CATALYSIS

VOLUME I

FUNDAMENTAL PRINCIPLES (PART 1)

Edited by

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PREFACE

Catalysis is now the keystone of the chemical structure of large sections of industries which together produce billions of dollars worth of products annually. For example, gasoline, synthetic rubber, methanol, higher alcohols, formaldehyde, ammonia, nitric acid, sulfuric acid, phthalic anhydride, toluene, benzene, acetic acid, plastics, and many other chemicals and commodities are now, wholly or in part, produced by catalytic processes. This industrial importance would in itself warrant the publication occasionally of a treatise designed to summarize the present status of the subject.

At this time, however, there is yet another cogent reason for presenting such a detailed discussion. It is to be found in the rapid change that is taking place in our way of interpreting catalysts and catalytic processes. In the past, catalysis has been correctly designated as an art. Those who have sought to improve catalysts have, accordingly, had to depend largely on empirical correlations and on a large measure of intuition in using effectively the mass of experimental results that have appeared in the literature. However, within the last thirty years, the art has gradually been acquiring a considerable coating of scientific luster. All of the research tools of science have been brought to bear on the continuing search for a better understanding of the detailed mechanisms through which catalysts are able to function. Though catalysis has not yet been placed on a firm scientific foundation, the signs of progress are numerous and unmistakable. The very recent approach which tends to link up the activity of a solid catalyst with its electronic structure seems particularly promising. At such a point it is timely to attempt to record, in an orderly fashion, all that is now known in regard to the theory and practice of catalysis.

The present series represents such an attempt. Every effort has been made to include all of the better ideas and interpretations of the past together with newer, though rapidly changing, ideas and theories that are currently being introduced. It has, of course, been impossible to refer to every published article but it is hoped that no outstanding, significant contributions have been overlooked.

The fundamental principles and theories of both homogeneous and heterogeneous catalysis are included in the first two volumes of the series. Catalysis as an art, however, has not been neglected. Along with the fundamental aspects of the theory, considerable new material has been included in Volume I relative to catalyst supports, carriers, and methods of preparation. In the same spirit in Volume II, discussions of catalysts according to current ideas of solid state physics are flanked by tables in which our knowledge as to the general types and classes of catalysts has been organized in a systematic but entirely empirical fashion.

In successive volumes, various subdivisions into which it has become customary to divide catalytic work will be treated, including: hydrogenation and dehydrogenation; synthesis of hydrocarbons, ammonia, methanol, and higher alcohols; alkylation, isomerization, polymerization, cracking, hydroforming, hydrocracking, and hydrodesulfurization; and finally, oxidation, hydration, dehydration, halogenation and miscellaneous reactions. The discussion of each of these topics will comprise a presentation of published factual matter as well as ideas and theories as to the mechanism of the reactions involved. Attention is focused on the catalysts and catalytic reactions and not on the engineering or economic characteristics of the processes. It should be noted, too, that the present series does not include a discussion of enzymes, the biochemical catalysts that are essential to life itself.

In any series of books in which several authors contribute to each volume, a certain amount of overlapping and duplication is unavoidable. The editor has endeavored, however, to organize the subject matter in such a way as to keep duplication to a minimum and at the same time assure a comprehensive coverage of all relevant facts and theories. Any shortcomings in this respect are necessarily the fault of the editor and not of the individual authors.

To all of those who have contributed material to this series, the editor wants to take this opportunity of extending his own personal vote of thanks. Without their cooperation, adequate coverage of the enormous field into which catalysis has developed would have been impossible. It is hoped that this joint effort by a large number of experienced specialists will succeed in drawing together into a clear and comprehensive treatise the catalytic art of today and the science of catalysis that now seems to be in the process of being formulated.

Pittsburgh, Pa.
December 25, 1953

PAUL H. EMMETT

CONTENTS

CHAPTER 1

PHYSICAL ADSORPTION

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INTRODUCTION

Adsorption is a process in which the atoms or molecules of one material become attached to the surface of another or, in a more general sense, become concentrated at an interface. An interface is a contiguous area between two phases. There are five types of interfaces: gas-solid, liquid-solid, gas-liquid, liquid-liquid, and solid-solid. Of primary concern in the present discussion is the combination of gas and solid, which is common to many systems in heterogeneous catalysis. The literature is abundant in the fields of adsorption and catalysis in gas-solid systems, particularly in recent years. Extensive bibliographies are readily available[18, 32-34, 63-66, 122, 134, 135, 137].

Adsorption at the liquid-solid interface has also been investigated in the study of solid catalysts, thin-film lubrication, and related fields[15, 16, 40, 54, 59, 60, 123, 130]. In adsorption at the liquid-solid boundary, the presence of a solvent provides a complicating factor, because it competes with the solute for positions at the interface. This difficulty is not present in simple gas-solid systems having only a single component in the gas phase.

Adsorption at the gas-liquid interface has been investigated by classical surface-tension methods and by means of the film balance with which surface pressure-area and surface potential experiments are performed on monomolecular films[1, 59, 103, 104, 121]. Adsorption at the liquid-liquid interface and the corresponding interfacial-energy relationships provide basic information for heterogeneous catalysis involving two liquid phases. Application of liquid-liquid studies is extensive in the fields of biology, lubrication, and emulsion systems in general. Liquid-liquid interfaces have been investigated by means of interfacial tensiometer measurements and related techniques. Investigation of solid-solid interfaces is basic to the study of catalyst promoters and to the study of friction between rubbing solids.

All adsorption processes, whether physical or chemical in character, are accompanied by a decrease in free energy. Solid surfaces are similar to liquid surfaces in that there are unbalanced or unsymmetrical forces present. These forces are satisfied to some extent by the adsorption or deposition of the adsorbate. The free surface energy is therefore decreased. Because the adsorption of gases or vapors also involves a decrease in entropy, such processes are exothermic. Conversely, the corresponding desorption processes are endothermic.

Definitions

If, in a two-phase system, the molecules of one phase move beyond the interface into the *bulk* phase of the second substance the process is one of *absorption*. These molecules may dissolve in the bulk phase or they may form a compound with it. Solution involves a weak interaction, whereas compound formation is the result of a strong interaction. A somewhat analogous differentiation may be made for processes at surfaces or interfaces. There may be a relatively weak interaction, which is known as *physical* or *van der Waals* adsorption, or a strong interaction of a chemical nature, known as *activated adsorption* or *chemisorption*.

The forces responsible for physical adsorption are considered to be van der Waals forces. These are the forces associated with liquefaction and with condensation in capillaries. The higher the boiling point or the lower the saturation pressure of an adsorbate material, the greater will be its physical adsorption under a given set of conditions. Although some chemisorption processes take place rapidly, others are sufficiently slow to be measurable. The term, "activated adsorption," is sometimes used to designate this slower type of chemisorption because the adsorption rate frequently increases with an increase in temperature to an extent corresponding to a considerable energy of activation.

Other distinguishing characteristics of adsorption phenomena are arbitrary but useful. Physical adsorption is easily reversible and involves relatively small heats of adsorption similar in magnitude to heats of liquefaction. Chemisorption, however, is irreversible or reversible only with great difficulty and is associated with high heats of adsorption often in the neighborhood of heats of chemical reaction. Physical adsorption is essentially nonspecific with respect to the adsorbent and adsorbate, whereas chemisorption involves a high degree of specificity[38]. It is also useful to distinguish between chemisorption and chemical reaction in the ordinary sense. In chemisorption the adsorbate-adsorbent interaction involves only the surface layer, whereas in chemical reaction in the conventional sense there are bulk phase changes.

Applications of Physical Adsorption

Adsorption is of fundamental significance in heterogeneous catalysis. Although chemisorption may be more intimately involved than physical adsorption in catalytic phenomena, the tools and techniques of physical adsorption have played a major role in catalyst studies of recent years. These techniques contribute to our knowledge of solid catalysts in at least two important respects. Adsorption measurements indicate the extent of the solid surface area and provide information on the pore structure of the solid. Both of these applications are discussed in detail in subsequent chapters[36, 144]. Nevertheless, it is important to realize the significance of these applications while considering the phenomena of physical adsorption.

The determination of catalyst area has become almost essential in the reproducible preparation and the systematic comparison of catalysts. The method of surface-area measurement as developed by Brunauer, Emmett, and Teller[20] has been an important factor in the transition of catalyst preparation from an art to a science. Until activities per unit area of catalyst could be assigned, comparison of catalytic reactions observed in different laboratories was extremely unsatisfactory. Other important properties of catalysts, such as thermal stability, can now be determined with greater ease and can be described with much more precision by means of area-temperature curves.

Pore-structure characteristics, such as pore volume and pore radius, obtained from adsorption data help to establish reproducibility of catalyst preparations and to define catalyst systems. Pore dimensions are undoubtedly critical in some cases for the inward diffusion of reactants, the outward diffusion of products, and related factors involved in regeneration processes. The function of catalyst supports is indicated by the basic information on structure obtained from studies of physical adsorption.

Although in this discussion our principal interest lies in the adsorption of gases on solids as related to heterogeneous catalysis, other applications of physical adsorption are important. Surface-area and pore-structure measurements are useful in studying many types of solids other than catalysts. Additional applications include: separation of gases by fractional adsorption, desiccation, chromatographic analysis, decolorization of oils, thin-film lubrication, corrosion protection, detergency, emulsions, foams, and molecular structure and orientation as determined in monolayer studies on liquids.

Experimental Methods

The physical adsorption of gases on solids is generally measured by either the volumetric or the gravimetric method. The former is more widely used because it is simple and versatile. However, correcting for the dead space introduces errors from which the gravimetric method is free. In the gravimetric method the use of a delicate, vibration-sensitive spring or beam balance introduces experimental difficulties. Nevertheless, for studies at elevated temperatures and for multiple sample measurements, it offers certain practical advantages. Other means for the measurement of adsorption include the use of accommodation coefficients, optical effects, and isotope tracers.

Degassing of the sample is required in all methods. The higher the temperature of the adsorbent, the better the vacuum, and the longer the pumping period, the more thorough will be the desorption of contaminants. However, care must be taken that the elevated temperature does not cause sintering or other transformations in the adsorbent. Periodic measurements of surface area are advisable in extended studies in order to be certain that sintering complications are avoided.

Volumetric

The apparatus employed for the volumetric measurement of adsorption is generally an all-"Pyrex" high-vacuum system equipped for degassing of the absorbent at elevated temperatures and with burette-manometers for measuring gas volumes. Because physical adsorption is usually studied at low temperatures, such convenient means as vapor-pressure thermometers must be provided for measuring temperatures. Discussions of equipment and procedures have been presented in some detail by Brunauer[18], Emmett[32, 33], Farkas and Melville[41], and Ries[122]. The complete description of adsorption equipment and techniques by Joyner[84] is particularly valuable. Frankenburg[45] presents many important details and precautions essential for precision work in the field of gas adsorption.

The volumetric determination of adsorption depends on the difference between the volume initially present in the burette-manometer system and that finally present in the system and in the dead space. A small adsorption or small difference will magnify errors in the relatively large measured volumes. Large adsorption and small dead-space volumes are therefore desirable. Helium of high purity is recommended for dead-space measurements because its adsorption is negligible over a wide range of temperature. With helium, the dead space may generally be determined at the temperature of the subsequent adsorption experiment and the helium may be removed with ease.

For several reasons, special care must be exercised to obtain reliable equilibrium data. In the first place, a system of finely divided solid plus adsorbate gas at low pressures has poor heat conductivity, and the heat of adsorption must be dissipated to maintain isothermal conditions. Secondly, diffusion of the adsorbate gas, whether through the gas phase or on the surface of a porous solid, may involve appreciable time. Time intervals required for equilibrium range from ten minutes to several hours and depend on the portion of the isotherm concerned and the amount adsorbed. After equilibrium is apparently achieved, the system should be allowed to stand for an appropriate period to confirm the equilibrium. It is particularly important to allow adequate time for equilibration in the study of adsorption-desorption hysteresis.

Gravimetric

The gravimetric method for the measurement of adsorption has been described by McBain and Bakr[106]. Recent refinements have been introduced by Milligan[110] and Rhodin[120]. Apparatus for the gravimetric determination of adsorption is similar to that used for the volumetric procedure. The principal difference is that the adsorbent sample is placed in a small container suspended on a helical spring inside the vacuum system. The spring may be constructed of quartz or of a phosphor-bronze alloy. Extension of the spring is observed by means of a cathetometer. Calibration and adsorption measurements are direct. The open bucket-like container for the sample may be hung a considerable distance below the spring, so that the sample and the spring may be thermostated at different temperatures.

The principal advantage of the spring method is that dead-space measurement and attendant errors are avoided. However, a buoyancy correction must be made. Adsorption measurements at higher pressures may be performed satisfactorily with the gravimetric system[111]. The buoyancy correction increases with increase in pressure. The correction requires that the density of the adsorbate vapor and the true solid volume of the adsorbent be known. The latter is probably best determined by measuring helium displacement; helium will penetrate the fine pores of the solid and will not be adsorbed under ordinary conditions.

Another gravimetric apparatus employs a beam balance in place of a spring balance[9, 17a, 53a, 107]. This type of balance greatly reduces the buoyancy factor and in some cases may eliminate the need for this correction. The sensitivity may be made much greater than that of the spring type. A detailed discussion of the beam apparatus with a number of refinements has been presented by Rhodin[120]. Direct weighing on an ordinary balance as a means for measuring adsorption has been reported by Mills, Boedeker and Oblad[110a] and by Zabor and Emmett[144a].

Other Experimental Methods

Three other methods for studying adsorption warrant mention. They utilize the accommodation coefficient, the optical properties of the adsorbed film, and radiotracer techniques. These methods are generally considered less direct than those in which the volume or the weight of gas adsorbed is measured.

In a determination of accommodation coefficient, the adsorption phenomenon is related to the exchange of energy between the gas and the solid surface. Energy exchange is indicated by the change in temperature of the gas as related to the temperature of the solid. The accommodation coefficient, a, is defined as follows:

$$a = \frac{T_2 - T_1}{T_2' - T_1} \tag{1}$$

where T_1 is the temperature of the gas before it collides with or is adsorbed by the solid, T_2 the temperature following the collision, and T_2' the temperature of the solid surface. Investigation of the accommodation coefficient has been described in detail by Roberts[128]. Adsorption measured by this method is usually performed on a wire of small surface. Precise measurement of small differences in temperature is required.

Optical methods for the study of adsorbed films involve experimental and theoretical difficulties not found in the more direct methods. An adsorbed film on a solid may cause an elliptical polarization of an incident beam of light. The ellipticity may then be related to the thickness of the adsorbed layer if a dielectric constant for the adsorbed phase is assumed. This method has been described by Frazer[47, 48] and by Bowden and Throssell[17].

In principle, the application of radiotracers to adsorption measurements appears to be direct. In gas-solid systems, an adsorption determination may be accomplished by measuring the accumulation of radioactive gas at the solid adsorbent or by measuring the loss of radioactivity in the gas phase. Such a method might be refined to measure the adsorption of quantities much below the limit of the other methods. This technique would thus provide an excellent means for determining adsorption rates. The radiotracer technique allows measurement of the adsorption of one of the components of a mixture. The method would be similar to the radiotracer techniques used for observing the adsorption of a solute at the surface of a liquid[4, 14, 92, 133].

THEORIES OF PHYSICAL ADSORPTION

Prior to the pioneering work of Langmuir, Harkins, and others, adsorbed films were generally considered to be many hundreds or even thousands of molecules thick. This viewpoint can be attributed in part to a gross underestimation of the surface area of the adsorbing solid. If better methods for estimating surface area had been available, theories of thin-film adsorption undoubtedly would have developed earlier. The extensive studies of monomolecular films on aqueous substrates supplied convincing evidence in the early development of monolayer adsorption concepts.

Early Contributions

Current research in adsorption, both theoretical and applied, has been guided to a great extent by the early contributions of Langmuir, Freundlich, and Polanyi. The work of these investigators represents three widely different approaches.

Langmuir. One of the first and most important adsorption equations based on theory was that developed by Langmuir[100, 101, 102]. His concept initially implied only monomolecular film adsorption and had other limitations. It was applied to both chemical and physical adsorption. Because many important subsequent developments were essentially extensions of the Langmuir relationship, its derivation will be briefly outlined. Langmuir used a direct kinetic derivation. Thermodynamic and statistical methods have since given similar relationships.

The dynamic equilibrium postulated by Langmuir was that the rate of evaporation or desorption equals the rate of condensation or adsorption. The adsorbate molecules remain on the adsorbent surface for a finite length of time and account for the adsorption effect. In physical adsorption, this time lag is short; in chemisorption, it is relatively long.

If, in a given system, θ is the fraction of the surface covered with an adsorbed layer and ν is the rate of evaporation when all the surface is covered, then, according to Langmuir, $\nu\theta$ represents the rate of evaporation. This assumes that the heat of adsorption does not depend on θ. Correspondingly, if μ is the rate at which molecules strike the surface and α the fraction of the striking molecules that condense or that have inelastic collisions with the surface, then $\alpha\mu(1 - \theta)$ is the rate of condensation. Since $1 - \theta$ is the fraction of surface not covered, it is assumed that only elastic collisions occur on the covered surface. This is the assumption of monomolecular adsorption.

At equilibrium, the rate of evaporation is equal to the rate of condensation:

$$\nu\theta = \alpha\mu(1 - \theta) \tag{2}$$

or

$$\theta = \frac{\frac{\alpha}{\nu}\mu}{1 + \frac{\alpha}{\nu}\mu} \tag{3}$$

Because μ is proportional to the pressure, p, by letting $k = \alpha/\nu$ times k', the constant of proportionality relating μ and p, the following equation is obtained:

$$\theta = \frac{kp}{1 + kp} \tag{4}$$

This expression indicates that at very low pressures the adsorption is approximately proportional to pressure, in agreement with Henry's law, and at high pressures the surface approaches saturation. The constant is a function of temperature.

The Langmuir equation may be translated into an expression that represents the special monolayer case of the BET multilayer adsorption theory (p. 14). If v_m is the volume of adsorbate required to complete the monolayer or saturate the surface and v is simply the volume adsorbed at the measured pressure, p, then the fraction of surface covered, θ, is equal to v/v_m. Thus,

$$\frac{v}{v_m} = \frac{kp}{1 + kp} \tag{5}$$

or

$$\frac{p}{v} = \frac{1}{kv_m} + \frac{p}{v_m} \tag{6}$$

This is the linear form of the Langmuir relationship that in many cases provides a method for obtaining the amount of adsorbate required to cover the surface.

Freundlich. The classical Freundlich equation[49] described the behavior of many systems in the slightly higher region of intermediate pressure:

$$v = kp^{1/n} \tag{7}$$

where v is the volume adsorbed, p the pressure of the adsorbate gas, k a constant, and n a constant greater than unity. The Freundlich equation was introduced simply as an empirical relationship. It deals most successfully with adsorption at intermediate pressures, but many adsorption systems even in this region do not obey the Freundlich relationship. Nevertheless, theoretical considerations of Halsey and Taylor[58] have shown that, if the Langmuir adsorption equation is applied to a series of sites the relative energies of which follow an exponential relationship, the Freundlich equation is obtained (see also Sips,[132]).

Polanyi. At approximately the same time that Langmuir was developing his monomolecular theory for gas adsorption, Polanyi[118, 118a] was formulating an entirely different concept known as the potential theory. This concept in its original form dealt only with physical adsorption and implied the existence of films many molecules thick. It attempted to make quantitative an early qualitative notion that the attractive forces of the surface extend out many layers and fall off with each succeeding layer.

The Polanyi contribution is called a potential theory because it defines an adsorption potential as the work done by the forces of adsorption in bringing a molecule from the gas phase to a point near the adsorbing surface. The theory is based throughout on the assumption that the van der

Waals forces of adsorption are similar to those of condensation. Thus three-dimensional equations of state are used to relate density and pressure. The density is greatest near the adsorbent and falls off with distance.

In the Polanyi concept the attractive force of the surface as well as the layers above each layer tend to compress the film. The attractive force of the surface does not change with temperature. Compression is greatest on the first layer, but no particular significance is attached to the monolayer. The Polanyi theory, which has been considered in detail by Brunauer[18], is of limited utility because it does not yield an equation relating pressure and adsorption. It provides little information about the structure or extent of the surface or the thickness of the adsorbed layer. Nevertheless, it indicates that the adsorbed gases behave much like compressed gases and liquids. It demonstrates the temperature dependence of adsorption.

The earlier potential theory was modified in a later contribution by Goldmann and Polanyi[51]. The later theory could apply to monomolecular films but it generally indicated thicker layers. According to the modified theory vapor is adsorbed in a monolayer for coverages ranging from five to eighty per cent. Patches of adsorbate or islands are formed next. These flow together to form a continuous coating. The molecular roughness and uneven adsorption potential of the surface determine the adsorption. Sites of highest potential are covered first and then those with progressively lower potentials.

In the "affinity curves" of Goldmann and Polanyi the adsorption potential is plotted against the amount of gas adsorbed at constant temperature. The adsorption potential, ϵ, is calculated from the equation:

$$\epsilon = RT \ln p_0/p \tag{8}$$

where p is the pressure in the gas phase, p_0 the liquefaction pressure, R the gas constant, and T the absolute temperature. The equation is based on three assumptions: the vapor phase obeys the ideal gas laws; the liquid adsorbed phase is incompressible; and the work required to produce the liquid surface is negligible. Affinity curves obtained at different temperatures may be very close and almost parallel[51], or may coincide[37]. Coincidence may mean that the temperature coefficient of expansion of the adsorbed layer is negligible. The potential plots of Emmett and Brunauer[37] cover adsorption of less than a monolayer, through the monolayer and multilayer regions, into the region of capillary condensation.

A polarization theory offered by de Boer and Zwikker[29] was also concerned with multilayers. It attributed adsorption by ionic adsorbents to the dipoles induced in nonpolar adsorbate molecules. The induced dipoles in the first layer induce dipoles in succeeding layers. Polarization theories may have produced empirical relationships of some use, but it is unlikely that the effect of induced dipoles even in a second layer could account for significant adsorption[18, 20].

Later Developments

Later work has been concentrated on efforts to describe adsorption in terms of isotherms and to analyze different types of such isotherms. An adsorption isotherm is the relationship between the pressure of the adsorbate gas and the amount adsorbed at a specified temperature. A typical example is shown in Figure 1[122]. It represents both the adsorption and desorption of nitrogen on a synthetic silica-alumina catalyst at the boiling point of liquid nitrogen. The relative pressure, p/p_0, in which p is the measured pressure of the adsorbate and p_0 the liquefaction or saturation pressure, is plotted against the volume adsorbed in cubic centimeters, at standard temperature and pressure, per gram. The relative pressure, p/p_0 is used as the independent variable rather than p because it tends to correct for small temperature fluctuations. The high degree of reproducibility of the adsorption measurements is indicated by the coincidence of the three separate determinations. In the hysteresis portion, the upper curve is the desorption branch and the lower part is the adsorption branch. The inset in the lower right corner of the figure is an expanded plot of the higher-pressure region.

The monolayer region for nitrogen is generally considered to be that portion of the isotherm below a relative pressure of approximately 0.1[19a]. In other words, the deposition of a statistical monolayer is approximately complete in the neighborhood of 0.1 relative pressure. This point is close to the "B" point of Emmett and Brunauer[39], defined as the lower extremity of a central linear portion of the isotherm. The multilayer region for nitrogen generally refers to that portion of the isotherm above 0.1 relative pressure. Capillary condensation for the most part involves the region from approximately 0.4 to 1.0 relative pressure. Three phenomena—monolayer adsorption, multilayer adsorption, and capillary condensation—with considerable overlapping, may be involved in the interpretation of a single adsorption isotherm. Consequently, there are inherent difficulties in the development of a unified theory or a generalized equation for adsorption isotherms.

The contour of a complete adsorption isotherm from zero pressure to the saturation pressure, where $p = p_0$, depends on the adsorbate, the extent and nature of the adsorbing surface, and the pore structure of the solid. Isotherms involving physical adsorption alone may be limited to five types having the contours shown in Figure 2, drawn after Brunauer, Deming, Deming, and Teller[19].

Type I is frequently referred to as the Langmuir type because it approximates monomolecular adsorption. Certain charcoal and silica xerogel structures give this type with oxygen or nitrogen at low temperatures because a monolayer saturates the surface or fills the pores. Examples of Type I isotherms are presented in Figure 3[138]. This contour is also characteristic of chemisorption phenomena in which a monolayer completes the significant interaction of adsorbent and adsorbate.

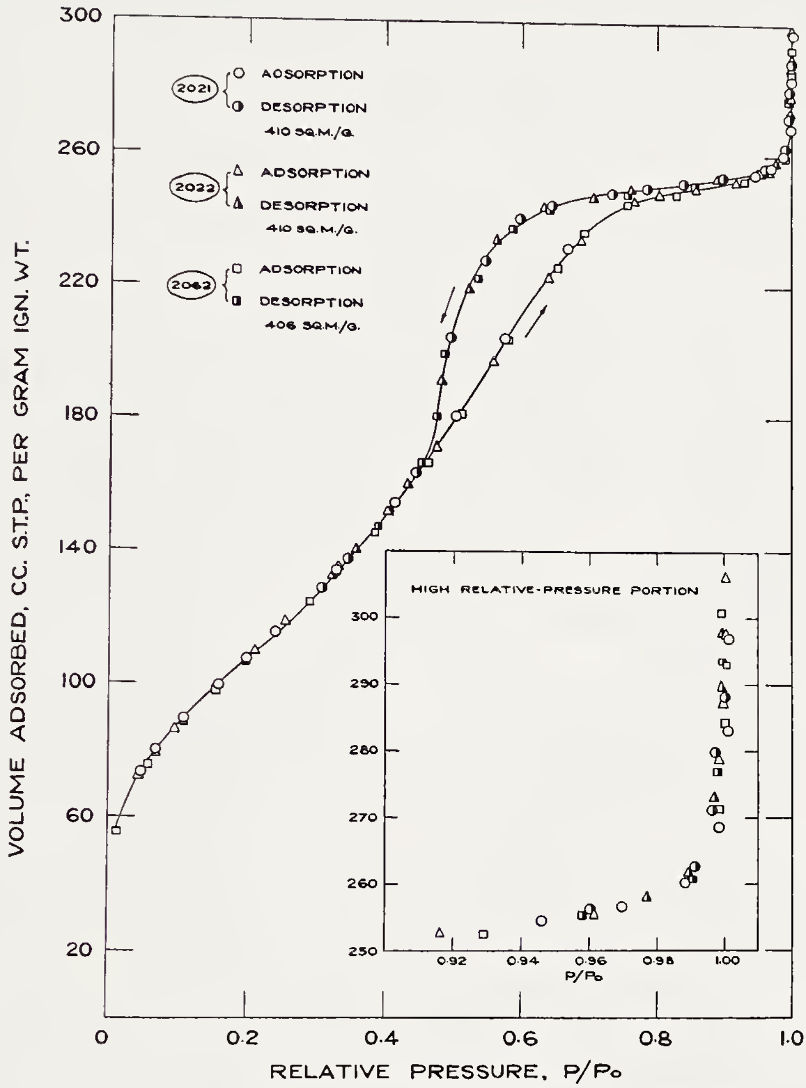

Figure 1. Nitrogen adsorption-desorption isotherms for virgin diakel.

Type II is the sigmoid or S-shaped isotherm with an asymptotic approach to the p_0 line. This contour is generally ascribed to multimolecular adsorption. Many monolayers are deposited to give this curve. Excellent examples include those for nitrogen on nonporous high-area silica and on nonporous titania. Isotherms for these materials of widely different areas are illustrated in Figures 4 and 5[122, 123].

Type III and Type V isotherms are relatively rare. The forces of monolayer adsorption here are small. One example of Type III is bromine on silica gel[119]; another is water on graphite[62]. The Type V isotherm has an upper limit to pore volume; an example is the adsorption of water vapor on charcoal[28].

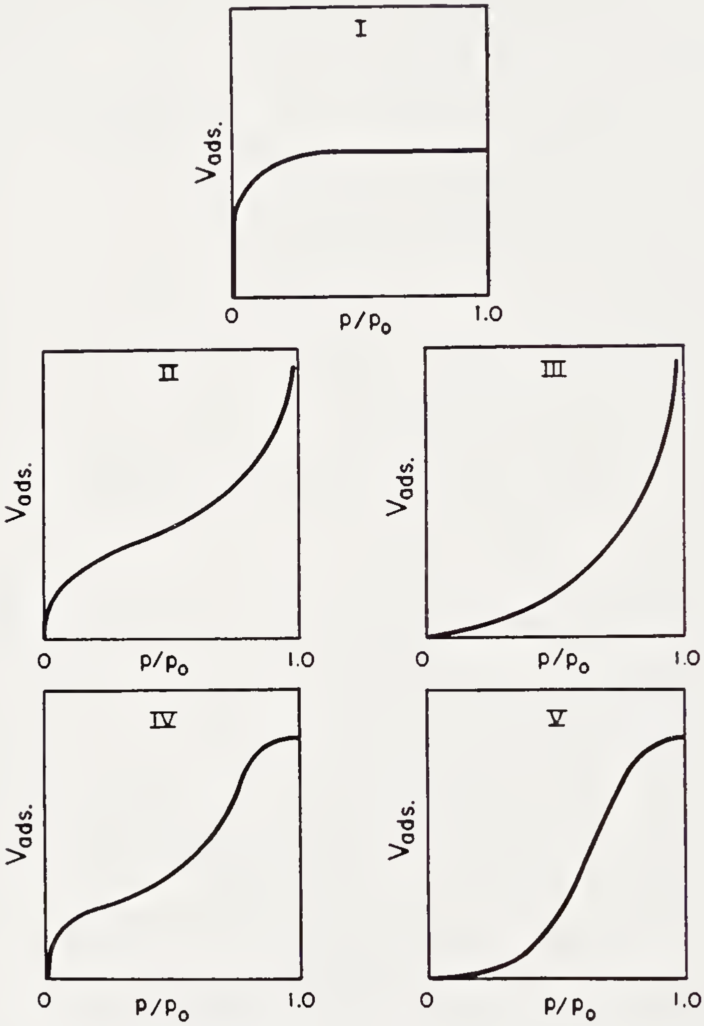

Figure 2. Five types of isotherms for physical adsorption according to Brunauer, Deming, Deming and Teller[19].

Type IV is similar to Type II except that a limited pore volume is indicated by a sharp approach to the p_0 line. The contour is relatively common for porous structures of many kinds. The examples shown in Figure 6 for a synthetic silica-alumina cracking catalyst[138] show a particularly sharp upper limit to pore volume.

In the lower-pressure region there is similarity in the contours of Types I, II, and IV. In the region of very low pressure, almost all types of isotherms approach a linear relationship between amount adsorbed and pressure; apparently a Henry's-law relationship describes the behavior in this region. However, as adsorption increases in Types I, II, and IV, the amount adsorbed does not increase as rapidly with increasing pressure as it does in the region in which Henry's law applies. In Types III and V, above this lowermost pressure region, the amount adsorbed increases more rapidly with increasing pressure than in the lowermost pressure region. The variation among the five types of isotherms makes difficult the development of generalized theories for physical adsorption.

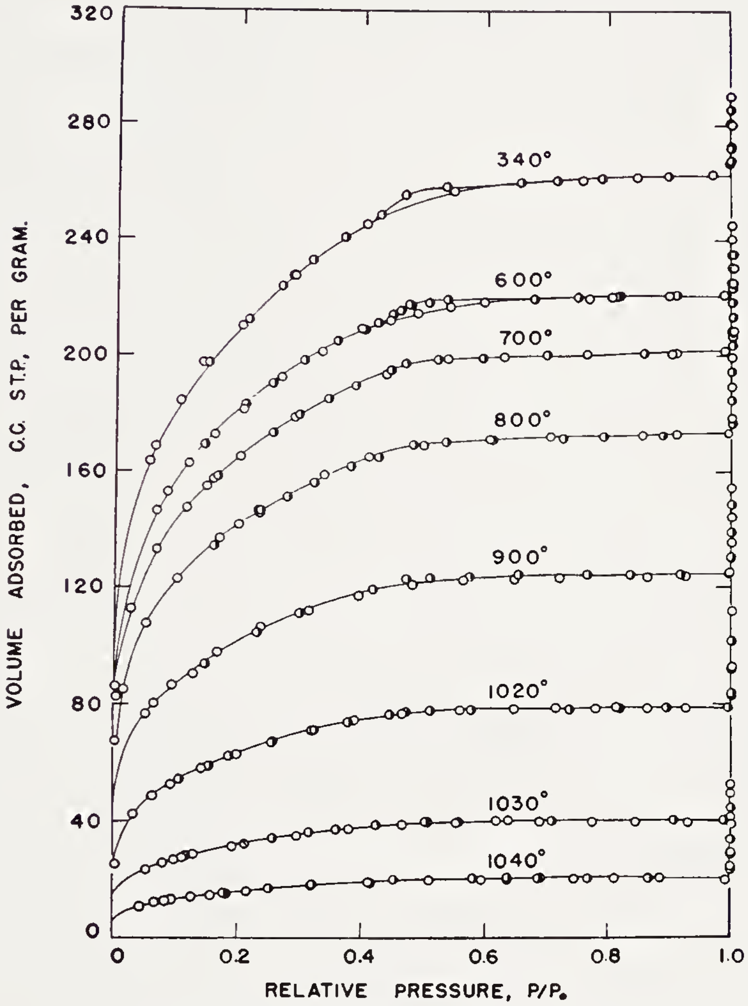

Figure 3. Nitrogen adsorption-desorption isotherms for silica xerogel sintered in vacuo.

In recent years the best known and most widely used of the multilayer adsorption theories is that developed by Brunauer, Emmett, and Teller and now known as the BET theory[20]. In view of its importance it is often referred to as the theory of multilayer adsorption. It was the first theory that attempted to describe more than one of the five types of isotherms. The BET theory was subsequently extended by Brunauer, Deming, Deming, and Teller[19]. In the extended form of the theory, all five types may be derived as special cases. The equations developed give curves that closely approximate the contours of the isotherms throughout a wide range of pressure.

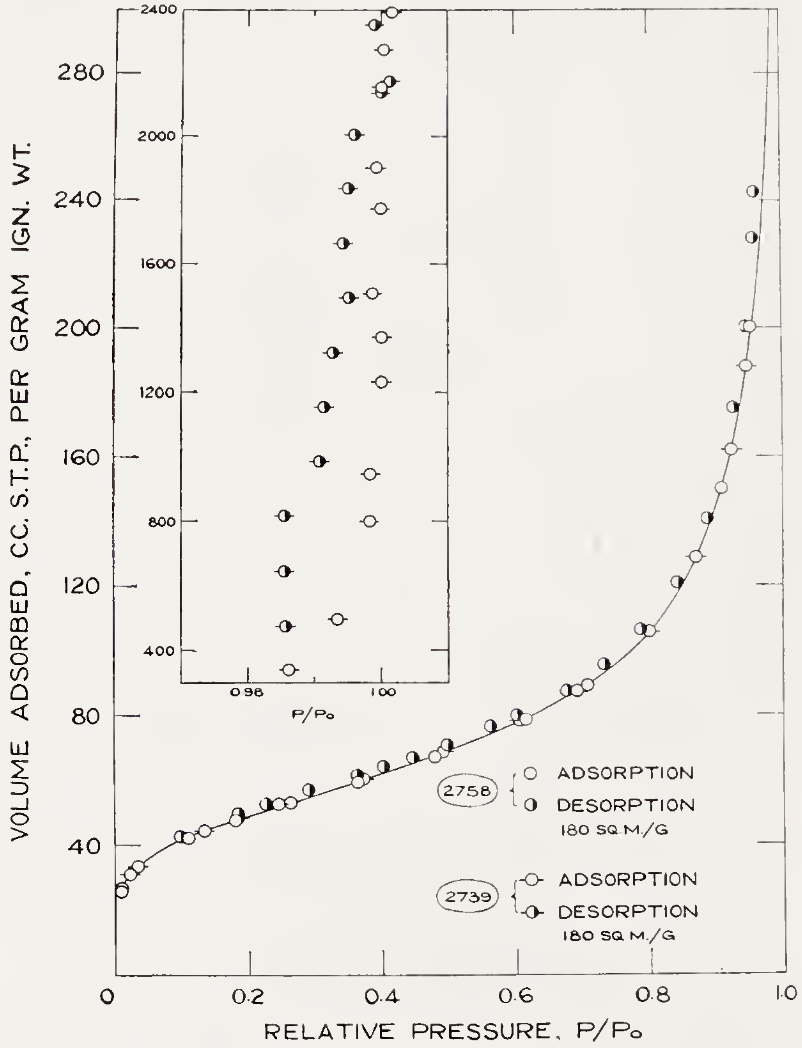

Figure 4. Nitrogen adsorption-desorption isotherms for Linde silica.

The BET Theory. The BET multilayer theory[20] is essentially an extension of the Langmuir interpretation of monomolecular adsorption. The derivation is based on the same kinetic picture and the assumption that condensation forces are the principal forces in physical adsorption. As in the

Langmuir theory, the rate of evaporation of the molecules in the first layer is considered to be equal to the rate of condensation on the uncovered surface. It is then similarly argued that the rate of evaporation from each succeeding layer is equal to the rate of condensation on the preceding layer. A summation is then performed. The heat of adsorption is involved exponentially in each of the equilibrium-rate expressions. It is assumed that the heat of adsorption in each layer other than the first is equal to the heat of liquefaction of the bulk adsorbate material. In other words, the van der Waals forces of the adsorbent are transmitted to the first layer only. Expressions are obtained for adsorption on a free surface and on a restricted surface.

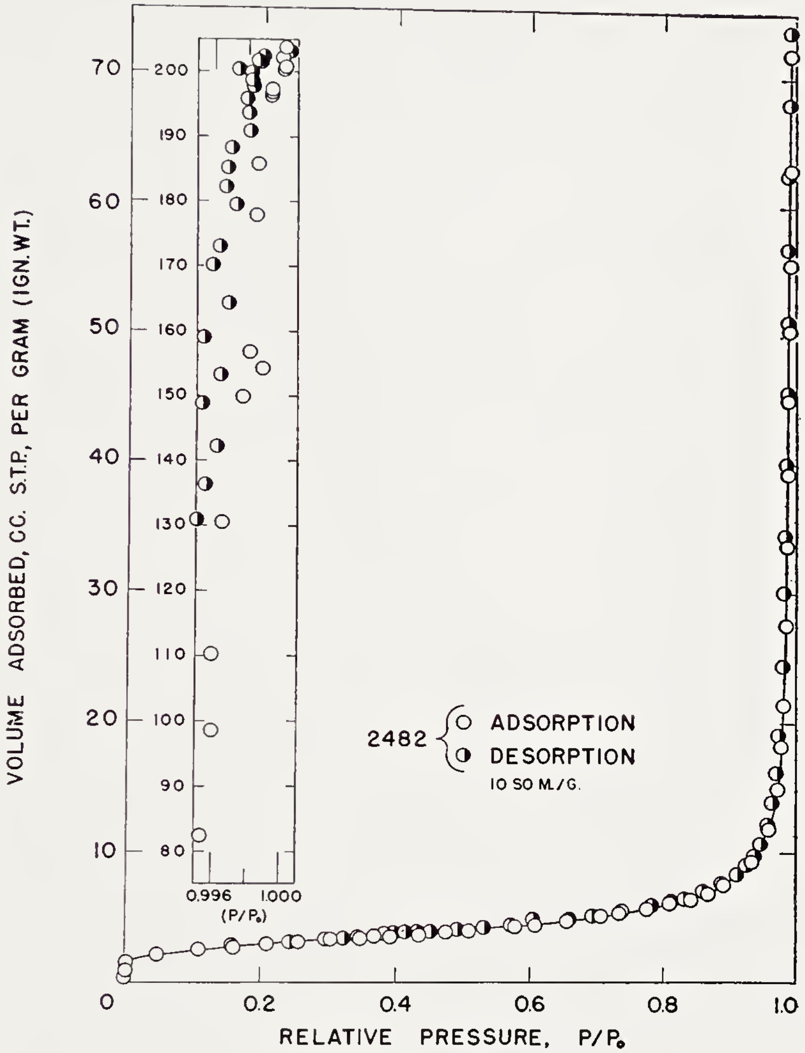

Figure 5. Nitrogen adsorption-desorption isotherms for titanium dioxide.

If it is assumed that on a free surface an infinite number of layers may be adsorbed, the BET isotherm equation can be derived:

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{v_m c p_o} \tag{9}$$

where v is the total volume adsorbed at the measured pressure, p; v_m is the volume adsorbed in the monolayer; p_0 is the saturation pressure of the adsorbate gas; and c is a constant related exponentially to the heat of adsorption and the heat of liquefaction of the adsorbate. Because the equation is linear, a plot of the data within limits will give a straight line from which the values of the two constants, v_m and c, may be obtained. The significance of v_m as related to other methods of determining the extent of surface is

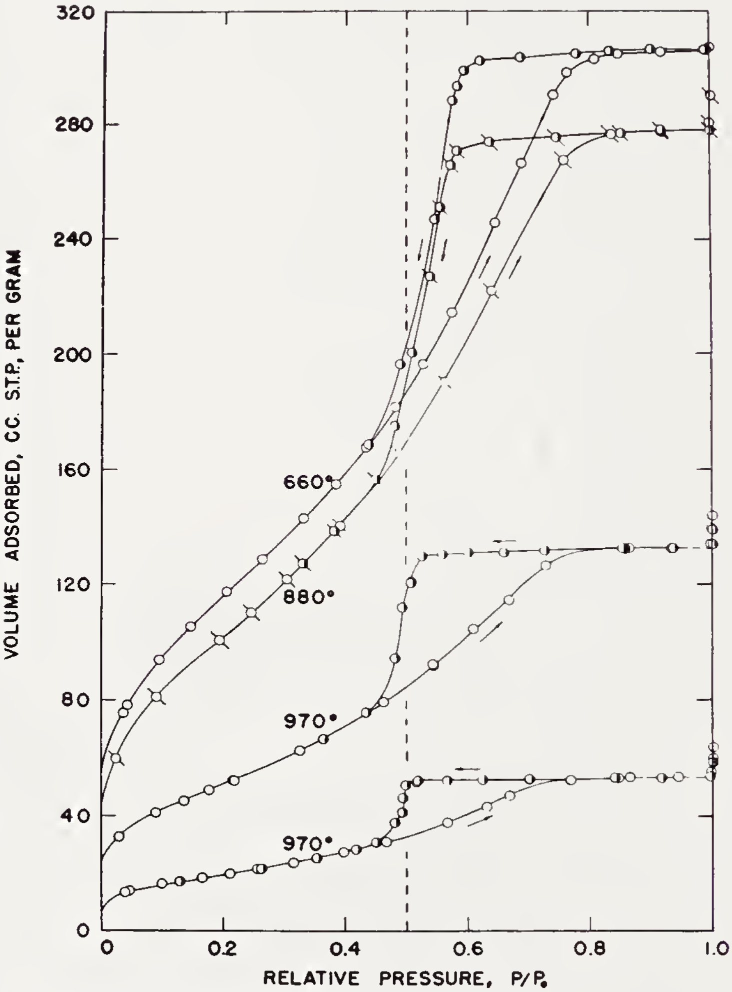

Figure 6. Nitrogen adsorption-desorption isotherms for Socony T.C.C. bead catalyst sintered in vacuo.

discussed in Chapter 2 by Emmett. The derivation of Equation (9) by a statistical mechanical approach is discussed by Hill[67].

The BET multilayer theory yields another adsorption expression if the adsorption is not on a free surface but is limited in amount by the walls of pores having very small diameters. When the number of layers on each pore wall is restricted to n, then the limited summation leads to the equation:

$$v = \frac{v_m c x}{1 - x} \cdot \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (c - 1)x - cx^{n+1}} \tag{10}$$

where x is the relative pressure, p/p_0. This more general equation reduces to the Langmuir relationship when $n = 1$. Under conditions in which the surface is free and adsorption is not limited, $n = \infty$, and Equation (9) is obtained. One may use Equation (9) with the data in the low-pressure region, obtain values for v_m and c, and then use the n form to indicate the number of layers. Thus, an equation that approximates a broader range is obtained, although the effects of capillary condensation have not been taken into account. Equation (10) above is especially valuable when applied to Type I isotherms and to the low-pressure part of Type IV isotherms.

In a subsequent extention of the theory by Brunauer, Deming, Deming, and Teller[19], an effort was made to obtain expressions for isotherms of Types IV and V. Because the pores in these two cases are filled before the saturation pressure is reached, it was assumed that the last layer to be adsorbed is attracted by the layers on both sides and hence has a higher heat of adsorption. This will change the rate of evaporation for the last layer in the BET derivation. A much more elaborate equation is thus obtained to account for isotherms of Types IV and V.

The multilayer theory of adsorption represents the first major effort to unify physical-adsorption concepts as applied to the complete isotherm from the monomolecular region through the multilayer and capillary-condensation regions to the saturation pressure. It may be applied to all five types of isotherms. The equations are most useful in the monomolecular-film region and the portions immediately preceding and following this region. At lower relative pressures, generally below 0.05, the theory fits rather poorly. The equations that apply at the high relative pressures in the capillary-condensation region become complex and unwieldy.

Refinements and New Approaches. Several defects in the multilayer theory of Brunauer, Emmett, and Teller have been pointed out by the authors themselves and others[6, 24, 52, 67, 70, 108]. One difficulty is the assumption that the heat of vaporization is the same for all layers following the first and is equal to the heat of vaporization for the bulk liquid. A common subject of criticism is based on the erroneous belief that the authors did not consider

$$\frac{\frac{p}{p_0}}{V(1 - \frac{p}{p_0})}$$

lateral interaction effects of adsorbed molecules. The BET authors recognized that lateral interaction would be negligible only at the lowest pressures or under conditions in which the adsorbed molecules are extremely dilute. They assumed that interaction effects increase as surface heterogeneity effects decrease, and that these effects tend to compensate each other in such a way as to make possible the use of an average heat of first layer adsorption in deriving Equation (9). These assumptions were initially justified principally on the basis of simplification.

Detailed analysis of adsorption theory by means of statistical and thermodynamic methods has been undertaken by Cassie[23], Everett[39a], Halsey[55], Harkins and Jura[61], and Hill[67, 78]. The more rigorous treatments include detailed consideration of horizontal interaction effects. Criticism has also been directed at an adsorption theory proposed by Hüttig[82] that is somewhat similar to the BET theory[67, 129]. The principal point of difference between the BET and Hüttig theories is that the Hüttig theory holds that molecules covered by succeeding layers may evaporate with the same facility as exposed molecules. This viewpoint of Hüttig is the subject of further examination by Hill[67, 78].

Hill. Employing the methods of statistical mechanics, Hill's treatment of multilayer adsorption indicates that the BET equation is correct for the model used[67-77]. Refinements in the model are made, although mathematical difficulties are introduced. Theoretical treatments based on the refined models suggest that multimolecular theory under certain conditions covers capillary condensation, generally considered a separate phenomenon.

Hill differentiates between mobile and localized adsorption in the first layer. In mobile adsorption, the adsorbed atoms have translational freedom in two dimensions; in localized adsorption, they have no translational freedom. Physical adsorption of a localized type should be observed only infrequently at the temperatures generally used. The BET theory assumes only localized adsorption, whereas both localized and mobile states should be considered. An approximate isotherm equation employing the mobile first-layer concept as developed by Hill approaches quantitative agreement with phase changes described for two-dimensional systems by Harkins and Jura and others[89, 90, 91]. Mobility, as used in this sense, implies that the motions of the molecules in two dimensions are the motions of a two-dimensional gas or liquid. Adsorption forces restrict the motion to two dimensions in the plane of the surface. Nevertheless, possible phases of the adsorbed film, such as gas, liquid-expanded, liquid-condensed, and solid, must be considered.

Hill has developed his statistical mechanical treatment in part by careful consideration of the horizontal interactions of the adsorbed molecules in the monolayer. Cassel has also considered horizontal interactions in a thermodynamic development of adsorption theory[22]. Hill has subsequently extended his argument into the region of capillary condensation and hysteresis. Not only should there be a single stable equilibrium curve but also various metastable states that permit hysteresis. Statistical mechanical theory is in accord with experiment in that the predicted desorption curve is always above the adsorption branch. The thermodynamics of solutions has also been applied to the problems of adsorption and there is a satisfactory equivalence[76]. Specific application of thermodynamic functions has been discussed, in the case of nitrogen adsorption on graphon, by Hill, Emmett, and Joyner[79]; see also Hill and Kemball[80].

A related viewpoint has been contributed by Sips[1, 2]. He has assumed localized adsorption with no interaction and has proposed a method for calculating an energy distribution of the adsorption sites from the isotherm. This is related to a distribution of adsorption energies described by Halsey and Taylor[58] for nonuniform adsorbent surfaces. Halsey and Taylor used an exponential energy distribution in developing an isotherm, rather than an isotherm to deduce a distribution. The Halsey and Taylor study was based on the hydrogen-tungsten system investigated by Frankenburg[45, 46].

Halsey. Refinements of the BET theory as well as independent derivations of adsorption-isotherm equations have been presented by Halsey[55, 56, 57]; and by Frenkel[48a]. In his analysis of adsorption on a uniform surface, he argues that, if the energy of adsorption in the second layer were equal to the liquefaction energy, as assumed in the BET derivation, no adsorption other than that in the first layer would occur. Furthermore, if the energy of adsorption decreased for each successive layer, the isotherm should consist of a series of steps. According to Halsey, this should hold whether localized or mobile adsorption is assumed. To smooth out the isotherm, either nonuniformity of the surface or interaction effects among the adsorbed molecules must be assumed.

These arguments involve the concept of cooperative adsorption which implies that adsorbate molecules influence each other during the adsorption process. This is related to the horizontal interaction considered in Hill's discussions. In developing his theory, Halsey divides the adsorption isotherm into three parts. The more active portions or active sites of the adsorbent surface are responsible for the steeply rising low-pressure portion of the isotherm. Here, adsorption takes place without cooperation. The second part of the isotherm is attributed to cooperative adsorption on the surface made heterogeneous by the initial adsorption. In the higher-pressure region near liquefaction pressures, the third portion results from cooperative multilayer condensation. In both the second and third parts, the adsorption is influenced by the diminishing van der Waals forces transmitted from the surface.

A given isotherm does not necessarily demonstrate all three of these parts. A Type I isotherm consists entirely of the first part. In Types III and V, the first portion is not observed. The heat of adsorption should rise with increasing amounts adsorbed on uniform surfaces because the adsorption is cooperative. Some support for this concept has been provided by heats of adsorption. Isosteric heat curves plotted from the precise adsorption data of Rhodin[120] rise to a maximum at approximately monolayer coverage for single crystal faces. Cooperative or horizontal interaction effects are evidently in operation. Rhodin employed a refined gravimetric method using a sensitive microbalance and studied the physical adsorption of nitrogen on copper crystals. An initial fall in the heat of adsorption may well indicate surface heterogeneity, but may also be accounted for by surface changes attributable to the adsorbate.

Harkins and Jura. Isotherm equations developed by Harkins and Jura[61, 88, 89] are closely related in certain respects to those derived by Halsey[55, 56]. Harkins and Jura, in developing their thermodynamic theory, observed an analogy between the relationships for monomolecular films on water and those for the physical adsorption of gases on solids. Similar observations have been presented by Gregg and Maggs[53]. Harkins and Jura found that the equation of state for condensed monolayers could be transformed by means of the Gibbs adsorption equation and applied to gas adsorption on solids. The relationship apparently applied to phases other than the condensed phase and extended into the multilayer region for gas-solid systems. The following isotherm equation was derived:

$$\log p/p_0 = B - A/v^2 \tag{11}$$

where v is the volume of gas adsorbed at the measured pressure, p, p_0 is the saturation pressure, and A and B are constants. Apparently this isotherm is a special case of an equation derived by Halsey[56] in which a specific value for the exponent of v is not initially assigned. Remarkable agreement of the Halsey equation with the data for nitrogen on anatase is found when a value of 2.67 is used for the exponent; agreement extends from $p/p_0 = 0.0026$ to $p/p_0 = 0.9936$.

Jura[87] has pointed out that in physical adsorption the solid adsorbent exerts only an extremely small effect on the isotherm after the completion of the monolayer. However, at low pressures and low coverage, the isotherm contour may be sensitive to the nature of the adsorbing surface. The Harkins and Jura studies are discussed further in the chapter on surface-area measurements[36].

Other Contributions. Anderson and Hall[2, 3] have endeavored to correct the BET theory for the differences in free energy of adsorption for the second and succeeding layers and of liquefaction of the bulk material. These authors have also introduced a correction factor for the decrease in effective pore diameter that accompanies the increase in thickness of the adsorbed layer. Pickett[114] has dealt with the multilayer-adsorption concept in the higher-pressure region. Both Anderson and Pickett have attempted to improve the theory in the region in which the pore volume becomes filled. Carman and Raal[21] have argued that capillary condensation cannot be ignored and must be considered along with multilayer adsorption phenomena.

Discussions of the BET theory and its modifications have been presented by Keenan[94, 95] and by Cook[27]. Constants of a more or less empirical nature, although related to adsorbate-adsorbate and adsorbate-adsorbent interactions, were introduced by Cook and tend to improve the equation principally for the higher-pressure portion of the isotherm. A "dual-surface adsorption theory" has been offered by Walker and Zettlemoyer[139, 140]. Pierce and Smith have also criticized the BET theory, principally as related to its application to systems having small pores and large areas[115, 116, 117]. Experiments tending to support the application of the BET theory to small-pore systems have been presented by Johnson and Ries[83].

A new approach to a theory for physical adsorption has been proposed by Wheeler[142, 143]; see also Ono[112]. He objects to the limitations of localized or fixed adsorption sites. He suggests that a general theory should allow mobility on the surface and at the same time a van der Waals type of interaction between the molecules and the surface as well as with each other. Wheeler has attempted to construct a picture of the adsorbed layer that is related to and in accord with modern theories of the liquid state. Interaction energies between the adsorbate molecules themselves and between the molecules and the adsorbent surface are assumed to be known. The equations developed involve these forces as well as the density of the adsorbate in the surface region.

For significant improvements in physical-adsorption theory, particularly in the multilayer and higher-pressure region, a satisfactory theory of the liquid state is needed because gases adsorbed on solid surfaces approach the liquid state. The development of rigorous equations is in progress for certain nonpolar liquids, but present equations are much too complex to apply to other systems. Until liquid-state theory has developed further, theories of adsorption must depend on approximate models.

Development of satisfactory theories will be enhanced by reliable data on heats of adsorption[96]. Both isosteric and direct calorimetric heats of adsorption are useful, although the application of the Clausius-Clapeyron equation to isosteric data has limitations. Nevertheless, excellent agreement between calorimetric and isosteric data on two carbon blacks has been reported[11, 85]. Precise adsorption data with small differences in temperature will be helpful. Reliable adsorption data for well-defined and controlled systems at low pressures are also needed.

The precise direct calorimetric measurements of heat of adsorption essential for many of the thermodynamic calculations of adsorption theory have been supplied for some time by Beebe and co-workers[10, 11, 12, 13, 98]. Contributions to the thermodynamics of adsorption and direct adiabatic calorimetric measurements have also been made by Aston[5] and by Kington and Aston[97]. Adiabatic systems have the advantage of temperature flexibility over the isothermal type. Close agreement between heats of adsorption and heats of desorption have been observed. Considerable study has been made of the low-temperature adsorption of helium, nitrogen, and oxygen on titania. Stepwise adsorption has been indicated in the case of helium. Work of this type will eventually establish the relationship between calorimetric and isosteric heats and other thermodynamic properties inherent in isotherm equations, whether kinetic, thermodynamic, or statistical-mechanical concepts are employed.

CAPILLARY CONDENSATION AND PORE STRUCTURE

Much attention has been focused on the higher-relative-pressure region of the isotherm partly because of interest in the pore structure of catalysts and related materials[35, 44, 81, 122-126, 141]. Although the true structure of pores involves a complicated geometry, the spaces between the solid particles are generally treated as simple cylinders or parallelepipeds. Interest in the interpretation of adsorption data in the neighborhood of liquefaction and the interpretation of adsorption-desorption hysteresis extends back to classical concepts of liquid surfaces and capillarity. Nevertheless, whether the classical capillary-condensation or the later multilayer theories are used, it is accepted that small pores are filled at lower pressures and large pores at higher pressures. At the liquefaction pressure, the pore volume is completely filled. For extremely small pores and for large adsorbate molecules, there may be screening or sieving effects, sometimes referred to as the relative availability of internal surface[7, 35].

Early Concepts

Zsigmondy[145] was the first to apply capillary-condensation theory to relationships between adsorption and pore structure. His interpretation was based on the Kelvin equation[136]:

$$\ln p/p_0 = -\frac{2\sigma V \cos\beta}{rRT} \tag{12}$$

where p is the measured pressure, p_0 the saturation pressure, σ the surface tension of the adsorbate, V the molal volume of the liquid adsorbate, β the angle of contact, r the capillary radius, R the gas constant, and T the absolute temperature. Thus, for a given relative pressure, p/p_0, a corresponding pore radius, r, could be calculated. Zsigmondy argued that, in porous structures such as gels, the same relationship between vapor pressure and meniscus radius applied as in the case of ordinary cylindrical capillaries. As the equilibrium pressure is increased in an adsorption experiment, condensation takes place in successively larger pores. This leads directly to the calculation of pore size from adsorption-isotherm data, but many assumptions are involved. Probably the principal assumption is that the liquid in the capillaries of the adsorbent has properties characteristic of the bulk liquid phase, such as the same surface tension and the same molal volume[135a].

For most adsorbates* it is customary to add the thickness of at least one molecular layer to the Kelvin radius, because an adsorbed layer or two undoubtedly functions as part of the solid surface independent of capillary condensation. Moreover, because the Kelvin equation involves capillary condensation and evaporation and implies liquid-phase properties, it is more reasonable to work with the desorption isotherm than the adsorption branch. At the saturation pressure, the adsorbate approximates as closely as possible the liquid phase; whereas, at the beginning of the adsorption branch, adsorption forces function independently of the effects of capillaries, and the point of initiation of capillary-condensation forces may be difficult to ascertain. Application of simple geometry to pore-volume and area data gives relatively good agreement with corrected Kelvin radii when rather narrow distributions are considered[122]. Structure curves for solids may be drawn by plotting volume adsorbed against the pore radius calculated from the relative pressure by means of the Kelvin equation. A pore-size distribution curve is obtained by differentiating the structure plot. Emphasis is generally placed on desorption isotherms for pore-size studies.

Additional understanding may be obtained by considering the complete adsorption-desorption isotherms or hystersis relationships. Hysteresis refers to a difference between adsorption and desorption isotherms (see Figure 1 p. 11). Ii the difference is reproducible, the hystersis is reversible; if the difference is temporary, the hystersis is irreversible. Zsigmondy interpreted hysteresis as a phenomenon related to differences in the angle of contact, β, caused by surface contamination, which interfered with adsorption. The contamination might be displaced partially or wholly before desorption, and the difference in contact angle could account for hysteresis according to Equation (12). This interpretation would apply only to irreversible hysteresis. Gleysteen and Deitz[50] have suggested that the BET multilayer

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* For water-desorption isotherms on charcoal, it is usually assumed that the Kelvin equation applies all the way to the walls of the capillaries, because at relative pressures below about 0.5 only a small fraction of a monolayer of water is adsorbed on a well-degassed charcoal surface[35, 86].

theory can account for hysteresis if it is assumed that the heat of desorption is greater than the heat of adsorption. This suggestion is related in a sense to the concept of cluster formation proposed by Mayer and Mayer[103]. They postulate that clusters or aggregates of adsorbate molecules form on adsorption and that these may then be difficult to break up on desorption. Reversible hysteresis, which is observed in many cases, has been explained by Kraemer[99] and McBain[105] by means of pore geometry rather than by wetting characteristics of the adsorbate.

In the Kraemer-McBain theory of hysteresis, a "bottleneck" pore having a narrow orifice and a relatively large body is assumed. During the adsorption process it is necessary that relatively high pressures are reached before the bodies with their large radii of curvature are filled. After the pores and their narrow necks are filled, a much lower pressure is required for desorption according to the Kelvin equation, because the emptying process must be initiated at the narrow pore necks. Emptying of a narrow neck "unlocks" the larger body which releases its contents quickly. Without the "neck" this emptying or desorption would proceed at a greater pressure. According to this picture, "funnel" or V-shaped pores oriented with their large openings to the surface would not exhibit hysteresis, whereas the inverted orientation would give hysteresis[86].

Later Interpretation

A more general explanation of reversible hysteresis has been offered by Foster[42, 43, 44] and Cohan[25, 26]. Their interpretations are based on an open-pore structure of the adsorbent. These pores may be visualized ideally as cylindrical tubes of uniform diameter throughout their length and open at both ends, or as parallel-platelet systems. It is suggested that the bottleneck structure is simply a special case of the open-pore theory. The open-pore theory in simple form holds that adsorption takes place normally in layers on the walls of the capillaries until the films are thick enough to bridge the pore at one point or throughout. If the pore is bridged at one point, capillary condensation may occur. When the pore is filled, the adsorption branch of the isotherm is completed. Desorption must obviously take place from the menisci formed at the ends of the filled pores, and thus the pressure must be reduced to relatively low values to initiate desorption. Consequently, the concept of bottle-neck structure is not required.

The theories of Foster and Cohan and the data indicate that the desorption branch of the hysteresis curve is much more significant for calculating pore radius than the adsorption branch, which in many cases may have little to do with capillary condensation. The radius of curvature for a meniscus of a filled pore is small and of the order of the radius of the pore proper, whereas the cylindrical surface formed on adsorption before complete filling has one small and one infinite radius of curvature. By means of such concepts, Cohan formulated an expression for the pressure required for filling and for emptying the cylindrical pores. Good qualitative agreement has been found in a number of cases between hysteresis data and these expressions[33]. Nevertheless, in a discussion of hysteresis data as related to both open-pore and bottle-neck theories, it has been argued that neither theory is acceptable[93].

Both the bottle-neck and the open-pore theories lead one to expect no hysteresis in the case of nonporous loosely packed adsorbents (Figures 4 and 5; see also[122, 123]). For systems with extremely small pores in which one or two layers fill the pores, hysteresis should be absent or negligible. This is because adsorbed layers presumably fill the pores without the benefit of capillary condensation; that is, deposition and removal may involve similar forces. As pore size increases within the small pore range, hysteresis generally becomes greater. With larger pores, condensation and evaporation involve different surface contours and consequently different forces. However, with systems of very large pores or V-shaped pores, hysteresis again diminishes and approaches that found with nonporous powders. The extreme of large pores is, in a sense, no pores at all. It is reasonable to measure the pore volume of large-pore structures, but the pore walls may be sufficiently separated that hysteresis is not observed.

Later developments in pore-structure interpretation of adsorption data incorporate refined methods for correcting the Kelvin relationship for adsorbed layers[8, 113, 131, 141]. A basic approach to hysteresis phenomena has been presented by Everett and Whitton[39b]. Wheeler's original concept[141] is that the pore radius is the sum of the Kelvin radius and the multilayer thickness calculated by the BET equation. Barrett, Joyner, and Halenda[8] have obtained pore-volume and area distributions of pore size by means of an analysis of desorption isotherms in which the Wheeler method of correcting capillary condensation for physical adsorption has been incorporated. These distributions appear reasonable and in addition are in agreement with some related pore distributions obtained by Drake and Ritter, who used high-pressure mercury-porosimeter techniques[31, 127]. The method cannot be applied rigorously to extremely small pores, because the Kelvin equation implies a liquid-phase meniscus. However, generally only small volumes are contained in pores of extremely small radii. The use of the Kelvin relationship, at least for pores larger than 10 A in radius, has received support from the studies of Juhola and Wiig[86] in which precise water-adsorption data were obtained on a series of charcoals.

A remarkable development in adsorption investigations related to pore size is that reported by Dickey and Pauling[30]. This study demonstrated that adsorbents may be prepared having affinities for specific substances.

Pores in the adsorbent structure that admit or fit the desired adsorbate molecules are obtained by preparing the adsorbent in the presence of the particular adsorbate. The original mechanism was concerned with the preparation of antibodies in the presence of the antigens under study and silica gels for the adsorption of specific dyes. This technique, if established on a wide basis, should have far-reaching effects in the fields of adsorption and catalysis.

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CHAPTER 2

MEASUREMENT OF THE SURFACE AREA OF SOLID CATALYSTS

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Introduction

Since the earliest experiments in catalysis the notion has been prevalent that, other things being equal, solid catalysts would attain their maximum activity if prepared in such a way as to give them large surface areas per unit weight. To this end, it has become customary to prepare catalysts either in a very finely divided form or in particles with high porosity and therefore large total surface areas. Until recent times, however, no general method was available for assaying the surface area of solid catalysts so that the entire interrelationship between surface area and catalytic activity was necessarily on a very qualitative basis. Within the past twenty years it has been shown, as pointed out in Chapter 1, that under suitable conditions, gases can be made to build up adsorption layers several molecules thick on the surface of a solid, and that methods can be devised for estimating the total surface areas of solid adsorbents from such gas adsorption.

Some idea as to the importance of being able to make surface area measurements in conjunction with catalytic studies was given recently by Taylor[1] who, in appraising the progress in catalysis that was made between the two World Wars said, "The final five year period (1935-1940) of our survey gave to contact catalytic science a tool of which it had long been in sore need." He was referring to the technique mentioned briefly in Chapter 1 for measuring surface areas of catalysts by the physical adsorption of gases at temperatures near their respective boiling points. In describing the method further he continued "The technique is a standardized one which can be reproduced by different workers in different laboratories with considerable accuracy and reproducibility. It therefore becomes a norm for expressing numerically what many believe to be very close to the accessible surface of a solid body." He further expressed the hope that in time such surface area measurements would become a standard part of all publications on solid catalysts and of all catalyst patent applications.

Before discussing the methods for measuring surface areas, it may be well to define what is meant by the surface area of a porous solid or a finely divided solid. Quite clearly, a porous solid may be said to have two different types of areas. One of these is made up of the external, the geometric, or the outer surface area of the porous particle. The other portion of the surface is usually called the "inner surface" and is made up of the surface of the walls of capillaries, crevices and cracks in the porous catalyst particle. Sometimes the ratio between the total surface area and the outer surface area needs to be stated. This ratio is usually known as the "roughness factor" of the solid. Such roughness factors may extend all the way from the value unity for perfectly smooth solids up to values of several hundred or several thousand for very porous materials.

The purpose of the present chapter is to summarize critically all that has been published relative to methods of measuring surface areas of catalysts and catalytic materials. This will include a critical discussion of the low-temperature gas adsorption method mentioned above, modern ideas as to the interrelationship of surface area and catalysis, a discussion of the limitations of the method, and a critical comparison of the method with all other procedures that have been suggested for obtaining surface areas of finely divided and of porous solids.

SURFACE AREA MEASUREMENTS BY LOW-TEMPERATURE GAS ADSORPTION METHODS

The general idea of measuring adsorption in order to determine surface areas is not new. Perhaps the earliest attempts to measure such areas by adsorption, however, involved some form of chemisorption. For example, Benton[2] tried to measure the surface area of platinum catalysts by the chemisorption of carbon monoxide and hydrogen; de Boer and Dippel[3, 3a] suggested measuring the surface area of calcium fluoride crystals by the chemisorption of water vapor; Emmett and Brunauer[4, 5] showed that it was possible to measure the surface area of a pure iron catalyst by the chemisorption of carbon monoxide at −195°C; and Beeck[6] and co-workers measured the surface of thin metallic films by the chemisorption of carbon monoxide at low temperature, as also did Rideal and Trapnell[7]. These latter authors also used the chemisorption of oxygen at low temperatures to measure films. In certain particular cases, chemisorption is a very effective means of measuring the surface of a solid catalyst. However, in general, there is considerable uncertainty as to whether a gas may chemisorb on the entire surface of a solid, or on only a portion of it; or whether, in some instances, it may react with more than the outermost layer of atoms of the solid.

Physical adsorption has often been used for obtaining some idea as to the relative surface areas of different catalysts or as to changes occurring in treating or sintering a particular catalyst. Thus, for example, Russell and Taylor[9] compared the extent of surface of an unpromoted nickel catalyst with that of a promoted nickel catalyst by noting the relative amounts of nitrogen, hydrogen or carbon dioxide that were adsorbed at temperatures at and above 0°C. However, physical adsorption, like chemical adsorption, to be effective must be used in such a way as to enable one to know the fraction of the total surface that is being covered in a given adsorption experiment. Only recently has serious attention been directed toward finding a way of selecting, on a particular adsorption isotherm, the point corresponding to a statistical monolayer of adsorbed gas.

About twenty years ago it became increasingly evident that a method was needed for determining the extent of the surface of a reduced synthetic ammonia catalyst. Only when such surface area was known would it be possible to ascertain whether particular promoters increased the extent of the surface or altered the quality of the surface. Furthermore, in order to be useful, the method had to be applicable to active metal surfaces and capable of being used without altering the catalytic activity of these surfaces. It occurred to the author that an observation made by Benton and White[10] in studying the low-temperature adsorption of carbon monoxide and nitrogen on iron synthetic ammonia catalysts might furnish a clue to a possible method for measuring the surface areas. When they obtained an S-shaped isotherm for the adsorption of nitrogen at -191.5°C on an iron synthetic ammonia catalyst, they noted a sharp break in the isotherm at about 120-mm pressure. They suggested that this might correspond to the completion of a first layer and the beginning of a second layer of adsorbed gas. It was evident that if a point could be found on such an adsorption isotherm corresponding to a single layer of adsorbed gas, a simple multiplication of the number of molecules in this layer by the estimated cross-section of each molecule would yield an absolute surface area. Accordingly, measurements were begun to determine the adsorption isotherms of gases such as nitrogen, argon, oxygen, carbon monoxide, carbon dioxide, etc., on iron synthetic ammonia catalysts at temperatures close to the boiling points of the respective gases. The first group of results obtained by Emmett and Brunauer[5] are shown in Figure 1. These isotherms marked the beginning of a research program that has culminated in the development of a simple, effective and accurate method of measuring the surface area of porous catalysts or of any finely divided or porous solid.

"Point B" Method

A cursory examination of the isotherms in Figure 1 showed that the sharp break observed by Benton and White was absent. The disappearance of this break resulted from applying corrections for deviation from perfect gas laws to the adsorbate gas in the adsorption bulb at liquid air temperatures. However, the corrected isotherms still seemed to contain a point that might well be related to the completion of a monolayer. All of them were characterized by a long linear portion usually extending over several hundred mm pressure. Furthermore, gases having molecules of approximately the same size all showed linear portions beginning at approximately the same volume of adsorbed gas. It seemed reasonable therefore to conclude that for the gases tried the long linear part of the isotherm might represent the filling up of the second layer of adsorbed gas. On this basis, the beginning of the long linear part of the isotherms of the type shown in Figure 1 would represent the point of completion of a monolayer; for convenience, it was labeled "point B". A series of adsorption isotherms for nitrogen, argon, carbon dioxide, carbon monoxide and oxygen at low temperature on iron[5], and also on a variety of other finely divided porous solids[5a], yielded a number of types of evidence that added to the conviction

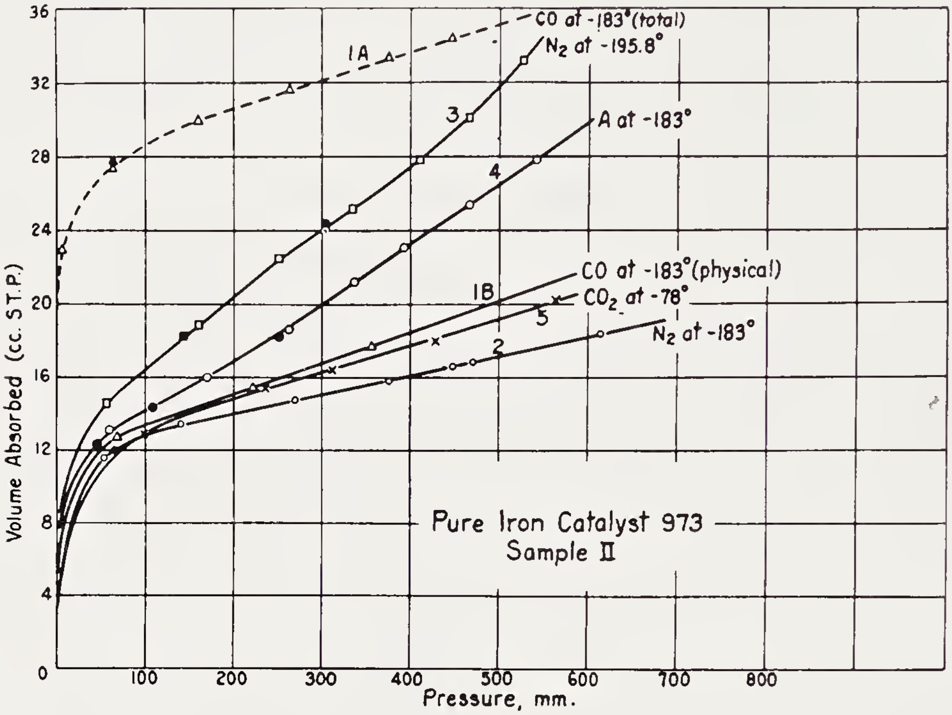

Figure 1. Adsorption isotherms[5] for various gases near their boiling points on 49 grs. of pure iron catalyst 973. Curves 2, 3, 4, and 5 are for N_2 at −183°, N_2 at −195.8°, A at −183°, and CO_2 at −78°, respectively, as indicated. Curve 1A is for the total CO adsorption at −183° and includes both physical and chemical adsorption; curve 1B is for the physical adsorption of CO on top of a layer of chemisorption. Solid symbols are for desorption.

that the point B method could be used for these gases to measure the surface areas of contact catalysts, provided the measurements were made at temperatures close to the boiling points of the respective adsorbates. However, similar adsorption experiments with butane soon showed that for many isotherms the point B method was inapplicable. Such a curve for butane is shown in Figure 2, together with isotherms for other gases. Clearly it would be almost impossible to select a point B on an isotherm that is so nearly a straight line through the origin as is the butane curve.

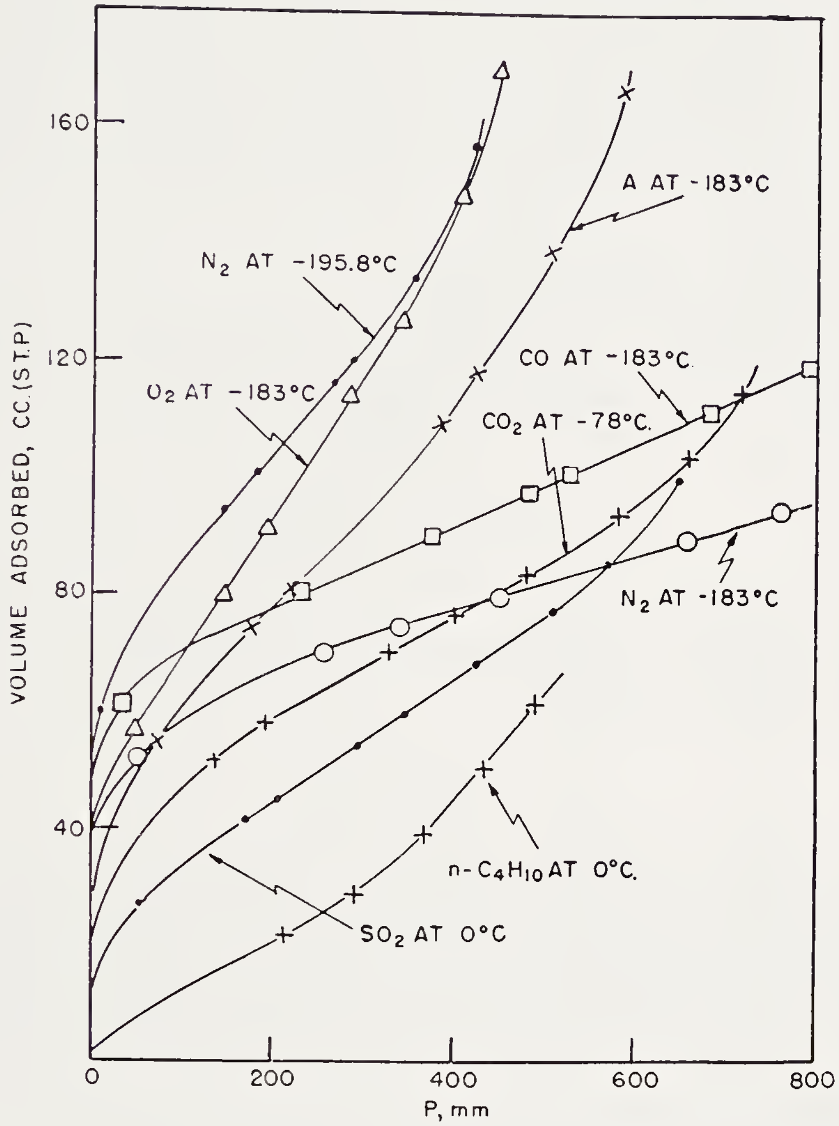

Figure 2. Low temperature adsorption isotherms for various gases on 0.606 grs. of silica gel[5a].

In view of the apparent failure of the point B method to be applicable to all types of gas adsorbates and solids, it seemed worthwhile to try to develop a quantitative theory of physical adsorption including an equation for plotting the experimental adsorption data in such a way as to yield a value for the surface area or at least for V_m, the volume of gas required to form a monolayer. This attempt culminated in the Brunauer, Emmett, Teller[12] theory of multilayer adsorption already described in Chapter 1. The equations of Harkins and Jura[13, 14, 15], and the approaches of Hüttig[16], Gregg[17] and others[18, 19] for interpreting adsorption isotherms followed. These will now be discussed in turn.

The Brunauer-Emmett-Teller Method

As pointed out in Chapter 1, Brunauer, Emmett and Teller derived an equation that has proved very useful in interpreting multilayer gas adsorption isotherms and in yielding information as to the surface area of solid catalysts. Their equation may be written in the form

$$\frac{x}{V(1 - x)} = \frac{1}{V_mC} + \frac{(C - 1)x}{V_mC} \tag{1}$$

where x is the relative pressure, p/p_0, for the adsorbate; V is the volume of gas (S.T.P.) adsorbed at relative pressure x; V_m is the volume of adsorbate required to form a monolayer on the surface of the adsorbent; and C is a constant given by the equation

$$C = \frac{a_1b_2}{a_2b_1} e^{\frac{(E_1-E_L)}{RT}} \tag{2}$$

The coefficient of the exponential is considered to be approximately unity; E_1 is the heat of adsorption in the first layer*; E_L is the heat of liquefaction of the adsorbate; R is the gas constant, and T, the absolute temperature. A plot of the left-hand side of Equation (1) against the relative pressure, x, yields† a value for V_m and for the constant C. Typical BET plots are shown in Figure 3.

As pointed out earlier, the use of the BET method for obtaining values for the surface area of a solid involves estimating the area covered by each

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* As pointed out in the original article[12], Brunauer, Emmett and Teller recognized that at best E_1 would be some kind of average value for the heat of adsorption in the first layer and that it would probably represent an average value for the last 20 per cent or so of the surface to be covered.

† The BET plots of data for the adsorption of N_2 at −195° are linear usually from about 0.05 to 0.35 relative pressure. The location of the linear portion depends upon the value of C and hence upon the heat of adsorption. In general, the linear portion will extend on both sides of the pressure corresponding to a monolayer. When $C = 100$, the monolayer point occurs at a relative pressure of about 0.1; when $C = 1$, a monolayer is reached at a relative pressure of 0.5.

adsorbed molecule. In the absence of any more certain criterion, Emmett and Brunauer[5] suggested calculating the area of each adsorbed molecule

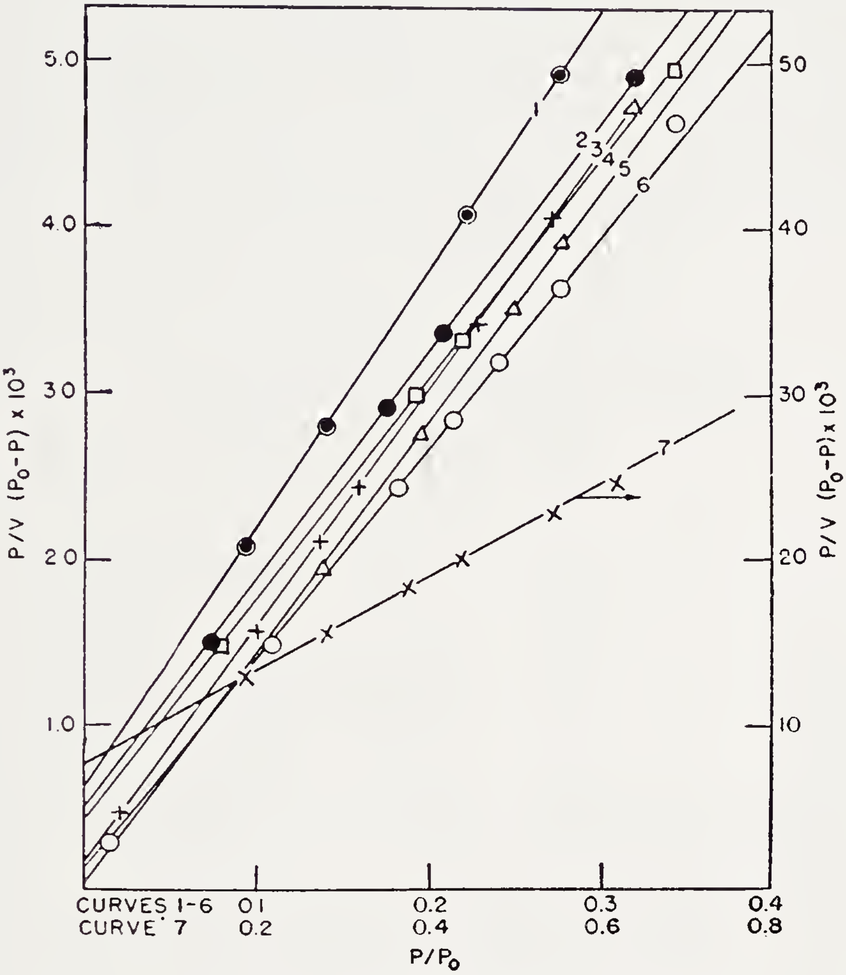

Figure 3. BET[12] plots for the adsorption of various gases on 0.606 g. of silica gel[5a] as follows: Curve 1, CO_2 at −78°; Curve 2, argon at −183°; Curve 3, nitrogen at −183°; Curve 4, oxygen at −183°; Curve 5, carbon monoxide at −183°; Curve 6, nitrogen at −195.8°; and Curve 7, n-butane at 0°C.

from the density of the liquefied or solidified adsorbate according to the equation

$$\text{Area per adsorbate molecule} = 4(.866)\left[\frac{M}{4\sqrt{2}Ad}\right]^{2/3} \quad (3)$$

where M is the molecular weight of the gas, A is Avogadro's number, and d is the density of the solidified or liquefied adsorbate. This equation is derived on the assumption that the adsorbate molecules are held in two-dimensional close packing on the surface, the area occupied by each molecule being the projected cross-section of the molecular volumes calculated from the density of the solidified or liquefied adsorbate. In Table 1 is given a list of the original areas as calculated by Emmett and Brunauer[5] from Equation (3). The choice of suitable areas and methods for possibly improving on the values listed in Table 1 will be discussed later in the chapter. At this point it is merely desired to emphasize that the BET method for measuring absolute surface areas does require an estimate of the area covered by each adsorbate molecule and that for adsorbed nitrogen the value 16.2Å^2 appears to be a reasonably satisfactory value for the cross-sectional molecular area.

TABLE 1. CALCULATED CROSS-SECTIONAL MOLECULAR AREAS OF TYPICAL ADSORBATES

Gas	Density of Solidified Gas[a]	Temp. (°C.)	Calcd. Mol. Area Å^2	Density Liquefied Gas[a]	Temp. (°C)	Calcd. Mol. Area Å^2
N_2	1.126	−253	13.8	0.751	−183	17.0
				0.808	−195.8	16.2
O_2	1.426	−253	12.1	1.14	−183	14.1
A	1.65	−233	12.8	1.374	−183	14.4
CO		−253	13.7	0.763	−183	16.8
CO_2	1.565	−80	14.1	1.179	−56.6	17.0
CH_4	[b]	−253	15.0	0.392	−140	18.1
n-C_4H_{10}			32.0[c]	0.601	0	32.1
NH_3	[b]	−80	11.7	0.688	−36	12.9

[a] The densities of all solids and liquids were taken from Volume III of the International Critical Tables.

[b] The densities for these solidified gases were calculated from the size of the unit cells as given by Wyckoff in "The Structure of Crystals" (Second ed.).

[c] The cross-sectional area of n-C_4H_{10} was calculated by assuming the butane molecules packed in oblongs 4.3Å wide and 7.45Å long (see S. B. Hendricks, *Chem. Rev.*, 7, 431 (1930)).

An early comparison of the value for V_m obtained from BET plots with the values obtained by selecting point B on nitrogen adsorption isotherms at low temperature quickly showed excellent agreement between the two procedures. Typical data are given in Table 2. It became evident therefore that the BET equation afforded a suitable method for plotting adsorption data in order to obtain an accurate value for V_m quickly and from relatively few measurements.

The repeated use of the BET plots for measuring surface areas revealed several advantages over the point B method. To begin with, the V_m values for adsorption isotherms such as that of butane in Figure 2 were still reasonable in comparison with the volume of nitrogen required to form a monolayer, when the estimate was made by the BET equation. On the other hand, it was considered impossible to select a point B on isotherms such as a butane isotherm for obtaining a value for V_m. Thus, the data shown in Figure 2 plot up as shown in Figure 3 to yield a value of 383 sq meters per gram for surface area estimated from a butane isotherm (using 32Å^2 per molecule for the adsorbed butane molecule as per Table 1) as compared to 477 sq meters per gram for the surface estimated from the nitrogen isotherms, using 16.2Å^2 as the area occupied by each adsorbed nitrogen molecule.

TABLE 2. VOLUME OF ADSORBED NITROGEN IN A MONOLAYER ON VARIOUS ADSORBENTS AS JUDGED BY THE BET[12] METHOD AS COMPARED TO THE POINT B METHOD[5]

Solid	V_m cc/g	Point B cc/g
Unpromoted iron catalyst 973 I	0.13	0.12
Unpromoted iron catalyst 973 II	0.29	0.27
$Fe\text{-}Al_2O_3$ catalyst 954	2.86	2.78
$Fe\text{-}Al_2O_3$ catalyst 424	2.23	2.09
$Fe\text{-}Al_2O_3\text{-}K_2O$ catalyst 931	0.81	0.76
$Fe\text{-}Al_2O_3\text{-}K_2O$ catalyst 958	0.56	0.55
$Fe\text{-}K_2O$ catalyst 930	0.14	0.12
Fused Cu catalyst	0.05	0.05
Commercial Cu catalyst	0.09	0.10
Cr_2O_3 gel	53.3	50.5
Cr_2O_3- glowed	6.08	6.14
Silica gel	116.2	127.0

One further advantage of the BET plots should be mentioned in passing. If nitrogen is used as an adsorbate, experience has shown that most of the BET plots have relatively small intercepts on the ordinate. Accordingly, for a solid known to have a Type II or a Type IV isotherm,* if a single point is determined on the nitrogen adsorption isotherm in the range 0.1 to 0.3 relative pressure and is then connected by a straight line to the origin in a BET plot, the value of V_m deduced from this curve will seldom differ by more than 5 per cent from the value of V_m determined by a large number of experimental points. This enables one to determine a large number of surface areas by a one-point method in a comparatively short time. Actually one can refine this method further by assuming an approximate value of C when the adsorption is on a type of material that is known to be characterized by a given C value. In this way Byck[20] claims to be able to

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* See Chapter 1 for a description of the various types of isotherms.

use the one point method to obtain areas on as many as thirty samples per day for a single operator, the uncertainties in the areas being no more than 2 or 3 per cent greater than those that would have been obtained from a large number of adsorption points on each adsorbent.

Space will not permit the reviewing of the many modifications that have been suggested for the BET equation[20a, 20b, 20c], nor the critical comments relative to its derivation[21]. Many of these have already been covered in Chapter 1 on Physical Adsorption. It will perhaps suffice to point out that at the present time it is generally admitted that the surface areas obtained by the nitrogen adsorption method are as accurate and reliable as any that we know how to obtain. Furthermore, even if the BET equation was derived on the basis of assumptions that are to be seriously questioned, it still serves as a useful and reliable method for plotting adsorption data to yield a value for V_m that is very close to that selected by the point B method, and that presumably can be used for calculating satisfactory values for surface areas.

The BET Equation for Narrow Capillaries

As pointed out in Chapter 1, an equation was derived by Brunauer, Emmett and Teller[12] with a view to obtaining a reliable V_m value also for solids having capillaries so narrow as to preclude the application of the general BET equation. The following equation for narrow capillaries was finally obtained in which all of the terms have the same meaning as previously and n represents the number of layers that can be formed on each wall of a narrow capillary without the layer meeting one from the opposite wall:

$$V = \frac{V_m C x}{(1 - x)} \left\{ \frac{1 - (n + 1)x^n + nx^{n+1}}{1 + (C - 1)x - Cx^{n+1}} \right\} \tag{4}$$

Joyner, Weinberger and Montgomery[22] have shown an easy method for applying this equation to obtain values for C, V_m, and n for materials in which the capillaries are so narrow as to compel the use of Equation (4) rather than Equation (1). The details of the method need not be discussed here since they have been fully described in the original paper. However, in Figure 4 are shown several isotherms for the adsorption on activated carbon, together with the values of n, C and V_m obtained by these authors. In this same figure are given plots made according to Equation (4) for narrow capillaries and also according to the following simplified equation to which Equation (4) reduces if n is assumed to be equal to 1:

$$\mathrm{p}/V = \mathrm{p}_0/CV_m + \mathrm{p}/V_m \tag{5}$$

The same authors point out that if Equation (5) is used for samples for which n is actually greater than 1, the calculated surface area would be considerably larger than that deduced by using Equation (4). On the other hand, if Equation (1) is used for such samples, the resulting surface area will be considerably smaller than that obtained with Equation (4). For example, if n is really equal to 1.5 for a given sample, the use of Equation (5) yields surface area value that would be about 115 per cent of that from

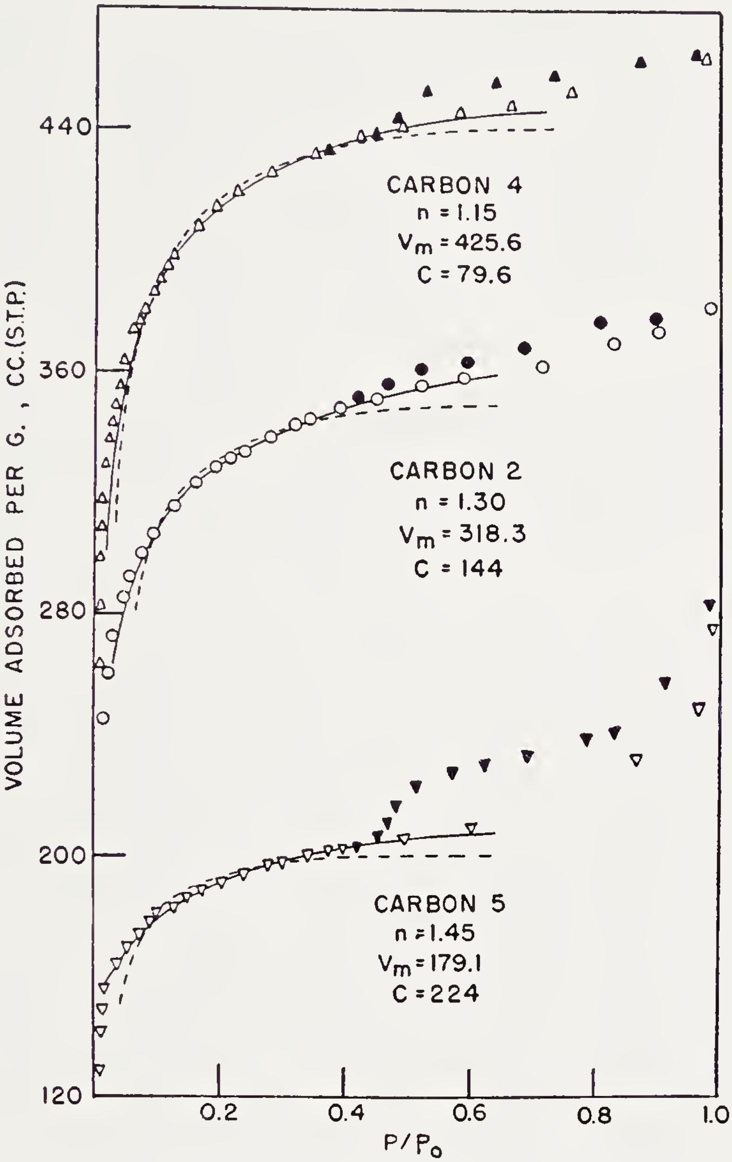

Figure 4. Adsorption isotherms for three activated carbons at −195°C[22]. The curves shown as solid lines are plotted according to the "n" form of the BET equation (Eq. 4) using the values for n, V_m and C indicated for each curve. The dotted lines were plotted according to the Langmuir equation (Eq. 6). Desorption points are indicated by solid symbols.

Equation (4), whereas Equation (1) will yield a value 82 per cent as large as that from Equation (4).

Harkins and Jura Method

A distinctly different approach to the interpretation of low-temperature gas adsorption isotherms has been employed by Harkins and Jura[13, 14, 15]. By assuming that the same type of equation is applicable to the adsorption of gases on solids that has been found applicable to correlating the surface spreading force of adsorbed films on liquids with the area occupied by adsorbed molecules, they[13] have been able to obtain the equation:

$$\log p/p_0 = B - \frac{A}{V_2} \qquad (6)$$

where V is the volume of gas adsorbed at pressure p and A and B are constants. Furthermore, they deduced that the area of a solid can be obtained from a plot of log p vs. $\frac{1}{V^2}$ by means of the equation

$$\text{area} = ks^{1/2} \qquad (7)$$

where s is the slope of the plot of Equation (6) and k is a constant that had to be evaluated by some independent means. In some very ingenious experiments they[14, 15] also provided an independent means of evaluating k by exposing a finely divided solid such as TiO_2 to a sufficient pressure of water vapor to form four or five statistical adsorbed layers, and then immersing in liquid water this sample coated with several layers of adsorbed water. They were then able to obtain from the evolved heat of immersion a direct measure of the surface area of the powder without any assumption as to the molecular cross-section of the water molecule. They merely divided the heat of immersion by 118.5 ergs, the value for the normal surface energy per sq cm of liquid water, to obtain a value for the number of sq cm of area in the sample[15a, 25]. Using this surface area for the powder they were then able to evaluate the constant k of Equation (7). For other solids they could apply Equation (7) by assuming that the constant k was independent of the type of surface. Proceeding in this way they obtained surface area values for six separate solids with their nitrogen adsorption isotherms and compared them with the areas that were obtained by plotting the adsorption data according to Equation (1). The results are shown in Table 3. A comparison of the values in column 2 with those in column 6 shows that the agreement between the two independent methods of interpreting the nitrogen isotherms is clearly remarkable and serves to strengthen the general conviction that gaseous adsorption isotherms can be used to obtain reliable surface area values for catalysts and other finely divided materials.

The close agreement between the area values calculated by the BET method and those obtained by the method of Harkins and Jura is surprising for a number of reasons. To begin with, if the sample of TiO_2 used in the water immersion experiments had any pores that would be filled up at the high relative humidities (80 to 90 per cent) used by Harkins and Jura in presaturating the samples, then one would have expected the immersion experiments to yield a surface area value smaller than those obtained by the BET method. The exact agreement between the two methods, each giving a value of 13.8 sq meters per gram for TiO_2 (Standard), presumably indicates the absence of any small pores in the sample. The more puzzling aspect of the agreement of these two methods is the queer coincidence that such divergent interpretations of the low-temperature adsorption isotherms should lead to the same surface area values for the adsorbents shown in Table 3. Halsey[23], in this connection, pointed out that the Harkins and Jura plot of the adsorption data according to Equation (6) may be taken as a special instance of his own more general equation relating the logarithm of the pressure to $1/\theta^r$, where θ is the adsorption expressed as number of layers. The constant r frequently has values ranging up to as high as 3 though for many materials over a considerable pressure range the plot is linear when r is given a value of 2. Several papers have been written[24, 24a, 25] in an attempt to make this agreement between the areas deduced from the BET plots and those from the Harkins and Jura plots appear more rational, but a complete and satisfactory explanation of the agreement has not as yet been given. It seems to be established, however, that data obeying the BET equations over the range 0.05 to 0.35 must also obey the Harkins and Jura plot (Equation 6). It should be noticed in this connection that the surface area deduced from the Harkins and Jura plots may differ by 25 to 30 per cent from those obtained by the BET plots (Equation 1). This deviation seems to be a function of the heat of adsorption as reflected by the BET C values[25]. Thus as C increases from 50 to 250 the cross-sectional area that has to be assigned to the nitrogen molecule to yield areas equal to those from the Harkins and Jura plots increases from 13.6 to 18.6Å^2. Nevertheless, since many gases, especially those boiling near $-190°C$, yield C values in the range between 50 and 150, the agreement between the two methods is, as a rule, very satisfactory.

Procedure of Askey and Feachem

In an article published in 1938, Askey and Feachem[26] pointed out that for several years they had used low-temperature adsorption isotherms for measuring the surface area of finely divided materials. The method was substantially the same as the first of the methods suggested by Brunauer and Emmett[27] according to which it was postulated that an extrapolation of the linear part of the S-shaped adsorption isotherm to zero pressure should yield a value for V_m and hence, with the assumption of a suitable value for molecular size, an absolute surface area. Although this method was judged by Emmett and Brunauer[5] to be somewhat less accurate and more often open to question than the point B method, it would certainly yield areas which are approximately (10 to 30 per cent smaller than by the point B method) correct and which are probably capable of giving fairly reliable relative areas for various finely divided solids.

Gregg's Approach to Surface Area Measurements

Even before Harkins and Jura published their work on measuring surfaces by plotting adsorption data according to Equations (6) and (7), Gregg[28] had suggested that films on solids can exist in the same states (gaseous, liquid-intermediate, and liquid-condensed) as films on water. However, his method of plotting the data for estimating surface areas made use of the variation of surface compressibility of the adsorbed layer as a function of pressure. Specifically, Gregg and Maggs[29] suggested that as the molecular concentration on the surface increases the molecules move closer and closer together and hence the surface film becomes progressively less compressible. When, however, a point is reached at which multilayers start to form the "apparent compressibility" rises since one is able rapidly to accumulate molecules on the surface of the catalyst. Accordingly, they suggested that a plot of log x against β/S, where β is the compressibility coefficient of the adsorbed layer, S is the surface area, and x is the relative pressure, should yield a minimum at a point corresponding to the completion of a monolayer on the solid adsorbent. Figure 5 contains such a plot together with an isotherm plotted as volume of gas adsorbed against relative pressure and also plotted as the volume of gas adsorbed as a function of the

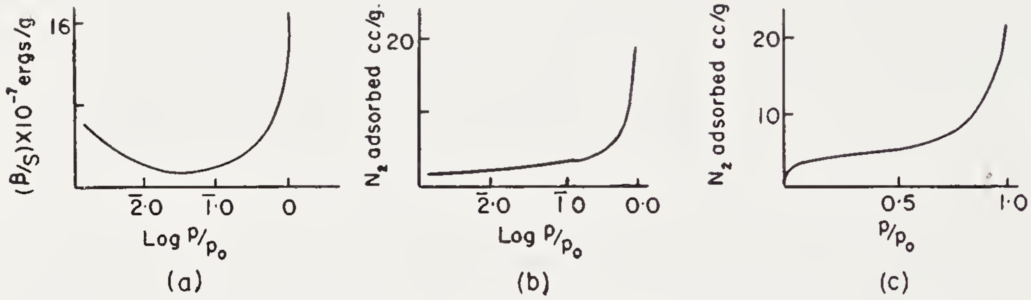

Figure 5. Compressibility plots[17] for nitrogen on anatase (TiO_2) at −195.8°C.

(a) contains a plot of the compressibility β/S (see Eq. 8) against the logarithm of the relative pressure.

(b) is a semilogarithmic plot of data for the adsorption of nitrogen on anatase at −195.8°.

(c) is the regular plot for the nitrogen adsorption isotherm, as volume adsorbed as a function of relative pressure[13].

logarithm of the relative pressure. This last form of the plot is needed in evaluating the term β/S since Gregg has been able to show that this compressibility per unit area is given by the equation

$$\beta/S = \frac{1}{RTw^2}\frac{dw}{dlnp} \tag{8}$$

where w is the adsorption per gram as measured at the pressure p. According to Gregg[17] the surface area[30a] estimated by this method from the plots shown in Figure 5 for the adsorption of nitrogen on TiO_2 agrees within a few per cent with that obtained by the BET method[12] using Equation (1).

Other Gas Adsorption Methods

Several other methods for calculating the areas of porous materials with the help of low-temperature adsorption and desorption isotherms[18, 19, 30b, 30c, 31, 32, 33] and rate curves have been proposed. In particular, attention should be called to the method proposed by Harvey[18], to that proposed by Kistler[19] and his co-workers, and to the detailed and critical discussion of both of these[25]. Their methods are based on the calculation of surface areas from the amount of liquid apparently capable of being held by porous solids in the form of capillary condensation. A somewhat similar proposal has also been made by Oulton[33] in assigning arbitrarily a value for the thickness of an adsorbed film at the point at which the desorption curve for a porous solid joins the adsorption isotherm. These are very specialized methods that are applicable in principle only to those porous solids for which hysteresis is observable. They do not, accordingly, seem to have the general applicability of the methods depending on the shape of the nitrogen adsorption isotherms over the relative pressure range 0.05 to 0.35. For this reason they will not be discussed further in the present chapter.

A few of the other special methods for using adsorption or heat of wetting in measuring surface areas will be described briefly. Gregg[30a] suggests the use of heat of wetting data to supplement information obtained by use of adsorption isotherms. Mizushima[30b] used both the adsorption isotherm and the angle of wetting of an adsorbent by the adsorbate to arrive at an equation for evaluating the surface area of a solid. Zhukhovitskiĭ and Rubinshteĭn[30c] point out that if the heat of adsorption is much higher than the heat of liquefaction, the adsorption data obey the equation

$$V/V_m = 1 - \frac{1}{ap} + bp \tag{9}$$

where a and b are constants and the other symbols have their usual meaning. The authors propose a graphical method for solving this three-constant equation and claim that V_m deduced for the adsorption of N_2 at $-195°C$

is in good agreement with that calculated by the BET equation[12]. Duncan[31] employed both the Harkins and Jura equation and the BET equation as modified by Anderson[20a] in interpreting low-temperature adsorption isotherms of both nitrogen and ethylene to yield values of the surface area and V_m, respectively. He also showed how for certain ranges of the heat of adsorption both of these equations can be reduced to one of the form

$$p/p_0 = C(1 - V_m/DV) \tag{10}$$

where C and D are constants. To a close approximation the constant D may be taken as unity and C as $1/k'$ where k' is the constant of the Anderson form of the BET equation and may be taken as 0.6. A plot of p/p_0 against $1/V$ then yields a value of V_m that should differ from the value obtained by the BET equation by not more than 20 per cent.

Hüttig Equation

One theoretical development very similar to that upon which the BET equation is based is that of Hüttig. This has already been discussed in Chapter 1. The Hüttig equation which can be used for measuring surface areas is similar to Equation (1) and can be written in the form

$$\frac{x(1 + x)}{V} = \frac{1}{V_m C} + \frac{x}{V_m} \tag{11}$$

where the various terms have the same meaning as for the BET equation. The surface area obtained from Hüttig's equation agrees usually within 10 per cent of that obtained by the BET plot. According to Hill[34a], however, the Hüttig derivation[16] contains all of the shortcomings that can be attributed to the derivation of the BET equation plus a few additional ones. Accordingly, as an interpolation equation for obtaining an estimate of V_m from adsorption isotherm data it probably is about as useful as the BET equation but of no more real significance.

In general, it seems fair to say that none of the alternate methods described above has any real advantage over the BET method. They require more experimental points and at least as many calculations without producing more significant or reliable area values than can be obtained by the simple BET equation or the point B method described above.

CRITIQUE OF THE MEASUREMENT OF SURFACE AREAS BY GAS ADSORPTION METHODS

In the present chapter, it is especially desirable to stress the utility of gas adsorption methods for measuring the surface areas of solids. On the other hand, it is equally important to emphasize the limitations and uncertainties of these methods. In summarizing the measuring of surface areas of catalysts by these gas adsorption methods, accordingly, attention should be called to the following points:

Molecular Cross-Sectional Areas

The BET method, as typified by Equation (1), yields a value for V_m, the volume of gas required to form a monolayer on the adsorbent. However, to convert V_m to absolute surface area in sq meters per gram, one has to select a value for the cross-sectional area estimated to be covered by each adsorbate molecule. It must be fully recognized that the areas obtained by the use of adsorbates other than nitrogen in many but not in all cases differ considerably from the area obtained by nitrogen if to these other molecules cross-sectional areas are assigned on the basis of Equation (3). Iodine adsorption[35] on MgO gives an area value in good agreement with that obtained using nitrogen as adsorbate. On the other hand, Harris and Emmett[35a] found that for another adsorbate, carbon disulfide, the area might be only one-third to one-half as large as that calculated by the nitrogen adsorption isotherms. In less extreme cases one may cite observations that have been made for butane, krypton, and argon. The areas obtained from isotherms with these three gases[36, 37, 38] must be multiplied by correction factors of about 1.5, 1.3 and 1.2, respectively, to make them agree with the ones obtained from the nitrogen isotherm.

The reason for these deviations is not fully understood. The explanation can certainly not be based entirely on the assumption that the larger molecules are screened out of some of the pores of porous solids, although in some instances with measurements on solids having very small pores this, too, may be a factor. Presumably, the result is due to irregularities in the packing of various molecules on the surface of a solid. Indeed, on MgO Walker and Zettlemoyer have shown that better agreement among the values for the surface area of a given solid as obtained by various adsorbates can be obtained by assuming that the adsorbate molecules space themselves according to the dimensions of the solid adsorbent[39]. At any rate deviations are almost invariably in the direction that areas obtained by other adsorbates either agree with or are smaller than those obtained using nitrogen. Livingston[38] has given a detailed list of the best values to use for the cross-sectional areas of a number of molecules in calculating surface areas from adsorption isotherms.

Harkins and Jura *k* Value

The method of Harkins and Jura[13, 14, 15] avoids this difficulty of selecting particular cross-sectional areas for the adsorbate molecules by determining an absolute value for the surface area of TiO_2 by the heat of wetting experiment described above. It is then possible to determine the constant *k* for each adsorbate that one wishes to use in examining the surface areas in a series of solids. When this is done the areas as obtained by different gases usually agree very closely with each other. This is illustrated by comparing columns 2, 3, 4, and 5 in Table 3. It must be realized, however, that the procedure used by Harkins and Jura is tantamount to making the areas by a series of gases such as nitrogen, butane, heptane, and water vapor agree on a given solid and then applying these same relative areas to other solids. In columns 6, 7, 8, 9 and 10 of Table 3, surface areas have been calculated from the adsorption isotherms by using various appropriate cross-sectional areas for the adsorbed molecules. It is evident that if one selects the cross-sectional areas for the various adsorbates in such a way as to make surface area values agree for some particular adsorbent, then very nice agreement is also obtained in BET measurements on other solids with the various adsorbates.

Table 3. Surface Areas[11] (in Square Meters per Gram) of Six Adsorbents as Calculated by the Method of Harkins and Jura[13] and the Method of Brunauer, Emmett and Teller[12]

Solids	Method of Harkins and Jura				BET Method[a]				
	N_2	H_2O	n-C_4H_{10}	n-C_7H_{16}	N_2 16.2Å^2	H_2O 14.8Å^2	H_2O 11.3Å^2	n-C_4H_{16} 56.6Å^2	n-C_7H_{16} 64.9Å^2
TiO_2 (standard)	13.8	13.8	13.8	13.8	13.8	13.8	10.5	13.8	13.8
TiO_2 II	8.7	8.4		8.7	8.6	11.7	8.8		8.7
SiO_2 (quartz)	3.2	3.3		3.3	3.2	4.2	3.2		3.6
$BaSO_4$	2.4	2.3	2.2	2.3	2.4	2.8	2.1	2.7	2.4
$ZrSiO_4$	2.9	2.7			2.8	3.5	2.7		
TiO_2 plus Al_2O_3	9.6	11.8			9.5	12.5	9.5		

[a] The cross-sectional area for the nitrogen molecule was taken from Table 1 to be 16.2Å^2 as calculated by Equation (3). The molecular area values for columns 7, 9, and 10 were so selected as to make the areas for the standard TiO_2 agree with the one calculated by the nitrogen isotherm. The molecular area of 11.3Å^2 for water (column 8) was so chosen as to make the area for the TiO_2-Al_2O_3 sample agree with that obtained by nitrogen adsorption.

Gas Adsorption Methods—Confirmation for Nonporous Solids

The areas obtained by using nitrogen adsorption isotherms at liquid nitrogen temperature on nonporous solids in conjunction with the point B method, with the BET equation, or with the equations of Harkins and Jura all appear to check each other and to be in agreement with areas obtained by independent means. Space will not permit a complete listing of all comparisons that have been made by way of checking the validity of these methods involving the physical adsorption of gases. It will perhaps suffice to point out that good agreement is obtained between the gas adsorption method and the areas estimated by (1) the heat of immersion method of Harkins and Jura[14] on TiO_2, (2) the electron microscope photographs for carbon black[40], (3) the direct microscopic observations[41] on sized glass spheres about 7 microns in diameter, (4) permeability measurements on zinc oxide pigments using various liquids as fluids[42], (5) ultramicroscopic observations on suspensions of these same zinc oxide pigments, (6) geometric measurements on single crystals of copper[43, 44, 45], zinc, and aluminum, (7) the adsorption of stearic acid and other molecules from solution on zinc oxide pigments[46], and (8) geometric measurements on smooth silver foil and on "Monel" ribbon[37].

In connection with these observations, it should perhaps be noted that surface area measurements on various solids of known geometric areas with nitrogen as an adsorbate have never revealed roughness factors smaller than unity if 16.2 sq Å was used for the cross-sectional area of the nitrogen molecule[37, 43, 44, 45]. There seems to be no reason to believe, therefore, that the molecular area calculated for nitrogen from the density of liquid nitrogen is too small. Certainly the agreement mentioned in the various examples given above is close enough to warrant the conclusion that with nitrogen as an adsorbate one obtains reasonable areas for finely divided nonporous solids whose surface areas can be determined by some independent means.

Confirmation of Gas Adsorption Methods on Large-Pore Solids

A method for measuring surface areas of catalysts must always be regarded with suspicion until it can be confirmed by some independent means. As pointed out above, for nonporous finely divided solids such independent verification is easily obtainable. For porous solids, however, there are very few independent means of confirming surface area measurements. One of the few methods for checking the size of crystallites or sub-particles in a porous solid is the use of low angle x-ray scattering. Thus, the measurements by Elkin, Shull and Roess[47] indicate that for a series of silica gels the sizes of the tiny amorphous blocks or sub-particles as revealed by low angle-scattering measurements yielded area values which were larger than the areas obtained by the nitrogen adsorption method by factors ranging from 1.14 to 1.5 for the various gels. Their results are summarized in Table 4. This really constitutes excellent agreement in view of the combined uncertainties of the two methods. The few data obtained by adsorption from solution may also be used to test the areas obtained by the adsorption method. Smith and Fuzek[48], for example, found that areas estimated by the adsorption of fatty acids from benzene on Raney nickel catalysts are approximately the same as those deduced from nitrogen adsorption isotherms by BET plots.

Area Measurements on Solids having Fine Pores

"Only for materials giving isotherms approaching the flat Langmuir type shown in Figure 4 does there appear to be much uncertainty relative to the surface area of porous solids as estimated by gas adsorption methods.

TABLE 4. COMPARISON OF THE SPECIFIC SURFACE AREAS AS MEASURED BY THE ADSORPTION OF NITROGEN AT −195°C WITH THOSE OBTAINED BY LOW-ANGLE SCATTERING OF X-RAYS FOR A SERIES OF SILICA GELS AND SILICA-ALUMINA CATALYSTS[47]

% Al_2O_3	Av. Diam. of Particles by Low-Angle Scattering of X-rays (Å)	Surface Area sq m/g		Ratio of Area by X-rays to Area by Ads. of N_2
		By Ads. of N_2	From Part. Size of Col. 2.	
Series A, prepared by precipitation on Silica Gel I				
0.0	31.5	829	1080	1.30
5.2	34.5	675	1020	1.51
19.8	43.5	580[a]	700	1.21
Series B, prepared by mixing of wet gels (Silica Gel II)				
0.0	58.3	414	560	1.35
5.2	54.2	571	650	1.14
17.5	65.7	388	530	1.37

[a] Value obtained by interpolation on a graph of specific surface vs. composition.

Obviously, when pores are sufficiently close to molecular dimensions, the very definition of surface becomes somewhat equivocal. For example, the surface of some of the smaller capillaries will probably be reached only by the smallest adsorbate molecules. Hence, the area calculated from the adsorption data would depend upon the size of the molecules being used as a measuring unit. However, even for a silica gel sample that has pores so small as to cause its nitrogen adsorption isotherm to resemble those obtained on charcoal, the x-ray low-angle scattering measurements of Elkins, Shull and Roess[47] give good agreement with the areas deduced from nitrogen adsorption isotherms. Unfortunately, this is about the only means available for checking the gas adsorption method when fine pores are involved though a few meagre comparisons have been made between areas deduced by the adsorption at −195° for charcoal and areas obtained by adsorption from solution[11]". Accordingly, one must admit that there is considerable uncertainty as to the validity of methods for obtaining V_m for solids having very small pores. However, as pointed out above, V_m values calculated with the help of Equation (4) by the method of Joyner, Weinberger, and Montgomery for solids having small pores seemed to be as reliable as we know how to obtain at the present time for the surface area accessible to molecules of the size used in the adsorption measurements.

Precautions

In conclusion it seems well to mention a few precautions that are needed in applying the BET method and to mention a few instances in which its applicability has been questioned.

(1) In applying the adsorption technique at -195° by the usual procedures a sample of 5 to 10 grams of finely divided or porous solid should have an area of at least 1 sq meter. By the use of suitable microgravimetric techniques, however, it is possible to make surface area measurements by the nitrogen adsorption method on single crystals having a total surface as low as 10 sq cm.[43, 44]

(2) For measuring areas smaller than about 1 sq meter it is ordinarily preferable to use some adsorbate having so small a p_0 value that the number of molecules left in the gas phase during the measurements is of the same order as the number that are actually adsorbed on the surface being measured. Krypton at -195°C[36], butane at -78°[37], and ethane and ethylene at -195° are adsorbate-temperature combinations that have been used in this connection. Wooten and Brown[50] first showed the potentialities of using the BET method for measuring small surface areas when they employed ethane and ethylene at -195°C for measuring surface areas of the oxides from radio tube filaments when the total sample had an area of only about 100 sq cm. They claim an accuracy of about 10 per cent in their measurements.

(3) The presence of a chemisorbed layer of gas on the adsorbent does not interfere seriously with the low temperature nitrogen adsorption measurements provided, of course, that the pores are not so small that a monolayer of chemisorbed gas can block or close up some of the tiny pores and hence actually decrease the amount of surface to which the nitrogen has access. This rule is generally true though there are a few experimental results[51, 52, 53] to suggest that covering a metal surface with a chemisorbed layer of carbon monoxide may cause a decrease of as much as 10 per cent in the value of the surface area as measured by nitrogen.

Phase changes have been reported[53a, 53b] for many adsorbates and solids. Such phase changes will, of course, interfere with the use of these adsorbates for measuring the area of a particular solid if they occur in the relative pressure range needed for surface area measurements. Fortunately, in no instance has such a phase change been observed for nitrogen at −195° over the relative pressure range 0.05 to about 0.25, though discontinuities resembling what are commonly called phase changes have been found at lower relative pressures for nitrogen[54]. Accordingly, for measurements with nitrogen as adsorbate such phase changes do not appear to constitute a problem; for other gases they may interfere with area determinations.

(5) On certain freshly graphitized carbon blacks, Smith and his co-workers[55] have observed stepwise isotherms with a number of different adsorbates. For nitrogen, however, the BET plots are still linear over a range from about 0.05 to 0.2. The authors elected to use the point B method for estimating the surface areas of these carbon blacks, though BET plots over this limited relative pressure range appear to be equally satisfactory. These stepwise isotherms for nitrogen have so far been noted for very few adsorbents and have not been observed at all on any of the substances that are used extensively as solid catalysts.

(6) In rare instances, BET plots have been found to be slightly concave with respect to the pressure axis between about 0.2 and 0.3 relative pressure for adsorbates such as nitrogen. This behaviour has been interpreted by Zettlemoyer and Walker[55a, 55b] as indicating that part of the surface has a high heat of adsorption, and part of it a low heat. For example, the data for nitrogen adsorption on active magnesia could be explained by assuming that 75 per cent of the surface was characterized by $C \cong 130$, and 25 per cent by $C \cong 1.4$ (see Equation 1). Against this interpretation is the absence of an adsorption isotherm for any inorganic compound with $C \leqq 35$. It seems more likely to the author that the slight concavity indicates a tendency toward the same type of stepwise adsorption found by Smith[55] and his co-workers and by Joyner and Emmett[55c] for partially graphitized carbon black and as such should not seriously interfere with the measurement of the area of porous and finely divided catalysts. It must of course be admitted that the usefulness of nitrogen for measuring surface areas by the adsorption method will be greatly diminished if many examples are found in which the C value of the adsorption according to Equation (1) is smaller than about 5. To the writer's knowledge only two such examples have so far been found, out of the tens of thousands to which the nitrogen method has probably been applied. They are the adsorption at −195° of nitrogen on tanned hide[56] and on layers of solid xenon[57]. In both instances, because of the low heat of adsorption the isotherms approach the type III variety and hence are not of much use for area determinations.

The detailed experimental technique and procedure used in applying the adsorption method have not been described in the present chapter because they have been fully presented in a number of previous publications[55c, 55d]. Furthermore, the technique used is very little different from that employed in standard gas adsorption work described in the literature for many years.

If the precautions and limitations outlined above are kept in mind, workers should be able to measure effectively both the relative and the absolute surface areas of any solid catalysts or catalytic materials in which they are interested. It seems likely that the gaseous adsorption methods will be supplemented by rather than replaced by other methods for obtaining area estimates for catalysts or other finely divided or porous solids.

Application of Surface Area Measuring Methods in the Study of Solid Catalysts

Activity vs. Surface Area

In general one will not expect[57a] to find the activity of a catalyst to be proportional to its surface area for a number of reasons. In the first place, there is good evidence that in many instances at least catalytic action is limited to certain active spots or active regions on the surface of the catalyst[58]. These active regions may constitute only a small fraction of the total surface area. Consequently, one would not expect to find the activity proportional to the area unless there happened to be some good reason to believe that the two catalysts being compared had equal fractions of their surfaces in the form of active points. In this connection it should be noted that the argument is not changed if we assume that active points are not preformed in preparing the catalyst but are created by one or more of the gaseous reactants during the catalysis as proposed by Volkenstein[58a]. Even on this new point of view one would expect proportionality between the activity and the total area only in the event that the fraction of the surface converted into active points by the reactant was constant and independent of the particle size and of methods of preparation.

The second reason for not expecting a linear relationship between catalytic activity and surface area arises from the fact that in porous solids frequently only the more easily accessible pores are available for the reaction that is being catalyzed[59, 60, 60a]. The influence of pore size and pore distribution on catalytic activities will be discussed in more detail in Volume II of this series. It will suffice to point out here that if one has a catalyst consisting of rather small pores, and is trying to catalyze a very fast reaction, the small pores most remote from the surface of the particle will have little chance to play their parts in helping to catalyze the reaction. Consequently, unless the two catalysts being compared have two identical pore distributions and pore sizes, they would not be expected to have activities proportional to areas even if the activity per unit accessible area happened to be the same.

If a solid catalyst possesses very small pores, then the absolute value of the surface area may depend upon the size of the molecules of the gas used in making the measurements. Furthermore, the very small pores probably are not participating in the catalytic reaction. Accordingly, the existence of such very small pores is still another reason for the lack of proportionality between catalytic reaction rate and the surface area of porous solids.

In spite of valid reasons for not expecting an exact correlation between the surface area of catalysts and the catalytic activity, a number of examples have been noted in which such a correlation does exist. These correlations are usually restricted to the variation of activity of a particular type of catalyst with its measured surface area. For silica-alumina cracking catalysts, surface areas have been measured by numerous workers[61a, 61b, 61c, 61d, 61e, 70a]. Furthermore, for a given type of catalyst the activity for cracking hydrocarbons is proportional to the surface area as measured by the nitrogen adsorption method. However, if one tries to compare silica-alumina catalysts, silica-magnesia catalysts and clay catalysts by this procedure, one will find that the activities are not directly proportional to the areas.

Chromia-alumina catalysts for the dehydrogenation of butane afford one of the best examples of a relationship between surface area and catalytic dehydrogenating activity[62]. Actually this correlation is so good that the measurement of surface area could probably be used as a standard for checking one batch of catalyst compared to another for this reaction. A plot of data illustrating the approximately linear dependence of rate on activity is given in Figure 6.

In general, it may be stated that the use of surface areas in comparing catalysts is much more valuable as a means of ascertaining the extent to which various treatments alter the total surface area than it is in obtaining a direct correlation between catalytic activity and surface area.

Surface Area Measurements in Studying Promoter Concentrations on Catalyst Surfaces

In some work published a number of years ago Brunauer and the author[4] were able to measure the fraction of the surface of an iron synthetic ammonia catalyst covered by such promoters as potassium oxide and aluminum oxide by comparing the total chemisorption of carbon monoxide on these catalysts with the total surface area as measured by nitrogen. The results seem to indicate that one or two per cent of a promoter in an iron catalyst is capable of covering 60 to 70 per cent of the surface with promoter molecules. Only the existence of a method for measuring the total surface area of these catalysts made possible the drawing of these conclusions relative to the fraction of the surface covered by promoter molecules.

It should be emphasized that the chemisorption of carbon monoxide and carbon dioxide at −195° and −78°, respectively, in comparison with the adsorption of nitrogen at −195° on a metallic catalyst may not always prove to be a reliable method for estimating the fraction of the surface covered with promoter molecules or impurities. For example, Skau and the author[63] found that a nickel catalyst chemisorbed a volume of carbon dioxide at −78° equal to 80 per cent and a volume of carbon monoxide equal to 200 per cent of the volume of nitrogen required to form a monolayer. Since the area per nickel atom in the three principal planes, 100, 110 and 100, are 6.19, 8.75 and 5.36Å^2, respectively, one can understand how the chemisorption of carbon monoxide on the metallic part of the surface could be several times as large as the nitrogen monolayer over the entire catalyst provided little residual alkali from the sodium hydroxide used in preparing the catalyst is left on the surface. It is difficult, however, to account for such an extensive chemisorption of both carbon monoxide and carbon

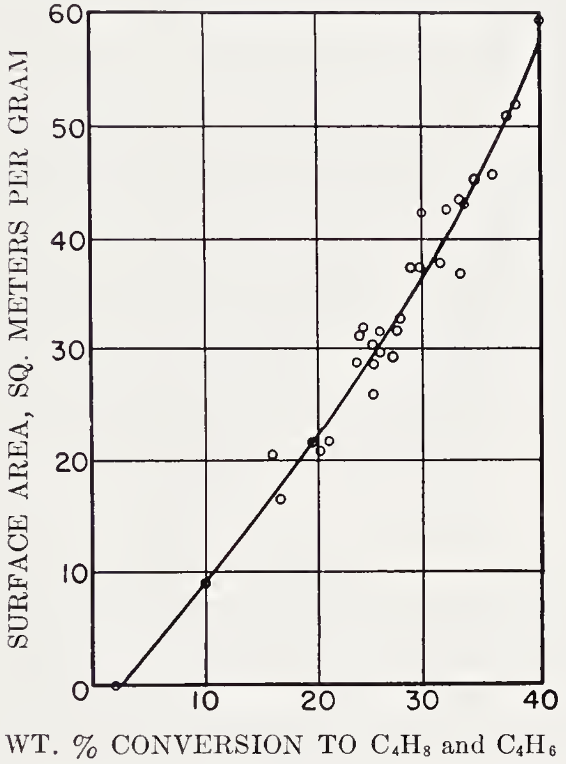

Figure 6. Correlation[62] of the surface area of chromia-alumina catalysts with their activity for the dehydrogenation of butane.

dioxide. Clearly, then, this method for estimating the concentration of promoters or impurities on the catalyst surface must be used with caution.

Surface Area Measurements and Pore Size Determination

One other use of surface area measurements of porous catalysts is connected with the determination of the average pore size of catalysts. If one assumes the pores of catalysts to be cylindrical, then the average radius of the pores of a given catalyst are related to the pore volume and surface area by the equation[42]

$$r = \frac{2V}{A} \tag{12}$$

where V is the volume of the pores in cc, A is the area in sq cm and r is the radius in centimeters. As will be pointed out in Volume II, there are other methods for measuring pore distributions and average pore size. However, this method which makes use of the total pore volume and the surface area of the solid is a good one for determining approximately the average size of capillaries and for serving as a general check on other methods that are capable of giving a pore distribution.

Examples of Measuring Surface Areas of Catalysts by Gas Adsorption Methods

Surface area measurements by gas adsorption methods were originally developed for the study of synthetic ammonia catalysts[4, 5]. They have proved useful not only for these catalysts but for a variety of other catalytic materials, including metallic catalysts for the Fischer-Tropsch synthesis[65, 66, 67, 68]; silica gel to be used as a catalyst or as a catalyst support for various reactions[69, 69a, 70]; silica-alumina catalysts used for cracking hydrocarbons[61a]; montmorillonite catalysts which when activated by acid washing are capable of cracking hydrocarbons[61b, 61d]; alumina gel[71, 72, 73] to be used either directly or as a catalyst support for various hydroforming and dehydrogenation processes; carbon blacks and charcoals[25, 40, 41, 55e, 74, 75, 76, 77, 78] that are useful as catalyst supports or as catalysts for certain processes; and a variety of other metallic[79, 80, 81, 82] and nonmetallic catalytic materials.

These few examples that are mentioned are among those relating to the direct application of the surface area method for the study of catalysts. Naturally the method has found much wider application than use with catalysts. However, the present chapter is necessarily restricted in principle to ways and means of measuring the surface area of catalysts so the many other applications of the method for measuring surfaces of solids other than catalysts will not be included.

The reader will be able to formulate his own opinion as to the general utility of the gas adsorption method by noting the large number of instances in which such measurements are being and will, it is hoped, continue to be mentioned as a standard part of the discussion of specific catalysts.

OTHER METHODS FOR MEASURING THE SURFACE AREAS OF FINELY DIVIDED AND POROUS SOLIDS

In view of the fact that this chapter is intended to summarize the most effective means available for measuring the surface area of catalysts, it has seemed wise to present first what seems to be the most convenient and accurate method so far devised—the gas adsorption method. However, a discussion of methods of measuring surface area by procedures not depending upon the observation of gas adsorption also seems desirable both because of the special instances in which some of these other methods may be very useful and because of confirmation that they afford of the correctness of the gas adsorption methods. Accordingly, brief mention will now be made of the following additional methods for obtaining information relative to the particle size, and surface area of finely divided solids: (1) sedimentation, (2) permeability, (3) light and electron microscopic techniques, (4) x-ray methods, (5) optical methods, (6) radioactive methods, and (7) miscellaneous procedures. These will now be discussed in turn.

Sedimentation

One of the oldest methods[83, 84] for obtaining an estimate as to the size of finely divided particles and the distribution of the particle sizes involves the sedimentation of the particles in some suitable fluid. By assuming the validity of Stokes' law[85] in such a process one can calculate particle size for particles larger than 1000Å by the equation

$$D = \sqrt{\frac{18\eta h}{(D_s - D_L)gt}} \tag{13}$$

where D is the diameter of the particles; η, the viscosity of the fluid medium through which the settling occurs; h is the distance settled in time t; g is the gravitational constant; and D_s and D_L are the densities of the solid particles and the liquid medium, respectively. For smaller particles in the range 100 to 1000Å, sedimentation methods can still be used provided a centrifuge is employed to accelerate the settling process. The following equation for the centrifugal sedimentation was derived by Svedberg[86] as a modification of Stokes' law:

$$D = \frac{6}{\theta} \sqrt{\frac{\eta \ln x_2/x_1}{2(D_s - D_L)t}} \tag{14}$$

where θ is the angular velocity of the centrifuge and is equal to $2\pi N/60$, N being the number of revolutions per minute; x_2 and x_1 are the distances from the center of rotation between which the particles move; and the other terms are the same as in the gravitational form of Stokes' law.

Sedimentation procedures have been used extensively for measuring the particle size and size distribution of soil colloids[85a], paint pigments, clays[87, 88, 89], abrasive powders[90], cement[91], and other finely divided materials[92]. However, for catalytic work it has the general drawback of giving information about the external size and surface of particles but not about the internal surface area of porous solids. One particular application that was made to catalysts has to do with the measuring of the average size of the agglomerates of fluidized catalysts that are used commercially today. Innes and Ashley[93], for example, have described a method by which particles of cracking catalysts that are used in fluidized processes for cracking hydrocarbons can be measured as to particle size distribution by permitting the particles to settle in a bath of isopropyl alcohol. Another sedimentation method using air as a fluid is the well known Roller[94] process and apparatus and also the recently described "Micromerograph"[94a] for obtaining size distribution curves for finely divided solids. The Roller method using air as a fluid when slightly modified to prevent fragmentation has been used for determining the particle size of fluid cracking catalysts[95].

In view of the fact that standard descriptions of this sedimentation procedure in all its ramifications have been available in the literature for many years[83, 84] no further elucidation of the details of the methods or of the results obtained wil be given in this chapter. It will suffice to point out that since it does not measure the internal surface area of porous catalyst particles its use will necessarily, for the most part, be restricted in catalytic work to determining the external particle size of porous catalyst particles or agglomerates.

Permeability Methods

Closely related to the methods of settling or sedimentation are the procedures that can be classed under the general term of permeability measurements, and that involve the measurement of pressure drop when a given fluid is caused to flow through a packed bed of finely divided solid at some known flow rate. The fundamental equation employed in permeability measurements is known as the Kozeny[96] equation. It is usually stated in the form[99]

$$u = Q/A = \frac{K_1 \Delta P}{\eta L} \tag{15}$$

where K_1 is defined by the equation

$$K_1 = \frac{g\epsilon^3}{5S_0^2(1 - \epsilon)^2} \tag{16}$$

and u is the apparent linear flow of the fluid through the packed bed, in cm per second; Q is the rate of flow in milliliters per second; A is the cross-sectional area of the bed; ΔP is the pressure drop through the packed bed in grams per sq cm; η is the viscosity of the fluid in poises; L is the length of the packed bed; g is the gravitational constant in cm per second per second; ϵ is the fractional voids in the packed bed and S_0 is the specific surface area of the particles in the packed bed in sq cm per cc. The equation has been independently derived by Fair and Hatch[96a]. However, only when Carman[97, 98, 99] critically reviewed and tested the equation experimentally did it begin to be used widely for measuring the particle size of powders. Carman employed various liquids for fluids; Lea and Nurse[101] and Blaine[102] have employed the method but have used air as a fluid.

Table 5. Surface Area and Particle Size Measurements on ZnO Pigments

	F-1601	K-1602	G-1603
Area by adsorption of nitrogen at −195°(m²/g)	9.48	8.80	3.88
Average Particle Size (microns)			
By microscopic count[a]	0.21	0.25	0.49
By adsorption of methyl stearate[46]	0.19	0.24	0.55
By ultramicroscopic count[a]	0.135	0.16	0.26
By permeability[98]	0.12	0.15	0.25
By adsorption of nitrogen[42]	0.115	0.124	0.28

[a] Values reported by the New Jersey Zinc Co. which furnished all three of these standard samples.

Some idea as to the agreement between the values of the surface areas of finely divided nonporous, solids by the permeability method as compared to the nitrogen adsorption method[42] can be obtained from the data on three samples of ZnO listed in Table 5. For all three samples the agreement is within about 15 per cent in spite of the fact that the particle size of the ZnO pigments is near the limit of the size range to which the permeability method using liquid as a fluid is applicable.

In recent years[103–110] a great deal of effort has been directed toward the use of air as a fluid in the permeability method. By applying certain corrections for slip at the gas-solid interface, values have been obtained for the surface areas of carbon blacks, cement, TiO_2, silica, slate powder, alumina hydrate powder, and miscellaneous other powders. Agreement between values of surface areas by the modified Kozeny methods and those by the nitrogen adsorption methods seems as a whole to be very satisfactory. The air permeability method when thus corrected seems to be applicable to particles that are smaller by a factor of at least ten then can be measured by the liquid permeability procedure.

Ordinarily the flow of gases in the viscous flow region has been employed in the permeability method for measuring particle sizes. However, recently it has been suggested[111, 112, 113] that similar measurements can be made, particularly on small particles, by using a flow method in which the pressure is in such a range that Knudsen flow will be obtained. There is some indication that this flow for nonporous particles will give better agreement with the particle size deduced from the nitrogen surface area measurements than flow measurements made at higher pressure in which the gas flow is viscous.

Although permeability methods are ordinarily considered to yield only the external or geometric surface area of a bed of packed particles, they can under certain conditions apparently be used to yield information about the "internal" surface area of solids. Probably the most extensive application of the method to "internal" surface area measurement has been concerned with the flow of gas through individual porous particles or through porous membranes. Illustrative of such measurements are those published by Schwertz[113a]. The area in his measurements is entirely "internal area." Even in this type of measurement, however, the surface area as measured by nitrogen adsorption will probably be larger than that measured by gas flow through the porous membrane or individual porous particle. This follows from the fact that there may well be blind pores somewhere within the membrane that are accessible to the adsorbate molecules such as nitrogen but do not contribute to the total flow of gas through the sample. This type of measurement can, when applied to individual catalyst pellets, be made to yield valuable information about the "internal surface" of the pellet, though clearly this measured "internal surface" will be smaller than the true and perhaps the catalytic surface if the tiny particles which go to make up the pellets are themselves porous.

The second approach that may prove to be especially useful in applying gas flow permeability measurements to catalytic materials has been given in two recent papers[113b, 113c]. In the first of these Kraus, Ross and Girifalco apply the standard gas flow steady state method to packed beds of CuO, glass spheres, $PbCrO_4$, $BaSO_4$ and TiO_2, respectively. They interpret their results in terms of the equation ordinarily used for gas flow measurements

$$Q = \frac{1}{\Delta P}\frac{dn}{dt}\frac{1}{A} = \frac{\epsilon^3 \bar{P}}{k(1-\epsilon)^2 S_0^2 \eta RT} + \frac{Z\epsilon^2 \pi}{(1-\epsilon) S_0 \sqrt{2\pi MRT}} \qquad (17)$$

where dn/dt is the flow rate in moles per second, k is the constant in the first (Poiseuille flow) term and may be taken as 5.0, $\bar{P}$ is the mean pressure in the bed, and Z is a constant for the second (Knudsen flow) term in the equation, and is taken to be $(48/13)\pi$. The other terms in the equation are identical to those mentioned above in connection with the general Kozeny equation. Their results are shown in columns 3 and 4 of Table 6. It will be noted that the area calculated from the term for Poiseuille flow is always considerably smaller than the area calculated from nitrogen adsorption (columns 6 and 7). This they interpret as being consistent with the idea that this viscous flow term measures the "rounded off surface"[113a, 113d] of the particles. The term for the Knudsen flow, on the other hand, gives an area value that is in good agreement with that obtained by the nitrogen adsorption methods for $PbCrO_4$ and TiO_2 and is 10 to 40 per cent lower than the nitrogen areas for the other solids. The authors suggest that the Knudsen flow is concerned with collisons of the molecules on the actual particle walls and therefore probably would be expected to give an area more nearly characteristic of the true outer area of each particle than would the Poiseuille term. The second paper by two of these authors describes the application to five of these solids of a transient state flow method proposed by Barrer and Grove[113d]. The method involves the rate of build up of pressure from a small value (a micron or smaller) up to several hundred microns as a function of time, the pressure on the high pressure side of the bed being at an approximately constant value many times higher than the low pressure side. When the pressure on the low pressure side is plotted against time a linear plot is obtained after a few minutes. This plot extrapolates back to a finite intercept on the time axis, this time value being called L, the time lag. The results are interpreted by the authors through the use of an equation of the form

$$S = \frac{144}{13} \frac{\epsilon}{1 - \epsilon} \frac{L}{l^2} \sqrt{\frac{2RT}{\pi M}} \tag{18}$$

l is the length of the bed and all other terms have been defined in connection with previous equations. The coefficient 144/13 is 18/13 times as large as that used by Barrer and Grove. Employing this equation Kraus and Ross[113c] obtain the area values shown in column 5 of Table 6. It will be noted that the area values obtained are in excellent agreement with those measured by nitrogen adsorption provided nitrogen is used in the flow experiments. On the other hand, for reasons not too well understood, as yet, the flow measurements by this method using helium yield values for the area that are about 15 to 20 per cent larger than those obtained by the nitrogen adsorption method. The authors suggest that this might be due to the penetration of helium in Knudsen flow into some of the tiny capillaries that are so small as to exclude nitrogen.

Barrer and Grove[113d] expressed the opinion that this transient flow method ought to give values for the total internal area including the area of "blind" capillaries. Kraus and Ross express some doubts as to whether the method will yield correct values when blind capillaries are present. The nice agreement on the five solids between the areas obtained by nitrogen using this transient flow procedure with those using nitrogen as adsorbate in low temperature adsorption measurements certainly suggests that at least a portion of the surface roughness is accurately measured by the transient flow method even though the extent to which blind or closed end capillaries are measured must for the present remain in doubt. It hardly seems reasonable that the "inner surface" of very porous solids such as alumina, silica gel and the like will be measured even by this transient flow variation of the permeability method when packed beds of these finely divided porous solids are being used.

Table 6. Comparison of Gaseous Permeability Steady State Flow and Transient Flow Surface Area Determinations[113b, 113c] with those Made by the Nitrogen Adsorption Method

Powder	Gas	Steady State Flow Areas, sq m/g		Transient Flow Area, sq m/g (Knudsen)	Area by N_2 Adsorption sq m/g	
		By Poiseuille Term	By Knudsen Term		BET	HJ
CuO	H_2	0.073	0.17			
	He	0.067	0.19	0.37		
	N_2	—	—	0.31	0.30	0.31
Glass Spheres IV	H_2	0.17	0.29			
	He	0.17	0.28	—		
	N_2	—	—	—	0.37	0.38
Glass Spheres II	H_2	0.29	0.47			
	He	0.29	0.47	0.64		
	N_2	—	—	0.55	0.55	0.59
$PbCrO_4$	H_2	2.1	3.73			
	He	1.9	3.63	4.60		
	N_2	—	—	3.89	3.75	4.01
$BaSO_4$	H_2	1.9	4.46			
	He	1.9	4.04	5.45		
	N_2	—	—	4.75	4.68	4.97
TiO_2	H_2	6.0	8.37			
	He	4.8	8.02	8.85		
	N_2	—	—	7.90	7.97	8.26

Light and Electron Microscopic Methods

Microscopic observations[113f] have long been used for obtaining information as to the particle size of finely divided solids. Svedberg[86] has placed the limit of resolution with the light microscope at about 0.2 μ when light of 0.5 μ wave length is used. By employing ultraviolet light the limit may be pushed down to about 0.1 μ. For still smaller particles the electron microscope has proved very effective. Particles as small as 50Å in size may be identified by proper electron microscopic technique[114, 115, 116].

Although both light and electron microscopic studies are capable of giving estimates of the size of particles, they do not yield values for the total intrinsic surface area. Only in the event that the roughness factor of a given solid is substantially unity is one able to obtain a reasonable estimate of its total surface area by either of these methods. This limitation of the microscopic methods is generally recognized and has been frequently mentioned in the literature. For example, in the study of carbon blacks[40] it was shown that the nonporous carbon blacks yield surface area values calculated from the size distribution estimated by electron micrographs that agree excellently with surface areas calculated from nitrogen adsorption isotherms at −195°C on these carbon blacks. On the other hand, for those carbon blacks that had been made porous as a result of after-treatment with either air or steam, the electron microscopic examination gives average particle sizes that yield surface areas much lower than those observed by gas adsorption methods[40]. It follows naturally, therefore, that these particular methods can for the most part be used to obtain reliable surface areas only for particles that are nonporous or that have only large pores of known size or general dimensions.

Although the electron and optical microscopes cannot yield accurate information about the inner surface area of porous catalyst particles, they can, nevertheless, give considerable information as to the number and size[117-120] distribution of large pores. As will be seen in Volume II, these large pores are very important to the catalytic activity of porous solids because they afford an access for reactants to the large internal area of the catalyst. Modern replica techniques for studying surfaces give promise of increased elaboration of the nature of the pore structure of a given solid even though they do not yield accurate values for the internal surface areas. It is entirely possible therefore that the electron microscope will be of considerable help in the future in giving us a better picture of the structure of porous catalyst particles.

X-Ray Methods

Another physical method for obtaining surface areas of catalysts closely related to the microscopic method is the use of low-angle scattering of x-rays.

Barkla and Crowther[120a] first observed this type of scattering in 1911. The theory of the scattering was explained by Debye[120b] in 1930. Guinier[120c] showed that the low-angle scattering of x-rays from spheres of uniform size can be represented by the Bessel function

$$I = 9MN^2 \left[\frac{\sin kR - kR \cos kR}{(kR)^3}\right]^2 \tag{19}$$

where I is the intensity of scattered radiation, R is the radius of the scattering particles, M is the number of particles, N is the number of electrons per particle, and k is defined by the equation

$$k = \frac{2\pi\epsilon}{\lambda} \tag{20}$$

where ϵ is the scattering angle in radians, and λ is the wave length in the same units in which R is expressed. Yudowitch[120d] points out that as long as kR is less than about 1.5, the Bessel function may be expressed over short intervals of kR by the equation

$$I = ce^{-\frac{(kR)^2}{5}} \tag{21}$$

It is apparent from Equation (21) that a plot of the logarithm of the intensity I of the scattered radiation against the square of the scattering angle gives a curve the slope of which at each particular angle with a given wave length of x-radiation can be related to the radius of the scattering particles. Thus, in principle an estimate can be made of the size distribution of the tiny crystallites or of the blocks of amorphous material of which the individual particles are composed. As pointed out above, for example, the size of the blocks of amorphous partially hydrated silica of which silica gel is composed has been estimated by the low-angle scattering technique by Elkins, Shull, and Roess[47, 124]. The agreement between the surface areas calculated from the nitrogen adsorption isotherms and those calculated from the low-angle scattering experiments is surprisingly good, the areas by the nitrogen method agreeing within a factor of two with the areas calculated by the low-angle scattering. Other measurements[122, 123, 125] on some of these same oxides have been reported elsewhere in the literature[47a] as have also measurements on charcoals and charcoal-supported catalysts[121a]. It should be remembered however that, as pointed out recently by Guinier[121], the method will be of most use when supplemented by some independent information relative to the size and size distribution of the tiny crystallities or of the blocks of amorphous material of which the particles that are being studied are composed. Actually, Shull, Elkins and Roess[124] show how supplementary information as to pore volume and surface area can be used to prove clearly that the size of the tiny crystallites or blocks composing the solid and not the size of the pores between the crystallites or blocks is being measured by low-angle scattering. In the absence of supplementary information the distinction between the size of the solid matter and the size of the capillaries is never certain since the scattering reveals primarily the size of units at which sudden changes in the density of the scattering electrons occurs.[120e]

One can summarize the low-angle scattering work by saying that it is the only means for obtaining size distributions on the tiny crystallites or on the blocks of amorphous material of which catalysts are composed, and that it is the only means of giving even approximate confirmation to the size of these crystallites or blocks deduced from measurements by gas adsorption techniques. These contributions would in themselves make the low-angle scattering very valuable in catalyst studies. Recently, however, Van Nordstrand and Hack[125] have called attention to some additional observations that suggest even greater utility for the low-angle scattering. Working at scattering angles that for the most part were outside the range suggested by Yudowitch[120d] for Equation (21), they found that a plot of the logarithm of the scattered radiation against the logarithm of the square of the scattering angle gave straight lines for a series of aluminas. Plots of this kind were also suggested and used by Elkins, Roess, and Shull[47]. Van Nordstrand and Hack have made the rather surprising observation that the surface areas of a series of alumina samples as measured by the low-angle scattering log-log plots are directly proportional to the surface area as measured by the nitrogen method. In making these area determinations they read off directly the intensity of the scattered radiation at some given angle such, for example, as 2 degrees. Because of the proportionality between scattering intensity at a given angle and surface area as measured by N_2 they suggest that the low-angle scattering method can be used on a series of similar samples for rapidly obtaining relative surface areas. The low-angle scattering runs, according to these authors, require only about 5 minutes per determination. A few measurements on silica samples by these authors also seem to show a linear relation between the intensity of scattering and the surface area. The authors give evidence for believing that the low-angle scattering also reveals other information about the structure of the catalysts that will prove to be useful. For example, the change in the log-log plots on sintering alumina samples is not at all the change that is observed when any one of the aluminas is simply diluted with an inert material prior to the low angle measurements. They obtain what they call a "uniform sintering type" rather than a "dilution type" of effect on the low-angle scattering. These results therefore suggest that low-angle scattering may prove to be even more valuable in studying catalysts than has been heretofore suspected and in certain cases may even prove to be the most rapid method for obtaining relative surface areas of catalysts and catalytic materials.

Closely related to the low-angle scattering is one other type of x-ray measurement consisting of measuring the width of lines in the x-ray patterns. The method depends fundamentally on an equation developed by Scherrer[126] in the form[127]

$$L_c = \frac{0.94\lambda}{B \cos \theta} \tag{22}$$

where L_c is the average crystallite dimension perpendicular to the particular set of diffraction planes in the lattice, λ is the wave length of the x-rays, θ is the Bragg angle of the diffraction maximum, and B is the angular width (corrected) of the line at half its maximum intensity. Actually B is more accurately given by the equation

$$B^2 = B_1^2 - b^2 \tag{23}$$

where B_1 is the actual measured width of the line at half maximum and b is a width correction for the instrument, in radians.

This method in theory should be useful in the study of catalysts because it gives a measure of the tiny crystallites of which the catalyst is composed. In practice, however, it has two drawbacks for catalytic work. In the first place, it is applicable only to crystalline materials and gives no information about the size of tiny blocks in particles of amorphous catalysts. In the second place the crystallite size as revealed by the line broadening method is frequently considerably smaller than the size deduced from gas adsorption methods. Apparently at times the tiny crystallites that are inferred from the breadth of the x-ray lines are grouped together in packets that are so compact that gas adsorption does not take place between the crystallites. Thus for example, x-ray work has shown[128] that carbon black particles appear to be made up of tiny packets of graphite-like flakes, which in a narrow dimension may be as small as about 12Å. A large number of these packets go to make up the more extensive carbon black particles which may have a diameter as high as 500Å and a roughness factor approaching unity. Similarly, Nielsen[54] has noted that line broadening indicates a crystallite size of about 350Å for promoted iron synthetic ammonia catalysts, whereas gas adsorption measurements yield areas indicating an average particle size of about 900Å. Possibly, as Nielsen suggests, the tiny crystallites are cemented together to form the larger units, the promoters themselves serving as the cement. On the other hand, possibly as for carbon black particles the larger crystals as measured by gas adsorption are simply composed of a number of smaller crystallites sufficiently displaced from each other to cause the x-ray pattern to be restricted to the smaller crystallites, but not sufficiently separated from each other to permit nitrogen molecules to penetrate between the crystallites during the low temperature surface area measurements.

One additional use of x-rays in studying catalytic materials should be mentioned. Mitchell[129] and his co-workers have studied the resistance and chemisorption characteristics of evaporated films of tungsten, copper and silver. They have found it[129a] possible to measure the thickness of these thin films by an x-ray interferometer method. By this procedure it is possible to determine the thickness of a film with an accuracy of about 1 per cent over the size range 500 to 1000 Å. This thickness measurement, together with a chemical determination of the total amount of film deposited on a given area of the glass surface, permits the calculation of the density of the film. The observation that [129a] even sintered films of copper still seem to have a density 10 to 20 per cent lower than that of the bulk metal shows that the films are still porous. It appears therefore that this particular use of x-ray affords at least qualitative information as to the porosity and roughness factors of the films.

Miscellaneous Methods

In conclusion, a few methods will be mentioned briefly that are useful in very special applications but that are probably not of value in measuring surface areas of catalysts. These include the electrolytic method for measuring the area of porous electrodes as developed by Rideal[132] and his co-workers[132a]; the use of light-scattering methods as proposed by Pfund[133], by Gamble and Barnett[134], by Skinner and Boas-Traube[135] by Rose and Lloyd[136], by Stutz[136a] and by Sharratt, Van Someren, and Rollason[137]; the measurement of the adhesion of particles to an inclined plane as a function of size[138]; and finally the rate of chemical reaction or of catalysis on a known geometric area of a solid compared to the rate on the unknown area chemically identical to the standard[139, 140, 140a, 140b, 140c, 140d]. This chemical procedure has been especially used for measuring the surface area of finely divided or porous metals by measuring rates of solution in acids.

One final method deserves special mention because it has from time to time been used in measuring the surface area of catalysts. It is the radioactive method originally developed by Hahn and his co-workers[142, 142a]. It involves the incorporation into a catalyst of certain elements in small traces that are capable of evolving some radioactive emanation such as radon at a steady rate. From the known concentration of the added radioactive component and the rate of evolution of radioactive gas into the surrounding atmosphere it is possible to obtain a figure for the total surface area of the solid. Obviously this method depends upon the fact that

TABLE 7. COMPARISON OF TYPES OF SURFACE AREA AND PARTICLE[a] SIZE INFORMATION OBTAINABLE BY VARIOUS EXPERIMENTAL TECHNIQUES ON POROUS SOLIDS COMPOSED OF TINY CRYSTALLITES OR TINY BLOCKS OF AMORPHOUS MATERIAL

Exptl. Method	Total Surface Area	External Area of Particles	Particle Size	Particle Size Distribution	Size of Crystallites	Size Dist. of Crystallites	Size of Amorphous Blocks	Size Dist. Amorphous Blocks	Remarks
Gas Ads. N_2 at −195°	Yes	No	No	No	Sometimes[b]	No	Yes	No	Area directly; size of blocks, indirectly
Sedimentation	No	Yes	Yes	Yes	No	No	No	No	Size directly; area of particles, indirectly
Permeability	No	Yes	Yes	No	No	No	No	No	Area, directly; size, indirectly
Light microscope	No	Yes	Yes	Yes	No	No	No	No	Size directly; area by calculation
Electron microscope	No	Yes	Yes	Yes	Qualitative	Qualitative	Qualitative	Qualitative	Size directly; area by calculation
X-ray low-angle scattering	Yes	No	No	No	Sometimes[b]	Sometimes[b]	Yes	Yes	Size directly; area by calculation
X-ray line width	No	No	No	No	Yes	No	No	No	Size directly; area by calculation

[a] The term "particle" is used to indicate the separate individual grains of a porous solid; it will therefore include undispersed agglomerates. Crystallites refer to the tiny crystals of which the particles may be composed. "Amorphous blocks" is a term used to describe the tiny sub-particles of which amorphous particles are composed. For example, silica-alumina cracking catalysts are believed to consist of "amorphous blocks" 50 to 100Å on a side, or in diameter.

[b] If the crystallites are sufficiently separated from each other to permit easy access of an adsorbate gas, the "sometimes" would be replaced by "yes."

only the radioactive atoms within a certain recoil distance σ of the surface of the tiny crystallites are able to evolve gas directly to the gas phase; other atoms within the crystals also form radon but presumably the radon atoms are trapped within the crystals and cannot escape. σ may have values ranging from 200 to 500Å. Tracers are also used either from solution or from the gas phase as tools for the measurement of the extent of adsorption[143, 144, 144a] and hence of surface area. These methods like the others mentioned in this section are very specailized and hence not of wide applicability in measuring the surfaces of catalysts and catalytic materials.

SUMMARY

Perhaps the easiest way to summarize the various methods that have proved to be useful in catalyst surface area work is to tabulate as accurately as possible the exact type of information furnished by each and to mention briefly the way in which each of the methods appears to be useful. Such a tabulation is attempted in Table 7.

From the table it is evident that only the gas adsorption method and the low-angle scattering of x-rays can yield accurate area values for the total internal and external surface of solid catalysts. The gas adsorption method measures the surface area directly, whereas the low-angle scattering measures the size distribution curves for crystallites and sub-particles of the catalyst grains, particles or pellets. On the other hand, the gas adsorption method gives no information as to the distribution curves for the tiny crystallities, whereas the low-angle scattering furnishes such information or at least is capable of so doing. In this connection, the detailed methods for calculating the area of a collection of crystallites or sub-particles from distribution curves have been given many times in the literature[130] and will not be considered here in detail. It will suffice to point out that the diameter used most frequently in estimating area from a distribution curve is defined as $\Sigma nd^3/\Sigma nd^2$, n being the number of particles of diameter d observed to be present. This relation is especially useful in calculating surface areas from electron microscopic photographs of finely divided nonporous solids.

The other size characteristic of catalyst particles aside from their true surface area in which one may be interested is the size and perhaps the size distribution of the gross particles or grains of catalyst. As is apparent in the table, sedimentation, permeability and either light or electron microscopy are capable of furnishing the size of the particles regardless of whether they are tightly knit agglomerates or nonporous solids. Furthermore both the sedimentation and light or electron microscopic methods are capable of yielding distribution curves for the size of particles or grains. The permeability measurements of course do not yield such a distribution curve.

In conclusion then it may be well to emphasize that catalytic work of the future will have at its command a relatively large number of methods for obtaining information as to the size and size distribution of the gross catalyst particles, and also the size, size distribution and total area of the tiny crystallites or of the blocks of amorphous material of which the larger particles are composed. With these tools and the quantitative treatments that can result from their use, progress in the elucidation of the nature and mechanism of catalytic reactions should prove to be much more rapid in the future than has been possible in the past.

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CHAPTER 3

CHEMISORPTION

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A large amount of evidence has now accumulated which shows that catalysis by solid surfaces invariably involves the adsorption of reactant molecules. The general problem of adsorption is therefore of fundamental importance in connection with a study of contact catalysis. The subject is a vast one, and the present discussion is confined to those aspects which are of particular significance in connection with the kinetics of surface reactions.

Work on the adsorption of gases on solid surfaces has led to the conclusion that two main types of adsorption are to be clearly distinguished, namely, van der Waals adsorption and chemisorption. In van der Waals adsorption, also known as physical adsorption, the molecules are held to the surface by physical forces which correspond to those involved in the van der Waals equation of state for gases. The heat evolved when physical adsorption occurs is usually similar to the heat of liquefaction of the gas, i.e., a few hundred cal per mole, and the reactivity of the adsorbed substance is consequently not markedly altered. This type of adsorption is therefore not of direct importance in connection with surface catalysis of the reactions of stable molecules; it does, however, play a role in the reactions of atoms and free radicals at surfaces. Physical adsorption studies also have great application in the measurement of surface areas and pore size distribution of catalysts, as pointed out in Chapters 1 and 2.

In chemisorption, the adsorbed molecules are held to the surface by valence forces of the same nature as those which bind atoms together in molecules. These forces are much stronger than those in van der Waals adsorption, and the heats evolved are of the same order as those liberated in chemical reactions, values of 10 to 100 kcal per mole being common. In view of the magnitude of the energy changes in chemisorption the reactivities of molecules may be greatly changed on adsorption, and may be markedly increased. A special case of this is when, as frequently occurs, chemisorption is associated with dissociation of the adsorbed molecule;

when hydrogen molecules are adsorbed by tungsten, for example, the bonds between the hydrogen atoms are broken, and the resulting adsorbed atoms are considerably more reactive than are free hydrogen molecules.

The nature of the interactions which occur in chemisorption will be considered briefly. Much work has been done on the chemisorption of gases at metal surfaces. At the surface of a metal there is at least one free valence electron per metal atom. It is therefore possible for each surface atom to combine with, for example, at least one hydrogen atom. When a hydrogen atom approaches a bare tungsten surface a bond can be formed with the liberation of about 70 kcal of energy. If a hydrogen molecule approaches the surface the process of adsorption involves the dissociation of the molecule, the atoms becoming absorbed separately. Since the dissociation of a hydrogen molecule involves the adsorption of about 103 kcal per mole, the net heat liberated in dissociative chemisorption is about $2 \times 70 - 103 = 37$ kcal per mole. The adsorption of oxygen proceeds in a similar manner; the adsorption of oxygen atoms on tungsten liberates about 130 kcal per gram-atom, and since 117 kcal are involved in dissociation, the adsorption of a molecule is accompanied by the evolution of about $2 \times 130 - 117 = 143$ kcal per mole. The adsorption of carbon monoxide on metal surfaces may not involve dissociation, since carbon monoxide has electrons available for covalent bond formation[1].

A number of special features of chemisorption may now be considered briefly, since they are of great importance in connection with the kinetics of surface reactions. The first is that after a surface has become covered with a single layer of adsorbed molecules it is essentially saturated so that additional chemisorption cannot take place; a complete chemisorbed layer is thus a unimolecular layer. The second feature is that the process of chemisorption may often have an appreciable activation energy, and hence may sometimes be a slow process. The third feature is that there is frequently a considerable variation in the adsorptive capacities of the various surface sites. These three features of chemisorption will now be discussed.

The Unimolecular Layer

The fact that chemisorption can only give rise to a unimolecular layer on a surface was emphasized by Langmuir[2] in his original treatment of the problem, and a number of investigations have shown this to be the case. Langmuir[3] made manometric measurements of the amounts of various gases adsorbed and found that the amounts required to saturate the surface corresponded to the formation of a unimolecular layer. A careful study of the adsorption of hydrogen on tungsten has more recently been made by J. K. Roberts[4]. If a tungsten surface were perfectly smooth and the 110 plane were exposed the number of surface atoms would be 7.8×10^{14} per sq cm.; if the 100 plane were exposed the number of atoms would be 5.5×10^{14} per sq cm. Roberts found that the number of hydrogen molecules that could be adsorbed was 4.4×10^{14}. This result is consistent with the hypothesis of a unimolecular layer if, as is probable, hydrogen is adsorbed atomically, one atom being attached to each surface tungsten atom; the number of atoms adsorbed is 8.8×10^{14} which is very close to the number of surface atoms.

Activated Adsorption

The suggestion that the process of chemisorption frequently involves an activation energy was first made by Taylor[5], and has proved to be extraordinarily fruitful in connection with the interpretation of adsorptive and catalytic phenomena. In a number of instances activation energies have been calculated from rates of chemisorption at different temperatures; some of the values obtained in this way are included in Table 1. In some cases, particularly on oxide surfaces, the energies of activation are relatively high, and adsorption at low temperatures takes place very slowly; under these conditions the van der Waals adsorption will predominate, since this requires very little activation energy.

This concept that chemisorption may require an activation energy provides a satisfactory explanation of many phenomena that are found to be associated with adsorption. Heats of adsorption for example, are frequently small at low temperatures and large at higher ones; this is because the van der Waals adsorption is more important at the lower temperatures, the process of chemisorption being slow, whereas chemisorption with its large heat evolution is predominant at higher temperatures. Rates of adsorption are frequently found to decrease as the temperature is raised, because at lower temperatures the process is rapid van der Waals adsorption, while at higher temperature it is slower chemisorption. The quantity of gas adsorbed sometimes[6] varies with the temperature in the manner shown in Figure 1. At the lowest temperatures the adsorption is mainly of the van der Waals type, and since the process is exothermic the extent of adsorption decreases with temperature. As the temperature is raised the rate of activated adsorption increases and the quantity of gas adsorbed becomes greater, so that there is an increase in the total amount adsorbed. In the higher temperature range chemisorptive equilibrium is established and since the process is exothermic the extent of adsorption again decreases with increasing temperature.

It is generally agreed that chemisorption on oxides and similar substances, and on metals which have not been especially cleaned (and which therefore probably have an oxide layer), involves appreciable activation energies. In the case of carefully cleaned metals, on the other hand, it has

TABLE 1. SUMMARY OF CHEMISORPTION DATA

Surface	Gas	Types of Investigation	Temperature Range (°C)	Pressure Range (mm)	Heat of Chemisorption (kcal/mole)	Activation Energy (kcal/mole)	Ref.
Ag (oxygen covered)	O_2	Isotherms, kinetics of chemisorption	−78.5 to 0	0 to 700	—	4–5	1
Ag (oxygen covered)	H_2	Isotherms, kinetics of chemisorption	−78.5 to 0	0 to 700	—	—	1
C (charcoal, activated by O_2)	H_2O	Isotherms, rates of adsorption	17 to 900	—	—	—	2
C (diamond)	H_2	Isotherms, rates of adsorption	450 to 819	0 to 0.4	58	14–22	3
C (graphite)	H_2	Isotherms	418 to 733	0 to 0.1	45	6–	3
Co	H_2	—	60 to 200	—	—	—	4
Co	CO	—	60 to 110	—	—	—	4
Co	H_2O	—	60 to 100	—	—	—	4
Co	CO_2	—	100 to 150	—	—	—	4
Cr	O_2	Isotherms	30	0 to 10	—	—	5
Cr	Cl_2	Isotherm	30	0 to 10	—	—	5
Cr	NO_2	Isotherm	30	0 to 10	—	—	5
Cr	NO	Isotherm	30	0 to 10	—	—	5
Cr_2O_3	H_2, D_2	Rates of adsorption	110 to 184	—	—	—	6
Cr_2O_3	H_2	Kinetics of chemisorption	130 to 220	0.25 to 1 atm.	—	—	7
Cr_2O_3	CO	Isotherms, kinetics of chemisorption	−195 to 0	0 to 1.6	9–15	0.2–0.7	8
Cr_2O_3	N_2	Isotherms	−183 to 0	0 to 1.6	8–9	—	8
Cr_2O_3	O_2	Isotherms	−183 to 0	0 to 1.6	20–27	—	8
Cr_2O_3	H_2, D_2	Isotherms	−183	0 to 1.6	3–6	—	8
Cr_2O_3	CO	Calorimetry	25	—	12–29	—	9
Cr_2O_3	H_2	Calorimetry	25	—	36–72	—	9
Cu	H_2	Calorimetry	160 to 300	—	7–18	—	10

Cu	H_2	Calorimetry	—	—	4–17	—	11
Cu	H_2	Isotherms, isobars	−195 to 0	0 to 600	—	—	12
Cu	CO	Isotherms, isobars	−183 to 110	0 to 800	—	—	12
Cu	H_2	Calorimetry	0	—	11–13	—	13
Cu	CO	Calorimetry	0	—	13–16	—	13
Cu	CO	Calorimetry	0	—	13–20	—	14
Cu	H_2	Calorimetry, isotherms	0	0 to 40	9–33	—	14
Cu	CO	Isotherms	−195 to −78	—	—	—	15
Cu	O_2	No. of molecules to saturate surface	−183 to −74	—	—	—	16
Fe	H_2, CO, H_2O	—	60 to 200	—	—	—	17
Fe	CO_2	—	25 to 300	—	—	—	17
Fe	H_2	Isotherms	−195 to −78.5	0 to 700	—	—	18
Fe	H_2	Calorimetry	−196 to 23	—	5–33	—	19
Fe (0.15% Al_2O_3)	N_2	Kinetics of chemisorption	402 to 451	760	—	—	20
Fe (0.15% Al_2O_3)	C_2H_4	Isotherms	−81 to 100	0 to 700	—	—	21
Fe (0.15% Al_2O_3)	C_3H_6	Isotherms	−40 to 23	0 to 800	—	—	21
Fe (0.15% Al_2O_3)	C_4H_8	Isotherms	−10	0 to 420	—	—	21
Fe (1.31% Al_2O_3)	N_2	Isotherms, kinetics of chemisorption	351 to 453	0 to 760	35.0	—	22
Fe (1.3% Al_2O_3; 1.59% K_2O)	H_2	Isotherms, kinetics of chemisorption	−196 to 460	0 to 760	—	10.4	23
Fe (1.3% Al_2O_3; 1.59% K_2O)	N_2	Isotherms, kinetics of chemisorption	224 to 452	0 to 50 atms.	35.0	16.0	24
Fe 1.3% Al_2O_3; 1.59% K_2O)	H_2	Isotherms, kinetics of exchange reactions	−195	0 to 50	—	—	25
Fe (0.8% Al_2O_3; 0.25% K_2O)	$N^{14}N^{14}$ $N^{15}N^{15}$	Rate of isotope exchange	500	60	—	—	26
Fe (1.55% Al_2O_3; 0.58% ZrO_2	$N^{14}N^{14}$ $N^{15}N^{15}$	Rate of isotope exchange	500	70	—	—	26

TABLE 1—*Continued*

Surface	Gas	Types of Investigation	Temperature Range (°C)	Pressure Range (mm)	Heat of Chemisorption (kcal/mole)	Activation Energy (kcal/mole)	Ref.
Fe (2.26% Al_2O_3; 0.21% ZrO_2 0.62% SiO_2)	$C^{12}O$, $C^{14}O$	Fractional adsorption (heterogeneity studies)	−195 to −78	—	—	—	27
Fe (with various promoters)	H_2	Study of amount of residual gas	500	—	—	—	28
Fe (Al_2O_3, K_2O, TiO_2)	H_2, N_2	Isotherms, isobars	50 to 350	50 atm.	—	—	29
Fe_2O_3	NH_3	Isotherms	−20 to 60	0.001 to 700	—	—	30
MnO	H_2	Isotherms, kinetics of adsorption	−78.5 to 444	400 to 700	—	12–20	31
MnO, Cr_2O_3	H_2	Isotherms, isobars, kinetics of adsorption	−78.5 to 444	0 to 700	20	—	31
MnO, Cr_2O_3	CO	Isobars	−78.5 to 450	165	—	—	31
Mn_2O_3	CO	Calorimetry	—	—	62–67	—	32
Mn_2O_3	H_2	Calorimetry	—	—	30–44	—	32
Mn_2O_3, Cr_2O_3	CO	Calorimetry	25	—	33–47	—	32
$Mn_2P_2O_7$	H_2	Isotherms	304 to 400	0 to 700	—	—	33
Ni	H_2	Calorimetry	—	—	10–30	—	34
Ni	H_2	Isotherms, isobars	−210 to 110	0 to 760	—	—	35
Ni	H_2	Kinetics of adsorption	−145 to −118	6–30 x 10^{-3}	—	2	36
Ni	C_2H_4	Theoretical	—	—	—	—	37
Ni	H_2	Calorimetry	−183 to 23	—	5–29	—	38
Ni	CO_2	Isotherms	150, 200	10^{-4} to 0.1	22	—	39
Ni (activated)	H_2	Isotherms	25 to 305	0 to 700	2.5	—	40
Ni (activated)	CO	Isotherms	−195 to −78	—	—	—	41
Ni (activated)	CO_2,	Isotherm	−78	—	—	—	41
Ni (supported)	H_2, D_2	Isotherm, rates of adsorption	110	—	—	—	42

Ni (with various promoters)	H_2, D_2	Isobars, rates of adsorption	−195 to 302	—	—	—	43
Pd	CO	Isotherms, isobars, kinetics of adsorption	−186 to 280	2 x 10^{-4} to 140	7.1–18.1	2.3–9	44
Pt (black)	H_2	Calorimetry	—	—	3–32	—	45
Pt	O_2	Calorimetry	—	—	7–161	—	45
Pt	SO_2	Calorimetry	—	—	18–39	—	45
Pt	CO	Calorimetry	—	—	11–35	—	45
Pt	H_2	Calorimetry	0	0 to 3	10–18	—	46
Steel (various types)	O_2, Cl_2, NO, NO_2	Isotherms	30	0 to 10	—	—	47
Ta	N_2	Calorimetry	23	—	85–135*	—	48
Ta (covered with hydrogen)	N_2	Calorimetry	23	—	23–35*	—	48
W (wire)	H_2	Calorimetry, rates of adsorption	−194, 22	4–30 × 10^{-4}	18–45†	—	49
W (film)	H_2	Calorimetry	−183 to 25	—	12–45†	—	50
W (film)	H_2	Isotherms	−183 to 0	10^{-6} to 10^{-2}	2–14†	—	51
W (film)	O_2	Calorimetry, rates of adsorption	—	—	43–145†	—	52
W (powder)	H_2	Isotherms	−194 to 750	10^{-6} to 1	15–46	—	53
W (powder)	N_2	Isotherms, kinetics of adsorption	400 to 750	10^{-6} to 35	20–75	10–25	54
W	H_2	Isotherms, isobars	90 to 200	0 to 2.5	—	—	55
W	NH_3	Isotherms	20 to 60	0 to 500	—	—	55
W (film)	N_2, C_2H_4	Isotherms	0 to 20	0–2 × 10^{-2}	2.8–11.6 (N_2)	—	56
WS_2	H_2	Isotherms	20 to 450	—	—	—	57
WS_2	C_2H_4	Isotherms	20 to 450	—	—	—	57
ZnO	H_2	Isotherms	−191 to 306	—	3.8–15.9	—	58
ZnO	H_2	Isotherms, isobar	0 to 302	1 atm.	—	3.3–15.3	59
ZnO	CO	Isobar	184 to 218	1 atm.	—	—	60

TABLE 1—*Continued*

Surface	Gas	Types of Investigation	Temperature Range (°C)	Pressure Range (mm)	Heat of Chemisorption (kcal/mole)	Activation Energy (kcal/mole)	Ref.
ZnO	CO	Calorimetry	25	—	18–30´	—	61
ZnO	H_2O	Isotherms	200 to 400	—	—	—	62
ZnO (activated)	H_2	Isotherms, isobars	0 to 302	1 atm.	0–12	—	63
ZnO (activated)	N_2	Isotherms	−196 to −56	—	—	—	63
ZnO, Cr_2O_3	H_2	Isotherms, isobars, kinetics of adsorption	255 to 302	¼ atm.	23	1–34	64
ZnO, Cr_2O_3	H_2, D_2	Isotherms, rates of adsorption	110 to 184	760	—	—	65
ZnO, Cr_2O_3	H_2	Calorimetry	25	—	10–48	—	66
ZnO, Cr_2O_3	CO	Calorimetry	25	—	11–44	—	66
ZnO, Cr_2O_3	H_2	Isobar	50 to 200	370	10	8.5	67
ZnO, Cr_2O_3	CO	Isobar	50 to 200	<1 atm.	6	5–85	67
ZnO, Mo_2O_5	H_2	Isotherms, isobars, kinetics of chemisorption	218 to 351	0 to 100	22.3	16–26	68
ZnO, Mo_2O_5	CO	Isotherms, isobars	−78.5 to 444	50–800	4–17	14–20	68

* Given as function of θ.

† Given as function of θ; the values of Rideal and Trapnell correspond to a more fully covered surface than those of Roberts and of Beeck.

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TABLE 1—*Continued*

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been suggested[7] that no activation energy is involved. As will be seen later (p. 202), however, the present indications are that such processes do involve a small but significant activation energy.

Surface Heterogeneity

The third feature of chemisorption, that surface atoms generally show a variation in adsorption power, was also first suggested by Taylor[8]. Even the most carefully polished surfaces are not perfectly smooth, and therefore consist of atoms of varying degrees of unsaturation. Certain atoms will be present at peaks on the surface, and the original idea was that adsorption would take place preferentially in such positions, which would also have the highest catalytic activity; atoms occurring along the edges of crystals were also supposed to be more active than those on plane surfaces. According to this concept, adsorption and chemical reaction would occur predominantly on certain "active points" or "active centers." It is well established that active centers play an important part in connection with chemisorption and catalysis, but recent work has indicated that the original idea that the active centers are peaks or edges on the surface requires modification. This idea has recently been the subject of a comprehensive review by Boudart[9], who concludes that active centers are not simply atoms present at certain positions on the surface; rather are they, as originally suggested by Volkenshtein[10], certain types of lattice defects on the surface. Boudart also emphasizes the fact that active centers are not to be envisaged as occupying fixed positions on the surface; they are constantly being created and destroyed with the movement of excited electrons in the lattice.

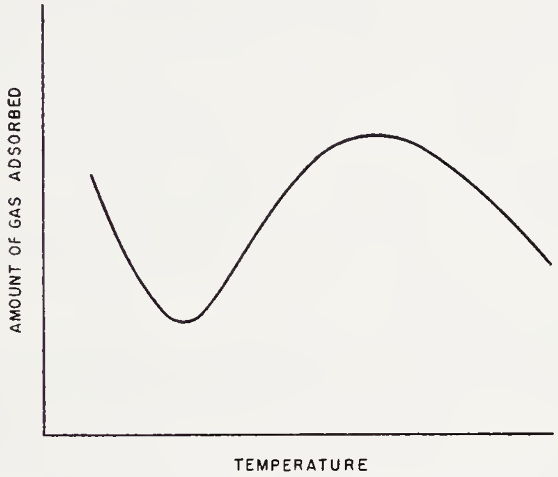

Figure 1. Typical curve for an adsorption isobar showing the variation of amount adsorbed at constant pressure as a function of the temperature.

The Data of Chemisorption

Space does not permit a comprehensive discussion of the extensive chemisorption data that have accumulated in the literature. All that will be attempted here is a brief consideration of the types of data that have been obtained, and a summary of the main results.

Work on chemisorption has been concerned with equilibria and with rates. The amount of gas or vapor absorbed when equilibrium is established depends on the nature of the surface, the nature of the adsorbate, the temperature, and the pressure. It is customary to hold constant all except one of these, and to study the dependence of the amount adsorbed on the remaining one. For example, work may be performed with a given surface and adsorbate, and at a constant temperature, a study being made of the variation of the amount adsorbed with the pressure; a graph showing the amount adsorbed at equilibrium *vs.* the pressure is known as an *isotherm.* An alternative procedure is to work at a given pressure of gas, and to determine the dependence of the amount adsorbed on the temperature; the resulting plot is known as an *isobar.* A third method, not so widely used, is to determine the variation of the equilibrium pressure with respect to the temperature for a definite amount of gas adsorbed; the plot in this case is known as an *isostere.*

Another type of investigation that is frequently made in connection with adsorption equilibrium consists of the measurement of heats of adsorption. Heats of adsorption are sometimes determined by direct calorimetric measurement; a quantity of gas is admitted to the surface, the rise of temperature determined, and the heat calculated. The heat can be expressed as calories of heat evolved per mole of gas adsorbed, and is the average heat of adsorption for that part of the surface which is covered with adsorbed gas at equilibrium; a heat measured in this way is known as an *integral* heat of adsorption. There is also a quantity known as the *differential* heat of adsorption which is the heat per mole calculated from the heat evolved when an infinitesimal amount of gas is adsorbed. This differential heat can be determined approximately by the calorimetric method, by admitting minute quantities of gas at a time to the surface. It is found that the differential heat varies with the fraction of surface covered, and that it is necessary to specify the fraction covered in stating the results. In view of this, the integral heat does not have any simple significance, since it represents an average of the differential heats over various fractions of surface covered. The reasons for the heat differential will be discussed later.

A more satisfactory method of measuring the differential heat of adsorption is to determine the equilibrium pressure, p, corresponding to a given fraction of surface covered (i.e., the isotere), at various temperatures, and to determine the heat, q, by using the Clapeyron-Clausius equation

$$\frac{d \ln p}{d(1/T)} = -\frac{q}{R} \tag{1}$$

This equation can be applied to the data by plotting $\ln p$ against $1/T$, the resulting slope being $-q/R$. This method gives q corresponding to the given value of the fraction covered, and q can be determined as a function of the coverage.

Kinetic studies on chemisorption usually consist of measurements of rates of adsorption and desorption; these may be made at constant gas volume by following the pressure change as a function of time, or at constant pressure by following the volume change. Activation energies for chemisorption and desorption may be determined by measuring rates at different temperatures and making use of the Arrhenius law. These activation energies, like the heats of adsorption, are usually strongly dependent on the surface coverage, owing to the existence of various types of activated adsorption on a given solid; care must therefore be taken in the application of the Arrhenius law, and in particular it must be applied only to rates which correspond to a given coverage.

Table 1 presents a summary of the main data that have been obtained on chemisorption*. The items are arranged alphabetically with respect to the absorbent, and the type of investigation and the results are indicated briefly. The specified temperature range is that of the entire investigation and does not necessarily imply that appreciable chemisorption occurs over the entire range. In the table have been included not only examples which pertain exclusively to chemisorption, but also some cases in which a limited amount of chemisorption occurs in the temperature range, even though the major part of the adsorption may be physical adsorption. It is not possible to give complete details in a table of this type, but it may be useful as an index to some of the publications which can be consulted if further information is desired.

Adsorption isotherms have in many cases been fitted to equations, and Table 2 summarizes the more important equations that have been employed. Some of these equations have some theoretical basis, while others are purely empirical, as has been indicated in the last column. The Langmuir isotherm is of great theoretical importance in connection with contact catalysis, and is discussed in detail in the following section.

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* The author is much indebted to Sister M. Lucetta, C.S.C., for preparing this Table.

TABLE 2. ADSORPTION ISOTHERM EQUATIONS

v = volume adsorbed; p = gas pressure; θ = fraction of surface covered; v_m = volume of gas required to form a unimolecular layer. The remaining symbols represent constants.

Name	Isotherm	Remarks	Ref.
Freundlich	$v = kp^{1/n}$ $(n > 1)$	Empirical, but has been interpreted theoretically; (p. 104) van der Waals adsorption and chemisorption	1
Chakravarti-Dhar	$v = \dfrac{kp^{1/n}}{b + p^{1/n}}$	Empirical; unimolecular layer; chemisorption	2
Langmuir	$\theta = \dfrac{bp}{1 + bp}$	Theoretical; unimolecular layer; chemisorption	3
Williams-Henry	$\ln \dfrac{v}{p} = \ln v_m b - \dfrac{nv}{v_m}$	Theoretical; unimolecular layer; chemisorption	4
Zeise	$v = \left(\dfrac{ap}{1 + Kp}\right)^{1/2}$	Empirical; unimolecular layer; chemisorption	5
Magnus	$v = \dfrac{k_1 k_2 p - k_3 v^2}{1 + k_1 p - \dfrac{k_3}{k_2} v^2}$	Theoretical; unimolecular layer; van der Waals adsorption	6
de Boer-Zwicker	$\ln \dfrac{p}{K_3 p_0} = K_2 K_1^{\,v/v_m}$	Theoretical; polymolecular layer; van der Waals adsorption	7
Frumkin-Slygin	$\theta = \dfrac{1}{f} \ln c_0 p$	Theoretical; unimolecular chemisorption	8
Brunauer-Emmett-Teller	$\dfrac{p}{v(p_0 - p)} = \dfrac{1}{v_m c} + \dfrac{c - 1}{v_m c} \dfrac{p}{p_0}$	Theoretical; polymolecular layer; van der Waals adsorption	9

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IDEAL ADSORPTION

The importance of the Langmuir adsorption isotherm is that it is the one that should theoretically apply to chemisorption on a perfectly smooth surface where there are no interactions between adsorbed molecules. The Langmuir isotherm therefore has a significance in adsorption theory which is equivalent to that of the ideal gas laws, and it is convenient to speak of adsorption which obeys the Langmuir isotherm as *ideal* adsorption. As is the case with the ideal gas laws there are very few systems in which the ideal adsorption laws are obeyed; this is attributed to the fact that in practice surfaces are seldom smooth, and there are interactions between neighboring adsorbed molecules. The modifications that are required to the Langmuir isotherm for these factors are considered later in this chapter. A kinetic derivation of the Langmuir isotherm and of certain other equations pertaining to ideal adsorption will be given in this section; ideal adsorption will be considered from a statistical point of view in the following section (p. 93).

The Langmuir Adsorption Isotherm

Consider a gas at pressure p in equilibrium with a surface. Let the fraction of the surface which is covered by adsorbed gas be denoted by θ, so that the fraction bare is $1 - \theta$. The rate of adsorption v_1 on the surface is proportional to the gas pressure and to the fraction of surface uncovered, since adsorption may only occur when a gas molecule strikes a bare part of the surface. The rate of adsorption may therefore be written as

$$v_1 = k_1 p(1 - \theta) \tag{2}$$

where k_1 is a constant. The rate of desorption, v_{-1}, depends only on the amount of gas adsorbed, and is therefore proportional to θ,

$$v_{-1} = k_{-1}\theta \tag{3}$$

At equilibrium the rates of adsorption and desorption are equal, so that

$$k_1 p(1 - \theta) = k_{-1}\theta, \tag{4}$$

or

$$\frac{\theta}{1 - \theta} = \frac{k_1}{k_{-1}} p \tag{5}$$

$$= Kp \tag{6}$$

where K, equal to k_1/k_{-1}, is an equilibrium constant for adsorption. Rearrangement of this equation gives,

$$\theta = \frac{Kp}{1 + Kp} \tag{7}$$

for the fraction of surface covered.

Two special cases, which are frequently encountered in practice, are worthy of special attention. If the surface is only sparsely covered by adsorbed molecules the term $1 - \theta$ in Eqs. (4) and (5) is practically equal to unity, so that

$$\theta = Kp \tag{8}$$

For this case of slight adsorption the fraction of surface covered, and therefore the amount of gas adsorbed, is directly proportional to the pressure.

The second special case corresponds to fairly complete coverage; θ is then approximately equal to unity. Equation (6) may therefore be written as

$$1 - \theta = \frac{1}{Kp}\,. \tag{9}$$

In this case, the fraction of surface uncovered is inversely proportional to the gas pressure.

Adsorption with Dissociation

In certain cases there is evidence that the process of adsorption is accompanied by the dissociation of the molecule on the surface, the adsorbed species therefore being the atoms. If this is so, the process of adsorption may be considered a reaction between the gas molecule and *two* surface sites, and the rate of adsorption may therefore be written as

$$v_1 = k_1 p(1 - \theta)^2 \tag{10}$$

The process of desorption involves reaction between *two* adsorbed atoms, and the rate is therfore proportional to the square of the fraction of surface covered

$$v_{-1} = k_{-1}\theta^2 \tag{11}$$

Equating the rates at equilibrium gives

$$k_1 p(1 - \theta)^2 = k_{-1}\theta^2 \tag{12}$$

whence

$$\frac{\theta}{1 - \theta} = \left(\frac{k_1}{k_{-1}}\,p\right)^{1/2} \tag{13}$$

$$= K^{1/2}p^{1/2} \tag{14}$$

where K is equal to k_1/k_{-1}. This equation rearranges to

$$\theta = \frac{K^{1/2}p^{1/2}}{1 + K^{1/2}p^{1/2}} \tag{15}$$

At low pressures, where the surface is sparsely covered,

$$\theta = K^{1/2}p^{1/2} \tag{16}$$

i.e., the fraction covered is proportional to the square root of the pressure.

The above derivation of the isotherm equation for the case of dissociation is not entirely satisfactory, since it employs kinetic laws of adsorption and desorption which are not necessarily obeyed; this point will be considered later. However, the same equilibrium equations are obtained from a statistical derivation such as that given on p. 96.

Adsorption of Two Gases on the Same Surface

The isotherm for two gases adsorbed on the same surface is of considerable significance in connection with chemical reactions between two substances (p. 151). Let the fraction of surface covered by molecules of Type A be θ, and the fraction covered by B be θ'. The rate of adsorption of A is given by

$$v_1 = k_1p(1 - \theta - \theta'), \tag{17}$$

where p is the partial pressure of A; $1 - \theta - \theta'$ is the fraction of surface that is bare. The rate of desorption of A is $k_{-1}\theta$, and equating these rates gives

$$\frac{\theta}{1 - \theta - \theta'} = Kp, \tag{18}$$

where K is equal to k_1/k_{-1}. In a precisely similar way it can be shown that for the equilibrium of the gas B,

$$\frac{\theta'}{1 - \theta - \theta'} = K'p' \tag{19}$$

where p' is the partial pressure of B and K' is equal to the ratio of the rate constants for the adsorption and desorption of B. Solution of Eqs. (18) and (19) gives

$$\theta = \frac{Kp}{1 + Kp + K'p'} \tag{20}$$

and

$$\theta' = \frac{K'p'}{1 + Kp + K'p'} \tag{21}$$

for the fractions covered by A and B respectively.

STATISTICAL TREATMENT OF IDEAL ADSORPTION

In the previous section kinetic derivations were given of the isotherms for ideal adsorption, by which is meant the case in which the surface is homogeneous and there is no interaction between adsorbed species. The equations will now be derived on a statistical basis, and it will be seen that the equilibrium constants used in the foregoing treatment can now be given a precise physical significance. The statistical treatments of adsorption on a heterogeneous surface and when there are interactions will be discussed later. First, however, a brief account will be given of the general statistical treatment of equilibrium.

According to the methods of statistical mechanics the equilibrium constant of a reaction

$$aA + bB \rightleftharpoons cC + dD \tag{22}$$

is given by

$$K_c = \frac{F_C^c F_D^d}{F_A^a F_B^b} e^{E/RT} \tag{23}$$

where the F's are the partition functions per unit volume of the molecules A, B, C, and D, and E is the energy decrease at the absolute zero when a moles of A react with b of B to give c moles of C and d moles of D, all substances being in their standard states; R is the gas constant and T the absolute temperature. The total partition function, f, for a molecule is defined by

$$f = \sum_i g_i e^{-\epsilon_i/kT} \tag{24}$$

where k is Boltzmann's constant, ϵ_i is the energy (with respect to the zero-point energy of the molecule) of a given energy level of the molecule and g_i, the statistical weight, is the number of quantum states corresponding to that level; the summation covers the electronic, translational, rotational, and vibrational states. The partition function F appearing in the equilibrium expression is simply f divided by the volume V in which the molecule is present.

To a good approximation the partition function f may be written as the product of independent factors referring to the four types of energy, i.e.,

$$f = f_e f_t f_r f_v \tag{25}$$

where the four subscripts apply to electronic, translational, rotational, and vibrational energy. The partition function for electronic energy is calculated directly from the observed electronic levels of the atom or molecule, but this function seldom differs appreciably from unity since the excited electronic states are usually of high energy and the lowest electronic states are usually singlet so that the statistical weight g_e is unity*. The partition function for the three degrees of translational motion of a molecule can be shown to be†

$$f_t = \frac{(2\pi mkT)^{3/2}}{h^3} \tag{26}$$

where m is the mass of the molecule, T the absolute temperature and k is Planck's constant. The rotational partition function for a linear molecule, having only two degrees of rotational freedom, is given by

$$f_r = \frac{8\pi^2 IkT}{h^2} \tag{27}$$

where I is the moment of inertia of the molecule; for a homonuclear molecule this function must be divided by two. In the case of a polyatomic molecule having no axis of symmetry the rotational partition function is given by

$$f_r = \frac{8\pi^2(8\pi^3 ABC)^{1/2}(kT)^{3/2}}{h^3} \tag{28}$$

where A, B and C are the moments of inertia about any three mutually perpendicular axes. This expression must also be divided by a symmetry number if the molecule has certain types of symmetry.

A molecule containing N atoms has a total of $3N$ degrees of freedom. If the molecule is in the gas phase, three of these apply to the translational motion, and in the case of a nonlinear molecule three are for rotational energy; the remainder, $3N - 6$, therefore apply to vibrational motion; there are then $3N - 6$ vibrational frequencies (of which some may be the same, in which case *degeneracy* is said to exist). If the molecule is linear, there are only two degrees of rotational freedom, and hence $3N - 5$ degrees of vibrational freedom; in the case of a diatomic molecule there is only one degree of vibrational freedom, and only one vibrational frequency. The partition function for vibrational motion is given by

$$f_r = \prod_i (1 - e^{-h\nu_i/kT})^{-1} \tag{29}$$

where ν is the vibrational frequency in sec.$^{-1}$, the product being taken over all the modes of vibration, so that there are either $3N - 6$ or $3N - 5$

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* The contribution of the lowest electronic state is $g_1 e^{-\epsilon_1/kT}$, where the subscript 1 refers to the lowest state; the energy levels are referred to the lowest electronic state, so that $\epsilon_1 = 0$ and hence the contribution is g_1. The contributions from higher electronic states are generally negligible owing to the large values of ϵ_2, ϵ_3, etc.

† This is actually the partition function per unit volume and is the one which should be used in the treatment of equilibrium problems.

factors to be multiplied together in the case of a gaseous molecule. In the case of a chemisorbed molecule there are usually no translational or rotational factors, and the total partition function is the product of $3N$ vibrational terms, each of the form $(1 - e^{-h\nu/kT})^{-1}$

The Langmuir Adsorption Isotherm

The above methods may now be applied to the derivation of a statistical expression for the equilibrium constant corresponding to the adsorption process. For this purpose the process of adsorption may be regarded simply as a bimolecular reaction between the surface atoms and the gaseous atoms or molecules, with the formation of an adsorbed atom or molecule; in the simplest case reaction occurs between a gas molecule G and a simple adsorption site S, and the process may be represented as

$$G + S \rightleftharpoons A \tag{30}$$

The surface is to be regarded as an assembly of surface sites upon which adsorption may occur; these may sometimes be surface atoms and in some cases pairs or sets of atoms. Let the number of sites that are uncovered at equilibrium be N_s, let N_g be the total number of molecules in the gas phase, and let N_a be the total number of adsorbed molecules. It is now convenient to define the concentrations corresponding to these numbers as follows, S being the total surface area in sq cm.:

Concentration in gas phase, $c_g = N_g/V$ molecules per cc.
Concentration of adsorption sites, $c_s = N_s/S$ sites per sq cm.
Concentration of adsorbed molecules, $c_a = N_a/S$ molecules per sq cm.

The equilibrium constant for the process is thus

$$K_c = \frac{c_a}{c_g c_s} = \frac{N_a}{(N_g/V)N_s} \tag{31}$$

This equilibrium constant is, as seen above, given by

$$K_c = \frac{F_a}{F_g F_s} e^{\epsilon/kT} \tag{32}$$

where the F's are the partition functions per unit volume and ϵ is the energy liberated at 0°K per molecule adsorbed. However, since neither the total partition function f_a for the adsorbed molecule nor f_s for the surface site contains a volume term explicitly, it is convenient to use the total partition function in each case; the equilibrium expression thus becomes

$$\frac{c_a}{c_g c_s} = \frac{f_a}{F_g f_s} e^{\epsilon/kT} \tag{33}$$

If θ is the fraction covered at equilibrium,

$$\frac{c_a}{c_s} = \frac{\theta}{1 - \theta} \tag{34}$$

so that

$$\frac{\theta}{1 - \theta} = c_g \frac{f_a}{F_g f_s} e^{\epsilon/kT} \tag{35}$$

The concentration c_g may be replaced by p/kT, and F_g may be written as

$$F_g = \frac{(2\pi mkT)^{3/2}}{h^3} b_g \tag{36}$$

where b_g represents the rotational and vibrational factors. Furthermore the adsorption sites have very little freedom of motion, and the partition function f_s may therefore be taken as unity. The partition function for the adsorbed molecules is also probably close to unity, since little motion can occur, but may be written as b_a which represents the contribution of the internal degrees of freedom of the adsorbed molecule. Making these changes the adsorption isotherm becomes

$$\frac{\theta}{1 - \theta} = p \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \frac{b_a}{b_g} e^{\epsilon/kT} \tag{37}$$

An expression equivalent to the above was first derived by Fowler[11]. Equation (37) may be seen to have the same general form as Equation (6), but now the constant K is given in explicit form.

Adsorption with Dissociation

It was seen earlier that in many cases adsorption involves dissociation of the adsorbed molecule. If this is so, the process of adsorption must be regarded as a reaction between a gas molecule and *two* surface atoms, to give *two* adsorbed atoms;

$$G_2 + 2S \rightleftharpoons 2A \tag{38}$$

The equilibrium constant for the process is thus

$$K_c = \frac{c_a^2}{c_g c_s^2} \tag{39}$$

c_a is the number of adsorbed atoms per sq cm and c_g and c_s are as defined previously. The equilibrium constant is now given by

$$K_c = \frac{f_a^2}{F_g f_s^2} e^{\epsilon/kT} \tag{40}$$

where ϵ is the energy liberated at 0°K when one molecule is adsorbed. Equations (39) and (40) give rise to

$$\frac{c_a}{c_s} = c_g^{1/2} \frac{f_a}{F_g^{1/2} f_s} e^{\epsilon/2kT} \tag{41}$$

Again writing c_a/c_s as $\theta/(1 - \theta)$, f_a as b_a, f_s as unity, F_g as $(2\pi mkT)^{3/2}/h^3$, and c_g as p/kT this equation becomes

$$\frac{\theta}{1 - \theta} = p^{1/2} \frac{h^{3/2}}{(2\pi m)^{3/4}(kT)^{5/4}} \frac{b_a}{b_g^{1/2}} e^{\epsilon/2kT} \tag{42}$$

This equation is readily seen to be of the same form as Eq. (14).

Nonlocalized Adsorbed Layers

In the above treatments it has been assumed that the adsorbed molecules are localized on the surface, and have no translational freedom. In some cases, particularly at elevated temperatures, it has been supposed that the adsorbed molecules may have complete freedom of motion on the surface although it is doubtful whether this is ever the case with chemisorption. The adsorption isotherm will now be derived for the case in which the adsorbed molecules move freely on the surface, i.e., have two translational degrees of freedom.

In this case the adsorption sites need no longer be regarded as reactants, but the equilibrium may be considered to be between molecules having two and three degrees of translational freedom. The equilibrium constant may therefore be written as

$$K_c = \frac{c_a}{c_g} = \frac{N_a/S}{N_g/V} \tag{43}$$

The numbers of molecules N_a and N_g are proportional to the complete partition functions, so that

$$\frac{N_a/S}{N_g/V} = \frac{F_a}{F_g} e^{\epsilon/kT} \tag{44}$$

where F_a is the partition function per unit surface area, and F_g per unit volume, as above. Hence

$$\frac{c_a}{c_g} = \frac{F_a}{F_g} e^{\epsilon/kT} \tag{45}$$

The partition function F_a for two degrees of translational freedom is $2\pi mkTb_a/h^2$ where b_a is the contribution of the rotational and vibrational factors, so that

$$\frac{c_a}{c_g} = \frac{\dfrac{2\pi mkT}{h^2}\, b_a}{\dfrac{(2\pi mkT)^{3/2}}{h^3}\, b_g}\, e^{\epsilon/kT} \qquad (46)$$

$$= \frac{h}{(2\pi mkT)^{1/2}} \frac{b_a}{b_g} e^{\epsilon/kT} \qquad (47)$$

If L is the total number of molecules that are adsorbed on one square centimeter when the surface is fully covered, c_a is equal to $L\theta$; putting $c_g = p/kT$ Equation (47) gives for the fraction of surface covered,

$$\theta = p \frac{h}{L(2\pi m)^{1/2}(kT)^{3/2}} \frac{b_a}{b_g} e^{\epsilon/kT} \qquad (48)$$

Adsorption of Two Gases on the Same Surface

For certain purposes it is necessary to consider the adsorption laws for a mixture of two gases; this was discussed from a kinetic point of view on p. 92; a statistical treatment will now be given. As before, let c_s be the concentration of bare surface sites, and let c_a and c_a' be the concentrations of adsorbed A and B, the corresponding gas concentrations being c_g and c_g'. The adsorption isotherm for A is then

$$\frac{c_a}{c_g c_s} = \frac{f_a}{F_g f_s} e^{\epsilon/kT} \qquad (49)$$

while that for B is

$$\frac{c_a'}{c_g' c_s} = \frac{f_a'}{F_g' f_s} e^{\epsilon'/kT} \qquad (50)$$

where f_a' is the partition function for adsorbed B, and F_g' that for gaseous B. These equations are obviously equivalent to Eqs. (18) and (19) and the significance of the constant K is readily seen, on reference to Eq. (37), to be

$$K = \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}} \frac{b_a}{b_g} e^{\epsilon/kT} \qquad (51)$$

A corresponding expression holds for K', so that if these expressions are introduced into Eqs. (20) and (21), the fractions of surface covered by the two gases are obtained in explicit form.

DEVIATIONS FROM IDEAL BEHAVIOR

The adsorption isotherms derived in the previous two sections have proved of very great value from a qualitative standpoint, but unfortunately most of the adsorption data do not follow them very closely. In a number of cases, for example, the surface coverage is related to the pressure by an equation such as that of Freundlich (Table 2), which does not have any simple theoretical significance (see however, p. 104). The present section is concerned generally with the reasons for the deviations from simple behavior. However, the matter is treated in greater detail in the following two sections (pp. 101 and 105).

There are two principal reasons why the simple isotherms do not apply exactly to the adsorption data: (1) they assume surfaces to be absolutely smooth; and (2) they neglect the possibility of interactions* between molecules which are adsorbed close to one another on a surface. These simplifications entered into the derivations of the simple equations in that each adsorption center on the surface was assumed to be the same as any other.

The idea that adsorption sites are of varying activity was first emphasized by Taylor,[8] who pointed out that a surface must consist of regions of varying degrees of unsaturation; isolated atoms at peaks on the surface and along crystal edges will be the most unsaturated, and adsorption will occur mainly in such positions. Various types of evidence have been presented in favor of this point of view regarding the nature of surfaces, and in particular of the existence of active centers where adsorption and chemical reactions occur preferentially. Certain catalytic phenomena can be explained only on such a basis. For example, there are many cases known in which the reduction in velocity through poisoning is much greater than the reduction in degree of adsorption; thus Pease and Stewart[12] found that mercury vapor decreased the adsorption of ethylene on copper to 80 per cent of normal and of hydrogen to 5 per cent of normal, but the velocity of hydrogenation decreased to 0.5 per cent of normal. Such results can only be explained if reaction occurs on a small fraction of surface. Other effects pointing to active centers are the abnormal sensitivity of catalysts toward poisons, methods of preparation and sintering, as compared with the sensitivity of degree of adsorption to these factors.

Another phenomenon which has also been interpreted in terms of surface heterogeneity is that the heats of chemisorption usually decrease markedly as adsorption proceeds and the surfaces become covered. This can be explained provided that, as is reasonable, the most active sites, i.e., the ones on which adsorption occurs with the highest heats of adsorption, are also the ones on which adsorption occurs with the least activation energy. Adsorption thus occurs most readily on these sites, which are therefore the first to be covered; the less active sites are covered later, and the heats

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* The question of the nature of these interactions is discussed on p. 108, where it is seen that the most important type of interaction is of an indirect nature, owing to the formation of an electrical double layer at the surface.

of adsorption thus decrease. Unfortunately, this type of evidence is not unequivocal, since exactly the same type of behavior is predicted on the basis of repulsive interactions between adsorbed molecules. If such interactions exist, the first molecules adsorbed will tend to be as far apart as possible* so that the repulsive energies are small; subsequent molecules, however, are required to be adsorbed close to previously adsorbed molecules, and the effect of the repulsive forces is to bring about a decrease in the heat liberated on adsorption. In some cases[13] attempts have been made to analyze heat data in a quantitative manner so as to decide between these two interpretations of the falling heats. However, the conditions existing at surfaces are so complex that a definite decision usually cannot be made. The same applies to attempts to distinguish between the two interpretations by detailed analysis of the adsorption isotherms; it is always possible to devise plausible distributions of adsorption sites, or plausible interaction laws, or a combination of the two, that will explain the isotherms to within the experimental error.

In view of this situation, which has been discussed by Roginsky and Todes[14], it is essential to have some crucial test for distinguishing between the two hypotheses in a given instance. Roginsky and Todes have suggested an experiment of this type, using isotopic gases such as hydrogen and deuterium. One of the gases, say hydrogen, is allowed to become adsorbed on part of the surface, after which deuterium is introduced to the system. The adsorbed gases are then pumped off in stages, and the fractions analyzed for the ratio of hydrogen to deuterium. If the surface was, in fact, heterogeneous it is clear that the hydrogen will have become adsorbed on the most active sites, and the deuterium on the less active ones; on pumping off the gases the deuterium will therefore be desorbed first, and the hydrogen last. If, on the other hand, the surface is smooth and the complexities of adsorption (as revealed by the isotherms and the variation in heat of adsorption) are the result of repulsive interactions, the hydrogen and deuterium molecules will all be on the same footing once they are adsorbed, and the various samples that are pumped off will have the same composition, the ratio of concentrations being in strict conformity with the composition of the adsorbed layer. If the second type of behavior is found to occur it is clear that surface heterogeneity may be excluded as a possible interpretation; the first type of behavior, however, in which the species adsorbed last comes off first, does not exclude the possibility that repul-

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* This is evidently so if the surface layer is mobile, since the adsorbed molecules will move away from one another because of the repulsive forces. For an immobile layer the same result will be obtained if, as is likely, the repulsive forces affect the activation energies for adsorption; adsorption will therefore occur less rapidly at sites which are close to already occupied sites, so that there will again be a tendency for the molecules to be adsorbed as far apart as possible.

sions occur in addition to surface heterogeneity. A more careful analysis of the results, however, may enable the question of the relative importance of the two types of phenomena to be examined.

SURFACE HETEROGENEITY

The evidence for the heterogeneity of various surfaces will be discussed in greater detail in this section and an outline will be given of the theories which treat adsorption on heterogeneous surfaces.

Experimental Evidence.

As mentioned previously, the most direct and positive evidence for surface heterogeneity involves the method suggested by Roginsky and Todes, in which isotopic gases are successively adsorbed and desorbed. The method was first employed by Keier and Roginsky[15], who worked with active charcoal and used hydrogen and deuterium. They found that the last fraction desorbed had approximately the same composition as the first fraction adsorbed, showing that the surface was heterogeneous. The same method was also employed by Kummer and Emmett[16] using an iron synthetic ammonia catalyst, the promoters being 2.26 per cent Al_2O_3, 0.21 per cent ZrO_2 and 0.62 per cent SiO_2. The gases used were ordinary carbon monoxide ($C^{12}O$) and the radioactive $C^{14}O$, and these were added in succession as two separate fractions, the work being done at −78 and −195°C. The results showed that there was a general tendency for the second fraction of gas added to be desorbed first, but this did not occur in as clear-cut a manner as would have been the case if only surface heterogeneity were involved. The data, in fact, were found to be consistent with the hypothesis that about one-half of the surface was heterogeneous, and that the molecules were then adsorbed without interaction between them, and that the other half was smooth but that there were repulsive interactions; on this second half there would be complete equilibration between adsorbed species. Of course, as Emmett and Kummer emphasize, such a picture of the surface is too simple: rather, the surface should be regarded as completely inhomogeneous; the repulsive interactions should operate all over the surface, but they are not strong enough to effect complete equilibration of the adsorbed species.

A somewhat similar investigation was also carried out by Emmett and Kummer[17] using N_2^{28} and N_2^{30} on the same surface. The results indicated complete equilibrium at all times in contrast to the results with carbon monoxide.

A less direct approach to the problem of surface heterogeneity has been made by Taylor and his collaborators[18]. The method employed is to measure the extent of adsorption at constant gas pressure and at successively increasing temperatures. The method was first applied by Taylor and Liang[19] to the adsorption of hydrogen on zinc oxide, and they worked in a temperature range in which van der Waals adsorption was negligible. A typical curve showing volume adsorbed *vs.* time is shown in Figure 2. At a given temperature the amount of adsorption increases steadily with time, but on raising the temperature, as at point A, they observed a rapid desorption of hydrogen, followed by a characteristic rise typical of slow chemisorption. The rapid desorption is, of course, to be expected even on a smooth surface, but the subsequent slow adsorption can be explained only on the assumption that it occurred on a part of the surface on which adsorption was unable to occur at the lower temperature (the activation energy being too high). Taylor and Liang discuss this phenomenon with reference to a simple system consisting of two types of surface, A and B, which are associated with activation energies E_A and E_B and with heats of adsorption q_A and q_B. If E_A is low and E_B is high there will be adsorption only on A at the lower temperature, the rate of chemisorption on B being too low. If the activation energy for desorption from A, $E_A + q_A$, is sufficiently low there may be rapid desorption from A as the temperature is raised, and adsorption on B may now occur at an appreciable rate, $E_B + q_B$ being large enough for B to be covered to an appreciable extent. The over-all result is that on raising the temperature from T_1 to T_2, gas is desorbed from A and adsorbed on B. It follows from this that the measurement of rates of adsorption at T_1 and T_2 will not lead to an activation energy which has any real significance, since different sites are involved.

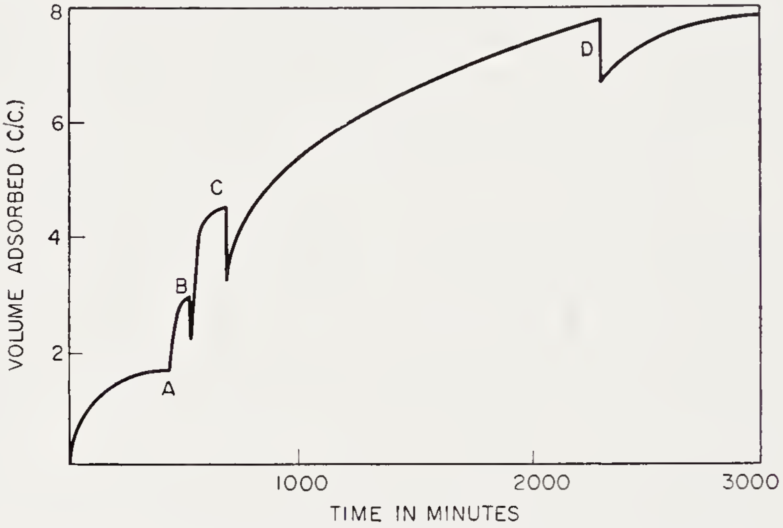

Figure 2. Typical adsorption rate curve (after Taylor and Liang[19]), for the adsorption of hydrogen on zinc oxide at 1 atm. pressure. The curve to the left of A applies to 0°C; at A the temperature is raised to 111°, at B to 154°, at C to 184°, and at D to 218°.

The same procedure as that of Taylor and Liang has been applied by Sadek and Taylor[20], who used hydrogen and six different promoted nickel catalysts and obtained evidence for heterogeneity in each case. Taylor[18] has also analyzed earlier data of the same type, using nickel and iron, zinc oxide, chromic oxide and certain mixed oxides, and has shown that the results again indicate surface heterogeneity. A similar procedure, with similar results, has also been applied by Keier and Roginsky[21] to the adsorption of hydrogen on sugar charcoal.

Theoretical Treatment

It was first pointed out by Langmuir[22] that if adsorption occurs on sites of varying activity the adsorption isotherm must take the form

$$\theta = \sum_i \frac{K_i p}{1 + K_i p} \tag{52}$$

the summation being made over all of the different types of sites. This equation forms the basis of most discussions of adsorption on homogeneous surfaces, but is usually put into a more tractable form by assuming a continuous variation of activity over the surface, thereby allowing the summation to be replaced by integration.

The problem of adsorption on an inhomogeneous surface can be attacked from two different directions. One method is to start from an experimental isotherm, and to deduce the distribution of sites; this treatment is more complete and satisfactory, but unfortunately it is mathematically very difficult. The second method is to try various plausible distribution functions in order to see whether the experimental isotherm can be fitted; this is considerably easier to carry out.

The second method was employed by Zeldowitch[23]. His treatment involved certain approximations, but he reached the important conclusion that the Freundlich isotherm was obtained if the sites were distributed exponentially with respect to the energy of adsorption. His treatment is equivalent to the following simplified version. Ideal adsorption with no interaction is assumed for each type of surface site, so that the isotherm for the i-th type of site is

$$\frac{\theta_i}{1 - \theta_i} = K_i p \tag{53}$$

If the difference between the various types of site resides solely in the energy of adsorption, and not at all in the entropy, this equation may be written as

$$\frac{\theta_i}{1 - \theta_i} = K p e^{\epsilon_i / kT} \tag{54}$$

where ϵ_i is an energy term appropriate for the i-th type of site. This equation may be written as

$$\theta = \frac{Kpe^{\epsilon_i/kT}}{1 + Kpe^{\epsilon_i/kT}} \tag{55}$$

and if there are N_i sites of the i-th kind the average, and therefore over-all, fraction of sites covered is

$$\theta = \frac{\sum_i \theta_i N_i}{\sum_i N_i} \tag{56}$$

Introduction of Eq. (55) into Eq. (56), replacing the summations by integrations, gives

$$\theta = \frac{\int_0^\infty [NKpe^{\epsilon/kT}/(1 + Kpe^{\epsilon/kT})]\, d\epsilon}{\int_0^\infty N\, d\epsilon}, \tag{57}$$

where N is some function of ϵ. Zeldowitch assumed an exponential distribution of sites with respect to ϵ, i.e., he took N to have the form

$$N = ae^{-\epsilon/\epsilon_0},$$

where a and ϵ_0 are constants. He was unable to obtain an exact integration of the expression, but found that for fairly small values of θ the solution is

$$\ln \theta = \frac{kT}{\epsilon_0} \ln p + \text{const.} \tag{59}$$

which is the Freundlich isotherm.

Another theoretical study of the problem using the second method was made by Halsey and Taylor[13], who were apparently unaware of Zeldowitch's work. Halsey and Taylor first showed that the Freundlich isotherm was not obtained if N was assumed to be independent of ϵ. They then tried the exponential distribution, Eq. (58), but performed the integration from minus infinity to infinity instead of, as is correct, zero to infinity. This allowed the integration to be carried out in the general case but they also found on making some approximations that Eq. (59) was obtained. Halsey and Taylor found that this equation agreed satisfactorily with the data of Frankenburg[24] for the adsorption of hydrogen on tungsten powder.

Unfortunately, the validity of the treatment of Halsey and Taylor seems doubtful in view of the integration from minus infinity to infinity, since negative values of ϵ have no physical meaning[25]. Their procedure weights very heavily those sites which are so inactive that there can be no adsorption on them, whereas, on general physical grounds it is known that even the least active sites have some appreciable affinity for gas molecules. Zeldowitch's treatment is therefore preferred, even though his solution was not as general as that of Halsey and Taylor.

Various attacks on the problem have also been made using the first method, in which the distribution is deduced from the experimental isotherm. Some progress was made by Roginsky[26], but his methods did not lead to an explicit solution of the problem. A much simpler procedure was followed by Sips[27], who showed that, starting with a given isotherm, a unique distribution function for the sites could be obtained, but who also integrated from minus infinity to infinity. In the case of the Freundlich isotherm, this distribution function is the exponential one, as had been found by Zeldowitch and by Halsey and Taylor. Sips pointed out that the Freundlich isotherm implies an infinite number of sites, since the amount of adsorption continues to increase as the pressure is raised; he therefore proposed to replace it by the modified form

$$\theta = \frac{kp^{1/n}}{1 + kp^{1/n}} \tag{60}$$

When n is close to two he found that this equation leads to a Gaussian distribution of sites. When n is unity the equation becomes the Langmuir equation, which corresponds to a completely homogeneous surface. Tompkins[28] has extended Sips' treatment to adsorption with dissociation, and has applied it to other isotherms.

As a result of the criticism by Hill[25] with regard to the integration between minus infinity and infinity, Sips[27] has modified his treatment, and now finds that a completely general treatment is not possible. However, the conclusion that an exponential distribution will give rise to a Freundlich isotherm is still correct.

One other matter of interest in connection with adsorption on nonuniform surfaces is the manner in which the differential heat of adsorption, q, varies with θ. The treatment of this problem[13] leads to the conclusion that when the Freundlich isotherm is obeyed, and the distribution is consequently exponential, q varies exponentially with θ.

INTERACTION BETWEEN ADSORBED MOLECULES

Experimental Evidence

A certain amount of evidence has now accumulated which indicates that there are repulsive interactions between atoms or molecules adsorbed on a surface. Some of this evidence is admittedly capable of alternative explanation, but it seems difficult to escape the general conclusion that these interactions are important and must not be overlooked in the theoretical treatment of adsorption.

The first significant evidence for repulsive interactions was obtained by Roberts[7], who measured heats of adsorption of hydrogen on tungsten filaments. These filaments were freed of contaminant by flashing before starting a series of experiments, and the surface was considered to be smooth. Roberts determined calorimetrically the differential heats of adsorption corresponding to various degrees of surface coverage, and his results are shown in Figure 3; it is seen that the heat falls approximately linearly, from about 45 kcal for a bare surface to 15 kcal for a fully covered one. He found that there was no appreciable change in the amount of hydrogen adsorbed at pressures higher than 3×10^{-4} mm, and concluded that the surface was fully covered at this pressure; as will be seen later, however, his conclusions have required modification.

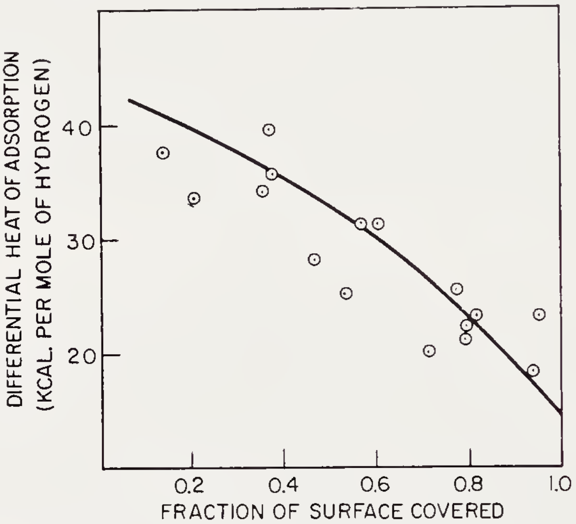

Figure 3. Roberts's[7] data for heats of adsorption of hydrogen on a tungsten surface.

Another investigation of the adsorption of hydrogen on tungsten was made by Frankenburg[29], who used the metal in powdered form; its surface area was about 10^6 times that of Roberts's wire. Between − 194 and 750°C, and from 10^{-6} to 10-mm pressure his system obeyed the Freundlich isotherm. For sparely covered surfaces his differential heats, derived from the isotherm, are consistent with those of Roberts; however, for a coverage Frankenburg believed to be 25 per cent, the heat had already fallen to about 15 kcal. In this investigation the heat was found to vary linearly with log θ, rather than with θ as in the studies of Roberts.

Frankenburg's tungsten powder contained 0.1 per cent of silica, and in order to account for the discrepancy between the results with the powder and those with wires and films (see below), Beeck[30] has suggested that the very small amount of impurity can have a very marked effect on the surface. He assumed that the fraction of the powder surface covered with silica is about three-quarters, so that when Frankenburg thought his surface to be 25 per cent covered it was actually almost fully covered. The logarithmic variation of the heat may also be caused by the heterogeneity of the surface.

Similar work has been carried out by Beeck and Wheeler[31], using evaporated tungsten films, the surface areas of which were of the order of 10^6 times greater than those used by Roberts. Experimental details of this work have not been published, but the data are apparently much more accurate than those of Roberts. The interesting result is that in spite of the very different methods of preparing the surfaces, the heats are in close agreement with those of Roberts. This would seem to render unlikely the explanation that the results are caused by surface heterogeneity, and indicates that the hypothesis of interactions must be invoked to explain the falling heats.

In agreement with Roberts's conclusion, Beeck and Wheeler also found the surface to be essentially saturated at about 10^{-4} mm. However, there is some difficulty about accepting this conclusion. When heats of chemisorption are low, high gas pressures are required for adsorption to occur; the fact that no further adsorption appeared to occur above 10^{-4} mm might therefore simply mean that adsorption occurs with difficulty, and would occur more readily at higher pressures. That this is actually the situation was found by Rideal and Trapnell[32], who continued the work up to pressures greater than 10^{-2} mm, using an evaporated film. Their conclusion was that when Roberts, and Beeck and Wheeler, thought they had reached complete coverage, they had only in fact reached about 70 per cent coverage. Trapnell continued the measurements of heat of adsorption to complete coverage. Trapnell's curve for heat of adsorption *vs.* θ is shown in Figure 4; the points up to 71 per cent coverage are taken from Beeck and Wheeler, the remainder from his own work.

It therefore appears that heats of adsorption of hydrogen on tungsten fall from about 45 kcal on a bare surface to a value very close to zero on a fully covered surface. If the surface can really be assumed to be homogeneous, this fall in heat must be attributed to very strong repulsive interactions between adsorbed molecules.

Evidence for repulsive interactions was also found in the investigations of Emmett and Kummer (p. 101) using the isotope method suggested by Roginsky and Todes. They found that surface heterogeneity was not adequate to explain the results, and that interactions must be involved as well.

Further evidence for repulsive interactions has been obtained by Weber and Laidler[33], who made semiquantitative measurements of rates of desorption of ammonia and deuterated ammonias from a copper surface and from an iron synthetic ammonia catalyst. They found that the rate of desorption of ammonia or of deuterated ammonia was increased by several orders of magnitude when other isotopic forms of ammonia were adsorbed on the surface. Although the surfaces used were undoubtedly heterogeneous, it appears that heterogeneity alone cannot explain the effect on rates of desorption. The most probable explanation of these results is that adsorbed molecules are put into higher potential energy states when other molecules are adsorbed next to them, i.e., that repulsive forces are involved.

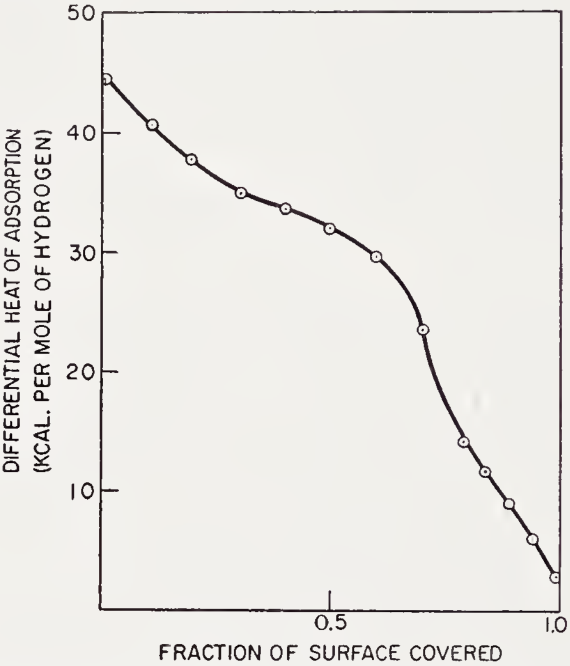

Figure 4. Trapnell's[32] curve for the heat of adsorption of hydrogen on tungsten; the data corresponding to lower surface coverages are those of Beeck and Wheeler[31], the others, those of Trapnell.[32]

Theoretical Treatment

Two aspects of the problem of interactions between adsorbed molecules need to be discussed; the first is the nature of the interactions, the second the statistical mechanics of adsorption with interaction.

A recent paper by Boudart[34] has thrown considerable light on the question of the nature of interactions between adsorbed molecules. Previous work had, for the most part, tacitly assumed that the effects referred to in the previous section are to be interpreted in terms of the ordinary repulsive forces existing between atoms which are not connected by valence bonds. On the quantitative side, however, there have been some misgivings[35] as to whether the repulsive forces were sufficiently strong to account for the results obtained. For example, in the case of the adsorption of hydrogen on tungsten, the fall in heat of chemisorption from about 45 kcal on a bare surface to practically zero on a fully covered surface appears to be much too large to be explained on the basis of direct repulsive forces between neighboring hydrogen atoms. However, Boudart points out that there is another and entirely different mechanism by which an adsorbed species may affect the heat of adsorption of a neighboring atom. In the case of the adsorption of a hydrogen atom on a metal, for example, the covalent H—M bond formed will have a certain ionic character depending on the relative electronegativities of hydrogen and the metal; this bond has a dipole moment and an electrical double layer at the surface. The effect of this double layer is to reduce the strength of H—M bonds subsequently formed, and to reduce the heat liberated on the chemisorption of further hydrogen atoms. A quantitative application of this theory showed that the effect was sufficiently great to explain the thermochemical data, including those for hydrogen on tungsten.

Boudart refers to this mechanism as *induction*, and shows that it is usually much more important than direct interaction between dipoles. In view of the fact that the effects of induction (which is an indirect interaction) are exactly the same as those of direct interaction, it seems convenient to employ the general term interaction for any case in which the adsorption of a molecule affects the adsorption of another; an alternative term used is "induced heterogeneity."

In connection with a theoretical discussion of the statistical mechanics of adsorption with interaction it is necessary first to distinguish between various types of adsorbed layers*. A distinction has already been made (p. 97) between localized and nonlocalized layers. In localized adsorption the adsorbed molecules have become attached to definite sites on the surface, so that the three translational degrees of freedom of the gas molecules have been converted to vibrational modes. In nonlocalized adsorption, on the other hand, the adsorbed molecules move freely in two dimensions over the surface, and cannot be considered to be attached to definite sites.

Even when a layer is localized, however, there is still the possibility that an adsorbed molecule may move to another site, either by a direct process or by evaporation and recondensation. If this can occur at an appreciable rate, the layer is said to be *mobile*. If a layer is *immobile*, on the

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* The treatment in the remainder of this subsection to some extent follows that of Roberts ("Some Problems in Adsorption," Cambridge University Press, 1939) and A. R. Miller ("The Adsorption of Gases on Solids," Cambridge University Press, 1949); however, the derivations are presented in a simpler form.

other hand, the adsorbed molecules remain fixed on the sites on which they were originally adsorbed; both the rate of evaporation and the rate of jumping from site to site must be neglibibly small. An immobile layer is clearly in a nonequilibrium state which changes slowly with time. It is evident that the nonlocalized layers are necessarily mobile, but that localized ones may be either mobile or immobile. However, it has been concluded[36] on theoretical grounds that in van der Waals adsorption the films are invariably mobile, and that in chemisorption they are nearly always mobile.

The distinction between mobile and immobile films becomes particularly important when interactions between adsorbed molecules are under consideration. If a film is immobile, and adsorption occurs without activation energy, it is clear that there will be a completely random distribution of adsorbed molecules on a smooth surface (since there is an equal probability of adsorption at any site, and since the molecules must remain where they land). If a mobile layer is formed, however, and there are repulsive interactions, the first molecules adsorbed will distribute themselves as far apart as possible, instead of being distributed at random. If adsorption involves an activation energy the behavior will correspond to that for the mobile layer, even if the layer is in fact immobile. This is so because the repulsive forces will inevitably affect the activation energy; there will be a greater activation energy for adsorption in positions close to already adsorbed molecules, so that there will be a tendency for adsorption to occur in positions as far as possible from one another.

Whether or not there is a random distribution of adsorbed molecules has an important effect on the manner in which the heat of adsorption varies with the fraction of surface covered. If the distribution is random, i.e., if the layer is immobile and there is no activation energy for adsorption, the number of near neighbors that a given molecule finds on becoming adsorbed increases steadily with θ, so that the repulsive energy increases linearly with θ; the heat of adsorption therefore falls linearly with θ. Consider, for example, a surface lattice in which the total possible number of near neighbors that an adsorbed molecule can have is s, and suppose that the interaction energy between a pair of molecules adsorbed side by side is V; the interaction between the molecules not adsorbed side by side will be neglected. If the differential heat of adsorption on the bare surface is q_0, that on the completely covered surface is $q_0 - sV$, since the repulsive energy suffered by the final adsorbed molecules is sV, and this is subtracted from the initial heat q_0. When the fraction of surface covered is θ the average number of molecules surrounding a given adsorbed molecule is now θ_s so that the differential heat of adsorption is $q_0 - \theta sV$. This linear variation of q with θ is shown in Figure 5.

The case of the mobile film may be considered with reference to the square lattice shown in Figure 6. The coordination number is taken here to be 4, the interactions across the diagonal being neglected. If the adsorbed molecules distribute themselves so as to avoid being in neighboring positions as far as possible, it is clear that up to $\theta = 0.5$ such positions can be avoided entirely; the distribution at $\theta = 0.5$ is shown in Figure 6, and it can be seen that there are no neighboring molecules. The heat of adsorption up to $\theta = 0.5$ therefore remains at q_0. After $\theta = 0.5$, however, every additional adsorbed molecule must necessarily be adsorbed between four already adsorbed molecules, and the heat of adsorption is therefore now $q_0 - 4V$. The variation of heat of adsorption with θ for this case is therefore as represented in Figure 5, curve *b*. However, this curve will not actually represent the situation since, owing to the Boltzmann distribution of energies in the adsorbed molecules, the molecules will not arrange themselves exactly as indicated above; the effect of taking this into account is to round off the corners of the curve, as shown in curve *c*.

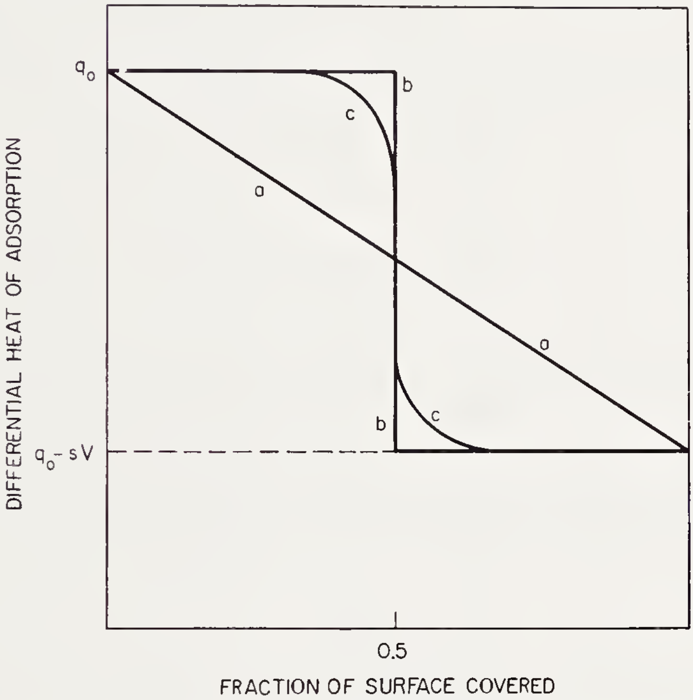


Figure 5. Theoretical curves for the variation of heat of adsorption with coverage for an immobile layer (curve a) and a mobile layer (curves b and c); in b the Boltzmann distribution of energies is neglected; in c it is included.

In view of the great importance of mobile films in the case of interaction between adsorbed molecules, a brief quantitative treatment of this problem will be presented. An isotherm will first be derived, after which an expression for the heat of adsorption as a function of θ will be obtained. The method of solving this type of problem was first given by Peierls[37], and has been employed extensively by Roberts and his co-workers[38]. The equations that will now be obtained are essentially those of Roberts, but the derivation will be somewhat different.

Consider a central site S_0 surrounded by four sites, S_1, S_2, S_3 and S_4 (see Figure 6). If there were no interaction and adsorption occurred without dissociation the isotherm would be

$$\frac{\theta}{1 - \theta} = Kp, \tag{61}$$

where θ, the fraction covered, may also be considered to be the probability that a given site is covered. Suppose now that S_0 is uncovered, and consider the probability P that S_1 is covered. This will be given by

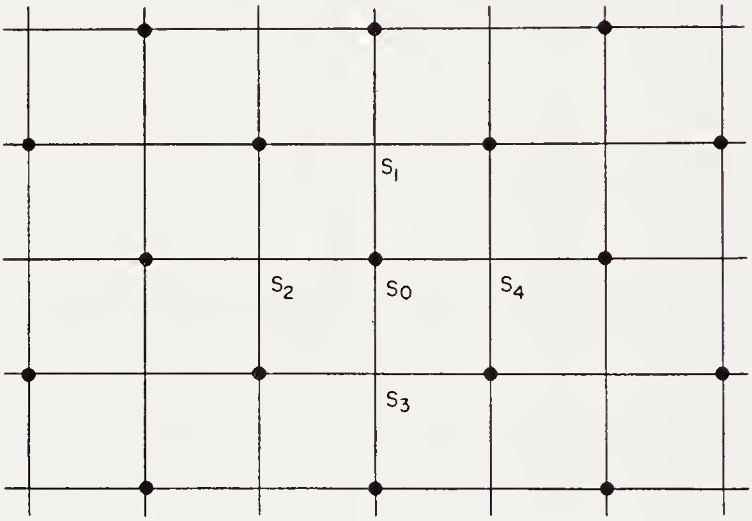


Figure 6. A square surface lattice showing the way adsorbed molecules will distribute themselves at half coverage in the case of a completely mobile layer.

$$\frac{P}{1 - P} = Kp\zeta \tag{62}$$

where ζ is a term that takes into account the interactions due to molecules adsorbed on the sites that surround the colony of five under consideration; $K\zeta$ will be written as κ. If, on the other hand, S_0 is occupied the probability P' that S_1 is occupied is given by

$$\frac{P'}{1 - P'} = Kp\zeta e^{-V/kT} \tag{63}$$

where the term $e^{-V/kT}$, which will be written as η, allows for the interaction between the molecules adsorbed on S_0 and S_1. Equations (62) and (63) give rise to

$$P(S_0 \text{ vacant}) = \frac{\kappa p}{1 + \kappa p} \tag{64}$$

$$P'(S_0 \text{ occupied}) = \frac{\kappa \eta p}{1 + \kappa \eta p} \tag{65}$$

The over-all average value of θ is

$$\theta = (1 - \theta)P + \theta P' \tag{66}$$

$$= \frac{(1 - \theta)\kappa p}{1 + \kappa p} + \frac{\theta \kappa \eta p}{1 + \kappa \eta p} \tag{67}$$

whence

$$\frac{\theta}{1 - \theta} = \frac{\kappa p(1 + \kappa \eta p)}{1 + \kappa p} \tag{68}$$

This is therefore the isotherm for the case of interactions. If there are no interactions κ becomes K and η is unity, in which case Eq. (68) reduces to the Langmuir isotherm, Eq. (6).

The application of this equation to heats of adsorption has been made by Wang[39]. The differential heat of adsorption per molecule, q, is the decrease in the energy of the system when one molecule is adsorbed, and is given by

$$q = u - \frac{\partial U}{\partial N_a} \tag{69}$$

where u is the energy of a gaseous molecule, U is the total energy of the adsorbed film and N_a is the number of adsorbed molecules. The total energy U can be expressed as

$$U = U_0 + \bar{X}V, \tag{70}$$

where U_0 is the energy apart from interactions, V is the interaction energy per pair of neighboring molecules and $\bar{X}$ is the average number of pairs for a given value of θ. The average number of pairs is given by

$$\bar{X} = (\tfrac{1}{2})sN_a \times (\text{average value of } P \text{ when central site is covered}), \tag{71}$$

the $\frac{1}{2}$ being introduced to avoid counting each pair twice. If L is the total number of molecules that can be adsorbed, $N_a = L\theta$, so that $\bar{X}$ becomes

$$\bar{X} = \frac{(\frac{1}{2})sL\theta\kappa\eta p}{1 + \kappa \eta p} \tag{72}$$

Elimination of Kp making use of the isotherm, Eq. (68), gives

$$\bar{X} = (\tfrac{1}{2})sL\left\{\theta - \frac{1 - [1 - 4(1 - \eta)\theta(1 - \theta)]^{1/2}}{2(1 - \eta)}\right\} \tag{73}$$

This equation, combined with Eqs. (69) and (70), gives rise to

$$q = q_0 - (\tfrac{1}{2})sV\left\{1 - \frac{1 - 2\theta}{[1 - 4(1 - \eta)\theta(1 - \theta)]^{1/2}}\right\} \tag{74}$$

where q_0 is the heat of adsorption when $\theta = 0$. The use of this equation for particular values of V (and therefore of η) gives rise to curves of the general form of c in Figure 5. A similar equation has been derived for adsorption with dissociation.

It remains to consider briefly the application of the above treatment to the data, particularly to the heats of adsorption of hydrogen on tungsten. On the basis of his original data, Roberts considered that the variation of q with θ was a linear one, and concluded that the layer was therefore immobile; this conclusion was originally accepted by Miller[40]. However, the new data of Trapnell appear to require a modification of this view[41]: at low coverage the surface is probably immobile, but at higher coverages, owing to the repulsive interactions, the layer is probably mobile.

THERMODYNAMICS OF CHEMISORPTION

It is very convenient to treat the subject of chemisorption from a thermodynamical point of view rather than from a statistical one. In the analysis of certain kinds of adsorption data, for example, it is frequently most useful to calculate heats and entropies of adsorption. The significance of heats of adsorption has already been considered in connection with the distinction between chemisorption and physical adsorption, and with the question of heterogeneity of surfaces and the possibility of interactions between adsorbed molecules. The subject of entropies of adsorption has been somewhat neglected, but Kemball[42] has recently demonstrated their significance in connection with the freedom of motion of adsorbed molecules.

The thermodynamical discussion of adsorption involves largely a consideration of equilibrium constants, free energies, entropies and heats. The magnitudes for all of these quantities, except the last, involve the question of standard states. The most fundamental, but perhaps not the most convenient procedure, is to use as the standard state one molecule per cc for the gas, one site per sq cm for the surface, and one molecule per sq cm for the adsorbate. This is the procedure used on p. 95, and Eq. (31) is the expression for the equilibrium constant. The free energy and entropy of adsorption would then be related to this constant by the usual equations

$$\Delta F = -RT \ln K_c \tag{75}$$

$$\Delta S = \frac{\Delta H - \Delta F}{T} \tag{76}$$

The entropy of adsorption ΔS can be calculated if K_c and the heat of adsorption $(-\Delta H)$ are known.

A more convenient procedure is to express the gas pressure in atmospheres, and express the concentrations of sites and of adsorbed molecules in terms of the fractions bare and covered. The equilibrium constant is then

$$K = \frac{\theta}{(1 - \theta)p} \tag{77}$$

(cf. Eq. (6)), and the free energy and entropy are calculated as previously. This method has the advantage of using the same units as are used in the Langmuir isotherm, the K in Eq. (77) above being the same as in Eq. (6). If the Langmuir isotherm is not obeyed the usual procedure is to determine the equilibrium constant when $\theta = \frac{1}{2}$; the ΔH value to be used in calculating the entropy should then, of course, be the value at this coverage.

The theoretical significance of some of the exponential heats and entropies of chemisorption will be considered in the remainder of this chapter.

Heats of Chemisorption

Very little progress has been made in the direction of giving a theoretical interpretation to the observed heats of chemisorption. The problem is basically a very complicated one owing to the complex nature of solid surfaces. A very interesting empirical approach to the problem has, however, recently been given by Eley[43], who assumes the chemisorptive bond to be of the covalent type and calculates its energy using the methods employed by Pauling[44]. The method may be illustrated with reference to the chemisorption of hydrogen on tungsten,

$$2W + H_2 \rightarrow 2W\text{—}H$$

The differential heat of chemisorption on a bare surface, q_0, is related to the bond energies E by

$$q_0 = 2E_{W-H} - E_{H-H} \tag{78}$$

The energy of the surface W—H bond is calculated from Pauling's equation

$$E_{W-H} = (\tfrac{1}{2})\,(E_{W-W} + E_{H-H}) + 23.06(x_W - x_H)^2, \tag{79}$$

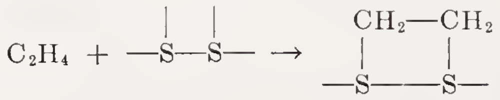
where x_W and x_H are the electronegativities of the elements. The term involving $x_W - x_H$ is estimated from Pauling's approximation that it is equal to the dipole moment of the bond, and this is obtained from the measured contact potential.

To obtain E_{W-W} Eley assumes that each metal atom has twelve nearest neighbors, and since two atoms are involved in each bond E_{W-W} is equal to one-sixth of the sublimation energy.

The values of q_0 obtained in this way for the adsorption of hydrogen and of ethylene on various metals are shown in Table 3, where the observed values are also given. In the ethylene calculations it is assumed that adsorption occurs in the following manner:

TABLE 3. CALCULATED AND OBSERVED HEATS OF CHEMISORPTION[43]

	Hydrogen		Ethylene	
Metal	Calc.	Obs.	Calc.	Obs.
W	44	45	64	102
Ni	17	31	36	58
Fe	17	32	36	68
Rh	23	28	42	50
Ta	32	39	51	138
Cr	16	45	35	102



$$C_2H_4 + -\overset{|}{S}-\overset{|}{S}- \rightarrow -\underset{}{\overset{CH_2-CH_2}{\overset{|}{S}}}\!-\!-\overset{}{\overset{|}{S}}-$$

The agreement is less satisfactory if other types of adsorption are assumed. The agreement is not particularly good, but there is probably a certain correlation between the observed and calculated values. The chief merit of the method is that in some cases it allows certain modes of adsorption to be eliminated as energetically improbable.

Entropies of Chemisorption

The entropy data for a number of examples of adsorption have recently been examined by Kemball[42]. It is possible to calculate, using the appropriate partition functions, what the entropy changes are corresponding to the loss of various types of freedom, and these calculated losses may be compared with the theoretical ones. Thus, if a non-linear molecule is adsorbed in a localized layer, there is a loss of three degrees of translational freedom, three degrees of rotational freedom, and perhaps some vibrational freedom, although the latter loss may be expected to be small. From the partition functions the entropy changes associated with the losses of translational and rotational freedom can be calculated, in terms of the molecular masses and moments of inertia. Similarly, the entropy loss associated with the formation of a nonlocalized layer can be calculated; in this case only one degree of translational freedom is lost. The loss of entropy is less in the case of a nonlocalized layer, and by comparing the data with the calculated values it is possible to draw conclusions as to the nature of the layer. It is, of course, essential to use the same standard states in comparing theoretical and observed values.

Proceeding in essentially the above manner Kemball has analyzed the entropy data for a number of cases of van der Waals adsorption and for three cases of chemisorption. The standard states were not always well defined for the data, since the surface areas were often not exactly known, but in spite of this Kemball was successful in distinguishing clearly between the different types of layer. The physical adsorption data were mostly consistent with nonlocalized adsorption, but in some cases there was evidence of localized layers. The three cases of chemisorption were water on zinc oxide[45], nitrogen on iron synthetic ammonia catalysts[46] and nitrogen on tungsten[47]. In all cases the entropies were consistent with localization of the adsorbed molecules on definite surface sites.

Kinetics of Chemisorption

Since the kinetic laws of adsorption and desorption, and the absolute rates of these processes, are closely related to those for certain types of chemical reactions, it has been thought expedient to deal with these topics in the following two chapters.

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CHAPTER 4

KINETIC LAWS IN SURFACE CATALYSIS

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This Chapter and the following one are concerned with the kinetics of reactions on surfaces, and an attempt has been made to treat this subject in as comprehensive a manner as possible. Those theories that seem to have made a significant contribution toward an understanding of the kinetics of surface reactions have been considered. A large number of data are presented, and the most important kinetic facts with regard to them are referred to and discussed in the light of the theoretical treatment.

The material has been organized in a manner which, it is hoped, will make the subject matter most readily available to the reader. The present chapter gives a general and fairly elementary review of the theoretical aspects of the subject and is mainly concerned with the effects of concentrations and temperature on the rates. The chapter which follows comprises a much more detailed and advanced theoretical treatment, and is particularly concerned with the statistical theory of the absolute rates of surface reactions. In both of these chapters the experimental data are presented in some detail, and are discussed as thoroughly as possible in the light of the theoretical treatment. The reader who is only interested in a purely general knowledge of the kinetics of surface reactions will probably find most of the information which he needs in this chapter.

BASIC KINETIC LAWS

Rates of Surface Reactions

There are a number of different ways of expressing the rates of reactions. Perhaps the most fundamental method is to express rates as moles or molecules of reactant disappearing per second. If n is the number of moles of a reactant present at time t the rate would be $-dn/dt$ moles per second. The rate may also be expressed in terms of the appearance of product. If the number of moles of a product present at time t is n', the rate is then dn'/dt. In general, there is a numerical difference in the rate according to which reactant or product is considered; if the stoichiometric equation for a reaction is

$$A + 2B = 3C$$

for example, the rate of disappearance of B is twice that of A, while the rate of appearance of C is three times the rate of disappearance of A.

A second method of expressing the rate is in terms of the concentration of any reactant or of any product of reaction. If a reactant is chosen the rate will be expressed as the rate of decrease of the concentration of this reactant; if a product is chosen the rate is rate of increase of the concentration of this substance. Thus, if a reactant is at a concentration c at time t the rate is $-dc/dt$; if a product has a concentration x at time t the rate is similarly dx/dt. Rates so expressed may be in moles per liter per second, molecules per cc per second, and so forth.

A third method, which is sometimes used for expressing rates, is in terms of pressures of reactants or product. Thus, if p is the pressure of a reactant at time t the rate is $-dp/dt$; if p' is the pressure of a product the rate is dp'/dt. Various units may be used for the pressure, and rates may be in atmospheres per second, millimeter of mercury per second, etc. In using concentration and pressure units it is again important to specify what reactant or product is being considered.

The rates expressed in these three different methods are all related. In the case of ideal gases, pressures are related to concentrations by the equation $p = cRT$ so that, at constant temperature, dp/dt is related to dc/dt by the constant factor RT. Since concentrations are related to numbers of moles by the equation $c = n/V$, where V is the volume of the system, it also follows that at constant volume dc/dt is related to dn/dt by the constant factor $1/V$.

In most fundamental kinetic studies the temperature of the system is maintained constant, but many investigations are made in which the volume is not constant. For example, reactions are sometimes studied statically in a reaction vessel in which the pressure, and not the volume, is maintained constant, and if the reaction involves a change in the number of molecules the total volume will then change. Reactions are also frequently studied in flow systems in which the pressure is constant, and in which the volume of gas passing through a given cross-sectional area of the reactor may therefore be variable.

If the volume is not constant some of the change in concentrations or partial pressures of reactants or products is caused not directly by the reaction itself, but by the change in volume. The rate in concentration units, $-dc/dt$, is equal to $-d(n/V)/dt$, which is not now related to $-dn/dt$ by any simple factor.

Order of Reaction: Systems of Constant Volume

Many kinetic investigations are carried out under constant volume conditions, and then the kinetic laws assume a particularly simple form. In such cases it is customary and convenient to express rates using concentration or pressure units (i.e., as $-dc/dt$ or $-dp/dt$ rather than as $-dn/dt$), and this will be done in the present treatment; in a later section (p. 124) a discussion is given of the modifications required when systems of variable volume are employed.

Order of a Surface Reaction

The rate of a surface reaction sometimes varies with the concentrations of the reactants in a particularly simple manner, and in this case the kinetics are specified by stating the *order* of the reaction; thus a reaction whose rate depends solely on the first power of the concentration or pressure of one reactant is said to be of the first order; if the rate is proportional to the product of two reactant concentrations it is of the second order. In general, if the rate is related to the reactant concentrations c_A, c_B, etc., by an equation of the form

$$-\frac{dc}{dt} = kc_A^{\alpha}c_B^{\beta}\cdot\cdots\cdot \tag{1}$$

where α, β, $\cdots$, are constants, the reaction is said to be of the α-th order with respect to A, the β-th with respect to B, and so forth. The over-all order n of such a reaction would be

$$n = \alpha + \beta + \cdots . \tag{2}$$

A number of reactions which show this simple type of behavior are known, and will be considered later; one or two examples may be referred to here briefly. The decomposition of hydrogen iodide on platinum[1] is a first order reaction under certain conditions, obeying the law

$$-\frac{dp}{dt} = kp \tag{3}$$

where p is the pressure of hydrogen iodide at any time. The decomposition of ammonia on tungsten[2] is a well-known example of a zero-order reaction, the rate under some conditions being independent of the ammonia pressure, i.e.,

$$-\frac{dp}{dt} = k \tag{4}$$

The reaction between ethylene and hydrogen on copper[3] is sometimes a second order reaction, the rate being proportional to the first power of the pressures both of ethylene and hydrogen,

$$-\frac{dp_{C_2H_4}}{dt} = kp_{C_2H_4}p_{H_2} \tag{5}$$

It must be emphasized that a great many reactions do not show such simple behavior, and cannot be said to have a simple order. Thus the exchange reaction between ammonia and deuterium on an activated iron surface[4] approximately obeys the law

$$-\frac{dp_{NH_3}}{dt} = \frac{kp_{D_2}{}^{1/2}p_{NH_3}}{(1 + k'p_{NH_3})^2} \tag{6}$$

where k and k' are constants at a given temperature. This reaction may be said to be of the one-half order with respect to deuterium, but it has no order with respect to ammonia (except in certain special cases which will be considered later). Clearly no over-all order can be assigned to this reaction.

Rate Constant for a Surface Reaction

The term *rate constant*, which is also known as the *rate coefficient* and as the *specific reaction rate*, is applied to the constant k in Eq. (1), and is best reserved for reactions having a simple order. The rate constant is numerically equal to the reaction rate when the reactants are present at unit concentrations. The units of the rate constants depend upon those employed for the concentration or pressure; thus if moles per liter are used, the constant has the units (moles per liter)/(sec) (moles per liter)^n, where n, equal to $\alpha + \beta + \cdots$, is the over-all order; this reduces to

$$\text{mole}^{1-n}\ \text{liter}^{n-1}\ \text{sec}^{-1}$$

The units for various simple orders are given in Table 1, for both concentration and pressure units.

Analysis of Experimental Data

The question of how the experimental kinetic data are analyzed in order to determine the order and the rate constants will not be discussed here in any detail, since this subject has been treated fully in various texts[5]. The commonest method is that of integration, according to which the amounts of reactant or product at various times are fitted to integrated forms of the rate equations. The integrated equations for various simple and useful cases are given in Table 2, in which a represents the initial amount of reactant, and x the amount of product at time t.

Other methods which are used are the half-period method, the differential method and the isolation method. The differential method is particularly valuable for the treatment of reactions that do not have a simple order.

TABLE 1. UNITS OF THE RATE CONSTANT

Order	Units		
	Concentrations units (moles/liter)	Pressure units	
		(mm)	(atm)
0	Moles liter^{-1} sec^{-1}	mm sec^{-1}	atm sec^{-1}
$\frac{1}{2}$	Moles$^{1/2}$ liter$^{-1/2}$ sec^{-1}	mm$^{1/2}$ sec^{-1}	atm$^{1/2}$ sec^{-1}
1	Sec^{-1}	Sec^{-1}	Sec^{-1}
$\frac{3}{2}$	Liter$^{1/2}$ mole$^{-1/2}$ sec^{-1}	mm$^{-1/2}$ sec^{-1}	atm$^{-1/2}$ sec^{-1}
2	Liter mole^{-1} sec^{-1}	mm^{-1} sec^{-1}	atm^{-1} sec^{-1}
3	Liter^{2} mole^{-2} sec^{-1}	mm^{-2} sec^{-1}	atm^{-2} sec^{-1}

TABLE 2. SUMMARY OF RATE EQUATIONS

Order	Differential form	Rate equation Integrated form
0	$\frac{dx}{dt} = k$	$k = \frac{x}{t}$
$\frac{1}{2}$	$\frac{dx}{dt} = k(a - x)^{1/2}$	$k = \frac{2}{t}[a^{1/2} - (a - x)^{1/2}]$
1	$\frac{dx}{dt} = k(a - x)$	$k = \frac{1}{t} \ln \frac{a}{a - x}$
$\frac{3}{2}$	$\frac{dx}{dt} = k(a - x)^{3/2}$	$k = \frac{2}{t}\left[\frac{1}{(a - x)^{1/2}} - \frac{1}{a^{1/2}}\right]$
2	$\frac{dx}{dt} = k(a - x)^{2}$	$k = \frac{x}{ta(a - x)}$

Dependence of Rates on Surface Area and Gas Volume

The rate of a surface reaction, and hence the rate constant also, is dependent on the area of the catalyst surface, and on the total gas volume. It is usually, although not invariably, the case that the number of molecules reacting per second is proportional to the surface area of the catalyst. Thus, if the amount of catalyst, and hence the surface area, is increased tenfold, the number of molecules transformed per second is increased tenfold; if the volume is the same in both experiments this means that the number of moles per liter per second, i.e., the rate, is increased tenfold. If the total volume of the reaction system is increased, however, the molecules transformed are distributed over the larger volume, and the rate is therefore reduced in inverse proportion to the volume; one can therefore write

$$-\frac{dc}{dt} = (k'S/V)c_A^{\alpha}c_B^{\beta}\cdots \tag{7}$$

where V is the total volume. Since, whatever the order of reaction, the rate constant is proportional to the rate, the ordinary rate constant k may be written as

$$k = k'S/V \tag{8}$$

For certain purposes it is convenient to define a new rate constant k', which is equal to kV/S, and which, unlike k, is independent of the gas volume and the surface area of the catalyst. However, this is rarely employed in practice, since the surface area is seldom known precisely.

Kinetic Laws when the Volume is Variable[6]

The relationships that have been discussed up to the present stage are not applicable if the volume of the reaction system is not constant. The chief importance of considering the case of variable volume stems from the fact that reactions are sometimes studied using the flow method, in which the gases are streamed through the reaction vessel. Under these conditions, the reaction occurs at constant pressure. The time of contact depends upon the volume of gas passing a given point in unit time, but if the reaction involves a change in the total number of molecules this volume varies through the vessel owing to the progress of the reaction. Consequently, it is not permissible to apply the equations previously given.

The case of a homogeneous, first-order gas reaction will be considered first. First-order reactions proceed by a mechanism[7] involving the initial activation of molecules by collision, a process which is followed by the reaction (decomposition or isomerization) of the activated molecules. According to statistical theory a certain fraction of the original number, n, of molecules of reactant are in the necessary activated state, and of this number a certain fraction undergo further reaction in unit time. It is therefore clear that the correct first-order rate law is

$$-\frac{dn}{dt} = kn \tag{8.1}$$

where n is either the number of molecules or the number of moles of reactant. In the special case of constant volume this equation is equivalent to

$$-\frac{dc}{dt} = kc \tag{8.2}$$

since $c = n/V$. If the volume is variable, however, Eq. (8.1) must be used, and Eq. (8.2) is not applicable. The difference between the two equations is conveniently seen in their integrated forms, which are

$$kt = \ln \frac{n'}{n} \tag{8.3}$$

and

$$kt = \ln \frac{c'}{c} = \ln \frac{n'}{n} \frac{V}{V'} \tag{8.4}$$

where the primes represent the conditions at zero time. If the k of Eq. (8.3) is truly constant, that of Eq. (8.4) will vary by the factor ln (V/V') during the course of reaction. In the case of a reaction $A \longrightarrow \nu B$ occuring at constant pressure, for example, V/V' varies from unity at $t = 0$ to ν at $t = \infty$; the "constant" k of Eq. (8.4) will therefore vary by the factor ln ν during the course of the entire reaction.

A further extension of the argument is required for the case of first-order gas reaction which is catalyzed by a solid surface; Eq. (8.1) is no longer applicable to this situation. The correct rate law for the case of variable volume may be obtained by considering the mechanisms of such processes. A surface reaction is of the first order either because (a) the velocity is controlled by the number of collisions of reactant molecules with the surface, or because (b) the velocity is controlled by the reaction of molecules sparsely adsorbed on the surface. In (a) the number of moles reacting in unit time is proportional to the number of molecules colliding with the surface, which is proportional to cS, where c is the concentration and S the surface area. In (b) the rate is proportional to the amount of gas adsorbed, and this is again proportional to cS. In either case the correct rate law is therefore

$$-\frac{dn}{dt} = k'Sc = \frac{k'S}{V} n \tag{8.5}$$

The correct rate law to use in the general case is best determined by considering the equilibrium between a surface reaction of the $\alpha + \beta \cdots$ order from left to right and of the first order from right to left. The rate from left to right may be written as

$$-\frac{dn_A}{dt} = kf(V, S)c_A^\alpha c_B^\beta \cdots. \tag{8.6}$$

where $f(V, S)$ is a function to be determined. The rate law for the first order reaction from right to left has been seen [Eq. (8.5)] to be

$$-\frac{dn}{dt} = k'Sc \tag{8.7}$$

At equilibrium these rates are equal, so that

$$\frac{c_A^\alpha c_B^\beta \cdots}{c} = \frac{k'S}{kf(V, S)} \tag{8.8}$$

Since the equilibrium constant is independent of V and S it follows that $f(V, S) = S$, so that the correct rate law for the general case is*

$$-\frac{dn_A}{dt} = kSc_A^\alpha c_B^\beta \cdots. \tag{8.9}$$

At constant volume, when $dn_A = Vdc_A$, this is seen to reduce the equation to the form of Eq. (7).

Reactions in Flow Systems[8]

The equations developed in the preceding section are particularly useful in analyzing the results of flow experiments. The principle of such methods is that the gas or mixture of gases is led at a known rate of flow through a reaction vessel, which may contain a contact catalyst. The issuing gases are analyzed in order to determine the amount of reaction occurring in the vessel. From the volume of the reaction vessel and the rate of flow it is possible to calculate the mean time spent by the reaction mixture in the vessel; the order of reaction can be determined by varying the rate of flow through the vessel and the concentrations of the entering gases.

The methods of calculating rate constants from the results of flow experiment will be indicated only briefly. The simplest situation is when there is no change in the number of molecules during reaction; in this case the volume of gas passing a given point in the reaction vessel is the same at all points, so that the volume rate of flow is constant. If this rate of flow, i.e., the volume of gas passing a given point per second, is denoted by V, the time that the gas resides in a small element dV_0 of the reaction vessel is given by

$$dt = dV_0/V \tag{8.10}$$

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* For the case of a *homogeneous* reaction it can similarly be shown, using Eq. (8.1), that the general rate equation is $-dn_A/dt = kVc_A^\alpha c_B^\beta \cdots$; this reduces to Eq. (1) if the volume is constant.

If the reaction is a first-order one, the kinetic equation is Eq. (8.5), so that

$$-\frac{dn}{[n]} = \frac{k'S}{V^2}\,dV_0 \tag{8.11}$$

This integrates to

$$\ln\frac{n_i}{n_f} = \frac{k'SV_0}{V^2} \tag{8.12}$$

where V_0 is the total reaction volume and n_i and n_f are the initial and final numbers of moles of reactant. The rate constant k' can therefore be calculated if n_i, n_f, V_0, V and S are determined; if, as is frequently the case, S is not known one must be content with calculating the quantity $k'S$. Reactions of higher order can be treated similarly.

If the reaction involves a change in the total number of molecules two procedures may be used. The first, which is simple but approximate, involves using Eq. (8.12) and for V taking the average of the rates of flow of the entering and exit gases. The second and exact procedure for the case of the first-order reaction $A \rightarrow \nu B$ is as follows. Suppose that the gas entering the reaction vessel per second occupies the volume V_i and is composed of n' moles of A and B. The volume of gas passing any given point in unit time is then

$$V = V_i\,[\nu - (\nu - 1)n/n'] \tag{8.13}$$

and in addition Eq. (8.10) holds. These values of dt and V may be substituted into Eq. (8.11), and the result of integration is

$$\frac{k'SV_0}{V_i^2} = \nu^2 \ln\frac{n_i}{n_f} - 2\nu(\nu - 1)\left(1 - \frac{n_f}{n_i}\right) + \frac{(\nu - 1)^2}{2}\left(1 - \frac{n_f^2}{n_i^2}\right) \tag{8.14}$$

Similar procedures are applicable to reactions of higher order.

MECHANISM OF SURFACE CATALYSIS

The foregoing discussion has been concerned with the purely experimental aspects of surface reactions—that is, with the phenomenological laws which are obeyed. Consideration must now be given to the question of how these laws may be interpreted in terms of the molecular mechanisms by which surface reactions occur. The only successful explanation of the behavior has been in terms of the theory that adsorption of reactant molecules must occur, and that reaction occurs in the adsorbed films; such a view was first proposed by Faraday in 1825. It was for a time thought that the main effect of the catalyst was to concentrate the reactant molecules and thus increase their chance of reaction. That this is not generally true is, however, shown by the fact that in certain cases different surfaces give rise to different products of reaction from the same reactants, a result which clearly indicates that specific chemical forces are involved.

The subject of chemisorption was treated in detail in Chapter 3, and it is now necessary to see to what extent the kinetic laws for surface reactions are related to the adsorption laws. It has been seen that the simplest treatment of adsorption involves the assumptions that surfaces are smooth and that there are no interactions between adsorbed molecules. These simple assumptions will be made, and it will be seen that on the basis of these a simple and reasonably satisfactory qualitative interpretation of surface kinetics can be given. In the first part of Chapter 5 moreover, it will be shown that absolute rates can even be calculated, to within an order of magnitude, using these assumptions.

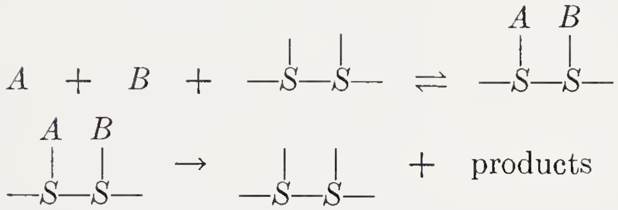
The application of the more exact adsorption laws, taking account of surface inhomogeneity and interactions, is much more difficult, and not too much progress has yet been made along these lines. Some indications of what progress has been made will be found on pages 182 and 188.

Diffusion Theory of Surface Catalysis

In order for a reaction to occur on a surface it is necessary for the reactant molecules to diffuse to the surface and for the product molecules to diffuse away. At one time one of these processes was considered the slowest, and therefore the rate-determining step in the reaction. This, however, generally is not the case, and is certainly not so when nonporous catalysts are employed. In order for diffusion to be the slow step on such surfaces it would be necessary for the diffusion layer to be very thick and, in fact, to be a visible layer. When certain technical catalysts of a porous nature are used[9], however, there is no doubt that diffusion may be the slow and rate-controlling step. The influence of porosity is treated in detail in Chapter 6.

Langmuir's Treatment of Surface Catalysis

Adsorption and desorption processes both involve appreciable energies of activation, and may therefore be the slow processes in surface catalysis. The actual chemical transformation on the surface may also be the slow step. In a classical paper Langmuir[10] considered a number of precise mechanisms for catalysis, and one type of mechanism was later applied, particularly by Hinshelwood[11], to a large number of reactions and was shown to offer an acceptable interpretation of these reactions. According to this type of mechanism, which will be referred to as a Langmuir-Hinshelwood mechanism, the reactant or reactants are considered to be in adsorptive equilibrium with the surface, and reaction then involves the adsorbed molecules. The quantitative treatment of reactions occurring by this mechanism therefore involves obtaining an expression, using the adsorption isotherms, for the concentrations of reactant molecules on the surface, and then expressing the rate of reaction in terms of these surface concentrations; the rate of reaction can then be expressed in terms of the concentrations of gaseous reactants. If there is a single reactant the surface process is probably a simple unimolecular reaction; if there are two, *A* and *B*, these must be adsorbed on neighboring surface sites for reaction to occur, and the probability that this occurs is proportional to the individual concentrations of adsorbed *A* and adsorbed *B*. For such a reaction between *A* and *B* the process may be formulated as



(1)

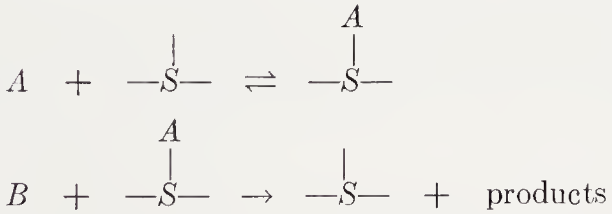
$$A + B + -\overset{|}{S}-\overset{|}{S}- \rightleftharpoons -\overset{\overset{A}{|}}{S}-\overset{\overset{B}{|}}{S}-$$

(2)

$$-\overset{\overset{A}{|}}{S}-\overset{\overset{B}{|}}{S}- \rightarrow -\overset{|}{S}-\overset{|}{S}- + \text{products}$$

Here reaction (1) is the process of adsorption, while (2) is the reaction itself. In the Langmuir-Hinshelwood formulation the concentration of adsorbed molecules would be calculated by considering the adsorption equilibria alone, neglecting the reaction of the adsorbed molecules [reaction (2)]. This implies that the adsorption equilibrium is established rapidly in comparison with reaction (2). If this assumption is not made, as on p. 131, the resulting kinetic law is somewhat different from that in which the equilibrium assumption is made.

Another type of mechanism for surface reactions, particularly applicable to reactions between two species, *A* and *B*, was also considered by Langmuir[10]. According to this mechanism only one reacting substance has to be adsorbed, since the reaction occurs between a gas molecule and an adsorbed molecule. Such a process may be represented as follows:



(1)

$$A + -\overset{|}{S}- \rightleftharpoons -\overset{\overset{A}{|}}{S}-$$

(2)

$$B + -\overset{\overset{A}{|}}{S}- \rightarrow -\overset{|}{S}- + \text{products}$$

In this case substance *A* is adsorbed in process (1), and adsorbed *A* reacts with gaseous *B* in reaction (2). It is not necessarily true that *B* is not at all adsorbed; however, it is postulated that adsorbed *B* does not react with adsorbed *A*. It appears, as will be seen later, that this type of mechanism is not of very general applicability. Interest in these mechanisms has recently been revived by Rideal[12], who has suggested that they apply to certain reactions involving hydrogen; the most recent work has, however, indicated that this is probably not the case[13]. This second type of mechanism, in which a gas molecule reacts with an adsorbed molecule, is now usually referred to as a Rideal mechanism.

Molecularity of Surface Reactions

In connection with the mechanisms of reactions of all types, including surface reactions, an important concept is the number of reactant molecules which come together during the course of reaction. This number is known as the *molecularity* of the reaction, and a reaction is said to be unimolecular, bimolecular, trimolecular, etc., depending on whether one, two or three molecules come together and react.

In the case of elementary homogeneous gas reactions there is usually a quite simple correspondence between the over-all order of the reaction and the molecularity. With surface reactions, on the other hand, the situation is a good deal more complex; in general the molecularity can only be deduced from the order on the basis of theoretical interpretation, about which there is frequently some uncertainty. The actual relationships between molecularity and order will be made clear in the following sections, in which reactions are classified according to their molecularity. One or two examples will be referred to here briefly. Reactions involving a single reacting substance, e.g., decompositions, are usually, but not invariably, unimolecular. Thus the mechanism of the decomposition of ammonia on most surfaces (p. 138) involves the reaction of single adsorbed ammonia molecules, and the reactions are therefore unimolecular. On the other hand, the kinetics of the decomposition of acetaldehyde on various surfaces[14] can only be interpreted on the hypothesis that two neighboring adsorbed acetaldehyde molecules undergo a bimolecular reaction. Reactions involving two reacting substances, such as the reaction between nitric oxide and oxygen on glass[15], are usually bimolecular. When dissociation of reactants occurs on the surface the reaction may involve interaction between an atom or radical and a molecule; for example, the exchange reaction between ammonia and deuterium on iron[16] must be regarded as a bimolecular interaction between a deuterium atom and an ammonia molecule.

KINETIC LAWS FOR UNIMOLECULAR REACTIONS

This section and the following two are concerned with the deduction of the kinetic laws for various mechanisms of surface reactions. Reactions are classified according to whether they are unimolecular or bimolecular (surface reactions of higher molecularity are not known), and the case of retardation by poisons is also considered.

If the reaction on the surface involves one molecule of a single reactant, the rate can be formulated in terms of the adsorption isotherm. According to the Langmuir-Hinshelwood hypothesis the adsorption equilibrium can be regarded as undisturbed by the occurrence of the reaction, and if the Langmuir isotherm is used the fraction of surface covered is therefore related to the pressure according to the equation

$$\theta = \frac{Kp}{1 + Kp} \tag{9}$$

The rate of reaction is proportional to θ and may therefore be written as

$$v = k_2\theta \tag{10}$$

$$= \frac{k_2Kp}{1 + Kp} \tag{11}$$

where k_2 is the proportionality constant.

If the assumption of adsorption equilibrium is not made, i.e., if it is not assumed that equilibrium is established much more rapidly than the reaction occurs, the steady state treatment must be employed[17]. The processes are formulated as

(1) $$G + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} G\text{—}S$$

(2) $$G\text{—}S \xrightarrow{k_2} \text{products}$$

where G is a gas molecule, S is a surface site, $G-S$ is a molecule adsorbed on the surface, and k_1 , k_{-1} and k_2 are the rate constants for adsorption, desorption and reaction, respectively. According to the steady-state hypothesis the concentration of adsorbed species is invariant in time; i.e., $d\theta/dt = 0$. The species $G-S$ is produced by the adsorption process, the rate of which is equal to $k_1p(1 - \theta)$ and is removed by desorption at the rate $k_{-1}\theta$ and by reaction, the rate of which is $k_2\theta$. Hence

$$\frac{d\theta}{dt} = k_1p(1 - \theta) - k_{-1}\theta - k_2\theta = 0 \tag{12}$$

so that

$$\frac{\theta}{1 - \theta} = \frac{k_1}{k_{-1} + k_2}\,p \tag{13}$$

or

$$\theta = \frac{k_1 p}{k_{-1} + k_2 + k_1 p}. \tag{14}$$

This is of the same form as Eq. (9) to which it reduces if $k_{-1} \gg k_2$, i.e., if desorption occurs much more rapidly than reaction. Equation (11) may be employed as the rate equation in the general case, if K is taken to be $k_1/(k_{-1} + k_2)$ rather than as k_1/k_{-1}. In most discussions of surface catalysis it is, however, tacitly assumed that the equilibrium case applies, i.e., that $k_{-1} \gg k_2$, although there is seldom any evidence for this.

Case I. Sparsely Covered Surface

If the pressure is sufficiently low the term Kp in Eq. (11) can be neglected in comparison with unity, and the rate equation becomes

$$v = k_2 Kp \tag{15}$$

If this type of law is obeyed, and there are no complicating features (such as inhibition by products), the partial pressure of the reacting gas changes in accordance with the equation

$$-\frac{dp}{dt} = Kp \tag{16}$$

This equation integrates to

$$\ln \frac{p_0}{p} = kt \tag{17}$$

where p_0 is the initial pressure. This equation may be written as

$$\frac{p_0}{p} = e^{kt} \tag{18}$$

or

$$p = p_0 e^{-kt} \tag{19}$$

The partial pressure thus falls exponentially with time.

Case II. Fully Covered Surface

If the pressure is sufficiently high the term Kp in Eq. (11) is large compared with unity, and the rate expression becomes

$$v = k_2 \tag{20}$$

i.e., the kinetics are of zero order. This case corresponds to a surface which is fully covered by adsorbed molecules, and the rate of the over-all reaction is equal to the rate of decomposition of the adsorbed molecules. This rate equation may be written as

$$-\frac{dp}{dt} = k \tag{21}$$

which integrates to

$$p = p_0 - kt \tag{22}$$

The partial pressure of the reactant thus falls linearly with the time.

Poisoning of Unimolecular Surface Reactions

Any substance which is adsorbed on a catalytic surface reduces the area of the surface available for reaction, and thus reduces the rate of reaction; it is therefore known as a *poison* or an *inhibitor.* In particular the product of a reaction may be adsorbed, thus inhibiting the reaction and at the same time modifying the kinetic laws. Various special cases of inhibition will now be considered.

Suppose that a substance A is undergoing a unimolecular reaction on a surface, and that a nonreacting substance is also adsorbed. If the fraction of surface covered by A is θ, and that covered by the poison is θ_p, the adsorption isotherms are as found on p. 92,

$$\frac{\theta}{1 - \theta - \theta_p} = Kp \tag{23}$$

$$\frac{\theta_p}{1 - \theta - \theta_p} = K_p p_p \tag{24}$$

where p_p is the partial pressure of the poison. Solution of these equations gives

$$\theta = \frac{Kp}{1 + Kp + K_p p_p} \tag{25}$$

for θ, and the rate of reaction is therefore

$$v = k_2 \theta \tag{26}$$

$$= \frac{k_2 Kp}{1 + Kp + K_p p_p} \tag{27}$$

The rate of reaction in the absence of the inhibitor is

$$v_0 = \frac{k_2Kp}{1 + Kp} \tag{28}$$

so that the ratio of the rates of inhibited to uninhibited reactions is

$$\frac{v}{v_0} = \frac{1 + Kp}{1 + Kp + K_pp_p} \tag{29}$$

A case of special interest is when the pressure of the reactant is sufficiently low that the available surface is only sparsely covered by the reactant. The term Kp is then negligible in comparison with $1 + K_pp_p$, and the rate of the inhibited reaction is

$$v = \frac{k_2Kp}{1 + K_pp_p} \tag{30}$$

The ratio of v to v_0 in this case is simply

$$\frac{v}{v_0} = \frac{1}{1 + K_pp_p} \tag{31}$$

If the inhibitor is strongly adsorbed the term K_pp_p is large compared with unity, so that the rate of the inhibited reaction is

$$v = \frac{k_2Kp}{K_pp_p} \tag{32}$$

and in this case

$$\frac{v}{v_0} = \frac{1}{K_pp_p} \tag{33}$$

A special case of Eq. (30) is when the product of a unimolecular first-order reaction is an inhibitor. If a is the original concentration or pressure of the reactant, and x is the amount transformed at time t, then p is proportional to a $- x$ and p_p is proportional to x. The rate equation therefore takes the form

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + bx} \tag{34}$$

where k and b are constants. This equation integrates to

$$kt = (1 + ab) \ln \frac{a}{a - x} - \frac{bx}{t} \tag{35}$$

Such an equation has been found to be obeyed by the decomposition of nitrous oxide on the surface of platinum, a reaction that is poisoned by the oxygen produced (p. 147).

If the surface is strongly poisoned by the product, Eq. (34) reduces to the form

$$\frac{dx}{dt} = \frac{k(a - x)}{x} \tag{36}$$

and this integrates to

$$kt = a \ln \frac{a}{a - x} - \frac{x}{t} \tag{37}$$

This law is obeyed by the decomposition of ammonia on platinum, which is inhibited by the hydrogen produced in the reaction (p. 139).

Activation Energies in Unimolecular Surface Reactions[18]

The rate constant k of any elementary process varies with the temperature according to the Arrhenius law, which may be expressed as

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{38}$$

where E is the energy of activation of the reaction; it was interpreted by Arrhenius as the energy that the reactant molecules had to acquire in order to react. The Arrhenius law is strictly applicable only to elementary processes (i.e., processes occurring in a single stage) such as an adsorption process or the reaction of an adsorbed substance. It is not necessarily applicable to over-all surface reactions, which involve both adsorption and reaction. However, the data for a surface reaction may be analyzed in terms of the Arrhenius law by proceeding in the following manner.

It has been seen [Eq. (11)] that the rate law for a unimolecular reaction on a surface takes the form

$$v = \frac{k_2 Kp}{1 + Kp} \tag{39}$$

The Arrhenius law applies to the rate constant k_2, which is the rate constant for the reaction of the adsorbed reactant molecules. The temperature variation of the equilibrium constant K follows the analogous law

$$\frac{d \ln K}{dT} = -\frac{\lambda}{RT^2} \tag{40}$$

where λ is the heat evolved per mole of reactant gas in the adsorption process. The temperature dependence of the rate may now be considered with reference to the two limiting cases.

If the pressure is low the rate is given by

$$v = k_2Kp, \tag{41}$$

so that the first-order rate constant k' is given by

$$k' = k_2K \tag{42}$$

From Eqs. (41) and (42) it follows that

$$\frac{d \ln v}{dT} = \frac{d \ln k'}{dT} = \frac{d \ln k_2}{dT} + \frac{d \ln K}{dT} \tag{43}$$

$$= \frac{E - \lambda}{RT^2} \tag{44}$$

The activation energy associated with k' or v, which may be called the apparent activation energy E_a, is therefore given by

$$E_a = E - \lambda \tag{45}$$

The apparent activation energy in this case is the "true" activation energy E reduced by the heat of adsorption of the reactant.

If the pressure is sufficiently high

$$v = k_2, \tag{46}$$

and the apparent activation energy is now equal to the true activation energy.

The relationships obtained above may be considered with reference to the potential-energy diagram shown in Figure 1. Reaction first involves the passage of the system over an initial energy barrier to give the adsorbed state, the energy of which is lower by λ than that of the initial state; then the system passes over a second barrier of height E. If the pressure is low, most of the reactant molecules are in the unadsorbed state, and to pass to the activated state they have to acquire only the energy $E - \lambda$. At high pressures, however, the equilibrium favors the adsorbed state, and the system has to acquire the energy E in order to pass to the activated state.

Another case of interest is when the reaction is inhibited by a poison. If the reactant is weakly adsorbed and the poison strongly adsorbed the rate has been seen to be

$$v = \frac{k_2Kp}{K_pp_p} \tag{47}$$

The equilibrium constant K_p varies with the temperature according to

$$\frac{d \ln Kp}{dT} = -\frac{\lambda_p}{RT_2}, \tag{48}$$

where λ_p is the heat of adsorption of the poison. It follows that

$$\frac{d \ln v}{dT} = \frac{d \ln k_2}{dT} + \frac{d \ln K}{dT} - \frac{d \ln K_p}{dT} \tag{49}$$

$$= \frac{E - \lambda + \lambda_p}{RT^2} \tag{50}$$

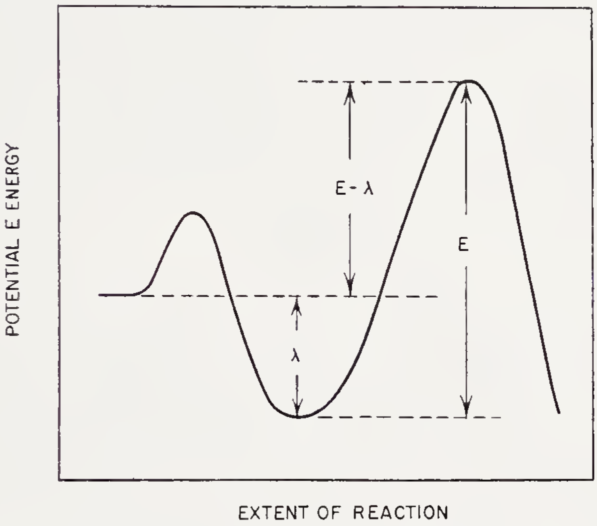


Figure 1. Potential-energy diagram for a unimolecular surface reaction.

The apparent activation energy is thus given by

$$E_a = E - \lambda + \lambda_p \tag{51}$$

The activation energy for the inhibited reaction is thus greater than that for the uninhibited reaction by λ_p, and this is due to the necessity for desorbing a molecule of poison in order for a molecule of reactant to react.

Discussion of Experimental Data on Unimolecular Reactions

In this section the principal experimental data on the kinetics of unimolecular surface reactions are summarized, largely in the form of tables, and are briefly discussed in the light of the general theoretical treatment of surface reactions. A large number of investigations of surface reactions have been carried out. A certain amount of selection has been made by attempting to confine the discussion (here and in the section on bimolecular reactions, p. 151) largely to work which is more or less complete in the kinetic sense, in that the reaction order and the activation energy have been determined; there are a few exceptions to this, however. There are many important papers which are concerned with such questions as the relative efficiencies of different types of catalyst, or with correlating efficiencies with other properties of the catalyst. However, a discussion of this work has not been considered to be within the scope of this chapter.

The information which has been collected for each investigation consists of the nature of the surface, the temperature and pressure ranges used, the rate law (in some cases obeyed only approximately) and the energy of activation. The temperature and pressure ranges quoted are given only to show the general experimental conditions: it is not always possible to be certain as to the exact range, since in some cases it appears that work has been done at temperatures and pressures not specified in the paper. The various rate laws are discussed briefly in this chapter with respect to the general theory of surface catalysis, but a detailed treatment is not given since the mechanisms of many of the reactions considered here are taken up elsewhere in this series.

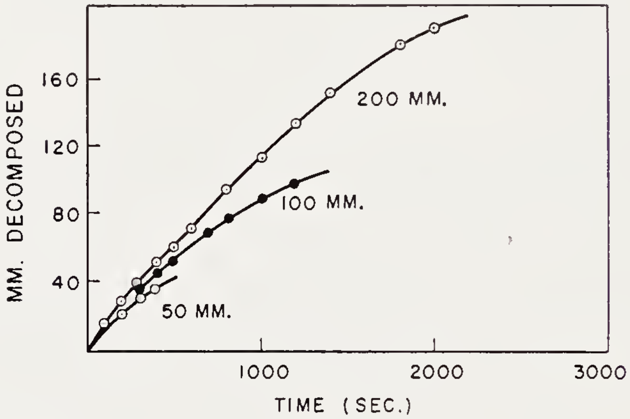


Figure 2. Pressure-time curves for the decomposition of ammonia on tungsten at three different initial pressures (Hinshelwood and Burk[19]).

Decomposition of Ammonia

The first complete study of the kinetics of ammonia decomposition on tungsten and platinum surfaces was made by Hinshelwood and Burk[19]. In their work with tungsten they used a commercial tungsten filament lamp as a reaction vessel. The reaction vessel was kept in melting ice and the filament was heated electrically to a constant temperature which was measured by determining its resistance. The reaction was followed by determining the change in pressure as a function of time.

Some of the results, obtained at 856°C, are plotted in Figure 2. It should be noted that the initial slopes are all the same, in spite of changes in the initial concentration; this indicates that the reaction is of zero order under the conditions of the experiments. The same conclusion is indicated by the fact that the pressure-time curves are linear over the initial range of pressures: deviations from linearity, however, occur at later times, since the kinetics approach first-order behavior at lower ammonia pressures. Application of the half-life method also leads to the conclusion that the reaction is approximately of zero order. Half-lives are proportional to a^{1-n}, where n is the order and a the initial amount of reactant; for a zero-order reaction the predicted ratios for 50-, 100- and 200-mm pressure are 1:2:4. Experimentally the half-lives at those pressures were found to be in the ratio 1:1.92:3.52, in satisfactory agreement. It was found that hydrogen had no inhibiting effect on this reaction. The zero-order kinetics indicate that the surface is fully covered by ammonia.

Hinshelwood and Burk also made a study of the decomposition of ammonia on platinum. In this case the kinetics were found to be of first order in ammonia, but the reaction was inhibited by hydrogen, the rate law being

$$v = \frac{k[\mathrm{NH_3}]}{[\mathrm{H_2}]} \tag{52}$$

Nitrogen had no inhibiting effect.

Subsequent to the investigations of Hinshelwood and Burk a number of workers have made studies of ammonia decomposition on various surfaces. The main results are summarized in Table 3. All of the investigators found that the reaction on tungsten was of zero order, but that there were differences in the activation energies obtained. The reason for this has been considered by Barrer; it is probably not caused by differences in the surfaces, but to errors in the measurement of the surface temperature. Barrer investigated this matter carefully, and his activation energy of 42.4 kcal is probably the most reliable.

The decomposition on platinum was found by several workers to be first-order in ammonia and to be inhibited by hydrogen but not by nitrogen. The very high activation energy found by Hinshelwood and Burk was confirmed by Schwab and Schmidt at higher pressures, but according to them the rate law is much more complicated. On the other hand at low pressures (0.25 – 4 mm) simple kinetics are obtained and the activation energy is now 44.0 kcal. The activation energy at the higher pressures is too high to be attributed to desorption of products, and Schwab[20] suggests that part of the reaction in this region occurs as a chain reaction, the high temperature coefficient being the result of an increase in chain length with an increase of temperature. Alternatively, since a hot filament was used, it is possible that the high value is the result of temperature gradients at the surface (see also p. 151).

The complex kinetic law found by Winter (and later by other workers)

TABLE 3. DECOMPOSITION OF AMMONIA

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	(Activation Energy (kcal)	Ref.
W	631–941	50–200	$v = k[NH_3]^0$	38.7	1
W	810–1300	16–265	$v = k[NH_3]^0$	47.3	2
W	950–1150	7–37	$v = k[NH_3]^0$	26.8–30.1	3
W (ND_3)	630–750	35–150	$v = k[ND_3]^0$	35.0	4
W	950–1180	50–150	$v = k[NH_3]^0$	42.1	5
W	680–880	6×10^{-3}–0.6	$v = k[NH_3]^0$	42.4	6
Pt	933–1215	100–200	$v = \frac{k[NH_3]}{[H_2]}$	140	7
Pt	1050–1160	20–76	$v = \frac{k[NH_3]}{[H_2]}$	—	8
Pt	1100–1485	0.25–4	$v = \frac{k[NH_3]}{[H_2]}$	44.0	9
Pt	1100–1485	10–300	$v = \frac{k[NH_3]^2}{[H_2]^2\{[H_2] + b[NH_3]\}}$	140	10
Mo	824–955	—	$v = k[NH_3]^0$	53.2	11
Mo	725–1125	100	$v = k[NH_3]^0$	31.8–42.7	12
Fe	430–455	—	$v = \frac{k[NH_3]}{[H_2]^{3/2}}$	54.0	13
Fe (1.3% Al_2O_3; 1.59% K_2O)	335–430	—	$v = \frac{k[NH_3]^{0.6}}{[H_2]^{0.85}}$	45.6	14
Os	290–370	50–300	$v = k[NH_3]^0$	47.6	15
Cu	495–620	760	$v = \frac{k[NH_3]}{[H_2]}$	46.0	16
Re	380–440	—	$v = \frac{k[NH_3]^{0.53}}{[H_2]^{0.89}}$	32.2	17
SiO_2	791–1050	75–330	$v = k[NH_3]\{1 - b[H_2]\}$	—	18

TABLE 3—*Continued*

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is a matter of some interest and is discussed theoretically by Temkin and Pyzhev[21]. Winter's original suggestion to explain the form of the law he obtained ($v = k[NH_3]/[H_2]^{1.5}$) is that there is an equilibrium

$$NH_3(\text{gas}) \rightleftharpoons N(\text{ads.}) + 1.5H_2(\text{gas})$$

the adsorption isotherm for which is

$$\frac{\theta}{1-\theta} = \frac{K[NH_3]}{[H_2]^{1.5}} \tag{53}$$

where θ is the fraction of surface covered by nitrogen. If the surface is only sparsely covered by hydrogen atoms this reduces to

$$\theta = \frac{K[NH_3]}{[H_2]^{1.5}} \tag{54}$$

Winter assumes that the nitrogen is liberated into the gas phase by the processes

$$N(\text{ads.}) \rightarrow N(\text{gas})$$

$$2N(\text{gas}) \rightarrow N_2(\text{gas})$$

and that the first of these processes controls the rate. The rate is therefore proportional to θ, and the experimental rate law is explained.

Temkin and Pyzhev, however, point out a serious difficulty with respect to this mechanism. The desorption of nitrogen atoms to give gaseous nitrogen atoms is highly endothermic, and would require considerable activation energy; a simple thermochemical argument in fact shows that the over-all activation energy corresponding to the above mechanism must be at least equal to the heat of the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$ plus one-half the heat of dissociation of nitrogen into atoms. The sum of these two quantities is about 97 kcal, whereas the experimental activation energy is 54 kcal; the mechanism is thus excluded.

It is evidently more reasonable to suppose that the rate of production of nitrogen is controlled by the process

$$2N(\text{ads.}) \rightarrow N_2(\text{gas})$$

but this would require that the rate is proportional to θ^2, and would [assuming Eq. (54) to hold] give rise to the wrong kinetic law. Temkin and Pyzhev avoid this difficulty by supposing that the Langmuir isotherm is not applicable to the system, and instead they use the isotherm of Frumkin and Slygin[22] according to which

$$\theta = \frac{1}{f} \ln a_0 p \tag{55}$$

where f and a_0 are constants. The equations for the rates of adsorption and desorption which correspond to this isotherm are, respectively,

$$v_1 = k_1 p e^{-g\theta} \tag{56}$$

and

$$v_{-1} = k_{-1} e^{h\theta} \tag{57}$$

where k_1 and k_{-1} are the rate constants and g and h are constants.

All of these equations conform with the facts that heats of adsorption and activation energies for desorption decrease with increasing surface coverage, and that activation energies for adsorption increase with surface coverage; these changes, as discussed in Chapter 3, are due to surface heterogeneity, to repulsive interactions between adsorbed molecules, to a combination of these factors, or to other factors not yet fully understood. If it is assumed that the difference between the activation energies for adsorption on two sites is a certain fraction α of the difference between the corresponding heats of adsorption, the constant appearing in Eq. (56) is a fraction α of the constant f in Eq. (55),

$$g = \alpha f \tag{58}$$

Similarly changes in activation energy for desorption may be a fraction β of the corresponding heat changes, so that

$$h = \beta f \tag{59}$$

The fractions α and β are related, since the increase in energy of activation for adsorption, plus the decrease in energy of activation for desorption, must equal the decrease in heat of adsorption; from this it follows that

$$\alpha + \beta = 1 \tag{60}$$

The application of the Frumkin-Slygin equation to Winter's data, as made by Temkin and Pyzhev, is as follows. The gas-phase equilibrium established at the surface is

$$2NH_3 \rightleftharpoons 3H_2 + N_2$$

so that the equilibrium pressure of nitrogen at any time is given by

$$[N_2]_{eq.} = \frac{K'[NH_3]^2}{[H_2]^3} \tag{61}$$

The fraction of surface covered, according to Eq. (55), is thus

$$\theta = \frac{1}{f} \ln a_0 K' \frac{[NH_3]^2}{[H_2]^3} \tag{62}$$

Eq. (57) therefore gives, for the rate of desorption of nitrogen,

$$v_{-1} = k_{-1} \exp\left\{\frac{h}{f} \ln a_0 K' \frac{[NH_3]^2}{[H_2]^3}\right\} \tag{63}$$

$$= k'_{-1} \left(\frac{[NH_3]^2}{[H_2]^3}\right)^{\beta} \tag{64}$$

where k'_{-1} is a new constant. This equation is identical with Winter's equation if β is taken to be one-half, which is an entirely reasonable value. Temkin and Pyzhev further show that their treatment is self-consistent from the thermochemical standpoint.

The high pressure data obtained by Schwab and Schmidt for the decomposition of ammonia on platinum (cf. Table 3) have also been explained by Temkin and Pyzhev in terms of their theory. The rate equation can be written approximately as

$$\frac{k[NH_3]^{1.4}}{[H_2]^{2.3}} \tag{65}$$

and this is almost identical with

$$v = k\left(\frac{[NH_3]^2}{[H_2]^3}\right)^{0.73} \tag{66}$$

The result may therefore be explained with a value of 0.73 for β. McGeer and Taylor have also interpreted their rate law on rhenium (Table 3) in terms of the theory, the rate equation being close to

$$v = k\left(\frac{[NH_3]^2}{[H_2]^3}\right)^{0.28} \tag{67}$$

This treatment of Temkin and Pyzhev is a semi-empirical one, since it employs the empirical equations (56) and (57). More recently Brunauer, Love and Keenan[23] have improved the theory so as to give more significance to the constants g and h which appear in the equations. They find that if the energy of activation for adsorption increases linearly with the fraction covered according to the equation

$$E_1 = E_1^0 + \gamma\theta \tag{67.1}$$

the constant g is related to γ by

$$g = \gamma/RT \tag{67.2}$$

Similarly, if the energy of activation for desorption varies linearly according to

$$E_{-1} = E_{-1}^0 - \delta\theta \tag{67.3}$$

the constant h is given by

$$h = \delta/RT \tag{67.4}$$

The constant β appearing in the Temkin-Pyzhev equation is equal to h/f or to $h/(g + h)$; it is therefore also equal to $\delta/(\gamma + \delta)$. If γ and δ can be determined from an analysis of adsorption data it is thus possible to calculate β.

This procedure was applied by Brunauer, Love and Keenan to the ammonia decomposition on an activated iron catalyst (No. 931). From an analysis of rates of adsorption of nitrogen they found that $\beta = 0.276$; the kinetic law for the ammonia decomposition [cf. Eq. (64)] should therefore be

$$v = \frac{k[NH_3]^{0.55}}{[H_2]^{0.83}} \tag{67.5}$$

This agrees within the experimental error with the rate law obtained by Love and Emmett with this catalyst and given in Table 3.

TABLE 4. DECOMPOSITION OF PHOSPHINE

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Glass	—	—	$v = k[PH_3]$	—	1
Porcelain	845–956	50–260	$v = k[PH_3]$	86.7	2
SiO_2	828–1042	37.5–751	$v = k[PH_3]$	40–50	3
W	360–560	0.01–300	$v = k[PH_3]$	25	4
W	610–720	10^{-3}–10^{-2}	$v = k[PH_3]$	26.5	5
W	610–720	0.2	$v = \frac{k[PH_3]}{1 + b[PH_3]}$	32.0	5
W	610–720	1–5	$v = k[PH_3]^0$	31.3	5
Mo	570–645	~0	$v = k[PH_3]$	15.1	6
Mo	570–645	0.06	$v = \frac{k[PH_3]}{1 + b[PH_3]}$	20.8	6
Mo	570–645	0.20	$v = k[PH_3]^0$	22.3	6

References

1. van't Hoff, J. H., and Kooij, D. M., *Z. physik. Chem.*, **12,** 155 (1893).
2. Trantz, M., and Bhandarkar, D. S., *Z. anorg. Chem.*, **106,** 95 (1919).
3. Hinshelwood, C. N., and Topley, B., *J. Chem. Soc.*, **125,** 393 (1924).
4. Melville, H. W., and Roxburgh, H. L., *J. Chem. Soc.*, **1933,** 586.
5. Barrer, R. M., *Trans. Faraday Soc.*, **32,** 490 (1936).
6. Melville, H. W., and Roxburgh, H. L., *Loc. cit.*

Decomposition of Phosphine

The phosphine decomposition was first investigated by van't Hoff and Kooij[24] on a glass surface. They found that the reaction was of the first order, so that the surface was sparsely covered by phosphine. The data for the reactions are summarized in Table 4. First-order kinetics were also first obtained for the reaction on tungsten, but Barrer[25] made an investigation over a wide range of pressures and found the expected transition from first-order kinetics at low pressures to zero-order at higher ones. The activation energy varies from 26.5 kcal at low pressures to 31.3 at high ones; the difference, 4.8 kcal, should be correlated with the heat of adsorption of phosgene on the surface [Eq. (45)].

A similar change from first-order to zero-order kinetics with increasing pressure was observed on molybdenum by Melville and Roxburgh[26]. The activation energy falls by 7.2 kcal over the pressure range, and this may be approximately the heat of adsorption.

Decompositions of Arsine, Stibine, Selenium Hydride and Methane

The decompositions of other hydrides have been studied in less detail. van't Hoff[27] found the composition of arsine on glass to be a first-order reaction. Stibine decomposes on an antimony surface according to the law[28]

$$v = kp^{0.6} \tag{68}$$

Table 5. Decomposition of Hydrogen Iodide

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Au	530–820	100–400	$v = k[\mathrm{HI}]^0$	25.0	1
Pt	720–950	100–300	$v = k[\mathrm{HI}]$	33.8	2

References

1. Hinshelwood, C. N., and Prichard, C. R., *J. Chem. Soc.*, **127**, 1552 (1925).
2. Hinshelwood, C. N., and Burk, R. E., *J. Chem. Soc.*, **127**, 2896 (1925).

but the data may equally well be fitted to a Langmuir equation of the form of Eq. (11). Selenium hydride decomposes on selenium according to a first-order law[29], as does methane on carbon[30].

Decomposition of Hydrogen Iodide

The data for hydrogen iodide decomposition are summarized in Table 5. Hinshelwood and Burk found a slight inhibition by hydrogen in their work on platinum.

Decomposition of Nitrous Oxide

The decomposition of nitrous oxide on various surfaces has been investigated extensively. The results of studies pertaining to the kinetic laws applicable to this reaction are summarized in Table 6. It will be seen that most of the rate laws found are special cases of the general law

$$v = \frac{k[\mathrm{N_2O}]}{1 + b[\mathrm{N_2O}] + b'[\mathrm{O_2}]} \tag{69}$$

indicating appreciable adsorption of both nitrous oxide and the product oyxgen. The results of Cassel and Glückauf, obtained at low pressures,

TABLE 6. DECOMPOSITION OF N_2O

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Pt (filament)	600–1200	50–400	$v = \frac{k[N_2O]}{1 + b[O_2]}$	32.5	1
Au	830–990	200–400	$v = k[N_2O]$	29.0	2
Var. pure and mxd. oxides	280–730	—	—	24–44	3
Pt (filament)	730–1530	0.1	$v = \frac{k[N_2O](1 + b[O_2]^{1/2})}{1 + b'[O_2]^{1/2}}$	—	4
MgO	800–1200	—	$v = k[N_2O]$	37.1	5
CaO	800–1200	—	$v = k[N_2O]$	34.8	5
SiO	800–1200	—	$v = k[N_2O]$	32.0	5
Al_2O_3	800–1200	—	$v = k[N_2O]$	29.3	5
La_2O_3	—	—	$v = k[N_2O]$	28.0	5
In_2O_3	—	—	$v = \frac{k[N_2O]}{1 + b[O_2]}$	28.5	5
CdO	—	—	$v = \frac{k[N_2O]}{1 + b[O_2]}$	36.6	5
CuO	495–590	—	$v = \frac{k[N_2O]}{1 + b[O_2]}$	27.0	6
CuO-Al_2O_3	505–610	—	$v = \frac{k[N_2O]}{1 + b[O_2]}$	34.0	6
Pt	450–570	7–48	$v = \frac{k[N_2O]}{1 + b[O_2]}$	—	7
Ag	450	50–400	$v = \frac{k[N_2O]}{1 + b[O_2]}$	—	8
Pt	850–875	0–270	$v = \frac{k[N_2O]}{(1 + b[N_2O])(1 + b'[O_2])}$	—	9

References

1. Hinshelwood, C. N., and Prichard, C. R., *J. Chem. Soc.*, **127**, 327 (1925).
2. Hinshelwood, C. N., and Prichard, C. R., *Proc. Roy. Soc.*, **A108**, 211 (1925).

Table 6—*Continued*

3. Schwab, G. M., and Schultes, H., *Z. physik. Chem.*, **B9**, 265 (1930).
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5. Schwab, G. M., Stager, R., and von Baumbach, H. H., *Z. physik. Chem.*, **B21**, 65 (1933).
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8. Steacie, E. W. R., and Folkins, H. O., *Can. J. Research* **B15**, 237 (1937).
9. Miyazaki, S., *J. Chem. Soc.*, (*Japan*), **72**, 723 (1951).

are exceptional in this respect, and indicate that inhibition is brought about by adsorbed oxygen atoms. This discrepancy has been resolved by the work of Schwab and Eberle[31] and of Steacie and McCubbin[32], who showed that oxygen formed in the reaction is more effective at inhibiting the reaction than is added oxygen.

Several other investigations, not directly concerned with the kinetic laws, are worthy of brief comment. Schwab and Schultes[33] studied the activities of a number of mixed oxides. Van Praagh and Topley[34] studied the decomposition on platinum, and found that the activity of the catalyst was very variable. Hedwall *et al.*[35] found that the catalytic effect of nickel on the decomposition changes at the Curie point, and correlated the activity of the catalyst with the paramagnetic properties. Wagner[36] proposed a mechanism for the decomposition of nitrous oxide on metals and oxides involving quasi-free electrons as reactants and adsorbed oxygen ions as intermediate products. He showed that this mechanism was consistent with the observed facts, such as the retardation by oxygen, a fractional order of the reaction with respect to indium oxide as catalyst, and the decrease of the electrical conductivity of zinc oxide in the presence of nitrous oxide. Boudart[37] applied Pauling's theory of metals to the decomposition of nitrous oxide on zinc oxide, and emphasized the importance of electronic structures in connection with the problem of active centers.

Decomposition of Nitric Oxide

The data on the decomposition of nitric oxide on platinum are summarized in Table 7. The results of Green and Hinshelwood and of Zawadzki and Perlinsky are consistent with Eq. (32) on p. 134, but according to Bachman and Taylor the kinetics should be second order with respect to nitric oxide; their own results show this, and in addition they reanalyzed the data of Green and Hinshelwood and concluded that the second-order law is more applicable.

Decomposition of Formic Acid

Hinshelwood and co-workers studied the kinetics of the decomposition of formic acid on a number of surfaces (see Table 8), and found that under the conditions of their experiments the first-order law was always obtained. On glass the reaction proceeds partly as

$$\text{(1)} \qquad HCOOH = CO + H_2O$$

TABLE 7. DECOMPOSITION OF NITRIC OXIDE

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Pt	882–1403	100–500	$v = \frac{k[NO]}{[O_2]}$	14.0	1
Pt	1210	201–479	$v = \frac{k[NO]^2}{[O_2]}$	—	2
Pt-10% Rh	1040–1390	193–477	$v = \frac{k[NO]^2}{[O_2]}$	24.6–26.9	2
Pt	860–1060	—	$v = \frac{k[NO]}{1 + b[O_2]}$	22.0–25.0	3

References

1. Green, G. E., and Hinshelwood, C. N., *J. Chem. Soc.*, **129,** 1709 (1926).
2. Bachman, P. W., and Taylor, G. B., *J. Phys. Chem.*, **33,** 447 (1929).
3. Zawadski, J., and Perlinsky, G., *Compt. rend.*, **198,** 260 (1934).

TABLE 8. DECOMPOSITION OF FORMIC ACID

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Glass	240–300	—	$v = k[HCOOH]$	16.0 (for $CO + H_2O$) 28.0 (for $CO_2 + H_2$)	1
Pt	140–210	—	$v = k[HCOOH]$	22.2 (for $CO_2 + H_2$)	2
Ag	140–250	—	$v = k[HCOOH]$	31.3 (for $CO_2 + H_2$)	2
Rh	160–190	—	$v = k[HCOOH]$	25.0 (for $CO_2 + H_2$)	3
Au	140–190	—	$v = k[HCOOH]$	23.5 (for $CO_2 + H_2$)	3
Pd	—	—	$v = k[HCOOH]$	33.0 (for $CO_2 + H_2$)	3
TiO_2	140–180	—	$v = k[HCOOH]$	29.6 (for $CO + H_2O$)	3

References

1. Hinshelwood, C. N., Hartley, H., and Topley, B., *Proc. Roy. Soc.*, **A100,** 575 (1922).
2. Tingey, H. C., and Hinshelwood, C. N., *J. Chem. Soc.*, **121,** 1668 (1922).
3. Hinshelwood, C. N., and Topley, B., *J. Chem. Soc.*, **123,** 1014 (1923).

and partly as

$$\text{(2)} \qquad HCOOH = CO_2 + H_2 ,$$

and activation energies for both processes were obtained. On various metals reaction (2) was found to predominate, while on titanium dioxide reaction (1) was more important.

In addition to the above studies, G. M. Schwab and his collaborators[38] made extensive investigations of the decomposition of formic acid on a large number of alloy surfaces. Under the conditions of these experiments the kinetics were generally of zero order. Since these studies were largely concerned with the relationship between activity and the nature of the surface they are outside the scope of the present discussion.

Decomposition of Alcohols

Alcohols decompose on surfaces with the splitting off of either hydrogen or water, the former being favored by metallic catalysts and the latter by oxide catalysts. Numerous studies have been made on such reactions, using various alcohols and various surfaces, but most are concerned with specific surface effects and are therefore outside the scope of this review.

Constable[39] studied the kinetics of the dehydrogenation of ethyl alcohol on copper in the presence of water vapor, acetone and benzene, which inhibit the reaction. He found that the rate law is

$$v = \frac{k[C_2H_5OH]}{b[C_2H_5OH] + b'[\text{poison}]} \tag{70}$$

which is evidently a special case of Eq. (27). Other important studies on reactions of this type are those of Dohse[40], Balandin[41] and Schwab[42].

Some Reactions at Hot Filaments

In the reactions already considered there would appear to be no doubt that the processes were actually catalyzed by the surface. Some of these reactions occurred at surfaces which were heated to a higher temperature than the surrounding gas. There are certain other reactions, carried out under the same conditions, for which there is considerable doubt that they are truly catalyzed reactions. These include the decompositions of acetone, dimethyl ether, diethyl ether, and propionaldehyde, all of which have been studied using heated platinum filaments. The activation energies for these reactions, and for the purely homogeneous reactions, are given in Table 9.

In contrast to the reactions discussed earlier, the activation energies for the filament reactions are seen to be equal to or higher than those for the homogeneous reactions. This strongly suggests that the filament reactions are not truly catalyzed but that they occur homogeneously in a layer of gas close to the filament. The cases in which the activation energies for the filament reactions are higher than those for the homogeneous reaction have been explained by Steacie and Reeve[43] on the assumption that the accommodation coefficient of the gas at the surface is less than unity and increases with temperature. Alternatively, the mere fact that there is a steep temperature gradient at the surface may be sufficient to account for this result.

KINETIC LAWS FOR BIMOLECULAR REACTIONS

Interaction Between Two Adsorbed Molecules

It appears that most surface reactions between two substances involve interaction between two adsorbed molecules, the adsorption occurring on neighboring surface sites; this is conveniently known as a Langmuir-Hinshelwood mechanism. The rate of a reaction between *A* and *B* is then proportional to the probability that *A* and *B* molecules are adsorbed on neighboring sites, and this is proportional to the product of the fractions covered by *A* and by *B*. For the case of mixed adsorption these fractions were seen (p. 92) to be given by

TABLE 9. ACTIVATION ENERGIES FOR REACTIONS OCCURRING HOMOGENEOUSLY AND AT HEATED FILAMENTS

Decomposition	Activation Energy (kcal.)		Ref. (for filament study)
	Homogeneous	Filament	
CH_3COCH_3	68.5	68.4	1
CH_3OCH_3	58.5	67.0	2
$C_2H_5OC_2H_5$	53.0	52.0	3
$C_2H_5OC_2H_5$	53.0	57.0 (Pt) 58.0 (W)	4
CH_3CH_2CHO	55.0	96.5	5

References

1. Taylor, H. A., *J. Phys. Chem.*, **33**, 1793 (1929).
2. Steacie, E. W. R., and Reeve, H. A., *J. Phys. Chem.*, **36**, 3074 (1932).
3. Steacie, E. W. R., and Campbell, H. N., *Proc. Roy. Soc.*, **128**, 451 (1930).
4. Taylor, H. A., and Schwartz, M., *J. Phys. Chem.*, **35**, 1044 (1931).
5. Steacie, E. W. R., and Morton, R., *Can. J. Research*, **4**, 582 (1931).

$$\theta = \frac{Kp}{1 + Kp + K'p'} \tag{71}$$

and

$$\theta' = \frac{K'p'}{1 + Kp + K'p'} \tag{72}$$

The rate of the reaction, being proportional to the product of these two fractions, may thus be written as

$$v = k_2\theta\theta' \tag{73}$$

$$= \frac{k_2KK'pp'}{(1 + Kp + K'p')^2} \tag{74}$$

If the pressure p' is kept constant, and p is varied, the rate may be seen to change in accordance with Figure 3; the rate first increases, passes through a maximum, and then decreases. A similar variation with p' is also found. The physical explanation of the falling off of the rate at high pressures is that the more strongly adsorbed reactant displaces the other from the surface as its pressure is increased. It is most convenient to consider a number of special cases of the general Eq. (74).

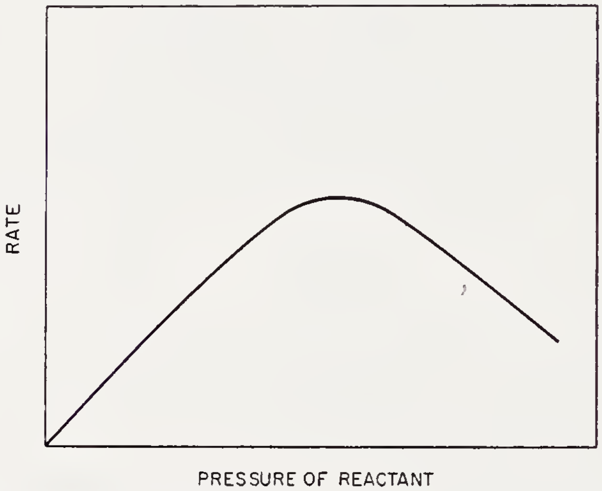


Figure 3. Schematic representation of the variation of rate with the pressure of either reactant in the case of a bimolecular surface reaction proceeding by interaction between the two adsorbed molecules.

Case I: Sparsely Covered Surface. If the pressures p and p' are sufficiently low, the terms Kp and $K'p'$ may both be neglected in comparison with unity, and the rate equation is

$$v = k_2KK'pp' \tag{75}$$

The rate is thus proportional to the product of the two partial pressures, and the reaction can be said to be of the first order with respect to both A and B, and therefore of the second over-all order. If both reactants are present at the initial pressure p_0, and the pressures at time t are p, the rate equation is

$$-\frac{dp}{dt} = kp^2 \tag{76}$$

and this integrates to

$$p = \frac{p_0}{1 + p_0 kt} \tag{77}$$

This equation may be put into the more familiar form

$$\frac{x}{a(a - x)} = kt \tag{78}$$

where a is the initial amount of each reactant and x is the amount of product formed at time t. If the reactants are present at different initial concentrations or pressures a and b the corresponding equation is

$$\frac{1}{a - b} \ln \frac{b(\mathrm{a} - x)}{a(b - x)} = kt \tag{79}$$

A number of reactions obey laws of this type; examples are the reaction between nitric oxide and oxygen on glass (p. 162) and the reaction between ethylene and hydrogen on copper under certain conditions of temperature (p. 168). The decomposition of acetaldehyde on various surfaces (p. 159) is also of this type, and therefore involves bimolecular interaction on the surface.

Case II: One Reactant Very Weakly Adsorbed. If reactant A is weakly adsorbed, the term Kp in the denominator of Eq. (74) may be neglected in comparison with $1 + K'p'$, and the rate equation becomes

$$v = \frac{k_2 K K' p p'}{(1 + K'p')^2} \tag{80}$$

The rate is now proportional to the pressure of A, but as the pressure of B increases the rate first increases, passes through a maximum, and then decreases. Such a maximum in the rate has been observed in the reaction between hydrogen and carbon dioxide on platinum (p. 165), and in the exchange reaction between deuterium and ammonia on an iron surface (p. 172).

If reactant B is sufficiently strongly adsorbed so that $K'p'$ is much greater than unity, the rate equation becomes

$$v = \frac{k_2 K p}{K'p'} \tag{81}$$

The rate is now inversely proportional to the pressure of the strongly adsorbed reactant B. There are several examples of this type of behavior. Under certain conditions the rate of the reaction between carbon monoxide and oxygen on the surfaces of quartz and platinum (p. 161) is directly proportional to the pressure of oxygen and inversely proportional to that of carbon monoxide; the latter is therefore strongly adsorbed, and as its pressure is increased it displaces the oxygen from the surface. Another example is the reaction between hydrogen and oxygen on platinum (p. 160) the rate of which, under certain conditions, is inversely proportional to the hydrogen pressure. Similar behavior is sometimes shown by the reaction between ethylene and hydrogen on copper (p. 168).

Interaction between a Gas Molecule and an Adsorbed Molecule

The foregoing treatment of bimolecular reactions has been in terms of the Langmuir-Hinshelwood type of mechanism, in which reaction occurs between adsorbed species. It was mentioned previously that there is also the possibility that reaction occurs between a gaseous molecule and an adsorbed molecule. The kinetic laws applicable to this will now be considered.

Suppose that reaction occurs between an adsorbed A molecule and a gaseous B molecule. The fraction of surface covered by A is given by Eq. (20) on p. 92 and the rate is now proportional to this fraction and to the pressure p' of B, i.e.,

$$v = k_2 p' \theta \tag{82}$$

$$= \frac{k_2 K p p'}{1 + Kp + K'p'} \tag{83}$$

It should be noted that it is not assumed that B is not at all adsorbed, since the term $K'p'$ in the denominator corresponds to the adsorption of B; adsorbed B molecules do not enter directly into reaction, but they affect the rate by occupying surface which might otherwise be occupied by A. If B is not at all adsorbed the rate equation becomes

$$v = \frac{k_2 K p p'}{1 + Kp} \tag{84}$$

These equations should be contrasted with those for the Langmuir-Hinshelwood mechanism, and it should be noted that there is now no longer any maximum in the rate as the pressure p increases; instead the rate varies with p in the manner shown in Figure 4. A decision between the two types of mechanism may therefore be made by applying the different kinetic laws to the data, and in particular this type of mechanism can be excluded if it can be shown that the rate passes through a maximum as the concentration of a reactant is increased.

It appears that there are few well-defined examples of reactions occurring by such mechanisms. The acetaldehyde decomposition (p. 159) may be of this type, but more detailed study would be desirable. The ammonia-deuterium exchange reaction has been thought to be of this type, but the kinetics on activated iron have been shown (p. 172) to fit the Langmuir-Hinshelwood law, and in particular the rate passes through a maximum as the ammonia pressure is increased. The hydrogenation of ethylene is a somewhat doubtful case, and is discussed in detail later; it has been stated that the rate remains constant over a wide pressure range, but on both copper and nickel maxima have been observed, so that at least under some conditions the Langmuir-Hinshelwood mechanism must apply. The para-ortho-hydrogen conversion (p. 178) was formerly believed to occur as a result of interaction between a gaseous hydrogen molecule and an adsorbed hydrogen atom, but on the whole the evidence is rather against this and appears to favor a mechanism involving interaction between adsorbed hydrogen atoms. The only clear-cut examples of a Rideal mechanism appear to be the surface combinations of atoms and free radicals. These are discussed on p. 180. These reactions almost certainly involve interaction between a gaseous radical *R* and an adsorbed radical;

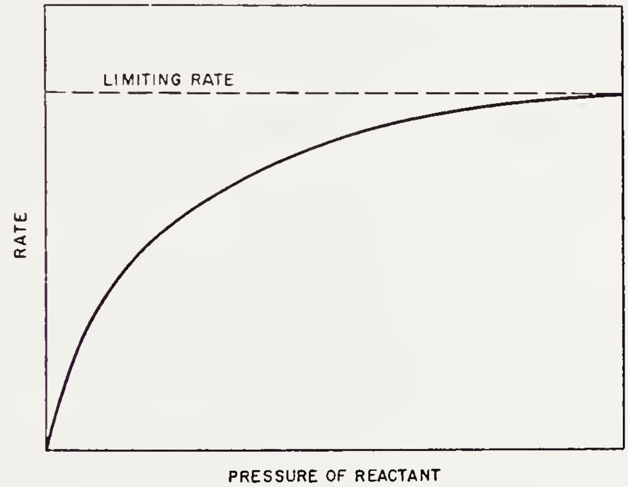
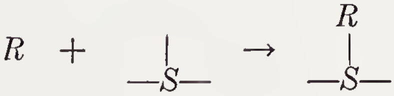


Figure 4. Schematic representation of the variation of rate with the pressure of either reactant in the case of a bimolecular surface reaction proceeding by interaction between an adsorbed molecule and a molecule in the gas phase.

$$R + \overset{R}{\underset{-S-}{|}} \rightarrow \underset{-S-}{|} + R_2$$

a radical subsequently becoming adsorbed on the bare surface site,



$$R + \underset{-S-}{|} \rightarrow \overset{R}{\underset{-S-}{|}}$$

Adsorption of Two Gases without Mutual Displacement

A third possibility, which arises in one or two instances, is that reaction occurs between two adsorbed molecules, but that the two gases are adsorbed on two types of surface site, so that they do not displace one another from the surface. The kinetic law applicable to this case is readily obtained from the Langmuir isotherms for the two types of site. The isotherm for sites of type 1, on which the first gas, at pressure p, is adsorbed, is

$$\frac{\theta}{1-\theta} = Kp \tag{85}$$

Similarly for sites of type 2,

$$\frac{\theta'}{1-\theta'} = K'p' \tag{86}$$

where p' is the pressure of the second gas. The rate is again proportional to $\theta\theta'$, so that

$$v = \frac{k_2KK'pp'}{(1+Kp)(1+K'p')} \tag{87}$$

This equation is seen to be quite different from Eqs. (74) and (83), and the three cases may readily be distinguished provided that rates are measured over a sufficiently wide range of pressure.

Equation (87) has been found to be applicable to the reaction between hydrogen and nitrous oxide on gold (p. 167) and to the reaction between hydrogen and carbon dioxide on tungsten (p. 166).

Inhibition of Bimolecular Surface Reactions

Equations for inhibited reactions proceeding by any of the above three mechanisms may readily be derived. For the Langmuir-Hinshelwood mechanism the adsorption isotherms are now, for A,

$$\frac{\theta}{1-\theta-\theta'-\theta_p} = Kp \tag{88}$$

for B,

$$\frac{\theta'}{1-\theta-\theta'-\theta_p} = K'p' \tag{89}$$

and for the poison,

$$\frac{\theta_p}{1-\theta-\theta'-\theta_p} = K_pp_p \tag{90}$$

Solution of these equations gives

$$\theta = \frac{Kp}{1 + Kp + K'p' + K_p p_p} \tag{91}$$

and

$$\theta' = \frac{K'p'}{1 + Kp + K'p' + K_p p_p} \tag{92}$$

The rate is therefore

$$v = k_2 \theta \theta' \tag{93}$$

$$= \frac{k_2 K K' p p'}{(1 + Kp + K'p' + K_p p_p)^2} \tag{94}$$

In the case that the surface is only sparsely covered by both reactant molecules this equation becomes

$$v = \frac{k_2 K K' p p'}{(1 + K_p p_p)^2} \tag{95}$$

If the poison is strongly adsorbed $K_p p_p$ is very large compared with unity and the rate equation becomes

$$v = \frac{k_2 K K' p p'}{K_p^2 p_p^2} \tag{96}$$

If the two reacting molecules are the same, and their pressure is p, the rate is proportional to p^2/p_p^2. It is of interest that in these cases of bimolecular reaction the inhibitor reduces the rate according to the square of its pressure.

If the inhibitor is a diatomic molecule which is adsorbed atomically, Eq. (90) must be replaced by

$$\frac{\theta_p}{1 - \theta - \theta' - \theta_p} = K_p{}^{1/2} p_p{}^{1/2} \tag{97}$$

and the rate equation then becomes

$$v = \frac{k_2 K K' p p'}{(1 + Kp + K'p' + Kp^{1/2} p_p{}^{1/2})^2} \tag{98}$$

In the case of sparse coverage by reactant molecules and large coverage by inhibitor the equation becomes

$$v = \frac{k K K' p p'}{K_p p_p} \tag{99}$$

The rate is now inversely proportional to the *first* power of the inhibitor pressure. Behavior of this type has been found for the decomposition of nitric oxide on platinum and on a rhodium-platinum surface (p. 148); in both cases, the reaction is inhibited by the product oxygen, which is adsorbed in the atomic form.

If reaction occurs between an adsorbed A molecule and a gaseous B molecule the rate is proportional to θ and to p'; θ is given by Eq. (91) on p. 157 so that the inhibited rate is

$$v = \frac{k_2KK'pp'}{1 + Kp + K'p' + K_pp_p} \tag{100}$$

Examples of this case do not appear to be known.

Finally, if reaction occurs between two adsorbed molecules but there is no mutual displacement the isotherms are

$$\theta = \frac{Kp}{1 + Kp + K_pp_p} \tag{101}$$

and

$$\theta' = \frac{K'p'}{1 + K'p' + K_pp_p} \tag{102}$$

The rate is therefore

$$v = \frac{k_2KK'pp'}{(1 + Kp + K_pp_p)(1 + K'p' + K'_pp_p)} \tag{103}$$

No cases of this appear to have been investigated.

Activation Energies in Bimolecular Surface Reactions

The expressions for the activation energies of bimolecular surface reactions are readily obtained by application of the methods employed on pp. 135 to 137. Details will not be covered here; the results will merely be given.

For the *Langmuir-Hinshelwood mechanisms:*

Case I (sparsely covered surface)

$$E_2 = E - \lambda - \lambda' \tag{104}$$

where E is the "true" activation energy and λ and λ' are the heats of adsorption of the two reactants.

Case II (with reactant B strongly adsorbed)

$$E_a = E - \lambda + \lambda' \tag{105}$$

For the *Rideal mechanisms:*

A weakly adsorbed,

$$E_a = E - \lambda \tag{106}$$

A strongly adsorbed,

$$E_a = E \tag{107}$$

The equations for the various cases of inhibition will be given with respect to the rate equations involved:

Eq. (96):

$$E_a = E - \lambda - \lambda' + 2\lambda_p \tag{108}$$

Eq. (99):

$$E_a = E - \lambda - \lambda' + \lambda_p \tag{109}$$

TABLE 10. DECOMPOSITION OF ACETALDEHYDE

Surface	Temp. Range (°C)	Pressure Range (mm)	Rate Law	Activation Energy (kcal)	Ref.
Pt	960–1200	25–300	$v = k[CH_3CHO]^2$ at lower pressures; $v = k[CH_3CHO]$ at higher pressures; slight retardation by products	42.4	1
Pt-10% Rh	—	—		45–47	1
				49–51	1
Au	—	—			
W	—	100–300		49–50	1

References

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DISCUSSION OF EXPERIMENTAL DATA ON BIMOLECULAR REACTIONS

Decomposition of Acetaldehyde

The results of Allen and Hinshelwood on the decomposition of acetaldehyde into methane and carbon monoxide on various surfaces are summarized in Table 10. Allen and Hinshelwood interpret the rate laws obtained as indicating that there is interaction between an adsorbed molecule and a gas molecule; at low pressures the concentration of adsorbed molecules is proportional to the pressure so that the kinetics are second order; at higher pressures the concentration of adsorbed molecules is independent of pressure and the kinetics are first order. If the reaction involved interaction between two adsorbed molecules the kinetics would become zero order at higher pressures, but the data show no indication of this.

Decomposition of Nitric Oxide

As discussed on p. 148 it is possible that the rate of decomposition of nitric oxide on platinum is proportional to the square of the pressure, in which case the reaction must be classed as a bimolecular one. The data are summarized in Table 7 on p. 149.

Hydrogen-Oxygen Reaction

The reaction between hydrogen and oxygen on various surfaces has been studied extensively. The results of the main investigation which have thrown light on the kinetic laws are summarized in Table 11. It will be seen that there is considerable variation from catalyst to catalyst and also as the pressures of the reactants are changed.

Bodenstein's results on porcelain clearly imply sparse coverage by both reactants. The kinetic law obtained by Bone and Wheeler on a variety of surfaces is consistent with the reaction occurring between gaseous hydrogen and a layer of adsorbed oxygen which fully covers the surface, although a different interpretation was given by these workers; that the above is the correct explanation is supported by Pease and Taylor[44] using copper, and by Benton and Emmett[45] using nickel. Working with a platinum surface, Langmuir found the rates to be irreproducible and was unable to obtain quantitative data. However, there is definite inhibition by oxygen and this must indicate reaction between adsorbed hydrogen and adsorbed oxygen in contrast to the behavior discussed above. In their work with platinum Donnelly and Hinshelwood found that the rate was independent of the hydrogen pressure, but varied in a complex manner with the oxygen pressure; at low pressures the increase was linear, with a falling off from linearity at higher pressures, but the rate continued to rise and never reached a limiting value. This is interpreted as a superposition of two Langmuir isotherms, one corresponding to saturation at low pressures, the other at higher pressures. This indicates two types of center for oxygen adsorption, and moreover the kinetics suggest that the hydrogen forms a saturated layer on a third type of center.

The data of Benton and Elgin on silver also require that the hydrogen and oxygen are adsorbed on different types of center, since there is no mutual displacement. The oxygen layer is evidently saturated, while the 0.63 power dependence indicates intermediate coverage by hydrogen. The results of Hinshelwood, Moelwyn-Hughes and Rolfe with silver indicate a very different behavior at higher temperatures; the results are consistent with interaction between gaseous oxygen and adsorbed hydrogen, or with adsorption on two different types of surface, the oxygen sparsely covering its centers, the hydrogen forming a saturated layer. Donnelly's data on nickel could also be explained in terms of either hypothesis.

Carbon Monoxide-Oxygen Reaction

Data for the oxidation of carbon monoxide on various surfaces are summarized in Table 12, in which it may be seen that there are considerable differences on the various types of surface. Of particular interest is the different behavior found by Bodenstein and Ohlmer and by Benton and Williams, both working with quartz glass. The surface used by Bodenstein and Ohlmer was evidently much more active than that used by Benton and Williams, who had to work at higher temperatures; the latter workers

TABLE 11. HYDROGEN-OXYGEN REACTION

Surface	Temperature Range (°C)	Pressure Range (mm.)		Rate Law	Activation Energy	Ref.
		H_2	O_2			
Porcelain	450–650	—	—	$v = k[H_2]\,[O_2]$	—	1
Porcelain, Ag, Au, Pt, Ni, spathic iron ore, CuO, NiO	—	—	—	$v = k[H_2]\,[O_2]^0$	—	2
Pt	25–1625	—	—	$v = \dfrac{k[H_2]}{[O_2]}$	—	3
Pt	100–150	12.5–500	38–500	See text	—	4
Pt	−120–100	12.5–50	12.5	$v = k[H_2]$; O_2 effect not determined	—	5
Ag	80–130	30–350	6–55	$v = \dfrac{k[H_2]^{0.63}\,[O_2]^0}{1 + b[H_2O]}$	—	6
Ag	650–700	200–400	30–200	$v = k[H_2]^0\,[O_2]$	—	7
Ni	173–330	300–1000	50–200	$v = \dfrac{k[H_2]\,[O_2]}{1 + b[O_2]}$	—	8

References

1. Bodenstein, M., *Z. physik. Chem.*, **29**, 665 (1899).
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3. Langmuir, I., *Trans. Faraday Soc.*, **17**, 621 (1922).
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attribute this to contamination of Bodenstein and Ohlmer's catalyst by some substance that had an activating effect.

Table 12. Carbon Monoxide-Oxygen Reaction

Surface	Temperature Range (°C)	Pressure Range (mm)		Rate Law	E (kcal.)	Ref.
		CO	O_2			
Quartz glass	230–320	5–160	24–700	$v = \frac{k[O_2]}{[CO]}$	—	1
Rock crystal, quartzite	303	60–140	60–110	$v = k[CO]\,[O_2]^{1/2}$	—	1
Quartz glass	500	—	47–71 (total)	$v = k[CO]^{1/2}\,[O_2]$	—	2
Pt	225–475	—	0–60 (total)	$v = \frac{k[O_2]}{[CO]}$	—	3
CuO	310–430	0.2–1.5	0.2–67.0	$v = k[CO]\,[O_2]^0$	18.0	4

References

1. Bodenstein, M., and Ohlmer, F., *Z. physik. Chem.*, **53**, 166 (1905).
2. Benton, A. F., and Williams, T. L., *J. Phys. Chem.*, **30**, 1487 (1926).
3. Langmuir, I., *Trans. Faraday Soc.*, **17**, 621 (1922).
4. Schwab, G. M., and Drikos, G., *Z. physik. Chem.*, **52**, 234 (1942).

Table 13. The Nitric Oxide-Oxygen Reaction

Surface	Temperature Range	Pressure Range (mm)		Rate Law	Activation Energy (kcal)	Ref
		NO	O			
Glass	83–88°K	$4\text{–}80 \times 10^{-3}$	$4\text{–}50 \times 10^{-3}$	$v = k[NO]\,[O_2]$	−4.3	1
Activated charcoal	15–120°C	—	—	$v = \frac{k[NO]^{1.5}\,[O_2]}{[NO_2]^{0.5}}$	Variable	2
Activated carbon	25–150°C	—	—	$v = \frac{k[NO]^2}{1 + b[NO]}$ in excess O_2	—	3

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1. Temkin, M., and Pyzhev, V., *Acta Physicochim. U.R.S.S.*, **2**, 473 (1935).
2. Boreskov, G. K., and Shogam, S. M., *J. Phys. Chem.*, (*U.S.S.R.*), **8**, 306 (1936).
3. Kurin, N. P., and Novgorodova, E. M., *Invesg. Tomsk. Ind. Inst.*, **60**, 61 (1940).

Nitric Oxide-Oxygen Reaction

Results for the oxidation of nitric oxide on various surfaces are given in Table 13. Temkin and Pyzhev explain their results in terms of the hypothesis that reaction occurs between two nitric oxide molecules and one oxygen molecule all adsorbed on neighboring sites, the rate being thus proportional to $\theta_{NO}^2 \theta_{O_2}$; the nitric oxide is supposed to be adsorbed to an intermediate extent so that θ_{NO} is proportional to $[NO]^{1/2}$. A somewhat similar explanation accounts for the results of Boreskov and Shogam, but here nitrogen dioxide must be adsorbed in addition. In the final example, the appearance of $1 + b[NO]$ in the denominator is consistent with a mechanism involving interaction between gaseous and adsorbed molecules.

Sulfur Dioxide-Oxygen Reaction

The oxidation of sulfur dioxide on the surface of platinum was the subject of a very careful investigation by Bodenstein and Fink[46]. The reaction is the only well-investigated example of a bimolecular surface reaction which is retarded by the products; unfortunately it is not a simple case and does not fit into the general scheme discussed on p. 151.

Bodenstein and Fink found that the reactions generally followed one of two equations; if oxygen was in excess (the exact condition is $[SO_2] < 0.75[O_2]$) the equation was

$$v = \frac{k[SO_2]}{[SO_3]^{1/2}} \tag{110}$$

while if $[SO_2] > 0.75\,[O_2]$

$$v = \frac{k[O_2]}{[SO_3]^{1/2}} \tag{111}$$

More generally the equations for these respective conditions are

$$v = \frac{k[SO_2]}{1 + b[SO_3]^{1/2}} \tag{112}$$

and

$$v = \frac{k[O_2]}{1 + b[SO_3]^{1/2}} \tag{113}$$

It may be seen at once that these equations are not consistent with the general equations derived above; Eq. (94) for example becomes

$$v = \frac{k_2KK'[SO_2][O_2]}{(1 + K[SO_2] + K'[O_2] + K_p[SO_3])^2} \tag{114}$$

which cannot reduce to Eqs. (110)–(113).

Bodenstein and Fink explained their results in terms of the diffusion theory of surface catalysis, which was discussed briefly on p. 128. They assumed that the platinum is covered by a multimolecular layer of sulfur trioxide the thickness of which is proportional to the square root of the pressure. For reaction to occur, the molecules of sulfur dioxide and of oxygen must diffuse through this layer to the surface of the catalyst, where they can react together. When sulfur dioxide is in excess in the gas phase there is a sufficient supply of it at the platinum surface, and the molecules of oxygen arriving there will react at once; the rate is therefore controlled by the rate of diffusion of oxygen. This is approximately proportional to the concentration of oxygen in the gas phase and inversely proportional to the film thickness, so that Eq. (111) follows immediately. Equation (110) is explained in a similar manner on the hypothesis that the rate is now controlled by the diffusion of sulfur dioxide.

This theory is clearly capable of explaining the kinetic equations but a variety of evidence has now accumulated which shows that the diffusion theory is not tenable. Accordingly, Bodenstein[47] has modified his original theory by assuming that the diffusion process occurs not through an adsorbed layer, but parallel to the surface. It is supposed that there are certain active centers to which adsorbed molecules must diffuse in order to react. With a slight modification of the arguments this explanation is also capable of explaining the kinetic laws observed. This type of process of diffusion across surfaces has also been postulated by Schwab and Pietsch[48], who emphasized the importance of edges, corners and phase boundaries as the seat of chemical reaction.

Ethylene-Oxygen Reaction

A detailed study of the oxidation of ethylene has been carried out by Twigg[49] who used both static and flow systems and who studied the adsorption of reactants and products in addition. The catalyst employed was prepared by plating glass wool fibers with a thin coating of silver (10^{-4} mm thick), and the work was performed in a temperature range from 200 to 350°C. The oxidation to carbon dioxide and water was found to occur by two independent routes—a direct one and the other proceeding via ethylene oxide:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{1}$$

and

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_4O \tag{2}$$

The adsorption studies showed that only oxygen was adsorbed, the oxygen being present on the surface as oxygen atoms.

To account for his results, Twigg proposed the following mechanism.

A gaseous ethylene molecule can react with a single oxygen atom to form a molecule of ethylene oxide,

$$C_2H_4 + O_{ads.} \rightarrow C_2H_4O$$

or may react with two adsorbed oxygen atoms to form some intermediate product that is rapidly oxidized further to carbon dioxide and water

$$C_2H_4 + 2O_{ads.} \rightarrow [C_2H_4O_2] \xrightarrow{2O_2} 2CO_2 + 2H_2O$$

Ethylene oxide can also pick up additional oxygen to form carbon dioxide and water.

On the basis of this scheme the following rate equations may be written, θ being the fraction of surface covered by oxygen atoms,

$$-\frac{d[C_2H_4]}{dt} = k_1[C_2H_4]\theta + k_2[C_2H_4]\theta^2 \tag{115}$$

$$-\frac{d[O_2]}{dt} = k_3[O_2](1 - \theta)^2 - k_4\theta^2 \tag{116}$$

$$-\frac{d[C_2H_4O]}{dt} = k_5[C_2H_4O] - k_6[C_2H_4]\theta \tag{117}$$

Twigg integrated these equations using a Bush differential analyzer and obtained excellent agreement with his kinetic curves showing the rates of change of the concentrations of ethylene, oxygen and ethylene oxide. This is a striking demonstration of the correctness of the mechanism proposed.

Carbon Dioxide-Hydrogen Reaction

The water gas reaction has been investigated kinetically on platinum and tungsten surfaces, and the results are summarized in Table 14. Prichard and Hinshelwood considered their results on platinum to indicate that interaction occurs between adsorbed carbon dioxide and hydrogen molecules, so that the rate law corresponds to Eq. (74); moreover they find that the hydrogen is more strongly adsorbed than the carbon dioxide, so that inhibition by carbon dioxide and not by hydrogen indicates that reaction occurs only on certain sites on which the hydrogen is less extensively adsorbed. Temkin and Mikhailova, however, presented serious objections to these views. They point out (1) that the data of Prichard and Hinshelwood indicate that the carbon dioxide pressure corresponding to the maximum rate is proportional to the hydrogen pressure, whereas the theory (according to which the maximum rate should occur when $[CO_2] = 1/b$) predicts that there should be no variation with the hydrogen pressure; (2) that the value of the carbon dioxide pressure corresponding to maximum rate should vary with temperature more than it was found to do (the variation should, according to the theory, be the same as that of $1/b$); and (3) that active centers cannot constitute a small fraction of the total sites at the temperatures used, owing to sintering.

In their own experiments Temkin and Mikhailova obtained the same rate at 800°K as Prichard and Hinshelwood did at 1323°K; they therefore conclude that the latter were using a highly poisoned surface.* They obtained varied results depending on whether or not the carbon dioxide was dried with phosphorus pentoxide, suggesting that the surface is very sensitive to traces of water. Their rate law, shown in Table 14, is different from that of Prichard and Hinshelwood, and to account for the behavior observed they postulate the following mechanism. The surface is practically fully covered by carbon monoxide as soon as a small amount is formed, hydrogen is adsorbed to a lesser extent, and carbon dioxide hardly at all. As carbon monoxide molecules evaporate they are replaced either by other carbon monoxide molecules or by hydrogen molecules. Reaction occurs between adsorbed hydrogen and gaseous carbon dioxide, but to account for the independence of the rate on the carbon dioxide pressure it is postulated that the slow process is the one in which hydrogen is adsorbed; its rate is the rate of desorption of carbon monoxide multiplied by the prob-

TABLE 14. THE CARBON DIOXIDE-HYDROGEN REACTION

Surface	Temperature Range (°C)	Pressure Range (mm)		Rate Law	Activation Energy (kcal)	Ref.
		CO_2	H_2			
Pt	870–1122	0–300	0–400	$v = \dfrac{k[CO_2]\,[H_2]}{(1 + b[CO_2])^2}$	—	1
Pt	529	100–200	100–200	$v = \dfrac{k[H_2]\,[CO_2]^0}{[H_2] + b[CO]}$	—	2
Pt	700–1200	0–0.3		See text	—	3
W	1000–1300	0–500	0–500	$v = \dfrac{k[H_2]\,[CO_2]}{(1 + b[H_2])\,(1 + b'[CO_2])}$	—	4

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* This seems to the writer to invalidate their third objection to the conclusions of Prichard and Hinshelwood, whose reaction was evidently occurring on a small fraction of the surface.

ability that the resulting space becomes filled by hydrogen rather than carbon monoxide. This mechanism is shown to account for the rate law.

Schwab and Naicker studied the reaction on platinum at very low pressures and obtained a different behavior. They also found that the reaction varies depending on the drying procedure used, and obtained entirely different kinetic laws when different methods were used for removing the water formed in the reaction; with phosphorus pentoxide, for example, the law was

$$v = \frac{[CO_2]}{1 + b([CO_2] + [CO])} \tag{118}$$

Hinshelwood and Prichard's results on tungsten suggest that the hydrogen and carbon dioxide are adsorbed on different types of site, as discussed on p. 156.

Reaction between Hydrogen and Nitrous Oxide

Several kinetic studies of the hydrogen-nitrous oxide reaction have been made, and indicate widely different types of behavior under different conditions (Table 15). The results of Hinshelwood on platinum suggest that the mechanism involves interaction between two adsorbed molecules, the hydrogen being more extensively adsorbed. Cassel and Glückauf's work was carried out using an excess of hydrogen, and the kinetic law was obtained by analyzing the course of reaction rather than by altering initial conditions. The existence of a limiting rate with increasing nitrous oxide pressure, instead of a maximum, suggests that reaction does not involve interaction between the two adsorbed molecules, and Cassel and Glückauf suggest that it occurs between adsorbed nitrous oxide and gaseous hydrogen. Dixon and Vance explain their result in terms of interaction between gaseous nitrous oxide and two adsorbed hydrogen atoms.

The kinetic law obtained by Hutchinson and Hinshelwood on gold was interpreted by them as implying that the hydrogen and the nitrous oxide are adsorbed independently on two different types of surface (cf. p. 156). Benton and Thacker explain their results on silver in terms of initial decomposition of nitrous oxide on the surface, followed by reaction between a gaseous hydrogen molecule and an adsorbed oxygen atom. Vance and Dixon's results on alumina indicate that reaction occurs on two different types of surface, and that poisoning by water occurs on only one of these.

Ethylene-Bromine Reaction

The results for the ethylene-bromine reaction on glass are shown in Table 16. The negative temperature coefficient is attributed to desorption with increasing temperature.

The Hydrogenation of Ethylene

In spite of considerable experimental study during the past thirty years there is still much uncertainty as to the facts regarding the hydrogenation on ethylene. Work has been done using various catalysts, and the main results are summarized in Table 17. The results of Pease on copper show that the rate passes through a maximum with increase of ethylene pressure, suggesting that the rate law is

$$v = \frac{k[H_2][C_2H_4]}{(1 + K[C_2H_4])^2} \tag{119}$$

which is of the same form as Eq. (80). This law applies to the mechanism involving interactions between an adsorbed ethylene molecule and two

Table 15. Reaction Between Hydrogen and Nitrous Oxide

Surface	Temp. Range (°C)	Pressure Range (mm)		Rate Law	Activation Energy (kcal)	Ref,
		H_2	N_2O			
Pt	507–580	50–400	300–400	$v = \frac{k[N_2O]}{[H_2]}$	25.0	1
Pt	327–1177	2×10^{-2}	$3\text{–}8 \times 10^{-3}$	$v = \frac{k[N_2O]}{1 + b[N_2O]}$ (H_2 in excess)	—	2
Pt	260–471	—	—	$v = k[N_2O]\,[H_2]^0$, slight inhibition by H_2O	22.6	3
Au	704–880	100–500	100–500	$v = \frac{k[H_2]\,[N_2O]}{(1 + b[H_2])\,(1 + b'[N_2O])}$	—	4
Ag	60–180	—	—	$v = \frac{k[H_2]\,[N_2O]^0}{1 + b[H_2O]}$	—	5
Al_2O_3	330–472	—	—	$v = k_1[N_2O]^{2/3}\,[H_2]^n + \frac{k_2[N_2O]^{2/3}\,[H_2]^n}{[H_2O]}$	$E_{k_1} = 30.0$ $E_{k_2} = 35.7$	6

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adsorbed hydrogen atoms, in which the ethylene is strongly adsorbed and the hydrogen is weakly adsorbed. The same conclusion applies to the data of Farkas and Farkas on platinum.

The data on nickel are the subject of considerable controversy. Apart from the results of Toyama, the data are not inconsistent with the equation

$$v = \frac{k[H_2][C_2H_4]}{1 + K[C_2H_4]} \tag{120}$$

and Twigg[50], in discussing the mechanism, has in fact concluded that a law of this type is obeyed. The simplest mechanism consistent with this law is of the Rideal type, involving interaction between an adsorbed ethylene molecule and a gaseous hydrogen molecule. Twigg has discussed in detail such a mechanism, and has considered both hydrogenation and exchange reactions. However, as seen on p. 171, there are serious objections to his explanation of the exchange process.

TABLE 16. REACTION BETWEEN ETHYLENE AND BROMINE

Surface	Temperature Range (°C)	Pressure Range (mm)		Rate Law	Activation Energy (kcal)	Ref.
		C_2H_4	Br_2			
Glass		—	—	$v = k[C_2H_4][Br_2]$	—	1
Glass	9–25	10–50	4–30	$v = k[C_2H_4][Br_2]$	−22.0	2

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Alternatively, it is suggested[50a] that the data on nickel also obey Eq. (119.) This law, unlike Eq. (120), predicts a falling-off of the rate at high ethylene pressures; the data of Toyama, who worked at higher pressures than the other workers, evidently support this conclusion. The rate according to Eq. (119) passes through a maximum, and the results of the other workers, namely, that the rate is independent of the ethylene pressure, may simply mean that they worked in the region of the maximum. Detailed consideration of the data of these workers reveals that the pressure range employed by them was in all cases too limited for a falling off at higher pressures to be detected. Their data are therefore equally well explained by Eqs. (119) and (120), but in view of Toyama's results Eq. (119) seems to be preferable.

The Methane-Deuterium Exchange Reaction

The exchange reactions between methane and deuterium have recently been the object of careful experimental study by Kemball[51], who used evaporated nickel surfaces. He measured the rates of formation of CH_3D, CH_2D_2, CHD_3 and CD_4, and determined an activation energy for each process. All of the rates were found to be proportional to the first power of

Table 17. Summary of Data on Ethylene Hydrogenation

Catalyst	Temperature Range (°C)	Ethylene Pressure Range (mm)	Rate Law	Ref.
Cu	150–300	—	$v = k[H_2]\,[C_2H_4]$	1
Cu	0–20	200–600	$v = \dfrac{k[H_2]}{[C_2H_4]}$	2
Pt	0–236	10–100	$v = \dfrac{k[H_2]}{[C_2H_4]}$	3
Ni (foil)	78–200	0–100	$v = k[C_2H_4]\,[H_2]^0$ with H_2 in excess; $v = k[H_2]\,[C_2H_4]^0$ with C_2H_4 in excess	4
Ni (wire)	−10–130	0.03–0.2	$v = k[H_2]\,[C_2H_4]^0$ at low T; $v = k[H_2]\,[C_2H_4]$ at high T	5
Ni (wire)	20–155	10–30	$v = k[H_2]\,[C_2H_4]^0$	6
Ni (mass)	−78–0	100–400	$v = k[H_2]$; rate retarded by increasing $[C_2H_4]$	7
Ni (wire)	70–200	10–50	$v = k[H_2]\,[C_2H_4]^0$	8
Ni (film)	—	—	$v = k[H_2]\,[C_2H_4]^0$	9
C (active)	−80–50	0–760	$v = k[H_2]\,[C_2H_4]$ at low pressures	10
Various Ni alloys	0–180	50–250	$v = \dfrac{k[H_2]\,[C_2H_4]}{1 + b[H_2] + b'[C_2H_4]}$	11

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the methane pressure. The rate of formation of CH_3D is inversely proportional to the square root of the deuterium pressure, while the rates of formation of CH_2D_2 , CHD_3 and CD_4 are inversely proportional to the first power of the deuterium pressure. As suggested by Kemball, this result implies that the methyl radicals do not rapidly undergo exchange with adsorbed deuterium atoms, but merely add on atoms to form CH_3D. The other deuterated methanes must then be formed in another manner, and the simplest hypothesis is that they are produced from adsorbed CH_2 radicals. Kemball has in fact produced evidence for two kinds of equilibria, one probably involving adsorbed CH_3 and the other adsorbed CH_2.

The reaction is discussed further on p. 224 in connection with absolute rate calculations.

The Ethylene-Deuterium Exchange Reaction

The deuteration of ethylene on a nickel surface at 150°C was studied by Twigg and Rideal[52], who concluded that the rate was independent of the ethylene pressure and directly proportional to the first power of the deuterium pressure—this is the same dependence as for the hydrogenation (p. 168). Evidently the deuterium covers the surface only sparsely, while the ethylene coverage is considerable. Twigg[53] explains the results in terms of adsorbed ethyl radicals; both exchange and hydrogenation are supposed to involve reaction between such a radical and an adsorbed H or D atom. The concentration of adsorbed ethyl radicals is (assuming full coverage by ethylene) independent of the ethylene pressure and proportional to the square root of the hydrogen or deuterium pressure, and the concentration of adsorbed D's is also proportional to the square root of the deuterium pressure; the kinetic laws are thus explained. However, this mechanism involves some difficulty. The activation energy of the exchange reaction is greater by about 9 kcal than that for hydrogenation; the rate of exchange is, nevertheless, about three times the rate of hydrogenation. On the basis of activation energy alone, the exchange rate is expected to be 10^{-5} times that of the hydrogenation, and there should therefore be a frequency factor ratio of about this figure. Twigg's mechanism, however, provides no interpretation of such a ratio. Absolute rate calculations give good agreement for hydrogenation (see Chapter 5), but the calculated exchange rates are too low by about 10^5.

The only way out of this difficulty[50a] would seem to be to reject Twigg's conclusion that the rate varies with the first power of the deuterium pressure, and to assume that, as in other exchange reactions, the square-root law is obeyed. In fact, examination of the data of Twigg and Rideal indicates that the first-power dependence was by no means well established. Only two deuterium pressures were used, and these differed only by a factor of 2. Moreover, there were large variations in catalyst activity from run to run, and these were corrected in terms of the variation of activity with respect to hydrogenation—evidently a very doubtful procedure. All in all, the data do not support the first-order law any better than the square-root law.

The Ammonia-Deuterium Exchange Reaction

The kinetics of the exchange reaction between ammonia and deuterium were first studied by A. Farkas[54] on a pure iron surface, and the process was found to be of zero order with respect to ammonia and of the one-half order with respect to deuterium. These facts can be explained in terms of interaction between an adsorbed ammonia molecule and an adsorbed deuterium atom, provided that the deuterium is weakly absorbed and the ammonia more strongly adsorbed. The rate law corresponding to this situation is

$$v = \frac{k[D_2]^{1/2}[NH_3]}{(1 + b[NH_3])^2} \tag{121}$$

which indicates a maximum in the rate as the ammonia concentration is increased; the zero-order obtained by Farkas could be explained on the assumption that the ammonia pressures were such that the rate was in the neighborhood of the maximum.

The data of Farkas could also be explained on the basis of interaction between an adsorbed deuterium atom and a gaseous ammonia molecule; if ammonia is strongly adsorbed the treatment[55] of this case gives the rate law

$$v = \frac{k[D_2]^{1/2}[NH_3]}{1 + b[NH_3]} \tag{122}$$

which becomes $v = k'[D_2]^{1/2}$ at sufficiently high pressures. In this case there is no falling off of the rate at high ammonia pressures.

In order to distinguish between these two possibilities, Weber and Laidler[56] have reinvestigated the reaction on an activated iron surface, using a microwave spectroscopic technique for following the disappearance of ammonia. Special attention was given to the dependence of the rate on the ammonia concentration, which was varied over a wide range at three different temperatures. The results at 141.5°C, which are typical of those obtained at the other temperatures, are shown in Figure 5, and it will be seen that there is definitely a falling off at higher pressures. The data are seen to be adequately represented by Eq. (121), the curve drawn in the figure being the best fit based on this equation. That the rate is proportional to the square root of the deuterium pressure is seen from Figure 6.

It may therefore be concluded that under the conditions of the experiments the mechanism involves interaction between adsorbed ammonia (or species derived from ammonia, e.g., NH_2) and adsorbed deuterium atoms.

The reaction has also been studied by Singleton, Roberts and Winter[57] on evaporated films of iron, tungsten and nickel. These workers state that the rates are first-order with respect to deuterium, but their data do not support this in all cases and a one-half order law is more accurately obeyed under certain of their conditions. The dependence of the rate on ammonia pressure is somewhat different on the three surfaces. On tungsten the rates are practically independent of ammonia pressure at pressures greater than 30 mm (they actually decrease slightly with increasing pressure). At the lowest deuterium pressure used the square-root law is approximately obeyed, but at higher pressures the rate is proportional to the first power of the deuterium pressure. With regard to the dependence on ammonia pressure the rates evidently pass through a maximum (at lower pressures than those used), but instead of falling steadily as in the experiments of Weber and Laidler the rates appear to fall only to a constant level. These results are most simply explained in terms of a composite mechanism consisting of (1) interaction between adsorbed deuterium atoms and adsorbed ammonia [Eq. (121)] and (2) interaction between adsorbed ammonia and gaseous deuterium molecules. Mechanism (1) alone would give rise to behavior of the type found by Weber and Laidler, the rate falling toward zero as the ammonia saturates the surface. At higher ammonia pressures mechanism (2) may be expected to predominate, so that the rate will not

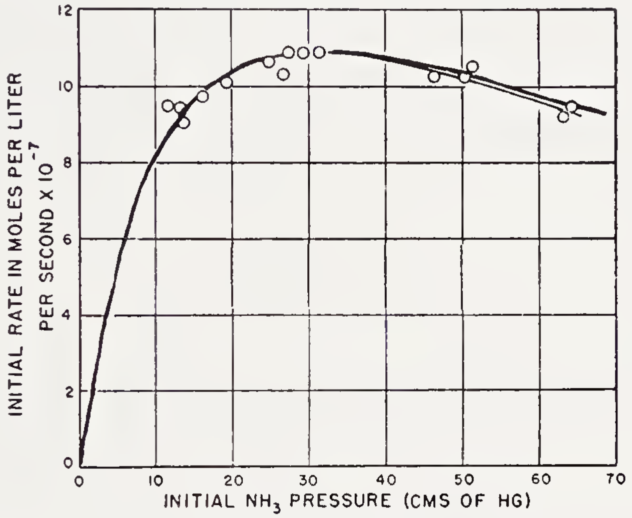


Figure 5. Rate of ammonia-deuterium exchange *vs.* ammonia pressure (Weber and Laidler[56]). The initial P_{D_2} was 8.2 (cms of Hg).

fall to zero. At low ammonia pressures, when mechanism (1) is most important, the rate will be proportional to the square root of the deuterium pressure, while at higher pressures, when mechanism (2) predominates, it is proportional to the first power; this is in agreement with the facts.

The situation regarding nickel and iron catalysts is less clear-cut; on nickel, for example, the dependences on ammonia and deuterium pressures have not been studied at the same temperature. On iron the rates evidently pass through a maximum at some lower ammonia pressure than those investigated, and at higher pressures the rates fall rather sharply; however, again they appear to approach a constant finite value rather than zero. The results on nickel and iron are again consistent with the idea of the two simultaneous mechanisms.

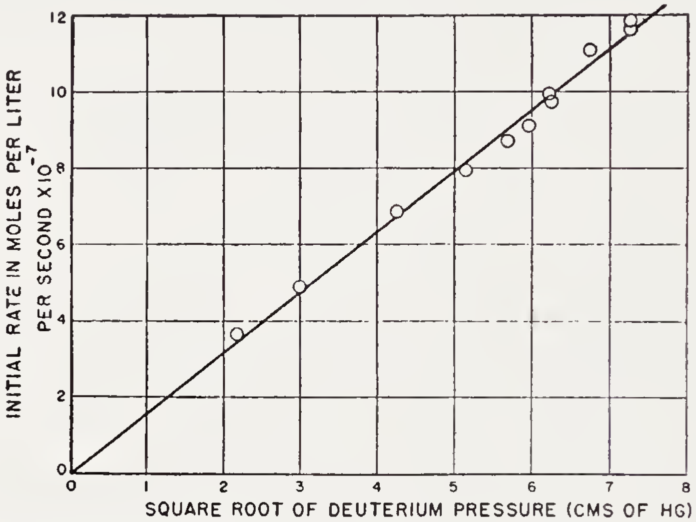


Figure 6. Rate of ammonia-deuterium exchange *vs.* square root of deuterium pressure (Weber and Laidler[56]). The initial P_{NH_3} was 18.4 (cms of Hg).

The reaction on evaporated nickel catalysts has also been studied by Kemball[58] who found the rate to be proportional to the square root of the deuterium pressure and to a slightly higher power of the ammonia pressure; the work was not extended to sufficiently high pressures of ammonia so that the question of the rate falling off was not settled. In a later investigation, Kemball[58a] has followed the rates of production of the various individual deuterated ammonias, NH_2D, NHD_2 and ND_3, using evaporated films of platinum, rhodium, palladium, nickel, tungsten, iron, copper and silver. In all cases it was found that the initial product was NH_2D, and that NHD_2 and ND_3 are produced in subsequent independent reactions; in other words, only one hydrogen can be exchanged at a time. This is most simply explained on the assumption that NH_3 on adsorption is dissociated into —NH_2 and —H, and that the former can merely add on deuterium; —NH_2 cannot undergo surface exchange with deuterium.

In spite of a very considerable variation in catalytic activity from metal to metal, Kemball found that the relative concentrations of the deuteroammonias formed throughout the reaction were identical in every case, and corresponded to the equilibrium concentrations. Kemball derived differential equations for the various rates on the basis of the following two assumptions: (1) only one exchange can occur at a time and (2) all rates and equilibria are uninfluenced by substituting deuterium for hydrogen. The equations were integrated numerically and shown to be in excellent agreement with the data; the assumptions made in the treatment are therefore justified.

Synthesis of Ammonia

The work on the synthesis of ammonia from nitrogen and hydrogen will be discussed only briefly in view of the fact that a chapter will be devoted to this topic in Volume III. Benton[59] carried out an analysis of some data obtained by Larson and Tour[60] on iron and concluded that the rate law for the synthesis was

$$v = \frac{k_1[H_2][N_2]}{[NH_3]} - k_{-1} \tag{123}$$

the second term applying to the reverse reaction, of zero order. Temkin and Pyzhev[61] made a more detailed study of the kinetics and concluded that the rate law is

$$v = \frac{k_1[N_2][H_2]^{1.5}}{[NH_3]} - \frac{k_2[NH_3]}{[H_2]^{1.5}} \tag{124}$$

They also showed that the data of Larson and Tour are more consistent with this equation than with Eq. (123).

Their rate law was interpreted by Temkin and Pyzhev in terms of the treatment considered earlier for ammonia decomposition. The second term, of course, corresponds to Eq. (64) for the decomposition. Just as the rate of decomposition is controlled by the rate of desorption of nitrogen, the rate of synthesis is equal to the rate of adsorption of nitrogen, which is given by Eq. (56). The equilibrium expression for nitrogen is given by Eq. (61), so that the rate of adsorption is

$$v = k_1[N_2] \exp\left\{\frac{g}{f} \ln a_0 K' \frac{[NH_3]^2}{[H_2]^3}\right\} \tag{125}$$

$$= k_1[N_2]\left(\frac{[H_2]^3}{[NH_3]^2}\right)^{\alpha} \tag{126}$$

Since β from Winter's data on the decomposition is equal to one-half, α

is also one-half, so that the rate of synthesis is

$$v = \frac{k_1[N_2][H_2]^{1.5}}{[NH_3]} \tag{127}$$

which corresponds to the first term of Eq. (124). The Temkin-Pyzhev theory therefore gives a satisfactory explanation of the data on the synthesis and decomposition of ammonia.

More recently, Emmett and Kummer[62] have reported kinetic results on the ammonia synthesis, using high pressures and an iron catalyst containing 0.94 per cent potassium oxide and 3.02 per cent alumina. The results were again consistent with the Temkin-Pyzhev theory.

SOME SPECIAL TYPES OF REACTIONS

Certain reactions which do not easily fall into the classification of reactions employed above, and which therfore require separate treatment, will be discussed here. The reactions considered are (1) the adsorption and desorption of gases (2) the parahydrogen conversion, (3) surface combinations of atoms and radicals, and (4) the production of atoms at hot surfaces.

Adsorption and Desorption[63]

The kinetics laws for the adsorption and desorption of gases are of importance in themselves, and also because they throw light on the kinetics of other processes, such as the conversion of parahydrogen into orthohydrogen (p. 178).

The simplest case to consider is that in which there is no dissociation of the adsorbed molecule on the surface. The kinetic laws followed are then the same as were assumed on p. 131 in the development of the Langmuir adsorption isotherm. Thus, the rate of adsorption is proportional to the pressure of the gas being adsorbed and to the fraction of the surface that is bare,

$$v_1 = k_1 p(1 - \theta) \tag{128}$$

Similarly the rate of desorption is proportional to the fraction of surface that is covered,

$$v_{-1} = k_{-1}\theta \tag{129}$$

The isotherm is obtained by equating these rates.

Of special interest are the laws obtained when the gas becomes dissociated when it is adsorbed on the surface. Two formulations of the kinetics are then possible. In the first case the adsorption process may be represented as the interaction between half a molecule of the gas and a single surface site,

$$\tfrac{1}{2}G_2 + S \rightarrow S - G$$

and the rate is then proportional to the square root of the gas pressure and to the fraction of surface that is bare,

$$v_1 = k_1 p^{1/2} (1 - \theta) \qquad (130)$$

The desorption rate is proportional to the fraction of surface covered,

$$v_{-1} = k_{-1}\theta \qquad (131)$$

Equating these rates gives rise to the correct adsorption law,

$$\frac{\theta}{1 - \theta} = \frac{k_1}{k_{-1}} p^{1/2} \qquad (132)$$

The second formulation regards the reaction involving interaction between a gas molecule and a *pair* of surface atoms. The number of pairs of bare sites is proportional to the square of the number of bare single sites, so that the rate in this case is proportional to the pressure and to the square of the fraction of surface that is bare,

$$v_1 = k_1 p(1 - \theta)^2 \qquad (133)$$

The desorption process is now the interaction of two neighboring adsorbed atoms, and the rate is proportional to the square of the fraction of surface covered,

$$v_{-1} = k_{-1}\theta^2 \qquad (134)$$

On equating these rates there is again obtained an isotherm of the same form as Eq. (132).

Kinetic laws of the form of Eq. (130), in which the rate is proportional to the square root of the pressure provided that $1 - \theta$ is pressure-independent, i.e., the surface is sparsely covered, are obeyed by a number of systems. Thus Smithells and Ransley[64] found that the rate of uptake of hydrogen by nickel is proportional to the square root of the pressure up to 112 atmospheres. A similar result was obtained by Lombard and Eichner[65] for the sorption of hydrogen by palladium, and by Borelius and Lindblom[66] for the sorption of hydrogen by iron. However, in all of these cases there is diffusion of the hydrogen into the metal, so that it is possible that the slow step is the diffusion of the atoms through the metal and not the adsorption process[67].

The case of the adsorption of hydrogen on tungsten is of special interest, since there is no possibility of diffusion into the metal. Unfortunately, there is no direct information as to the kinetic law; Roberts[68] studied rates of adsorption under carefully controlled conditions but did not determine the pressure dependence of the rate. However, the following indirect argument leads to the conclusion that the rate is proportional to the first power of the hydrogen pressure. It seems likely that the rate of the conversion of parahydrogen into orthohydrogen on tungsten is controlled by the rate of adsorption of parahydrogen. The data on this conversion (p. 210) indicate that when the reaction is studied at constant total hydrogen pressure, i.e., when the fraction of surface covered is kept constant, the rate of conversion varies linearly with the first power, and not the square root of the hydrogen pressure. The adsorption process under these conditions thus follows Eq. (133) and not Eq. (130).

The Parahydrogen Conversion

The conversion of parahydrogen into orthohydrogen on metal surfaces will be discussed separately, since the interpretation of the experimental data has given rise to considerable difficulty and the matter is by no means settled. Only the pressure dependence of the rate of conversion is considered in this section; the calculation of the absolute rate is discussed in Chapter 5 (p. 210), while a complete treatment of the reaction, by B. M. W. Trapnell, will be presented in Volume II.

Two mechanisms have been proposed for the reaction occurring on a tungsten surface, for which most of the experimental work has been done. According to the original mechanism of Bonhoeffer and Farkas[69] the conversion proceeds by adsorption and desorption of the hydrogen on the surface; adsorption involves dissociation so that the equilibrium mixture is produced on desorption. This mechanism may be represented as

$$p\text{-H}_2 + \text{W} \rightleftharpoons 2\text{W—H} \rightleftharpoons 2\text{W} + o\text{-H}_2$$

and the rate of the conversion is controlled by the rate of adsorption of parahydrogen.

It was seen in the previous section that the rate of adsorption of hydrogen on tungsten is probably proportional to the first power of the pressure; thus for the adsorption of parahydrogen

$$v_1 = k_1 p_p (1 - \theta)^2 \qquad (135)$$

where p_p is the pressure of parahydrogen. If the conversion is followed starting with pure parahydrogen the fraction covered θ is related to the parahydrogen pressure by the adsorption isotherm, and if the nature of the isotherm is known the rate can be formulated in terms of the parahydrogen pressure. If the Langmuir isotherm were obeyed $1 - \theta$ is given by (cf. p. 92)

$$1 - \theta = \frac{1}{1 + K^{1/2} p_p^{1/2}} \tag{136}$$

whence

$$v_1 = \frac{k_1 p_p}{(1 + K^{1/2} p_p^{1/2})^2} \tag{137}$$

At sufficiently high pressures $K^{1/2} p_p^{1/2} \gg 1$, under which conditions the rate should be independent of the parahydrogen pressure, i.e., the kinetics should be zero-order.

In fact, it has been found[70] that the order of the reaction is very close to zero, so that the above formulation of the reaction appears at first sight to offer a satisfactory interpretation of the reaction. However, a more careful consideration of the process has revealed that this treatment is not acceptable. The difficulty is that the Langmuir isotherm is not obeyed by the adsorption process. Two independent studies[71] of the isotherm have shown that $1 - \theta$ does not vary inversely as $p_p^{1/2}$ under the experimental conditions (in which the surface is fairly fully covered), but varies approximately as $p^{-0.2}$. The rate is thus given by

$$k_1 = k_1 p_p p_p^{-0.4} \tag{138}$$

$$k_1 = k_1 p_p^{0.6} \tag{139}$$

This law appears to be inconsistent with the observed zero-order kinetics, and on the basis of this Halsey[72] has rejected the Bonhoeffer-Farkas mechanism, preferring instead the Rideal-Eley mechanism, which is discussed below.

It should, however, be pointed out that this argument neglects the possibility that there is a pressure dependence of the adsorption constant k_1 itself[73]. This pressure dependence arises from the fact that the heat of adsorption varies strongly with the surface coverage, and therfore with the pressure. There is probably an activation energy for adsorption, and this is also pressure dependent. A careful consideration of the possible pressure dependence of the activation energy for adsorption does, in fact, lead to the conclusion that k_1 varies with the pressure approximately as $p_p^{0.6}$. According to Eq. (139) the rate is therefore pressure-independent, in agreement with the experimental data. There is, therefore, no objection, on kinetic grounds, to the Bonhoeffer-Farkas mechanims.

The alternative mechanism for the conversion was first proposed by Rideal[74]. The reason for its proposal was that the adsorption studies of

Roberts[75] appeared to indicate that adsorbed hydrogen atoms are held very firmly to the surface, so that desorption occurs too slowly for the Bonhoeffer-Farkas mechanism to be possible. Rideal's mechanism is that reaction proceeds through interaction of a chemisorbed atom and a gaseous molecule or one held in a van der Waals layer,

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

More recent adsorption studies[76], however, have indicated that Roberts's surfaces were not as fully covered as he believed them to be, and that at higher pressures than those used by Roberts the heats of adsorption fall to such low values that desorption can occur rapidly. The objection, on the grounds of rates of desorption, to the Bonhoeffer-Farkas mechanism therefore loses its validity and Rideal himself now prefers this mechanism[77].

The main objection to the Rideal mechanism is that it does not appear capable of explaining the zero-order kinetics. If the reaction occurred between an adsorbed atom and a molecule in the gas phase the rate would be given by

$$v = kp\theta \tag{140}$$

Since the surface is fairly fully covered under the experimental conditions the fraction θ varies only slightly with p; if k varies as $p^{-0.6}$ the rate is thus proportional to $p^{0.4}$. It is thus not possible to account for the zero order. A lower pressure dependence may be obtained by assuming the hydrogen molecule to be adsorbed in a van der Waals layer, but a very considerable coverage of this type is required for zero-order kinetics. Such a high degree of van der Waals adsorption is, in fact, precluded by the adsorption data.

Surface Combination of Atoms and Radicals[78]

The combinations of atoms and radicals on surfaces are first-order processes over a wide range of pressures and temperatures[79], but become second-order at higher temperatures[80]. Various mechanisms may be suggested for the processes, but most can be excluded since they do not explain the experimental behavior. One mechanism is the adsorption of atoms on neighboring sites of the surface. The rate would then be given by

$$v = kp^2(1 - \theta)^2 \tag{141}$$

but this equation cannot explain the fact that the kinetics are first-order over a wide range. A second mechanism would involve slow adsorption of the atoms followed by rapid migration and recombination on the surface. If the fraction of bare surface were pressure-independent (i.e., if the surface were sparsely covered) the kinetics would be first-order, but would remain so at high temperatures; this mechanism would also not appear to be satisfactory. The only remaining simple possibility is that reaction occurs between an adsorbed atom and a gaseous one. This may readily be seen to correspond to the observed behavior. If the surface is fully covered the rate is proportional to the pressure of the atoms, i.e., the kinetics are first-order. At higher temperatures the surface becomes sparsely covered and the fraction covered is proportional to the atomic concentration; the kinetics are then second-order in agreement with experiment.

The kinetic law may be formulated as follows. The fraction covered depends upon the atomic pressure according to the isotherm

$$\frac{\theta}{1 - \theta} = Kp \tag{142}$$

The rate is now proportional to θ and to p,

$$v = kp\theta \tag{143}$$

whence

$$v = \frac{kKp^2}{1 + Kp} \tag{144}$$

If the surface is fully covered, which will be so at lower temperatures, $Kp \gg 1$, so that

$$v = kp \tag{145}$$

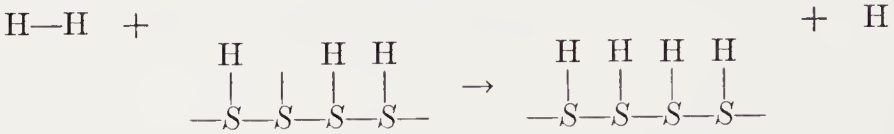
and the kinetics are first order. At higher temperatures, on the other hand, $1 \gg Kp$, so that

$$v = kKp^2 \tag{146}$$

i.e., the kinetics are first-order. This mechanism therefore offers a ready explanation of the transition from first- to second-order kinetics, and appears to be the correct one. It should be noted that the mechanism is of the Rideal type, the reaction occurring between a gas atom and an adsorbed atom.

The Production of Atoms at Hot Surfaces[81]

It was first shown by Langmuir[82] that hydrogen atoms are produced from the molecules at a hot tungsten surface, and Bryce[83] showed that the rate of reaction is proportional to the square root of the hydrogen pressure. As seen in the previous section, the combination of atoms probably occurs by the interaction of a gaseous atom and an adsorbed atom, and the production of atoms would be expected to occur by the reverse process; a hydrogen molecule strikes a bare site, whereupon one atom is adsorbed and the other passes into the gas phase. Such a mechanism was in fact proposed by Roberts and Bryce[84], and may be represented as



$$\mathrm{H{-}H} + \begin{array}{cccc} \mathrm{H} & & \mathrm{H} & \mathrm{H} \\ | & | & | & | \\ -S- & S- & S- & S- \end{array} \rightarrow \begin{array}{cccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \\ | & | & | & | \\ -S- & S- & S- & S- \end{array} + \mathrm{H}$$

This mechanism will account for the first-order law provided that, as is found to be the case[85], the surface is fully covered. The fraction of surface bare is then inversely proportional to the square root of the pressure of hydrogen, so that the rate, being proportional to the pressure and the fraction bare, is proportional to the square root of the pressure. The rate law for the general case may be derived as follows. The rate is given by

$$v = kp(1 - \theta) \tag{147}$$

where θ is given by the isotherm

$$\frac{\theta}{1 - \theta} = Kp^{1/2} \tag{148}$$

The rate is thus

$$v = \frac{kp}{1 + Kp^{1/2}} \tag{149}$$

The surface is fully covered at high pressures when $Kp^{1/2} \gg 1$ the rate is then

$$v = \frac{k}{K} p^{1/2} \tag{150}$$

in accordance with experiment. At lower pressures or higher temperatures the surface would be sparsely covered; in this case $Kp^{1/2} \ll 1$, and the rate is

$$v = kp \tag{151}$$

i.e., the kinetics are first-order. This behavior has not been observed experimentally. However, a more detailed study[81] (p. 209) of the data of Bryce has indicated that the behavior is not described exactly by Eq. (86), but that the kinetic law is intermediate between Eqs. (86) and (87), i.e., that Eq. (85) should be employed.

KINETICS ON HETEROGENEOUS SURFACES

So far in the development of the kinetic laws for surface reactions it has been tacitly assumed that the surfaces were smooth, all parts of the surface being of the same activity. This assumption is, of course, inherent in the use of the Langmuir isotherm for the adsorption process. It has been seen in the previous chapter, however, that strict conformity to the Langmuir equation is rarely if ever observed, and that this is frequently due to the variation of the surface activity. In view of this, it would be expected at first sight that the kinetic equations derived earlier in this chapter would be rarely adhered to. Surprisingly, however, it is actually found that the "ideal" kinetic laws derived above are obeyed very well for most reactions, the deviations being much less pronounced than the deviations from the ideal isotherm. A striking example of such conformity is found in the data of Dohse[86] on the decomposition of various alcohols on alumina. It was found that over a range of pressures the rate was strictly proportional to the amount of gas adsorbed, in spite of the fact that an alumina surface is one on which there are marked variations of heat of adsorption with surface coverage, indicating that the surface is highly heterogeneous.

There is an apparent discrepancy between the adsorption work and the kinetic work, the former indicating a wide range of activity of the surface sites, the latter being consistent with the assumption that reaction occurs on sites all of which have the same activity. The explanation of the anomaly is that on any catalytic surface there is one group of sites which are more active than the remainder, and that reaction occurs on this group with a lower activation energy than on the other sites. Since the rate varies exponentially with the activation energy the reaction proceeds mainly on the most active sites and only to an insignificant extent on the remainder. Reaction on the less active sites therefore does not introduce any complexity into the kinetic laws, which apply to the reaction on the group of most active sites. The calculations of absolute rates indicate that in the case of smooth metal surfaces the most active sites constitute the majority of the sites on the surface, but that with oxides and composite catalysts of various kinds the active sites may comprise only a thousandth or less of the total number of surface sites.

Constable's Treatment

A theoretical treatment of the distribution of surface sites and of the kinetics of reactions on inhomogeneous surfaces was given by Constable[87], whose treatment was later extended somewhat by Cremer and Schwab[88]. The theory proceeds essentially as follows.

Let the number of sites of the i-th type be n_i, and let reaction occur on these sites with an activation energy of E_i. The over-all rate of reaction may therefore be written as

$$v = k\sum_i n_i e^{-E_i/RT} \tag{152}$$

where the proportionality coefficient k may be a function of the pressure of the reacting gas; in the case of a first-order reaction k will obviously be proportional to the first power of the pressure. Constable presents theoretical reasons for supposing that n_i will be an exponential function of the activation energy E_i, of the form

$$n_i = ae^{E_i/b} \tag{153}$$

where a and b are constants. The rate is therefore

$$v = ka\sum_i e^{\left(\frac{1}{b} - \frac{1}{RT}\right)E_i} \tag{154}$$

If a continuous distribution of sites is assumed the rate equation becomes

$$v = ka \int_{E_1}^{E_2} e^{\left(\frac{1}{b} - \frac{1}{RT}\right)E} \, dE \tag{155}$$

where E_1 is the lower limit of the activation energy and E_2 the upper; the lower limit applies to the most active sites, the upper to the least active ones.

Integration of Eq. (155) gives rise to

$$v = \frac{ka\left[e^{\left(\frac{1}{b} - \frac{1}{RT}\right)E}\right]_{E_1}^{E_2}}{\frac{1}{b} - \frac{1}{RT}} \tag{156}$$

$$= \frac{ka}{\frac{1}{b} - \frac{1}{RT}}\left[e^{\left(\frac{1}{b} - \frac{1}{RT}\right)E_2} - e^{\left(\frac{1}{b} - \frac{1}{RT}\right)E_1}\right] \tag{157}$$

Analysis of experimental data, particularly the dehydrogenation of ethyl alcohol on various surfaces, showed that $(1/b) - (1/RT)$ is a negative quantity; writing it as $-r$, where r is positive, Eq. (157) becomes

$$v = \frac{ka}{r}\,(e^{-rE_1} - e^{-rE_2}) \tag{158}$$

The magnitudes of r, E_1 and E_2 were found by Constable to be such that the term e^{-rE_2} can be neglected in comparison with e^{-rE_1}; the rate is thus given by

$$v = \frac{ka}{r}\, e^{-rE_1} \tag{159}$$

$$= \frac{kae^{E_1/b}}{r}\, e^{-E_1/RT} \tag{160}$$

The over-all activation energy is therefore E_1, the lower limit, and the kinetics of the reaction correspond to the reaction occurring exclusively on sites of the highest activity.

Equation (160) has some interesting consequences. If a given reaction is studied on a series of similar catalysts, for example, on a surface that is given various temperature treatments, it may occur with a range of activation energies. However, the frequency factor of the reaction, since it involves the factor $e^{E_1/b}$ [Eq. (160)] will be lower the lower the activation energy. There will therefore be a tendency for low activation energies to be partly compensated by low frequency factors, the compensation being greater the smaller the term $(1/b)-(1/RT)$. Many examples of such correlations between frequency factors and activation energies will be found in the literature.

The question of the magnitude of the constant b has been the subject of some experimental investigation. Constable studied the dehydrogenation of ethyl alcohol on copper obtained by reduction of the oxide at various temperatures, and found that the activation energy varied between 21.6 and 25.6 kcal. At the same time the frequency factor varied in such a manner that the value of b was found to be constant within the experimental error. A similar result was found by Balandin[89] for the dehydrogenation of cyclohexanone, decalin, cyclohexane and other substances on various catalysts; b was the same for all the reactions studied and had a value of about 1000.

In the experiments of Constable and of Balandin the catalysts were prevented from sintering, so that the surface sites would not attain their equilibrium distribution. Cremer and Schwab[88] considered theoretically the situation in which catalysts were heated so that they would reach an equilibrium distribution, and concluded that under these conditions the value of b would be equal to $R\theta$ where θ is the temperature at which the equilibrium distribution is frozen. Cremer[90] studied the kinetics of the decomposition of ethyl alcohol on a number of oxides which had been heated to about 1000°K, and found that whereas the activation energies varied from 13 to 32 kcal and the rates in the ratio 1:10,000, the value of b was essentially constant. Its value, moreover, was about 2000, which is consistent with a value of about 1000°K for θ in accordance with the theory of Cremer and Schwab.

Halsey's Treatment

The simple conclusion of Constable, that on an inhomogeneous surface the kinetics will closely correspond to the occurrence of the reaction on the most active sites, may require modification in certain cases. In the above discussion it was tacitly assumed that the rate-controlling step is the same on all of the surface sites; thus in Eq. (155) it is supposed that k is the same, and has the same pressure dependence, for all of the sites. It is also necessary to consider the possibility that the rate-controlling step is different on different types of site; thus it might be an interaction between the gas molecule and site on some types, and desorption of the product on others. If this is so, the reaction will not show the simple kinetics that would be expected if the surface were uniform.

Suppose, for example, that E_1 is the activation energy for reaction to give adsorbed products on sites of type 1, and E_1' the activation energy for desorption of products; similarly let E_2 and E_2' be the corresponding quantities for reaction on sites of type 2. If E_1 is greater than E_1' the rate-controlling step on sites of type 1 is probably the formation of adsorbed products. If the product is more strongly adsorbed on sites of type 2 the activation energy for the formation of products will be reduced (i.e., E_2 is less than E_1), but at the same time the activation energy for desorption, E_2', will probably be high. The net effect may be that desorption controls the rate on the sites of type 2. The sites of type 2 will be more covered with product than those of type 1, and there will now be no simple relationship between the rate and the gas pressure.

A quantitative discussion of this situation has been given by Halsey[91]. He assumes that the relationship existing between the activation energy for the formation of adsorbed products on sites of the i-th type, E_i, and the activation energy for the desorption of products, E_i', is

$$rE_i + E_i' = E_0 \tag{161}$$

where E_0 and r are constants. If θ_i is the fraction of sites of the i-th type that are covered by reactant molecules, and θ_i' the fraction covered by product molecules, the isotherm for these sites is

$$\frac{\theta_i}{1 - \theta_i - \theta_i'} = Kp \tag{162}$$

whence

$$\theta_i = \frac{Kp}{1 + Kp}(1 - \theta_i') \tag{163}$$

$$= P(1 - \theta_i') \tag{164}$$

where P is equal to $Kp/(1 + Kp)$. The steady-state equation for adsorbed product molecules on the sites of the i-th type is

$$\frac{d\theta_i'}{dt} = A(\theta_i e^{-E_i/RT} - \theta_i' e^{-E_i'/RT}) = 0 \tag{165}$$

where A is a frequency factor, assumed to be the same for both processes.

Eq. (165) gives rise to

$$P(1 - \theta'_i)e^{-E_1/RT} = \theta_i e^{-E'_i/RT} \qquad 166)$$

whence

$$\theta'_i = \frac{Pe^{-E_i/RT}}{Pe^{-E_i/RT} + e^{-E'_i/RT}} \qquad (167)$$

The rate of reaction on sites of the i-th type is thus

$$v_i = A\theta'_i e^{-E'_i/RT} \qquad (168)$$

$$= \frac{APe^{-(E_i+E'_i)/RT}}{Pe^{-E_i/RT} + e^{-E'_i/RT}} \qquad (169)$$

In the special case that $r = 1$, Eq. (169) gives rise to

$$v_i = \frac{APe^{-E_0/RT}}{Pe^{-E_0/RT}e^{E'_i/RT} + e^{-E'_i/RT}} \qquad (170)$$

Putting

$$\varphi = \frac{e^{-E'_i/RT}}{P^{1/2}e^{-E_0/RT}} \qquad (171)$$

equation (170) may be written as

$$v_i = \frac{P^{1/2}e^{-E_0/2RT}}{\varphi + \varphi^{-1}} \qquad (172)$$

If there are N_i sites of the i-th type, the over-all rate is

$$v = \Sigma_i N_i v_i \qquad (173)$$

or, if a continuous distribution is assumed,

$$v = \int NvdE' \qquad (174)$$

Halsey assumes an exponential distribution of numbers of sites with respect to the energy of activation for desorption, as follows,

$$N = Ce^{-E'/E_m} \qquad (175)$$

where C and E_m are constants. Integration of Eq. (163) using this distribution gives, with certain approximations,

$$v = \text{const.} \times P^{\frac{1}{2} + \frac{RT}{E_m}} \qquad (176)$$

If, as is sometimes the case, RT/E_m is much smaller than one-half, the result is that

$$v = \text{const.} \times P^{1/2} \tag{177}$$

$$= \text{const.} \times \left(\frac{Kp}{1 + Kp}\right)^{1/2} \tag{178}$$

In spite of the many assumptions and approximations that were necessary to obtain an explicit solution of this problem, the final result obtained is a particularly interesting and valuable one. Whereas the simple Langmuir treatment predicts that the rate would vary with $Kp/(1 + Kp)$, Halsey's theory shows that under some conditions the rate may vary with the square root of this quantity. Fractional reaction orders have in fact been found for a few reactions on inhomogeneous surfaces, and the treatment throws some light on these. Thus Love and Emmett (cf. Table 3) found that the rate of the ammonia decomposition on an activated iron catalyst obeys the law

$$v = k \frac{p_{\mathrm{NH_3}}^{0.6}}{p_{\mathrm{H_2}}^{0.85}} \tag{179}$$

It is to be emphasized that the type of complexity considered by Halsey will not *necessarily* arise on an inhomogeneous surface; in order for the rate to be controlled by different processes on the different types of site the distribution of surface activities must be sufficiently broad. If this is not so the reaction will occur most rapidly on the most active sites, and the treatment of Constable will suffice; the simple Langmuir law will then apply. It appears from the discussion of the data given earlier in this chapter that in the majority of cases the simple laws are obeyed satisfactorily.

KINETICS IN THE CASE OF INTERACTIONS BETWEEN ADSORBED MOLECULES

Since a discussion of the effect of interactions on the kinetics of surface reactions largely involves a consideration of absolute rates, this will be taken up in Chapter 5 (p. 239). Attention may, however, be directed to the work, already discussed, of Temkin and Pyzhev (p. 141); by using the Frumkin-Slygin isotherm they take interactions and surface heterogeneity into account in an empirical manner.

THE TIME COURSE OF SURFACE REACTIONS

The kinetic laws discussed earlier in this chapter have been based on the assumption that the catalyst surface remains in a constant state of activity throughout an experiment and that the rate of reaction, accordingly, can be expressed in terms of the influence of the pressures of the reactants and products on the fraction of the surface covered with a given species. Within the last few years Thon and Taylor[93] have made the suggestion that the catalyst surface changes in the course of the reaction and that therefore the kinetic equations which represent the change of initial rate of reaction with partial pressures of reactants and products may be very different from the equation that accounts for the rate during the main course of reaction. We shall now briefly review the evidence cited by Thon and Taylor in support of their hypothesis.

Chemisorption

It was first pointed out by Zeldovich[94, 96] that the time course for the adsorption of carbon monoxide on manganese dioxide follows the exponential law

$$\frac{dq}{dt} = ae^{-\alpha q} \tag{180}$$

where q is the amount of gas adsorbed (or fraction of the surface covered) and a and α are constants. This same equation was reported later by Elovich and Zhabrova[95] to apply to the adsorption of hydrogen and the adsorption of ethylene on reduced nickel between −23 and 50°C. The equation is currently known as the Elovich equation and, according to Taylor and Thon,[92] is capable of representing many of the adsorption data that have been published.

Taylor and Thon's theoretical interpretation of the equation is as follows. The fact that the equation applies over an extended range of the chemisorption process, during which time the gas pressure may have varied considerably, suggests that of the two reactants, gas molecules and solid sites, it is the mass action of the latter only that determines the instantaneous rate. The mass action of the gas determines only the initial rate a. This, they say, is understandable if in an initial short period of time the gas and the surface interact to produce an active center; after this, in the subsequent slow process, the sites may be in relatively shorter supply as compared with an abundant supply of gaseous reactant (except in the final stages of the adsorption, where the law is no longer obeyed).

It follows from these considerations that the time course of slow chemisorption is governed by the availability of sites, and furthermore that the process of chemisorption eliminates sites over and beyond actual occupancy. Thus if the momentary rate of adsorption is proportional to the momentary surface concentration n of active sites, simple molecule-per-site inactivation would mean that $-dn/dq$ is constant; this leads to first-order kinetics. The actual inactivation law that is required in order to account for the

Elovich law, was derived by Taylor and Thon[92] as follows. It is assumed that the rate of adsorption at any time is proportional to n, the concentration of sites, and this law may be written as

$$\frac{dg}{dt} = \frac{a}{n_0} n \tag{181}$$

where n_0 is the initial value of n and a is the initial rate. Equations (180) and (181) give rise to

$$n = n_0 \, e^{-\alpha q} \tag{182}$$

so that

$$-\frac{dn}{dq} = \alpha n \tag{183}$$

From Eq. (183)

$$-\frac{dn}{dt} = \alpha n \frac{dq}{dt} \tag{184}$$

and, using Eq. (181),

$$-\frac{dn}{dt} = \frac{a\alpha}{n_0} n^2 \tag{185}$$

Equation (185) corresponds to a bimolecular interaction between sites.

The interpretation of Taylor and Thon represents an interesting and novel approach to the problem of chemisorption, but it must be emphasized that it is by no means the only one that will explain the experimental results. Another interpretation has in fact been given by Porter and Tompkins[97] in terms of a nonuniform surface with a continuous distribution function; the slow step is the migration of adsorbed atoms from one site to another. On the whole this theory of Porter and Tompkins is more satisfying than that of Taylor and Thon, since it takes into account the variation of activation energy with coverage, a result that has been well established experimentally. Indeed it seems to be a major weakness of the Taylor and Thon theory that it takes no account of these variations and gives no explicit mechanism for the bimolecular disappearance of sites. Porter and Tompkins give a detailed theoretical treatment, for which their paper should be consulted.

Chemical Reactions

In order to explain the time-dependence of the rates of chemical reactions Thon and Taylor[93] propose a similar scheme, which is in terms of "active centers" rather than of surface sites. By "active centers" they mean dissociatively adsorbed particles of *one* reactant of the system; for example in hydrogenation reactions, they identify the "active centers" as chemisorbed hydrogen atoms.

For a number of reactions, they contend, the rate data are best expressed by an exponential equation of the Elovich type. However, it is also possible in certain instances to maintain the "active centers" in approximately constant concentration throughout an experiment by a type of surface chain mechanism similar to that proposed by Rideal.[74] For example in the hydrogenation of ethylene the interaction would be between an adsorbed hydrogen atom and a gaseous ethylene molecule to form an adsorbed ethyl radical. This radical in turn would then react with a gaseous hydrogen molecule to reform a surface hydrogen atom and a molecule of ethane. In this way the supply of "active centers" (adsorbed hydrogen atoms in this case) could be kept constant. In support of this hypothesis with respect to the hydrogenation over nickel, data of Elovich and Zhabrova[95] are cited to show that ethylene added to a surface already covered with chemisorbed hydrogen will not react to form ethane in the absence of gaseous hydrogen; however, on this same surface containing its layer of chemisorbed hydrogen, reaction proceeds readily if a mixture of hydrogen and ethylene is added.

The author takes a rather dim view of the general importance of the Elovich equation either in chemisorption or in catalytic kinetics. As pointed out above and as emphasized by Porter and Tompkins,[97] surface heterogeneity seems to offer a more satisfying explanation of the frequently observed rapid decrease in the rate of reaction with the fraction of the surface covered by chemisorbed molecules. As to catalytic kinetics, a careful examination of the examples cited by Thon and Taylor[93] makes it doubtful that there are any examples in the published literature that are uniquely explained by the Elovich equation. Certainly, the numerous known flow systems such as ammonia synthesis in which the rate of reaction remains constant for months or even years does not suggest any bimolecular time dependent decay of "active centers" on the surface of a catalyst. Until some detailed theory is developed that will account for both the formation and the decay of "active centers" in the course of a catalytic reaction it does not seem likely that the application of the Elovich equation to explain the kinetics of catalytic reactions will be widely accepted.

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CHAPTER 5

THE ABSOLUTE RATES OF SURFACE REACTIONS

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Whereas Chapter 4 has been concerned only with the general form of the kinetic laws for surface-catalyzed reactions, the present one gives precise significance to the various constants that appear in the equations. The procedures for calculating the absolute rates of surface reactions are explained, and for a number of systems it is shown that there is good agreement between calculated and observed values.

As in the chapter on chemisorption, the first part of this chapter will be concerned with the "ideal" laws, i.e., the kinetic laws applicable when the surface is completely smooth and when there are no interactions between adsorbed molecules. The modifications required when surfaces are inhomogeneous and when interactions have to be taken into account will be discussed later.

THEORY OF ABSOLUTE REACTION RATES

The most useful modern treatment of the absolute rates of chemical reactions is an extension of the statistical theory of equilibrium that was considered in Chapter 4. In order for any process to take place it is necessary for the system to pass through what is known as an *activated state*, the system in this state being described as an *activated complex*. This complex is regarded as being at the top of an energy barrier lying between the initial and final states, and the rate of the reaction is controlled by the rate at which the complex travels over the top of the barrier. The calculation of the absolute rates of reactions has been much simplified by the assumption that the activated complexes are in statistical equilibrium with the reactants. This assumption is the basis of Eyring's[1] formulation of the rates of reactions, a formulation that has provided the only practicable method of calculating the absolute rates of reactions.

According to this theory, the important problem in the study of the rates of reactions is the determination of the structure of the activated complex, and in particular the determination of the energy of this complex with reference to that of the reactants. When this is done one can calculate, by the methods of statistical mechanics, the concentration of the activated complexes in terms of those of the reactants, assuming equilibrium to exist; then the rate of the reaction can be expressed. Since the structure of the activated complex controls not only the rate but its variation with the reactant concentrations (i.e., the order of the reaction) it is obviously necessary to define it correctly and precisely. In principle the configuration and energy of the activated complex can be calculated by the methods of quantum mechanics, but in practice this can be done only for the simplest systems, and even then the results are not very accurate. Some of the attempts to make such calculations for adsorption processes are considered in a later section (p. 236). A more practical procedure is to make use of the experimental results to obtain information as to the activated complex. The experimental activation energy does, in fact, give a value for the energy of the complex in excess of that of the reactants, while the configuration of the activated state can usually be inferred from the dependence of the rate on the concentrations of reactants.

This procedure for calculating absolute rates of reactions, although less fundamental than desired, is convenient and reasonably accurate, and is the one that will be followed here. The application of Eyring's theory to adsorption and desorption processes and to surface reactions was first made by Laidler, Glasstone and Eyring[2]. Other but less complete treatments of surface processes have also been made by Topley[3], Kimball[4] and Temkin[5].

The theory of absolute reaction rates will now be formulated for a simple adsorption process, in which dissociation does not occur. The theory will then be applied to adsorption with dissociation, to desorption processes, to atom and radical recombination, to the production of atoms at surfaces, and to the para-ortho-hydrogen conversion. The absolute rate laws will then be applied to various kinds of chemical reactions on surfaces. The modifications required when surfaces are inhomogeneous and when there are interactions between adsorbed molecules will be discussed later in the chapter.

Absolute Rates of Adsorption

The process of adsorption is a bimolecular reaction between surface sites and gas molecules; the case of the localized activated complex will be considered first. Let N_S, N_g and $N_\ddagger$ be the numbers of sites, gas molecules and activated complexes, respectively, and let the corresponding concentrations be $c_S(= N_S/S)$, $c_g(= N_g/V)$ and $c_\ddagger(= N_\ddagger/S)$. The assumption of equilibrium between the activated complexes and the reactants then gives rise to the equation

$$\frac{c_{\ddagger}}{c_g c_S} = \frac{f^{\ddagger}}{F_g f_S} e^{-\epsilon_1/kT} \tag{1}$$

which is analogous to Eq. (33) on p. 95; ϵ_1 is the energy of the complexes with reference to the reactants, at the absolute zero, and is therefore the activation energy at that temperature.

As pointed out earlier (p. 93), the partition function F_g can be factorized into translational, rotational and vibrational factors. The activated complex has no translational or rotational motion, since it is assumed to be localized on the surface, but it undergoes various types of vibrational motion. One of the vibrational factors in the partition function is of a very different nature from the rest, since it corresponds to a very loose vibration which allows the complex to dissociate into the products of reaction, i.e., into the adsorbed state in the present case of adsorption. For this one degree of freedom one may therefore employ, in place of the usual factor $(1 - e^{-h\nu/kT})^{-1}$, the value of this function in the limit at which ν tends to zero. This is evaluated by expanding the exponential and taking only the first term,

$$\operatorname*{Lim}_{\nu \to 0} \frac{1}{1 - e^{-h\nu/kT}} = \frac{1}{1 - (1 - h\nu/kT)} = \frac{kT}{h\nu} \tag{2}$$

The equilibrium constant may therefore be expressed by including this term $kT/h\nu$ and replacing $f^{\ddagger}$ by $f_{\ddagger}$, which now refers to one less degree of vibrational freedom; the resulting expression is thus

$$\frac{c_{\ddagger}}{c_g c_S} = \frac{f_{\ddagger}(kT/h\nu)}{F_g f_S} e^{-\epsilon_1/kT} \tag{3}$$

which rearranges to

$$\nu c_{\ddagger} = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_1/kT} \tag{4}$$

The frequency ν is the frequency of vibration of the activated complexes in the degree of freedom corresponding to their transformation into adsorbed molecules. The expression on the left-hand side of Eq. (4) is thus the product of the concentration of complexes $c_{\ddagger}$ and the frequency of their transformation; it is therefore the rate of the adsorption process, which is thus given by the expression on the right-hand side of the equation, viz.

$$v_1 = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_1/kT} \tag{5}$$

The partition functions may now be evaluated in the same manner as in the equilibrium equations. There are no translational and rotational factors in $f_{\ddagger}$, and the remainder, due to vibration, will be represented by $b_{\ddagger}$. As before, f_S is taken as unity, since the surface atoms can undergo only very restricted vibration, while F_g will be written as $(2\pi mkT)^{3/2}b_g/h^3$ where b_g represents the vibrational and rotational factors. Substitution of these values gives

$$r_1 = c_g c_S \frac{kT}{h} \frac{b_{\ddagger}}{\dfrac{(2\pi mkT)^{3/2}}{h^3}\, b_g} e^{-\epsilon_1/kT} \tag{6}$$

If the gas is diatomic the factor b_g contains the rotational factor $8\pi^2 IkT/h^2\sigma$, where σ is the symmetry number, and also a vibrational factor. However, at ordinary temperatures the latter is close to unity, and therefore can be omitted. Similary $b_{\ddagger}$ is very close to unity, apart from a symmetry factor $1/\sigma_{\ddagger}$: the rate expression can therefore be written as

$$r_1 = c_g c_S \frac{kT}{h} \frac{1/\sigma_{\ddagger}}{\dfrac{(2\pi mkT)^{3/2}}{h^3}\,\dfrac{8\pi^2 IkT}{h^2\sigma}} e^{-\epsilon_1/kT} \tag{7}$$

$$= c_g c_S \frac{\sigma}{\sigma_{\ddagger}} \frac{h^4}{8\pi^2 I(2\pi mkT)^{3/2}} e^{-\epsilon_1/kT} \tag{8}$$

In the above it has been assumed that in the formation of the activated state the gas molecule becomes attached to only one adsorption site. In many cases two adjacent sites, i.e., a dual site, are necessary for adsorption. If this is so Eq. (8) still gives the rate of adsorption provided that c_S is replaced by c_{S_2}, the concentration of such dual sites. If the surface is bare the number of dual sites is related to the number of single sites as follows. Each single site has a certain number, s, of adjacent sites; s is known as the coordination number of the surface and depends upon the particular type of surface lattice. If the number of dual sites were counted by counting s for each single site the result would be sc_S, but in this procedure each pair is counted twice so that the actual number of dual sites is $\frac{1}{2}sc_S$. The rate of adsorption on dual sites is thus given by replacing c_S in the above expression by $\frac{1}{2}sc_S$, viz.

$$r_1 = \tfrac{1}{2}\, sc_g c_S \frac{\sigma}{\sigma_{\ddagger}} \frac{h^4}{8\pi^2 I(2\pi mkT)^{3/2}} e^{-\epsilon_1/kT} \tag{9}$$

This expression is, however, only valid for adsorption on an initially bare surface, i.e., it applies only to initial rates of adsorption on dual sites.

If the fraction of surface already covered is θ, the average number of bare sites adjacent to any given site is, assuming random distribution, $s(1 - \theta)$. The total number of bare dual sites is therefore now $\frac{1}{2}c_S s(1 - \theta)$. If the concentration of covered single sites is c_a, θ is given by

$$\theta = \frac{c_a}{c_a + c_S} \tag{10}$$

so that the concentration of bare dual sites is

$$c_{S_2} = \frac{\frac{1}{2}\, c_S^2 s}{c_a + c_S} \tag{11}$$

$$= \frac{\frac{1}{2}\, s c_S^2}{L} \tag{12}$$

where $L = c_a + c_S$ is the total concentration of single sites when the surface is completely bare. The rate of adsorption on dual sites is thus generally given by replacing c_S in Eq. (8) by c_{S_2} using Eq. (12), and the expression obtained is

$$v_1 = \frac{s c_g c_S^2}{2L} \frac{\sigma}{\sigma_\ddagger} \frac{h^4}{8\pi^2 I (2\pi m k T)^{3/2}} e^{-\epsilon_1/kT} \tag{13}$$

This reduces to Eq. (9) if $L = c_S$, which is so if the surface is completely bare.

The rate equations are quite different if the molecules are not localized in the adsorbed state, and hence presumably in the activated state. The equilibrium between initial and activated states may now be represented by

$$K_c = \frac{c_\ddagger}{c_g} = \frac{N_\ddagger/S}{N_g/V} = \frac{F^\ddagger}{F_g} \tag{14}$$

where F_g and $F^\ddagger$ are the partition functions for unit volume of gas and per sq cm of activated complex, respectively. By the same methods as used previously it can be shown that the rate of adsorption is given by

$$v_1 = c_g \frac{kT}{h} \frac{F_\ddagger}{F_g} e^{-\epsilon_1/kT} \tag{15}$$

where $F_\ddagger$ differs from $F^\ddagger$ in lacking the $kT/h\nu$ factor corresponding to reaction. The activated complexes now differ from the reactants by having translational freedom in only two dimensions, and the ratio $F_\ddagger/F_g$ is thus simply $h/(2\pi m k T)^{1/2}$. The rate of adsorption thus becomes

$$v_1 = c_g \frac{kT}{h} \frac{h}{(2\pi m k T)^{1/2}} e^{-\epsilon_1/kT} \tag{16}$$

Replacement of $c_g kT$ by the pressure, p, and considering the special case of zero activation energy, gives

$$v = \frac{p}{(2\pi mkT)^{1/2}} \tag{17}$$

This equation is the classical Hertz-Knudsen equation for the number of gas molecules striking 1 sq cm of surface in unit time. Equation (16) is often used for calculating rates of adsorption when there is no activation energy, but it should be emphasized that it is only applicable when the adsorbed molecules are not localized on the surface, and this is generally not the case. For a localized layer Eq. (13) should be used; this corresponds to a very much lower rate of adsorption than does Eq. (16).

The Accommodation Coefficient

For certain purposes it is convenient to define a quantity, known as the accommodation coefficient γ, which is equal to the fraction of the molecules striking the surface which become adsorbed. For a localized layer, the number adsorbed is given by Eq. (6), while the number striking is given by Eq. (16) with ϵ_1 equal to zero; hence

$$\gamma = \frac{c_g c_S \dfrac{kT}{g} \dfrac{b_{\ddagger}}{\dfrac{(2\pi mkT)^{3/2}}{h^3} b_g} e^{-\epsilon_1/kT}}{c_g \dfrac{kT}{h} \dfrac{h}{(2\pi mkT)^{1/2}}} \tag{18}$$

$$= c_S \frac{h^2}{2\pi mkT} \frac{b_{\ddagger}}{b_g} e^{-\epsilon_1/kT} \tag{19}$$

Adsorption with Dissociation

When dissociation accompanies adsorption the rate laws may be formulated on the basis of two different mechanisms, which must be clearly distinguished. The first corresponds to dissociation which is not completed by the time the activated state is reached, the dissociation occurring in a subsequent stage; in the second mechanism, dissociation is completed in the slow process of adsorption, so that the activated complexes are adsorbed atoms.

In the first case the reaction may be written as

$$G_2 + S_2 \rightleftharpoons S_2G_2^{\ddagger} \rightarrow 2SG$$

where $S_2G_2^{\ddagger}$ represents the activated complex. The equilibrium between activated complexes and reactants may be expressed as

$$K_c = \frac{c_\ddagger}{c_g c_{S_2}} = \frac{f^\ddagger}{F_g f_{S_2}} e^{-\epsilon_1/kT} \tag{20}$$

In the same manner as before it can be shown that the rate is now given by

$$v_1 = c_g c_{S_2} \frac{kT}{h} \frac{f_\ddagger}{F_g f_{S_2}} e^{-\epsilon_1/kT} \tag{21}$$

$$= \frac{c_g s c_S^2}{2L} \frac{kT}{h} \frac{f_\ddagger}{F_g f_{S_2}} e^{-\epsilon_1/kT} \tag{22}$$

The rate is seen to be proportioned to the first power of the gas pressure. This expression is identical with that obtained when there is no dissociation but when adsorption occurs on dual sites.

If dissociation is completed during the slow and rate-determining process of adsorption, the activated complexes may be considered to be single adsorbed atoms, and the formation of these may be written as

$$\tfrac{1}{2}G_2 + S \rightleftharpoons GS^\ddagger$$

The equilibrium between reactants and activated complex is now

$$K_c = \frac{c_\ddagger}{c_g^{1/2} c_s} = \frac{f^\ddagger}{F_g^{1/2} f_S} e^{-\epsilon_1/kT} \tag{23}$$

In the same manner as before it can be shown that the rate is now

$$v = c_g^{1/2} c_S \frac{kT}{h} \frac{f_\ddagger}{F_g^{1/2} f_S} e^{-\epsilon_1/kT} \tag{24}$$

The rate is in this case proportional to the square root of the gas pressure.

Comparison of Theory with Data

In order to test the adsorption equations derived above it is necessary to have data on the rates of adsorption of gases on surfaces of known area, but unfortunately such data are not very common. All of the rate data to be considered apply to cases in which adsorption involves dissociation, so that either Eq. (22) or Eq. (24) would be expected to apply; in fact it appears that Eq. (22) is the one which is applicable.

Emmett and co-workers[6] have measured rates of adsorption of nitrogen and hydrogen on an iron-aluminum oxide-potassium oxide catalyst, the so-called catalyst "931". The observed and calculated data are given in

Table 1. The rates refer to half-covered surfaces and are expressed as molecules per second on the available surface.

On the whole, the agreement is satisfactory in view of the approximations involved, and particularly in view of uncertainties in the energies of activation. An activation energy of 8.9 kcal for the hydrogen adsorption would, for example, give exact agreement between theory and experiment. As discussed on p. 186, an observed activation energy may have no simple significance if the surface is not homogeneous, and this is certainly true in this example.

Data were obtained by Roberts[7] for the rate of adsorption of hydrogen on a clear tungsten wire of known area, but unfortunately there is some doubt as to the theoretical significance of the results. At 79°K, and at a pressure of 10^{-4} mm, the rate of adsorption was found by Roberts to be 5.9×10^{12} molecules per sq cm per sec. Unfortunately, it was not determined whether the rate is proportional to the first power or the square root of the pressure, so that at first sight it is difficult to know whether to employ Eq. (22) or Eq. (24). However, as seen on p. 211, a somewhat indirect argument based on the kinetics of the parahydrogen conversion on the same surface leads to the conclusion that the rate of adsorption is proportional to the first power of the hydrogen pressure, i.e., that Eq. (22) applies. Taking s as 4 and c_S as 10^{15} sites per sq cm the rate of adsorption is found to be $1.2 \times 10^{17}\, e^{-E/RT}$ molecules per sq cm per sec. The calculated and observed rates agree if an activation energy of 1.5 kcal is assumed, and this figure is not unreasonable. However, it was found by Roberts that the rates of adsorption were the same at 79 and 295°K, so that the activation energy should be zero. If the activation energy is in fact zero it would be necessary to assume that only one site in about 2×10^4 can act as an adsorption center, but this would seem unlikely and is not supported by any other data. The only other simple possibility is that diffusion through the apparatus, and not the actual adsorption process, was the slow step under the conditions of Roberts's experiments, a possibility that was in fact admitted by him[8]. If this is so, the actual rate of adsorption might be greater than observed, and might also be different at the two temperatures, thus allowing a small activation energy.

TABLE 1. RATES OF ADSORPTION ON CATALYST "931"

Gas	Temperature (°K)	E (kcal)	Rate of Adsorption (molecules sec^{-1}.)	
			Calc.	Obs.
N_2	544	14.4	35.8×10^{16}	3.4×10^{16}
H_2	194.5	10.4	5.7×10^{15}	1.8×10^{17}

It is evident from the above discussion that there do not exist in the literature anything like enough data to permit a satisfactory test of the equations for rate of adsorption.

ABSOLUTE RATES OF DESORPTION

The process of desorption of undissociated molecules held in a localized layer will be considered first. Desorption from such a layer involves an activated state in which the molecule has acquired the necessary configuration and activation energy to escape from the surface. If N_a and $N_\ddagger$ are the number of adsorbed molecules and activated complexes, and c_a and $c_\ddagger$ are the corresponding concentrations, in molecules per sq cm, the equilibrium between initial and activated states may be written as

$$K_c = \frac{c_\ddagger}{c_a} = \frac{N_\ddagger/S}{N_a/S} = \frac{f^\ddagger}{f_a} e^{-\epsilon_{-1}/kT} \tag{25}$$

where ϵ_{-1} is the activation energy for desorption at the absolute zero. The concentration of activated complexes is therefore given by

$$c_\ddagger = c_a \frac{f^\ddagger}{f_a} e^{-\epsilon_1 kT} \tag{26}$$

Application of the methods employed earlier gives rise to the rate expression

$$v_{-1} = c_a \frac{kT}{h} \frac{f_\ddagger}{f_a} e^{-\epsilon_{-1}/kT} \tag{27}$$

where $f_\ddagger$ differs from $f^\ddagger$ in no longer including the partition function $(kT/h\nu)$ for passage across the potential-energy barrier. By equating this rate with that of Eq. (5) for the rate of adsorption it may readily be seen that the adsorption isotherm, Eq. (33) on p. 95, is obtained, with ϵ equal to $\epsilon_1 - \epsilon_{-1}$.

In the case of adsorption with dissociation, two mechanisms for the desorption process are possible, corresponding to the two mechanisms for adsorption. In the first adsorption mechanism that was considered the dissociation did not occur in the rate-determining step, but occurred in a subsequent stage. The complete process may be represented as

$$G_2 + S_2 \rightleftharpoons G_2S_2^\ddagger$$

$$G_2S_2^\ddagger + 2S' \rightleftharpoons 2GS' + S_2$$

where S_2 is a dual site on which the molecule of G_2 is first adsorbed and S' represents a site to which each atom finally jumps. The equilibrium between adsorbed species and activated complex is given by

$$K_c = \frac{c_{\mp} c_{S'}^2}{c_a^2 c_{S_2}} = \frac{f^{\mp} f_{S'}^2}{f_a^2 f_{S_2}} \, e^{-\epsilon_{-1}/kT} \tag{28}$$

and the rate of desorption is

$$v_{-1} = \frac{c_a^2 c_{S_2}}{c_{S'}^2} \, \frac{kT}{h} \, \frac{f_{\mp} f_{S'}^2}{f_a^2 f_{S_2}} \, e^{-\epsilon_{-1}/kT} \tag{29}$$

By equating this equation with Eq. (21) the adsorption isotherm (Eq. (41) on p. 97) is obtained, as is necessary, with ϵ equal to $\epsilon_1 - \epsilon_{-1}$.

In the second mechanism, the activated complex for both adsorption and desorption is a dissociated species: the expression for equilibrium between initial and activated states for desorption is therefore again Eq. (25), where c_a now represents the concentration of an adsorbed atom or radical. The rate of desorption is therefore given by

Table 2. Rates of Desorption

Gas	Surface	Temp (°K)	E (kcal)	Relative Rate (molecules cm^{-2} sec^{-1}.)	
				Calc.	Obs.
CO	Pt	600	32.0	1.25×10^{28}	2.79×10^{29}
O_2	W	2000	165.0	4.16×10^{28}	13.4×10^{30}

$$v_{-1} = c_a \, \frac{kT}{h} \, \frac{f_{\mp}}{f_a} \, c^{-\epsilon_{-1}/kT} \tag{30}$$

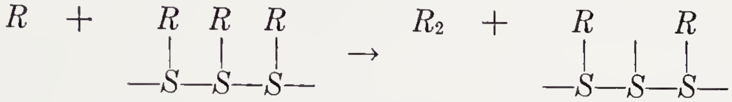
Equating this expression with that of Eq. (24) gives rise to the isotherm, with ϵ now equal to $2(\epsilon_1 - \epsilon_{-1})$.

Comparison of Theory with Data

Langmuir[9] has measured the rates of desorption of carbon monoxide from platinum and of oxygen from tungsten, and since both of these gases are probably adsorbed without dissociation, Eq. (27) should apply. It may be assumed that both the adsorbed molecules and the activated complex are immobile, so that $f_{\mp}/f_a$ may be taken to be unity. The calculated values of $c_a(kT/h)$ are compared with the corresponding experimental values in Table 2. The agreement between observed and calculated values is fairly satisfactory. Some of the discrepancy may be due to the fact that the activated molecules may have more rotational and vibrational freedom than the adsorbed molecules. This would make their partition functions greater than unity and hence would increase the calculated rates.

ABSOLUTE RATES OF SURFACE COMBINATIONS OF ATOMS AND RADICALS[10]

It was seen on p. 180 that the combination of atoms and free radicals on surfaces are first-order processes under a wide variety of conditions, and that the most plausible interpretation of this is that reaction occurs between a gaseous atom or radical and a surface-adsorbed atom or radical,



$$R + \begin{array}{ccccc} R & & R & & R \\ | & & | & & | \\ -S & - & S & - & S- \end{array} \rightarrow R_2 + \begin{array}{ccccc} R & & & & R \\ | & & | & & | \\ -S & - & S & - & S- \end{array}$$

If c_g is the concentration of gaseous atoms and c_a the concentration of adsorbed atoms the rate is therefore given by

$$v = c_g c_a \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_a} e^{-\epsilon_0/kT} \tag{31}$$

where $f_{\ddagger}$, F_g and f_a are the partition functions and ϵ_0 the activation energy at the absolute zero. If a rate constant k is defined by the equation $v = kc_g$ it is given by

$$k = c_a \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_a} e^{-\epsilon_0/kT} \tag{32}$$

Assuming, as previously, that $f_{\ddagger}/f_a = 1$, and expressing F_g as $(2\pi mkT)^{3/2} b_g/h^3$, where b_g is the product of the rotational and vibrational partition functions (unity in the case of atoms), the rate constant becomes

$$k = \frac{c_a h^2}{(2\pi m)^{3/2}(kT)^{1/2} b_g} e^{-\epsilon_0/kT} \tag{33}$$

This expression may thus be used for calculating absolute rates of surface combinations.

The Recombination Coefficient

The fact that surface recombinations are first order processes implies that each gaseous atom or radical arriving at the surface has a certain constant probability of recombining, which is independent of the pressure. One can therefore define a recombination coefficient γ, equal to the ratio of atoms striking the surface and combining and the total number striking the surface[11]. The relationship between γ and the rate constant k is readily obtained for a static system as follows. Consider a system of volume V cc containing n atoms recombining at a surface of S sq cm. The number reacting per second may be expressed as

$$-\frac{dn}{dt} = kn \tag{34}$$

where k is a different rate constant from that previously employed; the number of atoms striking a surface of S cm^2 per second is given according to kinetic theory by

$$Z = \left(\frac{n\bar{v}}{4V}\right)S \tag{35}$$

where $\bar{v}$ is the mean atomic velocity. The recombination coefficient is the ratio of these quantities,

$$\gamma = \frac{4kV}{\bar{v}S} \tag{36}$$

Usually the experiment is carried out in a cylindrical tube, so that $V = \pi r^2 L$ and $S = 2\pi rL$, where r is the radius and L the length, in this case

$$\gamma = \frac{2kr}{\bar{v}} \tag{37}$$

This equation is identical with that derived by Paneth and Herzfeld[11] for the case of a flow experiment involving an inert transport gas, and it has also been shown[10] that the equation is valid for a flow system where the transfer of the atoms or radicals is by diffusion alone.

The recombination coefficient may be expressed in terms of absolute rate theory as follows[12]. As seen on p. 200 the number of collisons on a surface is equivalent to the rate of adsorption to give a mobile layer when there is no activation energy for adsorption. The recombination coefficient is therefore given by

$$\gamma = \frac{c_g c_a \dfrac{kT}{h} \dfrac{f_{\ddagger}}{F_g f_a} e^{-\epsilon_0/kT}}{c_g \dfrac{kT}{h} \dfrac{F_{\ddagger}}{F_g}} \tag{38}$$

where $F_{\ddagger}$ is the partition function for the activated complex in the mobile layer. Evaluation of the partition functions gives

$$\gamma = \frac{c_a h^2}{2\pi mkTb_g} e^{-\epsilon_0/kT} \tag{39}$$

Expressions (33) and (39) for k and γ may be seen to be consistent with Eq. (37) when it is noted that

$$\bar{v} = \left(\frac{8kT}{\pi m}\right)^{1/2} \tag{40}$$

Comparison of Theory with Data

Calculations of rate constants and recombination coefficients have been made for various systems, and the results compared with experiment. Smith[13] has measured recombination coefficients for hydrogen atoms on various dry oxides (ZnO, Cr_2O_3, Al_2O_3, K_2CO_3, K_2SiO_3, Na_3PO_4) at 300°K, and obtained values varying from 3×10^{-2} to 6×10^{-2}. The total number of atoms adsorbed per sq cm of such surfaces is found[14] to be about 1.35×10^{15}, and this value is therefore taken for c_a. Employing methods to be discussed later (p. 238) the activation energy for this process was estimated as 0.6 kcal, and using this value the recombination coefficient on the basis of Eq. (39) is calculated to be 5×10^{-2}. This is in excellent agreement with Smith's results.

Semiquantitative measurements have also been made of the rates of recombination of hydrogen atoms on clean glass surfaces[15]. At liquid air temperatures the recombination coefficient is close to unity[16] but at higher temperatures the value becomes smaller[17]. In the region from -79 to 99°C the recombination coefficient increases in accordance with an activation energy of about 0.9 kcal[18]. As the temperature approaches 250°C, when there is rapid evaporation of hydrogen[19], the coefficient reaches a maximum and then decreases, the order increasing at the same time from unity to two. This effect is due to the depletion of the layer of hydrogen atoms (so that c_S varies with the pressure of hydrogen atoms), and it has also been noted for the recombination of methyl radicals on glass[20] and of nitrogen atoms on nickel[21]. The temperature dependence of γ is shown schematically in Figure 1, the curve being based on the data summarized above.

In the temperature region from -180 to -80°C the curve can be fitted by Eq. (39) taking $c_S = 1.35 \times 10^{15}$ and $E_0 = 0$; in the region from -80 to 250° C it can be fitted with $c_S = 1.35 \times 10^{15}$ and $E_0 = 0.9$ kcal. The calculated recombination coefficients and rate constants so obtained are shown in Table 3. These values are of the right order. Roberts[22] states that γ for glass at liquid air temperatures should be somewhat less than unity. The values of γ between 200 and 500°K agree with that found by Smith for dry oxides and are also in agreement with the observation of Steiner and Wicke[23] that γ on clean glass is several order of magnitudes higher than on water vapor poisoned glass surfaces.

In order to explain these results, including the fact that the reaction is of the first order over most of the temperature range, it is suggested that the surface is fully covered by hydrogen atoms, which react with gas-phase hydrogen atoms:

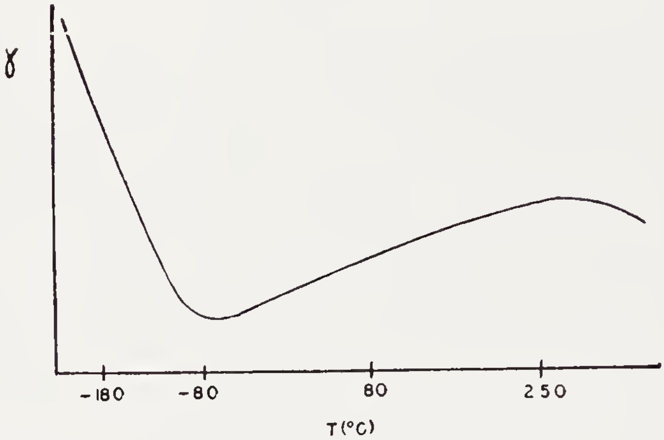


Figure 1. Temperature variation of the recombination coefficient for hydrogen atoms on clean glass surfaces.[16, 17]

Table 3. Calculated Values of γ and k' for Clean Glass Surfaces

Temperature (°K)	γ	k' (cm sec⁻¹.)
90	0.46	6.8×10^4
180	0.22	1.1×10^4
200	2.2×10^{-2}	1.1×10^3
300	3.1×10^{-2}	1.9×10^3
400	3.3×10^{-2}	2.4×10^3
550	3.2×10^{-2}	2.8×10^3

$$S\text{—H} + \text{H} \rightarrow S + \text{H}_2$$

$$S + \text{H} \rightarrow S\text{—H}$$

This is consistent with Langmuir's result[9] that hydrogen atoms are adsorbed on clean glass down to liquid air temperatures, with a packing of about 1.35×10^{15} atoms per cm^2 (the value used above); moreover, Johnson[19] found that desorption only sets in between 200 and 300°C. To explain the fact that the activation energy of the reaction is zero at low temperatures and 0.9 kcal at higher ones it has been suggested[10] that the hydrogen atoms are van der Waals adsorbed to the glass in the low temperature region and chemisorbed at the higher temperatures. Thus, Beebe and his co-workers[24] have shown that in certain cases the heat of adsorption increases with increasing temperature. Support for the mechanism proposed is provided by the fact that the estimated activation energies for the high temperature region are in satisfactory agreement with the experimental values.

THE PRODUCTION OF HYDROGEN ATOMS AT HOT SURFACES[25]

It has been seen on p. 181 that the kinetics of the production of hydrogen atoms at a hot tungsten surface are best explained on the basis of a mechanism in which a molecule strikes a bare surface site, whereupon an atom is adsorbed and one passes into the gas phase. The isotherm for the dissociative adsorption of hydgogen is

$$\frac{c_g}{c_S} = c_g^{1/2} \frac{f_a}{F_g f_S} e^{\epsilon/kT} = Kc_g^{1/2} \tag{41}$$

where ϵ is the heat of adsorption per hydrogen atom. Together with $c_a + c_S = L$ this gives for the concentration of bare sites

$$c_S = \frac{L}{1 + Kc_g^{1/2}} \tag{42}$$

where K is equal to $(f_a/F_g f_S)e^{\epsilon/kT}$. The rate, involving interaction between a bare site and a hydrogen molecule, is therefore

$$v = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon'/kT} \tag{43}$$

$$= \frac{Lc_g}{1 + Kc_g^{1/2}} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon'/kT} \tag{44}$$

This expression gives rise to half-order kinetics provided that $Kc_g^{1/2} \gg 1$, when

$$v = c_g^{1/2} \frac{L}{K} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon'/kT} \tag{45}$$

$$= c_g^{1/2} L \frac{kT}{h} \frac{f_{\ddagger}}{F_g^{1/2} f_a} e^{-(\epsilon+\epsilon')/kT} \tag{46}$$

If, on the other hand, $Kc_g^{1/2} \ll 1$, which will obtain at higher temperatures, the rate expression is

$$v = c_g L \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon'/kT} \tag{47}$$

On the basis of the result that the rate is proportional to the square root of the pressure it has generally been assumed that Eq. (46) is directly applicable, but there are some difficulties about this view. Equation (46) corresponds to the process $\frac{1}{2}H_2 = H$, which is endothermic by 51.6 kcal; the activation energy must therefore be at least this. However, the experimental energy of activation corrected to 0°K is 43.9 kcal, which is significantly less than 51.6 kcal. Some support for the conclusion that the activation energy is really less than one-half of the heat of dissociation of hydrogen is provided by the fact that rates calculated on the basis of 51.6 kcal are too low by a factor of about 100. The rates are given in Table 4, which includes calculations with an activation energy of 43.9 kcal. These rates agree better with experiment, but are still too low.

The best interpretation would appear to be that the limiting law, represented by Eq. (46), is not directly applicable, but that Eq. (44) should be applied. According to this interpretation the activation energy will lie between E' and $E' + E$, which, since E' is small, may be much less than 51.6 kcal. This interpretation implies that the rate is no longer exactly proportional to the square root of the pressure; the pressure range used in the experiments (3×10^{-2} mm to 3.7×10^{-2} mm) is hardly great enough to exclude this possibility.

TABLE 4. THE FORMATION OF HYDROGEN ATOMS ON TUNGSTEN
(p is in mm of Hg; v is in atoms cm^{-2} sec^{-1}.)

Temperature (°K)	$v/p^{1/2}$ (Observed)	$v/p^{1/2}$ (Calc. with $E = 51.6$)	$v/p^{1/2}$ (Calc. with $E = 43.9$)
1148	6.6×10^{15}	2.9×10^{13}	8.6×10^{14}
1243	3.0×10^{16}	1.6×10^{14}	3.6×10^{15}
1378	1.1×10^{17}	1.1×10^{15}	1.9×10^{16}
1421	2.9×10^{17}	1.8×10^{15}	2.8×10^{16}

THE PARAHYDROGEN CONVERSION ON TUNGSTEN[26]

The kinetic laws for the conversion of parahydrogen into orthohydrogen on a tungsten surface were discussed in detail in Chapter 4, and it was shown that the data strongly favor the Bonhoeffer-Farkas mechanism, according to which the conversion is controlled by the rate of the dissociative chemisorption of the parahydrogen. It now remains to check the possibility of this interpretation by an order of magnitude calculation of the rate.

According to Eley and Rideal[27] the absolute rate of the conversion is 2.1×10^{18} molecules per sq cm per sec. at -100°C, at a parahydrogen pressure of 1 mm, and the activation energy varies from 1.0 to 3.8 kcal. The adsorption process involves dissociation into hydrogen atoms, so that either

Eq. (22) or Eq. (24) may apply to the rate of adsorption. As previously mentioned (p. 202), the pressure dependence of the adsorption process was not determined by Roberts; however the data on the parahydrogen conversion require that Eq. (22) is applicable. When the conversion is studied at constant total pressure, i.e., when the fraction of surface covered is kept constant, the rate is found to be strictly proportional to $k(p - p_e)$, where p is the parahydrogen pressure at any time, and p_e is the equilibrium pressure. This is only understandable if Eq. (22) applies; Eq. (24) would lead to a conversion law of the form $k(p^{1/2} - p_e^{1/2})$.

Under the conditions of the experiments of Eley and Rideal the surface was about 90 per cent covered, so that c_S is equal to 10^{14} sites per sq cm; the concentration of bare dual sites, c_{S_2}, is $sc_S^2/2L$ and is 2×10^{13} if a coordination number s of 4 is assumed. Using these values, and values of unity for $f_{\ddagger}$ and f_a and 3.4×10^{23} for parahydrogen, Eq. (22) gives a rate at $-100°C$ and a pressure of 1 mm of $v = 3.0 \times 10^{18}\, e^{-E/RT}$ molecules $cm^{-2}\, sec^{-1}$. This is consistent with the value of 2.1×10^{18} if there is a small activation energy. The question of the influence of interaction forces on this calculation is considered on p. 239.

It was seen earlier (p. 180) that the Rideal mechanism seems to be incapable of explaining the order of the conversion. Absolute rate calculations also render unlikely this type of mechanism. The theoretical rate is now found to be $10^{20}\, e^{-E/RT}$, and this requres an activation energy of about 1.5 kcal for agreement with the data. This energy of activation is too low for this type of mechanism involving the dissociation of a hydrogen molecule by interaction with an adsorbed hydrogen atom; a value of 7 kcal applies to the reaction $H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$ even when the reacting atom is free, and the Rideal mechanism requires a value at least as great as this.

UNIMOLECULAR REACTIONS

The formulation of the absolute rates of ordinary chemical reactions is very similar to that of adsorption processes. The case of unimolecular reactions will be considered first: these involve reaction between a gas molecule and a surface site, to give an activated complex at the surface.

Consider a reaction involving one molecule of the gaseous reactant A, which is either decomposing or isomerizing on the surface. If the process occurs on a single site S it may be written as

$$A + S \rightleftharpoons AS^{\ddagger} \rightarrow \text{products},$$

and the equilibrium between initial and activated states is

$$\frac{c_{\ddagger}}{c_g c_S} = \frac{f^{\ddagger}}{F_g f_S}\, e^{-\epsilon/kT} \tag{48}$$

where ϵ is the energy of activation at the absolute zero. The rate of reaction is therefore given by

$$v = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{49}$$

The expression is formally identical with that for the rate of adsorption [Eq. (5)], but the activated states are different in the two cases. However, in both cases the value of the partition function $f_{\ddagger}$ may be taken as unity, since the activated state consists of a molecule immobilized on the surface.

Two limiting cases of Eq. (49) are of interest, according to whether c_S is large or small.

First-order Kinetics

If the surface is only sparsely covered by adsorbed molecules c_S, the concentration of bare surface sites, is approximately equal to L, the number of sites per sq cm of completely bare surface. Under these conditions c_S is therefore approximately independent of c_g, so that the rate of reaction is directly proportional to c_g; the process is therefore kinetically of the first order.

If a reaction of this type occurs on a dual surface site the concentration c_S in Eq. (49) must be replaced by c_{S_2}. As seen on p. 198, for a bare surface c_{S_2} is equal to $\frac{1}{2}sc_S$, i.e., to $\frac{1}{2}sL$, so that the rate is

$$v = \tfrac{1}{2}sc_g L \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{50}$$

If the reaction involves a diatomic molecule the rate equation becomes

$$v = c_g L \frac{\sigma}{\sigma_{\ddagger}} \frac{\frac{1}{2}sh^4}{8\pi^2 I(2\pi mkT)^{1/2}} e^{-\epsilon_0/kT} \tag{51}$$

where σ and $\sigma_{\ddagger}$ are the symmetry numbers of the molecules of reactant and activated complex, respectively, and I and m are the moment of inertia and the mass of the reacting molecule. For a nonlinear polyatomic molecule the rate is

$$v = c_g L \frac{\sigma}{\sigma_{\ddagger}} \frac{\frac{1}{2}sh^5}{8\pi^2(8\pi^3 ABC)^{1/2}(2\pi m)^{3/2}(kT)^2} e^{-\epsilon_0/kT} \tag{52}$$

where A, B and C are the three moments of inertia of the reactant.

Experimental data are available for the decompositions of phosphine[28], hydrogen iodide[29] and nitrous oxide[30], which obey the first-order law. The rates have been calculated using the above equation, s being taken as 4 in each case, and L being taken as 10^{15} sites per sq cm. The calculated and observed values are compared in Table 5; the rates quoted are the ordinary first-order rate constants which refer to the particular surface area involved in the experiment. The calculated and observed rates are in satisfactory agreement, considering the errors inherent in the calculations and in the experimental values (particularly in the activation energies). It should be noted that the observed rates are in two of the cases appreciably higher than the calculated. This may be due to roughness of the surface, which would make the value of L greater than the value employed, and partly to the fact that there may be some freedom of movement in the activated state. In the case of relatively complex molecules, such as phosphine and nitrous oxide, rotation or vibration in the activated state may well be appreciable, and the inclusion of a contribution for this would increase the calculated reaction rates.

TABLE 5. OBSERVED AND CALCULATED RATES FOR FIRST-ORDER REACTIONS

Decomposition of	Surface	Temperature (°K)	Rate Constant, sec⁻¹.	
			Calc.	Obs.
PH_3	Glass	684	2.2×10^{-8}	4.7×10^{-7}
HI	Platinum	836	1.2×10^{-3}	1.0×10^{-3}
N_2O	Gold	1211	3.4×10^{-6}	12.3×10^{-5}

Zero-order Kinetics

When the surface is almost completely covered by adsorbed molecules the concentration c_S varies with the pressure of the gas, and the kinetic law may be obtained by combining the rate equation (49) with the isotherm

$$\frac{c_a}{c_S} = c_g \frac{f_a}{F_g f_S} e^{-\epsilon/kT} \tag{53}$$

The rate law obtained is

$$v = c_a \frac{kT}{h} \frac{f_{\ddagger}}{f_a} e^{-(\epsilon_0+\epsilon)/kT} \tag{54}$$

When the surface is almost completely covered by adsorbed molecules c_a may be taken as constant, so that the rate is independent of the pressure of the reactant; the kinetics are therefore zero-order.

Since both $f_{\ddagger}$ and f_a may be taken as unity the rate law may be written as

$$v = c_a \frac{kT}{h} e^{-E/RT} \tag{55}$$

where E is the activation energy per mole at the absolute zero. An equation of this general form, with a frequency factor of 10^{12} per second in place of kT/h, was first proposed by Topley[31].

In Table 6 are given some of the calculated and observed rates, expressed as molecules per sq cm per sec., for reactions which exhibit zero-order kinetics; in all cases the value of c_a was taken to be 10^{15}. The agreement is seen to be satisfactory except for the decomposition of hydrogen iodide on gold; the discrepancy here is presumably due to the fact that the reaction occurs on a small fraction of the surface.

TABLE 6. OBSERVED AND CALCULATED RATES FOR ZERO-ORDER REACTIONS

Decomposition of	Surface	E (kcal)	Temp (°K)	Rate		Ref.
				Calc.	Obs.	
NH_3	W	38.0	904	8.0×10^{18}	4×10^{17}	1
NH_3	W	41.5	1316	3.4×10^{21}	2×10^{19}	2
NH_3	Mo	53.2	1228	8.5×10^{18}	$5\text{–}20 \times 10^{18}$	3
HI	Au	25.0	978	5.2×10^{22}	1.6×10^{17}	4
$HCOOCH(CH_3)_2$	Glass	35.0	714	7.5×10^{17}	5.8×10^{16}	5

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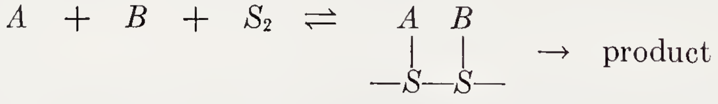
BIMOLECULAR REACTIONS PROCEEDING BY LANGMUIR-HINSHELWOOD MECHANISMS

When reaction occurs between two molecules, both of which are adsorbed (i.e., by a Langmuir-Hinshelwood mechanism), it may be supposed that it is necessary for the molecules to be adsorbed on adjacent sites. The reaction may thus be formulated as



$$A + B + S_2 \rightleftharpoons \begin{array}{c} A \quad B \\ | \quad\; | \\ -S-S- \end{array} \rightarrow \text{product}$$

where A and B are the reacting molecules and S_2 is a dual site. The rate of reaction is then given by

$$v = c_g c_g' c_{S_2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g F_g' f_{S_2}} e^{-\epsilon_0/kT} \tag{56}$$

where c_g and c_g' are the gas-phase concentrations of A and B and F_g and

F_g' are the corresponding partition functions per unit volume. On p. 199 it was seen that the concentration of bare dual sites is related to the concentration of bare single sites by

$$c_{S_2} = \tfrac{1}{2} s c_S^2 / L \tag{57}$$

so that the rate may be formulated as

$$v = \tfrac{1}{2} s \frac{c_g c_g' c_S^2}{L} \frac{kT}{h} \frac{f_\ddagger}{F_g F_g' f_{S_2}} e^{-\epsilon_0/kT} \tag{58}$$

This equation may be put into a more general form, using the isotherms

$$\frac{c_a}{c_g c_S} = K \tag{59}$$

and

$$\frac{c_a'}{c_g' c_S} = K' \tag{60}$$

where c_a and c_a' are the concentrations of adsorbed A and adsorbed B. Since in addition

$$c_a + c_a' + c_S = L \tag{61}$$

it is found that

$$c_S = = \frac{L}{1 + Kc_g + K'c_g'} \tag{62}$$

Insertion of this expression into Eq. (58) gives

$$v = \frac{\tfrac{1}{2} s c_g c_g' L}{(1 + Kc_g + K'c_g')^2} \frac{kT}{h} \frac{f_\ddagger}{F_g F_g' f_{S_2}} e^{-\epsilon_0/kT} \tag{63}$$

as the general equation for a bimolecular reaction. This may be seen to have the same form as Eq. (74) in Chapter 4. The equation is best applied to the data in its various limiting forms, as follows.

When the surface is sparsely covered Kc_g and $K'c_g'$ can be neglected in comparison with unity; the rate equation is then

$$v = \tfrac{1}{2} s c_g c_g' L \frac{kT}{h} \frac{f_\ddagger}{F_g F_g' f_S} e^{-\epsilon_0/kT} \tag{64}$$

so that the kinetics are second order.

This equation has been applied to the reaction between nitric oxide and oxygen on a glass surface. This reaction has been found experimentally to be of the second order, the rate at 85°K being given[32] by

$$v = 9.4 \times 10^{-27}\, c_{\mathrm{NO}} c_{\mathrm{O}_2}\, e^{-\epsilon_0/kT} \text{ molecules cm}^{-2} \text{ sec.}^{-1}$$

the concentrations of the reacting gases being in molecules per cc. The rate has been calculated assuming $f_{\ddagger}/f_S$ to be unity, L to be 10^{15} sites per sq cm, and s to be 4. The result was

$$v = 14.8 \times 10^{-27}\, c_{\mathrm{NO}} c_{\mathrm{O}_2}\, e^{-\epsilon_0/kT} \text{ molecules cm}^{-2} \text{ sec.}^{-1}$$

in satisfactory agreement with the experimental value.

If B is only weakly adsorbed, but A is not necessarily weakly adsorbed, $K'c_g'$ may be neglected, but not Kc_g; the rate equation is thus

$$v = \tfrac{1}{2}\, s\, \frac{Lc_g c_g'}{(1 + Kc_g)^2}\, \frac{kT}{h}\, \frac{f_{\ddagger}}{F_g F_g' f_{S_2}}\, e^{-\epsilon_0/kT} \tag{65}$$

The rate will therefore pass through a maximum as c_g is increased, the maximum occurring when $Kc_g = 1$.

If A is strongly adsorbed, Kc_g is large compared with unity, and the equation becomes

$$v = \tfrac{1}{2}\, s\, \frac{L}{K^2}\, \frac{c_g'}{c_g}\, \frac{kT}{h}\, \frac{f_{\ddagger}}{F_g F_g' f_{S_2}}\, e^{-\epsilon_0/kT} \tag{66}$$

If K is expressed in terms of partition functions equation (66) becomes

$$v = \tfrac{1}{2}\, sL\, \frac{c_g'}{c_g}\, \frac{kT}{h}\, \frac{F_g f_{\ddagger} f_S}{F_g' f_a^2}\, e^{-(\epsilon_0 + 2\epsilon)/kT} \tag{67}$$

The activation energy will be greater by 2ϵ then the value for a sparsely covered surface; the reason for this is that two molecules of A must be desorbed before the activated complex is formed.

Equation (67) has been applied quantitatively to the reaction between carbon monoxide and oxygen on a platinum surface. The observed rate at 572°K was found[33] to be equal to

$$v = 7.10 \times 10^{14}\, \frac{c_{\mathrm{O}_2}}{c_{\mathrm{CO}}} \text{ molecules cm}^{-2} \text{ sec}^{-1}$$

the activation energy being 33.3 kcal at this temperature. The calculated rate was found to be

$$v = 4.33 \times 10^{15} \frac{c_{O_2}}{c_{CO}} \text{ molecules cm}^{-2} \text{ sec}^{-1}$$

in satisfactory agreement with experiment.

When both reacting molecules are the same the general rate equation, (63), becomes

$$v = \tfrac{1}{2}\, s \frac{c_g^2 c_S^2}{L} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_S} e^{-\epsilon_0/kT} \tag{68}$$

If the surface is sparsely covered Eq. (68) reduces to

$$v = \tfrac{1}{2}\, s c_g^2 L \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_S} e^{-\epsilon_0/kT} \tag{69}$$

The general rate equation is

$$v = \tfrac{1}{2}\, s \frac{L c_g^2}{(1 + K\, c_g)^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_S} e^{-\epsilon_0/kT} \tag{70}$$

When the surface is almost completely covered

$$v = \tfrac{1}{2}\, s \frac{L}{K^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_S} e^{-\epsilon_0/kT} \tag{71}$$

$$= \tfrac{1}{2}\, sL \frac{kT}{h} \frac{f_{\ddagger} f_S}{f_a^2} e^{-(\epsilon_0 + 2\epsilon)/kT} \tag{72}$$

Interaction Between an Adsorbed Molecule and a Gaseous Molecule[34]

The equations for the absolute rate of a reaction involving interactions between a gaseous molecule and an adsorbed molecule may readily be derived, as follows. Suppose that reaction occurs between an adsorbed molecule A, of concentration c_g in the gas phase, and a gaseous molecule B, of concentration c_g'. Solution of Eqs. (59), (60) and (61) gives for the concentration of adsorbed A,

$$c_a = \frac{LKc_g}{1 + Kc_g + K'c_g'} \tag{73}$$

The rate of reaction is

$$v = c'_g c_a \frac{kT}{h} \frac{f_{\ddagger}}{F'_g f_a} e^{-\epsilon'_0/kT} \tag{74}$$

where ϵ'_0 is the activation energy for molecule at the absolute zero. Using Eq. (73) this becomes

$$v = \frac{LKc_g c'_g}{1 + Kc_g + K'c'_g} \frac{kT}{h} \frac{f_{\ddagger}}{F'_g f_a} e^{-\epsilon'_0/kT} \tag{75}$$

$$= \frac{Lc_g c'_g}{1 + Kc_g + K'c'_g} \frac{kT}{h} \frac{f_{\ddagger}}{F_g F'_g f_S} e^{-(\epsilon'_0 - \epsilon)/kT} \tag{76}$$

This is of the same form as Eq. (83) on p. 154.

If, on the other hand, interaction occurs between gaseous A and adsorbed B the equations become

$$v = c_g c'_a \frac{kT}{h} \frac{f_{\ddagger}}{F_g f'_a} e^{-\epsilon''_0/kT} \tag{77}$$

$$= \frac{LK'c_g c'_g}{1 + Kc_g + K'c'_g} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f'_a} e^{-\epsilon''_0/kT} \tag{78}$$

$$= \frac{Lc_g c'_g}{1 + Kc_g + K'c'_g} \frac{kT}{h} \frac{f_{\ddagger}}{F_g F'_g f_S} e^{-\epsilon_0'/kT} \tag{79}$$

It is of considerable interest that this equation is of exactly the same form as Eq. (76).

These equations have not been applied quantitatively to any reactions since, as discussed in Chapter 4, there are very few reactions for which there is unequivocal evidence that this type of process occurs; for none of these are the data sufficiently complete for comparative calculations to be made. It may, however, be noted here that the limiting rates predicted by Eqs. (76) and (79) are very close to the maximum rates for the Langmuir-Hinshelwood mechanism. It is not, therefore, possible to distinguish between the two types of mechanism on the basis of quantitative calculations. This is so, for example, in the case of the ethylene-hydrogen reaction (p. 168) for which there is controversy as to the mechanism. The rate equations for both mechanisms give rise to satisfactory agreement with experiment; a final decision must therefore await a more exhaustive investigation of the variation of rate with ethylene concentration.

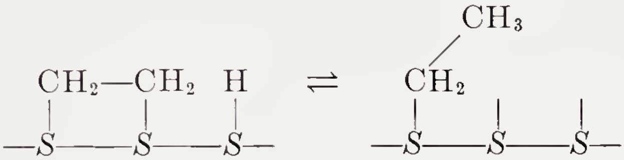
SOME SPECIAL REACTIONS

The Hydrogenation of Ethylene

The treatment given above requires modification and extension for the case of the hydrogenation of ethylene, since in this reaction the ethylene presumably occupies a pair of sites, and the hydrogen is adsorbed with dissociation. The kinetic laws applicable to this reaction were discussed in the previous chapter, in which it was shown that the Langmuir-Hinshelwood treatment is probably applicable.

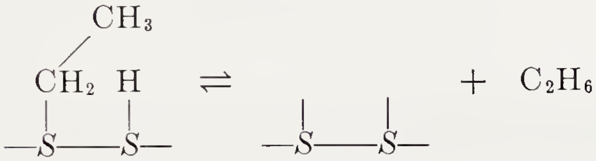
The mechanism on which the absolute rate treatment is based is as follows[35]. Ethylene is assumed to be adsorbed on dual surface sites, hydrogen atoms on single sites. Adsorbed ethyl radicals may be formed by interaction between adsorbed ethylene and hydrogen atoms,

(1)



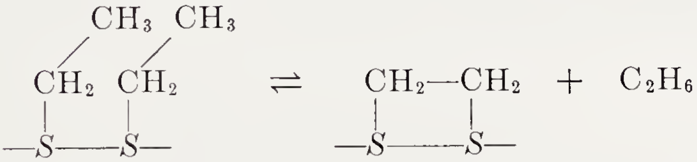
Ethane can be produced either by interaction between adsorbed ethyl and adsorbed H,

(2)



or between two ethyl radicals adsorbed on neighboring sites

(3)



In the formulation of the absolute rate equations[36] it will be assumed that the surface is sparsely covered by all species except ethylene, which is adsorbed on dual sites. The isotherm for ethylene adsorption is

$$\frac{c_a}{c_{S_2}} = Kc_g \tag{80}$$

where c_{S_2} is the concentration of dual sites, equal to $sc_s^2/2L$. Since the surface is only very sparsely covered by hydrogen,

$$L = 2c_a + c_S \tag{81}$$

and it is found that

$$2sKc_gc_a^2 - L(1 + 2sKs_g)c_a + \tfrac{1}{2}sKL^2c_g = 0 \tag{82}$$

The solution of this is

$$c_a = L\,\frac{1 + x - (1 + 2x)^{1/2}}{2x} \equiv LA \tag{83}$$

where $x = 2sKc_g$. Also,

$$c_S = L\,\frac{(1 + 2x)^{1/2} - 1}{x} \equiv LB \tag{84}$$

Plots of $c_a/L(= \theta/2)$ and $c_S/L(= 1 - \theta)$ against x are shown in Figure 2. The isotherm for hydrogen adsorption is

$$\frac{c_{a'}}{c_S} = K'^{\,1/2}c_{g'}^{\,1/2} \tag{85}$$

so that

$$\theta' = \frac{c_{a'}}{L}\,BK'^{\,1/2}c_{g'}^{\,1/2} \tag{86}$$

The concentration of adsorbed C_2H_5 radicals may be calculated as follows. The concentration of adsorbed ethylenes which have a hydrogen atom adsorbed on any one of a neighboring surface site is given by $c_{aa'} = sc_a\theta'$. According to reaction (1) the concentration of adsorbed ethyls, $c_{a''}$, is given by

$$\frac{c_{a''}}{c_{aa'}} = \frac{c_{a''}}{sc_a\theta'} = \frac{f_{a''}}{f_{aa'}}\,e^{\epsilon''/kT} \tag{87}$$

The fraction of surface covered by ethyls is thus

$$\theta'' = \frac{c_{a''}}{L} = \frac{sc_a\theta'}{L}\,\frac{f_{a''}}{f_{aa'}}\,e^{\epsilon''/kT} \tag{88}$$

If ethane is produced by reaction between an adsorbed ethyl and an adsorbed hydrogen atom [reaction (2)], the rate is as follows. The concentration of ethyls which are next to a hydrogen atom is

$$c_{a'a''} = sc_{a''}\theta' = s^2c_a\theta'^2\,\frac{f_{a''}}{f_{a'}}\,e^{\epsilon''/kT} \tag{89}$$

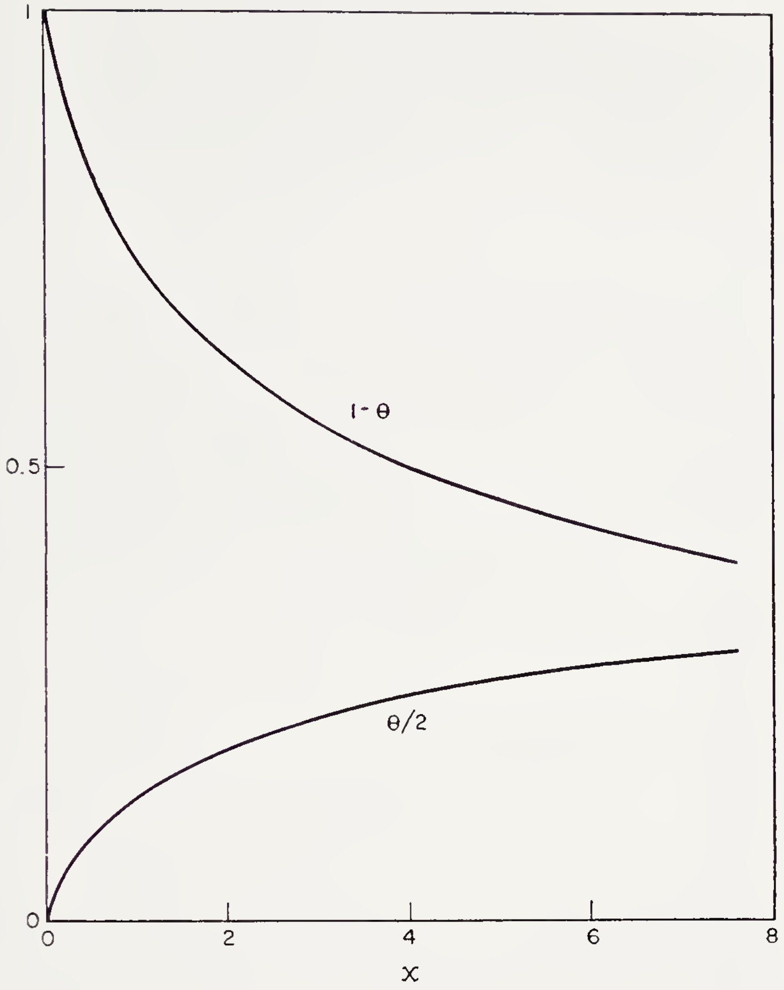


Figure 2. Plots of c_a/L $(= \theta/2)$ and c_s/L $(= 1 - \theta)$ against $x(= 2sKc_g)$. (See equations 83 and 84 for the adsorption of ethylene and the concentration of bare surface, respectively.)

The rate of reaction by this mechanism is therefore

$$v = \frac{kT}{h} s^2 c_a \theta'^2 \frac{f_{\ddagger} f_{a''}}{f_{a'a''} f_{aa'}} e^{-(\epsilon_0 - \epsilon'')/kT} \tag{90}$$

$$= s^2 LAB^2 c_{g'} \frac{kT}{h} \frac{1}{F_{g'}} e^{-(\epsilon_0 - \epsilon'' - 2\epsilon)/kT} \tag{91}$$

where A and B are as defined in Eqs. (83) and (84). In Eq. (91) the partition functions for adsorbed species have been written as unity, and K' is written as $(1/F_g)^{1/2} e^{2\epsilon/kT}$, where ϵ is the energy of adsorption per atom of hydrogen.

The rate is seen to vary directly with $c_{g'}$, i.e., the hydrogen pressure, but to vary in a complex manner with x, i.e., with the ethylene pressure.

The function AB^2 is plotted against x in Figure 3 (curve a), and it is seen that the variation is quite similar to that of $x/(1 + x)^2$, (curve b), which was given by the simpler treatment of Eq. (65). The function AB^2 passes through a maximum at $x = 1.5$, as can also be shown analytically. The value of AB^2 is then 0.074, so that the maximum rate is

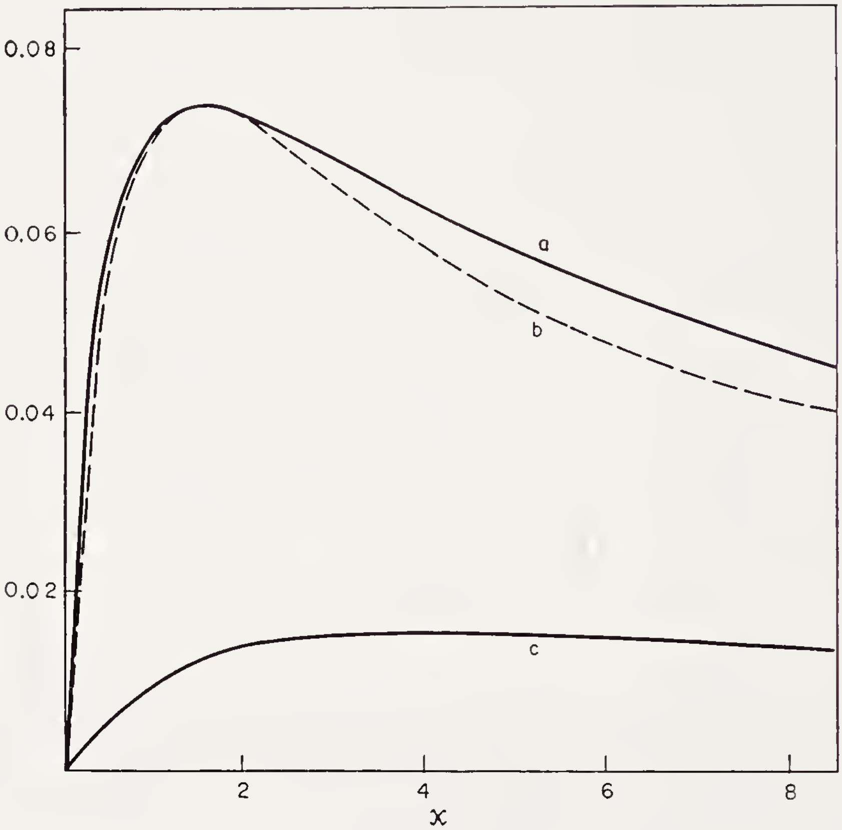


Figure 3. Plots of various functions for the rate of catalytic hydrogenation of ethylene against x: curve (a) AB^2; curve (b), $x(1 + x)^2$; curve (c), A^2B^2. The functions A and B are defined by Eqs. (83) and (84).

$$v_{\max} = 0.074 s^2 L \frac{kT}{h} \frac{1}{F_{g'}} e^{-(\epsilon_0 - \epsilon' - 2\epsilon)/kT} \tag{92}$$

The second possibility is that ethane is formed by interaction between two ethyl radicals adsorbed on neighboring sites [reaction (3)]. The concentration of ethyls adsorbed on neighboring sites is

$$c_{a''a''} = \tfrac{1}{2} s c_{a''} \theta'' = \tfrac{1}{2} s^3 \frac{c_a^2 \theta'^2}{L} \frac{f_{a''}^2}{f_{aa'}^2} e^{2\epsilon''/kT} \tag{93}$$

so that the rate of reaction by this mechanism is

$$v = c_{a''a''} \frac{kT}{h} \frac{f_{\ddagger}}{f_{a''a''}} e^{-\epsilon_0/kT} \tag{94}$$

$$= \tfrac{1}{2} s^3 L A^2 B^2 c_{g'} \frac{kT}{h} \frac{1}{F_{g'}} e^{-(\epsilon_0 - 2\epsilon' - 2\epsilon)/kT} \tag{95}$$

The rate is again seen to be proportional to $c_{g'}$, and the plot of the function A^2B^2, in Figure 3 (curve *c*) shows that the rate again passes through a maximum with increasing $c_{g'}$. The maximum value of the function is .0156, this value corresponding to $x = 4$.

The third possibility, which we consider unlikely (see p. 169), is Twigg's mechanism which involves interaction between adsorbed ethylene and gaseous hydrogen. The rate equation for this is

$$v = LAc_{g'} \frac{kT}{h} \frac{1}{F_{g'}} e^{-\epsilon_0/kT} \tag{96}$$

At high values of c_g the rate reaches a limiting value of

$$v_{\text{max}} = \tfrac{1}{2} L c_{g'} \frac{kT}{h} \frac{1}{F_{g'}} e^{-\epsilon_0/kT} \tag{97}$$

It is of particular interest that the present treatment leads to the conclusion that the rate passes through flatter maxima (curve *a*) than were predicted by the simpler treatment (curve *b*); this is especially the case when reaction involves interaction between two ethyl radicals. This makes it even more difficult, in considering experimental data, to exclude the possibility of a falling off of the rate at high ethylene pressures.

The numerical factors appearing in the rate expressions are $0.074s^2$ for the first mechanism [Eq. (92)], and $0.0156 \times \tfrac{1}{2}s^3$ by the second mechanism [Eq. (95)]; for $s = 4$, these factors are 1.2 and 0.5. These are too close to permit a decision as to the mechanism to be made on the basis of the data. In the numerical calculations a value of unity has been taken for the factor.

In Table 7 are quoted some experimental rates, calculated as molecules reacting per sec per sq cm of surface; a selection of values has been made from the work of various authors. Absolute rates have been calculated as indicated above, using a numerical factor of unity. The agreement with experiment indicates that both Eqs. (91) and (95) give a satisfactory interpretation of the reaction.

The Methane-Deuterium Exchange Reaction[37]

The data of Kemball[38] on the methane-deuterium exchange on evaporated nickel surfaces were discussed in some detail in Chapter 4 (p. 169). It was shown there that the results suggest that methane is adsorbed both as CH_3 and as CH_2 radicals, and that CH_3D is probably formed by addition of a deuterium atom to a CH_3 ; CH_2D_2 , CHD_3 and CD_4 , however, are formed from adsorbed CH_2 radicals. The conditions are such that the surface is sparsely covered by methane and well covered by deuterium which is adsorbed atomically.

Absolute rate expressions for the reaction have been formulated, the general approach being similar to that for parahydrogen conversion (p. 210). The exchange processes which occur on the surface, i.e., the production of adsorbed CH_2D from adsorbed CH_3 and D and of adsorbed CH_2D_2 , CHD_3 and CD_4 from adsorbed CH_2 and D, are considered to occur rapidly, the slow process in each case being the desorption of the products from the surface. Adsorption equilibrium, apart from exchange, is assumed to be established rapidly, and the concentrations of adsorbed CH_3 and CH_2 are therefore calculated from the equilibrium expressions. The rate of removal of CH_2 from the surface, equal to the rate of adsorption of methane as CH_3, controls the rate of production of CH_3D, the proportionality factor being the statistical weight expressing the probability that an adsorbed CH_2 will pick up a D rather than an H. Similarly the rates of production of CH_2D_2 , CHD_3 and CD_4 , are controlled by the over-all rate of desorption of CH_2 , which is initially equal to the rate of adsorption of methane as CH_2 ; the proportionality factors are now the statistical factors for the uptake of two, three and four deuterium atoms, respectively.

TABLE 7. ABSOLUTE RATES OF ETHYLENE HYDROGENATION

Surface	Temp. (°C)	Surface			Rate $\times 10^{-16}$ (molecules cm^{-2} sec^{-1}.)		Ref.
		p_{H_2} (mm)	Area (cm^2)	*E* exp (kcal)	Obs.	Calc.	
Ni	120	14	0.47	4.7	2.6	14.3	1
Ni	117	72.5	1.88	6.0	2.1	16.3	2
Ni	156	29.9	2.51	3.2	142	320	3
Ni-Si	156	760	0.04	5.5	150	250	4

1. Farkas, A., Farkas, L., and Rideal, E. K., *Proc. Roy. Soc.*, **A146**, 630 (1934).
2. Toyama, O., *Rev. Phys. Chem., Japan*, **12**, 115 (1938).
3. Twigg, G. H., and Rideal, E. K., *Proc. Roy. Soc.*, **A171**, 55 (1939).
4. Schwab, G. M., and Zorn, H., *Z. physik. Chem.*, **B32**, 169 (1936).

The equation for the rate of formation of CH_3D is derived as follows. Methyl radicals, hydrogen atoms and deuterium atoms are assumed to be adsorbed on single surface sites, and the rate of formation of CH_2D is the rate with which adsorbed CH_3 and D are desorbed together from the surface. The equilibrium for deuterium adsorption may be written as

$$\tfrac{1}{2}D_2 + S \rightleftharpoons S\text{—}D$$

The equilibria involving H_2 and HD may be neglected since initially D_2 predominates. The surface is sparsely covered by methane and well covered by deuterium, so that the concentration of bare sites is given by the equations

$$L = c_S + c_{a'} \tag{98}$$

and

$$\frac{c_{a'}}{c_S} = K' c_{g'}^{1/2} \tag{99}$$

where the prime indicates deuterium. These equations give rise to

$$c_S = \frac{L}{1 + K' c_{g'}^{1/2}} \tag{100}$$

$$\doteq \frac{L}{K' c_{g'}^{1/2}} \tag{101}$$

for full coverage.

The rate of adsorption of methane as methyl radicals is

$$v = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{102}$$

$$= \frac{c_g}{c_{g'}^{1/2}} \frac{L}{K'} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{103}$$

$$= \frac{c_g}{c_{g'}^{1/2}} L \frac{kT}{h} \frac{f_{\ddagger} F_{g'}^{1/2}}{F_g f_{a'}} e^{-(\epsilon_0+\epsilon)/kT} \tag{104}$$

since $K' = (f_{a'}/F_{g'}^{1/2} f_S)e^{\epsilon/kt}$ where ϵ is the energy of adsorption at 0°K per deuterium atom. The treatment is seen to account correctly for the pressure dependence of the rate. This equation essentially gives the rate of desorption of CH_3D, since the probability that an adsorbed CH_3 will pick up a deuterium atom is close to unity on account of the high surface coverage by deuterium atoms.

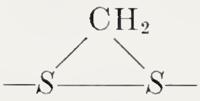
Equation (104) has been applied to Kemball's data, taking $f_{\ddagger}$ and $f_{a'}$

as unity and L as 13.6×10^{16} sites per milligram of catalyst, this value having been determined directly by Kemball. The calculated rates are seen to be in excellent agreement with the observed (Table 8).

TABLE 8. RATES OF FORMATION OF CH_3D

Temp (°K)	p_{D_2} (mm 0°C)	p_{CH_4} (mm 0°C)	Rate $\times 10^{-13}$ (molecules mg^{-1} sec^{-1}.)	
			Calc.	Obs.
499.4	2.49	12.4	13.0	19.0
503.2	4.82	3.26	2.3	3.0
499.4	4.85	3.26	2.3	2.6
501.1	4.85	6.46	4.6	5.3
499.4	4.85	9.69	6.9	6.9
503.0	4.85	12.7	9.3	13.0
498.6	14.4	3.20	1.3	1.5
498.6	14.5	6.46	2.6	4.6

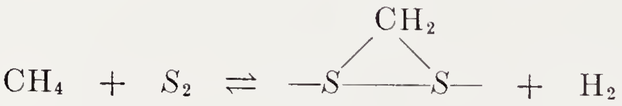
In addition to being adsorbed as methyl radicals it must be assumed that methane is also adsorbed as methylene radicals, which are presumably attached to two surface sites,



Whereas adsorbed methyl radicals can only add on deuterium atoms, methylene radicals can undergo rapid surface exchange and be desorbed as CHD_3 and CD_4 as well as CH_2D_2.

The initial equilibria are

(2)



$$CH_4 + S_2 \rightleftharpoons \overset{CH_2}{—S——S—} + H_2$$

and

(3)

$$\tfrac{1}{2} D_2 + S \rightleftharpoons SD$$

The methylenes only sparsely cover the surface, so that Eq. (101) again gives the concentration of single sites. The concentration of dual sites is equal to $\frac{1}{2}sc_S/L$, where s is the coordination number, so that

$$c_{S_2} = \frac{\frac{1}{2}sL}{K'^2 c_{g'}} \tag{105}$$

The rate of adsorption of methane in the form of methylene is given by

$$v = c_g c_{S_2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_{S_2}} e^{-\epsilon_0/kT} \tag{106}$$

$$= \tfrac{1}{2} s \frac{c_g}{c_{g'}} \frac{L}{K'^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_{S_2}} c^{-\epsilon_0/kT} \tag{107}$$

$$= \tfrac{1}{2} s \frac{c_g}{c_{g'}} L \frac{kT}{h} \frac{f_{\ddagger} F_{g'} f_S^2}{f_{a'}^2 F_g f_{S_2}} e^{-(\epsilon_0 + 2\epsilon)/kT} \tag{108}$$

Equation (108) also gives the total rate of desorption of CH_2 in the form of the various methanes, and is seen to give the correct pressure dependence for the formation of CH_2D_2, CD_3H and CD_4. To obtain the rates of formation of these Eq. (108) must be multiplied by suitable statistical factors, as follows. It is assumed that surface equilibration is established rapidly compared with the rates of desorption. Let q be the probability of a deuterium atom being picked up, and $1 - q$ the probability of a hydrogen atom being picked up. Then the relative probabilities that an adsorbed CH_2 will form CH_2D_2, CHD_3 and CD_4 are $6(1 - q)^2 q^2$, $4q^3(1 - q)$ and q^4. Kemball has listed experimental values of $q/(1 - q)$; the theoretical interpretation of q will now be considered.

The problem is primarily to calculate the concentration of adsorbed hydrogen atoms ($c_{a''}$) in terms of the concentrations of gaseous methane and deuterium. These hydrogen atoms arise from the adsorption of methane as methylene radicals, so that in addition to reactions (2) and (3) above the adsorption process

$$(4) \qquad \tfrac{1}{2}H_2 + S \rightleftarrows SH$$

must be considered. The equilibrium expressions corresponding to reactions (2) and (4) are

$$\frac{c_a c_{g''}}{c_g c_{S_2}} = K \tag{109}$$

and

$$\frac{c_{a''}}{c_{g''}^{1/2} c_{S_2}} = K'' \tag{110}$$

c_{S_2} is given by Eq. (105). Since an adsorbed methylene corresponds either to two adsorbed hydrogen atoms or to one gaseous hydrogen molecule it follows that

$$c_a = \tfrac{1}{2} c_{a''} + \frac{V}{S} c_{g''} \tag{111}$$

where V is the gas volume and S the surface area. Equations (109), (110) and (111) give rise to

$$c_{a''}^4 + \frac{SK''^2L}{sV} c_{S_2} c_{a''}^3 = \frac{4SK''^4L^2K}{s^2V} c_g c_{S_2}^3 \tag{112}$$

Consideration of the magnitudes of the quantities in this equation reveals that the second term can be neglected; hence

$$c_{a''} = \left[\frac{4SKK''^4L^2}{s^2V} c_g c_{S_2}^3\right]^{1/4} \tag{113}$$

$$= \left[\frac{sSKK''^4L^5}{2VK'^6}\right]^{1/4} \frac{c_g^{\ 1/4}}{c_{g'}^{\ 3/4}} \tag{114}$$

Since $c_{a'}$ is essentially L, it follows that

$$\frac{q}{1-q} = \frac{c_{a'}}{c_{a''}} = \left[\frac{2VK'^6}{sSKK''^4L}\right]^{1/4} \frac{c_{g'}^{\ 3/4}}{c_g^{\ 1/4}} \tag{115}$$

According to this a plot of $q(1-q)^{-1}$ vs. $c_{g'}^{\ 3/4}/c_g^{\ 1/4}$ should be linear, and this is found to be the case.

TABLE 9. RATES OF FORMATION OF CH_2D_2, CHD_3 AND CD_4

Temp (°K)	p_{D_2} (mm °C)	p_{CH_4} (mm °C)	Rate (molecules mg^{-1} sec^{-1}.) $\times 10^{-12}$								
			CH_2D_2			CHD_3			CD_4		
			Calc. (E = 32.0)	Calc. (E = 33.0)	Obs.	Calc. (E = 32.0)	Calc. (E = 33.0)	Obs.	Calc. (E = 32.0)	Calc. (E = 33.0)	Obs.
499.4	2.49	12.4	220	88	96	1260	380	340	2380	700	780
503.2	4.82	3.26	6	2.4	1.8	84	25	40	440	130	130
499.4	4.85	3.26	6	2.4	1.7	82	25	30	440	130	130
501.1	4.85	6.46	26	10	12	240	72	110	760	230	350
499.4	4.85	9.69	58	23	22	340	100	130	1100	330	460
503.0	4.85	12.7	72	29	28	520	170	230	1460	440	600
498.6	14.4	3.20	0.8	0.3	0.4	18	5	5	140	40	36
498.6	14.5	6.46	4.0	1.6	1.8	56	16	18	300	90	99

Equation (115) evidently permits an absolute calculation of $q(1-q)^{-1}$ and hence of the statistical factors for the formation of the various deuterated methanes. However, in view of the fact that the heats of adsorption (required for the calculation of K, K' and K'') are not accurately known, a more empirical procedure has been considered preferable. The calculations have accordingly been made using Kemball's experimental q's. Calculated values are shown in Table 9; Equation (108) has been used, together with the statistical factors. The calculations have been made using Arrhenius activation energies of 32 and 33 kcal, the former being the average of 34, 31 and 31 for the three reactions; the E_0 values used were obtained by subtracting $\frac{1}{2}RT$. The partition functions $f_\ddagger$, f_S, $f_{a'}$ and f_{S_2} were taken as unity, L as 13.6×10^{16} per mg and s as 4. The agreement between observed and calculated values in the case of 33 kcal is extremely good.

The Ethylene-Deuterium Exchange

The data of Twigg and Rideal[39] on the exchange reaction between ethylene and deuterium on a nickel surface were discussed in Chapter 4 (p. 171). It was concluded there that the best interpretation of the reaction appears to be that the rate is proportional to the square root of the deuterium pressure and is independent of the ethylene pressure. It is considered that a Langmuir-Hinshelwood mechanism is involved, the rate being at the maximum.

If this interpretation is accepted, the data admit readily of formulation in terms of absolute rate theory.[40] As discussed previously (p. 220) adsorbed ethylene is considered to react readily with adsorbed H or D to form an adsorbed ethyl radical, and these can revert to ethylene or deuterated ethylene in the gas phase by depositing a hydrogen atom on a bare site;

According to the treatment of a previous section [Eq. (87)] the concentration of adsorbed ethyl radicals is given by

$$c_{a''} = sc_a\theta' \frac{f_{a''}}{f_{aa'}} e^{\epsilon''/kT} \tag{116}$$

$$= sLABc_{g'}^{1/2} \frac{f_{a'}f_{a''}}{f_{aa'}f_SF_{g'}} e^{(\epsilon''+\epsilon)/kT} \tag{117}$$

where A and B are defined by Eqs. (83) and (84). It is assumed that there is always at least one bare site adjacent to an ethyl radical, so that the exchange rate can be considered to be controlled by the unimolecular breakdown of adsorbed ethyl radicals. Under the usual conditions H is in excess over D, so that the product is mainly CH_2CHD; the rate of production of this is thus approximately

$$v = sLABc_{g'}^{1/2} \frac{kT}{h} \frac{f_{a'}f_\ddagger}{f_{aa'}f_SF_{g'}} e^{-(\epsilon_0-\epsilon''-\epsilon)/kT} \tag{118}$$

The maximum rate is

$$v_{\max} = 0.0125\, sLc_{g'}{}^{1/2} \frac{kT}{h} \frac{1}{F_{g'}} e^{-(\epsilon_0 - \epsilon'' - \epsilon)/kT} \tag{119}$$

Comparison of this expression with that for hydrogenation [Eq. (85)] shows that the activation energy for exchange should be greater than that for hydrogenation by ϵ, the heat of adsorption per atom of hydrogen. Experimentally the activation energy difference is 9 kcal, and it is therefore most significant that Eley[41] gives the heat of adsorption per mole of hydrogen on a covered surface as 17 kcal, almost exactly twice the activation energy difference. This agreement provides strong support for the above mechanism and for the fact that the rate varies with the square root of the hydrogen pressure.

At 156°C and a deuterium pressure of 10.6 mm, Twigg and Rideal obtained an activation energy of 12.2 kcal and an absolute rate of 1.36×10^{18} molecules $\text{cm}^{-2}\,\text{sec}^{-1}$. The calculated rate using $s = 4$ is 7.9×10^{16} molecules $\text{cm}^{-2}\,\text{sec}^{-1}$; the agreement is not as good as usual, but this could be due to an error in the activation energy. The first-power law, which Twigg considers to be applicable, gives $\sim 10^{12}$, which is much too low.

Retardation by Poisons

When a substance other than a reactant, e.g., a product, is adsorbed on the surface, the concentration of bare surface sites is reduced, so that the reaction is inhibited. Various cases of inhibition will be considered.

Case I: Unimolecular Reactions. The general equation for a unimolecular reaction on a surface is

$$v = c_g c_S \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{120}$$

and the isotherms for adsorption by the reactant and the poison are

$$\frac{c_a}{c_g c_S} = \frac{f_a}{F_g f_S} e^{\epsilon/kT} = K \tag{121}$$

and

$$\frac{c_{ap}}{c_{gp} c_S} = \frac{f_{ap}}{F_{gp} f_S} e^{\epsilon_p/kT} = K_p \tag{122}$$

where the subscript p refers to the poison. Also,

$$c_a + c_{ap} + c_S = L \tag{123}$$

and Eqs. (121), (122) and (123) give rise to

$$c_S = \frac{L}{1 + Kc_g + Kpc_{gp}} \tag{124}$$

The rate equation may therefore be written as

$$v = \frac{c_g L}{1 + Kc_g + K_p c_{gp}} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{125}$$

If the reactant is only weakly adsorbed

$$v = \frac{c_g L}{1 + K_p c_{gp}} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{126}$$

and if the poison is very strongly adsorbed

$$v = \frac{c_g L}{K_p c_{gp}} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_S} e^{-\epsilon_0/kT} \tag{127}$$

$$= L \frac{c_g}{c_{gp}} \frac{kT}{h} \frac{f_{\ddagger} F_{gp}}{f_{ap} F_g} e^{-(\epsilon_0 + \epsilon_p)/kT} \tag{128}$$

If reaction occurs on dual sites c_S in Eq. (120) must be replaced by $\frac{1}{2} s c_S^2 / L$. Insertion of Eq. (124) into the rate equation then gives rise to

$$v = \tfrac{1}{2}\, s \frac{c_g L}{(1 + Kc_g + K_p c_{gp})^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_{S_2}} e^{-\epsilon_0/kT} \tag{129}$$

so that when the surface is well covered by the poison the rate is inversely proportional to the square of the concentration of the poison. However, this behavior is rarely found in practice, and it appears that usually the poison is adsorbed with dissociation. The adsorption isotherm is then

$$\frac{c_{ap}}{c_{gp}{}^{1/2} c_S} = \frac{f_{ap}}{F_{gp}{}^{1/2} f_S} e^{\epsilon_p/kT} = K_p \tag{130}$$

and c_S is then given by

$$c_S = \frac{L}{1 + Kc_g + K_p c_{gp}{}^{1/2}} \tag{131}$$

The rate equation is now

$$v = \tfrac{1}{2}\, s \frac{c_g L}{(1 + Kc_g + K_p c_{gp}{}^{1/2})^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_{S_2}} e^{-\epsilon_0/kT} \tag{132}$$

When the poison nearly covers the surface the rate is

$$v = \frac{\tfrac{1}{2}\, s c_g L}{K_p^2 c_{gp}} \frac{kT}{h} \frac{f_{\ddagger}}{F_g f_{s_2}} e^{-\epsilon_0/kT} \tag{133}$$

$$= \tfrac{1}{2}\, sL \frac{c_g}{c_{gp}} \frac{kT}{h} \frac{f_{\ddagger} F_{gp} f_S}{F_g f_{ap}} e^{-(\epsilon_0+2\epsilon_p)/kT} \tag{134}$$

The rate of decomposition of ammonia at low pressures on a platinum surface varies with the ammonia pressure and inversely as the hydrogen pressure. Both Eqs. (128) and (134) satisfy this condition, but since the hydrogen is adsorbed atomically it appears that Eq. (134) must be applicable. According to Schwab and Schmidt[42] the observed rate at 1423°K is given by

$$v = 2.60 \times 10^{22} \frac{c_{\mathrm{NH_3}}}{c_{\mathrm{H_2}}} \text{ molecules cm}^{-2} \text{ sec}^{-1}.$$

and the energy of activation is 44.3 kcal. Taking this value to be equivalent to $\epsilon_0 + 2\epsilon_p$, and assuming $f_{\ddagger}$, f_S and f_{ap} to be unity, L to be 10^{15} and s to be 4, the rate is calculated to be

$$v = 0.92 \times 10^{22} \frac{c_{\mathrm{NH_3}}}{c_{\mathrm{H_2}}} \text{ molecules cm}^{-2} \text{ sec}^{-1}.$$

in good agreement with experiment.

Case II: Bimolecular Reactions. The rate equation for a bimolecular reaction involving a single reactant is Eq. (68), but if there is poisoning L is equal to $c_S + c_a + c_{ap}$. The isotherms for reactant and poison then give rise to

$$L = c_S + c_S c_g K + c_S c_{gp} K_p \tag{135}$$

where

$$c_S = \frac{L}{1 + Kc_g + K'c_{gp}} \tag{136}$$

The general rate equation for this case is thus

$$v = \tfrac{1}{2}\, s \frac{c_s^2 L}{(1 + Kc_g + K'c_{gp})^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_{s_2}} e^{-\epsilon_0/kT} \tag{137}$$

If the reactant is very weakly adsorbed

$$v = \tfrac{1}{2} s \frac{c_g^2 L}{(1 + K_p c_{gp})^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_{s_2}} e^{-\epsilon_0/kT} \tag{138}$$

and if in addition the poison is very strongly adsorbed

$$v = \tfrac{1}{2}s \frac{Lc_g^2}{K_p^2 c_{gp}^2} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_{S_2}} e^{-\epsilon_0/kT} \tag{139}$$

$$= \tfrac{1}{2}sL \frac{c_g^2}{c_{gp}^2} \frac{kT}{h} \frac{f_\ddagger f_S^2 F_{gp}^2}{F_g^2 f_a^2 f_{S_2}} e^{-(\epsilon_0+2\epsilon_p)/kT} \tag{140}$$

A similar treatment applied to the case in which the poison is adsorbed with dissociation gives rise to

$$c_S = \frac{L}{1 + Kc_g + K_p c_{gp}^{1/2}} \tag{141}$$

and the rate is

$$v = \tfrac{1}{2}s \frac{c_g^2 L}{(1 + Kc_g + K_p c_{gp}^{1/2})^2} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_{S_2}} e^{-\epsilon_0/kT} \tag{142}$$

If the reactant is weakly adsorbed and the product strongly adsorbed

$$v = \tfrac{1}{2}s \frac{Lc_g^2}{K_p c_{gp}} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_{S_2}} e^{-\epsilon_0/kT} \tag{143}$$

$$= \tfrac{1}{2}sL \frac{c_g^2}{c_{gp}} \frac{kT}{h} \frac{f_\ddagger F_{gp} f_S^2}{F_g^2 f_{S_2} f_a^2} e^{-(\epsilon_0+2\epsilon_p)/kT} \tag{144}$$

Behavior of this type has been observed[43] for the decomposition of nitric oxide on platinum, and on a platinum-rhodium surface, the reaction being retarded by oxygen which is apparently adsorbed atomically. At 1483°K the rate on pure platinum is

$$v = 2.2 \times 10^{-4} \frac{c_{\mathrm{NO}}^2}{c_{\mathrm{O}_2}} \text{ molecules cm}^{-2} \text{ sec}^{-1}.$$

Using the activation energy of 14 kcal[44] the calculated rate was

$$v = 2.9 \times 10^{-4} \frac{c_{\mathrm{NO}}^2}{c_{\mathrm{O}_2}} \text{ molecules cm}^{-2} \text{ sec}^{-1}.$$

in excellent agreement with the observed value.

For the case of a bimolecular reaction involving two reactants the general rate equation is

$$v = \tfrac{1}{2}s \frac{c_g c_g'}{(1 + Kc_g\, K'c_g' + K_p c_{gp})^2} \frac{kT}{h} \frac{f_\ddagger}{F_g^2 f_{S_2}} e^{-\epsilon_0/kT} \tag{145}$$

when the poison is adsorbed without dissociation, and is

$$v = \tfrac{1}{2}s \frac{c_g c_g' L}{(1 + Kc_g + K'c_g' + K_p c_{gp}{}^{1/2})^2} \frac{kT}{h} \frac{f_{\ddagger}}{F_g^2 f_{S_2}} e^{-\epsilon_0/kT} \qquad (146)$$

when it is adsorbed with dissociation. No simple cases of this type of behavior are known.

ACTIVATION ENERGIES OF SURFACE REACTIONS

Comparison of Homogeneous and Heterogeneous Reactions[45]

It is instructive to compare the rate laws for homogeneous and heterogeneous reactions, with particular reference to the question of why certain reactions proceed more rapidly on the surface than in the gas phase. Such a comparison will be made for a bimolecular reaction. The absolute rate for a second-order heterogeneous reaction between the reactants A and B per sq cm of surface may be written [cf. Eq. (56)] as

$$v_{\text{het.}} = c_A c_B c_{S_2} \frac{kT}{h} \frac{1}{F_A F_B} e^{-E_{\text{het.}}/RT} \qquad (147)$$

The partition functions of the activated complex and of the surface sites have been taken as unity. For the corresponding gas phase reaction the rate is

$$v_{\text{hom.}} = c_A c_B \frac{kT}{h} \frac{F_{\ddagger}}{F_A F_B} e^{-E_{\text{hom.}}/RT} \qquad (148)$$

where $F_{\ddagger}$ is the partition function for the activated complex in the gas phase. The ratio of rates is thus

$$\frac{v_{\text{het.}}}{v_{\text{hom.}}} = \frac{c_{S_2}}{F_{\ddagger}} e^{\Delta E/RT} \qquad (149)$$

where ΔE is the amount by which the activation energy of the homogeneous reaction is greater than that of the surface reaction. For 1 sq cm of bare surface c_{S_2} is of the order of 10^{15}, while $F_{\ddagger}$ for a complex molecule may range from 10^{24} to 10^{30}; taking 10^{27} as a typical value it follows that

$$\frac{v_{\text{het.}}}{v_{\text{hom.}}} \approx 10^{-12} e^{\Delta E/RT} \qquad (150)$$

The heterogeneous rate considered refers to 1 sq cm of surface and to 1 cc volume of gas phase, the homogeneous rate to 1 cc of the gaseous reactant. It is evident from this equation that if the activation energies in the two phases were the same the rate in the gas phase would be very much greater than that on the surface. For the surface reaction to predominate either the surface area must be extremely large, or the activation energy for the surface reaction must be much lower than that for the gas phase reaction. At a temperature of 300°K the activation energy of the surface reaction would have to be 16.5 kcal lower than that of the gas reaction for the rates to be the same, assuming 1 sq cm of surface; at 500°K the difference is 27.6 kcal. For a larger surface area the differences are less.

Examination of the data for reactions which occur both in the gas phase and on a surface does in fact show that the surface activation energies are very much lower. A selection of data is given in Table 10.

TABLE 10. ACTIVATION ENERGIES FOR HOMOGENEOUS AND HETEROGENEOUS REACTIONS

Decomposition of	Surface	E het. (kcal)	E hom. (kcal)
HI	Au[1]	25.0	44.0
	Pt[2]	14.0	
N_2O	Au[3]	29.0	58.5
	Pt[4]	32.5	
NH_3	W[5]	39.0	>80
	Os[6]	47.0	
CH_4	Pt[7]	55–60	~80

1. Hinshelwood, C. N., and Prichard, C. R., *J. Chem. Soc.*, **127**, 1552 (1925).
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The way in which the activation energy of the surface reaction may be less than that of the homogeneous reaction may be considered with reference to the potential-energy diagram shown in Figure 4. The full line in this figure represents the variation in the potential energy as the homogeneous reaction proceeds, the height of the maximum with reference to the initial level being the activation energy $E_{\text{hom.}}$. The dotted curve represents the corresponding change which occurs in the surface reaction. In general, the system passes over a barrier to reach the adsorbed state, and then a second barrier is passed to give products in the adsorbed state; the height of this second barrier, with reference to the initial level, is $E_{\text{het.}}$. The difference between $E_{\text{hom.}}$ and $E_{\text{het.}}$ is clearly the difference between the energy of the gaseous activated complex and that of the absorbed activated complex. If reaction can proceed via an activated complex which is strongly adsorbed the reaction on the particular surface under consideration is therefore favored. Various more detailed discussions along the above lines have been published.[46]

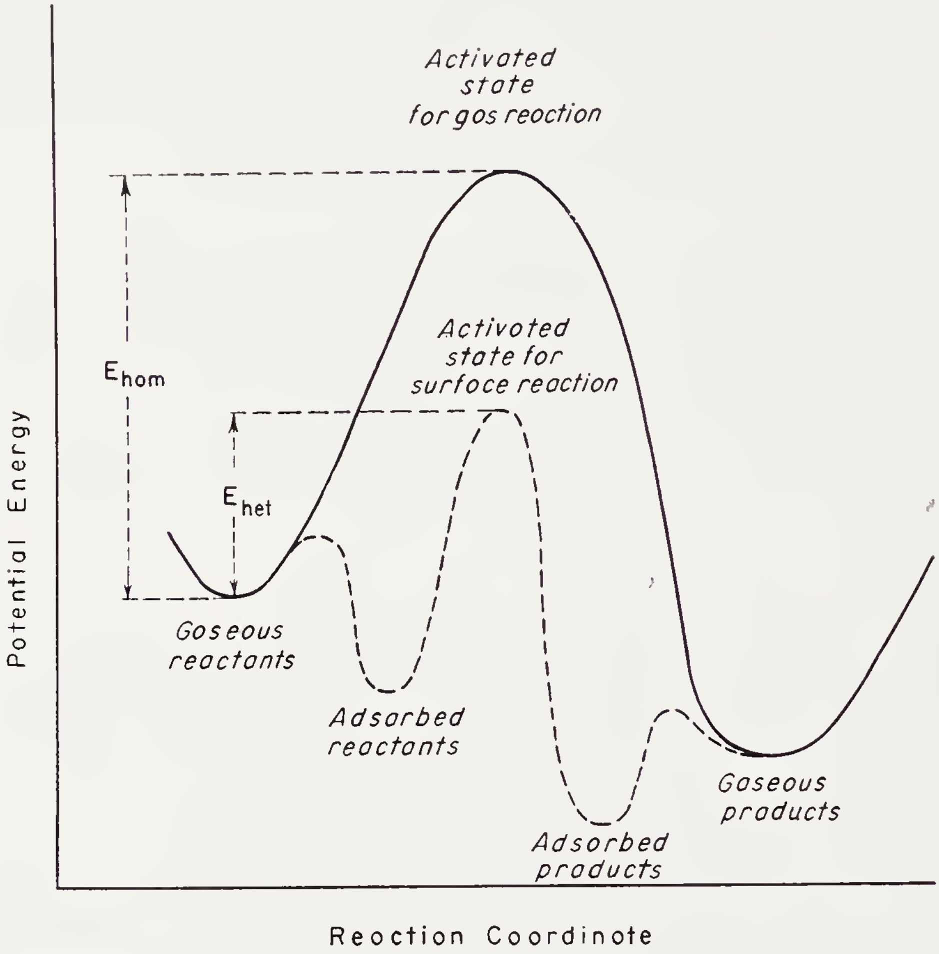
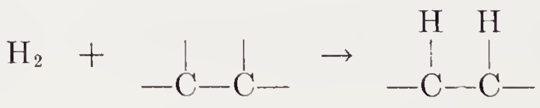


Figure 4. Potential-energy curves for a reaction proceeding homogeneously (full curve) and on a surface (dotted curve).

Calculations of Activation Energies for Surface Reactions

A few calculations have been made, using quantum-mechanical methods, of the activation energies for adsorption processes; none appear to have been made for chemical reactions on surfaces presumably because of the very considerable difficulty of doing so. Since these quantum-mechanical calculations have been reviewed elsewhere[47], the present discussion will not go into detail.

The first calculations were done for the chemisorption of hydrogen on carbon[48], a process that may be represented as



$$H_2 \;+\; -\overset{|}{C}-\overset{|}{C}- \;\rightarrow\; -\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}-$$

This can be regarded as a four electron problem, the two electrons of the hydrogen molecule interacting with the two unpaired electrons on the two carbon atoms. Calculations were therefore made using the London equation for four electrons, according to which the energy is given by

$$E = Q \pm \{\tfrac{1}{2}[(\alpha_1 + \alpha_2) - (\beta_1 + \beta_2)]^2 + \tfrac{1}{2}[(\beta_1 + \beta_2) - (\gamma_1 + \gamma_2)]^2 + \tfrac{1}{2}[(\gamma_1 + \gamma_2) - (\alpha_1 + \alpha_2)]^2\}^{1/2} \quad (151)$$

Here the greek symbols represent exchange energies corresponding to each pair of electrons, and Q is given by

$$Q = A_1 + A_2 + B_1 + B_2 + C_1 + C_2 \quad (152)$$

where A_1, A_2, B_1, B_2, C_1, and C_2 represent the corresponding coulombic energies. These quantities were obtained empirically, the coulombic and exchange energies being assumed to be certain fractions of the total energies as obtained from experimental Morse curves.

Proceeding in this way it was possible to calculate the minimum energy barrier that the system had to cross in order for the hydrogen to pass into the adsorbed state; this is the energy of activation.

Other calculations of the same kind for chemisorption processes have also been made.[49] Unfortunately the results are never very satisfactory, the calculated activation energies usually being much too high. There are various reasons for this; perhaps the most important is that the theoretical treatment regards the pair of surface sites as being essentially the same as if they were present in a molecule in the gas phase. A variety of evidence, however, has now accumulated which shows that surface atoms are in special states, and in particular it appears that electrons at surfaces are more freely mobile than in ordinary molecules, so that adsorption may occur more readily than the calculations indicate.

In spite of this drawback, the few calculations that have been made have been useful in various ways. They have, for example, called attention to the high sensitivity of activation energies, and therefore of rates, to the interatomic spacing at surfaces, and have so stimulated research in the direction of experimental investigations of reactions on different crystal surfaces. This work is of great interest and significance, but is outside the scope of the present discussion.

Empirical Methods

A number of empirical results have been of considerable importance in connection with an understanding of the magnitudes of activation energies in surface reactions, and will be referred to briefly. Schwab[50] has made a number of studies of reactions occurring on a wide range of alloys. For the decomposition of formic acid, which occurs as a zero-order process under all conditions investigated, he has shown that the activation energy is proportional to the square of the electron concentration. From this he concludes that the rate-determining step in the reaction is the transfer of two electrons from the formic acid molecule into the lowest unfilled level in the metal. Couper and Eley[51] have shown that the activation energy of the parahydrogen conversion on palladium rises sharply when gold is alloyed at the right concentration to fill up the holes in the *d*-band. This implies that unpaired *d* electrons at the surface are required for the activation energy to be low. Work along somewhat similar lines has been carried out by Dowden and Reynolds[52] who find, for example, that the decomposition of hydrogen peroxide is favored by a full *d*-band; this may be due to the fact that the slow step involves electron transfer from metal to hydrogen peroxide.

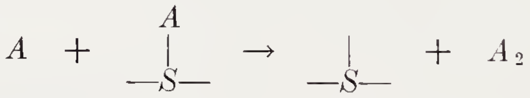
Another type of empirical approach to the problem of activation energies in heterogeneous reactions was applied by Shuler and Laidler[53] in connection with the estimation of activation energies for atom recombinations. According to Hirschfelder[54] the activation energy of an exothermic process $A + BC \rightarrow AB + C$ is given to a rough approximation by

$$E = 0.055D_{BC} \tag{153}$$

where D_{BC} is the energy of dissociation of BC; if the reaction is endothermic the activation energy is

$$E = 0.055D_{AB} + \Delta H \tag{154}$$

where $-\Delta H$ is the heat of reaction. This empirical equation was applied by Shuler and Laidler to heterogeneous atom combinations proceeding by the mechanism (cf. p. 205)



$$A + \underset{-S-}{\overset{A}{|}} \rightarrow \underset{-S-}{|} + A_2$$

Since these processes are exothermic the activation energy should be $0.055D_{SA}$, where D_{SA} is the heat of adsorption of the atom on the surface. Table 11 shows estimates derived in this way, together with the experimental values. The method appears to be quite satisfactory.

REACTIONS ON INHOMOGENEOUS SURFACES

The calculations of absolute rates that have been made earlier in this chapter have all been for surfaces which, as far as is known, are fairly smooth. It has accordingly been possible to make a reliable estimate of the number of surface sites, and in the calculations all of these are tacitly assumed to have the same catalytic activity. In the cases treated above the calculations have all been fairly successful, the agreement between theory and experiment usually being within a factor of ten. Such agreement tends to confirm that the assumptions of smoothness and of surface uniformity are correct.

It would clearly be desirable to extend this type of treatment to inhomogeneous surfaces on which the sites are of variable activity. This presents a formidable problem, and it cannot be said that much progress has been made in this direction. M. C. Wall and M. C. Markham, working in the author's laboratory, have made calculations for numerous reactions occurring on surfaces (particularly alloys) that were presumably inhomogeneous, but the results did not reveal any regularities upon which a satisfactory theoretical treatment could be based. In many of the cases it was found that there was good agreement (within a factor of ten) between calculated and observed values; this may mean either that the surfaces were more homogeneous than had been supposed, or that the reaction occurred largely on a group of active centers that constituted a significant fraction of the surface.

TABLE 11. EXPERIMENTAL AND ESTIMATED ACTIVATION ENERGIES FOR ATOM RECOMBINATIONS

Atom	Surface	Heat of Adsorption	Activation Energy (kcal)	
			Estimated	Observed
H	Glass	10–11	0.6	0.9
H	Various metals	50–60	2.7–3.3	2.5–3
N	Ni	55	3.0	2.5–3

In other cases it was found that the experimental values were lower than the calculated, by factors which were sometimes as low as 10^{-6}. This type of behavior is understandable if reaction occurs to an appreciable extent only on certain active centers which are present in small concentrations. No cases were found in which experimental rates were significantly higher than the observed, a result that is consistent with the theory.

Attempts to correlate the type of behavior found in these calculations with the nature and previous treatment of the surface have not proved successful. Progress in this important field must probably await further knowledge of the structure of solid surfaces and of its relationship to catalytic activity.

KINETICS IN THE CASE OF INTERACTIONS BETWEEN ADSORBED MOLECULES[55]

Recent work on adsorption[56, 57, 58] has indicated that there may frequently be strong repulsive interactions between atoms or molecules adsorbed on neighboring surface sites. It is therefore important to consider the effect of these interactions on the kinetics and absolute rates of surface reactions. In the preceding discussion these interactions have not been considered, but in spite of this the calculated rates have been satisfactorily in agreement with experiment. The present section is concerned with treating these effects, and it will be seen that interactions do not have an important effect on rates. The theory is applied to the para-ortho-hydrogen conversion, which was discussed on p. 210, but may readily be modified for other reactions.

The statistical treatment of adsorption with interaction that is employed here is equivalent to that of Peierls[59] and Roberts[60] (cf. p. 112). Consider a central site S_0 surrounded by four neighboring sites S_1, S_2, S_3, and S_4. The isotherm for dissociative adsorption without interaction is:

$$\frac{\theta}{1 - \theta} = K_p^{1/2} \tag{155}$$

Suppose that S_0 is bare; then the probability P that S_1 is covered is given by

$$\frac{P}{1 - P} = K\zeta p^{1/2} \equiv \kappa p^{1/2}, \tag{156}$$

Here ζ is a term that takes into account the interactions due to molecules surrounding the colony of five under consideration. If S_0 is occupied the probability P' that S_1 is occupied is given by

$$\frac{P'}{1 - P'} = K\zeta e^{-V/kT} \equiv \kappa\eta p^{1/2} \tag{157}$$

where V is the interaction energy and η is equal to $e^{-V/kT}$. Equations (156) and (157) give, for the probability that S_1 is bare when the surface is well covered ($P \rightarrow 1$ and $P' \rightarrow 1$),

$$1 - P = \frac{1}{\kappa p^{1/2}} \qquad \text{when } S_0 \text{ is bare} \tag{158}$$

$$1 - P' = \frac{1}{\kappa\eta p^{1/2}} \qquad \text{when } S_0 \text{ is covered} \tag{159}$$

If the total number of sites per sq cm when the surface is bare is L, the concentration of bare single sites is

$$c_S = L(1 - P') \tag{160}$$

The concentration of bare dual sites is given by

$$c_{S_2} = \tfrac{1}{2} s c_S (1 - P) \tag{161}$$

where s is the coordination number, assumed to be 4 in this case. Equations (158) to (161) give rise to

$$\frac{c_{S_2}}{c_S^2} = \frac{s}{2L} \cdot \frac{1 - P}{1 - P'} = \frac{s\eta}{2L} \tag{162}$$

The ratio of partition functions, f_{S_2}/f_S^2, is $\eta/2$, the two being the symmetry number for the dual site.

The rate of adsorption, i.e., the rate of reaction between gas molecules and bare dual sites, is equal to

$$v = c_g c_{S_2} \frac{kT}{h} \cdot \frac{f_\ddagger}{F_g f_{S_2}} e^{-E_0/RT} \tag{163}$$

In terms of single sites instead of dual sites,

$$v = \frac{s c_g c_{S_2}}{L} \frac{kT}{h} \frac{f_\ddagger}{F_g f_S^2} e^{-E_0/RT} \tag{164}$$

Since the η cancel, it is clear that the interaction terms have no effect on the rate. Equation (164) is the equation used earlier in calculating the rate of reaction by the Bonhoeffer-Farkas mechanism, and it is concluded that this mechanism is acceptable.

It is concluded, therefore, that the interaction terms exactly cancel out of the rate expressions, so that it is permissible to neglect interactions in making absolute rate calculations. Previous workers have come to different conclusions. Thus Trapnell[61] and Eley[62] calculate rates for the parahydrogen conversion by using the expression derived by Peierls.[59] Employing an interaction energy of 40.4 kcal derived from Trapnell's isotherm Eley calculates that the number of bare dual sites is about 10^{-6} of the number that would be present if there were no repulsive forces. His absolute rates moreover are about 10^{-6} of the observed ones, and on this basis Eley rejects the Bonhoeffer-Farkas mechanism (p. 210). There is, however, a serious objection to this procedure. The only way in which the repulsive forces appear in this treatment is to diminish, by 10^{-6} or so, the concentration of bare dual sites. It is clear, however, that they should also enter in another way: by making the dual sites intrinsically improbable they should increase the rate of reaction per dual site. Expressed differently, the rate equation contains in its denominator the partition function for the dual site, and this will be diminished by the repulsive interactions.

The theory outlined above in fact indicates that there is complete compensation between these two effects.

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CHAPTER 6

CATALYST CARRIERS, PROMOTERS, ACCELERATORS, POISONS, AND INHIBITORS

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Only very rarely do commercial catalysts consist of a single component. This chapter is concerned with the other components besides the primary active catalytic agent that may be present during catalytic action. Primary reactants or reaction derivatives such as coke are not considered. The components under consideration may be added during catalyst manufacture (carriers, promoters and inhibitors) or may be introduced to the catalyst from the gas stream during catalytic usage (poisons and accelerators). Sharp distinctions between the different component types given below are rare and definitions are somewhat arbitrary. Only recent work is covered (1942–1952) since earlier literature was reviewed by Berkman, Morrell and Egloff.*

CATALYST CARRIERS

The term catalyst carrier as used herein refers to a major catalyst constituent that serves as a base, support, carrier or binder for the active constituent but which by itself has little, if any, catalytic activity for the reaction in question. Literature in recent years has been pretty much confined to specific materials. Berkman, Morrell and Egloff[1] devote an excellent chapter to the subject.

Function of Carriers

The mechanical function of a carrier is to act as a base or framework for the catalytic component. It may serve to reduce shrinkage and lend physical strength. Aside from its purely mechanical function, other possible desirable effects of a carrier include:

(1) Giving a larger exposed surface of active agent and thereby greater

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* Berkman, S., Morrell, J. C., and Egloff, G., "Catalysis," New York, Reinhold Publishing Corp (1940).

catalytic activity in cases in which this agent by itself has low surface area, or giving an equal surface area and activity with much less active material. The latter is particularly important with expensive agents such as platinum. In some cases the active constituent may simply be physically adsorbed on the carrier material so that the active component is spread out in a monomolecular layer. A probable example of this is molybdena on alumina[2].

(2) Increasing catalyst stability by keeping fine crystals of the active constituent too far apart for sintering to occur[1].

(3) Favorably modifying the catalytic activity or selectivity, poison resistance, etc., of the active constituent. In some cases surface compound or complex formation may take place between the carrier and the supported material giving a complex which has better catalytic properties per unit area than the latter. Silica-alumina and silica-magnesia cracking catalysts fall in this category[3]. The surface complex is strongly acidic unlike alumina or magnesia and also has catalytic properties that are very different from those of the separate constituents.

The work of Selwood[4, 5, 6] on the magnetic susceptibility of catalytic paramagnetic oxides on diamagnetic oxide supports has shown that in many cases at high surface dilution, the catalytic agent simply adds on to the support crystal lattice and assumes the same valence state as the latter (phenomena of valence induction). Examples include manganese oxide on alumina, iron oxide on titania, nickel oxide on alumina and nickel oxide on titania. Of course, this would be expected to have a marked effect on the catalytic properties of the paramagnetic material though the nature of the effect, whether favorable or otherwise, would depend on the circumstances. In the case of manganese, copper and iron on alumina the highly dilute material was found to be relatively inactive for CO oxidation by O_2.

(4) Improving activity by increasing the accessibility of the active surface[7]. This is important in many industrial catalytic processes in which the catalyst is used in the form of large granules, pellets or rings. Supports with large pores such as diatomaceous earth would be expected to act in this manner. Physical structure has also been found to have an important effect on selectivity[8].

(5) The increase of active surface resulting from use of a carrier may result in a decrease in sensitivity to poisons[9].

(6) Catalyzing one of the steps where there is a dual action mechanism[10]. This is similar to the function of a dual action promoter except that the carrier acts also as a mechanical support for the other constituent.

(7) Helping to dissipate heat and prevent local overheating which would cause sintering with resultant loss in active surface. High heat conductivity carriers are favored for such purposes. In the catalytic oxidation of ethylene, metallic silver carriers are commonly used.

Incorporation of Catalyst with Carrier

A catalyst may be incorporated with a carrier in many ways, including the following:

Impregnation. The most common method involves mixing a soluble solution of the active component with the carrier and then heating the resultant mixture in order to decompose the salt and deposit the catalyst in the desired form on the external, and for porous carriers, also on the internal surfaces[11]. The soluble solution may be either a salt solution (usually a nitrate or other easily decomposable salt) or a colloidal dispersion. However, in the latter case, micelle size can be expected to be a factor both in regard to penetration of small pores of the support by the colloid and the extent of the final active catalyst surface. The carrier may be either a hydrous gel with a relatively open structure that undergoes shrinkage on drying or a preformed carrier that undergoes no physical change.

Impregnation, as described above, is a relatively simple operation. The amount of active constituent that can be introduced to the internal surface of a preformed carrier by a single impregnation can be calculated from the pore volume and the concentration of the catalyst solution if selective adsorption is negligible. For example, if the catalyst solution concentration expressed as the oxide is 10 per cent and the pore volume is 0.4 cc/g the final per cent catalyst oxide is:

$$\frac{(.4 \times .1)100}{1 + .4 \times .1} = 3.8 \text{ per cent}$$

However, if the deposited catalyst constituent can be rendered insoluble by heating, the process may be repeated in order to obtain higher catalyst concentrations.

The principal objection to simple impregnation is that is usually results in nonuniform catalyst distribution. During drying, the liquid evaporates from the pores near the external surface and the liquid from the interior pores continually migrates to the external surface. The catalyst component in the liquid deposits on evaporation, and becomes concentrated as relatively large crystals near or on the external surface.

Precipitation. A generally more satisfactory way of adding active component to carrier which eliminates migration of the catalyst component on drying involves the following steps:

(1) Introduction of catalyst to carrier as a solution or colloidal dispersion.

(2) Precipitation in situ by addition of an agent that lowers the solubility of the active agent so that it deposits on the carrier surface.

(3) Washing out undesirable constituents if necessary.

(4) Drying.

In preparing a silica-alumina catalyst, the common practice is to first make a silica gel (hydrous or xerogel), add a soluble aluminum salt, add a base such as ammonia to insolubilize the aluminum, wash out the undesirable soluble salts and dry[12, 13]. A somewhat different example involves adding salt solution of a reducible metal (Pt, Au, Ag) and then adding a reducing agent such as formaldehyde which causes insolubilization by reduction[14].

Coprecipitation. Another procedure that is sometimes used involves simultaneous precipitation of both carrier and catalyst constituent. This usually leads to a very intimate mixing of catalyst and carrier. Occasionally, when this procedure is used, the carrier strongly modifies the catalytic properties of the catalyst constituent and makes it difficult to say whether or not a new chemical species has been formed. X-ray studies usually are helpful in this connection. Usually both crystal lattices contain some of the other component. Examples include silica-alumina catalyst as made by the Houdry process[15] and molybdena-alumina hydroforming catalyst as made by the California Research Corporation[16].

Mechanical Mixing. Simple mechanical mixing of the catalytic component with the carrier both in insoluble form and usually in the presence of water is sometimes employed. Either, or both, may be in a hydrated state. Although such a procedure would not be expected to result in a high degree of dispersion of catalytic component unless a reaction occurred, the carrier may still serve to impart physical strength, dissipate heat or lessen shrinkage. Examples of this include cases in which hydraulic cements are used as the carrier material[17, 18].

Vapor Phase Adsorption. One method, which is seldom used, involves heating a mixture of catalytic component and carrier in a closed vessel to a temperature at which the former has a high enough vapor pressure to be adsorbed on the carrier. Russell[19] used this procedure for depositing molybdena on alumina.

Liquid Phase Adsorption. Where the catalytic component is selectively adsorbed from solution, liquid phase adsorption may be used as a means of getting the catalyst on the carrier surface although this is usually combined with impregnation.

Spraying. In cases of nonporous carriers it is common practice to apply the catalyst by spraying or sprinkling on the catalyst solution while rotating the bed of carrier material. A ribbon mixer is sometimes employed for this operation. Unless the product is pelleted, adhesion of the active agent to the carrier may be poor. This is particularly serious if the catalyst is used in a "fluid" form because attrition will soon wear off a surface coating. Binders are sometimes used to solve this problem.

Miscellaneous Methods. Other methods rarely used include electroplating[20] and vapor phase decomposition on the carrier as, for example, passing metal stearates through hot pumice causing decomposition thereon. An unintentional example of the latter occurs in petroleum cracking where heavy metals, such as nickel from the oil, deposit on the cracking catalyst causing it to have undesirable dehydrogenation activity[21].

Description and Properties of Carrier Materials

Because of pressure drop considerations, industrial vapor phase catalysts are almost entirely of two types: powders, 20–300 microns, for "fluid" bed operation, and granules, rings or pellets (1/16 to 3/4 inch diameter) for fixed bed processes[22]. Carrier materials must either meet these requirements or be capable of being formed or disintegrated to meet them before or after incorporation with the active agent.

Among the factors to be considered in the selection of a carrier are:

(1) Possible catalytic activity of the carrier component.
(2) Modification of the properties of the supported component by the carrier.
(3) Surface area.
(4) Porosity.
(5) Structure.
(6) Specific heat.
(7) Heat conductivity.
(8) Particle size.
(9) Density.
(10) Attrition resistance, hardness, and compressive strength.
(11) Stability under reaction conditions.

Although there is no easy way to classify carrier materials, and some carriers can be tailor-made to have widely varying properties (e.g., silica gel), the best way to classify them seems to be on the basis of structure. The main classes of structure are listed below. Data on specific products except where otherwise indicated are typical and were supplied by the manufacturer. These should be regarded as only approximate and current. Only representative suppliers and a few grades are included.

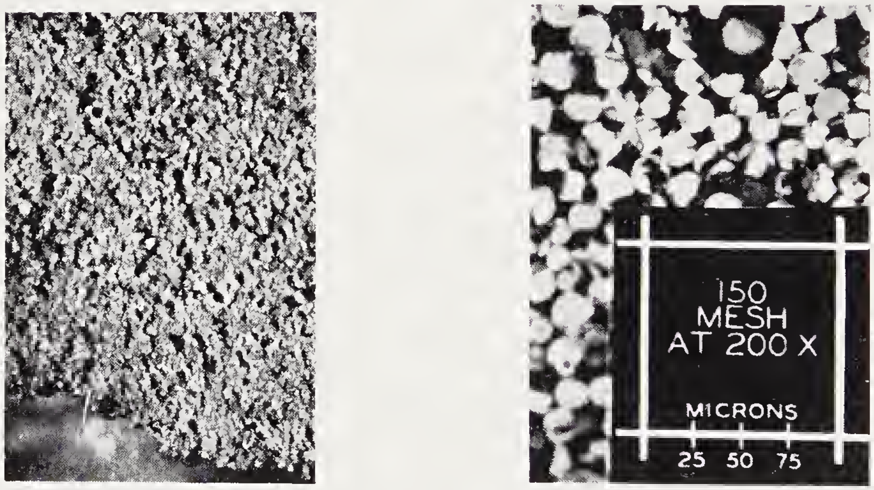
Low-Area Carriers. *Nonporous.* Nonporous macroscopically sized (+200) mesh) materials are included in this category. Substances available in this form and in common use are ground glass[23], Alundum[24, 25], silicon carbide[26, 27], and mullite (see Figure 1).

Carriers of this nature are used only in those instances in which the active component is extremely active for the reaction in question, and in which usually, as for partial oxidation reactions, the desired reaction product can undergo further reaction leading to poor selectivity. The distribution curve for the number of collisions of reactant molecules with the catalyst surface in passing through the catalyst bed is narrower than is obtained with porous materials. Molecules or reaction products that penetrate pores usually make more collisions with the catalyst surface than calculated from average residence time.

Nonporous

Silicon Carbide "Alundum"

Porous



Porous "Alundum" Porous Glass

Figure 1. Low-area-carriers.

One of the major problems with this type of catalyst is adherence of the catalytic component to the carrier, particularly with fluid-type catalysts. Sometimes carriers of this nature are used as secondary supports for a primary carrier-catalyst composite together with a binder to hold the mass together. This procedure would be expected to give a narrow contact time distribution since the catalyst-primary carrier composite is spread as a thin layer on the secondary carrier.

Porous. Available materials of this nature include diatomaceous earth, brick, pumice, silicon carbide aggregate, porous metals, chamotte, "Filtros" and many others. Carriers of this type are useful where the catalytic component is so active that only a small surface area is required. They may also be used as secondary carriers for a catalyst primary carrier composite. Their coarse pore system makes even the internal area of large pieces accessible. Details on the various porous low-area carriers are given below.

"Alundum" and Silicon Carbide Aggregates. These coarse pord materials are manufactured from nonporous alumina and silicon carbide powder by pelletizing or extruding and then heating to a high enough temperature to fuse the points of contact. A flux or binder may also be used to help cement the particles together. Data on commercial products of this nature are given in Table IA.

Virtues of these materials include a high degree of hardness and heat conductivity. The availability of many shapes and sizes is another important consideration in their usage. However, their very low specific surface limits their applications[28, 29, 30].

Pumice, Firebrick, Etc. Pumice is a cellular hard glossy lava of volcanic origin[31]. It is a complex silicate of sodium, potassium, calcium, magnesium and iron and is widely used for carrier purposes[32, 33, 34]. The physical properties are given in Table 1A. Firebrick has similar properties and finds occasional usage. Another coarse pore siliceous product ("Filtros")[35] is made by sintering graded pure sand.

Diatomaceous Earths. Diatomaceous earth, known also as kieselguhr and diatomite, is derived from marine life and has a diatom cellular structure (Figure 2). It is composed almost entirely of semiamorphous silica (cristobalite). The commercial materials are prepared by calcination, crushing and screening of the source material[36]. Some of the commercial products are "flux-calcined" to improve filtration characteristics or to produce aggregates. Data on commercial products are given in Table 1B and by Anderson *et al*[37].

Although diatomaceous earth carriers do not have a very high surface area, they usually give a catalyst with large pores which permit easy access to reactants. This is important for many fixed bed operations. Calcined grades are fairly heat stable. The attrition resistance of ground aggregate material now available appears to be too low for these products to offer much promise for fluid bed catalysts. The great porosity generally leads to a bulky catalyst product. Applications[38, 39, 40, 41] include the German, cobalt Fischer-Tropsch catalyst.

Metals. Although metals are not commonly used for carrier purposes,

TABLE 1A. POROUS LOW-AREA CARRIERS

Supplier		Carborundum Co.[2]					Norton Co.[1]		Alcoa[7]			K. F. Griffith[6]	Filtros, Inc.[5]	Westvaco[8]
Type or trade name		AMC	CEHF	SAEHF	SEHF	CMC	"Alundum[3]"	"Alundum"	T60–61	T74–75	T71	Pumice	A to H	Periclase S 93
Al_2O_3	Wt. % ignited basis	85	4	92	4.6	4.0	77	89	99.5	99.5	99.5			
SiC	Wt. % ignited basis		79			80								
SiO_2	Wt. % ignited basis	11	14		93	14	*ca.* 20	*ca.* 10	0.02	0.02	0.02	*ca.* 65	99.6	3.3
CaO	Wt. % ignited basis	0.4	1.6	1.2	1.2	0.4	low	low						2.0
MgO	Wt. % ignited basis	0.3					low	low						93.0
Na_2O	Wt. % ignited basis	0 1	0.3	0.5			low	low	0.02–0.15	0.16–0.26	0.35–0.40			
K_2O	Wt. % ignited basis	0.3	1		0.3	1.1	low	low						
Fe_2O_3	Wt. % ignited basis	0.9					low	low	0.03	0.03	0.03	<1		
TiO_2	Wt. % ignited basis	2.0												
B_2O_3	Wt. % ignited basis			5.8										
Principal phases							α-alumina			α alumina			quartz	periclase
Specific surface	m²/g						0–1 m²/g		0.07–0.34			0.04		
Porosity	% voids	42	64	63	63	41	35 to 45		8	21	37		36 to 26	25+
Av. pore diameter	microns	coarse grade = 350 medium = 125 fine = *ca.* 10											300 to 55	
Bulk density	g/cc	0.88	0.48	0.64	0.48	0.80	2.0	2.0	2.1		1.5	0.7	0.8	1.6
Skeletal density	g/cc	3.6	2.7	3.5	2.7	3.0			3.9	3.9	3.9			3.7
Compressive strength	% fines on compression 200 psi	4.2	<0.2	2.7	7.0	2.2	high strength	high strength				high strength	high strength	
Approximate softening pt.–	°F						2700	2700	3500	3500			*ca.* 1500[4]	3700
Available physical forms.		2-4 mesh and 4–8 mesh granules, etc.					wide variety shapes and sizes		granules		granules	as specified	as specified	¼″ to 1″ spheres

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[1] Worcester, Mass.

[2] Niagara Falls, N. Y.

[3] Fused magnesia, zirconia and mullite porous supports are also available.

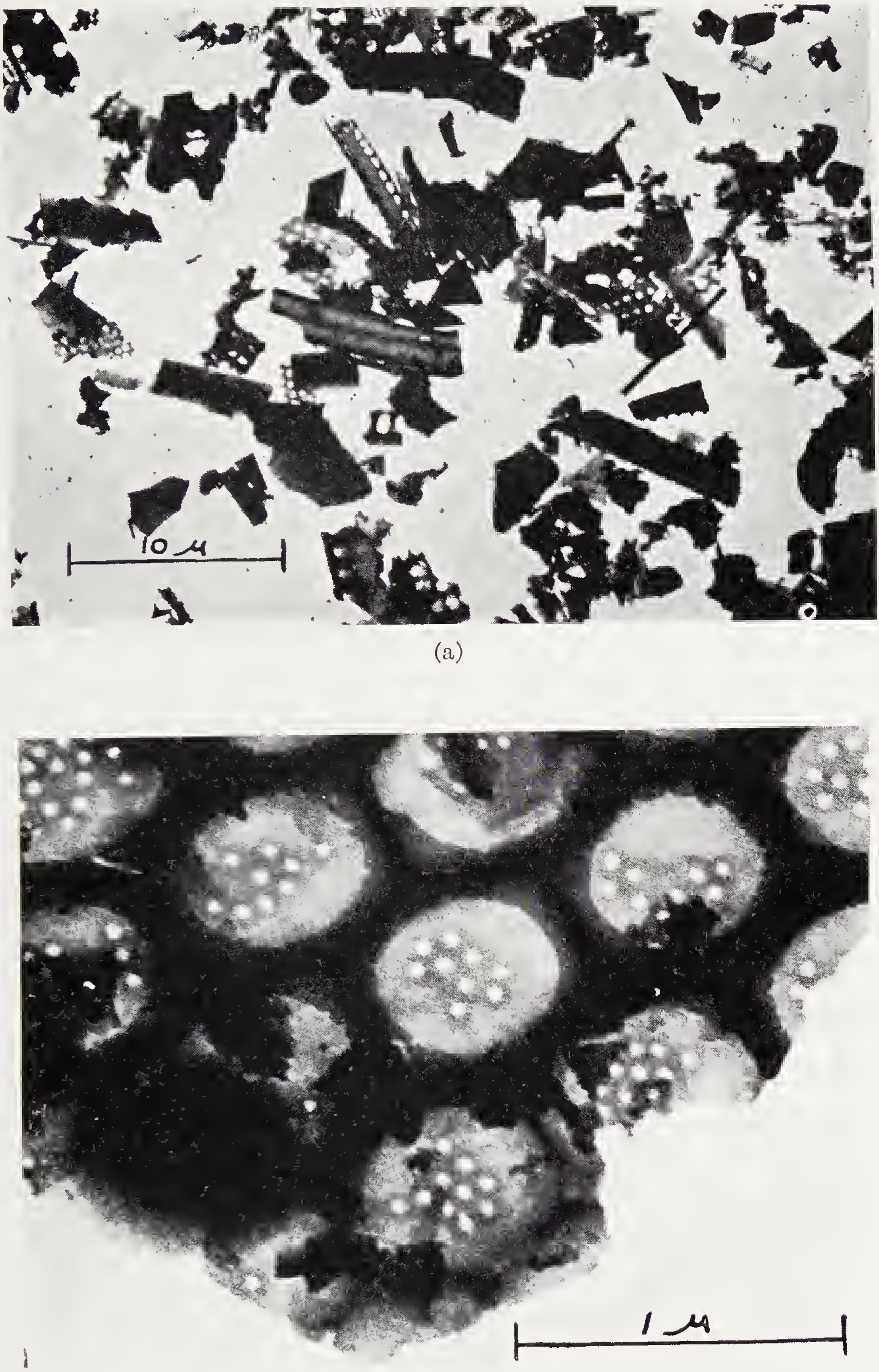
[4] Subject to fracture with sudden changes of temperature.

[5] East Rochester, N. Y. Porous carbon, clay and mullite also available.

[6] Newark, N. J., from Lipari Island, Italy.

[7] 1501 Alcoa Bldg. Pittsburgh, Pa.

[8] Westvaco Chemical Division, Food Machinery and Chemical Corp, 161 East 42nd St., New York City.



(a)

(b)

Figure 2. Low-area porous carriers. Typical diatomaceous earth (a) low magnification; (b) high magnification.

Table 1B. Diatomaceous Earths

Supplier		Great Lakes Carbon Corp.[3]							Johns Manville Corp.[4]										
Grade		#911[5]	SA 5 637T[6]	Speed Flow[7]	PS Grade[7]	Speed Plus[7]	#1	Aggregate	Aggregate	"Filter-Cel"[2]	"Snow Floss"	"Hyflo Super-Cel"	"Celite" 408	"Celite" 410	JM I	JM II	JM III	JM IV
Approx. cost	cents/lb	8	3	3	3	3	8	5	88	92	93	90	87	87	92	93	92	88
SiO_2	Wt. % ign. basis	79	79	90	90	85	79	87	6.0	4.0	2.3	3.8	7.5	7.5	2.3	2.3	4	6
Al_2O_3		8	6	5	5	5	8	9		3		3						
Fe_2O_3		2	2	2	2	3	2	2		1		1						
CaO		1	1	2	2	3	1	1				0.3						
MgO		0.4	0.5	0.3	0.3	0.3	0.4											
Ignition loss	Wt. %	4	6	0.2	0.2	0.2	4.4	4	0.5	3.5	3.5	0.2	0.5	0.5	0.2	0.5	3.5	3.5
S	Wt. %									0.03		0.03						
Principal phases		amorphous		cristobalite						amorphous		cristobalite			cristobalite		amorphous	
Skeletal density	g/cc	2.0	2.0	2.25	2.25	2.35	2.0		2.15	2.2	2.3	2.3			2.4	2.2	2.3	2.2
Bulk density[1]	g/cc	0.25	0.20	0.21	0.25	0.23	0.18			0.15	0.19	0.22	0.57	0.54	0.26	0.20	0.17	0.23
Total pore volume	cc/g	3.7	4.4	4.2	3.7	3.5	5.1		1.1–3.0	6.1	5.0	4.0	0.55	0.58	3.4	4.6	5.2	3.9
Specific area	m²/g	30	35	4	3		20		0.5–2.0	23	19	2	2.4	2.4	3	6	19	12
Particle Size	Wt. %							as specified	various sizes & shapes	powders					powders			
	-2μ	66	76	15		10	17						0.18″ pellets	0.28″ pellets				
	-10μ	100	100	75		53	72			4–6μ	1–2μ	7–9μ			2–4μ	2–3μ	4–6μ	4–6μ
	-40μ	100	100	95		96	99											
Compressive strength	psi												5200	2200				
Reference		36 and 37							36 and 37									

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[1] Packed or vibrated.

[2] Acid extracted.

[3] Dicalite Division, 612 S. Flower St., Los Angeles 17, Calif.

[4] Manville, N. J., from Lompoc, Calif., deposit.

[5] From Terrebone, Oregon, deposit.

[6] From Nevada deposit.

[7] Probably from Lompoc, Calif., deposit.

they possess several advantages over other materials, including high heat conductivity[42], mechanical strength and ease of fabrication. Poor adherence of active agent and nonavailability of anything but low-area nonporous products account for the lack of greater usage[43]. The introduction of porous metallic products such as the porous stainless steel and other sintered metal materials should lead to many carrier applications. The most important factor is that they may be fabricated in thin sheet form so that the reactants can be forced to penetrate the pore structure uniformly without excessive pressure drop. This should give very efficient contacting and uniformity of contact time. The latter is of great importance in cases where the desired product is capable of undergoing further reaction.

Table 1C. Porous Metallic Carriers

Supplier: Micro-Metallic Corporation[1]; Type: 18-8 Stainless*

	Grade				
	D	E	F	G	H
Specific surface (cm²/g†)	60	110	200	400	800
Porosity % voids†	50	50	50	50	50
Av. pore diam. (microns)	65	35	20	10	5
Permeability (CF air/min/ft² for ⅛ in. thickness and 1 psi pressure drop)	475	220	82	41	28
Skeletal density (g/cc)	7.7	7.7	7.7	7.7	7.7
Minimum tensile strength (psi × 10^{-3})	7	10	10	8	8
Maximum usable temp. (°C)					
Reducing atm.	800		775		750
Oxidizing atm.	650		625		600
Minimum thickness (inches)	0.06	0.075	0.06	0.04	0.03

* Also available in "Monel", "Hastelloy" B and C and other alloys.

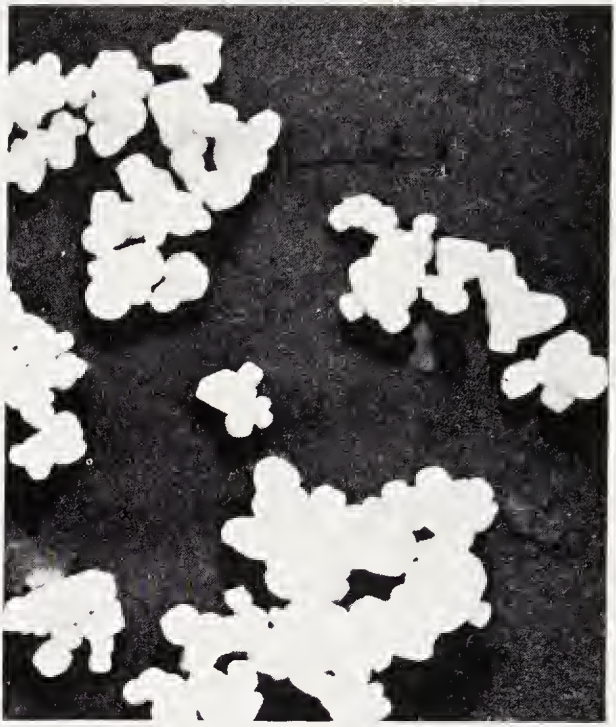
† Estimated.

[1] Glen Cove, New York.

Data on available porous metallic products are given in Table 1C. Fibrous metallic carriers are discussed under the heading of fibrous carriers.

High-Area Carriers. *Nonporous.* Available materials of this type include substances generally called pigments which have surface areas in excess of about 5 m²/g and submicron particle size. Examples include kaolin[44, 45, 46, 47], iron oxide pigments[48], carbon black[49, 50], titania[51] and zinc oxide[50] (see Figure 3).

The usual procedure in utilizing carriers of this type is to add a solution of the catalyst component (spray or otherwise) and then pelletize or extrude to obtain the desired particle size and shape. Heat treatment to eliminate water and to decompose the catalyst salt, etc., generally follows. Materials of this size are too small to be retained by dust collectors so that it is im-

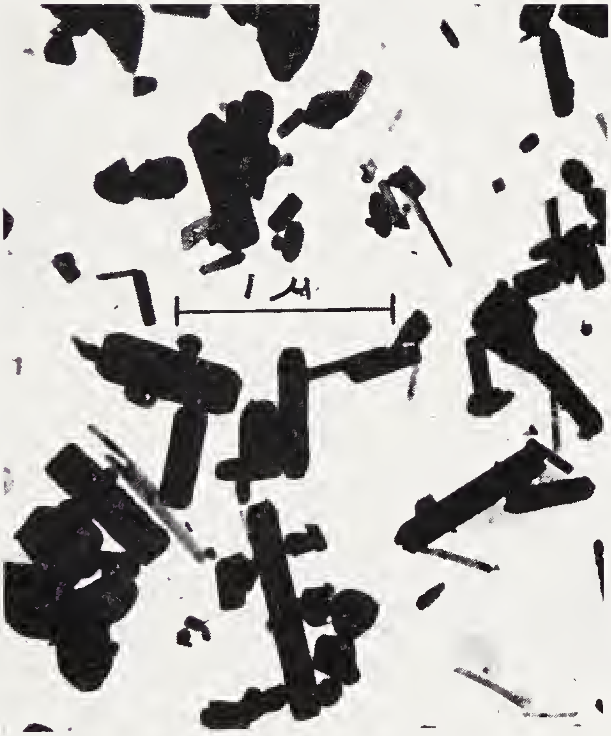


Titanium Dioxide

Ferric Oxide

Figure 3. Pigment-type carriers.

Kaolinite



Zinc Oxide
Figure 3 (*cont'd*)

practical to use them as fluid catalysts without aggregation, in which case they can be considered as porous supports. Data on a few of the commercially available products are given in Table 2.

Porous. Carriers of this type usually have surface areas in excess of about 50 m²/g and porosities greater than about 0.2 cc/g. Ultimate particle (micelle) and pore size is usually less than 200 Å. They are generally used where maximum activity and/or stability are wanted. However, the stability of the carrier must be considered as well as that of the active component. If the reaction product is capable of undergoing further reaction, and selectivity is of prime importance, lower surface area larger pore carriers may be preferable because of greater uniformity of contact time. Unless the catalytic agent is properly distributed on the carrier the use of a high-area carrier does not insure a high activity catalyst. Also, to realize maximum activity it is necessary to add enough active agent to completely cover the surface. The amounts necessary to cover the surface for high-area carriers are generally more than realized. If the catalytic agent deposits as a monomolecular layer, the amount necessary to cover the surface can be estimated from the expression:

$$\frac{\text{wt. of catalyst agent}}{\text{wt. of carrier}} = 10^4 S d^{2/3} \times M^{1/3}/N^{1/3}$$

where S = specific area of carrier in sq m/g
M = molecular wt of catalytic agent
d = density of catalytic agent
and N = Avogadro number.

This expression assumes the same spacings for the active agent as are present in the bulk phase which, of course, is only an approximation. For example, if the carrier was silica gel with an area of 500 m²/g and the active component was γ alumina ($M = 102$, $d = 3.5$):

$$\frac{\text{wt. alumina}}{\text{wt. carrier}} = \frac{10^4 \times 500 \times 3.5^{2/3} \times 102^{1/3}}{(6 \times 10^{23})^{1/3}} = 0.64$$

Russell and Stokes' work[52] with molybdena on alumina catalyst clearly indicated that a molecular layer of molybdena did form on an alumina support since a linear increase of activity with molybdena content occurred until enough molybdena was added to form a completed layer. If an incomplete layer was present, no drop in catalytic activity for dehydrocyclization of *n*-heptane was found on heat treating until there was not enough surface for a monolayer.

In cases where a surface complex or compound is formed, a stoichiometric ratio may exist between the exposed surface carrier atoms and the atoms of supported material for a monolayer. The work of Selwood and co-

Table 2. Nonporous, Low-Particle Size Carriers (Pigments)

Supplier		R. T. Vanderbilt Co.,[1]					Edgar Bros.,[2] Clay	C. K. Williams Co.[3]		R. T. Vanderbilt Co.[1]	
Type		Peerless #1	Continental	"Pyrax" B	Nytal 200	Cherokee		Iron Oxide R1599	Chromia G4099	Carbon Black "P33"	Carbon Black "Thermax"
Al_2O_3	Wt. %	40	37	74	1	38	41			0.5	0.5
SiO_2		45	46	20	57	46	45				
Fe_2O_3		0.3	1.3	0.1		0.4	0.3	>99			
MgO		tr.	tr.	0.1	31	0.1					
CaO		tr.	tr.	tr.	7	tr.	0.4		>99% Cr_2O_3		
K_2O		0.1	0.3	tr.		tr.	tr.				
Na_2O		0.1	tr.	tr.		tr.					
TiO_2		0.7	1.4	0.2		1.2	1.6				
Loss on ignition		14	14	4.0	4	14				1.5 ← moisture	→ 1.5
Principal phase		kaolin	kaolin	pyrophyllite	talc	kaolin	kaolin				
Skeletal density	g/cc	2.6	2.6	2.8	2.8	2.6	2.6	5.1	5.2	1.8	1.9
Bulk density	g/cc	0.4	0.4	0.6	0.6	0.5		0.9	1.0	.04	.03
Specific area	m^2/g		10*	2*	10*		7–15	11	10	22	8
Particle size	Wt. % -2μ	60	98	10	10	70	as specified				
	-10μ	90	99	50	44	90					
	-40μ	99	99	90	98	99					
	−200 mesh	100	100	99	100	100		>99	>99	>99	>99
	Av μ	1	0.2*	10	12	0.8		0.2	0.2	0.16	1.1

* Data obtained by Stamford Research Laboratories, American Cyanamid Co.

[1] 230 Park Ave., New York 17, N. Y.

[2] McIntyre, Ga.

[3] Easton, Pa.

workers[53, 54, 55] has indicated in the case of oxides on an oxide carrier that often the supported materials simply adds on to the existing crystal lattice.

It probably can be generally said that the use of high-area carriers results in a substantial modification of the catalytic properties of the supported material because of its high degree of dispersion.

There are a variety of high-area porous supports available as listed below:

Natural Products. High area, porous naturally occuring products[35, 46] are obtained by processing (washing, acid treating and calcining) naturally occurring materials such as deposits of bentonite[56], bauxite[57, 58], halloysite[46] and attapulgite[59, 60, 61] (Table 3A). (Figure 4).

Inorganic Skeletal Products. Alumina and magnesia products of high areas are made by the heat treating of crystalline hydrates or hydroxides to give a skeleton type product having the gross structure of the original material although perforated by small pores (50 Å diameter in the case of magnesia) resulting from water elimination (Table 3B). Porous glass can be obtained[67] by the leaching of soluble constituents from a glass having the composition: SiO_2 (50%), Al_2O_3 (10%), alkali metal oxide (5%), boria (20%) and P_2O_5 (15%).

Activated Carbon. The high area of activated charcoals which may be derived from soft coal, lignite, bone, wood or other carbonaceous matter[68] by calcination, steam treatment, etc., is also due to its skeleton structure which results from the elimination of hydrocarbons[69]. As might be expected, the surface area and porosities of skeleton type products are very dependent on activation procedure, and charcoals with areas in excess of 1000 m^2/g with pores of molecular size can be prepared[70]. Skeletal densities of chars vary widely with the fluid used for measurement because the limited pore size has a marked effect on packing efficiency.

Bone charcoal, which is extensively used for sugar refining[72], is obtained by dry distillation of bones at temperatures up to 2000°F. It differs from ordinary charcoal in that it has a very high ash content (basic calcium phosphate). A synthetic product (Synthad) of similar composition is also available[73]. Pore size distribution data are given in reference [74].

Figure 5 gives the pore size distribution of activated carbon from coal. Samples of this identical material are available from the Pittsburg Coke & Chemical Company's "Sample Bank." Charcoals find many carrier applications[75, 76, 77, 78]. Data are given in Table 3C and Figure 6.

Synthetic Dry Gels. Dry gel type products (Figures 6 and 7) are obtained by drying hydrogels which result from the aggregation of colloidal particles (micelles). The high area and porosity result from the small size of the micelles and inefficient packing due to acicular or spheroidal shape. Although recrystallization and merger may occur when gels are heated, leading to loss of surface and porosity, electron microscopic evidence indicates

TABLE 3A. HIGH-AREA, POROUS SUPPORTS DERIVED FROM NATURAL MATERIALS

Supplier		Attapulgus Minerals and Chemical Corp.		Floridin Co.[4]		Filtrol Corp.[5]	
Type		Porocel	Attapulgus clays	Fuller's earth	Act. bauxite	Act. sub-bentonite	Act. halloysite
SiO_2	Wt. % ignited basis	13[7]	67	69	15	73	59
Al_2O_3		76	13	15	80	17	39
Fe_2O_3		7[7]	4	4	4[2]	1.5	<0.5
MgO			11	8		4	
CaO			2	1		2	
K_2O			0.6	0.5		0.03	
Na_2O			0.3			0.01	
TiO_2		3	0.6	1	1		
Loss on ignition		6[7]	20	17			
Principal phases		γ alumina	95% attapulgite	attapulgite	γ alumina	montmorillonite.	halloysite
Skeletal densities	g/cc	3.4	2.6	2.6	3.4	2.6	2.6
Bulk densities	g/cc	0.9	0.5	0.5	0.8	0.75	0.93
Porosities	cc/g	0.31	0.6	0.5	0.25	0.46	0.31
Specific area	m^2/g	240[6]	120[8]	124	142	280	140
Particle size		as specified	as specified or extruded	as specified or extruded	as specified	as specified or extruded[1]	as specified or extruded[1]
Approx. sintering temp.	°C. (50% loss in area, 12 hrs in air or vacua)	780	750	750	780	820	
Reference		57	59	61	152	153	46

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[1] Also available in pelleted form.

[2] Available with lower iron content.

[3] 210 W. Washington Sq., Philadelphia 5, Pa.

[4] Warren, Pa.

[5] 727 W. 7th St., Los Angeles 17, Calif.

[6] Low temperature calcined "Porocel" has lower area.

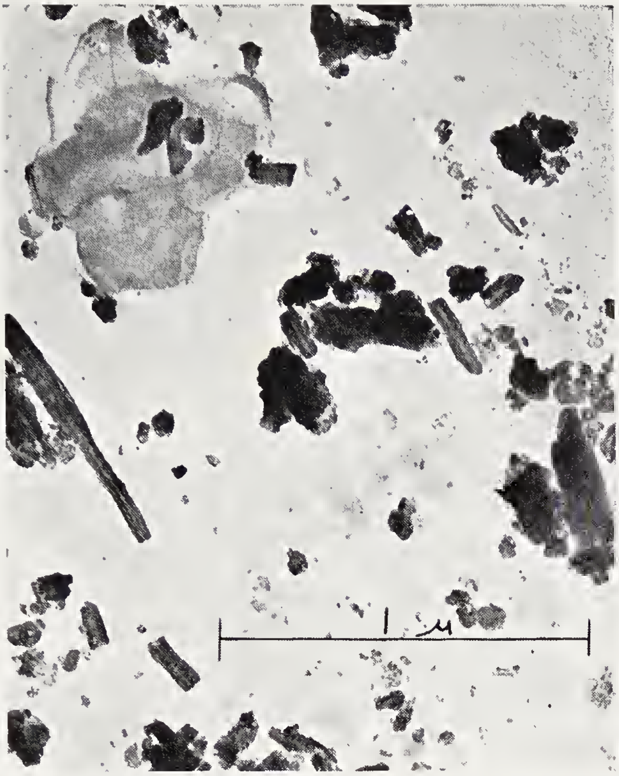
[7] Also available in low iron, low silica and lower volatile grades.

[8] Extruded Attapulgus clay has higher areas.

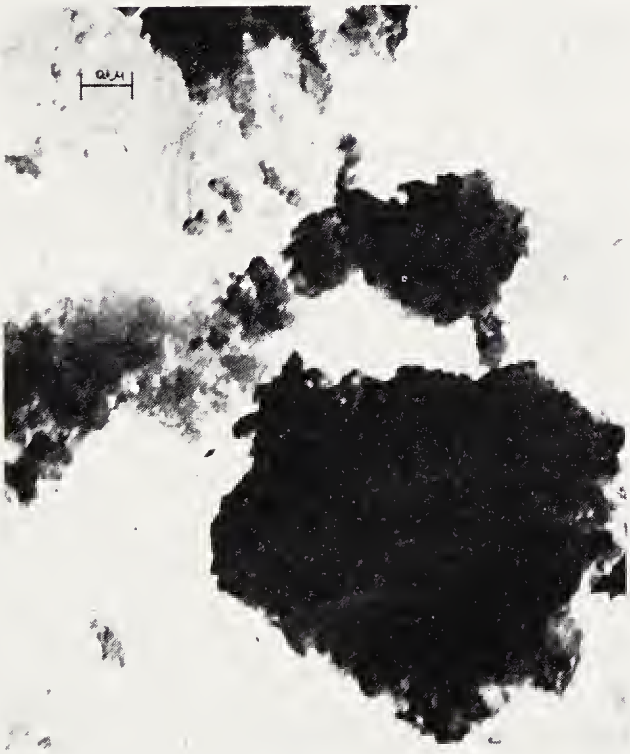
Attapulgite

Extruded Attapulgite

Figure 4. "Natural" high-area carriers.



Activated Halloysite



Activated Bentonite

Figure 4 (*cont'd*)

TABLE 3B. HIGH-AREA PRODUCTS FROM CRYSTALLINE HYDRATES

		Activated Magnesia				Activated Alumina	
Supplier		Westvaco Chemical Div., Food Machinery and Chemical Corp.[1]				Alcoa[2]	
Grade or trade name		2665	XP	"Sea Sorb"	2652	F 10	XF 21
Activation time	(hrs)	4.0			0.5		
Activation temp.	(°C)	375			625		
SiO_2	Wt. % ignited basis	0.6	0.9	4.4	0.8	<.1	.02
Al_2O_3		0.2	0.8	0.4	0.3	99	99
Fe_2O_3		0.2	0.3	0.3	0.4	.05	.02
$Na_2O + K_2O$							0.3
MgO		96	96	90	96		
CaO		1.2	1.5	4.0	2.6		
NaCl		0.3	.07	.3			
Sulfate		0.4		0.2			
Loss on ignition		6	5	10	7	3	8
Principal phase						χ alumina	
Skeletal density	g/cc	3.7	3.7	3.7	3.7	3.5	3.5
Bulk density	g/cc	0.6	0.10	0.6	0.77	0.88	1.0
Porosity	cc/g			.28			
Specific area	m²/g	30	230	140	125	100	200
Structure		perforated plates					
Particle size	Wt. % −10 μ				8 to 28 mesh	as specified	
	−20 μ						
	−40 μ						3
	−200 mesh	92		95			33
	−100 mesh						96
Av. particle size	microns	2	3	2			
Attrition resistance							good
Reference		64	64		64	62	62

---

[1] 161 E. 42nd St., New York City.

[2] 1501 Alcoa Bldg., Pittsburgh 19, Pa.

that the micelles in silica gel existing during gelation largely maintain their identity on dehydration at low temperatures, although surface tension forces tend to bring about a denser packing by breaking the weak bonds existing at the hydrogel points of contact[79].

The most important gel type carriers are silica gel base products which appear to have a spheroid (usually *ca.* 50 Å)[87] aggregate structure which is fairly stable up to 600°C and higher[79]. Increased bonding between micelles prior to dehydration which can be realized by hydrogel aging, heat treatment, etc., leads to less rearrangement on drying with consequent lessened shrinkage and higher porosity. Important carrier applications include catalysts commercially used for the manufacture of phthalic anhydride from naphthalene[81], for butadiene from alcohol[82], and for petroleum cracking.

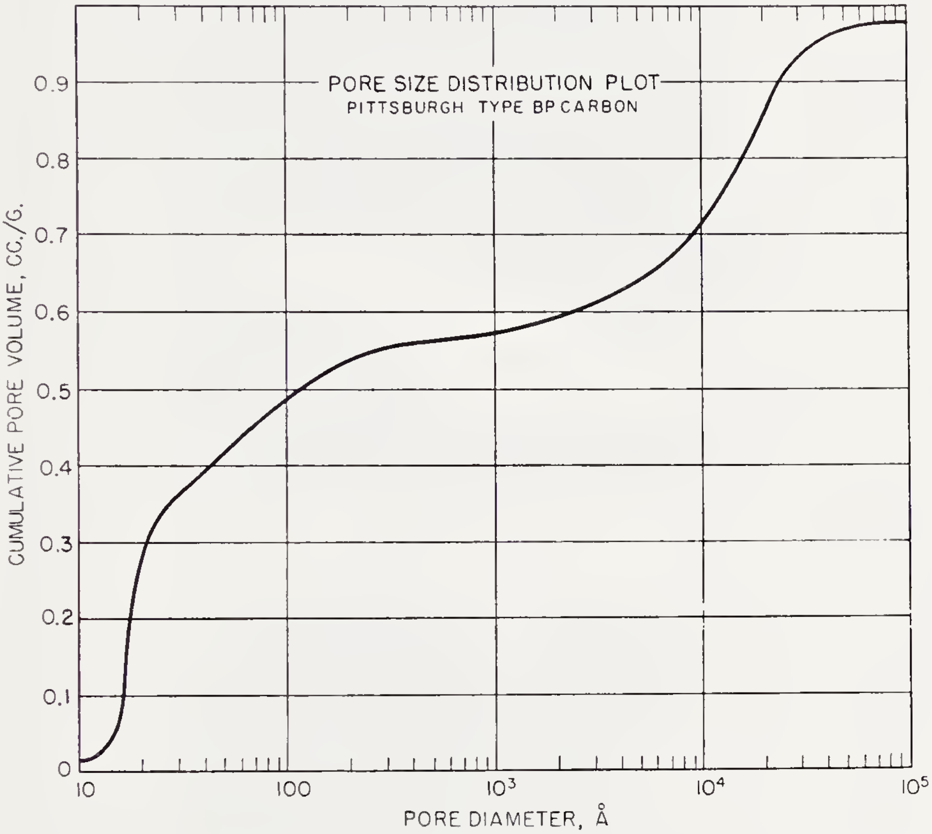


Figure 5. Pore size distribution plot for a typical activated carbon.

Gel type carriers can also be prepared from other oxides which form colloidal dispersions such as titania[82], alumina[84] and iron oxide[48], though in cases in which the colloidal particles are hydrates such as alumina, the high porosity and area may result from both inefficient packing of micelles and dehydration.

Commercial dry gel type products are listed in Table 3D.

TABLE 3C. ACTIVATED CARBONS

Supplier		Pittsburgh Coke & Chemical[5]	Darco[6]		Baugh & Sons[7]		West Virginia Pulp & Paper Co.[9]
Type		BP[4]	S51[1]	G60[2]	Bone Charcoal	"Synthad" C38	"Nuchar"[8]
C	Wt. %	87	80	97	8	6.5	96
SiO_2		7	13	2	natural basic calcium phosphate	synthetic basic calcium phosphate plus clay binder	0.5
Al_2O_3		3	5	0.3			tr.
CaO		0.2	0.6	0.1			0.5
Fe_2O_3		2	0.4	0.1			0.5
MgO		0.1	tr.				
Na_2O, K_2O		0.1	tr.				0.8
Principal phase		graphite			apatitic	apatitic	
Skeletal density	g/cc	2.3	2.3	2.3	2.8	2.8	2.3
Bulk density	g/cc	0.42	0.40	0.40	0.66	0.66	0.30
Porosity	cc/g	0.98	0.96		0.31	0.41	2.0
Specific area	m^2/g	1100	612	1190	115	90	750
Particle size	Wt. % −10 μ	4 x 10 mesh					
	−20 μ						
	−40 μ		70[3]	70			
	−200 mesh						
Approx. ignition temp. in air	(°C)	360	200	200			375
Reference		69			73	73	68

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[1] From lignite.

[2] From wood.

[3] Granular grades also available.

[4] From coal.

[5] Neville Island, Pittsburgh 25, Pa.

[6] 60 East 42nd St., New York 17, N. Y.

[7] Philadelphia 6, Pa.

[8] Derived from paper pulping by-products.

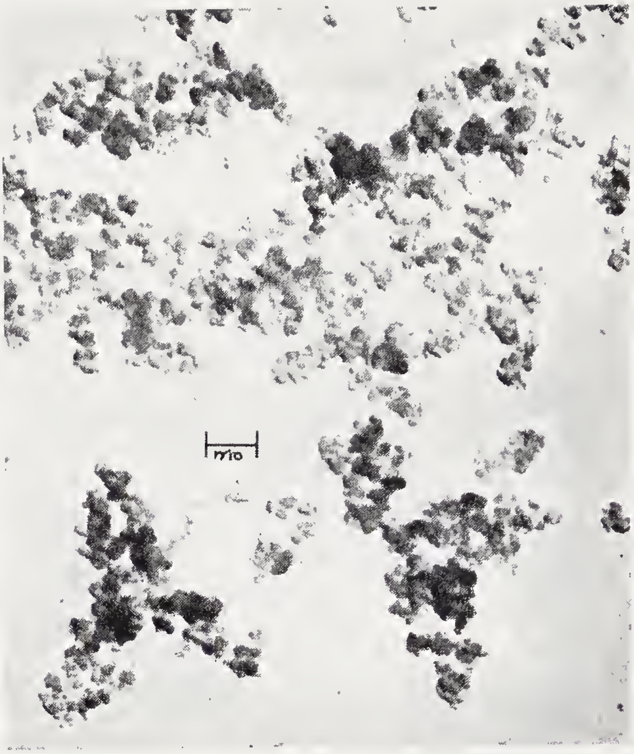
[9] New York City.

Miscellaneous Carriers. *Hydrous Gels and Hydraulic Cements.* Materials of this type are either hydrous gels or become so on the addition of water. They have important advantages for carrier usage. They may act as a

Activated Charcoal

Activated Magnesia

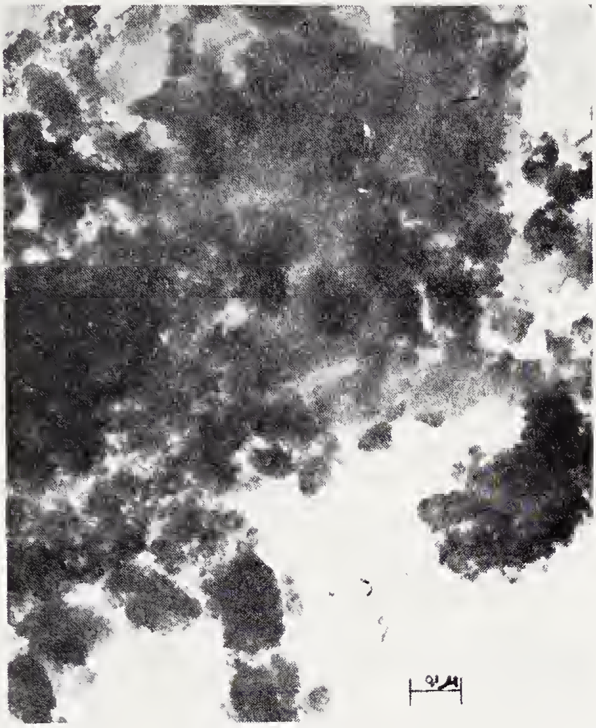
Figure 6. High-area skeleton-type carriers.



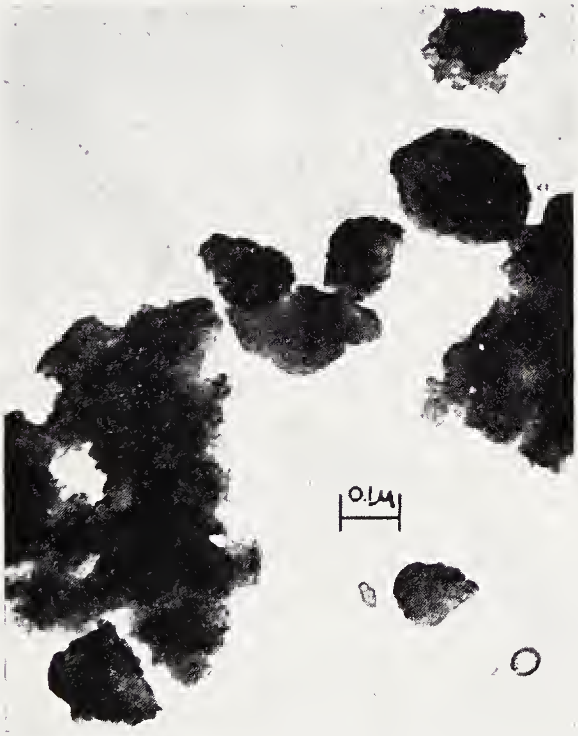
Silica Gel

Silica-Alumina Gel

Figure 7. High-area synthetic gel type carriers.



Alumina Gel



Silica-Magnesia Gel (Magnesol)
Figure 7 *(cont'd)*

TABLE 3D. HIGH-AREA SYNTHETIC GELS

		Silica Gel			Silica Alumina Catalyst				Alumina			Silica Magnesia	
Supplier..........		Davison[9]		Mon-santo[8]	Davison[9]	American Cyanamid[10]		National Aluminate Co.[11]	Alcoa[7]			Floridin Co.[12]	Westvaco Chemical Div., Food Machinery and Chem. Corp.[1]
Type		Normal	ID	"Santo-cel" C	MS-F-1	MS-A1	MS-B	MS-2	H-41[6]	H-42[4]	H 151	"Florisil"	"Magnesol"
SiO_2	Wt. % ignited basis	99.7	99.6	96	87	87	87	87	5	4	0.1–4	84	79
Al_2O_3		0.10		<1.0	13	13	13	13	95	95	94		
MgO												15	20
CaO		0.02	0.02										1
Na_2O		0.02	0.1		0.02				0.1	0.1	0.5		
K_2O													
Fe_2O_3		0.03	0.02	<1.0	0.03				0.1	0.1	0.1		
TiO_2		0.09	0.2										
Sulfate				1.4	0.2*	0.3*	0.3*	0.2*				1	
LOI (1000°C)		6.5	4.5	5	14*	15*	15*	16*	9	30	5		10
Principal phases		amorphous			amorphous							amorphous	
Skeletal density	(g/cc)	2.2	2.2	2.2	2.4*	2.5*	2.5*	2.5*	3.6			2.5	2.1
Bulk density	(g/cc)	0.77	0.45	0.09	0.52*	0.45*	0.43*	0.47*	0.8			0.45	0.2
Porosity	(cc/g)	0.4	0.8	4.0	0.55*	0.75*	0.75*	0.70*	0.40		0.4	0.4	1.0
Specific area	(m^2/g)	800	400	520	500	600	600	500	350			300[2]	515

Particle size	Wt. %											as specified	
	−10 μ				0	0	1	1		MS	¼″, ⅛″ ball		
	−20 μ	[3]	[3]		2	2	14	3	MS				
	−40 μ				11	15	50	15					
	−200 mesh				86	61	92	78					
	Av μ			4	64	68	40	57					50
Hardness (Mohs)		5	5										3.5
Attrition resistance*		excellent			exc.	exc.	exc.	exc.	exc.				fair
Approximate sintering temp. (50% area loss, 8 hr in air or vacua)	(°C)				900	900	900	900	1000				
Reference				155	12	13	154		62			156	[5]

[1] 161 E. 42nd St., New York, N. Y.

[2] Can be increased to 400 m^2/g by special treatment.

[3] Available in powder, grain or pellet form.

[4] Supplied in inactivated form. Activation achieved by heating at 450°C.

[5] Covered by U. S. patents 2,076,545, 2,163,526, 2,163,525 and 2,163,527.

[6] Also available in low silica grades.

[7] 1501 Alcoa Bldg., Pittsburgh 19, Pa.

[8] 445 Park Ave., New York 22, N. Y.

[9] Baltimore 3, Md.

[10] 30 Rockefeller Plaza, New York City.

[11] 6236 W. 66th Place, Chicago 38, Illinois.

[12] Warren, Pa.

* Data obtained by Stamford Research Laboratories, American Cyanamid Co. A manual of test methods is available.

binder to give good mechanical strength or plasticize the catalyst mix so that it can be extruded. Very intimate mixing is readily attained. Data on some commercially available materials of this nature are given in Table 4A. The surface area of Portland cement mixes has been measured by Blaine and Valis[85].

Fibrous Materials. Another class of carriers that find limited application includes materials such as asbestos[86, 87, 88], glass[89, 90], metals, etc., that can be manufactured in fibrous form. Since these can be woven into cloth or gauze mats or used in wool form it is possible to obtain very efficient contacting and narrow contact time distribution without excessive pressure drop. Carriers of this class are listed in Table 4B. A few photomicrographs of these materials are shown in Figure 8.

PROMOTERS

The most important patents in the field of catalysis are concerned with promoters and future progress in the field will probably be largely in this direction. The catalytic properties of pure substances are generally well known but possibilities for improvement through the use of suitable promoters are great. Earlier reviews of the subject have been given by Griffith[9] and by Berkman, Morrell and Egloff[92].

The term promoter is difficult to define since there are a great many types of promotion and it is often hard to make a distinction between the promoter, the active catalytic component, and the carrier. Sometimes more than one promoter is used. Therefore, any definition must be somewhat arbitrary. Other synonyms such as activator are also used in the literature. For the present purposes, a promoter is defined as "a substance added to the catalyst during its preparation in small amount (usually less than 10%) which by itself has little activity but which imparts either better activity, stability or selectivity for the desired reaction than is realized without it." Invariably there is some optimal amount, though sometimes this is just economic in the case of a high cost agent. In a few cases, these maxima are quite sharp as indicated by the work of Griffith[93] on the promotional effect of silica on molybdena.

Types of Promotion

Structural Promoters. Probably the most important type of promotion is the one in which the promoter increases the surface area of the active component. Usually, but not always, this involves increasing catalyst stability by inhibiting loss of surface during usage. This type of promoter has often been designated as a stabilizer in the literature. The classic case of this is the promotional action of alumina in iron synthetic ammonia catalyst which has been thoroughly discussed by Emmett[94]. Although not

TABLE 4A. HYDROUS GELS AND HYDRAULIC CEMENTS

		Hydraulic Cements			Natural Hydrogels			Synthetic Hydrogels	
		Aluminate[9]	Portland						
Supplier.		Atlas[4]	Lehigh[5]	Atlas[4]	R. T. Vanderbilt Co.[1]	Floridin Co.[2]	Attapulgus Minerals & Chemicals Corp.[8]	Alcoa[3]	Davison[7]
Grade.		Lumnite	Hi Early	White	"Veegum"	"Florigel"	"Attasol"	XH-1010	silica gel
SiO_2	Wt. % ign. basis	9	20	24	67	derived from fuller's earth	derived from fuller's earth	0.5	99.7
Al_2O_3		40	7	4	10			96	0.1
MgO		1	4	1	15				0.0
CaO		37	62	66	3			2	0.1
Fe_2O_3		4	2.5	0.4	1				0.03
FeO		4							—
$Na_2O + K_2O$							0.1		0.02
SO_3		0.2	2	2	3			0.15	—
Loss on ignition	(%)	<1	<2	<2	9	20	22	25	72
Particle size	% +100 mesh							9	
	−200 mesh	>95						69	
	−300 mesh							62	
Bulk density	(g/cc)	1.3						0.4	0.7
Compressive strength[6]	(psi)	>4000	2000						
Specific surface	(m^2/g)	.13	.28						

---

[1] 230 Park Ave., New York 17, N. Y.

[2] Warren, Pa.

[3] 1501 Alcoa Bldg., Pittsburgh 19, Pa.

[4] Universal-Atlas Cement Co., 100 Park Ave., New York 17, N. Y.

[5] Allentown, Pa.

[6] Standard mortar (1 cement to 2.75 sand) 1 day, 23°C.

[7] Baltimore 3, Md.

[8] 210 W. Washington Sq., Philadelphia 5, Pa.

[9] A chemically pure calcium aluminate cement has recently been introduced by Alcoa.

Table 4B. Fibrous Carriers

	Glass	Asbestos				
Supplier	Fiberglas Corp.[3]	Johns Manville[1] and The Ruberoid Co.[2]				
Grade	Fiber	Actinolite	Anthophyllite	Chrysotile	Amosite	Tremolite
Essential composition		$Ca(MgFe)_3(SiO_3)_4$ water up to 5%	Mg silicate with iron	Hydrous silicates of magnesia	Silicate of Fe and Mg Higher iron than anthophyllite	Ca and Mg silicate with some water
Fibril diameter	.0002″–.0008″		200Å	150Å	300Å	300Å
Fibril length	.2–.3″	variable	short	short to long	2–11″	short to long
Tensile strength (psi)	300,000	low	low	90,000	40,000	4000
Specific area m²/g	.04–.16			16		
Skeletal density (g/cc)	2.57	3.1	2.9	2.5	3.2	3.1
Thermal conductivity Btu/ft²/hr/in/°F				277		
Maximum recommended usage temp °F	1000			1000		
Resistance to alkalis	fair	poor	good	good	poor	good
Resistance to acids	good	fair	very good	poor	good	good
Flexibility		low	low	high	medium	varies

[1] Manville, New Jersey.

[2] South Bound Brook, New Jersey.

[3] Owens-Corning Fiberglas Corp., New York City.

very many clear cut cases of this type of promotion have been definitely established, it is a fertile field for investigation which can readily be attacked by measurement of surface area, x-ray diffraction, and electron microscopy as well as by catalytic activity tests. The increase in structural stability can probably be related in most cases to an increase in the melting point of the active component as a result of the presence of the promoter. This can occur when the promoter forms a solid solution with the active component. In some cases, a structural promoter may stabilize the structure of the carrier and only indirectly affect the surface area of the active component. An example of this is silica in a catalyst with molybdena as the active component on an alumina carrier[95]. The silica in this case probably stabilizes the structure of the alumina which supports the molybdena. The action may be even more complex in some cases. Molybdena has a deleterious effect on the structural stability of alumina but according to one patent[96], the addition of lime to form calcium molybdate reduces this harmful effect. Of course, the presence of a structural promoter may influence the catalytic performance in other ways in addition to preserving a high surface area. Melting point-composition data should be helpful in predicting structural promotion effects. Heuman[97] has related the melting points of binary crystal systems to molecular volumes. The nature of the promotional action is seldom made clear in the literature as only recently have surface area measurements become common, but it is probable that promotion of this type is achieved in the cases listed in Table 1 when the promoter is intimately mixed or coprecipitated with the catalyst component.

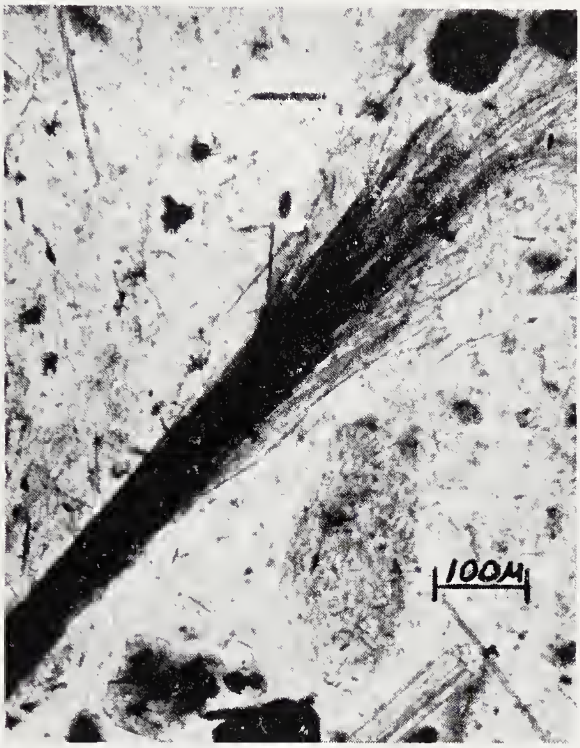
Dual Action Promoters. In some cases of catalysis more than one reaction must be catalyzed to achieve the over-all result. In such cases the promoter may act to catalyze one of the reactions. The best example of this dual action is the recent work of Ciapetta, Pitts and Leum[98] on the isomerization of paraffins with a nickel-silica-alumina gel catalyst. Neither the nickel on other carriers such as silica gel or the silica-alumina gel by itself are active but in combination high activity is achieved. Apparently active centers for both hydrogen and proton transfer are needed for this reaction. The alumina in this case could be considered as a dual action type of promoter. It is probable that there are many cases of promotion of this type but only those listed in Table 1 appear to have been recognized.

Electronic Promoters. Reactions on metallic surfaces involving hydrogen have been shown in recent years to be related to the electronic character of the metallic system[99, 100] or, in other words, to the ability of the metallic system to accept electrons from and give up electrons to the surface. Metals having many vacant orbitals or "holes," and having a high attraction for additional electrons, strongly adsorb hydrogen (e.g., tantalum), and the electrons from the hydrogen may become part of the

"Fiberglas"

"Fiberglas"

Figure 8. Fibrous carriers.



South African Asbestos

Canadian Asbestos (chrysotile)
Figure 8 *(cont'd)*

electronic system of the bulk metal. Metals without empty orbitals, such as copper and gold, have a low attraction for hydrogen and do not adsorb hydrogen strongly in the pure state. The first type of metal is a poor hydrogenation catalyst, probably because the adsorbed hydrogen is held too tightly to be available for reaction. The relatively poor catalytic power of unpromoted metals of the second type, without empty orbitals, can be attributed to the lack of adsorbed hydrogen. Highest catalytic activity is realized with metals such as nickel and platinum which have few empty orbitals so that hydrogen is adsorbed but can be readily released to the other reactant. If a foreign substance is added, this will affect the number of empty orbitals and therefore the catalytic activity. If it improves the activity more than expected from averaging because of the effect on the vacant orbitals, it may be considered to be an electronic promoter.

Studies on alloy catalysts by Schwab[101], Couper and Eley[102], Dowden and Reynolds[103] and Vol'kenshtein[104] illustrate this type of promotion and inhibition. Their work also indicates that mechanical and electrical properties such as resistance and hardness are also related to the degree of filling of the electronic orbitals.

It would appear that measurement of physical properties as well as the heat of adsorption can be used to study promotion of this nature.

Lattice Defect Promoters. This type of promotion has been expounded by Vol'kenshtein[105], Taylor[106] and others[107, 108, 109] in recent years. Taylor now tends to identify the active centers of many oxide catalysts with such lattice defects as occur near the surface rather than with surface peaks and valleys as he believed earlier (see Chapter by Hulburt). A small amount of impurity or additive can have a very large affect on the number of lattice defects since each interstitial foreign atom may be the center of a lattice defect which extends for 10 atom diameters or more. The number of defects may also be influenced by the temperature so that the apparent activation energy may be affected by the activation energy of defect formation. If the promoter increases catalytic activity by affecting the number of lattice defects, it can be considered to be a lattice defect promoter.

In order for interstitial substitution to occur it is usually necessary for the foreign ion to be about the same size as the one it replaces. Related to defect formation is the electrical conductivity and the valence state. Small amounts of impurities or promoters may affect the electrical conductivity of semi-conductors many fold and even change the stable valence state of neighboring atoms if the impurity has a valence different from that of the atom it replaces. The dissociation pressure of the oxide may also be affected. Therefore, it is possible to study this type of promotion by measurement of valence state, electrical conductivity and magnetic susceptibility as well as by adsorption measurements and catalytic performance. Examples of valence induction given by Taylor[106] include the following:

Catalyst	Promoter or Impurity	New Valence of Active Catalysts Cation	Unpromoted Valence of Catalyst Cations
NiO	Li_2O	3	2
CoO	Li_2O	3	2
MnS	La_2O_3	3	2

In the oxidation of ammonia on oxide catalysts such as ferric oxide, bismuth trioxide, nickel oxide, cobaltous and manganous oxide Taylor[110] states that yields of N_2O are directly proportional to the excess of oxide ions in the lattice.

Adlineation Promoters. It is reasonable to expect that boundary zones between phases or crystals will have different catalytic activity than the bulk phases. A promoter may act by creating or increasing the number of such active interfaces. This type of promotion is discussed at length by Berkman *et al.*[92] with reference to the work of Volmer, Koslelitz (CuO-ZnO interface), Cassel, Pease and Taylor (Cu-CuO interface), Balandin and Rubinshtein (Ni-Al_2O_3 interface), etc. Recent literature does not appear to have many examples (Table 5). Balandin and Vasserberg[111] explain data on the decomposition of isopropyl alcohol on zinc oxide promoted alumina on this basis. Herbo[112] who studied the hydrogenation of cyclohexene over a Ni:ZnO:Cr_2O_3 catalyst interpreted his results as indicating that the reaction occurred at the chromia-nickel interface.

Selectivity Promoters. In cases in which more than one reaction is possible, it is often desirable to have a selectivity promoter to guide the reaction along the proper path or prevent further reaction of desired product. More often than not this probably involves poisoning the sites active for undesired side or secondary reactions. A probable example of this is the usage of potassium with chromia on alumina (dehydrocylization) or with iron (Fischer-Tropsch synthesis) (see Table 5). In these cases the potassium possibly acts by poisoning the sites that are active in cracking (acid groups) and thereby decreases the gas yield. Thus, what is an inhibitor for one reaction may be a selectivity promoter for another.

In some cases in which the desired reaction product can be partially destroyed by undergoing further reaction (for example, naphthalene oxidation to form phthalic anhydride), it is undesirable to have a very active fine pore structure catalyst. Naphthalene molecules getting into such a pore system are very likely to be oxidized further than the desired product, phthalic anhydride. The promoter in such a case may function by simply filling up some of the fine pore space and thus giving less opportunity for further reaction of the desired product.

Diffusion Promoters. In most commercial catalytic processes, the catalyst is employed in the form of $\frac{1}{4}$ to $\frac{3}{4}$-inch granules, pellets, or rings; this tends to avoid high pressure drops which lead to channeling and high gas compression costs. Largely as a result of the use of catalyst in the form of rather large particles, diffusion into the catalyst particles is a major rate-determining factor in some reactions, particularly at high temperatures[113]. The diffusion characteristics may be improved by adding a diffusion promoter as well as by decreasing the particle size or by decreasing the compression during the pelleting operation. A satisfactory diffusion promoter must be capable of decreasing the resistance to diffusive flow without appreciably harming the physical strength or other catalyst properties. A system of interconnected macropores as well as micropores is preferable for obtaining both low diffusion resistance and high surface area. Examples are:

(1) Organic materials such as mineral oil, graphite, wood flour, starch dextrin, castor oil, oleic acid and cellulose[114]. These all decompose and tend to make the catalyst porous.

(2) High porosity diatomaceous earths which have many very large pores.

(3) Material with needle shaped particles (e.g., fuller's earth) which pack only to a low density unless a large amount of other filler is present that would fill this space.

(4) Hydrous oxides which lose a great deal of water on drying to give a porous residue.

(5) Decomposable salts, such as nitrates and carbonates, which evolve gas on heating. If these are in a molten state during decomposition so as to impart plastic properties to the mass, a highly porous product may result.

Phase Change Promoters. Catalyst surfaces must be considered as dynamic systems undergoing very rapid transitions. In many cases such as oxidation catalysis the catalytic action itself is probably dependent on the ability of local points of the surface to change back and forth between different oxidation states and crystal structures if other than surface atoms participate[115]. Hence, a possible mechanism for promotion and inhibition is by aiding and hindering phase or oxidation state transitions. Measurement of transition rates might be utilized to study this type of promotion.

Tables on Promoters

The literature pertaining to promoters (1942–1952) is summarized in Table 5. Doubtless there are many important omissions despite an attempt to achieve a complete listing. The valence state of the promoter may, of course, change during usage from that given in the table. Because mechanisms of catalytic action are seldom well understood, the listings of promotion type should only be considered as an opinion. To improve readability and reduce space requirements, the following abbreviations have been used in Table 5.

Reaction Type

H	hydrogenation
−H	dehydrogenation
H_2O	hydration
$-H_2O$	dehydration
Cr	cracking
FT	Fischer-Tropsch synthesis
Nit	nitrile formation
Am	amination
Alc	alcohol synthesis
Halo	halogenation
Ox	oxidation
Shift	$CO + H_2O \leftrightarrows CO_2 + H_2$
O	oxygen
Exc	exchange
Isom	isomerization
Poly	polymerization
Alk	alkylation

Promotion Types

sel.	selectivity
str.	structural
adl.	adlineation
elec.	electronic
diff.	diffusion

Companies

N.V. de B.P.M.	N.V. de Bataafsche Petroleum Maatschappij
I.C.I.	Imperial Chemical Industries
N.Z.	New Zealand
H.A.C. for S. & I.R.	Honorary Advisory Council for Scientific and Industrial Research (Canada)
Kyowa Chem. Ent.	Kyowa Chemical Enterprises Co. (Japan)

ACCELERATORS

No very satisfactory name has been given to agents that are continuously added to inlet vapors for the same purpose as promoter is added during catalyst preparation. They are gaseous agents which do not yield the product but which, in some way, promote the desired reaction. They can be considered as the opposite of poisons. For economic reasons these agents are largely limited to low cost materials such as steam, air and

TABLE 5. PROMOTERS FOR VARIOUS CATALYTIC AGENTS

Alumina

Promoter	Wt. (%)	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
Sulfamic acid			sel.	Nixon, A. C., and Davis, O.	**43,** 1161 (1949)	U. S. 2,450,766
KOH	5	—H	sel.[2]	Schulze, W. A., and Hillyer, J. C.	**44,** 1628 (1950)	U. S. 2,485,927
					42, 2410 (1948)	U. S. 2,431,427
NaF_2			str.	Thibon, H., Charrier, J., and Tertian, R.	**45,** 10023 (1951)	
K or Na			str.	Smith, A. E., and Beeck, O.	**41,** 6681 (1947)	Brit. 572,110
K_2O	0.5	Cr etc.		Bailey, W. A., Jr., and Bittner, C. W.	**42,** 1032 (1948)	Brit. 592,116
CaO, BaO, MgO	1–10	—H	sel.	Schulze, W. A., Hillyer, J. C., and Drennan, H. E.	**39,** 4887 (1945)	U. S. 2,380,876
BaO	5	—H	sel.[1]	Schulze, W. A., and Hillyer, J. C.	**44,** 1628 (1950)	U. S. 2,485,927
MgO	3	—H	sel.[3]	Schulze, W. A., and Hillyer, J. C.	**44,** 1628 (1950)	U. S. 2,485,927
Be_2OF_2		Cr		Darling, S. M.		U. S. 2,449,061
CaO, MgO	1–10	$-H_2O$		N.V. de B.P.M.	**44,** 5387 (1950)	
$Ba(OH)_2$		—H		Whaley, T. H.	**42,** 4600 (1948)	U. S. 2, 437,773
Al_2O_3	5–35	Cr		Garrison, A. D.	**44,** 317 (1950)	U. S. 2,483,130
SiF_4	5–35			Garrison, A. D.	**44,** 317 (1950)	U. S. 2,483,130
SiO_2	1–15	Cr etc.	str.	Bailey, W. A., Jr., and Bittner, C. W.	**42,** 1032 (1948)	Brit. 592,116
Fe_2O_3				Heinemann, H., Wert, R. W., and McCarter, W. S. W.	**44,** 1889 (1952)	*IEC*, **41,** 2928 (1949)
Fe_2O_3				Wicke, E.	**43,** 6497 (1949)	
ZnO	10	$-H_2O$	adl.	Balandin, A. A., and Vasserberg, V.	**41,** 1539 (1947)	

[1] Reduces cracking.

[2] Reduces carbon.

[3] Reduces isomcrization.

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
K_2O	3	Al_2O_3 MgO	−H	sel.	Yamazaki, G.	**44,** 1125 (1950)	
K_2O	12	Al_2O_3	−H	sel.	Visser, G. H.	**44,** 7636 (1950)	
K_2O	1	Al_2O_3	−H	sel.	Varga, J., Rabo, G., and Zalai, A.	**45,** 10022 (1951)	
Na, K, Rb		Al_2O_3	−H	sel.	Greensfelder, B. S., and Archibald, R. C.	**42,** 751 (1948)	Brit. 572,251
K_2O	0.07	many	−H	sel.	Carrozzi, R. C.	**43,** 8661 (1949)	
BeO	5–20	Al_2O_3	−H	str.	Owen, J. R.	**44,** 2004 (1950)	U. S. 2,483,929
BeO			−H	str.	Pitzer, E. W.		U. S. 2,536,085
BeO	1–10	Al_2O_3	−H	str.	Huffman, H. C.	**41,** 855 (1947)	U. S. 2,411,829
BeO	5	Al_2O_3	−H	str.	Parker, R. L., Jr., and Huffman, H. C.	**42,** 1049 (1948)	U. S. 2,426,118
CaO, MgO	2	$ZnO\cdot Al_2O_3$	−H	sel.	Kearby K. K.		U. S. 2,556,280
MgO		Al_2O_3	−H	str.	Layng, E. T.	**41,** 7738 (1947)	U. S. 2,423,328
$AlPO_4$	1.2	Al_2O_3	−H	str.	Stirton, R. I.	**42,** 5655 (1948)	U. S. 2,411,297
SiO_2	1	Al_2O_3	−H	str.	Parker, R. L., Jr., and Huffman, H. C.	**42,** 1049 (1948)	U. S. 2,411,829
CeO_2	0.2	Al_2O_3	−H	sel.	Varga, J., Rabo, G., and Zalai, A.	**45,** 10022 (1951)	
CeO_2	0.07	many	−H	sel.	Carrozzi, R. C.	**43,** 8661 (1949)	
SnO_2	5–10	Al_2O_3	−H		Burk, R. E.	**38,** 4764 (1944)	U. S. 2,342,247
ZrO_2		Al_2O_3	−H	str.	Ahlberg, J. E.	**39,** 3421 (1945)	U. S. 2,374,404
ThO_2	0.1	Al_2O_3	−H	sel.	Varga, J., Rabo, G., and Zalai, A.	**45,** 10022 (1951)	
SiO_2	4–6	Al_2O_3	−H	str.	Huffman, H. C.	**42,** 4340 (1948)	U. S. 2,437,533
Sb_2O_5	9	Al_2O_3	−H	sel.	Fisher, F. E., Watts, H. C., Harris, G. E., Hollenbeck, C. M.	**40,** 1647 (1946)	*IEC*, **38,** 61 (1946)
S	1		−H		Roy, A. N.	**42,** 3426 (1948)	

TABLE 5—*Continued*

Clay

Promoter	Wt. (%)	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
MgO	6	FT	str.	Craxford, S. R.	**42,** 3648 (1948)	*TFS*, **66,** 440 (1947)
MgO	2	Cr	str.	Spicer, W. E., and Pierce, J. A.		U. S. 2,431,206
ThO_2	3	FT	sel.	Craxford, S. R.	**42,** 3648 (1948)	*TFS*, **66,** 440 (1947)
MnO_2	3	Cr		Gary, W. W.	**42,** 5629 (1948)	U. S. 2,440,743
KOH, Fe_2O_3		$-H_2O$	dual	Nagai, H.	**43,** 5359 (1949)	
Al_2O_3	4	Cr		Oulton, T. D.		U. S. 2,440,756
Al_2O_3	2	Cr		Spicer, W. E., and Pierce, J. A.		U. S. 2,431,206
Be, Ti, Zn, oxyfluoride		Cr		Darling, S. M.	**44,** 2224 (1950)	U. S. 2,449,061

Copper and Its Oxides

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
K, Na			$-H$		I.C.I. of Australia and N. Z.	**44,** 4932 (1950)	
KOH			$-H$	sel.	Rutovskii, B. N., and Mulyar, P. A.	**36,** 442 (1942)	
Alkali		Al_2O_3	Alc		Nippon Chem. Ind.	**44,** 1127 (1950)	
Ca, Mg			$-H$		I.C.I. of Australia and N. Z.	**44,** 4932 (1950)	
CaO		Al_2O_3	H		Stewart, M. M.	**40,** 4860 (1946)	U. S. 2,400, 959
CaO, MgO	50		H		Brown, F. E., Menzel, R. E., Stewart, M. M., Lefrancois, P. A.	**45,** 3529 (1951)	*JACS*, **72,** 5602 (1950)
MgO			$-H$	str.	Yamanaka, T.	**42,** 6628 (1948)	
$Ba(NO_3)_2$	0.2	act. C	$-H$		Grekhnev, M. A.	**41,** 7214 (1947)	
U^{+3}	0.1		$-H$		Lel'chuk, S. L.	**40,** 5627 (1946)	
$Al_2O_3 + Ti_2O_3$	10 + 2		$-H$, $-H_2O$	dual	Lel'chuk, S. L.	**42,** 4436 (1948)	
Al_2O_3			$-H$, $-H_2O$		Lel'chuk, S. L.	**42,** 4436 (1948)	

H_3BO_3	10	Al_2O_3	Am		Nippon Chem. Ind.	**44**, 1129 (1950)	
CeO_2			$-H$		Lel'chuk, S. L.	**40**, 5627 (1946)	
CeO_2	2–20		$-H_2O$, $-H$		Lel'chuk, S. L., *et al.*	**42**, 4436 (1948)	
TiO_2		Al_2O_3	$-H$	sel.	Lel'chuk, S. L., *et al.*	**39**, 1130 (1945)	
SnO_2			H		Natta, G.	**44**, 1127 (1950)	
H_3PO_4	10	Al_2O_3	Am		Nippon Chem. Ind.	**44**, 1129 (1950)	
Ni	18		$-H$	elec.	Rienacker, G., and Bade, H.	**37**, 2253 (1943)	
Co, Cr_2O_3		many	$-H$		Church, J. M., and Joshi, H. K.		*IEC*, **43**, 1806 (1951)
Cr_2O_3, MnO_2, Fe_2O_3			$-H$		Kearby, K. K.	**41**, 2886 (1947)	U. S. 2,407,373
Cr_2O_3			H	str.	Lefrancois, P. A.	**39**, 663 (1945)	
Cr_2O_3	4.6	kies.	FT		Ghosh, J. C., and Basak, N. G.	**42**, 5643 (1948)	
Cr_2O_3		kies.	H	str.	Miyake, R.	**44**, 352 (1950)	
Cr_2O_3	4.4		CH_3OH	dual	Pospekhov, D. A.	**43**, 3351 (1949)	
Fe_2O_3	1		Ox	str.	Murdock, R. E., Brooks, F. R., and Zahn, V.	**42**, 2208 (1948)	*AC*, **20**, 65 (1948)
ZnO	35.6		CH_3OH	dual	Pospekhov, D. A.	**43**, 3351 (1949)	
ZnO		many	$-H$	str.	Church, J. M., and Joshi, J. K.		*IEC*, **43**, 1806 (1951)
ZnO			$-H$	str.	Yamanaka, T.	**42**, 6628 (1948)	
ZnO	5		H	str.	Natta, G.	**44**, 1127 (1950)	

[*Copper Chloride*]

KCl	30	Al_2O_3	Halo.		Kilgren, E. W., and Gorin, E.	**44**, 5575 (1950)	

[*Copper Chromite*]

PbO_2	0.1	act. C	Ox.		Zhabrova, G. M., Roginskii, S. Z., and Fokina, E. A.	**41**, 1539 (1947)	

TABLE 5—*Continued*

Cobalt and Its Oxides

Promoter	Wt. (%)	Carrier	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
Alkali		kies.	FT	sel.[4]	Russell, W. W., and Miller, G. H.	**44,** 8616 (1950)	*JACS*, **72,** 2446 (1950)
Alkali	2	inert	Nit	sel.	Teter, J. W.	**44,** 1128 (1950)	U. S. 2,479,879
Be_2O_3		kies.			Hamai, S., Hayashi, S., Shimamura, K., and Igarashi, H.	**41,** 4366 (1947)	
MgO		kies.	FT	str.	Anderson, R. B., Hall, W. K., and Hofer, L.	**42,** 8058 (1948)	*JACS*, **70,** 2465 (1948)
CeO_2			FT	str.	Russell, W. W., and Miller, G. H.	**44,** 8616 (1950)	*JACS*, **72,** 2446 (1950)
CeO_2 , ThO_2	12, 25	kies.	FT	str.	Hamai, S., Hayashi, S., Shimamura, K., and Igarashi, H.	**41,** 4366 (1947)	
ThO_2	18	kies.	FT	sel.	Friedman, A. H.	**44,** 4656 (1950)	U. S. 2,500,533
ThO_2		kies.	FT	sel.	Clark, Alfred	**44,** 4655 (1950)	U. S. 2,497,761
ThO_2	6	kies.	FT	sel.	Craxford, S. R., and Poll, A.	**44,** 8086 (1950)	
ThO_2	8	kies.	FT	sel.	Hofer, L., Peebles, W., and Bean, E.	**44,** 9223 (1950)	*JACS*, **72,** 2698 (1950)
ThO_2	18	kies.	FT	sel.	Craxford, S. R.	**41,** 262 (1947)	
ThO_2		kies.	FT	sel.	Anderson, R. B., Hall, W. K., and Hofer, L.	**42,** 8058 (1948)	*JACS*, **70,** 2465 (1948)
ThO_2	8	kies	FT	sel.	Hofer, L., and Peebles, W.	**42,** 1483 (1948)	*JACS*, **69,** 2497 (1947)
Cr_2O_3		kies	FT		Ghosh, J. C., and Basak, N. G.	**42,** 5643 (1948)	
Cu		kies	FT	dual	Russell, W. W., and Miller, G. H.	**44,** 8616 (1950)	*JACS*, **72,** 2446 (1950)
CuO	1–20	MgO		str.	Bilisoly, J. P.	**44,** 8092 (1950)	U. S. 2,509,204
MnO			Am.	sel.	Teter, J. W.	**39,** 5253 (1945)	U. S. 2,381,473

[4] Increases liquid yield.

Promoter	Wt. (%)	Carrier	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
Al_2O_3	2–3		FT		Keith, P. C.	**43,** 5574 (1949)	U. S. 2,470,216
Al_2O_3			NH_3	str.	Brill, J. L.		*JCP*, 1047 (1951)
Al_2O_3			NH_3	str.	Love, K. S., and Brunauer, S.	**36,** 3092 (1942)	*JACS*, **64,** 745 (1942)
Al_2O_3	5		H	str.	Komori, S.	**42,** 2228 (1948)	
Al_2O_3	50			str.	Cirilli, V.	**41,** 7215 (1947)	
Al_2O_3			shift	str.	Kirillov, I. P., and Sirotkin, G.	**43,** 3599 (1949)	
Bi_2O_3	33		O Exc	str.	Morita, N.	**41,** 2974 (1947)	
Bi_2O_3			O Exc		Morita, N.	**41,** 4366 (1947)	
SiO_2	2		NH_3		Grinevich, V. M.	**40,** 3576 (1946)	
SiO_2	40				Cirilli, V.	**41,** 7215 (1947)	
Cu			FT		Merkel, H.	**44,** 8564 (1950)	
Cu			FT	sel.	Kolbel, H., and Langheim, R.	**44,** 3235 (1950)	
Cu	10		FT		Kodama, S., Murata, Y., and Hari, I.	**44,** 9135 (1950)	
CuO	5		FT		Hall, W. K., Tarn, W. H., and Anderson, R. B.	**45,** 5907 (1951)	*JACS*, **72,** 5436 (1950)
CuO					Kolbel, H., and Engelhardt, F.	**43,** 4828 (1949)	
CuO	.08		FT		Kolbel, H., Ackermann, P., Juza, R., and Tentschert, H.	**43,** 8117 (1949)	
CuO	5	MgO	−H		Fulton, S. C., and Kearby, K. K.	**40,** 719 (1946)	U. S. 2,383,643
CuO			−H		Meinert, R. N., *et al.*		U. S. 2,518,354
CuO	5		−H	sel.	Kearby, K. K.	**44,** 3874 (1950)	*IEC*, **42,** 295 (1950)
CuO	5		−H		Morrell, C. E., and Slotterbeck, O. C.	**43,** 680 (1949)	U. S. 2,449,004
CuO	8		−H		Standard Oil Development Co.	**42,** 357 (1948)	Brit. 589,546
CuO			−H		Nickels, J. E., and Corson, B. B.		*IEC*, **43,** 1685 (1951)
CuO	4.6	MgO	−H		Klieber, C. E., Campbell, D. L., Stines, D. E., and Nelson, C. C.	**41,** 2426 (1947)	U. S. 2,414,817

TABLE 5—*Continued*

Iron and Its Oxides

Promoter	Wt. (%)	Carrier	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
CuO	0.5		Ox	str.	Krause, A., Kotkowski, St., and Karolewicz, St.	**45,** 10021 (1951)	
K_2CO_3	1		FT		Kodama, S., Tahara, H., Imai, O., and Yamada, T.	**44,** 9135 (1950)	
K_2CO_3	0.25		FT		Kolbel, H., and Engelhardt, F.	**43,** 4828 (1949)	
K_2CO_3	0.12		FT		Kolbel, H., Ackermann, P., Juza, R., and Tentschert, H.	**43,** 8117 (1949)	
K_2CO_3	7–10		FT		Kodama, S., *et al.*	**43,** 2397 (1949)	
K_2CO_3	7		−H		Davies, E. P., and Eggertson, F. T.	**43,** 7610 (1949)	U. S. 2,461,147
K_2O	5		FT		Hall, W. K., Tarn, W. H., and Anderson, R. B.	**45,** 5907 (1951)	*JACS*, **72,** 5436 (1950)
K_2O	2–3		FT		Keith, P. C.	**43,** 5574 (1949)	U. S. 2,470,216
K_2O	0.5		FT		Shultz, J. F.		*JACS*, **74,** 637 (1952)
K_2O			NH_3		Brill, J. L.		*JCP*, 1047 (1951)
K_2O			NH_3		Nelson, A., and Bohlbro, H.		*JACS*, **74,** 963 (1952)
K_2O			NH_3		Love, K. S., and Brunauer, S.	**36,** 3092 (1942)	
K_2O			−H		Meinert, R. N., *et al.*		U. S. 2,518,354
K_2O	5		−H	sel.	Kearby, K. K.	**44,**,3874 (1950)	*IEC*, **42,** 295 (1950)
K_2O	5		−H		Morrell, C. E., Slotterbeck, O. C.	**43,** 680 (1949)	U. S. 2,449,004
K_2O	8		−H	sel.	Standard Oil Development Co.	**42,** 357 (1948)	Brit. 589,546
K_2O			−H		Nickels, J. E., and Corson, B. B.		*IEC*, **43,** 1685 (1951)
K_2O	4.6	MgO	−H		Klieber, C. E., Campbell, D. L., and Stines, D. E.	**41,** 2426 (1947)	U. S. 2,414,817
K_2O	0.25		shift		Stowe, V. M.	**39,** 4204 (1945)	U. S. 2,364,562
KF	0.1–10		FT		Standard Oil Development Co.	**43,** 8121 (1949)	Brit. 621,902
KF	1		FT		Voorheis, A., Jr.	**43,** 9420 (1949)	U. S. 2,479,439
KF	1.4	MgO	−H		Fulton, S. C., and Kearby, K. K.	**40,** 719 (1946)	U. S. 2,383,643

KBF_4	0.2–10		FT	sel.[5]	Vesterdal, H. G.	**44,** 317 (1950)	U. S. 2,471,129–30
K_2CrO_4	10		−H		Sumerford, S. S.	**42,** 7312 (1948)	U. S. 2,436,616
$K_2Cr_2O_7$			shift		Kirillov, I. P., and Sirotkin, G.	**43,** 3599 (1949)	
Na_2O, K_2O					Maxwell, L. R., Smart, J. S., and Brunauer, S.	**45,** 8829 (1951)	*JCS*, **19,** 303 (1951)
Na silicate	0.2–20		FT		Herbert, W.	**39,** 2636 (1945)	
Alkali			FT	sel.[6]	Kolbel, H., and Langheim, R.	**44,** 3235 (1950)	
Alkali			−H	sel.[7]	Davidson, D. D.	**44,** 8625 (1950)	U. S. 2,513,994
Alkali ferrate	0.2–20		FT		Mosesman, M. A.	**43,** 6338 (1949)	U. S. 2,470,784
MgO	4		FT		Kodama, S., *et al.*	**44,** 9135 (1950)	
MgO			FT		Shultz, J. F., Seligman, B., Lecky, J., and Anderson, R. B.		*JACS*, **74,** 637 (1952)
MgO	30		shift		Stowe, V. M.	**39,** 4204 (1945)	U. S. 2,364,562
MgO	4		FT		Hall, W. K., Tarn, W. H., and Anderson, R. B.	**45,** 5907 (1951)	*JACS*, **74,** 5436 (1950)
$MgCrO_4$	10		shift		Ashley, K. D., and Innes, W. B.	**46,** 1188 (1952)	U. S. 2,567,140
CaO			NH_3	str.	Nelson, A., and Bohlbro, H.		*JACS*, **74,** 963 (1952)
CaF_2			−H		Fulton, S. C., and Kearby, K. K.	**40,** 719 (1946)	U. S. 2,383,643
BaO					Maxwell, L. R., Sm**art,** J. S., and Brunauer, S.	**45,** 8829 (1951)	*JCP*, **19,** 303 (1951)
H_3BO_3	20		FT	sel.	Kodama, S., *et al.*	**44,** 9136 (1950)	
TiO_2			NH_3		Sastri, M., and Srikant, H.		CS (India), **19,** 343 and 213
CrO_3	10		shift		Stowe, V. M.	**39,** 4204 (1945)	U. S. 2,364,562
Cr_2O_3			−FT		Davidson, D. D.		U. S. 2,513,994
Cr_2O_3	5		H		Komori, S.	**42,** 2228 (1948)	
Cr_2O_3	5		−H		Davies, E. P., and Eggertsen, F. T.	**43,** 7610 (1949)	U. S. 2,461,147
Cr_2O_3			shift		Atwood, K., Arnold, M. R., and Appell, E. G.	**44,** 9137 (1950)	*IEC*, **42,** 1600 (1950)
Cr, Mn chlorides	0.1				Strongin, G. M.	**41,** 1820 (1947)	
PbO			shift		Kirillov, I. P., and Sirotkin, G.	**43,** 3599 (1949)	

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[5] Favors olefin polymerization.

[6] Increases carbide and carbon formation.

[7] Reduces carbon.

TABLE 5—*Continued*

Magnesium Oxide

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
MoO_3, Fe_2O_3			$-H_2O$	dual	Gershbein, L. L., Pines, H., and Ipatieff, V. N.	**42,** 1185	*JACS*, **69,** 2888 (1947)
Salts of Mn			$-H_2O$		Waida, T.	**41,** 3038	
MnO, Cr_2O_3			$-H_2O$, $-H$	dual	Waida, T., and Yoshimoto, Y.	**41,** 3744	

Manganese Oxide

K_2O	5		$-H$	sel.	Guyer, W. R. F.	**42,** 5464	U. S. 2,440,471
Na_2O		Al_2O_3			Selwood, P. W., and Lyon, L.		*JACS*, **74,** 1051 (1952)
BaO			Ox.		Krauss, W.	**44,** 2711	
CaO, Al_2O_3, ThO_2	5		$-H$	str.	Guyer, W. R. F.	**42,** 5464	U. S. 2,440,471
CuO				dual	Takahashi, T., and Hikawa, F.	**43,** 5363	
Fe, Cd, Cu oxides			alc. syn.		Kyowa. Chem. Ent.	**44,** 1525	

Manganese Phosphate

$NaHPO_4$			Ox.		Field, E.	**44,** 10967	U. S. 2,519,751

Molybdena[8]

Promoter	Wt. (%)	Carrier	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
LiO	2	Al_2O_3	−H	sel.	Smith, A. E., and Beeck, O. A.	**43**, 6762	U. S. 2,474,440
BeO	5	Al_2O_3	−H	str.	Huffman, H. C.	**41**, 855	U. S. 2,411,829
BaO_2		Al_2O_3	−H		Edson, K. C., and Fisher, F. E.		U. S. 2,436,558
							U. S. 2,419,343
CaO + ZnO	4	Al_2O_3	−H	str.	Welty, A. B., Jr., and Holder, C. H.	**44**, 823	U. S. 2,447,043
CaO	4	CaO	−H		Smith, A. E., and Beeek, O. A.		U. S. 2,422,378
CaO, MgO	2	$ZnO-Al_2O_3$	−H	sel.[9]	Kearby, K. K.		U. S. 2,556,280
CaO, SrO	3	Al_2O_3	−H	str.	N. V. de B. P. M.	**43**, 4792	
						43, 5039	
$AlPO_4$	7	Al_2O_3	−H	str.	Stirton, R. I.		U. S. 2,441,297
							U. S. 2,440,236
SiO_2	4	Al_2O_3	−H	str.	Shiffler, W. H., and Claussen, W. H.		U. S. 2,485,073
SiO_2	5	Al_2O_3	−H	str.	Layng, E. T.	**44**, 2147	U. S. 2,487,564
SiO_2	5	Al_2O_3	−H	str.	Huffman, H. C.	**42**, 4340	U. S. 2,437,533
SiO_2	5		−H	str.	Griffith, R. H., and Lindars, P. R.	**44**, 7638	
TiO_2		Al_2O_3	−H	sel.	Layng, E. T.		U. S. 2,453,327
ZrO_2	5	Al_2O_3	−H	str.	Smith, J. O., Jr.	**41**, 6702	U. S. 2,424,636
Cr_2O_3	10	Al_2O_3	−H		Dague, A. B. C., and Myers, J. W.	**44**, 4668	U. S. 2,500,920
Cu, W, Ag, Au	3	Al_2O_3			Denton, W. I., and Plank, C. J.	**44**, 10728	U. S. 2,518,295
ZnO	10	Al_2O_3	−H	str.	Murphree, E. V.	**43**, 389	U. S. 2,451,041
ZnO	4	Al_2O_3	−H	str.	Roberts, R. M., Eggertsen, F. T., and Greensfelder, B. S.	**44**, 4168	U. S. 2,498,709
ZnO					Black, J. F.	**43**, 6818	U. S. 2,474,213
clay	15	Al_2O_3	−H	str.	Thomas, C. L., and Morrell, J. C.	**44**, 7027	U. S. 2,444,965

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[8] A fairly complete bibliography (to 1948) of molybdenum catalysts has been given by Killefer and Linz. "Molybdenum Compounds," Interscience Publishers, Inc., New York, 1952.

[9] Reduces carbon.

TABLE 5—*Continued*

Nickel and Its Oxides

Promoter	Wt. (%)	Carrier	Reaction Type or Product	Promotion Type	Author	Chem. Abstracts	Ref.
Alkali	0.1	kies.	H		Ueno, S.	**43**, 5210	
Alkali			H		Ungnade, H. E., and McLaren, A. D.	**38**, 957	*JACS*, **66**, 118 (1944)
Alkali			H		Grunfeld, M.	**43**, 682	U. S., 2,449,036
Alkali			H		duPont de Nemours & Co., Inc.	**42**, 3774	Brit. 596,006
KOH			−H	str.	Rutovskii, B. N.	**36**, 442	
Na_2S	10	kies.	H		Ohe, H.	**42**, 6735	
BeO			H	adl.	Herbo, C., and Hou, S.	**41**, 1537	
MgO			FT	sel.	Booth, N., Wilkins, E. T., Jolley, L. J., and Tebboth, J. A.	**43**, 2402	
MgO		pumice			Komatsu, S., and Kuraku, H.	**41**, 3267	
Al_2O_3	0.16				Chakrovarty, K. M., and Sarker, J. M.	**38**, 6178	
Al_2O_3		clay	FT		Strickland-Constable, R. F.	**43**, 7666	
Al_2O_3		kies.	FT		Perrin, M., and Michel, A.	**44**, 7638	
Al_2O_3	30		−H		Yamanaka, T.	**42**, 6628	
SiO_2			H	str.	Schuit, G. C. A.		*TFS*, 299 (1950)
SiO_2					van Voorthuijsen, J. J. B., *et al.*	**44**, 10473	
ThO_2			H	adl.	Herbo, C., and Hou, S.	**41**, 1537	
ThO_2			H Exc		Sadek, H., and Taylor, H. S.	**44**, 5199	*JACS*, **72**, 1168 (1950)
ThO_2		kies.	FT		Booth, N., Wilkins, E. T., Jolley, L. J., and Tebboth, J. A.	**43**, 2402	
ThO_2		kies	[10]	str.	Tebboth, J. A.	**42**, 5319	*JSCI* (*London*) **67**, 62 (1948)
HF	10	clay		dual	Voorhies, A., Jr., and Spicer, W. E.	**43**, 1162	U. S. 2,450,317
Cu			Isom.		Ipatieff, V. N., and Monroe, G. S.	**45**, 2662	U. S. 2,538,248
Cr_2O_3			H	adl.	Herbo, C., and Hou, S.	**41**, 1537	

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[10] $2CO \rightarrow CO_2 + C$.

Cr_2O_3			H Exc		Sadek, H., and Taylor, H. S.	**44**, 5199	*JACS*, **72**, 1168 (1950)
Fe	7		+ H_2O, −H		Standard Oil Development Co.	**44**, 11068	Brit. 641,945
Fe	10	kies.	H		Ohe, H.	**42**, 6735	
MnO_2		kies.	FT		Perrin, M., and Michel, A.	**44**, 7638	*TFS*, **4**, 193 (1948)
NiO				adl.	Rayet, J. R., and Lude, A.	**43**, 4933	
$PtCl_4$					Levering, D. R., Morritz, F. L., and Lieber, E.	**44**, 5199	*JACS*, **72**, 1190 (1950)
$PtCl_4$	0.1				Levering, D. R., and Lieber, E.	**43**, 6498	*JACS*, **71**, 1515 (1949)
$RhCl_3$			H		Sokol'skii, D. V., and Shmonina, V. P.	**45** 8337	
W			−H	str.	Tanida, S.	**42**, 330 **41**, 4368	

Phosphates

Promoter	Phosphate	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
KOH, NaOH	H_3PO_4	10	act. C	Isom	sel.	Korpi, K.	**39**, 609	U. S. 2,347,955
$CaPO_4$	Cu_2PO_4			Isom		Fawcett, E.	**42**, 7029	Brit. 601, 202
SiO_2	$FePO_4$	4.5	kies.	Poly	dual	Corson, B. B., and Brady, L. J.	**43**, 5419	Brit. 616,260
HCl	metal PO_4			Poly		Schmerling, L.	**43**, 5640	U. S. 2,470,190
Ag and Cu compd.	Cd & Zn		powdered glass or quartz	$+H_2O$	dual	Topsøe, H. F. A.	**44**, 8363	
CuO	$FePO_4$	0.65		Poly	dual	Corson, B. B., and Brady, L. J.	**43**, 5419	Brit. 616,202
Cu	H_3PO_4	1	act. C	$-H_2O$, $+H_2$		Dittrich, E.	**38**, 2349	
Cr_2O_3	$CaNiPO_4$			−H olefins		Britton, E. C., and Dietzler, A. J.	**43**, 2382	U. S. 2,456,367
$Cd_3(PO_4)_2$, $Cu_3(PO_4)_2$	H_3PO_4			Isom		Fawcett, E.	**42**, 7029	Brit. 601,202

Table 5—*Continued*

Platinum-Palladium

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
Bi	1	kies.	H		Kawamoto, O., and Furukawa, K.	**44**, 1524	
Halogen	4	Al_2O_3	−H	dual	Haensel, V.	**43**, 8578	U. S. 2,479,109
						43, 8664	U. S. 2,479,110
						46, 728	U. S. 2,566,521
Hg, Ag, Pb		kies.	H	sel.	Yamanaka, T.	**45**, 1857	
PtO			Ox	adl.	Roginskii, S., and Rozing, V. S.	**36**, 3092	
Rh	4				Panseri, C.	**44**, 1394	
Ru	2						
Ta	1.2						
Al_2O_3	10	SiO_2	Isom	dual	Fowle, M. J., Bent, R. D., Ciapetta, F. G., Pitts, P. M., and Leum, L. N.	**45**, 10557	*ACS*, **5**, 76 (1951)

Silica

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
Al_2O_3	1		alk		Schulze, W. A., and Stoops, C. E.	**44**, 8949	U. S. 2,514,419
TiO_2, ZrO	1		alk		Schulze, W. A., and Stoops, C. E.	**44**, 8949	U. S. 2,514,419
$CuCl_2$, Cu	0.2, 6			dual	Freidlin, L. Kh., Balandin, A. A., Lebedeva, A. I., and Fridman, G. A.	**42**, 2241	
$CuCl_2$			dehalo		Freidlin, L. Kh., and Fridman, G.	**44**, 4440	
Copper salts			dehalo	dual	Freidlin, L. Kh., Balandin, A. A., Lebedeva, A. I., and Fridman, G. A.	**40**, 5627	
ZrO_2-BeO			Cr		Bates, J. R.		U. S. 2,454,369

[*Silica-Alumina and Silica-Magnesia*]

Promoter	Wt. (%)	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
Alkali		$-H$, $-H_2O$	dual	Butterbaugh, D. J., and Spence, L. U.	**41**, 6272	U. S. 2,423,681
Alkali		$-H$, $-H_2O$	dual	Spence, L. U. Butterbaugh, D. J., and Kundiger, D. G.	**42**, 5463	U. S. 2,438,464
HF, BF_3		Cr		Plank, C. J.	**41**, 7730	U. S. 2,428,741
BaO	10,	Cr		Olsen, L. E.		
CaO	5	Cr		Marisic, M. M.	**44**, 5577	U. S. 2,456,072
CaO		Cr		Shexnailder, R. E., Jr.	**43**, 7162	U. S. 2,472,834
MgO	35	Cr	str.	Corner, E. S., and Kearby, K. K.	**45**, 1761	U. S. 2,529,283
BF_3	10	Cr	sel.	Paushkin, Ya. M., and Lipatov, Y. S.	**45**, 6371	
TiO_2		Cr	dual	Kimberlin, C. N., Jr., and Bilisoly, J. P.	**45**, 7346	U. S. 2,551,014
ThO_2		$-H$, $+Cr.$	dual	Dixon, J. K.	**41**, 6580	U. S. 2,422,165
ThO_2, ZrO_2		$-H$, $-H_2O$	dual	Spence, L. U., Butterbaugh, D. J., and Kundiger, D. G.	**42**, 5463	U. S. 2,438,464
Alk. hydroxide + MnO_2, CuO, MoO_2		$-H_2O$, $-H$	dual	Butterbaugh, D. J., and Spence, L. U.	**42**, 9102	U. S. 2,447,181
ZrO_2	4	Cr	str.	Thomas, C. L., and Lee, E. C.	**39**, 609	U. S. 2,347,648
ZrO_2		Cr	str.	Lee, E. C., and Thomas, C. L.	**40**, 7600	U. S. 2,406,613
ZrO_2		Cr	str.	Clark, I. T., and Harris, E. E.		*JACS*, **74**, 1031 (1952)
ZrO_2		Cr	str.	Thomas, C. L., and Lee, E. C.	**42**, 4724	U. S. 2,439,994
ZrO_2 + kies.		Cr	diff.	Ahlberg, J. E., and Thomas, C. L.	**41**, 7727	U. S. 2,428,257
BiO	0.5	Cr		Connolly, G. C.	**37**, 2559	U. S. 2,302,297
H_3PO_4		Cr		Plank, C. J.	**41**, 7730	U. S. 2,428,741
$(NH_4)_3PO_4$	2.5	Cr		Ehrhardt, C. H.	**44**, 7056	U. S. 2,507,625
HF	10	Cr	sel.	Pelzer, H. L.	**46**, 247	U. S. 2,507,220
HF + H_3PO_4		Cr		Plank, C. J.	**41**, 7730	U. S. 2,428,741
Cr_2O_3			str.	Natta, G., and Rigamonti, R.	**42**, 5839	
Pb. Cu			de S	Nachod, F. C.		U. S. 2,422,982

TABLE 5—*Continued*

[*Silica-Alumina and Silica Magnesia*]

MnO_2, ZnO, Fe_2O_3		Cr	dual	Kimberlin, C. N., Jr., and Bilisoly, J. P.	**45**, 7346	U. S. 2,551,014
Cu, Co, Ni, Cr_2O_3			Ox.	Kassel, L. S.		U. S. 2,436,927
Fe_2O_3	2.0	Cr		Marisic, M. M., *et al.*		U. S. 2,461,069
Ni	1.5	Poly	dual	Quigg, H. T.	**42**, 4338	U. S. 2,439,021
Lamp black	10	Cr	diff.	Marisic, M. M., and Schmitt, A. C.	**41**, 578	
MoO_3, V_2O_5, Fe, Co, Ni	4	Poly	dual	Clark, A.		ACS Meet., Sept., 1952

Silver and Its Oxides

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
BaO_2	10	Ag	Ox		Nevison, J. A., and Lincoln, R. M.	**44**, 2550	U. S. 2,491,057
Ca oxalate		Ag	Ox		McKim, F. L. W., and Cambron, A.	**44**, 2836	
$CaCO_3$	5	Ag	Ox		H.A.C. for S & I R	**42**, 1034	Brit. 591,670
SnO		Ag	Ox		McKim, F. L. W., and Cambron, A.	**44**, 2836	
Cr_2O_3		Ag	Ox	adl.	Schenck, R., Bathe, A., Keuth, K., and Suss, S.	**37**, 3659	
Rh_2O_3, V_2O_3		Ag	Ox	adl.	Schenck, R., Bathe, A., Keuth, K., and Suss, S.	**37**, 3659	
SnO, CdO	5	Ag	Ox		H.A.C. for S & I R	**42**, 1034	Brit. 591,670

Vanadia

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
K		SiO_2	Ox		Martinuzzi, E. A.	**42**, 8058	
K, Rb	18		Ox		Topsøe, H., and Nielsen, A.	**42**, 7946	
KOH		kies.	Ox		Hirai, T.	**42**, 6496	
KCl	4	SiO_2	Ox		Shogam, S. M.	**40**, 4860	
Alkalies		MgO	–H	sel.	Stanley, M., Salt, F. E., and Weir, T.	**41**, 2080	Brit. 580,088
BaO	3	SiO_2	Ox		Shogam, S. M.	**40**, 4860	
Ca		SiO_2	Ox		Martinuzzi, E. A.	**42**, 8058	
TiO_2				str.	Pongratz, A.	**43**, 7803	
H_3PO_4	2	MgO	Ox[12]	sel.	Margolis, L. Ya.	**45**, 2758	
$P_2O_5 + MoO_3$	0.05, 5		Nit		Erchak, M., Jr.	**44**, 3024	U. S. 2,486,934
$P_2O_5 + MoO_3$	0.034, 3.9		Nit		Cosby, J. N., and Erchak, M., Jr.	**44**, 6885	U. S. 2,499,055
HF	2	MgO	Ox	sel.	Margolis, L. Ya.	**45**, 2758	
Fe		SiO_2			Martinuzzi, E. A.	**42**, 8058	
Tl	18		Ox		Topsøe, H., and Nielson, A.	**42**, 7946	

Tungsten Sulfide

S			–H		Standard Oil Development Co.	**42**, 6850	Brit. 599,252

Urania

Ti, Ce, Th, Zn oxides	1		FT		Mills, G. A.	**44**, 4246	U. S. 2,453,152

Zinc Chloride

Promoter	Wt. (%)	Carrier	Reaction Type	Promotion Type	Author	Chem. Abstracts	Ref.
$AlCl_3$			Isom		Hokkaido Art. Pet. Co.	**43**, 2216	
HCl			Isom		Chel'tsova, M. A., and Petrov, A. D.	**39**, 1129	
Cd, Co chlorides			Isom		Hokkaido Art. Pet. Co.	**43**, 2216	

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[12] Complete.

TABLE 5—*Continued*

Zinc Oxide

Alkali			CH_3OH	sel.	Tomita, A.	**41,** 3353	
$NaO + MgO$			Poly.	dual	Standard Oil Development Co.	**42,** 2983	Brit. 587,475
Be_2O_3	3		$-H$		Schneider, H. G., and Mistretta, V.	**43,** 6650	U. S. 2,472,493
V_2O_5				dual	Broun, A. S., and Kuratova, O. S.	**38,** 2314	
Cu	5	Al_2O_3	$-H$		Ipatieff, V. N., and Haensel, V.	**40,** 600	U. S. 2,386,957
			Zirconia, Thoria				
Na_2O	4		$-H_2O$, $-H$	sel.	Spence, L. U., Butterbaugh, D. J., and Kundiger, D. G.	**42,** 5628	U. S. 2,436,125
CeO_2	1		FT		Rienacker, G.	**44,** 1314	
					Rienacker, G., Birckenstaedt, M., and Burmann, R.	**44,** 10473	

AC—Analytical Chemistry
ACS—Advances in Chemistry Series
CEP—Chemical Engineering Progress
CS (*India*)—Current Science (India)
IEC—Industrial and Engineering Chemistry
JACS—Journal of the American Chemical Society
JCP—Journal of Chemical Physics
JCS—Journal of the Chemical Society (London)
JPCC—Journal of Physical & Colloid Chemistry
JSCI—Journal of the Society of Chemical Industries (London)
OGJ—Oil and Gas Journal
TFS—Transactions of the Faraday Society

hydrogen. For lack of a better name, and to distinquish them from promoters added during catalyst preparation, they are termed *accelerators*. The different types are listed below. Some of the recent work on accelerators is tabulated in Table 6.

Diluents. Inert gases such as nitrogen, methane, water vapor, etc., may be added simply to dilute the reactants to:

(1) Reduce the partial pressure of the reactants and thus favor the thermodynamic equilibrium. An example of this is the dehydrogenation of butene to butadiene[116].

(2) Give better temperature control. They are often used in very exothermic or endothermic reactions to supply or carry away the heat of reaction[117]. Because of better temperature control, better yields of products and longer catalyst life are usually obtained.

Decoking Agents. Water vapor and hydrogen are sometimes added to reduce coke formation. For example, in the synthesis of butadiene from butene over iron catalyst it is possible to operate continuously without regeneration by adding steam to the inlet gases[116]. Hydrogen is recycled and mixed with the inlet naphtha in the dehydrogenation of naphthenes to aromatics in order to reduce coke formation (Hydroforming process).[118] The mechanism of coke reduction may or may not involve direct reaction of the incipient coke with the decoking agent.

Activity Accelerators. In some cases the presence of the accelerator may act as an auxilliary to the catalyst and thereby accelerate the reaction. Although this appears to be unusual[119], few investigations of gaseous additives other than very common gases have been carried out.

Selectivity Accelerators. An accelerator may also act to improve selectivity for the desired reaction. It may accomplish this by poisoning an undesired side or secondary reaction. Rideal and Taylor[120] quote the example of the use of steam in the dehydrogenation of methanol to formaldehyde for repressing secondary decomposition of formaldehyde to carbon monoxide and hydrogen.

Other Functions. One case is given[121] in which an accelerator (methanol) is used to prevent poisoning of a nickel catalyst in the hydrogenation of halogenated hydrocarbons.

In cases in which the active catalyst component is volatile and is slowly lost in usage (such, for example, as aluminum chloride) the loss may be replaced by adding small amounts of this catalyst compound to the gas stream[122].

Poisons

The term poison as used herein refers to an impurity present in the gas stream that has an adverse effect on catalyst performance. This does not

TABLE 6. RECENT LITERATURE ON ACCELERATORS

Reaction	Catalyst	Accelerator	Type	Author	Chem. Abstracts	Ref.
$C_2H_2 + HCN \rightarrow CH_2{=}CHCN$	Na_2CO_3-C	$H_2 + H_2O$	diluent	du Pont	**44**, 3006 **41**, 2072	Brit. 628,023 Brit. 581,035
Mesityl oxide → ketone + isobutylene	SiO_2-Al_2O_3	H_2O		Kagan, M. Ya., and Savachenko, R. I.	**44**, 2914	
$C_6H_5Cl + H_2 \rightarrow C_6H_6 + HCl$	Ni	MeOH	prevents poisoning	Ipatieff, V. N., and Schmerling, L.	**42**, 582	U. S. 2,427,791
n to isoalkenes	$Cu_3(PO_4)_2$	H_2O		Fawcett, E. W. M.	**42**, 7029	Brit. 601,202
Fischer-Tropsch	Fe	H_2O	decoking	Voorhies, A., Jr.	**43**, 9420	U. S. 2,479,439
Allyl alc. + NH_3 → picoline	Cu	N_2		Hoog, H., and Engel, W.	**43**, 5426	
Aldehyde oximes → unsat. nitrile	Cr_2O_3	H_2O, N_2	diluent	Dutcher, H. A.	**40**, 7231	U. S. 2,404,280
Oxo reaction	Co	Co comp.	replacement	N.V. de B.P.M.	**44**, 1526	
NH_3 + olefins → nitriles	Co	H_2O	selectivity	Teter, J. W.	**41**, 5144	U. S. 2,417,892
$C_2H_2 + CO \rightarrow AcH$ + acetone	V_2O_5	H_2O		Schwarz, R. and Bessel, G.	**40**, 4660	
Butadiene dimer → styrene	V_2O_5, Cr_2O_3, MoO_3	H_2		Voorhees, V.	**39**, 3553	U. S. 2,376,985
$2RNH_2 \rightarrow R_2NH + NH_3$	Al_2O_3	NH_3	selectivity	N.V. de B.P.M.	**44**, 7343	
$HCN + C_2H_2 \rightarrow CH_2{=}CHCN$	NaCN	H_2		Harris, C. R., and Sharples, W. C.	**41**, 2072	
$HCN + C_2H_2 \rightarrow CH_2{=}CHCN$	NaCN	H_2, H_2O		Green, H. D., and Taylor, D. S.	**41**, 1697	U. S. 2,413,496
Gas oil cracking	clay	H_2O	selectivity	Conn, A. L., and Bracken, C. W.	**43**, 8565	*IEC*, **41**, 1717 (1949)
Olefins → dimers	Ni-SiO_2-Al_2O_3	H_2	decoking	Moore, F. J., and Stewart, M. M.	**44**, 7340	U. S. 2,507,864
Olefins → liq. polymers	MoO_3-H_3PO_4	H_2	selectivity	Stewart, M. M., and Moore, E.	**42**, 7520	U. S. 2,446,619
Propylene → low m.w. polymers	Cu pyrophosphate	isobutene		Hughes, E. C., and Stine, H. M.	**44**, 3700	U. S. 2,494,510
$C_2H_4 + C_3H_6$ → pentene + heptene	alk. metals	polynuclear aromatics		Freed, Wm. V.	**44**, 4921	U. S. 2,492,693

O_2 + alcohol or ald. → carboxylic acid	Cu	H_2O	diluent	Lel'chuk, S. L., and Belen'kaya, A. P.	**41,** 2071	
O_2 + *o*-xylene → phthalic anhydride	V_2O_5	H_2O	diluent	Welty, A. B.	**44,** 2022	U. S. 2,485,342
$CH_3OH \rightarrow HCHO + H_2$	Ag, Pt	O_2 and H_2		Natta, G., and Baccaredda, M.	**44,** 2011	
$C_2H_4 \rightarrow C_2H_2 + H_2$	Ni	H_2O	decoking	Ohe, H.	**42,** 6735	
$H_2 + CO \rightarrow CH_4 + H_2O$	Ni	H_2O	decoking	Booth, N., *et al.*	**43,** 2402	
Butene → butadiene	$CaNiPO_4$	H_2O	decoking	Britton, E. C., and Dietzler, A. J.	**43,** 2382	U. S. 2,456,369
$C_4H_{10} \rightarrow C_4H_8 + H_2$	Mo	H_2O	decoking	Dague, A. B. C., and Myers, J. W.	**44,** 4668	U. S. 2,500,920
Butene → butadiene + H_2	Fe	H_2O	decoking	Kearby, K. K	**44,** 3874	*IEC*, **42,** 295 (1950)
$PhCHMe_2 \rightarrow PhCMe{=}CH_2$	Fe	H_2O	decoking	Morrell, C. E., and Slotterbeck, O. C.	**43,** 680	U. S. 2,449,004
$PhCHMe_2 \rightarrow PhCMe{=}CH_2$	Fe	H_2O	decoking	Kearby, K. K.	**42,** 198	U. S. 2,926,829
Diaryl paraffin → diaryl ethylenic comp.	Cu	H_2O	decoking	Dixon, J. K., and May, D. R.	**43,** 2235	U. S. 2,400,334
p-Cymene → H_2 + dimethyl styrene	Cr_2O_3	CO_2		Kobe, K. A., and Romans, R. T		*IEC*, **43,** 1755 (1951)
Aliphatics → aromatics + H_2	C	H_2	decoking	N.V. de B.P.M.	**43,** 3453	
Ethylene cyanohydrin → acrylonitrile	bentonite	$N_2 + CO_2$		*Jap. I.S.O.C.R.**	**44,** 3006	
Ethyl benzene → styrene + H_2	V_2O_5	H_2O		Stanley, H. M., Salt, F. E., and Weir, T.	**41,** 2080	Brit. 580,088
Diphenyl ethane → styrene + H_2	bentonite	H_2O	decoking	Morton, M., and Nicholls, R. V. V.	**43,** 1251	
$H_2 + C_2H_2 \rightarrow C_2H_4$	Cr-Ni-Fe	H_2S	selectivity	Welling, C. E., and Hepp, H. J.	**39,** 4444	U. S. 2,379,670
Bicyclohexyl → $Ph_2 + H_2$	Ni	1% thiophene		Adkins, H., Rae, D. S., Davis, J. W., Hager, G. F. and Hoyle, K.	**42,** 2247	*JACS*, **70,** 381 (1948)
$H_2O + C_2H_2 \rightarrow CH_3CHO$	phosphates	H_3PO_4	replacement	Mollerstedt, B. O. P.	**44,** 1528	
Ethyl alc. → butadiene + H_2O	SiO_2-MgO	C_2H_4		Rigamonti, R., and Russo, F.	**42,** 3309	
$CH_2{=}CHC{-}NH \rightarrow CH_2{=}CHCN + H_2O$	MnO_2	H_2O		Kung, F. E.	**39,** 4085	U. S. 2,375,005

* Institute Synthetic Organic Chemical Research, Japan.

include reactants, agents added during catalyst manufacture (inhibitors), or products of the reaction such as coke or wax. Almost every catalytic reaction is adversely affected by poisons of some sort and their effects are of greater economic importance than is generally realized. Reviews on the subject include those of Berkman, Morrell and Egloff[123], Griffith[124], Maxted[126] and others[127]. Poisons can best be classified on the basis of their mechanism of action though seldom is this well understood.

Chemisorbed Poisons. Probably the most important type of poisoning involves *adsorption of the poison on the surface.* This can decrease catalyst activity by: (1) converting the active sites into an inactive surface compound; (2) adversely affecting the number of free electrons, unpaired electrons or "holes" from the standpoint of the catalytic reaction. The two mechanisms perhaps do not differ fundamentally except that advocates of mechanism one assume either that the active surface is substantially uniform and that activity decline is proportional to the fraction converted to inactive surface compound or that certain favored spots responsible for the activity are preferentially covered by the poisons. The second mechanism considers the activity to be related to the over-all "electronic state" of the surface which can be affected to a high degree by chemisorption of poisons in quantities much less than required for complete surface coverage.

The first mechanism has been stressed by Roginskii[125, 128, 129, 130] and Maxted[126] and the second by Vol'kenshtein[131] and Pacault[132] and Taylor[133, 134].

This type of poisoning is characterized by a rapid activity decline until an adsorption equilibrium is reached and a steady state activity is realized. If the chemisorbed poison is tightly held and the steady state activity is very low, the poisoning may be termed permanent since on eliminating the poison source the activity is restored very slowly. If the poison is held loosely or is removed rapidly by the pure reactants so that the activity is rapidly regained, it has customarily been termed a temporary poison.

Selectivity Poisons. A second class of poisons includes those which influence selectivity. Selectivity usually becomes progressively poorer with time. By far the most important industrial example is heavy metal compounds (Ni, V, Cu, Fe) present in gas oils used for catalytic cracking[135, 136]. These deposit on the catalyst and because of their dehydrogenation activity bring about decreased gasoline and increased hydrogen, light gas and coke formation. So serious is this poisoning that a catalyst is often discarded on the basis of its heavy metal content rather than its activity level.

Stability Poisons. A third type of poisoning is the one in which the poison decreases the structural stability of the catalyst. The best example of this is steam poisoning of silica or alumina gel base catalysts[135, 137, 138, 139]. The major part of the deactivation of silica-alumina cracking catalysts has been attributed to this cause. Poisoning of this type is characterized by gradual activity and surface area decline.

The structural poisoning effect of steam appears to be related to the catalyst pore diameter. Catalysts of low pore diameter appear[140, 141] more subject to this type of poisoning than those of high pore diameter probably because material transfer necessary for fusion of particles or sintering is more difficult if pore walls are far apart.

Diffusion Poisons. A fourth type of poisoning involves diffusion blocking. This can occur if the pores become blocked so that the reactants are prevented from reaching the internal surface. The poison may deposit in the pores near the external surface or on the external surface forming a surface scale. This type of poisoning is encountered primarily with granular or pelleted catalysts which have relatively small external area. Organometallic compounds which decompose on contact with the catalyst leaving a residue can be cited as a possible example. Entrained solids may also act as diffusion type poisons[142]. Electrostatic precipitation or filtration can be used to remove this type of poison. Sulfur oxides may react with the alkali present in some catalysts to form an alkali sulfate scale which may block diffusion (unpublished data).

Influence of Process Variables on Poisoning

Poison Concentration. Of first consideration is the inlet gas stream poison concentration and its affect on steady state activity. Roginskii[125, 128, 129, 130] divides adsorbed poisons into three groups in which either:

(1) Equal adsorption occurs on sites of differing activity. This leads to a linear active decline with increased poison concentration.

(2) The poison is preferentially adsorbed on the more active sites. This results in a lowered rate of activity decline with increased poison concentration.

(3) Preferential adsorption occurs on inactive sites. This gives an increased rate of activity decline at high poison concentrations.

Most recent literature appears to indicate that a linear relation is usually obtained at low poison concentrations. For example, Maxted, Moon and Overgage[143] use the relation $k_c = k_0(1 - \alpha C)$ to express the effect of poison concentration in which k_0 is the original activity, k_c is the steady state activity in the presence of concentration C of the poison, and α is the poisoning coefficient. Herrington and Rideal[144] point out that it is unnecessary to introduce the concept of active centers to explain their linear results on the poisoning of Ni, Co, Pt and Pd. If poisoning is linear with poison concentration and also with the amount of chemisorbed poison, it follows that chemisorption is also linear with poison concentration.

The effect of poison concentration on other types of poisoning has received little attention in recent literature. One exception is the structural poison, steam, in gas oil cracking over silica-alumina catalyst. The data [135, 137, 138, 139] are rather scattered since no one investigator has attempted to cover a wide range of steam partial pressures. Combining the data gives the plot of Figure 9.

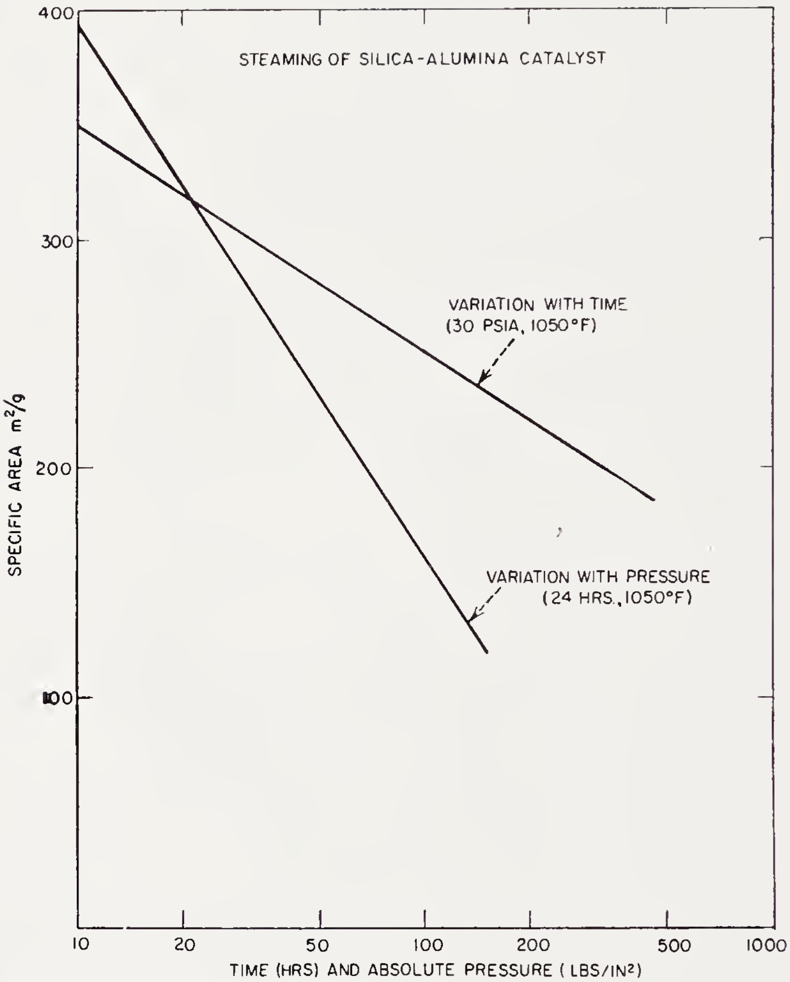

Figure 9. Change in surface area of a silica-alumina cracking catalyst with time and pressure of steaming at 1050°F.

The Effect of Surface Area and Pore Structure. In the absence of a poison, and assuming that the surface reaction is rate controlling, the activity of a catalyst is normally proportional to its surface area. Maxted, Moon and Overgage[143] demonstrated in the case of methyl sulfide poisoning of platinum catalysts that the poisoning coefficient, α, defined above is also a function of surface area so that αS is a constant where S is the specific surface. The net activity of a poisoned catalyst can then be related to the specific surface by the following relation.

$$k_c = k_0' S \left(1 - \frac{k}{S} C\right)$$

where k_0' = activity per unit surface area in the absence of poison,
S = specific surface area,
k = αS = poisoning coefficient for unit surface area,
c = poison concentration,
and k_c = specific activity of poisoned catalyst.

According to this relation, catalyst activity in the presence of adsorbed poisons increases more than proportionally with surface area.

The effect of surface area on other types of poisoning has received little attention in recent literature. However, it is clear that pore structure has a large bearing on diffusive poisoning. Catalysts having pores that can be readily plugged by the poison are more susceptible. That is, for example, catalyst having smaller pores than the poison material (e.g., dust) would not be expected to be as readily poisoned as a catalyst with larger pores which the poison can penetrate and plug up. Partial blocking of pore entrances may very markedly decrease catalyst activity[145].

The Effect of Temperature. Little new work has appeared on the effect of temperature on poisoning. According to older literature, as reviewed by Berkman, Morrell and Egloff[123], chemisorption poisoning generally decreases with increased temperature. This would, of course, be expected because adsorption also generally decreases with increased temperature. Reactions that are not feasible at low temperatures because of poisoning are sometimes possible at higher temperatures. Activation energies may be higher than values obtained in the absence of a poison.

Diffusion poisoning would be expected to be affected by temperature to a relatively small extent since diffusion varies only as $\sqrt{T}$. However, poison entrainment, decomposition and fusion on the external surface, etc., might be markedly affected by temperature so that this type of poisoning would likewise be affected.

The effect of temperature on selectivity poisoning depends on the case in question so that it is hard to generalize. Little information on the subject is available.

Stability poisoning increases markedly with increasing temperature[146] since the loss in surfaces is akin to melting.

The Effect of Pressure. No generalizations as to the effect of pressure can be made since there is very little information on the subject. However, what has been said about poison concentration probably also applies to the effect of pressure since the poison partial pressure is proportional to the total pressure. Data are available on the effect of steam pressure on the "structural poisoning" of silica-alumina cracking catalyst[135, 136, 137, 138]. Some of these data are given in Figure 9.

Common Poisons

Knowledge of poisons affecting various catalysts is sometimes of considerable help. Berkman, Morrell and Egloff go into this quite thoroughly so it is only necessary to condense and bring their listings up to date (Table 7).

TABLE 7. POISONS FOR VARIOUS CATALYSTS

Catalyst Component	Reaction	Poison Class	Poisons
Silica-alumina	cracking	ads. str. sel.	quinoline, other organic bases water heavy metal compounds
Nickel, platinum and palladium	H, −H Ox	ads.	compounds of S, Se, Te; P, As, Sb, Bi, Zn; halides, CO (<180°C), Hg, Pb, NH_3, pyridine, 1 ethyl cyclopentane, O_2 C_2H_2, H_2S, PH_3, iron oxide and silver dust, As compounds
Copper	H, −H	ads.	same as for nickel but poisoning not as severe
Cobalt	hydrocracking	ads.	NH_3, S, Se, Te, P compounds
Silver	$C_2H_4 + O \rightarrow C_2H_4O$	sel.	CH_4, C_2H_6
Vanadium oxide	Ox	ads.	As compounds
Iron	NH_3 syn.	ads.	O_2, H_2O, CO, S compounds, C_2H_2, PH_3
	H, −H	ads.	Bi, Se, Te, P compounds, H_2O
	Ox	ads.	VSO_4, Bi
	FT	ads.	S compounds
Platinum and palladium	H, −H	ads.	CO, S compounds, AsH_3, PH_3 and SbH_3, Pb and Hg salts, 1 ethyl cyclopentane

Catalyst Revivification

Poisoning problems may be solved by operating at conditions that minimize poisoning (high temperatures, etc.), by conversion of poison to a nontoxic material, by removal of the poison from the gas stream and by periodic catalyst revivification. The poison removal approach is outside the scope of this work.

Revivification of a catalyst poisoned by an adsorptive mechanism can usually be accomplished by bringing about the desorption or decomposition of the poison. Steaming is commonly used for such stripping operations. Often passage of air to effect combustion or oxidation and reduction[147] is employed to remove both poisons and tarry reaction products[148]. Treatment of the catalyst with acid or alkali solutions is sometimes used to remove poisons attacked by these reagents. Hydrogenation is often effective in removing poisons as well as tarry matter. Maxted[149, 150] has made use of peroxide and sodium molybdate solutions to restore the activity of sulfur poisoned catalysts. West[151] has reactivated Ag catalyst used for olefin oxidation by treating first with a stream of gas containing a halogen compound followed by a stream of gas containing $NH_3 + H_2O$ at 170 to 325°C.

Catalysts that have lost activity because of structural poisons cannot, as a rule, be easily restored to their former structure.

Catalysts which are poisoned by a diffusive mechanism can usually be completely rejuvenated by tumbling or other mechanical treatment to remove the outer blocked pores. If the poison is soluble in a liquid which does not injure the catalyst, it can be removed by leaching.

The revivification of selectivity poisoned catalysts depends on the individual case. In the important example of heavy metal poisoning of cracking catalysts, the heavy metals can be partly removed by acid treatment without much catalyst decomposition, but not completely enough to justify the cost (unpublished data).

Recent Literature on Poisoning

The importance of this aspect of catalysis would seem to warrant more work than that which is summarized in Table 8.

INHIBITORS

The term inhibitor as used herein is defined as a substance which when added during catalyst preparation in small amount results in poorer catalyst activity, stability or selectivity than is realized without it. Or to put it briefly, it is the opposite of a promoter.

Although, without doubt, much work has been done on the subject, little of this has appeared in print (antioxidants or antidetonating agents excepted). The lack of interest can, of course, be attributed to their negative effects and for the same reason the material that has appeared on the subject in recent years has only been surveyed to a limited extent.

The early literature is covered by Berkman, Morrell and Egloff[123]. Recent work is summarized in Table 9. For other work pertaining to the

Table 8. Summary of Recent Literature on Poisons*

Reaction	Catalyst	Poison	Type	Author	Chem. Abstracts	Ref.
Dehydrogenation	Ni, Co, Cu, Fe	S, Se, Te, P	ads.	Maxted, E. B.	**45**, 2608	Brit. 644,239
Dehydrogenation	Pd	Me_2S	ads.	Dilke, M. H., Eley, D. D., and Maxted, E. B.	**42**, 6184	*JCS*, 1916 (1948)
Dehydrogenation	Pt	S compounds		Maxted, E. B., and Walker, A. G.	**43**, 3407	
$C_2H_4 + H_2 \rightarrow C_2H_6$	Ni	H_2O	ads.	Burford, W. B., III, and Frazer, J. C. W.	**39**, 1350	*JACS*, **67**, 331 (1945)
Cyclization of paraffins	Cr_2O_3-Al_2O_3	nonaromatizable paraffins		Archibald, R. C., and Greensfelder, B. S.	**39**, 2629	*IEC*, **37**, 356 (1945)
Aromatization	Cr_2O_3-Al_2O_3	H_2O		Corson, B. B., and Webb, G. A.	**44**, 3247	U. S. 2,495,700
Gasoline reforming	Pt, Pd	S compounds	ads.	Haensel, V., and Gerald, C.	**45**, 10567	U. S. 2,478,916
$HCOOH \rightarrow CO_2 + H_2$	Pd	S compounds	ads.	Hernandez, L., and Nord, E.	**43**, 27	*JPCC*, 363 (1948)
Cyclohexane → benzene + H_2	5% Pt	1 ethyl cyclopentane		Shuikin, N. L., Novikov, S. S., and Tulupova, E. D.,	**42**, 4437	
Hydrocracking of solid paraffins	Co	NH_3	ads.	Koch, H., and Titzenthaler, E.	**44**, 9335	
Gas oil cracking	SiO_2-Al_2O_3	H_2O	str.	Makarov, S. K., and Kaliko, M.	**41**, 6697	
Fischer-Tropsch	Fe	S		Johnson, E. A.	**43**, 1551	U. S. 2,455,419
Fischer-Tropsch	Fe	S		Pichler, H.	**43**, 7664	
Fischer-Tropsch	Co	S, wax	ads.	Hart, M., Hoog, H., and Weeda, K.	**45**, 2607	U. S. 2,529,236
Oxo	Co	S	ads.	Hart, M., Hoog, H., and Weeda, K.	**45**, 2607	U. S. 2,529,236
Alcohol synthesis	many	S	temp.	Pichler, H., and Ziesecke, K. H.,	**44**, 7040	
$CO + H_2O \rightarrow CO_2 + H_2$	Fe_3O_4	dust	diff.	Bridger, G. L., Gernes, D. C., and Thompson, H. L.	**42**, 4723	*CEP*, **44**, 363 (1948)
$CH_4 + NH_3 + \frac{1}{2}O_2 \rightarrow HCN+$	Pt	C_3+ hydrocarbons		Merrill, D. R., and Perry, W.	**43**, 9396	U. S. 2,478,875
$CO + \frac{1}{2}O_2 \rightarrow CO_2$	MnO_2	H_2O	ads.	Dolique, R., and Galindo, J.	**38**, 2555	
$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$	Ag	CH_4, C_2H_6, $C_2H_4Cl_2$	sel. ads.	McKim, F. L. W., and Cambron, A.	**44**, 2836	
$3H_2 + N_2 \rightarrow 2NH_3$	Fe	S and O compounds Cu, Cl_2, P	ads.	Farrar, G. L.		*OGJ*, **51**, 82 (1952)

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* The following abbreviations are used: ads. = adsorptive poisoning, str. = structural poisoning, diff. = diffusive poisoning, sel. = selective poisoning.

TABLE 9. INHIBITORS

Reaction	Active Catalyst	Inhibitor	Probable Mechanism	Author	Chem. Abstracts	Ref.
Gas oil cracking	silica-alumina	sodium	neut. acid groups	Baker, M. O., Chesnutt, S. D., and Wier, T. P., Jr.	**43,** 2414	*JPCC*, **52,** 1364 (1948)
Fischer-Tropsch	Fe, Cu, Mn	boric acid		Kodama, S., *et. al.*	**43,** 2397	
Fischer-Tropsch	Fe	chlorides		Kodama, S., Tahara, H., Hongo, M., and Fujita, H.	**44,** 9135	
				Storch, H., Golumbic, N., and Anderson, R. B.*		
Fatty acid est. → unsat. higher alc. + H_2	iron oxides	Co, Cu, Ni		Komori, S.	**43,** 5363	
Naphthalene oxidation to phthalic anhydride	V_2O_5	iron oxide	causes complete oxidation	Tomeo, M., and Serrallonga, J.	**42,** 7274	
Gas oil cracking	silica-alumina	sodium	neut. acid groups	Ballod, A. P., Patsevich, I. V., Fel'dman, A. S., and Frost, A. V.	**45,** 7861	
	alumina	fluorides	increases sintering	Thibon, H., Charrier, J., and Tertian, R.	**45,** 10023	
Naphthenes → aromatics + H_2	Cr_2O_3-Al_2O_3	iron	cat. gas formation	Carrozzi, R. C.	**43,** 8661	
Olefin + NH_3 → nitrile	Co	sodium chlorides, sulfates		Teter, J. W.	**43,** 7498	U. S. 2,468,522

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* Storch, H., Golumbic, N. and Anderson, R. B., "The Fischer-Tropsch and Related Syntheses," New York, John Wiley & Sons, Inc., 1951.

subject the reader is referred to the sections on poisons and promoters. Poisons could be considered as inhibitors if added during catalyst manufacture.

Like promoters, inhibitors can act in many ways and can be similarly classified. The examples in Table 9 illustrate a few of these.

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CHAPTER 7

CATALYST PREPARATION

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The art of catalysis includes a very extensive "know how" of the procedures and experimental techniques employed in the preparation of solid catalysts. Chemical composition alone is not a sufficient guide in predicting the activity of catalysts. In many cases, the physical characteristics of the catalyst, such as the surface area, particle size, pore size and crystal structure, determine its activity and selectivity for a specific reaction.

The chemical and physical properties of a catalyst are determined by the total history of its preparation. To obtain active catalysts it is important to use established procedures and experimental techniques. Some of the guiding principles and techniques used in the laboratory preparation of solid catalysts are discussed in the first part of this chapter. Selected procedures, reported in the literature, for the preparation of some of the more important catalysts are reviewed in the second part. In the last part, standard laboratory procedures for the preparation of a number of useful active catalysts are given in detail. These procedures will illustrate some of the techniques discussed below, and provide working examples for the neophyte.

General Techniques of Catalyst Preparation

This discussion aims primarily to set forth the elementary principles of catalyst preparation in a manner most useful to experimenters having little specialized equipment. The generalized descriptions of laboratory techniques and the specific examples of catalyst preparations are slanted in that direction. In describing the preparative methods used in catalyst compositing, one assumption is made, namely, that the composition desired to catalyze a specific reaction is known. The remaining problem is then to decide on the specific means by which the compounding may best be carried out.

A great many catalysts can be prepared in a variety of ways, while a smaller number can be prepared in only a very highly specialized manner.

In the former case, the actual choice of methods may be guided by ease of preparation, homogeneity of the product, stability of the catalyst, and ease of duplication. For example, while impregnation of a granular support would seem to be the simplest possible way to prepare a catalyst, complications are quite apparent. First of all, the support must either be inert to the added component(s) or else interact to give only the desired properties. Second, the support must be a material of known constitution and properties. Finally, the specific condition necessary to give the desired concentration of the catalytic agent on the support must be determined experimentally.

The various methods of catalyst preparations may generally be considered as combinations of certain unit operations. The unit operations most frequently involved will be discussed in the following pages.

Methods of Preparation

Precipitation and Gel Formation. These two methods are treated together because they are very closely related chemically. However, the physical characters of the products are usually widely divergent. The phenomenon of gelation is a special aspect of precipitation which depends upon the lyophilic properties of the precipitate and the rate of precipitation. A great many hydrous oxides are of interest either as catalysts or catalyst supports, and many of them are amenable to gel formation.

It has often been stressed that the specific details of the preparation of a given catalyst composite are of the utmost importance. Said details may give rise to all-important properties of specificity and stability. However, in spite of the physical differences which show up in catalysts of a given composition when cogelled or coprecipitated, it has frequently been found that the catalytic properties of such products are quite similar. Nevertheless, even when preparing compositions for which the latter condition holds, there are certain practical advantages to using cogelation techniques. Some of these will be pointed out in the detailed discussions of the compositing methods.

Precipitation. This method is frequently employed in the preparation of single- and multiple-component catalysts. Precipitation techniques are applicable to materials such as the hydrous oxides, sulfides, carbonates, and phosphates. In general, one starts with aqueous solutions of the desired constituents and adds the required precipitating agent. On a commercial scale, use of aqueous solutions would probably be an economic necessity. However, for bench scale work nonaqueous solutions may be used when advantageous.

One of the primary problems arising in the preparation of a precipitated catalyst is that of purification from occluded or adsorbed impurities. One way in which to minimize the presence of such impurities is to carry out the precipitation by mixing very dilute solutions (e.g., Kohlschütter Cr_2O_3 gel[121]). Another method of minimizing the problem is to use ammonia or ammonium salts as the precipitants along with nitrates of the desired metals. The resulting precipitate then requires a minimum of washing, since any adsorbed material remaining can be removed by calcination of the product.

The use of nitrates as the source of the desired cations is recommended as a general rule unless otherwise specified. The reason for this is the fact that other anions (e.g., chloride or sulfate) sometimes act as catalyst poisons, if they are present in the final product. For example, such an effect has been described by Hofer, Peebles and Dieter[102] for chloride in precipitated iron catalysts for the Fischer-Tropsch synthesis.

In the case of coprecipitation of two or more components, it is generally desirable to maintain the greatest possible degree of homogeneity in the product. Since normally the solubility products of the constituents are divergent, it is possible to obtain a decidedly heterogeneous product. Such a situation would exist, for example, if one were to add a solution of aqueous ammonia to a solution of two metal nitrates to coprecipitate the two corresponding hydrous oxides. The ammonia would tend to precipitate first one hydroxide then the other. On the other hand, revising the procedure by adding the solution of the two nitrates to the ammonia solution would tend to give simultaneous precipitation of the two hydrous oxides. It is true that in the latter procedure the pH would change continuously throughout the process of precipitation. If a constant pH is desired, the method would have to be modified. To achieve the goal of precipitating at a constant pH it may be necessary to bring together two streams of the reacting solutions in such proportions as to maintain the desired pH.

Alternatively, it is possible to maintain homogeneity of a two-component precipitate by dissolving one of the reactants in an acid solution and the other in a basic solution. For example a silica-alumina coprecipitate may be made by mixing dilute solutions of aluminum sulfate (with added acid, if desired) and sodium silicate (water glass).

It is frequently desirable to increase the surface area of the product by precipitating the catalytic material on a support material. The method involves a combination of various catalyst preparation techniques as will be discussed subsequently.

Gel Formation. This particular method of catalyst preparation is especially suited to those catalysts whose major components are hydrous oxides. In particular those containing primarily silica or alumina are especially amenable to gel formation. The phenomenon of gel formation is, as mentioned, merely a special case of precipitation. Therefore, preparation of a catalyst composite in gel form rather than as a coprecipitate does not necessarily result in a change in specific catalytic activity. However, even when no such change occurs, there are frequently major physical advantages to gel formation. Specifically, the disadvantages inherent in processing the highly gelatinous precipitates are eliminated. As a result the gel-formed catalyst is usually considerably easier to prepare. In addition, by the very nature of the process, maximum homogeneity in the polycomponent composites will be produced by gelation.

The general conditions required for gel formation were described long ago by Von Weimarn[236]. However, for any particular gel it is usually necessary to specify the conditions very closely. Gels may be prepared not only in aqueous media but also in nonaqueous and mixed media. For example, alcoholates prepared from the various metal chlorides may be dissolved in alcohols and gelled either in the alcoholic or alcohol-water media. Certain gels such as those of magnesia[125] and $Cd(OH)_2$ or $Zn(OH)_2$[56] are prepared most easily as organo-gels.

Several examples of gel preparation will be described in detail later in the discussion on specific catalyst preparations. However, it should be pointed out that, as a last resort when other methods of gel formation fail, it is usually possible to form a gel by a dialysis method similar to that used by Weiser and Bloxsom[237] for the formation of arsenate gels.

Impregnation Methods. The technique of impregnating an active component (or components) on an inactive support is frequently the simplest possible method of producing a catalyst. However, as already stated, a number of complicating factors arise even in such a simple method of preparation.

Impregnation of a support normally involves the use of a soluble compound of the desired constituent dissolved in a liquid, which is usually water. It is also possible to perform a vapor phase impregnation of the support if one can find a volatile compound of the desired constituent. Impregnation by a solution may be carried out on either dried porous supports or on undried precipitates or gels. In the case of dried supports one may use either a powdered or granular material. A granular support is usually preferred since it eliminates pelleting or extrusion of the finished catalyst.

Impregnation of Granular Supports. In its simplest form this method of catalyst preparation may involve the following steps: (1) evacuating the support, (2) contacting the support with the impregnating solution, (3) removing the excess solution, (4) drying and (5) calcination and activation. Frequently it is necessary to add a precipitation and washing step either before or after drying. In addition, it is generally desirable to obtain preliminary information regarding the equilibrium distribution of the solution between the solid support and the impregnating solution. Such information is necessary to establish the quantity and concentration of the impregnating solution required to obtain the desired concentration of the active component on the support.

Evacuation of the support prior to contacting it with the impregnating solution gives more uniform distribution of the active component. Frequently, trapped air in the pores of the support prevents complete penetration of the solution. In many cases, this step is unnecessary, provided sufficient time of contact between the support and impregnating solution is allowed. Under certain circumstances it may not be desirable to use a prolonged contact time, e.g., when the support can be hydrolyzed. Thirty minutes to an hour is sufficient time to obtain uniform wetting of the support. An excess of impregnating solution is usually used. Removal of this excess solution can be accomplished by either filtration or decantation. Centrifuging is an effective method of removing liquid between the solid particles.

In several cases, the use of excess impregnating solution is undesirable. In these instances enough solution is added to completely wet the support. This can be done by spraying the solution on the support while it is tumbled in a rotating bottle.

Whether a precipitation step is necessary or not depends on the nature of the impregnating compound. If no undesirable component remains after simple calcination, e.g., as in the case of nitrates or ammonium salts, no precipitation will be required. However, if the impregnating compound involves an undesired component in the final product, it is probably necessary to precipitate the desired constituent and then to wash out the undesired material. For example, a cracking catalyst may be prepared by impregnating silica gel with aluminum sulfate. Since sulfate is not desirable in the final product, it is necessary to precipitate the aluminum as the hydrated oxide by adding ammonia. The sulfate ion is then removed by washing.

Impregnation of Powdered Supports. Powdered catalyst supports may be impregnated in a manner entirely analogous to that described for granular supports, with the additional steps of pelleting or extruding to form the final particles. Whereas one normally does not impregnate a granular support with a substance which will be precipitated by the support, it may be advantageous to do so with powdered supports. A procedure of this type would, of course, result in the active material on the external geometric surface of the particles rather than distributed throughout the catalyst pores. Occasionally, this may be used where the active component is expensive and high area is not important.

Vapor Phase Impregnation. Under certain circumstances, the simplest method of preparing a catalyst having the desired degree of purity may be to deposit the active material on a support from a vaporized source. Such a method has been employed in the n-butane isomerization process developed jointly by the Anglo-Iranian Oil Co. and the Standard Oil Development Co.[173] In this process the reactor is charged with a low-iron content bauxite ("Porocel"). At the start, a stream of hot butane is first contacted with $AlCl_3$ and then passed over the bauxite. When sufficient $AlCl_3$ has been deposited on the support, hydrogen chloride is added to the incoming n-butane and the charge is passed directly to the reactor. As the catalyst activity decreases, additional amounts of $AlCl_3$ are intermittently deposited on the bauxite using the hot butane as a carrier.

An analagous process has been patented by Burgin[37] as a method for maintaining the activity of an alumina-boria cracking catalyst. The variation involves passing an admixture of steam plus boric oxide with a hydrocarbon cracking charge over the alumina-boria catalyst. This catalyst is prepared initially by a simple impregnation technique. The catalyst loses boria rapidly in operation. Thus, the process serves to maintain the boria content and, therefore, the activity, much more nearly constant.

Wet Mixing of Catalyst Components. One technique of catalyst preparation frequently used is that of wet-mixing two or more components. The components may be hydrogels or hydrous precipitates or they may be dried materials, or both. Ball milling of the components represents the simplest technique for the preparation of small batches of catalysts. For example, Bailie and See[23] prepared an active silica-magnesia cracking catalyst by ball milling finely divided magnesia with a washed silica hydrogel.

Methods with Limited Application. Certain well known catalysts are prepared by methods which have little general applicability. Examples of these are: (1) thermal fusion, (2) chemical reaction, and (3) evaporation of metals. Let us consider a few examples of these methods with a brief description of each.

Thermal Fusion. The best known examples of catalysts prepared by thermal fusion are some of the fused iron catalysts used for the synthesis of hydrocarbons and ammonia. These catalysts may be prepared by the "schmeltz" method, electric fusion, or use of an induction furnace. The first of these involves burning iron powder in a stream of oxygen Promoters are added directly to the melt. Electric fusion of Fe_3O_4 may be accomplished by the use of water-cooled electrodes immersed in a bed of the oxide. For very small laboratory batches fusion of the desired powdered mixtures may be carried out in an induction furnace.

Chemical Reaction. Catalysts prepared by precipitation or gelation techniques usually involve simple metathetical reactions. Other chemical reactions such as decomposition, oxidation and reduction, etc., are frequently employed to prepare catalysts. These preparatory methods are best illustrated by the following examples. Copper chromite catalysts are prepared by the thermal decomposition of a precipitated copper ammonium chromate[8]. The copper ammonium chromate is preferably precipitated in the presence of a support such as kieselguhr[62]. A chromia-alumina catalyst is prepared by adding chromic acid to a concentrated solution of aluminum sulfate[144]. A solid mass is obtained on heating the mixture at 150 to 400°C. The finished catalyst is obtained by decomposing the dried solid in a reducing atmosphere at 350 to 650°C to remove all the sulfur as sulfur dioxide or hydrogen sulfide.

Another example is the preparation of cracking catalysts from montmorillonite clays. These catalysts are made by leaching the natural clays with dilute sulfuric acid, washing and drying the product. Increased surface area is produced by leaching out part of the alumina and other constituents of the clay. Active surface groups are produced which are acidic in nature and are probably amorphous as contrasted to the crystalline structure of the clay base.

In the case of Raney nickel, an active catalyst is prepared by leaching aluminum from a nickel-aluminum alloy with a base[187, 188]. Usually about a 20 per cent solution of sodium hydroxide is used to remove the aluminum from a 50-50 nickel-aluminum allloy. The washed product is an extremely active hydrogenation catalyst. The finished catalyst is pyrophoric and should not be allowed to dry in air.

Activated magnesia is prepared by alternate hydration of the oxide to the hydroxide at low temperature and dehydration of the hydroxide at temperatures up to 875°C[203]. The final activated magnesia may have an area of over 100 m^2/g.

An alternate oxidation-reduction procedure is used to prepare the copper-iron catalyst used in the Caterole process[240]. Here a mixture of copper and iron turnings in the ratio of 5:1 is placed in a steel tube and alternately oxidized with air at about 400°C and reduced with hydrogen at about 250°C.

Evaporation of Metals. The work of Beeck, Smith and Wheeler[24] has helped to bring into prominence the study of metal films as an aid to fundamental catalytic work. The films used by these investigators were prepared by evaporating the metal from a wire onto a glass support.

Another particularly interesting application of metal evaporation has been described by Rhodin[191]. In this work single crystals of Zn were produced by an evacuation technique described earlier by Bridgman. The crystals so produced were used in adsorption studies.

Processing Operations

Washing. The object of the washing step is primarily to remove impurities from the catalyst. For this reason many impregnated catalysts need not be washed. These materials usually involve decomposable compounds whose solid decomposition products are desired on the catalyst and whose gaseous products disappear. When working with precipitates or gels, washing is usually essential.

Washing techniques vary to a great extent. In the authors' laboratory where much work is done with gels, the method is as follows. The hydrogel is either formed originally in bead form or cut into blocks after gelation. The beads or blocks are placed in a large Büchner funnel which is closed at the bottom with a stopper. Using this simple apparatus, a batch-type washing operation is carried out. Washing is discontinued when the concentration of the contaminating ion reaches a specified concentration in the filtrate at the end of a wash period. This concentration is usually defined by addition of a counter-ion in sufficient quantity to precipitate the undesired ion when present in the filtrate above the prescribed limit. In the washing of certain hydrogels, such as zirconia, peptization is so serious that the temperature of the wash water must be controlled. Marisic and Griest[142] found, for example, that zirconia gels must be washed at temperatures not less than 60°C.

The procedure just described probably represents the simplest possible washing method. However, as previously mentioned, a great majority of catalysts cannot be formed as gels. Precipitates are washed most efficiently by slurrying the filter cake in a large volume of water (usually 5 to 10 times the volume of the cake) with vigorous stirring. The slurry is then filtered in a large Büchner funnel. This washing technique is repeated until the concentration of the contaminating ions in the filtrates, as determined by the addition of a counter-ion, is very low. When the precipitate peptizes on washing, the addition of a small amount of ammonia to the wash water helps to prevent the peptization. Elkin *et al.*[66] have described such a technique in the preparation of alumina. If the products are to be pelleted, some workers prefer to oven dry the precipitates before washing them.

It should be mentioned that when a coprecipitate possesses zeolitic properties, washing alone will probably not be sufficient to remove all contaminating ions. In this case an ion-exchanging operation will be required prior to washing. Such a situation arises in the preparation of cogelled silica-alumina cracking catalysts[156]. These are exchanged with NH_4^+ or Al^{+3} ions prior to washing. A number of oxide combinations possess zeolitic propperties. For example, it has been pointed out by Plank[181] that silica-zirconia gels may possess considerable base exchange capacity. Thus, the observation that the wash water shows no contaminating ions is no proof that the precipitate is also free from that contaminant. This can only be proved by analysis.

Drying. In the preparation of industrial catalysts the drying operation is frequently a complicated one. Many patents have been granted on specialized drying techniques for particular catalytic products. However, in general, these closely controlled operations are used to insure certain desired physical characteristics in the products. They are not usually important to the chemical and catalytic properties of the catalyst. Of course, extreme changes in physical properties should be avoided as they may change the catalytic properties.

Usually drying is carried out in air, in laboratory electric or steam ovens. The temperatures used vary from possibly 60 to 200°C. If one is not concerned with the structural qualities of his product he could use practically any temperature within this range. A safe working range would be from 100 to 150°C. Higher drying temperatures may result in severe fracturing of the gel particles so that the product cannot be tested without being pelleted.

Certain catalysts like Raney nickel or colloidal platinum used for low temperature hydrogenation are not dried at all.

Catalyst Forming or Sizing. The ultimate end of a catalyst preparation is its use in a catalytic reactor. Recently, attention has been focused on the problem of diffusion, particularly in connection with catalysts having surface area and small pores. Thiele[221], Wheeler[241], and Blue[26] have stressed the importance of this factor in catalytic reactions. Hence, it is important to insure freedom from diffusion limitations by sizing of the catalyst.

If properly handled, many of the gelled and precipitated catalysts can be obtained as hard lumps after drying. Grinding and sieving to the proper mesh size are the only operations required prior to calcination and activation. For most small scale testing of catalysts in fixed bed reactors, particle sizes between 6 and 30 mesh are used. The size range is normally defined in terms of the Standard Screen Scale. During the sieving operation catalyst fines which cause large pressure drops through a catalyst bed are eliminated. The shrinkage factor on calcination should be considered in sizing the dried catalyst.

If the dried catalyst crumbles to a powder, or its structure is too weak to withstand the grinding or sieving operation, pelleting or extrusion is required. These latter operations require specialized equipment and know-how to obtain the catalyst in the desired shape and size.

Calcination and Activation. Calcination and activation take several forms depending on the type of catalyst being prepared. These steps represent the final operations in catalyst preparation. In general, the dried catalyst is calcined and activated at temperatures at least as high as those used in the reaction. This treatment is carried out while a large volume of purge gas is passed through or over the catalyst to maintain a low partial pressure of the evolved vapors.

The hydrous oxide catalysts prepared by the techniques previously discussed require only a calcination treatment at temperatures of 350 to 750°C.

For example, the activity of silica-alumina cracking catalysts is stabilized by heating in an inert or air atmosphere at approximately 650 to 750°C[13]. The calcination may be carried out in a catalytic reactor or in a muffle furnace. If a muffle furnace is used, the catalyst should be placed in a shallow bed to insure uniform treatment.

Catalysts which are to be used for hydrogenation or dehydrogenation reactions are calcined and activated in a reducing atmosphere. Nickel, cobalt, iron, or copper catalysts are prepared by reduction of the corresponding oxides in a hydrogen atmosphere at 300 to 500°C. The initial activity of these metallic catalysts, as well as those of platinum and palladium, is a function of the extent of reduction and the temperature used. For the nonreducible oxides of the transition metals, such as chromium, molybdenum, and tungsten oxides, activation in a stream of hydrogen at high temperatures results in a reduction of the valence of the metal ion.

After reduction, these catalysts should be handled in an inert atmosphere such as nitrogen or carbon dioxide to avoid oxidation. Exposure of finely divided metallic catalysts to air frequently destroys their activity.

In the laboratory, the reduction step is normally performed in the catalytic reactor prior to the introduction of the reactants. If exact knowledge of catalyst weight and volume is required the reduced catalyst should be cooled in a stream of nitrogen to minimize the amount of hydrogen adsorbed on the catalyst surface.

Several catalysts require special activation and conditioning treatments to show maximum activity. Nickel and cobalt catalysts used in the Fischer-Tropsch synthesis of hydrocarbons require an induction step with a mixture of carbon monoxide and hydrogen. The reduction of molybdenum trisulfide to the disulfide is frequently carried out with hydrogen containing either hydrogen sulfide or carbon disulfide to minimize partial reduction to the metal.

Catalyst Preparation—Literature References

The art of catalyst manufacture is best illustrated by the large number of procedures reported in the literature for any one catalyst. Very few of these procedures would be considered as standard methods, since many of the factors affecting the activity of the finished catalyst have not been completely investigated. As would be expected, the important technical catalysts have been more thoroughly studied. A review of the literature on methods of preparing some of these catalysts is presented below. A sufficient number of references are included to indicate the various methods used to prepare these catalysts.

Copper

Copper salts, such as the halides, nitrate, sulfate, formate, acetate or oxalate, can be used as starting materials for the preparation of copper catalysts. The pure metal or alloys of copper with other metals, and the metal oxides can also be used.

Sabatier[198] reports the preparation of an unsupported copper catalyst by slow reduction of black "tetracupric" hydroxide in the presence of hydrogen at 200°C. Pease and Taylor[170] describe the preparation of copper catalysts by reduction of cupric oxide with hydrogen at 150 to 200°C. Brown and Henke[35] give the preparation of pure copper catalysts by (1) igniting copper nitrate to form the oxide followed by reduction with hydrogen, and (2) precipitation of the hydrous oxide by adding an aqueous solution of sodium hydroxide to an aqueous solution of copper nitrate. Piccard and Thomas[176] investigated the composition of a copper catalyst prepared by reduction of the oxide. Lewis and Taylor[134] prepared a copper catalyst by reduction of the oxide. Constable[47] describes the preparation of copper catalysts using cupric formate, acetate, oxalate, malonate or succinate as the starting material. Hara[98] describes the preparation of copper catalysts by (1) addition of sodium hydroxide to copper sulfate to precipitate the hydroxide, drying and reducing the oxide in hydrogen at 250°C, and (2) calcination of copper nitrate and reduction of the oxide at 570°C. Frolich, Fenski and Quiggle[83] investigated the effect of temperature of precipitation of copper hydroxide on the activity of the catalyst. The hydroxide was prepared by adding aqueous ammonia to a water solution of a copper salt. These investigators also compared the activity of the catalyst prepared by the above procedure with those produced by precipitating the hydroxide from a copper salt solution using sodium hydroxide instead of ammonia. Fauconau[73, 74] describes the preparation of finely divided copper catalysts by treating copper-zinc or copper-aluminum alloys with 30 per cent aqueous sodium hydroxide. Bessalov[25] gives the preparation of a copper oxide aerosol. Lewis and Taylor[134] described the preparation of pure copper catalysts by mixing an aqueous solution of sodium hydroxide with a solution of copper nitrate. Ipatieff and Corson[110] prepared a number of copper catalysts containing small amounts of nickel, cobalt, ceria and chromia as promoters. Lefrancois[133] also describes the preparation of a number of promoted copper catalysts.

Palmer[160] describes the preparation of a copper catalyst supported on china-clay. The support is impregnated with a saturated solution of copper formate, dried at 100°C, calcined in air at 300°C, and finally reduced with hydrogen. The effect of reduction temperature on the catalyst activity was also investigated. Palmer[159] also describes the preparation of copper catalysts supported on the oxides of iron, manganese and magnesium. These catalysts were prepared by coprecipitating the two oxides by adding the metal sulfates to a boiling solution of sodium carbonate. The carbonates were washed free of sodium ions and calcined to decompose the carbonates to the oxides. Taylor and Joris[219] prepared a magnesium oxide supported copper catalyst by coprecipitating the hydroxides from an aqueous solution of the metal salts, followed by washing, drying and reducing the copper oxide in an atmosphere of hydrogen. Schwab and Nakamura[202] investigated the effect of various methods of preparation on the activity of magnesium oxide supported copper catalysts. Taylor[217] investigated the effect of coprecipitation techniques on the homogeneity of magnesium oxide supported copper catalyst. In a second paper he investigated the effect of various other methods of preparation of the copper-magnesia catalyst on the activity of the finished catalyst. Ipatieff and Corson[110] describe the preparation of copper catalysts supported on alumina and thoria. Rienacker[193] gives the preparation of a nickel promoted copper catalyst supported on kieselguhr as the carrier.

A number of two-component catalysts containing copper are of considerable academic and industrial importance. Copper chromite has found considerable use in the hydrogenation of organic compounds containing functional groups. Adkins, Connor and Folkers[8, 45, 46] give detailed procedures for the preparation of this catalyst by decomposition of copper ammonium chromate. Connor also describes the preparation of copper chromite catalysts containing small amounts of the oxides of barium, calcium or magnesium. Dunbar[62, 64] describes the preparation of copper chromite catalysts supported on pumice, alumina, and "Celite." Lazier[131] gives a standard preparation of a barium copper chromite catalyst starting with an aqueous solution of the nitrates of these metals. Dunbar and Arnold[63] give several alternate methods of preparation of copper chromite catalysts supported on "Celite" or "Carborundum." Riener[194] describes an improved laboratory method of preparing copper chromite catalysts.

Several catalysts containing copper and zinc oxide are of use in the synthesis of methanol from carbon monoxide and hydrogen. Lewis and Frolich[135] describe the preparation of a copper-zinc oxide-alumina catalyst. The catalyst is prepared by precipitation of the hydroxides of these metals by the addition of ammonia to an aqueous solution of the nitrates. After drying, the catalyst is activated with a mixture of carbon monoxide and hydrogen at 180 to 200°C for 2 to 4 hours at a pressure of 100 to 400 psi. Frolich and co-workers[82, 84] also describe the preparation of copper-zinc oxide catalysts by a similar procedure. These investigators studied the effect of catalyst composition on the activity of the finished catalyst.

Aluminum

Aluminum nitrate, chloride or sulfate are preferred as starting materials for the laboratory preparation of alumina. The commercial trihydrate of alumina or the metal itself, dissolved in sodium hydroxide to form sodium aluminate, can be used to prepare this important catalyst and catalyst support. Aluminum alkoxides, expecially aluminum isopropylate, have also been used by several investigators.

Sabatier and Mailhe[200] describe several procedures for the preparation of alumina catalysts. The alumina catalyst most active for the dehydration of alcohols was prepared by addition of an aqueous solution of ammonia to a solution of aluminum nitrate. The precipitate was washed to remove nitrate ions, and dried at 300°C. Weiser[239], in 1920, summarized most of the previous information available on the effect of various factors on the physical and chemical properties of hydrous alumina. He discusses the composition and properties of precipitated alumina, the preparation and properties of colloidal solutions of alumina and methods of coagulating the alumina. Adkins and Krause[7] prepared an active alumina catalyst by the addition of concentrated ammonia to a boiling solution of aluminum nitrate. The precipitate was washed until free of nitrate ions and dried at 165°C. Adkins[5] describes the preparation of alumina catalysts by the hydrolysis of aluminum alkoxides. A pumice-supported alumina catalyst was prepared by melting a given weight of the aluminum alkoxide in contact with a known weight of ignited pumice. After cooling, the impregnated carrier was exposed to the atmosphere for 18 hours.

Willstäter and Kraut[243] prepared alumina by the addition of a hot (60°C) solution of aluminum sulfate to one containing ammonia and ammonium sulfate. During the precipitation of the alumina the temperature of the slurry was maintained at 60°C. The precipitate was washed free of sulfate ions and dried in a vacuum over phosphorous pentoxide. Pearce and Alvarado[167] prepared an aluminum oxide catalyst by the addition of ammonium hydroxide to a dilute solution of aluminum nitrate. The slurry was heated to expell excess ammonia, washed by decantation, filtered, and dried 18 hours at 120°C. The catalyst is activated by heating at 250°C for 24 hours. Perry[172] describes the preparation of an alumina gel. The gel is prepared by slowly adding ammonium hydroxide to a solution of aluminum sulfate at room temperature with vigorous stirring. The gel is washed to remove sulfate ion, filtered, dried at 60°C, and activated in air at 200°C. Bruckner and Hirth[36] prepared an activated alumina by the addition of 25 per cent ammonia to a 2 per cent solution of either aluminum chloride or aluminum sulfate. The gel was washed by decantation and dried at 300°C. Kistler, Kearby and Swann[120] describe the preparation of an alumina aerogel.

Goldwasser and Taylor[91] describe the preparation of an alumina catalyst for the dehydration of alcohols. The alumina is prepared by the addition of concentrated ammonia to a 1.5N aluminum nitrate solution with vigorous stirring. The slurry is filtered without washing and dried at 100°C. The catalyst is activated at 400°C. In a second paper, these investigators studied the effect of the concentration of the aluminum nitrate and ammonia solutions on the activity of the finished catalyst. Elkin, Shull and Roess[66] give a detailed procedure for the preparation of alumina from aluminum chloride hexahydrate using dilute ammonia as the precipitant. Elmore, Mason and Hatfield[67] investigated the pH of sodium aluminate solutions during the precipitation of alumina with carbon dioxide. They show that the precipitation starts at a pH of 11.4 and is essentially complete at about 9.0 pH. These workers give a procedure for precipitating alumina at a constant pH using an automatic controller on the addition of carbon dioxide. Russell and Cochran[195] investigated the influence of temperature, atmosphere and duration of heating on the surface area and crystal structure of various forms of alunina. The preparation of these aluminas is given in a later paper[213] which deals with the thermal transformations of alumina and alumina hydrates. These changes are followed by x-ray powder diffraction analysis.

Vanadium

In the preparation of vanadium oxide catalysts, vanadium pentoxide, vanadic acid or organic esters of vanadic acid, vanadyl chloride, sulfate or oxalate, or the alkali or ammonium vanadates have been used as starting materials. Gibbs[88] describes a procedure for the preparation of vanadium oxide catalysts by fusing pure vanadium pentoxide. A vanadium oxide catalyst supported on infusional earth is prepared by impregnating the carrier with molten vanadium pentoxide. Kuhlmann[126] impregnates pumice with a solution of vanadyl oxalate obtained by dissolving vanadic acid in oxalic acid. The oxalate is decomposed by calcining the impregnated carrier in air at 400 to 500°C. Weil and Rawlinson[235] describe a procedure for purifying ammonium vanadate and the preparation of vanadium oxide catalysts from the purified salt. Adadurov and Boreskov[1] describe the preparation of chamott-supported vanadium oxide catalysts by impregnation with an aqueous solution of ammonium vanadate. Craver[53] describes the preparation of vanadium oxide catalysts by the reaction of ammonium vanadate with oxalic, malic, citric, tartaric or succinic acids. Maklakov[141] gives the procedures for the preparation of vanadium catalysts promoted with calcium, barium, tin and potassium. Joseph[113] and Cummings[54] describe procedures for impregnating kieselguhr with a water solution of sodium vanadate. Milas and Walsh[145] give preparation of pumice-supported vanadium oxide catalyst starting with ammonium metavanadate. Foster[79] prepares a vanadium oxide catalyst starting with vanadyl sulfate. Douglas[61] prepares an alumina-supported vanadium oxide catalyst by impregnating a porous fused alumina with an aqueous solution of vanadyl chloride. The preparation of vanadium oxide-kieselguhr catalysts useful for the oxidation of sulfur dioxide to sulfur trioxide is described by Girsewald[89]. Adadurov[2] gives a procedure for the preparation of vanadium oxide-chromium oxide catalysts using aqueous solutions of ammonium vanadate and chromium nitrate. Foster[78] describes the preparation of vanadium oxide catalysts supported on pumice or alundum by reducing metavanadic acid with a hydrogen halide. Littmann[137] describes the preparation of vanadium oxide catalysts supported on alundum. The alundum is impregnated with a solution of butyl vanadate in butyl alcohol. Lyubarskii and Kagan[140] give the preparation of a vanadium oxide catalyst supported on alumina. Tuerck[226] prepared a supported vanadium oxide catalyst by impregnating alumina or silica gel with a solution obtained by dispersing vanadium pentoxide in an aqueous solution of hydrogen peroxide. Shagam[205] also gives a procedure for the preparation of vanadium oxide catalysts supported on silica gel. Komarewsky, Bos and Coley[122] give a detail procedure for the preparation of vanadia-alumina catalysts by coprecipitation using solutions of sodium vanadate and aluminum nitrate. Komarewsky and Knaggs[124] prepared a vanadium oxide catalyst by the addition of concentrated nitric acid to a hot saturated solution of ammonium vanadate. The gel formed by this method is washed to remove nitrate ions, dried at 110°C and activated at 400°C in a stream of hydrogen.

Chromium

Chromium oxide catalysts are most conveniently prepared by starting with an aqueous solution of one of the soluble compounds of trivalent chromium. Chromium salts such as the nitrate, chloride, sulfate, acetate, and oxalate are usually preferred. However, other compounds such as the ammonium and the alkali metal chromates and dichromates are frequently used.

Lazier and Vaughan[132] describe the preparation of chromium oxide catalyst by (1) the ignition of ammonium dichromate in a muffle furnace at 400°C, (2) thermal decomposition of chromium nitrate and chromium oxalate at 400°C, (3) reduction of ammonium dichromate with methanol in hot sulfuric or hydrochloric acid solution, and (4) precipitation of chromium oxide gel by the addition of an aqueous solution of ammonium or sodium hydroxide to a solution of chromium nitrate or chloride. These investigators discuss various aspects of the preparation of this catalyst. They also report a number of observations on the "glow" phenomenon which occurs when amorphous chromium oxide is heated above a temperature of 300°C. Frey and Huppke[81] give in detail the preparation of a chromium oxide gel catalyst by the addition of aqueous ammonium hydroxide to a solution containing chromium nitrate and ammonium acetate. After washing, the gel is first dried at 50°C, and then at 250°C in vacuo for 8 hours. The dried catalyst is activated in pure dry hydrogen over a period of 15 hours while the temperature is increased to 400°C. Kohlschütter[121] describes the preparation of a very active chromium oxide gel catalyst. The gel is prepared by the slow addition of 0.1N ammonium hydroxide to a 0.1N solution of chromium nitrate with vigorous stirring. The gel is washed with water, dried at 105°C and activated in pure dry hydrogen at 380°C. Goldwasser and Taylor[90] also prepared an active chromium oxide gel by this procedure, however, they prefered to activate the dried catalyst in hydrogen at 475°C.

The preparation of an alumina-supported chromium oxide catalyst is reported by Grosse and co-workers[95, 96]. This catalyst is made by impregnating activated alumina with an aqueous solution of either chromic acid, chromium nitrate, ammonium chromate or ammonium dichromate. Kistler, Kearby, and Swann[120] describe the preparation of a chromia-alumina areogel. Ethylene oxide is added to a solution containing aluminum chloride, chromic chloride and glycerol. The green firm gel which forms after standing for 15 hours is autoclaved, and the solvent removed. Zelinskii and coworkers[248] prepared a chromium oxide catalyst by the addition of aqueous ammonia to a soluble trivalent chromium salt. Chromia and alumina supported chromium oxide catalysts are prepared by impregnating the ignited carriers with an aqueous solution of chromium nitrate.

Turkevich, Fehrer and Taylor[228] give detailed directions for the preparation of chromia catalysts by several procedures. A chromium oxide jelly is prepared by the addition of aqueous ammonia to a solution containing chromium nitrate and ammonium acetate. The jelly is cut into cubes, washed by decantation, dried at 50 to 60°C and finally at 300°C overnight. A chromium oxide gel is prepared by adding concentrated ammonia to a boiling solution of black chromium acetate. After the gel is formed, it is washed, dried at 120°C for 15 hours and then heated to 350°C over a 24-hour period. The preparation of amorphous chromium oxide catalysts by the reduction of chromic acid with (1) ethyl alcohol, (2) sucrose and (3) oxalic acid are also given.

Komarewsky and Coley[123] prepared a chromia catalysts by precipitating chromium hydroxide from a cold 1.0N solution of chromium nitrate by the addition of 1.0N sodium hydroxide. The precipitate is washed free of nitrate ions, dried at 110°C, and activated in a stream of hydrogen at 500°C. A second preparation involves redissolving the precipitated chromia in excess sodium hydroxide. The chromite solution on standing overnight gives a precipitated chromia gel. Hughes and co-workers[38, 104] prepared chromia-alumina catalysts by coprecipitation techniques using solutions of chromium acetate and sodium aluminate. The pH of the slurry during precipitation is maintained at approximately 10. By this technique it is possible to vary the concentration of chromium oxide in the final catalyst from 18 to 31 mole per cent.

Molybdenum

Molybdic acid or ammonium paramolybdate are the usual starting materials for the preparation of molybdenum oxide or sulfide catalysts. Other molybdenum compounds, such as the chlorides and cyanides, and the mineral, molybdenite, have also been used to prepare active molybdenum catalysts. In general, molybdenum oxide catalysts can be prepared by the addition of hydrochloric acid to an ammoniacal solution of molybdic acid or ammonium paramolybdate. A supported molybdenum oxide catalyst is normally prepared by impregnation of the carrier with an aqueous solution of ammonium molybdate. The impregnated carrier is heated to a temperature of 400 to 500°C to decompose the molybdate to the oxide. Molybdenum sulfide catalysts are prepared by either acidifying an aqueous solution of ammonium thiomolybdate, or by treating the oxide at elevated temperatures with hydrogen sulfide.

Slotboom[211] describes the preparation of a norite supported molybdenum oxide catalyst starting with the mineral, molybdenite. King and Matthews[118] give the procedure for the preparation of a molybdenum oxide catalyst supported on active charcoal. Bahr and Petrick[21] describe the effect of supports, promoters, method of preparation and reaction conditions on the activity of molybdenum oxide catalysts. Galle and Michelitsch[86] investigated the preparation of molybdenum oxide catalysts and their resistance to sulfur poisoning. King and Cawley[117] describe procedures for the preparation of alumina-supported molybdenum oxide catalysts by impregnation of granular alumina with ammonium molybdate. Kingman[119] investigated the effect of various promoters on the activity of molybdenum oxide catalysts used in hydrogenation reactions. Griffith and Hill[93] studied the effect of silica concentration on the activity of molydenum oxide catalysts for the decomposition of *n*-hexane. Cawley and King[42] investigated the effect of various preparational methods on the activity of molybdenum oxide catalysts for the hydrogenation-cracking of tars. Demyb[59] gives a brief review of the methods of preparation of molybdenum catalysts and their catalytic activity. Helm[101] reviews the effect of carriers, promoters, poisons, crystal structure and gas sorption of catalysts of the molybdenum group. Ando[17] investigated the effect of carriers on the activity of molybdenum catalysts for the high pressure hydrogenation of low temperature tars. Fuchs and

Brendlein[35] discuss the effect of sulfur in hydrogenation reactions using molybdenum oxide as the catalyst. Ando[17] gives the preparation and compares the activity of molybdenum oxide and sulfide catalysts for the hydrogenation of phenols under high pressures. Maslyanski and Shenderovich[143] investigated the effect of reaction and catalyst variables on the activity of molybdenum oxide and sulfide catalysts. Russell and Stokes[196] studied the effect of preparational variables on the activity of alumina-supported molybdenum oxide catalysts for the dehydrocyclization of *n*-heptane to toluene. Webb and co-workers[234] describe the effect of various methods of preparation of alumina supported molybdenum oxide catalysts on their activity for the reforming of low octane naphthas. Greensfelder, Archibald and Fuller[92] describe the activity of alumina-supported molybdenum oxide catalysts for the reforming of naphthas in the presence of hydrogen.

The preparation of molybdenum sulfide catalysts used in the hydrogenation of phenols and cresols is described by Moldavskii and Levshitz[148]. Prokopetz and Eru[184] describe the preparation of colloidal molybdenum sulfide catalysts by the action of hydrogen sulfide on an ammoniacal solution of a molybdenum salt. Polozov[183] gives a method of preparation of molybdenum sulfide from molybdenum oxide and an aqueous acid solution of the sodium sulfide. Carlile and Cawley[39] describe the preparation of molybdenum sulfide and alumina-supported molybdenum sulfide catalysts used in the hydro-desulfurization of benezene and the cracking of low temperature tars. Prokopetz[185] investigated the effect of kaolin alone, and kaolin plus cobalt sulfide on the activity of molybdenum sulfide catalysts for the hydrogenation of benzene and the isomerization of cyclohexane. Cawley and Hall[41] describe the activity of pure molybdenum sulfide for the hydrogenation of cyclohexane and decahydronaphthalene.

Tungsten

The preparation of tungsten catalysts usually starts with either the metal, tungsten oxide, the tungsten halides, ammonium paratungstate, tungstic acid or the alkali metal tungstates. The thermally unstable ammonium paratungstate is used in many preparations, especially for supported tungsten oxide or sulfide catalysts.

Brown and Reid[34] prepared a tungstic acid gel by the slow addition of $6.4N$ nitric acid to a 12 per cent solution of sodium tungstate. After setting, the gel is thoroughly washed, dried at gradually increasing temperature and reduced with hydrogen at 300°C to give the blue oxide. This catalyst can also be prepared by the addition of a hot hydrochloric acid solution to a hot solution of sodium tungstate. These authors also give the preparation of a pumice-supported tungsten oxide catalyst. The sized carrier is impregnated with an aqueous ethylamine solution of tungstic acid.

Patrick and Barclay[161] describe a procedure for the preparation of a tungstic oxide gel. The gel is prepared by adding an aqueous solution of a strong acid, e.g., hydrochloric or sulfuric, to a solution of sodium tungstate. The concentration of both the acid and tungstate solutions is critical in order to obtain a firm gel. The gel is washed free of sodium ions prior to drying and calcination. Pearce and Rice[168] prepared tungstic oxide by dissolving tungstic acid in ammonium hydroxide. The solution is boiled to remove free ammonia. Sufficient nitric acid is added to precipitate tungstic oxide. The precipitate is washed by decantation until free of nitrate ions, and dried 24 hours at 130°C. Arnold[20] prepares a tungsten oxide-molybdenum oxide catalyst by mixing ammonium paratungstate and ammonium molybdate with water to form a thick uniform paste. Nitric acid is added to form the hydrated tungstic and molybdic acids. The precipitate is washed with water, dried and calcined in air at 450°C. •

The I. G. Farbenindustrie[107] has patented several methods for the preparation of tungsten sulfide catalysts. An active tungsten sulfide catalyst can be prepared by treating monoclinic needles of ammonium tungstate with hydrogen sulfide for 48 hours at 300°C and then for 24 hours at 350°C. A modified procedure consists of heating ammonium paratungstate with hydrogen sulfide at temperatures up to 410°C under five atmospheres' pressure for 24 to 36 hours in the absence of air. The tungsten sulfide is activated in a stream of hydrogen at 430°C before use. A third preparation involves passing hydrogen sulfide into a solution of tungsten oxide in aqueous ammonia until crystals of ammonium sulfotungstate are precipitated. The mixture is evaportated to dryness and the sulfotungstate decomposed at 300°C in a stream of hydrogen. A tungsten sulfide catalyst can be made by heating tungstic oxide with carbon tetrachloride to convert the oxide to the chloride, followed by treating with hydrogen sulfide[153].

Moldavskii[147] describes the preparation of a tungsten sulfide catalyst which is active for the dehydrogenation of cyclohexane. Piers[179] obtains a tungsten sulfide-zinc sulfide catalyst by heating a mixture of the oxides in a carbon disulfide-hydrogen atmosphere at 200°C and 200 atmospheres' pressure. Tiede and Lemke[224] give detailed directions for the preparation of crystals of tungsten disulfide. The disulfide is prepared by treating tungsten metal with sulfur at high temperatures. Cawley and Hall[41] give a method for preparing pure tungsten disulfide cataysts. Archibald[18] prepares a tungsten sulfide-nickel sulfide catalyst by saturating a solution of tungstic acid with ammonia and then with hydrogen sulfide at 40 to 50°C to give ammonium sulfotungstate. To this basic solution is added enough nickel nitrate to give a tungsten-nickel ratio of about 1:1.5. The sulfides are coprecipitated at 35 to 45°C by addition of sufficient sulfuric acid to give a pH of 1 to 1.5. The precipitate is dried and calcined in the presence of hydrogen prior to use. Piers[178] discusses the preparation and activity of tungsten sulfide catalysts. This catalyst is prepared by dissolving tungstic acid in a hot (70°C) aqueous ammonia solution and treating the solution with hydrogen sulfide. The crystallized ammonium thiotungstate is decomposed in a stream of hydrogen at 400°C.

Nickel, Cobalt and Iron

The main sources of these catalysts are the pure metals, metal alloys, the oxides, the inorganic salts such as the nitrates, sulfates, chlorides, basic carbonates, and the organic salts such as the formates or oxalates. Many of the procedures used for one of these metals can be applied to the preparation of the other metals in this group. These catalysts are used in the form of the massive metal, as gauzes or wires, as finely divided metals which include the so called "Raney" metals, and supported catalysts on a wide variety of carriers.

Nickel. The preparation and activation of unsupported nickel catalysts have been studied by numerous investigators. Sendersens and Abouleuc[204] studied the preparation of reduced nickel catalysts. Erdmand[69] investigated the preparation of nickel catalysts for the hydrogenation of oils. Richardson[192] describes a method for preparing an active, finely divided nickel catalyst by mechanical grinding of shot nickel. Brochet[32] studied the effect of temperature of decomposition of nickel organic salts such as the formate and oxalate on the activity of nickel catalysts for the hydrogenation of oils. Kelber[115] investigated the effect of reduction temperature and oxygen on the activity of nickel catalysts prepared from the basic nickel carbonate. Lietz[136] studied the preparation of nickel catalysts by reducing the basic carbonate prepared by mixing aqueous solutions of nickel sulfate and sodium carbonate. Adkins and Lazier[10] compared the properties of nickel catalysts prepared by reduction of the oxide with ethyl alcohol and hydrogen. Kusama and Uno[127] compare the activities of nickel catalysts prepared from nickel chloride and nickel nitrate. Cornubert and Borrel[50] studied the preparation of active nickel catalysts by the interaction of sodium carbonate with nickel nitrate, nickel sulfate and nickel chloride. The basic nickel carbonate from each of these salts was converted to the formate by reaction with 78 per cent formic acid. Covert, Connor and Adkins[52, 9] made an extensive study of the preparation of nickel catalysts. Jenness[111] describes a method of preparing very active nickel catalysts by a selective corrosion and etching action on a nickel foraminate. Fajans[72] studied the effect of temperature on the sintering of nickel catalysts. Moshken and Kazakova[150] studied the effect of small amounts of copper on the activity of nickel catalysts prepared from nickel acetate and nickel formate. Petryaev[174] studied the effect of drying temperatures on the activity of nickel catalysts prepared from nickel formate. Boswell[27] investigated the effect of temperature of preparation on the crystal size and composition of nickel oxide. Dupont and Piganiol[65] investigated the effect of the crystalline state of the metal on its activity. Dobychin[60] studied the effect of temperture and gaseous atmosphere on the activity of nickel catalysts prepared from nickel formate. Etinburg[71] describes a procedure for the preparation of a highly active nickel catalyst from nickel carbonate. Iki[108, 109] describes a method of preparing active nickel catalysts by the electrolytic corrosion of nickel in alkali solutions containing small quantities of alcohol. Constable[48] prepared nickel films on china clay electrodes by electrolysis of a nickel solution at a fixed rate of deposition. Beeck, Smith, and Wheeler[24] describe the preparation of nickel films by evaporation of the metal on a cold glass wall.

Grote[97] describes the preparation of a nickel catalyst supported on aluminum or magnesium silicate. These catalysts were prepared by interaction of a solution containing the nickel and aluminum or nickel and magnesium salts with a solution of sodium silicate. Zelinskii and Komarewsky[249] prepared a nickel-alumina catalyst by mixing an aqueous solution of nickel nitrate with a solution of sodium aluminate. Pfaff[175] describes a modified procedure for the preparation of a nickel-alumina catalyst. Waterman and Tussenbroek[233] prepared a kieselguhr-supported nickel catalyst by precipitating the oxide from nickel sulfate on kieselguhr. They investigated the effect of heat treatment on the activity of the catalyst. Turben[227] describes a procedure for preparing a nickel-kieselguhr catalyst in which the loss of nickel by formation of a soluble nickel bicarbonate is minimized. Gaverdovskaya[87] investigated alumina, silica, zinc oxide and carbon as supports for nickel catalysts. Normann[155] investigated the effect of calcination temperature on the activity of nickel-kieselguhr catalysts prepared from nickel sulfate. Etinburg[70] investigated the activity of nickel-kieselguhr catalysts in relation to the thermal conditions of precipitation, drying and reduction. The catalysts were prepared by treating a solution of nickel sulfate with a solution of sodium carbonate. Juliard[112] studied the activity of nickel catalysts supported on oxides of iron, copper, cadmium, lead, manganese, zinc, chromium, cerium, thorium, aluminum and beryllium. Yamaguti[245] investigated the activity of nickel formate-kieselguhr catalysts containing various amounts of copper; Tanida[215], the influence of tungsten and molybdenum oxides on the activity of nickel catalysts. Trambouze[225] determined the chemical nature of the nickel in Fischer-Tropsch catalysts, and investigated the effect of thermal reduction of nickel carbonate-silica-alumina catalysts on their activity. Fischer and Meyer[77] made an exhaustive study of the effect of alumina and thoria on the activity of nickel catalysts. These investigators also made an extensive study of the effect of preparation variables on the activity of the finished catalyst. Neumann and Jacob[154] investigated the activity of nickel catalysts supported on pumice, asbestos, unglazed burned clay and magnesia. Ciapetta and Hunter[44] describe the preparation of nickel catalysts supported on silica-alumina.

The preparation of Raney nickel catalysts has been minutely described by several investigators. Covert and Adkins[51] give a modified procedure for the preparation of this finely divided nickel catalyst. Delepine[58] prepares a Raney nickel catalyst which is activated by the addition of a metal from the platinum group. Paul and Helly[163] describe the method used for preparing metal-aluminum alloys as well as the procedure for the preparation of the Raney nickel catalyst. Rapoport[190] investigated the properties of metal skeletons obtained by treating nickel-cobalt-aluminum and nickel-aluminum alloys with alkali. Sully[214] describes the preparation of Raney nickel catalysts and compares the activity of this catalyst to one prepared by precipitating nickel carbonate from nickel sulfate with sodium carbonate. Raney[187, 188] describes in detail the processing of a nickel-aluminum alloy to form Raney nickel. Schröter[201] gives a comprehensive review of the preparation and properties of Raney metals. Mozingo[151] gives in detail directions for the preparation of Raney nickel. Paul[162] reviews the methods of preparation and catalytic activity of Raney nickel catalysts. Pavlic[166] and Adkins[6] give procedures for the preparation of very active Raney nickel catalysts by digestion with caustic at a higher temperature. Heilmann, Dubois and Berege[100] describe two different procedures for the preparation of a platinized Raney nickel catalyst.

General reviews of the methods of preparation of nickel catalysts have been published by Pollit[182], Brochet[33], Thomas[223], Lush[139], Adkins[9], Sabatier[199], Armstrong[19], Fraser[80], Zhabrova[252], Dean[57], and Bailey[22].

Cobalt. Many of the procedures used for the preparation of nickel catalysts can be applied to prepare cobalt catalysts. Hüttig and Kassler[106] describe the preparation of cobalt catalysts by (1) precipitation of cobalt hydroxide followed by reduction in hydrogen, and (2) by direct reduction of cobalt oxide. The former procedure was found to give a more active catalyst. These investigators also studied the effect of reduction temperature on the activity of the cobalt catalysts prepared by the above methods. Griffitts[94] gives the preparation of a pure cobalt catalyst using cobalt nitrate and sodium hydroxide as the starting materials. Preparational methods are also given for modified catalysts containing manganese and chromium.

Fischer and Koch[76] carried out an extensive study of the effect of available methods of preparing supported cobalt catalysts on their activity. Cobalt catalysts supported on kieselguhr were made by (1) impregnation of kieselguhr using a thermally unstable cobalt salt such as the nitrate, and (2) by precipitating cobalt hydroxide in the presence of kieselguhr. Cobalt-thoria, cobalt-magnesia, and cobalt-alumina catalysts were prepared by coprecipitation techniques using an aqueous solution of the nitrates and either ammonium or alkali metal hydroxides, or carbonates, as the precipitant. Tutumi[229] made a cobalt catalyst supported on kieselguhr by (1) precipitating cobalt hydroxide in the presence of kieselguhr using potassium carbonate as the precipitant, (2) by mixing a wet precipitate of hydrous cobalt oxide with kieselguhr, and (3) by impregnating the kieselguhr with a solution of cobalt nitrate followed by thermal decomposition of the nitrate to the oxide. The effect of the ratio of cobalt-to-kieselguhr as well as the reduction temperature on the activity of the final catalyst were studied. A cobalt-magnesia catalyst can be made by coprecipitation from a solution containing either the nitrates or the chlorides of these metals[230]. Sodium carbonate is used as the precipitant. The preparation of a cobalt catalyst supported on either silica gel or magnesium-silicate is described by Teter[220] Ciapetta and Hunter[44] give the preparation of a cobalt catalyst supported on silica-alumina.

The preparation of Raney cobalt catalysts is described by Schröter[201], Hawk[99], Rapoport[190], and Fauconau[74].

Iron. Weiser[238] summarized the factors which affect the physical and chemical properties of hydrous ferric oxide. He investigated the composition of colloidal ferric oxide and the effect of various precipitants on the nature of the precipitate formed. Hüttig and Garside[105] critically examined the ferric oxide-water system. They give details of the preparation of hydrous ferric oxide by the addition of aqueous ammonia to ferric chloride solutions. Rao[189] also describes the preparation of a ferric oxide gel from ferric chloride using ammonia as the precipitant.

Procedures for the preparation of precipitated and supported iron catalysts are similar to those discussed above for nickel and cobalt catalysts. Lazier and Adkins[130] prepared a ferric oxide catalyst by the addition of excess ammonium hydroxide to a solution of ferric chloride. The precipitate is washed free of chloride ions and dried at 140°C. Emmett and Gray[68] describe in detail the method used in the preparation of a precipitated iron oxide catalyst. The oxide is precipitated from a solution of ferric nitrate by the addition of an excess of ammonia. The precipitate is washed by decantation until neutral to litmus, and dried at 100°C for 16 hours. The dried solid is reduced in hydrogen for 24 hours at 360 to 405°C. Pease and Stewart[169] prepared an iron catalyst supported on diatomite brick by impregnating the brick with a solution of ferric nitrate. The impregnated support is heated in air at 350 to 400°C to decompose the nitrate. The oxide is reduced to the metal by heating in hydrogen at 450°C.

An extensive study of the preparation and activation of precipitated and supported iron catalysts was carried out by Fischer and co-workers in connection with the development of active iron catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen. Pichler[177] summarized a large part of this work in a special report issued by the U. S. Bureau of Mines. The preparation and activation of iron catalysts are discussed in detail by Storch, Golumbic and Anderson[212].

The preparation of fused synthetic ammonia iron catalysts is described by Larson and Richardson[129] and Bridger, Pole, Beinlich and Thompson[31]. These catalysts are usually prepared by fusing a suitable magnetite powder (or ore) together with promoters in an electric resistance furnace. Larson and Brooks[128] give the preparation of a number of singly-promoted iron catalysts containing either potassium oxide, aluminum oxide, zirconium oxide, silica, tungsten, manganese or nickel. Fused iron catalysts containing two promoters, one of which is potassium oxide are also described. Anderson, Seligman, Shultz, Kelly and Elliott[15] give the preparation of a number of sintered and cemented iron catalysts used in the Fischer-Tropsch synthesis. Anderson, Shultz, Seligman, Hall and Storch[16] give detailed directions for the preparation of iron nitride catalysts. These catalysts are prepared by first reducing an iron catalyst at 450 to 550°C in hydrogen. The reduced catalyst is nitrided with ammonia at 350°C.

Platinum and Palladium

Catalysts containing platinum or palladium are prepared from the metals, from an acid solution of the metal chlorides, e.g., chloroplatinic acid, or from the alkali metal salts of these acids, e.g., sodium chloroplatinate. These catalysts may be prepared as (1) a metallic sponge, (2) a colloidal suspension, (3) a black, (4) a metallic gauze and (5) a supported catalyst on an inert carrier.

Willstätter[244] describes the preparation of a platinum sponge by adding either sodium or potassium hydroxide to a solution containing chloroplatinic acid and formaldehyde. Feulgen[75] gives a modified procedure for the preparation of a platinum sponge which minimizes losses of the metal during the washing step. Breteau[30], using a procedure similar to Willstätter, gives the preparation of a palladium sponge catalyst from chloropalladic acid, formaldehyde and sodium hydroxide.

Active and stable colloidal platinum and palladium catalysts can be prepared by liberating the metal in the presence of a protective colloid such as gum arabic or collodium. Bredig[29] was among the first to prepare colloidal platinum and palladium catalysts by arcing the metals in the form of a wire under the surface of distilled water. Paal and Amberger[157] describe the preparation of platinum and palladium sols using sodium protalbinate or lysalbinate as protective sols. Skita and Meyer[210] obtained a colloidal platinum catalyst by treating a solution containing potassium chloroplatinate and gum arabic with the calculated amount of sodium hydroxide or with excess sodium carbonate. Skita[207, 208, 209] also describes the preparation of colloidal platinum or palladium catalysts in an anhydrous medium by reducing an alcoholic solution of chloroplatinic or chloropalladic acid with hydrazine and sodium ethylate, or metallic sodium. Collodium is used as the protective colloid. Pennycuick[171] has studied the nature of colloidal platinum catalysts. Pauli[164, 165] describes the preparation of platinum sols by arcing platinum wires in dilute hydrochloric acid followed by purification and concentrations by electro-decantation. Zenghelis and Stathis[251] prepared colloidal platinum and palladium catalysts by reducing their salts with nascent hydrogen in the presence of 5 to 10 per cent gum. Rampino[186] describes the preparation of colloidal palladium and platinum catalysts in which synthetic high polymers, e.g., polyvinyl alcohol, are used as protective colloids. Kelber and Schwartz[116] prepared a colloidal suspension of palladium in aqueous acetic acid, using partially hydrolyzed glutin as a protective colloid, by reducing palladium chloride with hydrazine. Mindel and King[146] describe a number of methods of preparing Bredig platinum sols in water, hydrochloric acid, air, oxygen and nitrogen.

Loew[138] was among the first to prepare platinum blacks by treating a solution of platinic chloride with a mixture of formaldehyde and sodium hydroxide. Boswell[28] gives a detailed description of the preparation of a platinum black catalyst by Loew's method. Voorhees[231, 232], Adams [3, 4], Taylor[218], Cook[49], and Carothers[40] have investigated very thoroughly the preparation of platinum blacks by fusing chloroplatinic acid with sodium nitrate. Adams[3] made a detailed study of the effect of fusion temperature on the activity of platinum blacks prepared by this procedure. Zelinskii[247] prepared a palladium black by adding formaldehyde to an ammoniacal solution of palladium chloride and then adding a 20 per cent aqueous solution of potassium hydroxide. Wieland[242], Tausz[216] and Piccard[176] describe several procedures for the preparation of palladium black catalysts. Shriner and Adams[206] prepared palladium black by fusion of palladium chloride with sodium nitrate. The effect of fusion temperature on the activity of the catalyst was investigated.

The preparation of supported platinum or palladium catalysts is usually carried out by wetting the support with an aqueous solution of chloroplatinic or chloropalladic acids, or with an aqueous solution of the ammonium salts of these acids. The impregnated support is dried at 105 to 110°C, and reduced in a hydrogen atmosphere between 100 to 450°C. Zelinskii and Borissov[246] give the procedure for the preparation of platinum or palladium catalysts on asbestos. Kaffer[114] and Zelinskii[250] describe the preparation of a platinum catalyst supported on charcoal. Holmes[103] and Morris[149] describe the preparation of platinum catalysts supported on chalky and glassy silica gels. Alekseevskii[11, 12] gives the preparation of platinum catalysts supported on kaolin and charcoal. Packendorff[158] investigated the activity of a number of platinum catalysts supported on charcoal and alumina. Mozingo[152] gives a detailed preparation of a palladium catalyst supported on barium sulfate or activated charcoal. Ciapetta and Hunter[44] describe the preparation of a platinum catalyst supported on a synthetic silica-alumina support.

The preparation of platinum alloy gauzes such as platinum-rhodium are described by Davis[55].

CATALYST PREPARATION—EXPERIMENTAL

Catalyst manufacture on a commercial scale has increased in recent years as the result of the development and industrial utilization of new catalytic processes. In the petroleum industry alone, thousands of tons of silica-alumina catalyst are in constant use for the production of motor gasoline by the catalytic cracking of gas oils. Several catalyst manufacturers have engaged in the preparation of special catalysts which can be used for various chemical reactions. For examples, activated alumina, Raney and supported nickel, colloidal and supported platinum and palladium, chromia-alumina, and molybdena-alumina catalysts are sold commercially. Hence, for many routine catalytic reactions, preparation of the catalyst is not required.

However, for effective and productive research in the field of heterogeneous catalysis, a knowledge of the methods and experimental techniques involved in the preparation of catalysts is indispensible. Detailed procedures for the preparation of a few well known catalysts and catalyst supports will serve to illustrate some of the guiding principles and unit operations discussed in the first part of this chapter.

Alumina Gel

Uses. Catalyst for dehydration of alcohols, and for catalyst base.

Reference. Elkin, Shull and Roess[66].

Reagents. CP $AlCl_3 \cdot 6H_2O$ and aqueous ammonia.

Procedure. Dissolve 1000 g of CP $AlCl_3 \cdot 6H_2O$ in 10 l of H_2O. Prepare an aqueous ammonia solution by diluting 840 ml. of concentrated ammonium hydroxide (about 28.5 per cent NH_3) to 1450 ml with H_2O. Add the ammoniacal solution to the $AlCl_3$ solution with stirring, to make the system basic to litmus. The pH will be approximately 8.0. Allow the precipitate to settle, then decant through a Buchner filter.

Wash five times with very dilute ammonia solution. In each case slurry the precipitate with 5 l of H_2O containing 5 ml of concentrated ammonia. Allow the precipitate to settle then decant through a Büchner funnel as in the original filtration. By the end of the fifth wash the precipitate is very difficult to filter as it has begun to peptize. If a water wash containing no ammonia is used, the peptization begins even during the first wash and filtration is exceedingly difficult.

Dry the washed precipitate in an electric oven for several hours at 100 to 150°C. Then calcine overnight at about 550°C in a muffle furnace.

Silica Gel

Uses. Catalyst base.

Reference. C. J. Plank[180].

Reagents. "N" brand water glass ($SiO_2/Na_2O = 3.22$) (Philadelphia Quartz Co.) and C.P. Hydrochloric acid.

Procedure. Prepare two solutions. Solution A = 500 ml of water glass (0.200 g SiO_2/ml) + 1000 ml of H_2O. Solution B = 245 ml of 4.0*N* HCl + 300 ml of H_2O. Cool both solutions to about 5°C, then add solution A to solution B with vigorous mechanical agitation. Pour into a flat tray.

The resulting sol will have a pH of approximately 6.2 and a gel time of about 2 minutes. The gel will be stiff enough to be cut into cubes (about one inch on a side) within 30 to 60 minutes. Transfer the cubes to a 3-l Büchner funnel as soon as possible. Treat immediately with 1*N* HCl for a 2-hour period. Repeat this treatment three times, using just enough of the HCl solution to completely cover the gel each time.

The gel is washed free of chloride ions and then dried for 4 hours at about 150°C. The product should be transparent at this stage. If any opacity is observed, the drying period should be prolonged. The dried solid is calcined in air at 550°C.

The calcined product has extremely small pores (radius ~ 10 AU) characteristic of the desiccant gels. The pore size of the product can be controlled over a very wide range using the same hydrogel, but changing the pH of the treating solution. For example, using 1 per cent NH_4Cl instead of 1*N* HCl gives a much lower surface area and density[181] and the pore size will be approximately three times as great.

Silica-Alumina Gel

Uses. Cracking petroleum gas oils.

Reference. C. J. Plank[180].

Reagents. CP aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ and HCl; "N" brand water glass ($SiO_2/Na_2O = 3.22$) (Philadelphia Quartz Co.)

Procedure. Prepare two solutions. Solution A = 465 ml of water glass (0.200 g SiO_2/ml) + 900 ml of H_2O. Solution B = 67 ml of HCl (4.0*N*) + 140 ml of $Al_2(SO_4)_3$ solution (0.05 g Al_2O_3/ml) + 400 ml of H_2O. Cool both solutions to about 5°C. Add solution A to solution B rapidly with strong mechanical agitation. Pour into a tray as soon as completely mixed. The gel time after complete mixing is about 45 seconds. In about one hour cut the gel into cubes about one inch, or less, on a side. Allow the gel to age for 48 hours then transfer to a 3-l Büchner funnel. Base exchange with a 2 per cent solution of $Al_2(SO_4)_3 \cdot 18H_2O$—three times for 2-hour periods, then once overnight. Wash with distilled water until free of sulfate ions. Dry at least 4 hours at about 140 to 180°C. The resultant gel pieces should be translucent. If any opacity shows up, continue the drying. Finally, calcine 10 to 15 hours at about 550°C.

Nickel-Aluminum Oxide (25 per Cent Ni-75 Per Cent Al_2O_3)

Uses. Hydrogenation of unsaturated hydrocarbons, dehydrogenation of cycloalkanes to aromatics.

Reference. Zelinskii and Komarewsky[249].

Reagents. CP $Al(NO_3)_3 \cdot 9H_2O$; $Ni(NO_3)_2 \cdot 6H_2O$; NaOH.

Procedures. Dissolve 454 g of $Al(NO_3)_3 \cdot 9H_2O$ in 3000 ml of water and cool solution to 5 to 10°C in an ice bath. Dissolve 200 g of NaON in 1000 ml of water and cool solution to 5 to 10°C. Add the sodium hydroxide solution dopwise to the aluminum nitrate solution while stirring vigorously. Time of addition should be between 1.5 to 2.0 hours. Dissolve 101 g of $Ni(NO_3)_2 \cdot 6H_2O$ in 600 ml of water, add 45 ml of concentrated nitric acid and cool solution to 5 to 10°C in an ice bath. Add nickel nitrate solution to sodium aluminate solution over a period of 0.5 to 1.0 hour. Stir the mixture vigorously during the addition. The light green precipitate is filtered on a 10-inch Büchner funnel. The filter cake is suspended in 2000 ml of water and stirred for 15 minutes. The mixture is filtered, and the cake again dispersed in 2000 ml of water. This washing procedure is repeated six times. The washed cake is cut into cubes (2″ x 2″), placed in an evaporating dish, and dried in an air oven for 16 hours at 105°C. The dried catalyst is crushed to give particles of approximately 8 to 12 mesh. Approximate yield 80 to 82 g.

Before use the required amount of catalyst is reduced in a stream of hydrogen (rate = 2 to 5 l per hour) for 16 hours at 350°C. The furnace temperature is raised to the reduction temperature over a 3-hour period.

Chromic Oxide Gel

Uses. Dehydrogenation, e.g., dehydroaromatization of *n*-heptane to toluene.

References. H. W. Kohlschütter[121] and R. F. Ruthruff[197].

Reagents. CP $Cr(NO_3)_3 \cdot 9H_2O$, $(NH_4)_2CO_3$ and conc. aqueous NH_3 (about 29 per cent).

Procedure. To prepare 1 mole of Cr_2O_3 gel make up four batches as follows. To 5 l of 0.10N $Cr(NO_3)_3 \cdot 9H_2O$ at 20°C add 2.5 l of 0.10N NH_3 solution dropwise with vigorous stirring. By continuing the stirring for 2 hours, the original precipitate disappears. The addition of the remainder of the ammonia is then continued at the same rate—about 6 ml per minute. After a permanent precipitate forms, the remainder of the alkali is added rapidly. The dark green hydroxide separates as a gelatinous precipitate. It is allowed to settle and the supernatant liquid is removed as completely as possible.

Ruthruff has showed that a more active catalyst is prepared if the gel is washed with a 5 per cent ammonium carbonate solution rather than H_2O. In washing, sufficient solution is added to bring the level up to the original mark. The suspension is stirred for one-half hour, allowed to settle and the supernatant solution again removed. This method of washing is repeated about five times, or until the precipitate begins to peptize.

The precipitate is filtered on a Büchner funnel. It is then oven dried at 100 to 105°C for 24 hours. Before use the catalyst should be stabilized by heating in hydrogen while bringing the temperature slowly to about 380°C.

Impregnated Chromia-on-Alumina Catalyst

Uses. Dehydrogenation or hydrogenation of hydrocarbons, e.g., dehydrogenation of *n*-heptane to toluene.

Reference. C. L. Thomas[222].

Reagents. Activated alumina (e.g., "Alorco," F-10) and CP chromic acid, CrO_3.

Procedure. Place 176 g of activated alumina of the desired mesh size in a 500-ml filter flask. Attach a dropping funnel through a one-hole stopper. At some point between the stopcock of the funnel and the rubber stopper make a flexible tubing connection which may be clamped shut. Attach the side arm of the flask to a vacuum pump. Dissolve 31.6 g of CrO_3 in sufficient water to make 65 ml of solution and place the solution in the dropping funnel. This volume of solution represents the average amount necessary to fill the actual pore volume of the recommended activated alumina. If some other activated alumina is used, the pore volume for that material should be determined* and the appropriate correction made to the volume of the CrO_3 solution.

Evacuate the flask, then admit the CrO_3 solution into the flask while shaking the catalyst to assure uniform absorption of the liquid. The presence of the flexible tubing in the line from the dropping funnel permits the flask to be shaken without disturbing the liquid remaining in the funnel. By having a clamp on the flexible tubing it is possible to add the liquid in small portions.

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* The pore volume may be determined by weighing a sample of the activated alumina, saturating it with water, centrifuging off all excess water and then reweighing the sample. The gain in weight is essentially equivalent to the pore volume in ml/g catalyst.

When all the solution has been added and the alumina is uniformly impregnated the catalyst is removed from the flask, dried at about 150°C and finally calcined in hydrogen at about 550°C.

Phosphoric Acid on Kieselguhr

Uses. Polymerization of alkenes.

Reagents. 85 per cent orthophosphoric acid, and Kieselguhr (Baker's).

Procedure. Place 75 g of kieselguhr in an evaporating dish and add 240 ml of 85 per cent phosphoric acid slowly, while stirring the mixture constantly. Transfer the thick paste to a shallow copper dish. Place the dish on a hot plate and stir constantly until the paste is dry (temperature of paste should be kept between 100 to 150°C). The solid catalyst is crushed to 8 to 12 mesh particles.

Before use the "solid" phosphoric acid catalyst is further dried for 1 hour at 200 to 250°C.*

Molybdenum Sulfide (MoS_2)

Uses. Destructive hydrogenation of organic compounds.

Reference. B. L. Moldavskii and S. E. Levshitz[148].

Reagents. CP Ammonium paramolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$; concentrated ammonia; hydrogen sulfide.

Procedure. Dissolve 162 g of ammonium paramolybdate in 1000 ml of distilled water and add 1100 ml of concentrated ammonia. Bubble hydrogen sulfide at a slow rate through the solution until it is saturated (time of saturation 4 to 6 hours). The color of the solution changes from yellow to a dark red. The H_2S-saturated solution is heated to 60°C and 625 ml of $3N$ HCl added slowly while vigorously stirring the solution. After complete addition of HCl the brown precipitate is filtered from the mother liquor. The precipitate is removed from the filter and dispersed in 1500 ml of $3N$ HCl solution by stirring vigorously for 15 minutes. The resulting mixture is filtered. The precipitate is washed three times with $3N$ HCl and after the final wash filtered from the mixture. The filter cake is washed three times with 96 per cent alcohol (200 ml each wash) and then dried overnight in an oven at 110°C. The dried catalyst is dark brown in color. The approximate weight is 300 g.

Reduction of molybdenum trisulfide to the disulfide is obtained by reducing the dried solid in a stream of hydrogen at 350 to 375°C for 1 hour. This is carried out by introducing the desired amount of the trisulfide into a glass reaction tube which is placed in a cold furnace. The furnace is raised slowly to 350 to 375°C (approximately 2 to 3 hours) while a slow

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* If catalyst is heated above 350°C, its activity will be lowered due to conversion of orthophosphoric acid to metaphosphoric acid.

stream of hydrogen is passed through the tube. After the catalyst has reached the reduction temperature, the hydrogen is continued for one hour.

The reduced catalyst is black in color and pyrophoric if exposed to air. The reduced catalyst should be handled only in an inert gas atmosphere.

Fischer-Tropsch Catalyst

100 Co-6 ThO_2-12 MgO-200 Kieselguhr

Uses. Synthesis of hydrocarbons from hydrogen and carbon monoxide.

Reagents. CP Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$); thorium nitrate $Th(NO_3)_4 \cdot 4H_2O$); sodium carbonate (Na_2CO_3). Kieselguhr (Baker's or Mansville's Filter-cel). Powdered magnesium oxide.

Procedure. Dissolve 246 g of $Co(NO_3)_2 \cdot 6H_2O$ and 6.3 g of $Th(NO_3)_4 \cdot 4H_2O$ in 1000 ml of water and add additional water to give final volume of 1300 ml. Heat solution to boiling point. Disperse 100 g of kieselguhr and 6.0 g of magnesia in 500 ml of water and heat the slurry to the boiling point. Dissolve 92 g of sodium carbonate in 500 ml and heat solution to boiling point. The boiling slurry of kieselguhr and magnesia and solution of sodium carbonate are added simultaneously to the boiling solution of the nitrates with vigorous stirring. The resulting slurry is filtered and the filter cake washed with distilled water until the filtrate is free of sodium ions. The washed cake is cut into cubes, transferred to an evaporating dish and dried overnight in an oven at 110°C. The dried solid is crushed and screened to 8 to 12 mesh particles.

The catalyst is slowly heated to 400°C in a stream of hydrogen (2 hours to get to temperature) and held at 400°C for 2 hours. The rate of hydrogen should be adjusted to a gas space velocity of approximately 3000 ml of hydrogen per ml of catalyst per hour.

The induction of this catalyst is described in detail by Anderson *et al.*[14]

Fused Iron Synthesis Catalyst

Uses. Synthesis of ammonia, hydrocarbons, and alcohols.

Reference. H. H. Storch, Norma Golumbic and R. B. Anderson[212].

Reagents. CP Chemicals: MgO, Cr_2O_3, $KMnO_4$, K_2CO_3, SiO_2 and powdered Fe (electrolytic or carbonyl), or commercial magnetite (Fe_3O_4).

Procedure. Mix the following quantities of dry powdered materials: 187 g of Fe_3O_4, 9.2 g of MgO, 1.3 g of Cr_2O_3, 0.21 g of $KMnO_4$, 1.65 g of K_2CO_3 and 1.2 g of SiO_2. If a high temperature furnace, such as an induction furnace, is available, place the mixture of powder in the furnace in an alundum crucible and fuse at about 1550 to 1600°C.

If, on the other hand, a high temperature furnace is not available, the following experimental technique may be used. Replace the Fe_3O_4 by 135.3 g of powdered pure iron. Place the powder in a 5 to 6 inch dished steel head (about ½-inch thick) which in turn sits tilted in a second dished head. The bottom head is placed on a transite sheet about ½-inch thick to protect the bench top from heat damage. The mixture is ignited by a glassblower's torch and the iron burned to the oxide, using a slow stream of oxygen supplied from a 1-inch pipe. The rate of oxygen supply is, of course, kept low enough not to blow the powder out of the dish, but rapid enough for adequate oxidation.

All the iron must be completely burned so that the melt can be cast to yield a hard brittle product. The use of the dished heads permits this to be accomplished rather easily. While directing the oxygen stream from the pipe onto the powder with one gloved hand the bottom dished head is rotated with the other hand. Since the dish containing the powder is tilted, the rotating of the bottom head brings fresh powder to the surface and facilitates oxidation of all the powder. That is, one does not obtain merely a surface oxide coating over a fused iron melt.

When complete oxidation of the iron has been achieved the melt is cast. If the product is not sufficiently oxidized, it will not be brittle, as it should be. In that case the preparation may be repeated or the product screened to recover those particles which do have the required properties.

Copper

Uses. Dehydrogenation of alcohols to aldehydes.

Reagents. CP $Cu(NO_3)_2 \cdot 3H_2O$; NaOH.

Procedure. Dissolve 285 g of $Cu(NO_3)_2 \cdot 3H_2O$ in 1600 ml of water and cool in an ice bath to 10 to 15°C. Dissolve 100 g of NaOH in 600 ml of water and cool to 10 to 15°C. Add sodium hydroxide solution dropwise to the stirred copper nitrate solution over period of 1 to 1.5 hour. The light blue precipitate is filtered on a 10-inch Büchner funnel. The filter cake is suspended in 2000 ml of water and stirred vigorously for 15 minutes. The mixture is filtered and the cake again suspended in 2000 ml of water. The washing procedure is repeated six times. The washed cake is cut into cubes (2″ x 2″), placed in an evaporating dish, and dried in an air oven at 105°C for 16 hours. The dried catalyst has a dark gray color. The catalyst is crushed to give particles of 8 to 12 mesh. The approximate yield is 70 to 75 g.

Before use, the catalyst is reduced in a stream of hydrogen (rate, 2 to 5 l per hour) for 4 hours at 300 to 350°C.

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CHAPTER 8

MAGNETISM AND CATALYSIS

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INTRODUCTION

It has often been remarked that many elements of major importance in catalysis are those which, like iron and nickel, show interesting magnetic properties. That this is no coincidence is now beginning to emerge with the proved relationship between activity on the one hand and semiconductivity, *d*-band character, and unpaired electrons on the other. As recently pointed out by Maxted[15], there is considerable evidence that certain types of catalytic activity are related to *d*-band deficiency or, to express it another way, to the degree to which *d*-orbitals are filled with paired electrons. Thus, for catalytic hydrogenation in the series Ru, Rh, Pd, Ag, and the series Os, Ir, Pt, Au, there are rises and falls of activity and paramagnetic susceptibility which seem too nearly parallel to be accidental. This view is further strengthened by the observation that poisons for the above catalysts are those substances which can eliminate the *d*-band deficiency by supplying electrons. Such substances are atoms or groups having free electron pairs in the valency shell, metals with half filled or completely filled *d*-bands, and compounds with unsaturated bonds. In at least one case[9] it has been shown that the adsorption of such a poison, dimethyl sulfide on palladium, causes a decrease of paramagnetism which is due, presumably, to filling of the partially unoccupied *d*-band of the metal by electrons from the free pair in the sulfide. This is not to say that there is at present any research area in which the course of a chemical reaction may be influenced by appropriate choice of a magnetic field[23]. With one or two exceptions, the application of magnetism to catalysis is like the application of x-rays and electron diffraction. Magnetic susceptibilities and related quantities serve as tools for structural identification of the catalyst.

Magnetic methods are of the greatest use for those elements and compounds which, when serving as catalysts or catalyst components, are either paramagnetic like chromia gel, or ferromagnetic like the iron carbides. These methods fall into two main classes: (1) those in which the dependency of paramagnetic susceptibility on temperature gives information concerning the oxidation state and degree of dispersion of the active element; and (2) those in which the identification and rate processes of a ferromagnetic component are established by thermomagnetic analysis. There are, in addition, some methods such as the nuclear induction experiment which may be expected to yield useful information in the future.

In this chapter some of the fundamental principles and current theories of magnetism will be reviewed. The chief applications of paramagnetism and of thermomagnetic analysis will be presented and the experimental methods for susceptibility and for ferromagnetic studies given. These will be followed by a description of the less well established techniques and their possible uses.

THEORIES OF MAGNETISM

Definitions[2]

The magnetic quantities of principal concern in catalysis are the field strength, the specific magnetization, and the susceptibility. Magnetic field strengths are expressed in oersteds, but the dimensional characteristics of the specific magnetization and the susceptibility are obscure and for the present purposes they must be considered as dimensionless.

A substance placed in a field H, produces an induction B, such that $B = H + 4\pi I$. The quantity I is called the intensity of magnetization; divided by the density this becomes $\sigma = I/d$, or the specific magnetization. This quantity is of primary interest in connection with ferromagnetic materials. If I, the intensity of magnetization, is divided by H, there is obtained $\kappa = I/H$, or the magnetic susceptibility per unit volume. This, divided by the density, yields the susceptibility per unit mass, $\chi = \kappa/d$. The susceptibility is of primary concern in connection with paramagnetic and diamagnetic substances.

Ferromagnetism, as in iron, tends to be a strong effect, dependent on both field strength and on temperature. Paramagnetism is a very weak effect, generally dependent on temperature; diamagnetism is an extremely weak effect, independent of field and generally independent of temperature. Diamagnetic susceptibilities are considered to be negative in sign, while para- and ferromagnetism are positive. The specific magnetization, σ, of iron, a typical ferromagnetic, is about 250; the susceptibility per gram of chromium sesquioxide, a paramagnetic, is about 30×10^{-6}, while that of water is -0.72×10^{-6}. The attraction of iron for a magnet exceeds that of Cr_2O_3, weight for weight, by over a million-fold.

Theory of Diamagnetism[35]

An electron moving in a closed orbit gives rise to a magnetic moment. If this electron is subjected to a magnetic field the electron will precess in such a fashion as to produce an additional, smaller, magnetic moment opposite in sign to that originally present. In most chemical substances all electrons are paired owing to the formation of covalent bonds. This pairing results in cancellation of all permanent magnetic moments but leaves the small negative precessional moment. This is the cause of diamagnetism, which will be present in all substances even though the substance may also contain a positive moment. For the purposes of research in catalysis almost the only application of diamagnetism lies in the small diamagnetic corrections which must be made in the study of paramagnetic substances.

The classical theory of diamagnetism is attributed to Langevin, and substantially the same result is given by quantum mechanics. In brief, it is shown that diamagnetism is a function of the square of effective orbital radii of all electrons present in an atom or molecule. Obviously, those electrons with large orbital radii will be the principal contributors to diamagnetism. In a few cases, such as in aromatic compounds, and especially in graphite, the effective radius for one or more electrons is quite large. This yields a greatly enhanced diamagnetism which may be restricted to one crystallographic direction. The dependence of diamagnetism solely on electronic orbital radii explains why, in general, diamagnetic susceptibilities are independent of temperature and of field strength.

Theory of Paramagnetism[35]

Those atoms or molecules possessing an odd number of electrons have permanent magnetic moments and are paramagnetic. Thus, nitric oxide, cupric ion, and triphenylmethyl are paramagnetic. Furthermore, many atoms and ions, which may or may not have an odd number of electrons, are paramagnetic because electrons in the 3*d*, and similar partially filled energy levels, tend to remain unpaired unless forced to do so. Thus the ions Fe^{+3}, Ni^{+2}, Nd^{+3}, and U^{+4} are all paramagnetic.

Under the influence of an external field the permanent magnetic moment present in a paramagnetic atom or molecule tends to orient against thermal agitation. A fairly simple application of statistical mechanics shows that the magnetic susceptibility under these circumstances will vary inversely as the absolute temperature. The law $\chi = C/T$ is known as the Curie law after Pierre Curie who first discovered it experimentally. The quantity C is known as the Curie constant. In a substantial number of cases the experimental data are better represented by the Curie-Weiss law, $\chi = C/(T + \Delta)$, in which Δ is a constant, the significance of which will be described below.

It may readily be shown that the magnetic moment is given by $\mu = 2.84 \sqrt{C_M}$ where μ is given in Bohr magnetons and C_M is the Curie constant per mole. With a few exceptions, the magnetic moment is independent of temperature.

As electrons have both spin and orbital motions it might be expected that both would contribute to the magnetic moment. This is actually the case for most ions of the rare earth elements, but these elements are of minor importance in catalysis. Our attention will be directed principally to the elements, such as iron, in the first transition series.

Ions of the Transition Elements[24]

It is an illuminating fact that the magnetic moments of many paramagnetic ions are accurately represented by the so-called "spin-only" formula, $\mu = \sqrt{n(n+2)}$ where n is the number of unpaired electrons in the ion. Thus in its $3d$ orbitals the Fe^{+3} ion has five unpaired electrons which may be represented thus:

$$\begin{array}{lcc} & \overbrace{}^{3d} & 4s \\ Fe^{+3} & \odot\ \odot\ \odot\ \odot\ \odot & \circ \end{array}$$

The experimentally found moment in a variety of ferric salts is quite close to 5.9 Bohr magnetons. This agreement is found to be quite accurate for ions which are in S spectroscopic states, such as Mn^{+2} and Fe^{+3}. The fact that the spin-only formula gives satisfactory agreement with many other transition elements such as V^{+4}, Cr^{+3}, Mn^{+4}, Cu^{+2}, must mean that in these elements the orbital contribution to the magnetic moment is quenched by the electric fields of neighboring ions and oriented solvent molecules. The only serious discrepancy is found for Co^{+2} in which the spin-only moment of 3.9 is much lower than the experimental of over 5. Other ions in which the experimental moment is sometimes moderately different from the spin-only value are Ni^{+2}, Fe^{+2}, and Mn^{+3}. The ion Cu^{+2} in some environments gives a moment nearer 2.0 than 1.8 which is the spin-only value for one unpaired electron.

It will be clear from the above that a change of oxidation state will generally produce a change of magnetic moment. This is especially valuable when one of the states possesses no unpaired electrons as in the reduction of cupric ions to cuprous. The method has been used for identification of ionic species and for rate studies involving oxidations and reductions such as, for instance, the reduction of manganese dioxide in an operating dry cell.

The formation of a coordination compound not infrequently involves a change in the number of unpaired electrons. Thus, the iron in potassium ferricyanide has a moment corresponding to only one unpaired electron because the other four normally present in ferric ion are paired in covalent bond formation with the cyanide groups.

Other factors which may alter magnetic moments include the influence of one magnetic atom or ion on another. This factor, of major importance in the applications of magnetism to catalysis, will be discussed in the following sections.

Exchange Forces

In ferromagnetic substances there may be virtually complete alignment of the atomic magnetic moments in an applied field of quite moderate intensity. In order to account for this phenomenon, Weiss introduced the idea of a "molecular field" which enables the elementary moments to work cooperatively in overcoming thermal agitation. This idea has proved fruitful and has received theoretical justification in quantum theory.

The Heisenberg exchange interaction and its importance in modern valence theory is well known to chemists. The importance of this effect in magnetism is perhaps less familiar. If adjacent atoms possess an unoccupied, or incompletely occupied, atomic orbital, and if there are available electrons for the occupation of this orbital, then the exchange (or resonance) of electrons will produce enough energy to modify the properties of the system. The exchange integral may be either positive or negative—both being important in magnetism. In gases and in molecular liquids and solids the exchange forces are negligible so far as their magnetic effects are concerned. But in nonmolecular solids containing transition elements such as the metals themselves, the oxides or sulfides of iron, manganese and similar substances the exchange forces are of paramount importance in determining the magnetic properties. In some cases these forces produce ferromagnetism, in others, antiferromagnetism.

Ferromagnetism[5]

Ferromagnetic substances are characterized by very large inductions which are a function of field strength up to the field at which the substance is said to be saturated. The magnetic moment per atom in ferromagnetics may readily be calculated by extrapolation of the saturation magnetization. Many ferromagnetic substances show the phenomena of hysteresis and of residual magnetism but thus far these effects have not played a part in the applications of magnetism to catalysis.

Above a temperature characteristic of each ferromagnetic substance the induction drops almost to zero. This characteristic temperature is known as the Curie point, above which the substance generally becomes merely paramagnetic. The Curie point serves as a means of identification not unlike the melting point of an organic compound.

Although ferromagnetism is a cooperative phenomenon the minimum particle, or "domain," size which will develop ferromagnetism is not known with certainty. Various estimates, both theoretical and experimental, suggest a minimum particle size of from 10 to 40 Å. The problem is one of considerable interest in the study of highly dispersed substances such as most catalysts and it would be desirable to have more precise information on this point.

Ferromagnetism is found only in those elements which possess an unfilled lower energy level such as the 3*d* in iron, cobalt, and nickel, and the 4*f* level in gadolinium. Further requirements are that the atoms thus possessing permanent moments should be arranged about each other in proper coordination and at an optimum inter-atomic distance. The structural requirements for ferromagnetism are fairly severe and this accounts for the rather moderate number of such substances actually known. Exchange effects between other than nearest neighbors appear to be of minor but not negligible importance.

Antiferromagnetism[7]

A substantial group of elements and compounds exhibit an effect known as antiferromagnetism. This phenomenon is characterized by a susceptibility which increases with rising temperature up to a critical point known as the antiferromagnetic Curie point. Above this temperature the substance behaves in general like a normal paramagnetic.

Antiferromagnetism is believed to be brought about by a cooperative effect not unlike that causing ferromagnetism, except that the electron spins in a domain tend to lock antiparallel rather than parallel. The theory of the effect is by no means complete but is engaging the attention of numerous investigators because of its general bearing on the properties of the solid state. This circumstance is fortunate for catalytic chemistry because many substances such as Cr_2O_3, MnO_2, α-Fe_2O_3, NiO, and CuO are typical antiferromagnetics and are well known as catalysts.

Recent theoretical developments by Néel and others have shown that in all probability antiferromagnetism in systems such as those above is caused by exchange interaction between second nearest paramagnetic neighbors. Thus, in the case of MnO it has been shown that exchange must almost certainly go through an oxygen, and that, because of the shape of the wave-function involving *p* orbitals in the oxide ion, it is much more probable that interaction goes in a straight line from one manganese through the oxygen to another manganese. Such manganese ions are actually farther from each other than the nearest manganese neighbors are to each other, but to go through an oxygen to a nearest manganese neighbor involves a right-angle bend.

Application of Magnetic Susceptibilities to Catalyst Structure

Gels[30]

Many substances of interest as catalysts may readily be prepared in a form characterized by high specific surface and high activity. The familiar chromia gel, for example, is one such substance.

Such substances tend to be amorphous, hence x-ray diffraction methods seldom yield much information of interest concerning their structure. It has been found, however, that gels of the paramagnetic oxides such as chromia have magnetic properties which are quite different from those of the same oxide in the crystalline form. Figure 1 shows the magnetic susceptibility plotted against temperature for a typical crystalline oxide, and for the same oxide in amorphous, or gel, form. It is understood that these two states of matter may not be identical in composition because the gel often contains a few per cent of water. The water content may be reduced by appropriate procedures. From a point of view of structure, the amorphous disperse state and the crystalline or massive state differ greatly. Figure 1 applies generally to most of the transition group oxides such as VO_2, Cr_2O_3, MnO, Mn_2O_3, MnO_2, and α-Fe_2O_3. In some, the antiferromagnetic Curie point is well defined, as in MnO; in others, it is poorly defined, as in Cr_2O_3.

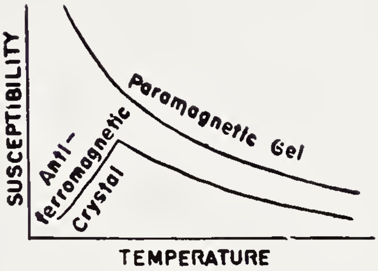

Figure 1. Magnetic susceptibility of a typical crystalline antiferromagnetic oxide and of the same oxide in the form of a catalytically active gel. Courtesy "Encyclopedia Chemical Technology," Vol. 8, p. 623—Sellwood (Interscience).

For the amorphous state, the Curie-Weiss law is followed throughout the observable temperature range, and there is no trace of the Curie point. Furthermore, the susceptibility per gram of gel is definitely higher than that of the crystal, even above the Curie point. Examination of the data shows that for Cr_2O_3, for example, the magnetic moment in the gel corresponds to three unpaired electrons, and that the chief magnetic difference between gel and crystal lies in the quantity Δ, the Weiss constant. Use of the magnetic method in determining gel structure seems therefore to rest on establishing a relation between structure and the Weiss constant.

An early, provisional theory of antiferromagnetism gave the Weiss constant as $-\Delta = 2JzS(S + 1)/3k$, where J is the exchange integral between nearest paramagnetic neighbors, z is the number of nearest paramagnetic neighbors, S and k are the spin quantum number and the Boltzmann constant, respectively. For a typical chromia gel, $\Delta = 100°$; for crystalline Cr_2O_3, above the Curie point ($\sim$ 50°C), $\Delta = 300°$. Hence, assuming the exchange integral to be the same in the two cases, and z to be nine in the crystal, we may write $z_{gel} = z_{cryst}\ \Delta_{gel}/\Delta_{cryst}$, or $z_{gel} = 9 \times 100/300 = 3$.

The many assumptions in the above procedure were, perhaps, justifiable only because they gave a result not inconsistent with other information concerning gel structure. A value of three for z calls for an exceptional degree of attenuation such as could be achieved only by monatomic sheets or by threads no more than a few Ångstroms in diameter. The specific surface area of chromia may be as high as 600 m^2g^{-1} which similarly calls for an extraordinary degree of attenuation.

The development of a new and expanded theory[7] of antiferromagnetism with its emphasis on second nearest neighbors suggests that it may soon be possible to establish a precise relationship between susceptibility and structure. For the present, we may say that we have a simple tool which will give quite definite qualitative information concerning the degree of dispersion of many active catalysts. The information obtained is parallel to, but not quite the same as that obtained by surface area measurements. The method, however, has its chief application in supported catalysts where estimation of the dispersion of the promoter on the surface of the support may be a most difficult problem.

One of the many interesting points in the magnetic properties of gels is in connection with hydrous ferric oxide. This substance shows the effects indicated in Figure 1, except that the magnetic moment of iron in the gel tends to be about 4.4 instead of 5.9 Bohr magnetons. This effect has apparently been recognized, if not explicitly stated, for a long time, but as yet no very satisfactory explanation has been given. The low moment has been attributed to a change of orbital hybridization leading to internal pairing of two of the five d electrons, or alternatively to a series of bonds between adjacent iron ions. The latter view is supported by the fact that the iron in solid solutions of Fe_2O_3 in Al_2O_3 shows a low moment down to quite low concentrations of iron, below which the moment rises to normal.[32]

Supported Oxides

The concentration of promoter in a catalyst may, as is well known, be varied almost at will. For instance, in a chromia-alumina dehydrocyclization catalyst the concentration of chromia may be varied within very wide limits by altering the chromium concentration in the solution used in the impregnation step. Figure 2 shows the susceptibilities per gram of chromium in such a series of catalysts consisting of chromia supported by impregnation and ignition on gamma-alumina[10]. The curve shown was obtained by susceptibility measurements at liquid air temperature where the magnetic changes observed become more striking. Such a curve is called a susceptibility isotherm. A few details not covered in the literature* will be given here as they apply in general to all the supported systems so far studied.

Alumina free from ferromagnetism and of a suitable high specific surface may be prepared by dissolving pure aluminum in potassium hydroxide, then by precipitating the alumina, first with nitric acid, and finally with carbon dioxide. The so-called gamma-alumina obtained in this way should have a diamagnetic susceptibility of about -0.4×10^{-6}, which is independent of field strength and of temperature. This dried material is now impregnated with a chromic acid solution, filtered (not washed), dried, and, for the purposes of this work, reduced in hydrogen. By altering the concentration of the chromic acid solution used for the impregnation it is possible to vary the chromium concentration in the finished catalyst within wide limits. The limits used in the work referred to were 0.1 to 40 per cent Cr.

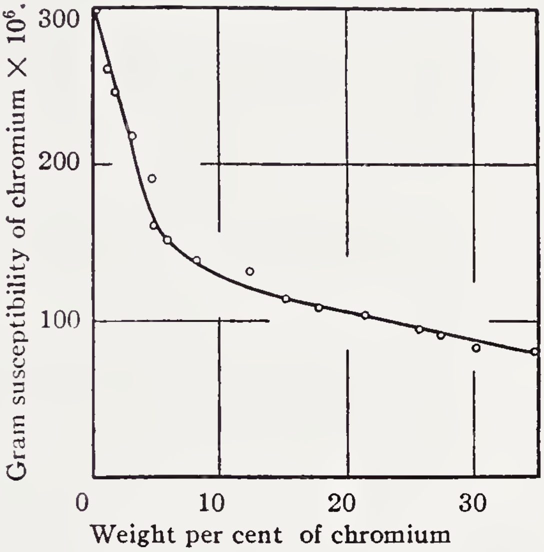

Figure 2. Susceptibility isotherm for supported chromia on high-area alumina, at −190°C[10].

Magnetic susceptibilities are measured for all samples at several temperatures, and the susceptibility per gram of chromium is found on the

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* The reader is referred to the original papers for the experimental details involved in the determination of the susceptibility isotherm.

assumption that the susceptibilities of Cr^{+3}, Al^{+3}, and O^{-2} are additive, and that the susceptibilities of Al^{+3} and of O^{-2} are independent of concentration. It is then found that the reciprocal susceptibility of Cr^{+3} is linear with temperature over a wide temperature range, or, in other words, that the Curie-Weiss law is followed. The data are characterized by a very large increase of Cr^{+3} susceptibility at low concentrations. This increase becomes larger as the temperature is lowered. Calculation of the magnetic moment and of the Weiss constant shows that while the moment is almost constant (for the Cr_2O_3-Al_2O_3 system) over the whole concentration range, the change of Cr^{+3} susceptibility is almost entirely brought about by a change of the Weiss constant. This constant changes from virtually zero at low chromium concentrations to values of 200 to 300° at the highest chromium concentrations. It may, therefore, be said, following the argument presented earlier, that the chromium ions are increasingly dispersed as the concentration is lowered, and that we have a method for comparing degrees of dispersion in different chromia-alumina catalysts.

Susceptibility isotherms, in general resembling those for chromia-alumina, are obtained for virtually all transition group oxides supported on high area alumina, silica, magnesia, or rutile. The rise of susceptibility at low promoter concentrations suggests in every case increasing dispersion of the catalyst on the support with increasing dilution, but the detailed interpretation of the isotherms may be somewhat different for each element. Thus, for chromia the interpretation is similar to that already suggested for chromia gel. It is possible in this way to compare the dispersion of chromia on two chromia-alumina catalysts. For the dehydrocyclization of *n*-heptane the catalytic activity appears to be linear with chromia dispersion. It is thus possible to predict the relative activity of two chromia-alumina catalysts on the basis of magnetic susceptibility measurements alone.

Another deduction from the magnetic studies concerns the manner in which the chromia is aggregated on the surface of the alumina. Specific surface areas of 200 to 300 m^2g^{-1} are common in the aluminas used for supported chromias and it is easily shown that a typical catalyst containing 10 per cent chromia does not contain nearly enough chromia to cover the alumina surface even in the thinnest possible continuous layer, the monatomic layer. Yet the magnetic results clearly indicate that some aggregation of chromium ions occurs at that concentration because the Weiss constant is far from zero, which is the value it actually approaches at the lowest concentrations measurable, namely, about 1 per cent. It must, therefore, be concluded that the chromia is at least partially aggregated into microcrystals at the concentrations often used in this catalyst system. This view of the surface leaves large portions of the alumina bare of promoter. It may be concluded that the chromia-alumina catalyst at concentrations of chromia in the neighborhood of 10 per cent consists of islands of chromia microcrystals relatively far apart, but that isolated chromium ions, that is to say, a true two-dimensional solid solution of chromia, probably does not occur. This view has important consequences in the interpretations of activity and these are discussed below.

In the case of supported chromia, interpretation of the susceptibility isotherm seems to be concerned only with the question of dispersion. This appears to be the case also for supported cupric oxide[25], but for several other systems the interpretation is considerably more complicated. In the case of supported manganese oxides[33], for instance, not only the Weiss constant but the magnetic moment also changes with changing manganese concentration. If manganous nitrate is impregnated on to high area alumina, then decomposed at about 200°C, the oxidation state of the manganese, and hence the magnetic moment of the manganese, is found to be a function of manganese concentration. At low concentrations the moment is about 4.8, corresponding to manganese in the $+3$ oxidation state, while at high manganese concentrations the moment is 3.8 and the oxidation state is $+4$. These oxidation states are confirmed by direct chemical analysis.

The influence of support structure on the oxidation state, and hence the structure of a supported oxide just described, is an example of the inductive action found for several catalyst systems, including manganese-rutile, iron-rutile[31], nickel-magnesia[11], nickel-alumina, and nickel-rutile. This effect has been shown to influence catalytic activity in some of these systems. For instance, in the catalytic decomposition of hydrogen peroxide by supported manganese oxide on alumina[18], the activity per gram of manganese reaches a high peak very close to the average oxidation state of 3.5. This behavior suggests that a necessary condition for activity in this system is the presence of a crystal interface involving the active element in two different oxidation states. There is now also a substantial amount of evidence that a certain minimum "domain" is essential for activity. This has been demonstrated for the hydrogenation of benzene over nickel-alumina[11], and for the oxidation of carbon monoxide over supported oxides of manganese, iron, and copper[19].

Many other properties of the susceptibility isotherm have been studied; a few of these will be mentioned. Some oxide phases of transition metals show ferromagnetism. When this occurs it greatly confuses interpretation of the magnetic data. Examples are sometimes found in systems containing vanadium[26] or chromium, and more often than not in iron oxide samples. Supported iron oxide[31] shows the anomaly previously referred to in connection with iron oxide gel, namely, that the magnetic moment tends to be low. By appropriate impregnation procedures it has been found possible to raise the moment to about 5.0 magnetons. These procedures involve washing the support with acid, and impregnating from an acid solution. It might be expected that a kind of infinite magnetic dilution would be reached at low promoter concentrations and that the susceptibility isotherm would become independent of concentration. But the only case in which the condition is even approached is possibly supported cupric oxide[25]. Another point is that changing the support phase, as from one polymorphic form of alumina to another, makes little difference in the shape of the isotherm, but gross changes in surface area have a marked effect, as does changing from one support to another, expecially in the low concentration ranges of the promoter. The presence of alkali in the support has a marked dispersing effect[27]. Molybdenum does not lend itself to the susceptibility isotherm method because the oxides of this element all seem to be diamagnetic or to have a small paramagnetism which is independent of temperature. This has been attributed to a species of covalent bonds between adjacent molybdenum atoms in the dioxide. The rare earth elements show virtually none of the effects described for the obvious reason that in these elements the 4*f* electrons responsible for the paramagnetism are protected by outer electron shells from external influence. The case of cobalt is also somewhat obscure by virtue of the rather strong spin-orbital coupling in the Co^{+2} ion. Rather surprisingly, it is found that tungsten and uranium oxides behave more like chromia than like either molybdena or the rare earths.

It will be clear that some of the catalysts described above are actually used in the reduced, or metallic state, rather than as oxides. If the metal happens to be diamagnetic, as copper, then useful data may sometimes be obtained by magnetic measurements on the reduced phases. In any event, the structural information obtained from the oxide phase is often of value for the reduced phase because it has been shown, by susceptibility measurements on reduced and reoxidized supported cupric oxide, that surface migration of supported elements during alternate reduction and oxidation is not nearly so rapid as was formerly believed. Extension of measurements such as those described seems to be a rich field for investigation. If the reduced phase happens to be ferromagnetic as iron, cobalt, and nickel, then the methods of study become those of thermomagnetic analysis described below.

The various supported catalyst systems so far studied by the method just described are listed in Table 1. In some cases, such as the chromia-alumina and manganese oxide-alumina systems, the magnetic and catalytic properties have been investigated thoroughly over a wide range of concentrations and conditions. In other systems, such as urania-alumina, the measurements have been limited to one sample only. The word "yes" under the heading Catalytic Activity indicates that the activity for at least one reaction has been studied in relation to the magnetic results.

TABLE 1

Promoter	Support	Dispersion Effect	Valence Inductivity	Catalytic Activity	Ref.
Cr^{+3}	Al_2O_3	yes	probably	yes	1
Co^{+2}	Al_2O_3	yes	doubtful	—	2
Cu°, Cu^{+2}	Al_2O_3	yes Cu^{+2}	no	yes	3
Fe^{+3}, Fe^{+4}	Al_2O_3, TiO_2, SiO_2	yes	yes	yes	4
Mn^{+3}, Mn^{+4}	Al_2O_3, TiO_2 and modified supports	yes	yes	yes	5
Mo^{+3}, Mo^{+4}	Al_2O_3	no	—	—	6
Nd^{+3}	Al_2O_3	no	—	—	6
Ni^{+2}, Ni^{+3}, Ni^{+4}	MgO, Al_2O_3, TiO_2	yes	yes	yes	7
Pd°, Pd^{+2}	Al_2O_3	no	—	—	2
Re^{+3}	Al_2O_3	no	—	—	6
Ru^{+3}	Al_2O_3	no	—	—	6
Ag°, Ag^{+1}	Al_2O_3	no	no	—	6
Ti^{+3}	Al_2O_3	yes	probably	—	2
W^{+4}	Al_2O_3	yes	—	—	6
U^{+4}	Al_2O_3	yes	—	—	6
V^{+3}, V^{+4}	Al_2O_3	yes	probably	—	8

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The heading Dispersion Effect refers to the increase of susceptibility observed at low concentrations as with chromium in the chromia-alumina system.

THERMOMAGNETIC ANALYSIS

Identification of Catalyst Components

It was pointed out above that ferromagnetic substances have a critical temperature, called the Curie point, above which the specific magnetization drops to near zero. Curie points for different ferromagnetic substances vary widely as do specific magnetizations below the Curie point. A few examples will show the wide range of values encountered. For iron $T_c = 770°C \pm 10°$, $\sigma_{25°} = 218 \pm 2$; for Ni the values are 355° and ~ 55; for Fe_3O_4, 572° and 95; for Fe_3C, 210° and 135. Curie points may be used for the identification of certain catalyst components in much the same way that melting points may be used for the identification of organic compounds. The Curie point is independent of the quantities involved, and of the rate of heating; it depends on the field strength to a slight degree only. But the Curie point is markedly dependent on the purity of the sample. For instance, a few per cent of copper in solid solution in nickel will depress the Curie point many degrees. The mere mechanical presence of an impurity does not affect the Curie point. In most cases an estimate of quantity present may be made by consideration of the specific magnetization. In a mechanical mixture of, say Fe_3C and Fe_3O_4, the specific magnetizations of the components are additive, depending on the quantities present.

When two or more ferromagnetic components are present the Curie point of each will, in general, be indicated. Resolution may become increasingly difficult as the Curie points approach each other. In many cases at least three ferromagnetic components have readily been identified. In favorable cases, a three-component mixture may be analyzed quantitatively by measuring the specific magnetization at temperature intervals lying between the several Curie points. However, the precision of this procedure will obviously depend on the spacing of the Curie points.

Qualitative and quantitative analysis by this procedure, referred to as thermomagnetic analysis, is a very powerful tool, but one which is unfortunately limited to the rather moderate number of ferromagnetic substances. The method is further complicated by the possibility of chemical reactions and solution processes which often occur in solids at temperatures in the neighborhood of the Curie points. This, however, has been developed into a major tool for the study of reactions in the solid state.

There is another aspect of thermomagnetic analysis which may be expected to yield interesting results. There is a large class of cubic oxides known as ferrites, or spinels, of which $MgFe_2O_4$ is an example. The oxides Fe_3O_4 and possibly γ-Fe_2O_3 belong to this group. Most of these substances are ferromagnetic but there has been no method for predicting the magnetic moment. Néel[21] has proposed a theory which makes it possible to account for the observed moments. He points out that the iron in such compounds may occupy two kinds of sites. He assumes that exchange interaction between nearest neighbor irons in the same kind of sites always leads to antiferromagnetism, but that exchange between irons in different kinds of sites leads to ferromagnetism. This theory lends itself to the study of synthetic ammonia catalysts. A start in this direction has been made by Maxwell, Smart, and Brunauer[16].

Solution Processes

One of the most searching uses of thermomagnetic analysis is in the detection and estimation of ferromagnetic substances in small or trace amounts. If the ferromagnetic substance is present in a moderate amount it may be studied by the usual methods of thermomagnetic analysis, which will be described below. But for trace amounts the Faraday method for measuring susceptibilities can be adapted to sensitivities at least as great as spectroscopic methods.

An example of this use is in the examination of supposedly pure copper. Copper is slightly diagmagnetic with a susceptibility which is, of course, independent of field strength. Most C.P. copper prepared in a finely divided, catalytically active form shows a susceptibility which falls moderately with rising field strength. Figure 3 shows typical samples[14], including one of "magnetically pure" copper prepared by repeated electrolysis or alternatively by coprecipitative removal of iron and nickel impurities. Those samples of copper which show considerable field strength dependence of susceptibility may be quite active for a reaction such as the hydrogenation of benzene, while magnetically pure copper is not. This test is so searching that no claim for activity in a diamagnetic metal such as copper should be taken seriously until the test has been made.

The method described is also useful in the study of systems such as copper-nickel where a deliberate addition of nickel as a promoter has been made. Morris and the writer[20] have investigated the thermomagnetic behavior and activity of copper promoted by one or two per cent of nickel and have shown that the active catalyst contains little or no pure nickel as such but that it does contain a continuous series of inhomogeneous solid solutions ranging from almost pure nickel to pure copper. Such catalysts are quite active for the hydrogenation of benzene. If the catalyst is now subjected to thermal inactivation the process of solid solution continues until, in the limit, a dilute homogeneous solid solution of nickel in copper is obtained. This is inactive. Thermomagnetic curves for the active, partially deactivated, and completely deactivated catalyst are shown in Figure 4. The interpretation in terms of inhomogeneous solid solutions is supported by studies of mechanical mixtures of copper and nickel powders

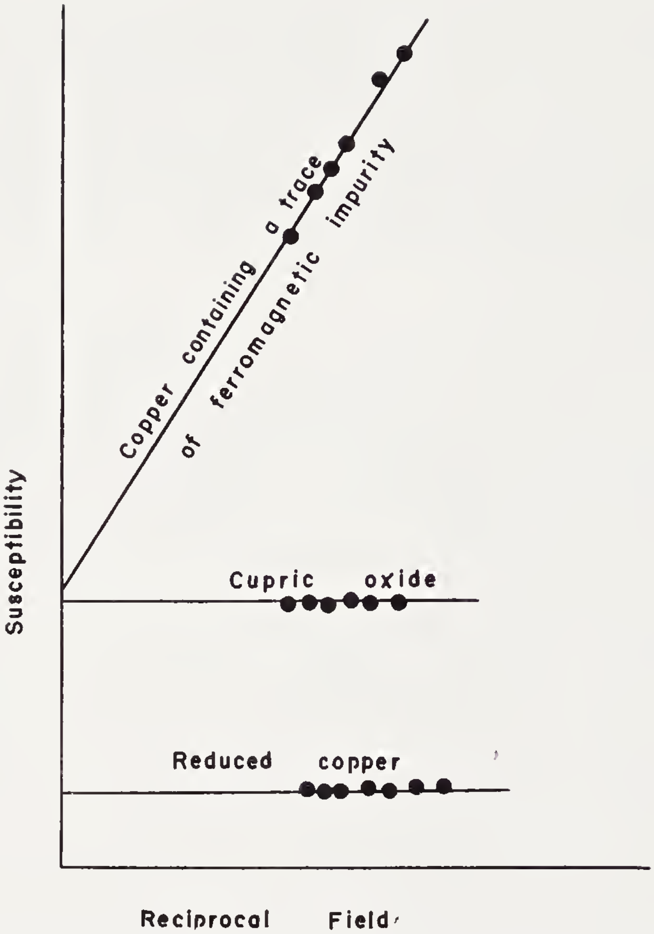

Figure 3. Susceptibility *vs* reciprocal field for pure copper, pure cupric oxide, and for copper containing a trace of ferromagnetic impurity such as nickel, but not in the form of a solid solution.

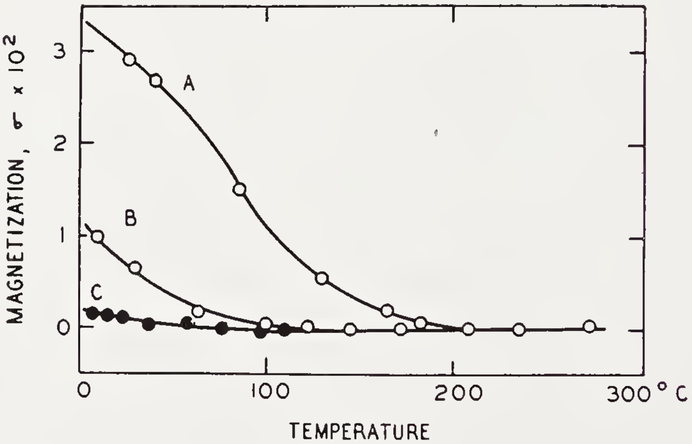

Figure 4. Thermomagnetic curves for nickel supported on copper for A, active; B, partially deactivated; and C, inactive samples. ("Advances in Catalysis," Vol. III, p. 100—Selwood (Academic Press)).

compressed and sintered according to the techniques of powder metallurgy[28]. The interpretation of activity loss attendant on dilution of the nickel with copper is consistent with current views relating unoccupied *d* electron orbitals in nickel and their filling by electrons from electron-rich elements such as copper. It must, of course, be understood that this process of solid solution is only one of those by which catalytic activity may be diminished; mere loss of specific surface through sintering will also diminish activity.

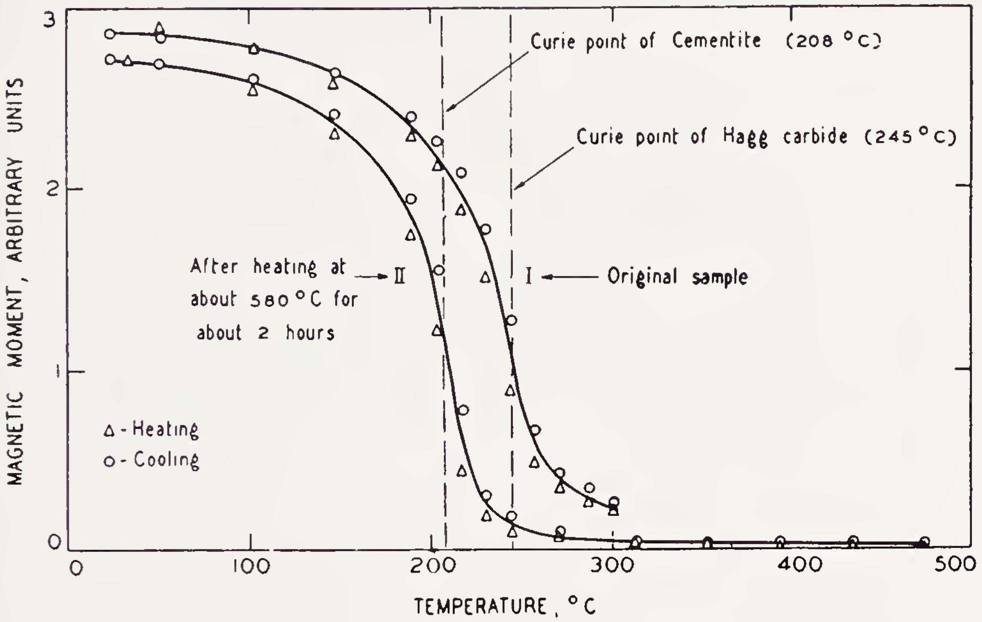

Figure 5. Thermomagnetic curves: I for Hägg carbide, II same after heating to 580°. ("Advances in Catalysis," Vol. III, p. 94—Selwood (Academic Press)).

Reaction Processes

Thermomagnetic analysis is a tool of quite extraordinary power for the study of reactions in the solid state. It will be illustrated by reference to four examples: the disproportionation of Hägg carbide, Fe_2C, to cementite and carbon, the decomposition of cobalt carbide to cobalt and carbon, the disproportionation of ferrous oxide, and the transformation of gamma-ferric oxide to alpha-ferric oxide.

Hägg carbide is one of several carbides studied by Hofer and co-workers[12] as of interest in Fischer-Tropsch catalysts. The Curie point of this carbide is at 250°C. A thermomagnetic curve taken for this substance is shown in Figure 5. This curve is reversible provided that the temperature is not taken too high. If the temperature is now held at 580°C for several hours, the specific magnetization at low temperature remains about the same, but the Curie point will be found to have dropped back to that for cementite, namely about 215°C. While in this case the Curie points lie rather too close together for accurate rate studies, there is no doubt that the method can effectively reveal the progress of reaction.

For the decomposition of the nonferromagnetic cobalt carbide, $Co_2C \rightarrow 2\,\alpha\text{-Co} + C$, the magnetic change is striking (Figure 6) owing to formation of the strongly ferromagnetic metallic cobalt. Hofer[13] and his assocates have studied this reaction as a function of temperature in order to obtain quite accurate rate constants and apparent activation energies for the transformation. The study of this and similar reactions is far less tedious by thermomagnetic analysis than by direct chemical analysis, or even by x-ray methods.

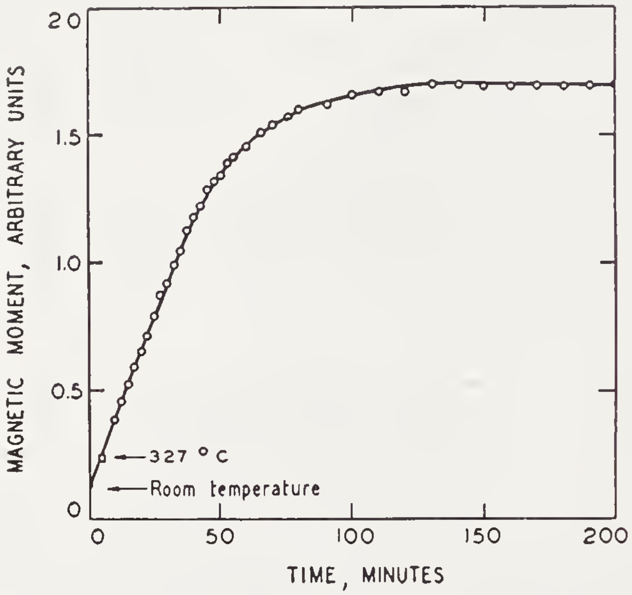

Figure 6. Specific magnetization *vs* time for decomposing cobalt carbide. ("Advances in Catalysis," Vol. III, p. 97—Selwood (Academic Press)).

Ferrous oxide[6] shows a complicated thermomagnetic behavior (Figure 7). It is well known that the wüstite phase corresponding to near FeO composition is unstable below 570°C but that the reaction $4FeO \rightarrow Fe + Fe_3O_4$ is immeasurably slow at room temperature. If a single phase corresponding closely to FeO is prepared by quenching from a high temperature the product will be almost free from ferromagnetism. If this is now heated there will be a strong ferromagnetism developed owing to the iron and magnetite formed by disproportionation of the ferrous oxide. But as the temperature approaches 570°C the equilibrium will begin to shift back toward FeO even before the Curie points of Fe_3O_4 and Fe are reached. The magnetization will then drop slowly with rising temperature and will fall sharply at the Curie point of magnetite. Finally, the magnetization will drop to zero above the Curie point of iron. If the temperature is now lowered slowly the thermomagnetic curve will be found not to retrace its

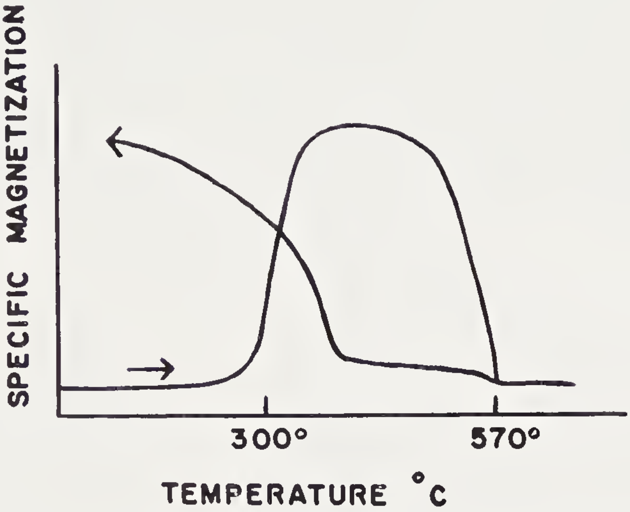

Figure 7. Irreversible magnetic changes during heating and cooling of FeO rich in oxygen. There is no Curie point for iron in the above curves because in a system rich in oxygen iron could not exist as such above 570°C which is 200° below its Curie point. (Colloques Internationaux, Paris, 1948, Reactions dans l'Etat Solide. Chaudron and Bénard, p. 89.)

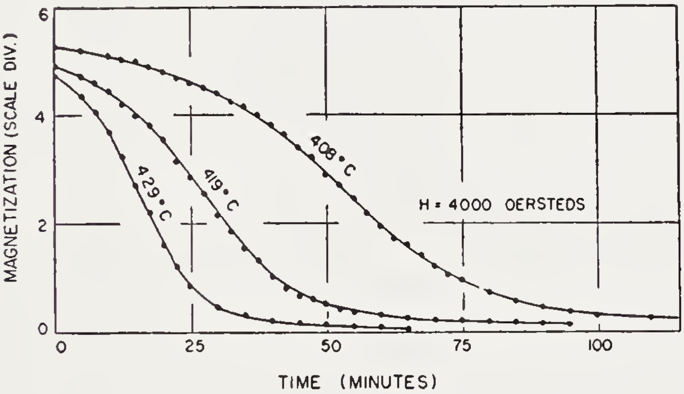

Figure 8. Plots of three kinetic runs for the transition γ-$Fe_2O_3 \rightarrow \alpha$-$Fe_2O_3$[22].

steps but to rise sharply at the Curie points for iron and magnetite, and to stay very high all the way back to room temperature.

Gamma-ferric oxide is, of course, strongly ferromagnetic but above about 400°C it transforms to nonferromagnetic alpha-ferric oxide[17]. This much-studied reaction hence lends itself well to thermomagnetic analysis. Studies have been made of the rate (Figure 8) and apparent activation energy of this process. It has been established that the gamma oxide is stabilized by the presence of alkali metal ions, or by alumina.

It will be clear from the above that thermomagnetic analysis has many applications in catalysis. It should, however, be pointed out that the method is subject to somewhat the same limitations that hamper x-ray diffraction studies of amorphous, or near amorphous, solids. This is that the ferromagnetism is a property of aggregates of atoms, while catalytic activity is, at least in some cases, an atomic property. Even in those cases where it has been shown that catalytic activity is also a function of minimum "domains" there is certainly no evidence that the catalytic domains are comparable in size with the minimum ferromagnetic domains.

EXPERIMENTAL METHODS

Magnetic Susceptibilities

For work on inorganic solids of the kinds (metals, oxides, sulfides) most frequently encountered in heterogeneous catalysis there is little doubt that the Faraday method of susceptibility determination is to be preferred.

In this method, sometimes called the Curie method, a sample is placed in a magnetic field which possesses a gradient in a direction in which the sample is free to move. The force acting on the sample will then be $f = \chi m H \partial H/\partial \mathrm{x}$ where χ and m are susceptibility per gram and mass of the sample, respectively; H is the field strength, and $\partial H/\partial \mathrm{x}$ is the field gradient in the direction of motion. For stability the sample should be placed in a region where the product $H\partial H/\partial \mathrm{x}$ is large and constant. Such a region may be achieved by proper shape of the pole pieces. One satisfactory arrangement is shown in Figure 9. Uniformity of $H\partial H/\partial \mathrm{x}$ is necessary over a small volume sufficient to enclose the sample, which need not weigh over 100 mg. Fields commonly used are from 5,000 to 20,000 oersteds produced by moderately large electromagnets.

The force acting on the sample has been measured in almost innumerable ways. One method, which has given satisfaction in the writer's laboratory, is to suspend the sample in a small glass (or Vycor) bucket from a silica spring such as is used in the McBain-Bakr gas adsorption balance. In this way the whole suspended system may be enclosed. It is convenient to attach the suspension and enclosure to a movable calibrated support such as may be made from the mechanical stage of a microscope. Motion of the sample in the field is observed with a micrometer microscope focused on some point at the lower end of the spring. In making a measurement the field is turned on and the mechanical stage adjusted until the sample is in the predetermined region of maximum, uniform $\mathrm{H}\partial H/\partial \mathrm{x}$. Then the field is turned off and the elongation, or contraction, of the spring is observed with the micrometer microscope. Calibration may be done with ferrous ammonium sulfate (Mohr's salt) for which $\chi = 31.8 \times 10^{-6}$ at 25°C or with sucrose, for which $\chi = -0.56$. Temperature control of the sample may be easily arranged by a slender heating coil, or an appropriately shaped Dewar flask to slip over the lower end of the enclosure.

In all substances used as catalysts, and in many other substances, there is a possibility of ferromagnetic impurities. The presence of these may easily be detected by making the susceptibility measurements at several field strengths, then plotting apparent susceptibility against reciprocal field. Extrapolation to $1/H = 0$ gives the true para- or diamagnetic susceptibility. No measurement of susceptibility on an inorganic solid should be accepted as reliable unless this procedure has been followed. This is the principal reason for favoring the Faraday method. The extrapolation to $1/H = 0$ gives uncertain results when applied to other susceptibility methods such as that of Gouy.

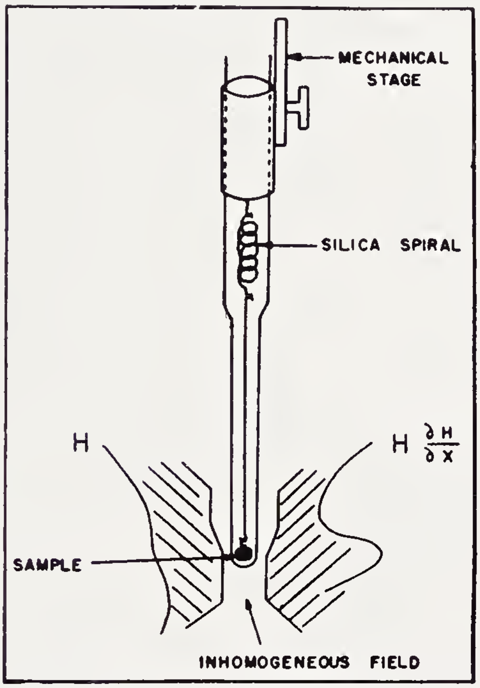

Figure 9. Faraday balance. (Research Reviews, published by the Office of Naval Research, Dept. Navy, Washington D. C., October 1951, p. 9, article by Selwood.)

The method of Gouy is convenient for use with liquids and for those solids in which no trace of ferromagnetism is present. The presence of ferromagnetism is easily detected by making measurements at two or more field strengths. If the results at several fields are not identical it is doubtful if accurate data may be obtained by this method. In this method a cylindrical sample or tube is suspended so that one end is in a uniform field, the other in a negligible field. The sample is often conveniently suspended from a balance as in Figure 10. The force on the sample is $f = \frac{1}{2} \kappa A H^2$ where κ

is the susceptibility per unit volume, A is the cross-sectional area of the sample.

Generally speaking, the Gouy method is the most convenient of all susceptibility methods. Calibration is made with ferrous ammonium sulfate or with water for which $\chi = -0.720 \times 10^{-6}$.

Thermomagnetic Balances

A ferromagnetic sample, suspended in an inhomogeneous magnetic field, is acted on by a force $f = \sigma m \partial H/\partial x$ where σ is the specific magnetization, m the mass, and $\partial H/\partial x$ the field gradient in the direction of motion. Thermomagnetic analysis consists of measuring the force on a sample as a function of temperature, and sometimes also as a function of time. A great many devices have been described for doing this. The simplest one consists merely of a sample suspended from a spring or balance in a field which has a more or less uniform gradient.

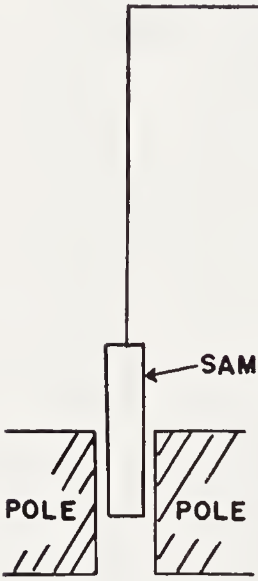

Figure 10. Gouy magnetic susceptibility balance. [Source: This has appeared in many places. The above is actually from an article by Selwood in "Encyclopedia of Chemical Technology," Vol. 8. (Interscience)].

The present discussion will be limited to a completely automatic balance built in the writer's laboratory by R. F. S. Robertson[22]. In this balance the sample moves horizontally on a torsion arm. Displacements are recorded on controlling and recording potentiometer, as is the temperature. A diagram of the apparatus is shown in Figure 11. The magnet pole pieces are cut to slope away from each other to produce a field gradient. Other methods for producing the gradient are equally satisfactory. The sample is

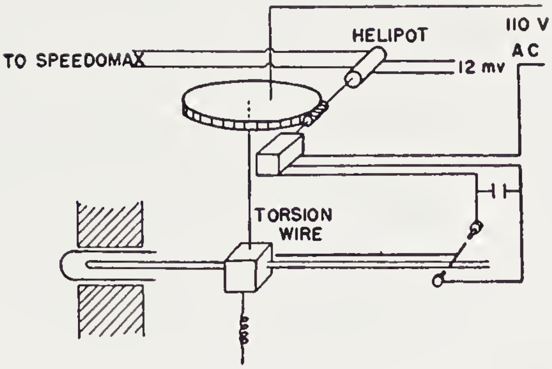

Figure 11. Diagrammatic representation[22] of a recording thermomagnetic balance.

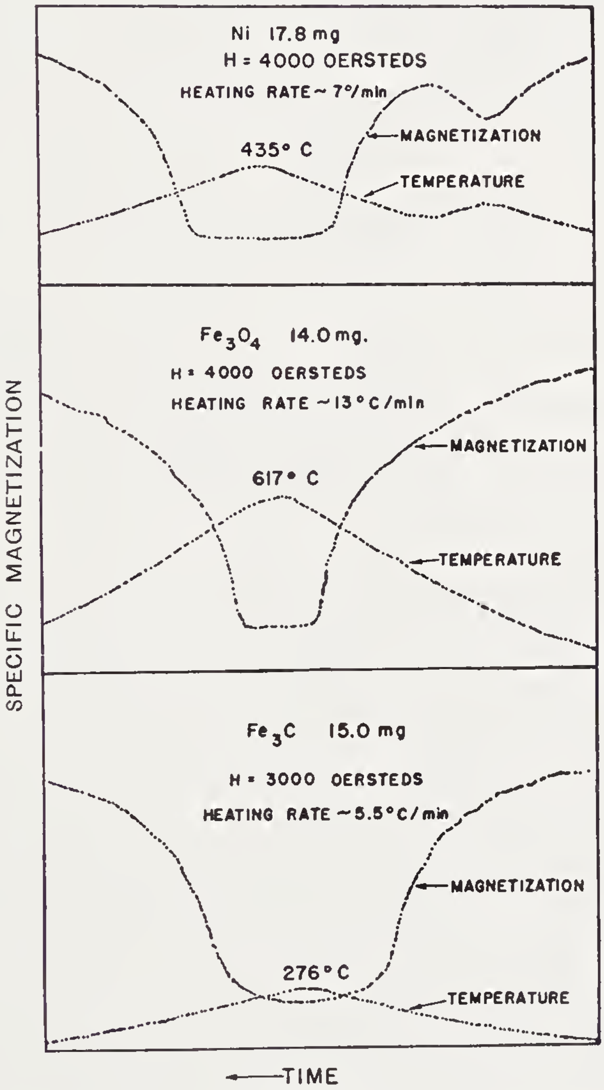

Figure 12. Direct tracing of specific magnetization and temperature for nickel, magnetite, and cementite on a recording thermomagnetic balance[22].

placed in a small furnace in such a position that it is free to move laterally in a region of uniform field gradient. The torsion arm hangs from a bronze torsion ribbon attached to a movable head. The head is turned by a small reversible motor. Displacement of the sample from its equilibrium position closes one of two contacts which causes the motor to turn the torsion head and thus return the sample to its equilibrium position. The shaft of the motor is also connected to a potential divider which feeds into the recording potentiometer. The voltage from the potential divider is directly proportional to the angular displacement of the torsion head necessary to restore the sample to its zero position.

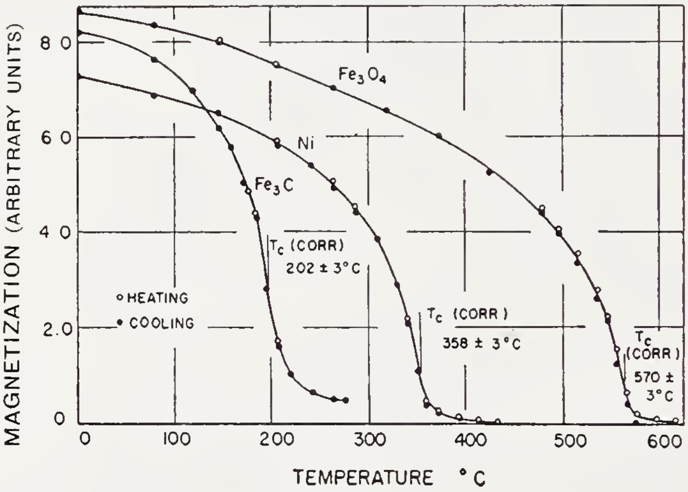

Figure 13. Runs of Figure 12 plotted on temperature-magnetization axes[22].

A small thermocouple is placed in contact with the sample. This gives a record on the recording potentiometer and also serves to actuate the furnace control mechanism which may be adjusted for any type of heating or cooling cycle. The motion of paper in the potentiometer gives the time axis for rate studies. With this apparatus there appear two lines as a function of time, one of temperature and one proportional to specific magnetiziation. Curie point curves must be obtained by replotting the data, but on the whole this is an advantage because so many thermomagnetic studies involve rate processes of one type or another. The apparatus has given considerable satisfaction. Samples of original and replotted data are shown in Figures 12 and 13.

In Table 2 there are shown specific magnetizations and Curie points for a few ferromagnetic substances likely to be encountered in work on solid catalysts.

Nuclear Induction and Paramagnetic Resonance

If a substance placed in a steady magnetic field is subjected to an alternating magnetic field at right angles to the first, there may appear certain phenomena of potential use in catalysis. At steady fields of 5,000 to 10,000 oersteds and alternating fields in the low megacycle range there appear certain effects related to the orientation of nuclear magnetic moments. This has had some application to the structure of catalytically active solids. On the other hand, at considerably higher frequencies, there arise effects known as paramagnetic resonance. So far as the writer is aware, this latter effect has not yet had any application to catalysis, but its growing success in related areas such as luminescent solids suggests that paramagnetic resonance is worth investigating.

TABLE 2* SPECIFIC MAGNETIZATIONS AND CURIE POINTS

	σ	T_c
		°C
Fe	218	770
Co	163	1180
Ni	55.5	355
γ-Fe_2O_3	95	675
Fe_3O_4	95	572
Fe_2C (Hägg)	135	247
Fe_2C (Hex.c.p.)	135	380
Fe_3C	135	210

* These data supplied by Dr. L. J. E. Hofer. Different investigators have reported values differing considerably from those above. The precision is ± 1 to ± 10 units for the specific magnetizations and ± 3 to ± 20° for the Curie points.

The theory and experimental basis[3] of nuclear induction will be outlined briefly, after which some applications of the method will be mentioned. The magnetic moments of atomic nuclei are about two thousand times smaller than the electronic (or atomic) moments referred to above. Nevertheless, satisfactory methods have been developed for measuring nuclear moments. If a nucleus possessing a resultant moment, most conveniently a proton, is placed in a steady field H_0, it may be excited with an alternating field of frequency υ given by $h\upsilon = 2\mu_0 H_0$ where μ_0 is the magnetic moment of the proton. Magnetic fields of the resonance frequency υ will stimulate transitions in the orientation of proton spins. If another coil is now placed at right angles to both H_0 and the alternating field it will acquire an induced e.m.f. from the changing nuclear spin orientation. The arrangement of the apparatus is shown diagrammatically in Figure 14.

Actually, orientation of nuclear magnetic moments is retarded through conservation of the angular momentum, and approach to equilibrium in an applied field is described by a simple exponential law with a characteristic time, called the longitudinal relaxation time, $2W = 1/T_1$, where W is the transition probability. The relaxation time is surprisingly long, being about three seconds for the protons in pure water. But if the water contains some paramagnetic ions such as Fe^{+3}, the relaxation time may be reduced to a few thousandths of a second. This effect is not unlike the paramagnetic ortho-para-hydrogen conversion. It has been shown by Purcell, Bloembergen, and Pound[4] that the relaxation time is related to the concentration and atomic moment of the dissolved ions by $1/T_1 = 12\ \pi^2\gamma^2\eta^2N\mu_{\text{eff}}^2/5kT$ where γ is the gyromagnetic ratio, η is the viscosity of the solution, N is the concentration of paramagnetic ions as number of ions per cc, μ_{eff} is the effective magnetic moment of the dissolved ions. It has recently been shown[8] that this relation does not apply to ions in which spin-orbital coupling is strong, but this excludes only Co^{+2} and most of the rare earth elements.

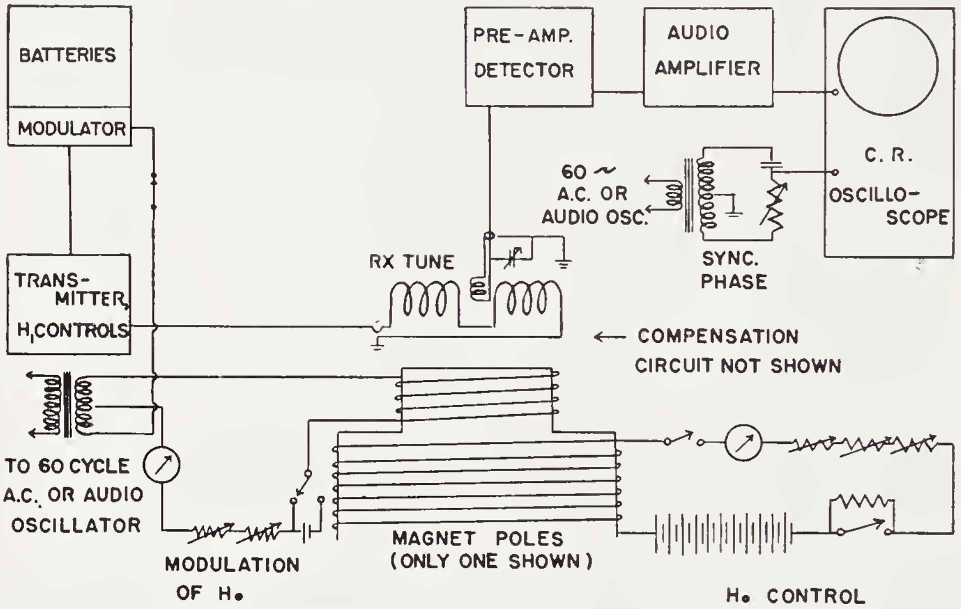

Figure 14. Bloch diagram of nuclear induction apparatus.

Experimentally it is found convenient to scan the resonance frequency by modulating H_0, generally at 60 cycles, by a few turns of wire on the poles of the electromagnet. The presentation on the oscilloscope is then as "pips," from the position of which the relaxation time is easily found.

It has been found that the relaxation time of protons in water is modified by contact of the water with typical supported paramagnetic oxides such as chromia-alumina[34]. This observation makes it possible to compare the effectiveness of different catalysts, and, in a sense, to compare the accessibility of the active part of the catalyst surface. A step in this direction has been taken by Schroyer and the writer[29] who, taking about one gram of solid powdered catalyst, covered it with 1 cc of water. The concentration of paramagnetic ions was defined as M, the moles of such ions present divided by the volume of water in liters. The proton relaxation time was then found. Next, a water solution containing the same paramagnetic ions (e.g., Cr^{+3}) was prepared, and the concentration of this solution was adjusted until it gave the same relaxation time as the powdered solid. The molar concentration of this solution is designated as M_0. Then the catalyst accessibility is defined as $a = 2\ M_0/M$, the factor 2 being added because of the shielding at the surface in the case of the powder. This rather crude method gives accessibilities which are linear with catalytic activity for such reactions as the dehydrocyclization of *n*-heptane. If the use of water for a proton source can be discarded in favor of a gas such as hydrogen, the method may become a very useful one.

The phenomenon of paramagnetic resonance is observed by placing the sample in an oscillating field and measuring the energy absorbed by the sample as a function of the intensity of a steady field applied perpendicular to the oscillating field. The experiment is not unlike the nuclear resonance experiment except that the oscillating field has a frequency of some thousands of megacycles. Absorption lines occur as the quantum of energy corresponding to an oscillation frequency equals the separation of energy levels in the paramagnetic ion. This experiment is capable of giving a substantial amount of information concerning the paramagnetic ion without much complication from diamagnetic substances also present[1].

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