

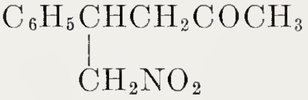
ALIPHATIC NITRO COMPOUNDS

In 1939, Johnson and Degering[1] reduced all of the nitroparaffins available from the vapor phase nitration of propane, butane, and isobutane to the corresponding amines in almost quantitative yields. The reductions were conducted over Raney nickel catalyst in a rocker-type high pressure bomb. The charge consisted of 0.25 to 0.33 moles of nitroparaffin, 175 ml of ethanol or methanol, and 7.5 g of catalyst. With hydrogen pressures from 6 to 110 atmospheres and temperatures of 40 to 50°C, the reduction took place in a few hours. Methylamine, ethylamine, 1- and 2-aminopropane, 1- and 2-aminobutane, and 1- and 2-amino-2-methylpropane were recovered in 82 to 94 per cent yields. The yields were increased to 93 to 97 per cent in the presence of ferric chloride.

Iffland and Cassis[2] studied the reduction of five nitroparaffins using 0.1 g of Adams' platinum oxide, 0.2 mole of the nitroparaffin dissolved in 95 per cent ethanol and 2 to 3 atmospheres hydrogen pressure. Yields of 48 to 91 per cent of amine were obtained, the yield increasing with increasing molecular weight of the nitroparaffin. The discrepancy between the yields as indicated by titration and by the essentially theoretical hydrogen absorption (91 to 100 per cent) is probably due to interaction between the product amine and the nitroparaffin. The use of larger quantities of catalyst (0.3 g) should improve the recoverable yields of amine by decreasing the reaction time.

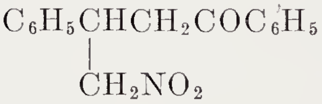
PARTIAL REDUCTION OF ALIPHATIC NITRO COMPOUNDS

In 1923, Kohler and Drake[3] reduced some γ-nitroketones in an effort to determine whether the oxime is produced as an intermediate step during the hydrogenation. These authors reasoned that if such is the case, the close proximity of the ketone and oxime groups should result in condensation and the formation of rings. The compounds studied were:



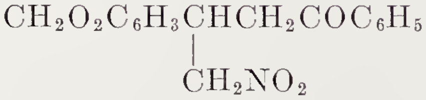
$$\mathrm{C_6H_5\underset{\underset{\displaystyle CH_2NO_2}{|}}{C}HCH_2COCH_3}$$

(I)



$$\mathrm{C_6H_5\underset{\underset{\displaystyle CH_2NO_2}{|}}{C}HCH_2COC_6H_5}$$

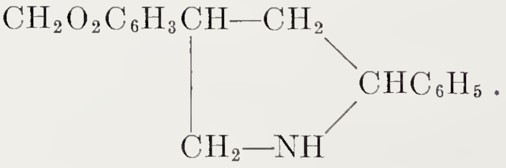
(III)



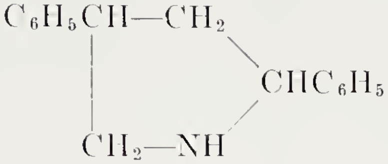
$$\mathrm{CH_2O_2C_6H_3\underset{\underset{\displaystyle CH_2NO_2}{|}}{C}HCH_2COC_6H_5}$$

(II)

The results were disappointing, for the ring systems were easily reduced, and the nature and relative amounts of the various products were not very reproducible. The reductions were accomplished in methanol solution with hydrogen in the presence of platinum black. (I) yielded a substituted pyrrolidine in 86.5 per cent yield. After absorption of two equivalents of hydrogen, (II) yielded unchanged nitroketone, aminoketone, a hydroxypyrroline the structure of which was postulated but not definitely established, and a substituted pyrrolidine with the structure



Beta-phenyl-γ-nitro-butyrophenone (III) was hydrogenated to yield noncrystallizable products. By indirect methods it was possible to show that the oil contained a hydroxy pyrroline and the pyrrolidine



The authors concluded that these products do not represent successive stages of reduction, but are formed simultaneously along different reduction routes.

During the hydrogenation of nitro compounds, the amines formed react slowly, even at room temperature with the unreduced nitro groups to yield complex derivatives. Hence a very active catalyst, thorough agitation, and low reaction temperature are essential for high yields of amines. Under these conditions unreacted starting material can be isolated from the reaction mixture throughout the reduction of a nitro compound. Hence, it is quite probable that the reduction does not involve the formation of stable intermediates when active catalysts such as Raney nickel or Adams' platinum are employed.

In 1923 Traube and Schulz[4], using a catalyst of palladinized barium sulfate, hydrogenated nitromethane and some nitroalcohols, producing methyl hydroxylamine and the hydroxylamine alcohols. Schmidt, Aschurl, and Mayer[5] prepared the intermediate alkylhydroxylamines without simultaneously producing the amine by using the same catalyst, but employing an aqueous or alcoholic solution of oxalic acid as solvent.

Doumani and Coe[6] have reported that the hydrogenation of nitrocyclohexane in the presence of a commercial catalyst yields cyclohexanone oxime. The reaction was conducted by passing steam and hydrogen through the nitrocyclohexane above 100°C.

Rockett and Whitmore[7] reduced dinitroneopentane with hydrogen at 1000 psi, using 6 per cent Raney nickel catalyst, ethanol as solvent, and a reaction temperature of 60°C. A 67 per cent yield of diaminoneopentane and a 5 per cent yield of α,α-dimethylmalonamide were obtained. The authors postulate that the amide was obtained from an intermediate oxime which rearranged as follows:

$$\begin{array}{ccc} (CH_3)_2C(CH_2NO_2)_2 & \xrightarrow{\text{Ni, H}_2} & (CH_3)_2C(CH{=}NOH)_2 \\ & & \downarrow \\ & & (CH_3)_2C(CONH_2)_2\ . \end{array}$$

NITRO ALCOHOLS

The condensation of aliphatic nitroparaffins with aliphatic aldehydes in the presence of basic catalysts yields various monohydric and dihydric nitro alcohols. Hydrogenation of these nitroalcohols gives corresponding amines. Such amines catalyze the decomposition of the alcohols to the nitroparaffin and aldehyde so that the yields are somewhat reduced. Vanderbilt and Hass[8] synthesized several nitroalcohols and reduced them with hydrogen over Raney nickel. They successfully prepared 2-amino-2-alkyl-1,3-propanediols, where the alkyl group was methyl, ethyl, *n*-propyl or isopropyl. These diols are useful as wetting agents, emulsifiers and detergents. Degering and Hoaglin[9] prepared 2-amino-2-methyl-3-pentanol, 2-amino-2-methyl-3-hexanol, and 3-amino-3-methyl-4-heptanol by hydrogenation of the corresponding nitro compounds in alcohol at room temperature with Raney nickel as the catalyst. The highest yield reported was 31 per cent.

TABLE 1. CATALYTIC HYDROGENATION OF NITROALCOHOLS

Compound	Amount (moles)	Catalyst (grams)	Pressure (psig)	Time Conversion	
				hrs	%
2-Nitro-1-butanol	½	1.5	1300	2	95
2-Nitro-1-butanol	½	7.5	600	8	74.5
2-Nitro-1-butanol	¾	7.5	1800	3	91
2-Nitro-1-butanol	¾	7.5	1800	10	91
5-Nitro-4-octanol	¼	7.5	1750	4	93
2-Methyl-2-nitro-1-butanol	¼	7.5	1700	4	86
3-Nitro-2-pentanol	¼	8.5	1600	3	92

Johnson and Degering[10] have reported the most thorough investigation of the reduction of nitrolalcohols. Working with a rocker bomb with Raney nickel as catalyst and ethanol as solvent these authors hydrogenated a series of nitroalcohols. The reactions were started at room temperature but enough heat was generated during the reduction to cause a temperature rise to 40 to 50°C. Catalytic hydrogenation was the only method found which gave good yields. The results are summarized in Table 1.

Similar studies with 2-alkyl-2-nitro-1,3-propanediols, where alkyl represents methyl, ethyl, propyl, or isopropyl, gave similar results.

NITROKETONES

In 1947 Kloetzel[11] prepared and catalytically reduced a series of γ-nitroketones. These ketones were prepared by the condensation of nitroparaffins with the appropriate α,β-unsaturated ketones in the presence of diethylamine. The hydrogenations were conducted in methanol over Raney nickel at 100°C and 1000 psig hydrogen pressure, both in the presence and absence of ammonia. Substituted pyrrolidines were the principal products of these reductions both in the presence and absence of the ammonia. Yields of these pyrrolidines ranged from 52 to 94 per cent. These results may be compared with those of Kohler and Drake[3] who found that reduction of γ-nitroketones over platinum by hydrogen at atmospheric pressure yielded a variety of products depending upon the nature of the nitroketone.

NITROVINYL POLYMER

Blomquist, Tapp, and Johnson[12] prepared nitrovinyl polymer but were unable to hydrogenate their product to the polyvinylamine because of the high degree of cross-linking involving the active hydrogen of the —$CH(NO_2)$— group. In the case of polymer from the olefin, 2-nitropropene, no such cross linking is possible, and hydrogenation was successfully achieved in dioxane solution over Raney nickel catalyst at 90°C and 1700 psig hydrogen pressure. A 68 per cent yield of 2-aminopropene polymer was obtained.

UNCONJUGATED NITROOLEFINS

The work of Nightingale and Tweedie[13] gives some insight into the relative ease of reduction of the nitro group and an isolated double bond. These investigators prepared three alicyclic nitro compounds from nitrostyrene and substituted butadienes by a Diels-Alder reaction. These compounds were 4-nitro-5-phenylcyclohexene, 4-nitro-5 phenyl-1-2-dimethylcyclohexene, and 1-nitro-3,5,6-triphenylcyclohexene. By control of temperature and pressure, using hydrogen, Raney nickel, and methanol as solvent, they found it possible to reduce each compound first to the cyclohexenylamine and then to the cyclohexylamine. No evidence was given to show whether the nitro group was reduced first because of a faster inherent rate of reduction or because it displaced the isolated double bond from the catalyst surface.

α-β-UNSATURATED NITROOLEFINS

The α-β-unsaturated nitrolefins exhibit reaction characteristics which are reminiscent of α-β-unsaturated ketones. When hydrogenation takes place, both the nitro group and the double bond are simultaneously reduced. The products which are obtained appear to result from the 1,4-addition of hydrogen to the conjugated system. When the double bond is also conjugated with a phenyl group, it is possible to hydrogenate selectively the arylnitroolefin to a 1-aryl-2-nitroalkane[14]. The reaction is carried out under controlled conditions at low temperatures with a platinum or palladium catalyst. In addition to the alkane, some 1-aryl-2-oxoalkane oximes and 1-aryl-2-oxoalkanes are obtained. The product distribution for reduction of some arylnitroolefins in various solvents in the presence of palladium on charcoal is given in Table 2. As noted in the previous section, the nitro group is ordinarily more readily reduced than an isolated double bond. However, the preponderence of yields of aryl nitroalkanes when the groups are conjugated (Table 2) suggests the possibility that the hydrogen adds to the 1,4-positions to give the *aci* form of the nitroalkane which then rearranges to form the normal nitroalkane.

Further impetus to such a postulate is given by the work of Sonn and Schellenberg[15] who reduced ω-nitrostyrene over platinum black with glacial acetic acid and ethanol as solvents. These investigators found that in alcoholic suspension the absorption of one mole of hydrogen by the nitrostyrene results in a mixture of isomeric compounds, the less soluble being 1,4-dinitro-2,3-diphenylbutane. The other compound, obtained in smaller yields, was a stereoisomer.

TABLE 2. REDUCTION OF ARYL NITROOLEFINS

Nitroolefin	Solvent	Temp (°C)	H_2 Pressure (psi)	Ketone	Yield Aryl Nitro-alkane	Per Cent Oxime
1-Phenyl-2-nitro-1-propene	water	31–35	500	4.9	63.0	17.3
1-Phenyl-2-nitro-1-propene	methanol	26–34	400–500	10.5	56.2	20.9
1-Phenyl-2-nitro-1-propene	acetone	30–35	200	6.8	43.0	41.0
1-Phenyl-2-nitro-1-propene	toluene	25–35	200	5.3	30.8	42.0
1-Phenyl-2-nitro-1-butene	methanol	30–38	400–500	17.3	45.6	13.2
1-Phenyl-2-nitro-1-butene	water	25–30	500	9.7	58.2	11.0
1-Phenyl-2-nitro-1-pentene	methanol	29–36	200–500	8.0	29.5	35.0
1-(*m*-Tolyl)-2-nitro-1-propene	methanol	20–21	300	11.5	40.5	9.8
1-(*p*-Isopropylphenyl)-2-nitro-1-propene	methanol	18–20	300	—	59.0	—

In glacial acetic acid the reduction proceeds in a different manner. The 1,4-dinitro-2,3-diphenylbutane was obtained together with methylphenylketoxime and an amorphous mixture. Similar results were obtained with piperonylidenenitromethane.

The reduction of 2-nitro-1-butene in glacial acetic acid over Adams' platinum catalyst results in the formation of oxime, saturated amine, and a deep red polymeric oil. No 2-nitrobutane was isolated[16]. Over Raney nickel with ethanol as solvent, the major product is polynitrobutylene and only about 10 per cent of the theoretical amount of hydrogen required for saturation is absorbed.

The reduction of nitroolefins to the amine is best accomplished by first reducing the nitrolefin to the ketoxime with iron and hydrochloric acid followed by hydrogenation over Raney nickel in ethanol to the saturated amine.

McPhee, Erickson, and Salvador[17] reduced some substituted α-nitrostilbenes to α-β-diphenylethylamines in the presence of palladium on charcoal and methanol as solvent. The reaction was conducted at 55°C and 50 to 60 psig hydrogen pressure. Table 3 shows the results of this study.

Clapp, Brown, and Zeftel[18] prepared 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene from 1-chloro-1-nitroparaffins by the action of aqueous alkali. The dinitroolefins were reduced with hydrogen over Adams' platinum or Raney nickel catalyst and gave 23 to 33 per cent yields of the corresponding diamines. The dinitroalkenes were also treated with ammonia gas to give 3-nitro-4-iminohexane and 2-nitro-3-iminobutane. These imines were reduced over Raney nickel catalyst to give 60 to 70 per cent yields of the diamines.

TABLE 3. HYDROGENATION OF SUBSTITUTED NITROSTILBENES

Ar—CH=C(NO_2)—C_6H_5

	Reduction Time (hrs)	Yield (%)
Substituted β-phenyl		
2-Methoxy	16	52
2-Hydroxy	3	86
4-Methoxy	3	67
4-Hydroxy	3	75
3-Methoxy-4-hydroxy	1	87

AROMATIC NITRO COMPOUNDS

In 1842 Zenin first reduced nitrobenzene with ammonium sulfide. Since that time many developments in the reduction of aromatic nitro compounds have taken place, and recently considerable attention has been given to reduction by catalytic hydrogenation. Nitrobenzene and related compounds have been hydrogenated over a variety of catalysts, in both liquid and vapor phases, at both low and high hydrogen pressures. The yields of amines are high with a minimum of by-product formation.

The heat of hydrogenation of the nitro group to form the amine and water is large, and the reaction proceeds readily under a wide variety of conditions. Care must be taken to maintain thorough agitation and to carefully control the rate of reduction by various means.

Condit and Haynor[19] have established the fact that nitrobenzene decomposes explosively at 356°C and that nitroxylene decomposes with explosive violence at 308°C. These explosion temperatures are relatively independent of the pressure of the surrounding gas.

In 1922, Brown and Henke[20] reduced nitrobenzene to aniline in almost quantitative yields. The reduction was accomplished by hydrogen over a copper catalyst at 260°C. Six years later, the superiority of nickel as a catalyst for the reduction of aromatic nitro compounds to aromatic amines was established[21]. Nitrobenzene, α-nitronaphthalene, *p*-nitrotoluene, *o*-nitrophenol, *p*-nitrophenol, and dinitrotoluene were reduced quantitatively to the amines by hydrogen at 215°C and 34 atmospheres hydrogen pressure in the presence of 0.52 g of reduced nickel oxide catalyst per gram of nitrophenol. Benzene and methanol were considered the best solvents. Nickel in the form of Raney catalyst was not available at this time. Brown and co-workers continued their study of nitrobenzene reduction in the vapor phase using a variety of catalysts including cadmium, cobalt, cobalt-manganese, cobalt-chromium and such compounds as Tl_2Pb, Tl_3Bi, NiS, CdS, PbS, etc. Optimum working temperatures were established for these materials[18, 20, 22, 23]. In all cases except one, high yields of aniline were obtained. The compound Tl_2Pb was found to promote the formation of azobenzene. Nickel sulfide was found to be superior to finely divided nickel, catalysing the reduction to aniline in 99 per cent yields. The sulfide catalyst was advantageous when sulfides were present in the nitro compound.

Condit[24] continued investigations in this field, and reduced nitrobenzene and nitroxylenes in the presence of molybdenum sulfide supported on active carbon. The reduction could be accomplished by hydrogen at atmospheric pressure, but the catalyst became less active as the reduction proceeded. For nitrobenzene the optimum temperatures were above 300°C with a large excess of hydrogen under a pressure or 400 to 500 psig. Under these conditions the catalyst maintained its activity over a long period of time. With nitroxylene, more difficulty was encountered because the catalyst became coated with carbonaceous material. Condit found that the catalyst was active at temperatures as low as 232°C under a hydrogen pressure of 3000 psig. This catalyst shows considerable promise for industrial applications. Many of the catalysts studied by Brown and co-workers could accommodate only low nitrobenzene space flows; in addition, many of them caused extensive ring hydrogenation.

Flamme[25] has made a detailed study of the reduction of nitrobenzene in the presence of Raney nickel. The latter was prepared by the method of Paul and Hilly[26]. He found that the optimum conditions were 20 to 25 atmospheres hydrogen pressure and a temperature of 200 to 220°C. The yields of aniline obtained were 97 per cent or greater.

In 1930 Komatsu and Amatatsu[27] studied the conditions at which the benzene nucleus as well as the nitro group may be hydrogenated over a reduced nickel catalyst. At 100°C and 50 atmospheres pressure, nitrobenzene was quantitatively reduced to aniline. At 200°C and 100 atmospheres pressure, 5 per cent aniline and 78 per cent cyclohexylamine were produced. For *p*-nitrophenol, aminocyclohexanol was formed at 160°C and 100 atmospheres of hydrogen. At 160°C, α-nitronaphthalene yielded predominantly α-*aci*-tetrahydronaphthylamine whereas a quantitative yield of α-naphthylamine was obtained at 50°C and 30 to 100 atmospheres pressure. Fuzitu[28] checked the results of the above investigators. He also established the relative rates of hydrogenation of the nitrophenols to be

ortho > *meta* > para

In 1934 Yoshikawa[29] hydrogenated nitrobenzene at 180 to 200°C and one atmosphere hydrogen pressure in the presence of a reduced nickel catalyst containing 1.5 to 2 per cent of nickel sulfate which tends to make the catalyst ineffective for ring hydrogenation. Aniline was produced in high space-time yields. Subsequently the same author[30] employed thiophene to prevent ring hydrogenation. The addition of copper to the nickel or the use of a copper support was found to be advantageous.

Table 4. The Reduction of Nitro Compounds

Compound	Moles	Temperature (°C)	Time (Hrs)	Catalyst and wt. (g)	Yield Amine (%)
m-Dinitrobenzene in diethyl ether	0.25	110	1.3	Ni (2)	95
m-Dinitrobenzene	0.21	175	1	$CuO \cdot Cr_2O_3$ (1)	70
Nitrobenzene in ethanol	0.5	100	1.1	Ni (4)	95
Nitrobenzene	0.61	175	0.8	$CuO \cdot Cr_2O_3$ (3)	98
p-Nitrophenol	0.25	100	0.6	Ni (2)	95
3,3′-Dinitrodiphenyl in ethanol	0.10	100	0.2	Ni (4)	95

Adkins and Connor[31] found that copper chromite can be used as a catalyst for the reduction of aromatic nitro compounds. The reaction takes place at 175°C and 100 to 150 atmospheres hydrogen pressure to produce 98 per cent yields of amines. There is little advantage in using this catalyst since reduced nickel is effective at lower temperatures. However, the copper chromite is not so sensitive to catalyst poisons. Adkins[32] summarized the art up to 1937 in Table 4.

Kinetics of Hydrogenation of Nitro Compounds

Because of the ease of reduction of the nitro group over Adams' platinum and Raney nickel catalysts at room temperature and a few atmospheres of hydrogen pressure, many studies of such reductions have been made during the last twenty years. These studies have included such aspects as the influence on rate of reduction caused by various substituent groups, by different solvents, and by the addition of promotors to the catalysts. In 1927 Adams, Cohen, and Rees[33] made a systematic study of the influence of solvent, temperature, and the presence of foreign materials as well as molecular structure upon the rate of reduction of certain aromatic nitro compounds over Adams' platinum catalyst. They employed 0.1 mole of nitro compound in 150 ml of solvent, 2–3 atmospheres of hydrogen pressure, and temperatures from 25 to 30°C. These authors concluded that more than 10 per cent water in ethanol used as solvent decreased the rate of reduction. A change of solvent to methyl or propyl alcohols had no effect on the reduction rate, but butyl or amyl alcohols had a retarding influence. Ethyl acetate or acetone were quite satisfactory solvents, but in glacial acetic acid the rate of reduction was only one sixth as fast as in ethanol.

The influence of structure on the rate of reduction of aromatic nitro compounds was investigated by use of the following compounds. Ortho, meta and para-nitrotoluenes; *o*- and *p*-nitrobenzoic acids; *p*-nitroanisole; and *p*-nitrophenol. It was concluded the *crtho* substituents produced no effect. The nitrobenzoic acids were reduced more rapidly than nitrobenzene. In the case of the nitrochlorobenzenes, good yields (85 per cent) of chloroanilines were obtained provided the reduction was stopped after 3 moles of hydrogen per mole of acceptor were absorbed. If the reaction were allowed to proceed further, certain amounts of cyclohexylamine hydrochloride were isolated.

The addition of hydrochloric acid, acetic acid, sodium carbonate, zinc acetate, or ferrous sulfate to the reaction mixture had a retarding influence.

Adams, Cohen, and Rees[33] also studied the reduction of substances having both a nitro and an olefin group. Both *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone gave quantitative reduction to the unsaturated amine. Since it appeared that these product amines might prevent the platinum from effectively catalyzing the addition of hydrogen to the double bond, acetic acid was added. Under these circumstances both the nitro group and the double bond were reduced, the former at a slower rate. Attempts to reduce the double bond rather than the nitro group by addition of alkali resulted in failure to produce any hydrogenation at all.

Blout and Silverman[34] reduced some nitrocinnamic acids and esters. Ethanol was employed as solvent and Raney nickel as the catalyst. In every case an 85 per cent yield of unsaturated amine was obtained. These experiments were carried out at 20 to 30°C under an initial hydrogen pressure of 30 psig. It thus appears that the nitro group when conjugated through a double bond with a benzene ring is more reactive than the olefinic bond. However, an olefinic bond in a nonconjugated system is reduced much more rapidly than an aliphatic nitro group, the relative rates being approximately ten to one.

Stevenson and Hamilton[35] converted some nitroarylarsonic acids to the monosodium salts which were readily reduced over Raney nickel at room temperature and 30 psig hydrogen pressure. However, the catalyst was rapidly inactivated. In order to determine the effect of various inorganic impurities which might be introduced during the synthesis of the acids, *p*-nitrophenol was reduced over Raney nickel in the presence of various inorganic substances. The results, shown in Table 5, indicate the retarding influence of nitrite, arsenite, and cyanide.

Beginning in 1939, Smith and co-workers[36, 37, 38] have made a rather complete study of the reduction of aromatic nitro compounds. They found no difference in catalytic activity for these reductions between Raney nickel made from a 30 per cent nickel-70 per cent aluminum alloy and that made from the conventional 50-50 alloy. They showed that platinum chloride enhanced the activity of the Raney catalyst at low hydrogen pressures. The increased activity was markedly greater than that which could be expected on the basis of the quantity of platinum metal involved. Sodium hydroxide acted as a catalyst poison.

TABLE 5. THE INFLUENCE OF INORGANIC MATERIALS ON THE HYDROGENATION OF *p*-NITROPHENOL OVER RANEY NICKEL

Contaminating Impurity (10% by weight)	Reduction Time (minutes)
None	11
Copper sulfate	8
Free sulfur	11
Sodium sulfite	11.5
Sodium hydrosulfite	11
Sodium nitrite	80
Sodium nitrate	12
Sodium arsenite	70
Sodium arsenate	11
Potassium cyanide	33
Sodium sulfate	11
Sodium chloride	11

Scholnik, Reasenberg, Lieber and Smith[37] demonstrated that the reduction does not proceed through various reaction intermediates, but goes directly to the amine. Nitrosobenzene, azobenzene, hydroazobenzene, azoxybenzene, and *β*-phenylhydroxylamine were found to hydrogenate more slowly than does nitrobenzene. The hydrogenations of these possible intermediates were not influenced by sodium hydroxide. Nitrobenzene itself was not hydrogenated in the presence of nitrosobenzene; the nitroso group coordinates with nickel to form complexes. Nitrosobenzene was hydrogenated to aniline over platinum.

In 1950, Samuelson, Garik, and Smith[38] reported a study of the influence of structure upon the rate of reduction of nitro compounds over Raney nickel. These hydrogenations were conducted at atmospheric pressure with

TABLE 6. THE INFLUENCE OF SUBSTITUENTS ON THE RATE OF HYDROGENATION OF THE NITRO GROUP OVER RANEY NICKEL CATALYSTS

Mono nitro compounds	Rates of Reduction			
	a	b	c	d
Nitromethane	69	114	84	149
Nitroethane	115	215	133	286
1-Nitropropane	103	207	100	283
2-Nitropropane	71	169	80	287
Nitrobenzene	200	330	0	144
o-Nitroethylbenzene	24	285	250	406
p-Nitroethylbenzene	32	479	157	394
2-Nitro-*p*-cymene	81	388	210	403
Nitrodurene	236	411	x	x
Nitromesitylene	217	340	310	481
2-Nitro-1,4-dimethylbenzene	121	451	213	554
5-Nitro-1,3-dimethylbenzene	123	523	1	x
4-Nitro-2-aminotoluene	125	479	55	286
6-Nitro-2-aminophenol	i	i	i	i
1-Nitro-2-methylanthraquinone	45	175	<1	x
Dinitro compounds				
o-Dinitrobenzene	80	450	0	80
m-Dinitrobenzene	<1	584	0	133
p-Dinitrobenzene	<1	436	<1	x
2,4-Dinitrotoluene	302	612	0	0
2,4-Dinitrophenetole	367	654	0	200
3,5-Dinitro-*o*-cresol	539	559	545	560
2,4-Dinitrophenylhydrazine	100	400	220	285
2,4-Dinitrophenol	422	581	424	584
2,6-Dinitrophenol	i	i	i	i
2,4-Dinitroaniline	409	427	159	292
4,6-Dinitro-2-aminophenol	i	i	i	i
3,5-Dinitrosalicylic Acid	i	i	i	i
1,5-Dinitronaphthalene	298	520	180	257
1,8-Dinitronaphthalene	450	454	0	0

0.05 moles of acceptor in 150 ml of ethanol as solvent. No temperature control was employed so that in some instances temperature increases as great as 10°C occurred during a run. A quantitative yield of amine was obtained for most of the compounds hydrogenated. The results of experiments with four catalysts are shown in Table 6. The catalysts used are identified as follows: (a) Raney nickel; (b) Raney nickel with approximately 5 per cent chloroplatinic acid; (c) Raney nickel with approximately 4 per cent sodium hydroxide; (d) Raney nickel with both the chloroplatinic acid and sodium hydroxide. All rates in the table refer to milliliters of hydrogen absorbed per 100 seconds calculated as an average rate over the first half of hydrogen absorption. The term "i" (incomplete reaction) indicates that the reaction ceased after absorption of an appreciable amount of hydrogen. "x" indicates that the reaction was not studied.

The authors drew the following conclusions:

(1) Some increase in rate occurred with *o*-substituted compounds, particularly polynitro compounds. However, chelation tends to lower the reduction rate.

(2) Platinum introduced as chloroplatinic acid is a true promoter since it does not initiate the hydrogenation reactions, but speeds up the hydrogenation of all nitro compounds over Raney nickel.

(3) The addition of a small amount of alkali usually retards hydrogenation of the nitro group over Raney nickel.

(4) The fact that the addition of platinum tends to oppose the poisoning action of alkali gives support to the idea that action of both alkali and platinum are probably at the catalyst surface.

Vesely and Rein[39] reported that hydrogen in the presence of platinum black acts selectively on one nitro group in dinitroaryl compounds. *m*-Dinitrobenzene yields *m*-nitroaniline, and *o*-nitro-*p*-toluidine may be similarly obtained. Strel'tsova and Zelinskii[40] studied the reduction of *m*-dinitrobenzene in alcohol in the presence of a platinum catalyst and obtained mixed *m*-phenylene diamine and *m*-nitroaniline. The same authors[41] found that the presence of methyl, hydroxy, chloro, carboxyl or methoxy groups on the benzene ring had no effect on the rate of reduction of aryl nitro compounds.

In 1948 Hernandez and Nord[42] made a systematic kinetic study of the reduction of *m*- and *p*-substituted nitrobenzenes with hydrogen on rhodium and palladium catalysts. Polyvinyl alcohol was used as a supporting colloid for these catalysts. The activity of the rhodium catalyst was markedly influenced both by the pH of the ethanol used as solvent and by the nature of functional groups attached to the benzene ring. The activity of the palladium catalyst seems to be almost unaffected by these factors. The authors concluded that rhodium ionizes the hydrogen so that the hydrogen ion is the effective hydrogenating agent, whereas hydrogen atoms are involved when the palladium catalyst is employed. Table 7 gives relative first order rate constants for hydrogenation of *para*-substituted nitrobenzenes in the presence of rhodium:

The rate constants given in Table 7 parallel rather closely the order of the "σ" constants in Hammett's equation[43].

A quantitative kinetic study of the catalytic hydrogenation of nitro groups has been published by Smith and Bedoit[16]. They find that under certain conditions these reductions are first order with respect to the nitro group and zero order with respect to hydrogen pressure. The reaction rate is given by

$$-\frac{dn}{dt} = kc$$

where c is the concentration of the nitro group in moles per liter and $\frac{dn}{dt}$ is the change in moles of this group per unit time. For a system of constant hydrogen volume, this may be integrated and finally expressed as

Table 7. Hydrogenation of Substituted Nitrobenzenes Over Rhodium

p-substituent	$k \times 10^6$
CN	11.1
CHO	10.8
NO_2	10.4
COOH	10.1
I	9.25
Cl	9.02
Br	8.79
none	8.33
OCH_3	6.25
NH_2	1.85

$$\log\left(P + \frac{n_0}{a} - P_0\right) = \frac{-k}{2{,}303V_1}\,t + \log n_0/a$$

where P_0 is the initial hydrogen pressure and P the pressure at any time, t, n_0 is the initial number of moles of organic compound, V_1 is the volume of liquid in the system, and a is a constant which is equal to $\frac{3Vg}{Rt}$, Vg being the hydrogen volume.

Under other conditions the rate of catalytic hydrogenation of the nitro group exhibits quite different kinetic behavior. Reactions are found which are first order with respect to hydrogen pressure and zero order with respect to concentration of the organic compound. Here the rate is expressed by the equation

$$-\frac{dn}{dt} = -k'P$$

If one assumes the ideal gas law for the hydrogen, this may be expressed as

$$-\frac{dn}{dt} = -\frac{RT}{V}k'P = \frac{kP}{V}$$

where k is constant for a given system at a given temperature, and V is the gaseous volume in the system. This may be integrated between limits and simplified to give:

$$\log P_0/P = \frac{kt}{2{,}303V}$$

Some molecules do not give rate data which fit either of the preceding expressions but appear to represent an intermediate situation. This behavior may be explained on the basis of the Langmuir equation

$$\sigma = \frac{s_1P}{s_1P + s_2}$$

TABLE 8. HYDROGENATION OF NITROPARAFFINS OVER PLATINUM CATALYST[44]

Nitroparaffin	$k_{1.0}$ at 30°C (ml g^{-1} $min.^{-1}$)	Activation Energy (cal. $mole^{-1}$)
Nitromethane	10.2	12,500
Nitroethane	6.9	12,500
1-Nitropropane	5.4	12,200
2-Nitropropane	1.6	13,800
1-Nitrobutane	6.0	12,000
2-Nitrobutane	0.64	15,000

where σ is the fraction of the catalytic surface covered by hydrogen and s_1 and s_2 are constants depending on the rate of adsorption and desorption. If there is a small rate of desorption, i.e., s_2 is quite small in comparison to s_1P, the expression reduces to the expression which is zero order with respect to hydrogen. On the other hand, if hydrogen is weakly adsorbed, i.e., s_1P is small as compared to s_2, the first order expression is obtained.

ALIPHATIC NITRO COMPOUNDS WITH PLATINUM CATALYST[44]

The hydrogenations of aliphatic nitro compounds over Adams' platinum catalyst in acetic acid solution are first order with respect to the concentration of the nitroparaffin and zero order with respect to hydrogen pressure. The rate constants and activation energies for a series of nitroparaffins are given in Table 8. The rate constants are listed as $k_{1.0}$. The subscript means that the rate constants are all referred to one gram of the platinum oxide.

This table shows that the rate of reduction of the 1-nitroparaffins is not greatly affected by chain length, although the rate for nitromethane is a little greater than for higher nitroparaffins The 2-nitro compounds are reduced more slowly, and activation energies are greater than for the 1-nitro groups.

When the reduction of 1-nitrobutane was carried out over platinum with ethanol as solvent, the kinetic behavior was changed and the rate under these conditions was almost linear with respect to hydrogen pressure. The rate of hydrogenation of 2-nitrobutane was only about 5 per cent of that of 1-nitrobutane under these conditions.

Aromatic Nitro Compounds with Platinum Catalyst

The hydrogenations of aromatic nitro compounds over Adams' platinum catalyst in acetic acid solution are zero order with respect to the aromatic nitro compound and first order with respect to hydrogen pressure. Data for the hydrogenation of a number of such compounds are given in Table 9. Since the benzene nucleus may also be reduced over this catalyst, very small amounts (5 to 10 mg) of catalyst were employed. Under these conditions, the hydrogenation essentially ceased after the nitro group had been reduced. When larger amounts of catalyst (0.1 to 0.2 g) are employed, the ring is also readily hydrogenated. The reaction proceeds step-wise and a very sharp reduction in rate occurs after the nitro group has been hydrogenated.

Table 9. Hydrogenation of Aromatic Nitro Compounds Over Platinum

Compound	$k_{1.0}$ at 30°C (ml g^{-1} $min.^{-1}$)	Activation Energy (cal. $mole^{-1}$)
Nitrobenzene	3050	3700
o-Nitrotoluene	3100	4100
m-Nitrotoluene	3100	4100
p-Nitrotoluene	3000	3400
p-Nitrobenzoic Acid	3100	3700
o-Nitrophenol	2700	3200
Nitromesitylene	585	4250
p-Dinitrobenzene	3300	5200
m-Dinitrobenzene	3800	6200
2,4,6-Trinitrotoluene	3550	6400

This table shows that within experimental error the substitution of a single methyl group into nitrobenzene does not influence the rate of reduction of the nitro group.

The low activation energy for the hydrogenation of *o*-nitrophenol may be due to the chelate ring in the molecule. The hydrogenation of the polynitro compounds proceeded without any breaks in the kinetic curves. It is of interest that the hydrogenations of the polynitro compounds exhibit a higher activation energy than for the mono-nitro compounds although there is no decrease in the reaction rate. The higher energies of activation must indicate a less negative entropy of activation which implies an increase in complexity of the activated complex. This may indicate that all of the nitro groups in these molecules are involved simultaneously in the activated state.

Nitromesitylene is a sterically hindered molecule in that the two methyl groups ortho to the nitro group prevent free resonance between this group and the benzene ring. Raman spectra studies on nitromesitylene indicate that the nitro group in this molecule has characteristics closely resembling those of aliphatic compounds. Measurements of the dipole[45] moments of nitromesitylene and nitrobenzene show quite different results, indicating a difference in structure[46]. From a kinetic standpoint, the catalytic hydrogenation of nitromesitylene is intermediate between that of aliphatic and aromatic nitro compounds The rate of hydrogenation of nitromesitylene depends on both the pressure of hydrogen and the concentration of the organic compound, and is somewhat lower than that for nitrobenzene

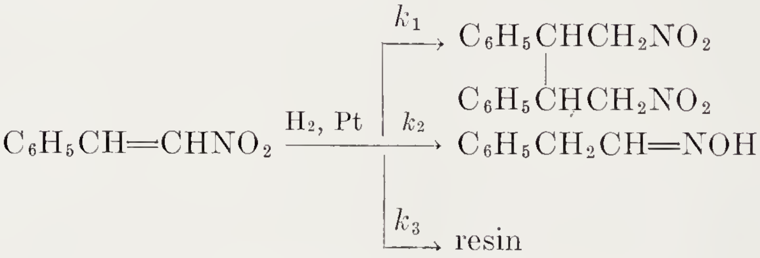
THE NITROOLEFINS WITH PLATINUM CATALYST[16]

ω-Nitrostyrene undergoes hydrogenation in acetic acid solution over Adams' platinum catalyst at a rate which is comparable to nitrobenzene until about 1.5 moles of hydrogen per mole of nitrostyrene have been absorbed; then the rate decreases sharply. The rate constant is 2500 cc g^{-1} $min.^{-1}$ at 30°C, and the activation energy is 4900 cal. $moles^{-1}$.

The hydrogenation of 2-nitrobutene-1 under these conditions is first order with respect to hydrogen pressure and zero order with respect to the concentration of the butene. Thus it behaves similarly to aromatic nitro compounds. The activation energy is 4900 cal. $mole^{-1}$, and the rate constant is 3500 cc g^{-1} $min.^{-1}$ at 30°C.

A comparison of the catalytic hydrogenation of nitroparaffins on the one hand and of nitrobenzene or conjugated nitroolefins on the other indicates that the kinetic analyses are quite different. While for nitrobenzene and the conjugated nitroolefins the reaction is very rapid, is first order with respect to hydrogen pressure and zero order with respect to the concentration of the organic compound, the situation with the nitroparaffins is quite reversed. For the latter compounds, the hydrogenations are slow, are zero order with respect to hydrogen pressure and first order with respect to nitroparaffin. In terms of the Langmuir theory of adsorption it would appear that the nitroparaffin is less strongly adsorbed than is hydrogen, while nitrobenzene is more so. This has been confirmed by studies of the influence of nitro compounds on the catalytic exchange reaction on platinum between deuterium gas and acetic acid[47]. The exchange reaction, which is first order with respect to hydrogen pressure and zero order with respect to acetic acid concentration (when diluted with *n*-heptane) is essentially unaffected by nitroparaffins but is completely stopped by very small concentrations of nitrobenzene.

Since the nitro and phenyl groups in the nitrobenzene are in conjugation with each other, it is probable that such conjugation is important in determining the kinetics of the reduction process. 2-Nitro-1-butene and ω-nitrostyrene represent systems in which double bonds are conjugated with the nitro group. The rate of hydrogenation of a simple double bond is not greatly different from that of nitrobenzene[48]. Therefore, the rapid hydrogenation of these nitroolefins could be caused by hydrogenation of the double bond rather than of the nitro group. However, this would lead to nitrobutane and phenylnitroethane on partial reduction, and these materials were not detected. The isolation of oximes as reduction products of these two molecules indicates that hydrogenation of both groups takes place simultaneously. The mechanism of the reduction of ω-nitrostyrene may be written to indicate several simultaneous reactions:



$$C_6H_5CH{=}CHNO_2 \xrightarrow{H_2,\ Pt} \begin{cases} \xrightarrow{k_1} \begin{array}{c} C_6H_5CHCH_2NO_2 \\ | \\ C_6H_5CHCH_2NO_2 \end{array} \\ \xrightarrow{k_2} C_6H_5CH_2CH{=}NOH \\ \xrightarrow{k_3} \text{resin} \end{cases}$$

Here $k = k_1 + k_2 + k_3$ if the latter are all first order constants.

Aliphatic Nitro Compounds with Nickel Catalyst[49]

The aliphatic nitro compounds in ethanol over Raney nickel catalyst exhibit kinetics which are first order with respect to hydrogen pressure but zero order with respect to the concentration of nitro compound. Dilution tends to increase the reaction rate. The nitroparaffins behave as weak electrolytes in alcohol and there is some correspondence between the rate of hydrogenation and the increase in equivalent conductivity with dilution. The results of experiments dealing with the hydrogenation of several nitroparaffins are given in Table 10. The influence of various solvents upon the rate of hydrogenation of nitromethane over Raney nickel catalyst is shown in Table 11.

It appears that basic media which tend to promote ionization of nitroparaffins increase the rate of reduction.

Aromatic Nitro Compounds Over Nickel Catalyst

The hydrogenation of aromatic nitro compounds is essentially zero order with respect to the concentration of the organic compound and first order with respect to hydrogen pressure. The nitro group is reduced almost quantitatively to the amine. The benzene nucleus is not reduced with hydrogen over Raney nickel at room temperatures. Table 12 shows the behavior of aromatic nitro compounds reduced over nickel.

The rate constant at 30° and the activation energy for the reduction of nitrobenzene over Raney nickel are very similar to those for the nitroparaffins. In fact, the main kinetic difference between the two is the change in rate with dilution of the nitroparaffins. The presence of the benzene nucleus and its conjugated unsaturation with the nitro group seems to have no influence on the reduction rate. Apparently the mechanism of hydrogenation involves only the nitro group.

TABLE 10. HYDROGENATION OF NITROPARAFFINS OVER RANEY NICKEL IN ETHANOL (1 ml of nitroparaffin in 50 ml of ethanol; hydrogen pressures around 50 psia).

Nitroparaffin	$k_{1,0}$ at 30°C (ml g^{-1} $min.^{-1}$)	Activation Energy (cal. $mole^{-1}$)
Nitromethane[a]	10.5	7000
Nitroethane	16.1	9000
1-Nitropropane	12.7	10,000
2-Nitropropane	10.5	10,500
1-Nitrobutane	11.9	10,000
2-Nitrobutane	9.7	11,000

[a] For 0.5 ml in 50 ml of ethanol.

TABLE 11. THE INFLUENCE OF VARIOUS SOLVENTS ON THE HYDROGENATION OF NITROMETHANE OVER RANEY NICKEL (0.5 ml acceptor per 50 ml. solvent; hydrogen pressure about 50 psia).

Solvent	$k_{1,0}$
Methanol	191
Ethanol containing 5% NaOH	159
Ethanol	144
Water containing 5% NaOH	110
Benzene	110
Water	82
Water with 5% Sodium palmitate	71
n-Hexane	71
Nitromethane	50
Water with 5% NH_4Cl	36

In general, Table 12 indicates that substituents on the benzene ring of nitrobenzene have not too great influence on the rate of reduction of the nitro group over Ni. For nitrophenol, however, the rate is considerably increased and the activation energy lowered. This is probably the result of chelation between the nitro group and the phenolic hydrogen. This would decrease the resonance in the nitro group thus decreasing the activation energy and increasing the reaction rate. When the phenolic hydrogen is replaced by a methyl group to give *o*-nitroanisole, chelation does not occur, the resonance in the nitro group is not destroyed, and the reaction proceeds at the same rate as for *m*- and *p*-nitrophenol.

One might expect the hydrogenation of the dinitrobenzenes to proceed somewhat faster than for nitrobenzene because of the presence of two nitro groups on the same molecule. This could explain the increased rate for *o*-dinitrobenzene, but not the lower activation energies found for both the *o*- and *m*-compounds. The more negative entropy of activation accompanying this decrease in activation energy may indicate participation of both nitro groups in the activated complex.

TABLE 12. LOW PRESSURE HYDROGENATION OF AROMATIC NITRO COMPOUNDS OVER RANEY NICKEL WITH ETHANOL AS SOLVENT

Compound	$k_{1.0}$ at 30°C (ml g^{-1} min.$^{-1}$)	Activation Energy (cal. mole^{-1})
Nitrobenzene	18.4	8,400
o-Nitrotoluene	12.4	9,400
m-Nitrotoluene	10.7	9,400
p-Nitrotoluene	11.1	9,600
Nitromesitylene	9.5	9,200
o-Nitrophenol	68.6	6,300
m-Nitrophenol	5.6	9,100
p-Nitrophenol	5.5	9,400
o-Dinitrobenzene	30.7	6,400
m-Dinitrobenzene	14.9	6,800
p-Dinitrobenzene	10.0	9,300
o-Nitroanisole	5.5	10,700
Trinitrotoluene	8.4	8,600

HYDROGENATION OF NITROOLEFINS OVER NICKEL CATALYST[49]

ω-Nitrostyrene is not appreciably hydrogenated over Raney nickel at room temperature and low hydrogen pressures with ethanol as solvent. 2-Nitrobutene-1 undergoes hydrogenation to the extent of about ten per cent of theoretical. The approximate rate found during this hydrogenation was 8.3 cc g^{-1} min.$^{-1}$. It is probable that this figure represents the rate constant for reduction of the nitro group to the amine. The value is reasonably comparable to that obtained for 2-nitrobutane under similar conditions. The rapid decrease in the rate of reduction is undoubtedly due to the formation of polynitrobutylene, the major product of the reduction.

One can conclude that the nitro group is not activated by the presence of a conjugated olefinic double bond when reduced over Raney nickel catalyst in alcohol solvent.

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CHAPTER 6

THE CATALYTIC SYNTHESIS OF AMMONIA FROM NITROGEN AND HYDROGEN

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The First Steps Toward a Catalytic Ammonia Synthesis

The catalytic synthesis of ammonia is a landmark in the development of catalytic processes. Ever since its appearance as an astonishing new technical achievement, it has drawn attention to catalysis as a powerful tool and has inspired many to extensive investigations into the nature of catalytic phenomena.

Over a period of more than one hundred years following the discovery of ammonia and its chemical composition, efforts were made to produce this compound directly by combining three parts of hydrogen with one part of nitrogen. First, merely a scientific puzzle, this problem rapidly became a challenge to industry after the great practical importance of "fixed nitrogen" had been demonstrated by Liebig's finding that ammonia-containing fertilizers can boost the yields of agricultural crops to unforeseen heights.

Early Attempts

In the years from 1820 to 1900 repeatedly futile efforts were made[93, 133, 139] to employ the newly discovered catalytic activity of platinum and also the reactivity of "nascent" hydrogen for "reducing elementary nitrogen to ammonia." A few positive results occasionally reported along this line proved faulty on closer scrutiny. Thus, at the turn of the century, it was a widely held belief that a direct synthesis of ammonia from its elements in one single chemical or catalytic process was merely a wishful dream.

Accordingly, the attention and activities of industrial laboratories shifted to alternative methods for the technical production of ammonia. Such methods were the indirect formation of ammonia *via* the preparation of metallic nitrides, cyanides, or cyanamides, followed by their reduction with hydrogen or decomposition with water; and the subjecting of hydrogen-nitrogen mixtures to electrical discharges[63].

At the same time, however, the groundwork for a systematic approach to a direct ammonia synthesis was laid in those laboratories where new ideas and new experimental investigations emerged from the rapidly growing field of physical chemistry. With the formulation of the law of mass action and of LeChatelier's principle, and with the mathematical derivation of chemical equilibria, a solid basis became available for evaluating quantitatively the possibilities of chemical conversions, especially of gas reactions. Seen from the viewpoint of chemical kinetics, the existence of definite equilibria for a given chemical system is synonymous with the concept that the corresponding reactions must be reversible, even when, under the usual experimental conditions, they appear to proceed in one direction only.

Applied to the well-known decomposition reaction

$$2NH_3 \rightarrow N_2 + 3H_2$$

this reasoning made a synthesis of ammonia from the elements conceivable provided that (1) such temperature and pressure conditions were chosen that would assure the presence of considerable amounts of ammonia in the equilibrium mixture, and that (2) catalysts were found which, at such favorable temperatures and pressures, would shift any given mixture of hydrogen and nitrogen toward its equilibrium with ammonia at a reasonable rate. An encouraging sign for the possibility of obtaining detectable equilibrium concentrations of ammonia could be seen in earlier results of Ramsey and Young (1884)[150]. These authors had studied the decomposition of ammonia over substances such as asbestos, glass and different metals, including iron, and had observed that, even at temperatures as high as 800°C, the hydrogen-nitrogen mixtures resulting from the decomposition reactions invariably contained minute but analytically detectable quantities of undecomposed ammonia. Even more promising were the experiments by Perman and Atkinson[148] (1904), who by passing a H_2-N_2 mixture through a glass tube containing iron nails, obtained enough ammonia to give a positive reaction with Nessler's reagent. Significantly, it was recognized in both these early studies that iron was superior to other metals, such as copper, in inducing the decomposition or formation of ammonia.

Equilibria

In the meantime, the correct mathematical formulation of the laws of chemical equilibria, particularly of gas equilibria, had become a major challenge to the scholars of physical chemistry. Theoretical as well as experimental work on this topic increased rapidly, with the equilibrium between N_2, H_2 and NH_3 being one of the favorite examples. Three prominent leaders in the field of physical chemistry, namely, Wilhelm Ostwald[147], Walter Nernst, and Fritz Haber, initiated in their laboratories quantitative studies on the decomposition and formation of ammonia. During the years

1904 and 1905 Haber and van Oordt carried out investigations of this kind at 1000°C and atmospheric pressure, using finely dispersed iron as a catalyst[83].

Both the results of the decomposition and of the synthesis experiments made Haber conclude that, at this temperature and pressure, a stoichiometric mixture of one part of nitrogen and three parts of hydrogen is in equilibrium with approximately 0.005 volume per cent of ammonia. The catalytic activity of the iron specimens used by Haber was too low to permit a reliable establishment and measurement of the equilibria at lower temperatures. Nevertheless, the approximate value ascertained by him for the equilibrium constant K_{1273}, namely,

$$K_{1273} = \frac{p_{NH_3}}{(p_{H_2})^{3/2}(p_{H_2})^{1/2}} = 10^{-3.8}$$

served him for a calculation or rather for an estimation of K_T values at any lower temperature T. He applied van t'Hoffs isochore equation:

$$\log K_{1273} - \log K_T = \frac{q}{2.302R}\left[\frac{(1273 - T)}{(1273 \cdot T)}\right]$$

where q is the heat of reaction in calories for the conversion

$$\tfrac{1}{2}N + \tfrac{3}{2}H_2 \rightarrow NH_3,$$

R the gas constant in calories and T the temperature in degrees Kelvin. Using the experimental value of 12,000 cal for q, Haber estimated that at a temperature of 327°C, about 8 volume per cent of NH_3 ought to be present in an equilibrium mixture. As shown by later measurements, this was an approximation only; the exact evaluation of K_T would have required additional, and at that time unavailable data on the temperature dependence of q, derived from a concise knowledge of the specific heats of all the reactants as functions of the temperature. Nevertheless, there was no doubt that at lower temperatures the equilibrium is shifted considerably in favor of ammonia. The problem now was to find, if possible, catalysts efficient enough to bring about, at such lower temperatures, a speedy combination of nitrogen and hydrogen to the extent predicted by thermodynamics.

Before a systematic search for such catalysts got under way, another important experimental variable was introduced by Nernst and co-workers[140] who studied the decomposition and formation of ammonia at *elevated pressures*. Considering the reactants, in first approximation, as ideal gases, one can see that the equilibrium concentrations of ammonia ought to increase proportionally to the pressure for any given temperature and composition of the H_2-N_2 mixture.

Here again, later investigations showed that this simple rule does not apply quantitatively, particularly not at pressures above 100 atmospheres, because the reactants deviate considerably in this range from ideal gases. An advantage of the higher ammonia yields obtained in the experiments at elevated pressures was the possibility of securing more exact values of the equilibrium constants in which Nernst was primarily interested. In these investigations, the ammonia or the hydrogen-nitrogen mixture was passed through an electrically heated pressure tube at temperatures between 685 and 1040°C and at pressures up to 75 atmospheres. The catalysts employed were platinum foil, and, in later runs, finely dispersed iron or electrolytically deposited manganese. The equilibrium concentrations of ammonia were approached for a given set of temperature and pressure values from both sides by means of decomposition and synthesis runs. The highest concentration reached was 0.896 volume per cent of ammonia in a synthesis run at 685°C and 50 atm. pressure, over a manganese catalyst.

Since the equilibrium constants derived by Nernst in these studies deviated somewhat from Haber's earlier experimental and calculated values, and since, for theoretical reasons, an exact determination and calculation of the constants appeared most desirable, a second series of decomposition and synthesis experiments, including high pressure runs, was started by Haber and LeRossignol in 1907[82]. These renewed measurements led to good agreement between the equilibrium values of both laboratories.

A comprehensive survey on the equilibrium data for the system H_2—N_2—NH_3 for a wide range of pressures and temperatures is given, in form of a monograph by Nielsen[141] who used the data of Larson and Dodge[118] and of Larson[114] for higher pressures and those of Haber for lower pressures[81].

THE INDUSTRIAL SYNTHESIS PROCESS

Development Work

In the course of these studies, the idea of an industrial, high-pressure synthesis of ammonia must have occurred to Haber and it is to his merit that he clung tenaciously to this idea in spite of the initial difficulties presented by the smallness of ammonia yields, the failure of the then employed catalysts to work efficiently at temperatures below 600°C, and the formidable industrial engineering problem of passing large amounts of gases compressed to more than 100 atmospheres through a bed of red hot catalyst. To solve some of these difficulties, Haber conceived a recycle process in which the reaction mixture, continuously circulated through the catalytic converter, is stripped of the ammonia formed, and returned to the converter. The gas losses caused by the conversion were, according to Haber's plan, replaced by bleeding into the cycle equivalent amounts of a fresh supply of the compressed nitrogen-hydrogen mixture[74]. This principle is used today in almost every ammonia plant and has found wide application in other fields of industrial catalytic gas reactions.

Since a high pressure synthesis of ammonia on an industrial scale involved the solution of problems far beyond the modest facilities of a scientific laboratory, Haber secured financial backing and technical help from the chemical industry in 1908 by entering into an agreement of cooperation with the Badische Anilin and Soda Fabrik (BASF).*

It was decisive for the success or failure of a new industrial ammonia synthesis to find inexpensive and efficient catalysts. After an intensive search conducted first by Haber and later by Mittasch such catalysts were finally discovered. Before a description of this phase is given, a few of the accessory problems that had to be solved to make the synthesis a profitable industrial process will be briefly presented.

Production of the Hydrogen-Nitrogen Mixture[33, 94, 139]

Ways had to be found for procuring, at acceptable costs, the vast amounts of hydrogen and nitrogen which are consumed in the synthesis[94, 139]. The quantities of gas fed into a typical ammonia plant, with an annual production of more than 100,000 tons of ammonia, can be visualized by considering that for the production of one ton of ammonia approximately 110,000 cu ft (NTP) of a $3H_2:1N_2$ mixture are required. Local conditions, such as the cost of power and the availability and cost of raw materials determine in every single case the most effective and economical method for producing the synthesis gas. As the principal source of hydrogen, either water is used, or if the plant is in the proximity of natural gas wells, methane is utilized.

A widely used process for manufacturing synthesis gas, the "Bosch Process," employs as its raw material coke or lignite, air and steam[139]. This process is based on the alternate production of generator gas and of water gas formed by blowing intermittently air and steam through the fuel

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* For this firm the technical conversion of gases by means of heterogeneous catalysis was no new field. Over a period of some twenty years its chemists and engineers had worked out a catalytic process for the production of sulfuric acid from sulfur dioxide, and had acquired considerable experience during this time on the technique of large scale gas reactions, including the purification of the reactants as a precaution against catalyst poisoning. Moreover, continuous efforts had been made by the same company to solve the problem of a technical fixation of atmospheric nitrogen, especially by Bosch and his associate Mittasch. From 1904 to 1909, these men had been engaged in systematic investigations of the various methods of forming cyanides and nitrides by the reaction between atmospheric nitrogen and the oxides or carbonates of barium, titanium, silicon and aluminum[132, 139]. In the course of this work, numerous observations had been made on the catalytic influence of small amounts of added substances on the rate at which elementary nitrogen acts on the various metal oxides and carbonates. All this experience proved to be a valuable asset in the work which was now started toward an industrial ammonia synthesis.

bed of a generator. The gases leaving this generator contain roughly 4 to 8 parts of CO_2 , 32 to 35 parts of CO, 28 to 37 parts of H_2 and 22 to 33 parts of N_2[33]. In a second step, water vapor is added to this gas, and the "water gas conversion reaction" between H_2O and CO is caused to take place by passing the mixture at 500°C over an iron oxide catalyst. Most of the CO reacts under these conditions according to the reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

which leads to a replacement of CO by an equal volume of H_2 . Only 1 to 3 per cent of CO is left in the gas leaving the water gas converter which now contains approximately 3 parts of hydrogen to 1 part of nitrogen.

By compression of this gas to 25 atmospheres, and passage through water, it is washed free of its CO_2 content as well as its content of hydrogen sulfide, formed in the water gas converter from organic sulfur compounds that were present in the generator gas. In some plants, the synthesis gas is subjected to a second pressure-wash with a solution of caustic or of organic amines in order to remove the last traces of carbon dioxide and hydrogen sulfide.

Of particular importance is the next step of purification, namely, the *removal of carbon monoxide*. Even in minute amounts, carbon monoxide acts as a strong poison on ammonia catalysts. In the Bosch process, ammoniacal copper solution is used for scrubbing CO from the synthesis gas after the latter has been compressed to 200 atmospheres; the CO-containing solution is then depressurized and simultaneously heated to 90°C for the release of the dissolved gas, whereupon it is returned to the absorption tower. A newer method of removing carbon monoxide from the gases is to use a small fraction of the hydrogen contained in the mixture to hydrogenate the carbon monoxide to methane in the presence of metallic hydrogenation catalysts. Since methane does not act as a poison, but merely as an inert dilutent in the ammonia synthesis, it can be left in the gases that are circulated through the ammonia converter. However, in order to avoid the excessive accumulation of methane and of other inert gases such as argon, a fraction of the circulating gases is continuously purged from the cycle.

Where hydrocarbons are available as raw material, such as natural gas rich in methane, the manufacture of synthesis gas is usually started with a reforming operation in which methane is subjected, usually in the presence of catalysts, to the combined action of steam and air at high temperatures. Essentially, the reforming process yields a mixture of CO, CO_2 and H_2 with additional nitrogen if air is included in the fresh gas. Subsequently, this mixture is subjected to the water gas shift reaction which replaces CO by H_2 as described above. The further purification of the gases is mostly achieved along lines similar to those used in the Bosch process. A modification of this method consists, as a first step, in subjecting the natural gas to a combination of cracking and reforming.

Among other processes we may mention briefly the following: (1) *Hydrogen production* methods include (a) the electrolysis of water or aqueous solutions; (b) liquefaction and fractionation of coke oven gas, and (c) a similar fractionation of tail gases from cracking units. (2) *Nitrogen production* is carried out by (a) liquefaction and fractionation of air (Linde Process), and (b) by the removal of residual oxygen with solid fuels or gaseous hydrocarbons from nitrogen-rich gases such as tail gases from the ammonia oxidation process.

Obviously, some of these methods are economically feasible only if coupled with other technical processes, as, e.g., the electrolytic production of hydrogen, which may be linked to the electrochemical manufacture of chlorine or caustic.

The considerable number of successive operations employed in any of these processes for the production of a sufficiently pure synthesis gas and their requirements of power and construction materials make the economy of any ammonia plant depend strongly on the manufacturing costs of the gases to be fed into the synthesis converter. For the same reason, the catalytic converter is but a small unit compared with the numerous compressors, reactors, washing towers, heat exchangers and other structures employed for preparing the hydrogen-nitrogen mixture. Nevertheless, the catalytic synthesis reaction proper has always remained the very heart of the entire process, and all the operations carried out as preparatory and as successive steps have to be tuned to the specific performance of the synthesis converter.

Variables of the Industrial Synthesis

The values for the ammonia equilibria, as, e.g., determined by the exact measurements of Haber and of Larsen, Tour, and Dodge[81, 114, 118, 119], permit a clear recognition of the limits to which the reaction

$$3H_2 + H_2 \rightarrow 2NH_3$$

can theoretically proceed at a given temperature and pressure. In spite of its stimulating effect on the development of the technical synthesis, this knowledge of the equilibria limitations is an insufficient guide in selecting the most favorable conditions for the synthesis reaction because it gives no information on the *rate of reaction* at which a hydrogen-nitrogen mixture moves toward its equilibrium with ammonia. For instance, the statement that according to thermodynamics a mixture of $3H_2 + N_2$ ought to be in equilibrium at 200°C and at 10 atmospheres pressure with over 50 per cent of NH_3 is mainly of theoretical interest because the reaction of the gaseous mixture at this low temperature proceeds at a very low rate, even with an extremely pure synthesis gas and with the most efficient catalysts known today. Therefore, in selecting the best conditions for the synthesis reaction, one must choose a range of temperatures and pressures not only favorable for the ammonia equilibrium but also capable of securing a reasonably high rate for the catalytic combination of a hydrogen-nitrogen mixture.

As early as 1909, Haber recognized this and recommended a procedure of passing the gases over the catalyst at such a high flow rate that the ammonia formed remained far below its equilibrium concentration[77]. In using this principle, one can obtain a much larger quantity of ammonia in a given converter in a given time than if, other conditions being equal, one passes the gases through the converter at such a slow speed that the ammonia formed per pass reaches its full equilibrium concentration.

For a given catalyst and composition of the synthesis gas, the three main variables, namely *flow rate*, *pressure* and *temperature* act differently on the equilibria and on the rates of ammonia formation. Table 1 illustrates this in a qualitative way; detailed quantitative data are given in surveys by Emmett[33] and by Nielsen[141].

TABLE 1

Increase of	Equilibrium Concentration of Ammonia	Rate of Ammonia Formation per pass (far from equilibrium)	Yield of Ammonia in lbs/hr/cu ft catalyst
Flow rate	Unchanged	Slightly decreased	Increased
Pressure	Increased	Increased	Increased
Temperature	Decreased	Increased	Increased

Both an increase of the flow rate and of the pressure result in higher space-time yields of ammonia. The upper limits for *technical flow rates* are set by the rapidly growing costs for circulating the compressed gases beyond a certain speed, and also by the difficulties of separating the ammonia from the off-gases if the latter flow at very high rates. In commercial units, flow rates are used up to 50,000 volumes (NTP) of synthesis gas passing per hour over one volume of catalyst space.

Increasing the *pressure* is advantageous in a twofold way, since it shifts the equilibrium conversion in a favorable sense, and also leads *ceteris paribus* to higher reaction rates. As to the upper limits of the pressures employed in industrial units, it is obvious that with higher pressures, the costs rise rapidly for the compression of the gases and for the construction of converters and adjoining units that have to resist the combined action of high pressures and temperatures over long periods of time. Moreover, high pressures concentrate the synthesis reaction on an increasingly smaller volume of converter space, and this introduces the technical problem of a fast dissipation and removal of the heat of reaction generated in the converter. These difficulties have been judged as being more or less serious, depending on the progress made in manufacturing high quality steels as construction materials, and on the exigencies of the patent situation. Accordingly, the pressures employed in the various modifications of the synthesis process used today range from about 100 to 1000 atmospheres.[160]

The effect of the *temperature* on the synthesis reaction is more complex insofar as high temperatures diminish the theoretical limits of ammonia obtainable per single pass (i.e., the equilibrium concentration of NH_3) but accelerate drastically the rate of ammonia formation. These two opposite effects make the choice of the operating temperature in the synthesis converter a matter of compromise. It is obvious that operation at relatively high temperatures is acceptable if combined with high pressures and high flow rates, whereas lowest possible temperatures have to be employed for operating at medium or low pressures and at moderate flow rates. Any decision regarding the synthesis temperature will necessarily also be influenced by the specific efficiency of the catalyst to be used for the contemplated process. Particularly active catalysts must be employed for any type of synthesis operated at low temperatures. In such cases, a very high degree of purity of the gases, especially very low percentages of oxygen and water vapor, is indispensable for maintaining these highly sensitive catalysts at optimum efficiency. The catalysts for a synthesis to be carried out at higher temperatures may have a lower activity, but must be mechanically rugged in order to resist over a reasonably long period the sintering and corroding effects of the high temperatures, pressures and flow rates.

Numerous variations of the synthesis process[94, 139] have been worked out because of the patent situation rather than because of their particularly high efficiencies. We shall therefore not describe all these modifications. Instead, the field of technical methods for the catalytic ammonia synthesis may be circumscribed here briefly by indicating three major processes, two of which represent extremes in conditions of operation, whereas the third represents an intermediate case.

In Table 2, these three processes are listed according to increasing severity of the conditions employed in the synthesis. With the step-up of pressure from process 1 to process 3, the space-time yields per single pass grow considerably. The smaller conversions per pass of process 1 and 2 are compensated for by recycling the gases which ultimately results in an almost complete conversion of the synthesis gas into ammonia. The special catalyst of process 1, characterized by its capacity to operate at low temperatures, calls for a very thorough purification of the H_2-N_2 mixture. A less drastic purification is permissible in processes 2 and 3 which employ conventional

TABLE 2[2, 16, 27]

Process	Temp. (°C)	Press. (atmos.)	Flow Rate cu ft gas NTP per hr (cu ft of catalyst)	Conversion per pass (% of gas)	Yield of NH_3 per pass (lbs /hr/cu ft of catalyst)	Catalyst		Remarks
						Type	Average life	
Mont Cenis	400–425	100	probably 20,000 to 40,000	5–12	approximately 50–100	Decomp. prod. of Al ferrocyanide	several years	Particularly high purity of synthesis gas is required to maintain catalyst active. Recycling of gases.
Haber-Bosch BASF	550	200–250	35,000 to 45,000	15–20	200	Promoted iron	2 to 5 yrs.	A number of processes exist which deviate from the BASF process in minor details only. Recycling of gases.
Claude	500–650	900–1000	30,000 to 50,000	40–80	400–600	Promoted iron	80 to 60 days	High pressure converters of special alloy steel. Usually 2 converters in series, but no recycling of the gas is used.

iron ammonia catalysts. Whereas the latter remain effective for several years in the BASF converter, their useful lifetime is limited to a few months at the high temperatures and pressures of the Claude process. Among the different methods for separating the catalytically produced ammonia from the off-gases, liquefaction has become the most widely accepted procedure.

The Technical Catalysts. *Early Work.* The early laboratory experiments on the decomposition and synthesis of ammonia in small reactor tubes had served the purpose of determining, over short periods of time, the composition of the reacted gas mixtures, and deriving therefrom the equilibrium concentrations of ammonia at various temperatures and pressures. No particular disadvantage was incurred in these exploratory experiments with catalysts of relatively low efficiencies and short lifetimes. All kinds of readily available solid substances including minerals, ceramics, salts, and oxides were tested in this early work as catalysts for the ammonia decomposition and synthesis. Soon it was recognized that the best catalytic action was obtainable with metals belonging to the sixth, seventh and eighth group of the periodic system of elements. Iron, chromium, and manganese proved to be superior to most of the other substances tested at that time.

The capability, however, of certain metal specimens to catalyze in laboratory experiments the formation of ammonia by no means suffices for making them fit for the industrial synthesis. The temperature threshold (about 600°C) above which these early catalysts show activity, at least for a synthesis at normal and medium pressures (up to 200 atmospheres), is too high to obtain economic yields of ammonia. Moreover, the catalytic action of these catalysts remains constant over only short periods, after which it declines in an erratic manner.

Thus, as soon as the technical synthesis moved into the focus of interest, a radical improvement of the early catalysts became imperative. Haber, in 1905, had already started a systematic search for better catalysts and continued this search into the year 1910. In these investigations he was evidently guided by the opinion that the insufficient performance of the previously employed iron, chromium, and nickel catalysts was an inherent property of these metals and that further progress had to come from a study of basically different substances. After an intensive search among many metals and metallic compounds, he found that metallic osmium[75], metallic uranium, and uranium carbide[76] excelled by far the earlier catalysts. With an osmium catalyst, 8 per cent of ammonia was obtained in the off-gas at 550°C and 175 atmospheres over prolonged periods and similarly good results were achieved with specimens of electrothermically prepared samples of carbide containing uranium. This substantial progress proved the existence of catalysts that, by operating at lower temperatures and over longer periods, were much superior to the catalysts of the earlier experiments[80].

For industrial purposes, however, osmium and uranium were unattractive. Osmium is very costly and available in small amounts only; moreover, the use of this metal involves the danger of losing substantial quantities in the form of volatile osmic acid when by accident air contacts the catalyst at high temperatures. Uranium, its carbides and nitrides share with manganese and cerium the undesirable property of being irreversibly oxidized and thereby inactivated by even small amounts of oxygen or water vapor present in the synthesis gas.

Promoted Catalysts. After the discovery of the relatively high catalytic activities of osmium and uranium, the further development of synthesis catalysts was carried out in the BASF by Mittasch and his co-workers[113, 132, 134]. Since at that time practically all metals and metallic compounds in their readily available forms had been checked in preliminary tests, efforts were now mainly directed toward an improvement of those catalysts that up to this point had shown promising but insufficient activities. Practically nothing was known in 1910 about the possibility of promoting catalysts by additional ingredients and about the outstanding catalytic properties of "multicomponent catalysts" which today dominate the field of industrial processes based on heterogeneous catalysis.

In earlier work on the formation of nitrides by the action of elementary nitrogen on metals such as aluminum and titanium, Mittasch had repeatedly observed that the addition of certain salts and oxides to these metals increased the rate of their reaction with nitrogen. Starting from this experience and from the concept that nitride formation of the catalyst is an immediate step in the catalytic synthesis, a vast number of new catalysts were prepared by combining the catalytic "base materials" such as osmium, uranium, nickel, chromium, manganese, tungsten, molybdenum[99] and particularly iron, with all sorts of other metals, oxides and salts[132].

After an initial period of erratic and contradictory results, it was recognized that traces of arsenic, phosphorus and especially of sulfur that were present as impurities in the various specimens are very strong catalyst poisons. These poisons obscured the effects of added promoters on the catalytic performance of the test samples. This was a particularly obnoxious effect with iron catalysts that proved to be extremely susceptible to minute amounts of sulfates or sulfides present in almost all of the then available iron preparations. Elimination of this disturbing factor by the use of highly purified reagents for the catalyst preparations, as well as a systematic investigation of a large series of iron-containing minerals, particularly of magnetites of various origins, finally led to a series of promoted metal catalysts of which the Al_2O_3-K_2O activated "doubly promoted" iron catalyst has become the classical example.

For the purpose of this survey on the general characteristics of ammonia catalysts, it is desirable to present briefly the various types of synthesis catalysts regardless of their commercial importance.

In Table 3, which represents a survey on results obtained by Mittasch and co-workers, relative performances and some other characteristics are listed for several catalysts consisting of single metals. The activity figures given in column (2) of Table 3 illustrate approximately the relative efficiencies of the different metals at standardized synthesis conditions. As can be seen from columns (4) and (5) of Table 3, the various catalysts are not equally susceptible to poisons. A further difference among the catalysts is indicated in column (6) which shows that some of them are present during the synthesis operation in the form of metals, and others in the form of nitride-containing metallic phases according to ordinary chemical analysis. These analytical findings do not exclude the possibility that the "metallic" samples contain very small amounts of chemically bound nitrogen. We shall see later that minute amounts of nitrogen are linked to the surface of all the catalysts and play a very important role in the synthesis reaction.

Except for cerium, which is a relatively poor catalyst, all the catalytically active metals belong to the sixth, seventh and eighth group of the periodic system.

Table 4, again based on data by Mittasch, illustrates the increase of the catalytic efficiencies of various base metals when they are combined with difficultly reducible oxides and with other metals.

Of these and many more multicomponent catalysts investigated in a number of laboratories, the promoted iron catalysts have proved to be the most suitable and least costly type for industrial use. They are about as effective as the much more expensive promoted osmium and molybdenum-nickel catalysts, durable in action, and reasonably resistant against catalyst poisons. The results obtained by Mittasch and co-workers in 1910 have been essentially confirmed and expanded by later investigations among which the thorough studies carried out by A. T. Larson and co-workers[114, 115, 116, 118, 119] in the Fixed Nitrogen Research Laboratory from 1923 to 1925 deserve specific mention. Particular attention was directed in this later work to the individual effects of various promoter oxides. One result of these studies was that "double promotion" by acidic or amphoteric oxides such as Al_2O_3, ZrO_2, SiO_2, and TiO_2 combined with an alkaline oxide such as K_2O gave iron catalysts of superior performance. Such doubly promoted iron catalysts yield about 13 to 14 per cent of ammonia in the exit gas at 100 atmospheres, 450°C and 5000 space velocity compared with singly promoted iron catalysts which yield only 8 to 9 per cent ammonia under the same conditions. In recent years, triply promoted iron catalysts, such as $Fe\text{-}Al_2O_3\text{-}CaO\text{-}K_2O$ combinations have been used to an increasing extent for the industrial synthesis[141, 143].

TABLE 3. EFFICIENCY OF PURE METALS AS AMMONIA CATALYSTS

Metals (1)	Yield of NH_3 Under Standard Conditions[a] (2)	Activity as a Function of Time (3)	Poisoning Effects		Composition, Under Conditions of Synthesis (6)
			Reversible (4)	Irreversible (5)	
Iron	2.0%	Rapid decrease to about 10% of initial activity	water, oxygen, CO_2	S, Se, Te, As, P, CO	Metal
Cobalt	0.2%	Slow decline of activity	water, oxygen, CO_2	S, Se, Te, As, P, CO	Metal
Nickel	0.0 to 0.1%	Soon becomes completely inactive	water, oxygen, CO_2	S, Se, Te, As, P, CO	Metal
Molybdenum	1.5%	Retains initial activity over long period	less susceptible than Fe, Co, Ni	less susceptible than Fe, Co, Ni	Metal–Metal nitride mixture (9% N content)
Tungsten	0.4%	Retains initial activity over long period	less susceptible than Fe, Co, Ni	less susceptible than Fe, Co, Ni	Metal–Metal nitride mixture
Manganese	0.8%	Rapid decrease due to high susceptibility to poisons	—	water, oxygen, S, Se, Te, As, P, CO	Metal–Metal nitride mixture
Uranium	1.0 to 2.5%	Slow decrease	—	water, oxygen, S, Se, Te, As, P, CO	Metal–Metal nitride mixture
Cerium	0.3 to 1.0%	Slow decrease	—	water, oxygen, S, Se, Te, As	Metal–Metal nitride mixture
Osmium	2.0%	Remains fairly constant	water, oxygen, CO	As, P	Metal
Ruthenium	Probably 1.0%		water, oxygen, CO	As, P	Metal

[a] 2 grams of catalyst in small reaction tube, 550°C, 100 atmospheric pressure, gas composition 1:1 $N_2:H_2$, space velocity = 30,000 to 50,000.

The conventional iron ammonia catalyst, containing between 0.6 to 2.0 per cent Al_2O_3 and 0.3 to 1.5 per cent K_2O, is usually prepared by fusion in an oxygen atmosphere of a mixture consisting of magnetite Fe_3O_4 and the promoting oxides, followed by reduction of the oxidic particles at synthesis conditions. Other kinds of preparation used for the various catalyst types involve the precipitation of hydroxides or oxides from aqueous solutions and their calcination and reduction, the addition of promoters by impregnation and as, e.g., in the case of osmium catalysts, the use of catalyst supports.

TABLE 4. PROMOTER EFFECTS ON METALS AS AMMONIA CATALYSTS

Metals	Promoting Oxides and Oxide Combinations	Promoting Metals	Effect on Activity of Unpromoted Metals
Iron	Al_2O_3 Rare earth oxides CaO Cr_2O_3 $Al_2O_3 + K_2O$ $Cr_2O_3 + MnO$	Mo W	2% → 4% → 5% Greatly prolonged useful lifetime
Cobalt	Al_2O_3	Mo W	0.2% → 1.5% Smaller effect of promoters than with Fe.
Nickel		Mo W	0.1% → 0.3%
Molybdenum	No promoter effects by oxides	Ni, Pd, Co, Pt. Fe	1.5% → 4%
Tungsten	No promoter effects by oxides	Ni, Pd, Co, Pt. Fe	0.4% → 1.2%
Osmium	Li_2O Na_2O K_2O ThO_2	Mn	2% → 4%
Manganese	Al_2O_3 CaO V_2O_5	Os	0.8% → 2.5%
Uranium	MgO ZrO		1.0% → 2.5%
Cerium	MgO		0.3% → 1.0%

THE THEORY OF THE CATALYTIC AMMONIA SYNTHESIS

The catalytic ammonia synthesis has been the object of numerous theoretical studies. Its investigation has remained an attractive topic, mainly because it differs from many newer technical catalytic conversions by its chemical simplicity, leading directly from the simple gases hydrogen and nitrogen to ammonia without any interference from side reactions or from the formation of secondary products. Various surveys on the results of earlier scientific investigations of the ammonia synthesis can be found in the literature[33, 35, 36, 38, 62, 63, 65, 134, 144].

General Principles of the Catalytic Process

Mechanism of Catalytic Activity. *The lowering of activation of energies.* So far, all efforts to combine hydrogen and nitrogen in a purely thermal uncatalyzed reaction in the gas phase, similar to the homogeneous reaction between hydrogen and oxygen, have failed. Moreover, it has proved impossible to obtain ammonia by a reaction in the gas phase between *atomic hydrogen* and *molecular nitrogen*[25, 146, 165, 174].

On the other hand, it has been shown that *atomic nitrogen* can be reduced to ammonia or to hydrazine, both in the gas phase and on metal surfaces[25, 33, 63, 164].

These observations, as well as the fact that typical hydrogenation catalysts, such as platinum, do not catalyze the synthesis of ammonia, indicate clearly that the main cause for the failure of obtaining ammonia directly in an uncatalyzed reaction is the *chemical inertia of the nitrogen molecule.* Its heat of dissociation has been estimated to be at least 160,000 cal per mole, against 117,000 cal for the heat of dissociation of O_2 and 100,000 cal for that of H_2. It is likely that the activation energy for a process initiating ammonia formation in the gas phase such as $N_2 + H_2 \rightarrow 2NH$ would amount to at least 100,000 cal. The necessity of such a high energy of activation means an extremely slow rate of reaction, even under otherwise favorable conditions.*

The only way to accelerate the reaction between nitrogen and hydrogen is by a *drastic lowering of the energy required for the activation of the reactants,*

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* Let us assume the most efficient mechanism of a gaseous reaction between N_2 and H_2 by postulating that every collision between a N_2-molecule and an H_2 molecule, for which an activation energy of 100,000 cal is provided would lead to the formation of 2NH radicals, and that the latter would be immediately and quantitatively further hydrogenated to ammonia. Even with these very advantageous assumptions, only about 10^9 NH_3 molecules would be formed per second in one liter of a N_2-H_2 mixture 1:3, at a temperature of 527°C and a pressure of 300 atm. This is a negligible amount if we consider that for a just measurable rate of reaction (1 part of NH_3 formed in 1000 parts of the gas mixture in 10 min.) approximately 10^{16} NH_3 molecules ought to be formed per one second in one liter. In order to obtain this conversion of 0.1 per cent of the gas mixture to ammonia in 10 min., the reaction temperature would have to be raised for the process considered above from 800 to 1210°K at which high temperature, however, almost no ammonia can be formed because of the unfavorable equilibrium conditions.

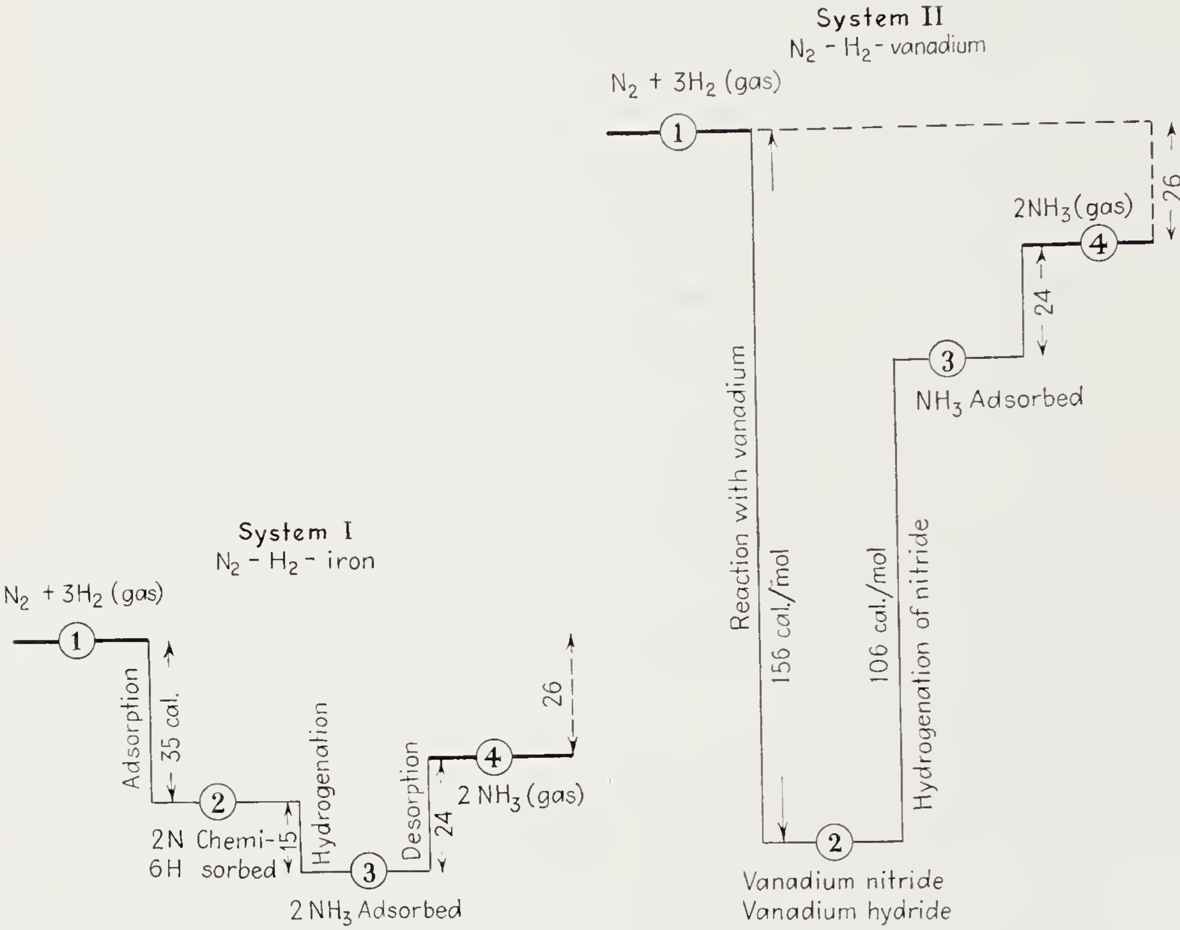
particularly of the nitrogen molecule. The fact that on efficient ammonia catalysts, the synthesis reaction occurs at a measurable rate at temperatures as low as 200°C proves that these catalysts offer to nitrogen and hydrogen new pathways of reaction, every single step of which requires activation energies not higher than, at the most, 30,000 to 40,000 cal/mole.

In order to understand how a catalyst can lower the activation energy of a given reaction, the activation process itself may be briefly discussed. The only means for achieving a considerable weakening of the interatomic bond within a nitrogen molecule in the gas phase is to increase its total energy content by raising the temperature of the gas mixture. This method of activation is both unspecific and wasteful since the energy imparted to every single molecule will be distributed over all its degrees of freedom and thus cause not only intensified intramolecular vibrations with a corresponding weakening of the N-N bond, but also accelerated translational movements and intensified rotations of the molecules both of which contribute little, if anything to their reactivity. Thus, merely a fraction of the total invested energy will be usefully employed.

If, however, a weakening of the N-N bond in a nitrogen molecule is induced by other more specific means, such as by a considerable stretching, or a total dissociation of the molecule under the influence of a catalyst surface of the appropriate spacing and specific affinity toward nitrogen, reactive configurations of the nitrogen molecules will be obtained without requiring the supply of the high amount of energy necessary for the activation of the isolated molecules.

Requisites for Ammonia Catalysts. Thus, the *first requisite* for a good ammonia catalyst is its capacity to force nitrogen molecules that have become attached to it into active configurations with a minimum expenditure of energy. The kind of chemical affinity and structure which enable a catalyst to satisfy this condition will be discussed later. These characteristics, however, in themselves do not suffice in making a given substance a good ammonia catalyst. Since the desired active configuration of the nitrogen molecule is brought about by forces of affinity projected from the catalyst surface, the price to be paid for the activation process is a more or less intimate linkage of the activated nitrogen to the catalyst in form of a catalyst-nitrogen complex of the general type Cat-N–N-Cat. The *second indispensable requisite* for an efficient ammonia catalyst is that the links established between its surface and the nitrogen atoms are not too strong. This is essential for limiting the activation energy of the next step of the catalytic process, namely of the partial or total hydrogenation of the nitrogen anchored to the catalyst to values not exceeding 30,000 to 40,000 cal. In chemical terms this means that the intermediary *complex between catalyst and nitrogen must have a limited stability.*

Figure 1 illustrates these relationships schematically. System I shows the energy levels of the processes of nitrogen activation and nitrogen hydrogenation for a doubly promoted iron catalyst which with nitrogen forms a *surface complex* of the desired low stability. System II represents the energy levels of the corresponding process for vanadium that reacts with nitrogen to form a stable *"bulk nitride,"* VN, of high stability.



Activation Energies A

Step process	Value
1 ⟶ 2	16 cal./mol N_2
2 ⟶ 3	7.5 cal./g. atom N
3 ⟶ 4	10 to 12 cal./mol NH_3

Activation Energies A

Step process	Value
1 ⟶ 2	10 to 15 cal./mol N_2 (estd)
2 ⟶ 3	= 53 cal. /g. atom N
3 ⟶ 4	10 to 12 cal./mol NH_3

The values in the diagram are the heats of reaction Q of the individual step processes

Figure 1.

Each of these two systems comprises successive steps whose heats of reaction Q and energies of activation A are indicated in the diagrams. As a simplification of the diagram and also for the purpose of emphasizing the predominant importance of the nitrogen activation for the catalytic synthesis, the steps of hydrogen activation are omitted from the diagrams of both systems. Another simplification is that for both systems the hydrogenation of the catalyst-bound nitrogen (2) → (3) is shown as one single act although it may actually occur in successive steps such as

$$\begin{array}{ll} \text{(a)} & N_{\text{activated}} + H_{\text{activated}} \rightarrow NH \\ \text{(b)} & NH + H \rightarrow NH_2 \\ \text{(c)} & NH_2 + H \rightarrow NH_3 \end{array} \left.\vphantom{\begin{array}{l} a \\ b \\ c \end{array}}\right\} \begin{array}{l} \text{in the} \\ \text{adsorbed} \\ \text{phase} \end{array}$$

Since, however, the speed of the entire hydrogenation process on many effective ammonia catalysts is high enough to eliminate this act of hydrogenation as the rate determining step, its finer differentiation may be omitted at this point. None of the individual processes of System I requires an energy of activation above 16,000 cal. whereas the reaction path of System II includes the highly endothermic hydrogenation of the stable vanadium nitride, requiring an activation energy of about 52,000 cal.

The rate v of an elementary process depends strongly on its activation energy A and decreases rapidly the larger A becomes according to

$$v = B \cdot e^{-A/RT}, \qquad B = \text{constant.}$$

Thus, the over-all conversion in System I will be very much faster than in System II, the latter coming practically to a standstill at point 2. In the following, we assume that in System I the process with the highest energy of activation, namely the formation (1) → (2) of the "surface nitride" is the slowest and rate determining step. If we use the experimental observation of Emmett and Brunauer[42] that the rate of this process is slower by a factor of 10^6 than the rate calculated from the number σ of collisions between nitrogen molecules with the surface of the iron catalyst, and if we calculate the rate for a temperature of 200°C, a nitrogen pressure of 0.25 atmospheres, and a catalyst surface of 8×10^5 cm^2 (5 g of promoted iron catalyst), we obtain the following result for the rate v of step (1) → (2) in System I:

$$v = \sigma \cdot 8 \cdot 10^5 \cdot 1.10^{-6} \cdot e^{-16000/473R}, \text{ or}$$

$$\begin{aligned} v &= 6 \cdot 10^{22} \cdot 8 \cdot 10^5 \cdot 1.10^{-6} \cdot 10^{-7.4} \\ &= 8 \cdot 10^{15} \text{ } N_2 \text{ molecules reacting per second, or} \\ &= 16 \cdot 10^{15} \text{ } NH_3 \text{ molecules formed per second.} \end{aligned}$$

This yield corresponds roughly to the formation of 0.001 cc of NH_3/sec., or to the production of about 400 parts per million of NH_3 in a synthesis mixture of $N_2 + 3H_2$ streaming over the catalyst at 1 atm. pressure and 200°C with a space velocity of 2,500. Considering the approximate character of this calculation, it agrees well with experimental results of Wright[181] who obtained in synthesis runs, over a doubly promoted iron catalyst, under conditions roughly corresponding to those assumed for the foregoing calculation, an ammonia yield of 650 parts per million, at 239°C.

Although step (1) → (2) in System II, namely the formation of vanadium nitride and the simultaneous rupture of the N-N bond of the N_2 molecule, may occur at a rate comparable to that of step (1) → (2) in System I, this is of little avail for the over-all speed of process II because of the extreme slowness of the hydrogenation step (1) → (2). The latter, other conditions being equal, will occur at 200°C at a rate that is smaller by a factor of about 10^{19} than the corresponding step (2) → (3) in System I.

Catalytic Activity and Capacity for Nitride Formation. Thus, the significant characteristic of an ammonia catalyst is the *delicate balance of its chemical affinity toward nitrogen.* This affinity must suffice for the formation of a catalyst-nitrogen association in which the *N-N bond is substantially weakened or completely broken,* but *it must not be strong enough to cause the formation of a stable, highly exothermic "bulk nitride."* Since many catalysts that form labile complexes with nitrogen do so only at their uppermost surface, the detection and quantitative investigation of these intermediates of the catalytic reaction require methods more refined than those commonly used in analytical chemistry. For the same reason conventional chemical data on the formation of bulk nitrides from molecular nitrogen and various metals cannot serve as dependable indicators for the effectiveness of the various metals as ammonia catalysts.

This is illustrated by the fact that the metals Li, Ca, and Al fail as ammonia catalysts although they react readily with nitrogen, forming well defined nitrides, and, at least as far as lithium is concerned, with the expenditure of a small activation energy[64]. The catalytic inactivity of these three metals may be correlated with the fact that their nitrides possess high heats of formation and an ionic structure.

However, the capacity for forming "bulk nitrides" is also no dependable criterion of catalytic activity even for the metallic elements listed in the periodic system under the atomic numbers 21 to 28, 39 to 46, 57 to 78 and 87 to 92, although these "transition elements" appear in principle to be better equipped for the activation of nitrogen than the elements forming nitrides of an ionic structure[85, 86].

Specifically, of the metals with atomic numbers 21 to 28, Sc, Ti, V, and Cr bind nitrogen in the form of very stable nitrides of the type MeN; Mn absorbs up to 40 atom per cent of nitrogen; Fe does not combine with molecular N_2 to form any bulk nitrides, except at nitrogen pressures far above those employed in the industrial synthesis. This metal, however, as well as Ni, forms several nitrides if reacted with ammonia. Of these seven metals, the first four do not catalyze the ammonia synthesis; Mn possesses weak catalytic activity; Fe serves as the basis of very efficient catalysts;

and Ni is a very poor catalyst by itself, but can be made into a good catalyst by combining it with nitrogen binding metals such as Mo and W[134]. Thus, in this series of transition elements, the metals suitable as *ammonia catalysts are not the typical nitride formers but are those elements that are incapable of forming nitrides with elementary nitrogen*, at least at the temperatures and pressures employed in the catalytic synthesis reaction.

For the second series of transition elements (atomic Number 39 to 46) catalytic activity becomes noticeable with Mo. Ru, it has been claimed, possesses considerable catalytic activity,* while Rh and Pd are inactive as ammonia catalysts.

In the series 57 to 78, W has frequently been reported to yield efficient catalysts, as does Re, which resembles iron in its activity[124, 183], and Os which we have already encountered as one of the best catalysts. No bulk nitrides can be obtained by any method from osmium. This last fact for many years puzzled those who postulated that a certain capacity for nitride formation is a prerequisite for ammonia catalysts.

In the last series of transition elements with the atomic numbers 87 to 92, U is known as a good catalyst.

All the metals that serve as base material for effective catalysts are thus to be found among the transition elements of the horizontal periods 4 to 7 of the periodic system where these periods intersect the vertical groups 6 to 8.

It thus appears that the catalytic ammonia synthesis does not involve as an intermediate step the formation of bulk nitrides of classical chemistry. Rather, the nitrogen molecules appear to become bound to the catalyzing metals and metal combinations by a process that remains limited to the catalyst surface. Such two dimensional surface reactions, being basically different from the formation of three-dimensional nitrides, can occur even on metals such as osmium that are locked against the deeper penetration of nitrogen atoms into their lattice, and are thus incapable of forming normal nitrides or nitride-containing bulk phases.

This concept of a formation on ammonia catalysts of nitrogen-containing *surface* phases, differing in their structures, free energies, rates of formation, and other properties from the known bulk nitrides, had to remain a speculation as long as no experimental evidence was brought forward for their existence. For the last twenty-five years such evidence has gradually accumulated from detailed studies of the catalyst surfaces and of the reactions by which nitrogen is incorporated into these surfaces.

The following paragraphs present the main results of this experimental work.

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* German Patents 252,997 (1912), 289,105 (1913), 288,496 (1914).

Experimental Studies on the Theory of Ammonia Synthesis

Measurement of the Surface Areas of Catalysts. The determination of surface areas is as important for the correct interpretation of surface reactions as is the measurement of reaction volumes for the interpretation of regular reactions in gases and liquids. Over a considerable time, the theoretical study of heterogeneous catalysis was retarded by the lack of an adequate method for evaluating the true "accessible" surface areas of catalysts which, particularly in the case of highly porous materials, can exceed the macroscopic "geometric" surface by a large factor.

Such a method became available as the result of numerous investigations by Emmett, Brunauer and co-workers. It is based on the quantitative measurement of the physical adsorption of a gas on the catalyst surface at temperatures slightly above the liquefaction point of the gaseous adsorbate. It has proved advantageous to use nitrogen as the physically adsorbed gas at temperatures between about −191 and −196°C. At these low temperatures no chemical links are established between the nitrogen molecules and the adsorbing surfaces.

The development of this highly useful and generally accepted method for measuring the accessible area of solids, including solid catalysts, originated from adsorption studies made on iron catalysts for the ammonia synthesis[43, 44]. The perfecting of this method[21, 46], the development of generally applicable equations for the evaluation of the surface areas from the measured isotherms (Brunauer, Emmett and Teller)[22], and the critical studies of the method and of its theoretical background[37, 39] have made it a reliable and indispensable tool for practical and theoretical studies of solid catalysts.* In discussing the various types of ammonia catalysts, we shall come back to this procedure.

Intermediates Formed between Nitrogen and Metallic Tungsten, Iron and Osmium. In most of the work aimed at detecting the activated complexes formed during the synthesis reaction between nitrogen and the catalysts, iron-based catalysts and metallic tungsten were studied as typical representatives of the active metals. A few investigations were also carried out with osmium.

Bulk Phases. Iron Nitrides. According to x-ray measurements by Hägg[84], the nitrides Fe_4N, Fe_3N and Fe_2N, and mixed phases of these nitrides can be obtained from iron by subjecting the metal, at temperatures varying from 400 to 600°C, to the action of *ammonia*. In earlier work Baur and Voermann[4] as well as Maxted[126] had shown that none of these nitrides can be obtained from iron and *molecular nitrogen* at temperatures of 400 to

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* For a detailed discussion of the method of measuring surface areas by gas adsorption see Chapter 2, Vol. I. of this series.

700°C and pressures as high as 200 atmospheres. Noyes and Smith[144] calculated for iron nitride preparations, consisting probably of mixtures of all three nitrides, dissociation pressures at 460°, ranging from 20,000 to 50,000 atmospheres.

Detailed studies of the iron-ammonia-hydrogen system and the iron-nitrogen system were carried out by Lehrer[120] and by Eisenhut and Kaupp[30] using magnetometric and x-ray methods. Similarly, extensive measurements were reported by Emmett, Hendricks and Brunauer[52a] and by Brunauer, Jefferson, Emmett and Hendricks[23].

These thorough investigations of the German and American workers, in good agreement, led to the conclusion that the dissociation pressure of the lowest nitride, Fe_4N, amounts to approximately 5,000 atm.* at about 450°, and that the phases richer in nitrogen which contain solid solutions of compositions varying from Fe_3N to Fe_2N exert dissociation pressures at 450° equal to or above 10^5 atmospheres. This proves that *none of these iron nitrides can be formed under the conditions of the catalytic synthesis.* In all those experiments in which the iron samples were exposed at a given temperature to NH_3-H_2 mixtures which in terms of the NH_3-N_2-H_2 equilibrium are equivalent to nitrogen pressures below the dissociation pressure of Fe_4N at the same temperature, no solid solutions of Fe_4N in the metal were formed. Rather, small amounts of nitrogen, never exceeding 0.2 weight per cent, were taken up under these conditions by the iron samples without any indication of changes in the lattice of α-iron. In some recent work Krichowskii and Khazanova[103] by exposing iron samples to nitrogen pressures as high as 2000 to 4000 atmospheres and to temperatures from 300 to 550°C, brought about the formation of various nitrides, showing that the dissociation pressures of the nitrides and nitride-containing phases are somewhat lower than those calculated by the earlier investigators.

Tungsten Nitrides. In contrast to the intensively investigated iron-nitrogen system, few quantitative data are available for the tungsten-nitrogen system. By treating tungsten with ammonia, various nitrides and nitride-containing phases can be obtained[86]. As to the action of molecular nitrogen on the metal, no "bulk nitrides" are formed by this method according to Smithells and Rooksby[163], and accordind to Martin[125]. Some uncertainty exists regarding the amounts of nitrogen, if any, that are taken up under these conditions by the metal in solid solution. In various investigations in which tungsten was exposed to nitrogen at very low pressures (10^{-5} to 30 mm) and at temperatures ranging from -78 to 750°C, no signs were observed of a formation of solid solutions of nitrogen in the metal. Similarly, Martin

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* In this calculation no attempt was made to correct for the imperfection of gaseous nitrogen, hydrogen or ammonia at high pressures.

found no nitrogen uptake by tungsten metal at atmospheric pressures in the range from 400 to 1200°C. On the other hand, detectable quantities of chemically bound nitrogen are present, according to Mittasch, in tungsten samples that, in serving as catalysts for the ammonia synthesis, had been exposed for many weeks at 500°C and 100 atmospheres pressure to a 1:3 mixture of N_2 and H_2.

It is likely that in its capacity for binding molecular nitrogen, tungsten stands between iron, with its very low uptake, and metallic uranium and molybdenum which can contain as much as 9 and 7.3 per cent nitrogen respectively[132, 134], after having been used as ammonia catalysts. In all probability, the dissociation pressures of the solid solution of nitrogen in tungsten vary as a function of the concentrations of this solid solution. Thus, this solid solution represents a system covering a considerable range of free energies and heats of formation.

In the field of chemisorption, we shall encounter surface phases characterized by a similarly wide and continuous spectrum of energy levels and by a corresponding gradation of chemical reactivities. Such systems are of basic importance for surface catalysis. The existence of a wide range of substrate molecules, activated to a varying extent and anchored to the catalyst by a series of strong to weak linkages, increases drastically the probability that a *certain fraction* of these molecules will be ideally suited for participation in the step reactions which compose the catalytic overall effect.

Osmium-Nitrogen. The situation regarding the osmium-nitrogen system is simple insofar as neither formation of a nitride nor of any solid solutions of nitrogen has been observed for this metal either on treatment with nitrogen or with ammonia[65, 134].

In summarizing these observations on the behavior of the three typical catalytically active metals, iron, tungsten and osmium toward molecular nitrogen, one must conclude that none of them is capable of forming, under the synthesis conditions, even small amounts of any bulk nitride that can be differentiated from the pure metal by x-ray analysis. With iron and particularly with tungsten, solid solutions of nitrogen in the metal may be formed slowly and to a limited extent during synthesis. Osmium does not show even this effect.

Surface Phases. Chemisorption of Nitrogen. General Characteristics. Around 1930 decisive progress was made at various laboratories in the study of the nitrogen-catalyst complexes that operate in the ammonia synthesis. This progress was essentially achieved from detailed investigations of various adsorption systems. As pointed out by Taylor[167], it became possible "to differentiate between types of association between gas and catalyst surfaces, to distinguish, in many cases, between *nonspecific*, physical or *van der Waals* *adsorption* of gases which has negligible significance in the phenomenon of catalysis, and on the other hand, *a chemical association between gas and surface, chemisorption*, involving valency forces between surface atoms and adsorbed species and requiring for the formation of the adsorption complex an activation energy of adsorption."

Both types of adsorption have been treated in detail in separate chapters in Volume I of this series.

Experimentally, the first type, or physical adsorption can be distinguished from the second type, or chemisorption, by the following criteria:

(1) Physical adsorption is shown by gases and vapors only at temperatures slightly above their points of liquefaction. The heats of adsorption involved are low (approximately 1.5 to 2 times the heats of liquefaction of the adsorbates) and the physically adsorbed gas is easily desorbed by evacuation of the system at the same temperatures at which the adsorption occurred. The chemical nature of the adsorbent is of negligible importance for the physical adsorption, and this makes the latter a suitable effect by which to determine the surface areas of all kinds of solids (see Chap. 2, Vol. I).

(2) In contrast to physical adsorption, chemisorption is selective, occurring only between gases and solids which have mutual chemical affinity. In most of the systems investigated, chemisorption does not set in until a certain threshold temperature has been reached. On raising the temperature gradually above this threshold, without changing the pressure of the gas surrounding the adsorbent, i.e., by following an isobar, one obtains increasing amounts of chemisorbed gas due to the acceleration with increasing temperature of the initially very slow process of chemisorption. No true adsorption equilibria are obtained within this range of ascending isobars. At appreciably higher temperatures, adsorption as well as desorption become sufficiently fast for the establishment of true equilibria of chemisorption. Increasing the temperature further along the isobars results in a decrease of the chemisorbed amounts as has to be expected for an exothermic process. The heats of adsorption for chemisorbed gases range from about 5,000 cal/mole to 80,000 cal/mole, comparable to the heats of reaction of many chemical conversions.

Figure 2 shows two isobars and illustrates some of the characteristics typical of chemisorption.

The amounts of gas adsorbed at the two pressures p_1 and p_2 ($p_1 < p_2$) are plotted as a function of the temperature T. In the low temperature range T_A–T_B, the adsorbed amounts decrease with increasing temperatures for both pressures p_1 and p_2. Direct calorimetric measurements, as well as calculations by means of the Clausius Clapeyron equation prove that the heats of adsorption in the range T_A–T_B are relatively small. The rate of adsorption in this range is high enough to obtain true equilibria for this "chemisorption Type A." On this type of chemisorption, the adsorbed molecules are held to the adsorbing surface by only moderate forces and the activation energies for adsorption and desorption are relatively small.

At higher temperatures in the section T_B–T_C of Figure 2, Type A chemisorption undergoes a gradual transition to Type B chemisorption. In this range, the adsorbed amounts *increase* with increasing temperature. The adsorption of the additional quantities of gas occurs very slowly at the temperature T_B. By raising the temperature from T_B to T_C, the rate of adsorption is gradually increased until above temperature T_C, the adsorbed amounts reach their true equilibrium values for Type B chemisorption, and from there on, decrease normally with increasing temperature.

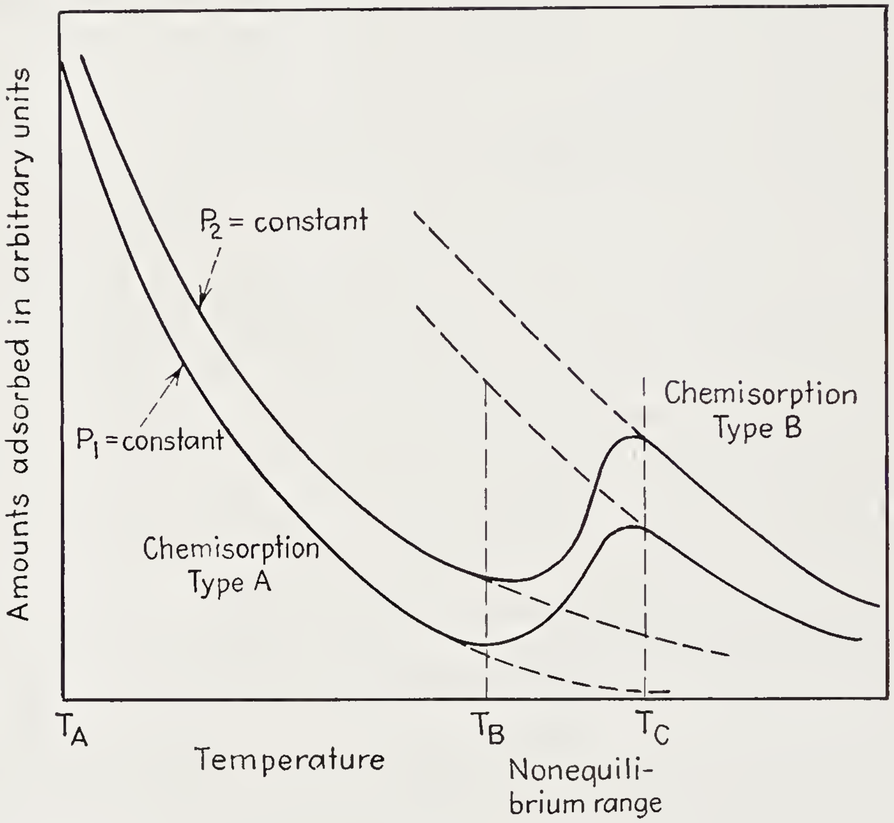

Figure 2. Isobars observed in a system showing two types of chemisorption.

The coexistence of two types of chemisorption in the transition range T_B to T_C causes in many systems a characteristic effect: If, in this range, the temperature of an adsorbent that has been partly covered with chemisorbed gas is raised, a rapid desorption occurs of some of the adsorbed gas which obviously correspond to the establishment of the equilibrium for Type A chemisorption. This is followed by slow readsorption of a quantity of gas that exceeds, after a long waiting period, the amount previously desorbed, an effect that demonstrates the approach to the equilibrium for the Type B chemisorption.

Various factors have complicated the study of chemisorption and have led to apparently contradictory experimental results and to divergent theories. These factors are:

(a) The existence in many systems of two or more different types of chemisorption involving weaker (Type A) and stronger (Type B) associations between the adsorbing surface and the adsorbed gas.

(b) Changes of the heats of adsorption and of the activation energies for adsorption and desorption concurrent with the gradual covering of the adsorbent with chemisorbed gas, and

(c) The fact that the heats of adsorption and the activation energies involved in the chemisorption of a given gas on a given solid can be profoundly altered by the presence of even small amounts of "foreign" molecules or atoms that are adsorbed on, or incorporated in, the adsorbing surface.

Experimental Observations. Nitrogen Chemisorptions on Tungsten, Iron and Osmium. Not all the phenomena connected with chemisorption were discovered and studied simultaneously. The first systematic observations were made by Taylor and co-workers[170, 171, 172], who studied the adsorption of hydrogen on various oxide surfaces. In this work, particular attention was directed toward the increase of chemisorption with temperature in the "nonequilibrium" range, and to the activation energy required for these chemisorptions. The term "activated adsorption" was suggested at that time by Taylor for differentiating this kind of surface association from that of physical adsorption.

In 1931, Messner and Frankenburger[131] reported on the first case of *chemisorption of nitrogen on a metallic surface,* namely, on a thoroughly reduced and outgassed *tungsten* powder. The progressive formation of a surface phase containing strongly bound nitrogen from a surface phase containing weakly bound nitrogen was clearly indicated in these studies by (1) the increase of the adsorbed amounts with rising temperature ("non-equilibrium range" between 100° and 400°C), (2) by the impossibility of removing this strongly adsorbed nitrogen by evacuation, and (3) by the phenomenon of a rapid desorption, followed by slow readsorption of nitrogen (change from chemisorption Type A to Type B) when the temperature in the adsorption system was raised between 100° and 400°C. These observations were, at that time interpreted as the strongly exothermic formation of a "surface nitride" from an adsorption system containing weakly bound nitrogen.

It was further concluded that the increase of nitrogen adsorption with rising temperature was caused by an accelerated formation of the new surface phase. Obviously, true chemisorption equilibria between nitrogen, tungsten, and surface nitride were not established below 400°, but readily obtained at temperatures of 550°C and higher. The maximum amounts of nitrogen that combined in these experiments with the metal surface corresponded to only a fractional covering (roughly 20 per cent) of the estimated surface area of the tungsten powder.

Another important step in our knowledge of a specific linkage of nitrogen to the surfaces of catalytically active metals was the discovery by Emmett and Brunauer[42] of a *chemisorption of nitrogen on iron synthetic ammonia catalysts*. According to these authors, nitrogen begins to be chemisorbed at a slow but measurable rate on iron catalyst samples at about 200°C. Between 400° and 450°C, at a nitrogen pressure of one atmosphere, this chemisorption reaches considerable values. On a doubly promoted (Fe + 1.3 per cent Al_2O_3 + 1.59 per cent K_2O) catalyst, at 224°C and a gas pressure of 760 mm, the nitrogen is still being adsorbed 2 hours after its admission to the adsorbent at nearly the same slow rate as immediately after its admission. It appears impossible to reach, at this temperature, final values for the adsorbed amounts, even over long waiting periods. This is typical for the "nonequilibrium" range. At about 400°C, however, the speed of the chemisorption is considerably higher: In the first minute after the admission of the gas the quantity of nitrogen taken up is about 70 per cent of that which is totally adsorbed after 2 hours. The amounts still being chemisorbed after 2 hours are negligible. Above 400°C true equilibria between the nitrogen-containing surface phase, iron and gaseous nitrogen are quickly established, and the chemisorbed amounts decrease in the usual way with further increase of the temperature.

Particularly interesting is the observation by Emmett and Brunauer[42] that in the chemisorption range above 400°C the adsorption of nitrogen on the iron catalysts occurs at a rate which makes it likely that this adsorption is the rate controlling process in the catalytic synthesis reaction. In the first evaluation of their chemisorption experiments, Emmett and Brunauer estimated an average heat of adsorption of 35,000 cal/mole, and an energy of activation for the adsorption process of 16,000 cal/mole. A detailed evaluation of the isotherms of Brunauer and Emmett shows, however, that the differential heats of successively chemisorbed portions of nitrogen actually decrease from an initial value of about 44,000 cal/mole N_2 for the first portions of chemisorbed gas, to a value of about 32,000 cal/mole for the higher coverage of the adsorbent obtained at one atmosphere of nitrogen pressure. Brunauer, Love, and Keenan[24] arrive at practically the same result by way of a thorough mathematical evaluation of the measured isotherms and of the observed rates of chemisorption. According to these authors, the heats of adsorption decrease in the range mentioned, from an initial value of 44,000 cal/mole to about 30,000 cal/mole as a linear function of the chemisorbed amounts. A further conclusion derived by Brunauer, Love and Keenan from the measurements of Emmett and Brunauer was that the activation energy of adsorption of nitrogen on the iron catalyst increases from about 10,000 cal/mole to about 21,500 cal/mole and that the activation energy of desorption decreases from 54,800 cal/mole to about 51,500 cal/mole, with the increasing coverage of the catalyst surface with chemisorbed nitrogen. Thus, the reactivity of the surface bound nitrogen varies with its concentration on the catalyst surface. The adsorption isotherms measured by Emmett and Brunauer follow Freundlich's equation.

The chemisorption of nitrogen on tungsten was investigated in the range of low pressures at room temperature by Van Cleave[179], who used as adsorbent the surface of a tungsten wire that had been thoroughly outgassed by flashing *in vacuo* at very high temperatures. By a method developed by Roberts[153], the accommodation coefficient of neon with this wire was measured and used as an indicator for the nitrogen adsorption on the wire surface. A considerable fraction of the surface was rapidly covered with nitrogen, at a nitrogen pressure of 10^{-4} mm, whereafter a slow adsorption of additional nitrogen continued over a considerable period. This effect was observed both at liquid air temperatures and at 100°C.

Numerous isotherms for the chemisorption of nitrogen on reduced, outgassed tungsten powder were measured by Davis[28] over a pressure range from 10^{-5} to 50 mm and a temperature range from 400° to 750°C. The evaluation of these isotherms gives an initial heat of adsorption for the chemisorbed nitrogen of about 75,000 cal/mole. The heat of adsorption remains at this high level for an uptake of nitrogen corresponding to surface coverings of 0.5 to 20 per cent, but decreases rapidly when further increments of nitrogen are chemisorbed. The activation energy of adsorption was found, in these experiments, to increase with increasing surface covering from about 15,000 cal/mole for sparse surface covering to about 30,000 cal/mole for coverings close to saturation of the tungsten surface with the chemisorbed nitrogen. Thus, nitrogen bound to a surface of metallic tungsten exhibits a variation of its binding energies to the metal similar to nitrogen bound to the surface of an iron catalyst. A difference between the two systems exists insofar as the nitrogen chemisorbed on tungsten includes a large fraction held by stronger forces than any part of the nitrogen adsorbed on an iron catalyst. It is very unlikely that this fraction of the nitrogen held by the tungsten surface with a force corresponding to heats of adsorption between 75,000 and 40,000 cal/mole participates to any extent in the catalytic formation of ammonia.

Of the nitrogen chemisorbed on iron and on tungsten, certain fractions have equal heats of adsorption on both metals. The existence of these fractions, which we may call "equivalent fractions," is a consequence of the gradual decline on both metals of the heats of adsorption with increasing surface coverage. Thus, any given fraction of nitrogen linked to an iron surface has its counterpart in an equivalent fraction adsorbed on a tungsten surface with the same heat of adsorption. A distinct difference, however, exists between both systems, insofar as any fraction of nitrogen linked with a given heat of adsorption to tungsten requires the previous chemisorption of larger amounts of nitrogen than does the equivalent fraction of nitrogen adsorbed on iron. It may well be that such equivalent fractions represent, on both metals, the same state of activation and that they participate at equal rates in the catalytic synthesis reactions, per unit of surface area covered with this particular adsorbate.

An interesting case of chemisorption of nitrogen is that occurring on an osmium surface. Qualitative observations pointing to a chemisorption of nitrogen on this metal were obtained by Frankenburger[65]. From some quantitative data for this system published by Guyer, Joris and Taylor[79], the following conclusions can be drawn:

(1) A weak and a strong chemisorption are superimposed within a certain temperature range in the systems described above.

(2) The strong chemisorption becomes apparent at about 80°C, is fairly rapidly established around 150°C, and enters the "equilibrium range" at about 155°C.

(3) The data by Taylor *et al.* do not permit an exact evaluation of the heats of this chemisorption of nitrogen on osmium, but there are indications that these heats are appreciably smaller, at equal surface coverings, than those for the nitrogen chemisorbed on iron catalysts, and *a fortiori*, on tungsten.

(4) The highest covering attained in these experiments for the chemisorption at 150° at a nitrogen pressure of one atmosphere, corresponds to only about 4 per cent of the osmium surface.

(5) The chemisorbed amounts decrease with increasing temperature beyond 158°C and reach very low values around 270°C at a N_2-pressure of one atmosphere. The fact that osmium is a good ammonia catalyst, in spite of the small extent to which nitrogen is held by it in a chemisorbed state under synthesis conditions, is a further support for the conclusion that only a narrow fraction of the nitrogen required to form a chemisorbed monolayer suffices to "feed" the synthesis reaction, provided it is in a suitable state of activation and linkage to the catalyst surface. Apparently, most of the nitrogen chemisorbed on osmium is in this state in spite of the fact that this state seems to be characterized by a relatively low heat of adsorption. This points again to the probability that most of the firmly bound nitrogen, such as is present on a large fraction of a tungsten surface, remains inert in the catalytic process.

The State of the Chemisorbed Nitrogen. Essentially, these studies on the chemisorption of nitrogen prove the existence of chemical associations between the catalysts and nitrogen that function as intermediaries in the catalytic synthesis reaction. Moreover, they reveal the heats of formation of these surface complexes and at different temperatures and pressures, the rates at which they are formed from, and dissociated into, their components. This knowledge has substantially contributed to a better understanding of the kinetics of the catalytic formation and decomposition of ammonia on certain catalysts.

Valuable as this information is, it gives but little direct evidence on the *actual state* of the chemisorbed nitrogen. The specific reactivity of the metal-bound nitrogen, the unequal intensity of its chemisorption over the catalyst surface, and other still unexplained elements are a challenge for further research both for a better understanding of surface catalysis, and for a fundamental solution of the exceedingly practical question of what makes a good catalyst. In this specific field, progress has not been as rapid as in other branches of catalytic research, mainly because our basic knowledge of the nature of chemical forces, particularly on surfaces of solids, is very limited. Nevertheless, several interesting contributions have been made to the fundamental aspects of the chemisorption and activation of nitrogen on catalysts.

Bond Type between Nitrogen and Transition Catalysts. The exceptional position held by metals of the transition groups as base materials for ammonia catalysts is obviously related to the incomplete *d*-shells of the electrons of these elements. One or more of the comparatively loosely bound electrons of the unfilled *d*-shells of the catalyst atoms can evidently "exchange" with electrons of adsorbed gas atoms or molecules, thus forming an essentially homopolar bond[31, 121]. This type of interaction will lead to a gas metal combination of a metallic rather than a salt-like or ionic character, the electrons of the chemisorbed species merging with the electron gas of the metal. This, however, does not exclude at least a fraction of the metalloid atoms from being strongly polarized and behaving like charged particles under the influence of strong electric fields.

The interatomic forces in diatomic gas molecules are decisively weakened by their interaction with the metal electrons. In their "metallic" state on the catalyst surface, the atoms of the chemisorbed gas easily enter into reactions with the molecules or atoms of other gases that on the same metallic surface have undergone a similar "predissociation" or total dissociation[149, 159]. Thus, the type of bonding and the resulting reactivity of a gas molecule dissolved in the surface of a metal of the transition group differs considerably from the bonding and reactivity of the same metalloid linked to a strong electropositive, nontransition metal, such as lithium, with which it forms typical ionic bonds.

An indirect support for this concept of a quasimetallic or "alloy" state of gases such as nitrogen and hydrogen, when chemisorbed on the surface of transition metals can be seen in the thorough investigations of Hägg[86, 87] on the crystal structures of the hydrides, borides, carbides and nitrides of the transition elements. According to Hägg, all the solid solutions and compounds formed between the transition metals and the metalloids mentioned are metallic in nature, in contrast to the phases formed between the same metalloids and the nontransition metals. Whenever the steric arrangement of the metal lattice and the size of the metalloid atoms permit, the latter enter into the metal structure without essentially changing this structure forming "interstitial phases." It is quite likely that the same type of binding forces that operate in the formation of the bulk phases investigated by Hägg are also responsible for chemisorption except that complete dissociation of the gas molecules is not as indispensable for the surface complexes as it is for the bulk phases that require the penetration of metalloid *atoms* into the metal lattice.

The Excess Reactivity of Metal Surfaces. Earlier in this chapter it was pointed out that nitrogen can enter into chemical association with the surface of a metal such as osmium even if this metal is unable to form any nitrogen-containing bulk phase. This excess reactivity of a surface layer can be correlated to the thermodynamic postulate that the surface of a solid possesses free energy exceeding that of its bulk phase. However, more specific and direct experimental evidence proving this increased reactivity is required for a better understanding of surface catalysts.

For iron and promoted iron, such evidence was obtained by Almquist and Black[1a] who investigated quantitatively the poisoning of these catalysts by oxygen and water vapor at atmospheric pressure, a study that was extended by Emmett and Brunauer to pressures up to 100 atmospheres[40]. Whereas according to detailed investigations of the equilibria in the system $Fe—Fe_3O_4—H_2O—H_2$[28a], massive iron is not oxidized at 440° by hydrogen-water vapor mixtures containing less than about 16 per cent water vapor, the two teams of investigators demonstrated by careful measurements of oxygen balances that appreciable amounts of oxygen were retained by iron and by promoted iron catalysts that were subjected to a stream of 3:1 hydrogen-nitrogen mixtures (5000 space velocity) containing as little as from 0.016 to 0.50 per cent water vapor. Evaluation of the experimental data indicated that this retention is due to the formation of a "surface oxide" involving about $1/2000$ of the total Fe-atoms with the pure iron samples, and about $1/200$ of the total Fe-atoms with the promoted catalysts. Concurrent with the formation of these surface oxides, the catalytic activity of the samples for ammonia synthesis was considerably diminished. This poisoning effect is reversible, the catalysts being restored to their initial activities on treatment with an oxygen-free hydrogen-nitrogen mixture. Obviously, the same parts of the catalyst surface that react by forming oxide with water vapor at very small partial pressures, are also active in the synthesis reaction. From the fact that oxide formation on the surface occurs readily at water vapor concentrations of 0.04 to 0.48 per cent in the 3:1 hydrogen-nitrogen mixture, that is, at concentrations far below the 16 per cent required for the "bulk oxidation" of iron at the same pressure and temperature, Almquist[1] concluded that the surface atoms involved in this reaction have an excess free energy of approximately 13,000 cal per gram atom Fe over that of ordinary iron.

As pointed out by Frankenburger[63], just as this excess of free energy of surface iron atoms permits their reaction with water vapor of a concentration insufficient for bulk oxide formation, it can also cause the formation of a "surface nitride" at nitrogen pressures insufficient for bulk nitride formation. An approximate calculation for the possible formation of Fe_2—N on the surface, and a similar calculation made by Emmett and Brunauer for a "surface Fe_4N"[40] show that the formation of such surface compounds is conceivable at the pressure and temperature conditions of the synthesis reaction. It must be pointed out, however, that these calculations are purely formalistic and do not prove that the nitrogen bound on the iron surface is actually arranged in a pattern resembling that of the known bulk nitrides. The merit of these calculations was mainly to point out the possibility of a nitrogen fixation in the metal surface at a time when the chemisorption of nitrogen on these catalysts had not yet been discovered.

Model Experiments with Metal Atoms and with Metal Films. The excess free energy of the boundary of a solid is to be ascribed to the free valencies of the surface atoms which, contrary to the atoms inside the solid, remain partly unsaturated. This applies to any surface in which the atoms are arranged in an ideal lattice plane. Atoms or assemblies of atoms located in exposed positions on top of such a lattice plane will have additional contents of excess free energy, and should have a correspondingly increased reactivity compared with the atoms of the regular surface. The sites of particularly pronounced activities of a catalyst surface, commonly called its "active centers" have been frequently correlated with the existence of such exposed surface structures. In following this hypothesis, it appeared interesting to go one step further, and to investigate the reactivity of completely free atoms of a catalytically active metal toward such gase as undergo catalytic activation on a surface of the same metal.

In 1914, Langmuir[113] reported interesting results on the chemical combination of tungsten atoms, obtained by the slow evaporation of a heated tungsten filament with elementary nitrogen in the gas phase. Langmuir interpreted this observation in terms of the formation, in the gas phase, of one molecule of WN_2 by the combination of one tungsten atom with one nitrogen molecule.

This example of a fast chemical reaction between single atoms of a metal of the ammonia catalyst-type with gaseous nitrogen, and the possible relationship of this effect to the operation of active centers on a surface of metallic tungsten led Frankenburger and Mayrhofer[68] and Frankenburger, Mayrhofer and Schwamberger[69] to investigate whether iron and nickel atoms as they are obtained by the controlled evaporation of these metals in an atmosphere of hydrogen or of nitrogen at gas pressures of the order of magnitude of $1 \cdot 10^{-2}$ mm would react in the gas phase with either one of the two gases.

No indications were observed in these experiments for a chemical combination of the metal atoms with hydrogen or nitrogen in the gas phase of the type found for tungsten and nitrogen by Langmuir. Substantial quantities, however, both of hydrogen and of nitrogen were taken up by the iron and nickel atoms as soon as these atoms condensed at the glass walls of the evaporation vessel at a temperature of −195°C in the hydrogen experiments and at −78°C in the nitrogen experiments. This gas uptake by the condensing metal atoms reached astonishingly high values (six H_2 molecules per one Fe-atom, and approximately one N_2 molecule per one Fe-atom) when the formation of coherent metal films at the cooled walls was prevented. This was achieved by condensing a large excess of sodium chloride vapor together with the metal vapor. The hydrogen and nitrogen that in this way become associated with the condensing metal atoms are linked to them by very weak forces. A large percentage (90 to 95 per cent) of the gases that at the low temperatures become bound in the metal-sodium chloride layers are given off when these layers are brought to room temperature. The remaining small fraction, however, of the initially adsorbed gas remains bound to the evaporated metal, and is only slowly and incompletely given off, even if the condensed layers are heated to temperatures as high as 300°C. This indicates that this part of the adsorbed gas switches from a weak van der Waals type* of association with the metal to a more stable gas-metal complex. It may well be that this effect is closely related to, or identical with, the transition from physical adsorption to chemisorption as observed for the same gases, on ordinary metal surfaces.

The failure of the free metal atoms present in the gas phase to combine with hydrogen or nitrogen proves that the activation of hydrogen and nitrogen is an effect that requires the cooperation of a large number of adjacent metal atoms.

* Editor's note: The question may well be raised as to whether the hydrogen is bound to the metal atoms in these experiments as a "weak van der Waals type" or as some weak chemisorption such as the type C chemisorption found by Kummer and Emmett on Fe—Al_2O_3 catalysts at −185°C[107].

There is a relationship between this early work on the uptake of gases by condensing metal atoms and the well known investigations of Beeck and his associates on the adsorptive and catalytic properties of various types of metal films that were obtained by evaporation of the metal *in vacuo*[8]. Tungsten films prepared in this way, according to Beeck, chemisorb nitrogen at room temperature with the high initial heat of adsorption of about 95,000 cal/mole, this heat remaining constant with increasing nitrogen uptake by the metal until about 60 per cent of the total surface of the tungsten film has been covered with chemisorbed nitrogen. On iron films, chemisorption of nitrogen was found by Beeck to occur also at room temperature and to require an activation energy. The heats of adsorption of nitrogen on these iron films decrease from 40,000 to 16,000 cal/mole over the fraction covered by nitrogen at this temperature, which according to Beeck is about one-fifth of the total surfaces.

These chemisorptions on vacuum-made extremely pure metal films differ in many respects from the chemisorption of the same gases on purified samples of the massive metals. The reasons for these discrepancies will be discussed later. Beeck's investigations are of considerable importance for our fundamental knowledge of the affinities between pure metal surfaces and diatomic gases. It would be misleading, however, to use these results obtained with "idealized" metals directly to interpret normal catalytic reactions, including the ammonia synthesis. The practical catalysts used in normal catalytic work represent, as we shall see, much more complicated systems than extremely pure or vacuum made metal films and accordingly exhibit quite different behavior toward diatomic gases, both in chemisorption and in catalytic activities.

Atomic or Molecular State of the Chemisorbed Nitrogen. The question has been frequently discussed whether diatomic gases such as hydrogen or nitrogen, if chemisorbed on a metal surface, exist as atoms or as molecules. In putting the question this way, it is assumed that the gaseous molecules and atoms, immersed in the field of an ensemble of metal atoms and electrons, can be distinguished from one another as can free atoms and molecules. Moreover the premise is made that atoms, known for their high reactivity in the free state, are characterized by a similarly high reactivity in the chemisorbed state.

As pointed out earlier, the activation of diatomic molecules in catalyst surfaces to be effective must bring about a considerable weakening of their interatomic bonds. For a given catalytic reaction in which diatomic molecules participate, it appears quite difficult to decide whether the activation of these molecules on a specific catalyst involves their total dissociation or whether it merely weakens their interatomic bonds, a type of activation which we designate here as "predissociation." Granted that atomic hydrogen and nitrogen, immersed in a metallic surface, are apt to enter into mutual reactions that result in ammonia as the end product, it does not follow that dissociation of the reactants in the catalyst surface is a *condition sine qua non* for the catalytic reaction. In the foregoing discussion, attention was drawn to the fact that the establishment of excessively strong linkages between reactants and catalyst can decisively impede the advancement of the catalytic process and it is conceivable that on some catalysts such strong linkages are formed between the metal and the atom of the chemisorbed metalloid. Generally, it will depend on the individual heats of adsorption of atoms on the one hand, and of pre-dissociated molecules on the other whether, on a given catalyst, the easiest and fastest pathways of the catalytic process lead over the atomic state of the adsorbed reactants, or over a state of predissociation.

In a discussion of results obtained by Bosworth[15] for the adsorption of nitrogen on a tungsten wire at 90°K, and of results obtained by Beeck for the adsorption of nitrogen on a tungsten film at 300°K (loc. cit.) Boudart[16] comes to the conclusion that, at the lower temperature, the nitrogen is chemisorbed without complete dissociation, whereas it is probably adsorbed in form of atoms at the higher temperature. Possibly the observation of the coexistence of a weaker Type A and of a stronger Type B form of chemisorbed hydrogen and nitrogen on certain transition metals corresponds respectively to the presence of predissociated and of fully dissociated molecules on the catalyst surfaces.

However, this interpretation is not tenable, according to Emmett, for the special case of Type A hydrogen adsorption occurring on iron catalysts in the temperature range of −100 to 0°C, and for the Type B hydrogen adsorption on the same catalysts at and above 100°C. Emmett's reason for refuting the possibility of a predissociated state for hydrogen adsorbed on a doubly-promoted iron catalyst in the Type A state is that this hydrogen was found to exert almost no poisoning effect on the ortho-para hydrogen interconversion at −195°C on the same catalyst (see p. 213). According to Emmett (private communication) steric factors make it more likely that adsorbed hydrogen molecules would interfere with the ortho-para interconversion than would adsorbed hydrogen atoms.

Several efforts have been made to obtain direct experimental information on the specific configuration of the chemisorbed gas molecules. Kistiakowsky[101] bombarded a synthetic iron ammonia catalyst with electrons in an atmosphere of nitrogen at low pressures in order to determine the ionization potential of the adsorbed nitrogen. Whereas this potential was 17 volts for free nitrogen molecules, ionization of the adsorbed nitrogen was obtained at 11 volts, a result that Kistiakowsky interpreted as indicating either a complete dissociation of the adsorbed nitrogen on the catalyst or a considerable weakening of the N—N bond of the chemisorbed molecules.* Thus, no clear cut decision was obtained from these measurements on the state of the chemisorbed nitrogen beyond the conclusion that the adsorbed gas is doubtlessly not present in the form of "normal" nitrogen molecules.

Brunauer and Emmett[21a] (1940) have established an experimental fact that they consider a strong argument for an atomic state of the nitrogen chemisorbed on iron catalysts. In their thorough investigations of the successive chemisorption of various gases on iron catalysts, these authors found that previously chemisorbed nitrogen does not decrease the successive chemisorption of carbon monoxide on the same catalyst at −78°C compared with carbon monoxide chemisorbed on the freshly outgassed catalyst. Sterical considerations suggest strongly the explanation that the chemisorbed nitrogen is dissociated into atoms and the latter are fixed on the catalyst surface at such sites that the iron atoms on the surface remain practically unaffected, retaining their capacity for the chemisorption of carbon monoxide.

A new method for investigating the state of chemisorbed nitrogen offered itself as soon as the nitrogen isotope N^{15} became available. With a mixture of normal and isotopic nitrogen molecules, reactions involving an exchange of isotopic N-atoms were studied of the type

$$N^{14}N^{14} + N^{15}N^{15} \rightarrow 2N^{14}N^{15}$$

Joris and Taylor[95] found that this type of exchange reaction did not occur to any measurable extent in the absence of specific catalysts even at temperatures as high as 750°C. It was to be expected that typical ammonia catalysts would facilitate the exchange reaction between N_2-molecules since both the ammonia synthesis and the exchange reaction probably require an identical or nearly identical type of activation of the nitrogen molecule.

In the investigation mentioned above, Taylor and Joris (loc. cit.) measured the rate of the exchange reaction over a singly and doubly promoted iron catalyst and over metallic tungsten.

In the presence of the iron catalysts, no isotope exchange was observed in the temperature range of 220 to 410°C, even over a period of 30 hours. The same catalysts, on the other hand, decomposed ammonia at a considerable rate at 400°C. At higher temperatures, the exchange reaction started to become apparent, but its rate remained low, even at a tempera-

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* The 11-volt ionization potential was also obtained with nickel, copper, and platinum that had been exposed to nitrogen. The ionization effects for these metals, however, were very much weaker than for the iron catalyst samples. After their exposure to nitrogen, treatment of all these metals with traces of oxygen caused a complete disappearance of the 11-volt ionization potential.

ture as high as 750°C. Small amounts of hydrogen that were present either in an adsorbed state on the catalyst, or in the gas phase, accelerated the exchange reaction to a very considerable extent.

The lack of a closer parallelism between the rate of the ammonia decomposition and that of the exchange reaction on the same catalyst led to a second investigation of the exchange reaction over iron catalysts by Kummer and Emmett[105]. These authors used the same experimental procedure as Joris and Taylor except that the composition of the promoted iron catalysts employed by the two laboratories differed slightly, and that in the second investigation the catalysts were reduced by a still more effective method prior to the admission of the isotopic nitrogen mixture. With these very thoroughly reduced iron catalysts, Kummer and Emmett obtained a rapid exchange reaction beginning at a temperature of 500°C which went to completion in about 10 to 15 minutes. A quantitative comparison was made of the rate of this isotope exchange with the rate of desorption of nitrogen from the same catalysts. On a doubly promoted (0.8 per cent Al_2O_3 + 0.25 per cent K_2O) catalyst, the exchange reaction proceeded at a slightly slower rate than the desorption of nitrogen, but its rate on a catalyst that contained no alkali promoters (2.26 per cent Al_2O_3 + 0.62 per cent SiO_2 + 0.21 per cent ZrO_2) equalled approximately that of the nitrogen desorption from this catalyst.

These authors, in agreement with Joris and Taylor found that hydrogen accelerated the exchange reaction, whereas small amounts of water vapor, introduced together with the isotopic nitrogen, retarded it substantially. This poisoning effect of traces of water vapor on the exchange reaction, according to Kummer and Emmett, suggests that the slow rates observed by Joris and Taylor were due to an incomplete reduction of the catalyst samples.

In a recent publication, McGeer and Taylor[124] have shown conclusively that this interpretation of their earlier work was correct by proving that strikingly different activities for the isotope exchange can be obtained with one and the same iron catalyst by intensifying its reduction with hydrogen[124]. Besides the removal of surface oxide, there may be an additional reason for the better performance of the thoroughly reduced catalysts. The particularly effective hydrogen treatment of the catalysts in the work of Kummer and Emmett and in the study of McGeer and Taylor may not only remove the last traces of oxide, but after evacuation of the reduced catalysts may also leave larger amounts of hydrogen in these catalysts than in those that were less thoroughly reduced. In a recent publication[106] Kummer and Emmett have shown that promoted iron catalysts contain, after a reduction with hydrogen and 24 hours of evacuation at 500°C, sufficient residual hydrogen to be equivalent to the covering of 5 to 35 per cent of the metallic surface, or to 1 to 10 per cent of the surface covered with promoter. Since, as found in both laboratories, hydrogen accelerates the exchange reaction considerably, the higher hydrogen contents of the drastically reduced catalysts may contribute to their better performance in the exchange reaction.

The fact that nitrogen molecules chemisorbed on an iron ammonia catalyst can exchange their atoms has been taken by Emmett as another proof for the atomic state of the chemisorbed gas. Taylor has discussed this possibility as well as that of an adsorption of nitrogen "still in the molecular form, with only a portion of its valence bonds involved in the attachment to the iron surface," a concept equivalent to the state of predissociation discussed earlier in this chapter.

The present experimental evidence, in the writer's opinion, does not permit any general and final decision in favor of the atomic or the predissociation state of the nitrogen chemisorbed on the different metals, and it may well be that both configurations are represented in the chemisorbed phases, depending on the catalysts and on the amount of surface coverage. The following conclusions, however, can be drawn from the experimental data: (1) The nitrogen that is formed during the catalytic decomposition of ammonia on an iron catalyst is essentially in the same state of activation as is nitrogen that is chemisorbed from the gas phase on the same catalyst. (2) In this state of activation, nitrogen can be hydrogenated to ammonia or can exchange atoms with other chemisorbed nitrogen molecules. (3) The presence of a certain amount of chemisorbed hydrogen on an iron catalyst may be essential for the activation of the nitrogen molecules. *This would mean that the actual catalyst for the nitrogen activation and ammonia synthesis is not iron, but a surface combination of iron and chemisorbed hydrogen.* (4) At given temperatures and pressures, the rate of desorption of chemisorbed nitrogen molecules from a given catalyst is the same, regardless of whether this nitrogen was produced by the catalytic decomposition of ammonia or had been adsorbed from the gas phase in the form of molecular nitrogen.

On *tungsten*, the exchange reaction between nitrogen molecules, according to Joris and Taylor (loc. cit.) proceeds still more sluggishly than on the iron catalysts. Here again, a more rapid reaction takes place in the presence of hydrogen. No experiments were made in the case of tungsten with samples that had been as thoroughly reduced as the iron catalysts in the work of Kummer and Emmett and of McGeer and Taylor.

In a study of the nitrogen exchange reaction on metallic *osmium*, Guyer[79] *et al.* found again a considerably slower rate for this process than for the ammonia decomposition on the same catalyst at equal temperatures.

A trace of oxygen poisoned the exchange on the osmium surface as it does on iron catalysts. Hydrogen acts on the exchange over osmium not as an accelerator as in the other two cases, but as an inhibitor. The slowness of the exchange reaction over osmium compared to the rate of ammonia decomposition on the same catalyst was ascribed by Taylor and co-workers to the small concentration of chemisorbed nitrogen on the osmium surface in the exchange experiment. This concentration is much lower than the concentration at which nitrogen is generated on an osmium surface during the decomposition of ammonia. The inhibiting effect of hydrogen was explained by the fact that, on the osmium catalyst, hydrogen adsorption is very much stronger than nitrogen adsorption. This creates a surface distribution of both types of gases unfavorable for a rapid exchange reaction among the widely separated nitrogen molecules.

It can be hoped that future studies on the exchange reaction of chemisorbed nitrogen will, in combination with thorough studies of the chemisorption proper bring further elucidation of the state of the chemisorbed nitrogen and of its concurrent activation.

The Association of Hydrogen with Ammonia Catalysts. *Relative Importance of the Activations of Hydrogen and Nitrogen for the Ammonia Synthesis.* The adsorption and activation of *hydrogen* on ammonia catalysts will be treated here more briefly than the activation of nitrogen discussed in the foregoing text. Both theoretical considerations and experimental evidence make it clear that the activation of the nitrogen molecule is far more difficult to achieve and occurs at a much slower rate than the activation of the hydrogen molecule. Accordingly, the nitrogen activation is the rate determining step of the ammonia synthesis. This is also revealed by the fact that on a given catalyst chemisorption of nitrogen and synthesis reaction make their appearance at about the same temperatures, whereas the chemisorption of hydrogen occurs at temperatures far below the range of the catalytic synthesis.

Many catalysts such as nickel, platinum, and various metal oxides that chemisorb hydrogen and catalyze the hydrogenation of a great number of compounds fail as ammonia catalysts because of their inability to activate effectively the nitrogen molecule. On the other hand, most of the ammonia catalysts are fairly effective hydrogenation catalysts. Thus, Emmett and co-workers have reported that promoted iron catalysts catalyze well the hydrogenation of ethylene[90], propylene and 2-butene[48].

Like the activation of nitrogen, the activation of hydrogen on metal catalysts occurs preferentially on metals belonging to the transition elements. The type of bonding formed between these metals and hydrogen appears to be of the same "metallic" type as that between these metals and nitrogen (see p. 201). Both systems are characterized by a collectivization of the valence electrons of the incorporated metalloid with the electrons of the metal[16, 121, 138]. Whereas only a few of the transition elements are suitable base metals for ammonia catalysts, most of them act as good to fair catalysts for hydrogenations of the general type, with the exception of those elements that form very stable, highly exothermic hydrides (e.g., Sc, Ti, Zr, Ta). The reason for this exception is the same as outlined earlier in this chapter for the inactivity as ammonia catalysts of typical nitride formers such as vanadium.

The greater ease of the activation of hydrogen, compared to that of nitrogen, and the wider range of catalysts available for simple hydrogenations are obviously related to the much smaller energies required for the predissociation and dissociation of the H_2 molecule. Moreover, the small radius of the hydrogen atom permits its incorporation into closely packed lattice planes that are locked against nitrogen atoms.

Hydrogen Chemisorption on Ammonia Catalysts. The activation of hydrogen in heterogeneous catalysis, like that of nitrogen, is brought about by its chemisorption on the catalyst surface. In contrast to the nitrogen activation which occurs on a few metals only, hydrogen activation takes place on numerous metals and metal oxides, all of which can serve as hydrogenation catalysts.

Many authors have investigated adsorption systems of this type, such as the pairs platinum-hydrogen, nickel-hydrogen and systems consisting of hydrogen and metal oxides[175] like ZnO, Cr_2O_3 and others. For our purpose, we shall limit this survey to hydrogen chemisorption on metals of the ammonia catalyst type.

Iron-Hydrogen. Informative measurements by Dew and Taylor[29] of the hydrogen adsorption at 760 mm pressure on pure iron samples indicated a decrease of the gas uptake between 0 and 110°C followed by a strong increase concurrent with the rise of the temperature to 218°C. These are characteristic signs of chemisorption. Similar effects were observed by Benton and White[11, 12] and by Benton[10]. According to these authors, the amounts of hydrogen adsorbed by a pure iron sample at constant pressure decrease by a factor of four between −183 and −78°C. On increasing the temperature to 0°C the first effect observed was a further small decrease of the adsorbed amounts of hydrogen. Over a long waiting period at 0°C, this initial desorption ceased and was superseded by a slow but continuous readsorption of hydrogen. After the sample had been kept at 0°C for 35 days, the readsorption had resulted in a tenfold increase of the amount of adsorbed gas compared with the quantity adsorbed initially at 0°C. In discussing this effect, Benton pointed out that either activated adsorption of hydrogen, or a diffusion of the gas into the interior of the iron sample, or a combination of both effects, cause this slow uptake of gas by the metal.

Extensive studies of the chemisorption of hydrogen on iron and of related phenomena were carried out by Emmett and co-workers[21a, 49, 50, 51, 52,

TABLE 5. CHARACTERISTICS OF HYDROGEN ADSORPTION ON IRON AND IRON CATALYSTS, ACCORDING TO EMMETT AND CO-WORKERS[21a, 49, 50, 51, 52, 106, 107]

Abbreviations: (a) Pure iron; (b) Singly promoted catalyst; (c) Doubly promoted catalyst.

Reactions: (1) $H_2 + D_2 \rightarrow 2HD$; (2) p-$H_2 \rightarrow o$-H_2 .

Type of Adsorption	Temp. Range in Which Observed	Heat of Adsorption (cal/mole H_2)	Activation Energy of Adsorption	General Characteristics of the Various Types of Hydrogen Adsorption
"Physical" adsorption on (a), (b) and (c)	−194° to −140°	2,000	—	On (b) a larger fraction of the hydrogen adsorbed at −194°C appears to be "chemisorbed" (Type C) than on (a) and (c). The physical adsorption on (a) and (c) is not affected by chemisorbed Type A hydrogen, but is diminished by previously chemisorbed Type B hydrogen[52, 92, 107].
Chemisorption *Type C* on (b) only	−194°C and higher	2,000 8,000 (estimated)	—	Pronounced on (b); very little, if at all on (a) and (c). Reaction (1) at −190° proceeds fast on (b), with H_2 and D_2 being in A′ state of chemisorption. Reaction (1) is hardly observable at −190° on (c)[50].
Chemisorption *Type A* on (a) (b) and (c)	−100° to 0°	—	10,000	Preadsorbed Type A hydrogen retards reaction (2) at −190° by about 25%, but does not influence subsequent "physical" adsorption of H_2 . Previously chemisorbed N_2 decreases Type A chemisorption, mole for mole. Chemisorbed Type A hydrogen does not react at −190° with D_2 (Reaction (1)) present in the gas phase[49, 52].
Chemisorption *Type B* on (a) and (c)	+100° and higher	8,500 (estimated)	—	Pre-adsorption of Type B hydrogen retards reaction (2) at −190° by a factor of 20. Preadsorbed Type B hydrogen diminishes considerably "physical" adsorption of H_2 . Previously chemisorbed N_2 decreases H_2 Type B chemisorption by an amount between one-half and total of the chemisorbed N_2 . Type B chemisorbed hydrogen does not react at −190° with D_2 (Reaction (1)) present in the gas phase[21a].

TABLE 5.—*Continued*

Type of Adsorption	Temp. Range in Which Observed	Heat of Adsorption (cal/mole H_2)	Activation Energy of Adsorption	General Characteristics of the Various Types of Hydrogen Adsorption
Chemisorption *Type B′* on (b)	+100° and higher	—	—	Pre-adsorbed Type B hydrogen does not retard reaction (2) at −190°. Previously chemisorbed N_2 does not decrease, but rather increases the Type B′ chemisorption of H_2 by as much as 30 to 50%[21a].

* It is likely that this adsorption is a composite effect consisting of a chemisorption of a weak type, probably combined with a typical physical adsorption. This is borne out by calorimetric measurements by Beebe[5] which indicate that at least a considerable part of this hydrogen adsorption at −194° on iron catalysts is chemisorbed; by work on the low temperature hydrogen adsorption on films of metallic iron[8]; and by the "poisoning" of this adsorption by Type B chemisorbed hydrogen[52].

Editor's Note: The amount of chemisorption of H_2 occurring on doubly promoted iron catalyst at −195° is known[5, 107] to be between 3 and 10 per cent of a monolayer on the metallic part of the surface. The H_2 is, however, so tightly bound as not to cause appreciable rate for reaction. It appears to account for less than 10 per cent of the total adsorption at 1 atm. and −195°C.

[106, 107]. In these investigations, the hydrogen chemisorption was measured on samples of pure iron as well as on singly and doubly promoted iron catalysts. Moreover, the influence was studied of previously chemisorbed CO, CO_2, N_2 and O_2 on the chemisorption of hydrogen on these catalysts as well as the reverse effect. Also included in this extensive work on the hydrogen-iron adsorption systems were measurements of reaction rates over the various iron catalysts, of the conversion H_2 ortho → H_2 para at −190°C, and of the exchange reaction $H_2 + D_2 \rightarrow 2HD$ at various temperatures. For both these reactions, Emmett and co-workers also investigated the influence of various pretreatments of the catalysts, particularly of their previous covering with chemisorbed hydrogen.

Instead of giving a detailed description of this extensive work of Emmett and co-workers, a condensed survey of their principal results is given in Table 5. In this table there are listed the types of hydrogen adsorptions on the three types of iron catalysts (unpromoted, singly and doubly promoted) as they were observed in specific temperature ranges.

In the data of Table 5, the following points appear to be of general significance:

(1) In measuring the hydrogen adsorption by following an isobar on a given iron catalyst from −194 up to 400°C, Emmett and Harkness observed the successive appearance of at least two* different types of chemisorp-

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* There are probably three different types of chemisorption if we include the low temperature adsorption at −196°C (see footnote below Table 5).

tion[133]. The isobar (see Figure 3) is shaped like that of Figure 2, (p. 196). The amounts of hydrogen taken up in the ascending branches of the isobars, i.e., in the nonequilibrium range, depend on the waiting time for every adsorption measurement at a given temperature.

(2) Emmett pointed out that the chemisorptions A and B cannot solely be ascribed to a diffusion of hydrogen into the metal, but must correspond to processes which result in changes of the catalyst surfaces. It would be hard to explain in any other way the retarding influence of preadsorbed Type A and Type B hydrogen on a typical surface reaction such as the ortho-para conversion at −190°C and its inhibiting effect on the weak chemisorption of hydrogen that occurs at −190°C.

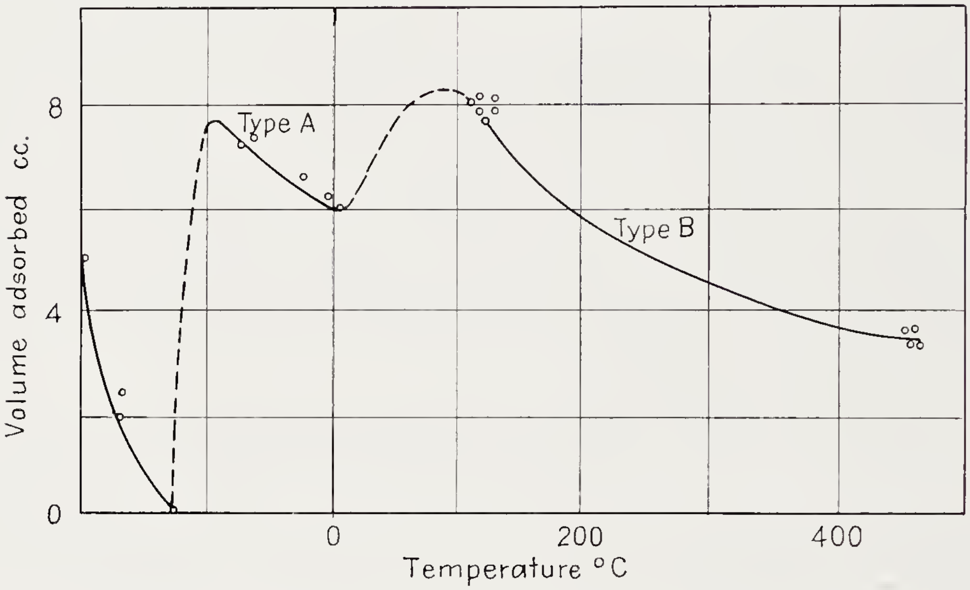

Figure 3. Adsorption isobar at 760 mm for hydrogen on doubly promoted iron catalyst, showing the existence of three types of adsorption[52]. The adsorption below −140°C is designated as "physical" adsorption, (see Table 5).

(3) *Nonpromoted* and *doubly-promoted* iron catalysts qualitatively show the same behavior in the chemisorption of hydrogen. Both of these catalysts are about equally efficient in promoting the ortho-para conversion at −190° and equally inefficient, at the same temperature, for the hydrogen-deuterium exchange.

(4) *Singly promoted* catalysts show a different behavior from that of nonpromoted and doubly promoted iron catalysts. At −194°C a specific type (C) of hydrogen chemisorption, different from the chemisorption found on the other iron catalysts, and a concomitant rapid hydrogen-deuterium exchange are observed on the singly promoted types.

(5) Strongly chemisorbed Type B hydrogen poisons the ortho-para con-

version at −190°C on pure iron and on doubly promoted catalysts, but does not do so on singly promoted catalysts.

(6) Interesting observations were also made on the effect of a previous chemisorption of *nitrogen* on the types A and B chemisorptions of hydrogen. Nitrogen preadsorbed on unpromoted and on doubly promoted catalysts causes an almost equivalent decrease (in moles) of the quantity of hydrogen chemisorbed (both Types A and B) compared with the amounts adsorbed on the catalysts containing no chemisorbed nitrogen. On singly promoted catalysts, however, previous chemisorption of nitrogen does not decrease, but *increases* the subsequent Type B chemisorption of hydrogen. In fact it increases to such an extent that the latter exceeds the chemisorption on the catalysts containing no chemisorbed nitrogen by 30 to 50 per cent.

(7) Previous chemisorption of hydrogen does not, for any of the catalysts, change the low temperature, physical adsorption of nitrogen.

(8) A treatment with hydrogen at 500°C followed by 24 hours evacuation at 500°C removes practically all the chemisorbed hydrogen from pure iron samples, but leaves considerable amounts on the singly promoted catalysts (see p. 212). No measurements of this kind were made for doubly promoted catalysts.

This is a rather complicated picture and interpretations of the various effects are necessarily of a hypothetical nature.

One interesting interpretation of Type A and Type B chemisorption has been suggested by Brunauer and Emmett[21a]. They tentatively assume that the Type A chemisorption on pure iron and on doubly promoted iron catalysts involves the association between hydrogen atoms and the metal atoms that are located in the uppermost lattice layer of the catalyst surface. Chemisorption Type B, following their suggestion, would be an adsorption of hydrogen on metal atoms arranged underneath the uppermost surface atoms as they occur in "open" lattice structure, for instance, in the (100)- and (111)-planes of the body-centered cubic structure of alpha-iron. According to this concept, the ratio of Type A to Type B chemisorbed hydrogen would vary with the quantitative distribution of the various crystal faces in the catalyst surface. Thus, they suggest that certain shifts between the two types of A and B chemisorption observed after the sintering of a catalyst are caused by a change, due to the sintering, in the relative ratios of the various crystal faces in the catalyst surface. The adsorbed hydrogen molecules for both Type A and Type B adsorption are interpreted by these authors as being dissociated into atoms.

The following alternative suggestions, occurring to the writer, for the existence of Type A and Type B chemisorptions may be mentioned:

(1) Different states may exist for these two types of chemisorbed hydro-

gen. For instance, Type A adsorption may be of the "predissociation" variety, whereas Type B may involve complete dissociation. On the other hand, Emmett and associates consider a "predissociated" state of Type A chemisorbed hydrogen unlikely in view of the fact that this type of chemisorption does not produce an appreciable inhibition on the amount of CO that can be chemisorbed.

(2) The presence on the catalyst surface of impurities such as oxides with specific adsorptive properties for hydrogen may be involved in Type A or Type B adsorption.

(3) A slow diffusion of hydrogen into the bulk of the metal may cause, for instance, the Type B chemisorption.

In the writer's opinion, no decisive arguments for or against any one of these speculations can be offered at present, except that diffusion of hydrogen into the bulk of the metal can account, at most, for only a fraction of Type B chemisorption for reasons already mentioned.

The abnormal effects observed with the *singly* promoted catalysts are obviously caused by the presence in the catalyst surfaces of the amphoteric or acidic oxides, Al_2O_3, SiO_2, ZrO_2, etc. Since neither pure iron nor the doubly promoted catalysts show the anomalies of the singly promoted type, it appears conceivable to the writer that hydrogen is preferentially chemisorbed (Type C) on the amphoteric or acidic oxides, or, more probably, on the interfaces between these oxides and the metallic iron present in the surface of the singly promoted catalyst. The presence of additional alkali oxides in the doubly promoted catalysts seems to counteract this type of chemisorption at interfaces between the acidic oxides and iron. We shall come back to this effect in connection with a detailed discussion of the various types of iron catalysts and their surface structure.

The chemisorption of hydrogen on iron films made by evaporation *in vacuo* has been investigated by Beeck[8]. The ultra-pure metal films used in this work differ considerably in their adsorptive capacity for hydrogen from the regular iron catalysts studied by Emmett *et al.*

An iron film that had been presintered *in vacuo* at 200°C adsorbed hydrogen at a rapid rate on exposure to a hydrogen atmosphere of 0.1 mm pressure at −196°C. On raising the temperature from −196 to −78°C (see ascending isobar, curve 1, Figure 4), a gradual increase of the hydrogen sorption occurred. Continued increase of the temperature to 200°C gave a maximum of the adsorption isobar at about −50°C, followed by a gradually steepening drop at still higher temperatures. When the sample is cooled back from 200 to −196°C, its isobar shows a gradual rise toward lower temperatures (Curve 2, Figure 4).

To explain these observations and the fact that the quantities of the slowly adsorbed hydrogen were proportional to the *weights* of the metal films, Beeck assumed that the chemisorption of hydrogen on these films is accompanied by a diffusion of the hydrogen into the interior of the metal, i.e., by a solution effect. The differential heats of adsorption of hydrogen on the iron films at room temperature were measured by Beeck calorimetrically. These heats dropped with increasing surface coverage from 32,000 cal/mole H_2 to *ca.* 18,000 cal/mole H_2, the latter value corresponding to an apparent saturation of the iron surface with the adsorbed gas. Quite in contrast to findings of Emmett and co-workers* for massive iron catalysts, all the adsorptions observed by Beeck on iron films occurred rapidly except the slow "diffusion" process observed during the initial adsorption measurements on fresh films. It must be emphasized here again that these results obtained on ultra-pure metal surfaces are not directly applicable to the processes occurring on practical ammonia catalysts.

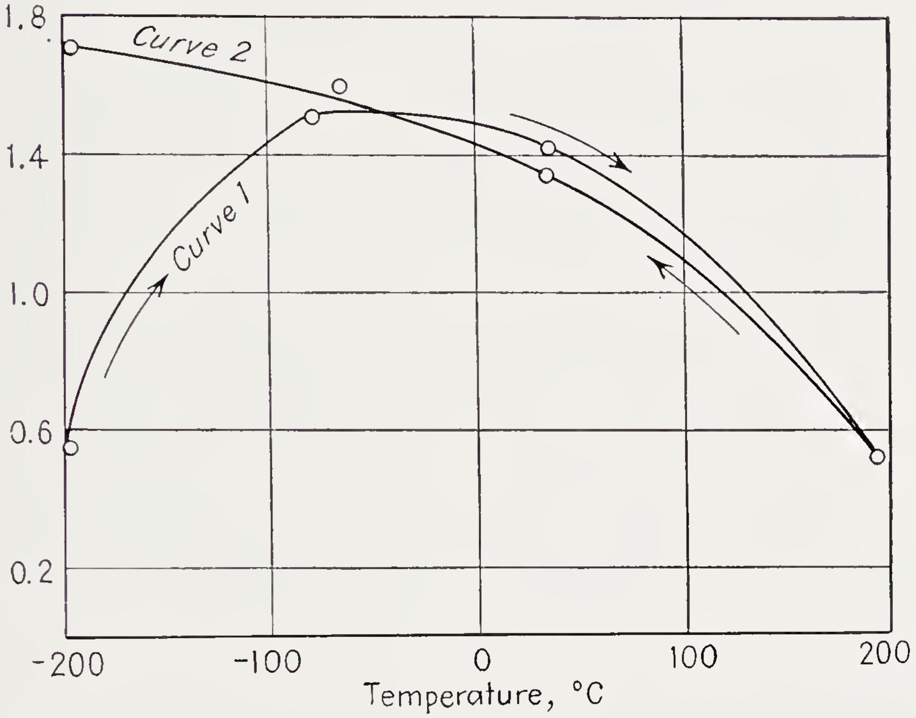

Figure 4. Sorption isobars of hydrogen at 0.1 mm pressure on an evaporated iron film sintered at 200°C. (Beeck, "Advances in Catalysis," Vol. 2, 170 (1950)).

As to other investigations of the iron-hydrogen system, mention has already been made of observations by Frankenburger, Mayrhofer and

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* *Editor's note:* Type C chemisorption of H_2 on an Fe—Al_2O_3 at −196°C is, like that on films, very rapid. For a comparison of the behavior of H_2 on Fe—Al_2O_3 catalysts and thin metal films see a paper by H. H. Podgurski and P. H. Emmett, *J. Phys. Chem.*, **57,** 159 (1953).

Schwamberger[69] on a loose association of hydrogen with iron atoms that condense on glass walls at low temperatures.

Tungsten-Hydrogen. Various studies have been made of the chemisorption of hydrogen on metallic tungsten. A comparison of the results obtained in different laboratories again shows, as in the case of the iron catalysts, the influence of even small amounts of impurities and of preadsorbed gases on the adsorptive properties of the metallic surfaces.

The adsorption of hydrogen on tungsten powders was measured by Frankenburger and Hodler[67] with the following results.

(1) The more thoroughly the metal surfaces were purified by a previous reduction of the powders with hydrogen and subsequent evacuation, the larger were the quantities of hydrogen adsorbed at a given gas pressure and temperature. (2) Regardless of the purity of the samples, the shape of all the isotherms conformed to Freundlich's formula rather than to Langmuir's isotherm equation. (3) A weak type of chemisorption was observed that yielded equilibrium values in the temperature range from 0 to about 50°C. Between 50 and 170°C, a "nonequilibrium range" was observed, characterized by ascending isobars. From 190° up equilibria were instantaneously established for a strong type of chemisorption. Powders of a low degree of purity gave the same indications for the existence of two types of chemisorption. However, the amounts adsorbed on these powders were smaller than on the highly purified powders and the transition from the weak to the strong type of chemisorption was shifted on these powders to higher temperatures. Whereas this transition occurred between 170 and 190° for the most thoroughly purified powders, it appeared between 220 and 240°C for a powder that had been subjected to a shorter reduction with hydrogen at 750°C.

Thus, the adsorption system tungsten-hydrogen resembles the iron-hydrogen system insofar as it shows the existence of two types of chemisorption that differ in their rates of adsorption and desorption and in their heats of adsorption. In both systems the linkage established between hydrogen and the metals is stronger for the chemisorption that takes place at high temperatures.

A new indirect method for obtaining information on the hydrogen adsorption on tungsten was developed by Roberts. This author worked with tungsten wires that had been freed from adsorbed gases and other contaminations by previously flashing the wires to very high temperatures, *ca.* 2000°C[153, 154]. From the change of the accommodation coefficient of neon with the surface of this wire before and after the admission of hydrogen at very low pressures, Roberts concluded that at hydrogen pressures as low as 10^{-4} mm and liquid air temperature, a monolayer of adsorbed hydrogen forms instantaneously on the tungsten surface. In following this observation further, Roberts measured the differential heats of adsorption evolved during this rapid uptake of hydrogen. This was done by determining the changes of the electrical resistance of the tungsten wire caused by the heats of adsorption of successive small increments of hydrogen.

These determinations[153, 154] gave a curve of the differential heats of hydrogen adsorption that, in a linear dependence on the quantities adsorbed, dropped from a value of 47,000 cal/mole of H_2 for the very first amounts of hydrogen adsorbed, to 18,000 cal/mole of H_2 for an almost completed monolayer of adsorbed hydrogen. The number of H-atoms held in the saturated layer equalled approximately the number of tungsten atoms contained in the total adsorbing surface. Roberts concluded from this numerical relationship that the adsorbed hydrogen is dissociated and forms a monolayer on the metal having the composition WH.

The most remarkable feature of Robert's investigation is the rapidity and completeness with which the hydrogen is adsorbed on the tungsten surface at very low pressures and temperatures, and the strength of the bonds established under these conditions between the gas and the metal. These characteristics make the adsorption of hydrogen on the ultra-pure surface of the tungsten wire used by Roberts quite different from the adsorption on the less thoroughly purified tungsten powders studied by Frankenburger and Hodler. The same type of strong chemisorption on the powders as that occurring on the tungsten wire requires an appreciable energy of activation and is therefore limited to considerably higher temperatures.

In view of this discrepancy, Frankenburg[61] renewed the investigation of the hydrogen adsorption on powders of metallic tungsten. Particular care was taken in these experiments to remove any residual surface oxides by reducing the tungsten powders at 750°C with purified hydrogen flowing at a rate of 30 l/hr over a period of at least 24 hours. The reduced powders were outgassed at 750°C in a high vacuum for 30 to 50 hours. The specific surface areas of the powders were determined by low temperature nitrogen adsorption according to the method of Brunauer and Emmett[21, 43] and Brunauer, Emmett and Teller[22] and found to be 0.7 sq m/g for one of the powder samples and 2.06 sq m/g for a second sample. The isotherms were measured for hydrogen pressures from 10^{-5} to 30 mm, and at temperatures ranging from −194 to 750°C. On tungsten powders, purified by this method, the adsorption of hydrogen was rapid at all temperatures between 100 and 750°C. In the same range, the measured equilibria were well reproducible on cooling and on heating the samples, in runs on replicate samples of the powders, and in measurements carried out in a second adsorption apparatus. Throughout the wide temperature and pressure range investigated, the isotherms followed Freundlich's equation. It can be shown that this conformity of the isotherms with Freundlich's exponential formula is caused by a strong decline of the differential heats of adsorption with increasing coverage of the metal surface with adsorbed hydrogen.

Below 100°C, the adsorption equilibria were not obtained as instantaneously as they were at the higher temperatures. At these lower temperatures, there occurred, after the admission of a given amount of hydrogen into the adsorption chamber, a rapid uptake of gas by the metal powder followed by an increasingly slower adsorption. Generally, the rapid adsorbed portions equalled about 75 per cent of the total amounts that were finally adsorbed over a long period. The slow uptake of a part of the gas is not due to the requirement of an activation energy; rather, it appears that at the small pressure gradients, low pressures and temperatures prevailing in these measurements a slow diffusion of the gas through the densely packed particles of tungsten powder becomes the rate controlling process.

The following results of these measurements on tungsten powders are in agreement with Roberts' findings: (1) The upper limit of the adsorption of hydrogen on tungsten surface is reached when a monolayer is formed consisting of one hydrogen atom for every tungsten atom located in the metal surface. (2) The differential heats of adsorption, Q, decrease gradually from high values for the initial amounts of hydrogen adsorbed to ever lower values with increasing coverage of the metal surface. (3) The initial differential heat of adsorption Q_0 that according to Roberts amounts to 47,000 cal/mole of H_2 was determined in Frankenburg's measurements as 46,000 cal/mole of H_2.

Differences exist between the results of both investigators on the following points: (1) According to Roberts, a complete monolayer of adsorbed hydrogen is formed on the metal at $-194°C$ and at a pressure as low as 10^{-4} mm. Under the same conditions, a hydrogen coverage of only *ca.* 40 per cent of the tungsten surface was observed on the tungsten powders. (2) Whereas according to Roberts the differential heats of adsorption Q decrease linearly with increased surface covering, ($\frac{-dQ}{dA} = K$ where A is the amount of hydrogen adsorbed per cm^2 of surface, and K is a constant) Frankenburg found no decrease of Q for low surface coverages below 1 per cent of the saturation value, but observed a rapid decrease for surface coverings $A > 1$ per cent according to $\frac{-dQ}{dA} = \lambda \frac{1}{A}$ where γ is a constant.

The adsorption of hydrogen on *films* of metallic tungsten prepared by evaporation of the metal *in vacuo* was investigated by Beeck[6, 8] and by Rideal and Trapnell[151]. Beeck reported briefly, without giving detailed experimental data, that a complete monolayer of adsorbed hydrogen was formed on his films at 10^{-4} mm and 0°C. The differential heats of adsorption in Beeck's calorimetric measurements decrease with increasing coverage of the surface in a manner similar to that found by Roberts for a tungsten wire. The initial heat of adsorption of hydrogen on a pure tungsten film was directly measured by calorimetry and found to be 46,000 cal/mole of H_2, in excellent agreement with both Robert's and Frankenburg's values.

Rideal's and Trapnell's adsorption measurements on tungsten films cover a pressure range from 10^{-7} to 10^{-2} mm and a temperature range from -183 to 0°C. Their investigation was not extended to higher temperatures, evidently because of the sintering of the tungsten films above 0°C. The authors observed a slow-down of the rate of adsorption resembling the effects observed by others for the low temperature adsorption of hydrogen on nickel and platinum, and by Frankenburg. at temperatures below 100°C, on tungsten. The slow uptake is ascribed by Rideal and Trapnell to a solution of hydrogen in the bulk phase of the film, although no convincing proof is given for this interpretation. At the most, 5 per cent of the total gas uptake by the tungsten is involved in the slow process, the remainder being chemisorbed. In this low temperature range the surface coverings of the metal observed by Rideal and Trapnell corresponded to values of 70 to 90 per cent of the saturation value. The isotherms measured for this range of high coverage follow Freundlich's equation, just as do the more extensive isotherms measured on tungsten powders. By an indirect method, based on measurements of oxygen adsorption by their films, and assuming that this oxygen adsorption corresponds to one monolayer of oxygen atoms on the tungsten surface, Rideal and Trapnell concluded that saturation of the tungsten films with chemisorbed hydrogen corresponds to the completion of a localized monolayer of WH. This conclusion is identical with that derived by the earlier workers. At 10^{-4} mm equilibrium pressure and -183°C, the quantity of hydrogen adsorbed, according to these authors, covers 85 and not 100 per cent of the surface as estimated by Roberts. At 10^{-4} mm equilibrium pressure and 0°C, a surface fraction of about 70 per cent was found to be covered with the chemisorbed gas. In the range of their measurements, Rideal and Trapnell obtained differential heats of adsorption which, with increasing coverage, fall from about 11,000 cal/mole for the 70 per cent coverage to about 2,000 cal/mole for 90 per cent coverage. This drop of the heats of adsorption is a nonlinear function of the surface coverage, and the shape of the heat curve obtained resembles that derived by Frankenburg for a wider range of surface coverings.

It is interesting to compare these results on the adsorption of hydrogen on tungsten samples. They include wires with less than one square centimeter of surface, powders with a total surface of about 300,000 cm², and tungsten films with total surfaces of about 8,000 cm² lying between these two extremes. With all these specimens adsorption equilibria were rapidly established at hydrogen pressures as low as 10^{-5} and 10^{-4} mm. The resulting gas uptakes, at these low pressures correspond to a considerable percentage, for instance at 0°C to 21 per cent on the powders and to 69 per cent on the films, of the saturation value. For all the samples investigated, the saturation of their surfaces equalled a quantity of hydrogen sufficient to form one monolayer of WH. At temperatures of 100°C and lower, the initial instantaneous uptake of gas by the samples was followed, both on powders and on films, by the slow disappearance of a relatively small additional quantity of gas. This effect is caused either by a gradual diffusion of hydrogen through narrow passages of the adsorbents or, less likely, by a slow solution of the gas in the bulk metal. At temperatures above 100°C chemisorption equilibra were established instantaneously on all the specimens investigated. For all the tungsten samples, the initial differential heats of adsorption was found to lie between 45,000 and 47,000 cal/mole H_2. A substantial decline was observed of the differential heats for successive increments of adsorbed gas, reaching very low values of the order of magnitude of 3,000 cal/mole on approach to completion of a monolayer.

The decline of the heats of adsorption on Frankenburg's tungsten powders is steeper in the range of low surface coverings than on the tungsten films of Beeck and on the tungsten wire of Roberts. This indicates that on the powder particles, the successively adsorbed increments of hydrogen are linked to the surface by weaker forces than on the other tungsten samples. As a consequence of these lower heats of adsorption for moderate surface coverings, higher hydrogen pressures are necessary on the powders for establishing a given surface coverage than on the wires and films. On none of these various specimens of thoroughly reduced and outgassed tungsten were types of a weaker chemisorption observed resembling those found in the earlier investigations of Frankenburg and Hodler who probably worked with metal surfaces of a lesser degree of purity.

Ammonia Chemisorption on Catalysts. In contrast to the numerous studies on the adsorption of nitrogen and hydrogen, only a few investigations have been made of the chemisorption of ammonia on catalytically active metals. One difficulty in these investigations is that in its state of chemisorption on active catalysts, ammonia is spontaneously decomposed at relatively low temperatures.

In 1927 Dew and Taylor[29] investigated the adsorption of ammonia on iron, nickel, copper and on an iron-molybdenum catalyst at temperatures between 0 and 445°C. The initial heats of adsorption are, according to these authors, 16,000 cal/mole for iron, 11,300 cal/mole for nickel, and 8,700 cal/mole for copper. On all these metals, the differential heats of adsorption decline rapidly with increasing coverage of the catalysts with adsorbed ammonia. Frankenburger and Hodler[67] found that isotherms of ammonia on tungsten follow Freundlich's equation in the temperature range of 25 to 60°C, and that the initial heats of this adsorption lie between 8,000 and 14,000 cal/mole adsorbed ammonia. In these experiments the adsorbed ammonia started to decompose at 90°C with the evolution of hydrogen, the nitrogen remaining in the adsorbed phase under these conditions.

Theoretical Considerations. On the Nonuniform Character of the Chemisorbed Phase and its Importance for the Catalytic Process. In almost all the adsorption systems discussed in the foregoing sections, the differential heats of chemisorption decrease as the coverage of the metal surfaces with the adsorbed gas increases.* This is true for the heats evolved in the chemisorption of hydrogen and nitrogen regardless of whether highly purified metal specimens or the usual types of ammonia catalysts are used as adsorbents.

This decline of the adsorptive potential of the catalysts with the gradual build-up of a chemisorbed monolayer is substantial, and in certain cases corresponds to a drop of 80 to 90 per cent from the initial to the final heat of adsorption. Thus, there is a wide spread of the forces that link successively adsorbed fractions of gas to the catalyst surface. As a consequence, the adsorbed particles in these systems must differ widely in their degrees of activity and reactivity, making it likely that there is included among the chemisorbed fractions of the reactant, one particular fraction that is especially adapted to a rapid participation in the successive steps of the catalytic process.

Thus, the nonuniformity of the chemisorbed phase appears to be of basic importance for surface catalysis and an essential feature of the catalytic ammonia synthesis. We shall discuss here briefly the factors that may be held responsible for the decline of the adsorptive potential with increasing coverage of the catalytic surface.

Pre-existing Heterogeneity of Catalyst Surfaces. In the last thirty years, the nonuniform potential of a catalyst surface for chemisorption has been envisaged as a point-to-point variation of its specific activity and has often been correlated to an *"a priori" structural* heterogeneity of the catalyst surface. That catalyst surfaces are disuniform and that their specific activity may reside in a finite number of isolated surface sites has been suggested since Maxted[127, 128, 129, 130] proved experimentally that certain poisons, even in amounts that can cover only a small fraction of the total catalyst surface, completely paralyze the activity of a given catalyst. Starting from these indications of the concentration of catalytic activity on a mere fraction of the catalyst surface, Taylor and co-workers studied a great

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* As a result of this decrease of the differential heats of adsorption, the isotherms follow Freundlich's equation (see page 218).

number of systems to get additional evidence for the intrinsic heterogeneity of the sites of catalytic action. These investigations led to the concept of "active centers" and demonstrated clearly that the disuniformity of solid surface is an important factor in surface catalysis[166, 167, 168, 169].

The presently accepted theoretical picture of the structure of "real solids" is in accord with the postulate that catalyst surfaces are topographically disuniform. According to this picture, the surfaces of most solids are agglomerates of numerous crystallites that, oriented at random, form irregular mosaic patterns of different crystal faces, edges, corners and other structural arrangements. On a submicroscopic scale, ordinary surfaces are usually composed of several crystal lattice planes, each of which contains atoms arranged in an individual pattern. Moreover, there are atoms and clusters of atoms arranged in exposed locations, particularly at edges and corners of the crystallites.

Theoretical considerations as well as experiments with specially prepared homogeneous oriented metal films[6, 7, 9] have confirmed the hypothesis that one of the factors governing the adsorptive potential and catalytic activity of a surface is the *specific steric arrangement of its atoms*. Thus, an irregular point-to-point variation of the catalytic activity has to result from the disuniform structure of ordinary catalyst surfaces, regardless as to whether this disuniformity is due to the exposure of different lattice planes, or to the presence of edges, corners, steps, and other discontinuities in one given type of lattice plane.

Induction Effects. Although this speaks clearly for a correlation between the structural imperfections of catalyst surfaces and the gradation of their adsorptive and catalytic properties, it is doubtful whether all the disuniformity effects observed in chemisorption and catalytic reactions can be satisfactorily explained solely on this basis. It appears, for instance, astonishing that an almost identical decline with increasing surface coverage has been measured for the successive differential heats of the chemisorption of hydrogen on tungsten wires and on tungsten films (see pp. 56, 219). One would expect the surface of a compact wire that was previously flashed at 2000°C would have a submicroscopic structure quite different from that of a porous metal film, formed in vacuo by the coalescence of condensing metal atoms. For this case, the structural hypothesis would demand that the different surface structures of the wires and films should be reflected in different declines of the heats of adsorption on the two adsorbents. Similarly it seems strange that two powder specimens of metallic tungsten, differing considerably in particle size and specific surface, yield identical curves for their differential heats of hydrogen adsorption[61]. Other examples could be given of effects that are difficult to explain exclusively on the basis of surface heterogeneity. It may suffice to refer to two recent publications by Boudart[16] in which such cases are discussed. All this makes it likely that many effects characteristic for chemisorptions and catalytic reactions are controlled by an additional factor of a more universal nature.

It has been pointed out by several authors[61, 70, 71, 72, 151, 161] that the continuous decline of the adsorptive potential of a surface during the build-up of a chemisorbed monolayer may be *a consequence of the act of chemisorption itself*, rather than the result of a preexisting heterogeneity of the surface. Such an "induced heterogeneity" or "induction" would act on the whole catalyst surface, rather than on a limited number of submicroscopic surface spots.

To produce induction effects of this kind, a medium is required in the catalyst that spreads the influence of widely separated chemisorbed particles over the total catalyst surface, or at least over large sections of the surface, decreasing its adsorptive potential for the chemisorption of addition amounts of the adsorbate. Such a "transmitter medium" is available in metallic catalysts as well as in catalysts of the semiconductor type in form of their free electrons. Several suggestions have been made on the specific mechanism by which this transmitter effect may operate[61].

Recently Boudart has outlined general viewpoints concerning induction effects of this kind on catalysts of the conductor type and of the semiconductor type. If we accept the notion that the activation of gases such as nitrogen or hydrogen on a metallic surface involves the merging of their valence electrons with those of the metal (see p. 201), it follows that every individual act of chemisorption necessarily changes the electron distribution within the entire metallic catalysts. This change will be spread throughout the "electron gas" within the solid and over its surface, imparting to the latter an adsorption potential different from that existing on the virgin surface.

Such an electronic mechanism of chemisorption can be correlated with experimental measurements of the work function ϕ of the metallic surface, that is, of the energy required to remove one electron from the metal surface. As has been known for some time, the ϕ-value of a given metal changes by an amount $\Delta\phi$, when traces of "impurities" are incorporated into the metal surface, regardless of whether these impurities are chemisorbed gases, or minute amounts of other metals or foreign oxides, etc. By using the $\Delta\phi$-values reported in the literature for several metal-gas adsorption systems, Boudart calculated for the decrease of the heats of chemisorptions in these systems values that check well with the experimental data.

Induction effects, according to this interpretation, will not remain limited to the influence of chemisorbed gases such as hydrogen and nitrogen on metallic or semiconducting catalysts. Rather, incorporation of any foreign substance into a catalyst containing free electrons ought to modify the activity of the catalyst via an electronic mechanism according to this concept. This would not only explain the fact that poisons and promoters change the intrinsic activity of a catalyst surface, but it also implies that all catalyst-bound reactants, intermediates, and reaction products must weaken or enhance this activity. Furthermore, the existence of induction effects would explain why ultra-pure metals are inadequate models of ordinary catalysts, since the latter invariably contain impurities in their surfaces.

For the special case of ammonia catalysts, Kummer and Emmett[104] have shown, in experiments in which radioactive and non-radioactive carbon monoxide gas were chemisorbed on a promoted iron catalyst at −195 and −78° until the surface was saturated with a fifty-fifty mixture of these isotopic molecules, that rapid mixing occurs in a portion of the mixed adsorption layer corresponding to about 50 per cent of the surface. The mixture of $C^{14}O$ and $C^{12}O$ on the rest of the surface did not show this rapid mixing, thus behaving as if this part of the surface had an *a priori* heterogeneity. The differential heats of adsorption of carbon monoxide on an iron catalyst were found by Beebe and Stevens[5] to decline rapidly with increasing surface coverage (from 35,000 to 8,000 cal/mole). The observed exchange of places among 50 per cent of the adsorbed carbon monoxide molecules might be more easily explained for this surface fraction by "induction" than by a pre-existent surface heterogeneity. More work will be necessary before it can be decided to what extent the concept of induction will advance the exploration of catalytic phenomena.

Studies of Individual Ammonia Catalysts

Iron Catalysts. *Influence of Additives.* While the preceding discussion deals with the general principles of catalytic ammonia synthesis, the following section presents a survey on investigations of individual catalysts, particularly of the technically important promoted iron catalysts.

Figure 5 based on a more detailed graph by Mittasch[132] depicts schematically the types of modifications that the catalytic activity of metallic iron can undergo, under the influence of different substances incorporated into the metal. Curve 1 illustrates the inactivation of iron by small amounts of sulfur, Curve 2, the slight activity increase resulting from supporting the metal on quartz pieces, Curve 3, the technically important activation of iron by alumina, and Curve 4, the mutual activation of the two catalytically active metals, iron and molybdenum.

This diagram demonstrates the variability of iron catalysts in a qualitative sense only. Actually, the extent to which second or third components increase or decrease the catalytic activity of metallic iron depends on the conditions under which this activity is tested. For instance, the activating effects of some promoters become clearly recognizable at elevated pressures only. This influence of pressure on the relative activities of unpromoted and promoted iron catalysts was studied thoroughly by Almquist and Crittenden[2], who obtained the results listed in Table 6 in comparative synthesis runs with different iron catalysts.

According to these data, K_2O acts on pure iron not as a promoter but as a moderately effective inactivator, both at 30 and at 100 atmospheres. If, however, K_2O is added to an Al_2O_3-promoted catalyst, it causes an increase of catalytic activity that is particularly pronounced at a higher pressure.

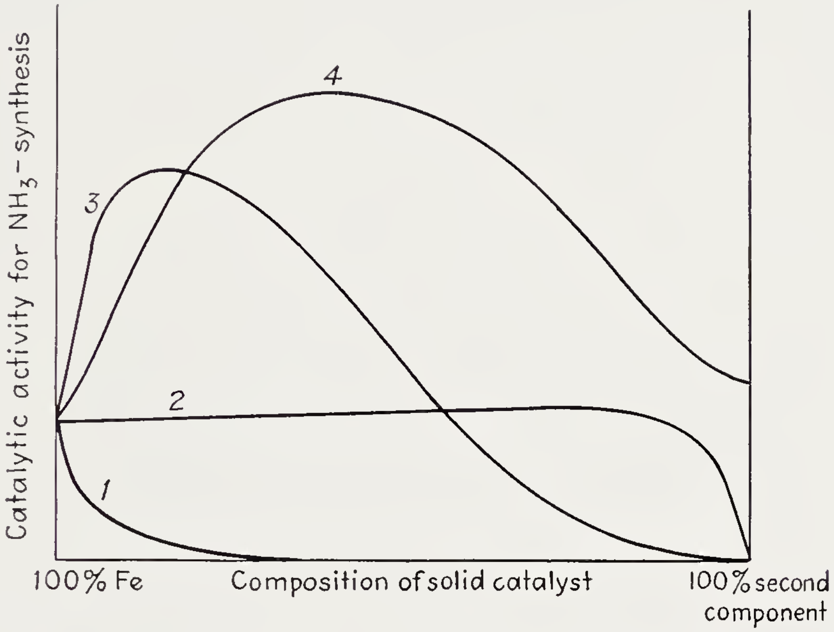

Figure 5. Modification of the catalytic activity of iron by other substances. (According to A. Mittasch).
Curve *1:* Fe + S: Poisoning
2: Fe on quartz: Effect of support
3: Fe + Al_2O_3 : Increase of activity by a substance which, by itself, is no catalyst.
4: Fe + Mo: Superadditive activity of mixtures of two catalysts.

Larson and Dodge[117] expanded these studies of the relationships between promoter action and catalytic activities as a function of the pressure used in the synthesis reaction. In Figure 6[38] (Fig. 3 from Emmett, *J. Chem. Educ.* **7**, 2580 (1930)) activity measurements are plotted that were made by these authors on eleven different promoted iron catalysts in the pressure range between 10 and 100 atmospheres. For comparing the activities of the different catalysts at low and high pressures, the term "efficiency" was introduced by Larson and Dodge. It is defined as the ammonia concentration in the off-gases of a given experiment, expressed as percentage of the equilibrium concentration of ammonia at the pressure and temperature conditions of this experiment.

TABLE 6. ACTIVITIES OF UNPROMOTED AND PROMOTED IRON CATALYSTS IN SYNTHESIS EXPERIMENTS AT 450°C, SPACE VELOCITY = 5000, WITH PURE 3:1 HYDROGEN-NITROGEN MIXTURE

(According to Almquist and Crittenden[2])

No.	Promoters weight percentages		Yields of NH_3 in % at	
	Al_2O_3	K_2O	30 Atmospheres	100 Atmospheres
1	—	—	3.30	5.49
2	—	1.20	1.57	3.43
3	1.31	—	5.35	9.35
4	1.05	0.26	5.80	13.85

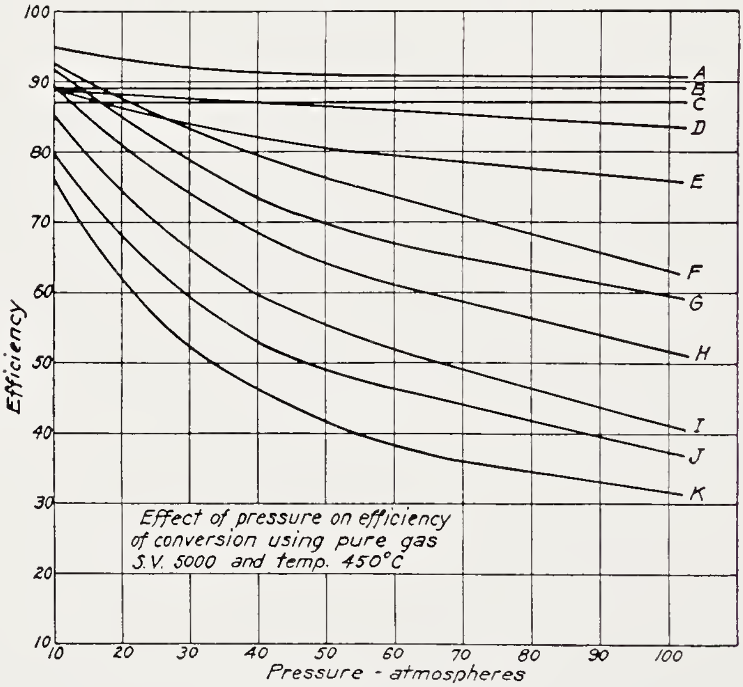

Figure 6. Variation of conversion efficiency with pressure for a series of promoted catalysts[38].

Effect of Promoters on the Catalyst Surface. Earlier Work. Per unit of catalyst weight and under ordinary synthesis conditions, the activity of an Al_2O_3-promoted iron catalyst is substantially higher than that of the unpromoted metal (see, e.g., Table 6, Catalyst 1 and 3). In addition, alumina-containing catalysts prove to be less sensitive to the presence of small amounts of oxygen or oxygen-containing impurities, such as H_2O, CO_2 and CO in the synthesis gas.

Soon after its discovery, the favorable effect of Al_2O_3 and of other acidic or amphoteric oxides (SiO_2, ZrO_2, etc.) on the activity of iron catalysts was tentatively explained by the assumption that these promoters preserve a large surface of the iron catalysts by counteracting their sintering at higher temperatures[65, 132, 133]. Specifically, it was suggested that Al_2O_3 and similar difficultly reducible promoter oxides cover, at least partly, the surface of the small iron crystallites that are initially formed when during the preparation of the catalyst iron oxide is reduced to the metal. The "skins" of foreign oxides deposited on the crystallite surfaces, according to this concept, prevent the formation of larger iron particles. This explanation had to remain a mere speculation as long as no method was available for the quantitative measurements of catalyst surfaces.

TABLE 7. SURFACE AREA OF IRON CATALYSTS, MEASURED BY LOW TEMPERATURE ADSORPTION OF NITROGEN

No.	Composition	Surface Area in m^2/g Catalyst	References
1	Fe_3O_4 unreduced	0.02	47 and 21
2	Fe, no promoter (0.15% Al_2O_3 as impurity)	0.55	47 and 21
2a	Same	1.24	47 and 21
3	Fe + 1.07% K_2O	0.56	47 and 21
4	Fe + 1.03% Al_2O_3	9.44	47 and 21
5	Fe + 10.2% Al_2O_3	11.03	47 and 21
6	Fe + 0.35% Al_2O_3 + 0.08% K_2O	2.50	47 and 21
7	Fe + 1.3% Al_2O_3 + 1.59% K_2O	4.04	47 and 21
8	Fe + Al_2O_3 + K_2O + CaO*	8.2	143
9	Fe + Al_2O_3 + K_2O + CaO*	12.6	143

* No quantitative data are given on the percentage composition of these triply promoted catalysts.

After they developed a method for measuring the surfaces of finely divided or porous solids, Emmett and his associates determined the specific surface areas of a series of promoted and unpromoted iron ammonia catalysts. The values listed in Table 7 confirm, in a concise way, the earlier notion on the role of oxidic promoters in iron catalysts by showing clearly that the specific surface areas of the Al_2O_3 promoted catalysts (samples #4 and #5) exceed greatly those of the unpromoted catalysts (#2 and #2a).

X-ray Work. That Al_2O_3 and related promoter oxides exert a profound influence on the physical structure of iron catalysts is also borne out by x-ray investigations of the crystal structure of these catalysts, both in their initially oxidized and in their reduced states. Wyckoff and Crittenden[182] and Brill[18] concluded from the x-ray patterns obtained of iron ammonia catalysts that the unpromoted catalyst, prior to its reduction to the metal, has the structure of magnetite, Fe_3O_4 and forms a lattice of the spinel type, characteristic for the compound $FeO \cdot Fe_2O_3$. Essentially the same lattice structure was found for catalysts that contain several weight per cent of Al_2O_3, or of the combined promoters, Al_2O_3 and K_2O.

The fact that in the presence of the promoter oxides, no crystalline phase is observed other than that of Fe_3O_4 indicates the formation of a solid solution of the spinel $FeO \cdot Al_2O_3$ in the $FeO \cdot Fe_2O_3$ lattice. It appears that this formation of a solution of alumina in the magnetite phase is essential for a satisfactory performance of the catalyst that is obtained by reducing the oxidic product. In 1932 Mittasch and Keunecke[136] and Brill[18] were able to show that a number of oxide preparations all consisting of 90 parts Fe_3O_4 and 10 parts Al_2O_3, if reduced, yielded catalysts of very different activities, depending on the extent to which a thorough mutual penetration of the two oxidic components had been achieved in the initial sample. Some of these preparations were mechanical mixtures of both oxides, some were obtained by the simultaneous precipitation of the hydroxides of iron and aluminum, and others were prepared by fusing together iron oxide with alumina. Both the α- and the γ-modifications of Al_2O_3 were tested as components of these mixtures. Of all these samples, only those yielded after reduction satisfactory catalysts that on x-ray examination revealed the formation of a mixed crystalline phase between Fe_3O_4 and Al_2O_3. All the oxide preparations that consisted, at least partly, of such a solid solution, proved to be more difficult to reduce than the mixtures in which Fe_3O_4 and Al_2O_3 were present as separate phases.

Nielsen[142] has recently made renewed x-ray investigations of iron ammonia catalysts in the oxide state, including an unpromoted type ("ferro-ferric-oxide") and samples promoted with $Al_2O_3 + K_2O$ and with $Al_2O_3 + CaO + K_2O$. All of these oxide catalysts showed again the magnetite structure. The only difference observed between the x-ray patterns of these "synthetic magnetites" and those of a specimen of natural magnetite was the presence in the x-ray diagrams of the synthetic samples of certain "satellite lines." These lines, missing in the diagram of the natural magnetite cannot be interpreted as due to the magnetite lattice. After a thorough discussion of these extra lines, Nielsen concluded that they probably originate from variations in the atomic scattering power and lattice parameter of the synthetic oxides caused by the occasional replacement of trivalent by divalent iron atoms, and by the substitution of iron ions with promoter ions, such as Al^{+++}.

In the *reduced state*, in which these catalysts are present during the synthesis reaction, they all show the lattice structure of α-iron[18, 141, 182]. This holds for all types of differently promoted iron ammonia catalysts examined by the various authors. The non-appearance of any reflections caused by the promoter substances can be explained only by assuming an extremely fine dispersion of the promoting oxides in the reduced catalysts, probably in the form of very thin surface layers of Al_2O_3 on the faces of small crystallites of α-iron. This confirms the assumption that the preservation of large specific surfaces in the promoted catalysts is due to the retardation of crystal growth, caused by a skin of promoter deposited on the iron particles. By dissolving the metallic iron of an Al_2O_3 promoted reduced catalyst, Brill obtained a residue of Al_2O_3 that had the γ-Al_2O_3 structure[18].

As to the average size of the α-iron crystallites in freshly reduced, "virgin" samples, no distinct differences were indicated between the unpromoted and the promoted catalysts in the x-ray patterns obtained by Wyckoff and Crittenden. A remarkable difference between both types, however, developed when the promoted and unpromoted catalysts were subjected by these investigators to a heat treatment for several hours at 600°C. After these "aging tests" the unpromoted catalysts gave x-ray patterns indicative of the presence of considerably enlarged crystallites of α-iron, whereas the types promoted with Al_2O_3 still showed the previously observed pattern characteristic for very small crystallite sizes. Nielsen confirmed this effect.

These results of the x-ray investigations are in accord with the surface measurements by the BET method (see chapter 2, Volume I of this series), insofar as both methods indicate that promoters of the Al_2O_3-type preserve the original structure of the reduced catalysts and thereby stabilize their large specific surface areas against the effect of sintering at higher temperatures.

It may be mentioned at this point that crystal growth in the unpromoted catalysts is apparently due not only to the elevated temperatures used in the aging tests, but also to the presence of minute amounts of oxygen or oxygen-containing substances in the nitrogen-hydrogen mixtures employed in these tests. Thus, Brill has reported in a recent publication[19] that, contrary to common assumptions, an unpromoted iron catalyst retains its catalytic activity for a very long time, even at 450°C, when this catalyst is reduced from its oxidic state with an ultra-pure, completely dry 3:1 mixture of hydrogen and nitrogen and when the same highly purified gas mixture is used for the activity tests. This unpromoted catalyst, however, proves to be much more sensitive to poisoning than a catalyst promoted with $Al_2O_3 + K_2O$. In supplementing this evidence, Nielsen has shown that the poisoning of ammonia catalysts by traces of oxygen or water vapor is not completely reversible, but causes a permanent decrease of catalyst activity, this decrease being caused by an accelerated rebuilding of the iron lattice under the influence of the oxygenated compounds in the usually employed synthesis gas.

In evaluating his x-ray diagrams, Nielsen[141, 142] concluded that a reduced promoted iron catalyst is made up of crystallites of pure iron, a few hundred Å units in diameter. The promoting oxides, according to Nielsen, do not only cover large parts of the crystallite surfaces, but also fill the interfacial layers between them. According to the same author, the total surface of all the crystallites contained in one gram of a promoted catalyst, as calculated from their linear dimensions estimated from the x-ray pattern, is several times greater than the specific surface area of the same catalyst measured by the BET method. From this, Nielsen concludes that the interfacial layers ordinarily coalesce with the iron crystallites to a coherent surface. Only where the iron crystallites are farther apart, or oriented at divergent angles, is the interfacial layer split up into two surface layers, "thus producing enlarged spacings developing into a rift network" (Nielsen). This network of crystallite clusters imparts to the reduced iron catalysts a porous structure and a large "internal surface," accessible to the reacting gases.

The high porosity of promoted iron catalysts is also proven by the fact that their densities range between about 2.7 to 3.5 g/cm^3,[139] compared with the density of 7.89 g/cm^3 for pure compact iron.

Distribution of Promoters on Catalyst Surfaces. Adsorption Measurements as an Analytical Tool. While these investigations strongly support the general concept that reduced iron catalysts contain innumerable agglomerates of tiny crystallites of pure α-iron and that the latter carry surface layers of the promoting oxides in the promoted types, no quantitative data can be obtained from the x-ray measurements on the exact chemical composition of the catalyst surfaces.

Here again, Emmett and Brunauer[45] succeeded in obtaining new and quantitative information by means of detailed adsorption studies on the different types of iron catalysts. These investigations started from comparative measurements of the adsorption of a number of gases, including nitrogen, argon, carbon monoxide and carbon dioxide on different reduced iron ammonia catalysts at temperatures between -195.8 and 0°C[43, 46]. Whereas nitrogen and argon showed the characteristics of a purely physical adsorption on all the catalysts this was not generally true for the adsorption of *carbon monoxide* and *carbon dioxide*. The total adsorption of CO at $-183°$ was for all the catalysts considerably higher than the physical adsorption of nitrogen and argon. On closer examination, Emmett and Brunauer[45] found that an uptake of carbon monoxide equal to that of nitrogen and argon could be obtained on a catalyst that had been pretreated as follows: The catalyst is permitted to adsorb CO at −183°C, is then subjected to an evacuation at −78°, and finally is used for measuring again the physical adsorption of CO at −183°C. This result, confirmed for numerous types of iron catalysts, indicates, according to Emmett and Brunauer[45], that the adsorbed carbon monoxide at −183° is actually a combined physical and chemical adsorption, and that the evacuation at −78° selectively removes the physically adsorbed carbon monoxide, leaving the chemisorbed portion of the gas intact on the catalyst surface.

The possibility of differentiating by this procedure between the physically adsorbed and the chemisorbed quantities of carbon monoxide led to other interesting results. On non-promoted iron catalysts, the chemisorbed amounts of CO are roughly equal to the physically adsorbed quantities of this gas, and both uptakes of CO are of the same magnitude as the amounts of nitrogen that are physically adsorbed by these catalysts. On promoted catalysts, however, the amount of chemisorbed carbon monoxide proved to be considerably smaller than the physically adsorbed quantity of the same gas. These observations led Emmett and Brunauer[45] to conclude that (1) the chemisorption of CO is selective and limited to that part of the catalyst surface that consists of metallic iron, and that (2) the surfaces of promoted iron catalysts are chemically disuniform and contain an unexpectedly small fraction of metallic iron. For instance, the surface of a catalyst promoted with 1.59 per cent of K_2O and 1.3 per cent of Al_2O_3 consisted of only approximately 40 per cent of metallic iron, the remaining 60 per cent of the surface being covered with promoter. The fact that a few weight per cent of promoter cover 60 per cent of the catalyst surface confirms and supports with quantitative data the qualitative evidence gained from x-ray studies that the promoter oxides accumulate on the surfaces of the iron crystallites.

Similar adsorption studies of Emmett and Brunauer[45] with *carbon dioxide* showed that this gas is selectively chemisorbed at −78° by alkali containing catalysts. This chemisorption of CO_2 can be used, in its turn, as an indicator of the amounts of alkali oxide present in catalyst surfaces. Using this technique, Emmett and Brunauer were able to show that the surface of a catalyst containing approximately one weight per cent of K_2O is covered to about 50 per cent with K_2O. In confirmation of the conclusion that CO is chemisorbed on iron and CO_2 on the alkali promoter, the volume of carbon dioxide, chemisorbed on a promoted catalyst at −78°, if added to the amount of carbon monoxide chemisorbed by the same catalyst at −183° is approximately equal to the amount of nitrogen required to form a complete physically adsorbed monolayer over the entire catalyst.

In a later investigtion[21a], Brunauer and Emmett made a detailed study on how the various gases chemisorbed on iron catalysts influence each other. Whereas these authors conclude that in their chemisorbed states hydrogen and nitrogen are dissociated into atoms, they postulate that carbon monoxide and carbon dioxide are adsorbed as molecules on the iron atoms, and on the promoter molecules of the surface, respectively. In their studies of combined adsorption, Brunauer and Emmett made the further observation that a previous chemisorption of CO_2 on the alkali promoter in the catalyst surface diminishes the chemisorption of CO on the iron atoms, and that conversely, preadsorption of CO on the iron diminishes the chemisorption of CO_2 on the alkali. From this, the conclusion was drawn that the metallic sites and promoter sites intimately intermingle in the surface and that neither the metal nor the promoter form large coherent homogeneous patches.

Effects of Promoters on the Intrinsic Catalytic Activity of Iron. These experimental findings on promoted iron catalysts leave no doubt that amphoteric and acidic oxides of the alumina, silica, zirconia type if incorporated into metallic iron create and preserve large specific surface areas of the promoted catalysts. The composite surfaces, consisting of metallic iron intimately mixed with the promoter oxides, are effectively stabilized against sintering at high temperatures and against recrystallization in the presence of oxygen-containing impurities in the synthesis gas.

The creation of extensive and stable surfaces does, however, not explain all the effects that are observed with oxide-promoted iron catalysts. Rather, the added promoters modify profoundly also the *intrinsic catalytic activity* of the exposed iron, *per unit surface of this metal.* The following experimental facts speak clearly in favor of this conclusion:

(1) Within a series of promoted iron catalysts containing different types and amounts of promoters, no strict parallelism exists between their "metallic surface areas," as measured by CO-chemisorption, and their individual catalytic activities for the ammonia catalysis. Table 8 presented in this form by Nielsen[142] demonstrates this nonparallelism by means of comparative data on the activities, total specific surface areas, and specific "metallic areas" for a singly promoted, a doubly promoted, and an unpromoted iron catalyst, as measured by Brunauer, Emmett and Teller[22] and by Brunauer and Emmett[21a]. It is obvious from these findings that these three types of catalysts are characterized by considerably different intrinsic catalytic activities per unit of their metallic surfaces. The inference from the data listed in Table 8 is that alkali-oxide added to the singly promoted (Al_2O_3) catalyst causes a large increase of its catalytic activity per unit of its iron surface.

That no parallelism exists between specific surface areas and catalytic activities even for catalysts of very similar compositions, has recently been shown by Nielsen and Bohlbro[143] who investigated two triply (K_2O-CaO-Al_2O_3) promoted iron catalysts that differed only by the relative proportions of the added promoters. The more active of these two catalysts had a smaller specific total surface area (8.15 m^2/g) than the second catalyst (12.6 m^2/g) and also a smaller number of available iron sites as determined by the chemisorption of carbon monoxide. Thus, it can be stated that, generally, the activities of different types of promoted iron catalysts are neither proportional to their individual total surface areas, nor to their total "iron surfaces."

Additional indications for qualitative changes of a catalyzing iron surface brought about by a promoter were reported by P. Zwietering[184]. This author studied the catalytic activities of a series of singly promoted iron catalysts containing increasing amounts of Al_2O_3, and compared these activities with the total specific areas, as well as with the specific "iron surfaces" of these catalysts. Here again, the activities of these catalysts showed no proportionality with the specific total surface areas nor with the specific surfaces of exposed iron. Rather, their catalytic activities varied proportionally to the *percentages of free iron* contained in their surfaces. This seems to indicate that, in this particular series of catalysts, the activity controlling factor is the specific distribution of the free iron in the promoter layer coating the catalyst.

TABLE 8

Catalyst	Promoters	Activity % NH_3 at 450°, 100 atm. and S.V. = 5000	Surface Area (m^2/g)	Equivalent Iron Area (m^2/g)
954	10.2% Al_2O_3	8.2	13.2	5.1
931	1.59% K_2O 1.3% Al_2O_3	12.3	3.72	1.5
973	0.15% Al_2O_3 as impurity	3.3	1	1

(2) Differently promoted iron catalysts, besides their dissimilar catalytic activities for the synthesis of ammonia, show also deviations in their adsorptive properties and in their catalytic efficiencies for chemical conversions other than the ammonia synthesis.[102] These deviations point again to a qualitatively different character of their active surface areas.

Significant discrepancies of this type have been observed by Emmett, Brunauer and co-workers to exist between the singly (Al_2O_3) promoted and the doubly (Al_2O_3 + K_2O) promoted types of iron catalysts. Table 9 gives a condensed survey on the most characteristic differences between these two types of promoted iron catalysts.

According to this, the singly (Al_2O_3) and the doubly (Al_2O_3 + K_2O) promoted types of iron catalysts exhibit such drastic discrepancies in several of their properties that one has to postulate for these two catalyst types the

TABLE 9. IRON AMMONIA CATALYSTS

No.	Property of Catalyst	Singly Promoted with Al_2O_3	Doubly Promoted with $Al_2O_3 + K_2O$	Reference
1	Hydrogen chemisorbed at −195°C	Existence of a chemisorption, whose heat of adsorption exceeds that of physical adsorption, but is smaller than that of type A and Type B hydrogen chemisorption	Extremely small chemisorption at this temperature.	107
2	Exchange between chemisorbed H_2 and D_2 in gas phase	H_2 chemisorbed at −195° exchanges. Type A and Type B adsorbed H_2 does not exchange	—	107
3	Effect of H_2 previously chemisorbed at 100°C (Type B) on adsorption No. 1.	Considerable decrease of H_2 chemisorption No. 1	—	107
4	Capacity for ortho-para H_2 interconversion at −195°C.	Very Rapid (half time 0.06 seconds)	Rapid but slower than on singly promoted catalyst. (half time 0.4 seconds).	52
5	Effect of H_2 previously chemisorbed at 100°C (Type B) on interconversion of o-H_2 to p-H_2	No effect	Strong poisoning (retarded by a factor of 20)	107, 52
6	Capacity for H_2-D_2 exchange at −195°C	Quite fast (half time 3–10 seconds)	Extremely slow (half time about 6000 seconds)	107
7	Effect of previously chemisorbed N_2 on H_2 chemisorption at 100° (Type B)	Increase of Type B-H_2 chemisorption, indicating formation of NH- and NH_2-groups in adsorption layer	Substantial decrease of H_2 chemisorption	21a
8	Kinetics of ammonia decomposition	Increases with increasing temperature up to 400°C and above 425°. Independent of temperature between 400 and 425°. Rate of ammonia decomposition increases with P_{H_2} and decreases with an increase in P_{NH_3} ("reverse kinetics").	Uniform increase of decomposition rate with increase in temperature. Rate increases with P_{NH_3} and decreases with an increase in P_{NH_2} .	122, 123

existence of catalytic centers that differ not merely by their degree of activity but by their very nature and function. Although according to the hypothesis of induction (see p. 224), the energy levels and distributions of electrons in an iron catalyst would be affected differently by the presence of Al_2O_3 than by the presence of the combination ($Al_2O_3 + K_2O$), this is too general a deduction to permit a satisfactory explanation of the striking dissimilarities between the two catalyst types.

A Tentative Explanation of the Different Behavior of Singly and Doubly Promoted Iron Catalysts. In the following an attempt will be made by the writer to interpret the individual character of the singly and doubly promoted iron catalysts in more specific terms. It is suggested that the singly promoted catalyst, after having been effectively stabilized with a promoter-oxide of the alumina, silica, zirconia type possesses a surface composed of metallic iron intimately mixed with centers of a slightly *acidic* nature, originating from the added promoter-oxide. The hydrogen ions typical for the acidic function are probably provided by small amounts of water associated with the surfaces of these oxides, and with the interfaces formed between these oxides and the iron crystallites present in the surface. The specific effects produced by these acidic "adlineation centers" on the adsorptive and catalytic properties of the composite surface can be neutralized by the addition of K_2O or of related basic oxides as second promoters, thus creating a qualitatively different type of surface, and therewith another type of catalyst.

Whereas the "acidic properties" of silica-alumina combinations used as cracking catalysts in the oil industry are widely known[89, 152] attention has been drawn less frequently to the fact that pure alumina can also act as an "acidic" catalyst. Oblad, Milliken, and Mills[145] in discussing the amphoteric character of Al_2O_3 have pointed out that, given a specific lattice arrangement, γ-Al_2O_3 can assume acidic properties. Schuit[156, 184] and Rijnders[152] express the view that the catalytic effectiveness of certain preparations of pure alumina catalysts for acid catalyzed conversions such as the isomerization of *n*-butane are due to certain anomalies of the crystal structure of these catalysts, as indicated by the diffuse character of their x-ray diffraction lines. In agreement with this, Rijnders and deBaus have found a strong chemisorption of ammonia on a pure Al_2O_3 catalyst prepared from aluminum-isopropylate with an initial heat of adsorption of 30,000 cal/mole. The same heat of adsorption of ammonia on alumina was found at temperatures between 600 and 700°C by Kagan, Morozov and Podurovskaya[97].

According to Nielsen, the alumina present in an unreduced promoted iron catalyst on x-ray analysis shows signs of a disturbed lattice structure (see p. 229). In the reduced catalyst, it is present, according to Brill[18] in its γ-modification, partly in such fine dispersion that it is not detectable by x-ray diffraction. All this makes it quite likely that this promoter in the presence of small amounts of tenaciously retained water acts as an "acidic component" in its surface combination with metallic iron, imparting special adsorptive and catalytic features to the singly promoted catalysts. The same applies *a fortiore* to iron catalysts promoted with typically acidic oxides, such as SiO_2 and ZrO_2 .

Referring back to Table 9, several characteristics of the singly promoted catalysts are in good agreement with the concept that these catalysts exert the combined effects of metallic iron and of acidic centers on their surfaces. The capacity of the singly promoted catalyst types of chemisorbing hydrogen at $-194°$ in considerably larger amounts than the doubly promoted types (Table 9, No. 1) and of catalyzing, at this low temperature, the deuterium-hydrogen exchange, again in contrast to the doubly promoted types (Table 9, No. 6), can, perhaps, be correlated to the capacity of typically acidic cracking catalysts[89] of promoting the exchange reaction between adsorbed deuterated water and gaseous hydrogen. In this connection, mention may be made again of the observation of Emmett and Kummer[106] that considerable quantities of hydrogen are tenaciously held by iron catalysts promoted with oxides of the Al_2O_3 type, possibly in the form of water.

A second support for the assumed acidic character of the singly promoted catalysts is the formation, on these catalysts, of adsorbed NH-radicals or NH_2-radicals from previously chemisorbed nitrogen and successively adsorbed hydrogen (Table 9, No. 7). Pointing in the same direction are the abnormal kinetics shown by singly promoted iron, if used as a catalyst for the decomposition of ammonia (Table 9, No. 8). Emmett, in discussing these anomalies, has shown that they can be explained by assuming that NH- or NH_2-radicals are formed on this catalyst type as the initial products of adsorbed ammonia, and that these radicals are more firmly held and more resistant against a split into nitrogen and hydrogen than when formed on the surfaces of doubly promoted catalysts. This effect, being observed exclusively on the singly promoted catalyst, is in line with the strong poisoning effects of nitrogenous bases on acidic cracking catalysts[145].

A strong support for this hypothesis is that all the effects that are ascribed here to the "acidity" of the singly promoted catalyst (see Table 9, 2nd column) disappear as soon as sufficient amounts of alkali (such as K_2O) are incorporated into this catalyst, transforming it into a catalyst of the doubly promoted type. The "neutralization" by alkali of the catalytic effects characteristic for solid acidic catalysts is well known in the field of cracking catalysts in the form of "alkali poisoning"[145] as a result of which the activity of these catalysts for splitting and isomerizing hydrocarbon molecules is greatly impaired.

The most effective way of incorporating alkali into an ammonia catalyst is the inclusion, in the oxidic melt employed in preparing the iron-alumina catalyst, of sufficient amounts of alkali carbonates or of earth alkali-carbonates or oxides. However, it has been shown by Love and Emmett[123] that the characteristic kinetics of the doubly promoted catalyst for ammonia decomposition can be gradually obtained with a singly (Al_2O_3) promoted iron catalyst by means of adding alkali directly to the reduced catalyst. This effect was confirmed and complemented by Love and Brunauer[122] who showed that by soaking the catalyst, prior to its reduction, in increasing amounts of alkali, it was possible to effect the transformation from a catalyst with the kinetic behavior of the singly promoted type to that of a catalyst with the kinetic characteristics of the doubly promoted type. Obviously, the alkali or earth alkali ions added to the singly promoted catalyst replace, at the alumina-iron interfaces, most of the protons derived from water molecules closely associated with γ-alumina. In this way the singly promoted catalyst is "deacidified" without losing the surface stabilizing effecting of the alumina-type oxides. The partial or complete neutralization of the acidic character of the surface results in a more efficient catalyst for the ammonia synthesis, probably because intermediates of this synthesis such as NH- or NH_2-radicals are less firmly anchored, and therefore less stabilized on the "neutral" surface of the doubly promoted catalysts, and possibly, also because of a speedier desorption of newly formed ammonia molecules from the latter. It would be interesting to test the validity of this hypothesis by comparative measurements of the heats of adsorption of ammonia and of other nitrogenous bases on the singly and doubly promoted types of iron catalysts. As to alumina proper, Kagan, Morozov and Podurovskaya[97] have shown that addition of K_2O to alumina decreases *ceteris paribus* the adsorption of ammonia and diminishes its heats of adsorption by about one-third.

Additional Observations on Alkali-containing Iron Catalysts. Two more facts may be mentioned in connection with the alkali content of the doubly promoted iron catalysts. Frankenburger, Andrussow and Dürr[66] reported that a mixture of metallic iron and lithium combines with molecular nitrogen to form the stable compound Li_3FeN_2, a complex resembling potassium ferricyanide in its structure. No corresponding compounds were obtained with mixtures containing metallic K or Na instead of Li, but it is nevertheless interesting that the chemical inertia of metallic iron toward molecular nitrogen can be overcome in the presence of one of the alkali metals. The second effect to be briefly referred to relates to the extensive observations made by Kunsman[108, 109, 110], on the thermic emission from alkali-containing iron catalysts of ions and atoms of the alkali metals, and from catalysts containing alkaline earth oxides, of ions and atoms of these alkaline earth metals. This effect exceeds in magnitude the ordinary thermionic emission of inorganic salts; it becomes perceptible at about 400°C and increases steadily with increasing temperature. The liberation of free metallic potassium from promoted iron catalysts that are heated *in vacuo* or in hydrogen had been observed previously[14]. That a certain percentage of the alkali metals and of the alkaline earth metals evaporating from the catalysts is in an ionized state, is, according to Kunsman, due to the fact that the ionization potentials of the emitted alkali metals and alkaline earth metals are substantially smaller than the electron affinity of the surrounding catalyst surface.

There is no straightforward parallelism between this thermionic emission and the catalytic activity of the doubly promoted iron catalysts. As pointed out previously (p. 227) an iron catalyst that contains alkali as its sole promoter is a relatively inefficient ammonia catalyst. On the other hand, these iron-alkali and iron-alkaline earth combinations show thermionic emissions equalling those of doubly promoted catalysts. Renewed studies of this interesting effect may be indicated in view of the recently discussed theories centered around the electronic structure of solid catalysts (see p. 225).

In concluding this condensed discussion of the technically important iron catalysts for the ammonia synthesis, the hope may be expressed that further studies of their electronic properties, of their kinetic behavior toward ultrapure hydrogen-nitrogen mixtures and toward synthesis gas mixtures containing well known amounts of selected impurities and poisons may lead to a fuller explanation of their working mechanism.

Special Studies of Other Ammonia Catalysts. Compared with the intensive work carried out on the structure and specific properties of the iron-ammonia catalysts, only sporadic investigations have been made of the other technically less important catalysts.

As mentioned at an earlier point, tungsten and molybdenum catalysts contain, under the operating conditions of the high pressure synthesis, considerable amounts of "bulk nitride." In an earlier survey on ammonia synthesis[34] Emmett mentions a study of Roiter, Gaukhman and Leperson[155] in which these authors found no activated adsorption of nitrogen on Fe-Mo and Fe-MoO-Al_2O_3 catalysts, in contrast to the finding of Emmett and Brunauer[34] that an Fe-Mo (1:1) catalyst shows a large activated adsorption of molecular nitrogen.

For catalysts consisting of the metal pairs Mo-Ni, Mo-Co, and Mo-Fe, Mittasch and Keunecke[135, 136] were able to specify the essential conditions for making good catalysts from these metal combinations. Catalytic effects exceeding those of the individual single components of these metal combinations can be obtained only when by suitable methods of preparation (1) the two metals composing the catalysts form an intermetallic compound with each other, and when (2) the metal representing the "basic material" of the catalyst is present in excess of the intermetallic compound formed. In the systems Mo-Ni and Mo-Co, molybdenum has to be present in excess. In the system Mo-Fe, either molybdenum or iron can act as "basic material," depending on which one of the two metals is present in excess of the Mo-Fe compound formed in the catalyst.

Kinetics of the catalytic decomposition and synthesis of ammonia

Early Investigations. In their pioneer work Haber and his co-workers[80, 82, 83] studied the rate of the ammonia synthesis as a function of the pressure, temperature, space velocity and composition of the reacting gases when they are passed, in a tubular reactor, over a bed of the catalyst. These investigations were continued and expanded in the I. G. Farben Laboratories by Mittasch and associates, particularly in regard to the synthesis rates obtained with the newly developed technical iron catalysts. In later years, a series of detailed and thorough investigations of the variables determining the synthesis rates under technical conditions were carried out in this country at the Fixed Nitrogen Research Laboratory by Almquist and Crittenden[2], Larson and Dodge[117] and others. Although they were of decisive practical value for the industrial development of the ammonia synthesis, these early measurements of the synthesis rates did not lead to a simple interpretation of the kinetics of the catalytic process.

Kinetics of the Catalytic Ammonia Decomposition in Static Systems. Starting in 1910, but mainly in the years from 1915 to 1935, efforts were made in several laboratories to elucidate the mechanism of the ammonia catalysis by measurements in a static reaction system.

Experiments were carried out with the reacting gas mixture enclosed in a vessel containing the catalyst in form of an electrically heated wire at pressures equal to or less than one atmosphere. Since, at these pressures, the equilibrium between hydrogen, nitrogen, and ammonia is highly unfavorable for the formation of ammonia, all these measurements in static systems were limited to determinations of the rates at which *ammonia is decomposed* into its elements on different catalysts. A number of investigations of this kind are listed in Table 10.

Contrary to expectations, these studies did not reveal simple and consistent kinetics for the decomposition reaction. Rather, the results obtained in different laboratories showed significant discrepancies. For instance, the kinetic expression for the rate of the ammonia decomposition on a platinum wire as derived by Hinshelwood and Burk[92] differs in its dependence on the pressure and on the temperature from the rate expression obtained for the same system by Schwab and Schmidt[158]. Similar discrepancies exist between the kinetic equations derived by various authors for the decomposition rates of ammonia on tungsten wires.

Of the several factors that may underlie these inconsistencies, mention will be made of the following ones:

(1) The metallic catalysts used in these investigations, mostly employed in the form of electrically heated wires, probably differed considerably from laboratory to laboratory as to their chemical purity, surface structure, extent of outgassing, etc.

(2) At the relatively high ammonia concentrations used by most of the investigators, several of the metals studied as catalysts were bound to become nitrided with a simultaneous profound change of their surface structure. For instance, the heated iron and tungsten wires used by several authors must have reacted with ammonia, forming nitrided phases during most of these static decomposition experiments. Thus, these catalysts in the course of the experiments assumed states quite different from that in which iron and tungsten catalysts are present during the synthesis reaction.

TABLE 10. KINETIC INVESTIGATIONS OF CATALYTIC AMMONIA DECOMPOSITION IN STATIC SYSTEMS

Catalyst	Authors	Year	Reference
Quartz	M. Bodenstein and C. Kranendieck	1912	14
Quartz	C. N. Hinshelwood and R. E. Burk	1925	92
Quartz	J. A. Christiansen and E. Knuth	1935	27
Platinum	C. N. Hinshelwood and R. E. Burk	1925	92
Platinum	G. M. Schwab and H. Schmidt	1926	158
Tungsten	C. N. Hinshelwood and R. E. Burk	1925	92
Tungsten	G. M. Schwab	1927	157
Tungsten	C. H. Kunsman	1928/1929	111
Tungsten	R. H. Hailes	1931	88
Tungsten	W. Frankenburger and A. Hodler	1932	67
Tungsten	J. C. Jungers and H. S. Taylor	1935	96
Tungsten	R. M. Barrer	1936	3
Iron	G. Engelhardt and C. Wagner	1932	55
Iron, promoted	C. H. Kunsman, E. S. Lamar and W. E. Deming	1930	112
Molybdenum	R. E. Burk	1927/1928	26
Molybdenum	C. H. Kunsman	1928/1929	111
Copper	J. K. Dixon	1931	29a
Osmium	E. A. Arnold & R. E. Burk	1931	2a
Cerium	G. Bredig, E. Elöd, and A. Koenig	1928	17

(3) The rates of ammonia decomposition measured in a static system are not necessarily determined by the chemical processes that occur at the catalyst surface proper. Rather, within certain ranges of gas pressures and temperature, the over-all speed of the ammonia decomposition will depend on the rate at which ammonia reaches the catalyst, or on the rate at which

hydrogen and nitrogen diffuse away from it. The size and shape of the reaction vessel, and the temperature distribution within it, the geometrical dimensions and location of the catalyst, and other external factors have a bearing on the extent to which these transport processes may obscure the "surface kinetics" of the ammonia decomposition.

(4) Even when the observed reaction rates were free from any interference by transport processes, there remained another complicating factor. In a static system, containing a reacting gas mixture, the composition of the gas phase changes concurrently with the progress of the reaction with the result that continuous changes occur of the amounts of the reactants and reaction products adsorbed on the catalyst surface. During the course of a single decomposition run, the fraction of the catalyst occupied by adsorbed ammonia will continuously decrease. This represents a particularly serious complication inasmuch as on many ammonia catalysts the activity of the surface sites seems to vary considerably as a function of the fraction of the surface occupied. Since the accumulated reaction products hydrogen and nitrogen will cover the catalyst to an increasing extent, the numbers of catalyst sites available for the decomposition of ammonia molecules, the specific activities of these sites, and the degree to which they are blocked by the reaction products will change continuously during a decomposition run in a static system. The disentanglement of these superimposed effects greatly complicates the deduction of simple kinetic relations from the decomposition rates observed in static systems.

Even though the studies in static systems failed thus to give a clear picture of the kinetics of the ammonia catalysis, they yielded useful information in regard to the "chemistry" of the decomposition process. According to Frankenburger and co-workers[63, 67, 131, 134] a rapid first step of the ammonia decomposition on metal surfaces is the process $[NH_3 \cdot Metal] \rightarrow [NH \cdot Metal] + H_2$ which may be pictured either as a dehydrogenation of adsorbed ammonia yielding an adsorbed NH-radical, or as formation of a "surface imide" of the catalyst metal. This first step of the decomposition process was clearly revealed by the observation that ammonia adsorbed on metallic tungsten at temperatures as low as 150° yielded pure hydrogen in an amount roughly corresponding to the equation

$$[NH_3 \cdot Me] \rightarrow [NH \cdot Me] + H_2$$

When the temperature was raised to approximately 200°, additional quantities of hydrogen were evolved, corresponding to the step

$$2[NH \cdot Me] \rightarrow 2[N \cdot Me] + H_2$$

or, in other words, to the formation of a "surface nitride." The same mechanism of a stepwise dehydrogenation of adsorbed ammonia was suggested by Emmett as an essential act of the catalytic ammonia decomposition and, in its reverse form, of the catalytic synthesis reaction[38]. Taylor and Jungers[173] obtained additional evidence that, on the catalyst, the attachment of hydrogen to the chemisorbed nitrogen and its detachment therefrom occur much faster than does the adsorption and desorption of the nitrogen. These authors found that the *exchange reaction between deuterium and ammonia* occurs on active iron catalysts at room temperature, far below the temperature required for the complete decomposition of ammonia and for the synthesis of ammonia on the same catalyst.

Thus, the studies of the catalytic ammonia decomposition in static systems helped to prepare the ground for intensified explorations of the catalytic kinetics by other techniques.

Studies of the Kinetics in Flow Systems. *General Principle.* As mentioned before, the earliest measurements of the synthesis rates were made in flow systems, using compressed nitrogen-hydrogen mixtures conducted over a catalyst bed. Primarily, the purpose of these experiments was an evaluation of the most favorable conditions for the technical process rather than a scientific analysis of its kinetics. After this exploratory first period, no further extensive studies in flow systems were made either of the rates of ammonia synthesis or of its decomposition prior to about 1930. At that time, systematic investigations of the decomposition rates of ammonia in flow systems were taken up by Emmett and his associates in this country and by others in Germany and Russia. A list of publications dealing with the kinetics of the ammonia catalysis in flow systems is given in Table 11.

The method of passing the reacting gases continuously through a reaction tube containing the catalyst, and of accumulating the reaction products present in the gases leaving the catalytic reactor offers the following advantages for kinetic studies:

(1) Both the decomposition and the synthesis of ammonia can be followed quantitatively with a high accuracy, permitting rate determinations of the synthesis process even at low pressures.

(2) The decomposition and synthesis rates can be measured far from equilibrium, thus minimizing the extent to which these rates are modified by those of the "back-reaction."

(3) After steady conditions have been attained in a flow reactor, a well defined, constant surface fraction of the catalyst will remain the seat of the rate determining process except in the case of progressive poisoning of the catalyst surface.

(4) At steady state conditions, the concentrations of the reactants and of the reaction product at the catalyst surface will remain constant, a fact that eliminates many of the complications encountered during measurements in static systems.

TABLE 11. KINETIC INVESTIGATIONS OF CATALYTIC AMMONIA DECOMPOSITION, AMMONIA SYNTHESIS AND NITRIDE REDUCTION IN FLOW SYSTEMS

Catalyst	Authors	Year	References
	Nitride Reduction and Ammonia Decomposition		
Glass, iron, copper	E. Elöd and W. Banholzer	1926	32
None, reduction of iron nitride	A. Mittasch, E. Kuss and O. Emert	1928	137
Iron foil	E. Winter	1928	180
None, reduction of iron nitride	P. H. Emmett and K. S. Love	1933	54
Promoted and unpromoted iron	P. H. Emmett and S. Brunauer	1934	42, 41
Promoted and unpromoted iron	V. S. Finkel'shtein	1934	56
Promoted and unpromoted iron	I. A. Khrizman	1936	100
Promoted and unpromoted iron	M. Temkin and V. Pyzhev	1940	177
Promoted and unpromoted iron	K. S. Love and P. H. Emmett	1941	123
Promoted and unpromoted iron	K. S. Love and S. Brunauer	1942	122
Iron (Theory of)	S. Brunauer, K. S. Love and R. G. Keenan	1942	24
Review	P. H. Emmett	1946	36
	Ammonia Synthesis		
Iron	V. S. Finkel'shtein	1934	56
Promoted iron (Al_2O_3, Mo)	V. S. Finkel'shtein and Z. M. Ya. Rubanik	1935	60
Promoted iron (Al_2O_3, Mo)	V. S. Finkel'shtein and Z. M. Ya. Rubanik	1935	57
Promoted iron (Al_2O_3, Mo)	V. S. Finkel'shtein and Z. M. Ya. Rubanik	1936	58
Promoted iron (Al_2O_3, Mo)	V. S. Finkel'shtein and Z. M. Ya. Rubanik	1936	59
Promoted iron (Mo-Al_2O_3)	S.S. Gaukhman and V. A. Roiter	1938	73
Promoted iron ($Al_2O_3 \cdot K_2O$)	M. Temkin and V. Pyzhev	1939	178
Promoted iron ($Al_2O_3 \cdot K_2O$)	M. Temkin and V. Pyzhev	1940	177
Promoted iron ($Al_2O_3 \cdot K_2O$)	P. H. Emmett and J. T. Kummer	1943	53
Promoted iron ($Al_2O_3 \cdot K_2O$)	I. P. Sidorow and V. D. Livshits	1947	162
Promoted iron ($Al_2O_3 \cdot K_2O$)	A. Nielsen	1950	141
Promoted iron ($Al_2O_3 \cdot K_2O$)	M. Temkin, S. L. Kiperman and L. I. Lukjanova	1950	176
Promoted iron ($Al_2O_3 \cdot K_2O$)	H. de Bruijn	1950	20
Promoted iron ($Al_2O_3 \cdot K_2O$)	R. Brill	1951	19
Promoted iron	A. Nielsen and H. Bohlbro	1952	143
Promoted iron	A. Nielsen	1953	142

(5) The yields of products, even if small can be determined with considerable accuracy by accumulating over an extended period sufficient amounts of the products, stripping them from the exit gases (e.g., collecting ammonia by passing the gases leaving a synthesis reactor through aqueous acid).

In order to take full advantage of these favorable characteristics of flow systems for kinetic studies, the following precautions are essential:

(1) The reacting gases should pass through a relatively short catalyst bed. Otherwise, the change of the gas composition along the catalyst bed introduces similar, although less severe complications, as does the change of gas composition that occurs as a function of time, in a static reaction system.

(2) In the case of porous catalysts, such as the iron-ammonia catalysts (see pp. 231–233), the size of the catalyst particles has to be such that at a given reaction rate, diffusion processes do not become rate controlling. (See chapter 2, Volume II of this series for a detailed discussion of the influence of pore size on kinetics.)

Development of Kinetic Rate Expressions for the Synthesis and Decomposition Rates on Iron Catalysts. Numerous useful data were gathered from experiments carried out in flow systems by Emmett[7] and co-workers. These authors investigated systematically the kinetics of the decomposition of ammonia over unpromoted, singly promoted, and doubly promoted iron catalysts at different temperatures, pressures, and in the presence of varied amounts of excess hydrogen.

The most consistent rate expressions for this process, applicable over a relatively wide temperature and pressure range were established by Emmett et al. for the decomposition reaction as it occurs over *doubly promoted catalysts* (Al_2O_3-K_2O). The latter are, as pointed out previously, the prototypes of the catalysts used for the industrial synthesis process.

The rate of ammonia decomposition over these catalysts was found to increase with increasing partial pressures of ammonia, and to decrease with increasing partial pressures of hydrogen, according to the equation

$$-\frac{dp_{\mathrm{NH_3}}}{dt} = k\,\frac{p_{\mathrm{NH_3}}{}^{\alpha}}{p_{\mathrm{H_2}}{}^{\beta}}$$

where k is a constant for a given temperature, and α and β are also constants both smaller than unity, amounting to 0.50 to 0.60 for α, and 0.83 to 0.90 for β.

These fractional values of α and β indicate that the kinetics of the catalytic surface processes cannot be successfully expressed in terms of simple expressions valid for reactions of the "first" or "second" order, such as have frequently been observed for conversions in homogeneous liquid or gaseous systems.

A satisfactory derivation of the observed decomposition rates and a successful kinetic interpretation also of the synthesis reaction over doubly promoted iron became possible in connection with a theory proposed by Temkin and Pyzhev in 1940[177] and with the subsequent thorough discussion of this theory by Brunauer, Love and Keenan[24]. The latter authors were able to correlate both the general form, as well as certain numerical constants of Temkin's and Pyzhev's equations with experimental results previously obtained by Emmett and Brunauer[42] and by Love and Emmett[123] in their experimental studies of the adsorption of nitrogen on iron catalysts.

This important progress in the kinetic interpretation of the ammonia catalysis has been described in comprehensive reports by Emmett[36] and by Emmett and Kummer[53]. In these publications it is shown how the mathematical expressions for the decomposition and synthesis rates were derived by Temkin and Pyzhev and how the theory was further developed and correlated with nitrogen adsorption data by Brunauer and co-workers.

Other important contributions to the theoretical aspects of the rate equations have been presented by Brill[19] in connection with new measurements on synthesis rates. Nielsen[142] has surveyed the kinetic equation of Temkin and Pyzhev for the synthesis reaction, particularly in regard to their application for evaluating specific activity constants of a number of industrial iron catalysts of the doubly and triply promoted type.

It appears superfluous to tabulate here once more the various rate equations that are derived and presented in detail in these publications.

Instead, an attempt will be made here to sketch the general background of this promising new approach to the mechanism of the ammonia catalysis by pointing out the basic concepts which, clad in a mathematical form, led to rate equations that agree satisfactorily with the observed decomposition and synthesis rates of ammonia over a wide range of pressures, temperatures, and gas compositions.

These concepts are:

(1) The slowest, and therefore rate-controlling process of the catalytic ammonia *synthesis* is the *adsorption of nitrogen* on the catalyst. The slowest step of the catalytic ammonia *decomposition* is the *desorption of nitrogen* from the catalyst.

In earlier parts of this survey, the attention of the reader was repeatedly drawn to observations which indicate that the chemisorption of nitrogen and its simultaneous activation on the catalyst surface is the "most difficult" step among the successive processes which, in their over-all effect, lead to the formation of ammonia. Whereas the chemisorption of nitrogen requires a considerable energy of activation, the subsequent steps of its hydrogenation on the catalyst surface, and of ammonia desorption occur at a fast rate, requiring small amounts of activation energy. The same relations hold conversely for the ammonia decomposition in which the fast and easy acts of adsorption and successive dehydrogenation of ammonia are followed by the slow process of the desorption of nitrogen in the form of nitrogen molecules from the catalyst surface.

Beyond confirming the earlier concepts regarding the nature of the rate-controlling processes, the new kinetic studies made it clear that, at least with the doubly promoted iron catalysts, the adsorption of nitrogen in the synthesis reaction and its desorption in the decomposition reaction *remain rate controlling throughout a wide range of pressures, temperatures and gas compositions*. This range covers the ammonia decomposition at pressures between one-thirtieth and one atmosphere, as well as the synthesis reaction performed at pressures between one and 300 atmospheres, reaction temperatures from 300° to 450°C, and gas compositions that were varied in the decomposition runs from 3 to 6 for the H_2/NH_3 ratio, and in the synthesis runs, from 0.3 to 3 for the H_2/N_2 ratio.

(2) With the kinetics of the catalytic reaction reduced to those of the *nitrogen adsorption and nitrogen desorption on doubly promoted iron catalysts*, the mathematical derivation of the rate functions of these two processes requires a detailed knowledge of the adsorption system involved. As shown by Brunauer, Love, and Keenan, the rate equations proposed by Temkin and Pyzhev imply a *nonuniform state of the adsorbed nitrogen, characterized by a substantial decline of the differential heats of adsorption as the fraction of the catalyst surface, F, covered with adsorbed nitrogen, increases*. Since the heat of adsorption of nitrogen at a given coverage equals the difference between the activation energies required for its desorption (E_d) and adsorption (E_a), these activation energies, too, are obviously functions of the surface coverage F.

The variations, over the catalyst surface, of E_a and E_d very substantially change the rates at which nitrogen is adsorbed and desorbed at different surface coverages of the catalyst: Relatively small variations in the values of E_a and E_d cause considerable changes of the adsorption and desorption rates since the latter are functions of $e^{-E_a/RT}$ and $e^{-E_d/RT}$, respectively. Inasmuch as E_a and E_d, in their turn, depend on the catalyst coverage F, the latter parameter enters the rate expressions in the form of $e^{-f(F)/RT}$, with $f(F)$ being a function still to be defined in more specific terms.

(3) *The adsorption equilibrium between nitrogen in the gas phase and nitrogen adsorbed on the catalyst surface* is, of course, decisively influenced by the decline of the differential heats of adsorption q with increasing F values. Qualitatively speaking, a given increase Δp of the nitrogen pressure in the gas phase causes a much larger increase of adsorbed nitrogen at low pressures than at high pressures. Expressed in mathematical terms, the uptake of additional nitrogen by the catalyst increases, even in the range of weak adsorption, not proportionally to the nitrogen pressure p in the gas phase, but to p^m where $m < 1$.

There is increasing experimental evidence that many adsorption systems show this p^m dependence (Freundlich's isotherm), over a wide range of gas pressures. In this connection, we refer back to a previous section on adsorption studies (pp. 194 to 200). At extremely low pressures and at very high pressures, close to the saturation of the adsorption isotherms, the p^m relationship becomes meaningless, and limiting conditions have to be introduced into the equation for the adsorption equilibrium in order to describe these marginal sections of the isotherms. This has been pointed out by various authors and, for the special case considered here, by Brunauer, Love and Keenan[24]. It seems, however, that the nitrogen adsorption on doubly promoted catalysts lies, for all the conditions that have been employed in the past for experimental rate measurements, well within the p^m range of the adsorption isotherms.

(4) In their derivations, Temkin and Pyzhev assumed that the nitrogen adsorbed on the catalyst under decomposition or synthesis conditions is in *full equilibrium, not with the nitrogen pressure in the gas phase surrounding the catalyst, but with a "fictional nitrogen pressure P" that would exist in the gas phase if, in this phase, complete equilibrium were established between nitrogen and the actually existing partial pressures of hydrogen and ammonia.* This fictional nitrogen pressure P_{N_2} is easily evaluated by means of the equation for the gas equilibrium

$$K_T = \frac{(P_{NH_3})^2}{(P_{H_2})^3(P_{N_2})} \tag{1}$$

where K_T is the constant for the ammonia equilibrium at the temperature T. This postulate of Temkin and Pyzhev is a logical consequence of the concept outlined previously, namely, that all the processes that occur at the catalyst surface between chemisorbed nitrogen, hydrogen, and ammonia, proceed at very much faster rates than the desorption and adsorption of nitrogen. *This results in the establishment of full equilibrium between the adsorbed forms of hydrogen, ammonia and nitrogen with the gaseous H_2 and NH_3, whereas no equilibrium is reached between the adsorbed and the gaseous nitrogen.* Thus, these very acts of nitrogen adsorption and desorption become, due to their slowness, rate controlling for the overall reaction.

These in essence are the concepts from which the kinetic equations for the synthesis and decomposition rates have been developed. As shown by Brill[19], the synthesis rate at a given temperature can be expressed in its most general form by the equation

$$\frac{dp_{NH_3}}{dt} = k_1 \cdot p_{N_2}{}^3 \left(\frac{p_{H_2}{}^3}{P_{NH_3}{}^2}\right)^n - k_2 \left(\frac{p_{NH_3}{}^2}{p_{H_2}{}^3}\right)^{1-n} \tag{2}$$

where $n < 1$.

The numerical value of n in (2) depends on the mathematical relationship by which the differential heats of nitrogen adsorption on the catalyst q, the differential activation energies of nitrogen adsorption E_a, and the differential activation energies of nitrogen desorption E_d vary with the extent, F, to which the catalyst surface is covered with adsorbed nitrogen.

The following simple linear equations have been adopted for these relationships:

$$q = Q - (a + b)F \tag{3}$$

$$E_a = A + aF \tag{4}$$

$$E_d = D - bF \tag{5}$$

where Q, A and D are limiting values of the heat of adsorption, the activation energy of adsorption, and the activation energy of desorption, for extremely low surface coverages of the catalyst.

As can easily be seen, Eqs. (3) to (5) imply that increasing surface coverage of the catalyst causes a linear decrease of the adsorption heat and of the activation energy for desorption, and a linear increase of the activation energy for adsorption.

The exponents n and $(1 - n)$ in equation (1) are related to the constants a and b in equations (3) to (5) as follows:

$$n = \frac{a}{(a + b)} \tag{6}$$

$$1 - n = \frac{b}{(a + b)} \tag{7}$$

The measurements of Love and Emmett[123] yield a numerical value of about 0.3 for the value of $(1 - n)$ for the ammonia decomposition on a doubly promoted iron catalyst. Brill[19] by means of very precise measurements of synthesis rates on pure iron, and on singly and doubly promoted iron catalysts, came to the conclusion that these synthesis rates can well be expressed by means of Eq. (2) when the values of $n = 0.7$, and $(1 - n) = 0.3$ are substituted in this equation.

In their earlier work, Temkin and Pyzhev assumed equality of the constants a and b, an assumption that leads to $n = 0.5$. Whereas the observed rates of the ammonia synthesis, under technical conditions, agree fairly well with equation (2) containing the exponent $n = 0.5$, more consistent agreement between calculated and observed rates seem to be obtained by using in equation (2) the value $n = 0.7$ as proposed by Brill.

The graphs of Figures 7 and 8 may help to illustrate more clearly the interrelationships between the constants n, a, and b and their connection with the variations of q, E_a, and E_d as a function of F, the catalyst coverage with adsorbed nitrogen.

Both figures show the changes of q, E_a and E_d in the range from a low coverage F_1 of the catalyst, to a denser coverage F_2, under the assumption that the linear Eqs. (3) to (5) hold for all coverages lying between F_1 and F_2.

The values of Q_0, A and D, and the decrease of the differential adsorption heats q in both graphs are identical. The decrease of E_d and the increase of E_a are, however, different in both cases, inasmuch as Figure 7 represents the special case $a = b$ (or $n = 0.5$, Temkin's equation), and Figure 8, the special case $a = 2.3b$ (or $n = 0.7$, Brill's equation). The more pronounced relative increase of E_a with decreasing q, in the latter case is, according to Brill, reasonable. It means, according to him that the "depth of the potential of the chemisorption of nitrogen varies less than the height of the potential wall which has to be overcome if activated adsorption occurs."

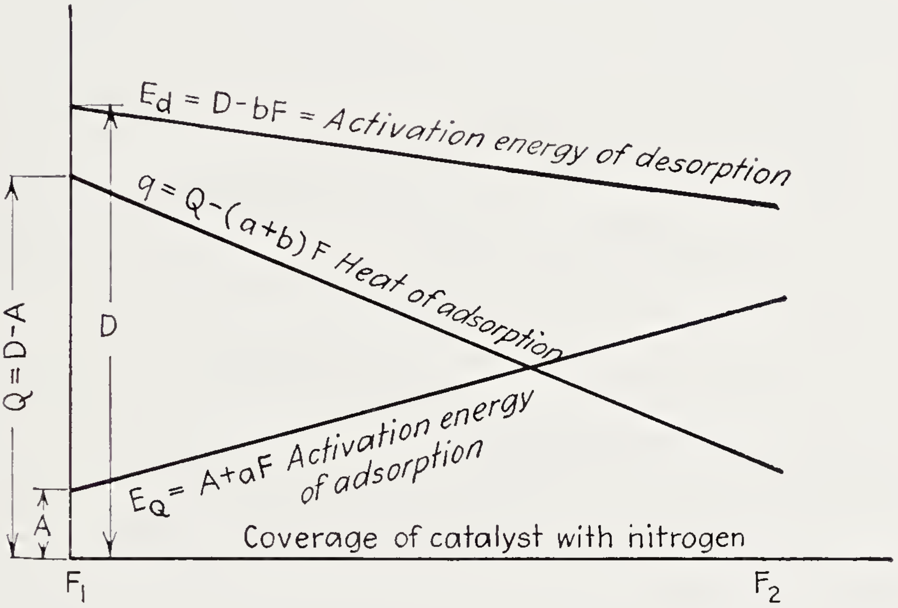

Figure 7. Heats of adsorption and activation energies for adsorption and desorption, as function of catalyst coverage.
Case a = b

The following correlations strongly support the concept that the rate at which nitrogen is being adsorbed on the catalyst and desorbed from it control the catalytic synthesis and decomposition of ammonia:

(a) Brunauer, Love and Keenan[24] derived a general equation for the rate of nitrogen adsorption on doubly promoted iron, using as a basis the measurements by Emmett and Brunauer[42].

(b) Using the numerical contents of this rate equation, the same authors developed a general formula for the adsorption isotherm of nitrogen on the catalyst in good agreement with the observed adsorption equilibria.

(c) The constants appearing in these equations were used for setting up a quantitative expression for the rate of ammonia decomposition, and this equation yields values that agree closely with the decomposition rates measured directly by Love and Emmett[123].

(d) The apparent activation energy of the catalytic decomposition of ammonia as derived from the observed temperature coefficient of this process is in satisfactory agreement with its theoretical value, calculated from the activation energy of nitrogen adsorption on the catalyst, the heat of this adsorption, and the heat of formation of ammonia.

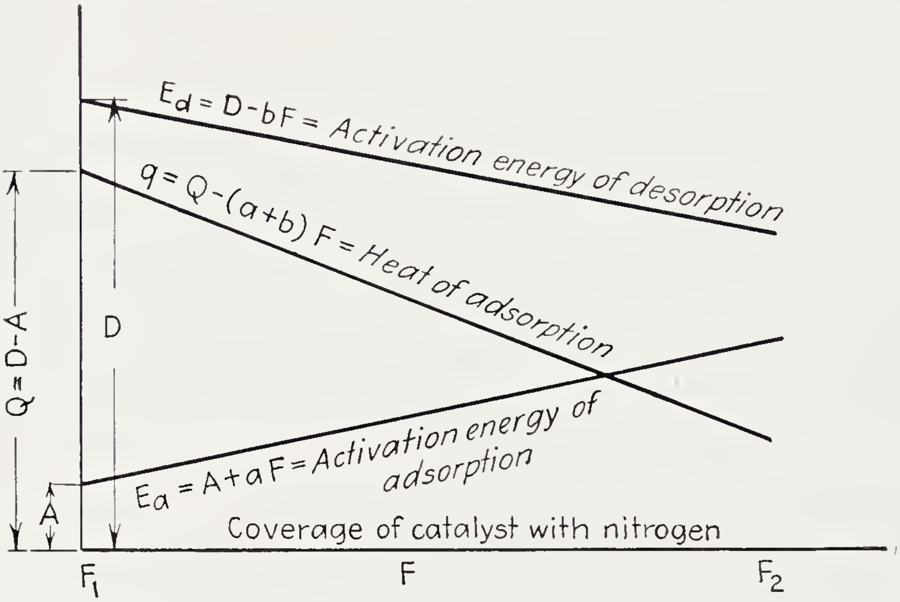

Figure 8. Heats of adsorption and activation energies for adsorption and desorption as function of catalyst coverage.

Case a = 2.3b

Residual Problems. The derivation of these rate equations for the synthesis of ammonia over doubly promoted catalysts is a gratifying achievement both for the theorist and the experimental worker in the field of surface catalysis. The applicability of these equations over a wide range of synthesis conditions proves the validity of their theoretical background and invites a deeper penetration into this background.

There are still several unsolved problems inherent in the kinetic analysis which represents a challenge for future investigators of the mechanism of the ammonia catalysis:

(1) Absolute reaction rates. As pointed out in the preceeding text, the synthesis rate at a sufficient distance from equilibrium is exclusively con-

trolled by the rate at which nitrogen becomes chemisorbed at the catalyst surface under the conditions prevailing in the reaction system. The equation for the synthesis rate far from equilibrium (i.e., the minuend of equation (2) (p. 249) expresses correctly the dependence of this adsorption rate on the nitrogen pressure and on the coverage of the catalyst with pre-adsorbed nitrogen.

The only empirical factor in the rate equation is the constant k_1 which is needed for expressing the rate of nitrogen adsorption in absolute terms. The question may be asked whether there is a way to derive the numerical value of this constant from our present theoretical picture of the synthesis reaction. In connection with their measurements of the rate of nitrogen chemisorption on iron ammonia catalysts, Emmett and Brunauer pointed out that the actual rate of this adsorption process is slower by a factor of approximately 10^6 than the adsorption rate calculated on the assumption that every nitrogen molecule that possesses the necessary activation energy will be chemisorbed when it strikes the catalyst surface.

Similar discrepancies between experimental and calculated rates of activated adsorption and desorption processes have been reported by other investigators. Taylor[172] has pointed out that the observed rate by which hydrogen is chemisorbed on a surface of zinc oxide is very much lower than the rate calculated on the assumption that every hydrogen molecule striking this surface with an energy equal or larger than the activation energy of adsorption becomes permanently attached to the zinc oxide.

On the other hand, the desorption rates that have been observed for several systems appear to exceed substantially the desorption rates calculated in the usual way. It is commonly assumed in these calculations that the adsorbed molecules vibrate with a certain frequency $\nu = \frac{KT}{h} = 1.10^{12}$ to 1.10^{14}, and become desorbed as soon as they are endowed with the activation energy required for the act of desorption. Davis[28] has shown that chemisorbed nitrogen leaves a tungsten surface at a much higher rate than at the rate calculated in this conventional way. Similarly, unpublished calculations of Frankenburg on the kinetics of hydrogen adsorption and hydrogen desorption from tungsten[61] have led to the conclusion that the rates of adsorption are considerably slower, and those of desorption, faster, than the calculated rates for both processes.

These discrepancies between the calculated and observed rates for adsorption and desorption of gases on solids suggest that an important factor has been overlooked in the frequently employed calculations of adsorption rates and desorption rates which follow the simple lines mentioned above. In his recent treatises on reaction kinetics including the kinetics of catalytic conversion, Eyring and co-workers[78] as well as Kemball[98] have pointed to the necessity of including in any theoretical equation of a chemical reaction rate, the *changes of entropy* associated with the process under consideration. The well known fact that every chemical equilibrium between two systems depends not only on the energy difference ΔE, but also upon the entropy difference ΔS between these systems, and the rule that the rates of the forward and backward reaction at equilibrium are equal, lead to the following conclusions: Every complete mathematical expression for a reaction rate ought to contain not only a factor $e^{-\Delta E/RT}$, designating the fraction of molecules endowed with the necessary energy to enter the reaction, but also a factor $e^{\Delta S/R}$, designating the probability that the reactants undergo the specific change of entropy associated with the reaction. Thus, a more intimate knowledge of the entropy of adsorbed, and particularly of chemisorbed molecules is an essential requisite for a deeper theoretical penetration into the kinetics of catalytic surface processes.

Generally speaking, adsorbed and particularly chemisorbed molecules will be considerably lower in entropy than the same molecules in the gaseous state. This means that the rate of adsorption will be lower, and the rate of desorption, higher than the rates calculated by means of the conventional equations.

A detailed investigation of the entropy changes associated with the chemisorption of hydrogen on a tungsten surface indicate that these entropy changes, just as the differential heats of adsorption, vary substantially with increasing coverage of the tungsten surface, indicating that the state of the chemisorbed hydrogen is greatly influenced by the composition of the surface layer to which it is added as an additional increment.

Renewed precision measurements of the adsorption equilibria and of the rates of adsorption and desorption for the nitrogen chemisorption on doubly promoted iron catalysts beyond the range explored by Emmett and Brunauer would throw more light on this important question.*

The specific mechanism by which entropy changes influence the rate of adsorption and desorption can be envisaged in several ways. One conceivable way of interpreting their mutual relationship is to assume a two-step mechanism for the acts of adsorption and those of desorption, by postulating as the first act of adsorption an attachment of the nitrogen molecules in a short-lived kind of "physical" adsorption at the surface, followed by a process of dissociation of the nitrogen molecules after which the nitrogen atoms are held in a more permanent state of chemisorption.

A satisfactory solution of this fundamental question would be an important contribution toward a more complete understanding of the ammonia catalysis, and of other surface catalyses as well.

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* *Editor's note:* Such measurements have recently been made by P. Zwietering and J. J. Roukens (*Trans. Faraday Soc.*, **50,** 178 (1954), and are discussed in Chapter 7).

(2) The influence of the catalyst coverage on the reaction rates. As pointed out on p. 251, a satisfactory kinetic expression for the catalytic synthesis and decomposition of ammonia was derived by postulating linear decreases of q and E_d, and a linear increase of E_a with increasing F. The question to what extent this linear rule is confined to a limited range of the adsorption isotherm will not be discussed here since apparently this range extends far enough so as to control the rates of nitrogen adsorption and nitrogen desorption under the usually employed conditions of the catalytic ammonia synthesis and ammonia decomposition.

Brunauer et al.[24] suggested that the variations of the differential heats of adsorption of nitrogen and of the activation energies of its adsorption and desorption over the catalyst surface can be explained by assuming (a) that the *surface is heterogeneous*, or (b) that there are, even *on an entirely homogeneous surface, forces of attraction or repulsion between the adsorbed particles.* To this we may add a third possibility, (c) that *previously adsorbed particles influence the entire catalyst and particularly its surface* in such a way that it exerts forces of attraction or repulsion toward nitrogen molecules from the gas phase different from those exerted by the completely bare surface.

As to details of this "induced heterogeneity" or "transmitter effect," reference is made to the earlier section on Induction Effects (pp. 224 to 226).

Without much more experimental evidence, it is difficult to decide for or against any one of these three possibilities. It may be mentioned, however, that the following considerations point more into the direction of hypothesis (b) or (c) than that of (a).

An *a priori* heterogeneity of the catalyst surface as postulated by this latter hypothesis is usually correlated to particular features of its submicroscopic structure. It is commonly assumed that the latter varies, depending on the specific mode of preparation and on the pretreatment of the catalyst. Accordingly, differently prepared samples of the same iron-ammonia catalyst and *a fortiori* catalysts of different chemical compositions ought to have surfaces of different degrees of heterogeneity. This would mean, according to hypothesis (a) that the adsorption isotherms, the rates of nitrogen adsorption and desorption, and the rate equations for synthesis and decomposition would vary substantially among these individual catalysts. This conclusion, however, is contradicted by the results of Brill's measurements on the synthesis rate, at different flow velocities over (1) pure and exhaustively reduced metallic iron, (2) a singly promoted Fe-Al_2O_3 catalyst, and (3) a doubly promoted Fe-Al_2O_3-K_2O catalyst.

On these three catalysts, the synthesis rates at about 320°C were found to obey the general rate Eq. (2) on p. 249, with nearly identical values in all three cases for the exponent n and for the rate constant k_1. In the light of the presently accepted theory of the synthesis mechanism, this remarkable equality in the efficiency of the three iron catalysts means that the rate of nitrogen adsorption must be nearly the same on their surfaces. This again leads to the conclusion that the heats of adsorption and the activation energies for adsorption and desorption of nitrogen are the same for the three different surfaces and that they show, moreover, the same dependence on the extent to which the three surfaces are covered with adsorbed nitrogen. It is extremely unlikely that the surfaces of pure iron, of an iron-alumina catalyst, and of an iron-alumina-potassium oxide catalyst possess exactly the same structural surface heterogeneity as would have to be the case if we accept hypothesis (a). Rather it appears that a more general phenomenon underlies the astonishing identity of the kinetics observed with the three catalysts.

Both the hypotheses (b) and (c) are of a more general character. Of these two, the concept of induced heterogeneity (c) seems to fit the observations somewhat better than that of interaction among the adsorbed particles (b), for the following reasons: (1) At very low coverage, interaction between adsorbed particles ought to be considered to be less pronounced than at high coverage. This is difficult to reconcile with the fact that the linear dependence of the adsorption heats and activation energies starts within the range of low surface coverage. (2) In the adsorption system consisting of the iron catalyst and nitrogen the changes of the differential adsorption heats and of the activation energies for adsorption and desorption with increasing nitrogen coverage of the catalyst surface are in no way influenced by the extent to which the surface is covered with adsorbed hydrogen and ammonia. This insensitivity of the energetics of nitrogen adsorption toward the presence of chemisorbed particles is difficult to reconcile with the interaction hypothesis (b).

The hypothesis of "induced heterogeneity" (c) is based on the concept that chemisorbed particles, especially particles exerting a high affinity to electrons, disturb the electron distribution within the adsorbent to such an extent that, even at a considerable distance from the chemisorbed particle, the surface of the adsorbent exerts weaker forces toward newly arriving particles of the adsorbate. Such a "transmitter" effect will operate even at very low surface coverages. Since this induced heterogeneity is chiefly caused by the specific electron affinity of the adsorbed molecular species, it is conceivable that certain adsorbates of a relatively low electron affinity such as hydrogen or ammonia will induce very little or no heterogeneity in the metal surface, whereas nitrogen or to a still larger extent highly electronegative particles such as oxygen atoms can be expected to weaken very substantially the adsorption potential and the rates of adsorption on the remaining free surface fraction of the metal.

Following this concept, the strong poisoning action of very small amounts of oxygen on iron ammonia catalysts becomes understandable without the necessity of postulating an *a priori* heterogeneity of the catalyst surface. For their final analysis, the energetics of nitrogen adsorption on iron will have to be studied more closely, both by additional measurements and by subjecting them to a deeper searching theoretical approach.

It can be expected that the concept of "induced heterogeneity" will become clearly defined and receive better support by future experimental work. There are indications that thorough studies of the electric conductivity and of the thermionic and photoelectric properties of catalyst surfaces, and of the changes of these parameters in the presence of chemisorbed gases will contribute valuable evidence to our understanding of surface catalysis.

Efforts to coordinate these physical phenomena with surface catalysis have been made in the past: In an early investigation by Brewer[17a] on the effect of adsorbed gases on the photoelectric emissivity of iron and platinum, substantial changes of the photoelectric effect were observed on iron surfaces, depending on the extent to which these surfaces were covered with adsorbed hydrogen, nitrogen, and ammonia. Characteristically, adsorption of oxygen depressed the photoelectric emission from the iron surface almost completely. Renewed and refined investigations of this and related types may shed more light on the influence exerted by chemisorbed particles on the electronic characteristics of catalyst surfaces.

(3) *Kinetic characteristics of other ammonia catalysts.* Whereas the technical types of ammonia catalysts as represented by the doubly and triply promoted iron catalysts have been used for a considerable number of kinetic studies, relatively few investigations have been carried out with the simpler types of iron catalysts, and with catalysts containing, as their main component, metals other than iron such as molybdenum, tungsten, or osmium.

As mentioned above, the kinetics of the ammonia synthesis carried out at one atmosphere pressure and approximately 320°C were found by Brill[19] to be essentially the same on pure iron, on an iron catalyst containing 3 per cent Al_2O_3, and on an iron catalyst containing 3 per cent Al_2O_3 and 2 per cent K_2O. It must be added, however, that this catalytic activity of pure iron is observed only after a very thorough reduction of this catalyst, and that the latter is much more easily poisoned than the promoted types.

In apparent contradiction to these observations by Brill are the findings of Love and Emmett who stated that the kinetics of *ammonia decomposition* are very different over iron catalysts promoted with Al_2O_3 only, from those obtained with a doubly promoted ($Al_2O_3 + K_2O$) catalyst. It must be considered, however, that the nitrogen adsorption on the catalysts in Brill's synthesis experiments were very much smaller (partial nitrogen pressure = ¼ atm.) than those employed in Love's and Emmett's decomposition experiments[123] in which the "fictional nitrogen pressures" calculated from the gas equilibrium for ammonia formation amounted to at least several hundred atmospheres. Thus, under the experimental conditions employed by Love and Emmett, the catalysts were undoubtedly covered to a very much higher degree with chemisorbed nitrogen than under the conditions employed by Brill.

Love and Emmett suggested, as a possible picture for the peculiar kinetics of ammonia decomposition over a singly promoted $Fe_2 \cdot Al_2O_3$ catalyst that on this catalyst an accumulation occurs of NH radicals, or of NH_2-radicals, and that the dehydrogenation of these radicals to chemisorbed nitrogen and hydrogen constitutes the slowest step of the successive acts of decomposition rather than the desorption of nitrogen from the catalyst. It was suggested in an earlier section of this survey (pp. 237–238) that singly promoted iron catalysts have an "acidic" nature, and that the lifetime of adsorbed basic radicals such as NH or NH_2 on the surface of these catalysts is probably much longer than it is on the doubly promoted "neutralized" catalysts. This possibly explains the anomalous kinetics of the decomposition reaction, particularly in a range in which the decomposition products of ammonia densely cover the catalyst surface. Love's and Emmett's studies indicate that at higher temperatures the decomposition kinetics over the singly promoted catalysts gradually assume the characteristics of the kinetics found for the doubly promoted types. In this higher temperature range, the split of the NH_2- or NH_2 radicals into chemisorbed nitrogen and hydrogen may have been accelerated to such an extent that the desorption of nitrogen becomes the slowest, rate-controlling step.

CONCLUSION

From the preceding survey, we may conclude that our knowledge of the working mechanism of the ammonia catalysis has made a slow but steady progress. The "chemistry" of this mechanism has become fairly clear, and the kinetics of the overall process as it occurs in the presence of certain catalysts has been successfully analyzed. This, however, does not mean that a full explanation of this catalysis has been attained. There is still no completely satisfactory answer to the challenging question as to why certain metals are highly superior to others in their catalytic activity for the ammonia synthesis. Equally obscure are the peculiar energetics and kinetics of the chemisorption of nitrogen on the catalyst surface.

There can be no doubt, however, that the past studies of the ammonia catalysis have prepared the ground well for new and more deeply probing investigations. Due to its relative simplicity, the catalytic ammonia synthesis presents a particularly attractive and promising subject which may well serve as a "test case" for future progress in the exploration of surface catalysis.

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CHAPTER 7

RESEARCH ON AMMONIA SYNTHESIS SINCE 1940*

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INTRODUCTION

During the past fifteen years, hence since about 1940, various experimental methods have been developed which give far more detailed information about the structure and texture of catalysts than had been available before. Methods for estimating the surface areas available for adsorption, for determining the total pore volume of catalysts and for estimating the width of the capillaries have resulted in a general realization that the microporous structures of catalysts play a far more dominant role than previously suspected. It will be clear that this development has also influenced strongly the research on ammonia synthesis since 1940.

Experiments have been performed to learn how the porous iron structure is formed by reduction of the oxide, and how it could be made relatively stable at the working temperature of ammonia catalysis by the addition of some nonreducible metal oxides, empirically known already as "promoters". The ways in which these promoters are distributed have been investigated. The pore structure has been studied and the total area of the catalyst available for physical adsorption and the free iron surface available for chemisorption of nitrogen and hydrogen have been estimated. The chemisorption itself of both nitrogen and hydrogen and the rates of chemisorption have been studied as well as the mutual influence of the two gases. Kinetic experiments on the synthesis reaction and the decomposition reaction of ammonia have been made.

The porous structure of the iron catalyst depends on the composition of the magnetite and on the method of reduction. The available surface area of the catalyst depends on the porous structure; its thermal stability on its composition, which also determines the free iron surface. The extent of chemisorption depends on the free iron surface area, and the rate of chemisorption on the character of the surface and on the porous structure. The rate of the synthesis reaction may be determined either by one of the chemi-

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* Introduction and concluding remarks by J. H. de Boer and D. W. van Krevelen.

cal reaction steps alone or by the rates of the diffusion of the gases into and out of the porous structure.

The above will have made it clear that the study of the porous structure and the consequences of this structure has formed a central theme of the investigations in the ammonia catalysis during the last fifteen years. It is understandable, therefore, that this study will constitute a prominent part of this chapter about the research on amonia synthesis since 1940.

This chapter has been composed by a few research-workers of the physicochemical department of the Central Laboratories of "Staatsmijnen" (State Mines) in the Kingdom of the Netherlands. These research-workers have, themselves, performed many investigations in the field of this synthesis and many of their results are being published in this chapter for the first time. Until a few years ago this physicochemical department was headed by Dr. H. de Bruijn, who at the present time is engaged in other work. He and his successor, Dr. C. van Heerden, have had a very stimulating influence on the research work done in this department.

Of the various topics of this chapter, those related to the structure and the texture of the catalyst have been treated by Dr. R. Westrik. The chemisorption part has been written by Mr. P. Zwietering, the kinetics by Dr. C. Bokhoven, whilst Dr. C. van Heerden dealt with the influence of internal diffusion problems. It goes without saying, however, that the collaboration of this team of authors has resulted in a strong mutual influence of all of them on each part of the chapter.

Pages 268–286 deal with the structure and the texture of the catalyst. The iron catalyst is practically always made by reduction of magnetite, Fe_3O_4 , to which some small amounts of other oxides (promoters) are added. The discussion clearly shows that it must be considered possible that different ways of preparing the magnetite-phase may yield different products. One of the most important promoters, Al_2O_3 , may or may not be dissolved completely. Depending on the ratio between three-valent and two-valent metal ions, one, or sometimes even two FeO-phases may exist beside the Fe_3O_4-phase. It is obvious that the reduction products may show different properties in those cases. The way the reduction process is carried out also influences the properties of the catalyst greatly. During this process the large surface on which the catalysis takes place has to be formed and its character and composition have to be developed.

It is very important to know that after reduction the resulting iron granules have the same volume as the original magnetite particles. From a crystallographic point of view it is interesting to learn that an ionic structure, the lattice of which is completely determined by a closely packed arrangement of the oxygen ions, yields, on reduction, hence on removal of all these structure determining oxygen ions, a porous assembly of iron of exactly the same volume and shape as the original magnetite. As found by Westrik and Zwietering[1] the crystal particles of α-Fe formed by this reduction show a remarkable orientation predetermined by the original magnetite crystal. The outer surfaces, found to be 111-planes, provided sintering and/or recrystallization processes have not disturbed the original orientation too seriously, are parallel to the 111-planes of the original magnetite. The pseudomorphism is, therefore, not restricted to the outer form only; there is also a micropseudomorphism which causes specific iron-surfaces to form the outer surface of the catalyst.

It is obvious that such a porous assembly must possess many holes and cavities and—at first sight—one may be inclined to expect an adsorbing surface of great heterogeneity. A supposed heterogeneous character of the surface of the catalyst is often held responsible for many features in catalysis. The experimental fact that the heat of chemisorption decreases substantially with an increasing degree of coverage is, in the literature, ascribed either to a heterogeneous character of the surface, or to a mutual repulsion of the adsorbed atoms. It is for this reason that the theoretical considerations on adsorption on heterogeneous surfaces are included (pages 288–294). The adsorption on homogeneous surfaces and the influence of a mutual repulsion of the adsorbed atoms is also treated. A subsequent discussion shows that neither of these possibilities can explain the experimental facts. The solution has to be found in the gradual change of the work function of the metal by the adsorbed atoms, as was pointed out by Boudart[2], following a treatment of the adsorption of metal ions on metal surfaces by one of the authors of these introductory remarks[3].

The experimental data for the adsorption of hydrogen and nitrogen are also given on pages 299–317. There was a time when chemisorption and activated adsorption were taken as identical phenomena. However, recently there has been a tendency to deny the activated character of chemisorption and many investigators believe that the dissociative chemisorption of hydrogen on a pure metal surface does not require an activation energy. The dissociative chemisorption of nitrogen, however, undoubtedly requires an appreciable amount of activation energy. This activation energy determines the rate of the nitrogen chemisorption which, in all practical cases, is determinative of the rate of the ammonia synthesis.

The activation energy for the chemisorption of nitrogen increases with a rise in the degree of coverage, whereas, as already mentioned, the heat of adsorption decreases. The adsorption phenomena, consequently, are not in agreement with Langmuir's conceptions. The adsorption isotherm is well described by an equation given by Temkin[4] who performed many important investigations in this field.

The importance of Temkin's work becomes even more obvious from the discussion dealing with kinetic problems (pages 317–343). The choice of the year 1940 as the starting point for the present review may even be defended by the fact that the fundamental work of Temkin and Pyzhev[5] was published in that year. The discussion on kinetics of ammonia synthesis starts, therefore, with an outline of the principles of what is now known as the Temkin theory, and is followed by experimental data of the ammonia synthesis as well as of the decomposition of ammonia. The experimental data must in many cases be corrected for internal diffusion retardations occurring in the pores of the catalyst granules. The great importance of this influence of the porous catalyst structure has induced the authors to end with a condensed treatment of these internal diffusion problems.

Structure and Texture of the Catalyst

To obtain a correct and comprehensive picture of the structure and texture of the iron catalyst for the synthesis of ammonia, it is desirable to study the various stages of its preparation because these are known to have an influence on its catalytic properties. This influence is mainly bound up with structural factors.

All over the world the iron catalyst for ammonia synthesis is prepared in substantially the same way. Pure iron is burnt to magnetite which, together with small amounts of promoter components, is fused electrically. Sometimes natural magnetite is also added (Bridger, Pole, Beinlich and Thompson[6]). After the melt has been allowed to cool it is crushed to the desired size. Subsequently, the particles are loaded into the ammonia synthesis column and reduced to α-Fe, the active constituent of the catalyst.

The promoters, consisting of metal oxides of a high melting point, are not reduced by this treatment. The favorable effect of the promoters can be ascribed either to the stabilizing of the large accessible surface area or to increasing the specific activity of the catalytic surface.

Unreduced Catalyst

To find out in what manner the promoters are distributed over the magnetite phase, the crystal structure of the magnetite should first be subjected to a closer examination.

Verwey and de Boer[7] and Verwey and Heilmann[8] found that magnetite possesses a spinel structure which should be considered as a cubic close packing of O-ions. Among these O-ions there occur two types of interstices, viz., octahedral and tetrahedral ones. In the elementary cell of a spinel, which contains 32 O-ions, 16 octahedral and 8 tetrahedral interstices are available to the metal ions. With spinel itself, $MgAl_2O_4$, the octahedral interstices are occupied by Al^{+++}, the tetrahedral by Mg^{++}. In the case of magnetite the situation is somewhat different; half of the Fe^{+++} ions are held in the tetrahedral interstices, the other half, together with an equally large number of Fe^{++} ions, being statistically distributed over the octahedral ones. This statistical distribution of Fe^{+++} and Fe^{++} over crystallographically equivalent sites is conducive to the good semiconductive properties of this oxide which are taken advantage of in the fusion process.

The iron ions may be substituted by others without causing a change in the crystal structure. In this case it is necessary, however, that the substituting ions should meet certain requirements as regards valency and size. It will be clear therefore that certain metal ions, such as Al^{+++} and Mg^{++}, can be homogeneously distributed over the magnetite lattice. This was already known from the experiments of Wyckoff and Crittenden[9]. In this way the promoter (Al_2O_3 or MgO) is excellently distributed throughout the magnetite phase with the result that the large internal surface area of the porous iron phase, obtained after reduction, is preserved. This property of the promoter has become apparent from X-ray patterns taken in the aforementioned experiments and was afterwards confirmed by Brill[10] and by Nielsen[11].

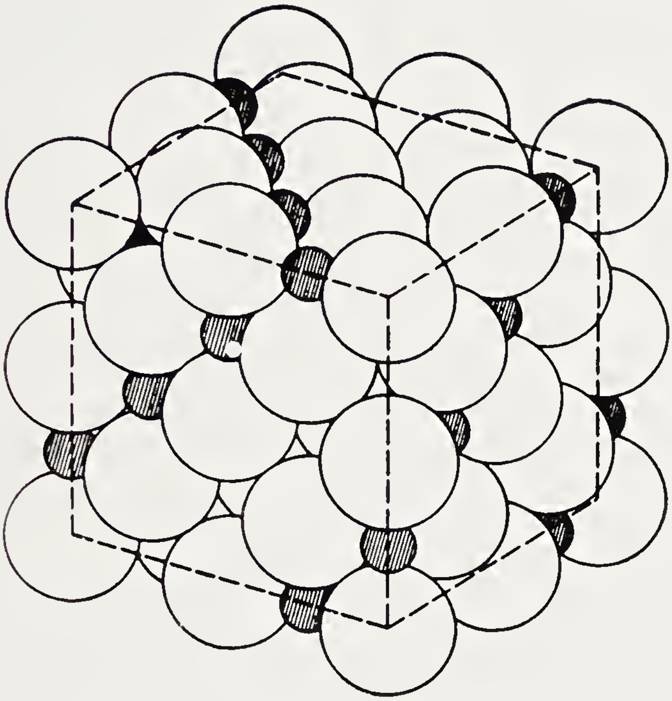

Figure 1. Crystal structure of magnetite. Large open circles: oxygen ion; medium-sized hatched circles: Fe^{3+} and Fe^{2+} in octahedral interstices; small black circles: Fe^{3+} in tetrahedral interstices, only one ion is visible. (Verwey and Haayman[12])

Moreover, X-ray patterns of magnetite phases in which the ratio of ferrous to ferric ions is higher than 0.5, appeared to contain FeO-lines (Verwey and Haayman[12]). X-ray examinations of a promoted unreduced catalyst possessing a similar composition but containing such an amount of Al_2O_3 as approximately corresponded to the excess of FeO, did not reveal FeO-lines; this points to the formation of the spinel $FeAl_2O_4$ in solid solution with Fe_3O_4 .

It will be evident that in order to insure a proper mixing, the fused mass of catalyst must be kept in the liquid state for some while. Moreover, there are indications that the rate of cooling is also an important factor[11]. Yamaguchi[13] found that an unreduced catalyst which by means of electron diffraction examinations had been found to contain big crystallites, possessed, after reduction, a higher activity than a catalyst whose magnetite phase consisted of much smaller particles.

As already remarked, magnetite with an Fe^{++}/Fe^{+++} ratio higher than 0.5 contains an FeO-phase. The presence of FeO in Fe_3O_4 may be due to minor shifting of Fe^{++} ions as could be demonstrated by Goldschmidt[14]. This investigator pointed out that FeO and Fe_3O_4 possess very kindred structures with the same cubic close packing of O-ions. FeO has the same structure as rock salt but invariably contains less Fe than would follow from the stoichiometrical composition. It is possible to prepare FeO-specimens with different Fe contents, and it appears that the lattice constant varies linearly with the composition, as was actually found by Bénard[15]. When the *double* value of the lattice constant is plotted versus the composition (the elementary cell of Fe_3O_4 contains eight times as many O-ions as the FeO cell) the extrapolated line appears to pass exactly through the point corresponding with the lattice parameter of the Fe_3O_4 (Figure 2).

Determinations of particle morphology from quantitative chemical analysis carried out by Wilchinsky[16] confirm the view that Al_2O_3 is dissolved in the magnetite lattice. Moreover, it was found that the K_2O and SiO_2 present in the same catalyst do not dissolve in the lattice.

Thermomagnetic investigations by Maxwell, Smart and Brunauer[17] led to an entirely different conclusion as to the distribution of Al_2O_3 in the magnetite lattice. These studies showed that the Curie points of singly promoted catalysts prepared with Al_2O_3 , Na_2O, K_2O, Cs_2O, BaO, B_2O_3 or SiO_2 as promoting components, are either equal to or only a few degrees lower than that of pure magnetite. Michel and Pouillard[18], however, noticed that if increasing amounts of Fe^{+++} in Fe_3O_4 are replaced by Al^{+++}, the Curie point and also the lattice constant decline regularly until 14 per cent of the Fe^{+++} has been substituted by Al^{+++}; at higher Al-contents the two quantities remain constant. This is in agreement with the conception that the Curie point varies steadily with a regular substitution of the nearest neighbors.

Maxwell, Smart and Brunauer, failing to observe an appreciable lowering of the Curie point, concluded therefore that only a very small amount of these promoters (about 1 mol per cent) had gone into solid solution with the magnetite. While for the majority of promoters this conclusion is entirely obvious, it seems to be rather surprising in the case of Al_2O_3. In this connection attention should be drawn to the work by Brill[10] who fused together magnetite with a small amount of α-Al_2O_3. The melting temperature is so high that this modification of Al_2O_3 is the stable one. After reduction of the magnetite phase formed, the Fe was dissolved in acid. The residue of Al_2O_3 appeared to be the γ-modification. Apparently the Al_2O_3 was forced into the γ-form which has a spinel structure, like magnetite itself. This clearly shows that the Al_2O_3 must have been in solid solution with Fe_3O_4.

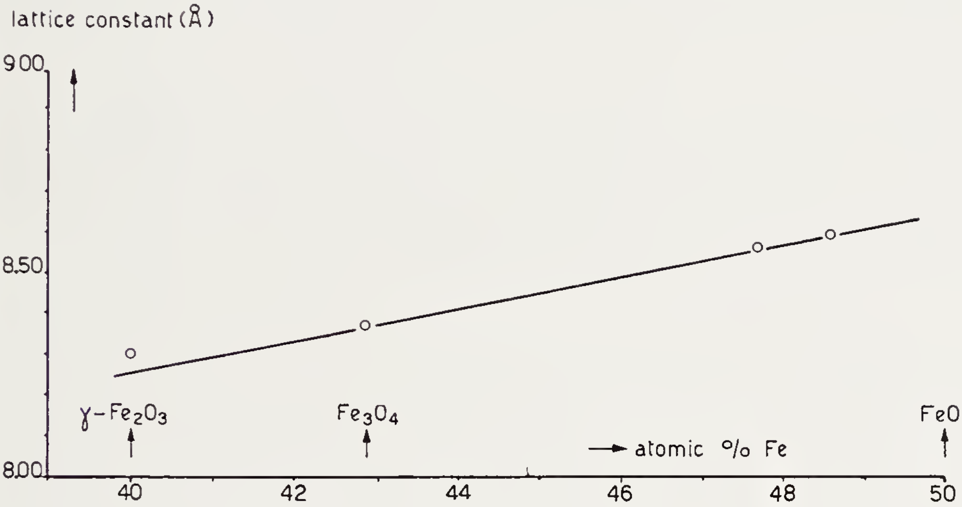

Figure 2. Variation of the lattice constant of iron oxides with Fe content. For FeO the double value of the lattice constant has been plotted.

To determine which of these discrepant views is the correct one, Westrik[19] measured the Curie points and the lattice constants of a series of catalysts with increasing amounts of Al_2O_3 which had been prepared by a fusion method.

The results are illustrated in Figures 3 and 4. The lattice parameters appear to decrease linearly with the ratio $Al^{3+}/(Fe^{3+} + Al^{3+})$; the Curie point, too, shows a distinct decrease with the amount of Al_2O_3. However, these measurements did not confirm the view advanced by Michel and Pouillard[18] that these two quantities should remain constant at Al_2O_3 contents higher than 14 mol per cent. It must be remarked, however, that these investigators employed an entirely different mode of catalyst preparation. By coprecipitation they prepared a mixed crystal containing Al_2O_3 and Fe_2O_3 which by a subsequent reduction at 400°C was converted into a spinel phase. It seems probable that in this method less Fe^{+++} is substituted by

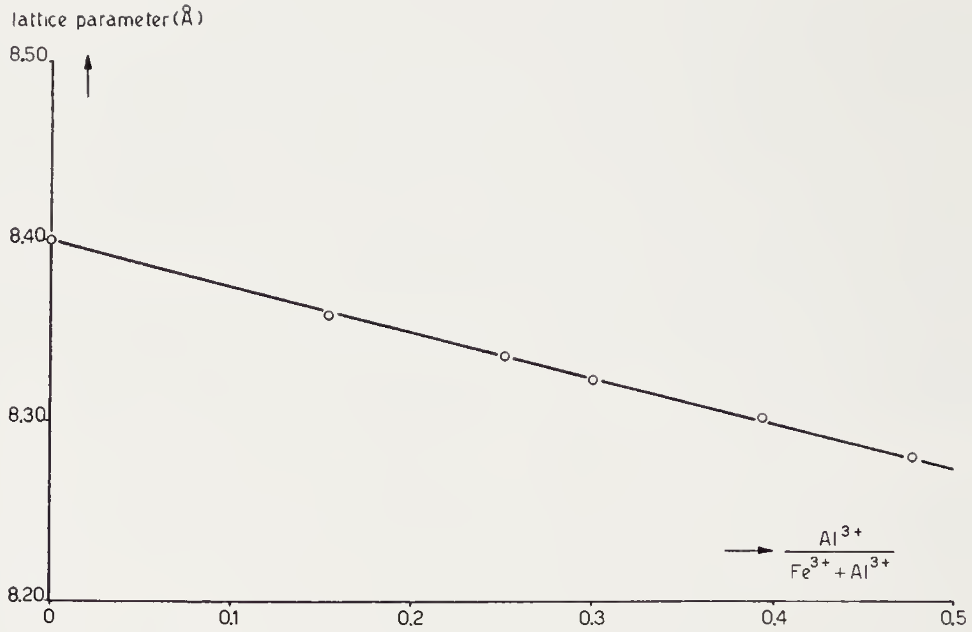

Figure 3. Variation of the lattice parameter of Al_2O_3 containing unreduced catalysts with the ratio $\frac{Al^{3+}}{Al^{3+} + Fe^{3+}}$. (Westrik[19])

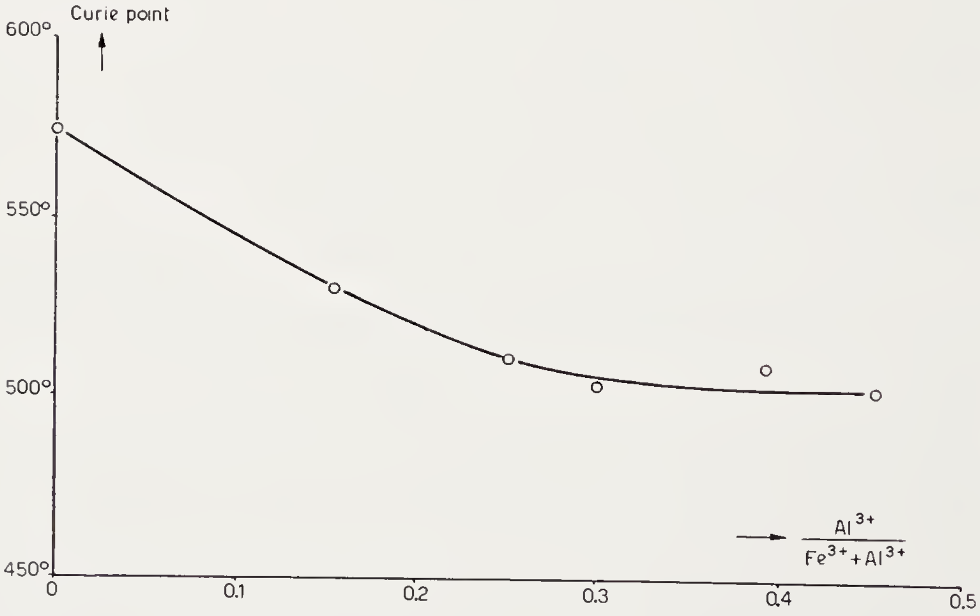

Figure 4. Variation of the Curie point of Al_2O_3 containing unreduced catalysts with the ratio $\frac{Al^{3+}}{Fe^{3+} + Al^{3+}}$. (Westrik[19])

Al^{+++} than is done in the fusion method. So, Westrik's results are contradictory to those found by Maxwell, Smart and Brunauer[17], but confirm the view that Al_2O_3 is dissolved in the magnetite lattice.

Nielsen[11], by means of the X-ray method, studied unreduced catalysts, i.e., ferrous-ferric oxide and the triply promoted Al_2O_3—CaO—K_2O iron catalyst. As in either case the ratio of ferrous to ferric ions was higher than 0.5, it was to be expected—as already remarked—that besides the Fe_3O_4 reflections FeO lines should occur in the diagrams.

In X-ray powder patterns taken of ferrous-ferric oxide, however, he noticed several deviations: at three points where FeO lines should have occurred a doublet was found; moreover, two more thin weak lines could be distinguished at two other points. It is certain that these lines cannot have been produced by Fe_2O_3 .

The observance of the doublets brings to mind the result of an investigation by Tombs and Rooksby[20] who found that at lower temperatures FeO adopts a rhombohedral structure. As a result most reflections are doubled, but it cannot be understood why this structure should occur in the case of the aforementioned catalyst. Nielsen[11] concluded that the extra lines cannot be FeO-reflections, and extended this conclusion to those cases where no doubling had been observed.

In connection with this conclusion we want to call attention to a paper by Goldschmidt[21] who studied a solid solution of MgO in FeO. It was to be expected that the lattice parameter of this compound should be smaller than that of FeO (Mg^{++} being smaller than Fe^{++}). However, this did not appear to be the case, but a doubling was observed into two FeO-phases possessing the same structure but different lattice parameters, viz., 4.298 and 4.317 Å, both of which are higher than the value of 4.284 Å for the original FeO. He explained this phenomenon by assuming that the Mg-ions, instead of replacing the Fe-ions in the FeO-lattice, occupy the empty interstices in this lattice with the result that an approximately ideal and an Fe-deficient FeO-lattice will occur beside each other. The value of 4.317 Å is very close to the value of 4.328 Å which by extrapolation can be calculated for a stoichiometrical composition (see Figure 2).

Although this explanation cannot be straightforwardly applied to the case described by Nielsen[11], still it is striking that the three doublets found by him can be exactly accounted for by assuming that there are two FeO-phases with lattice parameters of 4.279 and 4.321 Å. The latter value approximately corresponds to that for ideal FeO.

Nielsen[11] himself pointed to the possibility that the extra reflections may be connected with certain lattice defects. For, it is known, that certain lattice distortions may result in extra reflections. Daniel and Lipson[22] found that a sinusoidal variation in lattice parameter or in scattering power gives rise to symmetrical satellites of the main reflections, whereas Preston[23] showed that a combination of these two effects may lead to unsymmetric sidebands.

In Nielsen's opinion the extra reflections, found by him, are unsymmetric sidebands of the magnetite reflections. He remarks that the extra lines may probably be attributable to an exchange of two Fe^{+++} against three Fe^{++} ions. This would imply that some interstices in the spinel structure are occupied by Fe^{++}, with the result that an interstitial compound is obtained. In view of the survey on the relationship between the Fe_3O_4 and FeO-structures it will be clear that such a substitution of Fe^{+++} by Fe^{++}, and the occupation of empty interstices by Fe^{++}, may lead to the formation of small regions of FeO.

Nielsen noticed a broadening of the main diffraction lines of the unreduced catalyst examined by him. Broadening of X-ray diffraction lines may be due to the presence of small particles but also to lattice disturbances. In this case line broadening must have been caused by lattice disturbances because some lines, besides a line broadening, showed a certain degree of spottiness which points to a big size of the crystallites.

The lattice disturbances may be easily accounted for by the fact that the presence of promoters in the spinel structure may give rise to a change in the lattice constant and hence to a line broadening. The Ca^{++} used in this case is of too big a size for the spinel lattice, but will nevertheless dissolve in it to a certain extent (Verwey and co-workers[24]). There is no doubt that as a result hereof, stresses will be set up in the lattice which will become stronger as more promoter is dissolved. This has been borne out by experiments. Attention should also be directed toward another cause of lattice disturbances. The magnetite phase is obtained from a melt so that—especially in the case of rapid cooling—there is a possibility of certain metal ions penetrating into the wrong interstices, which will lead to stress formation.

Finally, it can be remarked that Nielsen[11] did not find a difference between the lattice constant of a natural magnetite, of a synthetic triply promoted Al_2O_3—Cao—K_2O iron catalyst and of pure ferrous-ferric oxide. This might be regarded as a confirmation of the results obtained by Maxwell, Smart and Brunauer[17]. On the other hand, the equality of these lattice constants may also be explained from the fact that whereas the Ca^{++} ion tends to raise the lattice constant, this influence may be neutralized by the lowering effect of the Al^{+++} ions. This point, however, cannot be checked until more experimental material becomes available.

Reduction

The conditions under which the reduction process is carried out, such as temperature and space velocity, have a great influence on the activity of the catalyst. This will be easily understood because this process is determinative both for the size and for the character of the surface on which the reaction is to take place.

The location of the equilibrium of the system iron, oxygen and hydrogen has been examined by various investigators. The most reliable data are those found by Emmett and Shultz[25, 26]. Their experimental results have been fully confirmed by the thermodynamical calculations of Tatievskaya, Chufarov and Antonov[27] and are in agreement with the experimental values found by Neuman and Köhler[28] as shown in Figure 5. This equilibrium diagram does not permit the formation of FeO during the reduction of magnetite below 570°C.

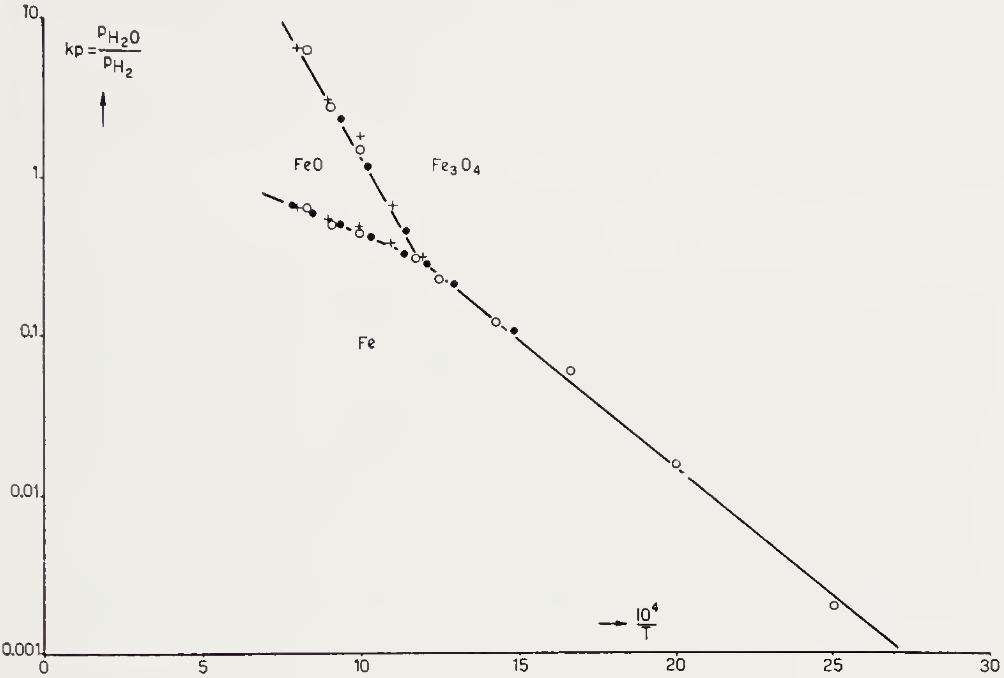

Figure 5. Equilibrium diagram of the system iron, oxygen, and hydrogen.
• Emmett and Shultz (exp.)[26]
○ Tatievskaya (calc.)[27]
+ Neumann and Köhler (exp.)[28]

Mosesman[29] studied the reduction of an iron catalyst (containing Al_2O_3 and K_2O as promoters) in an apparatus by means of which X-ray patterns could be taken during the reduction process. He found FeO as an intermediate, notwithstanding the temperature did not rise beyond 413°C. This is contradictory to the equilibrium diagram, although it might quite well be possible that a metastable phase is formed as an intermediate.

Various investigators pointed out that the reduction of a magnetite grain takes place along a clear-cut boundary line, which penetrates slowly but gradually toward the core. Udy and Lorig[30] succeeded in proving this with the aid of photographs of partially reduced grains.

The reduction starts on the outer surface of the magnetite grain. It is possible that the nonreproducible induction time, which is often noticed at the beginning of the reduction, and during which reduction proceeds at a very slow rate, is due to impurities on this surface. Considering that the reduction front has to be initiated, it is also possible that a nucleus formation process has an influence here.

If the supply of hydrogen and the discharge of water vapor through the already reduced porous portion proceeds at sufficient speed, the reduction rate will always be proportional to the surface of the reduction front. In that case it can easily be shown that (for spherical particles) the following expression applies:

$$-\frac{dO}{dt} = k[\mathrm{O}]^{2/3} \qquad (1)$$

where [O] is the oxygen content of the partially reduced grain. This expression is supported by reduction experiments which Chufarov and Tatievskaya[31] carried out on separate cubes of natural magnetite and by the reduction of a magnetite sphere at 500°C executed by Tikkanen[32]. Elaboration of the results found by Hall, Tarn and Anderson[33] in reducing a bed of catalyst particles, as well as the result Zwietering[34] obtained by reducing an isolated single crystal, yielded the same expression.

If this reaction rate is determined by the diffusion rate of water vapor through the porous reduced portion, the kinetic relation becomes much more complicated, as pointed out by Woods[35]. It is, however, almost certain that under the usual conditions the reduction rate is much lower than the diffusion rate.

Hall, Tarn and Anderson[33] carried out an investigation on a Fischer-Tropsch catalyst which was very analogous to the iron catalyst for ammonia synthesis. This catalyst was prepared by a fusion process and contained—besides magnetite—MgO and SiO_2. Using partially reduced samples of this type of catalyst, these investigators determined the available surface area and the amount of CO that can be chemisorbed thereon (a measure of the surface fraction occupied by Fe-atoms, Emmett and Brunauer[36]).

The results are illustrated in Figure 6. The accessible surface area increases linearly with the degree of reduction, but decreases slightly during the removal of the very last traces of oxygen. The iron surface (CO-adsorption) also increases linearly at first but, unlike the surface area, starts expanding more rapidly after a high degree of reduction has been attained. An increase in the reduction temperature appears to have a diminishing effect upon the accessible surface area as well as on the bare iron surface. As previously stated, calculations show that the experimental data of Hall, Tarn and Anderson obey Eq. (1).

The accelerated increase of the iron surface area toward the end of the reduction shows that the last amounts of oxygen occur on the surface. This is in entire agreement with the picture one can form of the sensitiveness of iron catalysts to oxygen-containing poisons, such as water. With this type of poisoning, also, the surface probably becomes covered with oxygen. As is well-known, removal of this oxygen restores the iron surface to its original catalytic properties (reversible poisons).

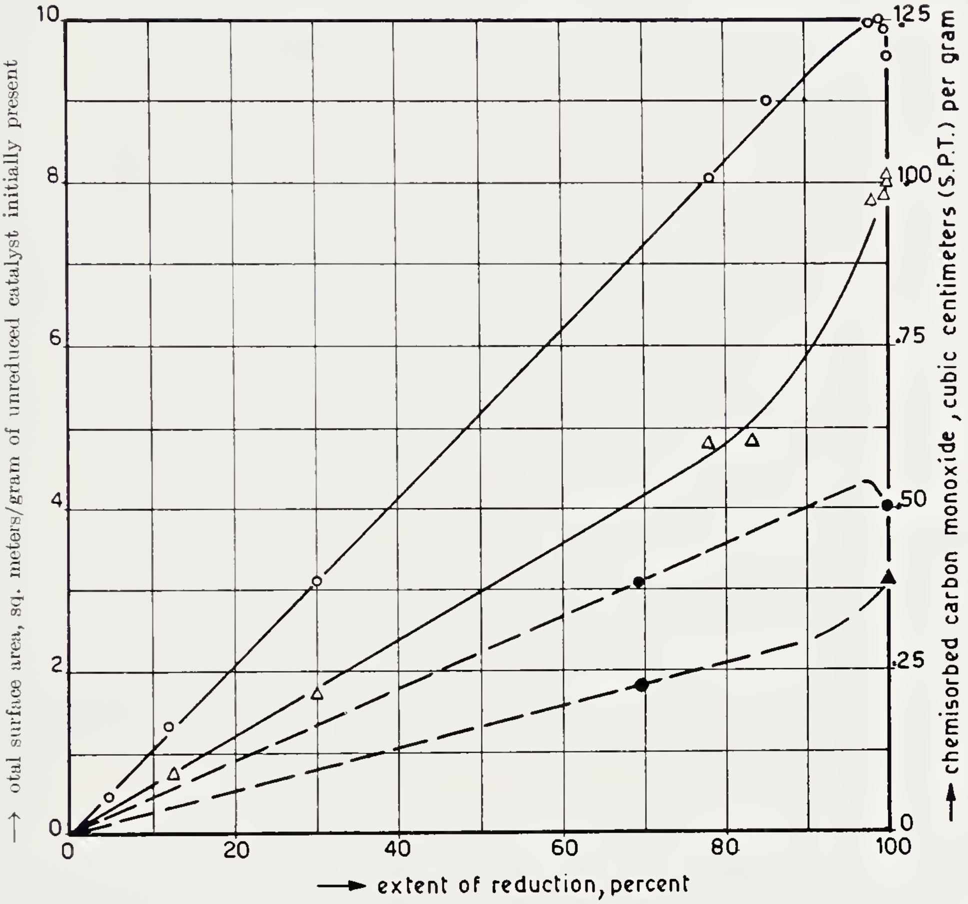

Figure 6. Variation of surface area and of carbon monoxide chemisorption with extent of reduction. The surface areas of samples reduced at 450°C are represented by ○ and their carbon monoxide chemisorptions by △. The solid points represent samples reduced at 550°C. (Hall, Tarn and Anderson[33])

The decrease of the accessible surface area attendant upon the growth of the iron surface, may be explained by assuming that the last amounts of oxygen have a strengthening effect on the iron lattice.

Zwietering[34], who carried out reduction experiments, also determined the relationship between the accessible surface area and the degree of reduction. The results obtained for an MgO-promoted catalyst were equal to those found by Hall et al.[33]. From experiments with an Al_2O_3-promoted catalyst, Zwietering found that the accessible surface *per gram of iron already reduced*

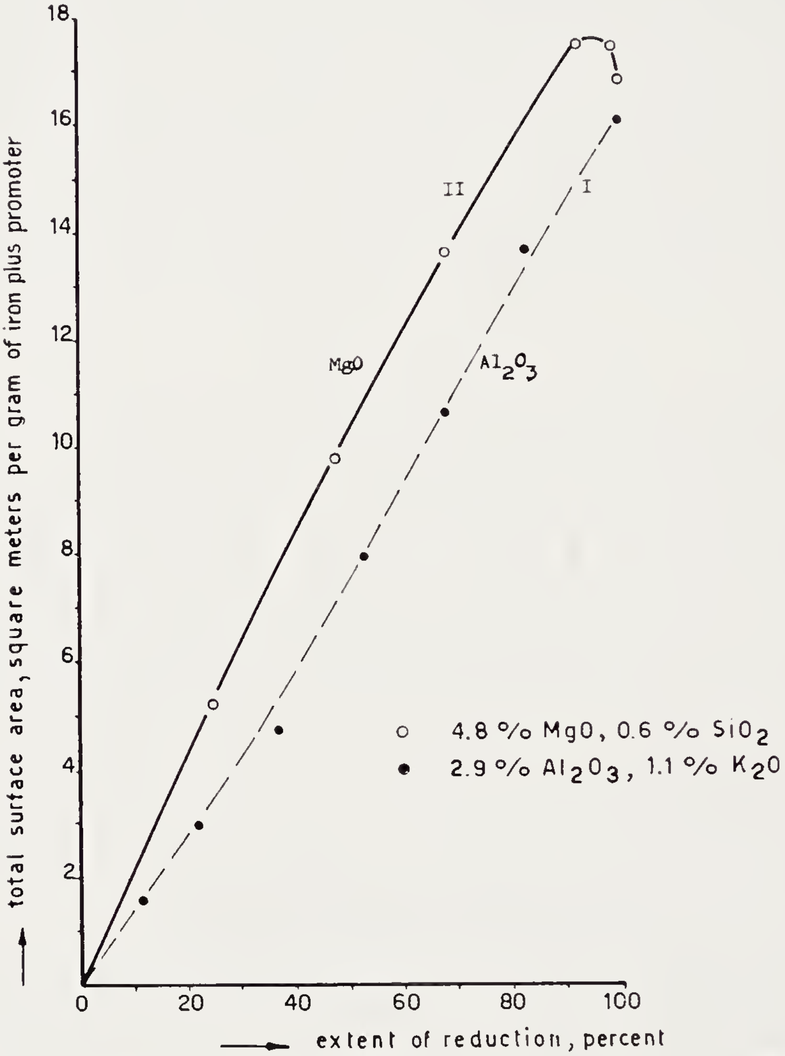

Figure 7. Variation of surface area with extent of reduction of an MgO and an Al_2O_3 containing catalyst. (Zwietering[34])

increases with the degree of reduction. These results are illustrated in Figure 7. The surface of an MgO-containing catalyst decreases upon removal of the last traces of oxygen, whereas in the case of an Al_2O_3-containing catalyst no such phenomenon was observed. This might suggest that Al_2O_3 is a better stabilizer than MgO. The ultimate surfaces of the two catalysts, however, are practically equal because, during the reduction, the surface of the MgO-containing catalyst was always larger.

Now that a picture has been formed of the reduction process, the various factors that may have an influence on this process will be reviewed.

Promoters. It has long been known that—depending on the character and quantity—the usual promoters have a retarding effect upon the reduction rate. The general opinion is that promoters dissolving in the spinel lattice are responsible for a greater decrease in the reduction rate than others, such as K_2O, which do not dissolve. We may even say that oxides which greatly retard the reduction rate will be good promoters. Further, the addition of increasing amounts of promoters will result in an increased lowering of the reduction rate and make it necessary to reduce at ever higher temperatures, in order to obtain a completely reduced catalyst (Lachinov[37]).

Space Velocity. The rate of reduction increases with increasing space velocity of the reducing gas owing to the fact that water vapor retards the reaction. All investigators agree that a high space velocity has a favorable effect on the activity of the catalyst formed. The reason may be that the higher the reduction rate the greater will be the surface area developed during the reduction.

Reduction Temperature. The reduction rate increases with temperature, the energy of activation is $\backsim 16$ kcal[32]. There are no data available about the influence of promoters on this energy.

As stated above, a high reduction rate has a favorable effect on the activity. On the other hand, an increase of the reduction temperature causes a higher rate of sintering, especially of the iron phase in its state of forming. So it will be clear that, provided other factors are kept constant, there will generally exist an optimum reduction temperature. This was found by Kurin[38].

Hydrogen Pressure. Only few reliable data are known on the influence of hydrogen pressure. Tatievskaya, Chufarov and Antonov[27] noticed that the reduction rate depends on hydrogen pressure, p, according to the expression

$$v = kp^n, \qquad \text{where} \qquad n < 1 \tag{2}$$

A more detailed interpretation of this relationship is still lacking.

In view of all these factors it need not be surprising that the literature contains several reduction schedules[6, 11, 37, 39] in which the space velocity and the temperature distribution are described accurately.

Reduced Catalyst

Texture. As already explained, the reduction process yields a porous α-Fe structure with a large accessible surface area. The normal Fe-catalysts have a surface area of about 10 m²/g (Hall, Tarn, and Anderson[33]), Nielsen and Bohlbro[40]).

Al_2O_3 largely contributes to the establishment and stabilization of this large surface. Emmett and Brunauer[36] already pointed out that the surface of a singly-promoted catalyst (954, 10.2 per cent Al_2O_3) is at least six times that of a gently reduced pure Fe-catalyst (973). After the catalyst had been treated for a while at 450°C this ratio increased to a value of twenty. From this it follows that Al_2O_3 may be regarded as a stabilizer of this porous and relatively instable α-Fe structure (see also pages 282–286).

The function of K_2O is entirely different; the presence of K_2O results in a decrease of the free iron surface area but nevertheless in a higher activity at elevated pressures. It must be concluded therefore that K_2O has a favorable effect upon the catalytic properties of the surface and must consequently be considered as a real promoter.

Since the iron phase formed by reduction is pyrophoric, it is necessary in most of the studies on reduced catalyst to passivate the catalyst beforehand. The method given by Kiperman and Temkin[41] is to pass a stream of hydrogen with about 0.1 per cent of oxygen over the catalyst.

Hall, Tarn and Anderson[33], in their experiments on the MgO-containing catalysts, determined the helium and mercury densities of all of the specimens investigated. From these examinations it appeared that the volume of mercury displaced by the reduced grains per gram of unreduced material initially present, remains constant, i.e., the external volume does not change during the reduction. The pore volume is formed therefore by the removal of the relatively big O-ions from the spinel lattice (see Figure 1).

Calculating the mean pore diameter from the helium and mercury densities and the available surface area, Hall and co-workers[33] found that during the reduction from 20 to 95 per cent, this quantity rises only from 330 to 348 Å, whereas the completely reduced catalyst has a mean pore diameter of 370 Å. When the reduction temperature is raised, the surface area decreases and the mean pore diameter gradually increases; at 650°C for example it is equal to 2420 Å.

McCartney and Anderson[42] carried out a supplementary electron microscopical investigation in which various replica techniques were employed. When the microstructure found from the micrographs is identified with the pore structure, the pore diameter can be estimated. The order of magnitude of this pore diameter is in reasonable agreement with that found by Hall *et al.*[33] but the inaccuracy of this quantity becomes apparent from the fact that no difference is observed between two samples reduced at 450 and 550°C (Hall's d-values of 371 and 917 Å).

Zwietering and Koks[43] determined the pore size distribution from the penetration of mercury under pressure according to the method described by Ritter and Drake[44]. A catalyst with 3 per cent Al_2O_3 and 1 per cent K_2O reduced at 450°C, yielded the pore size distribution curve illustrated in

Figure 8. The total pore volume and the accessible surface area of this specimen have also been determined. From these values, the mean pore diameter was calculated in the usual manner. Further, it was possible from the distribution curve to calculate the accessible surface area. The various data have been compiled in Table 1. The value of the mean pore diameter, 354 Å, deviates not inconsiderably from the value corresponding to the top of the distribution curve, 240 Å; this is imputable to the nonsymmetrical shape of the curve.

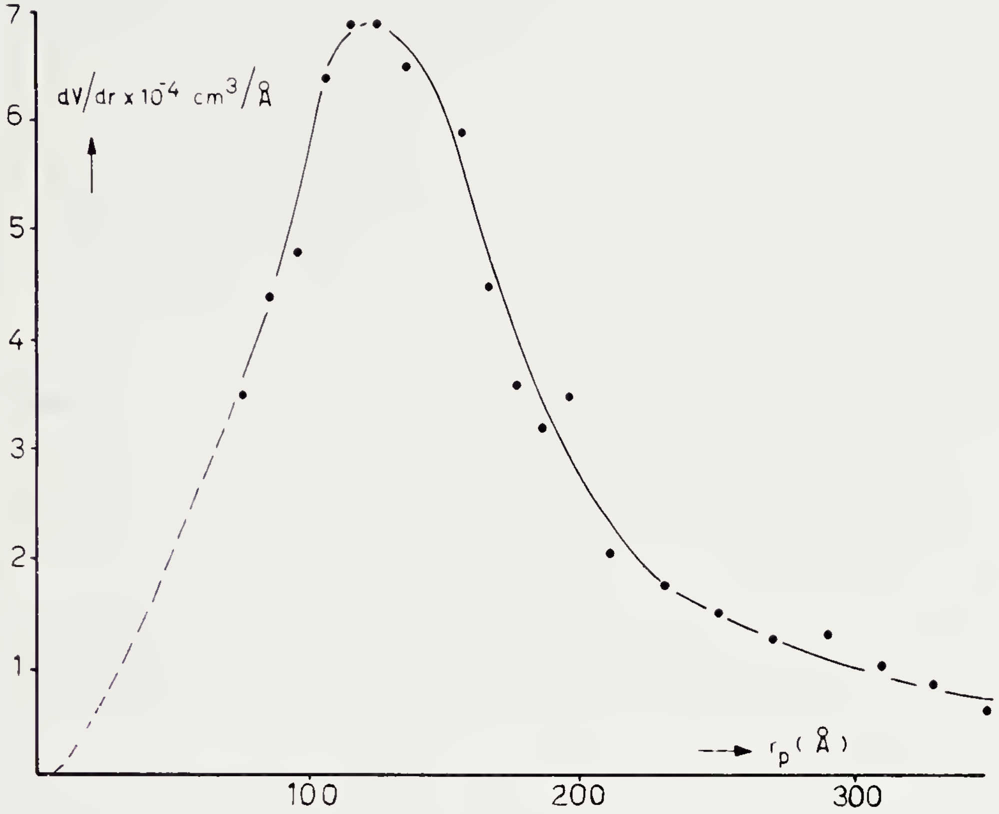

Figure 8. Pore size distribution of an iron catalyst containing 2.9% Al_2O_3 and 1.1% K_2O. (Zwietering and Koks[43])

TABLE 1. PORE ANALYSIS OF AN Fe-Al_2O_3-K_2O CATALYST (ZWIETERING AND KOKS[43])

Specific Volume (cm³/g)		Pore Volume V, cm³/g	Accessible Surface Area, F, m²/g		$\bar{d} = \frac{4V}{F_{BET}}$ Å	$d_{max.}$ Å
In mercury	In helium		BET	Calculated from pore size distribution		
0.258	0.142	0.116	13.1	15.1	354	240

The pore size distribution found by Zwietering and Koks[43] shows that the free volume of this catalyst is composed, rather homogeneously, of pores of about 300 Å. This conclusion is fully confirmed by the results of investigations on the restriction of the reaction rate by internal diffusion (see pages 339–343).

From the broadening of the X-ray diffraction lines of reduced catalysts—which in this case can almost entirely be accounted for by the occurrence of small iron crystallites—Nielsen and Bohlbro[40] determined the size of the crystallites. For a catalyst with a specific surface area of 8 m^2/g they obtained a value of 360 Å. From this result and an assumed porosity of 50 per cent the mean pore diameter is found to be 470 Å. Thus the value of the mean pore diameter is of the same order as the crystallite size.

If the catalyst granules are considered to consist of a loose packing of subparticles and the surface area found by the BET-method is identified with the outer surface of these subparticles, the dimensions can be calculated provided a definite choice is made about the shape of the particles. For plate-shaped subparticles a thickness of about 320 Å is calculated, which would be in good agreement with the linear dimension of 360 Å found from X-ray line broadening. If the subparticles are supposed to be of a spherical or cubical shape, a linear dimension of about 900 Å is calculated, which value is much larger than 360 Å. Thus, if the subparticles have this latter form it must be assumed that they consist of about 10 to 20 crystallites.

On the other hand, the catalyst granule may be considered to be a continuous spongy iron structure, channelled by pores. In this picture the mean pore diameter calculated from specific area and pore volume has a real physical meaning, but any connection between this diameter and crystallite size is lacking.

The X-ray diffraction line broadening is, in this case, determined by the thickness of the walls between the pores, or by crystallite dimensions smaller than that.

Thus, neither of the two extreme views about the porous structure of the catalyst—viz., a loose packing of subparticles or a continuous solid phase channelled by pores—is in contradiction with the experimental data, and a definite choice cannot be made as yet. Of course it is quite possible, and perhaps probable, that the actual structure is something intermediate between the two.

Nature of the Surface. There is no doubt that the excellent research by Emmett and Brunauer[36, 39, 45, 46, 47] on the surface structure of reduced catalysts ranks foremost among the work done in this field. In a series of articles these investigators described the occurrence of chemisorption of CO_2, O_2, CO, H_2 and N_2 on various promoted (Al_2O_3, K_2O and Al_2O_3 +

K_2O) and unpromoted iron catalysts. A detailed treatment of this chemisorption will be found on pages 299–304.

From the results of these investigations a method could be derived for determining the fraction of the surface covered with Al_2O_3 in a singly promoted catalyst and by Al_2O_3 or K_2O in a doubly promoted catalyst. This was done by determining in succession the total surface area with the BET-method, the iron surface from the CO-chemisorption and the alkali-oxide covered surface from the CO_2-chemisorption.

Their experiments disclosed the interesting fact that a considerable fraction of the surface area is occupied by the promoters, notwithstanding that these are present only in small amounts. This is clearly illustrated by some examples cited in Table 2. The catalysts used were taken from the well-known series developed at the Fixed Nitrogen Research Laboratory in Washington.

TABLE 2. SURFACE COMPOSITION OF SEVERAL PROMOTED IRON CATALYSTS FROM THE FIXED NITROGEN RESEARCH LABORATORY

Catalyst No.	Promoter Content per cent		Surface Composition, per cent of Surface Covered by		
	Al_2O_3	K_2O	Fe	Al_2O_3	Alkali
191	0.42	—	65	35	—
954	10.2	—	45	55	—
930	—	1.07	30	—	70
191 A	0.42	0.09	55	29	16
441	0.84	0.35	48	14	38
931	1.30	1.59	40	—	60

Indications were found that the K_2O and Al_2O_3 of doubly-promoted catalysts prepared by the fusion method have reacted with each other with the formation of K_2AlO_4 (see Table 2, Catalyst No. 931). Finally, the effect which the CO- and CO_2-adsorptions have upon one another, showed that the promoters are very intimately mixed with the Fe-atoms.

From their research on the structure of the iron surface, Brunauer and Emmett[39] concluded that this must be heterogeneous owing to different developed crystal faces of α-Fe. For the sake of convenience, they divided the Fe-faces into two groups, viz.

(a) those with a closed structure, such as the 110 plane, which is the most densely packed plane in the body-centered cubic structure of α-Fe

(b) those with an open structure, exemplified by the 100, 111 and 211 planes.

The outer iron atoms ("A") in the planes of the second group are more loosely packed and also an underlying layer ("B") is exposed, as in the 100 plane, or even a second underlying layer ("C"), as in the 111 plane (Figure 9). The 111 plane is the most loosely packed simple plane of α-Fe and probably possesses the highest surface energy and the highest catalytic activity.

During sintering, planes of open structure (e.g., 111) will disappear, resulting in the preferential increase in planes of closed structure (e.g., 110).

In calculating the surface fractions occupied by Al_2O_3 and K_2O, use must be made of a conversion factor for expressing the amount of free iron surface in terms of CO- chemisorption. For this purpose they determined the ratio of the CO-volume (V_{CO}) which at −78°C is chemisorbed on a pure iron catalyst, to the nitrogen volume physically adsorbed at −183°C (monolayer V_m). This ratio was found to be 1.25.

Assuming that the surface of a nitrogen molecule is 13.7 Å² and that

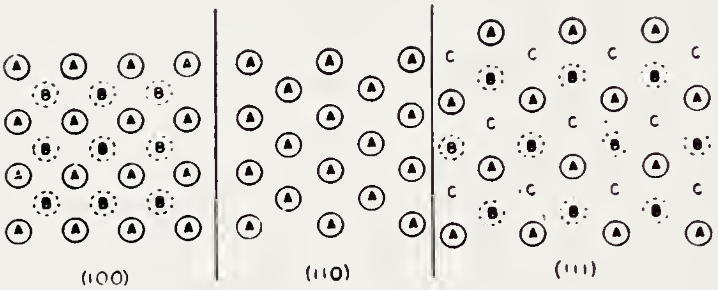

Figure 9. Arrangements of iron atoms in the (100), (110), and (111) planes. The distances between the centers of the iron atoms are drawn to scale, a_0 being taken as 2.86 Å. The circles are not intended to represent the sizes of the iron atoms. (From Brunauer and Emmett[39])

every CO-molecule is bound to one Fe-atom (except in the 110-plane where it is assumed from geometrical considerations that two Fe-atoms are required) one can calculate the value V_{CO}/V_m for the case that the surface would consist solely of 100, 111, 211 and 110 planes. These values were found to be 1.68, 0.97, 1.35 and 1.19, respectively, so that the experimental value of 1.25 appears to be in reasonable agreement with the concept that the surface is heterogeneous.

Westrik and Zwietering[1] arrived at a different picture for the surface structure. From adsorption and X-ray experiments they concluded that the surface of a catalyst prepared from a magnetite phase must consist almost entirely of 111-planes. They studied the adsorption by the method of Brunauer and Emmett.

An amount of pure magnetite, prepared by the fusion method, was reduced very carefully at 225°C, whereafter reduction was repeated a few times for short periods at 300°C. Then, they measured the accessible surface area and the amount of chemisorbed CO, from which they calculated the number of CO-molecules chemisorbed per cm^2 of surface (n_{CO}). In these calculations the surface area of the nitrogen molecule was taken to be 16.2 Å^2, because it was found (Harkins and Jura[48]) that this was in better agreement with reality than that of 13.7 Å^2. Their results are listed in Table 3.

In view of the strong chemisorptive bond between the CO-molecules and the iron surface, Westrik and Zwietering[1] assumed that each iron atom will tend to adsorb one CO-molecule localized on top of the iron atom. From simple geometrical considerations they concluded that due to the dimensions of the CO-molecule this one-to-one bonding is only possible on the 111-faces, whereas on the 100- and 110-faces a maximum coverage of $\frac{1}{2}$ and $\frac{1}{3}$ (expressed as n_{CO}/n_{Fe}) can be expected. By means of these data the theoretical value of n_{CO} could be calculated for these faces. They found:

TABLE 3. SURFACE AREA AND CO CHEMISORPTION (cm^{3}NPT/g IRON) AFTER REDUCTION AT 300°C (WESTRIK AND ZWIETERING[1])

Reduction Time (hr)	Monolayer Volume cm^3 N$_2$/g	CO Chemisorbed cm^3/g	Area m^2/g	n_{CO}/cm^2 × 10^{15}
40	0.68	0.805	2.96	0.73
88	0.61	0.73	2.66	0.74
128	0.57	0.675	2.48	0.73

$$110 \text{ face: } n_{CO} = 0.58 \times 10^{15}$$

$$100 \text{ face: } n_{CO} = 0.61 \times 10^{15}$$

$$111 \text{ face: } n_{CO} = 0.71 \times 10^{15}$$

As the experimental value was found to be in good agreement with the one calculated for the 111-plane, it was concluded that the Fe-particles obtained by careful reduction of magnetite expose almost exclusively 111-planes.

To obtain a better insight into this phenomenon, a single crystal of magnetite was reduced with the utmost care. Upon reduction it appeared that the (octahedral) form and the size of the original crystal had been preserved (Figure 10). X-ray patterns of the reduced crystal disclosed a preferred orientation of the Fe-atoms; the 111-planes of the Fe-crystallites appeared to run parallel to the surface and hence also parallel to the surface of the original magnetite.

So, there has been observed a very interesting case of pseudomorphosis in which both the habit and the orientation of the iron formed are very strongly affected by the oxide from which it has originated.

The observed pseudomorphosis and the attendant orientation consequently account for the conclusions drawn from adsorption investigations, viz., that the surface of the α-Fe phase prepared by careful reduction of magnetite is primarily substantially composed of 111-planes.

Possibly the study by Westrik and Zwietering may also explain the well-known phenomenon which as far back as 1909 was observed by Mittasch[49], who noticed that a catalyst obtained by reduction of a magnetite phase possesses a higher activity than catalysts prepared by another method. As pointed out previously, it is very probable that the 111-planes of α-Fe are the most active planes for the synthesis of ammonia.

It may be said, therefore, that this investigation has shown how the characteristics of the ammonia synthesis catalyst are influenced by its method of preparation.

(a) (b)

Figure 10. Single crystal of magnetite before (a) and (b) after reduction. (Westrik and Zwietering[1])

Chemisorption in Ammonia Synthesis

It may well be regarded a matter of course that the study of chemisorption has played an important role in the development of the research into the synthesis of ammonia. The necessity for making a profound study of the chemisorption phenomena was the more cogent because at a rather early stage already there was a growing opinion that the *chemisorption rate* of the nitrogen should be the rate-determining step of the total reaction[45].

This circumstance made it necessary for scientists, therefore, not only to make a study of the adsorption equilibria—and possibly also of the influence which the various reactants have upon one another—but also to go deeply into the kinetics of the nitrogen adsorption on the catalytic surface.

The high sensitiveness of the industrial iron catalyst to minute amounts of impurities in the synthesis gas may be likewise attributed to the formation of strong chemisorptive bonds. The strength of these bonds is so great that the partial pressures of these components need only be exceedingly low to cause the metal surface to be covered with poison to such an extent that the catalytic activity drops appreciably.

In view of this phenomenon it is understandable why a large part of the exploratory work has not been carried out on the technical iron catalyst, but on other metals—also possessing catalytic properties—which are capable of withstanding a more rigorous purification treatment, without it being necessary to raise their thermostability by the addition of stabilizers.

A larger number of data have therefore been collected from experimental work on tungsten which, having a high melting point and a volatility lower than that of its components, may be purified at a very high temperature. In the last few years it has become possible to supplement these data, because the adoption of the technique of making measurements on evaporated metal films has enabled the investigation to be extended to pure specimens of less stable metals.

An important disputed point which keeps cropping up in the existing observations on chemisorption and heterogeneous catalysis in general is the question as to how the experimental datum that the differential heat of adsorption (q) decreases with increasing coverage with adsorbed atoms (θ) may be accounted for. Many investigators have attempted to explain this phenomenon by assuming that the surface should be heterogeneous, in such a sense that the sites with the highest "activity" (q) are occupied first, and the less active sites are filled in the order of their degrees of activity.

However, it might also be assumed that the surface should a priori be *homogeneous* and that all adsorption sites should therefore possess the same degree of activity, i.e., give rise to the same heat of adsorption. According to this assumption the experimental decrease in the differential heat of adsorption would then be caused by a gradual change in the binding energy, which keeps step with the number of atoms adsorbed. During this process, however, *all of the adsorbed particles are always in the same energy state.*

From the standpoint of chemisorption, it will be self-evident that, strictly speaking, only the perfectly pure boundary plane of an ideal metallic single crystal may be considered as a homogeneous surface. Probably, this utopia is approached the most closely in the ingenious experiments on evaporated films in which, by applying a special method of preparation, it is possible to orient all the metal layers in one definite crystallographic direction. However, the contact material commonly employed in industrial applications (which is prepared by reduction of previously molten Fe_3O_4 to which several nonreducible oxides have been added as promoters and stabilizers) does certainly not correspond to this ideal picture. Whereas the surface iron atoms which, according to the generally accepted view, are the adsorption sites for the chemisorption of nitrogen and hydrogen, are most probably arranged in the regular pattern of the 111-plane of alpha-iron, the promoters added are largely accumulated at the surface, where they occupy 40 to 70 per cent of the total area. These promoter molecules are not concentrated in batches but are widely scattered across the entire surface area*.

Great importance should be attached to the question as to whether the adsorbing metal surface *behaves* as a homogeneous surface or as a heterogeneous surface, and as to whether it is possible by starting from the present views based on either of these two possibilities, to give a qualitative and especially a *quantitative* interpretation of the experimental data.

Before proceeding to a discussion of the experimental material, it might be useful here to give a brief outline of those theories which on the basis of either of the above possibilities enables a reliable formulation to be made of the adsorption isotherm, adsorption kinetics or of the relation between heat of adsorption and coverage.

Adsorption on Heterogeneous Surfaces

The Isotherm. The theory of chemisorption on heterogeneous surfaces has greatly benefited from the work by Russian investigators in the field of heterogeneous catalysis. A survey of their achievements has been given by Levin[50]. The contributions by investigators from the United States and other countries have been outlined by Halsey[51].

Representing the distribution function of all the adsorption sites toward the heat of adsorption by:

$$N(q)\,dq \equiv \text{fraction of sites with adsorption energy between } q \text{ and } q + dq \tag{3}$$

normalized according to

$$\int_{q_{\min}}^{q_{\max}} N(q)\,dq = 1 \tag{4}$$

the total degree of coverage is given by

$$\theta = \int_{q_{\min}}^{q_{\max}} \theta_q N(q)\,dq \tag{5}$$

where θ_q is the degree of coverage on sites with a heat of adsorption $= q$.

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* For a detailed discussion of the surface structure of the iron-catalyst see pp. 279–286.

As early as 1918, Langmuir derived a relationship for the isotherm*, viz.

$$\theta_q = \frac{1}{1 + \frac{a}{p} e^{-q/RT}} \tag{6}$$

p = pressure; a = constant.

which, neglecting the interaction forces between the adsorbed molecules holds for all the sites with the same adsorption energy. By combining Eqs. (5) and (6) it follows for the heterogeneous surface that:

$$\theta = \int_{q_{\min}}^{q_{\max}} \frac{N(q)}{1 + \frac{a}{p} e^{-q/RT}} \, dq \tag{7}$$

The solving of this integral for specially selected distribution-functions has led to an intensive mathematical study, especially by Russian authors[50, 51, 52].

A very interesting method of approximation, which rapidly leads to good results, was introduced by Roginskii[53]. This investigator established that the $q(\theta)$ curve, obtained by the Langmuir formula:

$$\frac{\theta_q}{1 - \theta_q} = \frac{p}{ae^{-q/RT}} \tag{8}$$

shows a bend at $\theta_q = \frac{1}{2}$ for definite values of p and T, and rises sharply if $q_{\min} \gg RT$, as is normally true.

In view of these findings, Roginskii now put the degree of coverage of that part of the surface where, according to (8), $\theta_q > \frac{1}{2}$, equal to one and neglected the adsorption on the less covered part of the surface. The limiting value of $q_{1/2}$ is given by:

$$\frac{p}{ae^{-q_{1/2}/RT}} = 1 \qquad \text{or} \qquad \frac{q_{1/2}}{RT} = \log \frac{a}{p} \tag{9}$$

When using this method of approximation, the solving of the integral (7) will amount to solving:

$$\theta = \int_{q_{1/2}}^{q_{\max}} N(q) \, dq \tag{10}$$

For an exponential distribution function

$$N(q) = ce^{-\alpha q} \tag{11}$$

---

* Strictly speaking this formula holds only for molecular adsorption; if the molecule dissociates into two atoms, p is to be replaced by $p^{1/2}$.

there results the well-known empirical formula given by Freundlich:

$$\theta = \text{const } p^{\alpha RT} \tag{12}$$

which has thus found a possible "theoretical" explanation[54, 55, 56].

For a constant distribution function:

$$N(q) = \text{const.} \tag{13}$$

the following well-known logarithmic isotherm may be derived from (10)

$$\theta = \frac{RT}{q_{\max} - q_{\min}} \cdot \log \left[\frac{p}{a} e^{q_{\max}/RT} \right] \tag{14}$$

Temkin[4] originally derived this expression directly from Eq. (7). Making use of (13) it follows from (7) that

$$\theta = 1 + \frac{RT}{q_{\max} - q_{\min}} \cdot \log \frac{1 + \frac{a}{p} e^{-q_{\max}/RT}}{1 + \frac{a}{p} e^{-q_{\min}/RT}} \tag{15}$$

In the case of $q_{\max} \gg q_{\min}$ and medium pressures it may be put that

$$\frac{a}{p} e^{-q_{\max}/RT} \ll 1 \qquad \text{and} \qquad \frac{a}{p} e^{q_{\min}/RT} \gg 1.$$

so that (15) changes to (14).

The reverse procedure—calculating the distribution function from a given empirical description of the isotherm—was treated by Roginskii[53] with the help of the approximation given above. For, by differentiating once toward the lower limit, it follows from (10):

$$N(q_{1/2}) = \frac{-d\theta}{dq_{1/2}} = \frac{1}{RT} \frac{d\theta}{d \log p} \tag{16}$$

The value of q pertaining to the calculated value of $N(q)$ is given by (9) which, however, still contains the unknown factor a. By performing the analysis on two isotherms, measured at two different temperatures, both a and q can be calculated.

Sips[57] tried to reach the same goal by the mathematical approach. In his first integration this author used the limits ∞ and $-\infty$. In a following article[58] he demonstrated also that in the case ∞ and 0 are chosen, a mathematical analysis can be made, provided certain conditions are satisfied. An interesting result of his calculations was that the isotherm

$$\vartheta = \frac{ap^n}{1 + ap^n} \quad (n < 1) \tag{17}$$

which may be regarded as a combination of the Langmuir and the Freundlich formulas, agrees with a distribution function which is practically equal to a Gaussian distribution.

Heat of Adsorption. The great experimental difficulties connected with the direct calorimetric determination of the heat of adsorption accounts for the fact that many data on this quantity have been calculated from experimental isotherms at different temperatures by means of the well-known Clausius-Clapeyron equation:

$$q(\theta) = -R\left(\frac{d \log p}{d\,\dfrac{1}{T}}\right)_{\theta} \tag{18}$$

The significance of the quantity calculated in this way has been clearly brought out by Hill[59].

The strong decrease which the adsorption energy generally shows with increasing coverage has been the main cause for the development of the conception of the heterogeneous surface. The shape of the $q(\theta)$ curves required according to the heterogeneity theory, can be derived in a simple manner from the calculated isotherms stated above. For example, from the formula for the Freundlich isotherm it is possible, by using (18) to derive:

$$q(\theta) = \text{const} - \alpha \log \theta \tag{19}$$

whereas from the Temkin equation it follows that

$$q(\theta) = q_{\text{max}} - (q_{\text{max}} - q_{\text{min}})\theta. \tag{20}$$

So, in these cases, the resulting $q(\theta)$ curves, after being differentiated once toward θ, give a picture of the distribution function $N(q)$. However, Halsey and Taylor[56] showed that this is certainly not always so.

Rates of Adsorption and Desorption. With the majority of technical catalysts chemisorption equilibrium is reached at a low rate which is governed by an activation energy E ("activated adsorption"). On the other hand, it appears that, even at very low temperatures the adsorption rate of hydrogen on very pure metal surfaces (wires and evaporated films) is often very high. In these cases the value of E is negligible. Naturally, the rate of desorption is governed by an activation energy equal to the sum of E and q. The development of the theory of the kinetics of ad- and desorption on heterogeneous surfaces is determined partly by the question as to whether there exists a relationship between the heat of adsorption for a given site and its activation energy, and partly by the mobility of the adsorbed particles along the surface[50].

If the velocity of migration of the adsorbed particles along the surface is low in comparison with the rate of adsorption, the adsorption kinetics are determined by the distribution function toward the activation energy $N(E)$. For sites of the same activation energy and a negligible rate of desorption the following relation holds:

$$\frac{d\theta}{dt} = k_a p(1 - \theta)e^{-E/RT} \tag{21}$$

and thus

$$(1 - \theta) = \exp\left[-k_a pte^{-E/RT}\right] \tag{22}$$

so that for the entire surface we get:

$$1 - \theta = \int_{E_1}^{E_0} \exp\left(-k_a pte^{-E/RT}\right)N(E)\,dE \tag{23}$$

However, in case the particles are mobile and q and E do not depend upon each other the rate of adsorption will always be determined by the number of vacant sites with the lowest activation energy, and the measured value of the activation energy will therefore be independent of coverage.

It is more reasonable, however, to assume that E and q will be correlated. In view of the potential curves illustrated in Figure 11 an antibatic correlation (E increases as q decreases) would seem to be the most probable on theoretical grounds[60]. This supposition has been borne out by most experiments[61]. On the other hand, there are the results of a few other experiments that seem to point to a symbate-correlation[62]. Should the relationship between E and q be antibatic, the sites with the highest heat of adsorption will always be covered first, so that the mobility will have but little influence on the adsorption kinetics. In that case Eq. (23) remains applicable.

Temkin[4], as well as Brunauer *et al.*[61], demonstrated that in those cases where a constant distribution function and the linear relation:

$$E = E_0 - \alpha q \tag{24}$$

hold, Eq. (23) is reasonably approximated by the simple relationship:

$$d\theta/dt = k'p\cdot e^{-g\theta} \tag{25}$$

The rate of desorption is then given by:

$$-d\theta/dt = k''\cdot e^{h\theta} \tag{26}$$

Roginskii[63], by using his approximation method dealt with before, arrived at the same result.

In cases where an exponential distribution function (11) applies he could derive:

$$d\theta/dt = \gamma A^{1/\gamma}\theta^{(\gamma-1)/\gamma} \tag{27}$$

In this customary representation[64], the constants A and γ are directly related with the constants of the distribution function. When there exists a symbate relation between E and q, it is very important to know whether

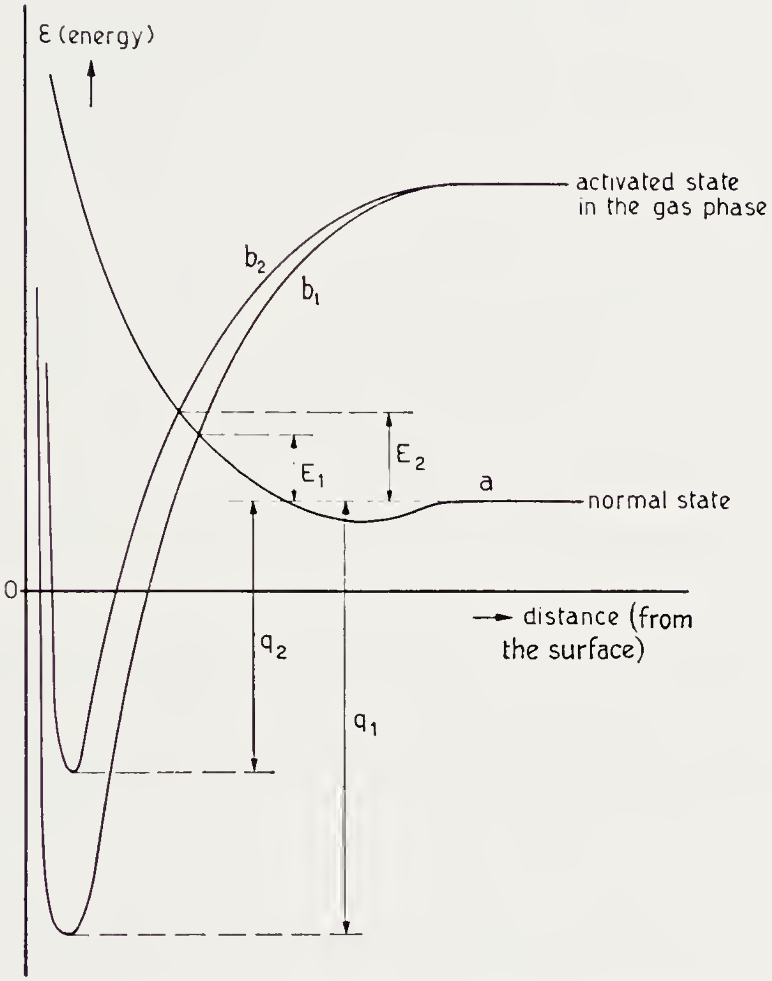

Figure 11. Theoretical representation[60] of probable relation between the energy of activation, E, and the heat of adsorption q, on a heterogeneous surface. Curve a represents the energy of a normal van der Waals interaction between the molecule and the surface as a function of the distance from the surface. Curves b_1 and b_2 refer to the chemisorptive bond between the molecule and the surface on two different sites with adsorption energies q_1 and q_2. (Comparable figures in ref 13, 31, 32.)

the adsorbed particles are mobile or not. For, if the particles are capable of a rapid reorientation in the course of the adsorption process, they will enter the adsorption layer via the sites with the lowest E and q values, to be immediately retained, however, by the sites where the heat of adsorption is highest. As a first approximation, therefore, the measured rate should be independent of the coverage and is characterized by a low activation energy. The alternative, that the particles are not capable of reorientation and

$$E = r \cdot q \tag{28}$$

has been mathematically treated by Halsey[65].

In conclusion it may be stated that the experimentally established relations giving a description of the adsorption data may be qualitatively explained by introducing a given distribution function $N(q)$. However, Roginskii[66] has already pointed out that the accuracy of the experimental data is generally insufficient for enabling a well-founded choice of the shape of the $N(q)$ curve. This view was confirmed by Kruyer[101], who proved that many experimental isotherms can be naturally described both by the Temkin and by the Freundlich formula. Finally, it should be remarked here that as long as no independent method is available of making a quantitative approximation of the heterogeneity of the adsorbing surface, the results of the analysis dealt with so far are in fact entirely unverifiable.

Adsorption on Homogeneous Surfaces

Experimental data obtained with pure surfaces—whose homogeneous character may well be taken for granted, considering the special way of preparation—often appear to be comparable to data measured on technical catalysts. These phenomena, added to the drawback that the distribution function cannot be verified independently, has induced several investigators to make an attempt at describing the experimental results by introducing the conception of the homogeneous surface, on which the change in the heat of adsorption with coverage should be caused by the interaction forces between the adsorbed particles.

In this theory it is extremely important of course to pay attention to the condition of the adsorbed particles on the catalytic surface. When diatomic or polyatomic molecules are being adsorbed, a dissociation may occur, in which case every one of the molecule fragments will occupy one site on the surface. Moreover, the adsorbed particles may be completely immobile, giving rise to a random distribution of occupied sites or pairs of sites. If, on the other hand, the particles are mobile an equilibrium distribution will be established under the influence of the interaction forces. Here again two possibilities may be distinguished:

(a) Although the mobility suffices for enabling the particles to move rapidly from one site to the other, the average distances between the particles are still determined by the lattice distances of the underlying surface (hopping).

(b) The mobility is so high that the lattice distances are of no account, because the average kinetic energy of the adsorbed particles is much greater than the potential barriers at the surface. In this case a mean distance is established under the influence of the interaction forces which distance is only dependent on coverage. The adsorbed phase may be regarded as a two-dimensional gas.

Table 4 gives a survey of the possible combinations.

The conception of the shortest distance interactions with a constant interaction energy V is based on the picture of the localized adsorption. The repulsive interaction force between two adsorbed particles is assumed to decrease so rapidly with the distance that it can exert an influence between particles adsorbed on the nearest site-site distance only. At the next larger distance (in a cubic lattice $d\sqrt{2}$) the interaction energy is neglected.

Table 4. Survey of Different Types of Chemisorption

	Molecular Adsorption		Dissociative Adsorption
	I one mol on one site	II one mol on more than one site	III one particle on one site
(A) Localized immobile	random distribution of occupied sites	random distribution of pairs of occupied sites	as A II
(B) Localized mobile (hopping)	equilibrium distribution of occupied sites	equilibrium distribution of pairs of occupied sites	as B I
(C) Non localized mobile two-dimensional gas	Equilibrium distribution as in a two-dimensional gas with an interaction energy $V = f(r)$		

The theory of the nearest-neighbors-interactions has been elaborated by Roberts[67] and his school. In the case of localized immobile adsorption where each molecule occupies one site (see (A) I, Table 4) $q(\theta)$ and $p(\theta)$ are very easy to calculate. For, owing to the resulting random distribution, the probability that a given site will be occupied is always numerically equal to the degree of coverage. The total number of interacting pairs (X) can therefore be written as:

$$X = M_s \theta z/2 \qquad (29)$$

where z = number of nearest neighbor sites to any site (coordination number); M_s = total number of occupied sites.

Representing the total number of sites by N_s, so that

$$\theta = M_s/N_s \qquad (30)$$

the total interaction energy is given by

$$XV = \frac{M_s^2}{N_s}\frac{z}{2}V \tag{31}$$

so that the differential heat of adsorption becomes a linear function of the degree of coverage:

$$q(\theta) = q_0 - zV\theta \tag{32}$$

For the adsorption isotherm we then find:

$$p = a\frac{\theta}{1-\theta}e^{-(q_0 - zV\theta)/RT} \tag{33}$$

It will be clear that in the range of medium coverages this formula also changes into the Temkin formula (15); it should be remarked, however, in this connection that strictly speaking the conception of the localized immobile adsorption is incompatible with the existence of a measurable equilibrium pressure. For, as the activation energy needed for the surface migration is always smaller than the total adsorption energy, there will invariably be a high degree of mobility before the equilibrium pressure gets an opportunity to attain a measurable value.

In the event the molecules tend to dissociate during the adsorption process, or are so big as to occupy more than one adsorption site, groups of occupied sites will be distributed at random. As a result, isolated gaps are left that are not capable of participating in the primary adsorption process. Roberts[67] calculated that with dissociative adsorption the number of gaps left on the surface may constitute 8 per cent of the total number of sites, whereas if big molecules are involved as many as 36 per cent remain unoccupied. By means of a statistical calculation this investigator determined the influence of this effect on the shape of the $q(\theta)$ curve[67, 68]. The slightly bent curve found can hardly be distinguished from a straight line, however.

If the mobility of the adsorbed particles is so high that there will be established an equilibrium distribution within a relatively short time, the shape of the $q(\theta)$-curve will be entirely different. For at low coverages the average number of pairs of occupied sites will remain very small, so that the adsorption energy is substantially independent of θ. It is only at medium degrees of coverage that, due to the rapid increase of the number of pairs, the heat of adsorption decreases considerably. For molecular adsorption the following equation holds[67]:

$$q_\theta = q_0 + \tfrac{1}{2}zV\left[1 - \frac{1-2\theta}{\{1 - 4(1-\eta)(1-\theta)\theta\}^{1/2}}\right] \tag{34}$$

where

$$\eta = e^{-V/kT}$$

In Figure 12 the shape of the $q(\theta)$ curve, calculated from (34) for different values of η, is demonstrated.

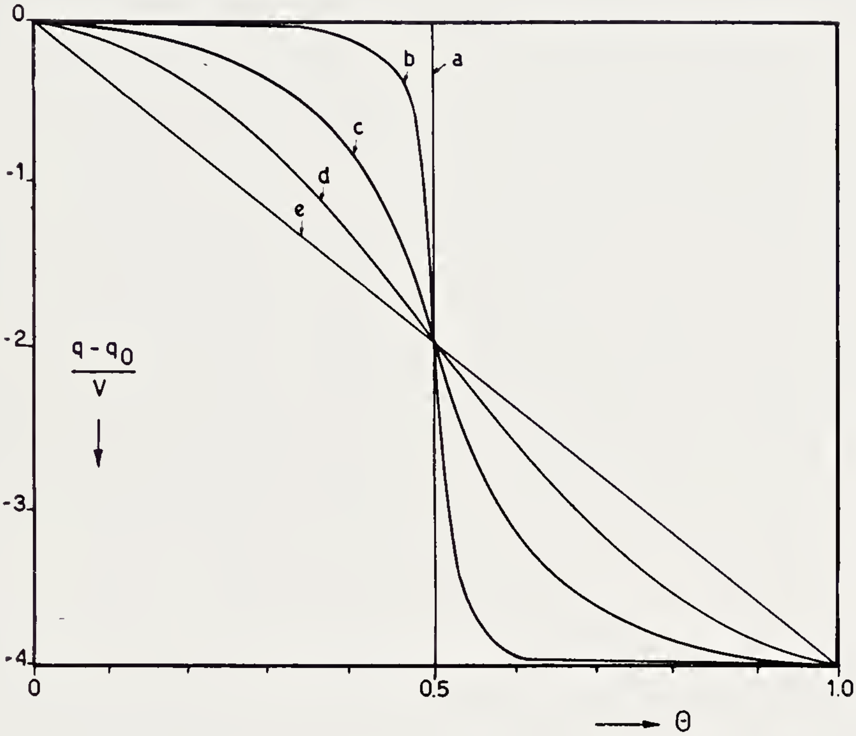

Figure 12. Variation of heat of adsorption with fraction of surface covered. Curve (a) $\eta = e^{-V/kT} = 0$; (b) $\eta = 3.6 \times 10^{-3}$; (c) $\eta = 8.2 \times 10^{-2}$; (d) $\eta = 0.368$; (e) $\eta = 1$. The subscript 0 refers to $\Theta = 0$; and V is the interaction energy between particles adsorbed on neighboring sites. The calculations are for $z = 4$. (According to Roberts[67])

The isotherm formula also becomes more complicated:

$$\frac{\theta}{1-\theta} = A\left\{\frac{1+\eta\epsilon}{1+\epsilon}\right\}^z pe^{q_0/RT} \qquad (35)$$

where ϵ is determined by:

$$\frac{\theta}{1-\theta} = \frac{\epsilon(1+\eta\epsilon)}{1+\epsilon} \qquad (36)$$

Analogous relations may also be derived for other cases (B II and B III).

As stated before, the mobility of the adsorbed atoms may eventually become so high that the distances between these particles are no longer determined by the lattice distances at the surface. By means of this picture, and on the basis of the experimentally found $q(\theta)$ curves, it is possible to make a formal calculation of the interaction function $V(r)$. This method is especially being applied by Russian authors[4, 69]; the resulting $V(r)$ functions seem to be improbable, however.

Thermo-ionic Work Function

From the previous discussion it has become clear that the experimental data may be formally described by starting either from the premise that the catalytic surface is heterogeneous with respect to the adsorbing particles, or from the hypothesis that the adsorbed particles may exert a repulsive interaction upon each other. However, the results thus calculated, namely a distribution function $N(q)$ or an interaction energy V, have both been the subject of well founded criticism in quantitative respect. Several times it has been pointed out[70] that the interaction energy V calculated from the experiments is so high that it cannot be explained from the repulsive action between the dipoles formed at the surface. This is elucidated by the following example: Both Roberts'[71] and Beeck's[72] experimental data on the heat of chemisorption of hydrogen on tungsten, may be excellently described[73] by the statistically derived formula for dissociative immobile adsorption:

$$\frac{q_\theta - q_0}{zV} = \frac{(z-1)^2}{z} \frac{\theta(2z-\theta)}{(z-\theta)^2} \tag{37}$$

putting $z = 4$ it follows that

$$q_0 - q_1 = 7V \tag{38}$$

From experiments it appears that $q_0 - q_1 = 25$ to 30 kcal/mol, so that V amounts to about 2.10^{-13} erg/pair.

The interaction energy between two dipoles is given by:

$$V = \mu^2/r^3 \tag{39}$$

the distance between these dipoles at a tungsten surface being 3.8 Å. From the value found for V it follows, therefore, that the dipole moment should amount to 3.3 Debye units. The dipole moment of a hydrogen atom, however, cannot be imagined to be so high, as this would not be in agreement with the values calculated from contact-potential-differences (0.46 D.[74]; 0.29 D.[75]).

De Boer[76] pointed out that although the presence of cracks, fissures and angles at the surface may have a considerable influence on the van der Waals attraction and on the electrostatic attraction on ionic lattices, the influence on the heat of chemisorption on metal surfaces is only very small. This view is confirmed by the results of Beeck[72] concerning the heat of adsorption of hydrogen on oriented and nonoriented nickel films. The heat of adsorption was found to be entirely independent of the way in which the film had been prepared, notwithstanding the fact that electron diffraction diagrams showed a strong difference in film structure. In view of these considerations it is not possible, therefore, to obtain a clear picture of the background of the calculated distribution function. This accounts for the fact that Beeck arrived at the remarkable conclusion that the only cause for a wide distribution function has to be sought in the interaction between the adsorbed particles and foreign molecules present at the surface as impurities. Whether this factor enables a quantitative interpretation to be made of the distribution function is to be questioned.

A very valuable contribution to the quantitative interpretation of the adsorption on metals was made by Boudart[2].

Previously attention has already been drawn to the fact that during the formation of an—at least partially—ionized adsorptive bond, the value of the work function of the metal (ϕ) must have an influence on the heat of adsorption. Since the formation of a double layer on the surface causes the work function to change, it follows that the heat of adsorption will also change as the coverage increases[77].

Boudart demonstrated that in many cases the decrease of the adsorption energy Δq may be put equal to about 0.5 $\Delta\phi$:

$$\Delta q = 0.5\ \Delta\phi \tag{40}$$

This relation, though not yet adequately founded perhaps, seems to offer interesting possibilities for linking the modern adsorption data with the very extensive material collected on the thermo-ionic emission of metals[78]. In the case of a constant dipole moment, and in the absence of interaction forces, q will consequently decrease linearly with the coverage, independent of the mobility of the adatoms. Possibly occurring interaction energies, or changes in the average dipole moment with coverage[74], or the heterogeneity of the surface, give rise to second order effects, which are superposed on the straight line as a result of which $q(\theta)$ curves of different shape may be obtained[77].

Experimental Data

Adsorption of the Pure Reactants on Iron and Other Metals.

a. *Hydrogen and Nitrogen on Iron Catalysts.* Hydrogen can be chemisorbed on a large number of metals. However, a complication met with is that hydrogen tends to dissolve in the metal at elevated temperatures; this phenomenon is not easy to distinguish from the chemisorption. The number of metals which are also capable of chemisorbing nitrogen is less great, as is the tendency of nitrogen to dissolve in the metal phase. The chemisorption of hydrogen and nitrogen on technical iron catalysts has been thoroughly investigated by the group at the Fixed Nitrogen Research Laboratory in Washington, D. C. A large part of these investigations was already published before the outbreak of World War II. As early as 1934 Emmett and Brunauer[45] published important data on the chemisorption of N_2 on several technical iron catalysts. Although the reproducibility was not always sufficient, due to undefined poisoning phenomena, the heat of adsorption and the activation energy on a doubly-promoted iron catalyst (No. 931, containing 1.3 per cent of Al_2O_3 and 1.6 per cent of K_2O) could be calculated at about 35 kcal/mol and 16 kcal/mol, respectively. Later on, these measurements were recalculated by Brunauer, Love and Keenan[61]. The investigators showed that the rate of adsorption at 397°C could be described by a linear dependency of E and q on the degree of coverage (Eqs. (25) and (26));

$$dv/dt = 0.02\ p(\text{mm Hg})e^{-2100v/RT} - 0.000957e^{800v/RT} \tag{41}$$

(see Figure 13), where v is volume (cm^3) adsorbed per gram.

By putting $dv/dt = 0$, the following isotherm formula results:

$$\log p = \log 0.04785 + 2900\ v/RT \tag{42}$$

which was also found to be in agreement with the experimental figures (Figure 14). Measurements on a singly-promoted catalyst (No. 921; 1.3 per cent Al_2O_3) could be described by a similar formula.

Measurements on the rate of chemisorption of nitrogen on a singly-promoted catalyst were also reported by Gaukhman and Royter[79]). At temperatures of 250 to 450°C an activation energy of about 17 kcal/mol was found at low coverage. The activation energy increases rapidly with increasing coverage.

The rate of chemisorption of N_2 on a singly-promoted catalyst containing 0.8 per cent Al_2O_3 was also studied by Zwietering and Roukens[80]. These measurements were carried out in the temperature range of 200 to 250°C at such a distance from equilibrium conditions that the rate of desorption could be safely neglected. A good reproducibility was obtained by using gases of the highest purity. The fraction of the iron surface (measured by the fast chemisorption of CO) covered by N_2 was found to range from 0.08 to 0.25. The activation energy appeared to vary linearly with coverage (Figure 15), but the resulting decrease in the rate of adsorption was found to be offset by a strong compensation effect. The experimental results at a pressure of 20.1 cm Hg could be described by:

$$d\theta/dt = 446.5e^{107\cdot 2\theta/R}e^{-(9200+727000\theta)/RT}\ \text{min}^{-1} \tag{43}$$

Some experimental data for the rate of chemisorption of N_2 on a doubly-promoted catalyst were recently published by Takao Kwan[81]. The measurements were performed in a constant-volume apparatus at different initial pressures (p_0). The temperature was not varied. The conclusion of the author that his results can best be described by a formula of the type:

$$-dp/dt = k_a p(p_0 - p)^{-\alpha}, \tag{44}$$

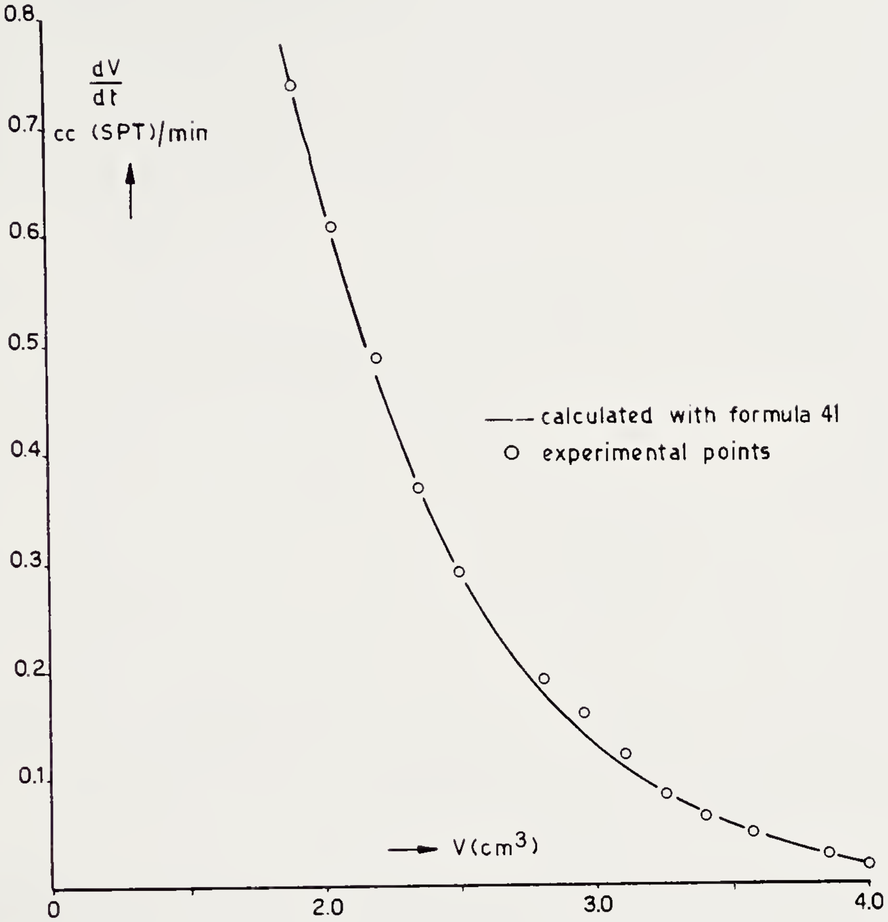

Figure 13. Rate of chemisorption of nitrogen on an iron catalyst as a function of the amount adsorbed. (Brunauer et al.[61])

cannot be subscribed to by us, however. From an analysis of the published material it appears that a relationship of the type (25):

$$-dp/dt = k_a p e^{-\beta(p_0 - p)}, \tag{45}$$

leads to much better results, in accordance with the aforementioned results of all other investigators.

The dissociative character of the nitrogen adsorption on iron is demonstrated by the carefully conducted tests by Kummer and Emmett[82]. Contrary to Joris and Taylor[83], these investigators could prove that the isotopic exchange reaction:

$$N_2^{14} + N_2^{15} = 2N^{14}N^{15}$$

proceeds on an iron catalyst at a measurable rate, provided the catalyst has been carefully reduced. The rate of exchange is of the same order of magnitude as the rate of desorption of nitrogen, calculated from the results of Brunauer, Love and Keenan[61].

Emmett and Harkness[84] showed that the chemisorption of hydrogen on an iron catalyst may proceed by two different ways, as appears from the adsorption isobar taken from their work (Figure 16). The chemisorptions observed at −90 and at +100°C were called type A and type B adsorption, respectively. The activation energy for type A was calculated at 10.4 kcal/mol, while the heat of adsorption for type B appeared to be about 8.5 kcal/mol. Later these measurements were repeated by Gaukhman and Royter[79] and by Taylor and Liang[85], who also found two maxima in the adsorption isobar. The latter investigators observed special discontinuities in the isobar, known from their work on ZnO catalysts[85], demonstrating that a sudden increase in temperature is accompanied by an initial desorption, followed by a slow readsorption. According to the authors this phenomenon should point to a special type of heterogeneity, with a symbatic relationship between E and q, and $\Delta E > \Delta q$. As has been pointed out before, this symbatic relationship is in contradiction to all the experimental results that have become known so far. The phenomenon, observed by Taylor and Liang can be understood, therefore, only if it is assumed to be due to a

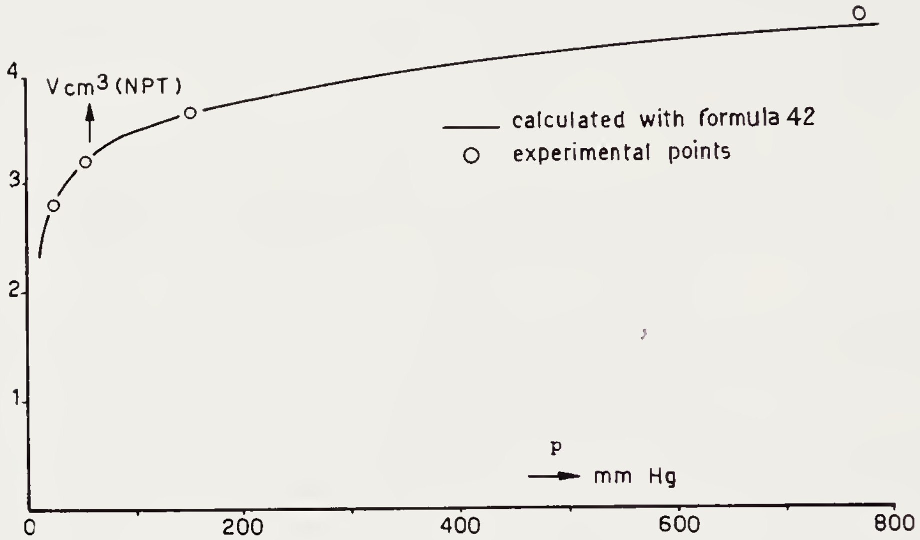

Figure 14. Chemisorption of N_2 on iron catalysts at 397°C–comparison of experimental and calculated curve. (S. Brunauer et al.[61])

transition to another type of adsorptive bond, either on the same or on other sites of the surface.

Kummer and Emmett[86] recently found that at very low temperatures (−196°C) there may occur a third type of hydrogen chemisorption (type *X*) especially on singly-promoted iron catalysts. Evidently, this chemisorption is responsible for the H_2-D_2 exchange reaction at low temperature whereas type A or B chemisorption appears to have a poisoning effect on this reaction. Contrary to the H_2-D_2 exchange, the ortho-para hydrogen conversion proceeds rapidly even on a doubly-promoted catalyst. This seems to suggest that this conversion does not proceed via a chemisorption process but via a magnetic perturbation.

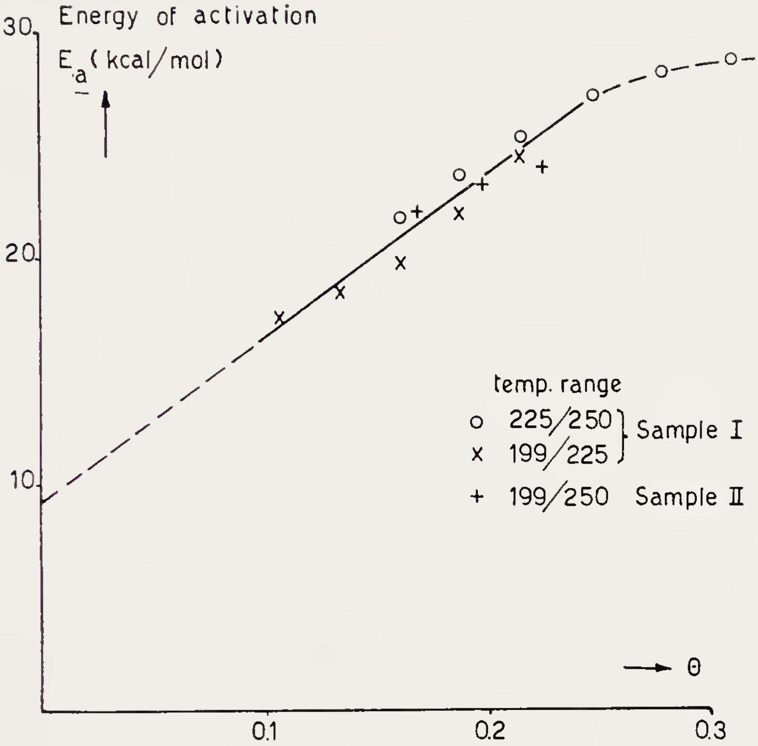

Figure 15. Activation energy of the chemisorption of nitrogen on a singly promoted iron catalyst. (Zwietering and Roukens[80])

The experimental results of Kummer and Emmett are in accordance with the calorimetric measurements of Beebe and Stevens[87], who found a heat of adsorption of 5.3 kcal/mol for H_2 on an iron catalyst at −183°C, which is too high to be ascribed to physical adsorption.

All of the above mentioned data on the chemisorption of hydrogen on iron catalysts were confirmed by the results of a recent investigation by Podgurski and Emmett[88]. The observation that type B chemisorption appears to increase strongly with pressure and the Al_2O_3 content of the catalyst, seems to be especially valuable for a better understanding of the different processes occurring on the catalytic surface.

In conclusion, reference may be made here to the measurements of Takao Kwan[100] concerning the type B chemisorption; these experimental isotherms could be described by a Freundlich formula (12). The heats of adsorption, calculated from the isotherms, decrease strongly with coverage (Figure 17). As regards this figure it should be noted that the coverage values were calculated using the total BET-surface area of the sample and neglecting the fact that the free iron surface is much smaller than the total surface.

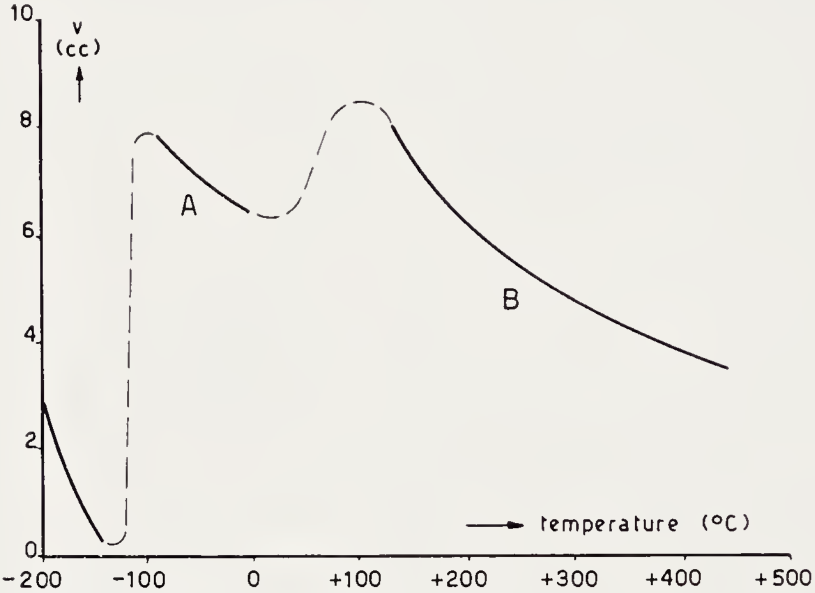

Figure 16. Adsorption isobars of hydrogen (1 atm.) on synthetic ammonia catalyst No. 931, containing 1.59% K_2O and 1.3% Al_2O_3. (Emmett and Harkness[84])

b. *Hydrogen and Nitrogen on Tungsten.* After this survey of the experimental material collected on technical iron catalysts, it is pertinent here to call attention to the extremely accurate measurements on the chemisorption of H_2 and N_2 on tungsten powder, carried out by Frankenburg[89] and by Davis[90]. These measurements were executed with very pure gases on carefully degassed specimens. Different samples with varying surface areas proved to yield identical results per square meter. The hydrogen adsorption[89] was measured across the temperature range from −194 to 600°C. At very low coverages the heat of adsorption was constant and amounted to 46 kcal/mol. The isotherms could be described by:

$$\theta = cp^{1/2} \tag{46}$$

in this region, which points to a dissociative adsorption of the hydrogen molecules. At higher coverages the heat of adsorption decreases considerably (Figure 18); in this region the Freundlich formula appears to hold for the isotherms at all temperatures. In a log v *vs.* log p plot, all straight lines appear to pass through one common point of intersection, which corresponds to a coverage of one hydrogen atom for every two surface tungsten atoms.

Rates of adsorption were not measured, equilibrium appeared to be established at a fairly high rate, especially when it was approached from the high temperature side. It is also noteworthy that, unlike the experience with iron catalysts, no different types of bonds (A or B) could be detected.

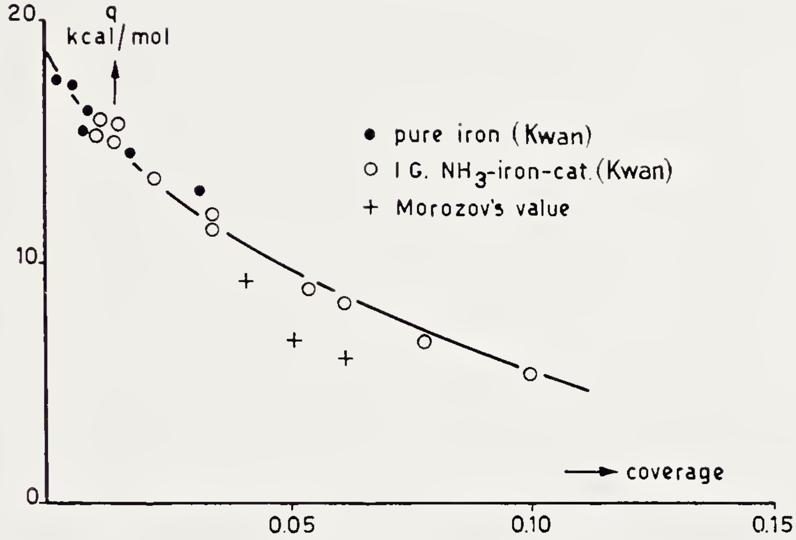

Figure 17. Heats of adsorption of H_2 on iron (Type B) according to Takao Kwan[100], compared with previous results of Morozov[102].

Davis[90], studying the chemisorption of nitrogen on the same samples at temperatures over 400°C, obtained very similar results. Here again, at low coverages a proportionality was found between θ and $p^{1/2}$, whereas the Freundlich formula described the experiments at higher coverages. The common point of intersection S corresponded with the value found for hydrogen. The heat of adsorption q_0 amounted to 78 kcal/mol and was considerably higher than for hydrogen. The decrease of the heat of adsorption with coverage is shown in Figure 18. Besides equilibrium measurements, Davis also carried out rate-measurements at constant pressure and calculated activation energies (Figure 19). The results, which at a later date were obtained by Zwietering and Roukens[80]) on an iron catalyst, are remarkably similar to Davis's data.

c. *Chemisorption on Wires and Evaporated Films.* The experimental results, found by Frankenburg and by Davis have given rise to animated discussions, especially because they differ so markedly from the data collected on tungsten wires and evaporated films. Generally, this discrepancy is attributed to the possibility that, notwithstanding the precautions taken, the surface of the powders used by Frankenburg might still be contaminated (see p. 308).

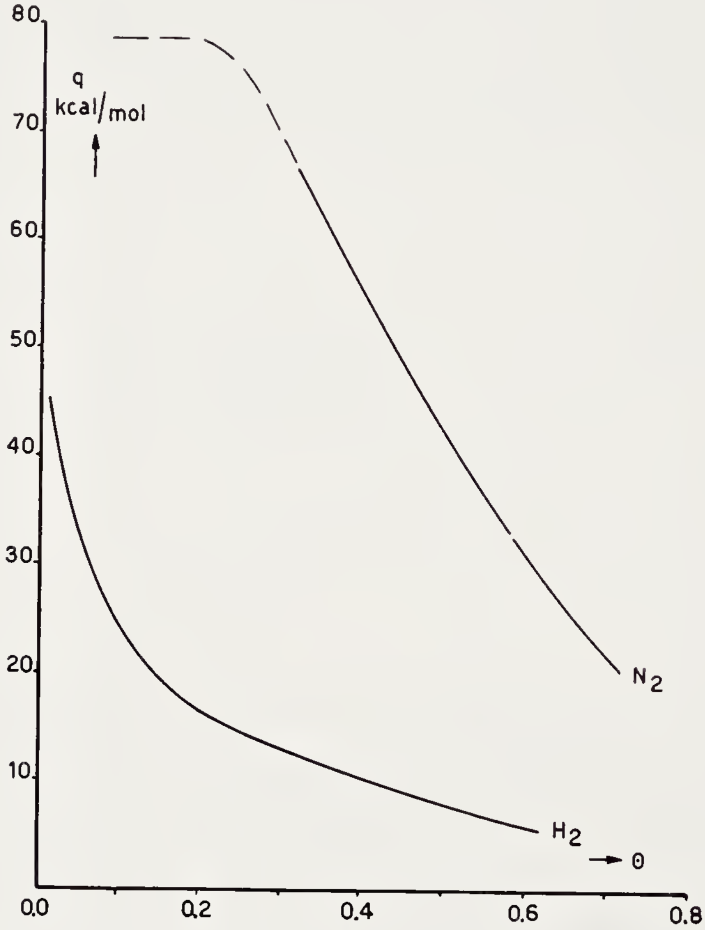

Figure 18. Heat of adsorption of H_2 and N_2 on tungsten powder. (According to W. G. Frankenburg[89] and R. T. Davis, Jr.[90])

Wires, while possessing an extremely high purity, have the drawback of a very small surface area, which makes the direct determination of the amount adsorbed almost impossible. Quantities which change greatly with the formation of the adsorbed layer such as the accommodation coefficient and the contact potential difference are measured instead; unfortunately, this increases the possible source of errors. The very rapid and strong adsorption on these specimens causes the surface to be covered completely at very low equilibrium pressure (about 10^{-3} mm Hg). This renders the complete measurement of the adsorption isotherm difficult. Besides the determination of the rate of ad- and desorption, most measurements comprise the calorimetric determination of the adsorption energy as a function of coverage.

Measurements on wires were chiefly carried out by Roberts[67] and his school (accommodation coefficient and direct calorimetric estimation of q) and by Bosworth[74] (contact potential difference, rates of ad- and desorption).

Measurements on films were carried out by Beeck[72], Eley[91] and Trapnell[92]. For these films the surface areas were about 1000 times greater than for wires, and the surface adsorption could therefore be estimated directly by volumetric methods.

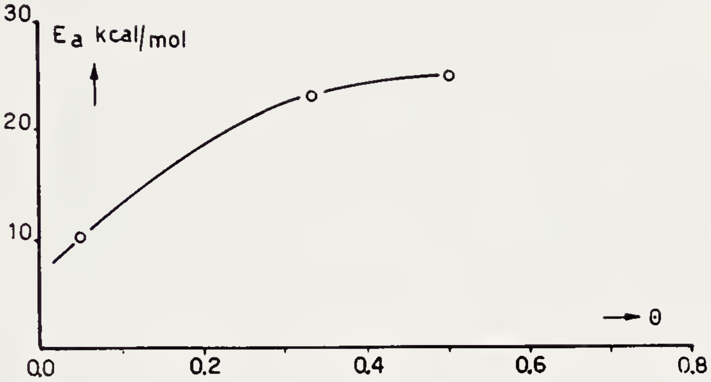

Figure 19. Activation energy for chemisorption of N_2 on tungsten powder. (R. T. Davis, Jr.[90])

Roberts determined the heat of adsorption of hydrogen as a function of coverage. These results were excellently confirmed by measurements of Beeck on tungsten films, as appears from Figure 20, in which Beeck's results, represented by a solid line, are compared with the experimental values found by Roberts and Frankenburg. It is remarkable to note that although the results of Frankenburg show a considerable divergence, the value q_0 is in good agreement with the others. Obviously therefore the explanation of the divergence must be sought in the definition of the coverage. Roberts, by starting from the geometric wire surface multiplied by a roughness factor of 1.4, calculated the coverage as the quotient of the number of adsorbed hydrogen atoms and the number of Wo atoms on the surface. At a very low pressure and temperature the surface appears to be already fully occupied. Frankenburg determined the accessible surface area with the BET-method and stated that his data would have been in agreement with Roberts', if the latter had used a roughness factor of 4.5. However, in the light of Beeck's results on films whose area had been determined by physical as well as chemical adsorption, this viewpoint seems to be untenable. Beeck points to the fact that Frankenburg's tungsten powder contained a fairly high SiO_2-content (0.1 per cent). This amount is amply sufficient for covering the entire metal surface. A strong accumulation of a nonreducible oxide on the surface of a reduced metal oxide is generally known from the work of Emmett and Brunauer[36] on the adsorption of CO on reduced iron catalysts. If it is true that 75 per cent of the powder surface should have been covered with SiO_2 the discrepancy between the measurements largely disappears, while moreover the results found by Beeck and by Davis on the chemisorption of nitrogen on tungsten also appear to be in good agreement.

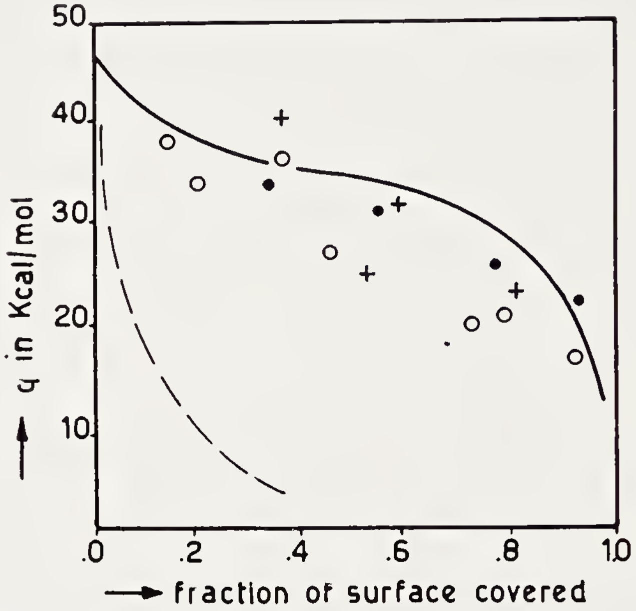

Figure 20. Heats of adsorption of hydrogen on evaporated tungsten films at 23°C in comparison with the results of Roberts (points) and of Frankenburg (broken line) as a function of surface covered. (Beeck[72])

Beeck also measured the heat of adsorption of hydrogen on iron films both at 23°C and −183°C. These measurements yielded the remarkable result (Figure 21) that at −183°C the adsorption energy proved to be constant up to full coverage (curve II), whereas at 23°C the q-values decreased gradually with increasing coverage (curve I). The same effect was found earlier with oxygen on nickel films[94]. As to this, Beeck rightly remarks that the constant value of q, which moreover equals the average value of the heat of adsorption measured at the higher temperature, should be an argument for a nonselective adsorption in the finely-porous system of the adsorbing film caused by the complete absence of any mobility of the adatoms. As soon as the adatoms have acquired a certain mobility at higher temperatures, they are capable of distributing across the entire surface, so that the descending curve is obtained. As a contrast, Miller[73] contends that curve I can excellently be described by the formula which Roberts and Miller[68] derived for immobile dissociative adsorption (37). As explained earlier, however, the application of this formula leads to incompatible high values for the interaction energy between the adsorbed hydrogen atoms, which makes the merits of this relationship questionable.

A better explanation was given by Boudart[2]. He showed that the relationship[40] given above enables a contact potential difference to be calculated from the decrease in the heat of adsorption, which is in good agreement with direct measurements of Bosworth[74].

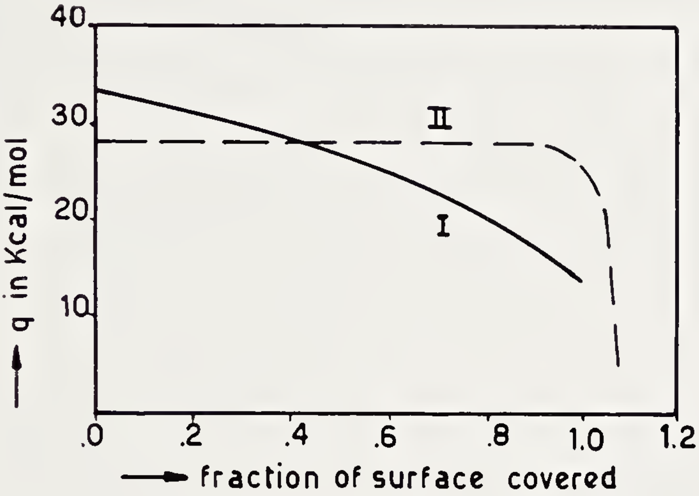

Figure 21. Heats of adsorption of hydrogen on evaporated iron films at −183°C (Curve II) compared with the heats obtained at 23°C (Curve I) as a function of the surface covered. (Beeck[72])

If in the experiments on films the gas pressure is raised to moderate values, an additional uptake of hydrogen is found which depends on the pressure. Beeck's opinion that this uptake must be explained as a dissolving process is based on the observation that the amount of gas taken up at a given pressure is not affected by the sintering of the film, notwithstanding the resulting large reduction of the film area and the rapid decrease of the initial adsorption of hydrogen at low pressure. Extensive measurements on the isotherms of hydrogen on tungsten films at high coverages, have led Trapnell[92] to the belief that most of the slow uptake of hydrogen is still a monomolecular adsorption with a strongly decreased heat of adsorption. This would imply that all θ-values of Beeck, as well as those found by Roberts, should have to be multiplied by a factor 0.7. The same standpoint is taken by Porter and Tompkins[93] who published extensive measurements on the isotherms and the rate of chemisorption of hydrogen on evaporated iron films at high coverages. In the range examined, the well-known relationship:

$$\frac{d\theta}{dt} = k_a p^{1/2} e^{-g\theta} \tag{47}$$

indicating a linear relationship between activation energy and coverage, proves to describe the experimental results excellently. Accordingly, the isotherms can be described by a logarithmic formula. Finally, Eley and Couper[91] consider that the observations may also be explained by second-layer formation. In this connection it is of importance to state that Mignolet[75] has shown that both on nickel and on tungsten a second type of hydrogen may occur, attended with a decrease of the thermo-ionic work function. This is in agreement with a theoretical calculation by Bosworth[95].*

Experiments have also been carried out on the chemisorption of nitrogen on metal films by Beeck[72] and on wires by Bosworth[97]. From the contact potential difference (c.p.d.) Bosworth found a dipole moment of 0.515 Debye units. The heat of adsorption was calculated from the rate of desorption as a function of temperature:

$$q_0 = 29.0 \text{ kcal/mol}$$

$$q_1 = 17.0 \text{ kcal/mol}$$

The entire curve can be described by the formula for dissociative adsorption calculated by Roberts and co-workers. The figures given do not agree with the result measured by Beeck at 300°K, on a tungsten film:

$$q_0 = 95 \text{ kcal/mol}$$

Boudart tried to explain this discrepancy by starting from the assumption

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* As a personal suggestion Professor J. H. de Boer offered a very interesting alternative explanation of the slow uptake of hydrogen, which was based on the experimental results, found by him, on the chemisorption of caesium vapor on evaporated CaF_2 films[96]. In these experiments it was found that the strong chemisorption of Cs might cause a desintering of a previously sintered film, which thus shows a slow but high uptake of Cs-atoms as compared to the physical adsorption of iodine. After slow desorption of the chemisorbed Cs-atoms, the iodine adsorption proved to be equal to the value measured before the sintering! As in all modern experiments on evaporated metal films a "stabilized," hence a more or less presintered film is used, the effect of a desintering, caused by the chemisorption, may also play a role here. Also in the experiments of Taylor and Liang[85], mentioned above, the phenomenon of desintering might form an explanation of the discontinuities found in the isobar with sudden temperature changes. This hypothesis is the subject of an experimental investigation in our laboratory at the moment and will be treated in a forthcoming publication.

that in the experiments of Bosworth, who measured the c.p.d. at −180°C, the adsorbed nitrogen should not have dissociated. This author overlooks, however, the fact that the rates of desorption from which q was calculated, had been measured at very high temperatures (500°C and upwards).

In conclusion, reference should be made to Beeck's calorimetric measurements on the heat of adsorption of nitrogen on iron films. Unlike in the experiments with tungsten films, a chemisorption of the activated type was found in this case; moreover, the highest coverage obtained amounted to no more than 0.2. Across this range q decreases from 40 to 16 kcal/mol.

The dissociative character of this chemisorption could be demonstrated by means of a test in which the entire film, saturated with nitrogen, was dissolved in an acid. The adsorbed nitrogen appeared to be quantitatively converted into NH_3 . At low temperature (90°K) another type of chemisorption of nitrogen (molecular ?) is found, with a far lower heat of adsorption (10 to 5 kcal/mol). The same result was obtained by Porter and Tompkins[93]).

Simultaneous Adsorption of the Reactants, Interaction between the Adatoms. Having dealt with the chemisorption of hydrogen and nitrogen on metals capable of a catalytic acceleration of the NH_3-synthesis, an outline of the present knowledge on the simultaneous adsorption of the two reactants and on the influence which these two will have upon one another will now be presented.

To collect data about this point, Beeck[72] executed some experiments on tungsten and iron films. He found that the heat of adsorption of hydrogen on tungsten, 60 per cent covered with nitrogen, exactly equals the value which q, the heat of adsorption per mole of H_2 , would have if the total surface were covered with hydrogen (Figure 22). Similar results have been obtained on iron films, but as already stated, the maximum degree of coverage with nitrogen amounts to only 20 per cent in this case. By reversing the sequence and measuring the adsorption of nitrogen on an iron film partially covered with hydrogen, it appeared that the maximum adsorption of nitrogen is invariably equal to 20 per cent of the fraction not covered with hydrogen. In other words, Beeck noticed a strict linear relationship between the surface coverage with hydrogen and the maximum coverage with nitrogen afterwards:

$$\theta_N = 0.2\ (1 - \theta_H) \tag{48}$$

From these two experiments it appears therefore that all adsorption sites are equivalent as regards the chemisorption of H- and N-atoms, and moreover that the interaction between both atoms is of the same order as between the adatoms of the same kind. Beeck rightly remarks that the results represented by (48) are not compatible with the assumption that the surface should be heterogeneous. For in that case a coverage of 20 per cent of the surface with H-atoms would completely prevent a subsequent adsorption of nitrogen. Boudart[2], on the other hand, showed that these results can be naturally accounted for by the view proposed by him. Porter and Tompkins[93] showed that the nitrogen chemisorption on an iron film at *low* temperature can be displaced by hydrogen in a 1:1 ratio.

The results obtained on metal films have been partly confirmed by measurements on technical iron catalysts by Brunauer and Emmett[39], who studied the chemisorption of a great number of gases, as well as their mutual interaction on several singly- and doubly-promoted catalysts. On all samples examined the hydrogen sorbed at low temperature (type A) could be replaced in a 1:1-ratio by chemisorbed nitrogen (see also Podgurski and Emmett[88]). In the case of type B chemisorption, however, this effect was observed only on a doubly-promoted catalyst. With singly-promoted catalysts even an increase in the chemisorption of hydrogen, after previous nitrogen adsorption, was observed.

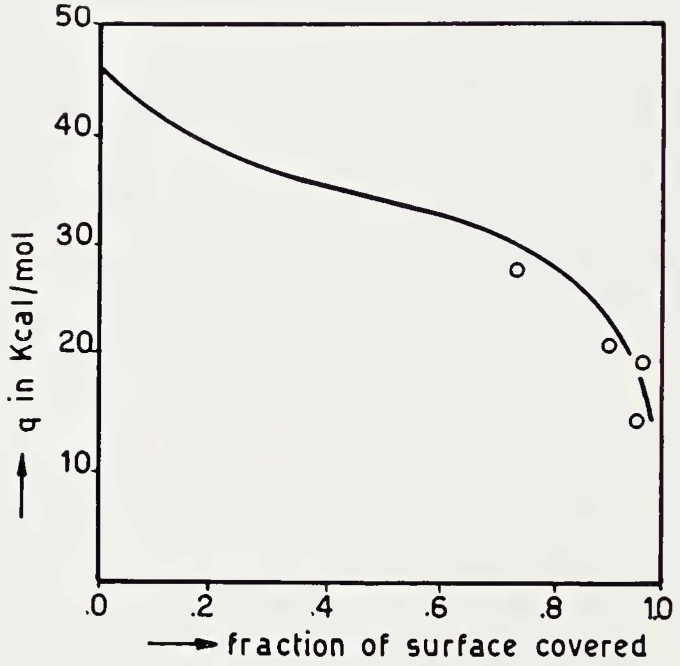

Figure 22. Heats of adsorption of hydrogen on evaporated tungsten films 50 per cent covered with nitrogen. (Beeck[72])

The results mentioned were confirmed by Zwietering[34] who measured, as had been done by Brunauer and Emmett, the chemisorption of hydrogen on a singly-promoted catalyst, before and after chemisorption of nitrogen. His results are given in Table 5.

At the temperature and pressure given in columns 1 and 2 the hydrogen volumes of column 3 are adsorbed on the catalyst if no nitrogen is present on the surface. If, however, nitrogen is preadsorbed (column 4), then the adsorption of hydrogen increases to the values given in column 5. At higher temperatures also NH_3-formation (column 6) was found. As the saturation value for both hydrogen and nitrogen, estimated from CO-chemisorption measurements, amounts to about 30 cm³ for the sample used, it is clear that for the lowest temperature the θ-values for the combined adsorption of nitrogen and hydrogen on the surface approach unity.

Discussion

Having arrived at the end of our account of the experimental data on the chemisorption of gases that are of interest with reference to the synthesis of ammonia by means of iron, the reader will probably experience the same feeling as the authors. On the one hand we are filled with admiration for the ingenuity displayed by the investigators and the perseverance with which they have assembled a wide array of valuable results in this field, which is so difficult to explore experimentally. On the other hand, it appears that even this multitude of experiments has not been able to provide an unambiguous answer to the questions facing us. However, a careful study of the available data reveals a few bright spots.

TABLE 5. SIMULTANEOUS CHEMISORPTION OF H_2 AND N_2 ON AN IRON CATALYST*

1	2	3	4	5	6
Temp. (°C)	Pressure (mm Hg)	H_2 (cm³)	N_2 (cm³)	H_2 on N_2 (cm³)	NH_3-formation
168	9.8	15.4	12.0	17.7	—
220	12.3	12.1	12.0	13.8	traces
276	14.1	9.4	12.0	10.0	0.71

* Zwietering[34]

Discussions concerning the homogeneity or heterogeneity of the catalytic surface such as whether the experimentally found relationships (as the Temkin or Freundlich isotherm, linear or bent $q(\theta)$ curves, etc.) should be explained on the basis of statistical heterogeneity theories, or from interaction forces between adsorbed particles, have made a few things clear. For, in the course of this argument it has appeared that the interaction energy, caused by the dipoles found, does not provide an explanation for the strong variation of q with coverage. *Mutatis mutandis* applies with equal force to the influence of the active centers. Irregularities in the crystal lattice, different crystal planes, etc., have too small an effect on the heat of chemisorption on a metal surface to account for the differences observed.

So, neither of the two theories is capable of a quantitative interpretation of the experimental facts.

It is of great importance to note therefore that—especially since the discussion on heterogeneous catalysis of 1950—there has been a growing perception that the decrease in the heat of adsorption with increasing coverage is substantially due to the change in the work function of the metal caused by the double-layer formed[2, 77].

This has led again to the conception that the metal surface should in a certain sense be considered as a continuum and that the adsorbed poisons, promoters, etc., exerting an influence upon the work function of the metal, influence all adsorption sites to the same extent and thus characterize the entire activity.

Thus, the influence of the surface heterogeneity on the heat of chemisorption on metals is less great than had been thought, and it must be concluded therefore that it is not possible to form an unambiguous judgment as to the structure of the metal surface on the basis of adsorption measurements. In this connection we want to point to an ingenious method to obtain information in another way, as indicated by Roginskii and Todes[66]. With this method the surface is covered in two steps, in one of which use is made of a labeled gas. Should the surface be heterogeneous, the latter gas, which is adsorbed on the less active sites, will be the first to leave the surface when the adsorbed layer is being pumped off. In case the surface should be homogeneous, the mixture pumped off will be constant in composition. Kummer and Emmett[98], as well as Eischens[99] executed such measurements on iron catalysts, both using $C^{14}O$-$C^{12}O$ mixtures. As in both cases the first and the second portion appeared to be mixed to no more than 50 per cent, it was concluded that the surface-structure must be at least partially heterogeneous. However, as already indicated by Kummer and Emmett[98] (*loc. cit.*) this result is still disputable because:

(1) on a heterogeneous surface homogenization of the sorbate may occur, owing to a high mobility of the adsorbed molecules.

(2) on a homogeneous surface there may persist a separation of the sorbate, especially where big molecules are involved, due to the occurrence of various types of bonds.

As far as the iron surfaces studied by the two investigators are concerned, the authors are of the opinion that there is every reason to assign a real significance to the latter phenomenon[1].

As regards the ammonia-synthesis, we have noted that both nitrogen and hydrogen may be chemisorbed under synthesis conditions. It may be assumed that the Fe—N bond will be a polar one, just as has been found for the W—N bond (Bosworth[52]). The chemisorption of nitrogen, therefore, may be considered to lead to the formation of an at least partially ionic bond. When the adsorption process is being considered as a chemical reaction it may be imagined to comprise the following steps:

$$N_2 = 2N - \epsilon_D \qquad (a)$$

$$2N + 2e = 2N^- - 2\epsilon_e \qquad (b)$$

$$[Fe] = 2e - 2\phi \qquad (c)$$

$$2N^- + [Fe] = 2[Fe]N^- + 2\epsilon \qquad (d)$$

$$\overline{N_2 + [Fe] = 2[Fe]N^- + q}$$

$\epsilon_D = 225$ kcal; $\epsilon_e = 17$ kcal; $\phi = 100$ kcal.
From this gross equation it follows therefore that (with $q = 40$ kcal/mol)

$$\epsilon = \frac{\epsilon_D + 2\epsilon_e + 2\phi + q}{2} = 250 \text{ kcal} \qquad (49)$$

This high gain in energy, obtained when an N-ion is being bound to the metal surface, cannot be explained by the normally used "image force" theory[76]. However, the N-ion formed on the 111 face of iron need not remain entirely on the outer surface, for the lattice is sufficiently loose-packed to enable the ion to penetrate between the iron atoms of the first layer where it comes to rest upon the atoms of the second layer[39]. Calculation of the Coulomb attraction between a univalent positively charged Fe-atom and an N-ion at the distance of closest approach gives a bond energy of the right order of magnitude:

$$\epsilon = \frac{e^2}{r_N + r_{Fe}} + (\alpha_N + \alpha_{Fe}) \frac{e^2}{2(r_N + r_{Fe})^4} \qquad (50)$$

putting $r_N + r_{Fe} = 1.95$ Å and $\alpha_N + \alpha_{Fe} = 5 \times 10^{-24}$ cm^3 we find:

$$\epsilon = 230 \text{ kcal.}$$

So the N-ions appear to be bound with a high energy. However, the energy needed for dissociation and ionization is so great that the activation energy also becomes appreciable. Technical iron catalysts require a temperature of about 300°C to show an appreciable rate of chemisorption, while in the case of very active iron films chemisorption can only be measured over 100°C. This entails the important consequence that the chemisorption of nitrogen constitutes the rate determining step of the entire synthesis reaction.

The chemisorption of hydrogen on iron has a more complicated character. For there exist at least two types of chemisorption, whose properties have been found to differ in many respects. Moreover, at low temperature a third type of chemisorption is sometimes observed. This type, which probably is of molecular character will not be discussed here.

Type A, with the lowest heat of adsorption and the lowest value for the activation energy, has the nearest resemblance to the chemisorption which at slightly lower temperatures is observed on metal wires and films. For, in either of these cases it has appeared that the adsorbed H-atoms behave entirely indifferently with respect to the simultaneously chemisorbed N-adatoms. From contact potential measurements it follows that both are chemisorbed with a negative dipole moment, which may account for this indifferent behavior. It is logical to assume, therefore, that type A adsorption on iron catalysts is caused by the H-atoms possessing a negative dipole moment with respect to the catalytic surface (H^-). In the case of type B chemisorption however, matters are different. There are indications that this type of adsorption is *stimulated* by the presence of nitrogen on the surface. Moreover, it is known that in measuring the photo-emission of metals at high temperatures the presence of hydrogen tends to shift the long wave limit to higher wavelengths[78], which means that the thermoionic work function is *lowered*. This leads to the view that the hydrogen chemisorbed at high temperatures (type B) should consist of positive ions. From a study of the energy contributions (shown schematically in Figure 23) which must play a part in the occurrence of the two types of bonds, it becomes clear that not only the activation energy but, by the virtue of the greater Fe-H distance, also the heat of adsorption will be lower for type A chemisorption than for type B, as is found experimentally. Alkali-oxides or metals also form positive dipoles on the metal surface, so that the favorable effect of adsorbed N-atoms on the type B chemisorption of hydrogen will be smaller on doubly-promoted catalysts than on surfaces where no K_2O is present. The combination of H^+ and N^- on the surface probably forms the first step toward the formation of ammonia, which process is completed by the capture of an impinging hydrogen molecule with the formation of a weakly bound NH_3 group. This group, which may be compared to an adsorbed alkali atom, will also have a positive dipole moment. All of the steps involved proceed rapidly in comparison with the chemisorption of the nitrogen.

In conclusion it may be remarked that the desorption rate of the NH_3 groups formed will depend on the binding energy and on the partial pressure of the NH_3 in the gas phase. Consequently, it is to be expected that this desorption rate will show a relative decrease as, in high pressure synthesis, P_{NH_3} starts to rise considerably. The important promoting action of K_2O, which becomes only apparent at high pressures (at low pressures K_2O acts as a poison!) can probably be explained from the lowering effect which these positive dipoles exert on the heat of adsorption of the NH_3-complex, and as a result of which the desorption rate is raised beyond the limit where it ceases to be the rate determining factor.

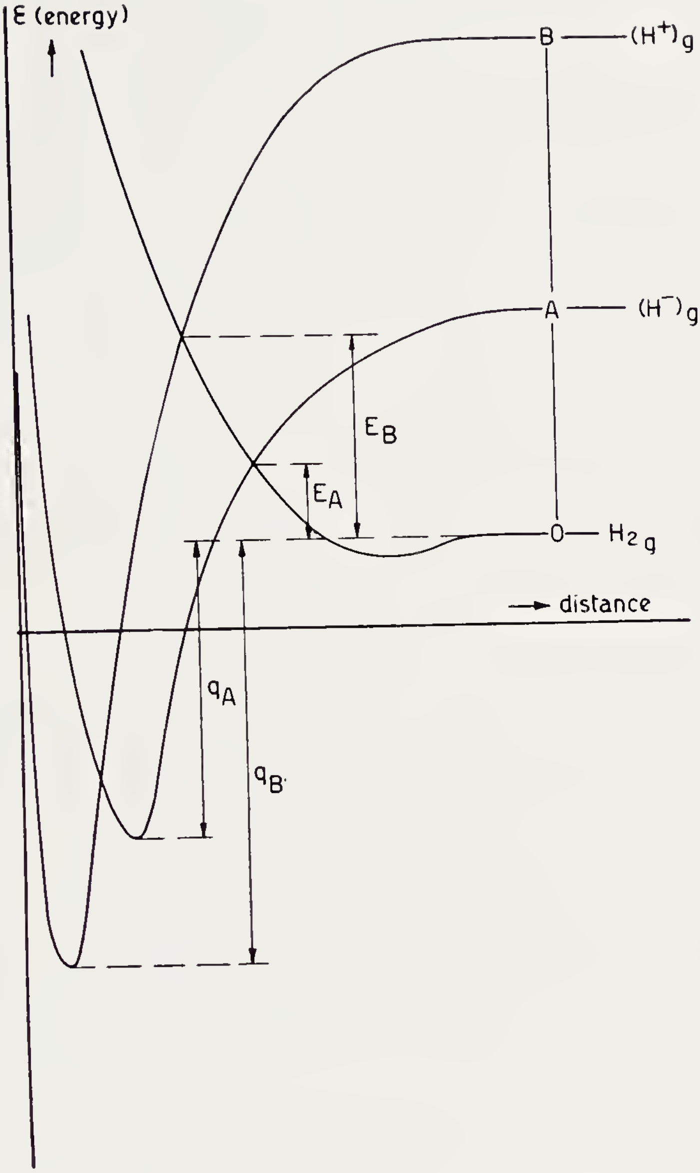

Figure 23. Energy diagram for H_2, H^+ and H^-.
$OA = E_D + 2\Phi_{Fe} - 2E_e = 270$ kcal/mol.
$OB = E_D - 2\Phi_{Fe} + 2\,E_I = 527$ kcal/mol.
Diss. energy $H_2 = 103$ kcal/mol.
Electron aff. H-atom = 16.4 kcal/mol.
Ionization energy H-atom = 312 kcal/mol.

KINETICS OF AMMONIA SYNTHESIS

Whereas the literature prior to 1940 makes hardly any mention of the kinetics of ammonia synthesis, it contains a large number of records of investigations dealing with the kinetics of ammonia decomposition which, unlike the former, can be studied easily. Furthermore, since interest in general was focused rather on the practical aspect of ammonia synthesis, only occasional attempts were made[103] to develop a reaction rate equation. The publication by Temkin and Pyzhev[5], dealing with the kinetics of ammonia synthesis on promoted iron catalyst, greatly enhanced the knowledge of the kinetics of heterogenous reactions in general and furnished a powerful impetus to the making of kinetic measurements. In view of the great importance which nowadays is assigned to the Temkin theory, we think it desirable to subject the principles underlying this theory to a more detailed consideration. After that, we shall test the theory with the aid of experimental data and conclude by examining how the reaction rate may be retarded by the restricted diffusion rate.

Principles of the Temkin Theory

Before giving a discussion of the principles on which the Temkin theory is based, we shall first consider what was known about the mechanism of ammonia synthesis prior to its development.

The catalytic synthesis of ammonia may comprise the following processes:

Transport of the reactants to the catalytic surface.

Adsorption of N_2 : $N_{2_{gas}} + [Me] \rightleftarrows [Me]N_2 \rightleftarrows 2[Me]N$

Adsorption of H_2 : $3H_{2_{gas}} + [Me] \rightleftarrows 3[Me]H_2 \rightleftarrows 6[Me]H$

Surface reaction: $2[Me]N + 6[Me]H \rightleftarrows 2[Me]NH_3$

Desorption of NH_3 : $2[Me]NH_3 \rightleftarrows 2NH_{3_{gas}} + 2[Me]$

As yet it is not quite certain whether or not the formation of ammonia really proceeds via a Langmuir-Hinshelwood mechanism, i.e., by reaction of adsorbed nitrogen with adsorbed hydrogen. It is well-known, however, that the adsorption of nitrogen may be regarded as the rate-determining step.

Emmett and Brunauer[45] succeeded in proving that the rate of nitrogen adsorption on an iron catalyst is approximately equal to the rate of formation of a corresponding amount of ammonia on this catalyst. Moreover, experiments by Kozhenova and Kagan[104] have shown that the hydrogenation reaction proceeds much more speedily than the nitrogen adsorption. Finally, it was found that the exchange reaction as illustrated by the formation of ND_3 :

$$2NH_3 + 3D_2 \rightleftarrows 2ND_3 + 3H_2$$

over an iron catalyst occurs at room temperature[105]. From this it follows that at a high temperature, neither the adsorption of hydrogen nor the desorption of ammonia can be the rate-determining step.

Consequently, Temkin and Pyzhev could start from the assumption that the adsorption of nitrogen is the rate-determining step in the synthesis of ammonia. In the course of their derivation of the kinetic expression they further introduced the following premises:

(1) the nitrogen adsorption is not influenced by hydrogen and ammonia and

(2) the adsorption and desorption of nitrogen at constant temperature can be described by the following expressions:

$$\text{adsorption rate } V = k_a P_{N_2} e^{-g\theta} \tag{51}$$

$$\text{desorption rate } W = k_d e^{h\theta} \tag{52}$$

where P_{N_2} is the nitrogen pressure in the gas phase, θ is the degree of coverage, and k_a, k_d, g and h are constants.

As explained on pages 291–294, it follows from these relationships that the isotherm describing the adsorption equilibrium must be equal to:

$$\theta = 1/f \ \ln a_0 P_{N_2} \tag{53}$$

where a_0 and f $(= g + h)$ are constants and k_a, k_d and a_0 are dependent upon the temperature.

Temkin and Pyzhev, in their original publication, supposed that nitrogen is adsorbed in the form of molecules. In later articles by Temkin[106], however, adsorption was always assumed to be of an atomic character, which is in agreement with the results of exchange experiments with N_2^{28} and N_2^{30} carried out by Kummer and Emmett[107]. The assumption of atomic adsorption, however, does not affect the general form of the kinetic expression.

According to the above premises the amount of ammonia produced per unit of time corresponds to the difference between the rates of adsorption and desorption of nitrogen:

$$\frac{dP_{NH_3}}{dt} = k_a P_{N_2} e^{-g\theta} - k_d e^{h\theta} \tag{54}$$

To eliminate θ, Temkin now introduces the quantity $P_{N_2}{}^*$ which may be considered as the fugacity of the adsorbed nitrogen. It is the fictitious nitrogen pressure which is in equilibrium with the degree of coverage θ:

$$\theta = 1/f \ln a_0 P_{N_2}{}^* \tag{55}$$

Substituting (55) in (54) gives:

$$\frac{dP_{NH_3}}{dt} = k_a P_{N_2} (a_0 P_{N_2}{}^*)^{-\alpha} - k_d (a_0 P_{N_2}{}^*)^{1-\alpha} \tag{56}$$

where $\alpha = g/f$. Following Winter[108], Temkin assumes that $P_{N_2}^*$ is determined by the hydrogen and ammonia pressures in the gas phase. The following may serve to elucidate this important point. As the Temkin theory assumes that all reaction stages—with exception of the nitrogen adsorption—are in equilibrium with one another, there must be equilibrium at the catalyst surface between the adsorbed nitrogen, hydrogen and ammonia. The value of the equilibrium constant $K = \dfrac{a[N_2]a^3[H_2]}{a^2[NH_3]}$, where $a[N_2]$, $a[H_2]$ and $a[NH_3]$ denote the activities of the adsorbed phases, is equal to that of the equilibrium:

$$N_2 \text{ gas} + 3H_2 \text{ gas} \rightleftarrows 2NH_3 \text{ gas}$$

As the adsorbed hydrogen and ammonia are always in equilibrium with the hydrogen and ammonia in the gas phase, the activities in the two phases are equal:

$$a[H_2] = P_{H_2} \qquad \text{and} \qquad a[NH_3] = P_{NH_3}$$

By definition, the fictitious nitrogen pressure $P_{N_2}^*$ introduced by Temkin is equal to the activity of the adsorbed nitrogen.
So,

$$a[N_2] = P_{N_2}^* = K^{-1}\frac{P_{NH_3}^{\,2}}{P_{H_2}^{\,3}} \tag{57}$$

Substitution of (57) in (56) finally gives the Temkin equation for the reaction rate:

$$\frac{dP_{NH_3}}{dt} = k_1 P_{N_2}\left(\frac{P_{H_2}^{\,3}}{P_{NH_3}^{\,2}}\right)^{\alpha} - k_2\left(\frac{P_{NH_3}^{\,2}}{P_{H_2}^{\,3}}\right)^{1-\alpha} \tag{58†}$$

where the constants k_1 and k_2 are equal to:

$$k_a a_0^{-\alpha} K^{\alpha} \qquad \text{and} \qquad k_d a_0^{1-\alpha} K^{\alpha-1} \text{ respectively.}$$

At equilibrium the rate of the forward reaction is equal to that of the back reaction so that

$$k_1/k_2 = \frac{P_{NH_3\,\text{equil.}}^{\,2}}{P_{N_2\,\text{equil.}} P_{H_2\,\text{equil.}}^{\,3}} = K \tag{59}$$

When integrating (58), it is customary to eliminate the constant k_1 (see pp. 321–325). In that case, the apparent energy of activation for ammonia decomposition will be determined by the temperature dependency of k_2.

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† Temkin[109] also investigated whether it is necessary to correct for the deviations from the ideal gas laws. Since at 300 atm. the activity coefficients differ but little from unity ($f_{NH_3} = 0.91$ and $f_{H_2} = 1.09$) the correction up to this pressure is still unimportant.

As $k_2 = k_d a_0^{1-\alpha} K^{\alpha-1} \sim \exp\,[-(E_a^0 + q_0) + (1 - \alpha)q_0 - (1 - \alpha)Q]/RT$, it follows from the Temkin theory that the apparent energy of activation for ammonia decomposition must be equal to:

$$E = E_a^{\;0} + \alpha q_0 + (1 - \alpha)Q \tag{60}$$

where E_a^0 and q_0 are the energy of activation and the heat of adsorption respectively of N_2, both at a surface coverage = 0, and Q is the enthalpy of the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$. The value of the constant α does not follow from theory and must therefore be determined experimentally. For this purpose Temkin, in his original paper, made use of the expression which Winter[108] has developed for the kinetics of the ammonia decomposition

$$-\frac{dP_{NH_3}}{dt} = k\,\frac{P_{NH_3}{}^{0.9}}{P_{H_2}{}^{1.5}} \tag{61}$$

from which it follows that the value of α must be somewhere near 0.5, so $g = h$. Putting $\alpha = 0.5$, the kinetic expression changes into

$$\frac{dP_{NH_3}}{dt} = k_1\,\frac{P_{N_2}P_{H_2}{}^{3/2}}{P_{NH_3}} - k_2\,\frac{P_{NH_3}}{P_{H_2}{}^{3/2}} \tag{62}$$

For $\alpha = 0.5$, Temkin using the values of E_a and q given by Emmett and Brunauer[45] (see p. 300), calculates the apparent energy of activation for iron catalyst at $15 + \frac{35}{2} + 13 = 45.5$ kcal/mol. In a following discussion we shall see that this value is in good agreement with those found from kinetic measurements. To check the kinetic relation (58) with the experimental data, the differential equation must be integrated. Therefore we shall carry out this integration for a number of conditions.

Integration of the Differential Equation (58)

Synthesis at 1 Atmosphere. In view of the low value of $P_{NH_3\,\text{equil.}}$ in the synthesis at 1 atmosphere, P_{N_2} and P_{H_2} may be put approximately equal to $P_{N_2\,\text{equil.}}$ and $P_{H_2\,\text{equil.}}$. After elimination of k_1, (58) consequently changes into

$$\frac{dP_{NH_3}}{dt} = \frac{k_2}{P_{H_2}{}^{3-3\alpha}}\left\{\frac{P_{NH_3\,\text{equil.}}{}^{2}}{P_{NH_3}{}^{2\alpha}} - P_{NH_3}{}^{2(1-\alpha)}\right\} \tag{63}$$

or:

$$\frac{d\eta}{dt} = k_2\,\frac{P_{NH_3\,\text{equil.}}{}^{1-2\alpha}}{P_{H_2}{}^{3-3\alpha}}\left\{\left(\frac{1}{\eta}\right)^{2\alpha} - \eta^{2(1-\alpha)}\right\} \tag{64}$$

where the efficiency $\eta = \dfrac{P_{NH_3}}{P_{NH_3\,\text{equil.}}}$.

In describing kinetic measurements it is customary to make use of the concept space velocity. Therefore we shall define the space velocity as the ratio of the gas rate (in cm^3(NTP)/hour) to the catalyst volume. The contact time t will then be equal to $\frac{\phi 273P}{T} \cdot \frac{1}{V}$, where ϕ is the free volume per unit volume of catalyst.

Integration of (64) finally yields:

$$k = \gamma^{3/2}(4 - 3\gamma)^{\alpha-0.5}P^{\alpha}V \int_0^{\eta} \frac{\eta^{2\alpha}}{1 - \eta^2}\, d\eta \tag{65}$$

where the constant k† is equal to:

$$k = \frac{k_1^{0.5-\alpha}k_2^{0.5+\alpha}(1/4)^{0.5-\alpha}(3/4)^{-1.5}273\phi}{T} \tag{66}$$

Further $\gamma = \frac{P_{H_2}}{0.75P}$ is a measure of the deviation from the stoichiometrical composition for which $\gamma = 1$.

For the special case that $\alpha = 0.5$, integration of (65) gives:

$$k = -1/2\gamma^{3/2}P^{1/2}V \ln (1 - \eta^2) \tag{67}$$

Since for $\alpha = 0.5$, the rate constant $k \sim \frac{1}{T} k_2 \sim \frac{1}{T} e^{-E/RT}$ the apparent energy of activation for ammonia decomposition calculated from the temperature dependence of k is equal to:

$$\frac{4.57T_1T_2}{T_1 - T_2} \log \frac{k'T_1}{k''T_2} \tag{68}$$

where k' and k'' are the rate constants at the temperatures T_1 and T_2, respectively.

Synthesis at Pressures above 1 Atmosphere. As has been done for the synthesis at 1 atmosphere, the integration of (58) will again be carried out for arbitrary values of α and γ. Therefore we put:

$$P_{N_2} = \frac{2 + (1 - 3\gamma)ZP}{2(1 + 3\gamma)} \tag{69}$$

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† It is customary to express the results of synthesis measurements in the rate constant k. From equation (66) it appears that for $\alpha = 0.5$ temperature dependence of k may be identified with that of decomposition reaction. From the relationship $k_1/k_2 = K$ it follows that the apparent energy of activation of the synthesis reaction differs by an amount Q (the reaction enthalpy) from that of the decomposition reaction. Throughout the whole reaction we shall follow, however, the usual procedure and specify the apparent energy of activation as the temperature dependence of the rate constant k.

$$P_{H_2} = \frac{3\{2\gamma - (1+\gamma)Z\}P}{2(1+3\gamma)} \tag{70}$$

$$P_{NH_3} = PZ \tag{71}$$

where P is the total pressure and Z the mole fraction of ammonia present. To eliminate k_1 we put:

$$L^2 \equiv \frac{Z_{\text{equil.}}^2(1+3\gamma)^4}{[2+(1-3\gamma)Z_{\text{equil.}}][2\gamma-(1+\gamma)Z_{\text{equil.}}]} = \frac{27}{16}\frac{k_1}{k_2}P^2 \tag{72}$$

Generally, in high pressure ammonia synthesis the volume contraction during the reaction may no longer be neglected. For this reason we shall define $V_0 = \frac{U_0}{w}$ and $V_z = \frac{U_z}{w}$ as the space velocities on the inlet and outlet sides of the reactor. In these expressions w is the volume of the catalyst and U_z is the gas volume (calculated for standard conditions) leaving the reactor with a mole fraction of ammonia $= Z$; so that:

$$\frac{dP_{NH_3}\,(\text{outlet})}{dt} = \frac{d\,\frac{U_z}{U_0}P_{NH_3}}{dt} = \frac{P}{(1+Z)^2}\frac{dZ}{dt} \tag{73}$$

Using (71), (72) and (73), and substituting $dt = \phi\,\frac{273}{T}\,P\,(1+Z)\,d\,\frac{1}{V_0}$, integration of (58) yields

$$k = P^{1-\alpha}V_0 \times \int_0^Z \frac{Z^{2\alpha}(1+3\gamma)^{3\alpha+1}[2\gamma-(1+\gamma)Z]^{3(1-\alpha)}dZ}{(1+Z)^3[16L^2\{2+(1-3\gamma)Z\}\{2\gamma-(1+\gamma)Z\}^3 - Z^2(1+3\gamma)^4]} \tag{74}$$

where the constant

$$k = \phi\,\frac{273}{T}\,(2/3)^{3(1-\alpha)}k_2 \tag{75}^*$$

For $\alpha = 0.5$ and $\gamma = 1$, the rate constant takes the following form

$$k = P^{1/2}V_0 \int_0^Z \frac{Z(1-Z)^{1,5}\,dZ}{(1+Z)^3\{L^2(1-Z)^4 - Z^2\}} \tag{76}$$

This integral can be solved numerically.

According to Temkin[109] a good approximation for the integral in (76) is:

$$I(Z) = -1/2(1-Z)^4 \ln\left[1 - \frac{Z^2}{(1-Z)^4L^2}\right] \tag{77}$$

Even at high ammonia contents, the values of $I(Z)$ calculated with the

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* Some authors do not include the factor $(2/3)^{3(1-\alpha)}$ in the constant k.

aid of (77), appear to deviate but slightly from those computed by numerical integration.

At first sight the dependence on the total pressure in Eq. (74) seems to differ from the expression given in Eq. (65). On closer consideration, however, it appears that for small values of $Z_{\text{equil.}}$ (74) may be transformed into:

$$k = P^{1-\alpha} V_0 Z_{\text{equil.}}^{2\alpha-1} \int_0^{\eta} f(\eta, \alpha)\, d\eta \tag{78}$$

Since

$$Z_{\text{equil.}}^{2\alpha-1} \sim P^{2\alpha-1}$$

the following expression holds:

$$k \sim P^{\alpha} V_0 \int_0^{\eta} f(\eta, \alpha)\, d\eta \tag{79}$$

which shows that Eqs. (65) and (74) are really equivalent. Under certain conditions (low temperature or high space velocity), the synthesis reaction may take place so far from equilibrium that the contribution of the decomposition reaction to the over-all reaction rate may be disregarded. In that case the following equation applies:

$$\frac{dP_{NH_3}}{dt} = k_1 P_{N_2} \left(\frac{P_{H_2}{}^3}{P_{NH_3}{}^2} \right)^{\alpha} \tag{80}$$

The integration of (80) is analogous to that of the general expression. The rate constant is given by:

$$k = P^{1-\alpha} V_0 \int_0^{Z} \frac{Z^{2\alpha}(1 + 3\gamma)^{3\alpha+1}\, dZ}{(1 + Z)^3[16L^2\{2 + (1 - 3\gamma)Z\}\{2\gamma - (1 + \gamma)Z\}^{3\alpha}]} \tag{81}$$

where k is given by Eq. (75).

For low values of Z, (81) changes into:

$$k = \text{constant } P^{1-\alpha} V_0 Z^{2\alpha+1} \tag{82}$$

Decomposition of Ammonia. As a rule the decomposition of ammonia is studied under conditions which permit the reverse reaction, i.e. the synthesis reaction, to be disregarded. In that case, it follows from the Temkin equation that:

$$\frac{-dP_{NH_3}}{dt} = k_2 \left(\frac{P_{NH_3}{}^2}{P_{H_2}{}^3} \right)^{1-\alpha} \tag{83}$$

The decomposition experiments are frequently carried out in such a way that variations in volume and partial hydrogen pressure may be neglected.

Integration of (83) then gives:

$$k = \frac{1}{2\alpha - 1} V_0(1 - P_{\mathrm{NH_3inlet}})^{3(1-\alpha)} \{P_{\mathrm{NH_3inlet}}{}^{2\alpha-1} - P_{\mathrm{NH_3outlet}}{}^{2\alpha-1}\} \quad (84)$$

With $\alpha = 0.5$, the rate constant becomes:

$$k = -V_0(1 - P_{\mathrm{NH_3inlet}})^{3/2} \ln \frac{P_{\mathrm{NH_3outlet}}}{P_{\mathrm{NH_3inlet}}} \quad (85)$$

Testing of the Temkin Expression

Before considering the experimental data, we shall outline a method by which the kinetic expression can be tested. The most obvious way would be to find out whether or not the rate constant, calculated from the kinetic expression, is independent of the space velocity, H_2/N_2-ratio and total pressure. Moreover, the value of the apparent energy of activation found from the temperature dependence must be constant for all conditions.

The validity of the kinetic expression becomes established only if all experimental data conform to the above conditions. With this in view, it is of the utmost importance that all of the available data be used. The validity of the Temkin expression will be tested in succession for the synthesis at 1 atmosphere, high pressure synthesis and for the decomposition of ammonia.

Kinetic Measurements at 1 Atmosphere. Temkin and co-workers carried out a fairly extensive investigation on the kinetics at 1 atmosphere for the following metals: iron[5], molybdenum[41], tungsten[110], ruthenium[111] and osmium[112]. Kinetic measurements were made on iron catalysts also by Brill[113], Nielsen[114] and Bokhoven[115]. The principal results of these measurements have been compiled in Tables 6, 7, and 8. All rate constants listed in these tables have been calculated with $\alpha = 0.5$, except where noted.

From the considerations on the transport factor (see pp. 339–343) it will appear that at 1 atmosphere and a high temperature the reaction rate is already retarded by internal diffusion. Therefore we must bear in mind that the results of the kinetic measurements at 1 atmosphere may be affected if the reaction rate also becomes determined by the diffusion process.

Measurements by Temkin and Pyzhev, however, always yielded a constant value for the apparent energy of activation which is equal to the value predicted by theory. From the rate constants listed in Table 1 it appears furthermore that the catalysts employed by Temkin and Pyzhev possessed a much lower activity than the catalyst on which Bokhoven and Hoogschagen[116] observed a retardation by diffusion at 1 atmosphere.* It therefore

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* The particle diameter of Temkin's catalyst being unknown, a direct estimation of the degree of retardation can not be made.

TABLE 6. KINETIC MEASUREMENTS AT 1 ATM ON IRON CATALYSTS

Authors	Catalyst	Temp. (°C)	Space Velocity cm³ (NTP)/cm³ cat. hr.	H_2/N_2	Efficiency $\frac{P_{NH_3}\text{ (outlet)}}{P_{NH_3}\text{ (equil.)}}$	Rate Constant		Apparent Energy of Activation for NH_3 Decom. kcal/mol
						$k = -\frac{\frac{1}{2}\gamma^{3/2}P^{1/2}}{V\ln(1-\eta^2)}$	$k = P^{\alpha}V\int_0^{\eta}\frac{\eta^{2\alpha}}{1-\eta^2}d\eta$	
Temkin and Pyzhev[5]	$Fe\text{-}Al_2O_3\text{-}K_2O$	400	13450	2.93	0.373	1000		40
		400	20550	3.0	0.320	1100		
		400	29550	3.0	0.258	1010		
		400	29700	1.48	0.294	960		
		400	30600	6.0	0.259	1210		
		450	29800	3.0	0.629	7730		
		450	20000	3.0	0.738	7840		
		450	9100	3.0	0.934	(9300)		
		400	ca 30000	0.5	0.332	511		
		400	ca 30000	1.0	0.275	643		
		400	ca 30000	1.5	0.247	676		
		400	ca 30000	3.1	0.208	641		
		400	ca 30000	6.1	0.201	758		
		400	ca 30000	8.5	0.184	674		
Nielsen[114]	$Fe\text{-}Al_2O_3\text{-}CaO\text{-}K_2O$	400	30000	0.5	0.149	100		
		400	30000	1.0	0.132	144		
		400	30000	1.5	0.120	137		
		400	30000	2.0	0.089	100		
		400	30000	3.0	0.070	74		
		400	30000	6.0	0.073	97		
		400	30000	12.0	0.065	87		
Bokhoven[115]	$Fe\text{-}Al_2O_3\text{-}K_2O$ SBB 1714	350	1980	3.0	0.786	953	842 $\alpha = 0.6$	
		350	3980	3.0	0.626	989	827	
		350	6710	3.0	0.518	1046	845	
		350	10930	3.0	0.431	1120	874	
		350	32800	3.0	0.262	1170	802	
Brill[113]	$Fe\text{-}Al_2O_3\text{-}K_2O$	317	4140	3.0	0.230	112	76 $\alpha = 0.6$	
		317	6270	3.0	0.188	113	73	
		317	8310	3.0	0.170	121	77	
		317	14120	3.0	0.134	128	77	

does not seem likely that the results of Temkin's measurements at 400°C have been influenced by internal diffusion. It is not impossible, however, that the measurements listed in Table 8 (from which fairly high values for the rate constants can be derived) have been retarded by diffusion. However the fact that these measurements too yielded a high value for the energy of activation points to the contrary.

TABLE 7. KINETIC MEASUREMENTS AT 1 ATM ON MOLYBDENUM AND TUNGSTEN

Authors	Catalyst	Temp. (°C)	Space Velocity cm³ (NTP)/ cm³ cat. hr	H_2/N_2	Efficiency $\frac{p_{NH_3(outlet)}}{p_{NH_3(equil.)}}$	Rate Constant	Apparent Energy of Activation for NH_3 Decom. kcal/mol
Kiperman and Temkin[41]	Molybdenum	494	11950	3.0	0.569	3700	
		494	15350	3.0	0.510	3700	
		494	21600	3.0	0.417	3300	
		494	28600	3.0	0.385	3700	
		494	45000	3.0	0.313	3700	
		494	45650	3.0	0.303	3500	42.5 (447–550°C)
		494	83500	3.0	0.218	3200	
		494	86000	3.0	0.227	3600	
		494	103000	3.0	0.207	3600	
		494	28400	2.0	0.415	3600	
		494	28650	1.5	0.447	3700	
		494	27700	1.0	0.510	3700	
		494	29300	0.5	0.627	3500	
Kiperman and Temkin[110]	Tungsten	672	18350	3.0	0.510	4500	
		672	33300	3.0	0.388	4300	
		672	34250	3.0	0.393	4600	
		672	36750	3.0	0.381	4500	
		672	73800	3.0	0.276	4700	
		672	76750	3.0	0.270	4600	
		672	104000	3.0	0.237	4700	45.3
		672	39000	3.0	0.282	2500	
		672	38000	1.5	0.319	2300	
		672	38350	3.0	0.281	2500	
		672	38400	1.0	0.381	2600	
		672	38200	3.0	0.286	2600	
		672	38500	0.5	0.530	2300	

From the results stated in the Tables 6 and 8 it follows that in a large range of H_2/N_2 ratios and of space velocities the k-values are practically constant. On the other hand, Brill[113], and Bokhoven[115] found that in some instances a variation in efficiency (space velocity) gives rise to a systematic deviation of the rate constant. According to Brill a better constancy can be obtained by choosing an α-value different from 0.5. This was confirmed by Bokhoven, who in his measurements on an Fe—Al_2O_3—K_2O-promoted catalyst found an α-value of 0.6. In the discussion of high pressure synthesis and ammonia decomposition, it will be seen that this deviating value of α is also obtained from entirely different experiments on the same Fe—Al_2O_3—K_2O catalyst.

From the temperature dependency of the rate constant it follows that in all measurements the apparent energy of activation is relatively constant. For all of the metals examined (with the exception of ruthenium) this value lies between 40 and 50 kcal/mol. Finally, it is interesting to note that during the synthesis at 1 atmosphere some metals (molybdenum and osmium) become converted into the nitrides.

Table 8. Kinetic Measurements at 1 Atm on Ruthenium

Author	Temp. (°C)	Space Velocity cm³ (NTP)/cm³ cat. hr.	H_2/N_2	Efficiency $\frac{p_{NH_3(outlet)}}{p_{NH_3(equil.)}}$	Rate Constant	Apparent Energy of Activation for NH_3 Decom. kcal/mole
Kiperman[111]	736	50400	3.0	0.673	15200	59.5 (608–740°C)
	736	53000	3.0	0.697	17600	
	736	72100	3.0	0.605	16500	
	736	73000	3.0	0.622	17900	
	736	109000	3.0	0.525	17900	
	736	111000	3.0	0.527	18200	
	736	56890	0.5	0.912	15000	
	736	57020	1.0	0.798	15700	
	736	59160	3.0	0.631	15000	
	736	54700	5.2	0.601	14400	
	736	51400	6.5	0.623	16200	
	736	53460	15.9	0.572	14800	

Summing up, we may conclude that for the synthesis at 1 atmosphere the Temkin expression reasonably satisfies the criteria stated. It is clear, however, that even at 1 atmosphere the applicability of the expression is bound to certain limits. We shall return to this in our discussion.

Kinetic Measurements at Pressures above 1 Atmosphere. Hitherto only few purely kinetic investigations have been carried out at a high pressure. Temkin used the results of previous measurements by Larson and Tour[117] for testing his theory. Since, as described on page 339, the majority of these measurements have been carried out under such conditions that the reaction rate depends also on the diffusion process, these results obtained by Larson and Tour will not be used here. Among the other investigations, mention must be made of the rather extensive measurements carried out by Emmett and Kummer[118] in the pressure range between 33.3 and 100 atmospheres, and of the measurements by Sidorov and Livshits[119, 120] in the range from 10 to 500 atmospheres. In conclusion we shall refer to the kinetic measurements described in Nielsen's thesis[114]. The results of these measurements are compiled in Tables 9 and 10.

On page 322, the requirements that must be satisfied by the kinetic expression were stated. We shall examine these data for the dependency of the rate constant on the efficiency, the H_2/N_2-ratio and the total pressure. As appears from Emmett and Kummer's results listed in Tables 10 and 11, the rate constants are somewhat dependent on variations in the H_2/N_2-ratio and the efficiency. In this connection it must be noted, however, that most measurements by Emmett and Kummer were carried out in a limited range of efficiencies (see Table 9). These measurements also show that for all temperatures and gas compositions examined, the rate constant decreases with increasing pressure. Bokhoven and van Raayen[121] noticed a similar deviation in their measurements at 1 and 30 atmospheres in the temperature range 350 to 450°C. Further, the determination of the temperature dependence of the rate constant yields only a fairly constant value for the apparent energy of activation (see Table 9).

Before a discussion of the results obtained by Nielsen and by Sidorov and Livshits (Table 11), we want to point to an experimental difficulty that may affect the results of high pressure measurements. This difficulty is due to the fact that the equilibrium percentage increases with pressure, which may give rise to a considerable heat release in the reactor. Owing to the nonisothermal temperature distribution, a variation in the space velocity will result in a systematic deviation of the rate constant. To appreciate the correctness of the Temkin expression, use shall only be made of such measurements as have been carried out either in an isothermal reactor (Sidorov) or at a constant space velocity (Nielsen).* Measurements at 300 atmospheres carried out by Sidorov and Livshits, and by Nielsen, show that the rate constants are practically independent of the efficiency, but clearly depend on the H_2/N_2-ratio. Both from Nielsen's measurements and from those by Sidorov and Livshits it appears that the rate constant decreases with increasing pressure. In the latter measurements, however, the pressure dependence was found to be small.†

Emmett and Kummer also investigated whether a better description of their measurements could be obtained by choosing another value for the constant α. They chose $\alpha = 2/3$, the value Love and Emmett[123] obtained

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* Though the recent measurements by Adams and Comings[122] were also carried out under isothermal conditions, considerable variations in the Temkin rate constants were found, especially for their measurements at 350°C and variable space velocity. It is probable, however, that these measurements were affected by the back diffusion of ammonia, due to the shallow catalyst bed used.

† The difference between the rate constants at high and low pressures decreases still further if a correction is made for the deviation from the ideal gas law.

TABLE 9. KINETIC MEASUREMENTS BY EMMETT AND KUMMER[118]

(Rate constants calculated with $\alpha = 0.5$)

Space Velocity cm³ (NTP)/cm³/cat. hr.	H_2/N_2	Rate Constants k at 450°C						Rate Constants k at 400°C						Rate Constants k at 370°C						Apparent Energy of Activation for NH_3 Decom. for the Temp. Range 370–450°C kcal/mol		
		100 atm.		66.6 atm.		33.3 atm.		100 atm.		66.6 atm.		33.3 atm.		100 atm.		66.6 atm.		33.3 atm.				
		Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	Eff. η^*	k	100 atm.	66.6 atm.	33.3 atm.
25000	3	0.47	(30100)[a]	0.53	(38100)	0.63	(55000)	0.19	2390	0.21	3400	0.25	5240	0.08^7	298	0.09^8	506	0.12	915	54.6	51.3	48.7
50000		0.36	(31200)	0.38	(39500) 34600	0.46	(54000) 49500	0.13	2290	0.14	3350	0.17	4950	0.05^5	218	0.08^4	465	0.08^0	828			
75000		0.30	(31000) 25200	0.32	(38800) 34500	0.37	(51900) 44100	0.10	2080	0.12	3250	0.14	4760	0.03^9	192	0.05^1	402	0.06^5	790			
100000		0.26	(29300) 23800	0.28	(37000) 33600	0.33	(50900) 43200	0.08^8	1860	0.09^8	2960	0.12	4540	0.03^1	164	0.04^1	359	0.05^6	764			
125000		0.23	(30300) 23200	0.25	(36500) 32400	0.29	(49000) 41006	0.07^2	1680	0.08^3	2660	0.09^9	4110	0.02^7	130	0.03^5	326	0.04^6	749	61.2	54.5	47.6
35000	1	0.46	24200	0.41	29600[b]	0.59	37000	0.21	2590	0.17	3000^2	0.23	3520	0.10	436	0.07^6	415^2	0.08^6	449	47.7	50.6	52.3
75000		0.35	26200	0.30	33200	0.41	35800	0.14	(3090) 2500	0.12	3050	0.15	3860	0.06^8	391	0.05^3	465	0.06^7	532			
100000		0.31	27600	0.26	31600	0.36	34600	0.12	(2660) 2310	0.09^6	2690	0.13	3550	0.05^7	351	0.04^4	487	0.05^7	530			
125000		0.27	25500	0.23	29200	0.32	34000	0.09^9	(2400) 2100	0.08^1	2380	0.12	3300	0.04^5	302	0.03^7	391	0.05^2	470	52.6	51.2	50.8
35000	⅓	0.52	16450	0.57	20410	0.66	22900	0.23	2030	0.25	2380		3710	0.12	436	0.13	460	0.16	692	43.3	45.2	41.8
75000		0.39	17700	0.44	21000	0.51	24400	0.16	2170	0.18	2485	0.24	3780	0.08^3	423	0.09^2	501	0.12	770			
100000		0.35	17800	0.39	20200	0.47	25200	0.15	2180	0.16	2390	0.21	3820	0.07^2	403	0.07^6	494	0.09^7	701			
125000		0.31	17800	0.34	19600	0.43	25600	0.13	2090	0.13	2295	0.18	3560	0.06^5	369	0.06^7	450	0.08^2	621	46.1	44.9	44.3

* $\dfrac{P_{NH_3(\text{outlet})}}{P_{NH_3(\text{equil.})}}$.

[a] Numbers in parenthesis refer to activities before the accidental poisoning preceding run 12 (see [118]). The 400 and 370°C runs on 3:1 gas were the same after run 12 as before.

[b] The intermediate pressure runs with 1:1 gas were at 50 instead of 66.6 atmospheres pressure.

from decomposition measurements on a similar type of catalyst. After recalculating their results with $\alpha = 2/3$ it was found, however, that this value certainly does not give a better result (see Table 10), in contrast to the results of Brill and of Bokhoven included in the discussion of the synthesis measurements at 1 atmosphere, where it was shown that as the space velocity was varied, α-values larger than 0.5 led to a better constancy of k.

In view of the question as to what is the true value of α, mention should be made of the results of some other measurements by Bokhoven[115]. In this investigation the exponents of the partial pressures occurring in the expression for the synthesis reaction were determined directly. For this purpose the reaction was carried out in a differential reactor in such a way that:

TABLE 10. KINETIC MEASUREMENTS BY EMMETT AND KUMMER[118]

Rate constants calculated with $\alpha = 2/3$

Space Velocity cm³ (NTP)/ cm³ cat. hr.	H_2/N_2	Rate Constants k at 450°C			Rate Constants k at 400°C			Rate Constants k at 370°C		
		100 atm.	66.6 atm.	33.3 atm.	100 atm.	66.6 atm.	33.3 atm.	100 atm.	66.6 atm.	33.3 atm.
25000	3	(6080)	(7700)	(10810)	402	570	888	41.6	87.0	140
75000		(5200)	(6520)	(8540)	285	463	662	20.6	47.6	96.4
125000		(4760)	(5410)	(7310)	204	334	517	11.9	33.8	82.7
35000	1	5650	6660	7850	525	610	665	76.4	68.9	69.6
75000		5590	6710	6910	440	545	650	58.4	69.2	74.5
125000		4850	5240	6000	328	376	495	39.7	51.9	69.5
35000	1/3	4650	5400	5850	515	585	900	97.7	99.1	149
75000		4460	5100	5810	478	544	835	82.0	97.0	148
125000		3950	4350	5480	397	450	693	65.1	77.2	104

(a) the reaction always proceeded far from equilibrium

(b) the mean partial pressure of one component was varied whereas the mean partial pressures of the other components remained constant.

If we write the rate of the synthesis reaction in the general form:

$$\frac{dP_{NH_3}}{dt} = kP_{N_2}{}^{a}P_{H_2}{}^{b}P_{NH_3}{}^{c} \tag{86}$$

plotting of log $\frac{\Delta P_{NH_3}}{T}$ *vs.* log $\bar{P}_{N_2}$, log $\bar{P}_{H_2}$ and log $\bar{P}_{NH_3}$ ($\bar{P}_{N_2}$, $\bar{P}_{H_2}$ and $\bar{P}_{NH_3}$ being the mean partial pressures) must yield a straight line. The slope of this line directly gives the values of the exponents a, b and c. These measurements showed that for the pressure range examined and at 350°C, $a = 1.1$ ($P_{N_2} = 2.7 - 10$ at); $b = 2.0$ ($P_{H_2} = 9.4 - 22$ at) and $c = -1.2$

TABLE 11. KINETIC MEASUREMENTS BY SIDOROV AND LIVSHITS[119, 120] AND NIELSEN[114]

1. Measurements at 300 atm, variable temperature and space velocity[119] ($Fe-Al_2O_3-K_2O$ catalyst)

Space Velocity cm³ (NTP)/cm³ cat. hr.	450°C		475°C		500°C		Apparent Energy of activation (NH_3 Decom.) kcal/mol
	Efficiency*	Rate Constant	Efficiency*	Rate Constant	Efficiency*	Rate Constant	
15000	0.552	8400	0.791	19600	0.872	51400	42
30000	0.412	9500	0.648	23200	0.690	49100	
45000	0.358	9450	0.557	23500	0.625	57200	
60000	0.315	9250	0.487	24900	0.553	57200	
90000	0.288	10300	0.385	22400	0.432	49600	

2. Measurements at 500°C, variable pressure and space velocity[120]

Space Velocity cm³ (NTP)/cm³ cat. hr.	10 Atm.		100 Atm.		200 Atm.		300 Atm.		400 Atm.		500 Atm.	
	Efficiency*	Rate const.	Efficiency*	Rate const.	Efficiency*	Rate const.	Efficiency*	Rate const.	Efficiency*	Rate const.	Efficiency*	Rate const.
30000	0.875	6170	0.698	6130	0.695	6200	0.689	4910				
60000	0.734	6800	0.544	6800	0.537	5570	0.553	5720	0.542	4450	0.530	3700
90000	0.642	7050	0.456	6800	0.437	5320	0.434	5320	0.449	4660	0.422	3350
120000	0.550	6400	0.396	6700	0.390	5210	0.359	5210	0.398	4630	0.368	3740

3. Kinetic measurements at 330 atm, 450°C, space velocity 15000 and variable H_2/N_2-ratio[114]

H_2/N_2	per cent NH_3	Efficiency $\frac{P_{NH_3(outlet)}}{P_{NH_3(equil.)}}$	Rate Constant
1	15.5	0.65	5900
3	20.1	0.52	7000
6	17.5	0.61	10800

4. Measurements at 450°C, space velocity 15000 and variable pressure[114]

Pressure (atm.)	per cent NH_3	Efficiency $\frac{P_{NH_3(outlet)}}{P_{NH_3(equil.)}}$	Rate Constant
360	21.9	0.54	5400
295	19.1	0.55	7600
240	17.4	0.56	8900
175	13.7	0.56	11700
130	11.3	0.59	14400

$* \frac{P_{NH_3\ (outlet)}}{P_{NH_3\ (equil.)}}.$

($P_{NH_3} = 0.2 - 1.1$ at). These values are in agreement with the Temkin theory if α is put equal to about $\frac{2}{3}$. The α-value thus determined comes very close to the value of 0.6 obtained from synthesis measurements on the same catalyst at 1 atmosphere and 350°C, and to the value of $\frac{2}{3}$ found by Love and Emmett. However, the difficulty remains that with $\alpha > 0.5$, the rate constants become more dependent on the total pressure.

A closer consideration of the general expression (79):

$$k \sim P^{\alpha} V_0 \int_0^{\eta} f(\eta, \alpha)\, d\eta \tag{87}$$

reveals that the increase of the difference between the rate constants at high and low pressures is ascribable to the α-dependency of $f(\eta, \alpha)$. So, notwithstanding there being a number of indications that α may have a value different from 0.5, it seems to be the most reasonable, with a view to the practical application of the Temkin expression, to retain the value of 0.5.

From a summary of the results discussed above it will be clear that no definite decision can be given as yet on the validity of the Temkin expression. Whereas the results obtained by Sidorov and Livshits are in good agreement with theory, other measurements deviate distinctly. This applies especially to the dependence on the total pressure. For this reason it is necessary to discuss these deviations in more detail (see pp. 337–339).

Kinetics of Ammonia Decomposition

The older literature contains descriptions of several measurements on the decomposition of ammonia. In most cases the decomposition was carried out in the presence of pure ammonia. This condition always leads to the formation of the *nitride phase*. It is obvious that if the results of the decomposition reaction are to be used for testing the Temkin theory, the formation of this nitride phase must be avoided. The decomposition will have to be carried out, therefore, in the presence of an excess of hydrogen. Such measurements were carried out for the first time by Winter[108] who developed the following kinetic relation:

$$\frac{-dP_{NH_3}}{dt} = k\,\frac{P_{NH_3}^{\;0.9}}{P_{H_2}^{\;1.5}} \tag{88}$$

This expression agrees reasonably with the Temkin theory, provided $\alpha = 0.5$. After the Temkin theory had been developed, Love and Emmett[123] and Love and Brunauer[124] studied the kinetics of ammonia decomposition on iron catalysts. Kiperman[125] and Temkin[125] and McGeer and Taylor[126] did the same on copper and rhenium catalysts, respectively.

Love and Emmett made use of different types of iron catalysts, viz., a catalyst with K_2O (No. 931: 1.3 per cent Al_2O_3 and 1.59 per cent K_2O) a catalyst without K_2O (No. 954: 10.2 per cent Al_2O_3) and a pure iron catalyst. For the decomposition over catalyst No. 931, the following relationship was found:

$$\frac{-dP_{NH_3}}{dt} = k_2 \frac{P_{NH_3}{}^{0.6}}{P_{H_2}{}^{0.85}} = k_2 \left(\frac{P_{NH_3}{}^2}{P_{H_2}{}^3}\right)^{0.3} \tag{89}$$

For the temperature range examined (335 to 430°C) and the H_2/NH_3-ratio chosen, the energy of activation appeared to be constant and to amount to 45.6 kcal/mol. This value is in agreement with that of the apparent energy of activation for ammonia decomposition which Emmett and Kummer have found from synthesis measurements on an identical type of catalyst.

TABLE 12. ENERGY OF ACTIVATION E FOR THE AMMONIA DECOMPOSITION ON CATALYST NO. 954

I. Decomposition with 75% of H_2 and 25% NH_3

From low to high temperatures	*From high to low temperatures*
$E_{387-411°\mathrm{C}}$ = 18.7 kcal/mol	$E_{442-421°\mathrm{C}}$ = 31.4 kcal/mol
$E_{411-420°\mathrm{C}}$ = 0 kcal/mol	$E_{421-406°\mathrm{C}}$ = 16.7 kcal/mol
$E_{420-442°\mathrm{C}}$ = 22.7 kcal/mol	$E_{420-386°\mathrm{C}}$ = 26.1 kcal/mol

II. Decomposition with 87.5% H_2 and 12.5% NH_3

From low to high temperatures
$E_{387-418°\mathrm{C}}$ = 31.7 kcal/mol
$E_{418-464°\mathrm{C}}$ = 8.6 kcal/mol
$E_{464-490°\mathrm{C}}$ = 28.6 kcal/mol

The decomposition of ammonia on catalysts without K_2O on the other hand, presented an entirely different picture. For these catalysts the energy of activation was found to be dependent upon the temperature and the H_2/NH_3-ratio (see Table 12).

As appears from Table 12, hysteresis effects occurred in these measurements; in going from low to high temperatures there was found a lower activation energy than in the reverse case. Moreover, in a wide temperature range the reaction rate appeared to increase with the partial hydrogen pressure and to decrease with the partial ammonia pressure. The deviations in the behavior of catalyst No. 954 could be eliminated by soaking the reduced and subsequently passivated catalyst in a KOH-solution. Upon repeated reduction, however, the activity proved to have considerably dropped (see Figure 24).

Finally, Love and Emmett did not notice an influence of the particle size of catalyst No. 954 upon the rate of decomposition.

No satisfying explanation has been given so far for the abnormal behavior of K_2O-free catalysts. The results of some decomposition experiments carried out by Bokhoven[127] enable us to consider the decomposition of ammonia over K_2O-free catalysts from a different point of view. In these experiments the decomposition of ammonia was studied with mixtures of 6 per cent NH_3 and 94 per cent H_2 both on catalysts with and without K_2O. The former catalysts were prepared by soaking the unreduced catalysts in a KOH-solution. In accordance with the decomposition experiments by Love and Emmett, Bokhoven's results obtained on the K_2O-promoted catalyst could be described by the Temkin expression. In the temperature range examined (400 to 450°C) a constant value (59 kcal/mol) was found for the apparent energy of activation (see Figure 25). However, between 371 and 411°C, the decomposition over the catalyst without K_2O also proceeded in accordance with the Temkin expression. The apparent energy of activation for this temperature range was found to be 60 kcal/mol. At higher temperatures, on the other hand, much lower values were obtained. Moreover, hysteresis effects occurred, though to a far less extent than in the case of catalyst No. 954.*

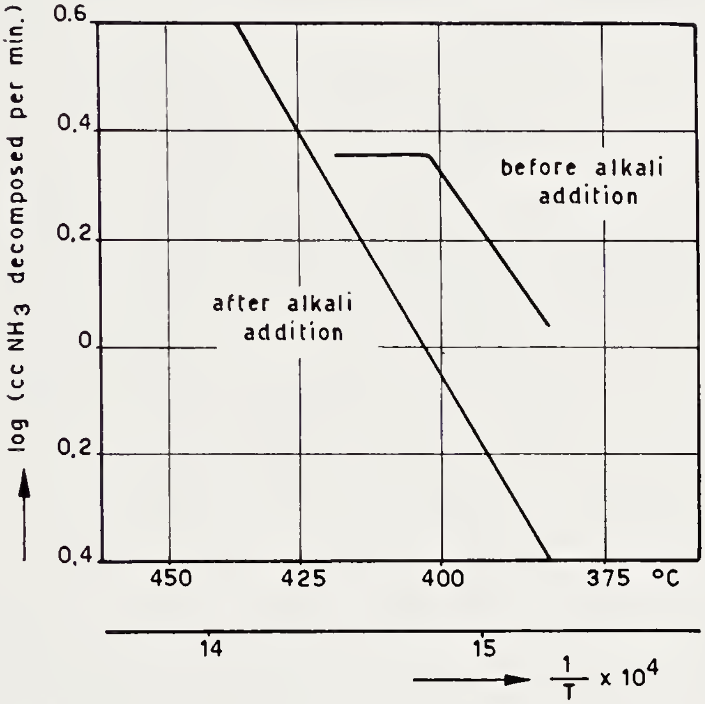

Figure 24. Rate of ammonia decomposition. (Love and Emmett[123])

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* On page 340, it will be demonstrated, that in the decomposition measurements

In explanation of the hysteresis effects observed by Love and Emmett, it must be remarked that their measurements were carried out at high ammonia contents, and hence at high nitrogen fugacities. Since the nitrogen fugacity in a mixture of 25 per cent NH_3 and 75 per cent H_2 at 420°C amounts to 1280 atmospheres and 2470 atmospheres at 444°C, the fact that nitrogen dissolves in the iron must certainly be taken into account. From data† on the solubility of nitrogen in iron it follows, that at the above nitrogen fugacities and temperatures, the amount of dissolved nitrogen may be 0.02 per cent (420°C) and 0.03 per cent (444°C) by weight, respectively. It seems likely now, that the hysteresis effects noticed by Love and Emmett (see Table 12) are ascribable to the slow adjustment of the adsorption equilibrium. This accounts for the fact that the activity at 420°C, after the measurement at 444°C appears to be lower than before said measurement.

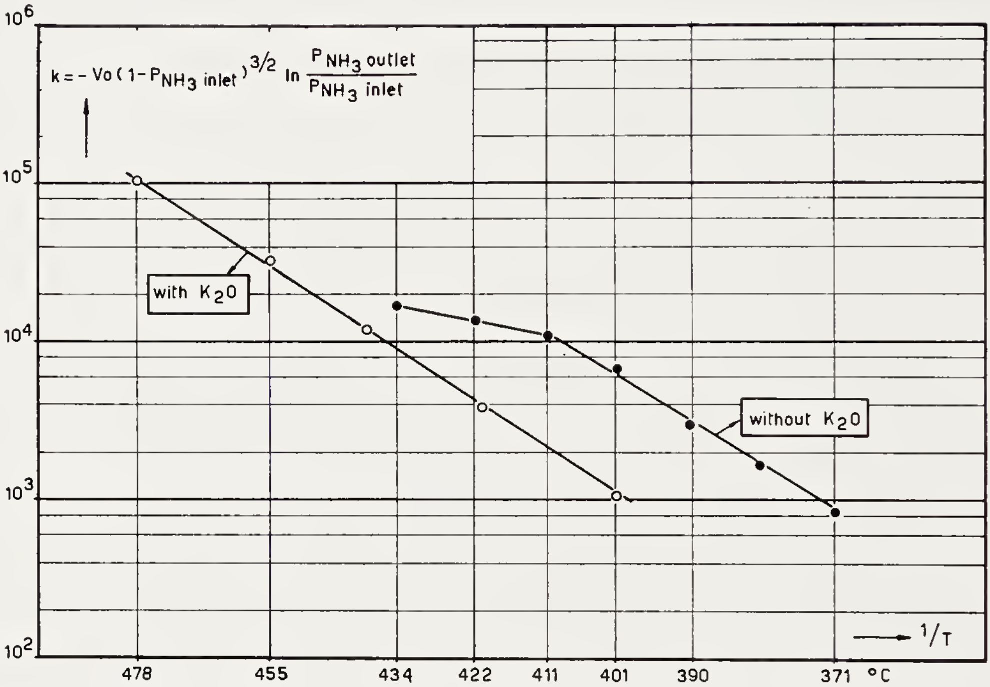

Figure 25. The Temkin rate constant (corrected for internal diffusion), according to experiments by Bokhoven[127] with iron catalyst ($MgO + SiO_2$) before and after the addition of K_2O.

According to the foregoing, the activity of the catalyst would depend therefore on the amount of dissolved nitrogen. This view is supported by the fact that the rate of decomposition increases with the hydrogen pres-

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both with catalysts without K_2O and in those with K_2O-promoted catalysts, retardation by diffusion has occurred. The values plotted in Figure 26 have been corrected for this influence.

† Private communication by J. D. Fast, Philips Laboratories, Eindhoven.

sure. Hence it is obvious to assume that the kinetics of ammonia decomposition over catalysts without K_2O will be in better agreement with the Temkin theory according as the H_2/NH_3-ratio is higher. This makes it possible, under certain conditions (high H_2/NH_3-ratio, low temperature) to describe the kinetics by the Temkin theory.

Now it is noteworthy that in the ammonia decomposition on K_2O-promoted catalysts no deviations from the Temkin theory were observed, notwithstanding the high nitrogen fugacities employed. Hence it might be concluded that K_2O has a promoting effect upon the tendency of the nitrogen to dissolve in the iron. With a view to this, one might expect that at fugacities in the vicinity of the equilibrium value for Fe_4N, the kinetics on K_2O-promoted catalysts will also start deviating.

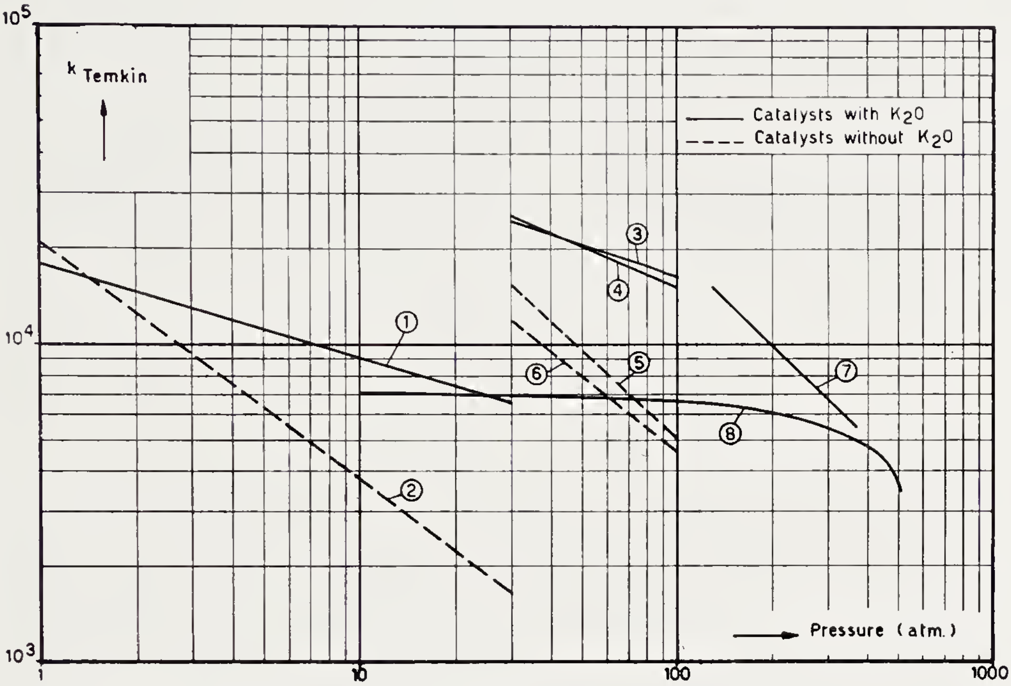

Figure 26. Pressure dependence of the Temkin rate constant.

1. Fe + Al_2O_3 + K_2O. 400°C. (Bokhoven and van Raayen[121])
2. Fe + MgO. 400°C. (Bokhoven [115])
3. Fe + 1.1% Al_2O_3 + 0.2% K_2O. 450°C. (Almquist and Crittenden[131])
4. Fe + 0.8% Al_2O_3 + 0.4 % K_2O. 450°C. (Larson[132])
5. Fe + 1.3% Al_2O_3 . 450°C. (Almquist and Crittenden[131])
6. Fe + 1% Al_2O_3 . 450°C. (Larson[132])
7. Fe + Al_2O_3 + CaO + K_2O. 450°C. (Nielsen[114])
8. Fe + Al_2O_3 + K_2O. 500°C. (Sidorov and Livshits[120])

Final Discussions on the Temkin Theory

We want to start this final discussion by pointing out that Temkin's approach to the theory of the kinetics of ammonia synthesis differs principally from the customary formulations (see e.g.,[128]). The essential feature in Temkin's derivation is the introduction of the nitrogen fugacity

$$P_{N_2}{}^* = K^{-1}\frac{P_{NH_3}{}^2}{P_{H_2}{}^3}, \tag{57}$$

This makes it possible to account directly for the fact that the synthesis reaction and the decomposition reaction are retarded by ammonia and hydrogen, respectively. Consequently, the Temkin theory furnishes a reasonable picture of the general kinetic behavior.

The derivation of the kinetic expression is but little affected by the choice of the isotherm. De Bruijn[129] showed that by starting from a more general basis (Langmuir adsorption and a given distribution function of the active sites) a reaction rate equation can be derived which apart from a factor $f(\theta)$, is equivalent to the Temkin expression.

$$\text{The factor } f(\theta) = \frac{\displaystyle\int \frac{(aP_{N_2}{}^*)^{1/2}e^{q/2RT}}{[1 + (aP_{N_2}{}^*)^{1/2}e^{q/2RT}]}\,N(q)\,dq}{\displaystyle\int N(q)\,dq} \tag{90}$$

in this equation is still dependent upon the partial pressures.

In view of the foregoing, it will be understood that the Temkin expression, though giving a sufficiently representative picture of the general character of the reaction kinetics, is bound to certain limits when applied to extreme cases. This limitation directly appears, i.e., from the fact that the reaction rate becomes infinite for $P_{NH_3} \rightarrow 0$.

Temkin already pointed out that the logarithmic isotherm is valid only in the region of mean coverages (see page 290). As at low coverages the adsorption rate is independent of coverage, it follows, according to Temkin[106], that in the range of low coverages a different type of kinetics must apply. This change in kinetics was actually confirmed by the measurements of Kiperman and Granovskaya[130]. It appeared that at very low efficiencies (in the order of 1 per cent) the reaction rate could be represented by:

$$\frac{dP_{NH_3}}{dt} = kP_{N_2} \tag{91}$$

The reaction rate in the very first part of the reactor will consequently obey expression (91). However, after a very small amount of ammonia has been produced, the reaction rate will be determined by the Temkin expression (58). As a result, integration of (58) will only result in a minor error. This was confirmed by the results of some experiments by Bokhoven[127], in which no systematic difference was revealed between the measurements in an integral reactor and those carried out in a differential reactor.

In testing the Temkin equation, its validity was examined both for the synthesis and for the decomposition of ammonia. This investigation showed that the kinetic expression for ammonia synthesis reasonably satisfies three of the four conditions mentioned above. For, it was found that both at 1 atmosphere and at 300 atmospheres, the rate constants were but little dependent upon the space velocity and the H_2/N_2-ratio. Moreover, the apparent energy of activation in this pressure range proved to have a constant value. In most cases, however, the rate constants are dependent on the total pressure (see Figure 26). The degree of this dependency is not always the same, but is evidently determined by the composition of the catalyst. This is confirmed by personal experiences from which we have learned that, whereas the addition of K_2O at 1 atmosphere has a lowering effect upon the activity, the activity at 100 atmospheres tends to be raised by the presence of this promoter. This typical influence of K_2O on the reaction kinetics was also observed in the decomposition of ammonia. Finally, Figure 26 shows that the pressure dependency of the rate constants is lowest in the case of Al_2O_3- and K_2O-promoted catalysts.

In conclusion, it may be stated that the Temkin equation gives a reasonable description of the kinetics of ammonia synthesis on a number of catalysts and especially on the technically important $Fe—Al_2O_3—K_2O$-promoted catalysts.

Restriction of the Reaction Rate by Diffusion

Because of the high activity of many industrial solid catalysts the restriction of the over-all reaction rate by the finite diffusion velocity of reactants and reaction products through the pores of the solid becomes more and more important. A summary of this aspect of the kinetics of heterogeneous catalysis is given by Wheeler[133].

Two phenomena are characteristic for a restricted internal diffusion velocity:

(1) the activity of the catalyst decreases with increasing particle size.

(2) in general, a plot of the log of the reaction rate constant *vs.* the reciprocal absolute temperature is a straight line, whose slope corresponds to the energy of activation of the reaction. In the temperature region, where the diffusion rate inside the pores begins to restrict the reaction rate, the Arrhenius plot shows a bend, the apparent activation energy decreasing from the true low temperature value to ultimately half of this value.

Ammonia Synthesis. It is generally accepted that under the usual conditions the ammonia synthesis reaction is too slow to be retarded by internal diffusion. This belief is supported by the results of some old experiments at 100 atmospheres of Larson and Tour[117], who failed to find any influence of particle size on catalyst activity.

More recent estimations by Wheeler[133] and Wagner[134] show however, that under industrial conditions (300 atmospheres, 450°C, particle size 5 to 10 mm) restriction by internal diffusion is probable. On account of this, Wagner suggests the possibility that at high pressure, surface migration of the chemisorbed molecules or radicals contributes considerably to the diffusion rate through the porous catalyst.

In a recent publication, Bokhoven and van Raayen[121] give the results of an extensive experimental study on this subject. At pressures of 1 and 30 atmospheres the activities of a catalyst of the normal type (2.9 per cent Al_2O_3 , 1.1 per cent K_2O) were measured for two different particle sizes as a function of temperature. The results of these kinetic experiments show both the phenomena mentioned above, which are characteristic for diffusional retardation. The effective diffusion constant of atmospheric oxygen through nitrogen at room temperature was determined for a similar type of catalyst by a method devised by Hoogschagen[116, 135]. From this value the effective diffusion constant of ammonia in a 3:1 hydrogen-nitrogen mixture was calculated for the conditions of the kinetic experiments (see Figure 27).

The method developed by Wagner[134] was employed for calculating the effectiveness factor β, the ratio of the experimental rate constant and the rate constant in the absence of diffusional retardation. This ratio depends on the dimensionless number $\frac{kR^2}{D_{\text{eff}}}$, where k is the pseudo first order reaction rate constant, R the particle radius and D_{eff} the effective diffusion constant.

After correction of the experimental Temkin rate constant for this factor β, the particle size effect and the decreasing slope of the Arrhenius plot disappears, which proves that both phenomena can be interpreted quantitatively by diffusional retardation.

It is definitely clear that under some of the experimental conditions of this investigation, the reaction rate is considerably restricted by internal diffusion. For the effectiveness factor of particles of 2.6 mm a value $\beta = 0.05$ (!) was found at 450°C and 1 atmosphere and a value $\beta = 0.25$ at 550°C and 30 atmospheres.

Because of the quantitative agreement there is no reason to assume that surface migration contributes significantly to the diffusion rate, at least not up to pressures of 30 atmospheres.

The experimental conditions of the investigation by Bokhoven and van Raayen lie outside the range of industrial practice, where higher pressures and larger particle sizes are applied. It was found by these workers that the retardation by internal diffusion decreases at increasing pressure. The reason is that the pseudo first order reaction rate constant decreases according to the Temkin theory as $1/P^{1.5}$, whereas the diffusion constant decreases as $1/P$. Moreover, there is experimental evidence that the reaction rate decreases even more rapidly with pressure than would follow from the Temkin relation.

In this connection the old experiments of Larson and Tour[117] are of interest. These investigators carried out a series of kinetic experiments at pressures from 1 to 100 atmospheres in a temperature range from 400 to 475°C and investigated the influence of particle size only at 100 atmospheres. At this pressure they did not notice a dependence of the activity on the particle size. It is especially at low pressures, however, that such an influence must be expected. This supposition is confirmed by the result of a recalculation of their experimental figures, also given by Bokhoven and van Raayen. The Temkin rate constants were calculated and the activation energy determined from the experiments at different temperatures (see Table 13). The decrease in the activation energy at decreasing pressure is significant, and furnishes ample proof that at lower pressures the experiments of Larson and Tour were highly affected by diffusional retardation. This conclusion is confirmed by the calculated values of the effectiveness factor at 450°C for 1 and 100 atmospheres recorded in the last column of Table 13.

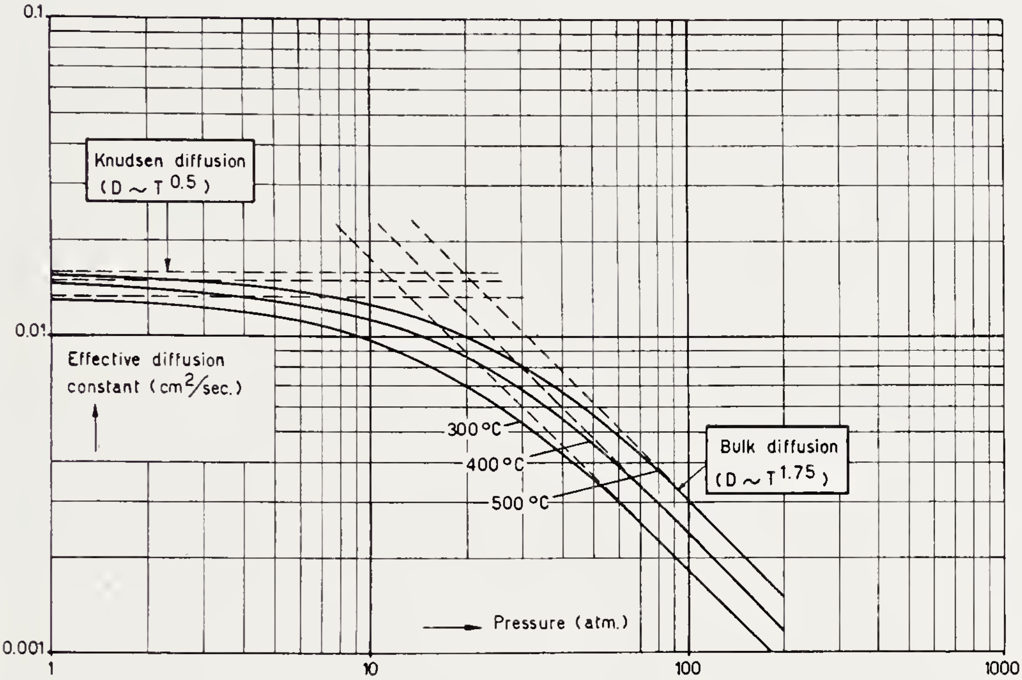

Figure 27. Effective diffusion constant of NH_3 in a $3H_2{:}1N_2$ gas mixture. (Bokhoven and van Raayen[121])

Although it is clear that at increasing pressure the diffusional retardation decreases rapidly, it remains of importance to carry out an estimation for industrial conditions because here the particle size (5 to 10 mm) is larger than in most of the laboratory experiments. The only kinetic experiments in the region of 300 atmospheres, for which the particle size is mentioned are those by Nielsen[114]. Some representative results are given in Table 14, also taken from Bokhoven and van Raayen. From the calculated value of the effectiveness factor it may be concluded that Nielsen's experiments are only very little affected by diffusion. If, however, the value of β is estimated for a particle size of 10 mm, a strong retardation is found. From this result it may be concluded that under industrial conditions diffusional retardation can be considerable, in particular in that part of the convertor, where the temperature is high and the ammonia concentration still low.

TABLE 13*. APPARENT ACTIVATION ENERGY AND EFFECTIVENESS FACTOR β CALCULATED FROM MEASUREMENTS OF LARSON AND TOUR[117]

Particle Size (mm)	Pressure (atm)	Act. Energy (kcal/mol)	β (450°C)
1.4–2.4	1	23	0.20
†	10	29	—
†	31.6	37	—
2.4–3.3	100	50	0.80

* Taken from Bokhoven and van Raayen[121].
† Not mentioned.

TABLE 14*. EFFECTIVENESS FACTOR β CALCULATED FROM MEASUREMENTS OF NIELSEN

(Catalyst E, particle size 1.2–2.3 mm)

Pressure (atm)	Temperature (°C)	β	β (10 mm)
330	450	0.96	0.38
330	450	0.89	0.15
330	480	0.93	0.23
360	450	0.98	0.40

* Taken from Bokhoven and Van Raayen[121]

It should be remarked that this conclusion is derived from the results of laboratory experiments only, where, because of the more favorable reduction conditions and the higher purity of the synthesis gas, catalyst activity may be substantially higher than actually obtained in industrial convertors.

Ammonia Decomposition. The only published experiments on ammonia decomposition to which the preceding considerations on diffusional retardation can be applied are those of Love and Emmett[123], who investigated the decomposition rate on conventional iron catalysts. In particular, the peculiar behavior of catalyst No. 954 (see page 336 and Figure 25) invites the question whether the experimental results might be affected by diffusional retardation. Love and Emmett themselves investigated the influence of particle size and found no significant difference in reaction rate for particles of 35 to 40 and 10 to 14 mesh. This result is in agreement with an estimation of the effectiveness factor. For the experiment most favorable for diffusional restriction of the reaction rate a value of 0.80 for the effectiveness factor was calculated. Thus it may be concluded that the experiments of Love and Emmett were not affected by internal diffusion.

However, for some experiments by Bokhoven[127], who measured (page 335) the decomposition rate of ammonia on iron catalysts before and after the addition of K_2O as promoter, the situation is completely different. Because of the higher activity of the catalyst the decomposition rate was much faster than in the experiments by Love and Emmett. The correction for diffusional retardation proved to be considerable. The corrected activity line (see Figure 25) of the alkali-promoted catalyst is straight and its slope corresponds to a value of the activation energy of 60 kcal/mol. The corrected line for the catalyst without K_2O, however, still shows a transition to a lower value of the activation energy at a temperature of about 400°C, which is in qualitative agreement with the results of Love and Emmett.

Thus it can be stated that, although the experiments by Bokhoven were strongly affected by diffusional retardation, the kinetics of the ammonia decomposition reaction on catalysts with and on catalysts without K_2O differ significantly.

Concluding Remarks

After reading this chapter one cannot fail to acknowledge that the research on ammonia synthesis since 1940 has greatly increased the understanding of the fundamentals of this catalytic reaction. It will, at the same time, be clear that many problems are still unsolved and that many new problems have arisen as the result of the investigations. The latter fact, of course, is quite normal and a healthy consequence of experimental research work.

The study of the magnetite phase, prior to reduction, has led to questions relating to the solubility of some metal ions which may form oxides which are not reduced during the reduction process and which may stabilize the favorable porous structure of the iron catalyst. It still remains to be investigated whether or not calcium can be dissolved into the Fe_3O_4-phase or whether a simultaneous dissolution of aluminium is required to permit calcium to enter the magnetite phase. Similar questions arise for elements like titanium and zirconium. These problems are now under investigation in this laboratory.

The process of the reduction itself is certainly not well defined. Even when no FeO-phase is present in the unreduced catalyst, it may be formed, temporarily, during the reduction process. The rate of the reduction reaction depends largely on the presence of stabilizing oxides, such as Al_2O_3 and others, as mentioned above. The rate of reduction, which is relatively high for pure Fe_3O_4 , may, by the action of such oxides, be lowered to such a degree that the type of reduction is altered. If the chemical reaction of this reduction is slow enough, this reaction will govern the rate of the reduction, whereas at a high speed of reduction diffusion may determine the rate.

Important properties of the iron catalyst after reduction are its pore structure and, probably, the orientation of the exposed outer iron surface. The mean size of the pores of a catalyst containing MgO and of one containing Al_2O_3 proved to be roughly the same at the same reduction temperature. The real shapes of the pores and the actual structure of the iron walls, bordering the pores, cannot be deduced from the present experimental data. If, however, an iron catalyst, reduced at say 450°C, may be described as a lamellar structure, the average thickness of the lamellae is of the same order of magnitude as the width of the capillary spaces between them. Similar structures are frequently obtained when thin layers of metals (or of inorganic salts) are prepared by evaporation in vacuo or in a diluted gas atmosphere. It may be pointed out that many of Beeck's fundamental experiments, referred to in the discussion on chemisorption (pp. 305–311) were conducted on such layers. Although our knowledge of the structure of iron layers obtained by evaporation is certainly far from perfect, a comparative study of such layers and of reduced magnetite particles may, in future, yield more conclusive results as regards the orientation of the iron surface and the chemisorption properties.

A study of the discussion on chemisorption will reveal that gradually a better understanding of the chemisorption phenomena is being obtained. Still many questions have remained unsolved while for a few outstanding ones only a possible explanation can be offered. One of the major problems is the decrease of the heat of adsorption with increasing degree of coverage. The great controversy in describing catalytic phenomena is at the back of the question, whether the adsorbing surface is to be considered as heterogeneous or whether the surface is more or less homogeneous. A careful study of all the pros and cons seems to lead to the last view. This must, with respect to the porous structure of the reduced magnetite, be understood in such a way that the surface of the catalyst mainly consists of a great number of identical, homogeneous areas of sufficiently large atomic dimensions. Extruding or intruding corners or edges offer, generally, but a minor part of the total amount of the sites available for adsorption. Chemisorption, contrary to physical adsorption, moreover, is rather insensitive to surface irregularities such as given by a porous structure. The nitrogen atoms and the hydrogen atoms are all bound to their own iron atoms and all these bonds must be considered to be practically the same. The strong decrease of the heat of adsorption with increasing amount of adsorbed atoms means that all adsorbed atoms are less strongly bound when more atoms are adsorbed.

We may say that the affinity of the metal to the adsorbed atoms depends on the amount of adsorbed atoms per unit surface. This affinity is always smaller when more atoms are adsorbed. This decrease in affinity is caused by the change in work function of the metal by the dipoles which the adsorbed atoms form. Adsorbed atoms forming dipoles, the positive part of which points away from the metal, decrease the work function. Those adsorbed atoms which form dipoles with their negative side pointing away from the metal increase the work function. In both cases the affinity of the metal to all adsorbed atoms decreases.

Nitrogen atoms bound by chemisorption on an iron surface form negative dipoles (the negative part pointing away from the metal) and so do hydrogen atoms chemisorbed at relatively low temperature. As is argued in the discussion on chemisorption, however, the type of hydrogen chemisorption, effective during ammonia synthesis, may well be a reversed one, forming positive dipoles. If this view is correct, it even offers a suggestion for a possible explanation of the promoting action of K_2O at high pressures.

The decrease of heat of adsorption with increasing degree of coverage leads to an equation for the adsorption isotherm of a form as given by Temkin. In the introductory remarks as well as in the discussion on kinetics the great importance of Temkin's work has been pointed out. The general conclusion of a thorough analysis of the kinetics of ammonia synthesis as well as of the decomposition of ammonia, has revealed, as can be seen in the discussion on kinetics, that all experimental data may reasonably well be described by the Temkin theory. In all kinetic experiments, however, one must be aware of the possibility of retardation of the rates by internal diffusion in the pores of the catalyst. Such retardations may play a role in industrial reactors.

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CHAPTER 8

SYNTHESIS OF METHANOL

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Introduction

Among the main industrial organic reactions, the synthesis of methanol is an outstanding example of the practical importance of catalytic processes.

In 1924 methanol was produced almost exclusively by the destructive distillation of wood wastes. That year, the world production of CH_3OH was as low as 45,000 tons[74]. As a consequence of the development of the catalytic synthesis, production of methyl alcohol in the United States in 1953 exceeded 480,000 tons[27], matching that of ethyl alcohol.

While in the past the destructive distillation of 60 to 100 lbs of wood gave only about 1 lb of CH_3OH, with the synthetic process 1 lb of CH_3OH may be produced starting from CO and H_2, obtainable from the conversion of 315 grams of methane.

The large-scale synthesis of methanol was first carried out by Badische Anilin und Soda Fabrik (B.A.S.F.) which also developed the synthesis of ammonia on an industrial basis. The remarkable analogies between the synthesis of ammonia and that of methyl alcohol are shown in Table 1.

The experience in high-pressure operations, acquired previously in the synthesis of ammonia, has certainly contributed to the development of the methanol catalytic process. However, the synthesis of methyl alcohol had to overcome many more difficulties of a chemical nature.

In the synthesis of ammonia side reactions are not possible; molecular H_2 and N_2 can interact directly to give only ammonia. On the contrary, carbon monoxide reacts with hydrogen in many different ways; among the possible reactions, the synthesis of methyl alcohol is thermodynamically one of the least favorable. Methyl alcohol is formed only if certain selective catalysts are used, which are different from the typical hydrogenation catalysts. This synthesis is therefore representative of the importance of selective catalysts in directing a process in a definite way, and avoiding other reactions which would be preferred in the absence of highly selective catalysts.

This explains the fact that the methanol synthesis was developed in a relatively recent period, while other catalytic organic syntheses (i.e., that of methane) were found much earlier. From the historical point of view, however, the formation of methanol by high pressure synthesis was first reported by the Badische Anilin und Soda Fabrik[2] in its endeavors to produce liquid hydrocarbons from water gas, using as catalysts either mixtures of cobalt and osmium oxides with sodium hydroxide, or alkali treated iron oxide. Methyl alcohol was at that time present as a minor component among the products of the reaction, which were mainly hydrocarbons, alcohols, esthers, aldehydes, etc.

Only in 1923[3] did B.A.S.F. find that methanol became the main product of the hydrogenation of carbon monoxide, when certain mixed catalysts containing ZnO and Cr_2O_3 were used, and when the reaction apparatus did not contain iron or iron alloys, which might react with CO to give iron pentacarbonyl. Similar results were reported by Schmidt and Ufers[67], who used a copper-base catalyst which also contained oxides of various metals

Table 1

	Synthesis of NH_3	Synthesis of CH_3OH
$\Delta F°_{400°C}$ per mole of H_2	+4,000 kcal	+7,400 kcal
$\Delta H_{400°C}$ per mole of H_2	−8,530 kcal	−12,325 kcal
$\Delta H_{400°C}$ per mole of synthesis gas	−6,300 kcal	−8,200 kcal
Temperature of synthesis	400–500°C	300–450°C
Pressure range	100–1000 atm	100–500 atm
Number of gas moles reacting	4	3
Volume diminution (referred to 1 volume of reacted N_2 or CO)	2	2

In the years which followed a number of processes for the synthesis of methanol, based on the use of some particularly selective catalysts or on particular methods for the production of the water gas, have been developed in other European Countries (France, Italy, England) and in the United States.

The synthesis of methyl alcohol from carbon dioxide and hydrogen has also been successfully realized. This process was introduced in the United States by the Commercial Solvent Corporation[32], which had to overcome many difficulties. During World War II, the Lonza Company in Switzerland succeeded in the industrial realization of methanol synthesis from CO_2 and electrolytic hydrogen[47]. Carbon dioxide was a by-product of the process for producing $Ca(NO_3)_2$. Therefore, in order to be used in the synthesis of methyl alcohol, it had first to be purified from nitrous vapors and then partially reduced by coal to carbon monoxide. The same ZnO-base catalysts were used on this synthesis which had been developed in Italy by G. Natta for the synthesis of methanol from CO and H_2.

Nowadays, both in the United States and in Italy, the main starting material for the methanol synthesis is methane from natural gas, which is converted to $CO + H_2$ by partial combustion with oxygen or water.

THERMODYNAMIC CONSIDERATIONS*

As has already been pointed out, carbon monoxide and hydrogen may interact to give several different end products.

A thermodynamical approach to the equilibria related to all the possible reactions is quite useful in order to understand the reasons why the synthesis of methanol requires the use of highly selective catalysts and high pressures for its industrial realization.

The following reactions for the synthesis of methanol from carbon monoxide are of interest:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta H_{350°C} = -24{,}450 \quad (1)$$
$$\Delta F°_{350°C} = +12{,}100$$

Reaction (1) could be considered as divided into the two consecutive reactions:

$$CO + H_2 \rightleftarrows HCHO \qquad \Delta H_{350°C} = +5{,}050 \quad (2)$$
$$\Delta F°_{350°C} = +16{,}100$$

$$HCHO + H_2 \rightleftarrows CH_3OH \qquad \Delta H_{350°C} = -29{,}500 \quad (3)$$
$$\Delta F°_{350°C} = -4{,}000$$

The synthesis of methanol from carbon dioxide

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta H_{350°C} = -15{,}335 \quad (4)$$
$$\Delta F°_{350°C} = +15{,}800$$

may be considered as a composite equilibrium, whose individual reactions are the conversion of CO_2 into CO

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta H_{350°C} = +9{,}115 \quad (5)$$
$$\Delta F°_{350°C} = +3{,}700$$

and the synthesis of methanol from carbon monoxide (Eq. 1). Reactions subsequent to that of Eq. (1) are:

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* The thermodynamical data considered in this paragraph are those published by Parks and Huffman[54], by Rossini and co-workers[63], and by Smith[71].

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta H_{350°C} = -4{,}600 \quad (6)$$

$$\Delta F°_{350°C} = -1{,}400$$

$$CH_3OH + nCO + 2nH_2 \rightleftarrows C_nH_{2n+1}CH_2OH + nH_2O \quad (7)$$

$$CH_3OH + nCO + 2(n-1)H_2 \rightleftarrows C_nH_{2n+1}COOH + (n-1)H_2O \quad (8)$$

These products may go through reactions of condensation, dehydration or ketonization, giving rise to the formation of olefins, esters, ketones, etc. The formation of these compounds may reach quite considerable values when alkali is contained in the methanol catalysts.

Reactions competitive to the synthesis of methanol are:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \qquad \Delta H_{350°C} = -52{,}222 \quad (9)$$

$$\Delta F°_{350°C} = -15{,}826$$

In practice the synthesis of methane, according to Eq. (9), is associated with the production of carbon dioxide, because the water vapor produced in reaction (9) participates in the water gas conversion reaction and converts a part of the carbon monoxide into dioxide. Accordingly, the reaction

$$2CO + 2H_2 \rightarrow CO_2 + CH_4 \qquad \Delta H_{350°C} = -61{,}337 \quad (10)$$

$$\Delta F°_{350°C} = -19{,}526$$

which is reported in the old technical literature, must be regarded as derived from reactions (9) and (5).

Elementary carbon may also be formed, according to the reaction

$$2CO \rightarrow CO_2 + C \qquad \Delta H_{350°C} = -41{,}430 \quad (11)$$

$$\Delta F°_{350°C} = -16{,}730$$

in the presence of metals of the eighth group.

The formation of hydrocarbons is also possible in the direct hydrogenation of carbon monoxide (Fischer-Tropsch synthesis):

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O \quad (12)$$

This reaction is not generally associated with the synthesis of methanol, because as a rule it takes place at considerably lower temperatures. However, substantial amounts of hydrocarbons are formed when thorium-containing catalysts are used in the temperature and pressure ranges of the synthesis of methanol.

Table 2 shows the dependence of the free energy of reaction on temperature for some typical reactions of hydrogenation of carbon monoxide. The ΔF° values for the synthesis of methanol are higher than those of the competitive reactions.

Although ΔF° of reaction (1), referred to standard conditions, is positive at temperatures $>180°C$, the synthesis of methyl alcohol is made possible by the use of high pressure, since this reaction is associated with a considerable volume contraction.

In the curve of Figure 1, the equilibrium constant K_{eq} of the methanol synthesis is plotted versus temperature. Whenever high pressures are used a correction has to be made for the non-ideal behavior of methyl alcohol. Figure 2 shows the values of the activity coefficient ratios, K_γ at different temperatures.

In practice the methanol synthesis is performed by operating at high space velocities and with low conversions at each cycle. This device helps to keep down the side reactions; on the other hand, CH_3OH concentrations are reached which are much lower than those corresponding to equilibrium.

TABLE 2. FREE ENERGY OF REACTION, ΔF° (kcal/mole)

T (°C)	27	127	227	327	427
$CO + 2H_2 \rightarrow CH_3OH$	−6.30	−0.80	+5.00	+10.80	+16.70
$2CO \rightarrow CO_2 + C$	−28.57	−24.31	−20.02	−15.73	−11.44
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−33.87	−28.56	−23.01	−17.29	−11.44
$2CO + 2H_2 \rightarrow CH_4 + CO_2$	−40.67	−34.36	−27.87	−21.22	−14.49
$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O (n = 2)$	−27.23	−19.34	−11.10	−2.67	+5.90
$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O (n = 2)$	−51.32	−40.46	−29.18	−17.62	−5.87

Experimental data, obtained (under conditions very close to the equilibrium) at 350 to 380°C with gas mixtures containing an excess of hydrogen, show methanol concentration figures which are practically coincident with those predicted by thermodynamical calculations.

CATALYSIS IN THE SYNTHESIS OF METHANOL

Classification of the Catalysts Used. The patent literature between 1920 and 1930 on catalysts for the production of methanol is somewhat chaotic. The catalysts listed in the patents of the B.A.S.F. cover complex mixtures of oxides or metals, including all the elements except those of the eighth group of the periodic system. Practically from the start all investigators discarded the iron group elements, which are active catalysts for the concurrent synthesis of methane.

In spite of the many papers describing the performance of the different catalysts, it is practically impossible to relate the results of the different experimenters, because of the wide differences in the experimental methods which were followed; while some investigators studied the catalysis of the synthesis of methyl alcohol, most of the publications deal with studies of the catalysis of the decomposition of methanol. Now, particularly from the point of view of selectivity, there is lack of a satisfactory similarity between the catalytic activity in the reaction of synthesis and in that of decomposition of methyl alcohol. The activity of a catalyst in the de-

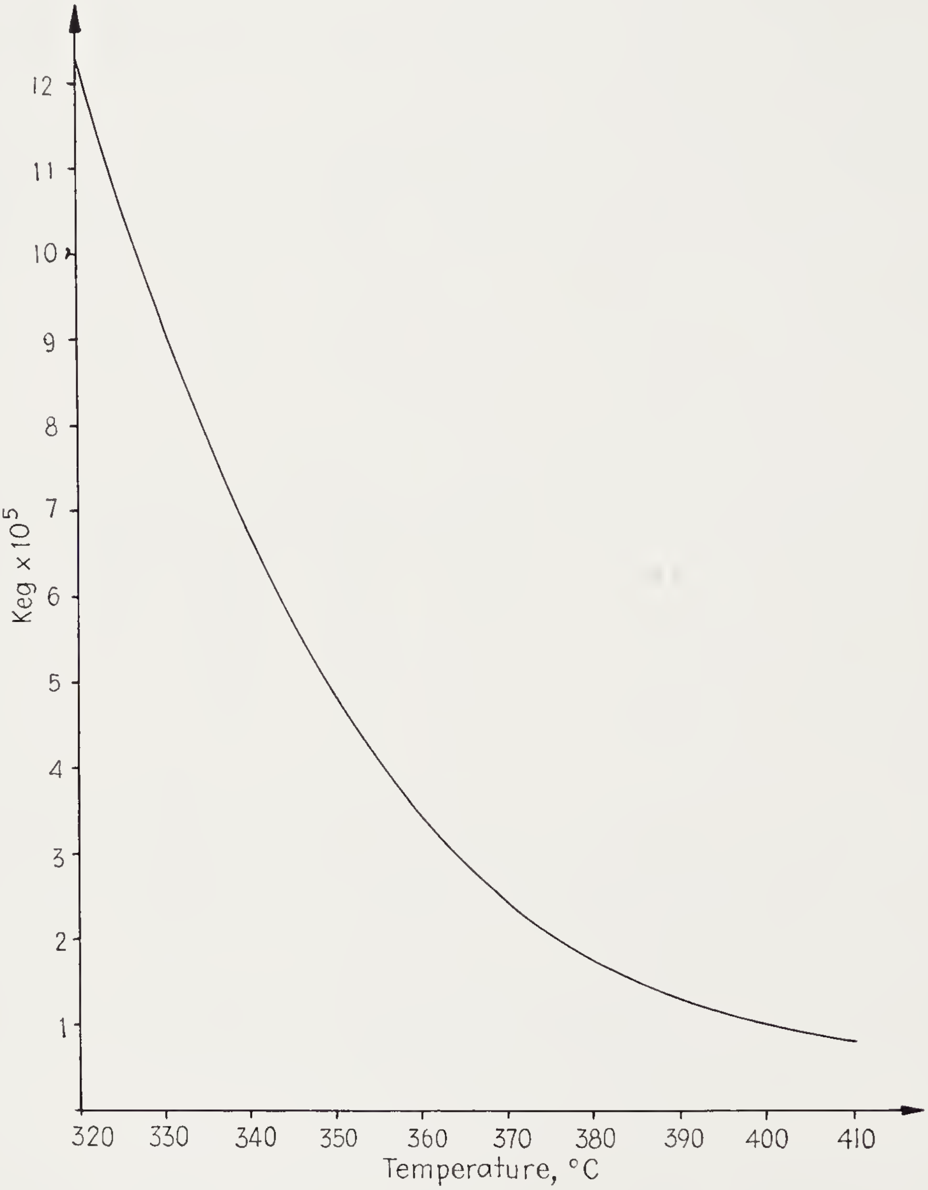

Figure 1. Equilibrium constant for the reaction $CO + 2H_2 \rightleftarrows CH_3OH$.

composition of CH_3OH has often been measured from the total volume of gas produced, but some catalysts cause the formation of methyl formate, or formaldehyde, in addition to that of CO and H_2.

Catalysts made with the same precipitation method show activities which depend a great deal on the conditions of precipitation (i.e., excess or deficiency of the precipitating agent, temperature of calcination before use, and so forth). In spite of these circumstances, it is possible to make a qualitative comparison among the catalysts prepared according to different methods.

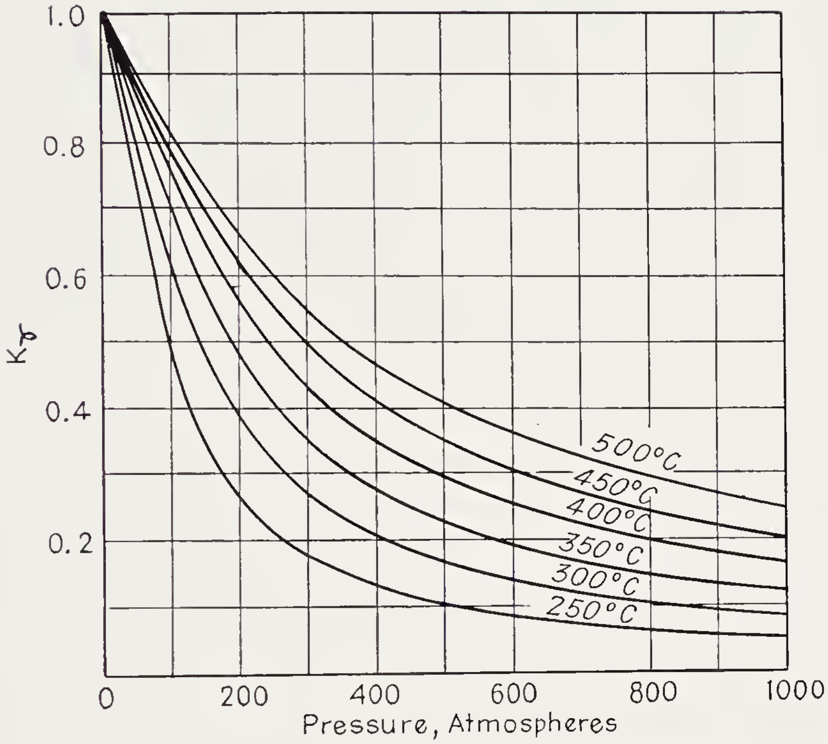

Figure 2. Values of Kγ for the reaction $CO + 2H_2 = CH_3OH$. Ewell, R. H., *Ind Eng. Chem.*, **32,** 152 (1949).

Among the various catalysts which have been proposed for the synthesis of methyl alcohol, only those containing ZnO or CuO have a real practical interest. The complexity in the composition of the majority of the catalysts listed in the various patents is somehow justified by the fact that the catalytic activity of pure ZnO or CuO is fairly low, while that of mixtures of these compounds with oxides of other metals is much higher and much more lasting.

In practice, the catalysts of industrial importance contain, beside ZnO, a promoter, in the form of a difficultly reducible oxide (i.e., Cr_2O_3). Several substances act as promoters, enhancing the catalytic activity of ZnO and

CuO. The German investigators who first studied this problem (Mittasch and co-workers) explained the high selectivity of mixed catalysts on a purely topochemical basis. As will be shown later, very active catalysts have been obtained with ZnO containing extremely small percentages of promoters of various kinds. These promoters have in common the property of being by themselves very poor hydrogenation catalysts, and of having high melting points; they also tend to prevent the aging (due to the growth of crystals) of the main catalytic agent.

In 1929–1930, G. Natta[40, 41] showed that very selective catalysts for the methanol synthesis may be obtained without the use of mixtures of metallic oxides. In fact, zinc carbonate (Smithsonite) heated at 350°C, gives a variety of zinc oxide, which is very active for the synthesis of methyl alcohol. The same investigator has obtained another very active variety of ZnO by the thermal decomposition of melted zinc acetate. The activity of such a catalyst is enhanced by the addition of a promoter. The next section is devoted to a detailed survey of the different types of catalysts which may be used for the synthesis of methanol.

Catalysts Containing Only One Metal Oxide

Preparation Methods and Activities of Zinc Oxide Catalysts.* Pure ZnO is not used at present for the industrial synthesis of methyl alcohol; however, this compound is considered as the most important component of the majority of the widely used mixed catalysts. Therefore the knowledge of the behavior of catalysts made with pure ZnO is of special interest for the interpretation of the mechanism of catalysis with mixed catalysts.

Zinc oxide is no doubt the most selective of all the catalysts for the synthesis of methyl alcohol. Certain forms of ZnO which are particularly active give pure methyl alcohol when used at temperatures lower than 380°C. Almost all these catalysts have the disadvantage of a rather short life.

In the technical literature several methods are given for the preparation of pure zinc oxide catalysts. Zinc oxide, when produced by the combustion of metallic zinc, is a very poor catalyst for the synthesis of methanol but is remarkably active in the decomposition reaction. Under the electron microscope, this catalyst appears to consist of trigonal star-like crystals.

The activity of ZnO catalyst obtained by calcination of precipitated zinc hydroxide seems to depend on the anion originally combined with

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* In this class those catalysts have been included, which consist of imperfectly crystallized zinc oxide. These catalysts are slightly reduced during their performance, and actually contain a deficiency of oxygen compared to the stoichiometric value for ZnO. Their very high catalytic activity is probably related to this imperfection of the crystalline lattice.

the zinc. Starting from $ZnCl_2$ or $ZnSO_4$, one obtains catalysts that are considerably less active than those obtained from $Zn(NO_3)_2$. This, according to Hüttig and co-workers,[20] is due to the adsorption of traces of Cl^- or SO_4^{--} by the precipitate of $Zn(OH)_2$*.

Frolich and co-workers[14] on the basis of their experience with copper catalysts advised precipitating all catalysts with NH_4OH rather than NaOH. They showed that the $Cu(OH)_2$ precipitated with NaOH is very active in the decomposition of methyl alcohol only if it is not previously washed free of its impurities. Purification of this precipitate by prolonged dialysis leads to a very poor catalyst. The catalyst prepared by precipitation with NH_4OH is not very active and its activity in the decomposition of methanol does not seem to be influenced by dialysis. The activity of catalysts containing traces of adsorbed NaOH decreases rapidly by heating them at temperatures above 300°C; this is probably related to the melting of the occluded sodium salts. The experiments dealing with the reaction of synthesis of methanol are not in agreement with those concerning its decomposition. In fact, the catalysts obtained by precipitation of $Cu(OH)_2$ with NaOH show lower activities and selectivities than those precipitated with NH_4OH.

Molstad and Dodge[38] operated with an ammonia-precipitated catalyst at a pressure of 178 atm. The conversions obtained by these authors with a gas ratio $CO:H_2 = 1:2$ and with space velocities of 25,000 are given in Figure 3. Similar results were obtained by several authors[5, 6, 15, 36], while other investigators[39] found much lower conversions with a similar catalyst.

Hüttig and Goerk tested a number of different catalysts in the decomposition of methyl alcohol[22]. They obtained the best results with catalysts prepared from the decomposition of complex zinc salts. Molstad and Dodge[38] pointed out that the catalysts precipitated with Na_2CO_3 are more active than those precipitated with ammonia. This is in good agreement with the decomposition experiments performed by Ipatiev and Dolgov[28].

Table 3 shows some results obtained by Molstad and Dodge. It can be noticed that the best conversion is obtained by the use of a catalyst prepared with a slight deficiency of Na_2CO_3 .

G. Natta[40] noticed a considerable decrease with time of the activity of a

* $Zn(OH)_2$ is isomorphous with $Ni(OH)_2$. Schwab and Block[70] have recently observed that in the precipitation of $Ni(OH)_2$ from $NiCl_2$ solutions there are formed lamellar crystals grown regularly only in two directions (bidimensional crystals). The chloride ions are adsorbed on the surface of the planes composed of hydroxyl groups, thus hindering (because of their large size) the growth of the crystals along the z axis. It is possible that the chloride ions are adsorbed by the crystals through substitution of the hydroxyl ions located at the external lattice planes of the crystals. Possibly zinc hydroxide, whose crystals structure is similar to that of $Ni(OH)_2$, behaves in a similar manner.

catalyst prepared with precipitated basic zinc carbonate. The activity is reduced to one-third of the original value after only 10 hours of operation at 400°C. The same investigator has found that when ZnO is prepared by the thermal decomposition of melted zinc acetate (at 300 to 350°C) its activity is more prolonged. This thermal decomposition must be carried on in the absence of air. One then obtains a gray catalyst, the long life of which is probably due to the action of traces of elemental carbon, which prevents the recrystallization of ZnO.

Even more active and durable catalysts were obtained by the thermal decomposition of smithsonite (mineral $ZnCO_3$), whereas hydrozincite (basic zinc carbonate) gives a rather impermanent catalyst. The high activity of ZnO from smithsonite may be attributed to its high and uniform porosity, and its resistance to sintering. The higher activity of ZnO from smithsonite has been confirmed by the experiments of Kostelitz and Hensinger[35]. Zinc oxide obtained from smithsonite is not completely pure ZnO. It can generally be observed that the zinc minerals which give the most active catalysts contain, in the form of solid solution, small amounts of other divalent oxides (CdO, MgO, CuO) which are believed to behave as promoters.

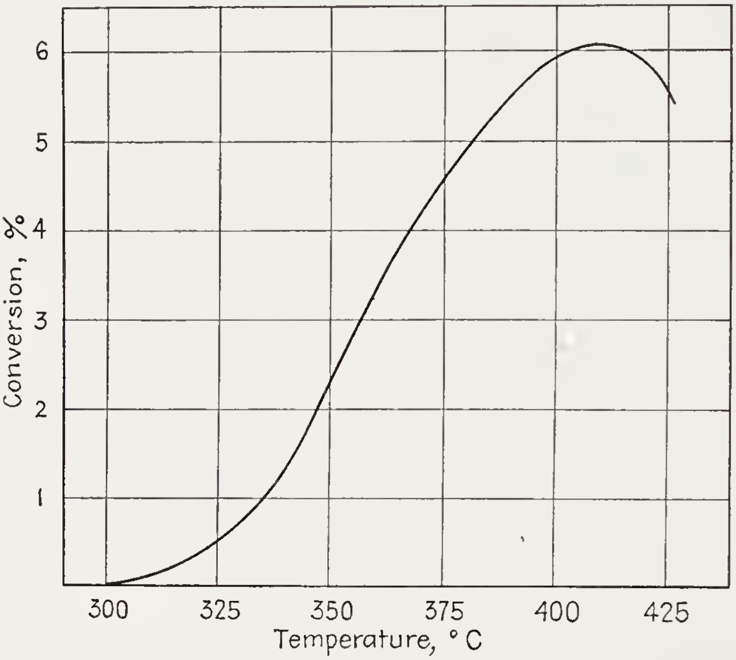

Figure 3. Synthesis of methanol from a 1:2 $CO:H_2$ mixture at a space velocity of 25,000 and a pressure of 178 atms[38].

Whereas many varieties of ZnO go through a rapid aging, the zinc oxides obtained from acetate or from smithsonite are very durable, provided they are used below 390°C, and, more generally, at temperatures lower than that of their formation. Because of their stability, it was possible to study the action of these catalysts and to perform experiments at various temperatures, obtaining reproducible results. Thus Natta and Corradini[49] worked with two varieties of ZnO, one from a smithsonite of Val Brembana, Italy, and the other from zinc acetate. Figures 4 and 5 show the results of some of their experiments, in which the produced methanol had a high degree of purity (above 99 per cent). The two catalysts present similar values of the activation heat (27 kcal/mole for ZnO from smithsonite and 30 kcal/mole for ZnO from zinc acetate).

TABLE 3. EFFECT OF THE PRECIPITATING AGENT ON ACTIVITY OF ZnO CATALYSTS

(Gas composition 1 CO:2 H_2 ; at 385°C and 178 atm.)

Catalyst Prepared from $Zn(OH)_2$ Precipitated by	Inlet Space Velocity	Conversion (%)
NH_4OH	92,000	3.0
NH_4OH	95,700	2.6
Na_2CO_3 excess	94,500	4.7
Na_2CO_3 insuff.	95,000	8.5
Na_2CO_3 excess	95,000	5.5

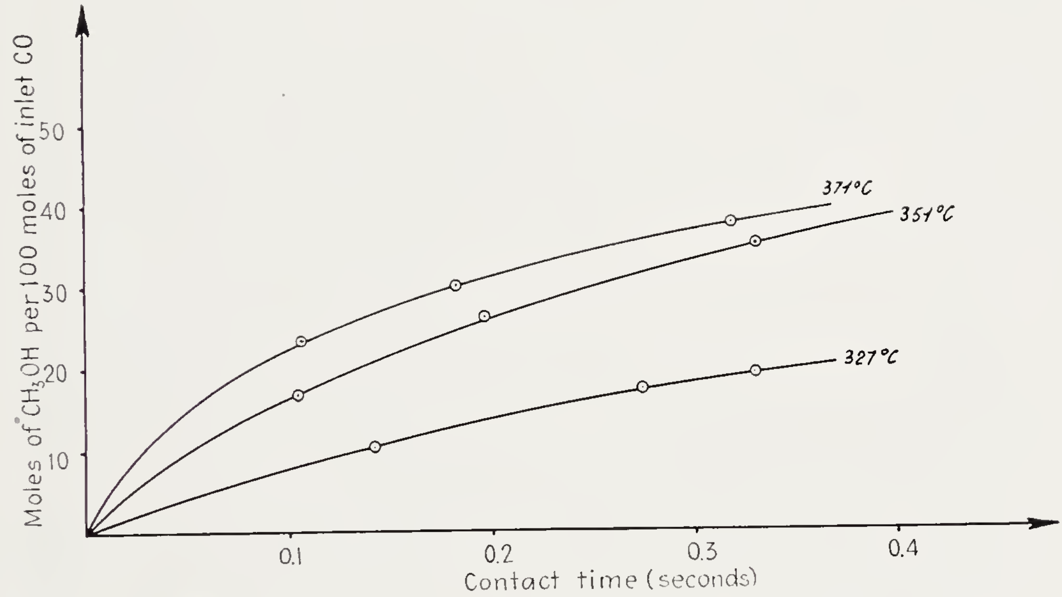

Figure 4. Moles of CH_3OH produced per 100 moles of inlet CO, as function of contact time at different temperatures with a ZnO catalyst from smithsonite. Pressure: 250 atm., inlet gas: CO:H_2 = 1:10. Contact time is defined as 3,600 times the ratio of the volume of the catalyst to the inlet volume of H_2—CO mixture per hour.

The data of Natta and Corradini should not be directly related with those of Molstad and Dodge[38], which are shown in Table 3. However, extrapolation of the data of Molstad and Dodge from 385 to 352°C, with the assumptions that the activation heat has a value of 30 kcal/mole and that for low conversions the amount of CH_3OH formed varies inversely with the space velocity, leads to the conclusion that among the different catalysts of Molstad and Dodge only the ZnO prepared from basic zinc carbonate, by precipitation with a slight deficiency of Na_2CO_3 yields initially an activity which is equal to that of ZnO from zinc acetate, if not to that of ZnO from smithsonite. The activity of the catalyst from basic carbonate, however, drops much more rapidly with aging than that of ZnO from smithsonite or from zinc acetate.

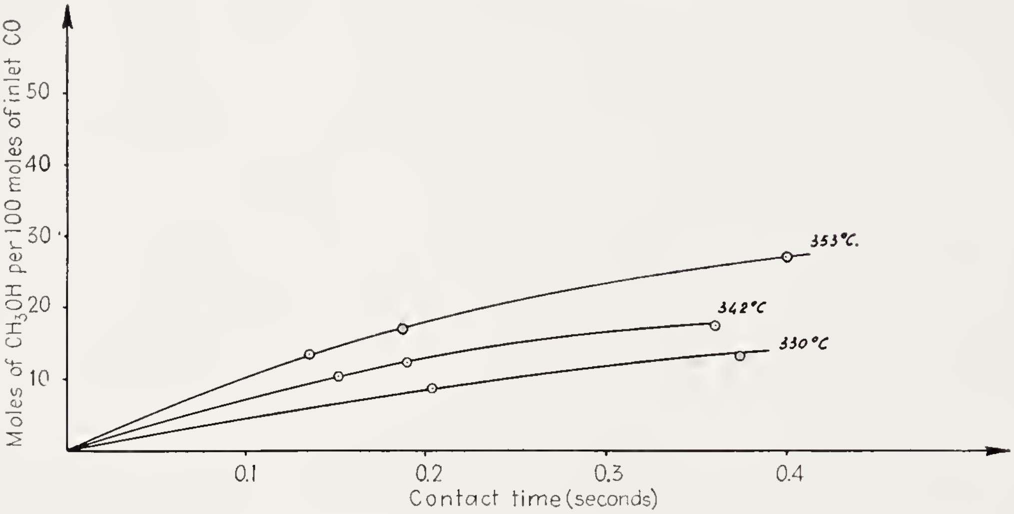

Figure 5. Moles of CH_3OH produced per 100 moles of inlet CO, as function of contact time at different temperatures, with a ZnO catalyst from zinc acetate. Pressure: 250 atm. Inlet gas: $CO:H_2 = 1:10$. Definition of contact time same as in legend of Figure 4.

Relationship between Activity and Crystal Size of Zinc Oxide. Several authors have established that the catalytic activity of ZnO obtained by the thermal decomposition of zinc compounds, is a function of the preparation temperature. The size of ZnO crystals increases with an increase in temperature, whereas the catalytic activity undergoes a corresponding decrease[29, 49]. It has to be pointed out that the catalytic activity is influenced much more by the crystalline size, than by the particle size (each particle being composed of a great number of individual crystals)[20].

Structural studies with X-rays and electron microscope observations by Natta and Corradini[49] have confirmed that the greater activity of some varieties of ZnO is due to the smaller crystalline size, and that the decrease of their activity is associated with an increase in the size of the individual crystals. As shown in Figures 10 and 11, the most durable catalysts show low variations in crystal size with time. Correspondingly, the activity of ZnO from zinc acetate is higher than ZnO from zinc nitrate, formate, or oxalate.

Table 4 shows some results of the X-ray examinations. A Geiger counter-recording type instrument was used, and the average crystalline size was calculated from the width of the diffraction bands.

The greater activity of ZnO from smithsonite appears to be associated with the smaller size of its crystals, the dimensions of which are not altered sensibly upon heating at 500°C. Similarly, the very low activity of ZnO from $Zn(NO_3)_2$ or from the combustion of metallic zinc should be considered as associated with the large crystal size.

TABLE 4

Method of Preparation of ZnO	Average Crystal Size (Å)
From zinc basic carbonate heated at 300°C	200
From zinc basic carbonate heated at 500°C	400
From zinc carbonate (smithsonite) heated at 350°C	100
From zinc carbonate (smithsonite) heated at 500°C	170
From zinc acetate, heated at 300°C	250
From zinc nitrate, heated at 500°C	>1000
From zinc formate, heated at 500°C	500
From zinc oxalate, heated at 500°C	500
From the combustion of metallic zinc	>1000

In the evaluation of the average crystal size of ZnO from zinc acetate there is an appreciable divergence between that obtained from electron microscopic examination and that calculated with the formula of Warren on the basis of X-ray diffraction measurements. The larger crystal size observed with the electron microscope may be justified by admitting that some of the biggest crystals observed should be regarded as aggregates rather than as individual crystals.

The gradual growth of the crystals of ZnO from zinc acetate, when heated with air at 500°C, can be followed by means of the electron microscope. Presumably the traces of elemental carbon present are eliminated by the calcination in air, and therefore crystallization can proceed much faster than in samples heated in the absence of air.

The variety of ZnO obtained from basic zinc carbonate (heated at 500°C) appears to consist of crystals which are very small and yet are in the visibility range of the electron microscope. The average crystal sizes of the zinc oxide from smithsonite and from basic carbonate (heated at 350°C) as calculated from X-ray measurements are in the range 100 to 200 Å; however, the individual crystals are not visible with the electron microscope (under a magnitude of 20,000).

Luminescence of ZnO. Schleede, Richter and Schmidt[66] have studied the luminescence of several varieties of ZnO, and have attempted to relate it to the catalytic activity of ZnO in the decomposition of methanol. ZnO obtained by the thermal decomposition of $Zn(NO_3)_2$ at 360°C presents an orange-red luminescence and does not act as a catalyst for the decomposition of CH_3OH at 360°C, while ZnO obtained by the decomposition of $Zn(OH)_2$ or $ZnCO_3$ is not luminescent and acts as a good catalyst.

Other investigators[69] have found no relationship between luminescence and catalytic activity of ZnO. Natta and Corradini[49] have pointed out that ZnO from basic zinc carbonate does not exhibit luminescence unless it was previously heated above 550°C. Whenever it is heated above 550°C, it exhibits a luminescence whose intensity grows with the heating temperature; meanwhile, its catalytic activity disappears. These investigators have also noticed that some other active forms of ZnO (for example, ZnO from basic zinc carbonate, or from smithsonite, or also from zinc oxalate) are not luminescent; this holds also for the most active mixed ZnO-Cr_2O_3 catalysts. On the contrary ZnO from nitrate, which is not very active, shows a fair luminescence. In other words, it seems that luminescence is characteristic of those varieties of ZnO which consist primarily of large crystals. With the exception of ZnO from acetate, which gives a greenish luminescence (and which consists of elongated, thin crystals), those varieties of ZnO which are good catalysts for the methanol synthesis are not luminescent.

Partially Reduced Copper Oxide. Although some mixed catalysts containing copper oxide are among the most active catalysts for the synthesis of methyl alcohol, pure copper oxide has a very weak catalytic activity. Copper oxide reduces itself rapidly to metallic copper, which then crystallizes readily. The crystals of metallic copper which are thus formed, according to the X-ray measurements performed by Natta and Corradini[49] appear to be of medium size (those which were brought to 350°C are as big as 500 Å). Reduced copper oxide gives a catalytic activity which depends very much upon the reduction temperature[1, 60]. According to the experiments of Veltistova, Dolgov and Karpov[75] with a copper catalyst, methane, carbon, and about 10 to 15 per cent methanol are obtained.

Chromium Oxide. Almost all the different types of the more of less hydrated chromium oxide are very poor catalysts for the synthesis of methyl alcohol. The highest activity in this group seems to be shown by the variety of Cr_2O_3 prepared by the decomposition, in an atmosphere of CO and H_2, of $Cr(OH)_3$, which in turn is obtained from solutions of $Cr(NO_3)_3$

and ammonia. Molstad and Dodge[38] have found that this catalyst has an activity which is considerably higher than that of the chromium oxide obtained by Lazier and Vaughen from chromium oxalate[37]. Figure 6, based on the experimental data of Molstad and Dodge, shows the dependence upon temperature of the conversion of CO, when pure Cr_2O_3 is used as a catalyst. A comparison of these conversion data with those obtained when ZnO is used as the catalyst, leads to the conclusion that Cr_2O_3 has an activation energy lower than that of ZnO.

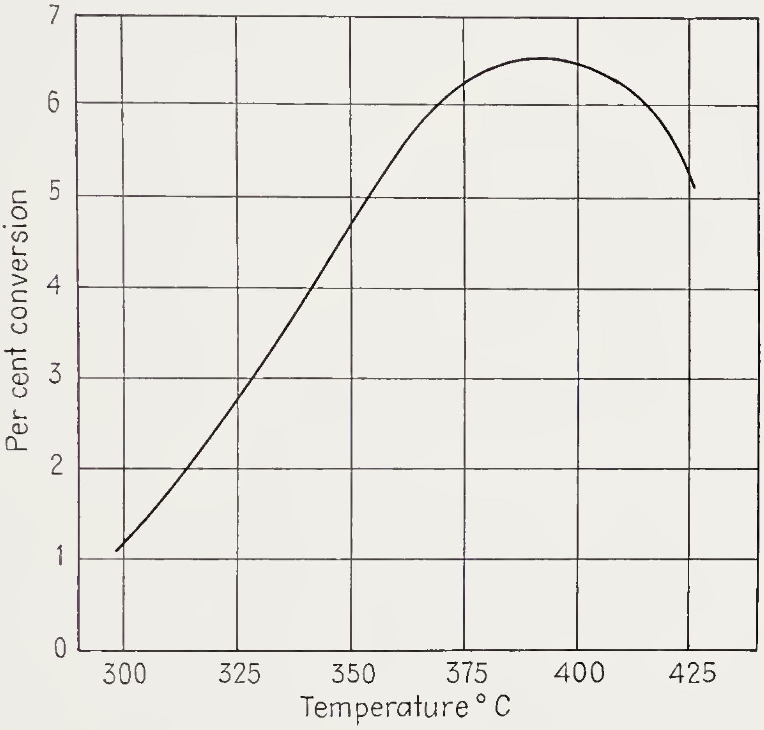

Figure 6. Percentage conversion of entering CO to methanol, under standard testing procedure at 178 atm., with a Cr_2O_3 catalyst[38].

The chromium oxide prepared by Molstad and Dodge has an activity, which is equivalent to that of the zinc oxide obtained from $Zn(NO_3)_2$ and ammonia. According to these investigators, the selectivity of their Cr_2O_3 is much higher than that of ZnO from $Zn(OH)_2$ precipitated with ammonia. The purity of methanol prepared over Cr_2O_3 is, however, not greater than that prepared over certain other ZnO catalysts (see, for example, Table 5).

The remarkable influence of the method of preparation of Cr_2O_3 on its catalytic activity for the methanol synthesis has been emphasized also by Hüttig[24], who has found that only a very few varieties of Cr_2O_3 (for example, that from $Cr(OH)_3$ obtained by treating $Cr(NO_3)_3$ with ammonia) possess a relatively high catalytic activity.

G. Natta[40] tested a chromium oxide catalyst, and found it to have a very poor activity. Lazier and Vaughen[37] found that their Cr_2O_3 catalysts showed a poor selectivity, but this may be due to the high working temperature (>400°C).

In conclusion all the catalysts made with Cr_2O_3, with the only exception of that prepared from $Cr(NO_3)_3$ and ammonia, show poor activities and low selectivities (see Table 6). Chromium oxide, however, has a considerable importance as a promoter of ZnO or CuO.

TABLE 5. PURITY OF SYNTHETIC METHANOL AS A FUNCTION OF THE TYPE CATALYST

Catalyst	% Methyl Alcohol in the Condensed Reaction Products	
	375°C	400°C
Chromium oxide from ammonia precipitated $Cr(OH)_3$ (Molstad and Dodge)[38]	96	91
Zinc oxide from ammonia-precipitated $Zn(OH)_2$ (Molstad and Dodge)	86	78
Zinc oxide from acetate (Natta)	99	97

TABLE 6. SYNTHESIS OF METHYL ALCOHOL WITH Cr_2O_3 AS CATALYST

Catalyst	Temperature (°C)	Pressure (Atm.)	Space Velocity	Yield in Raw Material cc. per hr. per 100 cc. Catalyst	Composition of raw product	
					Methanol %	Higher Alcohols (%)
Hydrated Cr_2O_3 gel	439	290	5,000	27.5	40	—
	440	290	10,000	36.0	60	—
	450	290	20,000	74.0	70	—
Cr_2O_3 from oxalate	375	280	10,000	43.0	41	—
	420	280	10,000	36.0	40	—
	450	280	10,000	39.0	34	23
Cr_2O_3 from $(NH_4)_3CrO_4$	425	280	10,000	14.0	48	7
	450	280	10,000	19.0	30	17
Chromium chromate	400	272	19,200	22.0	63	14
	448	272	19,000	26.0	49	22

Other metallic oxides, which have been proposed for the preparation of mixed catalysts (for example MnO, MgO, etc.) when used by themselves do not show any remarkable activity in the synthesis of methanol; therefore, they will not be considered in this section.

Mixed Catalysts

The catalysts of actual industrial importance for the synthesis of methyl alcohol are composed of mixtures of two or more oxides. In this treatment ZnO base and CuO base mixed catalysts are given separate attention.

ZnO Base Mixed Catalysts. All the varieties of pure ZnO (for example, that from smithsonite or that from zinc acetate), which were widely used in the past for their fairly good resistance to aging, have their activity inincreased upon addition of small amounts of promoters. The most widely used promoter is Cr_2O_3 , which, as we have seen in the preceding paragraph, shows by itself a very limited catalytic activity and a low selectivity. Here promoters of ZnO will be considered as divided into two groups, namely intracrystalline and intercrystalline promoters, depending upon whether they are internal or external to the crystalline lattice of ZnO.

Intracrystalline promoters include the oxides of those cations, whose ionic radius is in the range 0.6—0.9 Å, and hence very close to that of zinc oxide (0.75 Å); these oxides therefore may give rise to solid solutions with ZnO. Special care must be taken when a reducible oxide is used as a promoter. For example, G. Natta[40] has shown that solid solutions ZnO—FeO containing up to 12 to 13 per cent FeO are very active catalysts for the synthesis of methanol. These catalysts may be obtained by the thermal decomposition, in an atmosphere of hydrogen, of solid solutions of zinc and ferrous iron hydroxides or carbonates. This author points out that, if iron is initially present in the ferric form, or if the ferrous iron is not in solid solution with ZnO, it will go through reduction to mtallic iron during the performance of the catalyst and it will thereafter catalyze the formation of methane.

Cadmium is often present as solid solute in smithsonite, and its presence was noticed in some particularly active catalysts obtained from smithsonite. During the performance of the catalyst, CdO is reduced to Cd, which has a relatively high vapor pressure, and may therefore be carried away by the reaction products. In the crystal lattice of ZnO a number of empty spaces are thus obtained, which appear to act favorably toward catalysis.

Also MgO, when present in solid solution is an efficient promoter of ZnO. Magnesium oxide has an extremely low solubility in the crystalline lattice of ZnO[40, 49]; on the contrary ZnO has a relatively high solid solubility (20 per cent by weight) in the lattice of MgO. The mixed catalysts ZnO—MgO are rather mixtures of ZnO with its saturated solid solution in MgO.

Intercrystalline promoters of ZnO include difficultly reducible, high melting oxides. These compounds, which by themselves show very low activities and selectivities for the synthesis of methanol, are widely used in industrial practice as promoters. The most important of them is chromium oxide, which deserves separate consideration.

Chromium oxide may be introduced in the catalyst in several different ways. The following are some of the simplest methods for obtaining good ZnO-Cr_2O_3 catalysts:

(1) The preparation of mechanical mixtures of zinc and chromium oxides does not lead to the production of very active catalysts if Cr_2O_3

is directly used. Veltistova and co-workers[75], however, claim that a mechanical mixture of ZnO and Cr_2O_3 is more active than other ZnO-Cr_2O_3 catalysts obtained by coprecipitation. Better results are obtained with the use of CrO_3, which appears to react more strongly with ZnO. The I. G. Farbenindustrie has used in its industrial operations[26] a catalyst prepared by mixing mechanically ZnO and Cr_2O_3. The grain density of such a catalyst has the value of 1.70–1.75.

(2) Adsorption of a solution of H_2CrO_4 by an active form of a pure ZnO catalyst leads to a surface corrosion of the crystals, with formation of $ZnCrO_4$ and of basic zinc chromate, which can be reduced to zinc chromite and to zinc oxide. Zinc chromite, $ZnO \cdot Cr_2O_3$, appears to act as an intercrystalline promoter: this may explain its property of preventing the recrystallization of ZnO in the temperature range of the industrial methanol synthesis. Very small quantities of H_2CrO_4 are often sufficient for improving at least the durability of ZnO. The treatment of ZnO with chromic acid has in general the effect of improving the catalytic activity of zinc oxide; however, care must be taken in adding the chromic acid, because an excess of H_2CrO_4 leads to an appreciable lowering of the quality of the produced methanol[72].

(3) Reduction, at low temperatures, of zinc chromate or zinc basic chromate, gives a mixture of zinc oxide and amorphous zinc chromite, which exhibits a high catalytic activity. Zinc chromite obtained by reducing zinc dichromate at low temperatures ($<400°C$) appears amorphous to X-rays, but has a low catalytic activity. This would indicate that zinc chromite is not a good catalyst for the synthesis of methanol, but rather a good promoter of ZnO.

(4) Calcination, at temperatures lower than 400°C, of coprecipitated zinc and chromium hydroxides or carbonates, leads to a mixture of zinc and chromium oxides, which contains some residual OH groups, and which (at the high percentages of Cr_2O_3) is completely amorphous to X-rays. Natta and Corradini[49] have noticed that a catalyst, composed of zinc and chromium oxides ($Zn:Cr = 1:1$) obtained by heating the corresponding carbonates at 300°C, gives only the diffraction lines of zinc chromite, with a line broadening effect due to the semi-amorphous condition of the catalyst. The diffraction lines of zinc chromite and zinc oxide appear in this catalyst, when the temperature is increased above 300°C (see Figure 7). Hüttig[21, 23, 25, 33], who studied the system ZnO-Cr_2O_3 by the determination of water adsorption, by magnetic susceptibility, by solubility, and through X-ray examinations, believes that there is a solid state reaction at 600°C with the formation of spinel. According to Kauffe and Pschera[18] the formation of spinel is related to the sublimation of the more volatile ZnO on the surface of Cr_2O_3. At high ratios of ZnO:Cr_2O_3, the diffraction lines of ZnO appear very clearly.

(5) Thermal decomposition of melted zinc acetate, containing small quantities of dissolved chromium acetate, according to Natta, gives a very good catalyst, which is more active than that obtained by the decomposition of pure zinc acetate. Similarly, the catalyst obtained by decomposition of a mixture of zinc and chromium acetates previously treated with chromic acid, is more active than the corresponding catalyst from pure zinc acetate treated with chromic acid. Figure 8 reports some reaction rate curves which were obtained with this type of catalyst. It has been pointed out that addition of Cr_2O_3 makes it possible to work in a temperature range, at which pure ZnO would lose its activity very easily[37]. All the ZnO-Cr_2O_3 mixed catalysts present a high resistance to "aging."

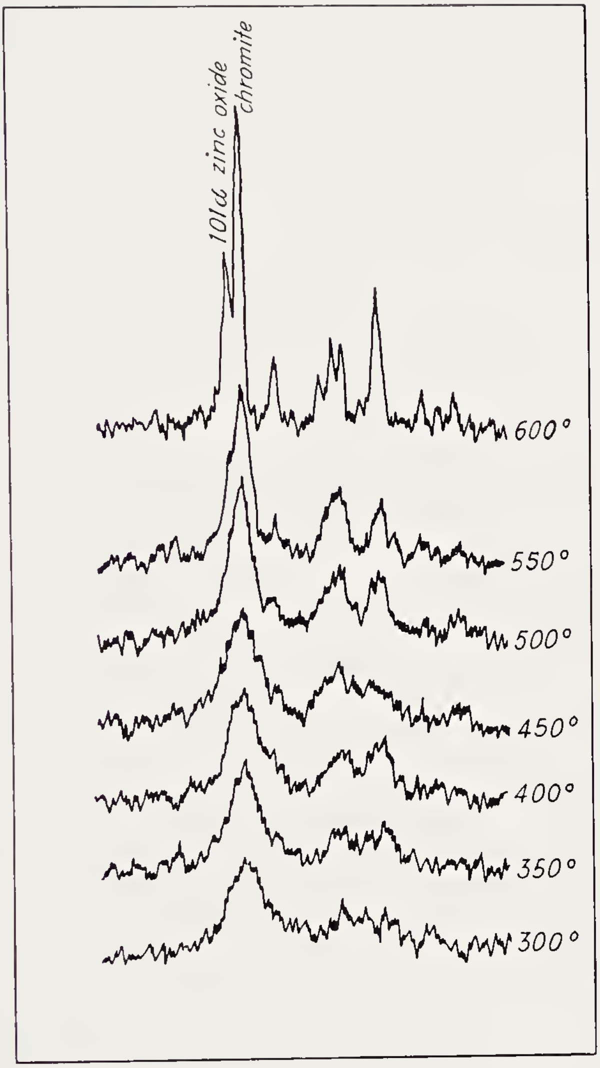

Figure 7. Development of pattern of ZnO and zinc chromite on heating a 1:1 ZnO:Cr_2O_3 catalyst[49].

Relationship between Cr_2O_3 Concentration and Activity of ZnO-

Cr_2O_3 Mixed Catalysts. There are several different opinions among the various investigators concerning the influence of chemical composition upon the catalytic activity of this class of catalysts. It has to be realized that, from a practical point of view, a catalyst should possess high activity, good resistance toward aging, and high selectivity. For evaluating the over-all influence of the promoter's concentration upon the catalyst's performance, it should be observed that the resistance of a ZnO catalyst toward aging varies directly with concentration of Cr_2O_3, while beyond a definite Cr_2O_3 concentration limit, the selectivity of a ZnO catalyst at a defined temperature appears to vary inversely with the concentration of the promoter. It is important to point out that some very active catalysts require considerably lower working temperatures, and thus generally work under conditions of relatively higher selectivity.

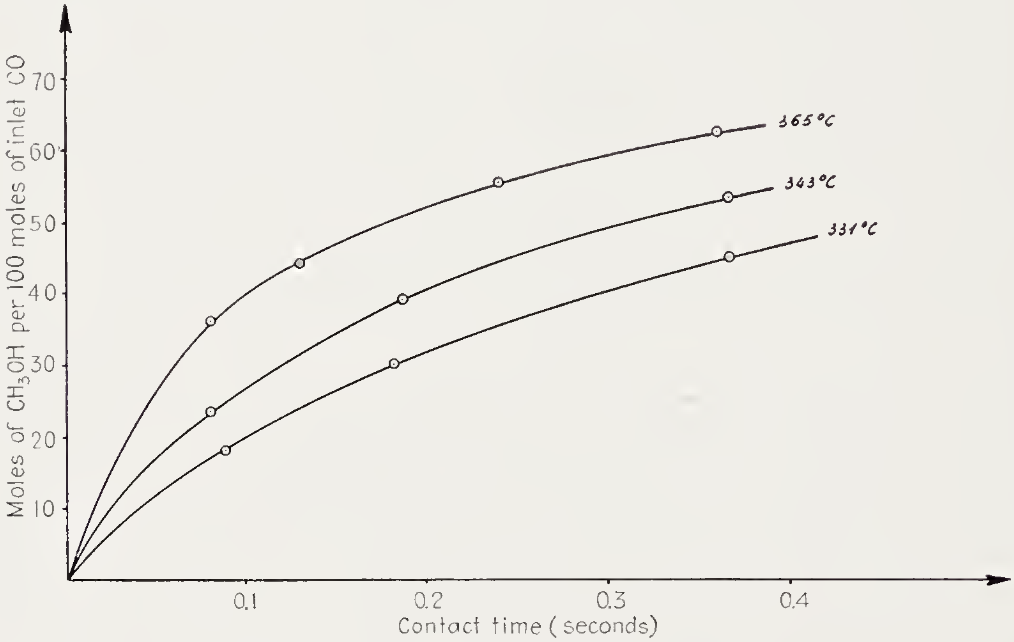

Figure 8. Moles of CH_3OH produced per 100 moles of inlet CO, as a function of contact time (see Figure 4 legend for definition of contact time) at different temperatures, with a $ZnO:Cr_2O_3$ catalyst prepared from a mixture of the acetates treated with chromic acid. Pressure: 250 atm. Inlet gas: $CO:H_2 = 1:10$.

As far as activity is concerned, the optimum composition depends on the catalyst preparation method. The optimum percentage of Cr_2O_3 is lower if this compound is used as promoter of some active ZnO catalysts, whose minute crystals are stabilized by a surface coating of chromium oxide or of zinc chromite. In the case of a real coprecipitation of zinc and chromium hydroxides or basic carbonates, the most active catalysts are those with higher perentages of chromium.

Extensive work on $ZnO-Cr_2O_3$ catalysts, obtained by precipitation of the hydroxides with ammonia from the solutions of the nitrates has been carried on by Molstad and Dodge[38].

Figure 9 shows the variation of the CO conversion to methanol with the catalyst composition, according to the experimental data of Molstad and Dodge[38]. It appears evident that the highest conversions are obtained with catalysts containing 20 to 30 per cent of chromium oxide. According to Molstad and Dodge, who studied also the effect of aging, the catalysts containing less than 25 per cent Cr_2O_3 lose their activity rapidly, while on the contrary, the catalysts containing more than 25 per cent Cr_2O_3 seem to present an activity that increases as time goes on. The catalysts with high percentages of Cr_2O_3 show a shrinkage which varies directly with the percentages of chromium. One of the best catalysts, $Zn_{58}Cr_{42}$ exhibits a shrinkage of 53 per cent after its regular performance. With the use of "preshrunk" catalysts, it has been noticed that the highest activity is given by catalysts with very high chromium contents.

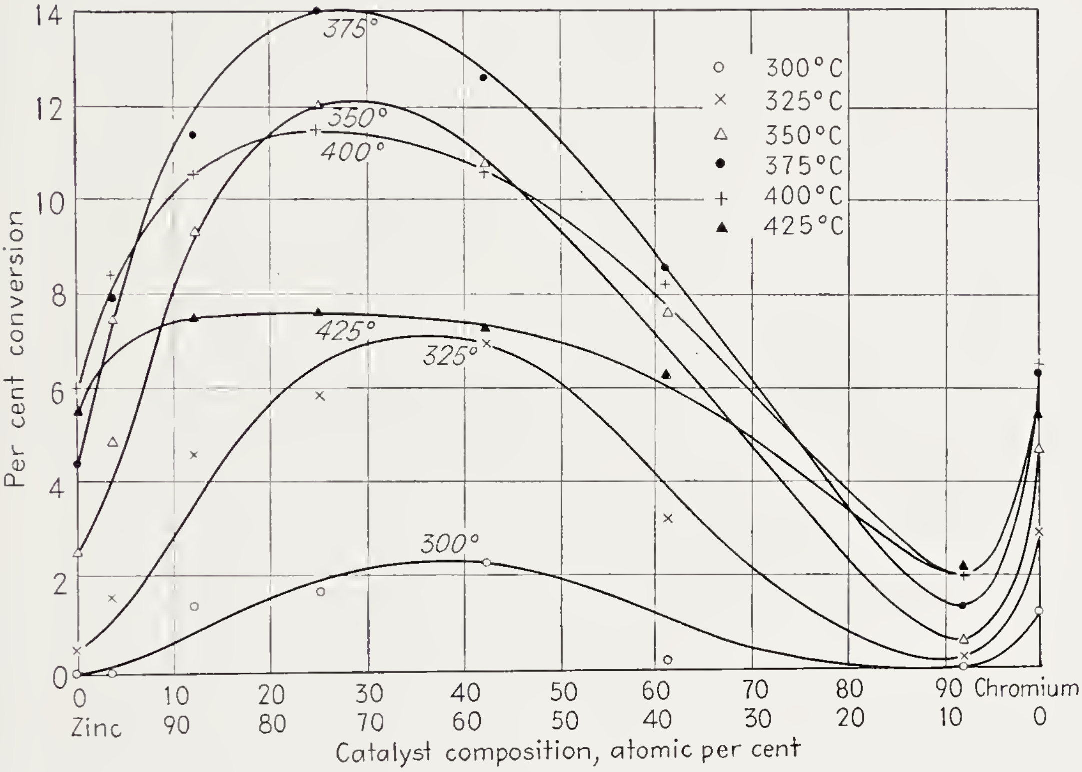

Figure 9. Percentage conversion of entering carbon monoxide to methanol during standard testing procedure at 178 atm[38].

Table 7 gives the conversion values for some catalysts with high chromium contents. The maximum conversions are obtained with catalysts whose Zn/Cr ratio is equal approximately to one.

The catalysts in which chromium was present in amounts insufficient for the formation of spinel are formed after a run, made up of crystals of ZnO, the sizes of which vary inversely with the percentage of chromium oxide present. Table 8 shows the result of crystal size determination of $ZnO-Cr_2O_3$ catalysts performed by Natta and Corradini by the X-ray diffraction method.

TABLE 7. VARIATION OF CONVERSION WITH CATALYST COMPOSITION FOR PRESHRUNK CATALYSTS* [38]

Composition	Temperature (°C) at which maximum Conversion Occurs	Inlet Space Velocity	Per cent Conversion
$Zn_{59}Cr_{41}$	320	25,000	24.4
$Zn_{58}Cr_{42}$	340	29,000	25.2
$Zn_{46}Cr_{54}$	340	30,000	26.4
$Zn_{45}Cr_{55}$	300	33,000	26.9
$Zn_{40}Cr_{60}$	300	25,000	21.8
$Zn_{35}Cr_{65}$	320	25,000	17.8
$Zn_{26}Cr_{74}$	340	25,000	7.4

* The temperature data reported in this table should be considered strictly on a comparative basis. The type of apparatus used, and the high conversion values, made it impossible to keep the temperature constant. The local temperature in certain zones of the catalyst's space reached values considereably higher than the indicated ones.

TABLE 8. PARTICLE SIZE OF PREHEATED CATALYSTS FROM PRECIPITATED BASIC ZINC AND CHROMIUM CARBONATES

Preheating temperature: 400°C

	Average Crystal Size in Å after a Heating Period of		
	2 hr	6 hr	15 hr
Pure ZnO	250 Å	300 Å	350 Å
Zn:Cr = 10:1	130	150	170
Zn:Cr = 5:1	110	150	170

The same authors have also studied the growth of the ZnO crystals, provoked by prolonged heating at definite temperatures. Figures 10 and 11 show clearly that ZnO from carbonate is less resistance to aging than ZnO from smithsonite, or than catalysts containing $ZnO + Cr_2O_3$.

In spite of the lack of data in the technical literature, the methanol industry is now successfully using some very active and resistant catalysts, which contain Cr_2O_3 in concentrations lower than those which were classified as "optimum." These catalysts present the advantage of being very selective: for example, a catalyst of Montecatini Chemical Co., containing

11 per cent by weight of chromium oxide, examined by Natta and co-workers[50] produced, at 375°C, a raw methyl alcohol of high purity (per cent methanol >99).

The activation energy of such a catalyst is about 30 kcal/mole, equal to that of pure ZnO. This seems to corroborate the hypothesis that the promoting action of Cr_2O_3 is mainly due to its hindering action upon the recrystallization of ZnO.

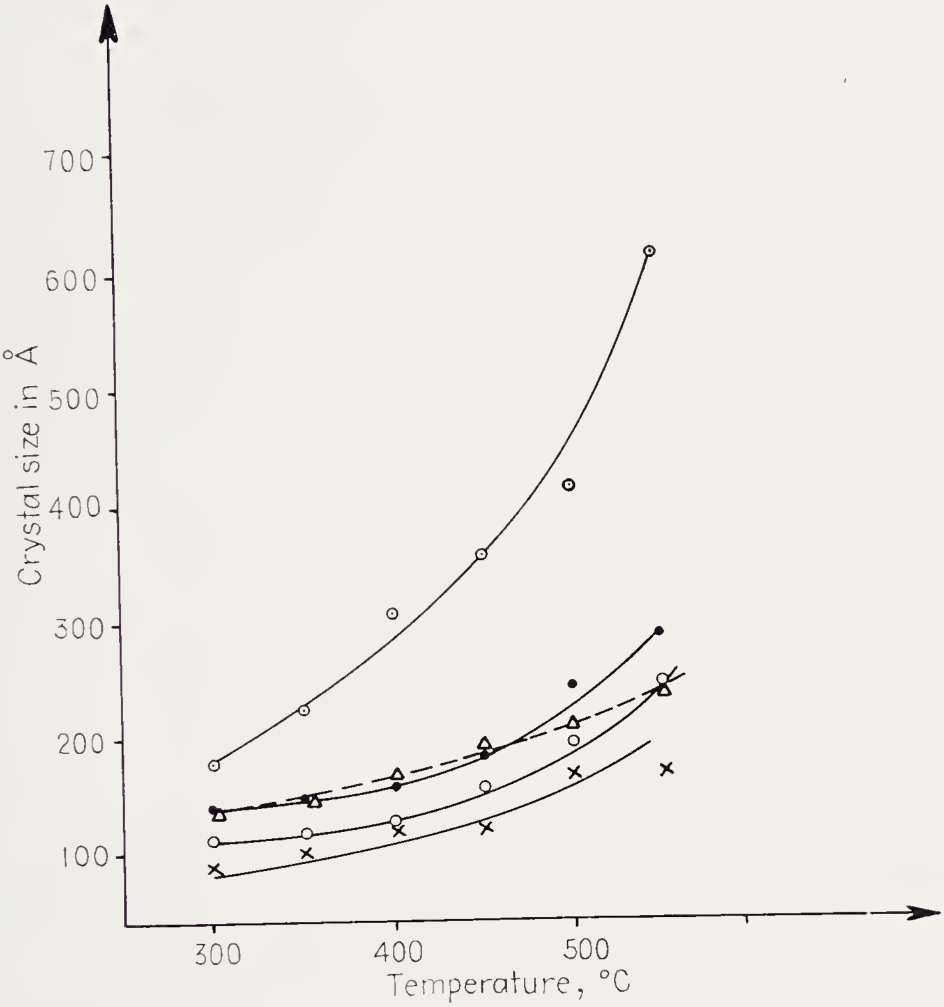

Figure 10. Growth of ZnO crystals in various catalyst preparations: ×, Smithsonite; ○, hydrozincite; △, basic zinc and chromium carbonates (Zn:Cr = 5:1); ●, basic zinc and chromium carbonates (Zn:Cr = 10:1); and ⊙, basic zinc carbonate[49].

Other Promoters of ZnO

In spite of the abundance of patents which claim the use of many promoters of ZnO besides Cr_2O_3, the available experimental data are extremely scarce. Aluminum oxide has an action, which is somewhat similar to that of Cr_2O_3. Al_2O_3 may combine with ZnO to give a spinel, $ZnO \cdot Al_2O_3$[18], which may be also obtained by calcination of the coprecipitated basic carbonates. However, Al_2O_3 seems to be far less efficient as a promoter than Cr_2O_3.

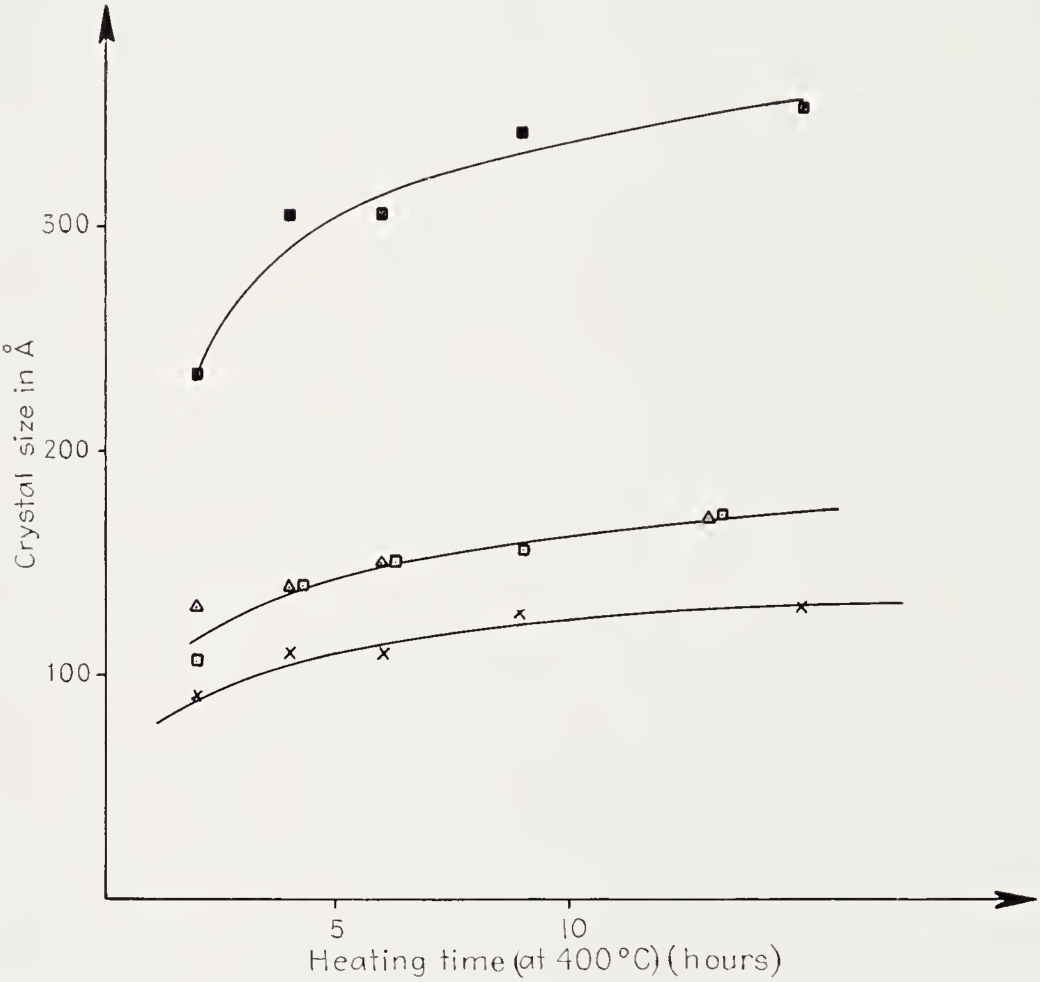

Figure 11. Growth of ZnO crystals as a function of heating time at 400°C: ×, Smithsonite; △, basic zinc and chromium carbonates (Zn:Cr = 5:1); ⊡, basic zinc and chromium carbonates (Zn:Cr = 10:1); and ■, basic zinc carbonate[49].

It has also been observed that Al_2O_3 favors the dehydration reaction of CH_3OH to give $(CH_3)_2O$; therefore $ZnO\text{-}Al_2O_3$ catalysts have had no practical interest.

Weltistowa and co-workers[75] claimed that ThO_2, when added in amounts of the order of 1 per cent to $Al_2O_3\text{-}Cr_2O_3$ catalysts, causes a yield increase of 50 per cent, provided pure gases are used; with technical gases, the authors reported no apparent improvement of yield. The results of Weltistowa were corroborated by Dolgov and Karpinskii[9], who used successfully small quantities of ThO_2, ZrO_2 and TaO_2 as promoters of a ZnO-Cr_2O_3 catalyst. According to Veltistova[75], vanadium oxide (V_2O_5) acts as an activating agent, by increasing considerably the yield of methyl alcohol when used in concentrations of the order of 1 per cent. Several other nonreducible oxides have been proposed, but comparative data concerning their behavior as promoters are missing.

Copper-containing Catalysts

While in the old scientific literature certain catalysts containing ZnO, CuO, Cr_2O_3 are considered very active for the synthesis of methyl alcohol, these catalysts have had only slight practical interest owing to their poor resistance to aging, and to their high sensitivity to poisons. These copper-containing catalysts were not considered in the discussion concerning ZnO-Cr_2O_3 catalysts, because copper oxide behaves in a manner which is different from that of Cr_2O_3, which acts mainly by hindering the recrystallization of ZnO, and which does not bring about any variation of the activation heats of the catalysts. The catalysts composed of CuO and ZnO have activation energies lower than those of the corresponding ZnO catalysts, even in the presence of chromium oxide. The catalysts containing ZnO and CuO are examples of mutual promoting action (Wechselverstärker). Kostelitz and Hüttig[34] have observed that in the decomposition reaction of methanol all the mixed catalysts CuO-ZnO exhibit activities higher than those of each of the two oxides, separately. Also certain mixed catalysts containing CuO, but without ZnO (for example, Cr_2O_3-CuO catalysts) have a good activity for the synthesis of methanol; their activity increases considerably when ZnO is present.

Pure cupric oxide is practically inactive for the synthesis of methyl alcohol, but small amounts of promoters are sufficient for raising its activity to relatively high values. Tagashi Eguchi[10] has activated CuO by the addition of traces of alkali. (See p. 357.) This investigator obtained conversions of the order of 20 to 30 per cent operating at 230° and 80 to 100 atmospheres, with an inlet space velocity of 10,000. Methanol production was in the range 1.3 to 2.8 pounds per hour per liter of catalyst. With different CuO-base catalysts the same author has obtained conversions as high as 70 per cent. Patart[56] had shown in a previous work that very good conversions in the synthesis (or in the decomposition) of methanol were obtained using a CuO catalyst containing 10 per cent ZnO. While the experiments of Fleury[12] confirmed Patart's conclusions on the behavior of the mixed copper-zinc catalysts, Folich and co-workers[15, 16, 17] found that the most efficient catalysts contain 30–40 per cent CuO. Nussbaum and Frolich[53] worked with a catalyst of the composition 58.3 per cent ZnO, 41.7 per cent

CuO. The catalytic activity in the decomposition of methanol seems to vary directly with temperature of reduction up to a certain temperature limit, after which it drops rapidly. The concentration of carbon monoxide in the decomposition products follows exactly the catalytic activity, while the concentration of formaldehyde in the same decomposition products varies inversely with the activity of the catalyst. The catalyst's activity decreases when the reduction time is prolonged.

Cupric oxide is progressively reduced to Cu, and in the meantime a small amount of ZnO is also reduced to metallic zinc, which forms a solid solution with Cu. X-ray analysis gave for the side of the elementary cell the value of 3.624 Å (correspondent to a brass containing 13 per cent Zn). Zolotov and Shapiro[76] noticed that complete reduction of CuO and partial reduction of ZnO occurred only at temperatures higher than 220°C.

Ternary Catalysts $Cu\text{-}ZnO\text{-}Cr_2O_3$. According to Fenske and Frolich[11] the catalyst $Cu_{49}Zn_{43}Cr_8$ is more active than all the binary catalysts $ZnO\text{-}Cr_2O_3$ or ZnO-CuO. At 220°C, this catalyst decomposes methyl alcohol to the extent of 90 per cent. In the synthesis, at 322°C and 200 atm., equilibrium is easily reached even with much higher space velocities. The catalysts $ZnO\text{-}CuO\text{-}Al_2O_3$ have a lower activity and are not as resistant as $ZnO\text{-}CuO\text{-}Cr_2O_3$ catalysts.

Frolich and Lewis[13] have worked with a catalyst of the composition:

$$(ZnO)_{36}(CuO)_{44}(Al_2O_3)_{20},$$

precipitated from a mixture of the acetates with ammonia, using a copper support. This catalyst, at 300 to 350°C and 204 atm. gives pure methyl alcohol, with negligible side reactions. It should be noticed that Al_2O_3, which does not act as a good promoter of ZnO, has a very good promoting effect upon copper. One should be careful, with Al_2O_3-containing catalysts, not to work at too high temperatures, because of the dehydrating action of Al_2O_3 on methanol.

According to Ivanov[30, 31] and to Plotnikov[57-59] the activity of copper oxide-base catalysts is affected only to a limited extent by the addition of ZnO, while it increases considerably upon addition of Cr_2O_3. The best catalysts used in experiments by these authors have the composition

$$Cu_{82}(ZnO)_{16}(Cr_2O_3)_2 \quad \text{and} \quad Cu_{60}(ZnO)_{35.6}(Cr_2O_3)_{4.4}$$

Similarly, Dolgov[8] gives the following compositions for the best of his catalysts:

$$Cu_{49}Zn_{43}Cr_8 \quad \text{and} \quad Cu_{50}Zn_{40}Bi_{10}$$

This investigator had obtained with the above catalysts yields of 86 to 87 per cent and 75 per cent at 360 to 400°C and 100 to 150 atm.

Ivanov[30, 31] prepared his catalysts by precipitation, and reduction of the dry precipitates in an atmosphere of hydrogen at 200 to 220°C. X-ray examination indicates that the primary function of Cr_2O_3 is to prevent the reduction of a small portion of the CuO; the existing active centers are thus attributed to Cu-CuO interfaces. During the catalyst's performance Zn and Cu form the α phase of brass, with an increase of the lattice constant of Cu, and with a consequent decrease in the catalytic activity.

Pospekhov[61] has observed a high initial activity, even at temperatures as low as 190 to 230°C and at pressures of the order of 100 atm., in a catalyst of the composition: $Cu_{60}(ZnO)_{35.6}(Cr_2O_3)_{4.4}$. This catalyst is reduced at a space velocity of 80,000 and at an initial temperature of about 200°C; it becomes very active, giving rise to a complex mixture of CH_3OH, water, and oxygenated compounds. The activity of this catalyst decreases with time, and at low space velocities (13,000 to 20,000) there is formation of CO_2 and CH_4. It is practically impossible to relate all the data of the technical literature on this matter, because of the wide differences in the operating conditions of the various investigators. The temperature data in particular are not very reliable, because of the carelessness in avoiding local overheating due to the reaction heat.

Natta and his co-workers[51] have recently studied the behavior of several catalysts containing Cu-Cr_2O_3 and Cu-ZnO-Cr_2O_3, obtained by the thermal decomposition of the acetates. Their apparatus was especially designed to give over the entire length of the catalyst a temperature that was constant to 1°C; therefore, it was not too difficult to obtain good comparable results. The catalysts examined by these investigators showed a good initial activity, which then decreased with time. For example, the catalyst Zn:Cu:Cr = 6:3:1 showed at 320°C a very high activity; after 72 hours of performance its activity was reduced by 40 per cent. A copper chromite catalyst, obtained by the thermal decomposition of copper and ammonium chromate (precipitated from a copper nitrate solution) has an activity which is lower than that of other catalysts containing ZnO and Cr_2O_3. The high resistance to the aging of this catalyst has to be attributed to the high concentration of Cr_2O_3. In Figure 12 the aging curves of three different catalysts listed by Natta and co-workers are shown.

Under X-ray examination, the reduced catalyst shows the lines of copper, and their intensity increases with time. With such low working temperatures the authors did not notice the formation of brass which had been noticed by other investigators[17], who probably have worked at higher local temperatures. The average crystal size of the copper crystals is 400 to 500 Å after about 100 hours of performance. The average size of the crystals of ZnO increases also, from 300 Å to about 350 Å.

If the catalysts are submitted to "aging" by prolonged heating at 330°C in an atmosphere of CO and H_2, they are sufficiently stabilized to make kinetic measurements possible at temperatures lower than 330°C.

In Figures 13 and 14 the results of such kinetic determinations are given for the copper chromite catalyst and for the catalyst Cu:Cr:Zn = 1:1:8. Such catalysts showed the following values for the apparent activation energy: Copper chromite, activation energy at 292 to 326°C of 14 kcal per mol; Copper-chromium-zinc catalyst (1:1:8) activation energy at 307 to 325°C) of 17 kcal per mol.

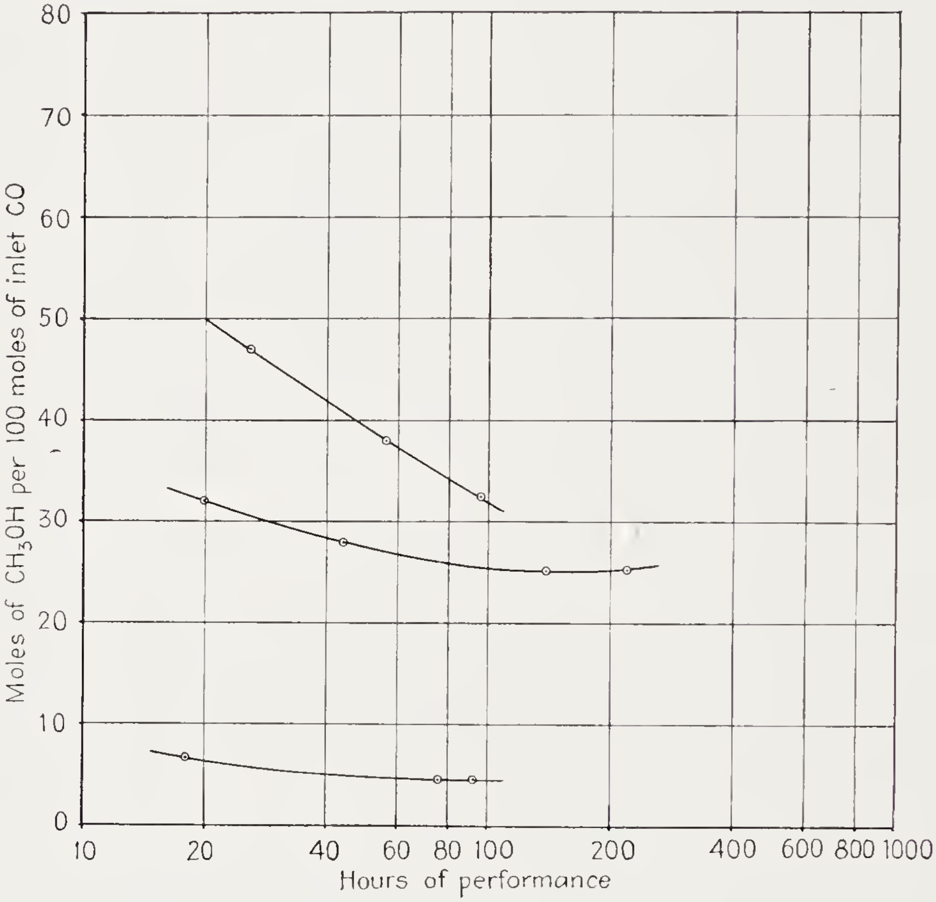

Figure 12. Aging runs on Zn–Cu–Cr methanol synthesis catalysts. Time of contact 0.1 sec for each run. Top curve is for a catalyst of the composition Zn:Cu:Cr = 6:3:1 and an operating temperature of 321°C; middle curve, Zn:Cu:Cr = 8:1:1 and temperature, 325°C; bottom curve, copper chromite and temperature, 292.5°C.

From the reaction isotherms of Figure 15, obtained with the catalyst Zn:Cu:Cr = 6:3:1, which had previously worked for 70 hours at higher temperatures (320 to 350°C), a value of 18 kcal per mol has been calculated for the activation energy in the temperature range 276 to 321°C.

From a practical point of view, the use of copper-containing catalysts which show high activities at temperatures lower than 300°C (at which the ZnO-Cr_2O_3 catalysts do not give any appreciable activity), is advisable only when any overheating (due to the reaction heat) which would rapidly reduce the activity of the catalyst, is avoided.

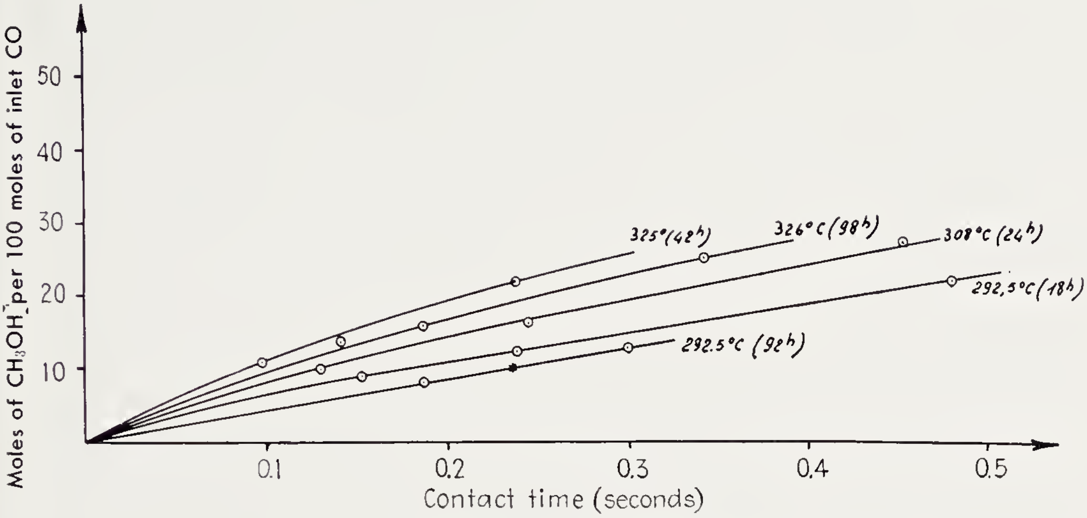

Figure 13. Moles of methanol produced per 100 moles of inlet CO, as function of contact time at different temperatures, with a copper chromite catalyst. Pressure: 250 atm. Inlet gas: CO:H_2 = 1:10. See legend of Figure 4 for definition of time of contact.

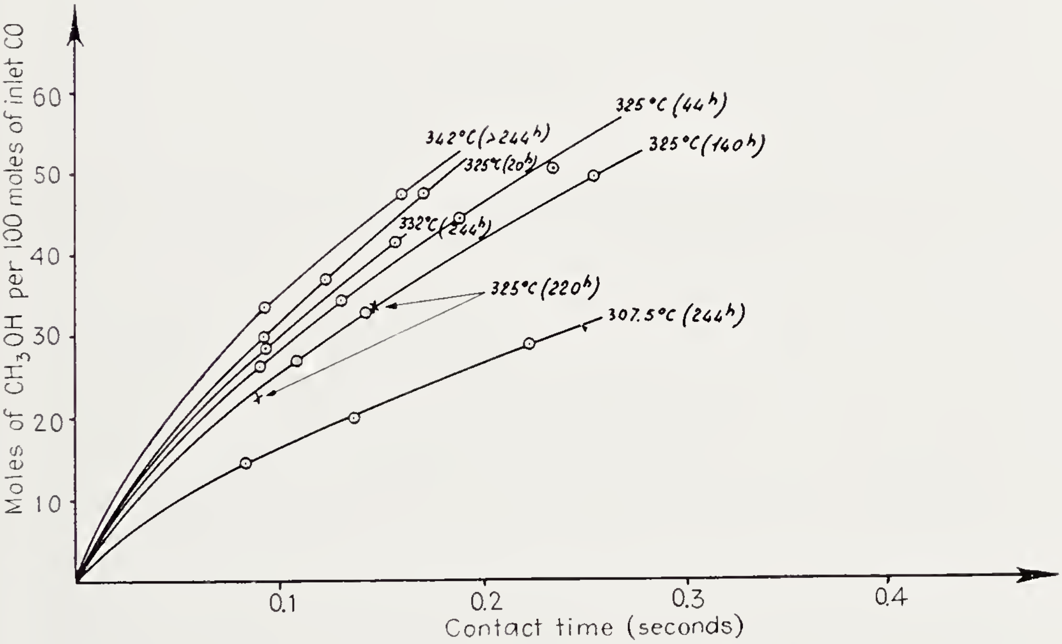

Figure 14. Moles of methanol produced per 100 moles of inlet CO as a function of contact time at different temperatures with a catalyst ZnO:CuO:Cr_2O_3 = 8:1:1. Pressure = 250 atm. Inlet Gas: CO:H_2 = 1:10. See Legend of Figure 4 for definition of time of contact.

ANTISELECTIVITY AGENTS AND POISONS

Antiselectivity Agents

The synthesis of methanol is greatly influenced by the presence of certain substances, even at low concentrations. For example, the presence of metallic iron or nickel in the catalyst leads to the formation of methane while the presence of strongly alkaline substances inhibits the formation of methane and synthesizes the higher alcohols. For this specific action on the selectivity of the catalysts, it would be erroneous to consider these compounds as real poisons, because a poison is a substance which, when adsorbed at the active surface of a catalyst, inhibits the activity of the catalyst itself. Iron and nickel when present in very low concentrations do not inhibit the activity of zinc oxide, but behave rather as independent catalysts for a concomitant reaction, the synthesis of methane, which is thermodynamically more favorable and kinetically faster than the synthesis of methyl alcohol. Therefore these metals should be named "antiselectivity agents," rather than "poisons." Traces of finely divided Fe or Ni in the catalyst are sufficient to cause the formation of a large quantity of methane. The synthesis of CH_4 is strongly exothermal and, when performed in the presence of Ni or Fe, proceeds very rapidly; therefore, local temperatures, high enough (600 to 700°C) to prevent the formation of methanol are

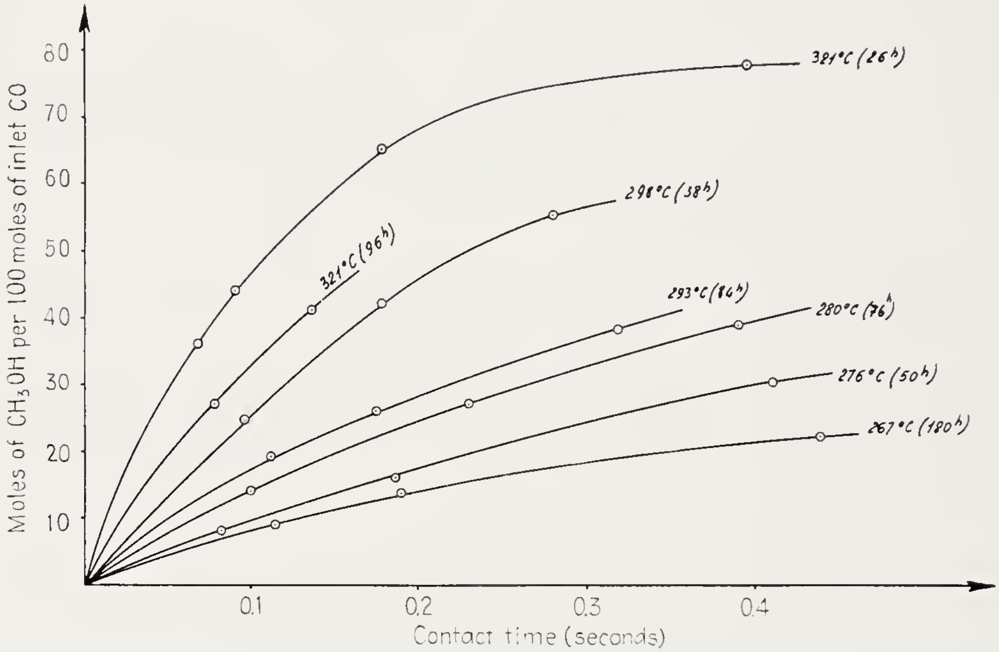

Figure 15. Moles of CH_3OH produced per 100 moles of inlet CO as a function of contact time at different temperatures. Pressure 250 atm. Inlet Gas: $CO:H_2 = 1:10$. The experiments were performed with a catalyst $ZnO:CuO:Cr_2O_3 = 6:3:1$. Time of contact is as defined in Figure 4.

easily reached. A considerable diminution of the yield of methyl alcohol is due also to the lowering of the partial vapor pressure of CO and H_2, caused by the formation of CH_4, H_2O, and CO_2. The formation of water causes the lower concentration of the methanol obtained. When the reaction is performed with gases rich in CO and poor in H_2 (for example, with water gas) a small part of the carbon monoxide is disproportioned to give elemental carbon and carbon dioxide.

The rate of the synthesis of methane is very high only at temperatures higher than 400°C; therefore when the reaction is carried out at lower temperatures (350 to 370°C) small amounts of iron in the catalyst may be allowed, particularly when iron is present as ferrous oxide (which may be dissolved in ZnO) or as ferric oxide (combined with ZnO as spinel $ZnO—Fe_2O_3$).

The most active forms of metallic iron or nickel in the catalysis of the synthesis of methane are those obtained by the thermal decomposition of iron or nickel carbonyls,[62] $Fe(CO)_5$, $Ni(CO)_4$, etc., which may be accidentally present in the reacting gases. For this reason the early patents of the Badische Anilin und Soda Fabrik claim that for the synthesis of methyl alcohol gases should be used free from carbonyl iron, and catalysts free from metals belonging to the iron group. In order to avoid the formation of iron or nickel carbonyls no iron or nickel-base apparatus which might react with CO is being used for the synthesis of methanol.

Natta[40] showed that when FeO is present in relatively high amounts, as solid solution in ZnO, it behaves as a promoter for the synthesis of methanol, without causing the formation of appreciable amounts of methane, which would take place if iron were present as free iron oxide or in the metallic state. Such solid solutions are greenish and ferrous iron is not reduced to the metallic state, if the working temperatures are not too high.

Natta observed that catalysts containing traces of iron (which may be present as impurity in the mineral smithsonite) transfer it to the circulating gases (as carbonyl iron) during the synthesis, provided these gases are initially free of carbonyl iron. After a period of performance at temperatures lower than 400°C, the iron originally present in the catalysts is almost entirely gone, so that eventually the produced methanol has a higher degree of purity and it contains less water than the methyl alcohol produced with fresh catalyst.

The reaction of formation of carbonyl iron is an equilibrium process:

$$Fe + 5CO \rightleftarrows Fe(CO)_5$$

Therefore the percentages of iron which may be present in the gases without damaging the synthesis of methanol depend on the partial pressure of CO, on total pressure, and (even more strongly) on temperature.

The data of Table 9 were calculated[46] with the assumption that the activity is equal to the partial pressure of each reacting gas; this assumption, however, does not hold for iron carbonyl, the critical temperature of which is relatively high; therefore, the above data should be considered as approximate, and probably lower than the real ones.

A catalyst, whose selectivity has been reduced as a consequence of the deposition at its surface of iron (or nickel) carbonyl coming from the reacting gases, may recover its original selectivity, provided it is used at lower temperatures with gases free from $Fe(CO)_5$ or $Ni(CO)_4$.

Some strongly alkaline substances (NaOH, Na_2CO_3, $Ca(OH)_2$, etc.), behave as antiselectivity agents, provoking the formation of higher alcohols. These substances are often present in methanol catalysts prepared by precipitation from zinc salts, and not previously washed carefully. When these compounds are present in the catalyst there is a decrease of activity with time, because of the formation of high molecular weight organic compounds which remain adsorbed in the catalysts.

Table 9. Equilibrium of the Reaction $Fe + 5CO = Fe(CO)_5$

Temp. (°C)	$\log Kp = \log \frac{(CO)^5}{Fe(CO)_5}$	Equilibrium Concentration of $Fe(CO)_5$ (g $Fe(CO)_5$ per Cubic Meter of Total gas at a CO Pressure of 100 Atm.)*
250	10.67	18.7
300	12.37	3.7
350	13.81	.01
400	15.12	.007

* These figures are the grams of $Fe(CO)_5$ per cubic meter of gas at 0°C and one atmosphere pressure.

Alkalies act also as inhibitors of the synthesis of methane when iron group metals are present.

Poisons

The catalysts composed of ZnO together with difficultly reducible oxides (Cr_2O_3, MgO, Al_2O_3, etc.) as promoters are not very sensitive to the common poisons of hydrogenation catalysts (H_2S, PH_3 etc.). For this reason, and for their good resistance toward aging, zinc-base catalysts are generally preferred to the copper-base catalysts, though the latter may show higher initial activities. The copper-base catalysts are rapidly and completely poisoned by sulfur compounds. Not only H_2S, but also COS and CS_2 behave as poisons for copper-base catalysts, even when their concentration in the gas is of the order of a few milligrams per cubic meter.

The different behavior of ZnO and CuO is due to the different values of the equilibrium constants for the reactions:

$$\text{(a)}\ ZnO + H_2S \rightleftarrows ZnS + H_2O$$

$$\text{(b)}\ Cu + H_2S \rightleftarrows CuS + H_2$$

While reaction (a) is reversible at temperatures of the order of 300 to 400°C, reaction (b) is shifted completely to the right. The reversibility of reaction (a) was shown in the case of a zinc-chromium catalyst containing 4.8 per cent of sulfur combined as sulfide. Sulfur had totally disappeared from the surface of the catalyst after 18 hours of performance[75].

The small amounts of water which are always present in the synthesis gases* are sufficient to regenerate zinc oxide from ZnS, or, in other words, to prevent the formation of zinc sulfide. Catalysts containing ZnS have been proposed by some authors[4, 7, 36]. It should be pointed out that sulfur originally present in the catalysts may be elminated also combined in organic compounds as, for example, according to one of the following equilibria which lead to methyl mercaptan:

$$ZnS + CH_3OH \rightleftarrows ZnO + CH_3SH$$

$$H_2S + CH_3OH \rightleftarrows CH_3SH + H_2O$$

It is therefore advisable to work with gases and catalysts free from sulfur if methyl alcohol without a bad odor is desired.

If the catalysts are obtained by precipitation from solutions of the sulfates, they may contain basic sulfates; these slowly eliminate their sulfur as H_2S or CH_3SH.

The presence of NO in the gases has to be avoided because it may cause the formation of amines. On the other hand the use of nitrogen-containing gases does not lead to the formation of ammonia; this agrees with the fact that CO acts as a poison for catalysts for the synthesis of ammonia from N_2 and H_2.

Copper-base catalysts are poisoned by compounds containing chlorine or sulfur. Therefore, good copper-base catalysts may not be obtained by precipitation from solutions of copper sulfate or chloride, whereas they are easily made by precipitation from solutions of copper acetate or nitrate.

According to Tagashi Eguchi[10] acetylene and (to a smaller extent) ethylene behave as poisons for the methanol synthesis. However, olefines are always present during the synthesis of higher alcohols with alkaline catalysts, and their addition to the synthesis gases causes an increase in the production of higher alcohols. Therefore, it is unlikely that small quantities of olefins act as poisons for the ZnO-base catalysts.

Occasionally small amounts of lubricating oils are carried by the reacting

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* Water is also formed in the reaction $2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$.

gases, and then are strongly adsorbed by the catalysts. These substances are not real poisons, but they have, naturally, a tendency to lower the activity of the catalysts. Similarly, the easily reducible oxides (PbO, SnO) whose corresponding metals have low melting points act as depressants. Cadmium, which may be formed by the reduction of CdO contained in ZnO as a solid solute, does not behave as a poison, because of its high vapor pressure; it is slowly carried away by the circulating hot gases. In other cases the catalytic activity of ZnO may be reduced by some low-melting compounds that facilitate the recrystallization of ZnO.

Rate of Reaction

The first attempts at a thorough kinetic study of the synthesis of methanol gave results which can be considered only as approximate, and valuable only within narrow intervals of composition and pressure. It is the opinion of the author that the oldest kinetic data for the synthesis of methanol should not be considered valid as a basis for a rigorous kinetic interpretation of this reaction, owing to the experimental difficulty of maintaining the entire mass of the catalyst at a strictly constant temperature. In order to avoid secondary reactions, one must use very short contact times. This can be done only by operating the reaction continuously. The constancy of temperature indicated in the reports of the old experiments should be interpreted as referring to only a small part of the bulk of the catalyst. The rate of the reaction is very high when active catalysts are used. Therefore in a typical continuous operation of synthesis of methyl alcohol performed at 250 atm. and 380 to 400°C, methanol is actually produced in amounts corresponding to 80 to 110 pounds per hour per cubic foot of catalyst, with a corresponding reaction heat as high as 25,000 to 45,000 kcal per hour. The synthesis, even if performed with high space velocities, may cause an adiabatic temperature rise of the order of 100°C in the reacting gases.

The experimental data which may be obtained by systematic experiments performed in large industrial apparatus should not be used for kinetic interpretations because of the considerable temperature rise along the reactor despite the efficient systems employed for cooling the catalyst. As far as laboratory-scale experiments are concerned, the data of the different authors are not mutually comparable because of the wide differences in the reaction apparatus, and of the uncertainty in the value of the temperature rise through the catalyst. The systematic experiments performed by Molstad and Dodge[38] with stoichiometric mixtures of CO and H_2, and with a specially designed apparatus, had pointed out the existence of a considerable rise in the temperature of the catalyst (about 25°C), with conditions under which the adiabatic temperature rise due to the reaction then taking place would have been about 125°C.

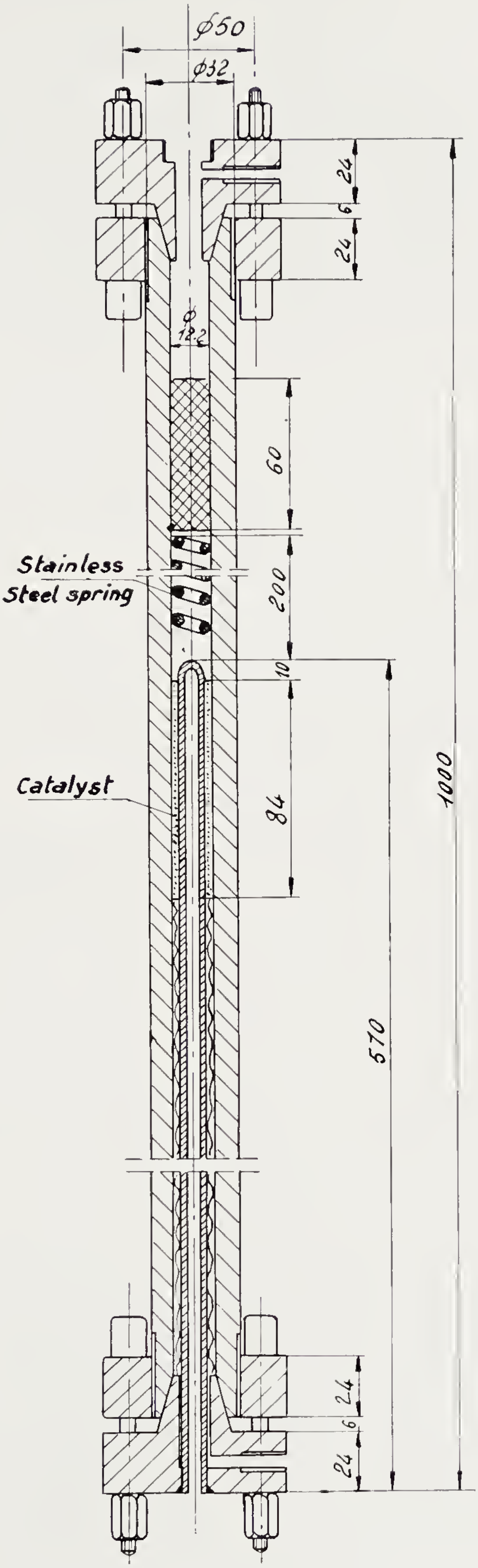

Figure 16. Reactor belonging to the laboratory apparatus used by Natta and his co-workers for the kinetic measurements on the synthesis of methanol.

Only very recently, Natta and his co-workers[50, 51] have performed systematic experiments with a laboratory apparatus particularly designed for kinetic measurements. These investigators used a reaction in which the catalytic space had an annular shape (see Figure 16). The relatively great thickness of the well of the reactor, and the close contact between the catalyst and the reactor's well, have made possible the performance of kinetic experiments in which the temperature measured along the catalyst maintained a constant value (within ±1°C) for over 90 per cent of the length of the catalyst. The temperature of the catalyst could also be kept constant (within ±1°C) for the entire time of each experiment. The apparatus used by these investigators is shown in Figure 17. The experiments were performed with a catalyst whose composition is ZnO, 89 per cent; Cr_2O_3, 11 per cent; and with another catalyst of the composion ZnO, 60.9 per cent; Cu, 29.8 per cent; Cr_2O_3, 9.3 per cent. The first of these has shown a very high resistance toward aging; the stability of the second was obtained, as it was already pointed out, by a prolonged (350 hours) treatment at 335°C in the presence of CO and H_2. The very high degree of purity of the methyl alcohol obtained under such conditions showed that

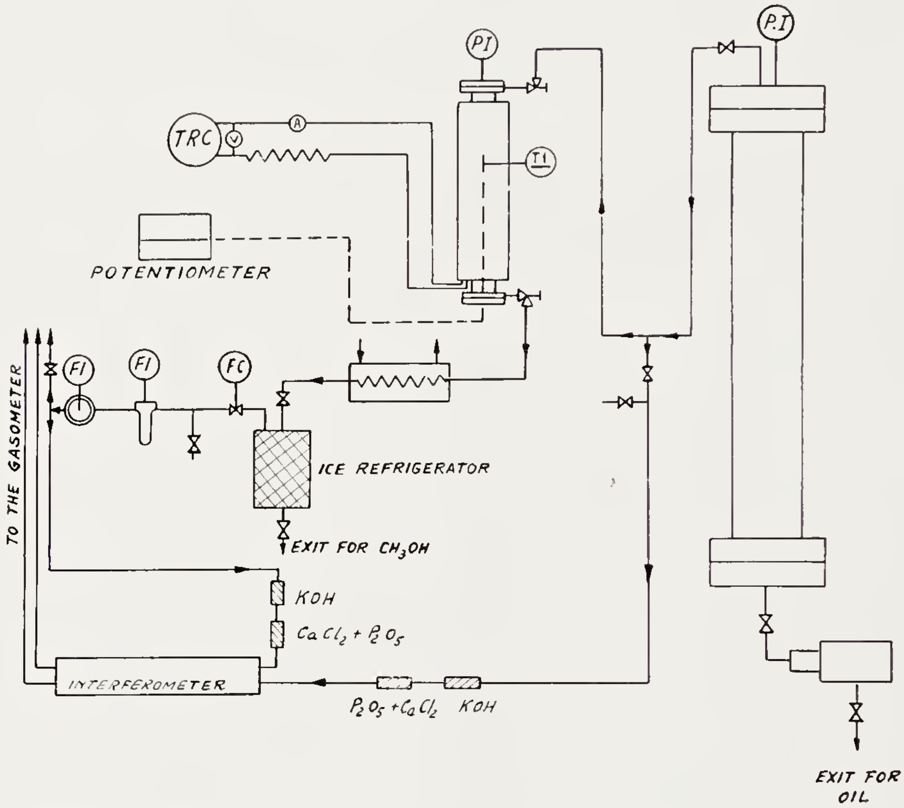

Figure 17. Apparatus used by Natta and his co-workers for the kinetic study of the synthesis of CH_3OH.

secondary reactions were practically eliminated, and that the catalysts were very selective.

Figures 18 and 19 give some of the isotherms obtained with constant pressure experiments. In the plots the moles of CH_3OH per 100 moles of inlet gas (referred to one mole of total input gases) are plotted against a time-depending factor, grams of catalyst per mole of inlet gas per hour. All the isotherms reproduced deal with gaseous mixtures containing an excess of hydrogen over the stoichiometric composition, because with such mixtures it is easier to transfer away by conduction the heat evolved in the reaction, and to calculate the quantity of converted carbon monoxide from the variation of the H_2:CO ratio. From such isotherms it may be concluded that practically complete equilibrium is reached with space velocities lower than 15,000, with gases having $\frac{H_2}{CO} > 10$, at temperatures of at

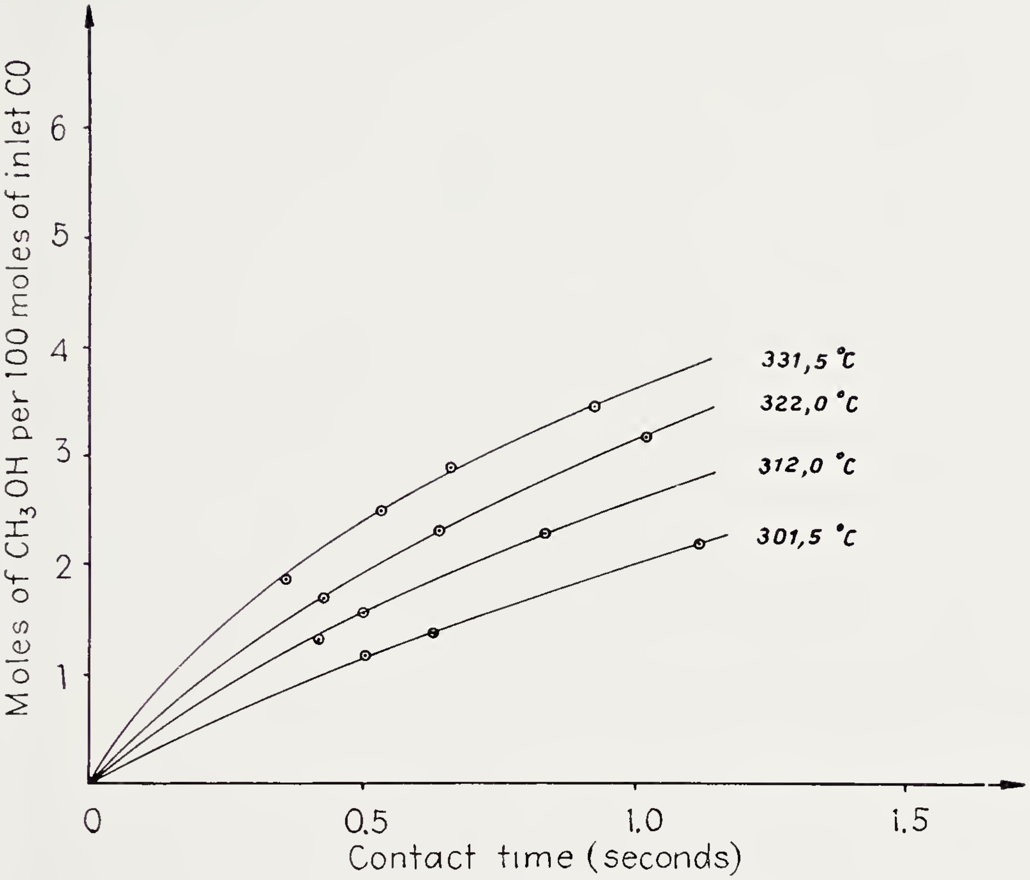

Figure 18. Rate of CH_3OH synthesis at constant temperatures as a function of the time of contact expressed as 3600 times the grams of catalyst per mole of inlet gas per hour. Catalyst composition: ZnO:CuO:Cr_2O_3 = 2:1:1. Inlet Gas: CO:H_2 = 9.3:90.7. Pressure: 200 atm.

least 390°C. From calculations of mass transfer and of thermal conductivity of the gas, it may be concluded that, even in the least favorable experimental conditions considered, the catalyst temperature is higher than the gas temperature by approximately 1°C, and that the gas temperature is about 1°C above the temperature of the external wall of the reaction vessel. The temperature values indicated in the plots of Figures 18 and 19 refer to the thermocouple located in the well inside the reactor; therefore, they may be considered equal to the temperatures of the gas.

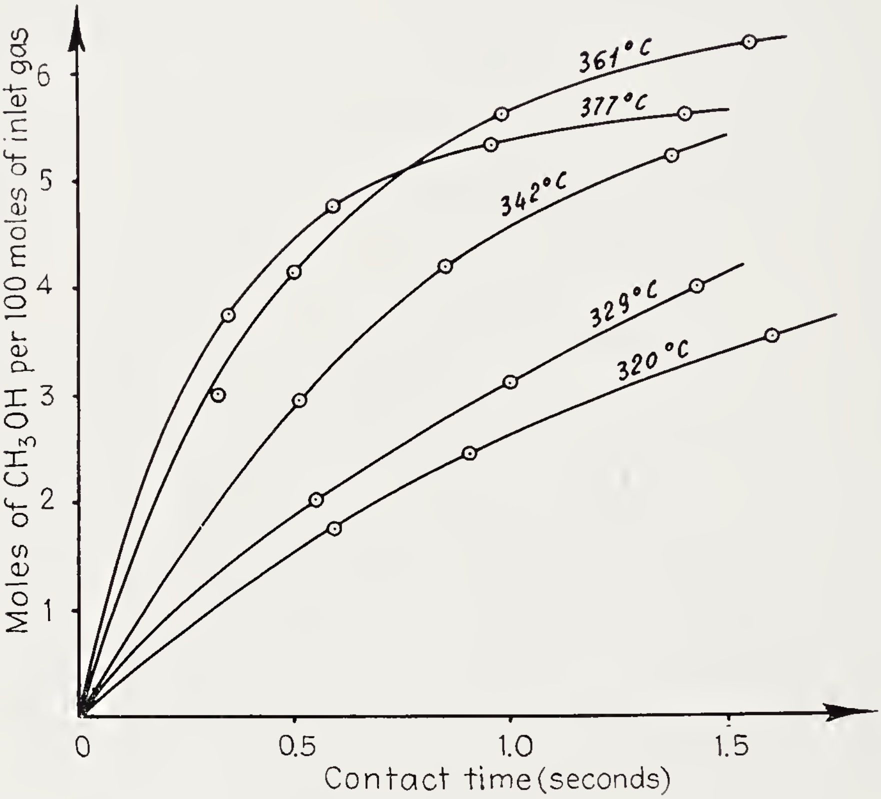

Figure 19. Rate of CH_3OH synthesis as a function of time of contact expressed as 3600 times the grams of catalyst per mole of inlet gas per hour. $CO:H_2$ = 9.1:90.9. Prsesure: 300 atm[32].

Interpretation of Kinetic Data

Older Experiments. The first attempts[43] to interpret the quantity of methanol produced as a function of temperature and contact time, with the assumption that the rate of reaction varied directly with the partial pressure of the reacting gases, led to results which were valuable only in a limited field of application, and with gases of a limited range of composition. In fact, the kinetic study of a catalytic reaction, taken as a homogeneous reaction* leads to valuable conclusions only whenever the concentrations of all the reacting gases in the adsorbed phase are proportional to their respective gas phase activities. The old adsorption measurements had given, for long adsorption periods, molar concentrations of adsorbed CO approximately equal to those of adsorbed H_2 ; this seemed sufficient to justify the kinetic classification of the synthesis of methanol as that of a homogeneous reaction, at least at the beginning of the reaction, when the amounts of CH_3OH formed are not too high.

Natta and Pastonesi[45] found a fair agreement between experimental data, and theoretical rate equations for the yield as a function of space velocity, assuming that the synthesis of methanol was a second-order reaction (i.e., proportional to the first power of CO concentration, and to the first power of H_2 concentration) and that the decomposition of methanol was a first-order reaction (i.e., proportional to the first power of the CH_3OH concentration). These two investigators worked with gaseous mixtures of constant composition ($H_2/CO = 2:1$) and made a few measurements, all at constant pressure but at different temperatures. They used an apparatus which was not strictly isothermal, and in which the temperature was measured in the central part of the catalyst. The authors assumed that the synthesis of methanol was divided into two consecutive reactions: (1) synthesis of formaldehyde (slow); (2) hydrogenation of formaldehyde to methanol (fast). The slower reaction of synthesis of formaldehyde would then be determinant for the apparent order of the over-all reaction. This hypothesis was corroborated by the fact that the formaldehyde concentration in the reacted gases was approximately equal to the equilibrium concentration for the hydrogenation of HCHO to CH_3OH under the conditions of the experiments.

The incorrectness of this kinetic interpretation was not noticed till recently because of the lack of experimental measurements with different $CO:H_2$ ratios. However, the forms of the isothermal rate curves calculated with this hypothesis are not very different from those calculated on the basis of a different kinetic interpretation, provided that mixtures having equal initial values of the $CO:H_2$ ratio are considered.

Recent Studies. When experimental data, conducted with different $CO:H_2$ ratios under the best conditions of temperature constancy, were available, it was possible to undertake a more rigorous kinetic study of the

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* *Editor's note:* Since a catalyst was needed, the reaction of carbon monoxide and hydrogen could never be considered as occurring as a homogeneous reaction in the gas phase. By the words "taken as a homogeneous reaction" the author means that the kinetics were interpreted in terms of the concentrations as partial pressures of the gaseous components and not in terms of the function of the surface covered by the reactants and products.

synthesis of methyl alcohol. The treatment of this reaction, interpreted as a heterogeneous catalytic process, was based on the method described by Hougen and Watson[19]. For this purpose Natta and his co-workers[50] have used the data of isothermal rate curves which were obtained with the apparatus described above. This approach is probably the first thorough study of a heterogeneous catalytic reaction operated at high pressures; therefore, a detailed discussion of the method of treatment follows.

The following parts of the complex process have been considered separately:

(1) Diffusion of the gases from the bulk of the gaseous phases to the gas-catalyst interface.

(2) Chemisorption of each component gas at the active surface of the catalyst.

(3) Reactions among the chemisorbed gases, according to different kinetic hypotheses.

(4) Desorption of the reaction products.

(5) Diffusion of the reaction products from the gas-catalyst interface to the bulk of the gaseous phase.

Assumption was made, that the gaseous phase behaves as an ideal mixture of real gases, in which the following equality is valid:

$$a_i = x_i P \gamma_i$$

where

a_i = activity of the ith component in the gaseous phase.
P = total pressure of the system.
x_i = molar fraction of the ith component.
γ_i = fugacity coefficient of the ith component, calculated for the pressure P and for the temperature of the experiment.

The processes (1) and (5) were so fast with the experimental values of space velocities and reactor shape, that their effect upon the kinetics of the reaction could be neglected. Therefore, with the assumption that the activity of each component at the interface catalyst-gas is equal to that of the component in the flowing gas phase, the adsorption rates of CO(A) and H_2(B) are:

$$r_A = k'_A a_A C_L - k''_A C_A$$

$$r_B = k'_B a_B C_L - k''_B C_B$$

where $r = \frac{dx}{dt}\frac{1}{W}$ is the resulting adsorption rate (the difference between adsorption and desorption rates expressed as the number of moles adsorbed by 1 gram of catalyst in unit time).

k' = adsorption rate constant
k'' = desorption rate constant
a = activity of the considered component at the interface catalyst-gas
C_L = molar concentration of the free active sites referred to the unit mass of the catalyst
C_A , C_B = concentrations of A and B, expressed in moles of A or B adsorbed by the unit mass of catalyst
W = weight of the catalyst in grams.

The following mechanism was assumed for adsorption on the active sites:

$$A + L \rightleftarrows A^*$$

$$B + L \rightleftarrows B^*$$

where L represents an active site. With the assumption that the reaction proceeds in the adsorbed phase, the following distinct schemes were considered:

(1) Bimolecular reaction

$$H_2^* + CO^* \rightleftarrows H_2CO^* + L$$

$$r_{s_1} = \frac{s}{C_{L_0}} k'_{s_1} C_A C_B - \frac{s}{C_{L_0}} k''_{s_1} C_F C_L$$

$$H_2CO^* + H_2^* \leftrightarrows CH_3OH^* + L$$

$$r_{s_2} = \frac{s}{C_{L_0}} k'_{s_2} C_F C_B - \frac{s}{C_{L_0}} k''_{s_2} C_R C_L$$

where s is the number of active sites located next to a given active site, and C_{L_0} is the molar concentration of active sites per unit of mass of the catalyst, and C_F and C_R the molar concentrations of formaldehyde and methanol, respectively, adsorbed by unit mass of catalyst.

(2) Trimolecular reaction

$$CO^* + 2H_2^* \rightleftarrows CH_3OH^* + 2L$$

$$r_s = \frac{s^2}{2C_{L_0}^2} k'_s C_A C_B^2 - \frac{s^2}{2C_{L_0}^2} k''_s C_R C_L^2$$

where k'_s and k''_s are the rate constants for the direct and reverse reactions in the adsorbed phase.

For the desorption of methyl alcohol (R) the following mechanism, similar to the last one, was chosen:

$$R^* \rightleftarrows R + L$$

$$r_R = k_R C_R - k'_R a_R C_L$$

From the experimental work of Natta and his co-workers[50] it has been concluded that the processes of adsorption and desorption proceed at much higher rates than the reaction at the surface, and that the process which determines the rate of the reaction is that of reaction among the adsorbed molecules. On that basis, it was possible to admit the existance of equilibrium between the activity of each component in the gas phase and its concentration in the adsorbed phase. It follows then:

$$C_A = K_A a_A C_L$$

$$C_B = K_B a_B C_L$$

$$C_R = K_R a_R C_L$$

where the constants K_A, K_B, K_R are the equilibrium constants for the adsorption of the components A, B, R.

The concentration of free active sites is given by the difference between the molar concentration of all the sites C_{L_0}, and that of the filled sites:

$$C_L = C_{L_0} - (C_A + C_B + C_R + C_I)$$

where C_I represents the concentration of the sites filled with other components which may be present (for example, inert substances). Operating in the absence of inert gases, it follows that

$$C_L = \frac{C_{L_0}}{1 + K_A a_A + K_B a_B + K_R a_R}$$

Substitution of the above value of C_L in the expressions which give the rate of reaction in the adsorbed phase, leads to expressions which give the reaction rate as a function of the rate constants of the direct and inverse reactions, of the constants of adsorption, and of the concentrations of active sites C_{L_0}.

These constants may be calculated on the basis of the kinetic data, whenever a sufficient number of accurate experimental data are available.

It has been shown[50, 51] that the kinetic equations, based on the hypothesis that the surface reaction is bimolecular, do not fit the isothermal rate curves.

Only with the hypothesis of a trimolecular reaction was it possible to solve this problem. The rate of a surface reaction for a trimolecular reaction results:

$$r = \frac{s^2 k_s' C_{L_0} K_A a_A K_B^2 a_B^2 - s^2 k_s'' C_{L_0} K_R a_R}{2(1 + K_A a_A + K_B a_B + K_R a_R)^3}.$$

Considering that the ratio $\frac{k_s'}{k_s''}$ is equal to K^*, i.e., to the equilibrium constant of the reaction in the adsorbed phase, and that the thermodynamical equilibrium constant K_{eq} is related to the constants of equilibrium for the surface reaction by the relationship

$$\frac{K^*K_AK_B^2}{K_R} = K_{eq}$$

the following equation is easily obtained:

$$r = \frac{a_Aa_B^2 - a_R/K_{eq}}{(A + Ba_A + Ca_B + Da_R)^3}$$

The four constants A, B, C, D represented in this equation are all positive and all of them are functions of the temperature only, if the assumption is made that the number of active sites C_{L_0} is independent of temperature. Substitution of the activities with the products of partial pressures and fugacity coefficients:

$$a_A = \gamma_Ap_A\,; \qquad a_B = \gamma_Bp_B \cdots$$

gives:

$$r = \frac{\gamma_{CO}p_{CO}\gamma_{H_2}^2p_{H_2}^2 - \dfrac{\gamma_{CH_3OH}p_{CH_3OH}}{K_{eq}}}{(A + B\gamma_{CO}p_{CO} + C\gamma_{H_2}p_{H_2} + D\gamma_{CH_3OH}p_{CH_3OH})^3} \tag{1}$$

Equation (1) interprets the surface reaction according to the following scheme:

$$CO^* + 2H_2^* \rightleftharpoons CH_3OH^* + 2L$$

For a very short contact time, starting with methanol-free gases, the concentration of methyl alcohol is nearly zero, and therefore Eq. (1) is thus simplified:

$$A + B\gamma_{CO}p_{CO} + C\gamma_{H_2}p_{H_2} = \sqrt[3]{\frac{\gamma_{CO}p_{CO}\gamma_{H_2}^2p_{H_2}^2}{r_0}} \tag{2}$$

In Eq. (2) r_0 is the initial reaction rate, or, in other words, the tangent of the reaction isotherm at the origin.

Equation (2) contains three unknowns, whose correspondent constants may be determined by measuring the initial rates of reaction in three experiments performed at the same temperature, but at different pressures and composition. This was done at several different temperatures, and the values of A, B, C were determined as functions of temperature. To establish the values of the constant D, the values of A, B, C, as previously determined, were substituted in Eq. (1) which was solved by introducing the experimental r values resulting from different values of time factor and with the experimental values of the partial pressures of CO, H_2, CH_3OH. Figures 20 and 21 give the values of A, B, C, D at several different temperatures for the catalysts $ZnO\text{-}Cr_2O_3$ and $Zn_{50}Cu_{25}Cr_{25}$. It results that the ratio $\frac{B}{C} = \frac{K_{CO}}{K_{H_2}}$ varies between 5 (at 330°C) and 8 (at 390°C).

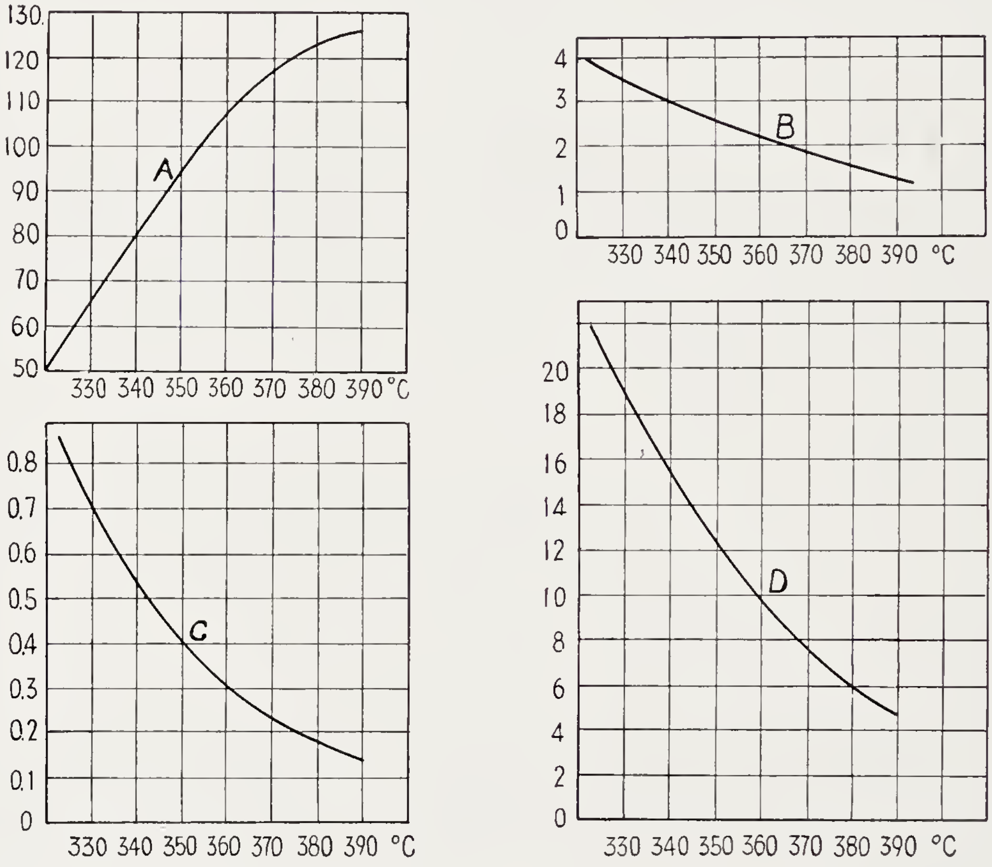

Figure 20. Dependence on temperature of the constants A, B, C, D ($ZnO\text{-}Cr_2O_3$ catalyst) (See Eqs. (1) and (2)).

The ratio $\frac{D}{C} = \frac{K_{CH_3OH}}{K_{H_2}}$ varies between 26 (at 330°C) and 37 (at 390°C). In the Zn-Cu-Cr catalyst the ratio $\frac{B}{C}$ has the constant value of 5 between 300 and 330°C while the ratio $\frac{D}{C}$ varies between 35 (at 330°C) and 29 (at 330°C). Such constants vary continuously with temperature. It is worthwhile to notice that the two above ratios have approximately equal values for the two catalysts. The adsorption heats vary in the sense $CH_3OH >$

CO > H_2. Such values of the ratios of the adsorption constants explain the facts that the reaction rate is higher when $\frac{H_2}{CO} > 2$, and that the produced methanol acts as a depressant of the reaction rate, because of its strong adsorption energy, which reduces the number of active sites available for the adsorption of CO and H_2.

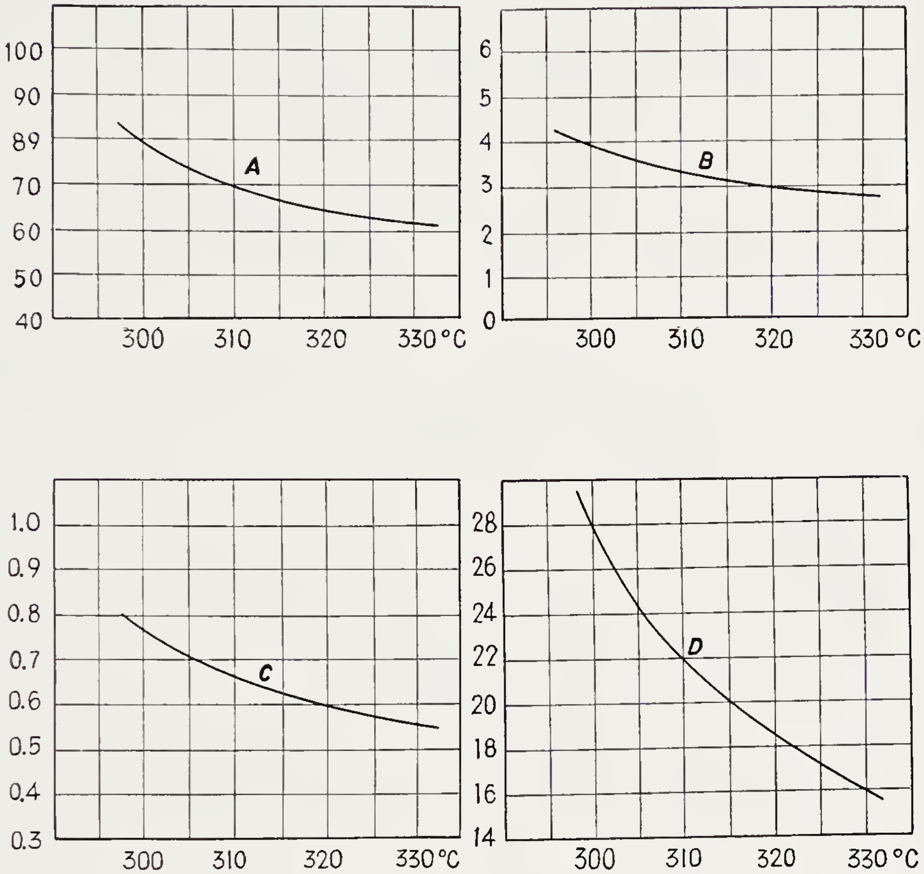

Figure 21. Dependence on temperature of the constants A, B, C, D. Catalyst composition = Zn:Cu:Cr = 2:1:1 (See Eqs. (1) and (2)).

Verification of the Kinetic Equations

Once the values of the constants A, B, C, D in the kinetic equation of the surface reaction (which is assumed to be the rate-controlling reaction) have been established, it is possible to predict the reaction rate for any values of temperature, gas composition, and pressure, within the field of applicability of the kinetic equation considered.

For a verification of such possibility, Natta and his co-workers[50] have integrated the differential equation:

$$r\,dW = F\,dx \tag{3}$$

where F is the input rate (or the moles of gas introduced in the reactor in unit time, W is the weight of the catalyst, x the moles of produced methanol per input gas mole, and r is the rate of the reaction, expressed as moles of methyl alcohol produced in the unit time with the unitary weight of catalyst. Integration of (3) gives:

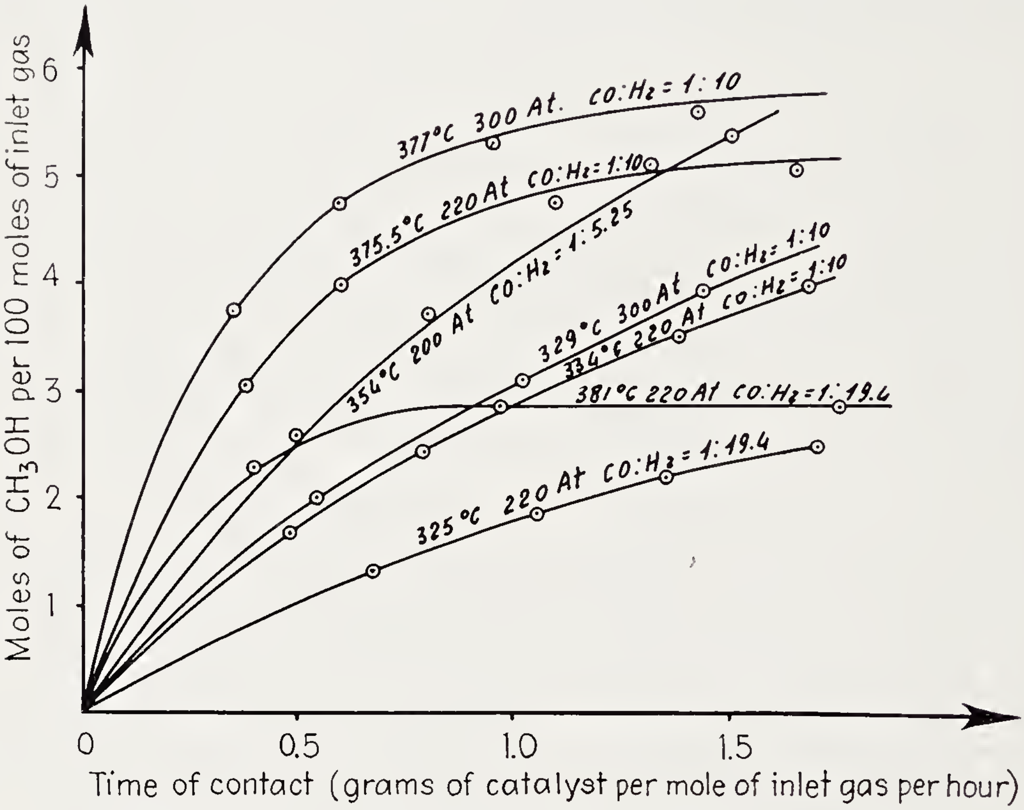

Figure 22. Verification of the kinetic equation proposed by Natta and his coworkers for a ZnO-Cr_2O_3 catalyst. Time of contact (3600 times the grams of catalyst per mole of inlet gas per hour). ⊙ Represents experimental points.

$$\frac{W}{F} = \int_0^x \frac{dx}{r}$$

or:

$$\frac{W}{F} = \int_0^x \frac{(A + B\gamma_{CO}p_{CO} + C\gamma_{H_2}p_{H_2} + D\gamma_{CH_3OH}p_{CH_3OH})^3}{\gamma_{CO}p_{CO}\gamma_{H_2}^2p_{H_2}^2 - \dfrac{\gamma_{CH_3OH}p_{CH_3OH}}{K_{eq}}}\,dx \qquad (4)$$

If one determines on the basis of just a few isotherms the values of A, B, C, D, and then introduces these values into Eq. (4), one can compare the moles of experimentally produced methanol with those calculated from

Eq. (4) for different values of temperature, pressure, and gas composition. Figure 22 shows the theoretical curves and the experimental data for the ZnO-Cr_2O_3 catalyst.

It appears clear that the experimental data agree exactly with the calculated ones, whenever the temperature and the concentration of CH_3OH are sufficiently low (in other words, whenever the production of methanol, and therefore the heat evolved in the reaction, are sufficiently low). Small divergencies of experimental from theoretical data (lower than 3 per cent referred to the moles of produced methanol) have been measured at higher temperatures with gases richer in CO, for long contact times. These divergencies are probably due to the greater difficulty of maintaining the temperature rigorously constant.

The good agreement between experimental and theoretical results is an evidence of the hypothesis that the rate-controlling process of the synthesis to methanol is the trimolecular reaction in the adsorbed phase.

A mechanism based on the hypothesis that the surface reaction is the resultant of two equally slow consecutive stages was not considered; the reason for this is that such a mechanism would require a more difficult mathematical treatment. The good agreement between experimental and calculated data in the case of the trimolecular reaction may be considered sufficient to establish the reliability of such an hypothesis. It should be pointed out that when dealing with surface phenomena, one finds reactions of the third or fourth order rather frequently, whereas, on the contrary, one usually finds complex homogeneous reactions to be divisible into simpler mono- or bimolecular stages.

Effect of Total Pressure

Since the synthesis of methanol is a reaction which proceeds with a considerable volume contraction, pressure has a very marked effect on the composition at equilibrium. When catalysts of normal activity are used, which react at temperatures higher than 350°C, it is necessary to operate at very high pressures to obtain good conversions.

Whenever in the synthesis of methanol gas mixtures containing N_2 or other inert gases are used, it is necessary to operate with pressures higher than the normal, the rate of reaction being a function of the activities of CO, H_2, and CH_3OH, which in turn are functions of the corresponding partial pressures of such gases.

This is the main reason why in industrial practice very often the synthesis of methanol is carried out at rather high pressures (200 to 250 atm.); equivalent conversions could be obtained at much lower pressures if pure gases were used. With very active copper-base catalysts, which may be used at temperatures close to 300°C, high conversion values may be obtained even with pressures of 100 to 120 atm., but such catalysts as a rule have the drawback of aging too rapidly.

Effect of Gas Composition

The first investigators of the synthesis of methanol observed that when the reaction was performed with a gas containing CO in excess of the stoichiometrical value, a greater decrease in the yield was noticed, than could be predicted on the basis of the law of mass action; some authors noticed also a kind of poisoning of the catalysts under such conditions. On the contrary, with H_2 greatly in excess of the stoichiometric composition, the yield of conversion decreases less than would be predicted theoretically. This effect was at that time attributed to the activating action of water vapor upon the catalysts.*

However, such an hypothesis is not sufficient to explain satisfactorily this remarkable effect, which is also noticed at lower temperatures (300 to 350°C) and with highly selective catalysts under such conditions as to make practically impossible the formation of water vapor. With highly selective catalysts the maximum rate of reaction occurs with $\frac{C_{H_2}}{C_{CO}} \gg 2$.

Natta and Casazza[42] attributed the favorable effect of a relative excess of H_2 upon the methanol yield in the experiments performed with very high space velocities, to the fact that the rate of adsorption of CO is higher than that of H_2. At that time, however, experimental data of adsorption at high pressures were missing. The data referring to adsorption experiments conducted at considerably lower pressures show that the volumes of CO and H_2 which are adsorbed under the same conditions are approximately equal, provided the gas quantities adsorbed over relatively long periods are considered. If, however, very short adsorption periods are considered, the adsorption rate of CO appears to be higher, although the rate of diffusion of H_2 is much higher than that of CO.

The apparently greater slowness of the adsorption of hydrogen is probably due to its diffusion into the inner part of the crystals; the part of hydrogen which is adsorbed slowly, therefore, is not concerned with the catalytical process, which takes place on the surface of the catalyst.

* When the reaction is performed with an excess of carbon monoxide, the water vapor (which is always present at least in small amounts among the reacting gases) disappears in the well known conversion reaction of carbon monoxide:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

and therefore it may no more exert its activating action. The presence of traces of water vapor is probably due to the formation of dimethyl ether:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O.$$

The results of the kinetic experiments performed by Natta and his co-workers[50] are able to explain the fact of a higher initial rate of reaction, as it is measured with ratios $\frac{C_{H_2}}{C_{CO}}$ higher than two. The values of the adsorption constants, as deduced from the results of the kinetic measurements, on the over-all reaction, which was interpreted as a surface reaction, show that hydrogen is adsorbed to a smaller extent than carbon monoxide. Accordingly, in order to obtain a stoichiometrical $2H_2:1CO$ composition in the adsorbed phase, it is necessary to operate with concentration ratios in the gaseous phase of the order at least of $10H_2:1CO$. Methyl alcohol itself is strongly adsorbed, thereby acting as an inhibitor of the synthesis reaction.

The presence of small quantities of CO_2 in the gas has a favorable effect on the conversion to methanol, when the reaction is performed at high space velocities. Such favorable effect of CO_2 is probably due to the combination of the following factors:

(1) It causes a decrease in the formation of dimethyl ether.

(2) It prevents the conversion of CO into CO_2, which would take place in the presence of water vapor.

(3) It allows a better temperature regulation, because the heat evolved in the reaction:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$$

is about 10 kcal per mole lower than that which is evolved in the reaction:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

Therefore, for a given amount of produced methanol, a smaller temperature increase along the reactor is noticed in the presence of CO_2. Furthermore, Natta and Rigamonti[44] noticed that the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

which proceeds toward the right at the higher temperatures, is catalyzed by zinc oxide: this endothermic reaction acts in the sense of regulating the temperature of the system, thus preventing any overheating of the catalyst.

The only apparent negative effect of the presence of carbon dioxide is that the amount of hydrogen consumed for a given quantity of methanol produced is higher. However, in the presence of small quantities of CO_2, the total amount of $CO + H_2$ consumed in the industrial practice is found to be slightly lower than in the absence of CO_2. It should be pointed out that when the synthesis is performed with recycle of the reacting gases, it is not convenient to work with gaseous mixtures containing high percentages of carbon dioxide, because in such cases a relatively large amount of carbon dioxide is dissolved in the produced methanol during the separation of the latter (through condensation) from the circulating gases.

Effect of Inert Gases

Some of the oldest patents dealing with the synthesis of methanol (Badische Anilin und Soda Fabrick, Terni Co., etc.) mentioned the fact that the presence of an inert gas (N_2, CH_4, etc.) may exert a favorable action upon the synthesis by preventing competitive reactions. However, the lessening of the amount of methane produced should not be attributed to a mass action effect of the methane already present upon the reaction:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O.$$

In fact, such reaction is at the high pressures almost completely shifted toward the right, and the effect of the presence of a small amount of methane would be negligible. Such effect would become important only with very high concentrations of methane (80 to 90 per cent) in the reaction gases. A high concentration of methane in the circulating gases would be harmful when operating at low pressures, because it provokes a diminution of the conversion at each passage of the gases through the catalyst. If, nevertheless, the synthesis of methanol is conducted at high pressures, a fairly high concentration of methane in the gas appears to be advantageous for the purity of the produced methanol. This may be connected with an effective reduction of the temperature rise of the reacting gases (due to the heat evolved in the reaction), as a consequence of: (1) the diminution of the production of methanol, on account of the lower partial pressures of CO and H_2; (2) the increased thermal capacity of the gas, because the specific heat of methane is higher than that of CO and that of H_2.

Pressures greater than 300 atm. may be conveniently used in the synthesis of methanol, if inlet gases containing 4 to 5 per cent of inert components are used, and if the reaction is operated with high inert gases concentrations (40 to 50 per cent) in the circulating gases.

Kinetic experiments in the presence of inert gases were performed by Natta and co-workers[50] with a $ZnO\text{-}Cr_2O_3$ catalyst. The molar concentrations of the produced methanol correspond exactly to those which may be predicted theoretically with Eq. (4), by simply admitting that the activities of CO and H_2 are proportional to the respective partial pressures, and to the fugacity coefficient related to the total pressure (see Table 10). It turns out, therefore, that neither methane nor nitrogen is sensibly chemisorbed by the catalyst, and that the only influence of these gases is their lowering of the partial pressures of CO and H_2 in the reaction gases, thus behaving effectively as inert gases.

Effect of Temperature and Space Velocity

The old data which appeared in the technical literature, concerning the optimum temperature range for the synthesis of methanol, are rather contradictory. Furthermore, the data of the various authors are not mutually comparable, because their experiments were not performed under strictly isothermal conditions. The experiments by Molstad and Dodge appear to be the most reliable of the earliest published work. The experiments of these authors were performed under well defined physical conditions, and the temperature rise due to the heat evolved in the exothermic reaction was pointed out. According to these authors, the optimum temperature for a space velocity of 25,000 and for catalysts containing 10 to 50 per cent Cr_2O_3, and not submitted to preshrinkage, is 375°C. With preshrunk catalysts the optimum temperature appears to be lower (see Table 8). If one considers carefully the type of apparatus used by Molstad and Dodge, the conclusion may be drawn that the reaction temperatures may be considerably lower than the actual catalyst temperatures; the temperature difference may be as high as 10 to 20°C. The optimum temperature for the reaction varies with the type and activity of the catalyst employed, and it also depends on space velocity.

TABLE 10. Comparison of Experimental and Calculated Rates of Methanol Synthesis*

Pressure Atm.	Temp. (°C)	Time factor	Moles of produced methanol per mole of inlet gas	
			Experimental	Theoretical
295	363	0.40	2.70×10^{-2}	2.60×10^{-2}
295	363	0.84	3.65×10^{-2}	3.55×10^{-2}
295	363	1.40	4.00×10^{-2}	3.95×10^{-2}
265	353	0.48	2.20×10^{-2}	2.20×10^{-2}
265	353	0.70	2.85×10^{-2}	2.80×10^{-2}
265	353	1.13	3.75×10^{-2}	3.75×10^{-2}
250	340	0.53	2.15×10^{-2}	2.10×10^{-2}
250	340	0.75	2.70×10^{-2}	2.65×10^{-2}
250	340	1.15	3.55×10^{-2}	3.50×10^{-2}

* For the runs at 250 atm. the inlet gas contained 7.8% CO, 73.5% H_2 and 18.7% CH_4; for the other runs shown, it contained 6.6% CO, 70.1% H_2 and 23.3% N_2.

As far as the optimum temperature is concerned, two cases should be considered separately: (1) the optimum temperature for the maximum production in unit time for unit of catalyst volume; (2) the optimum temperature for maximum production, in unit time, obtained with unit volume of circulating gases.

In (1) it is concluded that the production of methanol at a definite temperature varies directly with space velocity, while in (2) it varies inversely with space velocity, provided that the reaction is performed at such a temperature as to insure a good selectivity of the catalyst. For example, with a ZnO-Cr_2O_3 catalyst it is possible to obtain raw methanol of high purity (98 per cent CH_3OH) only by operating at temperatures lower than 390°C. If the synthesis of methanol is performed at temperatures higher than about 400°C, some secondary concurrent reactions take place, the extent of these side reactions increasing with an increase in temperature. Only with extremely high velocities of gas circulation is the occurrence of these secondary reactions kept negligibly small.

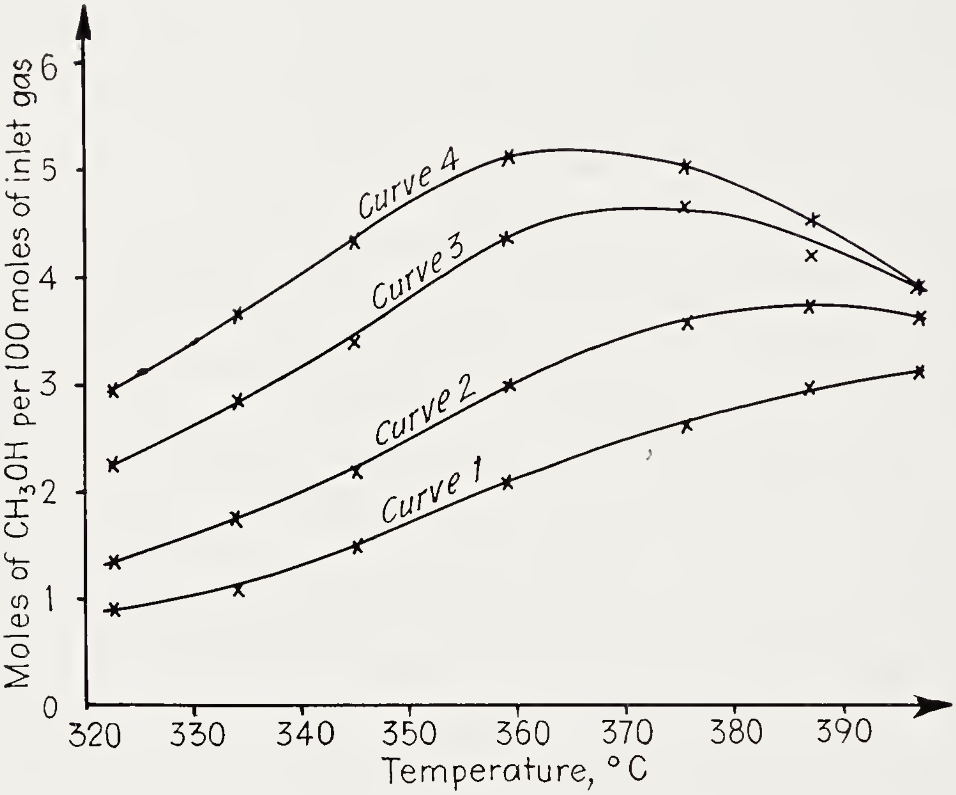

Figure 23. The conversion of a 1:10 $CO:H_2$ mixture to methanol as a function of temperature at 22.0 atm. pressure over a 89:11 $ZnO:Cr_2O_3$ catalyst at times of contact (as used in Figure 22) of 0.3, 0.5, 1.0, and 1.5 seconds, respectively for Curves 1, 2, 3, and 4.

Figures 23 and 24 show the conversion values obtained as a function of temperature, for different time factors, for a catalyst containing 89 per cent ZnO and 11 per cent Cr_2O_3 and for one in which $ZnO:CuO:Cr_2O_3 = 4:2:1$.

Activation Heat

The oldest data concerning this subject, which appeared in the technical literature may not be considered in our treatment, because the kinetic mechanism of the synthesis of methanol and that of the reverse reaction (dissociation of methanol) were almost completely unknown till recently.

Although the older literature contains abundant experimental data on the decomposition of methanol, it is practically impossible to consider them as starting points for the prediction of the catalyst's behavior in the synthesis of methyl alcohol, because the experiments on the decomposition of methanol were performed at low pressures, while the synthesis reaction was generally conducted at much higher pressures; furthermore, the types of side reactions which may take place are different in the two cases. Only when pure zinc oxide is used as the catalyst are the undesired side reactions really negligible. In this case a direct comparison between the synthesis and the decomposition data may be of some interest. For this reason the kinetic data obtained by Shekhter and Moshkovskii[68, 69] are reported in Table 11. These investigators worked with ZnO catalysts, one of which was prepared by the decomposition (at 350°C) of zinc carbonate, the other by the direct combustion of zinc in an electric arc in a current of air.

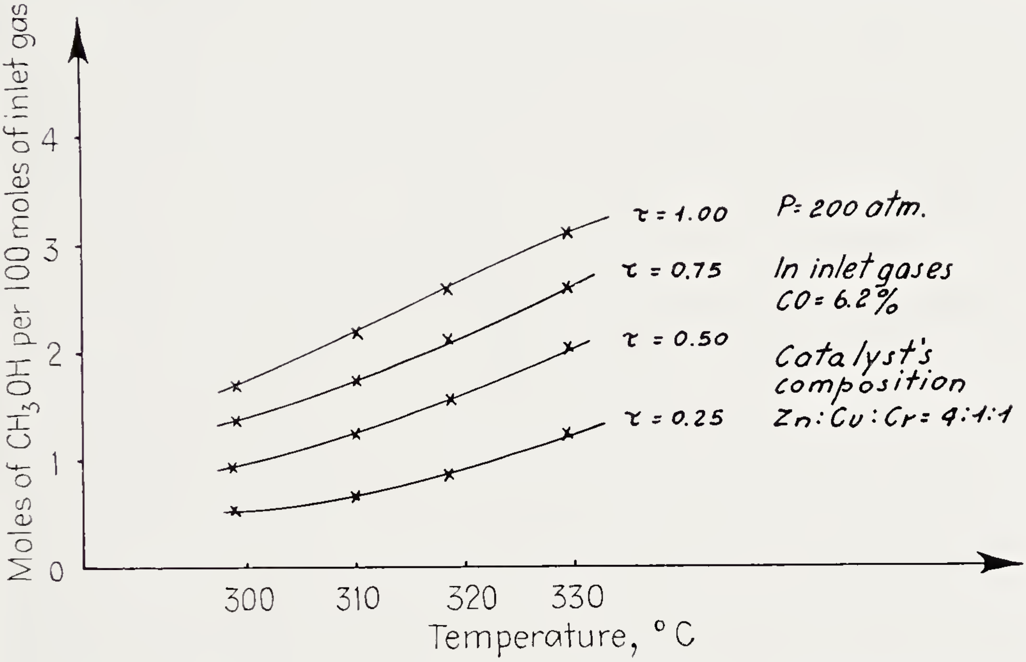

Figure 24. The conversion of a CO-H_2 (1:10) mixture to methanol as a function of temperature over a Zn-Cu-Cr (4:1:1). τ is the time of contact as defined in legend of Figure 22.

For the synthesis of methanol, Natta and his co-workers[49, 50, 51] have recently obtained the apparent values of the activation energy reported in Table 12. It should be noticed that the activation heats for the ZnO-Cr_2O_3 mixed catalysts are approximately equal to those for pure ZnO catalysts. This is in good agreement with the hypothesis that Cr_2O_3 behaves as promoter mainly through its action of preventing the decrease of the surface area of ZnO. The copper-containing catalysts have lower activation energies, and may be used also at relatively low temperatures. It may be noticed that the lowest activation heat is that for the CuO-Cr_2O_3 catalyst.

Mechanism of the Synthesis of Methanol

It has been pointed out that zinc oxide is the most important component of the catalysts for the synthesis of methyl alcohol. ZnO, when conveniently prepared, shows by itself a fairly good catalytic activity. Its durability may be increased by the addition of a promoter, which is generally a difficulty reducible oxide, whose hydrogenating properties are extremely poor. Chromium oxide (Cr_2O_3) is one of the most used promoters of ZnO, even when it is combined to it as zinc-chromite, ZnO—Cr_2O_3 .

Table 11. Kinetic Data Obtained in the Decomposition of Methanol
(Reaction of Zero Order in the Range 0.04–0.09 ml CH_3OH/min.)

k = cc of gas evolved per minute per gram of catalyst

Catalyst I: ZnO prepared by the thermal decomposition of $ZnCO_3$; (Specific surface area of 80 m^2/g).

Catalyst II: ZnO prepared by combustion of Zn at 1,000°C; (Specific surface area of 12 m^2/g).

Catalyst I	Temp. (°C)	322	300	290	
	k	153	61	41	
	E_{act} =	28 kcal per mole			
Catalyst II	Temp. (°C)	339	328	319	300
	k	152	101	36	10.5
	E_{act} =	51 kcal per mole			

Table 12. Energy of Activation for Methanol Synthesis

	Temp. Range (°C)	E (cal/mole)
Pure ZnO catalysts		
ZnO from smithsonite	325–370	27,000
ZnO from zinc acetate	330–353	30,000
Mixed catalysts		
CuO 34.6%-Cr_2O_3 65.4%	292–326	14,000
ZnO 90%; Cr_2O_3 5%; imbibed Cr_2O_3 5%	331–365	28,000
ZnO 89%; Cr_2O_3 11%	325–380	30,000
ZnO 80.8%; CuO 9.9%; Cr_2O_3 9.3%	307–325	17,000
ZnO 60.9%; CuO 29.8%; Cr_2O_3 9.3%	280–320	18,000
ZnO 51.3%; CuO 25.1%; Cr_2O_3 23.6%	300–330	18,000

Most of the promoters have the main function of inhibiting the sintering of ZnO, and, therefore, stabilizing the lattice vacant sites, and the anionic deficiencies, which are present to a greater or lesser degree in zinc oxide, according to its method of preparation. It should be here pointed out that a slight excess of zinc over the stoichiometrical value (10^{17} atoms per ml) is present even in the zinc oxide obtained by combustion of metallic zinc; there is evidence of a real homogeneous phase $ZnO_{(1-x)}$. The ZnO prepared from the combustion of metallic zinc is a rather poor catalyst while on the contrary ZnO obtained from zinc salts whose anion has a reducing action (for example, ZnO from $Zn(CH_3COO)_2$) is catalytically much more active. This appears to be connected with the greater number of anionic deficiencies in the lattice of ZnO, due to the presence of metallic zinc.

The introduction into the lattice of ZnO of oxides of trivalent cations in solid solution leads to the formation of cationic vacant sites, which may be filled by the excess of zinc present in ZnO. These trivalent ions have the function of stabilizing the excess of zinc atoms in the lattice, and therefore they increase the number of available electrons in the catalyst. This is in agreement with the higher conductivity measured in those zinc oxides which contain trivalent cations. The high catalytic activity of certain types of zinc oxide appears to be connected with the presence in the ZnO lattice of these available electrons due to elemental zinc.*

Taylor and Kistiakowsky noticed[73] that CO, H_2 and CO_2 are strongly adsorbed by ZnO, and that the mixed catalysts ZnO-Cr_2O_3 adsorb such gases to an even greater extent. The same authors pointed out that the adsorption heats are higher than the liquefaction heats. Several investigators in later works have shown that the mechanism of the synthesis of methanol with ZnO-base catalysts has to be correlated to the activated adsorption of CO and H_2 on the surface of zinc oxide. The temperature range at which the activated adsorption is possible (200 to 450°C) includes the temperatures at which ZnO acts as a catalyst for methanol synthesis.

Some active hydrogenating metals (Fe, Co, Ni) chemisorb carbon monoxide; however, the chemical reaction involved in the adsorption of CO by ZnO is quite different from that involved in the adsorption of CO by the above metals. If a finely divided or partially amorphous zinc oxide is heated in atmosphere of CO or H_2, traces of CO_2 or H_2O are found in the desorption of the adsorbed gases, as a consequence of the partial reduction of ZnO to Zn. For example, Natta and Agliardi[48] noticed that the number of Zn gram-atoms per mole of ZnO, which are formed in a single adsorption-desorption operation is of the order of 1×10^{-4}.

Fe, CO, and Ni chemisorb carbon monoxide because of their tendency to

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* The catalytic experiments with such semiconductive ZnO catalysts[55, 70] have been performed generally with catalysts obtained at very high temperatures (for example, ZnO—Al_2O_3), and having low catalytic activity for the synthesis of methanol. Al_2O_3 is not a good promoter of the ZnO and CuO-base catalysts, in which it is present as a solid solute. In the case of Cr_2O_3, however, one may conclude that Cr_2O_3, which is in contact with the surface of zinc oxide or of copper oxide, has a stabilizing action upon the surface cationic deficiencies.

combine with this gas to give carbonyl compounds. These metals, however, in the absence of hydrogen may provoke the disproportionation of CO to C + CO_2, and also may cause the formation of metallic carbides. It is reasonable to believe that the synthesis of hydrocarbons, catalyzed by these metals, proceeds through the transformation of CO into chemisorbed elementary C, which in turn is hydrogenated by the chemisorbed hydrogen.

Chemisorption of carbon monoxide on the surface of a metal belonging to the iron group is not entirely reversible. In fact, it is impossible to recover through desorption all the carbon monoxide chemisorbed on these metals, because a part of it is reduced to elementary carbon or to metallic carbide.

Chemisorption of carbon monoxide (or H_2) on zinc oxide is also not completely reversible, but in this case a part of the chemisorbed CO (or H_2) is desorbed as CO_2 (or H_2O), while ZnO is reduced to Zn. This reduction of ZnO to Zn proceeds sensibly only if the crystals of ZnO are defective; those promoters which hinder the complete crystallization of ZnO also make easier its partial reduction, stabilizing, therefore, the ZnO lattices containing an excess of electrons.

In the chemisorption of CO on the iron group metals there is a tendency toward the reduction of the carbon atoms, through removal of the oxygen previously linked to it; on the contrary in the chemisorption of CO on ZnO the divalent carbon is saturated, and there is no removal of the oxygen atoms combined with it. For this reason, when CO and H_2 are simultaneously present, iron group metals cause the formation of methane and higher hydrocarbons, while ZnO catalyzes the formation of methanol.

A complete reduction of ZnO to Zn, under the conditions of the synthesis of methanol, is impossible because small traces of CO_2 and H_2O are sufficient[65] to prevent the reaction of reduction. In fact, the equilibrium constant of the reaction

$$ZnO + CO \rightleftarrows Zn + CO_2$$

has extremely low values in the temperature range of the synthesis of methanol. The partial oxidations of CO to CO_2 and of H_2 to H_2O, which take place during the desorption of the chemisorbed CO and H_2 from active ZnO, have to be attributed to the presence of amorphous or imperfectly crystallized ZnO, for which the free energy of the reduction reaction assumes more favorable values, because of the absence of the contribution of the free energy of crystallization to the free energy of formation of ZnO.

The unusual behavior of ZnO, which is the most selective catalyst for the synthesis of methyl alcohol, may be thought of as being correlated with its crystal structure. Zinc oxide is, together with copper oxide, the only divalent metallic oxide having an ionic radius in the range 0.5 to 1.1 Å, which does not crystallize in the cubic system. ZnO crystallizes in the hexagonal system. Therefore, some planes of its lattice are composed entirely of oxygen atoms; others, entirely of zinc atoms. Eucken[10a] (private communication) attributed to the crystalline structure of zinc oxide its unusual catalytic behavior, which is shown, for example, in the decomposition of ethyl alcohol. In fact, while metals dehydrogenate ethyl alcohol to acetaldehyde, and, on the other hand, the nonreducible oxides (Al_2O_3, Cr_2O_3) dehydrate ethyl alcohol to ethylene, zinc oxide behaves intermediately, giving rise simultaneously to both ethylene and acetaldehyde.

The catalysts containing copper oxide behave substantially like the ZnO-base catalysts, the main difference being due to the higher reducibility of CuO. The short durability of copper-base catalysts, obtained through reduction of CuO in the presence of promoters, has to be attributed to the fact that the true catalyst of the methanol synthesis is not the metallic copper phase (cubic), but the copper oxide which is present in the incompletely reduced catalysts (for example, as copper chromite in the CuO-Cr_2O_3 catalysts). During a synthesis run there is a gradual reduction of CuO to Cu, and the separation of crystals of pure cubic metallic copper provokes the lowering of the catalyst's activity. The copper-containing catalysts are very active at the low temperatures, at which the reduction of CuO (specially when combined with Cr_2O_3) is fairly slow, but they lose their activity rapidly if the temperature is raised.

The behavior of copper-base catalysts in the synthesis of methanol is in many respects similar to that of the copper-base catalysts used in the hydrogenation of fatty acids to alcohols. These catalysts (for example, copper chromite) have a very short life when used at temperatures higher than 300°C, and lose their activity entirely when the copper oxide is completely reduced to copper.

The hypothesis that copper oxide, and not metallic copper, is the real catalyst for the synthesis of methanol, is substantiated by considering the behavior of silver-base catalysts, whose properties are in many cases similar to those of copper-base ones. In some instances (for example, in the oxidation of methanol to formaldehyde) silver is an even more active catalyst than copper. In the synthesis of methanol, however, silver is a bad catalyst: this is probably connected with the higher reducibility of silver oxide with respect to copper oxide.

The combination ZnO and CuO gives catalysts which are extremely active in the synthesis of methanol. This has been attributed to an improvement in the hydrogen adsorption capacity of the catalyst. However, this idea has not been corroborated by kinetic experiments on mixed Cu-Zn-Cr catalysts[51].

It has been mentioned that the activity of copper-base catalysts is connected with the presence of nonreduced copper oxide. This is shown also by the activating action of oxygen in the dehydrogenation of methanol to formaldehyde. The copper catalysts, which were widely used in the industrial production of formaldehyde from methanol, have a durable activity only when the reaction is performed in the presence of air or oxygen.

Activated adsorption of CO and H_2 on various oxides takes place generally starting from temperatures much lower than those corresponding to the complete reduction of the oxides. From this point of view, it is interesting to correlate the reducibility of some metallic oxides to their free energies of formation at the temperature of the methanol synthesis.

Oxide	$\Delta F^\circ_{400^\circ C}$
MnO	−89.9
$\frac{1}{3}Cr_2O_3$	−75.2
ZnO	−67.0
CdO	−54.7
$\frac{1}{2}WO_2$	−51.9
FeO	−51.5
NiO	−43.3
CoO	−43.2
CuO	−32.0

Of the above oxides, Cr_2O_3 and MnO were used as promoters. CdO also is a very active promoter (as it is shown by the high activity of certain ZnO catalysts from smithsonites containing cadmium as impurity) but it is easily reducible. FeO, CoO, NiO are also easily reducible, but they act as catalysts for the competitive synthesis of methane. The hydrogenating (and dehydrogenating) properties of Cr_2O_3 are generally observed at higher temperatures, and they are utilized in the industrial dehydrogenation of some hydrocarbons.

The free energies of the reactions of formation of spinels from the corresponding oxides have values of a few kcal per mole. Therefore, spinels are not reduced as easily as the corresponding free oxides; accordingly, zinc chromite is less active than the mixtures ZnO-Cr_2O_3 richer in ZnO. The reducibility of copper chromite is intermediate between that of CuO and that of ZnO; therefore copper chromite gives catalysts which last longer than those made with ZnO-CuO mixtures containing an equal amount of CuO.

The equilibrium constants for the adsorption of CO, H_2, CH_3OH on the active sites which are of interest in the catalysis have been deduced from the kinetic interpretation of the experimental data, as reported by Natta and his co-workers[50] for a catalyst, the composition of which is 89 per cent ZnO and 11 per cent Cr_2O_3. The values of such constants were obtained by calculating the ratios B/A, C/A, and D/A for the four constants in Eq. (1)

for different temperatures (page 391). Natta and co-workers[51] have calculated the analogous constants for a catalyst containing 50 per cent ZnO, 25 per cent CuO and 25 per cent Cr_2O_3. In Figure 25 the logarithms of the values of such equilibrium constants are plotted versus $\frac{1}{T}$. The higher reactivity of CO in the surface reaction is probably connected with the higher absolute value of the free energy of the reduction of ZnO with CO, with respect to that of ZnO with H_2. As was pointed out in one of the preceding paragraphs, the fact that the values of the equilibrium constants for the

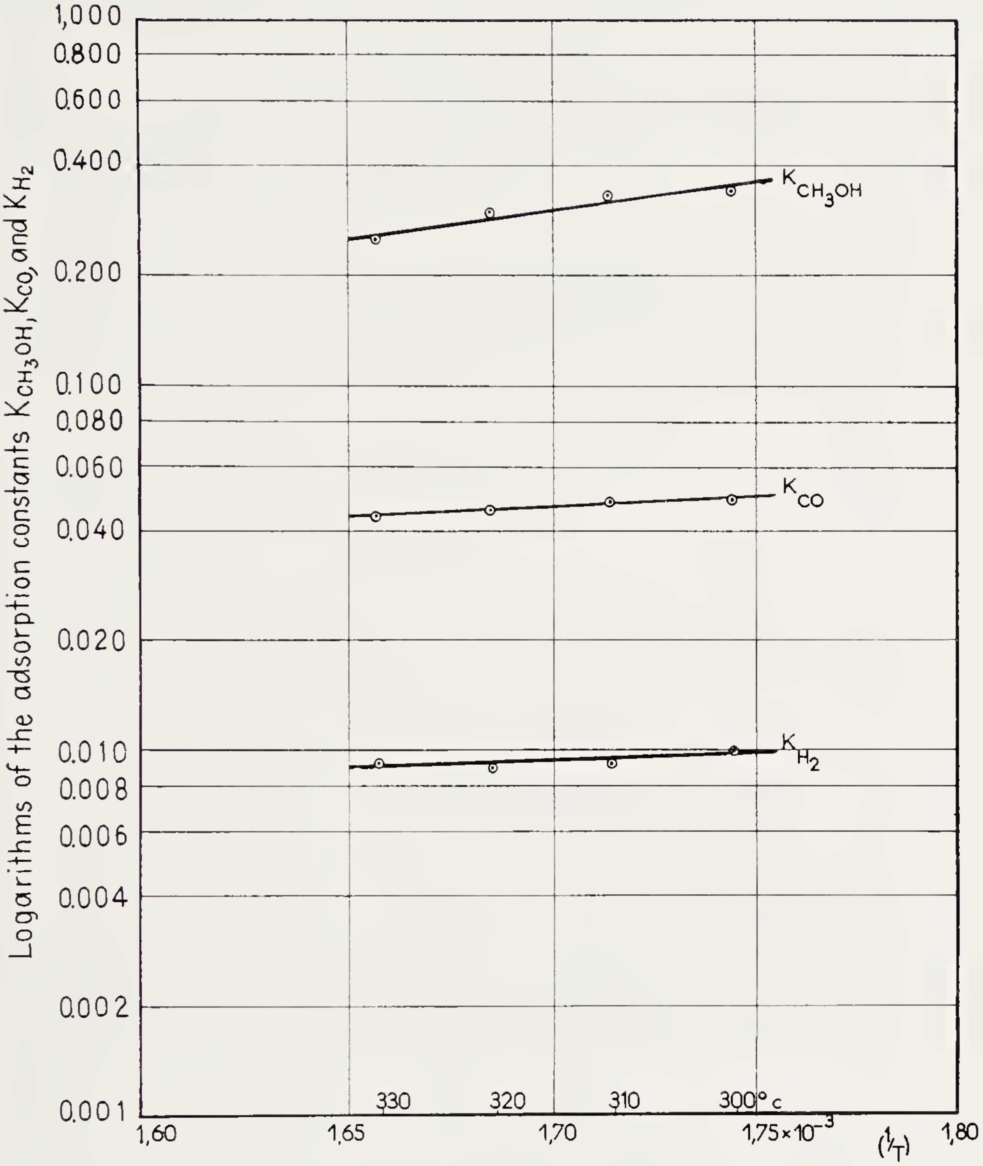

Figure 25. Logarithmic plots of K_{CH_3OH}, K_{CO}, and K_{H_2} as a function of temperature.

adsorption of CO are higher than those corresponding to the adsorption of H_2, explains the apparent abnormality of having the maximum reaction rate at each temperature with ratios H_2:CO much higher than the stoichiometrical ratio for the synthesis of methanol. These results corroborate the hypothesis that the heterogeneous catalysis occurs with CO and H_2 in the adsorbed phase, and that the rate of such reaction is a function of the concentrations of CO and H_2 in the adsorbed phase. However, if a comparison is made between the kinetically deduced chemisorption data and the experimental data concerning low pressure adsorption of CO and H_2 at the surface of ZnO, an apparent disagreement is found. In fact, for long adsorption periods at low pressures CO and H_2 are adsorbed in about equal molar concentrations. If one considers the experimental data of Sartori[64], related to the adsorption of CO and H_2, it is clear that, for very short adsorption periods, carbon monoxide is adsorbed much more readily than H_2. This is in good agreement with the results obtained from the kinetic interpretation of methanol synthesis.

TABLE 13. COMPARISON OF ADSORPTION CONSTANTS FOR CO, H_2, AND CH_3OH AT 325°C AS CALCULATED FROM KINETIC DATA FOR METHANOL SYNTHESIS CATALYSTS*

Catalyst	A	B	C	D	K_{CO}	K_{H_2}	K_{CH_3OH}	Ratios K_I/K_{II}		
								K_{CO}	K_{H_2}	K_{CH_3OH}
I	50.0	3.80	0.82	21.2	6.6×10^{-2}	14×10^{-3}	3.9×10^{-1}	1.44	1.52	1.44
II	62.5	2.85	0.57	17.1	4.6×10^{-2}	9.2×10^{-3}	2.7×10^{-1}			

* Catalyst I) ZnO:Cr_2O_3 = 89:11
Catalyst II) ZnO:CuO:Cr_2O_3 = 50:25:25
(For the meaning of the constants A, B, C, D see page 391.)

It appears therefore evident that not all the molecules of adsorbed CO and H_2 are actually related to catalysis, but, only those which are rapidly adsorbed on the most easily available active sites. The slow adsorption in the inner part of the crystals (or else on sites of lower activity) most probably are not involved in the catalytic processes which occur at very high space velocities.

The fairly high value of the adsorption constant for CH_3OH explains the fact that the presence of CH_3OH in the reacting gases inhibits the synthesis, and that therefore when high values for the concentrations of methanol are reached, a further conversion of CO and H_2 is slower than would be predicted by virtue of the reversibility of the reaction. Similar results were obtained with copper-base catalysts, whose adsorption constants are quite different from those pertaining to ZnO-base catalysts. However, the ratios $\frac{K_{CO}}{K_{H_2}}$ and $\frac{K_{CH_3OH}}{K_{CO}}$ are almost equal in the two cases (Table 13)[51, 52].

We may conclude this chapter by pointing out that the accurate kinetic study of the reaction of synthesis of methanol has given a remarkable contribution to the understanding of the mechanism of this reaction. Such a kinetic approach has also contributed to a better knowledge of the phenomena connected with activated adsorption.

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CHAPTER 9

HYDROGENATION OF GLYCERIDE OILS

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INTRODUCTION

Hydrogenation of the ethylenic linkages in glyceride oils to produce products of improved properties is one of the major processing operations in the fat and oil industry. Approximately two billon pounds of glycerides are hydrogenated annually in the United States. The primary objective generally is to convert the more plentiful oils into plastic fat products like margarine oil and the various types of shortening. Insofar as possible, the course of the reaction is controlled to produce products of a specific melting point, plastic range, creaming quality, etc.

In the production of edible fats a secondary objective is the improvement of keeping quality; that is, the reduction of the more unsaturated constituents, which are relatively susceptible to oxidation, the development of other off flavors, and polymerization. For certain nonedible products, the primary objective of hydrogenation may be to eliminate the more reactive unsaturated constituents of a fat or to produce stearins. Removal of color and destruction of peroxides are other incidental benefits attained through hydrogenation.

Cottonseed, soybean, and similar oils ordinarily subjected to hydrogenation possess a low vapor pressure: about 0.001 mm of mercury at 250°C[63]. Consequently, hydrogenation must be accomplished in the liquid phase.

One of three systems of hydrogenation has generally been employed in commercial practice. The simplest of these makes use of a so-called dead-end converter consisting of an upright, cylindrical pressure vessel containing heating and cooling coils and at least two agitators, the latter usually being mounted on a common shaft. The lower agitator mixes thoroughly the oil and finely divided catalyst while the upper agitator draws hydrogen from the head space of the vessel and mixes this with the oil and catalyst. Hydrogen is introduced in the lower part of the vessel and causes additional mixing as it travels to the head space.

The second system also employs an upright, cylindrical pressure vessel, but mixing of the reactants is accomplished by circulating, with the aid of external pumps, either the oil and catalyst mixture or hydrogen or both.

In the third system hydrogenation is accomplished in a continuous fashion by passing the hydrogen and oil either countercurrently or concurrently through a bed of nickel turnings whose surfaces have been activated by special treatment.

TYPES OF CATALYSTS AND METHODS OF PREPARATION

Catalysts for the hydrogenation of fats and oils can be classified in various ways. One of these is definitive of the method of reduction, the terms wet reduced and dry reduced being employed depending upon whether or not reduction of a salt or oxide is accomplished while it is suspended in oil. Ordinarily this classification distinguishes between catalysts derived from nickel formate (wet reduced) and catalysts derived from other salts or oxides of nickel. While nickel hydroxide and carbonates can be wet reduced, particularly if coprecipitated with salts of copper[26], such reduction is not widely practiced. Catalysts are also classified according to whether or not they are supported on an inert and refractory carrier, like diatomaceous earth. This division is useful in the practical field of hydrogenation, where it is considered that a supported catalyst is one to which a support or carrier has been deliberately added. However, it must be stated that some catalysts which are assumed to be of the nonsupported type actually may contain an inert material. For example, the wet reduction of nickel carbonates is usually incomplete and the final product may contain a large proportion of inert carbonates.

Catalysts for the hydrogenation of fats and oils can be classified according to type of metal or, if the metals are compared with mixtures of metals, according to whether or not the catalyst is promoted. Classifications of this type are made infrequently because in the commercial hydrogenation of oils nickel is practically the only metal used as a catalyst, and promoters in the normal sense are generally not incorporated.

In this chapter, the classification of catalysts will be somewhat arbitary and serve as a guide rather than a rigid division. The catalyst preparations which will be discussed will include, in addition to the commercially important preparations, some of those which have been used in laboratory and experimental work.

CATALYSTS OF NICKEL

Unsupported Type

Nickel Formate. In the hardening of glyceride oils, one of the two most widely used catalysts is that obtained through the pyrolysis of nickel formate.

According to Dean[25], nickel formate for this purpose is prepared commercially from nickel sulfate which is obtained in turn by the reaction between sulfuric acid and steam-shattered, high-sulfur nickel shot. A strong, hot solution of nickel sulfate and a solution of sodium formate which has been neutralized with formic acid, are mixed in equivalent amounts, care being taken that the concentration is maintained below the point at which sodium sulfate precipitates. Under these conditions nickel formate precipitates from the hot solution and is separated by filtration. The crystals are then washed with cold water and dried at a temperature below 100°C to obtain the dihydrate, $Ni(HCOO)_2 \cdot 2H_2O$. Alternate methods for the preparation of nickel formate can be employed and are desirable when the presence of small amounts of sulfate ion is considered to be objectionable. Most frequently in these alternate methods nickel hydroxide or carbonate is interacted with formic acid. In a recently described method[45], nickel formate dihydrate was produced on treating steam-shattered nickel shot with an excess of boiling, 85 per cent formic acid for four hours. While the yield was relatively low, it was claimed that the end product was of high purity and that the process could be operated in a continuous fashion.

On heating nickel formate dihydrate decomposition occurs according to the reactions[15]

$$Ni(HCOO)_2 \cdot 2H_2O \rightarrow \underline{Ni} + 2CO_2 + H_2 + 2H_2O \tag{1}$$

$$Ni(HCOO)_2 \cdot 2H_2O \rightarrow \underline{Ni} + CO_2 + CO + 3H_2O \tag{2}$$

The water of hydration begins to come off at about 150°C. Decomposition of the nickel formate itself apparently occurs over the temperature range of 170 to 240°C[97]. According to Dean[25] the main reaction is that given by Eq. (1).

A typical plant-scale preparation of catalyst from nickel formate has been described by Wurster[97]. The reaction, according to him, is carried out in a vented vessel provided with electrical heating and an agitator. Oil of the same type as that which is to be hydrogenated is placed in the vessel and finely divided nickel formate dihydrate is stirred in, usually until a ratio of one part of salt to four parts of oil is reached, though the ratio can be as high as one to one. Heating is then begun. When the temperature reaches 150°C, decomposition usually starts. It is at this point that the bubbling of a small amount of hydrogen gas through the mixture is begun. The hydrogen aids in stripping out the gaseous reaction products and aids in hydrogenating the oil carrier which is desirable. The temperature rises at a uniform rate until at the end of about one hour it reaches 185°C. The temperature then rises at a slower rate as decomposition becomes more rapid. At the end of the next one-half hour the temperature will have reached about 190°C. Then in the course of another one-half hour the temperature will rise to 240°C, at which temperature the mixture is kept for an additional hour and a half to complete the reaction. The total time required is three to four hours. The length of time at a given temperature may vary somewhat according to the age of the nickel salt, freshly precipitated salt reducing more readily at low temperatures.

The catalyst-oil mixture is ready for immediate use, but if desired, the mixture can be cast into blocks or flaked on chilling rolls and then stored for future use. The highly hydrogenated fat protects the catalyst surfaces from oxidation and is itself quite stable. Under ordinary conditions the mixture apparently keeps for years without any appreciable loss of catalytic activity.

The above described details for the processing of nickel formate are not, of course, inflexible. It is believed by some plant operators that the maximum temperature mentioned by Wurster is higher than desirable. Also, in the preparation of high-quality edible products it is considered good practice by some operators to remove from the catalyst the oil used in the pyrolysis, which always deteriorates to some extent, and replace it with fresh oil. The replacement is carried out with the help of a siliceous filter aid, which is added to the oil at about 300°F (149°C).

The formate is not the only salt of nickel which can be transformed into a catalyst by simple pyrolysis. Nickel oxalate decomposes in an analogous manner:

$$NiC_2O_4 \cdot 2H_2O \rightarrow \underline{Ni} + 2CO_2 + 2H_2O \qquad (3)$$

As in the case of the formate, decomposition commences at about 150°C and proceeds readily at 200°C. Side reactions do occur to some extent, and if the heating is not conducted in a reducing atmosphere[1], the reaction product may contain small amounts of nickel oxide and nickel carbonate.

Raney Nickel. Alloys composed of nickel and either aluminum or silicon or both were found by Raney[67] to yield nickel having catalytic activity when the other portion of the alloy was removed by selective reaction with appropriate reagents. The elements magnesium and zinc can also be employed. However, for all practical purposes nickel-aluminum alloys containing 42 to 50 per cent of nickel are employed. At these percentages it is believed that the nickel-aluminum compounds in the alloy include Ni_3Al, and NiAl, Ni_2Al_3, and $NiAl_3$, but not $NiAl_2$ or $NiAl_5$[5, 20]. The compositions $NiAl_3$ and Ni_2Al_3 are thought to be the ones which most readily yield an active catalyst. The NiAl reacts only slightly with the alkali employed to remove the aluminum from the alloy[74].

Alloys containing 42 to 50 per cent of nickel are prepared by working nickel shot into molten aluminum heated to about 1200°C and protected from oxidation by a salt flux or an inert atmosphere. After solidification the alloy is usually reduced to a fine powder, which is easily accomplished because the alloy possesses little tensile or compressive strength and is friable.

Conversion of the powdered alloy into catalyst is accomplished by digesting it with alkali and removing the aluminum as a salt. Numerous procedures describing this conversion, which differ only in detail, have been published. Those described by Raney[68] and Bailey[8] are typical for plant-scale hydrogenations, while those described by Adkins and Billica[4] and by Paul and Hilly[62] are good for laboratory use.

The preparation of Raney catalyst for plant use is very simple. A 20 per cent to 30 per cent solution of sodium hydroxide in water is placed in an open vessel equipped with an agitator and a steam jacket, the amount of the solution being such that the sodium hydroxide is considerably in excess of that theoretically required to react with the aluminum in the amount of alloy to be treated. The powdered alloy is added at a slow rate. The reaction is vigorous, particularly at first, and the heat liberated quickly brings the solution to the boiling point. Later the heat is dissipated by generating steam, which is vented to the atmosphere together with the hydrogen which is formed as a by-product. Water is added to the reaction vessel to keep the volume of the solution approximately constant. After all of the powder has been added and the reaction has subsided somewhat, the mixture is digested with the occasional addition of water for an additional 2 or 3 hours at about 250°F (121°C). Then the steam is turned off, the agitation is discontinued, and the nickel in the form of a sludge is allowed to settle. Most of the solution, which contains sodium aluminate and the unreacted sodium hydroxide, is drawn off; and the sludge is washed repeatedly with cold water until all traces of alkali have been removed. Because the sludge is highly pyrophoric, it must be kept wet at all times.

When the washing is completed, the sludge is flushed with water into a second vessel where as much as possible of the water is withdrawn and oil is added. The mixture is heated and agitated, preferably under vacuum, until all water has been removed. The catalyst is then ready for use.

In catalyst preparations for laboratory use it is desirable to have products of the highest possible activity. Adkins and Billica[4] claim this is obtained in the case of Raney nickel by observing certain precautions. To 160 grams of sodium hydroxide in 600 ml of water, they add, in the course of 25 to 30 minutes, 125 grams of nickel-aluminum alloy, being careful to maintain the temperature at all times at 50 ± 2°C. Then, while being agitated gently, the mixture is digested for 50 minutes at 50°C. The catalyst, after digestion, is washed three times by decantation and then transferred immediately to a vertical glass tube and washed countercurrently with 15 liters of distilled water while the water and catalyst are kept under an atmosphere of hydrogen. After the water washing the catalyst is transferred to a centrifuge bottle and washed three times with 150-ml portions of 95 per cent ethanol. Each time, the catalyst is stirred to disperse it in the ethanol and then is centrifuged to separate it from the ethanol. The washing is repeated with three 150-ml portions of absolute ethanol. The total time elapsed during the preparation should not be more than three hours. The finished catalyst should be kept in a closed bottle filled with absolute ethanol and stored in the refrigerator until used, which should be within two weeks of the time of preparation.

Massive Nickel. In the early development of the industrial hydrogenation of oils a continuous process (Bolton and Lush) was used, mostly in Europe, in which oil and hydrogen were passed over a mass of nickel turnings or wire whose surfaces had been treated to make them catalytically active[49, 50]. The first step in the activation of the turnings, which were confined in cages of monel screen, was to oxidize their outer surfaces. According to one published description[50], cages measuring 3.5 feet in length by 0.5 foot in diameter were made the anode in an electrolytic bath consisting of a dilute solution of sodium carbonate. After the passage of a current of about 40 amperes at 4 volts for 36 to 48 hours the surfaces of the nickel were covered with a black film of nickel oxide, estimated to have a thickness of 0.0003 mm. An alternate procedure was to immerse the cages in a dilute solution of sodium hypochlorite. The cages with the oxidized turnings were washed to remove the salt solution, dried, and placed in the hydrogenation apparatus where they were heated under hydrogen to 250°C to produce catalytically active surfaces.

Miscellaneous Unsupported Catalysts. In the literature on the hydrogenation of fats and oils there exist numerous descriptions of the preparation of unsupported nickel catalysts which have never become important either in the plant or laboratory. Nearly all of them may be considered as lying outside the scope of the present chapter. One or two of them, however, do yield interesting data relative to the nature and extent of the active nickel surfaces.

Richardson[72] and Elder[29] have described the preparation of active catalysts by mechanically grinding nickel sheets and pellets. The simplest preparation was obtained by grinding together by hand two nickel plates coated with cottonseed oil and powdered silica. In other experiments pellets were used and the grinding was performed in a ball mill, either with or without the addition of abrasives. To establish whether or not the accidental formation of nickel oxides and their subsequent reduction during hydrogenation might account for the activity of the nickel, grindings were performed under hydrogen as well as under air. In one case a dry grinding was performed in air. All preparations were active.

Early in the development of hydrogenation processes the idea was conceived that colloidally dispersed nickel should possess an unusual amount of activity because of its high ratio of surface area to mass. Because nickel tetracarbonyl is soluble in fatty oils and on heating can be readily decomposed according to the equation,

$$Ni(CO)_4 \rightarrow \underline{Ni} + 4CO \qquad (4)$$

to yield pure nickel in an extremely fine state of division, it seemed to be well suited for the preparation of colloidally dispersed nickel. Such preparations have been examined by several investigators among whom Shukow[75] apparently was the first. He passed carbon monoxide over finely divided nickel warmed to 60°C, and the resulting nickel tetracarbonyl was passed into cottonseed oil heated to 180°C. Later the temperature of the nickel-oil mixture was raised to 230 to 240°C and hydrogen was introduced. The oil hydrogenated under these conditions. Other investigators tried variations of this preparation, and in one instance[96] claimed to have obtained a highly active catalyst—though it appears from the data which are reported that the activity was about the same as that which might be expected from good nickel catalysts prepared by more conventional methods.

Supported Type

Supports in the form of siliceous material, like diatomaceous earth, can and frequently are added to catalysts prepared from nickel formate and nickel-aluminum alloys. In these instances the support serves primarily as an aid in handling the catalyst in filtering and other operations. A truly supported catalyst is prepared by precipitating nickel carbonate or hydroxide on diatomaceous earth or other refractory material, then drying and grinding the mixture and reducing the nickel in an atmosphere of hydrogen at a high temperature.

This mode of preparation serves admirably to attain the conditions sought in a hydrogenation catalyst; namely, the spreading of a given quantity of nickel over the largest possible surface area and simultaneous production of a surface consisting of very minute and extensively defective crystals. For an effective catalyst of this type the precipitated nickel compound itself must be deposited in a thin film on an inert carrier of high specific area (high area per unit mass of solid). This film must consist of very minute crystals which should be fairly uniform in size and free of adsorbed or occluded foreign matter which can poison the hydrogenation reaction. To activate the nickel, it is necessary to reduce the nickel compound in such a way as to avoid sintering and thereby destroying the relatively isolated or active nickel atoms which, according to the active point theory[82], are the points where reaction between hydrogen and oil occurs.

The salts of nickel which can be used in the production of precipitated catalysts are the chloride, nitrate, and sulfate. The latter is employed by far the most frequently, primarily because of its lower cost, and is one of the two main compounds used to prepare catalysts for the plant-scale hydrogenation of fats and oils. The other compound, as mentioned earlier, is nickel formate. The chloride and nitrate of nickel are used for precipitated catalysts when it is necessary to eliminate, insofar as possible, impurities which can poison the hydrogenation reaction. The nickel nitrate, in particular, is desirable because on heating it decomposes into oxides of nitrogen and nickel oxide, NiO.

As precipitants for nickel salts, successful use has been made of sodium, potassium, and ammonium hydroxides, the corresponding carbonates, and bicarbonates. Of these, sodium carbonate and sodium bicarbonate are the most generally suitable and are used predominantly. The use of ammonium hydroxide does have one advantage: traces of ammonium salts which remain behind in the precipitated mass are easily volatilized during the reduction process.

The reaction of sodium carbonate or bicarbonate with nickel sulfate in aqueous solution never produces pure nickel carbonate, even when sodium bicarbonate saturated with carbon dioxide is used, and the reaction is carried out at a low temperature[25]. Voluminous basic nickel carbonates of variable composition always are precipitated.

The preparation of precipitated, dry-reduced nickel catalysts requires close attention to many operational details, established mainly by trial and error methods. Factors reflecting the performance of the final product include the selection of the type of precipitant, solution concentrations, relative quantities of reactants, method of adding reactants, temperatures, washing procedure, and drying procedure. The necessity for close attention to this myriad of details becomes clear on remembering that they are all factors in determining the size, shape, and purity of the crystals obtained by a simple metathetical reaction between a soluble metal salt and a base to obtain an insoluble metal compound.

Nickel Sulfate. Since Normann[57] first described the preparation of a supported catalyst from nickel sulfate and sodium carbonate for use in the hydrogenation of fats and oils, numerous descriptions of similar preparations have appeared in the literature, but relatively few of the descriptions give the exact operational details. Most commercial firms regard these as trade secrets.

A procedure essentially as described by Bailey[8] yields a good, active catalyst. According to this procedure 70 parts of chemically pure nickel sulfate hexahydrate is dissolved in 2500 parts of water. The solution is heated to boiling; and 15 parts of a fine grade of diatomaceous earth is added. A second solution is prepared consisting of 42 parts of chemically pure sodium bicarbonate and 650 parts of cold, distilled water. The second solution, which must be used while fresh, is added to the first solution at a uniform rate over a period of 1.0 to 1.5 hours while the latter is kept boiling and is being agitated vigorously with a mechanical stirrer. The final solution containing the diatomaceous earth and nickel carbonates in suspension should be alkaline to phenolphthalein. At this point an additional 15 parts of diatomaceous earth is added, and boiling and agitation are continued for an additional 0.5 to 1.0 hour after which the mixture is filtered to remove the spent solution. The solids are resuspended in 2200 parts of distilled water, and the mixture is boiled for a short time and refiltered. The washing operation is repeated once or twice, care being taken not to prolong it unduly. Immediately after washing, the solids are dried at 105 to 110°C and pulverized to a fine powder which is the unreduced catalyst. If the operation has been carried out properly, the dried solids are soft and friable and can easily be crushed between the fingers. After pulverization the solids are of high specific volume and fluffy in nature. Nickel content is approximately 25 per cent. Reduction is accomplished by heating in a stream of hydrogen for about 8 hours at 900 to 950°F (482 to 510°C).

As in the reduction of all catalysts of this type, care must be exercised to remove entrapped air before the catalyst is heated in the presence of hydrogen; otherwise an explosion may result. The reduced catalyst is highly pyrophoric and must not come in contact with air. After reduction, the hydrogen over the catalyst can be replaced with carbon dioxide and thus lessen the possibility of explosions. A general practice is to suspend the catalyst in oil in which form it is stable.

Hugel[42] cites a somewhat different procedure for preparing catalyst from nickel sulfate. He states that for plant-scale preparations a boiling and mechanically stirred solution of nickel sulfate is treated with a solution of sodium carbonate. The sodium carbonate is added in a step-wise fashion, partly to prevent excessive foaming and partly as an aid in adding the exact amount required for the reaction. In the course of the addition samples are withdrawn and tested for soluble nickel salts. An excess of sodium carbonate is avoided because it makes difficult the washing of the unreduced catalyst. When all of the nickel has been precipitated, diatomaceous earth is added to the mixture, and the boiling and stirring are continued for a short time. After a final check for the absence of soluble nickel salts, the mixture of diatomaceous earth and nickel carbonates is separated from the solution by filtration, washed well with water, dried, and pulverized. The mixture is then heated to 350°C to transform the basic nickel carbonates into nickel oxide after which hydrogen is introduced and the temperature is increased to 450 to 500°C.

Electrolytically Precipitated Nickel. One form of supported catalyst currently being used to some extent for the hydrogenation of oils is prepared by converting, in an electrolytic cell, metallic nickel to nickel hydroxide, which is later reduced with hydrogen.[60]

A sheet of the metallic nickel to be converted to nickel hydroxide is made the anode of the electrolytic cell while another sheet of nickel or other corrosion resistant metal is employed as the cathode. On passing a direct current through the electrolyte (a dilute solution of sodium chloride) the following reactions occur:

$$2Na^+ + 2H_2O + 2e \rightarrow 2NaOH + H_2 \quad \text{(cathode)} \qquad (5)$$

$$2Cl^- + Ni \rightarrow NiCl_2 + 2e \quad \text{(anode)} \qquad (6)$$

$$Ni + 2H_2O \rightarrow Ni(OH)_2 + H_2 \quad \text{(net result)} \qquad (7)$$

In addition to the reactions indicated, a small amount of side reaction occurs: some basic nickel chloride is formed. This tends to increase the pH of the electrolyte as the reaction continues. In the original procedure, as described by Sieck[76], this tendency for the pH to increase was overcome to some extent by employing a mixture of sodium acetate and ammonium chloride as the electrolyte because of their buffering qualities. Current practice is to introduce an acidic material to control the pH.

The following is one of the proven procedures for preparing electrolytically precipitated nickel catalyst: The nickel sheet to be corroded (anode) is suspended in a vat made of wood or other inert material. Two cathodes (one on each side of the anode) are suspended to within 1 to 4 inches of the anode. The vat is almost filled with a 1 per cent solution of chemically pure sodium chloride, and an amount of fine diatomaceous earth equal in weight to the nickel to be corroded is added. The mixture of earth and electrolyte is heated to 122°F (50°C); and while it is kept in uniform suspension by mechanical stirring, direct current is passed through the cell at a current density of 44 to 57 amperes per square foot, based on the total anode surface. To produce this current density, about 6 volts is required. The temperature of the electrolyte is maintained at 122°F (50°C). The pH is maintained between 9.0 and 9.5 by introducing carbon dioxide at a slow, uniform rate. When the proper amount of nickel has been corroded, electrolysis is discontinued; and the suspended catalyst is separated from the electrolyte by filtration, washed, dried, and ground to a fine powder. This unreduced catalyst should contain about 38.5 per cent of nickel. Reduction is accomplished by heating it at 700 to 900°F (371–482°C) in a stream of hydrogen for 2 to 4 hours.

MIXTURES OF NICKEL AND OTHER METALS OR METAL OXIDES

Generally when a catalyst is composed of a mixture of metals or metals and metal oxides, the purpose of the mixture is to secure promoter action. This can be defined as occurring when a mixture of two or more substances is capable of producing a greater catalytic action than would be anticipated on the supposition that each substance in the mixture acts independently and in proportion to the amount present.

With the possible exception of the use of siliceous carriers, the use of promoters is limited in the industrial hydrogenation of fats and oils. The main reason for this is the good activity of the ordinary nickel catalysts. There is little practical advantage to increasing this activity. Also, promoters can be incorporated only with difficulty in at least one of the catalyst preparations commonly employed.

While mixtures of nickel with other metals or their oxides are used to a limited extent as promoted catalysts in the industrial hydrogenation of fats and oils, there are numerous descriptions of such promoted catalysts in the literature. Some of these descriptions are worthy of mention. Some mixtures of nickel with other metals or metal oxides have been used or have been suggested for use because of certain desirable properties other than promoter action.

It has been stated that aluminum oxide is a useful promoter for precipitated nickel catalysts[11, 30, 36]. The oxide can be incorporated in the required form by adding a minor proportion of an aluminum salt to a nickel nitrate solution before the latter is treated with a solution of sodium carbonate or other alkali. Reduction then is carried out in the usual manner.

The mode of operation of the aluminum oxide differs from that of diatomaceous earth. The latter provides an extended surface area and isolates the metallic nickel in pores or interstices[53]. On the other hand, the aluminum oxide forms stable oxides with the nickel, which are reduced only slowly and permit the formation of large numbers of reduction nuclei[28].

In the patent literature it has been stated that nickel catalysts can be promoted by chromium, cobalt, thorium, zirconium, copper, or their oxides, as well as by platinum and palladium[26, 54]. A number of other metals or their salts and oxides have also been mentioned. However, in many instances the claims which were made have not been clearly proven or substantiated by other investigators.

Some commercial use has been made of catalysts consisting of nickel and copper. Their most desirable characteristic is ease of preparation. When nickel and copper are coprecipitated in the form of their oxides, hydroxides, or carbonates, the resulting mixtures can be reduced at a relatively low temperature and directly in the oil to be hydrogenated, if desired[26]. Armstrong and Hilditch[6] have reported that compounds of nickel and copper distributed on suitable carriers can be reduced at 180°C, whereas nickel compounds alone under similar conditions are not reduced by hydrogen below 300°C and not rapidly below 350 to 400°C. For the reduction of nickel at this low temperature an intimate mixture of the nickel and copper compounds is necessary; that is, they are coprecipitated from a solution of their salts. However, even coprecipitation does not always produce the necessary degree of intimacy. It was suggested that the local heat needed to provide a sufficiently high temperature for the reduction of the nickel is furnished by the reduction of the copper, provided the latter is in sufficiently close proximity to the nickel.

Recently it has been claimed that mixtures of nickel and oxides of silica and aluminum can be employed to simultaneously hydrogenate and decolorize oils[61]. Such mixtures are prepared by treating aqueous solutions containing nickel and aluminum salts with an aqueous solution of an alkali metal silicate and then with a solution of an alkali bicarbonate, followed by filtering, washing, and drying. The catalyst is reduced and employed in the usual manner.

CATALYSTS OTHER THAN NICKEL

As mentioned earlier, catalysts other than those composed primarily or wholly of nickel are not used for the plant-scale hydrogenation of oils. Nevertheless, some non-nickel catalysts have been used extensively in laboratory experiments with fats and oils and continue to be of importance in the laboratory.

The earliest disclosures that oils could be hydrogenated in the liquid phase mentioned not only nickel but also copper, platinum, and palladium as catalysts for the reaction[35, 57]. Other metals have been mentioned subsequently. Iridium, rhodium, ruthenium, and osmium have been specified in a French patent[92]. Kahlenberg and Ritter[46] demonstrated that cobalt and bismuth possess a fair amount of catalytic activity while zinc and iron possess some. A British patent[43] claims that a number of metals including gold, tin, silver, lead, and thallium are catalysts for oils when reduced from their salt solutions by silicon-oxygen compounds of a lower degree of oxidation than silicon dioxide.

Some of the metals mentioned apparently possess little activity when used with fats and oils. Indeed, it appears that in a few instances evidence of their activity amounts to little more than a claim in a patent specification.

The metals (other than nickel) which are used in laboratory experiments are generally platinum and palladium. Both can be converted by a variety of methods into catalysts of either the supported or nonsupported type[30]. Only two of the better preparations will be described here.

The preparation of a platinum catalyst by the method of Adams and coworkers[2, 3, 94] consists of a simple reaction between chloroplatinic acid and sodium nitrate, followed by fusion of the reaction product and washing of the catalyst with water. The following reactions are involved:

$$H_2PtCl_6 + 6NaNO_3 \rightarrow Pt(NO_3)_4 + 6NaCl + 2HNO_3 \qquad (8)$$

$$Pt(NO_3)_4 \rightarrow PtO_2 + 4NO_2 + O_2 \qquad (9)$$

$$PtO_2 + H_2O \rightarrow PtO_2 \cdot H_2O \qquad (10)$$

According to one of their detailed procedures for preparing the catalyst, 35 grams of chemically pure sodium nitrate is added to 3.5 grams of chemically pure chloroplatinic acid in 10 ml of water. The mixture is evaporated to dryness by gentle heating over a gas flame while being stirred with a glass rod. Then while stirring is continued, the temperature is increased fairly rapidly to 350 to 370°C at which temperature fusion starts. The temperature is gradually increased to 500 to 550°C in the course of 20 minutes and held at this temperature for an additional 30 minutes. Then the mass is cooled, treated with 50 ml of water and finally washed with water until practically free of nitrates. After being dried, the final platinum oxide is added directly to the oil to be hydrogenated.

Platinum oxide is not reduced with hydrogen before being added to an oil. The reduction to platinum black occurs readily in the oil-catalyst mixture. When such a mixture is stirred and hydrogen is introduced, the brown oxide becomes black and disperses into a fine suspension. Usually after completion of the hydrogenation the platinum black tends to coagulate and drop out of suspension.

The preparation of an active palladium catalyst supported on charcoal has been described by Mannich and Thiele[51]. To a solution of palladium chloride (preferably 2 per cent) there is added some ignited animal charcoal and the mixture is agitated while hydrogen is introduced and the following reaction occurs:

$$PdCl_2 + H_2 \rightarrow \underline{Pd} + 2HCl \qquad (11)$$

When no more gas is absorbed, the powder is washed with water and then dried, after which it can be kept unaltered.

It was claimed that this palladium catalyst will hydrogenate the common oils to an iodine value of a few tenths when used at a temperature of 100°C and atmospheric pressure. An example was given to show an oil could be hydrogenated even when the weight ratio of metal to oil was 1:150,000.

CHARACTERISTICS OF VARIOUS CATALYSTS

Nickel Formate. One of the main advantages of catalyst from nickel formate is its ease of preparation—the salt is simply heated in the oil to be hydrogenated. The need for a dry-reduction furnace and the attendant hazards of handling a pyrophoric material admixed with hydrogen are eliminated.

The catalyst also has other advantages. Its activity is reasonably uniform and compares favorably with that of the other nickel catalysts used with oils. The selectivity is good; *i.e.*, the catalyst possesses a marked tendency to hydrogenate preferentially the more unsaturated components of an oil. Also, the formation of isomers during hydrogenation is not excessive.

Petryaev[64] on comparing a catalyst made by reducing nickel formate in oil at 240°C with one obtained by dry-reduction of nickel carbonate precipitated on diatomaceous earth, found that the latter was affected considerably by the presence of soap and albuminous, mucilaginous, and pectic substances, while the former was affected but little. On this basis it can be said that the nickel formate produces a relatively rugged catalyst.

The main disadvantage of the nickel formate catalyst is that it forms metallic particles of colloidal or near-colloidal size, even when close attention is paid to the details of preparation. Some of these particles pass through the filter paper and bed of filter aid used to filter the hydrogenated oil and impart a dark cast to the finished product. Subsequent treatment with bleaching clay or other adsorbent is necessary.

Certain precautions should be exercised in the preparation and use of the nickel formate catalyst. They are: adequate washing of the formate with cold water when the formate is prepared by metathesis between nickel sulfate and sodium formate, adequate stripping of the formate-oil mixture with hydrogen during reduction, and replacing of the oil used during reduction with fresh oil so as to remove, insofar as possible, any catalyst poisons formed through degradation of the oil at the high temperatures used in the reduction.

Raney Nickel. From a physical-chemical standpoint Raney nickel is prepared under almost ideal conditions. As Taylor and Weiss[81] have pointed out, the reaction of sodium hydroxide with a nickel-aluminum alloy to remove the aluminum leaves highly defective crystallites of nickel having a very large surface. These defective crystallites are maintained largely intact because the temperatures employed in the processing are low enough to prevent sintering. Empirically the onset of sintering of a normal crystalline solid can be associated with a temperature somewhere between the surface Tammann temperature (0.3 × melting point, °K) and the Tammann temperature of the bulk (0.5 × melting point, °K)[13]. Therefore, with metallic nickel, lattice mobility or regrouping of the active nickel atoms can be expected at about 250°C, which is well above the temperature used in the preparation of Raney nickel.

It has been pointed out that the operating conditions used in the preparation of Raney nickel do have some effect on its activity. Adkins and Billica[4] have shown that the activity is increased when the reaction between the sodium hydroxide and the aluminum alloy is carried out at a low temperature, the reaction time is short, air is excluded insofar as possible, and the finished catalyst is washed thoroughly (countercurrently) with water stored under hydrogen. It is not necessary that all of the aluminum be removed by the alkali treatment. Indeed, 20 per cent or more of aluminum does not appear to have much effect on the activity. Generally, the aluminum content is about 1 to 3 per cent and is believed to be in the form NiAl.

Raney nickel catalyst prepared from the standard alloy loses a sizable proportion of its activity on storage. Highly active preparations may lose as much as half of their activity on storage under alcohol for 20 days[78]. According to the data of Pattison and Degering[59] as much as 75 per cent of the activity can be lost on storage for 10 days under hydrogenated cottonseed oil if air is allowed to come in contact with the oil, but no activity is lost if air is excluded.

Several investigators have claimed Raney nickel to be more active than other types of nickel catalysts but not as active as those from platinum and palladium, which is probably correct when several per cent or more of Raney nickel is used in a hydrogenation. When activities are compared at concentrations of 0.05 to 0.10 per cent nickel, the concentrations used in the commercial hydrogenations of oils, Raney nickel is not nearly as active as are supported nickel catalysts[9]. The ratio of surface area to weight of nickel is of course much higher for the latter.

Nickel Sulfate. As mentioned earlier, close attention to details is required to produce a good catalyst of the dry-reduced, supported type by precipitating nickel as the basic carbonate or hydroxide from its sulfate solution. Unavoidable occlusion of at least some basic sulfates, which later become catalyst poisons, is one of the difficulties. Precautions, like the use of hot, dilute solutions of nickel sulfate, are taken to minimize occlusion. Without these precautions the amount of sulfate in the precipitate can be large. For example, if $2N$ solutions of nickel sulfate and sodium hydroxide are simply mixed in approximately equivalent quantities and the resulting precipitate very thoroughly washed with distilled water to the point that peptization causes difficulty, the dried product may contain over 3 per cent of sulfate retained as insoluble basic sulfates and adsorbed or occluded salts. For an inactive catalyst to be poisoned completely only 0.5 to 1.0 gram of sulfur per 100 grams of nickel is needed, while for an active catalyst 3.0 to 5.0 grams is needed[8].

Growth of the precipitated crystallites of basic nickel carbonates or hydroxide, either during the actual precipitation or during the subsequent washing operation is another factor which reduces the activity of the finished catalyst. Excessive crystal growth is more easily avoided when carbonates and bicarbonates are used as precipitants instead of hydroxides. However, catalysts made with the carbonates or bicarbonates can be damaged extensively or ruined completely if washing is prolonged or the basic nickel carbonates are stored in the wet state.

When nickel hydroxide is precipitated from an alkaline sulfate solution, crystallites of colloidal dimensions (less than 20 Å) are formed. To preserve these crystallites, alkali may be added to the first wash waters while the bulk of the sulfate ion is being removed. The alkali serves the double purpose of reducing the solubility of the nickel hydroxide and keeping it dispersed through adsorption of its ions on the surface of the crystallites. Subsequently, all excess alkali must be removed to prevent its poisoning the finished catalyst.

The nature of the diatomaceous earth or siliceous material used as support is claimed to have an effect on the activity of the finished catalyst. Catravas[23] prepared catalysts using two types of diatomaceous earth, one consisted essentially of disks perforated by pores of different diameters and hence possessed a relatively large surface area, while the other consisted essentially of smooth spheroidal particles without perforations and hence possessed a smaller surface area. The catalyst supported on the diatomaceous earth having the larger surface area hydrogenated peanut oil at an appreciably faster rate even though in both cases a portion of the nickel was not supported but was in the form of independent clusters of particles.

It is generally assumed that the function of a siliceous support is merely to extend the surface area of a given quantity of nickel, the precipitated hydroxide or basic carbonates tending to form a thin film on the siliceous surface which results in minute, isolated patches of nickel crystals on reduction. The crystals of nickel and nickel oxide present in supported catalyst are said to show their usual lattice parameters on x-ray examination, and in one preparation the linear dimensions of the nickel and nickel oxide particles were approximately 330 and 160 Å, respectively[73]. However, some evidence has been presented[91, 93] that, at least to some extent, a siliceous support may be involved chemically. In the precipitation of nickel hydroxide by the addition of sodium hydroxide to a mixture of a solution of nickel salt and diatomaceous earth, there is formed, as appears from x-ray investigations, a nickel hydrosilicate, which on reduction produces nickel atoms surrounded by silicate residues.

The use of a support for nickel compounds which are to be reduced at elevated temperatures has the advantage of permitting a higher reduction temperature—up to about 500°C. Without a support reduction temperatures would be limited to about 250°C, above which extensive sintering occurs, the specific area tends to approach the geometric area, and loss of activity results. However, even though a supported catalyst is relatively rugged, the temperature and the length of the reduction time should not be greater than required to obtain good activity. On the basis of this consideration the basic nickel carbonates have some advantage over the hydroxide because they reduce at a lower temperature.

Supported nickel catalysts possess other characteristics which contribute to their ruggedness. Raney[68] has pointed out that of the total nickel and nickel compounds in some good reduced catalysts one-third may be metallic nickel while the other two-thirds consists of various nickel oxides. This proportion does not always remain constant during the life of the catalyst. Under some conditions of use, reduction of the oxides continues until the proportions in the spent catalyst may actually be reversed. Thus new catalyst may constantly be formed during the hydrogenation of an oil. Raney's observations may serve to explain statements made by a few investigators that some supported nickel catalysts are not highly pyrophoric.

A patent has been issued[31] for a supported type catalyst which is stable in air. It is prepared by heating in air at 400°C a mixture of basic nickel carbonates precipitated on diatomaceous earth, followed by reduction with hydrogen at 400°C and then oxidation in air at 150°C to produce Ni_2O_4. The mixture is flushed with nitrogen or carbon dioxide between each operation. Probably precautions also are taken to carry out the final oxidation at a slow rate to prevent sintering. It is claimed that the catalyst will hydrogenate fats and oils.

When compared with other nickel catalysts, those prepared by dry reduction of basic nickel carbonates or the hydroxide can be as active as any, though there is the possibility of the activity and other characteristics varying from one preparation to the next. Their selectivity is about average, but their tendency to produce geometrical and positional isomers of the fatty acids normally combined in oils is marked. These catalysts, unlike that made from nickel formate, can be removed cleanly from a hydrogenated oil by simple filtration.

Electrically Precipitated Nickel. Much of what has been said about catalysts from nickel sulfate applies to catalysts obtained by way of electrolytic precipitation of nickel hydroxide on diatomaceous earth. The latter does have some special advantages: chiefly it can be prepared with a high degree of uniformity and there is no possibility of its containing occluded basic sulfates which will act as a poison and also produce relatively large proportions of isomers in hydrogenated oils. Electrolytically precipitated nickel hydroxide is, of course, relatively free of undesirable impurities.

Anodic corrosion of nickel in an alkaline medium produces colloidal nickel hydroxide, the characteristics of which are affected by the pH. For a good catalyst the pH must be kept between 9.0 and 9.5. Below this level it will be inactive and in addition will be hard to filter. Apparently there is little tendency for the crystallites of nickel hydroxide to grow in size during their preparation, which can be carried out over a period of 8 hours or more. The hydroxyl ions in the solution reduce the solubility of the nickel hydroxide in accordance with the solubility product law and probably also stabilize the crystallites by being adsorbed on their surfaces. While the author has never had any difficulty with the growth of nickel hydroxide crystals during washing and drying of the unreduced catalyst, these operations should be performed as rapidly as possible.

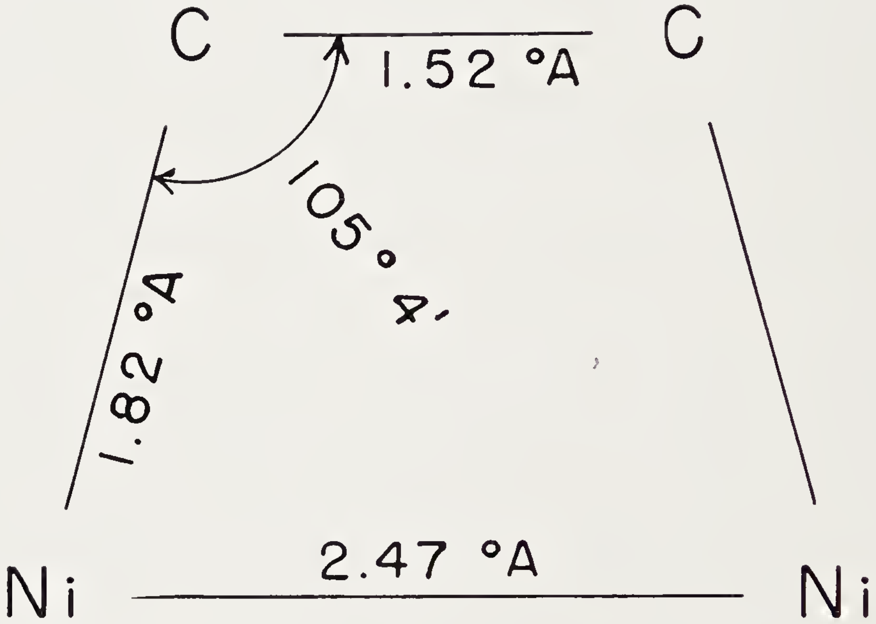

Figure 1. Interatomic distances and valence angle for C═C adsorbed on nickel.

Reduction of the supported nickel hydroxide can be performed over a rather wide temperature range (370 to 480°C) without reducing the activity of the finished product, provided the weight ratio of nickel to support is not greater than 1:1. Higher ratios will present problems in reduction.

Platinum and Palladium. For the hydrogenation of fats and oils platinum and palladium yield the most active catalysts known. Of the two, palladium possesses the greater activity. Hydrogenation of cottonseed oil can be effected with platinum catalyst at a concentration of 0.05 per cent when atmospheric pressure and a temperature of 40°C are used[71]. To measure the degree of unsaturation of an oil, analytical hydrogenations are frequently made in the laboratory at atmospheric pressure and temperatures below 60°C. Under these conditions the hydrogenations readily go to completion.

Twigg and Rideal[85] have correlated the catalytic activity of various metals with their interatomic distances. Using the distances 2.47 Å for Ni—Ni, 1.52 Å for C—C, and 1.82 Å for C—Ni, they showed that for adsorption of the C—C group the valence angle for the bond would have to be 105°′ 4 (Figure 1), which is considerably less than the tetrahedral angle 109° 28′. For the valence angle of the bond to equal the tetrahedral angle the interatomic distance for the metal would have to be 2.73 Å. Significantly, the interatomic distances for platinum and palladium are 2.76 and 2.74 Å, respectively. They should fit the C—C group without appreciable strain and probably are very good catalysts for that reason.

For a number of other good reasons platinum and palladium are not used for the hydrogenation of fats and oils, except in the laboratory. A most important consideration is that they are much more expensive than is nickel. Also, they are relatively unselective. Because all unsaturated bonds which are adsorbed are apparently hydrogenated with relatively equal facility, there is no marked preferential hydrogenation of the more unsaturated components of an oil. Finally, the noble metal catalysts are said to become poisoned easily.

Behavior of the Components of an Oil During Hydrogenation

The course of the catalytic hydrogenation of the ethylenic linkages in oils depends upon a complex interplay of a number of factors. The relative reactivity of a given ethylenic linkage is affected not only by its position in an acyl group and its proximity to other ethylenic linkages in the same group but also by the amount and type of catalyst and other operating conditions. Very frequently a given linkage does not undergo a straightforward reduction, but rather the first reaction is a shift to a new position or a rearrangement of the geometric form or both. To better elucidate the course of the hydrogenation reaction and the various side reactions involved, the reactions occurring in individual acyl groups will be described first. Then a description of the behavior of mixtures of acyl groups, such as occur in natural fats, will be undertaken.

Reactions of Individual Acyl Groups

Oleoyl Group.* Glycerides of normal oleic or *cis*-9-octadecenoic acid are widely distributed in nature and hence this fatty acid group represents

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* The terms methyl oleate, oleoyl group, etc., will be used in the general sense and will refer to any octadecenoic acid group and its esters unless indicated otherwise, either specifically or by context. Other common names like linoleate and linolenate will be used in an analogous manner. The term normal will be employed to indicate the use of a common name in its strict sense; thus normal oleic acid will indicate *cis*-9-octadecenoic acid.

not only one of the simplest involved in the hydrogenation of oils but also one of the two or three most frequently encountered. Its behavior during hydrogenation can be regarded as representative of all monoethenoid fatty acids occurring in oils.

Simple reduction of the oleic acid group to a stearic acid group is for all practical purposes an irreversible reaction. Thermodynamically this can be predicted on the basis of free energy of formation values for the normal paraffins and normal olefins[32]. According to these values dehydrogenation can occur only at temperatures well above 400°C. Before these temperatures are reached, other types of decomposition occur. A number of unsuccessful attempts to dehydrogenate saturated fatty acids with the aid of hydrogenation catalysts have been reported.

During the hydrogenation of oleic acid or its esters a sizable proportion of isomers of the acid or acid group are produced. These isomers are a by-product of the hydrogenation reaction and cannot be produced by simply heating oil and catalyst in the absence of hydrogen.

While it has been known for many years[48] that the reduction of oleic acid yields so called iso-oleic acids, their identity has still not been fully established. Relatively few investigators have concerned themselves with this particular aspect of hydrogenation. When the term "iso-oleic acids" is used in the literature, it usually refers to the high-melting, monoethenoid acids (usually derived from polyunsaturated fatty acids combined in the original oil) which appear with the saturated acids in the conventional lead soap separation employed in the determination of fatty acid composition.

Generally, determination of the positional isomers of the oleoyl group formed during the hydrogenation of esters of oleic acid has been confined to a qualitative establishment of the presence of one or two of them through examination of the high-melting, iso-oleic acids obtained from the hydrogenation product. Thus Moore[55], employing an ozone oxidation of the high-melting iso-oleic acids, came to the conclusion that a shift of the double bond from the 9-carbon to the 11- and possibly 10-carbon occurred. Hilditch and Vidyarthi[40] on hydrogenating methyl oleate using a nickel catalyst concluded that the shifts were to the 8- and 10-carbon. Benedict and Daubert[12] identified the *trans*-8-octadecenoic acid group as one of those formed during the hydrogenation of triolein with a Raney nickel catalyst.

Unlike earlier investigators, Boelhouwer and his co-workers[16] made a quantitative analysis of the positions of all of the double bonds in methyl oleate partially hydrogenated with the aid of a supported nickel catalyst. Their analytical procedure involved a potassium permanganate oxidation in acetic acid solution followed by chromatographic analysis of the resulting dicarboxylic acid mixtures. They found (Table 1) that migration of the double bond toward the ester group was limited to a shift of one position and was relatively small in amount. Migration toward the free end of the fatty acid chain was much more extensive in amount and involved shifts of at least three positions. Similar results obtained with methyl elaidate indicate that the original geometrical configuration of the double bond had no significant effect on the direction or amount of shift. In all probability the shifts toward the free end of the chain were more extensive than indicated by the analyses because it has been observed that in the hydrogenation of octadecenoic acids the highest rate occurs when the bond is farthest removed from the carboxyl group[65].

TABLE 1. DISPLACEMENT OF DOUBLE BONDS DURING HYDROGENATION OF METHYL OLEATE AND ELAIDATE[66, a]

Ester	Reaction Time (min.)	Iodine Value	Positional Distribution of Double Bond in Fatty Acid Group (%)					
			7:8	8:9	9:10	10:11	11:12	12.13[b]
Methyl oleate	0	85.0	—	5[c]	95	—	—	—
Methyl oleate	20	55.2	—	20	35	27	11	7
Methyl oleate	37	30.2	—	21	26	21	15	17
Methyl elaidate	0	87.8	—	2[c]	98			
Methyl elaidate	15	52.0	—	19	50	22	7	2
Methyl elaidate	30	25.7	—	17	32	25	13	13

[a] Catalyst concentration, 3 per cent nickel; temperature, 170–180°C; hydrogen pressure, atmospheric.

[b] And higher.

[c] There were no 8:9 double bonds in the starting materials. These values indicate the accuracy of the method.

As mentioned above, the formation of *trans* isomers during the hydrogenation of esters of oleic acid is a recognized fact of long standing. Moore[55] examined samples of ethyl oleate after partial hydrogenation in the presence of palladium and nickel catalysts. He concluded that as hydrogenation progressed an equilibrium was eventually reached such that the ratio of liquid oleic acid and solid iso-oleic acids obtained from the reaction product was about 10:15. Among the solid iso-oleic acids he identified elaidic acid. Mazume[52] investigated the hydrogenation of methyl oleate and concluded that a large amount of the combined oleic acid was converted to iso-oleic acid at the initial stage of hydrogenation and the iso-oleic acid thus formed was gradually transformed into oleic acid on further hydrogenation. Others determined the extent of *trans* isomer formation during the hydrogenation of oleic acid or its esters; but because of inadequate methods of analysis, never established the true facts.

In 1950 Swern and co-workers[30] described an infrared spectrophotometric method for the determination of *trans*-octadecenoic acids and esters in the presence of *cis*-octadecenoic and saturated acids and esters. This new technique, which is much more reliable than any heretofore available, was used by Feuge *et al.*[34] to follow the course of hydrogenation of methyl oleate and triolein.

According to the infrared method of analysis, *trans* isomers do form at a rapid rate during the initial stages of the hydrogenation of methyl oleate and triolein. The exact rate depends in some measure on the conditions employed, as is evident from the data for methyl oleate shown in Figure 2. The rate of formation of *trans* isomers in methyl oleate was found to increase as the temperature and catalyst concentrations increased and the degree of hydrogen dispersion decreased. Under identical operating conditions *trans* isomers formed at a slower rate with triolein than with methyl oleate. At the highest rate observed for the methyl oleate 38 per cent of *trans* isomers formed while the first 10 per cent of methyl stearate formed.

Examination of Figure 2 reveals that as hydrogenation of the methyl oleate progressed the ratio of *trans* to *cis* isomers came to an equilibrium which was unaffected by the temperature. From the slope of the straight line representing the later stages of hydrogenation it is evident that this equilibrium ratio of *trans* to *cis* isomers is 2:1, which is the same as that obtained on elaidinization of methyl oleate with selenium or oxides of nitrogen.

Linoleoyl Group. The double bonds in the linoleoyl group can shift during hydrogenation in the same manner that the double bond shifts in the oleoyl group. However, for the double bonds in the normal linoleoyl group, that is, the *cis*-9,*cis*-12-octadecadienoic acid group, the amount of shifting may not be as extensive under the operating conditions normally employed. This group is hydrogenated more readily than is the oleoyl group, and the probability of desorption from the catalyst without hydrogenation of one of the double bonds occurring is less. Also, a small amount of shifting of the two double bonds is likely to form a conjugated system which is regarded as being relatively resistant to further shifting. Some shifting of double bonds to relatively widely separated positions does seem to occur[24].

While the distance that the double bonds in the linoleoyl groups shift is probably limited under most conditions, a large proportion can shift by at least one carbon atom. The reason that large proportions of conjugated isomers of the linoleic acid group are seldom found on hydrogenating esters of normal linoleic acid is that the conjugated isomers are relatively reactive and are reduced about as rapidly as they are formed. Feuge and co-workers verified these facts by analyzing data on the hydrogenation of methyl linoleate[33]. The results obtained are recorded in Table 2.

A large amount of data is available showing that only one of the double bonds of the normal linoleoyl group is hydrogenated at a time. It is generally believed that the bond farthest removed from the ester linkage tends to be reduced first. Suzuki and Inoue[79] found that hydrogenating one mole of normal methyl linoleate with one mole of hydrogen produced oleates having the double bond in the 9:10 position. Similar experiments with isolinoleic acid[44] also showed that the bond farthest removed from the ester linkage was hydrogenated first. Reduction of the 12:13 bond in the normal linoleoyl group appears to be always accompanied by at least a minor amount of reduction of the 9:10 double bond[90] to produce an oleoyl group. Under certain conditions either the proportion of the 9:10 double bond being reduced first is extensive or extensive shifting of this bond occurs on reduction of the original 12:13 bond. Boelhouwer *et al.*[16] presented data on the hydrogenation of methyl linoleate from which it is evident that on hydrogenation to an iodine value of 96.0 (original iodine value 174.0) the double bonds in 71 per cent of the remaining unsaturated fatty acid groups were at the 11-carbon or higher.

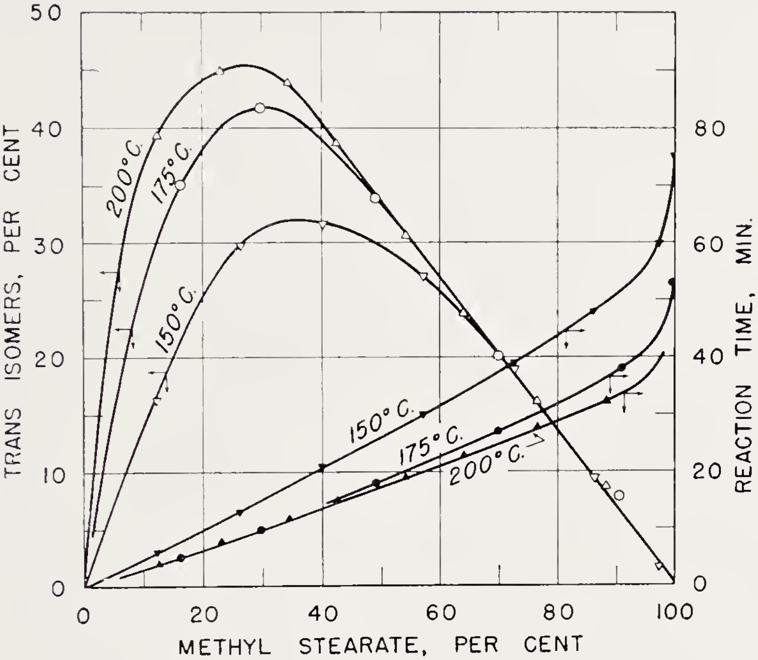

Figure 2. Effect of temperature on the formation of *trans* isomers (calculated as methyl elaidate) during the hydrogenation of methyl oleate at atmospheric pressure with 0.25 per cent nickel and good dispersion of hydrogen. Catalyst was of the supported, dry-reduced type prepared by electrolytic precipitation.

Partial hydrogenation of the normal linoleoyl group produces relatively large proportions of high-melting iso-oleic acid groups early in the course of the reaction[87, 99]. Possibly some are positional isomers of the *cis*-9 oleic acid group produced either by hydrogenation of the 9:10 double bond of the normal linoleic acid group or the wandering of the double bond in the oleic acid group which is produced during hydrogenation. It is generally assumed that the high-melting, iso-oleic acids are geometrical isomers of *cis*-oleic acids; that is, they possess the *trans* configuration. The latter assumption is supported by the fact that as a group the trans isomers of 6- through 12-oleic acid possess melting points appreciably above those for the corresponding *cis* isomers[41]. By the newly developed infrared spectrophotometric technique mentioned above it has been shown quantitatively how early and at what rate *trans* isomers can form during the hydrogenation of methyl linoleate[33], Figure 3.

TABLE 2. RELATIVE REACTION RATES IN THE HYDROGENATION OF METHYL LINOLEATE AND FRACTION OF ORIGINAL LINOLEATE UNDERGOING CONJUGATION

Run No.	Condition[a]	Fraction of Nonconjugated Linoleate to Conjugated Linoleate	Relative Reaction Rate		
			Nonconjugated Linoleate to Oleate	Nonconjugated Linoleate to Conjugated Linoleate	Conjugated Linoleate to Oleate
1	150°C, 0.25 per cent Ni, good hydrogen dispersion	0.05	1	0.06	3.7
2	200°C, 0.25 per cent Ni, good hydrogen dispersion	0.60	1	1.5	7.5
3	200°C, 0.25 per cent Ni, poor hydrogen dispersion	0.77	1	3.3	8.7
4	200°C, 0.05 per cent Ni, good hydrogen dispersion	0.34	1	0.52	6.0

[a] All hydrogenations conducted at atmospheric pressure using dry-reduced, supported catalyst prepared by way of electrolytic precipitation of $Ni(OH)_2$.

It is evident from Figure 3 that in these hydrogenations of methyl linoleate the amount of nonconjugated *trans* isomers formed in the early stages of the hydrogenation was directly proportional to the amount of reduction, the exact ratio of the proportion depending upon the hydrogenation conditions. In one case (Run 3) 80 per cent of *trans* isomers were produced by the time the iodine value was reduced to 80 and the last portions of the linoleoyl group had just about disappeared. It must be concluded that the initial formation of nonconjugated *trans* isomers observed during the early stages in the hydrogenation of methyl linoleate is mainly the result of hydrogenating one double bond of the methyl linoleate and simultaneously converting the remaining double bond to the *trans* form and that this occurs in a fixed percentage of the total number of molecules of linoleate undergoing hydrogenation.

Evidence has been obtained that the nonconjugated *trans* isomers formed during the hydrogenation of methyl linoleate are not equally reactive[71]. In the later stages of hydrogenation when only isomers of the oleoyl group are present the ratio of *trans* to *cis* isomers does not become 2:1, like it does during the hydrogenation of the normal oleoyl group. Instead, a higher ratio is obtained, indicating that some of the *trans* isomers obtained from the methyl linoleate are effectively removed from further reaction until the very late stages.

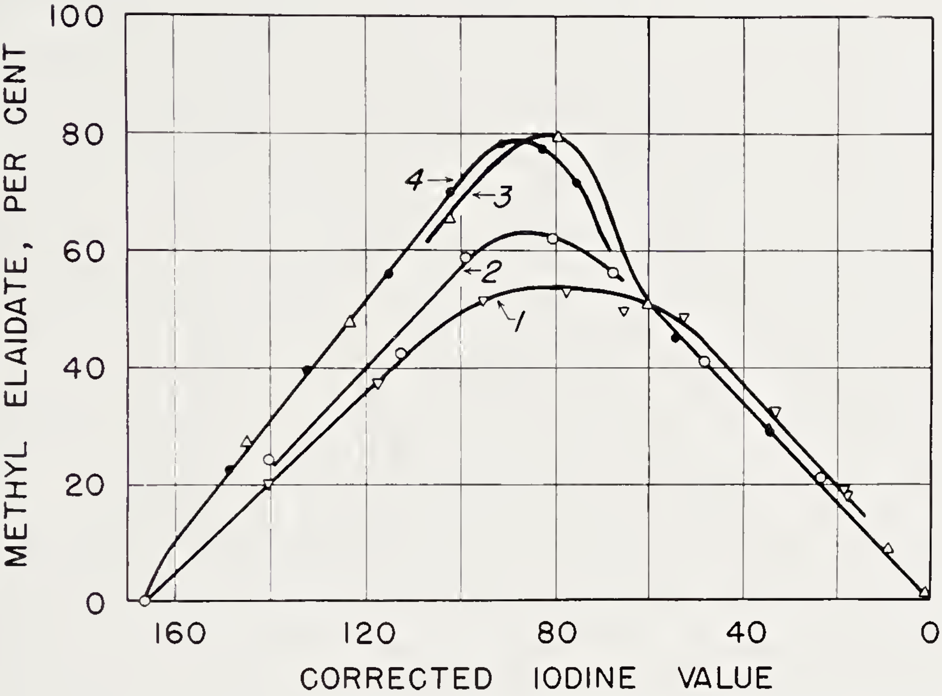

Figure 3. Content of nonconjugated *trans* isomers, as methyl elaidate, *vs*. corrected iodine value for progressively hydrogenated methyl linoleate. Curve numbers refer to hydrogenation runs listed in Table 2.

Linolenoyl Group. The normal linolenoyl or *cis*-9,*cis*-12,*cis*-15-octadecatrienoic acid group can undergo stepwise reduction in several ways and not all of the reports concerning this reduction are in agreement as to which of the double bonds is the most reactive. As Rebello and Daubert[69] have pointed out, 15 positionally isomeric linoleic acids, in which the double bonds are separated by more than one methylene group, are possible on saturation of one double bond of the normal linolenoyl group, accompanied by a shift of one or both of the remaining two unsaturated bonds by one carbon atom. It is not surprising that the course of reduction of the linolenoyl group is not yet fully understood.

Most of the later investigators agree that a sizable proportion of the reduction occurs first at the middle double bond[7, 10, 47, 69, 90]. Bailey and Fisher[10] found in experiments with glycerides that as much as 65 per cent of the hydrogen used in the first stage reduction may go to the middle bond. Bailey and Fisher also found that, unlike the reduction of the linoleoyl group, a single adsorption of the linolenoyl group on the catalyst can result to some extent to a reduction directly to an oleoyl group.

On analyzing partially hydrogenated methyl linolenate, Rebello and Daubert[69] found among the combined fatty acids the 8,14-, 9,15-, and 10,14-isolinoleic acids. The infrared absorption spectrum of these isolinoleic acids indicated the presence of a *trans* bond. It was assumed that the acids were formed by the preferential hydrogenation of the 12:13- or middle bond and that some shifting of the 9:10- and 15:16-bond occurred with simultaneous formation of at least some trans configuration.

Van der Veen[90] hydrogenated methyl linolenate at 180°C using a supported nickel catalyst and demonstrated the formation of 9,15- and 10,14-linoleic acid groups. These groups were considered as having been obtained by the preferential saturation of the 12:13- or middle bond and a partial shift of the 9:10- and 15:16-bond.

Eleostearic or 9,11,13-octadecatrienoic acid, which may be regarded as a conjugated isomer of linolenic acid, is the primary fatty acid combined in tung oil, and as such hydrogenation of its esters has been investigated by a number of workers. Unfortunately, the methods used for analyzing the reaction products have been largely inadequate. Until recently the *cis-trans* configuration of eleostearic acid itself was not known with any degree of certainty. The natural or alpha-eleostearic acid is believed to be the 9-*cis*,11-*trans*,13-*trans*-octadecatrienoic acid[14, 58].

Boeseken[17] and others of the earlier investigators believed partial hydrogenation first reduced the bond farthest removed from the ester linkage and that the two remaining bonds shifted to a new conjugated position farther out on the carbon chain. After hydrogenation of the second double bond, the one remaining was believed to be in the 11-position. Regardless of the mode of formation, 11-oleic acid has been obtained by several investigators in major proportions from hydrogenated tung oil.

Hilditch and Pathak[39] hydrogenated methyl eleostearate and examined the reaction products spectrophotometrically. They concluded that the primary action is the simultaneous addition of two moles of hydrogen to one mole of the ester to form very large proportions of 11-oleic acid esters.

Planck *et al.*[66] progressively hydrogenated tung oil at 170°C and a hydrogen pressure of 5 pounds per square inch gage, using 0.1 per cent of nickel supported on diatomaceous earth. Examination of the reaction products by what they considered to be an improved spectrophotometric technique showed a maximum of about 13 per cent of diene conjugated esters was obtained, at which point the hydrogen iodine value was 140.1 and the content of monoethenoid esters was about 48 per cent. These values appear to be in agreement with the mechanism of reduction suggested by Hilditch and Pathak, though there is a possibility that large concentrations of conjugated diene never accumulated because of their relatively high activity.

Relative Rates of Reaction of Acyl Groups

Much of the literature on the catalytic hydrogenation of fats and oils is concerned with the selectivity of the reaction, which simply means the preferential saturation of the more highly unsaturated components. That the various types of unsaturated acyl groups in fats and oils hydrogenate at different rates apparently was first discovered by Bömer[18]. Shortly afterward Burchenal[21] discovered that the selectivity could be controlled. Since then a number of extensive investigations have been reported including those of Moore, Richter, and Van Arsdel[56]; Richardson, Knuth, and Milligan[70]; Dhingra, Hilditch, and Rhead[27]; and Bailey, Feuge, and Smith[9]. It is now recognized that the hydrogenation reaction is inherently quite selective but that the selectivity is never perfect. An indication of the course of the reaction and the degree of selectivity which can be attained on hydrogenating soybean and linseed oils under conditions such as might be used in commercial practice is given in Figures 4 and 5, which present data obtained by Bailey and Fisher[10].

The hydrogenations represented in Figures 4 and 5 were carried out under selective conditions. A temperature of 350°F (177°C), a hydrogen pressure of 15 pounds per square inch gage, a moderate degree of agitation, and 0.1 per cent of nickel (electrolytically precipitated and dry reduced) was employed with the soybean oil. For the linseed oil, Figure 5, identical conditions were employed, except that the temperature was 375°F (190°C) instead of 350°F (177°C). The hydrogenator used had a capacity of about two gallons[9].

In Figures 4 and 5 the term "isolinoleic" refers to linoleic acid in which the double bonds are separated by more than one methylene group.

From data obtained by Bailey and Fisher[10], Bailey[7] recalculated the relative reaction rates for the component fatty acids of cottonseed and linseed oils hydrogenated under both selective and nonselective conditions. The rates obtained are reproduced in Table 3. In calculating these rates it was assumed that in the case of a number of different fatty acids existing together as glycerides and competing for hydrogen the fraction going to each acid for an infinitesimal amount of hydrogen absorbed will depend upon the concentration of the acid and a constant expressive of the affinity of the acid for hydrogen under the particular conditions of hydrogenation then obtaining.

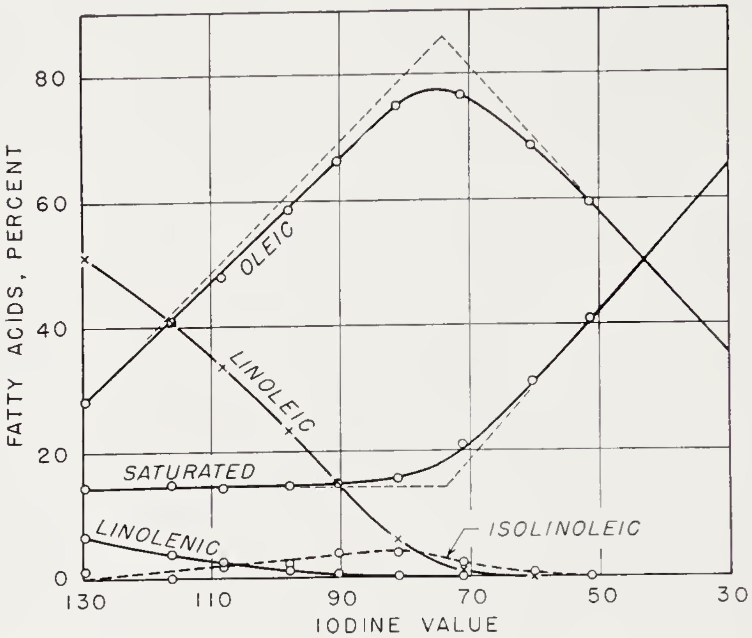

Figure 4. Fatty acid composition of selectively hydrogenated soybean oil.

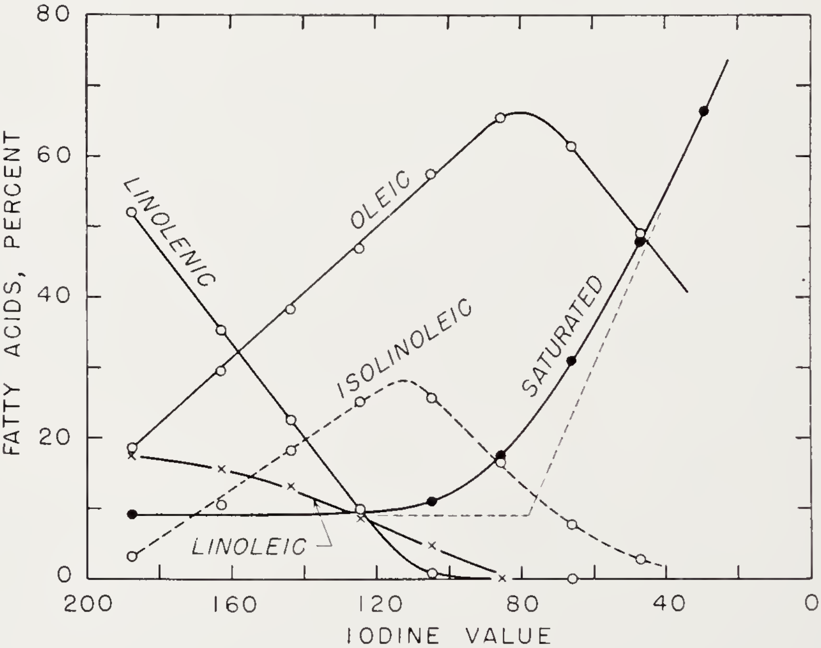

Figure 5. Fatty acid composition of selectively hydrogenated linseed oil.

Examination of the data in Table 3 reveals that changing the hydrogenation conditions so as to change greatly the relative reactivities of the oleic and linoleic acid groups has little effect on the relative reactivities of the linoleic and linolenic groups. Insofar as reactivity is concerned the oleic and isolinoleic acid groups may be considered as being in one class while the linoleic and linolenic acid groups are in another. Comparison of the oleic and linoleic acid groups makes it obvious that the additional double bond in the latter does not double the reactivity but, instead, increases it many fold. This greatly enhanced reactivity is attributed to the active methylene grouping, $—CH{=}CH—CH_2—CH{=}CH—$, in the normal linoleic acid group and is presumably related to the readiness with which a hydrogen atom may be detached from the central carbon atom[37, 38].

The relative reactivities of the fatty acid groups formed during the hydrogenation of methyl linolenate have been calculated[69] for operating conditions useful in the laboratory. The hydrogenations were carried out at room temperature and atmospheric pressure using 1.65 per cent of palladium in the form of palladium black supported on barium sulfate. Ethyl acetate was used as a solvent for the methyl linolenate. Under these conditions the relative reactivities of the various acids in the form of their methyl esters were: oleic, 1; isolinoleic, 5; linoleic, 27; linolenic, 27. The isolinoleic acid includes those linoleic acids in which the double bonds are separated by more than one methylene group.

TABLE 3. RELATIVE HYDROGENATION RATES OF COMPONENT FATTY ACIDS OF COTTONSEED AND LINSEED OILS

Fatty Acid	Relative Rate	
	Nonselective Conditions	Selective Conditions
Cottonseed oil		
Oleic[a]	1	1
Linoleic	4	50
Linseed oil		
Oleic[a]	1	1
Isolinoleic[b]	2.5	3.8
Linoleic	7.5	31
Linolenic	12.5	77

[a] Includes all isomers of oleic acid.

[b] All isomers of linoleic acid in which the double bonds are separated by more than one methylene group.

Reactivities involving the eleostearic acid group have been determined by Hilditch and Pathak[39] on the basis of the hydrogenation of mixtures of methyl esters at atmospheric pressure and 110 to 170°C, using Raney nickel catalyst at a concentration of 2 per cent of the esters. By making use of some of the data obtained by Bailey and Fisher[10] it was concluded that the relative activities of the eleostearate, linolenate, linoleate, and oleate are of the order 80:40:20:1.

Thompson[83] established the approximate reactivities of the main, unsaturated fatty acids combined in tung and linseed oils by hydrogenating a 50:50 mixture of these oils and analyzing the reaction products. The hydrogenation was performed at 150°C, and a hydrogen pressure of 20 pounds per square inch gage, using 0.1 per cent of nickel catalyst prepared electrolytically. While the accuracy of the methods used for analyzing the end products was limited it does seem that during the initial stages of the hydrogenation the eleostearin was many times more reactive than normal linolenin for equivalent concentrations. Also, for equivalent concentrations the conjugated linolein formed from the eleostearin was many times as reactive as the normal linolein when present in considerable amounts. Normal linolenin and normal linolein had similar reactivities.

OTHER FACTORS IN HYDROGENATION

Operating Variables

While hydrogenation tends to be naturally selective, the plant operator has four variables under his immediate control which he can manipulate to change the selectivity to a marked extent. The variables are temperature, type and concentration of catalyst, hydrogen pressure, and agitation. These variables exert their influences in a complex manner by controlling the following six steps involved in hydrogenation:

(1) Solution of hydrogen in the oil
(2) Adsorption of dissolved hydrogen on the catalyst
(3) Prior, simultaneous, or later adsorption of an unsaturated bond
(4) Formation of a hydrogen-nickel-unsaturated bond complex
(5) Decomposition of the complex
(6) Desorption of the saturated bond.

The effect of each variable is of course not exclusive. For example, the degree of agitation of the oil-catalyst-hydrogen mixture and the hydrogen pressure both control the rate of solution of the hydrogen in the oil. Bailey[7] has gone so far as to suggest that the hydrogen pressure, the degree of hydrogen dispersion through the oil, the catalyst concentration, and the temperature all affect the selectivity of the hydrogenation through their influence on the concentration of hydrogen in the reaction zone, with selectivity being favored by a low concentration.

In commercial practice the values assigned to the variables are a reflection of economic and technical considerations. Natural oils of a certain composition are available and are to be transformed at the lowest possible cost into specific fat products having a certain consistency, plastic range, melting point, etc. In the hydrogenations to produce the various fat products, the selectivity, degree of reaction, and the formation of isomers must be controlled insofar as practical. In spite of the diverse factors involved in commercial practice, the ranges over which the operating conditions are varied are generally well fixed.

The choice of an operating temperature is usually limited to those between 80 and 200°C. Below this range the nickel catalyst employed possesses insufficient activity, and above this range there is danger of damaging the oil. Also above 200°C the rate of reaction which at first increases with temperature begins to decrease. Between 135 and 175°C the rate of reaction is approximately doubled for an increase of 22°. Increasing the temperature at which a hydrogenation is performed increases the selectivity of the reaction and also the formation of iso-oleic acids in the oil.

The hydrogen pressure used in the reaction vessel is generally between atmospheric and 75 pounds per square inch gage, within which range the reaction rate is roughly proportional to the pressure. Decreasing the pressure tends to increase selectivity and simultaneously increases the formation of iso-oleic acid glycerides. Below atmospheric pressure the reaction rate is generally too small to be useful.

When agitation is mentioned in connection with hydrogenation, it is understood to mean the mixing of the body of oil containing the catalyst and extending the interface between the oil and hydrogen. Because agitation is capable neither of quantitative representation nor easy reproduction, its influence cannot be as well defined as that of the other variables. Qualitatively, increased agitation decreases the degree of selectivity and the rate of formation of iso-oleic acid glycerides.

Increasing the concentration of the nickel catalyst increases the degree of selectivity and the formation of isomers so long as the rate of hydrogenaion is not the sole function of the rate at which hydrogen dissolves in the oil. It is possible to add so much catalyst that additional amounts will not change the rate of hydrogenation. Very large amounts of catalyst may even decrease the selectivity[95]. The latter situation is thought to occur when the concentration of the highly unsaturated component is so low that it can not cover all of the catalyst surface under the given conditions. Generally, a catalyst concentration between 0.02 and 0.25 per cent nickel is used in the commercial hydrogenation of vegetable oils. The type of catalyst has, of course, also an effect on the mode of reduction.

Data obtained in a systematic investigation of the four operating variables[9] are shown in Table 4. These data indicate that temperature is the variable capable of exerting the most influence on selectivity. In the table the lower contents of saturated and linoleic acid glycerides indicate the better selectivities.

By the proper choice of operating variables differences in selectivity greater than those shown in Table 4 may be attained. The curves in Figure 6 indicate the range of differences which were readily attained with the same cottonseed oil, catalyst, and apparatus used in securing the data in Table 4. Curve 1 represents the course of a highly selective hydrogenation at 149°C, a hydrogen pressure of 10 pounds per square inch gage, a low rate of agitation, and a catalyst concentration of 0.3 per cent nickel. Curve 2 represents a nonselective hydrogenation made at 121°C, a hydrogen pressure of 27 pounds per square inch gage, a medium rate of agitation, and a catalyst concentration of 0.05 per cent nickel. The iodine value of 65.7, which is shown as a broken line in Figure 6, represents the iodine value of the fatty acid mixture at the instant the last trace of linoleic acid would

TABLE 4. INFLUENCE OF VARIOUS OPERATING VARIABLES ON THE COMPOSITION OF COTTONSEED OIL HYDROGENATED TO AN IODINE VALUE OF 62.9[a, b]

Variable	Value of Variable	Hyd. Time, (min.)	Percentage Composition of Fatty Acids			
			Satu-rated	Iso-oleic	Normal Oleic	Linoleic
Temperature	121°C	72	39.6	8.5	39.3	12.6
	149°C	31	34.1	11.2	47.5	7.2
	177°C	19	32.5	14.3	47.6	5.6
Pressure	5 psig	67	32.8	13.2	48.1	5.9
	27 psig	31	34.1	11.2	47.5	7.2
	50 psig	21	35.2	10.2	46.2	8.4
Agitation	290 rpm—16 lbs oil	101	31.7	15.8	47.7	4.8
	208 rpm—12 lbs oil	24	32.8	12.4	48.9	5.9
	528 rpm—8 lbs oil	12	34.2	10.7	47.8	7.3
Amount of catalyst	0.025% Ni	98	35.1	11.0	45.7	8.2
	0.050% Ni	31	34.1	11.2	47.5	7.2
	0.100% Ni	24	32.8	12.4	48.9	5.9
Nature of catalyst	0.050% Ni—No. 1[c]	31	34.1	11.2	47.5	7.2
	0.050% Ni—No. 2[d]	35	35.2	19.2	37.2	8.4
	0.100% Ni—No. 3[e]	85	34.1	10.7	48.0	7.2
Composition of oil before hydrogenation			26.9	—	27.1	46.0

[a] Unless shown otherwise the conditions for each run were temperature, 149°C; pressure, 27 psig; agitation, 408 rpm—12 lbs oil; and amount of catalyst, 0.050% Ni.

[b] The iodine value of 62.9 represents the maximum value of the glyceride mixture at which all of the linoleic acid could be converted into oleic acid in a completely selective hydrogenation.

[c] Dry-reduced, supported catalyst prepared by way of electrolytic precipitation of $Ni(OH)_2$.

[d] Dry-reduced, supported catalyst prepared from $NiSO_4$.

[e] Raney nickel catalyst prepared according to directions of manufacturer.

disappear during a completely selective hydrogenation. For a completely selective hydrogenation the curve representing it would pass through the intersection of the line for iodine value 65.7 and the line for zero content of linoleic acid.

In the hydrogenation of cottonseed oil the operating variables are chosen so that the selectivity of the reaction usually lies somewhere between the extremes represented in Figure 6.

When operating conditions are used which vary widely from those generally employed, the effects on selectivity and *trans* isomer formation may differ somewhat from those mentioned above. Sims[77] found on hydrogenating soybean oil at pressures up to 700 pounds per square inch that the effects of catalyst concentration and agitator speed on selectivity were reversed from those found under ordinary conditions. That is, at high pressures the selectivity varied directly with the amount of agitation and inversely with the catalyst concetration.

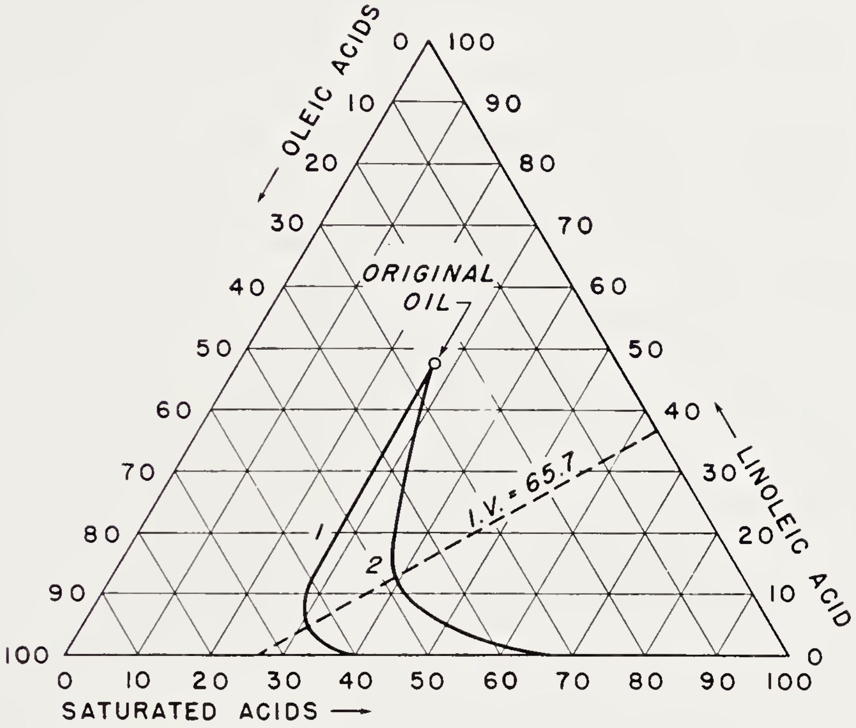

Figure 6. Fatty acid composition of cottonseed oil during the course of hydrogenation under (1) selective and (2) nonselective conditions.

The order of the hydrogenation reaction has been measured by a number of investigators. As might be expected, their conclusions varied widely, depending upon the operating conditions employed. Some who used average conditions of pressure, agitation, and catalyst concentration at moderate or low temperatures (below about 150°C) obtained first-order reactions. When a low pressure of hydrogen and a high concentration of catalyst were used so that the rate of hydrogenation was determined by the rate of solution of hydrogen in the oil, the reactions were of zero order. Still others came to the conclusion that the reaction was of the second order or higher. From the nature of the reaction it should not be expected that any definite order can be assigned to it.

Influence of Molecular Weight and Glyceride Configuration

The course of the hydrogenation reaction is influenced to some extent by the molecular weight of the components undergoing hydrogenation. It is general knowledge that under a given set of conditions the methyl esters of unsaturated fatty acids hydrogenate several times as rapidly as do the corresponding glycerides. Ueno[89] found that the higher molecular weight fatty acids (C_{20} and C_{22}) are more slowly reduced than those of lower molecular weight. Tsuchiya[84] hydrogenated equimolecular mixtures of oleic acid and each of several esters. The oleic acid hydrogenated 2.28–2.82 times faster than did the methyl oleate. This figure for other esters was: ethyl, 3.01; propyl, 3.58; isopropyl, 3.50; butyl, 3.82; and isoamyl, 3.09.

It is apparent that components of lower molecular weight hydrogenate more readily than do components which have a higher molecular weight but contain the same number and position of double bonds per acyl group. This, however, is generally not a factor in the selective hydrogenation of oils. Differences in the molecular weights of the unsaturated fatty acids combined as the glycerides are usually not great, and these differences are further reduced by the fact that the individual molecules contain a mixture of fatty acids. For example, Bushell and Hilditch[22] found that oleodipalmitin and oleodistearin hydrogenated with practically equal readiness.

The position of an unsaturated acyl group in a glyceride molecule appears to have no measurable effect on the readiness with which the acyl group hydrogenates. Oleic acid in the 2-position of a glyceride molecule has been found to be no different from oleic acid in the 1-position[22]. Bushell and Hilditch have obtained evidence that for triglycerides consisting of a given unsaturated acyl group and saturated acyl groups the readiness to hydrogenate depends upon the number of unsaturated acyl groups per glyceride molecule, being greater the higher the number. However, this effect on reactivity or selectivity is slight. As secondary evidence of these facts, the writer has found that the consistency of well-hydrogenated oils is changed very little after interesterification or random rearrangement.

Catalyst Poisons

A large number of compounds which might be present in the catalyst, hydrogen, or oil employed in a hydrogenation can poison the reaction, either completely or partially. If the poisoning is partial, the activity of the catalyst is reduced. Selectivity may or may not be impaired, and in certain instances the tendency of the catalyst to form *trans* isomers is enhanced.

Among the strongest poisons for nickel catalysts are the sulfur compounds, hydrogen sulfide, carbon disulfide, and sulfur dioxide, which can occur as impurities in the hydrogen produced by several of the common processes. Basic nickel sulfate left in catalyst prepared from nickel sulfate also is a poison. These and certain other sulfur-containing compounds exert their effect by forming nickel sulfide. This not only destroys some of the nickel crystallites but produces a compound which has a low melting point. The effect of sulfur poisoning is irreversible; the catalyst cannot be reactivated.

Bailey[8] has found that when a single catalyst is progressively poisoned by the addition of successive portions of a sulfur-containing compound, the activity of the catalyst after each addition corresponds closely to the residue of active nickel, as calculated from the sulfur added and the sulfur required for complete poisoning. The latter quantity varies, according to the original activity of the catalyst, between 0.5 and 5.0 grams of sulfur per 100 grams of nickel.

Sulfur-containing nickel catalysts possess the tendency to produce large amounts of *trans* isomers in partially hydrogenated oils. Ordinarily this is an undesirable characteristic, except when margarine oils are produced. In this connection a patent has recently been issued[98] which covers the addition of a small amount of sulfurated oil (1.38 to 5.00 per cent sulfur based on the nickel) to the oil to be hydrogenated.

Carbon monoxide, which can be present as an impurity in the hydrogen, is another commonly encountered poison. Its effect, unlike that of sulfur, is reversible. Catalyst poisoned with carbon monoxide can be reactivated by simply flushing with clean hydrogen the oil-catalyst mixture at the hydrogenation temperature. If the temperature of a hydrogenation is high enough, about 200°C, carbon monoxide poisoning will not occur. On the other hand, if a hydrogenation temperature as low as 100°C is used a concentration of 0.01 per cent of carbon monoxide in the hydrogen will interfere seriously with the reaction according to Bailey[8]. This situation is explained by the fact that carbon monoxide reacts with nickel to form relatively unstable nickel tetracarbonyl. When this compound is heated to 200°C or is heated in the presence of an inert gas at a lower temperature decomposition to nickel and carbon monoxide results. If the decomposition takes place in oil, the nickel will be catalytically active.

Natural oils contain a number of minor components which act as catalyst poisons. These include phosphatides[86], oxidized glycerides[19], proteins and proteinaceous materials, and unidentified gummy materials. Hence natural oils are always refined and bleached before being subjected to hydrogenation. Ordinary refining may not suffice because it tends to leave in the oil traces of alkali soaps which are poisons.

Ueno[88] made an extensive investigation of the hydrogenation of oil with a nickel catalyst and found that in addition to some of the compounds already mentioned the following had a retarding effect: soaps of lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold. He also found that glycolic and lactic acids, hydroxy-stearic acids, oxalic, succinic, and fumaric acids, and hydroxy acids such as malic, citric and tartaric had a retarding effect. Glycerol, gelatin, and a number of other compounds were also found to have an inactivating influence. It seems probable, however, that many of these compounds have only a very mild poisoning action.

Among the compounds which had no poisoning effect Ueno found the soaps of calcium, strontium, aluminum, cerium, nickel, manganese, copper, silver, vanadium, thorium, and platinum, as well as nickel acetate, butyrate, stearate, lactate, oxalate, and succinate. Among the nonmetallic compounds having no effect he included cholesterol, squalene, and glycogen.

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CHAPTER 10

CATALYTIC DEHYDROGENATION

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During the past twenty years dehydrogenation processes have risen to a position of major importance, especially in the field of petroleum chemistry. In addition to the production of aromatic hydrocarbons large quantities of butadiene and styrene are made by dehydrogenation. The history of these developments constitutes an interesting phase of recent advances in industrial chemistry.

The production of olefins, diolefins and styrenes by dehydrogenation is represented by the following typical reactions:

(1) Propane → propene + H_2

(2) Butene → butadiene + H_2

(3) Ethylbenzene → styrene + H_2

(4) Butane → butadiene + $2H_2$

When the equilibrium is favorable for dehydrogenation at temperatures below those of thermal cracking, these reactions are greatly benefited by the use of suitable catalysts. For example, the dehydrogenation of propane, butene and ethyl benzene is thermodynamically possible at temperatures below those at which these compounds decompose thermally. On the other hand, for dehydrogenating C_2 hydrocarbons thermodynamic equilibrium requires such high dehydrogenating temperatures that little, if any, advantage has been shown for the use of catalysts. Hexane and higher molecular weight hydrocarbons have a strong tendency to form aromatics or to crack and therefore have not given good yields of corresponding olefins or diolefins.

The production of olefins and of diolefins is discussed separately in the following pages.

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* Formerly named Standard Oil Development Company

DEHYDROGENATION OF PARAFFINS

The production of olefins from gaseous paraffins over catalysts such as nickel, platinum, palladium, iron, cobalt, copper etc., was studied by early investigators in the period 1919–1932[44, 113, 141, 142, 171]. However, the catalysts studied were generally unstable and produced secondary cracking reactions. Real impetus to studies of producing olefins from paraffins was given when Frey and Huppke studied the equilibrium of the reaction and found the superior properties of chromia catalysts[51].

Equilibrium Considerations in Paraffin Dehydrogenation

The studies of Frey and Huppke with chromia gel catalysts indicated that equilibrium could be closely approached in dehydrogenations to form ethylene, propylene, isobutylene and normal butylenes. It is commendable that these results, shown in Figure 1, are in better agreement with the best equilibrium data[99] presently available than are some of the equilibrium data published subsequently. Their work indicated that selective dehydrogenation required a proper choice of feed rate and temperature to avoid degradation reactions. Degradation reactions resulted in more hydrogen being produced than olefin, except in the case of isobutane, which formed methane and consumed hydrogen.

The curves in Figure 1, and values read from those curves in Table 1, have been calculated from the data of Pitzer, Rossini *et al.*[99] and are considered to be the best available at the present time. It is apparent from these results that ethane requires considerably higher dehydrogenation temperatures than propane. Butane and higher paraffins have equilibrium yields of normal 1-alkene olefins about the same as propane. The formation of *trans* 2-butene requires about the same temperatures as 1-butene, but the formation of *cis* 2-butene requires higher temperatures. The possibility of forming several normal butenes and pentenes and five normal hexenes results in higher equilibrium conversions to total normal alkenes for these hydrocarbons. It is also apparent in Figure 1 that isobutane can give higher yields of isobutylene at a given temperature than normal butane can of mixed normal butylenes.

The data of Figure 1 are in fair agreement with most of the published data on equilibria. However, some differences exist. For the dehydrogenation of ethane there is good agreement with the data of Frey and Huppke[51], Grosse and Ipatieff[63] and Komarewsky *et al.*[148], but not with those published by Pao Teh Wan[139]. The values for propane are about the same as those of Grosse *et al.*[63] and Komarewsky *et al.*[148], but are somewhat higher than those reported by Burgin *et al.*[26]. The data for equilibrium conversions of *n*-butane are in good agreement with calculations by Hackmuth *et al.*[71], but are lower than reported by Grosse *et al.*[63] and by Komarewsky *et al.*[148].

Komarewsky reported obtaining experimental yields agreeing with his higher calculated values for the equilibrium conversions. However, the differences are relatively small (only 3 to 5 per cent conversion).

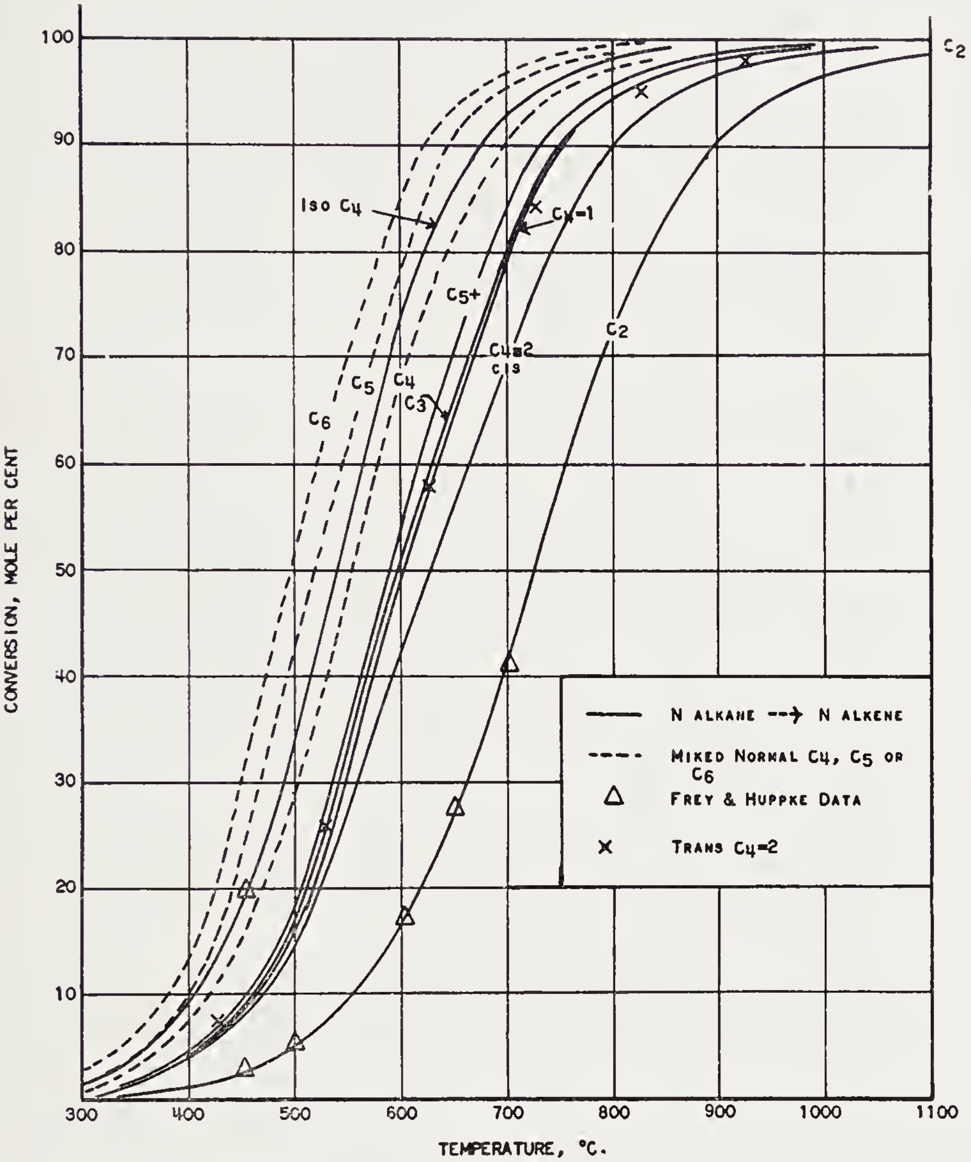

Figure 1. Dehydrogenation equilibria for paraffins to olefins. Total pressure of one atmosphere.

The data in Figure 1 and Table 1 are for a total pressure of one atmosphere. In commercial dehydrogenation plants, these conversions are frequently increased by using lower pressures or by using diluents with the feed. For dehydrogenations forming one mole of organic product and one or two moles of hydrogen, respectively, the effect of pressure is given by the following equations:

(1) $$C^2/1 - C^2 = K/P$$ (for 1 mole H_2)

(2) $$4C^3/(1 - C)(1 + 2C)^2 = K/P^2$$ (for 2 moles H_2)

where C is the fraction dehydrogenated, K is the equilibrium constant and P is the pressure in atmospheres. The first equation holds for the conversion of olefins into diolefins and alkyl benzenes into styrenes as well as for paraffins into olefins. The conversion of butane to butadiene is represented by Eq. (2). The equilibrium conversion for any of these reactions at any pressure is easily obtained from the values of K/P shown in Tables 2 and 3.

TABLE 1. DEHYDROGENATION EQUILIBRIA

Temperatures °C Required for Given Conversions at a Total Pressure of One Atmosphere

(Paraffin → Olefin + H_2)

Conversion Mole %	C_2	C_3	1-butene	2-butene Cis	2-butene Trans	Normal Mixed	Iso-butene	Pentenes		Hexenes Normal Mixed
								1-pentene*	Normal Mixed	
5	500	410	415	415	405	375	360	405	360	335
10	555	456	460	470	450	420	405	450	410	380
20	615	510	515	525	505	470	435	505	440	425
30	660	540	545	555	540	505	490	535	465	445
40	695	570	575	590	572	530	515	560	490	470
50	725	595	600	625	598	555	540	585	520	495
60	755	625	630	660	630	580	560	615	545	520
70	790	660	670	700	640	610	590	650	575	550
80	830	700	705	740	710	645	625	685	605	585
90	900	750	753	800	760	700	680	730	650	625
95	960	815	815	860	820	745	730	790	695	670

* Same values hold for 1-hexene and higher olefins.

That pressure has a marked effect on dehydrogenation conversions is illustrated in the following table for the equilibrium dehydrogenation of *n*-butane to mixed normal butylenes at 527°C.

Pressure, atm.	0.01	0.1	1.0	10	100
K/P	17.4	1.74	0.174	0.0174	0.00174
Conversion to butenes (%)	97	80	38.5	13	4

The thermodynamic data discussed above have not taken into consideration the simultaneous formation of butadiene from butane. If both

TABLE 2. VALUES OF PER CENT CONVERSION FOR VALUES OF K/P*

% Conv.	K/P	% Conv.	K/P	% Conv.	K/P	% Conv.	K/P	% Conv.	K/P
1.0	0.000101	21	0.04601	41	0.2021	61	0.5926	81	1.908
2	0.000400	22	0.05086	42	0.2142	62	0.6244	82	2.053
3	0.000901	23	0.05584	43	0.2268	63	0.6581	83	2.144
4	0.001603	24	0.06112	44	0.2401	64	0.6938	84	2.397
5	0.0025	25	0.06667	45	0.2539	65	0.7316	85	2.604
6	0.003613	26	0.07250	46	0.2684	66	0.7718	86	2.840
7	0.004924	27	0.07863	47	0.2835	67	0.8146	87	3.114
8	0.006441	28	0.08507	48	0.2994	68	0.8601	88	3.433
9	0.008166	29	0.09182	49	0.3160	69	0.9088	89	3.811
10	0.01010	30	0.09890	50	0.3333	70	0.9608	90	4.263
11	0.01225	31	0.1063	51	0.3515	71	1.017	91	4.817
12	0.01461	32	0.1141	52	0.3706	72	1.076	92	5.510
13	0.01719	33	0.1222	53	0.3906	73	1.141	93	6.402
14	0.01999	34	0.1307	54	0.4116	74	1.210	94	7.591
15	0.02302	35	0.1396	55	0.4337	75	1.286	95	9.256
16	0.02627	36	0.1489	56	0.4569	76	1.367	96	11.76
17	0.02976	37	0.1586	57	0.4813	77	1.456	97	15.92
18	0.03348	38	0.1688	58	0.5069	78	1.554	98	24.25
19	0.03745	39	0.1794	59	0.5340	79	1.660	99	49.25
20	0.04167	40	0.1905	60	0.5625	80	1.778	99.5	99.25

* For simple dehydrogenation reactions giving one molecule of hydrogen and one of hydrocarbon per molecule of feed converted.

$$\frac{C^2}{1 - C^2} = K/P$$

where C = fraction converted
K = equilibrium constant K_p
P = pressure in atmospheres.

olefins and diolefin are formed in equilibrium amounts, normal butane gives the conversions* shown in the following table.

EQUILIBRIUM BETWEEN n-BUTENE, n-BETENES, AND 1,3-BUTADIENE

Temperature (°C)	550	600	650	700	750	800	850
Conversion at 1.0 atm.							
To n-butenes	—	62.5	69	64.5	54	37.5	23
To 1,3 C_4H_6	—	6.0	14	27.5	45	61.5	74
Conversion at 0.167 atm.							
To n-butenes	68.5	64.5	48.5	31	17.5	—	—
To 1,3 C_4H_6	11.5	27.5	48.5	68	82	—	—

* Calculations made by Dr. D. W. Wood, Esso Research and Development Company.

Experimental Investigations of Paraffin Dehydrogenation Catalysts

Dehydrogenation with Chromia or Alumina-Chromia. Alumina-chromia catalysts are still the most satisfactory for dehydrogenating paraffins to olefins. In addition to the use of alumina-chromia, the Frey and Huppke patent[51] described the use of difficultly reducible oxides of Zr, Ti, Si, Th, B, and Mg with equimolar amounts of chromia and with or without minor amounts of other additives such as oxides of Tl, Bi, Pb, and Hg. However, none of these compositions proved as satisfactory as their alumina-chromia catalyst prepared by coprecipitation of aluminum and chromium nitrates with ammonium hydroxide. Numerous modified alumina-chromia catalysts have since been developed.

TABLE 3. VALUES OF PER CENT CONVERSION FOR K/P^2

% Conv.	K/P^2	% Conv.	K/P^2	% Conv.	K/P^2	% Conv.	K/P^2	% Conv.	K/P^2
1	0.0000039	21	0.02325	41	0.1421	61	0.4724	81	1.6298
2	0.000030	22	0.02633	42	0.1509	62	0.4846	82	1.758
3	0.000172	23	0.02966	43	0.1613	63	0.5292	83	1.9014
4	0.000229	24	0.03322	44	0.1721	64	0.5602	84	2.063
5	0.000435	25	0.03704	45	0.1836	65	0.5932	85	2.246
6	0.000733	26	0.04112	46	0.1956	66	0.6284	86	2.456
7	0.001135	27	0.04548	47	0.2082	67	0.6659	87	2.699
8	0.001654	28	0.05011	48	0.2214	68	0.7056	88	2.982
9	0.002301	29	0.05504	49	0.2354	69	0.7483	89	3.317
10	0.003086	30	0.06026	50	0.2500	70	0.7940	90	3.719
11	0.004019	31	0.06581	51	0.2654	71	0.8429	91	4.212
12	0.005109	32	0.07166	52	0.2815	72	0.8955	92	4.827
13	0.006362	33	0.07785	53	0.2885	73	0.9523	93	5.620
14	0.007787	34	0.08444	54	0.3165	74	1.0135	94	6.676
15	0.009398	35	0.09130	55	0.3353	75	1.0800	95	8.156
16	0.011194	36	0.09857	56	0.3552	76	1.1521	96	10.962
17	0.01319	37	0.10622	57	0.3762	77	1.2305	97	14.08
18	0.01538	38	0.1143	58	0.3983	78	1.3166	98	21.48
19	0.01779	39	0.1228	59	0.4217	79	1.4107	99	43.70
20	0.02041	40	0.1317	60	0.4463	80	1.5147	99.5	87.56

$$K/P^2 = \frac{4C^3}{(1 - C)(1 + 2C)^2}$$

where C = fraction converted
K = equilibrium constant K_p
P = pressure in atmospheres.

Burgin *et al.*[26] found that activated alumina itself could be used as a catalyst for dehydrogenating isobutane. At 650°C and 1200 to 4560 v/v/hr initial yields of 32 to 36 per cent olefins were obtained from both isobutane and propane, but the conversions did not hold up after 2 hours on feed.

The beneficial effect of small amounts of water on dehydrogenation previously reported by Beeck[20] were confirmed by Burgin *et al.*[26] for dehydrogenation over activated alumina. Large amounts of water were harmful.

Mole % H_2O in isobutane	0.0	0.1	0.2	0.4	0.6
Max. isobutene yield, mole %	35	40	36	24	15

Appreciably less severe dehydrogenation conditions were required when components such as oxides of Cr, V, Fe, Zn, or Ni were added to the activated alumina. Of these materials Cr_2O_3 on alumina gave the best results. Using chromic acid or chromium nitrate, 10 to 20 per cent Cr_2O_3 resulted in catalysts which could be used at temperatures 50 to 70°C lower than activated alumina. It was found that the optimum chromium content was higher for *n*-butane than for propane. Burgin and Groll[27] patented the use of alumina-chromia catalysts containing 6 to 40 per cent Cr_2O_3 for dehydrogenation. The advantages of adding chromia to alumina are illustrated by their data summarized below:

Effect of Chromia on Activated Alumina

1200 V/V/Hr Propane, Butane or Isobutane

Catalyst Period (hr) Temperatue (°C)	Alumina 3 650		Al_2O_3 + 2% Cr_2O_3 1.5 625		Al_2O_3 + 12–15% Cr_2O_3 1.0 550–575	
	Yield	Ratio*	Yield	Ratio*	Yield	Ratio*
Olefin						
Propene	23.6	0.87	37.4	0.95	25.8	0.95 (575°C)
n-butene	†	†	22	.60	30.1	.97 (550°C)
Isobutene	31	.74	35.5	.78	37	.83 (550°C)

* Ratio of olefins by dehydrogenation to total olefins. Yields are mole per cent.

† Excessive carbon (above the 1 to 4 per cent on feed for the other tests).

Extensive studies of paraffin dehydrogenation were published by Grosse and Ipatieff[63] in 1940. Their work indicated that ultimate yields as high as 90 per cent were possible while obtaining by-product hydrogen of 90 per cent purity. A fairly critical choice of feed rate was required to obtain maximum olefins yields without excessive degradation. At a given temperature in the range 500 to 600°C, the olefin concentration in the product gas increased with increasing contact time, but dropped off sharply when contact times greater than an optimum value were used. Their maximum concentrations of olefins in the exit gas are illustrated in the following table:

Contact Time (Sec.)	Volume per cent Olefins in Exit Gas				
	n-Butane		Isobutane		
	500°C	600°C	500°C	550°C	600°C
1	—	24.5	—	9.5	25
2	14	30	—	16	31
4	20	24.5	7.5	22	33
8	18.5	—	12	24.5	22
20	14.5	—	18	22.5	—
100	—	—	13	—	—

Grosse and Ipatieff also obtained excellent yields of propylene from propane. At a 25 per cent conversion to propylene their exit gas contained only 0.5 per cent methane when using a 2.7 second contact time at 600°C and 1 atmosphere pressure. Grosse[60] described a preferred catalyst as containing less than 10 per cent chromia on alumina.

A specific composition contained 96 per cent Al_2O_3 and 4 per cent Cr_2O_3 and was prepared by adding 100 parts of Alorco Grade A (now Grade F-10) activated alumina (6–10 mesh) to 50 parts by weight of a 10 per cent solution of chromium trioxide in water. After the suspended alumina was stirred for a few minutes it was freed of excess liquid and dried first at 100°C and then at 220 to 230°C.

Other Universal Oil Products Co. patents[64, 59, 128] concerned with making cyclopentadiene from cyclopentane describe similar catalysts containing molybdena and vanadia instead of chromia, but these are probably inferior.

Komarewsky *et al.*[148] claimed advantages for coprecipitation of alumina and chromia as compared with impregnation of activated alumina with chromia. Studies of the dehydrogenation of *n*-butane and isobutane showed that only the coprecipitated catalyst gave equilibrium yields at 500°C. With their catalyst higher yields of olefins were obtained before degradation reactions set in.

Their 75 Al_2O_3-25 Cr_2O_3 (weight per cent) catalyst was prepared by dissolving aluminum and chromium nitrates in excess sodium hydroxide solution at 0 to 5°C and neutralizing with nitric acid. It is possible that some of the improved characteristics of this catalyst were caused by the relatively high Cr_2O_3 content used, and by occlusion of soda.

Numerous other alumina-chromia catalyst compositions have been investigated. It is claimed that activity and carbon formation can be reduced by incorporating Group I or II alkaline oxides. The I. G. Farbenindustrie[78] preferred an alumina-chromia catalyst promoted with potassia. Alkalized alumina-chromia catalysts have also been described by Grosse[61]. Corson *et al.*[33] claimed to reduce carbon deposition on alumina-chromia catalysts by calcining the catalyst at 700 to 1100°C with or without addition of magnesia. Parker and Huffman[140] patented alumina-chromia compositions containing 1 to 15 per cent BeO and 0.5 to 15 per cent of an oxide of Si or Ti. They also described the use of other Group VI oxides and of nickel chromite and cobalt molybdate in place of chromia.

Studies of Other Catalyst Compositions. In addition to chromia on alumina catalyst, chromia on magnesia compositions have been studied. Also, considerable work has been done with other active dehydrogenating components on alumina.

Magnesia-chromia catalysts may be second only to alumina-chromia for dehydrogenating paraffins to olefins. Tropsch[181] has patented numerous modifications of magnesia-base catalysts. With calcined (1652°F) magnesite containing 10 per cent Cr_2O_3, isobutane at 1112°F and 50 to 80 v/v/hr formed a product containing about 24 per cent isobutylene and 30 per cent hydrogen. This $MgO—Cr_2O_3$ catalyst is less active and selective than the best alumina-chromia catalysts. The use of the magnesia base with other active components including molybdates, chromates, uranates, titanates, permanganates, and perrhenates is also disclosed. Salts of potassium and lead are mentioned specifically.

Grosse[62] prepared alumina-molybdena dehydrogenation catalysts by impregnating activated bauxite or other alumina hydrate with ammonium molybdate solution. For a contact time of 5 seconds *n*-butane at 500 and 600°C gave products containing 14.7 and 20 per cent butenes, respectively. High selectivity at 500°C was reflected by the 15 per cent H_2 content (*vs.* 14.7 butenes) of the product. At 600°C the hydrogen content of 27 per cent (*vs.* 20 per cent butenes) indicated a less selective reaction.

Huppke[84] claimed considerably improved results were obtained with alumina-urania or alumina-vanadia catalysts when zinc oxide was included. Catalysts containing about equal mole percentages of the three components could be used for periods two to three times longer than the two-component catalysts containing no zinc oxide.

Atkinson[6] claimed an ultimate yield of 87 per cent olefins using a catalyst containing 20 per cent phosphomolybdic acid on 80 per cent activated alumina for dehydrogenating mixed butanes. However, even at 1100°F the conversion per pass was only about 10 per cent.

Pao Teh Wan[139] studied 49 catalysts for ethane dehydrogenation without obtaining results superior to those given by noncatalytic thermal dehydrogenation. He studied inert materials such as procelain, chamotte, pumice, brick, active carbon, lamp black and quartz. Nickel, copper, bronze, iron, platinum and nichrome were investigated in the form of fine wire. Iron oxide with and without 0.5 to 10 per cent added oxides of Be, Mg, Cu and Ni was studied. Chromia with and without 0.5 to 5 per cent of Al_2O_3 , NiO, or Bi_2O_3 was compared with 80 Al_2O_3-20 Cr_2O_3 and with Cr_2O_3 or Al_2O_3 on chamotte. Other compositions included 20 Cr_2O_3-80 ZnO, $CuCr_2O_4$, and MgO with and without added Cr_2O_3 , CuO, ZnO, MoO_3 , K_3PO_4 and Na_2CO_3 .

Many other compositions have been reported in the patent literature, but judged by actual use alumina-chromia is the best catalyst for converting gaseous paraffins into olefins. References to some additional catalyst compositions studied are given in Table 4. These patent references do not give data which permit a quantitative comparison of the compositions described.

Effect of Feed Diluents on Dehydrogenation

Advantages have been claimed in several patents for the use of various additives or diluents with paraffin feed stocks undergoing dehydrogenation. However, it does not appear that any of these have sufficient merit to be in actual use. In general, steam suppresses the activity of alumina-chromia catalysts and sulfur appears to have an activating effect under certain conditions.

The poisoning effect of water on an alumina-chromia-magnesia catalyst was offset by Hackmuth[72] by initiating the dehydrogenation reaction at a high temperature (1163°F) at which water adsorption was low and then decreasing the temperature to 1095°F at a rate of 1°F per minute to obtain increased selectivity.

With steam, dilution catalysts comprising molybdena, vanadia, or tungsten oxide have been claimed[36] to be superior to alumina-chromia for dehydrogenating butane. However, the best results showed ultimate recycle yields of butenes plus butadiene of only 20 per cent. With addition of chromia to these catalysts the ultimate yields increased to 40 to 60 per cent, but only at low conversion levels of 12 to 17 per cent.

Mattox[114] found in dehydrogenating heptane that added water suppressed the yields of aromatics to a greater extent than it did the yields of heptene. For example, at 550°C addition of one mole of water per mole of heptane reduced the toluene yield from 63 to 12.3 per cent based on the heptane reacted, whereas the yield of heptene increased from 16.8 to 28.9 per cent. However, with water addition the yields per pass based on feed were only 6.1 per cent heptene and 2.6 per cent toluene, with 6.5 per cent gas and 0.85 per cent carbon being formed. Less gas and carbon were obtained by using short contact times in the absence of added water.

Other diluents and additives claimed in the patent literature to be bene-

TABLE 4. REFERENCES TO MISCELLANEOUS CATALYSTS FOR DEHYDROGENATION OF PARAFFINS

	Ref.
Alumina Support Plus	
MoO_3	36, 62, 87
V_2O_5	36, 84, 127, 174
UO_3	84
WO_3	36, 175
MnO_2	28
Fe_2O_3 or FeS	58
Phosphomolybdate	6
Cu—ZnO	92, 93, 94
Cr_2O_3 frozen hydrogel	168
Cr_2O_3 calcined 700–1100°C	33
$Cr_2O_3 + BeO$	82, 138, 177
Cr_2O_3 + CaO, BaO, SrO	32
$Cr_2O_3 + Ce_2O_3$	178
$Cr_2O_3 + ZrO_2$	1
$Cr_2O_3 + MnO_2$	179
Cr_2O_3 + salts of Pb, Zn Mg Cd, Fe, Ni, or Co	180
$Cr_2O_3 + MgO + K_2O$	194
Chromates of Cu, Zn, Ca, Fe, U, Mn, or Na	75
Other Supports	
$MgO—ZnO—Cr_2O_3$	181
$MgO—V_2O_5$	126
$ZnO—Cr_2O_3$	52
Molten B_2O_3 + ZnO , Fe_2O_3 , V_2O_5 or UO_3	85
$SiO_2—Cr_2O_3$	154
SiO_2 or C + Fe or Zn humate	86
$ZrO_2—Fe_2O_3$	19
zeolite support	95
pumice + Cu + K_2CO_3	173
ZrO_2 or ThO_2—ZnO	84
Other Compositions	
Cu + ZnO	3
charcoal	145
Sn naphthenate	7
supported selenium	103
Nd_2O_3 or Pr_2O_3	125
Cr_2O_3 gel	123, 182
Cr_2O_3 gel + alkali	21
chromites	4, 105, 155
NiB_2O_4 + Co or Fe borates	81
Pd black	171

ficial are: S^{31}, COS^{106}, thiophenes[106], CO_2^{45}, H_2S^{30}, and Hg^{176}. However, it does not appear that any of these materials are being used commercially.

Commercial Dehydrogenation Processes

Following extensive investigations by the petroleum industry in the period 1934–1940, several commercial processes were designed for dehydrogenating paraffins, especially butanes, into olefins. It is probable that most of the major oil companies considered the installation of butane dehydrogenation plants to make olefins for polymerization to motor gasoline, but found them uneconomical at that time. Later, the demand for butylenes for alkylation and for making synthetic rubber made it practical to dehydrogenate butanes to butylenes, although the increased demand was largely supplied by new catalytic cracking units. Several commercial processes for converting butane into butylene are described briefly below. Processes for converting butane to butadiene are covered in the following discussion on butene dehydrogenation.

Phillips Dehydrogenation Process. The Phillips Petroleum Company carried out extensive pilot-plant work on butane dehydrogenation and a plant of their design has been operated by them for the Rubber Reserve Corporation[73]. A fixed bed of alumina-chromia catalyst in heated tubes is used. The feed consists of fresh 98 per cent normal butane and recycled butane, the total feed containing about 3 mole per cent of normal butylenes. It is dried in bauxite towers and heated to 1100°F before passing through the catalyst in 2-inch diameter tubes.

The operation of the plant consists of 1-hour cycles on dehydrogenation followed by 1-hour regenerations in which carbon is burned off the catalyst with flue gas-air mixtures containing 2 to 3 per cent oxygen. Multiple catalyst beds permit dehydrogenation to take place continuously; half of the reactors are regenerated while the others are being used for the dehydrogenation reaction.

The ultimate recycle yield of butenes from butane feed is about 80 per cent, the conversion per pass dropping from 40 to 30 per cent after about 110 days of operation. The coke formation at these conditions is in the range of 0.8 to 1.6 weight per cent on feed. The operating conditions for these yields are 685 volumes (S.T.P.) *n*-butane per volume of catalyst per hour and 1100°F butane inlet temperature.

Pilot-plant studies[71] carried out in the development of the Phillips process indicate that operating pressure in the Phillips process is essentially atmospheric (1 to 2 psi gauge). This work showed 2-inch tubes to be superior to 3-inch tubes and that with tubes made of alloys containing nickel, (types 304, 410 and 430) coke deposition was excsssive. A 27 per cent Cr steel (type 446) was found to be the most satisfactory material for reactor tubes.

Universal Oil Company Dehydrogenation Process. In 1940 Grosse and Ipatieff[63] published results of extensive pilot-plant work on catalytic dehydrogenation and indicated that the process was sufficiently developed for plant application. A summarized description of the U.O.P. commercial design[183] shows a cyclic process involving alternate dehydrogenation and regeneration using fixed bed catalyst in tubular reactors. This is generally similar to the Phillips process described above. Operating temperatures of 1000 to 1100°F at pressures of 10 to 50 psi absolute result in conversions of 30 per cent per pass with ultimate yields of 75 to 80 volume per cent (butylenes from butanes). The earlier U.O.P. publication indicates that an alumina-chromia catalyst is used.

Houdry Butane Dehydrogenation Process. The Houdry process for dehydrogenating butane is operated primarily to make butadiene, although it is equally suitable for production of monoolefins. It is also a cyclic, fixed-bed process and utilizes an alumina-chromia catalyst, but the reactor is not tubular. Further details describing its use for making butadiene are given in a following section.

I. G. Butane Dehydrogenation Process. During World War II the I. G. Farbenindustrie[78] operated a butane dehydrogenation plant to obtain butylenes for making alkylate for aviation gasoline. This plant utilized a moving catalyst bed in which the catalyst moved continuously downward through banks of gas-fired tubes. The catalyst moved continuously for 3.5 hours and was stationary for ½ hour, having a total residence time in the reactor of 4 hours per cycle. This corresponded to a total transfer of 3090 pounds of catalyst every 4 hours. The catalyst was moved by bucket elevators from the reactor to the regenerator. The 2¾-inch diameter reactor tubes consisted of 8 per cent Cr, 1 to 2 per cent Si alloy steel ("Sicromal") and were 26 feet long. Operating at 1040 to 1076°F and 680 v/v/hr, conversions of 20 to 25 per cent per pass with ultimate recycle yields of 85 per cent were obtained.

The catalyst used contained 8 per cent CrO_3 and 1 to 2 per cent K_2O (I. G. No. 6448). Descriptions of the preparation of this catalyst in IC 7370 differ somewhat from that in IC 7375.

A specially prepared activated alumina was kneaded with a solution of KOH, CrO_3, and nitric acid, formed into spheres and calcined at 450°C. The activated alumina was made by dissolving alumina trihydrate in NaOH and precipitating below 50°C by rapid addition of nitric acid to a pH of 5.5 to 6.5.

Present Status. As late as 1946 the production of butylenes by catalytic dehydrogenation did not appear to be economical for making motor gasoline. The M. W. Kellogg Company published[143] results of a cost study on making gasoline from butane and propane by processes involving catalytic dehydrogenation. This study was based on laboratory data indicating yields of 89, 80, and 74 per cent olefins from propane, isobutane, and *n*-butane, respectively. The yields of carbon were 3.0 weight per cent for isobutane and 5.0 per cent for *n*-butane. Considering cases in which the olefins were either polymerized or alkylated, the study generally indicated that propane and butane were not attractive materials from which to manufacture gasoline. This article gives 1946 costs of gasoline as 13.8¢ per gallon when made by dehydrogenation plus polymerization and only 9.8¢ per gallon when made by dehydrogenation plus isomerization plus alkylation. It is probable that even today catalytic dehydrogenation of butane and propane can be used only for making more valuable products such as aviation gasoline and chemicals.

Dehydrogenation of Olefins and Alkyl-Aryl Hydrocarbons

Prior to World War II dehydrogenation processes for making butadiene and styrene had been patented extensively, but were being used to a relatively small extent. Styrene was being manufactured commercially by catalytic dehydrogenation, but the catalysts used were not satisfactory for dehydrogenating butene to butadiene. The dehydrogenation of 1-butene to butadiene is similar to the dehydrogenation of ethyl benzene to styrene except that the double bond is formed in 1-3 conjugation with an unsaturated bond instead of an aromatic bond.

When the need for synthetic rubber in the United States was forseen, intensive research programs were undertaken to obtain satisfactory processes for making butadiene. By the time the United States government decided to build synthetic rubber plants, American industrial laboratories had produced an improved dehydrogenation catalyst which was satisfactory for making butadiene from butene. The availability of this catalyst made possible the allocation at that time of plants for making cheap butadiene from petroleum rather than from alcohol at a fourfold greater cost. The improved catalyst also proved superior for dehydrogenating ethyl benzene to styrene and resulted in improved yields and increased capacities for the styrene plants.

Prior to the use of catalytic dehydrogenation, butadiene was produced in the United States by high temperature, steam cracking of naphthas and oils. The yields of butadiene were only 3 to 4 per cent, but numerous other useful products were also obtained. At the time it became necessary for the government to make a decision on building synthetic rubber plants, expansion of the high-temperature cracking process was authorized because in a number of cases this could be done by minor modification of existing refinery equipment. In addition to the 10,000 tons per year of butadiene capacity already in operation and under construction by the Standard Oil Company of New Jersey, Rubber Reserve authorized an additional 34,200 tons per year of this so-called "Quickie" butadiene[152].

Three other processes for making butadiene were available. These used ethyl alcohol, butene and butane as feed stocks. Allocations for construction of new plants were divided as follows:

Raw Material Used	Rated Capacity, Short Tons/Yr
Alcohol	220,000
Butene	305,000–350,000*
Butane	75,000*–30,000

* 45,000 tons/yr made from butenes which were isolated from dehydrogenated *n*-butane.

The relatively low capacity allocated to the direct dehydrogenation of butane to butadiene was based on a conclusion that this process was not tested to a sufficient degree to warrant substantial inclusion in the rubber program. The government allocated an appreciable part of the butadiene program to the alcohol process, even though the alcohol had to be taken from the wartime grain supply. It was stated that butylenes were required for making aviation gasoline and that the alcohol plants required less strategic materials. In actual plant construction the alcohol butadiene plants received higher priorities and came on stream ahead of the butene dehydrogenation plants. Government figures[152] for 1945 showed that butadiene from alcohol at 90¢ per gallon cost 40.2¢ per pound as compared with 11.6¢ per pound for that made from petroleum. However, it has been estimated that if alcohol becomes available at 25¢ per gallon the cost of butadiene can be lowered to one-third of its cost with alcohol at 90¢ per gallon[152].

The butane and butene dehydrogenation plants allocated by Rubber Reserve[152] are listed in the following table:

Company	Location	Rated Capacity, Tons per Year
Cities Service Refining Company	Lake Charles, La.	55,000[1]
Humble Oil and Refining Company	Baytown, Texas	30,000[1]
Neches Butane Products Company	Port Neches, Texas	50,000[1]
Shell Union Oil Company	Torrance, Calif.	55,000[1]
Sinclair Rubber, Inc.	Houston, Texas	50,000[1]
Phillips Petroleum Company	Borger, Texas	45,000[2]
Esso Standard Oil Co.	Baton Rouge, La.	15,000[1]
Sun Oil Company	Toledo, Ohio	15,000[3]
Standard Oil Company of California	El Segundo, Calif.	15,000[3]

[1] Butene dehydrogenation.

[2] Same as [1] but butenes made from butane.

[3] Houdry process from butane.

Thermodynamic Equilibria for Diolefins and Styrenes

Equilibrium conditions permit butadiene to be made from either butane or butenes. Below 650°C at 1 atmosphere pressure higher yields are obtainable from the olefin (curves, Figure 2) than from the paraffin (curve 1, Figure 2). Below 725°C the formation of butadiene from *n*-butane requires higher temperatures than its simpler dehydrogenation to 1-butene. This is apparent in comparing curves 1 and 2 of Figure 2, which represent equilibria at atmospheric pressure. These equilibrium data represent calculations based on the data of Pitzer, Rossini *et al.*[99, 150]. The opposite trend at higher

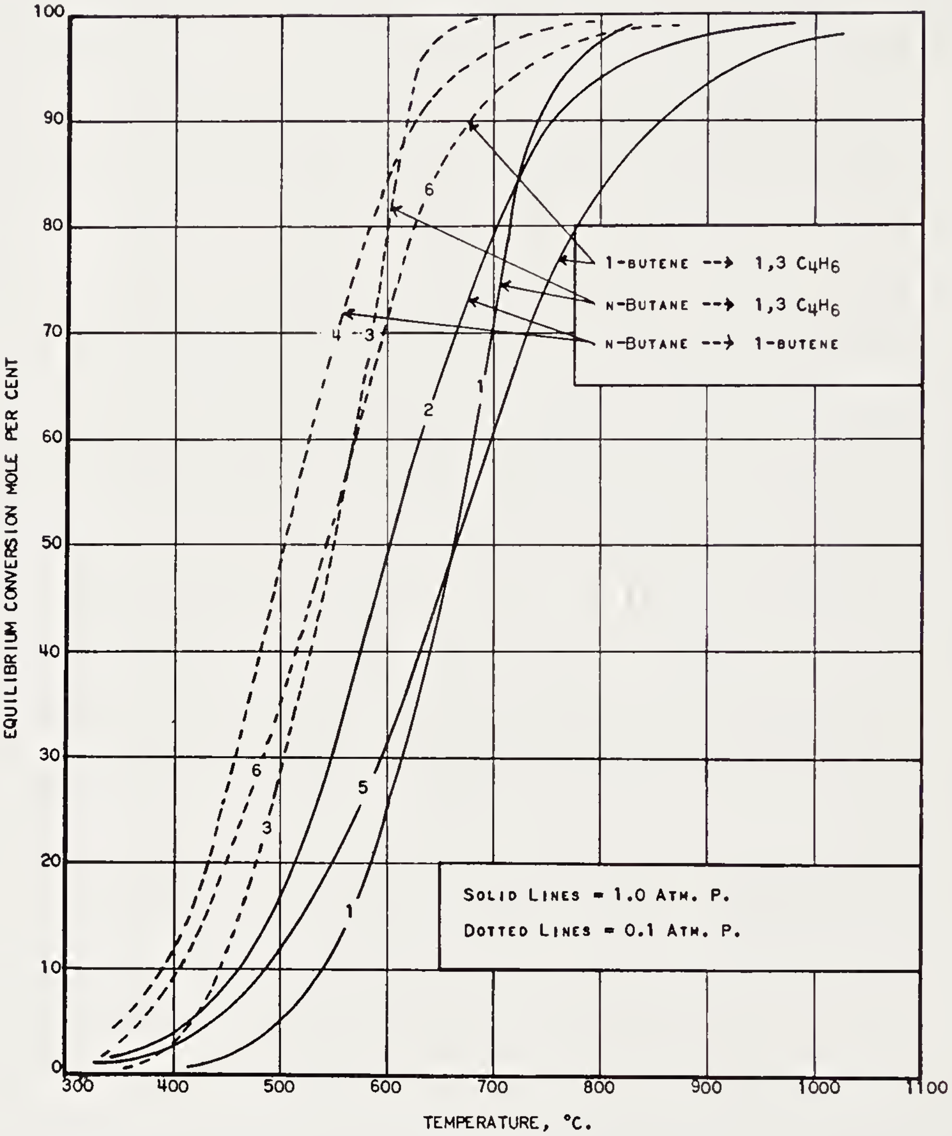

Figure 2. Dehydrogenation equilibria Butane-Butene-Butadiene.

temperatures is not of practical significance because degradation reactions become excessive. Curves 3 and 6 show that by reducing the pressure to 0.1 atmosphere it is possible to reduce by 100°C the temperature corresponding to a given per cent conversion to butadiene. The advantage of this lower pressure operation is utilized in commercial processes for making butadiene. These results are for the independent formation of olefins and diolefins. Data for their simultaneous formation were given on page 456.

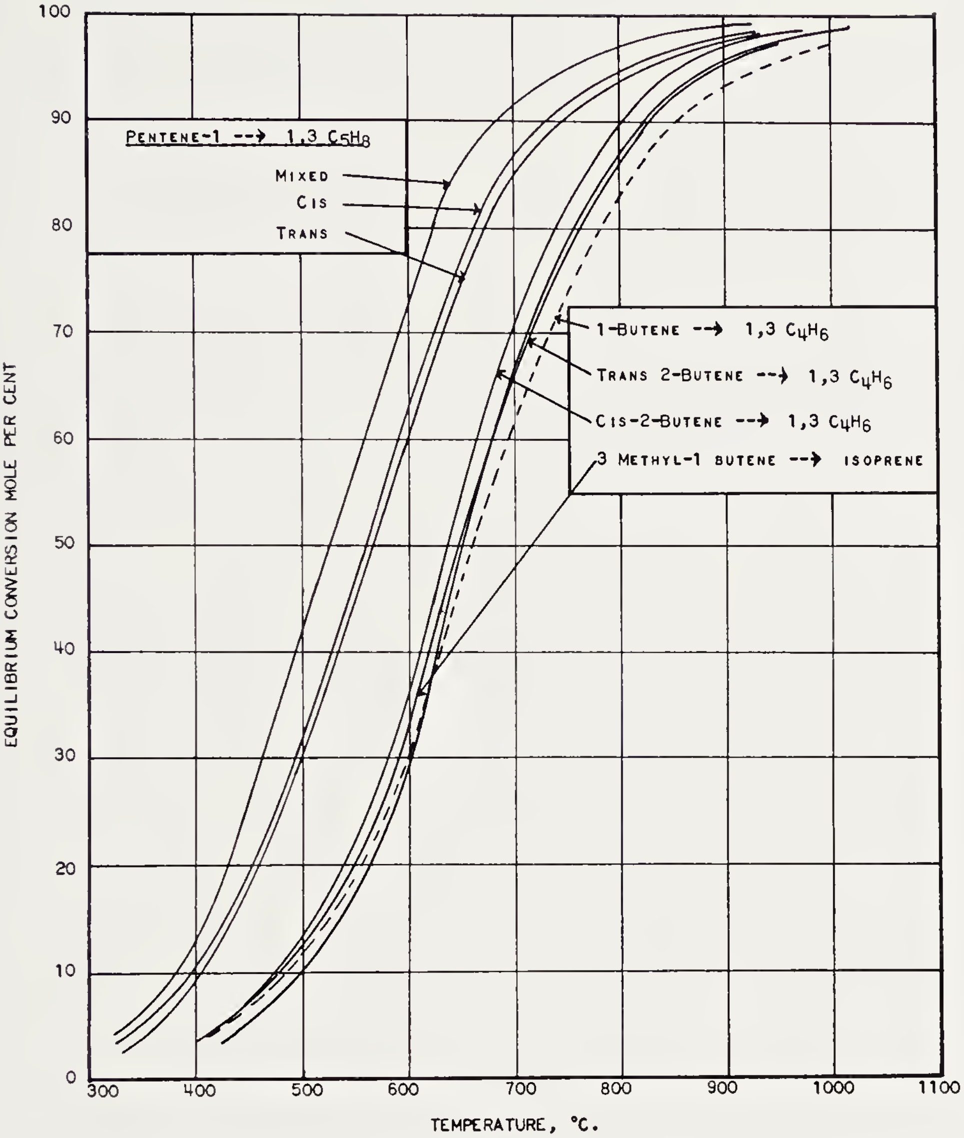

Figure 3. Dehydrogenation equilibria: comparison of butenes and pentenes.

Comparison of the curves in Figure 3 shows only small differences in the equilibrium yields of 1,3-butadiene from 1-butene as compared to *cis* and *trans* 2-butenes. The equilibrium yields of isoprene from 2 methyl, 1-butene are about the same as those of butadiene from the butenes. Normal pentene-1 is in equilibrium with larger yields of its diene than are the butenes or methyl butene. Data for these hydrocarbons are summarized in Table 5.

Equilibrium yields for the conversion of ethyl benzene to styrene are higher at a given temperature than those for butadiene from 1-butene. The formation of styrene is also benefited by reduction in pressure, equivalent equilibrium yields at 0.1 atmosphere pressure being obtained about 100°C below those at 1.0 atmosphere pressure. These comparisons are shown in Figure 4 and Table 5. At a given temperature the equilibrium conversion of isopropyl benzene to methyl styrene is much greater than that of ethyl benzene to styrene, the yields of methyl styrene at atmospheric pressure being about the same as those of styrene from ethyl benzene at 0.1 atmosphere pressure.

Table 5. Temperatures °C Required for Various Equilibrium Conversions

% Conv.	*n*-Butane to 1-Butene		*n*-Butane to 1.3 C_4H_6		1-Butene to 1,3 C_4H_6		*Cis*-2-Butene to 1,3 C_4H_6	*Trans*-2-Butene to 1,3 C_4H_6	1-Pentene to 1,3 C_5H_8			2-Methyl 1-Butene to Isoprene	Ethyl Benzene to Styrene		Isopropyl benzene to Methyl Styrene
									Cis	*Trans*	Mixed				
	1.0 Atm.	0.1 Atm.	1.0 Atm.	0.1 Atm.	1.0 Atm.	0.1 Atm.	1.0 Atm.	1.0 Atm.	1.0 Atm.	1.0 Atm.	1.0 Atm.	1.0 Atm.	1.0 Atm.	0.1 Atm.	1.0 Atm.
5	415	350	500	420	435	370	430	450	350	365	335	430	415	350	340
10	460	390	540	440	485	405	480	495	400	410	380	480	465	390	380
20	515	430	585	475	550	445	540	560	455	460	430	545	525	430	420
30	545	455	615	505	595	480	580	600	495	500	460	590	565	455	450
40	575	480	640	525	630	510	610	630	530	535	495	615	595	480	475
50	600	500	660	545	665	540	635	655	560	570	525	650	620	505	500
60	630	525	680	565	700	570	665	685	595	600	555	680	645	535	530
70	670	555	700	585	730	600	695	720	625	630	590	715	675	565	560
80	705	585	720	605	780	625	735	760	665	670	625	760	715	595	595
90	753	625	740	620	855	675	805	825	730	745	680	830	780	630	640
95	815	670	775	630	925	725	855	885	805	825	750	890	845	670	690

The values shown for styrene are slightly higher than predicted by the equilibrium equation published by Guttman *et al.*[67]. On the other hand, they are lower than found by Ghosh *et al.*[54] and higher than indicated by Mitchell[122].

Dehydrogenation of Olefins

Early Studies of Butene Dehydrogenation. Methods of producing diolefins by dehydrogenation of monoolefins were patented by Mathews *et al.* as early as 1910[110, 111, 112]. Their 1912 patent[112] described the use of catalysts such as metals (copper), oxides and salts. The dehydrogenation of butene under partial vacuum or with N_2, CO_2 or H_2O diluents over strontium uranate was disclosed in an I.G. patent filed in 1926[156]. Apparently no intensive investigations of butene dehydrogenation were made before about 1934 when Russian investigators published their results. Following this, German and American industrial laboratories became interested in the field. Patent applications were filed in 1936 by the Standard Oil Development Company[53] and in 1937 by the I. G. Farbenindustrie[88]. Butene dehydrogenation was studied intensively during the years 1938–1942, resulting in the development of commercial processes.

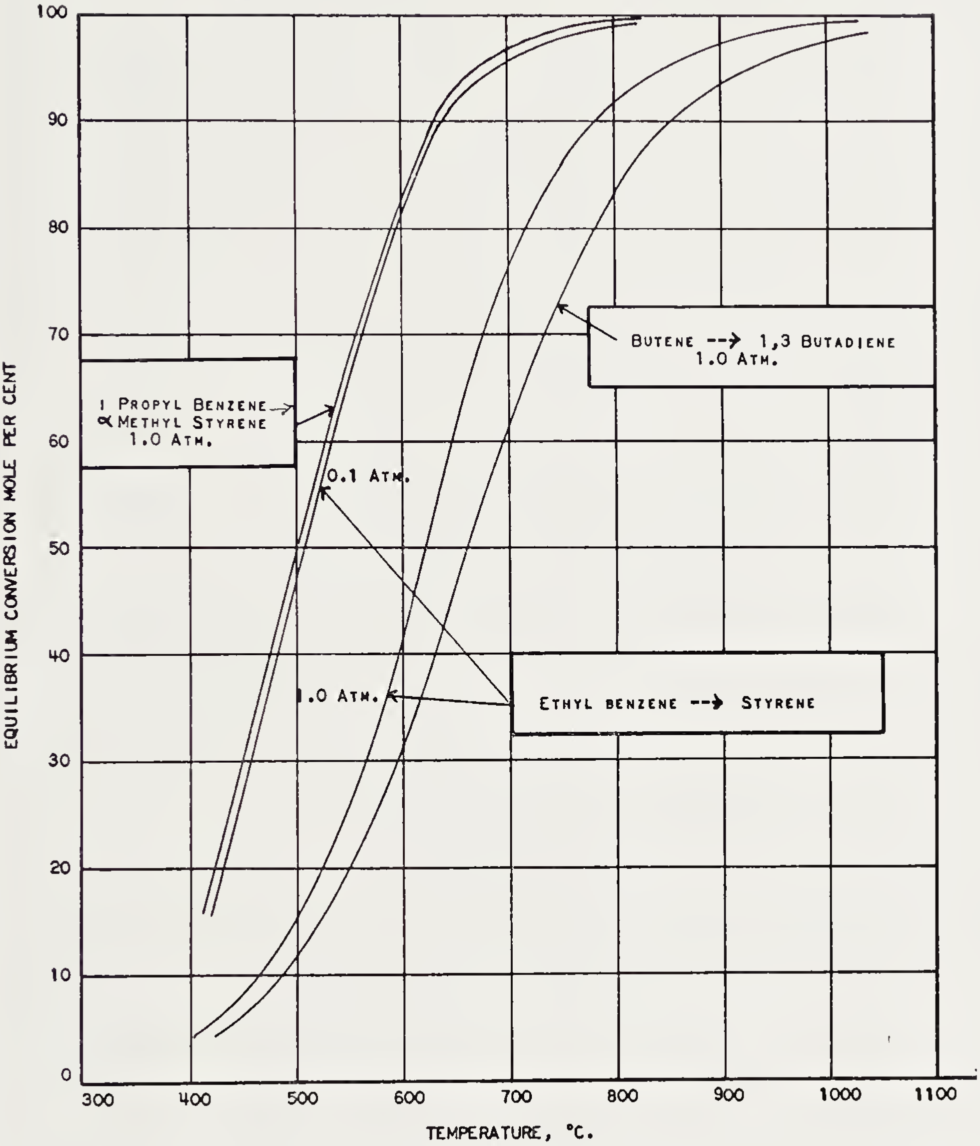

Figure 4. Dehydrogenation equilibria: comparison of styrenes with butadiene.

It is interesting that the early work on butene dehydrogenation disclosed some of the pertinent operating features of modern processes, for example, obtaining reduced pressure either by vacuum or by dilution with steam. However, the early researches failed to provide a catalyst which operated satisfactorily in the presence of diluent steam.

The early work[47] of the Russian investigators on butene dehydrogenation was done with relatively poor catalyst giving butadiene yields of 25 to 29 per cent with 27 to 29 per cent degradation to other products. Magnesia was reported to be superior as a catalyst to ZnO, Cr_2O_3, silica gel, Pt, Fe, Cu or C, which materials gave lower yields than thermal dehydrogenation. Nitrogen was used as a diluent to reduce the partial pressure of the butene. Batalin *et al.*[18] used steam as a diluent and glossy carbon as a catalyst, but obtained maximum butadiene yields of only 18 per cent when operating at 750°C and 14 to 23 seconds contact time. Much improved results were claimed by Yakubchik[193]. At 22 per cent butadiene yield per pass, he reported an ultimate recycle yield (per cent selectivity) of 78 per cent over an unspecified catalyst, when using steam dilution and quenching the products. Other catalysts included in the study were MgO, Cu, glossy carbon, Glukhov clay and the Lebedev catalyst ($ZnO \cdot Al_2O_3$).

Later Russian work by Balandin *et al.*[15] appeared to favor the use of CO_2 as a diluent. Maximum butadiene yields of 34.2 per cent with a 77 per cent selectivity were obtained over a chromic oxide catalyst. Balandin did not describe the "specially prepared chromic oxide catalyst," but indicated that inferior results were obtained with catalysts comprising Cr_2O_3 with Al_2O_3, ZnO, CuO, MoO_3, kieselguhr or zircon and with alumina-vanadia, silver vanadate or magnesia catalysts.

During the period 1936–1938 numerous patent applications were filed on dehydrogenating olefins to diolefins. A 1936 application[53] filed by the Standard Oil Development Company described the dehydrogenation of normal butenes over a chromia-activated alumina catalyst as the second stage of a process for making butadiene from butane. At 50 mm Hg pressure, 577°C and 132 v/v/hr (STP) an 18 per cent yield of butadiene was obtained with 51 per cent selectivity. The I. G. Farbenindustrie filed applications in 1937 on a two-stage process of making butadiene from *n*-butane, in which the butene from the first stage was diluted with 10 volumes of carbon dioxide and dehydrogenated over procelain at 680°C[89, 90]. The two-stage process included the use of silver nitrate for concentrating olefins and cuprous ammonium chloride for concentratin diolefins. Another I. G patent[91] on the use of steam as a diluent for butene dehydrogenation disclosed graphite and glossy carbon as catalysts, claiming a 35 per cent conversion and 70 per cent selectivity at 700°C, 0.2 seconds contact time and 8/1 steam to butene ratio. A 75 per cent selectivity at 25 per cent conversion was obtained over a silver vanadate catalyst[88]. The very good yields claimed in the above patents appear questionable since the best I. G. catalyst for butene dehydrogenation would appear, on the basis of very extensive patent coverage, to be 72 ZnO-9 $CaCrO_4$-18Al_2O_3[66]. At 20 per cent conversion per pass this catalyst was claimed to give 70 per cent selectivity when dehydrogenating butene diluted with 6 volumes of steam at 580°C and 0.5 second contact time. This reference broadly disclosed the use of catalysts containing 1 to 10 per cent of an oxide of Cr, V, Mo, U, or W on 90 to 99 per cent ZnO. As discussed later, a somewhat similar catalyst was used in Germany for styrene production but was inferior to catalysts subsequently developed.

Extensive studies of butene dehydrogenation at reduced pressures over alumina-chromia catalysts were reported by Grosse, Morrell and Mavity to the American Chemical Society in 1939[65]. Ultimate recycle yields of butadiene as high as 79 per cent could be obtained by operating at a 12 per cent butadiene yield per pass, but selectivities of only 50 to 60 per cent were obtained at yields per pass of 16 to 22 per cent. Methyl butenes and normal pentenes could also be dehydrogenated to the corresponding diolefins, but cyclopentane gave poor yields of cyclopentadiene. The catalyst was made by impregnating Grade A activated alumina with 4 per cent Cr_2O_3 from chromic acid or chromic nitrate solution.

Roy[151] has shown that the dehydrogenation of butene over alumina-chromia is benefited by the addition of small amounts of water vapor. Butene dried over sodium gave inferior yields (11.3 *vs.* 30.8 per cent C_4H_6). Addition of 1 to 1.5 per cent sulfur gave increased yields as did also the addition of 1 volume of air per volume of butene.

Best Catalysts for Producing Butadiene. For partial vacuum-type butene dehydrogenation an alumina-chromia catalyst is still the best available and is used in the Houdry designed plants. For operating with diluent steam the following catalysts have been used commercially:

(a) Standard Oil Development Company 1707
(b) Phillips promoted bauxite
(c) Shell 105
(d) Dow nickel calcium phosphate.

Catalyst 1707. Initial operations in all but one of the butene dehydrogenation plants were carried out with a catalyst known by the number 1707. Its composition was 72.4 MgO-18.4 Fe_2O_3-4.6 CuO-4.6 K_2O. This was only one catalyst of a number of suitable compositions which had been developed by the Standard Oil Development Company. At the time the Rubber Program was frozen it was selected as most suitable for initial operations.

Kearby[96] has described the development and characteristics of this type of catalyst. The potassium oxide acts as a promoter and is effective in increasing the conversion at given conditions from 20 to 40 per cent and in increasing the selectivity at 20 per cent conversion from 65 to 85 per cent. The potassium oxide reduces the amount of carbon deposited on the catalyst and causes deposited carbon to be removed during steaming periods. Oxides of rubidium and cesium are also good promoters, but those of sodium and lithium are inferior. Iron and copper are active dehydrogenating components and copper also can function as a stabilizer. In place of these active components, catalysts can also be made using chromium, manganese, cobalt and nickel. The magnesia serves as a catalyst support. Good catalysts can also be made with no support or with oxides of zinc, beryllium, or zirconium as supports. Alumina is inferior as a support in the presence of diluent steam.

1707 catalyst is prepared by adding a solution of iron and copper sulfate to magnesium oxide suspended in water. The reacted mixture is filtered, washed incorporated with a solution of potassium carbonate, dried and calcined at 1200°F.

Data[96] comparing some 1707-type catalysts are summarized in Table 6.

Several modifications of the use of 1707 catalyst for butene dehydrogenation have been disclosed. Sumerford[170] proposes the use of potassium chromate as a promoter. Meinert and Vesterdal[121] show methods of replenishing the potassium promoter lost during use. Methods of carrying out butene dehydrogenation in a fluid catalyst unit are described by Murphree *et al.*[130], Hemminger[77], and Roetheli[149]. Watson[186] describes the use of 1707 catalyst in the second stage of a process of making butadiene from butane.

Phillips Promoted Bauxite Catalyst. During initial operations of their butene dehydrogenation plant the Phillips Petroleum Company used a catalyst made by impregnating bauxite with about 5 per cent of barium hydroxide and/or strontium hydroxide. It is probable that the activity of this catalyst is due to the iron which it contains as an impurity. Phillips Laboratories found sodium hydroxide was inferior as a promoter. However, they later patented potassium hydroxide as a promoter[159]. Because of the poor selectivity (low ultimate recycle yields of only 50 to 37 per cent) obtainable with the bauxite catalyst[160] the Phillips plant was converted to the potassium promoted iron oxide type catalyst.

Shell 105 Catalyst. Following the decision to use 1707 catalyst in government owned plants the work of the Standard Oil Development Company showing the merits of potassium promoted iron catalysts was made available to the Office of Synthetic Rubber and various laboratories working in this field. Efforts to improve this catalyst or develop others were continued at laboratories such as those of Princeton University, Shell Development Company and Dow Chemical Company.

The Shell Development Company carried out extensive development work on an unsupported, potassia promoted, chromia stabilized iron oxide catalyst. This catalyst, known as 105 catalyst, is stated[41] to have the composition 93 Fe_2O_3, 5 Cr_2O_3, 2 KOH, but later preparations are believed to contain about 7 per cent K_2CO_3[43]. With relatively high steam dilution ratios, it is possible to use this catalyst for very long periods of continuous operation, without intermittent steaming of the catalyst. This advantage led to its replacing 1707 catalyst in commercial butene dehydrogenation plants.

The catalyst can be made[42] by simply mixing finely powdered calcined ferric oxide, chromic oxide and potassium carbonate, wetting and forming into pellets. Shell patents emphasize the importance of calcination at 800 to 950°C of either the iron oxide or the finished catalyst[68, 160]. Wright has patented the use of rubidium and cesium as alternate promoters for the 105 catalyst[191], and Pine and Ray (Harshaw Chemical Co.) its preparation from ferrous carbonate[144]. The use of catalysts having the composition of the 105 catalyst for butene and ethyl benzene dehydrogenation appears to be dominated by a Standard Oil Development Company patent[97].

TABLE 6. COMPARISON OF 1707 TYPE CATALYSTS FOR BUTENE DEHYDROGENATION
1200°F; butene flow 800 v/v/hr (STP); 7/1 steam/butene mol ratio

Catalyst Composition	Conversion (%)	Selectivity to C_4H_6 (%)	% Conversion to Carbon
80 MgO-20 Fe_2O_3-5 CuO	22	63	1.8
80 MgO-20 Fe_2O_3-5 CuO + 1.5% K_2O	45	68	0.05
80 MgO-20 Fe_2O_3-5 CuO + 1.5% Na_2O	22	72	.27
80 MgO-20 Cr_2O_3-5 CuO-1.5 K_2O	46	52	.08
80 MgO-20 MnO_2-5 CuO-1.5 K_2O	31	65	1.3
85 MgO-10 CuO-5 K_2O	28	80	0.3
90 MgO-10 Co_2O_3-5 CuO-1.5 K_2O	34	57	1.8
80 ZnO-20 Fe_2O_3-5 CuO-5 K_2O	50	66	0.3
80 ZrO_2-20 Fe_2O_3-5 CuO-5 K_2O	44	72	.1
80 Beo-20 Fe_2O_3-5 CuO-5 K_2O	39	75	.1
93 Fe_2O_3-5 CuO-2 K_2O	28	66	.7

Dow Nickel Calcium Phosphate Catalyst. Both the 1707 and 105 type catalysts can be regenerated by treating with steam. A new calcium-nickel phosphate catalyst* developed by Britton and Dietzler (Dow Chemical Company)[23] requires air regeneration. However, this is compensated for by

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* The Dow catalyst is a calcium nickel phosphate of the formula $Ca_8Ni(PO_4)_6$ stabilized with chromium oxide[24]. It is prepared by precipitating a solution of nickel and calcium chlorides with an ammonia-phosphoric acid solution. The flocculent precipitate is washed, filtered, dried, ground and mixed with 2 per cent graphite and 2 per cent chromium oxide. The commercial production of this catalyst has been described by Heath[76].

the higher ultimate yields of butadiene obtained at relatively high steam to butene ratios (20/1). The high selectivity of this catalyst is illustrated in Figure 5. These high selectivities drop off with increasing catalyst age as shown below[24]:

Butene Dehydrogenation Over Dow Ca—Ni Phosphate Catalyst

Cycle No.	123	817	1588	1972	2399
Temperature (°C)	610	620	620	630	630
% Conversion	30.9	37.1	28.2	26.7	29.4
% Selectivity	92.3	86.4	79.3	83.0	70.7

The Dow catalyst gives ultimate butadiene yields as high as 90 to 95 per cent in laboratory test units. Also, the selectivity does not fall off rapidly

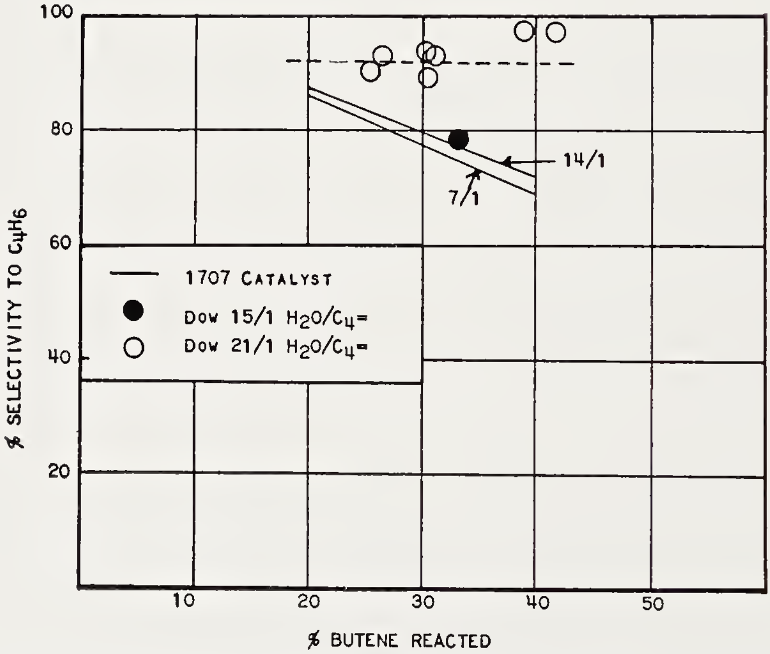

Figure 5. Comparison of butene dehydrogenation catalysts.

with increasing conversion levels up to 40 to 50 per cent as it does with iron catalysts. However, it requires a steam/butene ratio of at least 18/1.

The Dow catalyst was used for a while in the Baytown plant operated by the Humble Oil Company and is still preferred for use in the copolymer plant at Sarnia, Ontario. However, it is more expensive than the 105 catalyst and requires modification of other existing plants to provide for air-steam regeneration[129]. It also gives a product containing different impurities than those obtained with 105 catalyst. Whether its use will be extended to other plants depends on whether all considerations indicate an over-all advantage for a given plant[129].

Other Investigations of Butene Dehydrogenation. Numerous other catalyst compositions have been investigated for dehydrogenating olefins to diolefins. Studies have also been carried out on the effect of various diluents on the dehydrogenation of olefins. The dehydrogenation of pentenes has been studied fairly extensively.

Other Catalyst Compositions and Diluents. References on a number of catalysts studied for butene dehydrogenation are summarized in Table 7, which also lists references on the use of various diluents or additives. It is probable that none of these compositions is equal to the best catalysts described above. However, directly comparable data are not available. It is also doubtful that any of the diluents shown in Table 7 offer real over-all advantages.

Dehydrogenation of C_{5+} Hydrocarbons. Branched pentenes can be dehydrogenated to isoprene fairly readily, but normal pentenes and C_6 olefins tend to crack and give lower molecular weight diolefins. Using 1707 catalyst, Guyer[70] obtained an ultimate yield (selectively) of 66 per cent isoprene at a 42 per cent conversion level of trimethyl ethylene, but only a 27 per cent ultimate yield of *n*-pentadiene from 2-pentene. In the latter case the selectivity to butadiene was 33 per cent. The yields of isoprene were at least as good as those of butadiene from normal butenes under similar conditions. Using an alumina-chromia catalyst Mavity and Zetterholm[117] obtained a 67 per cent selectivity to isoprene at a 71 per cent conversion level and 83 per cent at a 43 per cent conversion level. Also, with an alumina-chromia catalyst Frey[49] has obtained 60 per cent selectivity to total dienes from hexene, but only 22 per cent selectivity to C_6 diolefins. The dehydrogenation of mixed butenes and pentenes has been described by Seyfried *et al.*[162] and by Kilpatrick[98].

Commercial Processes for Butene Dehydrogenation. In the discussion of catalysts reference was made to two commercial dehydrogenation processes for making butadiene from petroleum gases. The Jersey and Houdry processes are described briefly below.

The Jersey Dehydrogenation Process. The Jersey butene dehydrogenation process has been described by Russell *et al.*[153], by Kleiber *et al.*[101], and by Nicholson *et al.*[136]. A feed containing about 70 per cent normal butylenes is heated to 1100°F and fed into special jet-type mixers with 10 to 20 volumes of steam preheated to 1300°F. The mixed gases then pass through a 42-inch deep bed of catalyst in a 16-foot diameter reactor. The butylene feed rate is in the range of 200 to 800 v/v/hr (STP). The products are quenched as they emerge from the catalyst by injecting steam or water. Butadiene is then separated from the products by extractive distillation with cuprous ammonium acetate (or other solvent) and the rest of the product recycled. The catalyst reactor is designed to insure rapid heating of the feed, uniform passage of it through the bed and rapid cooling to minimize degradation reactions. When catalyst activity decreases due to carbon deposition, the butene feed is stopped, and the carbon is removed by reaction with the steam.

TABLE 7. REFERENCES ON OTHER CATALYSTS AND DILUENTS
Butene Dehydrogenation

	Ref.
CATALYSTS	
Alumina Supported	
1–15% BeO + 1–10% Gr. IV, V or VI	82, 83
V_2O_5—Ag	69, 88
Left side Group VI	116, 184, 185
5% Ni	131
Left side Group IV, V, VI (V_2O_5)	184
Alpha + 10 Cr_2O_3	172
Cr_2O_3 + Ce_2O_3, ThO_2 or MnO	178
Other Compositions	
Copper	189
Carbon	91
SiO_2 or clay + 5% Ni	131
Brucite (MgO—Fe_2O_3—SiO_2)	41, 158
SiO_2, MgO Clay + Left side Group IV, V, or VI	184
80 Cr_2O_3-15 Fe_3O_4-5 Al_2O_3	56
Asbestos-CuO-CaO or Na_2O	100
DILUENTS	
SeO_2 or SeO_2 + HX*	2
Cl_2	8
HX*	29
SO_2	167
SO_3	166
O_2	100
CO_2	88, 131
Propylene	157
Benzene	50
Thermally cracked olefins	48

* X represents a halogen.

The process normally operates at a conversion level of 20 to 25 per cent. Ultimate recycle yields vary with feed stock purity, operating conditions, and catalyst, but are usually in the range of 70 to 80 per cent.

Phillips Butadiene Process. The Phillips plant at Borger, Texas, included a butane dehydrogenation plant as described on page 474, and a steam-dilution butene dehydrogenation plant which originally used a bauxite catalyst, but later changed to the promoted iron type catalyst.

Houdry Butane Dehydrogenation Process. The Houdry process for making butadiene from butane indirectly involves the dehydrogenation of butylenes which are formed as intermediate products from butane, but are recycled until converted to butadiene. As mentioned earlier, this process was considered insufficiently developed when the Rubber Program was frozen and only two small plants were authorized. It appears that the government's decision was sound, because initial operations of the two Houdry plants were beset with difficulties. Sun's Toledo plant, with a rated capacity of 15,000 tons per year, produced only 2,479 tons in 1944 and 9,046 tons in 1945. Standard Oil of California's El Segundo plant, with a rated capacity of 18,000 tons per year, produced 3,975 tons in 1944 and 8,742 in 1945[152]. However, subsequent operations were improved[129] and later information indicated that design capacity could be attained.

The Houdry process appears to be a new engineering design for applying the earlier studies by the Universal Oil Products Company[102, 152] and by Komarewsky *et al.*[102] It involves dehydrogenation and air regeneration cycles of very short length (5 to 10 minutes). The heat released during regeneration is stored in the mixture of catalyst and inert "Alundum" and used to furnish the heat required by the dehydrogenation reaction. Dehydrogenation is carried out in a partial vacuum at a pressure of 3 to 10 inches of mercury, at about 1050 to 1100°F and at a butane feed rate of about 0.8 to 2.0 liquid v/v/hr[79, 196]. An alumina-chromia catalyst steamed for 20 hours at 1400°F and mixed with 2 volumes of "Alundum" has been described [79, 80]. The Houdry process operates both for the dehydrogenation of a butane stream and for the dehydrogenation of products obtained from the butane stream. An over-all selectivity or ultimate butadiene yield of 67 per cent was obtained in laboratory work[196].

The original Houdry design included either single-stage or two-stage operations, but only one of the two commercial units was equipped to operate as a two-stage unit[104]. In the two-stage process one reactor can be used for obtaining a butene-rich stream and two reactors for converting this to butadiene[196]. In a one-stage operation butane feed is admixed with recycle product from which butadiene has been removed and this represents the only feed stream contacting the catalyst[81]. A careful control of operating variables is required to insure that the carbon formed does not furnish excessive heat during regeneration. Carbon forming tendencies of the catalyst are controlled by its chromia content and calcination temperature[196]. The process is equally applicable for making monoolefins[81].

Dehydrogenation of Alkyl-Aryl Hydrocarbons

The dehydrogenation of ethyl benzene to styrene was developed and applied sooner than that of butene to butadiene. Considerable interest in this process was shown as early as 1929–1930 when both DuPont and I. G. Farbenindustrie filed patent applications[57, 109, 169, 192].

Prior to World War II, one plant was operating in the United States. This was the Dow plant at Midland, Michigan. During World War II the use of the process was greatly increased, and the Rubber Reserve Company authorized the building of new plants with a capacity of 187,500 short tons per year. The location and design capacities of these plants are summarized below[152]:

Company	Location	Rated Capacity Short Tons/Yr
Carbide and Carbon Chemicals Corp.	Institute, West Virginia	25,000
Dow Chemical Company	Los Angeles, California	25,000
Dow Chemical Company	Velasco, Texas	50,000
Koppers Company	Kobuta, Pennsylvania	37,500
Monsanto Chemical Company	Texas City, Texas	50,000

Development of Styrene Process. The earlier patents on dehydrogenating ethyl benzene describe a wide variety of catalysts and it is difficult to make a selection of a specific preferred composition from them. Both the Graves and Suida patents[57, 169] stressed the use of catalysts containing cerium oxide. The Suida patent taught the importance of carrying out the reaction at reduced pressures, showing ultimate recycle yields of 70 to 90 per cent of styrene at pressures of 10 to 20 mm Hg. This early patent also described application of the process to the dehydrogenation of diethyl benzene, isopropylbenzene, methyl ethyl benzene, ethyl naphthalene, propyl naphthalene, and butyl naphthalene.

Mark and Wulff[109] disclosed that the reduced pressure could be obtained advantageously by using steam or CO_2 as diluents. These diluents served to reduce carbon deposition on the catalyst and to prevent reduction of components like iron, cobalt or nickel to metallic form. This early patent limited the amounts of such reducible components to 3 per cent. Although numerous catalyst compositions are disclosed in this patent, the fourteenth and last example describes a 50 ZnO-40 Al_2O_3-10 CaO composition which was used in I. G. styrene plants up to about 1942[147]. A later patent of Wulff and Roell[192] extended the amount of the reducible metals to quantities greater than 3 per cent, while maintaining them in unreduced form by H_2O or CO_2 dilution or by combining them as vanadates, molybdates, tungstates, chromate, borates, or phosphates. It is interesting to note that the best iron and nickel catalysts in use today for making butadiene and styrene contain oxides, easily reducible to metals, but used under conditions which prevent reduction to the metal (steam dilution or combination with phosphate).

During 1940 and 1944 the I. G. Farbenindustrie carried out an extensive catalyst development program[147] which resulted in increasing the ultimate yield of styrene from ethyl benzene from 80 to 82 per cent to 90 per cent. This is the same yield as obtained in United States plants after changing to the catalysts developed for butadiene production. The improved I. G. catalyst had the composition 77.4 ZnO-7.6 Al_2O_3-9.4 CaO-2.8 K_2CrO_4-2.8 K_2SO_4 or the same with half the CaO replaced by MgO.

In the United States commercial production of styrene was carried out over a bauxite catalyst in the early part of World War II[190]. However, this catalyst was replaced by 1707 (see p. 473) catalyst when it became available. Since ethyl benzene dehydrogenates more readily than butene, the advantages of 105 catalyst are less for making styrene than for making butadiene, but it is believed to be in general use today.

Studies of Various Catalysts. Since ethyl benzene can be dehydrogenated thermally without any catalyst (although with poor yields), it is not surprising that many dehydrogenating components show some beneficial effect. In addition to the catalysts discussed above, a large number of other compositions have been studied for dehydrogenating alkyl-aromatic type hydrocarbons. These catalysts are of the same general type as have been investigated for the dehydrogenation of butane and normal butenes.

Webb and Corson[187] reported maximum yields of 55 to 60 per cent of styrene to be obtainable by thermal dehydrogenation. They found steam dilution to have only a small beneficial effect for the thermal reaction. Mitchel[122] found that an ultimate yield of only 45 per cent styrene is obtainable by thermal dehydrogenation of ethyl benzene at 700°C, with only 20 per cent conversion per pass.

In addition to the two iron-type catalysts discussed above, which have been used in commercial plants, natural products containing oxides of iron, such as bauxite and dolomite, have been found to be fairly good dehydrogenation catalysts for ethyl benzene in the presence of diluent steam[133, 188, 190]. Wood and Capell[190] obtained best results with an Alabama bauxite containing 19.9 per cent Fe_2O_3, 0.3 per cent CaO and 0.1 per cent MgO. Nickels[133] claimed to obtain an improved catalyst by adding 10 per cent of K_2CO_3 or Rb_2CO_3 to a low iron bauxite. Their best ultimate yields were only 70 to 82 per cent. Webb and Corson[188] obtained ultimate yields of about 70 per cent of styrene, vinyl naphthalene, etc., using a calcined dolomite ore containing 12 per cent Fe_2O_3. The alkalinity of the magnesium and calcium carbonates in this support are beneficial in promoting the water gas reaction between the diluent steam and deposited carbon.

Catalysts containing nickel have a greater tendency than iron to form carbon. Even in the presence of diluent steam, excessive carbon is frequently formed and the Germans considered reactors made of nickel-containing alloys to be unsatisfactory. The Dow nickel-calcium-phosphate catalyst overcomes this difficulty by combining the nickel as a phosphate[23]. Wulff and Roell[192] had recommended this technique for Cu, Cr, Fe, and Ni, but implied that Ni was to be used "cautiously or not at all." One of the catalysts described by Suida[169] contained nickel carbonate, iron nitrate and copper carbonate held on pumice. This catalyst was promoted with an alkaline additive, sodium silicate, but it apparently was not used with diluent steam.

Stanley and Salt of the Distillers Co. have taken out extensive patent coverage on the use of vanadium catalysts for dehydrogenating ethyl benzene in the presence of steam[163]. They described catalysts containing 3 to 10 per cent V_2O_5 on activated alumina granules. MgO is also mentioned as a catalyst support. With a 5 per cent V_2O_5-95 per cent Al_2O_3 catalyst they claimed a very high, 95 per cent, selective dehydrogenation. A 98 Al_2O_3-2 V_2O_5 catalyst was reported by Lyrbraskii and Kagan to give only a 46 per cent yield of styrene at 630°C[108]. A more recent Stanley *et al.* patent[164] describes MgO—V_2O_5 catalyst and MgO-Kaolin-V_2O_5 catalysts promoted with alkalies to reduce carbon deposition.

Alumina-chromia compositions are excellent catalysts for dehydrogenating ethyl benzene at reduced pressure in the absence of steam. Mavity *et al.*[118] obtained ultimate styrene yields of 89 per cent over U.O.P. alumina-chromia catalyst. At 250-mm Hg pressure and 600°C their yield per pass was 49.5 per cent as compared with only 1 per cent over quartz chips. The ultimate yield of styrene was found to decrease both with increasing conversion level and with increasing pressure of operation. Modified alumina-chromia catalysts (70 Cr_2O_3-15 Al_2O_3-15 Cu and 80 Cr_2O_3-5 Al_2O_3-15 Fe_3O_4) were used by Ghosh *et al.*[54, 55] for dehydrogenating ethyl benzene and ethyl naphthalene. A yield of 35 per cent vinyl naphthalene could be obtained at 600°C. Oblad *et al.*[137] compared the dehydrogenation of ethyl benzene over chromia gel and 90 Al_2O_3-10 Cr_2O_3 catalysts with that of various paraffins and naphthenes. Working at atmospheric pressure and the relatively low temperature of 482°C they found that ethyl benzene reacted slowly and strongly poisoned the catalyst.

Many other catalyst compositions have been investigated for dehydrogenating alkyl-aromatic hydrocarbons. Although it is difficult to make exact comparisons among these, it is unlikely that they are equal to the catalysts used commercially in the United States and Germany. References to some of the compositions studied are summarized in Table 8.

Dehydrogenation of Various Alkyl-Aromatic Hydrocarbons. Of the alkyl-aromatic hydrocarbons susceptible to dehydrogenation, ethyl benzene has received the greatest attention. However, isopropylbenzene has also been studied fairly extensively and numerous other hydrocarbons have been investigated.

Isopropylbenzene dehydrogenates primarily to alpha-methyl styrene over 1707 catalyst at conversion levels below 40 per cent[124]. Nickels *et al.*[134] attempted to dehydrogenate isopropylbenzene and simultaneously convert the product to styrene, but were unable to get good yields of styrene without excessive degradation. They studied both thermal and catalytic reactions. The best catalytic results obtained at about 20 per cent conversion gave a selectivity to total styrenes about the same as the ultimate yield of styrene obtainable in dehydrogenating ethyl benzene. Alumina-chromia was markedly poisoned by the addition of water to the feed, but this effect could be compensated for with regard to activity, by using a lower feed rate and a higher temperature. Comparative results at 0.7 second contact time are summarized in the following table:

TABLE 8. MISCELLANEOUS CATALYSTS FOR DEHYDROGENATION OF ALKYL-AROMATICS

Catalyst	Refs.
Cu—Al alloys, pptd. Cu, Cu—Cr_2O_3	16
CuO—Cr_2O_3	11
CuO—Cr_2O_3—V_2O_5	9
CuO—ThO_2—Al_2O_3	17
CuO—Cr_2O_3 or CuO—MnO (alkaline pptn.)	46
CaO—MgO or C on SiO_2, Florida earth, LiOH on C	109
Active charcoal	40
Zn chromate-Cr_2O_3	161
ZnO—Al_2O_3	109, 195, 196
ZnO—Ce_2O_3 or Ce_2O_3 on clay	169
ZnO—Al_2O_3—WO_3	109
ZnO—Ce_2O_3 + WO_3, UO_3 or MoO_3	57
10–25 Ce_2O_3 + UO_3 on MgO, BeO, CaO, SrO or BaO	165
Cr_2O_3—Al_2O_3	134
Cr_2O_3, MoO_3, V_2O_5 ± Al_2O_3	37
Cr_2O_3—Al_2O_3 + MgO or ZnO	13
Chromates of metals (at. No. 23–29)	135
MoO_3 on pumice	109
V_2O_5 on Al_2O_3	16
Ni—Al_2O_3	35, 134
Ni or Pt + support (carbonized)	25
Ni on SiO_2—Al_2O_3	35

Dehydrogenation of Isopropyl benzene

Catalyst	$85\ Al_2O_3$-$15\ Cr_2O_3$			$99\ Al_2O_3$-$1\ NiO$		1707		
Temperature (°C)	600	600	650	600	650	600	600	650
Liquid v/v/hr	5.9	0.5	0.5	5.9	0.9	5.9	0.5	0.5
H_2O/HC, Mol R	0	10	10	0	5	0	10	10
Yield per Pass (Wt. per cent)								
Methyl styrene	25.7	13	57.6	25.3	48.7	18.7	20.2	35
Styrene	0.8	1.1	11.2	1.0	7.0	1.0	1.2	10.7
Selectivity*	85	85	81	84	73	84	89	68

* To styrene plus methylstyrene.

The early Graves[57] patent described the dehydrogenation of isopropylbenzene as well as diethyl benzene, ethyldiphenyl, cymene, ditolyl ethane, and ethyl naphthalene. Stanley *et al.*[163] studied the dehydrogenation of isopropyl benzene over vanadia on alumina and other carriers. Butyl benzenes can be dehydrogenated fairly well. Balandin *et al.*[13] obtained products containing 71 to 74 per cent of butenyl benzene from tertiary butyl benzene. Ditertiary-butyl benzene gave a product containing 68 per cent of dibutenyl benzene.

Nickels *et al.*[135] have made an extensive study of ethyl naphthalene dehydrogenation over 19 catalysts. Ultimate recycle yields of 90 per cent vinyl naphthalene were obtained when using 100-mm Hg pressure without diluent as compared with 81.5 per cent with steam dilution. The reaction conditions with steam dilution were suitable for operation in existing styrene plants. Over calcined dolomite Corson *et al.*[34] obtained a 70 per cent ultimate yield of olefin from ethyl naphthalene as compared with 71 per cent from ethyl benzene, 46 per cent from isopropylbenzene and 62 per cent from diethyl benzene. In the case of diethyl benzene 41 per cent was to the monovinyl and 21 per cent to the divinyl benzene. Various other alkyl aromatics have been dehydrogenated, as shown by the list in Table 9.

Studies of Diluents and Additives. As in the case of butene dehydrogenation, the dehydrogenation of ethyl benzene is benefited over many catalysts by using diluent steam or CO_2 to reduce carbon deposition. This is particularly true of catalysts containing oxides of iron and zinc as the active components. Carbon dioxide has been shown to be advantageous in ethyl benzene dehydrogenation by Balandin *et al.*[14] The use of steam in place of CO_2 offers many operating advantages such as its ready availability and its ease of separation from the product gases.

Benzene was found to be a fairly stable diluent when used in ratios up to 10 parts per part of ethyl benzene[119]. With a 5 to 1 dilution ratio at 581°C over U.O.P. Al_2O_3—Cr_2O_3 catalyst, a 34.8 per cent conversion of ethyl benzene was obtained with a 90 per cent ultimate yield. The use of benzene as a diluent was described in an early Naugatuck Chemical Company patent[132].

Addition of 10 to 25 per cent sulfur to ethyl benzene is reported to be effective in converting it to styrene at temperatures of 670 to 700°F without a catalyst[120]. At conversion levels of 30 to 45 per cent an ultimate recycle yield of 90 per cent is claimed.

Styrene Dehydrogenation Plants. In the United States the Dow process for dehydrogenating ethyl benzene was used[122] in six of the seven plants operated for Rubber Reserve using the Standard Oil Development Company 1707 catalyst. These plants gave a 90 per cent yield of styrene from the ethyl benzene feed, operating at 35 to 40 per cent conversion level. These yields appear identical with those obtained by different type plants operated in Germany.

TABLE 9. REFERENCES ON DEHYDROGENATION OF VARIOUS ALKYL-ARYL HYDROCARBONS

Hydrocarbon	Refs.
Diethyl benzene	11, 12, 34
1,3,5,triethylbenzene	12
Sec. butyl benzene	40
Diphenyl ethane*	10, 38
Ethyl naphthalene	34, 55, 135, 169
Isopropylbenzene	34, 115
Ethyl toluene	115
Menthane, terpenes	39
p-Cymene	13
Ethyl cyclohexane	115

* More easily dehydrogenated than ethyl benzene.

The ethyl benzene feed is mixed with preheated steam (2.6 pounds H_2O per pound feed) just before entering the catalyst chamber. The diluent steam reduces the feed partial pressure to 0.1 atmosphere and serves to remove carbon from the catalyst. This allows it to operate for a year or more without regeneration. Fresh 1707 catalyst gives a conversion of 37 per cent at 600°C and this temperature may be increased to 660°C as the catalyst ages.

The catalyst is weighted down in the reaction chamber by a ram in such a way that shrinkage is automatically compensated for. Nickel containing alloys can be used for preheating the steam, but not for the ethyl benzene.

Since the process operates at somewhat less severe conditions than butene dehydrogenation, there is less need for replacing the potassium promoter or using a more stable catalyst. However, since the end of the war many of the styrene plants have shifted from using 1707 catalyst (72.4 MgO-19.4 Fe_2O_3-4.6 CuO-4.6 K_2O) used during the war to 105 catalyst (7 per cent K_2CO_3 and about 5 per cent Cr_2O_3 on iron oxide).

In Germany a reactor containing banks of gas-fired 8-inch I.D. tubes which were 30 meters long was used. The 18-8 alloy tubes were copper lined[5, 22]. About 40 per cent conversion per pass and an 89 per cent ultimate yield were obtained. A mixture in the ratio of 1.25 pounds of steam per pound of ethyl benzene was preheated to 560°C and passed over the catalyst heated to 610°C. Through about 1941 a 50 ZnO-40 Al_2O_3-10 CaO catalyst was used, which gave only about a 75 per cent yield[107]. It was then found that a catalyst having the composition 77.4 ZnO-7.6 Al_2O_3-4.7 CaO-4.7 MgO-2.8 K_2CrO_4-2.8 K_2SO_4 would give 90 per cent yield and a catalyst life of 12 to 20 months[147]. The studies leading to this catalyst included the use of Na_2O in place of K_2O, variations in the alumina content, and omission of the Cr_2O_3 component. The added MgO appears to be a late development used to strengthen the catalyst.

The catalyst was[5] made by dry mixing calcined zinc carbonate, Bayerite alumina and calcium oxide, and then adding a solution of KOH, K_2CrO_4 and K_2SO_4 to form a stiff paste which was extruded, dried, and granulated. Presumably the MgO was added with the CaO when this improvement was made.

Present Status of Dehydrogenation Processes

The major use of catalytic dehydrogenation for producing olefins and diolefins is dependent on the amount of synthetic rubber produced. Following the war the production of GR-S synthetic rubber decreased from about 760,000 long tons per year to about 275,000 tons per year in 1950[146]. However, the price of natural rubber increased from 18.3¢ per pound in January 1950 to 73¢ per pound in November 1950 and the synthetic plants were reactivated. Production for 1951 was about 530,000 tons per year. Capacity for petroleum butadiene for 1953 was estimated at 637,000 tons per year. The expanding use of butadiene and styrene in the chemical field, as well as for synthetic rubber, will probably result in continued operation of the dehydrogenation plants for many years.

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