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CHEMISORPTION

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Proceedings of a Symposium held at
The University College of North Staffordshire
Keele, Staffordshire
by
THE CHEMICAL SOCIETY
16–19 July 1956

Edited by
Prof. W. E. GARNER, C.B.E., D.SC., F.R.S.

LONDON
BUTTERWORTHS SCIENTIFIC PUBLICATIONS
1957

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88 KINGSWAY, LONDON, W.C.2

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U.S.A. Edition published by
ACADEMIC PRESS INC., PUBLISHERS
111 FIFTH AVENUE
NEW YORK 3, NEW YORK

Printed in Northern Ireland at The Universities Press, Belfast

PREFACE

The symposium on 'Chemisorption' was held under the auspices of the Chemical Society, and the President opened the meeting. Those attending were the guests of the University College of North Staffordshire at Keele, who very kindly placed the amenities of its quarters and two hundred acres of park and woodland at their disposal. Dr. I. J. Faulkner and Dr. B. W. Bradford of Imperial Chemical Industries, Billingham, suggested the idea of the discussion, and assisted in its organization in many ways.

The present symposium may be regarded as a continuation of those on 'The Adsorption of Gases' at Oxford in 1932 and on 'Heterogeneous Catalysis' at Liverpool in 1950, both of which were held under the auspices of the Faraday Society. It was singularly appropriate that the present discussion took place at Keele, in view of the classical contributions made on chemisorption at the Oxford meeting in 1932 by Sir John Lennard-Jones, who until recently was the Principal of the North Staffordshire College.

The symposium was deliberately restricted in scope in order that ample time could be provided for the discussion of the more fundamental aspects of catalysis. It was desirable to hold it in this country so that the younger generation in Industry and at the Universities could take part. We were fortunate in that some of the distinguished continental scientists, well known in this field, were able to attend and read papers. Visits were made by members to the I.C.I. Alkali works and to the Joseph Wedgwood & Sons potteries.

The meeting was divided into five sections, (1) The Theory of Chemisorption, (2) Chemisorption on Insulators, (3) Chemisorption on Metals, (4) Chemisorption on Semiconductors, (5) Chemisorption on Carbon, and each section was followed by a discussion.

W. E. G.

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SECTION 1

THEORY OF CHEMISORPTION

Chairman: W. E. GARNER

1.1

CHEMISORPTION AND VALENCY

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SUMMARY

The dependence of chemisorption upon the electronic configuration of the solid is discussed in terms of the valencies deployed at the surfaces of metals, semi-conductors and insulators. It appears that there are at least two kinds of chemisorption upon conductors, a weak form involving essentially d-*orbitals and a strong form using* dsp *valencies like the cohesive bonds of the solid.*

The properties of the metals are further treated in terms of band theory and resonating-valence-bond theory leading to the suggestion that manganese should show anomalous behaviour. Crystal field theory indicates how the properties of the ionic oxide semiconductors can depend upon the filling of the d-*shell in analogy with the metals. Insulators behave like acids and bases or like feeble* n-*type semi-conductors.*

INTRODUCTION

Chemisorption, the chemical reaction between molecules and the surfaces of solids, is a primary step in processes involving solids; the free-energy changes occurring on establishment of the activated and equilibrium states can in principle be positive or negative, as is crudely represented in *Figure 1* (after Lennard-Jones[1]). Chemisorption can frequently be distinguished from physical adsorption by its greater heat of reaction, but the distinction becomes somewhat arbitrary as concepts of valency alter.

Chemisorption is controlled by the valencies of the solid surface and of the adsorbate and one seeks relationship with the electronic and geometric configurations of the system as it moves from its initial to its final state through one or more recognizable intermediates. In this way the intractable problem of deriving energy surfaces in hyperspace is replaced by the simpler one of recognizing likely configurations along the reaction path.

Good data are scarce, but there are a number of behaviour patterns which it is the purpose of this paper to probe and explain.

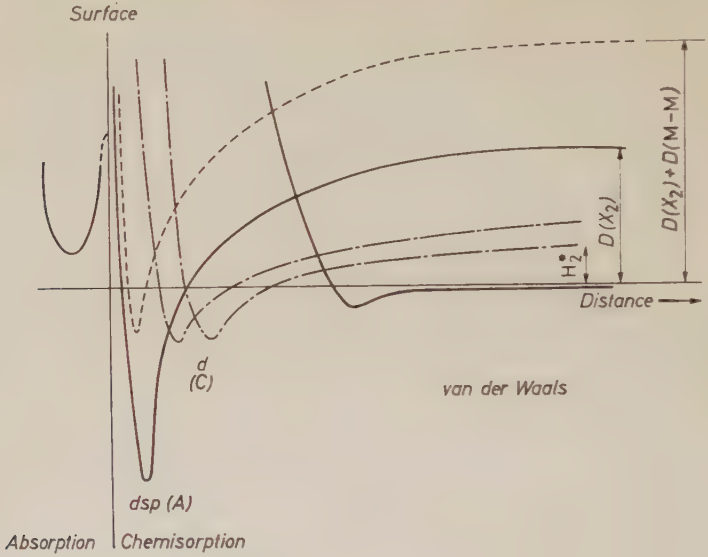


Figure 1. Sorption with residual valencies.

THE DESCRIPTIVE CHEMISTRY

The involved information can be simplified if the adsorbents are grouped[2] into electronic conductors (metals, semiconductors) and insulators (ionic, covalent), where the latter description is reserved for solids of very high electronic resistance.

Electronic Conductors

These chemisorb or activate (i.e. render active in catalysis) one or more of the simple molecules (H_2, N_2, O_2, CO), even at 195°K and below. They can be further classified into those (*d*-type) having low-lying, unfilled *d*-orbitals and those without such orbitals (*s,p*-type), a distinction that proves to be fundamental.

METALS

All metals, except perhaps gold, chemisorb oxygen. Only *d*-metals chemisorb hydrogen and nitrogen; *s,p*-metals chemisorb gases such as carbon monoxide and unsaturated hydrocarbons by processes which seem to be markedly different from those on *d*-metals.

Whether the division between the two classes occurs sharply at the alloy composition where the *d*-band is just full, is not known. Catalysis of hydrogen[3] and oxygen[4,5] reactions suggests some change, in at least one kind of chemisorption, close to the critical composition.

SEMICONDUCTORS

Superposition of the orbital classification upon the more usual semiconducting types gives the following groups:

n-type: $n_{s,p}$(ZnO) and $n_d(V_2O_5)$
intrinsic: $i_{s,p}$(Si, Se) and i_d(CuO, Fe_3O_4)
p-type: $p_{s,p}$(none) and p_d(NiO)

Like *s,p*-metals, $i_{s,p}$ semiconductors are relatively inert towards all gases except oxygen. Only *n*-type oxides chemisorb hydrogen readily, but *some* transition oxides (e.g. Cr_2O_3) appear to be more active than any $n_{s,p}$-oxide in hydrogen–deuterium exchange. In oxygen reactions, the most active oxides are p_d-type, the less active but more selective are n_d-type, and the least active are $n_{s,p}$-type.

For hydrogen and carbon monoxide, probably for all gases, the valencies of the cations are essential to the adsorption process; this is especially clear in oxygen-poisoning experiments at low temperatures.

Insulators

The most studied examples are all oxides, simple or mixed, drawn from groups 2 to 4 of the short periods; little is known of covalent insulators, such as diamond. The cations are in their highest valency state so that the solids have marginal semiconductivity of $n_{s,p}$-type.

Although chemisorption of neutral molecules (H_2, N_2, CO, O_2, C_nH_{2n+2}) is slow and small, slow hydrogen and oxygen exchanges are catalysed above 630°K. Polar molecules are strongly chemisorbed and many of the oxides cause typical acid or base catalysis. Although not so evidently as with the electronic semiconductors, the cations again play a significant role.

Weak Chemisorptions and Residual d-*Valencies*

An important feature of recent studies is the growing realization of the presence, on conducting surfaces at least, of states of chemisorption intermediate between physical adsorption and strong chemisorption[6,7,8,9]. Because active metals are *d*-metals, and because possible weak bonding has been found so far only on active solids, it will be supposed that the *d*-solids differ from the *s,p*-solids, by the possession of residual valencies, mainly of *d*-character, which produce the additional third potential curve[10] of *Figure 1*. Above energy-zero the minimum represents a stable activated complex, below zero it is a weak non-activated chemisorption (type *C* after Emmett[11]); both are precursors of a strong chemisorption (type *A*) which uses bonds like the cohesive bonds of the metal.

At a sufficiently low temperature only type *C* exists; in a higher range this transforms to type *A*, probably according to the Elovitch equation[12] (rate $\propto$ exp $(-bx)$; x, the amount of gas adsorbed in the slow process). On active solids, the curves intersect at low energies and *A* is rapid and inactivated up to high coverages, but when the falling heat has raised curve *A* sufficiently to inhibit formation of *A*, the weak chemisorption can still occur on the bare surface.

There may be more than two kinds of chemisorption on some planes, one only on others, but all will be sensitive to electron configuration.

THEORY

The universality of the relationship between chemisorption and the electronic configuration of the *bulk* solid, especially the domination of surface processes by the structure of the *d*-levels, is outstanding. Thus a correspondence, hardly an identity, exists between the configuration of the bulk and the surface atoms and the difference must arise from the asymmetry at the interface and at defects in the surface lattice.

The *d*-orbitals of the free atom are split by ionic and covalent interactions in the solid into groups

$$d\gamma(d_{z^2}, d_{x^2-y^2}) \qquad \text{and} \qquad d\varepsilon(d_{xy}, d_{yz}, d_{zx})$$

for cubic fields, separated by gaps of variable width and sharpness which depend upon the nature of the solid. Thus the total energy of the solid depends upon the displacement of the centre of gravity of the electron levels, the extent of the splitting, the number of electrons to be accommodated, and the rules for the filling of the levels. Because these factors cannot be calculated with any accuracy, and are in any case interdependent, the following discussion is purely qualitative.

Metals

Nearest-neighbour interactions are strong and this sets the metals apart from the semiconductors.

THE BULK

Recent data[13] for the density of electron levels ($n(E)$) clearly show the two sub-bands suggested by earlier calculations. Then, in the molecular-orbital approximation (band theory), the metals of the long periods can be crudely represented by the filling of a potential box to various maximum kinetic energies (E_M). *Figure 2* gives the position of the energy of the bottom of the band (E_0), where it can be guessed, the work function ($\phi = E_0 - E_M$) and $n(E_M)$ for the first long period together with the sublimation energies and the range of ionization potentials for simple molecules.

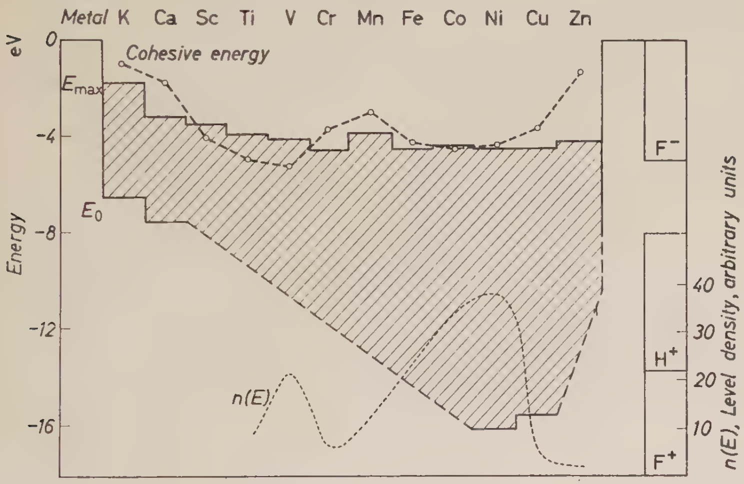


Figure 2. Energy levels of solids and adsorbates.

Pauling uses the one-electron wave-functions $nd\varepsilon^3$, $(n+1)s$, $(n+1)p^3$ to form strong, covalent σ-bonds to the eight nearest neighbours of the $A2$ lattice leaving $nd\gamma^2$ ('atomic orbitals') to accommodate the electrons giving magnetic properties. The set $nd\gamma^2$, $(n+1)s$, $(n+1)p^3$ is used for the six next-nearest neighbours with $nd\varepsilon^3$ as atomic orbitals. Then the ground state of iron can be represented[14] as a resonating hybrid of

	$3d\gamma^2$	$3d\varepsilon^3$	$4s$	$4p^3$
$A(nn)$	↑ ↑	. . .	.	. . 0
$B(nnn)$	. .	↑ ↑ ↑	.	. . 0

with A predominant.

The ground-state diagrams for $A1$ and $A3$ will be similar, so that to the transitional metals, by empirical arguments[15], can be assigned up to six valency electrons in orbitals of varying d-content, a number of magnetic electrons in atomic orbitals, and vacant 'metallic' orbitals to allow 'unsynchronized resonance'.

THE SURFACE

The valency state and the hybridization of the bare surface atom will differ from the bulk to yield stronger pairwise bonding[16] to its nearest (*nn*) and next-nearest neighbours (*nnn*). Thus the bonding electrons of α-iron will associate with the smaller number of ligands (4 *nn* and 5 *nnn*) but the two forms contributing to the ground state could rearrange to a surface state somewhat as follows:

$$A(nn),\ d^3sp^2 \rightharpoonup d^2p \text{ (trigonal pyramid)} + dsp \text{ (bent planar)}$$

$$B(nnn),\ d^2sp^2 \rightharpoonup d^2sp^2 \text{ (distorted tetragonal pyramid)}$$

together with other forms for smaller valencies.

Fractions of the metallic orbitals now lie in the surface and the metal atom is negative when this orbital is occupied, and positive when the atom has lost a bonding electron in the conductivity process.

The atomic orbitals, d_{z^2}, d_{zx}, and d_{zy} project from the surface but can form only weak, mutual π-bonds as suggested by ferromagnetic Curie points and the small σ-symbatic overlap of d_{z^2} orbitals on adjacent atoms[17].

Band theory must ultimately provide surface states similar to these, and in so far as they are separated from the band edges by an energy gap, such states can be said to form a 'surface metal'.

WEAK CHEMISORPTIONS

Molecules during sorption overlap first with d_{z^2}, then with (d_{zx}, d_{zy}), and lastly with $d_{x^2-y^2}$ and d_{xy}, both of which lie in the surface. Bond strength at points along the z-axis then depends upon the fraction of each orbital available, its energy, and its electron content; the atomic orbitals are full at d-electron concentrations greater than 10·5 in each long series.

For closed-shell molecules such as hydrogen, ethane, etc., and for lone-pair molecules, there will be no binding when the d-orbitals are all full. As holes appear in d_{z^2} and $d_{x^2-y^2}$ of valency state A (as in α-iron), several combinations are feasible for hydrogen:

$$M(d_{z^2} \leftarrow \mathrm{H} \ldots \mathrm{H}^+)$$

in the end-on position,

$$M_a^- \ldots \mathrm{H}_2^+ - M_b \rightleftharpoons M_a\text{—}\mathrm{H}_2^+ \ldots M_b^-$$

and even 2(M—H) where the orbitals used by the metal are composite. Still weaker binding can arise from the smaller residue of $d\varepsilon$ orbitals.

Unsaturated molecules (C_2H_4, C_2H_2, O_2, CO, N_2) can react with the vacant d_{z^2}-orbital to give Dewar π-complexes. At copper, σ-bonding to these molecules can be achieved by a rearrangement of the metallic orbital together with formation of a π-bond by overlap of the filled $d\varepsilon$-orbitals with the anti-bonding orbitals of the adsorbate.

Weak chemisorption of this type must always eliminate physical properties due to unpaired spins and will replace physical adsorption, in the orthodox sense, if it is of sufficiently small heat.

If Zener's ideas[18] concerning the stability of half-filled shells in manganese are correct, there should be no weak chemisorptions on that metal.

THE STRONG CHEMISORPTIONS

Unlike the atoms of the metal, adatoms do not exert significant mutual attractions in the surface plane, nor do they possess metallic orbitals. Yet the relative success of the Eley[19]-Stevenson[20] estimation of bond energies, using a term which contains one-sixth of the metal cohesive energy, suggests that the metal employs surface valencies similar to those of the bulk. Thus, at higher temperatures, the surface atoms assume states more like those of the interior, and complete their ligancy by strong chemisorption; the nature of the bonding orbitals depends upon the model of the solid which is chosen.

Pauling's theory. The bonds must be very like the *dsp*-bonding hybrids. This conclusion, however, leads to difficulties with the Eley-Stevenson derivation because the calculation contains no endothermal term for initial breaking of metal—metal bonds at the surface; this suggests that *dsp* bonds exist essentially free at the surface. On the other hand, the calculated heat for hydrogen on copper is close to that found for 'active' copper[20], yet pure copper does not chemisorb hydrogen.

Strictly, this paradox can be resolved by assuming that appropriate valencies are free at lattice defects (e.g. edge dislocations, 'dangling electrons')[21], that the endothermal factor is compensated by some extra resonance energy in the surface complex, or that a residue of metallic orbitals is available. Although it is likely that each of these situations can arise, the third appears most generally useful. The metallic orbital of the surface states of the $A2$ structure, lying in the surface and directed towards next-nearest neighbours is a *dsp*-hybrid in *d*-metals and exists nearly free because of its minor role in the unsynchronized-resonance process. In *sp*-metals it is an *sp*-hybrid of small capacity.

Whatever the nature of the hybrids used in strong chemisorption, whether originating in atomic or metallic orbitals, the saturation magnetization of ferromagnetics and the susceptibility of strong paramagnetics will both decrease due to pairing of atomic spins and interference with the *d*-shell/conductivity-electron interaction.

Initial heats have been correlated in many ways[22] with the bond character of the metal; emphasis is seldom laid on the tendency, especially in the first long period, for the heats (e.g. C_2H_4, H_2, N_2) to fall into two sets, a moderate heat almost constant within group 8 and larger heats, rising rapidly with decreasing atomic number, below group 7. The break occurs at the point where there is a relative minimum in cohesive energy, an appearance of variable valencies and filled-zone structures[23], and where bonding orbitals cease to be fully occupied. In these regions, for instance at chromium, it is possible that the reduction of the ligancy in the surface is accompanied by a halving of the metal valency in the surface state; chemisorption might then restore a bulk-like resonance and an extra evolution of heat, so accounting for the large discrepancy between experiment and calculation.

Heats of chemisorption must fall rapidly with increasing coverage because of increasing interference with the unsynchronized resonance of the metal until, in effect, a point is reached at which the endothermal term for breaking metal bonds must be included in the Eley-Stevenson equation; in this way the heat of hydrogen on nickel can fall from 29 to 12 kcal mole^{-1}. Ignorance of energy values makes a unified calculation, including steric and dipolar effects, impossible and the rate of fall of the heat with coverage cannot be found without resort to empiricism. It is clear, however, that heats must fall off more rapidly when the adatoms have more than one electron to be accommodated in the surface states.

Band theory. FRIEDEL[24] has recently shown that the binding between a solute atom and its solvent depends upon the value of the solute's ionization potential (I) and electron affinity (E) relative to E_0 and E_M. If $I > E_0$ then, for the hydrogen atom, the proton is shielded by an electron in a bound level subtracted from the bottom of the band, whereas for $E < I < E_0$ shielding is due to conduction electrons. Both models give heats of solution (H_2/Cu) in fair accord with experiment; the same could be done for chemisorption, but in this approximation it is hardly worth while; the qualitative results appear more useful.

If chemisorption is similar to an interstitial solid solution at the surface, then the adsorbate always behaves like a solute with more valency electrons than the matrix. Under these conditions, and when valency is the controlling factor, the following conclusions are relevant:

1. The donated electrons enter the bands overlapping at E_M in proportion to their respective densities, $n(E_M)$. Chemisorption then always reduces the saturation magnetization of nickel in the absence of polar factors.
2. The radius (R) of the screening increases when $n(E_M)$ decreases, when $\partial n(E_M)/\partial E$ becomes negative, and when the ratio of the number of donated electrons to the number of holes in the d-band (both per metal atom) increases.

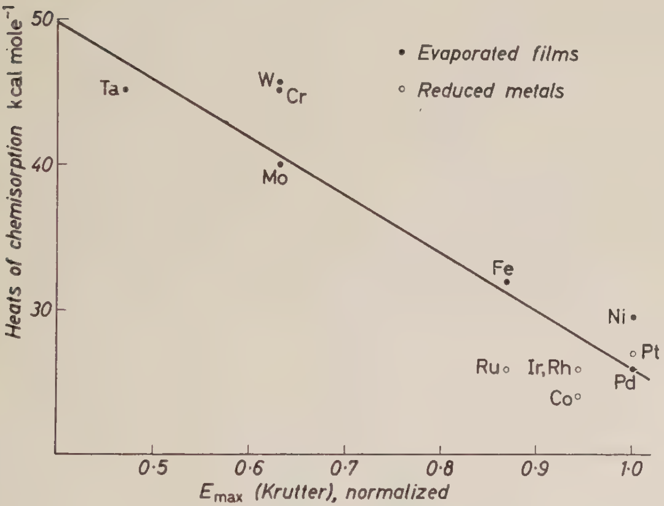


Figure 3. Hydrogen heats versus $E_{\max}$.

Heats of chemisorption fall off as soon as the screening radii are in contact and the slope is zero at zero coverage, but thereafter concave toward the zero. R is of the order of several atomic diameters for copper because of the small value of $n(E_M)$; it is of the same order for nickel, of large $n(E_M)$, because of the fraction of a hole in the d-band. The saturation coverage of nitrogen on the transition metals should then be close to that for hydrogen, in so far as the molecule uses only one electron per nitrogen atom in bonding, and this seems to be so at low temperatures[25]. The dissociated nitrogen molecule produces nitrogen adatoms with at least three extra electrons; R will be large on nickel, cobalt, and iron, because there are less than three d-band holes per atom and the resulting coverage less than unity. At tungsten, however, despite the large number of holes, $n(E_M)$ is small and again coverage will be incomplete. In the surface regions left uninfluenced by the circles of interaction it should be possible to chemisorb molecules having fewer electrons to donate[26] (H_2, molecular N_2).

A general view of the density-of-states curve gives a strong impression of two sub-bands with a finite gap; $n(E_M)$ is small in the centre of the first period and the work function parallels the drop in sublimation energy. Then the heats of chemisorption should decrease with increasing kinetic energy of the anti-bonding electrons in the metal. *Figures 3* and *4* show how the heats vary with E_M and $E_M - E_{\text{mean}}$ taken from the theoretical work of KRUTTER[27] and FLETCHER and WOHLFARTH[28], respectively. *Figure 4* shows in exaggerated form the sharp rise in heats in the region where the lower half-band presumably begins to empty.

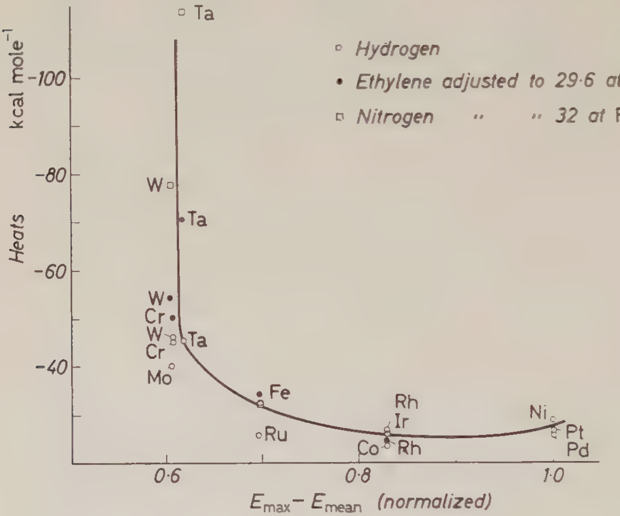


Figure 4. Heats of chemisorption versus electron energy (Fletcher and Wohlfarth).

According to ZENER[18], this half-band is particularly stable in chromium and manganese because of Hund's rule concerning half-filled shells. Then manganese should be like copper, and exhibit anomalously slow or small hydrogen chemisorption.

Semiconductors

In metals, atoms of positive polarity are shielded by those of negative polarity and the conductivity process alternates the polarity at each atom. In semiconductors, this image is, so to speak, 'fixed', and the magnetic evidence shows that the oxides of the first long period are essentially ionic; the $d\gamma$ and $d\varepsilon$ levels in octahedral sites are separated[29] by *c.* 28 kcal and 56 kcal in divalent and trivalent ions, respectively.

If weak, magnetic, cation–cation interactions are at first ignored and lattices are taken to be stoichiometric and of simple sodium chloride structure, then VERWEY's model[30] of a (100) surface can be used with isolated cations centred in distorted tetragonal pyramids of oxygen anions. The C_{4v} symmetry about each cation splits the five-fold *d*-level into three singlet levels and one doublet which qualitative considerations place in order of decreasing energy $d_{x^2-y^2}$, d_{z^2}, d_{xy} and (d_{zx}, d_{zy}). The positive lobe of the d_{z^2}-orbital is directed perpendicularly outward from the surface and this orbital, together with (d_{zx}, d_{zy}), provide the greater immediate overlap with adsorbates; as in metals, they should have the greatest effect in the formation of loose complexes.

The centre of gravity of the *d*-levels in the surface lattice is fixed by the electrostatic potential at the cations. Even in the purely ionic solid this is hardly susceptible to calculation, but since the divalent ions from manganese onwards possess not very different radii and exist in either the NaCl structure or structures similar to it, the bonding properties will be supposed to depend upon the electronic configuration alone. The conclusions may apply also to ions of higher valency, because their greater electrostatic potentials are cancelled to some extent by greater cation ionization potentials.

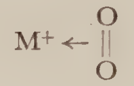
Other things being equal, then, the filling of the *d*-levels with electrons will control the rate of formation and the stability of the surface complexes, much as for metals.

WEAK CHEMISORPTION

The electronic configurations d^0, d^5, and d^{10} (*S*-states) are not split in this approximation and as full or half-full shells they are relatively stable. Thus, regardless of the electronegativity of the adsorbate, weak bonds are not likely to be formed by Ti^{4+}, Mn^{2+}, Zn^{2+}, Cu^+, etc. Bond formation should still be difficult at d^9 (Cu^{2+}) and d^8 (Ni^{2+}) for neutral molecules because the $d_{x^2-y^2}$-orbital lies in the surface and is shielded by the repulsions due to the full, projecting *d*-lobes. When d_{z^2} begins to empty at d^7 (Ni^{3+}, Co^{2+}), weak chemisorption and low activation energies become possible (hence the importance of non-stoichiometry and valency induction in NiO) and should be facile as the low-lying doublet begins to empty at d^3 (Cr^{3+}) and below. In real surface lattices, where there will certainly be covalent single and double bond contributions, these conclusions must be modified in a molecular-orbital treatment[31]; qualitatively, the results will be similar. Again, π-complexes are possible for unsaturated molecules.

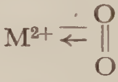
STRONG CHEMISORPTION

As for metals, simple adatoms should give negative dipoles at the surface of *n*-type and stoichiometric oxides; the lattice cations seek to restore their missing negative ligand. Thus oxygen bound weakly as



$$M^+ \leftarrow \begin{array}{c} O \\ \| \\ O \end{array}$$

or more strongly as



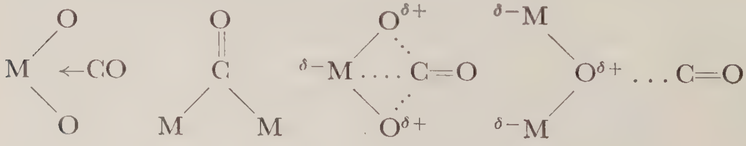
$$M^{2+} \overline{\leftarrow} \begin{array}{c} O \\ \| \\ O \end{array}$$

will dissociate to give $2O^{\delta-}$ and the surface complexes will relax from pyramidal towards octahedral symmetry with reinforcement of ionic character and alteration of surface strains.

In principle, the heats could be calculated using the ionic-lattice theory (with polarization), but such efforts are unprofitable. Although the bond will possess covalent character, it is probably sufficiently ionic to allow the application of exhaustion-layer theory[32] to the decline in heat with surface coverage.

Chemisorbed hydrogen will be 'hydride-like' or hydroxyl according to whether the weak complex goes over to $(H \ldots H)^{\delta-}$ on M—M or $H^{\delta-} \ldots H^{\delta+}$ on M—O. The usual concept of a primary homopolar dissociation is inapplicable, except at special sites, because of the large (3Å) cation–cation distance in the divalent oxides. Complexes such as $M^+ \ldots H_2^+{-}M^{2+}$ and $M^{2+} \ldots H^- \ldots H^+ \ldots O^{2-}$ seem more probable as intermediates with the proton held by molecular orbitals constructed from (d_{zx}, d_{zy}) of M^{2+} and p_z of adjacent oxygen ions. The state $2OH^-$ will be attained if the ion and lattice energies allow the reduction; again calculation is unprofitable.

Double bonded $p\pi$ and $p\sigma$ complexes can again be formed by ethylene and carbon monoxide, respectively, over cations with full or just filled *d*-shells[33]. Carbon monoxide can also provide intermediate states between such configurations as



using hybrid orbitals of the kind suggested for hydrogen. Then Garner's 'CO_3' ion[34] is the limit corresponding to the hydroxyl group.

Insulators

The same principles must operate in chemisorption by these oxides, but now the affinity for electronegative species is so great that almost the whole of the surface is covered with a tightly bound layer up to moderately elevated temperatures. Loss of oxygen to give *n*-type conductivity will occur preferably at lattice defects which cause a local tendency to crowding of anions; these may well exist at regions of misfit which, in the $Al_2O_3 \cdot xH_2O$ system for instance, can give rise to the 'γ-alumina' structures[35]. Thus the Bronsted-acid centres present at low temperatures give way to Lewis-acid or semiconducting centres at elevated temperatures, with loss of water and distortion of the surface polyhedra (e.g. tetrahedron to trigonal plane). The residual orbital is now p_z, which can provide weak or strong chemisorption depending upon whether it is pure or hybridized with *s*; it accepts lone pairs or π-electrons in Dewar bonds, but cannot react with hydrogen molecules with anything like the ease of *d*- and *dsp*-orbitals.

GENERAL DISCUSSION

It is now becoming clear how the electronic configuration of the solid controls all the degrees of interaction with sorbates, from the accommodation coefficient through physical adsorption and the several chemisorptions to final solution or occlusion. The *s*,*p*-metals, except copper, do not dissolve hydrogen; copper dissolves a little (endothermally) whereas the *d*-metals of the first long period dissolve appreciable amounts with heats which are endothermal from nickel to iron, endothermal and exothermal in different temperature ranges at manganese and chromium, but exothermal at vanadium and titanium[36]. The critical electron concentrations occur near copper and manganese, and the latter would repay a detailed investigation in both metallic and oxide systems.

The weak chemisorptions do not only replace the physical adsorptions operative in the Rideal-Eley type of mechanism, but can operate also in Bonhoeffer-Farkas processes and provide a natural explanation of Mignolet's observations[37] and Erlich's precursors of chemisorption[38].

It will be seen that chemisorption is a special case of Mulliken's 'inner' and 'outer' complexes[39], and that crystal-field theory, with appropriate molecular-orbital modifications, allows an easy transition to homogeneous catalysis where somewhat similar activity patterns apply[5,40].

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1.2

SOME ASPECTS OF THE QUANTUM MECHANICS OF CHEMISORPTION

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SUMMARY

The quantum mechanics of the chemisorption of hydrogen on to a metal surface is discussed. It is shown that the assumption that there are H^- *ions on the surface involves an approximation which cannot be justified for any metal. An investigation of the one-electron functions for the combined system metal + hydrogen atom shows that certain of these functions are localized about two centres: one centre is the proton, the other is the metal atom immediately below it in the surface. If there is a localized orbital with energy lying below the Fermi level of the metal, it will be doubly occupied and a covalent bond is formed between the hydrogen atom and the metal.*

INTRODUCTION

When a hydrogen atom is near the surface of a metal, the simplest situation that can be imagined is that an electron is transferred from the metal to the atom to give a negative hydrogen ion at the surface. The interaction energy Q of the system hydrogen atom + metal would then be given by a formula of the form

$$Q = \phi - \chi + K + J \tag{1}$$

where ϕ is the work function of the metal and χ the electron affinity of the hydrogen atom. K is the Coulomb interaction and J the quantum mechanical exchange interaction of H^- with the metal; both these terms depend upon R, the distance of the ion from the surface of the metal. If the right-hand side of (1) is negative, the system is stable against dissociation into clean metal and hydrogen atoms. The dissociation energy of H_2 is 4·5 eV, so that unless (1) leads to a binding energy greater than about 2·3 eV, the system is unstable against dissociation into clean metal and hydrogen molecules. To explain the known heats of chemisorption of H_2 on the transition metals, values of $-Q$ near 3 eV are required. Using a simplified form of (1) obtained by neglecting J and replacing K by the ordinary image potential, several authors[1,2] have shown that values of $-Q$ as large as this cannot be obtained. One concludes, therefore, that H_2 is not chemisorbed by metals as the H^- ion. We shall discuss the quantum mechanics of this 'anionic chemisorption' in the next section. Apart from the fact that this discussion leads to expressions for the quantities K and J in (1), it is of importance because it shows what assumptions must be made in the general quantum mechanical problem to obtain a description of the system which corresponds to the presence of H^- ions at the metal surface. It is then easy to see how these assumptions must be modified to obtain a more accurate description of the system. When this is done it turns out that there are one-electron functions (orbitals) for the system metal + hydrogen atom which are localized about two centres. One centre is the proton, the other is the metal atom adjacent to it in the surface. The importance of these localized orbitals in the theory of chemisorption is that, when such an orbital is occupied by a pair of electrons, the bond between the hydrogen atom and the metal is essentially a covalent bond. It is natural to assume, therefore, that if chemisorption is to occur, a surface bond of this type must be formed. Then the condition for chemisorption is that there must be a localized orbital with energy lying below the Fermi level in the metal.

ANIONIC CHEMISORPTION

In a quantum mechanical treatment of the binding of a hydrogen atom to a metal surface by means of the ordinary Hartree-Fock approximation, the first problem is to find the one-electron functions and energies for the system metal + hydrogen atom. This is a very difficult task.

Suppose we have a metal containing $(N + 1)$ Fermi electrons. Let $\psi_k^0(x_k)$ $(k = 1, 2, \ldots N + 1)$ be the Hartree-Fock functions for the isolated metal. Here x_k stands for the space and spin coordinates of the kth electron, i.e. $(x_k) = (r_k, s_k)$. These spin-orbitals are formed by multiplying the orbital $\psi^0(r)$ by either of the two spin functions $\alpha(s)$ or $\beta(s)$. Let $u(x)$ be a Hartree-Fock spin-orbital for a $1s$-electron in H^-. Then, as the zero-order wave function for the system we might take

$$\Psi(x_1 \ldots x_{N+2}) = C^0 \det|\psi_1^0(x_1) \ldots \psi_N^0(x_N) u_1(x_{N+1}) u_2(x_{N+2})| \quad (2)$$

where C^0 is a normalizing constant. This function represents the state in which an electron is transferred from the metal to the hydrogen atom so that H^- is the species in interaction with the metal. There is no loss of generality in assuming N to be even, so that (2) is a singlet state. For convenience in what follows, we use the bold-face symbol $\boldsymbol{\psi}_N^0$ to represent the set $\psi_k^0 (k = 1 \ldots N)$ of spin-orbitals on the metal and $\mathbf{u}$ to represent the two spin-orbitals of H^-.

In calculating the total energy of the system for the wave function (2), there are difficulties associated with the overlapping of the orbitals of the set $\boldsymbol{\psi}_N^0$ with those of $\mathbf{u}$ at any finite distance of the proton from the metal surface. This lack of orthogonality can be removed if the set $\mathbf{u}$ is replaced by a new set in which each orbital is a certain linear combination of all orbitals in the original set $(\boldsymbol{\psi}_N^0, \mathbf{u})$. For the moment we ignore this overlapping problem and treat the set $(\boldsymbol{\psi}_N^0, \mathbf{u})$ as though all orbitals were orthogonal. If the inner-shell electrons on the metal atoms together with the nuclei are treated as structureless ion-cores, the interaction energy of the system is given by a formula of the form (1). K and J are defined by

$$K = W - 2 \sum_k \int \psi_k^{0*}(\mathbf{r})(\mathbf{r} - \mathbf{R})^{-1} \psi_k^0(\mathbf{r})\, d\mathbf{r} + 2 \int u^*(\mathbf{r} - \mathbf{R}) V(\mathbf{r}) \times$$
$$u(\mathbf{r} - \mathbf{R})\, d\mathbf{r} + 4 \sum_k \iint \psi_k^{0*}(\mathbf{r}_1) u^*(\mathbf{r}_2 - \mathbf{R}) \times$$
$$(1/\mathbf{r}_{12}) \psi_k^0(\mathbf{r}_1) u(\mathbf{r}_2 - \mathbf{R})\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (3)$$

$$J = -2 \sum_k \iint \psi_k^{0*}(\mathbf{r}_1) u^*(\mathbf{r}_2 - \mathbf{R}) (1/\mathbf{r}_{12}) \psi_k^0(\mathbf{r}_2) u(\mathbf{r}_1 - \mathbf{R})\, d\mathbf{r}_1\, d\mathbf{r}_2 \quad (4)$$

Here $\mathbf{R}$ is the position of the proton with respect to any convenient origin. We choose the origin to be in the surface of the metal and take $\mathbf{R}$ perpendicular to the surface. $V(\mathbf{r})$ is the potential energy of an electron in the field of the metallic ion-cores and W is the potential energy of the proton in this field.

An important conclusion can be reached at once. It is that both K and J are short-range interactions. J, the exchange integral, is naturally a short-range term. The short-range nature of K, the Coulomb integral, follows from the fact that, for large R, it represents the potential energy of a negative charge (the hydrogen ion H^-), in the electrostatic field of a clean metal. This field is due to the dipole moment of the metal surface and when R is so large that the atomic structure of the metal may be neglected, the field is zero. This conclusion is not altered by a proper treatment of the overlapping problem between the orbitals of the sets $\boldsymbol{\psi}_N^0$ and $\mathbf{u}$. Hence, with the wave function (2), there are no long-range terms in the expression (1) for the interaction energy, and, if short-range terms are neglected, one has $Q = \phi - \chi$, which is positive for all metals.

The actual evaluation of the short-range terms requires a knowledge of the behaviour of the wave functions for the Fermi electrons near the free surface of the metal. This is a problem needing separate investigation. We note, however, that the function (2) describes two closed-shell systems. The short-range interaction energy of such systems is known to be positive. It does not appear, therefore, that the wave function (2) can lead to the binding of a hydrogen atom to the metal surface.

We may point out at this stage that, in writing the wave function in the form (2), we are not necessarily assuming that the set ($\boldsymbol{\psi}_N^0$, $\mathbf{u}$) is itself an approximate solution of the Hartree-Fock equations for the system. The assumption is that the approximate solutions may be expressed as linear combinations of the basic set ($\boldsymbol{\psi}_N^0$, $\mathbf{u}$). (This follows from the property that the total energy of the system is invariant under unitary transformations of the occupied one-electron functions.) Now this assumption is a very bad one because in the metal there is a large number of unoccupied states with energies very close to that of the highest occupied state. Hence, one would only expect to get an adequate approximation to the actual Hartree-Fock functions if the set $\boldsymbol{\psi}_N^0$ were supplemented by a large number of these normally unoccupied states. This inadequacy of the set ($\boldsymbol{\psi}_N^0$, $\mathbf{u}$) must be regarded as the underlying reason why the function (2) does not lead to any binding of the hydrogen atom.

It is now natural to ask for that total wave function which yields an expression of the form (1) for the interaction energy where the Coulomb term K degenerates to the image potential for large values of R. This function, Ψ', is given by

$$\Psi'(x_1 \ldots x_{N+2}) = C' \det |\psi_1'(x_1) \ldots \psi_N'(x_N) u_1(x_{N+1}) u_2(x_{N+2})| \quad (5)$$

where the orbitals $\psi_k'(k = 1, 2, \ldots N)$ are the N lowest Hartree-Fock functions for an electron moving in the self-consistent field of the metal and the H^- ion. Like (2), the function (5) represents the state in which an electron is transferred to the hydrogen atom so that H^- is the species in interaction with the metal. We note also that the essential assumption in (5) is that the actual Hartree-Fock functions may be expressed linearly in terms of the set ($\boldsymbol{\psi}_N'$, $\mathbf{u}$). This assumption is open to the same objection as that already mentioned in connection with the set ($\boldsymbol{\psi}_N^0$, $\mathbf{u}$). Namely, there is a large number of states with energies lying very close to the highest state of the set $\boldsymbol{\psi}_N'$ and these states cannot be neglected if one wishes to obtain an adequate approximation. Thus the function (5) suffers from the same defect as the function (2), and the presence of a long-range

Coulomb interaction which enhances the binding with (5) is of little significance.

THE COVALENT BOND IN CHEMISORPTION

The discussion in the previous section shows how the approximation is to be improved. The set ψ_N^0 has to be supplemented by a large number of normally unoccupied states to give a new set ψ^0, and hence a new basic set $(\psi^0, \mathbf{u})$, in terms of which the Hartree-Fock functions are to be expressed. If all the states of the isolated metal were included in ψ^0, this set would be complete and could be used alone as the basic set. The convergence would be slow, however, and for practical purposes it seems better to retain the hydrogen-ion functions in the basic set and to include in ψ^0 only those states of the metal which are considered important for the problem on hand. A simple example will make this clear. Consider a hypothetical metal which has a non-overlapping band system and in which the Fermi electrons occupy an *s*-band. All states in the *s*-band must be included in the set ψ^0, but states in the higher unoccupied bands will be of lesser importance and may be neglected in a first approximation. If the *s*-band is completely filled, we have the set ψ_N^0 again. Since this situation does not arise in any real metal, we have a little more insight into the failure of the function (2) to predict any binding. All real metals have a complicated overlapping band system, and states from several bands will be needed in the set ψ^0.

In this section we investigate, in the simplest manner possible, the orbitals for the system metal + hydrogen atom, assuming that only the states from a single band are important in the set ψ^0. We use the tight binding or LCAO approximation, and assume a simple cubic structure for the metal. The important result emerges that there exist orbitals which are localized about two centres. One centre is the proton, the other is the metal atom adjacent to it in the surface.

Let the proton be located at a perpendicular distance R from an atom in the metal surface. With the origin of coordinates at this atom, the position of any atom in the metal is defined by the vector

$$(l, m, n) = l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$$

where l, m, and n are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the vectors which map out the unit cell of the crystal. We take the x- and y-axes in the surface and the z-axis perpendicular to it so that

$$l = -\infty \ldots 0 \ldots +\infty, \quad m = -\infty \ldots 0 \ldots +\infty, \quad n = 0 \ldots \infty$$

Let v_{lmn} be the atomic orbital centred on the metal atom at the point (l,m,n), and let u be the $1s$-orbital centred on the proton. We assumed that any orbital ψ for the system metal + hydrogen atom can be expressed in the form

$$\psi = au + \sum_{lmn} c_{lmn} v_{lmn} \tag{6}$$

ψ is here expressed in terms of the atomic orbitals v_{lmn}. However, the orbitals v_{lmn} may be expressed linearly in terms of all the crystal states ψ_k^0 which arise from this atomic level. Hence ψ may be expressed in terms of the set $(\boldsymbol{\psi}^0, \mathbf{u})$, where only those crystal states which arise from the atomic state v are included in the set $\boldsymbol{\psi}^0$. This is our fundamental approximation. If H is the one-electron Hamiltonian operator for the system $(H\psi = \varepsilon\psi)$, put

$$\int v_{lmn}^* H v_{lmn}\,\mathrm{d}\tau = \begin{cases} \alpha & \text{if } (l,m,n) \text{ is in the interior of the crystal} \\ \alpha' & \text{if } (l,m,n) \text{ lies in the surface } (n = 0) \\ \alpha'' & \text{if } l = m = n = 0 \end{cases} \tag{7}$$

$$\int v_{lmn}^* H v_{pqr}\,\mathrm{d}\tau = \begin{cases} \beta & \text{if } (l,m,n) \text{ and } (p,q,r) \text{ are nearest neighbours} \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

$$\int u^* H u\,\mathrm{d}\tau = A, \qquad \int u^* H v_{000}\,\mathrm{d}\tau = \beta' \tag{9}$$

The need for $\alpha' \neq \alpha$ arises whenever there is a free surface of the metal; α'' differs from α' because of presence of the proton, whilst β' gives the interaction between the hydrogen atom and the metal. Neglecting all overlap integrals, we have the usual linear equations

$$(\varepsilon - \alpha) c_{lmn} = \beta(c_{lmn+1} + c_{lmn-1} + c_{lm+1n} + c_{lm-1n} + {} + c_{l+1mn} + c_{l-1mn}) \tag{10}$$

for (l,m,n) in the interior of the crystal. The boundary conditions are

$$(\varepsilon - \alpha') c_{lm0} = \beta(c_{l+1m0} + c_{l-1m0} + c_{lm+10} + c_{lm-10} + c_{lm1}) \tag{11}$$

$$(\varepsilon - \alpha'') c_{000} = \beta(c_{100} + c_{-100} + c_{010} + c_{0-10} + c_{001}) + \beta' a \tag{12}$$

$$(\varepsilon - A) a = \beta' c_{000} \tag{13}$$

When the hydrogen atom is at large distances from the metal surface, $\beta' = 0$, $\alpha' = \alpha''$, and the states for the isolated metal are obtained by solving equations (10) and (11). This problem has been treated by GOODWIN[3]. If v_{lmn} are s-orbitals, β is negative. Goodwin shows that if $(\alpha - \alpha')/\beta > 1$ then, apart from the usual crystal orbitals with energies forming a quasi-continuous band, there is a band of surface states. These states correspond to coefficients c_{lmn} of the form

$$c_{lmn} = C(-)^n \exp [i(l\theta_1 + m\theta_2) - n\xi] \tag{14}$$

with θ_1, θ_2 and ξ real and $\alpha - \alpha' = \beta \exp \xi$. These surface orbitals are therefore periodic, parallel to the surface, but decay exponentially into the metal perpendicular to the surface.

When the hydrogen atom is at any finite distance from the metal surface so that the extra conditions (12) and (13) have to be satisfied, it is easy to show that, provided surface states exist for the isolated metal, *localized states* exist for the combined system. These states have finite values of a in (6) and, if the v_{lmn} are s-orbitals, coefficients c_{lmn} of the form L_1 or L_2,

$$L_1\colon \quad c_{lmn} = C(-)^n \exp [-(|l| + |m|)\eta - n\xi] \tag{15}$$

$$L_2\colon \quad c_{lmn} = C(-)^{|l|+|m|+n} \exp [-(|l| + |m|)\eta - n\xi] \tag{16}$$

These localized orbitals therefore decay exponentially into the metal both perpendicular and parallel to the surface. States of the form (15) lie below the usual band of crystal states if $2 \cosh \eta - \cosh \xi > 3$, within the band if $-3 < 2 \cosh \eta - \cosh \xi < 3$, and above the band if $2 \cosh \eta - \cosh \xi < -3$. States of the form (16) are always above the band. There is always one localized state, and it may be of the form L_1 or L_2. The maximum number of such states which may be formed from the s-band is two, and any combination of the states L_1 and L_2 is possible. If we write

$$\begin{aligned} x &= [(\alpha' - A)/\beta] - [\beta/(\alpha - \alpha')] \\ y &= (\alpha' - \alpha'')/\beta \\ \Gamma^2 &= (\beta'/\beta)^2 \end{aligned} \tag{17}$$

then all possibilities for the existence of localized states may be shown as in *Figure 1*. The rectangular hyperbolas $(x - 4)y = \Gamma^2$, $(x + 4)y = \Gamma^2$ split the xy-plane into five regions. In every region localized states occur. L_1 indicates one state of the type L_1, L_1L_2 means that there are two states, one of each type, and so forth. For a given metal, both the number and type of localized states depend upon the nature of the interacting atom, while for a given atom they vary from metal to metal. We note that, in general, the localized orbitals spread over several atomic distances into the metal. Only if both η and ξ are large is just one metal atom mainly involved.

Suppose now that there is a localized state with energy lying below the Fermi level in the metal. The corresponding orbital will be occupied by two electrons with opposite spins. If this orbital is derived from an s-band it must be of the form L_1. Define a function ϕ by the equation

$$\phi = N^{-1/2} \sum_{lmn} (-)^n v_{lmn} \exp\left[-(|l| + |m|)\eta - n\xi\right] \tag{18}$$

where N is chosen such that ϕ is normalized. Then the localized orbital, which we denote by χ to distinguish it from the non-localized orbitals for the combined system, may be expressed in the form

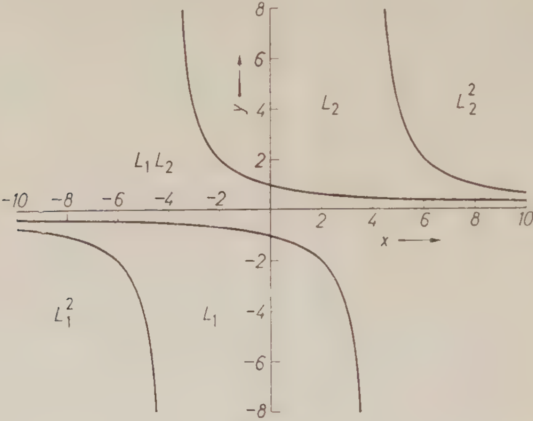

Figure 1.

$$\chi = au + b\phi \tag{19}$$

Now ϕ is localized on the metal atom at the origin, whilst u is, of course, centred on the proton. Hence, the orbital (19) has essentially the same form as the molecular orbitals for a diatomic molecule obtained by the simple LCAO theory. The wave function for the system is (compare (2) and (5))

$$\Psi(x_1 \ldots x_{N+2}) = C \det \left|\psi_1(x_1) \ldots \psi_N(x_N)\chi_1(x_{N+1})\chi_2(x_{N+2})\right| \tag{20}$$

where the $\psi_k (k = 1 \ldots N)$ are the N lowest non-localized spin-orbitals for the system. When the total energy is calculated with the function (20), we find that it contains a set of terms characteristic of the expression for the energy of a diatomic molecule. One nucleus of the 'molecule' is the proton, the other is the field of force provided by the metallic ion cores together with all the electrons except the two which are localized in the orbital χ.

It should be clear from the above remarks that, when a localized orbital is doubly occupied, something quite like a covalent bond is formed between the hydrogen atom and the metal. The analogy with the qualitative quantum mechanical description of the covalent bond in molecules can be made closer. The function ϕ of equation (19) may be formed by linear superposition of the states ψ_k^0 of the isolated crystal just as one forms, for example, the sp^3-hybrids from the s- and p-states of a carbon atom to describe the tetravalent state. One may therefore regard the state in which ϕ is singly occupied as the *valence state* of the isolated metal.

It seems natural to suggest that important binding of a hydrogen atom to a metal surface is not to be expected unless a covalent bond of the type described in this section is formed. The condition for chemisorption is then that there must be localized states with energy lying below the Fermi level of the metal. For a real metal, where we have an overlapping band system, the location of the energies of the localized states with respect to the Fermi level is a difficult problem even with the simplest model. Further work on this matter is in progress.

FURTHER REMARKS AND GENERALIZATIONS

We have seen that the interaction of an s-orbital on the proton with the s-band* of the metal gives the localized states L_1 and L_2. These orbitals are unchanged under those symmetry operations which transform the atoms of the metal surface into one another and leave the interacting atom unchanged. In the language used to describe diatomic molecules, they are σ-orbitals, and the resulting bond is a σ-bond. Consider now the interaction with a p-band. Only one of the three p-bands interacts with an s-orbital in the atom, namely, that derived from the atomic function p_z. From the p-band, therefore, we have a maximum of two localized orbitals. Again, these are σ-orbitals. The overlapping of the s- and p-bands does not alter the character of the localized orbitals, but even in the tight-binding approximation it does not appear possible to obtain either the wave functions or the energies of the resulting states.

If we have p-orbitals available on the interacting atom, the p_z-orbital interacts with the s- and p_z-bands of the metal to give localized σ-orbitals. In addition, the p_x-orbital interacts with the p_x-band and the p_y-orbital with the p_y-band to give localized π-orbitals. These orbitals are doubly degenerate. This situation, which is relevant to the case of oxygen in interaction with a metal surface, shows how double bonds may be formed. Similar conclusions may be reached for interactions involving d-bands.

An important consequence of the present picture of the surface

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* The s-band is always held to include the surface states which arise from the atomic s-level.

bond for hydrogen is that a decrease in the heat of chemisorption with increasing surface coverage is to be expected. This follows because, if the bonding of a hydrogen atom involves the presence of a pair of electrons in a localized orbital, the total energy, when there are two such bonded atoms, contains a term corresponding to the repulsion between two closed-shell systems. Now if η in equation (18) is not too large, the localized orbital is large over several metal atoms in the surface, and two localized orbitals will begin to overlap when the associated hydrogen atoms are rather far apart. The effect will thus set in much earlier than the usual short-range repulsion between closed-shell atoms or ions.

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1.3

THE CAUSE OF THE DECREASE IN THE HEAT OF CHEMISORPTION ON METALS WITH COVERAGE[1]

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SUMMARY

Various suggestions have been offered to explain this decrease, such as heterogeneity of the surface and mutual repulsion of dipoles. In 1934, for alkali-metal atoms on metal surfaces, the author described the effect as a consequence of the change of the work function of the adsorbing metal. Such a work-function effect or surface-potential effect may also be responsible in other cases of chemisorption on metals. Boudart introduced the name 'induced heterogeneity', which is not recommended.

An a priori *heterogeneity is, in all practical cases, superimposed on the surface-potential effect, even with the adsorption of caesium on tungsten.*

Recent attempts to explain the phenomenon by a change in the kinetic energy of the electrons are discussed, especially Temkin's conception of a surface electron gas.

The work-function effect results in a mutual hindrance or a mutual assistance of adsorbed atoms of different species. Many effects caused by contamination on adsorbing surfaces may be understood along these lines.

SOME CURVES

The heat of chemisorption Q is in most cases a function of the degree of coverage θ. *Figure 1* gives a few curves representing the following equations:

$$\text{curve A:} \quad Q_\theta = Q_0 \tag{1}$$

$$\text{curve B:} \quad Q_\theta = Q_0 - a\theta \tag{2}$$

$$\text{curve C:} \quad Q_\theta = Q_0 - b\theta^{3/2} \tag{3}$$

$$\text{curve D:} \quad Q_\theta = Q_0 - \frac{a\theta}{1 + c\theta} \tag{4}$$

$$\text{curve E:}\quad Q_\theta = Q_0 - \frac{a\theta}{1 + c\theta^{3/2}} \tag{5}$$

$$\text{curve F:}\quad Q_\theta = Q_0 - \frac{b\theta^{3/2}}{[1 + c\theta]^2} \tag{6}$$

$$\text{curve G:}\quad Q_\theta = Q_0 - \frac{b\theta^{3/2}}{[1 + c\theta^{3/2}]^2} \tag{7}$$

$$\text{curve H:}\quad Q_\theta = Q_m - k \log \theta \tag{8}$$

$$\text{curve I:}\quad Q_\theta = Q_a \tag{9}$$

In these equations Q_0 represents the initial heat of chemisorption at $\theta = 0$, and Q_m is the lowest value of Q_θ, reached at $\theta = 1$. Q_a is the average value of the heat of chemisorption, while a, b, c, and k are constants. In *Figure 1* the constants are chosen in such a way

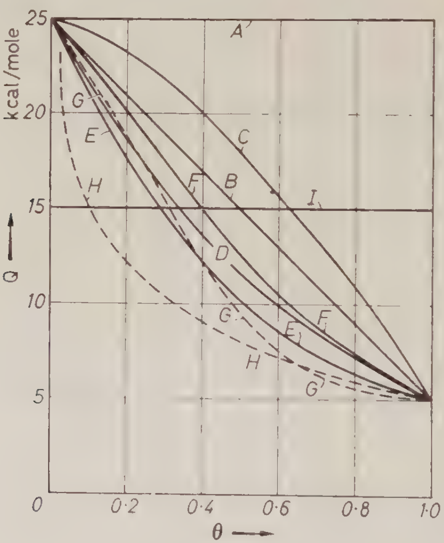

Figure 1

A: equation (1); $Q_0 = 25$ kcal/mole.
B: equation (2); $Q_0 = 25$ kcal/mole; $a = 20$ kcal/mole.
C: equation (3); $Q_0 = 25$ kcal/mole; $b = 20$ kcal/mole.
D: equation (4); $Q_0 = 25$ kcal/mole; $a = 40$ kcal/mole; $c = 1$.
E: equation (5); $Q_0 = 25$ kcal/mole; $a = 40$ kcal/mole; $c = 1$.
F: equation (6); $Q_0 = 25$ kcal/mole; $b = 80$ kcal/mole; $c = 1$.
G: equation (7); $Q_0 = 25$ kcal/mole; $b = 80$ kcal/mole; $c = 1$.
H: equation (8); $Q_m = 5$ kcal/mole; $a = 10$ kcal/mole.
I: equation (9); $Q_a = 15$ kcal/mole.

that for all curves (except curve I) $Q_0 = 25$ kcal/mole and (except for curves A and I) $Q_m = 5$ kcal/mole.

In chemisorption phenomena on metals a constant heat of chemisorption, independent of θ (curve A), is rarely found. If it is, it still does not mean that equation (1) is followed; a constancy of Q_θ also results when the molecules do not move freely over the surface before entering into chemisorption[2]. When they stay at the first point of the surface that they reach, the adsorbed layer will be built up gradually from those parts of the microporous system (e.g. metal films or powders) that are in direct contact with the gas, and will proceed gradually to the interior of the pore system. In this case, the average value of the heat of chemisorption is found, independent of the amount adsorbed (equation (9), curve I).

All the other curves show a decrease of Q with increasing θ. Such behaviour is mostly found in chemisorption on metals. In the following sections we shall discuss some possible physical interpretations of such curves.

MUTUAL REPULSION OF CHEMISORBED MOLECULES

Many authors have tried to explain the decrease of Q as a result of a mutual repulsion of the chemisorbed particles[3]. A short-range repulsion caused by the mutual interpenetration of electron clouds would lead to a linear relationship as indicated by equation (2). Such an effect can only be expected in the case of immobile adsorption, when statistically a certain number of direct neighbours may always be expected, or in the case of mobile adsorption at high degrees of coverage. A necessary condition is, moreover, that the covalent or electrostatic forces, which cause the chemisorption, compel the molecules to approach each other nearer than their mutual van der Waals attractive forces would allow. An effect of this sort has been found with the intercrystalline distances in soap crystals[4], but the author is not aware of any example in the field of chemisorption.

Repulsive forces of long range, such as the mutual repulsive forces of parallel oriented dipoles, would, in the case of immobile adsorption, lead to equation (3). In the case of mobile adsorption, sigmoid curves of $Q = f(\theta)$ would result, resembling curves F and G, but of a more pronounced form. In all known cases, the actual dipoles of the chemisorbed molecules are too small to account quantitatively for the experimentally found values of the decrease[3] of Q.

THE WORK-FUNCTION EFFECT

In 1934 the author[5] suggested that the decrease of the heat of chemisorption of alkali and alkaline-earth metal atoms on tungsten or molybdenum surfaces is caused by the change of the work function of the adsorbent metals by the adsorbed ions. The work function is changed (lowered in this case) by an amount

$$\Delta V = 4\pi\theta\sigma_0\mu \tag{10}$$

where σ_0 is the maximum number of atoms that can be adsorbed per square centimetre and μ is the effective part of the dipole caused by the chemisorption. As one would expect the work function to contribute with its full amount in the heat of chemisorption, one might expect a decrease of Q by the same amount, hence

$$Q_\theta = Q_0 - \varepsilon\Delta V \tag{11}$$

which is equation (2) with $a = 4\pi\varepsilon\sigma_0\mu$, where ε is the charge of an electron.

The adsorption of caesium on tungsten causes a decrease of the work function from 4·52 V at $\theta = 0$ to about 1·65 V at $\theta = 0{\cdot}60$, hence $\Delta V =$ about 2·9 V which would lead to $a =$ about 111 kcal/mole. The heat of adsorption decreases from 68·8 kcal/mole at $\theta = 0$ to 44·8 kcal/mole at $\theta = 0{\cdot}60$, hence $\theta a = 24$ kcal/mole and $a = 40$ kcal/mole. The predicted effect, therefore, is quantitatively too high.

The adsorption of hydrogen on nickel leads to an increase in work function of $\Delta V = 0{\cdot}345$ V for a fully occupied layer[6], which would lead to $a = 7{\cdot}95$ kcal/mole. The decrease in the heat of chemisorption is 14·4 kcal/mole H_2 for a fully occupied layer[7], which means $a = 7{\cdot}2$ kcal/mole H. The predicted effect is of the right order of magnitude in this case. The same is found with the adsorption of hydrogen on other metals (MIGNOLET[18]).

A DISCONTINUOUS CHARGE DISTRIBUTION

As pointed out in 1934[5], the dipole layer, which is formed by the chemisorbed caesium ions, may not be treated as a layer with a continuous charge distribution. It is a double layer of discrete charges and its electric field extends far beyond the dimensions of the dipoles. Consequently, a tungsten layer which is already covered with caesium ions adsorbs a newly arriving caesium *ion* stronger than a bare surface does. The heat of chemisorption of the caesium *atoms*, consequently, decreases less than calculated above.

An attempt to express the influence of the discreteness of the dipole layer more quantitatively led the author recently[8] to the equation

$$Q_\theta = Q_0 - 2\varepsilon \frac{\delta}{d}\pi\theta\sigma_0\mu \tag{12}$$

where δ is the length of the dipoles and d their mutual distance. As the effective part of the dipole $\mu = \varepsilon\delta/2$ and as $1/d = \sqrt{\sigma_0\theta}$, we obtain:

$$Q_\theta = Q_0 - 4\pi(\sigma_0\theta)^{3/2}\mu^2 \tag{13}$$

This equation is of the form of equation (3) and $b = 4\pi\sigma_0^{3/2}\mu^2$. Recently Mignolet[18] derived an equation for the 'structural factor' of the double layer. Following his conception, we can again derive (3) with $b = 18\sigma_0^{3/2}\mu^2$. With the known figures for $\sigma_0 = 3{\cdot}56 \times 10^{14}$ cm^{-2} and $\mu = 6{\cdot}8$ debye, b amounts to 56·4 kcal/mole; the decrease of Q, between $\theta = 0$ and $\theta = 0{\cdot}60$, therefore, would amount to about 26 kcal/mole, which compares well with the figure of 24 kcal/mole found experimentally. Equation (3), however, gives a $Q = f(\theta)$ curve which is concave to the origin (curve C of *Figure 1*). The experimental curve, on the other hand, which is given as curve A in *Figure 2*, is convex to the origin. This discrepancy must be

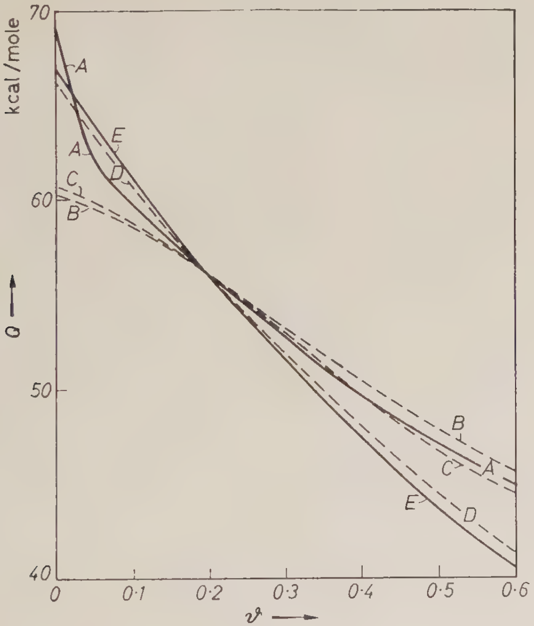

Figure 2

A: the heat of chemisorption of Cs on W (Taylor and Langmuir).
B: calculated curve, using equation (6).
C: calculated curve, using equation (7).
D: calculated curve, using equation (4).
E: calculated curve, using equation (5).

ascribed to the fact that we have assumed μ to be a constant, whilst, being caused by the mutual depolarization, it is a function of θ itself.

INFLUENCE OF THE DEPOLARIZATION

Using the conception of immobile dipoles, μ is given by

$$\mu_\theta = \mu_0/[1 + 9a\theta\sigma_0^{3/2}] \tag{14}$$

while mobile dipoles lead to

$$\mu_\theta = \mu_0/[1 + 9a(\theta\sigma_0)^{3/2}] \tag{15}$$

where a stands for the polarizability (a mean value, taken to be constant). Equation (14), together with (13), leads to an equation of the form of equation (6) with $b = 4\pi\sigma_0^{3/2}\mu_0^2$ and $c = 9a\sigma_0^{3/2}$, while equation (15), together with (13), gives an equation of the form of (7) with the same values of the constants. Both curves are given in *Figure 2*, B being the curve calculated with equations (14) and (13) and C with equations (15) and (13). They have been fitted on to curve A at $\theta = 0{\cdot}2$; the following figures were used: $\mu_0 = 6{\cdot}88$ debye (based on $\mu = 6{\cdot}8$ debye at $\theta = 0{\cdot}07$), $\sigma_0 = 3{\cdot}56 \times 10^{14}$ cm^{-2}, and $a = 10 \times 10^{-24}$ cm^3. Both curves, especially C, follow the experimental curve A quite well in the range of $\theta = 0{\cdot}1$ to $\theta = 0{\cdot}6$; they deviate distinctly from the initial part of curve A. This could be expected from the shapes of curves F and G of *Figure 1*.

It is only curves D, E, and H of *Figure 1* which start with a convex part. Curves D and E, representing equations (4) and (5), respectively, picture a dipole layer with continuous charge distribution, together with depolarization of the dipoles. In trying these equations we have to use $a = 111$ kcal/mole, as mentioned previously, which makes the total decrease of the heat of chemisorption far too large. Boudart[9], following up the conception of the work-function effect, but using the somewhat strange picture of sticking the charge halfway along the dipole layer, concludes

$$\Delta Q = \tfrac{1}{2}\varepsilon\Delta V \tag{16}$$

Assuming for a moment that this factor $\frac{1}{2}$ accounts, empirically, for the effect of the discreteness of the dipole layer, we shall use equations (4) and (5) with $a = \frac{1}{2} \times 111$ kcal/mole $= 55{\cdot}5$ kcal/mole and $c = 9a\sigma_0^{3/2} = 0{\cdot}603$; fitting the curves on curve A at $\theta = 0{\cdot}2$, curves D and E of *Figure 2* result. They do not give the desired effect.

HETEROGENEITY OF THE SURFACE

The remaining possibility is an equation of the shape of equation (8). This equation has not, as far as the author knows, any other background than a distribution of heats of chemisorption, leading to an isotherm equation of the so-called Freundlich type. The physical meaning is heterogeneity of the surface.

As the experimental curve A of *Figure 2* was obtained by TAYLOR and LANGMUIR[10] from experiments with tungsten wires heated to a high temperature, the only heterogeneity which one can visualize is the presence of some crystallographic faces other than the main face which is present. The work functions of various faces of tungsten may differ[11] by an amount of 1·1 V, corresponding to about 25 kcal/mole, and it is known that the heat of chemisorption of caesium differs on various faces of tungsten[12].

The author, therefore, suggests that the fall of the heat of chemisorption of caesium on tungsten, as measured by Taylor and Langmuir, is mainly due to the work-function effect, but that a certain degree of heterogeneity of the surface is present.

HYDROGEN ON NICKEL

The dipole, formed by this chemisorption, has only a very small dipole moment. The mutual depolarization may, therefore, be negligible. MIGNOLET[6] states that, in his experiments, the dipole moments of the chemisorbed H atoms on nickel seem to be independent of θ.

The best experimental curves are those of SCHUIT and DE BOER[7]; they show a linear relationship

$$Q_\theta = 25{\cdot}1 - 14{\cdot}4\theta \text{ kcal/mole H}_2 \qquad (17)$$

which for the heat of chemisorption of H atoms means

$$Q_\theta = \tfrac{1}{2}(D_{\mathrm{H}_2} + 25{\cdot}1 - 14{\cdot}4\theta) = 64{\cdot}5 - 7{\cdot}2\theta \text{ kcal/mole H} \qquad (18)$$

A linear decrease is only given by equation (2); a physical picture leading to this equation is the existence of a dipole layer with a homogeneous charge distribution. In that case we expect (*see*, however, the following section)

$$\Delta Q = \varepsilon \Delta V \qquad (19)$$

which, as we have seen earlier, holds here within 10 per cent.

A homogeneous charge distribution of a dipole layer, the negative side of which is pointing outwards, means that the electrons of the negative layer of this double layer are not restricted to localized spots, whereas the positive charges also may move relatively easily.

Such a layer could be formed if the H atoms constitute the *positive* part of the dipoles and at the same time penetrate deep enough into the surface to be situated below the uppermost layer of nickel atoms, or at least below the first layer of conducting electrons.

Such a picture has been suggested[9] and it would explain the existence of a negative double layer combined with an increase of the electric conductivity of the surface, as found by SUHRMANN[13]. At the same time, equation (19) would hold, whereas the decrease of Q would be linear. Linearity also requires the surface to be homogeneous, which SCHUIT[14] found to be true in this case. His nickel crystallites seem to possess one crystallographic face only. EISCHENS, FRANCIS, and PLISKIN[15], studying the infra-red spectra of CO adsorbed on Pd, Ni, and Pt prepared in a similar way, found that their Pd and Ni crystallites showed two or three crystallographic faces; with their Pt crystallites no evidence of more than one face could be found.

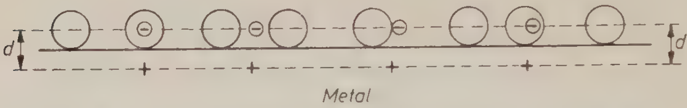

Figure 3. n-atoms, containing m additional electrons, moving freely among the chemisorbed atoms, are adsorbed per unit area ($m < n$); the distance between the extra electrons and their counter-charges is d.

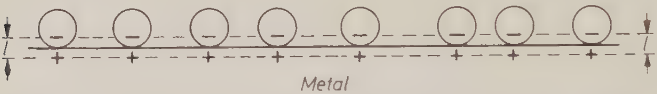

Figure 4. The distance between the electrons and counter-charges, l, is smaller than twice the distance of the centres of the atoms from the metal surface.

VARIOUS TYPES OF DIPOLE LAYERS

The dipole layers in chemisorption are mostly not of a purely ionic character. It is only for the chemisorption of alkali metal atoms, such as caesium, that this picture holds.

In most cases, the dipoles of the chemisorbed layer are formed by atoms, which are bound by covalent bonds. Using the conception of image charges and assuming that the metallic conduction starts at the metal surface[5], the magnitude of the dipole may then either be expressed as (a) the product of a small charge $f\varepsilon < \varepsilon$ and half the distance d of the centres of the two atoms bound together, hence

$$\mu_{\text{eff}} = f\varepsilon \times d/2 \tag{20}$$

or (b) by the product of the charge of an electron, ε, and half the distance of charges, $l < d$, hence

$$\mu_{\text{eff}} = \varepsilon l/2 \tag{21}$$

(a) An array of atoms, bound as pictured in *Figure 3*, consisting of n atoms per unit area, but containing m extra electrons ($m < n$) leads to equation (20). The average charge per atom is $(m\varepsilon)/n$, hence $f = m/n$.

(b) A distribution of atoms and charge as given in *Figure 4*, however, leads to equation (21).

Both cases are indistinguishable with respect to electron emission; in both cases the work function is raised (negative charge pointing outwards) by an amount

$$\Delta V = 4\pi\theta\sigma_0\mu_{\text{eff}} \tag{22}$$

It is only the value of μ_{eff} that matters.

When, however, new atoms are added in the course of chemisorption, the two cases differ. In case (a) the newly added atom has a probability m/n that it has to take up an electron from the metal base; if so, this electron has to penetrate the existing double layer. If that double layer has a continuous charge distribution, the average contribution decreasing the heat of chemisorption is

$$\Delta Q = \frac{m}{n} \times 4\pi\varepsilon\theta\sigma_0\mu_{\text{eff}} \tag{23}$$

Equations (22) and (23) lead to

$$\Delta Q = \frac{m}{n}\,\varepsilon\Delta V \tag{24}$$

In case (b) the probability of shifting the negative charge is unity; the charge is, however, only shifted over a distance $\frac{1}{2}l$. The decrease of the heat of chemisorption, nevertheless (in the case of a homogeneous charge distribution), is

$$\Delta Q = 4\pi\theta\sigma_0\varepsilon^2 l/2 = 4\pi\theta\sigma_0\varepsilon\mu_{\text{eff}} \tag{25}$$

and

$$\Delta Q = \varepsilon\Delta V$$

In this section we have taken the charge distribution to be homogeneous. This means that in case (a) we have to accept that the m charges move freely over the n atoms, a situation which seems quite reasonable. It is a picture similar to that which the author[16] originally used to describe the behaviour of F centres in crystals, and which has proved its usefulness[17].

This picture (case (a)) leads, therefore, to a linear decrease of Q

and, at the same time, probably to an increase of the surface conductivity, despite the fact that electrons are bound by the adsorbed atoms. ΔQ, however, is essentially smaller than $\varepsilon \Delta V$. Many cases, reported by BOUDART[9], may probably be explained by this phenomenon, which would account for his 'empirical' factor $\frac{1}{2}$.

A NEW SUGGESTION BY TEMKIN

Some authors[18] have tried to explain the fall in the heat of chemisorption by the changes of the electron distribution in the metal by the chemisorption process. These electrons occupy successive levels in the conductivity band and the more electrons have to be withdrawn the more energy it will cost, or the more electrons are added to the metal, the smaller the energy gained in the process. It is unlikely, however, that the withdrawal from, or the adding to, the bulk of the metal would involve a sufficient amount of energy to play a part in the process of chemisorption.

TEMKIN[19], therefore, suggested the existence of a surface electron gas, which takes part in the chemisorption process. He derived the following equation:

$$\Delta Q = \frac{h^2 \sigma_0}{4\pi m} \theta \tag{26}$$

where h is Planck's constant and m is the mass of an electron. This expression would give a linear decrease of Q. Generally speaking, the constant a in equation (2), which has to be used in this case, turns out to be too large when calculated by means of equation (26). Consequently, Temkin suggested that m should be replaced by an 'effective mass'. Equation (26) fails to contain any specific properties of the metals used as adsorbents.

If this surface effect exists, the solution of gases into metals, or the formation of alloys, would lead to a corresponding volume effect. There are few quantitative data available. Temkin cites the work of FEDEROVA and FRUMKIN[20] who found that the solution of hydrogen in the β phase of the Pd–H system (Pd with 60 atomic per cent of H) depends on the concentration of the extra H which is dissolved in this phase. The relation is:

$$Q_s = 46{\cdot}7 - 55{\cdot}2 \frac{[\mathrm{H}]}{[\mathrm{Pd}]} \text{ kcal/mole} \tag{27}$$

where Q_s is the heat of solution and the expression [H]/[Pd] stands for the proportion of the atomic concentrations. Equation (27) holds only for the range

$$0{\cdot}6 < \frac{[\mathrm{H}]}{[\mathrm{Pd}]} < 0{\cdot}8$$

When [H]/[Pd] $< 0{\cdot}6$, hence in the region of co-existence of the α and β phases of the Pd–H system, the heat of solution *increases* with the amount of H taken up, as found by LACHER[21]. Lacher's expression, written in a form similar to equation (27), amounts to:

$$Q_s = 4{\cdot}08 + 15{\cdot}3\,\frac{[\mathrm{H}]}{[\mathrm{Pd}]}\ \mathrm{kcal/mole} \qquad (28)$$

valid for [H]/[Pd] $< 0{\cdot}59$.

At [H]/[Pd] $= 0{\cdot}6$, expression (27) gives $Q_s = 13{\cdot}6$ kcal/mole and equation (28), $Q_s = 13{\cdot}2$ kcal/mole.

As long as no more data are available on the dependence of heats of solution in metals on the concentration of the dissolved atoms, it cannot be decided what value should be ascribed to Temkin's suggestion. If his picture is true, it means that the changes in work function and in contact potential are not caused by dipoles. If it is partly responsible for the effect, all data on dipole moments and contact potentials will consequently have to be revised quantitatively.

CONCLUSION

Whatever the cause of the change of the work function may be, we may conclude that the decrease of the heat of chemisorption with increasing degree of coverage is mainly caused by the change of the work function. The author does not recommend the term 'induced heterogeneity' introduced by Boudart. He prefers 'work-function effect'. The chemisorption of Cs on W can be described as a discontinuous distribution of dipoles, and their mutual depolarization. The chemisorption of hydrogen on metals seems to lead to a layer with a continuous charge distribution.

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1.4

THE THERMODYNAMICS OF THE ADSORPTION OF HYDROGEN AND THE EXCHANGE REACTION WITH D_2 OVER METAL CATALYSTS

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SUMMARY

The heats of adsorption of H_2, *the rate of exchange between* $H_2 + D_2$, *and the rate of exchange between adsorbed* D *and gaseous* H_2 *on some metal-on-*SiO_2 *catalysts (especially* Ni–SiO_2) *were measured. The surface-gas exchange shows the metal surface to be heterogeneous. With the aid of the theory of the transition state one can calculate the activation energies of surface-gas exchange on the basis of either the Bonhoeffer-Farkas* (I) *or the Eley-Rideal* (II) *mechanism. The most frequent activation energy according to mechanism* I *agrees satisfactorily with the most frequent heat of desorption at full coverage, but the extrapolated value for the rate of the* $H_2 + D_2$ *exchange is too high by a factor* 10^3. *On the other hand, an activation energy much lower than the heat of desorption can be calculated from mechanism* II, *and this is found to agree in rate with the* $H_2 + D_2$ *exchange. However, if this is accepted, it is not clear why mechanism* I *does not operate as it should.*

INTRODUCTION

This paper contains a survey of a number of experiments performed on the adsorption of hydrogen and the exchange reaction with deuterium over metal-on-SiO_2 and especially Ni-on-SiO_2 catalysts, and is intended for a comparison of the results with the current theories in this field. The subject has been treated recently by Trapnell in considerable detail[1,2], and there is hence no need to point out its main problems. It is assumed throughout that hydrogen is adsorbed by the formation of a covalent bond (Eley[3]) between a hydrogen atom and a surface metal atom. The heat of adsorption is known to decrease with increasing coverage for reasons not fully understood so far, which may or may not have to do with a hypothetical heterogeneity of the metal surface.

There are two hypotheses to account for the readily occurring exchange between H_2 and D_2 over metal surfaces. The first was given by BONHOEFFER and FARKAS[4] and connects the exchange with the adsorption-desorption process

$$\mathrm{H_2} + 2\text{Ⓢ} \rightarrow 2H, \quad \mathrm{D_2} + 2\text{Ⓢ} \rightarrow 2D, \quad \mathrm{D} + \mathrm{H} \rightarrow \mathrm{HD} + 2\text{Ⓢ}$$

in which Ⓢ is an empty site and H or D is an adsorbed atom. (This hypothesis will further be denoted as mechanism I.) The second was proposed by RIDEAL[5] and particularly advocated by Eley: it is further referred to as mechanism II:

$$\mathrm{H_2} + D \rightarrow H + \mathrm{HD}$$

The process may involve either a triatomic complex on one site or the transition state may occupy more than one site and hence necessitate the simultaneous presence of an occupied and at least one empty site.

EXPERIMENTS

The catalysts used by us were made either by coprecipitation of the metal hydroxides and silica or by impregnation of Davison silica gel grade 22 (surface 720 m^2/g, pore volume 0·39 cm^3/g after evacuation at 400°C) with metal salt solutions. The reduction temperature was generally 500°C, the temperature of evacuation 400°C. With these catalysts the following observations were made.

1. If hydrogen is admitted at room temperature to a $Ni-SiO_2$ catalyst and the heat evolved measured calorimetrically, the heat of adsorption is found to be constant so long as the gas pressure remains low, but it drops suddenly when the pressure becomes of the order of millimetres of mercury. The heat of adsorption measured was 17 ± 3 kcal $mole^{-1}$ (*see Figure 1*).

2. As was published earlier[6], the dependency of the amounts of hydrogen adsorbed on the temperature and pressure at equilibrium could be given by equation (1)

$$RT \ln p + T\left(\frac{\mu_T^\circ - h_0^\circ}{T}\right)_{\mathrm{H_2}} - 2\,RT \ln \frac{\theta}{1-\theta} = \varphi(\theta) \qquad (1)$$

in which p = pressure (atmospheres)

T = temperature °K

$\left(\frac{\mu_T^\circ - h_0^\circ}{T}\right)_{\mathrm{H_2}}$ = 'free-energy function' of gaseous H_2

$\theta = V/V_m$

where $V = \text{cm}^3\ H_2$ (STP) adsorbed at T and p while $V_m = \text{cm}^3\ H_2$ adsorbed at 195°K and $p = 1$ after evacuation of the reduced catalyst for 4 hours at 400°C (10^{-6} mm Hg). $\varphi(\theta)$ is a function of θ and proves to be nearly or completely independent of T. It therefore can be supposed to be a good approximation to $\Delta h(\theta)$, the heat of adsorption at coverage θ. In first approximation φ is linear in θ

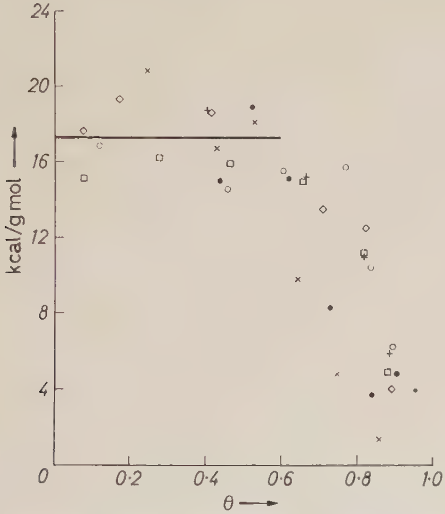

Figure 1. Heats of hydrogen adsorption to nickel-on-SiO_2; calorimetric data. (Separate runs are indicated by different signs.)

$$\varphi(\theta) = \Delta h_0(\theta) + \alpha\theta = -24000 + 14400\ \theta \text{ cal mole}^{-1} \qquad (2)$$

On closer inspection, the dependency proves to be slightly sigmoidal in character, the experimental values being somewhat greater at low θ and somewhat lower at high θ. This curvilinear character becomes somewhat more pronounced if it is assumed that a 'bare' surface, as obtained after pumping at 400°C, still contains some residual hydrogen from the reduction, and that a 'full' surface is not completely filled. The first supposition is probably not realistic since the adsorption of D_2 on a 'bare' surface and subsequent desorption showed only traces of hydrogen in the pumped-off gas. It is, however, very probable that the metal surfaces investigated here were not completely covered even at 195°K and 1 atm. This is shown by *Figure 2*, in which the adsorption at a pressure of 100 mm and various temperatures together with the adsorption on an equal amount of the carrier material has been plotted. As is evident, saturation is not yet attained at −78°C, while the slope in the V–T curve cannot be ascribed to van der Waals adsorption on the carrier.

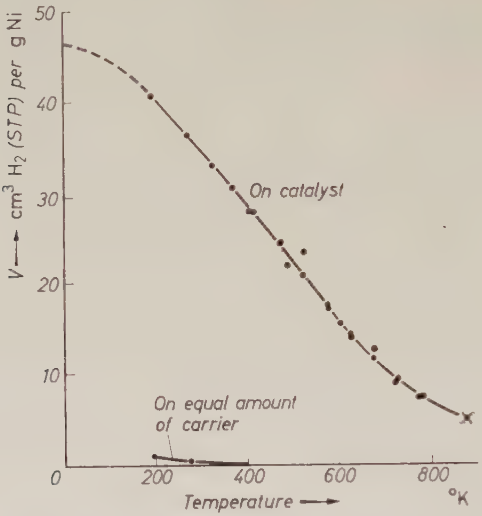

Figure 2. Hydrogen adsorption on Ni–SO_2-impregnated catalyst as a function of temperature at constant pressure (100 mm Hg). Reduction temperature: 700°C; evacuation at 600°C.

Figure 3 shows a comparison of various metals. The 'high coverage' ends of the curves are always suspect in view of the foregoing, but the sections between 20 and 80 per cent are probably correct.

3. The H_2–D_2 exchange over Ni–SiO_2 catalysts follows the kinetics

$$\ln \frac{\gamma_e - \gamma_0}{\gamma_e - \gamma_t} = kt \tag{3}$$

in which γ_e is the fraction of HD at equilibrium in the gas mixture
γ_0 that at time 0
γ_t that at time t

The temperature dependency of k is given by

$$\log k = -\frac{3000}{2{\cdot}3\,RT} - 0{\cdot}15\ (k\ \text{sec}^{-1}) \tag{4}$$

for a ratio of number of sites to number of gas molecules at 1 atm. of 10^{-3} (*see Figure 4*). We do not possess enough data to state the pressure dependency of k.

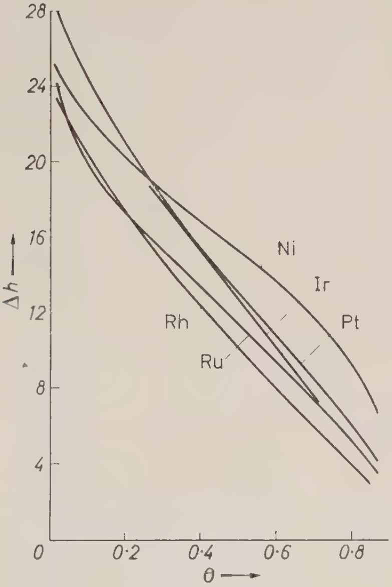

Figure 3. Heats of adsorption on various metals-on-SiO_2 as a function of coverage.

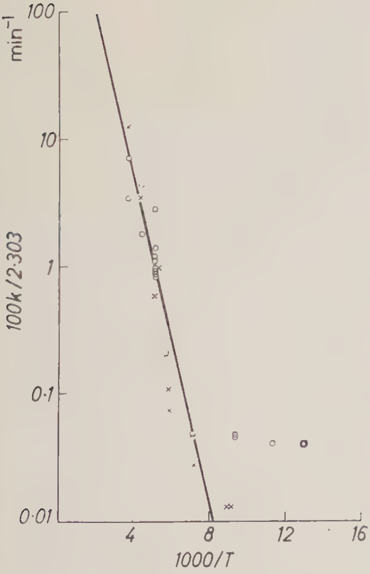

Figure 4. Reaction $H_2 + D_2 \rightleftharpoons 2HD$ over Ni–SiO_2. (Separate runs have been indicated by different signs.)

The activities of various metals for this reaction vary widely. The ratio of activities is roughly given by

$$k_{\mathrm{Pt}} = k_{\mathrm{Rh}} = k_{\mathrm{Ru}} = 10^2 k_{\mathrm{Ni}} = 10^2 k_{\mathrm{Co}} = 10^4 k_{\mathrm{Fe}} = 10^4 k_{\mathrm{Cu}}$$

The activation energies are respectively

$$\Delta E_{\mathrm{Pt}} = 1, \qquad \Delta E_{\mathrm{Ni}} = 3, \qquad \Delta E_{\mathrm{Fe}} = E_{\mathrm{Cu}} = 8 \text{ kcal mole}^{-1}$$

The log A factors therefore increase with increasing ΔE.

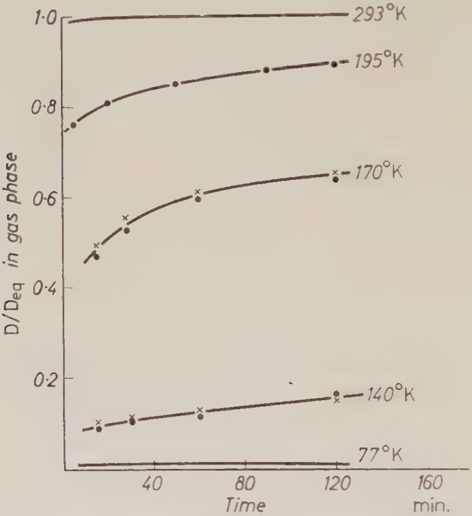

Figure 5. Surface-gas exchange on a Ni–SiO_2 catalyst as a function of time and temperature. (Separate runs have been indicated by different signs.)

4. If a catalyst is covered with D and then brought into contact with gaseous H_2 at a mole ratio of adsorbed isotope to gaseous isotope of the order of 1, the rate of exchange between adsorbed and gaseous isotope can be observed. As is shown by *Figure 5*, this exchange follows an unusual pattern. A part of the adsorbed isotope exchanges very rapidly, another part does so at a measurable rate, while a third part virtually remains stagnant. The higher the temperature, the greater the fraction of rapid exchange: at 77°K there is no, or almost no, exchange, while at 293°K the whole D content of the surface comes to rapid equilibrium with the gas phase. This phenomenon is not caused by an isotope effect since adsorbed H shows the same behaviour towards gaseous D_2 as adsorbed D towards H_2 (*Figure 6*).

Another interesting fact observed is given by the ratios $HD:D_2:H_2$ in the gas phase. As far as could be ascertained, these ratios are

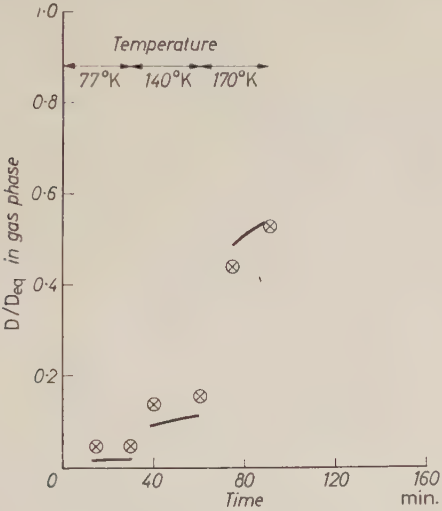

Figure 6. Comparison of exchange of adsorbed D with gaseous H_2: —; and adsorbed H with gaseous D_2: ⊗.

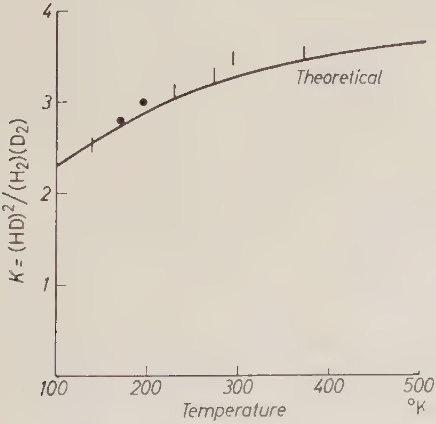

Figure 7. Exchanged atoms, originally on the surface, observed to be in thermodynamic equilibrium with the gas.

always those of thermodynamic equilibrium (*see Figure 7*). Hence, although a considerable part of the adsorbed isotope remains inert, the fraction that exchanges with the gas phase finds some means (either at a very active part of the surface or by a special way of reacting) which rapidly brings it to equilibrium in the gas phase.

THEORETICAL CONSEQUENCES OF THE EXPERIMENTAL RESULTS

It is immediately evident from the characteristics of the exchange between adsorbed and gaseous isotopes shown in *Figure 5* that not all adsorbed H or D atoms are energetically in the same situation and that hence *the nickel surface is heterogeneous.* On those parts of the surface that do not, at a certain temperature, exchange their adsorbed atoms, thermodynamic equilibrium cannot have been attained, since otherwise the dynamic equilibrium between gas and adsorbed phase would have automatically taken care of exchange. Robert's concept of a surface that thermodynamically should have been completely filled, but owing to the absence of pairs of adjacent empty sites necessary for adsorption cannot attain complete coverage, would meet the situation. Since this state of affairs is apparently stable, *the adsorbed atoms appear to be immobile.* This also seems to follow from the impossibility for atoms to cross over from 'inert' to 'active' spots of the surface, but in this case the conclusion might be erroneous and another factor might interfere. If a different exchange activity might arise from a different crystal size, 'crossing over' would be inhibited by the spatial separation of the nickel crystals.

How can the heterogeneity be reconciled with the form of equation (1)? This equation was originally derived for a homogeneous surface, assuming random distribution of the adsorbed atoms, while the heat of adsorption was supposed to decrease with increasing coverage. One of its results was that the standard entropy of the adsorbed atoms appeared very low so that one had to conclude that these were immobile.

By assuming either the heats of adsorption at zero coverage, the decrease in heat of adsorption with increasing coverage, or both to be distributed according to some simple binomial or Poisson-distribution, it was found by numerical calculation that the results of the introduction of a heterogeneous surface in the basic assumptions were remarkably insignificant and were generally in the direction of the experimental deviations from (2). The value —24000 in (2) appears a reasonably good approximation to the initial heat of adsorption of the most frequently occurring sites, while 14400 represents the decrease in heat of adsorption with increasing coverages of these sites. We thus now know that the concept of heterogeneity is reconcilable with equation (1) and that the most we can hope to extract from it is information about the most frequent sites, with some indications as to whether we may or may not have to do with a heterogeneous surface. Since there still is appreciable chemisorption at +195°K, there must be a section of the surface, partially covered or empty, that adsorbs hydrogen with a heat less than about 6 kcal mole^{-1}.

The conclusion as to the immobility of the hydrogen remains valid. Hence, if adsorbed hydrogen is mobile, this is not caused by the atoms 'hopping' from site to site but either by adsorption-desorption of the molecule or by a mobility of the nickel atoms to which the hydrogen atoms are bonded.

The only conclusion which we can derive from the calorimetric measurements is that they represent essentially integral heats instead of differential heats, since this assumption explains the numerical value observed. Therefore, either the gas penetrates into the sample in a zone-like fashion, or it does so into the catalyst grains.

The situation is completely comparable to those observed in chromatography and has no relation to thermodynamic equilibrium.

So far, therefore, our information is confined to a quantitative knowledge of the heat of adsorption at low coverage and the decrease in heat of adsorption with increasing coverage for the most frequently occurring sites, together with a notion that the surface is heterogeneous and that both quantities may show a 'spread'. We will now see whether we can arrive at more quantitative information as regards this spread. To do so we assume that the surface is divided into a number of homogeneous sections. The numbers of sites in these sections are supposed to be distributed according to a Poisson-function. Hence for section r

$$\frac{N_r}{\sum N_r} = \frac{r}{r!}\,e^{-\lambda} \tag{5}$$

in which λ is an adjustable parameter. The activation energies of the surface-gas exchange will vary with r according to

$$\Delta E_r = \Delta E_0 + r\,\Delta^2 E \tag{6}$$

If we neglect a possible contribution of vibratory partition functions to the free energy of the transition state and assume complete coverage, the theory of absolute rates predicts, for the reaction constant of mechanism I:

$$k_{\mathrm{I}} = Z\,\frac{kT}{h}\exp\left(-\frac{\Delta E_{\mathrm{I}}}{RT}\right) \tag{7}$$

where Z is the number of nearest neighbours of a site (= 6) and ΔE_{I} is the activation energy.

For mechanism II on one site, the following equation is valid:

$$k_{\mathrm{II}} = \frac{1}{3} p \frac{kT}{h} \exp\left(-\frac{S^{\circ}_{\mathrm{H}_2}}{R}\right) \exp\left(-\frac{\Delta E_{\mathrm{II}}}{RT}\right) \tag{8}$$

in which p is the pressure (1 atm.), $S^{\circ}_{\mathrm{H}_2}$ is the entropy (cal mole^{-1} degree^{-1}) of gaseous hydrogen, while ΔE_{II} is the activation energy.

At a certain temperature we observe, as shown before, a section that exchanges too fast to follow the rate, another that exchanges at measurable rate, and a third that exchanges very slowly. If we consider the three temperatures 140°, 170°, and 195°K, we can discern seven sections: three sections that exchange at measurable rate, two intermediate sections that exchange slowly at one temperature and fast at the next higher temperature, one section that exchanges fast at the lowest temperature, and one that exchanges slowly at the highest temperature. If now we assume that a fast exchange involved a value of k equal to 10^{-2} sec^{-1}, a measurable rate a k of 10^{-3} sec^{-1} and a slow exchange a k of 10^{-4} sec^{-1}, we can express our rates in terms of activation energies. The intermediate sections allow for a check as to whether the choice of the k values is satisfactory. *Figure 8* illustrates the result. According to mechanism

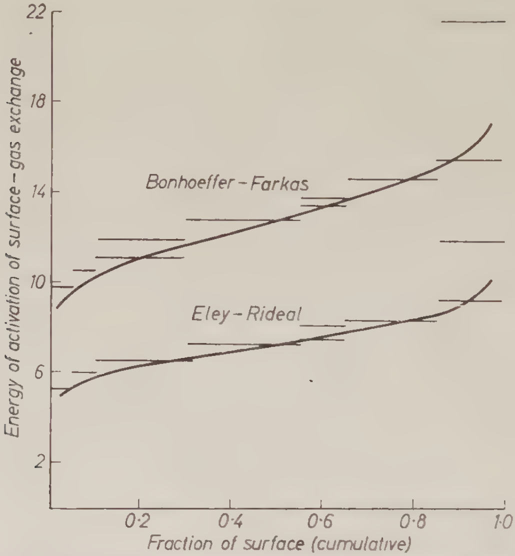

Figure 8. Calculated activation energies of surface-gas exchange, according to Bonhoeffer-Farkas and Eley-Rideal, with Poisson distribution.

I, the most frequent sites possess an activation energy of about 13 kcal mole^{-1}, which is remarkably in accordance with the heat of adsorption at complete coverage (e.g. 9·6 kcal mole^{-1} according to equation (2)). Mechanism II predicts a lower value equal to 7·5 kcal mole^{-1}. The curve through the 'experimental points' represents a Poisson distribution with $\lambda = 10$, while the parameters of equation (6) are: $\Delta E_0 = 6700$, $\Delta^2 E = 640$ for mechanism I; and $\Delta E_0 = 3700$, $\Delta^2 E = 380$ for mechanism II. Other values of λ give an analogous 'fit', although the parameters are different.

The equation for the rate of the $H_2 + D_2$ exchange in a certain temperature interval (170–270°K) can be calculated from these data. We assume that all the sections remain completely covered. Mechanism I then gives for its reaction constant

$$k_{\mathrm{I}} = \frac{1}{2}\frac{\mathrm{I}}{p}\frac{N_s}{N_g^\circ} Z \frac{kT}{h} \exp\left(-\frac{\Delta E_0}{RT}\right) \sum_r \frac{\lambda^r}{r!} e^{-\lambda} \mathrm{e}^{-\frac{r\Delta^2 E}{RT}}$$

and the *ER* mechanism (one-site transition state)

$$k_{\mathrm{II}} = \frac{1}{3}\frac{N_s}{N_g^\circ}\frac{kT}{h} \exp\left(-\frac{S^\circ_{\mathrm{H}_2}}{R}\right) \exp\left(-\frac{\Delta E_0}{RT}\right) \sum_r \frac{\lambda^r}{r!} e^{-\lambda} \mathrm{e}^{-\frac{r\Delta^2 E}{RT}}$$

Here, N_s is the total number of sites and N_g° the total number of gaseous molecules at one atm. ($N_s/N_g^\circ \sim 10^{-3}$).

A numerical evaluation of these constants in the temperature range indicated showed that, more or less independent of the choice of λ, if

$$\log k = -\frac{\Delta E}{2{\cdot}3\,RT} + \log A$$

then for mechanism I:

$$\Delta E = 6{\cdot}5 - 8{\cdot}5 \text{ kcal mole}^{-1}$$

$$\log A = 6 - 8$$

and for mechanism II:

$$\Delta E = 5 - 5{\cdot}5 \text{ kcal mole}^{-1}$$

$$\log A = 1 - 2$$

We are hence confronted with the following difficulties:

1. There is a reasonable agreement between heats of desorption and calculated energies of activation for a surface-gas exchange calculated on the basis of the mechanism I, assuming an activation energy for the adsorption of about 3 kcal mole^{-1}, and one could therefore surmise that the surface-gas exchange occurs via the adsorption-desorption mechanism.

2. This, however, does not agree with the properties of the H_2–D_2 exchange, which properties could be made to agree with those of the surface-gas exchange, if this reaction is assumed to proceed according to the 'one-site' mechanism II.

3. If, however, we adopt mechanism II, we have to account for the fact that mechanism I does not occur, since this should, according to the calculations, be much faster than its alternative.

This dilemma probably arises from our neglect of the influence of partial coverage on rate of exchange. However, as soon as we try to take this factor into account, the lack of information on the distribution of the numerical values of the heat of desorption becomes so important that further attempts in this direction rapidly appear futile. The decision between the applicability of the Bonhoeffer-Farkas mechanism or the Eley-Rideal mechanism for our catalysts (and, according to our belief, also for other systems reported in the literature) cannot, therefore, be made at the moment.

In fact, it is possible that attempts to arrive at such a decision will in any case be in vain. It is now well known that exchange reactions of D_2 with paraffins often proceed simultaneously according to two different mechanisms, a stepwise and multiple exchange. Since mechanism I is a typical example of a multiple, mechanism II of a stepwise exchange, and since they in general possess so much resemblance to the paraffin exchanges, their simultaneous occurrence in this case appears quite probable. We believe that the long-lived problem discussed in this paper will only be solved by proceeding from the latter point of view.

The authors thank the management of the Koninklijke/Shell-Laboratorium, Amsterdam, for permission to publish this paper.

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1

DISCUSSION

Chairman: W. E. Garner

On Paper 1.1

G. C. A. Schuit: This remark is also connected with my own paper, and it has as its object to show that under certain circumstances the 'weak chemisorption' postulated by Dowden may explain the dilemma discussed there. The situation is as follows:

1. At 77°K, when surface-gas exchange between adsorbed D (or H) and gaseous H_2 (or D_2) does not occur, the $H_2 + D_2$ exchange (both in the gas phase) still occurs at a relatively rapid rate.
2. This $H_2 + D_2$ reaction could be presumed to occur via a 'weak, chemisorption. However, since at this temperature practically complete coverage with strongly bonded chemisorbed H (D) occurs, this weak chemisorption apparently can find no place to occur.
3. Since, as has been shown, the nickel surface is heterogeneous, one might surmise that a very small fraction of the total surface still remains incompletely covered.
4. On this part of the surface, therefore, the coverage is only partial, which presumes that either the *heat* of adsorption for the 'strong' chemisorption is already very low at low coverage, or that that *activation energy* of adsorption for the same process is high.

Hence, only by a combination of the assumptions of 'weak' chemisorption, heterogeneity of the surface, and probably locally high activation energies of adsorption of the 'strong' chemisorption is it possible to account for the experimental facts observed.

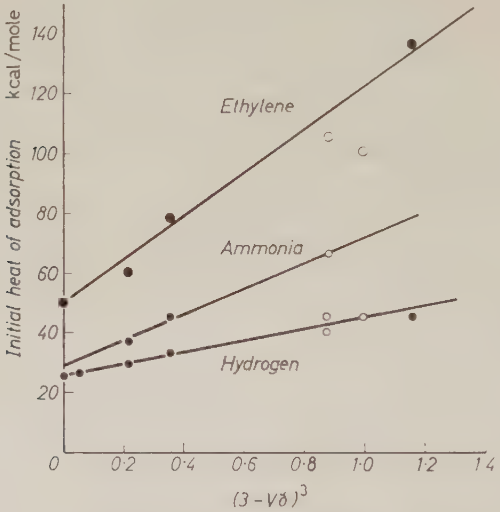
Such a combination might occur on very small nickel crystals.

G. C. Bond: The calculation of heats of adsorption by the Eley-Stevenson method yields results which are only in approximate agreement with observation. In particular, the values obtained for rhodium, palladium, iridium, and platinum are significantly different, due to their unequal latent heats of sublimation, whereas experimentally they are all close to 26 kcal/mole.

Initial heats of chemisorption have been shown to increase with decreasing percentage *d*-bond character of the metal, δ; there is little dependence of heat on δ between 40 and 50 per cent (<10 kcal/mole for hydrogen), but there is a very sharp dependence between 39 and 40 per cent. This seems illogical, and a smoother curve is obtained if heats of adsorption are plotted against valency times $\delta (V\delta)$: the Group VI elements are anomalous, although chromium fits if assigned a metallic valency of 5·1, which value brings it on the Schuit linear relationship between rate of ethylene hydrogenation and $V\delta$. Applying this relationship to tungsten, it is found that $V\delta$

should be 2·04, and using this value both for tungsten and molybdenum, the points for these metals now lie close to the curve.

Heats of adsorption versus $V\delta$ plots have been made for hydrogen, ethylene, and ammonia, and log-log plots show that the relationship is approximately a cubic one. The accompanying figure shows plots of heats of adsorption versus $(3 - V\delta)^3$. The equations describing the lines are



The dependence of heats of adsorption on $V\delta$.

$$C_2H_4: \quad -\Delta H_a = 50 + 61(3 - V\delta)^3$$
$$NH_3: \quad -\Delta H_a = 29 + 42(3 - V\delta)^3$$
$$H_2: \quad -\Delta H_a = 26 + 19(3 - V\delta)^3$$

These empirical expressions may be of use in predicting unknown heats of adsorption; for example, it is to be expected that the heat of adsorption of ammonia on rhodium would be close to 30 kcal/mole.

On Paper 1.3

J. H. de Boer: Two models of hydrogen adsorption on nickel may explain a negative surface potential and an increased conductivity at the same time, viz. the model of positively-charged hydrogen atoms, penetrating into the surface to some depth, as described in my paper, and the model of hydrogen atoms on top of nickel atoms to which they are bound by covalent forces, sharing a certain amount of electrons. In this latter case, the increase of conductivity is due to a surface conductivity of such an assembly of hydrogen atoms sharing a certain number of extra electrons. I prefer the latter model for the following reasons.

As already stated in 1937[1], thin metal films have somewhat greater atomic distances than bulk metals[2]. Thin films consequently have lower values of the work function, as, for example, found by MIGNOLET[3]. BEECK[4] found that the heat of chemisorption of hydrogen on nickel films is greater than on bulk nickel. This is in accordance with an electron transfer from the nickel to the hydrogen and not with the formation of positive hydrogen ions.

I therefore recommend the picture of *Figure 3* of my paper for cases like this.

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R. F. DEACON: I would like to suggest a further possible factor causing a variation of the heat of adsorption with the fraction of the surface covered, particularly for a graphite surface, but also possibly applicable to metals.

The unsaturated carbon atoms in what may be called the 'surface' of an aromatic hydrocarbon molecule attain a position of low potential energy by the formation of a molecular orbital, and the stability of this 'surface' orbital is greatly enhanced when it is a closed-ring orbital, or a system of such closed orbitals. For instance, the heat of hydrogenation of anthracene is greater than that of phenanthrene, and that of 1:2-dihydronaphthalene is proportionally much greater than that of naphthalene.

The surface of a graphite crystal cleaved along the 0001 plane can be considered as an infinite system of closed molecular orbitals of this type. When hydrogenating this surface, the first molecules adsorbed would be expected to have a low heat of adsorption because of the P.E. increase caused by breaking the stable π-orbitals on the surface into linear unstable ones. Subsequent adsorption would then give much higher heat of adsorption. One would thus expect the adsorption to grow out in rings from the initially formed active centres and the heat of adsorption curve to show a gradual increase with coverage. (This may be an alternative explanation for the results obtained by BARRER[1], although he was using charcoals with a wide variety of crystal faces exposed.)

If the valency electrons in a metal surface form similar closed surface orbitals, this may be a further factor in the variation of the heat of adsorption with coverage, due to a redistribution of the surface-bonding orbitals. In this case, the effects will probably be quite different from those in graphite (due to the *d*-electrons taking part), and also for different crystal faces.

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On Paper 1.4

P. T. LANDSBERG: Although the concept of 'coverage' is almost universally used in the literature on chemisorption, it is becoming recognized that it may not always be applicable. Its use implies that a definite number of sites is available and that these are used up in turn by the chemisorbed atoms. However, a chemisorbed atom may, by its action on the electronic structure of the surface, create new sites. Also, it may invalidate a variable number of sites, the number depending on the neighbourhood in which it finds itself. In fact, in the case of the logarithmic rate law of chemisorption, the notion of a percentage coverage becomes inapplicable (LANDSBERG[1]). It seems preferable, therefore, to speak of directly measurable quantities such as 'volume of gas taken up', and to restrict the evaluation of a percentage coverage to situations in which it can be shown to be probably applicable. For instance, one might estimate the number of sites on a surface, provided a reliable value for its area is available, and see if the chemisorption process terminates when the approximately correct number of atoms has been adsorbed. One might restrict the use of the concept of a percentage coverage to situations in which some such criterion is satisfied.

It would be interesting to know to what extent Dr. Schuit believes the concept of a percentage coverage to be applicable to the situations which he has envisaged.

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G. C. A. SCHUIT: There appears, indeed, room for doubt whether the concept of a 'site' is sufficiently proven by experiment. However, for our special case, we believe that such a proof can be given on the strength of the following arguments.

1. One can measure the surface area of a Ni–SiO_2 catalyst and its hydrogen adsorption. It is, moreover, possible to remove the nickel from the catalyst by passing CO over it at 80°C, which converts the nickel to $Ni(CO)_4$ that distils out of the silica residue. The difference in surface area of the catalyst and its silica residue can be presumed to be the surface area of the nickel. If the ratio of this nickel surface area to the number of hydrogen atoms adsorbed is calculated, the surface area for adsorbed H atoms proves to be 6 $Å^2$, i.e. the area of a surface nickel atom in the [100] or [111] crystals form. Hence, a 'site' is a surface nickel atom.

2. The decrease in ferromagnetism of the nickel by adsorption of H_2 is strictly proportional to the amount of H_2 adsorbed. This decrease is of the same order as the number of holes in the *d*-band per nickel atom (0·6), being equal to about 0·4. This again suggests that every time a H atom is adsorbed, essentially the same process occurs, which is in agreement with the concept of a well-defined 'site'.

Eisschen's infra-red absorption work on adsorbed CO on Ni that reveals either a ketonic or a carbonyl binding again makes the concept of a well-defined site a useful one.

J. H. DE BOER: Is it possible that the quick H_2–D_2 exchange takes place on the carrier (reduced nickel -silicate or silica heated in a reducing atmosphere) instead of on the nickel metal? Experiments by P. Zwietering of Geleen (Central Laboratories of Staatsmijnen, Netherlands) have shown that a quick exchange takes place on alumina surfaces, even proceeding quickly at low temperatures. Could a similar reaction take place on silica, heated in a reducing atmosphere?

G. C. A. SHUIT: None of the silica samples investigated so far in our laboratory shows any low temperature activity for H_2–D_2 exchange, completely different from the behaviour of, for instance, Al_2O_3. Whether the silica becomes different in character by the proximity of Ni could not, of course, be ascertained.

D. A. DOWDEN: Arising from Professor de Boer's question and Dr. Schuit's reply, it is worth pointing out that because silica does not chemisorb hydrogen appreciably in the absence of nickel, this does not remove the possibility that it may so do in the presence of nickel. Such questions are a frequent problem in catalysis—for instance, in 'Platforming' and its equivalents. Silica chemisorbs hydrogen only slightly and with difficulty, and the reaction can be described by the Lennard-Jones diagram with a high activation energy. However, at the nickel-silica boundaries, the activated hydrogen may migrate on to the silica from the nickel.

D. D. ELEY: It may be that hydrogen activated by nickel can attack silica. Dr. Hilnokuch, in my laboratory, has recently found that H_2 gas lowers (reversibly) the conductivity of diphenyl picryl hydrazyl if Pd electrodes are used, but not with Al electrodes. He still has the matter under investigation, so my remarks must be very tentative, but it is our preliminary view that H_2, dissociated into atoms on the thin Pd film, passes over to adsorb on the hydrazyl, thereby localizing its free electron.

G. C. BOND: Dr. Schuit finds incomplete exchange of chemisorbed deuterium with gas-phase hydrogen over a nickel–silica catalyst below room temperature. Several years ago I found[1] a similar behaviour with a pumice-supported platinum catalyst, but only about 3 per cent of the deuterium present exchanged at 0°C; however, on heating to 200°C and exchanging at that temperature, the full amount was released. Unfortunately, separate experiments on the support were not performed, and the possibility that the observations involved deuterium adsorbed on the pumice cannot be ruled out. The phenomenon of incomplete exchange may, however, be quite a general one.

With reference to Mr. Dowden's remark concerning the possibility that the nickel may induce adsorption on the silica, I have recently studied the ethylene–deuterium reaction over colloidal platinum supported on alumina, silica, and silica-alumina[2]. Significant differences in kinetic behaviour were detected, and a specific chemical interaction between metal and support was thereby established.

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General

D. D. ELEY: I should like to emphasize points made in this section that seem to me to be of special interest for the experimental part of the discussion. In connection with Dowden's postulate of weak chemisorption as occurring on *d*-orbitals, Couper and I in the Faraday Discussion (1950) suggested that H_2 was held in a second layer by weak exchange forces, to satisfy the requirements of the reaction order of the pH_2 conversion on tungsten which shows a partly saturated second layer at temperatures around 140°K. A number of metal orbitals, *d* and *dsp*, are available, and it may be that some kind of bonding of H_2 as *molecules* can occur to *d*-orbitals. Personally, I have always laid emphasis on the role that atomic *d*-orbitals and holes in the *d*-band play in bonding activated complexes in hydrogen reactions, and clearly Dowden's idea takes this a stage further. Work with the field emission microscope should help in solving problems of weak chemisorption, as Müller's work has shown. Dr. Grimley's paper leads to the view that a chemisorbed H atom is located over a metal atom, which accords with conclusions to be drawn from Pauling's equation in calculating the activation energy. Dr. Schuit's results on equilibration of H_2, D_2 on sites of weak adsorption at low temperatures very clearly parallels the findings of Emmett for the same reaction for a promoted iron (synthetic ammonia) catalyst.

ADDENDUM

THE THERMODYNAMICS OF THE ADSORPTION OF HYDROGEN AND THE EXCHANGE REACTION WITH D_2 OVER METAL CATALYSTS

Since the time of the symposium further work has been done and subsequent analysis of the experimental data has led to the following conclusions:

(a) The desorption-adsorption mechanism I gives a much closer 'fit' to experiment than the 'one site' mechanism II. An Eley–Rideal mechanism with an activated complex possessing two sites, one adsorbed atom and one molecule from the gas phase, gives a less good 'fit' than mechanism I but cannot be excluded in view of the experimental accuracy.

(b) The 'equilibration' of $H_2 + D_2$, accepting the rates measured in the 'exchange' and the textural properties of the catalysts investigated, proves to be diffusion-limited. The theoretical rate is then

$$K_{\text{eff.}} = N_s/N_g^\circ \sqrt{K_{\text{exchange}}}$$

The experimental results are rendered to within a factor of 10 but the various mechanisms become inseparable.

SECTION 2

CHEMISORPTION ON INSULATORS

Chairman: D. A. DOWDEN

2.1

CHEMISORPTION AT ROOM TEMPERATURE ON ALUMINA AND SILICA GEL

J. J. Kipling and D. B. Peakall

University of Hull

SUMMARY

The adsorption of water vapour and of four alcohol vapours by alumina and silica gel has been examined at room temperature. Four criteria are suggested for distinguishing between physical adsorption and chemisorption in this case: (1) The chemisorbed material cannot be removed by desorption at room temperature; (2) the amount of adsorbate irreversibly adsorbed increases (up to a limit) with the time of contact allowed before desorption is commenced; this indicates that there is a slow (chemisorption) reaction; (3) the chemisorption can be attributed to a definite reaction at specific sites on the surface, the oxide ions; (4) the extent of chemisorption can be calculated from a knowledge of the surface area of the adsorbent and its crystal structure.

The first criterion separates the total adsorbate into two parts; one is chemisorbed, the remainder is physically adsorbed onto the chemisorbed layer. The distinction is made clear by reference to desorption of vapours of benzene, ethylene dichloride and other relatively non-polar and non-reactive materials. These can be desorbed completely within a period of 100 hours.

These criteria might well apply more generally, but the fourth criterion is of less use when the surface reaction does not go to completion at the relevant temperature.

In the course of examining what was expected to be physical adsorption at or near room temperature, a number of authors have encountered irreversible phenomena which have suggested that chemisorption might be taking place to some extent. Examples include irreversible hysteresis in the adsorption of methyl alcohol on silica gel[1], and of water on silica gel[2,3] and on alumina[3]. It would clearly be valuable to establish criteria for distinguishing between chemisorption and physical adsorption in such cases. de Boer[4] has suggested that the magnitude of the heat of adsorption is not always an adequate criterion. This may be so for the cases in point, as the expected heats of chemisorption and physical adsorption are quite close together. From the data of ROSSINI *et al.*[5], it can be calculated that the heat of reaction of water vapour with $Al_2O_3.H_2O$ to give gibbsite is 13·6 kcal/mole of water at 25°, and to give amorphous $Al(OH)_3$ is 10·9 kcal/mole. These figures may be compared with the latent heat of condensation of water of 10·5 kcal/mole and the maximum expected heat of physical adsorption of 14·0 kcal/mole[6].

We have examined the adsorption of water and of four alcohols on various forms of alumina and on two samples of silica gel and have arrived at four criteria which form the basis for differentiating between physical adsorption and chemisorption in these cases; some or all may be useful for recognizing chemisorption more generally.

1. That the chemisorbed portion of the adsorbate is irreversibly adsorbed. This is shown by attempts to desorb the adsorbate when, after allowing for any decomposition which may occur, the rate of desorption falls below a measurable limit while substantial amounts of adsorbate remain on the solid surface.
2. That the amount of irreversible adsorption is markedly dependent on the time of contact between adsorbate and adsorbent before desorption is commenced.
3. That adsorption can be shown to occur at specific sites on the surface, as can sometimes be made clear by altering the surface.
4. That the amount of adsorbate chemisorbed can be related to the number of accessible sites on the surface.

These criteria are now discussed in turn in relation to the experimental data.

IRREVERSIBLE ADSORPTION

Table 1 shows the end results of two sets of experiments, in which desorption was followed gravimetrically. In the first set, desorption went rapidly to completion in all cases, and we assume that the adsorption of the vapours concerned was entirely physical in character.

In the second set, considerable desorption took place, but the rate of desorption had reached zero (or a significantly small value in the case of the alcohols, which are known to decompose even at room temperature when adsorbed on alumina[7]) at the time when desorption ceased, leaving an appreciable amount of adsorbate still on the surface. This amount we assume to be chemisorbed. At room temperature, these vapours can, of course, be physically adsorbed on the chemisorbed material.

Table I. DESORPTION OF VAPOURS FOR PERIODS UP TO 100 HOURS

Complete Desorption

Adsorbent	*Adsorbate*
γ-Al_2O_3	benzene
γ-AlO.OH	benzene, *cyclo*hexane ethylene dichloride
silica gel I	benzene, *cyclo*hexane ethylene dichloride
MgO	carbon tetrachloride, acetone chlorobenzene, *n*-propylamine
ZnO	carbon tetrachloride

Irreversible Adsorption

Adsorbent	*Adsorbate*	*Time of contact* (*days*)	*Residual amount adsorbed* (millimoles/g)	*Final rate of desorption* (mg/g/hr.)
γ-Al_2O_3	H_2O	7	3·42	0·0
	MeOH	7	1·47	0·1
	EtOH	7	0·88	0·1
	n-BuOH	7	0·71	0·0
γ-AlO.OH	H_2O	1	3·36	0·0
		7	4·08	0·0
		21	4·17	0·0
	MeOH	1	1·57	0·1
		7	1·89	0·0
	EtOH	1	0·80	0·1
		15	1·01	0·1
		30	0·98	0·1
	n-PrOH	7	0·89	0·1
	n-BuOH	7	0·87	0·07
silica gel I	H_2O	1	0·78	0·0
		7	1·03	0·0
	MeOH	1	0·76	0·1
		7	1·12	0·1
	EtOH	1	0·76	0·1
		7	1·09	0·07
	n-BuOH	7	1·05	0·06
silica gel II	H_2O	14	1·83	0·0
	MeOH	14	1·70	0·0
	EtOH	14	1·41	0·05
	n-BuOH	14	1·24	0·03

Table I includes data for adsorption on two oxides [MgO and ZnO] which were not the main object of our study. These were included because SCHREINER and KEMBALL[8] have referred to the irreversible adsorption of some vapours on these oxides when desorption was found to be incomplete after 15 hours. They did not state, however, whether desorption was continuing after that time. We presume that it was, as we have been able to show that desorption can be completed if continued for a period up to 100 hours. It is clearly important, in such experiments, to record the rate of desorption occurring at the conclusion of the experiment. *Table I* shows that similar complete desorption can be carried out from alumina and silica gel when these solids hold vapours which can be expected to be physically adsorbed only.

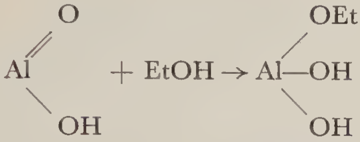
TIME OF ADSORPTION

Table I shows that the extent of irreversible adsorption of water and the alcohols on alumina and silica gel depends on the time of contact before desorption. This result would accord with there being a slow reaction at room temperature. It would not accord with physical adsorption at room temperature unless there were a rate-determining diffusion process, which seems most unlikely for these particular solids, especially as no such effect is found in cases where physical adsorption only occurs.

SPECIFICITY

Irreversible adsorption of water occurs on both anhydrous alumina [γ-Al_2O_3] and on boehmite [γ-AlO.OH]. The specific reaction can only be the conversion of the oxide to hydroxide groups. The surface then takes on the character of gibbsite [γ-$Al(OH)_3$], as has been found in x-ray studies[9]. This we believe to affect only the outermost layer of solid at room temperature, whereas DE BOER and HOUBEN consider that a double layer of boehmite is formed from anhydrous alumina[10]. Their result, however, seems to be inconsistent with our finding that water is chemisorbed by boehmite. It is also inconsistent with our finding that γ-Al_2O_3, on which the maximum amount of water has been chemisorbed, does not adsorb alcohols irreversibly, whereas we have shown that boehmite does this (*see* below).

Chemisorption of the alcohols on boehmite might occur at the oxide or the hydroxide groups. The fact that it occurs on anhydrous alumina, but not on a sample of boehmite treated so as to give it a surface like that of gibbsite, shows that the reaction is specific to the oxide groups. It can be formulated thus:



$$\mathrm{Al}{\overset{\textstyle \diagup\!\!\diagup\, O}{\underset{\textstyle \diagdown\, OH}{}}} + \mathrm{EtOH} \rightarrow \mathrm{Al}{\overset{\textstyle \diagup\, OEt}{\underset{\textstyle \diagdown\, OH}{—OH}}}$$

Silica gel, unlike alumina, is not prepared as a substance of definite composition. It seems, however, that most of the 'constitutional' water of normal silica gels is present in the form of surface hydroxide groups[11,12], and we may therefore assume that the surface contains oxide and hydroxide groups in proportions which vary with the conditions of preparation of the gel.

From the original gel we prepared a second sample by high-temperature dehydration (reducing the 'constitutional' water from 4 to 2·5 per cent), thus presumably increasing the ratio of oxide to hydroxide groups at the surface. The irreversible adsorption of alcohols was thereby increased, and we again conclude that chemisorption is specific to oxide groups.

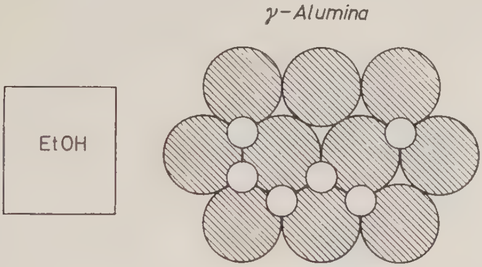


Figure 1. Size of the ethyl radical in relation to that of the ions in the γ-Al_2O_3 crystal.

CALCULATIONS OF THE EXTENT OF CHEMISORPTION

We have investigated the possibility of calculating the extent of chemisorption from the known dimensions of the crystalline materials and the surface areas of the particular samples used. The unit cell of γ-Al_2O_3 can be represented as a cube of side 7·84 Å, presenting eight oxide ions at each face[13]. The sample used had a surface area of 156 sq.m/g, and therefore sufficient surface oxide ions to chemisorb 3·37 millimoles of water per gram. This agrees well with the observed value of 3·43 mmole/g. The spacing of the oxide groups[13] is too close in relation to the size of the alkyl groups for an alcohol molecule to be adsorbed at each oxide ion (*Figure 1*).

From a consideration of the size of the alkyl groups it can be shown that, at most, one methyl alcohol molecule can be adsorbed for every two oxide ions, and one molecule of each higher alcohol for every three oxide ions. The observed values (*Table II*) are reasonably near those calculated on this basis, but are distinctly lower. The discrepancy may be due to inefficient packing on the surface[14], or to exclusion of the alcohol molecules (particularly as the chain length increases) from the smallest pores.

The corresponding calculations for boehmite can be made less precisely, as the 'molecule' of AlO.OH presents different areas in the three planes of the crystal[15]. The figures in *Table II* are therefore based on an average value for the number of surface oxide ions in the sample, which had a surface area of 250 sq.m/g. Allowance is also made for the fact that the material (a commercial sample) had been slightly over-calcined, as was shown by the amount of water lost at 1,200°.

Table II

Chemisorption by γ-Al_2O_3	*Chemisorption* (millimoles/g)	
	Calculated	*Observed*
water	3·37	3·42
methyl alcohol	1·68	1·47
ethyl alcohol	1·12	0·88
n-butyl alcohol	1·12	0·71
Chemisorption by γ-AlO.OH		
water	3·70	4·08
methyl alcohol	1·24 1·85	1·89
ethyl alcohol	1·03	0·98
n-butyl alcohol	1·03	0·87

The calculation for chemisorption of the alcohols requires a consideration of each face of the crystal separately. From models prepared by RUSSELL[16] (*Figure 2*), it can be shown that one alcohol molecule can be adsorbed for every three oxide ions in the *a* plane (or, for the smaller methyl alcohol molecule, every two oxide ions), and for every two oxide ions in the *c* plane. In the *b* plane, the oxide ions are recessed below hydroxide ions and are inaccessible to alcohol molecules in general. It has been suggested, however, that in silicate minerals, hydrogen bonding may take place between oxide ions and the methyl group in methyl alcohol[17]. If the same mechanism were to operate here, the higher figure for adsorption of methyl alcohol would obtain.

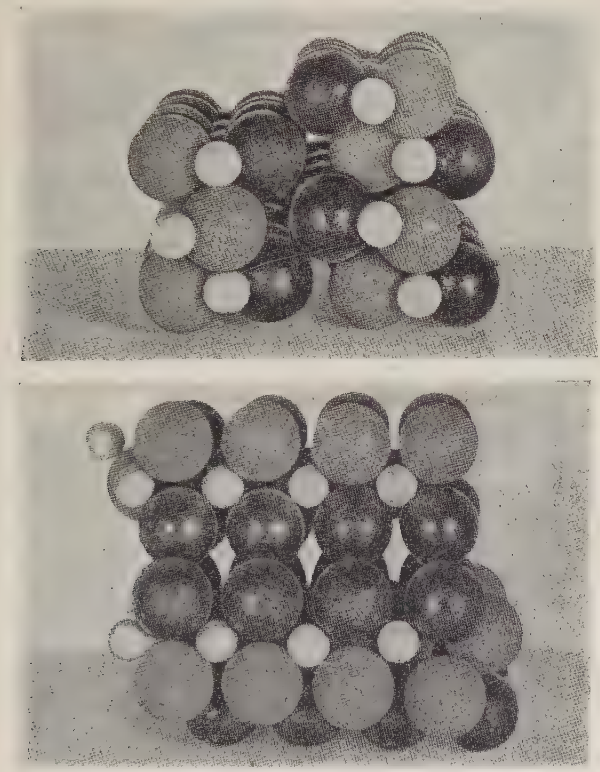


Figure 2. Models of the γ-AlO.OH crystal showing (above) the *a* plane, (below) the *c* plane. Black balls: hydroxyl ions; grey balls: oxygen ions; white balls: aluminium ions. (From Technical Paper No. 10 of the Aluminum Company of America, by courtesy of Dr A. S. Russell.)

Similar calculations cannot be carried out for silica gel, but some interesting qualitative conclusions can be drawn. The results of Shapiro and Weiss[11], together with our own observations that the chemisorption of water on silica gel is low for an adsorbent of relatively high surface area, lead to a picture of the surface in which the oxide ions are spaced well apart from one another among an excess of hydroxide ions. Thus boehmite, with a surface area of 250 sq.m/g, chemisorbs 1 mmole of ethyl alcohol per g, whereas silica gel, with more than twice this area (590 sq.m/g) chemisorbs only 1·20 mmole/g. Consequently, each oxide ion can chemisorb an alcohol molecule, and the extent of chemisorption of each alcohol is approximately equal to that of water. In the second sample, however, more oxide ions have been formed at the expense of hydroxide ions, and the extent of chemisorption of the alcohols again suggests that adsorption is restricted as with alumina.

This last criterion is of greatest value when the surface reaction goes to completion. We have also investigated a number of other systems in which the amount of irreversibly adsorbed material is considerably less than the calculated figure, and have assumed that in these cases the surface reaction does not go to completion.

A preliminary announcement of some of these results has been made[18], and further details will be published in due course[19].

EXPERIMENTAL

Desorption experiments were carried out as follows: (a) A weighed amount of dry solid contained in a small flask was saturated with the adsorbate at room temperature. The flask was then attached to a vacuum system, and removed at intervals to be weighed. (b) Alternatively, the solid was formed into a short column through which a stream of dry air was passed. It was shown that the two methods gave almost identical results.

The surface area of the boehmite was given by the manufacturers. That of the γ-Al_2O_3 was obtained by comparing the monolayer value for benzene on this solid with that for boehmite. The values for the silica gels were obtained in the same way.

Further experimental details will be found elsewhere[19].

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2.2

SOME OBSERVATIONS ON THE SORPTION OF WATER BY OXIDES

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SUMMARY

Active oxides prepared by calcination of the corresponding hydrous oxide or hydroxide retain a small percentage of 'water' to temperatures far above that at which the major portion is expelled. It is probably chemisorbed as hydroxyl groups, the fraction θ *of the surface thus covered gradually falling from near unity to zero as the temperature rises.*

The sorption isotherms of water vapour at 25° *on the oxides reveal the presence of a type of binding of water intermediate between chemisorption and physical adsorption: a small amount of water sorbed at* 25° *can only be removed by pumping at the original temperature of outgassing, say* 200°. *It is probably molecular water bound to the surface by hydrogen or hydroxyl bonds.*

Liquid *water will—at least for* TiO_2*—convert the surface oxide completely into hydroxyl groups.*

Silica, heated above 600°, *is 'hydrophobic'* (*Type V isotherm*) *but becomes hydrophilic after exposure to about half-saturated water vapour. This points to a rather profound modification of the surface by the adsorption of water.*

INTRODUCTION

Oxide catalysts are frequently prepared by the thermal decomposition of a parent solid, e.g. a hydrous oxide or a carbonate or nitrate; it is necessary that the heat treatment shall not be too drastic, otherwise sintering, with loss of specific surface, will ensue. It is, therefore, customary to arrest the heating at a point just short of complete decomposition, for it is found that the last traces of volatile product can only be driven off by using a far higher temperature than was necessary to effect the major portion of the decomposition.

Thus by two hours' heating of a particular sample of magnesium hydroxide at 450°, 96·3 per cent of the water was driven off, yet a temperature of 800–900°C was necessary to ensure complete expulsion of the water with the same duration of heating.

Since, then, oxides so often contain an appreciable residue of volatile product remaining from the preparation, it is important to know whether it is located at the surface of the sample; if so, it will, of course, markedly modify many of the surface properties of the solid. Such a location of the 'impurity' would, in general, seem probable: the volatile product (P) must move from the interior of the solid to the exterior by a Platzwechsel (place-exchange) mechanism and the energy required for evaporating a P molecule from the outermost layer is diminished because the P molecule immediately below it is able to move into its place. The energy required to release the P molecules from the last layer will accordingly be greater, so that a higher temperature will be required to expel them at a reasonable rate.

WATER CONTENT

In *Table I* is given the water content w for a number of typical oxides (formed by calcination of the corresponding hydrous oxide or hydroxide), together with the specific surface S' determined by nitrogen sorption. It seems clear that this 'water' must be present as hydroxyl ions, for molecular water could scarcely remain sorbed after some hours at the high temperatures in question; and assuming one molecule of chemisorbed water to occupy 15 Å^2 (= area of 2 OH ions) the values of θ, the fraction of the surface covered by OH ions, can be readily calculated. The resultant values of θ can be no more than approximate, for w has to be determined as the small difference of two much larger weights; moreover, one has to assume that the nitrogen molecules involved in the measurement of S' can reach

Table I. WATER CONTENT OF 'OXIDES'

(I) *Silica*[2]

T°C	200°	400°	600°	800°	900°
S'	715	639	546	397	237
w	65	40	17·5	5·5	2
θ	0·46	0·32	0·16	0·07	0·04

(II) *Stannic Oxide*[2]

T°C	200°	300°	400°	500°	600°	700°	800°
S'	172	119	45	26	19	15	9
w	52	33	13	6	3	1	0·5
θ	1·5	1·5	1·5	1·2	0·8	0·3	0·3

(III) *Stannic Oxide*[2]

T°C	220°	320°	420°	520°	625°	825°	1000°
S'	177	158	106	24	12	7	2
w	8·8	60	26	6	3	1	0
θ	2·4	1·9	1·2	1·3	1·2	0·7	

(IV) *Ferric Oxide*[2]

T°C	200°	400°	600°	800°
S'	153	64	34	10
w'	44	6	3	0·5
θ	1·4	0·5	0·5	0·3

(V) *Alumina*[3]

T°C	400°	500°	600°	700°	800°	900°	1000°
S'	300	243	224	166	148	118	99
w	69	35	19	14	12	8	6
θ	1·15	0·7	0·4	0·4	0·4	0·3	0·3

(VI) *Magnesia*[1]

T°C	400°	500°	600°	700°
S'	185	117	95	71
w	23·6	16·6	5·1	2·8
θ	0·65	0·7	0·3	0·2

(VII) *Magnesia*[1]

T°C	400°	450°	500°	600°	700°
S'	126	211	171	84	38
w	25·7	11·4	4·6	2·9	1·5
θ	1·0	0·27	0·13	0·14	0·20

(VIII) *Titania*[4]

T°C	110°	205°	306°	406°	505°
S'	308	161	122	80	72
w	91·0	22·2	9·6	2·4	1·4
θ	1·5	0·7	0·4	0·15	0·1

T: Temperature of calcination; S': specific surface, m^2 per g of anhydrous solid; w: water content, mg per g of anhydrous solid; θ: fraction of surface covered with OH.

Preparation: (I) Silicon ethoxide + pure water; (II) stannic ethoxide + pure water; (III) aqueous stannic chloride + aqueous ammonia; (IV) aqueous ferric chloride + aqueous ammonia; (V) aluminium ethoxide + pure water; (VI) aqueous magnesium chloride + aqueous ammonia; (VII) aqueous magnesium sulphate + ammonia; (VIII) titanium sulphate in aqueous sulphuric acid, + water.

Time of calcination usually 2 hours.

the whole of the hydroxyl-bearing surface; but the order of θ is appropriate for a monolayer, more or less completed, and it varies in the expected sense, i.e. it diminishes with rise in temperature. (Incidentally, it will be noted that the amount corresponding to a completed monolayer is often surprisingly large; thus with the sample of alumina calcined at 400°C it corresponds to a composition $Al_2O_3.O.4H_2O$.) This evidence for the chemisorbed layer is to some extent circumstantial, and it does not exclude the possibility that a fraction of the water content is *within* the lattice. Hydrous titania, for example, whilst yielding up most of its water below 500°C, gives off a small residue at about 700°C (near the Tammann temperature) in a sudden, almost explosive, manner which suggests that it comes from the lattice of the solid. DE BOER and HOUBEN[5] have suggested that active alumina, whilst covered with a monolayer of chemisorbed water, requires a small percentage of water within the lattice in order to stabilize the spinel structure of γ-Al_2O_3.

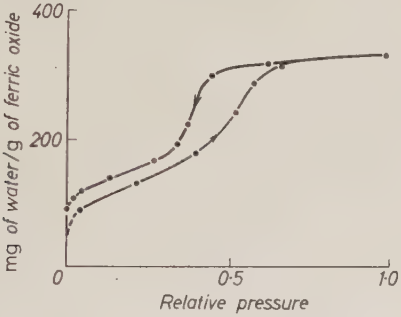

Figure 1. Sorption at 22°C of water vapour by ferric oxide gel outgassed at 200°C.

RETENTION

In the sorption of water vapour by oxides a phenomenon is sometimes encountered which may best be described by reference to an actual example[2]. A sample of ferric oxide gel was outgassed at 200°C and an adsorption isotherm of water vapour at 22°C was measured, first the adsorption and then the desorption branch (*Figure 1*). The system was next pumped out at 22°C, and after 5 hours, though the rate of loss of weight was too small to measure, the water content of the solid was higher than after the initial outgassing by 70 mg per g of solid. The temperature was now raised to 100°C, and after 5 hours' outgassing, accompanied by a loss of 38 mg, the rate of further loss became very small (<1 mg per hour). On raising to 200°C, the residual 32 mg was completely lost in 3 hours of pumping, the weight of the sample thus returning to its original figure for this temperature. Similar results were obtained[2] with stannic oxide gel and silica gel: in a number of experiments a residue of water was 'retained', i.e. it could not be pumped off in reasonable time (30 hours was sometimes allowed) at 22 °C, but it was comparatively quickly removed by outgassing at the temperature, whether 100°, 150°, or 200°C, used for the initial outgassing.

Retention also occurs with alumina—though detailed data as to the temperature required for removal are lacking—and it seems reasonable to suppose that many other oxides would show a similar effect. It is interesting that kaolin, though not an oxide, exhibited retention[6] in the water isotherms measured after outgassing at fixed temperatures between 50° and 720°C; the retained water could be completely removed only by pumping at the particular temperature of outgassing.

These facts indicate that, for a given temperature of outgassing, there is a proportion of 'water' which is reversibly expelled and which requires the same energy to drive it off the second time as the first. This bespeaks a distribution of sites of different energies which are stable enough to remain unchanged for at least two outgassings at a particular temperature. The water cannot be held merely by van der Waals forces, otherwise it would be removed by pumping at 25°C, but without further data one cannot decide its exact mode of binding. One needs, for example, to know whether a retention effect is still present when the outgassing temperature is much above 200°C; if so, it could not be wholly explained in terms of adsorption of molecular water through H bonds, for such water should be completely driven off *in vacuo* at 200°C. The results with kaolin do indeed suggest that it is possible for chemisorbed water, i.e. water present as OH groups, to be reversibly expelled.

All the cases of retention here reported occurred with adsorbents formed by calcination of hydrous oxides (or, with kaolin of a hydroxyl-containing body) and some, at any rate, of the 'water vacancies', whence the water was expelled, may still remain intact. Such vacancies could then readily resorb water with the same energy of binding as before expulsion. In this connection it would be interesting to know whether truly anhydrous oxides (e.g. smokes, or those produced by ignition at very high temperature) would fail to show a retention effect.

ADSORPTION OF WATER ON SILICA GEL

Some curious results have been obtained[2] when studying the adsorptive behaviour of water vapour on silica gel. The gel was prepared, almost free of ions, by hydrolysing silicon ethoxide with pure water, and separate portions were calcined for two hours at 200°, 600°, and 900°C, respectively. The sample calcined at 200°C gave a water isotherm (*Figure 2a*) of the expected kind—approximately Type IV—with a small retention effect; but the sample calcined at 900°C showed quite unusual behaviour: the first adsorption run produced an isotherm of Type V (*see Figure 2b*), and

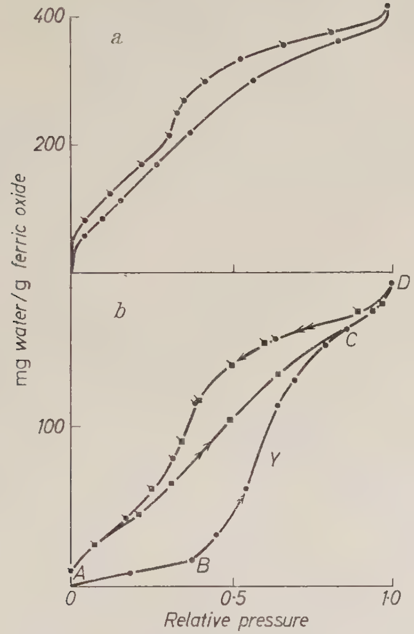

Figure 2. Sorption at 22°C of water vapour by silica gel, outgassed at 100° after calcining for 5 hours at (*a*): 200°; (*b*): 900°. ●, ●: first adsorption and desorption runs; ■, ■: second adsorption and desorption runs.

was indeed very similar to the isotherm of water on charcoal (cf. Dubinin) with the addition of a final upward turn; but on desorbing, the isotherm obtained was of Type IV. The second adsorption graph was quite different from the first, being typical of the adsorption branch of an ordinary Type IV isotherm, but the second desorption run coincided with the first. The results with the 600°C sample, though incomplete, would seem to represent a behaviour intermediate between the 200° and 900°C sample.

The close similarity of the first adsorption curve *ABCD* to the isotherm for water on charcoal suggests a similar explanation to that usually given for the latter system, viz. that, initially, most of the surface of the silica, like that of the charcoal, is hydrophobic, and that water is adsorbed only at the relatively few hydrophilic centres (probably OH groups and H_2O vacancies), probably by means of hydrogen bonds; that islands of adsorbed water molecules thus form and merge to form a monolayer which is completed at Y, the point of inflection; and that from Y upwards a multilayer begins to build up. This interpretation is supported by the fact that the amount of water required to fill a monolayer calculated from the specific surface (assuming each molecule to occupy 10 $Å^2$) is 72 mg, close to the actual adsorption at Y.

Dubinin has put forward a formula for the monolayer region of the isotherm (viz. $h/x = 1/x_0c - (1/x_0)h$, where x_0 is the sorption capacity of the hydrophilic centres, c is a constant, and x is the sorption for a relative humidity h). This applies fairly well to the present results, and gives a value of $x_0 = 17{\cdot}5$ mg. The hydrophilic centres would thus appear to comprise approximately one-quarter of the total number of sites available.

After completion of the first adsorption-desorption cycle, it is clear that the surface has become hydrophilic and that it remains so during at least one further adsorption-desorption cycle. It seems that exposure to saturated water vapour is not necessary, however; in the experiment with the 600°C sample the system was pumped out when the first adsorption branch had reached only approximately half the *saturated* vapour pressure, yet the second adsorption run indicated hydrophilic behaviour. The hydrophobic nature of the original surface can perhaps be explained qualitatively in terms of surface distortion in which the silicon ions are drawn inwards, i.e. towards the body of the material, so that the surface becomes essentially an array of negative (oxygen) ions. Adsorption occurs on the relatively few hydrophilic sites, probably those where OH ions are still present. Once the whole surface has become covered with liquid water, however, the field at the surface becomes more symmetrical, the silicon ions move outwards again, and the surface is thus rendered more hydrophilic.

EFFECT OF LIQUID WATER ON TITANIA

When calcined titania is soaked in liquid water it seems that the surface becomes completely covered with water, which is either chemisorbed or at least is held by hydrogen bonds: the water content w remaining after such soaking and then long heating at 110°C in air to drive off physically adsorbed water, is approximately proportional to the specific surface S (w was determined by raising the temperature to 1000°C and registering the loss in weight[4]).

Curiously, the area per molecule of the water works out at near 10 Å^2, characteristic of molecular water rather than of chemisorbed water (15 Å^2). Preliminary studies by thermogravimetric analysis suggests that the water w comes off gradually over the range 150° to 500°C, which would suggest a mixture of chemisorbed and hydrogen-bonded water.

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2.3

PROTIUM-DEUTERIUM* EXCHANGE BETWEEN ETHYLENE AND γ-ALUMINA

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SUMMARY

The isotope exchange between deuterium-containing aluminium oxide and ethylene has been studied. Our previous investigations have shown that it is theoretically possible to obtain, from the distribution of deuterium over the ethylene molecules, detailed information on the mechanism and rates of the reactions occurring at the surface. The experimental distributions show that an ethylene molecule is adsorbed at one carbon atom and that only the hydrogen atoms on the other carbon atom are exchangeable. The probabilities for desorption and exchange of one hydrogen atom are equal. The kinetics of the reaction show that two molecules are involved in one act of desorption. The combination of these data leads to a definite concept of the chemisorption and reactions of ethylene on aluminium oxide, of which the most striking feature is the adsorption of two molecules at one active site.

THE GENERAL THEORY OF ISOTOPE DISTRIBUTIONS IN EXCHANGE REACTIONS

In a system where an isotopic exchange between a hydrocarbon and a deuterium-containing solid occurs, hydrocarbon molecules containing 0, 1, 2, . . . , N deuterium atoms are present, where N is the number of exchangeable hydrogen atoms in the hydrocarbon molecule. The question as to what information can be derived from these N data, as obtained by mass-spectrometric analysis, has been recently investigated[1].

If, during the interaction between the hydrocarbon molecule and the surface, there is only one chance for the exchange of a hydrogen atom—a process which may be called stepwise exchange —then at any time the deuterium is distributed according to a

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* The nomenclature ^1H = protium, ^2H = deuterium is used, whereas 'hydrogen' is used as the generic term.

binomium over the hydrocarbon molecules if all N atoms are equally reactive. This distribution is determined by one parameter, the average degree of deuteration $\bar{d}$, and is independent of the mechanism by which the exchange occurs.

If, however, there is more than one chance for exchange, non-binomial distributions will be found. The general formulae for these distributions have been derived with the only restriction that the pool of hydrogen atoms in the deuterating agent is large as compared to the total number of protium atoms of the hydrocarbon molecules. These distributions are determined by an additional parameter β, which is the ratio of the rate with which the adsorbed species undergoes exchange to the rate of desorption. They may depend upon the actual mechanism assumed. Such processes may be called multiple-exchange processes.

EXCHANGE PATTERNS OF ETHYLENE

The theory developed has been applied to the exchange between ethylene and deuterium-containing γ-alumina, for which a number of mechanisms have been investigated. Suppose that an ethylene molecule is adsorbed as an ethyl radical by the addition of a deuterium atom and desorbs by loss of a hydrogen atom. If nothing else happens, a binomial distribution will be obtained at any time during the reaction. But if, during its existence, the ethyl radical can undergo exchange with the surrounding deuterium atoms of the alumina—the chance of which is β times the chance for desorption—polydeuterated species will be formed in amounts greater than according to a binomial distribution. If all five hydrogen atoms are equally reactive and the fraction of D in the hydrogen of the alumina (S) is unity, the distribution is as follows:

$$\begin{aligned}
d_0 &= p^{\frac{\beta+5}{\beta+5/4}} \\
d_1 &= 4\left(-p^{\frac{\beta+5}{\beta+5/4}} + p^{\frac{\beta+5}{\beta+5/3}}\right) \\
d_2 &= 6\left(p^{\frac{\beta+5}{\beta+5/4}} - 2p^{\frac{\beta+5}{\beta+5/3}} + p^{\frac{\beta+5}{\beta+5/2}}\right) \qquad (1) \\
d_3 &= 4\left(-p^{\frac{\beta+5}{\beta+5/4}} + 3p^{\frac{\beta+5}{\beta+5/3}} - 3p^{\frac{\beta+5}{\beta+5/2}} + p\right) \\
d_4 &= p^{\frac{\beta+5}{\beta+5/4}} - 4p^{\frac{\beta+5}{\beta+5/3}} + 6p^{\frac{\beta+5}{\beta+5/2}} - 4p + 1
\end{aligned}$$

Where p (average protium content) $= 1 - \bar{d} = e^{-\frac{\beta+1}{\beta+5}kt}$ and k is the rate of desorption.

Note that $\beta = 0$ leads to the binomial distribution and that for $\beta = \infty$ only d_0 and d_4 are present. In the case where $S \neq 1$, the expressions are somewhat more complicated.

If, however, only the methyl group in the ethyl radical can exchange, and desorption occurs by loss of a hydrogen atom from the methyl group the result*, for $S = 1$, reads

$$d_4 = p^{\frac{2(\beta+3)}{\beta+3/2}} - 4p^{\frac{2\beta+9/2}{\beta+3/2}} + 6(\tfrac{2}{3}p^2 + \tfrac{1}{3}p^{\frac{\beta+3}{\beta+3/2}}) - 4p + 1 \qquad (2)$$

with

$$p = 1 - d = e^{-\frac{\beta+1}{2(\beta+3)}kt}$$

For $\beta = 0$ the binomial distribution is again obtained and for $\beta = \infty$ only d_0, d_2, and d_4 are present (according to a binomial distribution over two groups of two atoms).

So far the mechanism for the exchange on the surface has not been defined.

A logarithmic rate law is (approximately) expected if either all hydrogen atoms in the alumina are equally reactive or if there are active centres and a great mobility of the hydrogen atoms in the alumina.

EXPERIMENTS AND RESULTS

In the experiments D-containing alumina was prepared by repeated exchange with D_2O, followed by evacuation at 500°C. The remaining hydrogen content is proportional to the surface area and amounted to $3{\cdot}8 \times 10^{-6}$ gram atoms per m^2. Such an alumina exchanges at reasonable rates with ethylene (pressure 5–45 cm Hg) at 100–200°C. In all cases the distributions are binomial (*Figure 1*). The deviations from a least-squares fit do not exceed 0·1 per cent which is an indication of the analytical accuracy. The simple log rate law is not obeyed. The pressure dependence at 140°C is of zero order.

If an additional amount of heavy water is added after the evacuation, non-binomial distributions occur and the rate of exchange decreases (*Figure 2*). With increasing amounts of added D_2O the deviations from the binomial distribution are first small and can be fitted by any set of formulae which gives a binomial distribution for $\beta = 0$. On addition of more D_2O, a critical region is passed where the deviations from the binomial distribution are large and cannot be fitted by any mechanism as developed above;

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* Only the expression for d_4—C_2D_4—is given, since, by comparison with equation (1), the other expressions can readily be obtained.

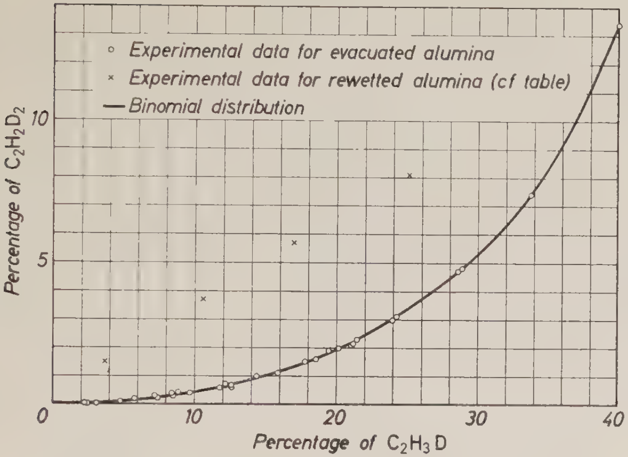


Figure 1. Results of exchange between D-containing alumina and ethylene.

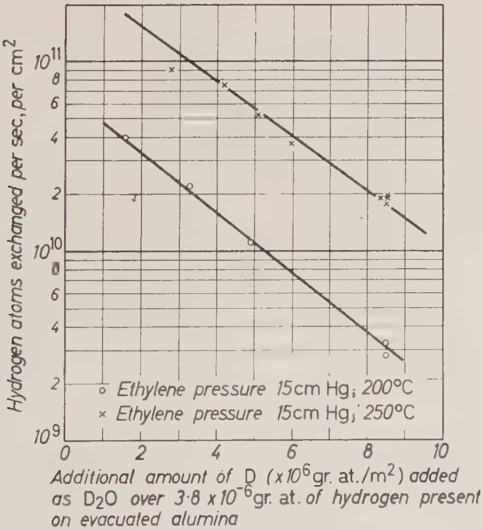


Figure 2. Rate of exchange as a function of degree of rewetting.

they are all based on the assumption that the adsorbed species can exchange with the large pool of deuterium in the immediate neighbourhood.

Addition of still more D_2O gives rise to the logarithmic kinetics and distributions which deviate markedly from the binomial distribution (*Figure 1*). Some type of multiple-exchange process hence takes place. Its absence with a relatively dry alumina must, on the basis of the above observations, be ascribed to the scantiness and relative immobility of deuterium near the adsorbed species.

The multiple-exchange patterns obtained with the rewetted alumina correspond to a mechanism which is characterized by adsorption of an ethylene molecule at one carbon atom, whereas the hydrogen atoms at the other end can undergo exchange (equation (2)) as shown in *Table I.*

Table I. SAMPLE AFTER 45 MIN REACTION AT 250°C BETWEEN 3·37 g OF ALUMINA (260 m^2/g) CONTAINING $1{\cdot}06 \times 10^{-2}$ GRAM ATOMS HYDROGEN (92% D) AND $1{\cdot}4 \times 10^{-2}$ MOLES ETHYLENE (PRESSURE 45 cm Hg)

	Exchangeable:	*All*	*Only methyl group*
	(experimental)	*(calculated minus experimental)*	
d_0	0·767	−0·0013	0
d_1	0·170	−0·0006	0
d_2	0·057	−0·0047	0
d_3	0·006	+0·0054	−0·0007
d_4	0	+0·0013	+0·0007

The distributions (see *Table I*) are least-square fits obtained by adjusting the parameters $\bar{d}$ and β. The latter will further be discussed in the form of the 'exponent' $\frac{2(\beta + 3)}{\beta + 3/2}$ to which p has to be raised to obtain d_0 (equation (2)).

One would expect this parameter β to have either a large or a small value, since it is the ratio of two presumably unrelated rates (exchange on the surface and desorption from the surface). It turns out that by changing either the D_2O content or the C_2H_4 pressure, the exponent tends to go to a limiting value of about 3. It may be remarked that, disregarding the evidence given in *Table I* concerning the mechanism, we could not find a mechanism yielding a distribution which would give an exponent of ~3 for an extreme value of β(0 or ∞). From *Figure 3* it is seen that, with increasing water content, the exponent suddenly changes from a value of approximately 3·9 (corresponding to $\beta \approx 0{\cdot}1$) to a value of approximately 3·2 (corresponding to $\beta = 1$) over an interval where the rate of exchange, which is essentially the rate of desorption, does not change more than by a factor 2 (*Figure 2*). This is the critical region, mentioned above, where mobility of the hydrogen in the alumina becomes fast as compared with exchange and desorption. From *Figure 3* it is also seen that over an interval where the rate of exchange is changing by a factor 4, the exponent, i.e. β, remains constant. This means that the process of desorption is related to the process for the further exchange on the surface. Moreover, a value of 3·2 corresponds to equal rates for both processes ($\beta = 1$).

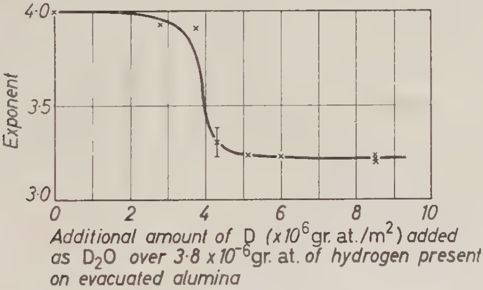


Figure 3. Exponent as a function of degree of rewetting at 250°C and 15 cm ethylene pressure.

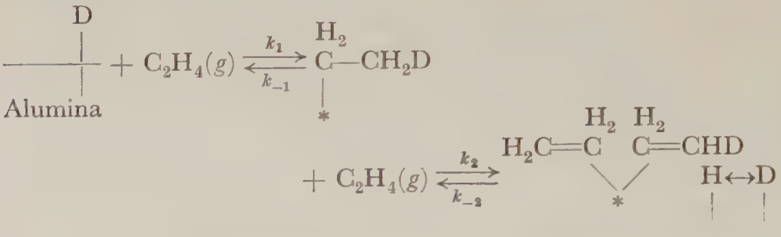
Actually, values somewhat smaller than 3·2 are observed (at higher pressures). This can be ascribed to an isotope effect. An approximate treatment leads to the reasonable value of 1·8 for the isotope effect at 200°C, corresponding to a limiting value of 2·8 for the exponent.

It further transpires that the value of β depends upon the pressure; the lower the pressure, the smaller the chance for multiple exchange, a surprising result, because one cannot, for instance, see off-hand that a lower pressure will decrease the residence time of an adsorbed molecule. Moreover, it turns out that, under appropriate conditions, the pressure dependence of the rate with which D appears in the gas phase is greater than 1. This means that in the multiple exchange and desorption process, respectively, two molecules are involved.

PROPOSED MECHANISM

The last conclusion, together with the conditions that these two molecules at some stage of the process become equivalent ($\beta = 1$)

and that exchange occurs only at the methyl group, leads to the following reaction mechanism:



The adsorbed bicomplex is a stable state, because during its existence the hydrogen split off must be replaced by deuterium through interchange of the oxide-hydrogens, before it decomposes again into a gaseous ethylene molecule and an adsorbed ethyl radical.

The mechanism of the multiple-exchange process has thus been defined. If the coverages with ethyl radicals and bicomplexes are θ_1 and θ_2, we define a new parameter α, which is the contribution of the decomposition of the bicomplex to the total rate of desorption.

$$\alpha = \frac{k_{-2}\theta_2}{k_{-1}\theta_1 + k_{-2}\theta_2} \qquad (0 < \alpha < 1)$$

If adsorption equilibrium is reached, the solution of this system leads to the same distribution as given in equation (2) with

$$\alpha = \frac{2\beta}{1 + \beta}$$

with the exception that

$$p = 1 - \bar{d} = \exp\left\{-\frac{1 - \frac{1}{2}\alpha}{6(1 - 1/3\alpha)}\,kt\right\}^{\alpha/3}$$

where k is the total rate of desorption.

It is readily seen that, on increasing the pressure, the contribution of the multiple exchange (formation of the bicomplex) increases, with $\alpha = 1$ as the limiting value. If a Langmuir adsorption isotherm is assumed, θ_2/θ_1 is proportional to the pressure. In an approximate treatment, the isotope effect can be incorporated in the exponent and be derived from the pressure dependence of the exponent, with the above-mentioned result. From the value of the exponent, the contributions of the rate of desorption of the ethyl radicals and of the bicomplexes to the total rate of desorption can be derived. On account of uncertainties in the isotope effect, a

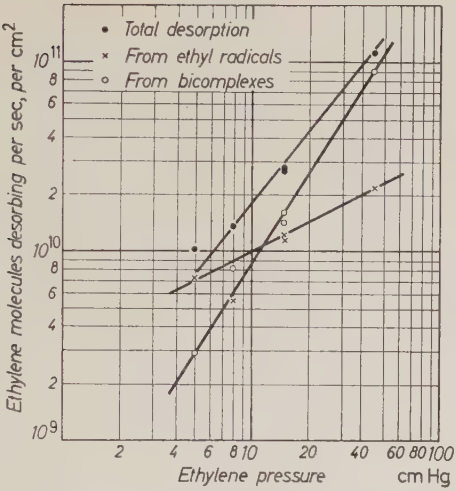


Figure 4. Pressure dependence at 250°C and $8{\cdot}5 \times 10^{-6}$ gr. at. D/m^2 (additional).

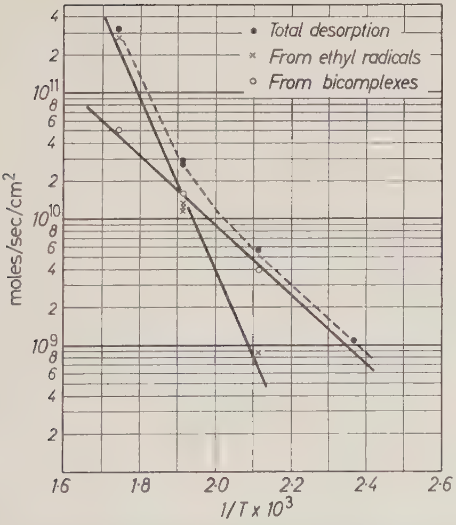


Figure 5. Temperature dependence at C_2H_4 pressure = 15 cm Hg and $8{\cdot}5 \times 10^{-6}$ gr. at. D/m^2 (additional).

small contribution of the former process ($\alpha \approx 1$) cannot accurately be determined.

Figure 4 shows the pressure dependences of the various rates for one set of conditions. For the total reaction, the desorption of ethyl radicals, and the decomposition of the bicomplexes, they have the values 1·2, 0·5, and 1·6. The difference between the latter two should be 1.

Similarly, the temperature dependences are given in *Figure 5* for a certain set of conditions. The apparent activation energies for the ethyl radical mechanism is 14 kcal/mole and for the bicomplex contribution about 30 kcal/mole. It is not yet known whether the adsorption or the desorption steps are rate-determining.

THE ROLE OF ALUMINA

Under our experimental conditions, the adsorption of water by alumina is a surface property, as was also found by FORTUIN[2]. The complete absence of multiple exchange with an evacuated alumina points to the absence of adsorbed water molecules. The hydrogen is present as isolated hydroxyl groups, in accordance with recent infra-red spectroscopic findings[3]. It seems reasonable to assume that the site that adsorbs two ethylene molecules is an aluminium ion. It may be thought that the formation of this bicomplex is linked up with the change from a tetrahedral surrounding to an octahedral one. The assumption of such bicomplexes may lead to a better understanding of various hydrocarbon reactions occurring on catalysts containing alumina, such as silica–alumina, chromia–alumina and fluorinated alumina.

The author thanks the management of the Koninklijke/Shell-Laboratorium, Amsterdam for permission to publish this paper.

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DISCUSSION

Chairman: D. A. Dowden

J. H. de Boer: I am not quite sure whether I understood Dr. Kipling correctly, but I would like to ask him whether he considers adsorption caused by hydrogen bonding to be chemisorption?

J. J. Kipling: No. I do not include hydrogen bonding as a cause of chemisorption.

J. H. de Boer: Dr. Kipling is inclined to indicate a very strong adsorption as chemisorption. Some 20 years ago I studied the adsorption of water on calcium fluoride[1] surfaces. The first layer of water molecules is very tightly bound; they cannot be removed by any means. Heating produces HF and a surface Ca–OH combination. I, nevertheless, consider this strong dipole-adsorption (hydrogen bonding) as a case of physical adsorption, which on heating gives the chemisorption of OH groups, while HF gas escapes.

In the thesis of one of my pupils (J. M. H. Fortuin), which has been released recently, experiments are described which give indications of the relative strength of the adsorption forces of water, and of lauric acid on alumina. Various samples of alumina, all prepared in different ways, but all pre-heated to about 700°C, are exposed to different relative water-vapour pressures, whereupon the adsorption of lauric acid from pentane solutions is studied. The dimensions of the pores in all samples are such that lauric acid has access to the total surface. Lauric acid is adsorbed to form a completely filled unimolecular layer. When water is pre-adsorbed, lauric acid is adsorbed on top of those water layers that are bound with strong forces; from a certain amount of water per unit surface area, however, water is replaced by lauric acid. Lauric acid cannot replace the first OH layer, nor the first H_2O layer on top of this OH layer. All successive water layers are desorbed by the action of lauric acid, which is, itself, adsorbed on top of the strongly bound H_2O layer, which in its turn is adsorbed on the chemisorbed OH groups. This strongly adsorbed H_2O layer, which cannot be replaced by lauric acid, is presumably bonded by strong dipole effects (hydrogen bonding).

With respect to the difficulty of driving off the last water molecules from an oxide surface, one might ask whether this difficulty is not due to the large distance between the OH groups on a sparsely covered surface? They have to react together to form a water molecule, which can desorb, but they are far apart.

Dr. Gregg referred to work, published by Houben and me, about the absorption of water in γ-Al_2O_3 to form a hydrogen spinel. In later years we have not been able to repeat these results and we, for the moment, have some doubt whether such a hydrogen spinel really exists.

Experiments made by two of my pupils (M. E. H. Hermans and J. M. Vleeskens) in recent years also point to the irreversible character of the OH chemisorption from water vapour on heated silica. We have found that only a treatment with liquid water, preferably at about 90°C, will restore the original properties of the (OH-covered) surface.

Whilst lauric acid is adsorbed on OH-free surfaces as well as on OH-covered surfaces of alumina, it was found that on silica surfaces fatty acids are bound only to OH groups. The adsorption of lauric acid from pentane solutions can be used to study the properties of the heat-dehydrated and the rehydrated silica surfaces.

Heated and rehydrated silica contains, after drying at about 110°C or over P_2O_5 at room temperature, one OH group for about every 23 $Å^2$. This may indicate that the arrangement of the Si and of the O atoms in silica is comparable to the arrangement in crystobalite, and that heated and rehydrated silica contains one OH group per surface Si atom. Silica preparations which have never been heated to high temperatures may contain more than one OH group per surface Si atom.

The type V isotherm of the H_2O adsorption on heated SiO_2 is shown by any SiO_2 sample heated at a sufficiently high temperature. Rehydration restores the hydrophilic character and the process can be repeated indefinitely.

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K. S. W. SING: We have found a difference in character between adsorption isotherms of water vapour and ethanol vapour, determined on the same samples of silica gel. With three different gels, outgassing at 200° led to irreversible water isotherms at 25°. Ethanol, however, gave reversible isotherms, although the adsorbed vapour could not be removed completely by pumping at 25°. A relatively large amount of ethanol was adsorbed at low pressure and the isotherm showed a well-marked 'point B', whereas the water isotherm was only slightly concave towards the pressure axis, with an ill-defined 'point B'. Again, although no relation could be found between the B.E.T. monolayer capacity for water vapour and the residual-water content of the gel, there are signs that the latter is related to the ethanol monolayer capacity. These results will be published elsewhere.

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W. F. K. WYNNE-JONES: I agree with Professor de Boer that, while the concept of chemisorption is clear enough, the criteria for distinguishing chemisorption are difficult to establish. The position is analogous to that obtaining in the field of solutions where for many years people agreed on the basis of the values of thermodynamic functions as to whether or not there was chemical interaction. It is now realized that deviations from simple or ideal laws may arise from a variety of reasons, and neither heat changes nor free-energy changes can be regarded as decisive for discriminating between chemical combination and van der Waals or dipole interaction.

The criterion of irreversibility cannot be considered as applicable since this is not a necessary consequence of chemical interaction. If a perfect crystal of a hydrate is placed in a high vacuum, decomposition does not occur, but a scratch on its surface will initiate decomposition, and a powder can be dried by passing a stream of dry air through it. Irreversibility would, therefore, be much more related to geometrical conditions that to straight chemical binding.

It seems probable that rate of sorption and changes in the optical and magnetic properties of adsorbed molecules afford better criteria of chemisorption than do energy changes.

W. E. GARNER: When water is abstracted from the surface of a hydrated oxide, cavities will be left in the surface, which will repair themselves by adjustments between the atoms in the solid. In an oxide, the process of repair probably takes place in stages, each with its own activation energy. During re-absorption, the activation energy required to produce a cavity to receive the adsorbed atoms or molecules may be the rate-determining factor, and this will depend on the state of repair of the cavity. If the activation energy for the reception of water molecules is sufficiently high, then the surface will be hydrophobic.

J. H. DE BOER: It may be relevant that we have never found this effect with alumina. Alumina is always reversible.

B. M. W. TRAPNELL: Chemisorption of water, in particular with reversible formation of OH groups, should give exchange between H_2O and D_2O. This is probably the best criterion of chemisorption available.

S. J. GREGG: I agree with Professor Wynne-Jones that it is very difficult to obtain a satisfactory criterion for chemisorption. Chemical reaction between a gas and a bulk solid is characterized by (a) a change of lattice, (b) a stoichiometric relation between the reactants and (c) an energy change usually several-fold greater than latent heats of sublimation or of condensation. When the reaction is confined to the surface, however, criterion (a) is difficult to apply, for one would have to detect a change of lattice confined to a layer one or two ions thick. Criterion (b) implies localized adsorption on definite sites; it is not easy to apply directly, but it must, in general, be associated with a high energy of adsorption, otherwise the adsorbed film could be mobile and the stoichiometric relation would not need to apply. Thus (c) is frequently our only available criterion. There can be no sharp line of demarcation between physical adsorption and chemisorption, but it is surely safe to say that very high heats, of the order of tens of thousands of calories per mole, must denote chemisorption, and low ones, of the order of the latent heat, physical adsorption. 'Water' which is not liberated at a reasonable rate until temperatures of some hundreds of degrees centigrade are reached, must be present as OH groups, and if these are confined to the surface, must be regarded as chemisorbed. With the 'retained' water which is lost at temperatures as low as 200° or even 100°, we are probably in the border region between physical and chemical sorption.

Professor Garner's model of vacancies is extremely useful, and the loss of these when heating involves properties of the solid such as m.p. Vacancies in themselves are insufficient to explain the hydrophobic nature of strongly ignited silica, for other hydrous oxides do not become hydrophobic when similarly ignited.

Professor de Boer has rightly emphasized that chemisorbed OH groups can only evaporate as water where two such groups occupy neighbouring sites; but this geometrical factor can only operate when the surface is less than one-quarter covered with OH, and energy factors must still be invoked to account for the difficulty of removing water from more fully occupied surfaces.

Finally, I would like to support Dr. Sing's observations of methanol adsorption. We obtain a similar curve with a branch, steep yet reversible, at low pressures.

E. R. S. WINTER: In reply to Dr. Trapnell, there has been some work reported on the use of D and ^{18}O to study the interaction of water with insulator-type oxides. Dr. WHALLEY and I[1] examined briefly the system γ-Al_2O_3–$H_2{}^{18}O$ at temperatures between 20 and 400°C and TiO_2–$H_2{}^{18}O$ and ThO_2–$H_2{}^{18}O$ at 120°C. In all cases, ready exchange of oxygen occurred. MILLS *et al.*[2] referred briefly to similar work on silica–alumina catalysts at the Faraday Society Symposium in 1950, and this work has since been published[3] (*see also* MILLS and HINDIN[4]).

Communicated: Mention should also be made of the work of the Russian workers, KARPACHEVA and ROZEN[5], dealing with Cr_2O_3–Al_2O_3 and with Al_2O_3, kaolin, and ZnO. In the last of these papers the exchange of ^{18}O between catalyst and EtOH is also dealt with.

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E. H. MILLWARD: Preliminary experiments on the adsorption of water vapour by certain chrysotile asbestos surfaces at 25°C indicate that hydrophobic (type V) isotherms, similar to those obtained by Dr. Gregg, occur. At low temperatures of outgassing (say, 25°C) the adsorption-desorption loop for the second cycle duplicates that for the first cycle. However, the loop for the first adsorption-desorption cycle, for outgassing at a temperature of about 300°C, lies above those for the second and subsequent cycles, which are virtually identical.

J. J. Kipling: I was glad that Dr. Winter referred to his work on oxygen isotope exchange on alumina, as it seems to support strongly, in the way Dr. Trapnell suggested, our views on the chemisorption of water.

I agree with Professor Wynne-Jones about the difficulty of defining chemisorption and one of the main purposes of presenting our paper was to encourage the kind of discussion which would lead to a better appreciation of what is, and what is not, chemisorption. While geometrical factors may sometimes be important in explaining irreversible adsorption, I doubt if they alone will explain such adsorption occurring over a complete monolayer.

Energy considerations are, I think, difficult to use for the kind of system dealt with here because the reactions are so slow that precise measurement becomes difficult.

Finally, it seems to me that by reference to the effects one normally associates with hydrogen bonding with water and simple alcohols, hydrogen bonding is not adequate to explain the irreversible adsorption we have observed.

J. F. Goodman: We have measured adsorption-desorption isotherms in ferric oxide, stannic oxide, and silica gels, using carbon tetrachloride, water, and methyl alcohol as adsorbates. The solid was outgassed at a definite temperature (usually 100°C) before measuring the isotherm. On desorption it was found that carbon tetrachloride could be removed from all three solids by outgassing at room temperature. With ferric oxide and stannic oxide, water could be removed by outgassing at the temperature originally used to outgas the solid, after which the isotherms were reproducible. When the type V isotherm, described by Dr. Gregg, was obtained with silica, the water could not be completely removed by outgassing at this temperature and, as he has observed, a change in the nature of the surface occurred during this run. With all the solids, a small quantity of methyl alcohol was found to be irreversibly held, even on outgassing at the temperature originally used to outgas the solid, but apart from this the isotherms were completely reproducible on subsequent runs.

It appears that carbon tetrachloride is only physically adsorbed in all cases. On ferric oxide and stannic oxide gels the water is held rather strongly, but apparently not as strongly as the methyl alcohol. It is attractive to attribute the retention of water to hydrogen bonding and the retention of methyl alcohol to definite chemisorption, but this, of course, can be little more than purely speculative from the present data.

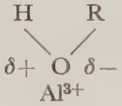
R. M. Barrer: I would like to comment upon the use of sorption heats as a criterion of chemisorption. This is, in my view, a dangerous procedure. In some crystalline minerals, molecules may be located in intracrystalline cavities which are joined by 'windows' to other similar cavities. The free diameters of these cavities may vary considerably. They are ~7·3 Å in chabazite, ~11·8 Å in a synthetic zeolite (e.g. Linde Molecular Sieve 4A), and ~16 Å in synthetic faujasite. Some initial heats of sorption in chabazite, for example, are:

H_2	~3 kcal mole^{-1}	CO_2	~14 kcal mole^{-1}
A	~4·5	NH_3	~24
N_2	~6	H_2O	~30
CO	~8		

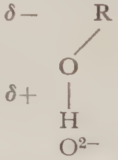
The heats for the more polar gases, in particular, are very large, and yet we do not think of the sorption as being other than physical. The high heat is due to ion-dipole interaction, and no criterion, such as colour change, intervenes to suggest otherwise. There is, indeed, no mystery about these large heats for physical sorption.

One may also refer to occlusion by faujasite. Quite large hydrocarbon molecules such as *iso*octane are speedily occluded, and we have measured isosteric heats of sorption for C_1 to C_8 paraffins. These heats are some two and one-half to three times as large as the corresponding latent heats of vaporization, and there is the expected regular change in the sorption heat and carbon number for *n*-paraffins. There seems to be nothing chemical here, yet the heat of sorption for *n*-heptane, for example, is 20–22 kcal mole^{-1}. I would, therefore, comment that there can be no simple relationship between energy change and chemisorption.

D. D. ELEY: Two points are relevant concerning high heats of physical adsorption. Very high heats for water on ionic oxides are forthcoming from ion-dipole interactions of the kind shown for alcohols:



$\Delta H_{ads} \equiv -56$ kcal mole^{-1}



$\Delta H_{ads} \equiv -63$ kcal mole^{-1}

These values will be found in a paper published by me three or four years ago in the *Symposium on Adhesion* (Society of Chemical Industry). In the case of hydrocarbons, the measurements and calculations for hydrocarbons on mercury carried out by Professor C. KEMBALL[1] are relevant. The adsorption energies, due to London forces, increase regularly with molecular size, reaching values of *c.* 20 kcal mole^{-1}. The reason, of course, is that the polarizability of the molecule which enters the equation for the London forces, increases with the size of the molecule. The shape of this molecule is, of course, important in deciding how close it may approach the surface.

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S. J. GREGG: The high heats of physical adsorption referred to by Professor Barrer represent a special case in that the molecules are surrounded on all sides by solid. If it were possible to remove the energetic results of this enclosing geometry, then I consider that energy would still be a useful criterion in chemisorption.

R. M. Barrer: To Dr. Gregg's comment that high heats for sorption in zeolites arise because the sorbed molecules in the intra-crystalline cavities are largely surrounded by the anionic framework of the crystal, I would point out the large size of the cavities in faujasite, for example. Some pockets, no bigger, exist in many gas-sorbing carbons and in silica gels, and here also large physical sorption heats can be expected. It is just such systems which are difficult to outgas at room temperatures and where sorption energy considerations could, if not carefully employed, lead to erroneous inferences of chemisorption. The influence on sorption heats of the geometrical or environmental factor cannot, in my view, be ignored, for it is an intrinsic factor in many porous gels.

F. Deacon: Dr. Gregg and others have quoted results showing that surfaces which are initially hydrophobic can become hydrophilic on contact with water. Many dried ionic solids show a decrease in contact angle on leaving in contact with water, sometimes to complete wetting. There may be a similar mechanism operating here, probably one involving a reversible but slow reaction with the surface, or a change in the electronic state of the oxygen ions.

E. C. Baughan: I would just point out that in some few cases where films of high polymers, about 0·01 mm thick, are exposed to organic vapours (e.g. polystyrene–CCl_4), there is practically no absorption under a certain partial pressure, above which absorption becomes complete. The reversible equilibrium curve can then be measured down to the lower pressures. In such systems, compound formation can hardly take place, so the effect must be essentially geometrical, in agreement with the fact that it is only observed where the absorbed molecule is larger than that of the solvent from which the film was cast[1,2,3].

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Anon: I would like to ask whether the films mentioned by Professor Baughan were completely dry?

E. C. Baughan: The films are made by casting from a solvent and drying them out to constant weight. There is no water, they have never touched water.

Anon: Not even enough water to form a single monolayer?

E. C. Baughan: The polystyrene films were made from benzene dried with P_2O_5; I have not considered whether this would involve one monolayer of water. The effect occurs only under the appropriate conditions, for instance, with polystyrene it happens for carbon tetrachloride, but not for xylene or toluene. On nitrocellulose films it occurs with some ketones, but not with others; certainly it appears that geometry cannot be excluded.

A. L. Papadopoulos: I would like to ask Dr. Kipling whether he has related the results of his experiments on alumina and silica gel to chemisorption of moisture on the surface of soda glass?

From tests which we carry out for product-quality control, we found that the first two criteria given by Dr. Kipling were obeyed by the glass-moisture system. The moisture present on the inside surface of the glasses of a Double Glazed Unit, i.e. two pieces of glass hermetically sealed together at the edges and separated by an air space, could be reduced by blowing through the unit a stream of dry air with a dew point of −70°C. The initial dew point of the unit was −40°C, and its equilibrium dew point which was obtained four days after sealing the vent holes was −18°C. This indicated that part of the adsorbed moisture was removed by the dry air during flushing, part of it was diffused into the dry atmosphere until equilibrium was obtained, and part of it remained on the glass. The latter could only be removed from the glass by more drastic conditions.

When the glasses were heated at 400°C for 3 hours and processed immediately after cooling to room temperature, the resultant Double Glazed Unit had an equilibrium dew point of −50°C. If the heat-treated glass was exposed to room atmosphere for 3 hours before processing, the unit produced had a dew point of −18°C, and it was proved that the amount of moisture adsorbed by the heat-treated glass was a function of the exposure time.

J. J. Kipling: We have avoided working with glass because adsorption might be complicated by formation of solutions between the vapour being offered to the solid and free alkali therein.

E. W. Jackson (*Communicated*): With regard to the difficulty of deciding whether adsorption is chemical or physical, I have found, in some experiments carried out in the liquid phase at A.R.L. Teddington, that the measures required to bring about desorption enabled one to differentiate between the two kinds of adsorption.

In this work barium 140 was adsorbed from aqueous solution on to films of polystyrene and other polymers. It was found that about half of the barium ions could be reversibly desorbed, but that the remainder could only be removed by treating the surface with solutions of chelating agents such as sodium ethylene–diamine tetraacetate, which forms soluble non-adsorbing complexes with barium. It seems that in this adsorption the two actions are proceeding simultaneously and that the reversible part is physical, but the desorption requiring the use of complexing agents is chemical.

F. A. P. Maggs: I would like to suggest an alternative explanation of these phenomena whereby it is possible, on heating to high temperatures such as 700–800°C, for the pore dimensions to be reduced so much that a molecular-sieve effect appears even for water. Then to talk of hydrophobicity is somewhat incorrect; for silica at a certain point in the isotherm the water is held up in the pores and the return loop is the normal curve as for hydrated silica. With some carbons one appears to get such molecular-sieve effects.

I notice that Dr. Kipling refers to the very long time effects which he observes; this suggests the presence of pores only just large enough to allow passage of the adsorbate.

S. J. GREGG: The time required for adsorption is not exceptionally large on the upward branch, a very small quantity of water being sufficient to produce this effect; it is difficult for me to think of such a small quantity of water opening up such a large area to further quantities of water.

J. H. DE BOER: This possibility has been thoroughly investigated in our case; the pore-size distribution has been measured before and after and does not change.

D. J. C. YATES: Mr. Chairman, I wish to point out that there is another method of differentiating between chemisorption and physical adsorption, namely the infra-red spectroscopy of adsorbed materials. The well-known work of Eischens and his collaborators in America has shown that in cases of undoubted chemisorption, e.g. carbon monoxide on a palladium, the spectrum of the adsorbate is quite different from that which it has in the liquid or gas phase. The bands obtained were assigned by means of analogies with the spectra of metal carbonyls and give definite information on the structure of the adsorbed phase.

At Cambridge, in the Department of Colloid Science, I have been working recently with Dr. N. Sheppard on the infra-red spectra of simple molecules physically adsorbed on to porous silica glass. For instance, in the case of ethylene, it is found that the adsorbed molecules have absorption spectra similar to those of liquid ethylene. The frequencies to be expected for ethane-like and acetylene-like complexes are known and thus we can be fairly certain that we are dealing with ethylene physically adsorbed. Although the cases mentioned are of definite chemisorption and definite physical adsorption, it is possible that further development of the technique may enable the status of borderline cases to be decided.

SECTION 3

CHEMISORPTION ON METALS

Chairman: D. D. ELEY

3.1

INTRODUCTION TO CHEMISORPTION ON METALS

D. D. Eley

Department of Chemistry, The University of Nottingham

The main points may be made clear by reference to the Lennard-Jones potential-energy curves for the chemisorption of hydrogen (*Figure 1*), as an example

$$H_2 + 2M \rightleftharpoons H_2 \ldots 2M \rightleftharpoons 2M - H$$

While an activation energy is usually absent at low surface coverage, it may clearly appear as $\sigma \to 1$. To understand the nature of chemisorption, heat measurements (employed by Trapnell in work described at this meeting) have been of the first importance, together with contact-potential measurements, discussed here by Mignolet. Contact-potential measurements, in so far as they indicate surface dipole moments and lead to electronegativities, should link up with values for the heat of chemisorption. Measurements of electric resistance of transparent films have been shown by Suhrmann to reveal the effects of adsorbed gases. Here I believe that in future we must not neglect to separate the resistance of the crystals from that of the intercrystalline gaps, and it has occurred to me that work at high frequencies might prove useful, although it may be that the effects will prove too small to be detectable.

The papers by Eley and Rossington, and Gundry and Tompkins, both tackle chemisorption from the kinetic point of view, considering the question of the activation energies involved in the process. The first of these papers also considers the relation between the log frequency factor and E, which is also discussed by Bond and Addy. Finally, the paper by Leck deals with a subject of practical importance, since ion-bombardment is a recognized cleaning method for metals used in chemisorption work. His paper also adds to our knowledge of slow-desorption phenomena.

Before closing, I would mention briefly some recent work, including new techniques, which we may expect to aid considerably our studies in the future. EISCHENS' work has shown how the infra-red spectrometer can identify chemisorbed radicals in favourable instances[1]. MÜLLER has used the field emission microscope in numerous important problems; e.g. he has shown that a second layer of hydrogen exists on tungsten, which is complete at 100°K and 10^{-3} mm Hg[2]. GOMER has used this instrument to determine activation energies for mobility of chemisorbed gases, and shown that the primary W-H layer is immobile at $\sigma = 1$ up to 205°K[3]. EHRLICH has developed a desorption technique so as to identify three different kinds of adsorption of nitrogen on tungsten[4]. Ferro-magnetic measurements have been correlated with photoelectric measurements and electrical conductivity of films for the adsorption of hydrogen on nickel[5]. These are only a few examples of work in progress on chemisorption.

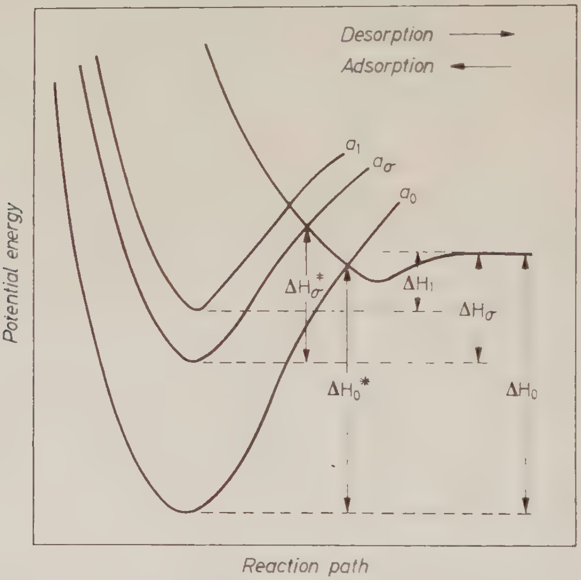

Figure 1. Lennard-Jones potential energy curves for the chemisorption of hydrogen. To the usual curve a_0 for M—H bond at surface coverage $\sigma = 0$ are added curves for higher coverages $\sigma = \sigma$ and $\sigma = 1$. They show how the heat of adsorption $-\Delta H$ and the activation energy for desorption ΔH_σ^* fall with increase in surface coverage. (D. D. Eley, *Trans. Faraday Soc.*, 49 (1953) 673.)

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3.2

MECHANISMS OF CHEMISORPTION

B. M. W. Trapnell
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SUMMARY

Recent and current work at Liverpool on this topic is described. Particular attention is paid to the structure of oxygen layers, calorimetric data being presented together with volumetric data and data on the variation in affinity for oxygen shown by different elements. This leads to a discussion of the possible existence of surface states, and experimental results relating to this question are described for chemisorption of oxygen and nitrogen, and for recombination of hydrogen atoms. Finally, brief mention is made of the variation of velocities of paraffin sorption on different metals, and the possible importance of such differences in deciding relative catalytic activities is outlined.

INTRODUCTION

We shall be mainly concerned with how velocities and heats of chemisorption vary among metals. The variation of heats is not, of course, a new problem, but the variation of velocities, in spite of its potential significance to catalysis, has so far been largely neglected.

In attempting to correlate experimental data with physical properties of metals, the fundamental problem arises as to the nature of the surface. Inasmuch as the surface metal atom is part of the crystal, it may be valid to attempt correlations of adsorption characteristics with bulk properties. On the other hand, the unsaturation of surface atoms may imply a difference from bulk property. An extreme view is that the surface atom is substantially a free gaseous atom, and in this case one should expect to be able to relate surface behaviour to properties of free atoms.

HEATS OF CHEMISORPTION

Mr. D. O. Hayward has investigated the variation among heats of oxygen chemisorption of different metals, and has so far obtained data at 15°C on films of W, Ta, Mo, Nb, Cr, Mn, and Ni. Of these, W, Ta, Mo, Nb, and Ni films were made by direct evaporation, while Cr and Mn films were obtained from electrodeposits on W filaments. Mn films are of interest in that their surface areas remain almost constant beyond a certain weight, and in that they give less hydrogen chemisorption than any transition metal so far studied.

Except for Ta and Cr, the heat remains constant as most of the surface is covered, falling only during the last 10–15 per cent of adsorption. The layers are therefore immobile, and the heats integral rather than differential. With most metals, the fall at the end of chemisorption may be due to the onset of oxidation, or to a little second-layer chemisorption of the type first suggested by Morrison and Roberts[1,2]. With Ta, the fall commences rather earlier, at about 70 per cent coverage, which is similar to the behaviour of nitrogen on Ta[3].

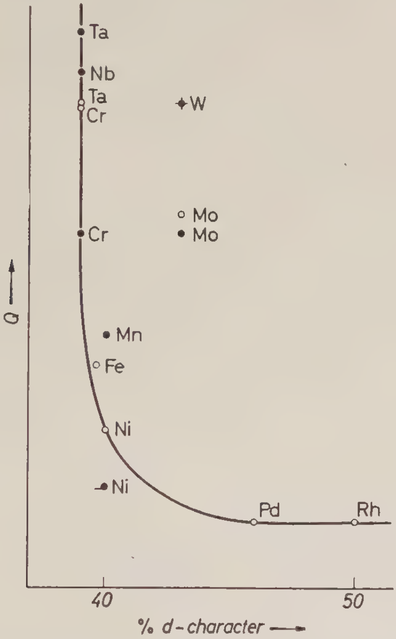

Figure 1. Heats of chemisorption of oxygen and hydrogen.
● : O_2 ○ : H_2

If we follow precedent by plotting heats against *d*-character, a very similar pattern emerges to that found with hydrogen and ethylene. This is shown in *Figure 1*, in which the heats of oxygen and hydrogen[4] chemisorption are plotted on the same graph, with the oxygen heats multiplied by a constant, chosen so that the heats of oxygen and hydrogen chemisorption on W coincide. The actual values of the oxygen heats vary between 210 kcal/mole (Ta) and 120 kcal/mole (Ni).

We note, however, that the close parallel between oxygen and hydrogen heats does not necessarily imply identity of bond types in the two cases. The Eley method of calculating heats[5] gives the ratio of heats on a metal M as

$$\frac{q_{O_2}}{q_{H_2}} = \frac{2E_{M-M} + 46{\cdot}12\ \mu^2_{MO}}{E_{M-M} + 46{\cdot}12\ \mu^2_{MH}}$$

where E is the bond energy and μ the dipole moment. With all metals for which oxygen and hydrogen heats are available, q_{O_2}/q_{H_2} is considerably greater than 2 and usually greater than 4. This suggests that the ionic contribution is more important with oxygen than with hydrogen.

In any case, the correlation between heat and *d*-character is obviously only partial. With oxygen the heat can vary substantially among metals with identical *d*-characters (40 kcal/mole between Cr and Ta; 25 kcal/mole between W and Mo), yet be virtually identical on metals with very different *d*-characters (Cr and Mo; W and Nb).

In seeking to correlate heats with some other property we found that if values for oxygen are plotted across individual periods, the anomalies of the *d*-character plot largely disappear. Across each period there is a uniform decrease in passing from left to right: first- and second-period heats are about equal at corresponding positions in the periods, and rather less than third-period heats. A similar plot is possible with hydrogen heats. Unfortunately, properties of metal *crystals* such as lattice spacing, *d*-character, and melting point tend to oscillate across a transition period, and no very relevant property changes progressively as a period is traversed. It is primarily the properties of free atoms, such as the electronic configuration, which change most steadily across a period. Thus, if the above method of plotting heats is significant, it may imply the existence of surface states with a partial atomic character. It is pertinent to examine further this rather drastic implication.

SURFACE STATES

Hitherto, only theoretical approaches have been made to the question of surface states. Several such approaches indicate the possibility of surface states, and one at least, due to GOODWIN[6], does conclude that the surface state of a metal is essentially that of a free atom. However, the treatment is based on the very simple model of a one-dimensional metal with a tight-binding approximation and cannot perhaps be regarded as very conclusive.

PICKUP[7] has recently considered whether there is any experimental evidence for surface states. The evidence proves to be very slender, but three sets of data are worthy of mention:

1. For no catalytic reaction are data available for a complete period, but in hydrogen atom recombination the activity of metals of the first period rises smoothly across the period in the sequence $Cr < Fe < Co$, then falls smoothly in the sequence $Co > Ni > Cu > Zn$[8]. Thus activity varies continuously with atomic number, which may indicate the existence of surface states, particularly since, on the basis of *d*-characters, Co should have a lower activity than both Fe and Ni.

2. The incomplete coverage of transition metals by nitrogen can best be ascribed to some kind of electron deficiency in the metal surface for covalent-bond formation[9]. However, if the surface metal atoms participated fully in the band structure of the crystal, it is not easy to see how such a deficiency could arise. The nitrogen data may indicate the existence of surface states.

3. The pattern of occurrence and non-occurrence of oxygen chemisorption presents a rather conflicting picture. We have remarked[10] that among the metals the unique inactivity of Au and Hg towards oxygen cannot readily be associated with any crystal property. Au and Hg do, however, possess uniquely high ionization potentials and as a result are unable to form ionic compounds. Since the surface bond with oxygen is largely ionic, a high ionization potential could preclude chemisorption if partly atomic surface states were involved.

However, GREENHALGH[11] has recently investigated the behaviour of the metalloids and elemental semiconductors towards oxygen. These, too, show low activity, and the essential result is that the further we depart from the metallic state the smaller is the ability to adsorb oxygen. Thus Se and Te are quite inactive up to 140°C, while among the metalloids the activity order is $As < Sb < Bi$. Of all these five elements, only Bi is capable of fast oxygen chemisorption. Departure from the metallic state is characterized by a decreasing density of levels near the Fermi level, and among the above elements there is an exact correlation between this density and the activity towards oxygen. Thus, a normal bulk property can explain the surface property, and, furthermore, there is no correlation between surface activity and any property of the atom such as the ionization potential.

VELOCITIES OF CHEMISORPTION

The velocity of a fast non-activated chemisorption will not often determine the rate of a catalytic reaction, and equally the variation of such velocities from metal to metal may well be small. More interesting data are likely to emerge from slow chemisorptions, the best-known examples of which on metals are those of the paraffins. The chemisorption of CH_4 and C_2H_6 has therefore been studied on films of ten transition metals, W, Mo, Ta, Cr, Fe, Co, Ni, Rh, Pd, and Ti, all of which other than Cr were prepared by direct evaporation. Temperatures up to 70°C were used; with C_2H_6 layers appreciable liberation of hydrogen was detected on W, Mo, and Rh and allowed for in calculating the hydrocarbon sorption. On all metals the chemisorption was small, even at the highest temperature, and coverage was probably incomplete. The sorption tended to increase with temperature.

Two methods were used in attempting to establish a hierarchy of velocities. First, some attempt was made to compare fast chemisorptions at —195°C. Since there is also strong physical adsorption at —195°C, the fast chemisorption was obtained indirectly, from ascending and descending isobars between —195 and 0°C. At 0°C there is no physical adsorption, and the measured uptake is the sum of the slow sorption and any fast chemisorption which may have occurred. The difference between initial and final sorptions at —195°C may to a first approximation be equated to the slow sorption, and hence the fast chemisorption can be calculated. For the W/CH_4 and Mo/CH_4 systems this amounted to 1·6 and 0·4 × 10^{18} molecules/100 mg, respectively, compared with hydrogen monolayer adsorptions at —195°C, 12·4 and 22·2 × 10^{18} molecules/100 mg, respectively. Thus on W there is appreciable fast chemisorption, but on Mo very little.

The indirect approach is, however, open to objection, and a comparison of sorptions at 0°C, where physical adsorption is negligible, gives more interesting results. The data of *Table I* were obtained after 30 minutes exposure of films to 5 × 10^{-3} mm pressure of gas at 0°C.

Most of the metals behave rather similarly even though their electronic configurations and lattice spacings are very different. In this connection it is interesting to compare the behaviour towards C_2H_6 of Ti, which lies at the beginning of a transition period, W, at the centre, and Rh at the end. The striking feature is the almost complete inactivity of the Fe, Co, Ni triad.

Probably the best, though not the only, explanation of this inactivity is the ferromagnetism of these metals. If the stable alignment of electrons persists at the surfaces of ferromagnetic crystals, chemisorption with formation of covalent bonds might well be very slow because of the disturbance of this alignment. The few extra kilocalories activation energy necessary to explain the unique behaviour of Fe, Co, and Ni could well arise from such an effect.

There is some correlation between ease of sorption and activity in paraffin–deuterium exchange. Thus in CH_4–D_2 exchange W and Rh are highly active, whereas Ni and Fe are relatively inactive[12]. In C_2H_6–D_2 exchange, W, Mo, Ta, and Rh are all active whereas Fe, Co, and Ni are again far less active[13]. Exchange activity may therefore be decided largely by the sorption velocity. However, Pd and Cr may be exceptions in that both give ready C_2H_6 chemisorptions at −78°C and above, yet possess low exchange activities, nearer to those of Co and Ni than of W, Mo, Ta, and Rh. With Pd, the low activity may be due to the low surface area, but this can hardly be the case with Cr.

Table I. CH_4 AND C_2H_6 SORPTIONS AT 0°C (MOLECULES $\times 10^{-18}$/100 mg)

Metal	CH_4 *sorption*	C_2H_6 *sorption*	*Monolayer chemisorption*
Ti	0·5	2·1	16·5 (H_2)
W	3·9	2·5	12·4 (H_2)
Mo	2·6	3·8	22·2 (H_2)
Ta	1·4	2·7	20·0 (O_2)
Cr	2·0	2·8	19·0 (H_2)
Fe	<0·01	0·04	11·0 (H_2)
Co	<0·02	<0·02	3·1 (H_2)
Ni	<0·02	0·09	2·5 (H_2)
Rh	0·58	2·0	9·5 (H_2)
Pd	0·03	0·36	1·25 (O_2)

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3.3

CHANGES IN CONDUCTIVITY ON ADSORPTION OF GASES ON METAL FILMS

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SUMMARY

Besides the work function, the concentration of the conduction electrons is of considerable importance for electron transfer between a chemisorbed molecule and the metal surface. This is shown by the changes in conductivity of nickel films, on the one hand, and bismuth films, on the other, caused by adsorption of carbon monoxide, oxygen, and hydrogen.

INTRODUCTION

If free gas molecules enter the electric field of a phase boundary, e.g. if they are adsorbed on a metal surface, their electric equilibrium is disturbed and their electron clouds are shifted with respect to their positive charges. Intensity and direction of the polarization depend on the electron affinity of the surface, the polarizability of the molecule, and its electron affinity. When the interaction between the molecule and the surface is very strong, the molecule can decompose, provided that the energy of decomposition of the adsorbed molecule is available. In this case the products of dissociation are chemisorbed.

The electronic interaction is usually studied by determining the change in the work function of metal surfaces either from photoelectric, thermionic, or field emission measurements or indirectly by determining the contact potential of the catalyst surface with reference to an unchanged electrode surface. The observed decrease or increase in the work function on adsorption of foreign molecules indicate only an electron shift to or from the catalyst surface. But if the electrons of the adsorbed molecules become part of the metal electron gas, or if the metal electrons become part of the electron shells of the molecules, a change in the electric resistance of the metal will be observed in addition to a change in the work function[1].

The change in resistance will become measurable when the adsorbing catalyst layer is not thicker than approximately a hundred or a thousand times the thickness of the layer undergoing electronic interaction.

In the following, the results of such investigations are described in which carbon monoxide, oxygen, and hydrogen were adsorbed on thin films of nickel and bismuth. They show that besides the work function, the concentration of the conduction electrons is of considerable importance for the type of the electron transfer between a chemisorbed molecule and the metal surface.

The transparent metal films were condensed on glass surfaces in high vacuum, observing all precautions of modern vacuum technique. The residual gas in the prevacuum flask was the same as that to be adsorbed. During evaporation of the metal the diffusion pump was connected with this flask.

Whereas the electric resistance of an evaporated nickel film increases with increasing temperature, as does the resistance of the bulk metal, the resistance of an evaporated bismuth film decreases. The interaction between the atoms of such a film is so weak that its energy bands do not overlap[2]; the electron concentration in the conduction band is therefore low and increases with increasing temperature. By the addition of atoms serving as electrons donors, e.g. of tellurium atoms, the concentration of conduction electrons can be increased to such an extent that the film becomes metallic in character[3].

CARBON MONOXIDE ON NICKEL AND BISMUTH

When carbon monoxide is adsorbed on a nickel film at 90°K the electric resistance of the film increases[4]. The amount of the increase depends markedly on the temperature of the entering gas: If the gas is as cold as the film, the over-all increase in resistance is only 7 to 12 per mille (*Figure 1*)*; if it is warm, the increase is 70 to 80 per mille (*Figure 2*)[5]. It is possible that the exchange of energy between the molecules and the cold surface occurs so slowly that the thermal energy of the molecules serves as activation energy for the place changes on the nickel surface.

In this case, metal electrons are displaced towards the adsorbed molecules because the electron affinity of the CO molecule is greater than that of the surface. If the work function were the only cause of electron affinity, electron transfer from a bismuth film to the adsorbed molecules would be easier than from a nickel surface, as the work function of the bismuth film is smaller than

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* The points on the curves shown in this and the following figures are actually measured values.

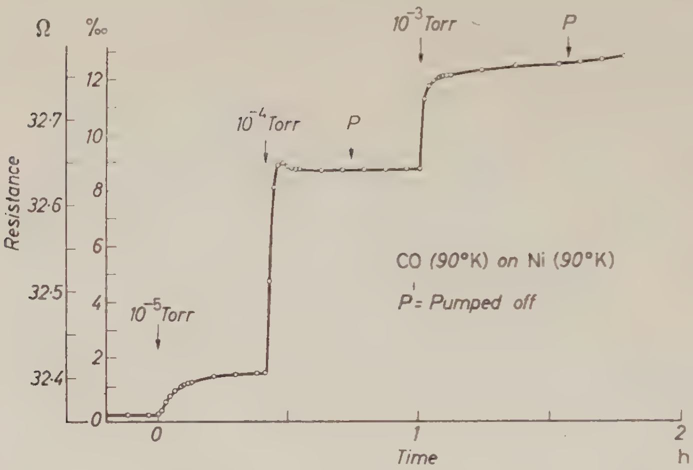

Figure 1. Resistance increase of a transparent nickel film on the adsorption of cold (90°K) carbon monoxide at $T = 90$°K. (Wedler, Dissertation, Braunschweig, 1955.)

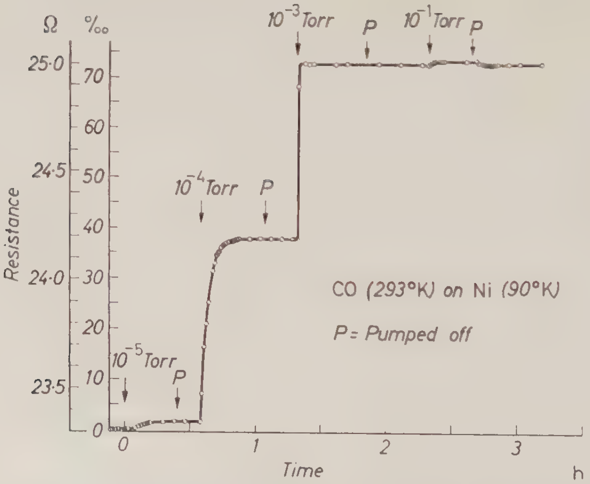

Figure 2. Resistance increase of a transparent nickel film on the adsorption of warm (293°K) carbon monoxide at $T = 90$°K. (Wedler, Dissertation, Braunschweig, 1955.)

that of the nickel film by 0·65 volts[6]: nevertheless, the resistance of the bismuth film decreases when carbon monoxide is adsorbed (*Figure 3*)[7]. Part of the decrease is not reversible by pumping off, but gas additionally adsorbed at pressures of 10^{-3} or 10^{-1} mm Hg at 90°K can be pumped off, whereby the resistance of the film increases again to the former value. The chemisorbed molecules are not strongly bound because the decrease of the resistance amounts only to 2·4 per mille.

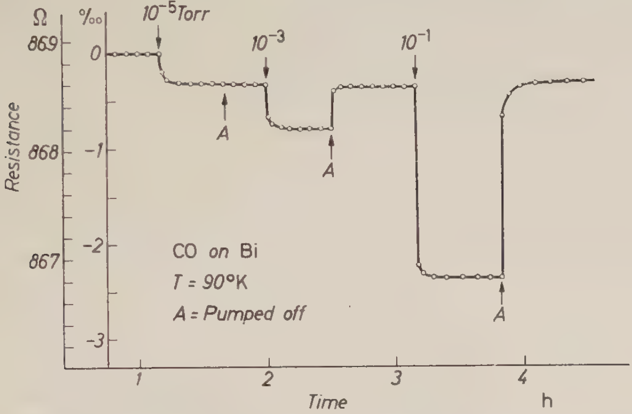

Figure 3. Resistance decrease of a transparent bismuth film on the adsorption of warm (293°K) carbon monoxide at $T = 90°K$. (Keune, Dissertation, Braunschweig, 1956.)

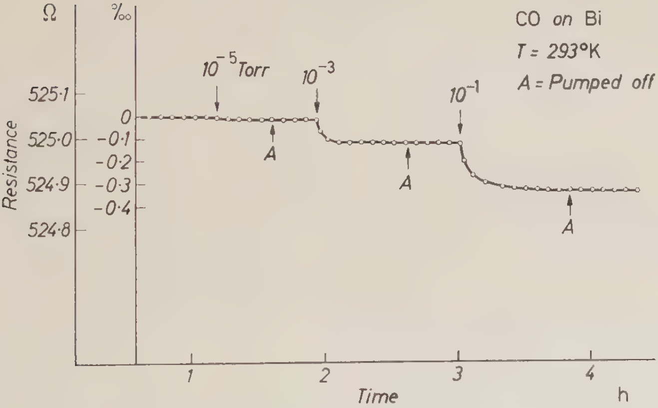

Figure 4. Resistance decrease of a transparent bismuth film on the adsorption of warm (293°K) carbon monoxide at $T = 293°K$. (Keune, Dissertation, Braunschweig, 1956.)

At room temperature the electron concentration of the film is larger than at 90°K, and we observe now in fact only a small decrease of the resistance when carbon monoxide is adsorbed, and no reversible effect occurs (*Figure 4*). When only 2 to 3 atoms per cent of tellurium are added to the bismuth metal the film can deliver electrons to the CO molecules so that the resistance *increases* (*Figure 5*), if carbon monoxide is adsorbed.

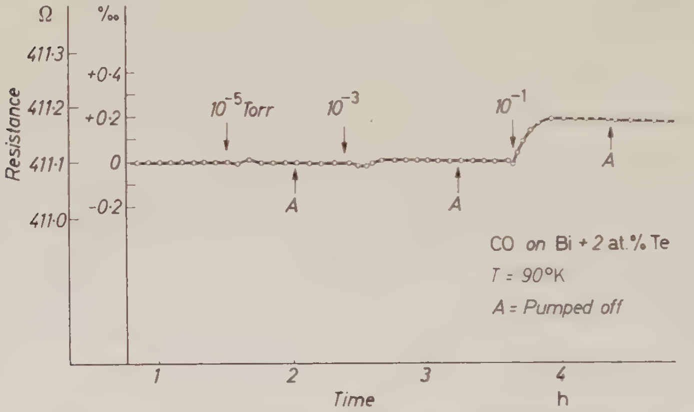

Figure 5. Resistance increase of a transparent bismuth film with 2 to 3 atom per cent of tellurium on the adsorption of warm (293°K) carbon monoxide at $T = 90$°K.
(Keune, Dissertation, Braunschweig, 1956.)

It follows from these results that electron concentration plays a very important role in the electronic interaction. Electron concentration is another factor which, besides the work function, governs the electron affinity of a metal surface.

OXYGEN ON NICKEL AND BISMUTH

On account of the high electron affinity of the O atom, decomposition into atoms of O_2 molecules striking the metal surface occurs if the electron affinity of the surface is not too high and if the necessary activation energy is available. The O atoms should draw electrons out of the metal surface and raise its resistance. In fact, if oxygen acts on the surface of a nickel film at 90°K, its resistance increases, first instantaneously and later more slowly but irreversibly (*Figure 6*). At pressures higher than 10^{-4} mm Hg more oxygen is adsorbed, but a further increase in the resistance is not observed. The oxygen additionally adsorbed shows no electronic interaction with the metal surface and can be pumped off.

As the work function of an evaporated bismuth film is larger than that of a nickel film by 0·65 V, one should expect bismuth to deliver electrons to the oxygen molecules more easily than nickel. But if oxygen of 10^{-5} mm Hg acts upon the bismuth surface at 77°K,

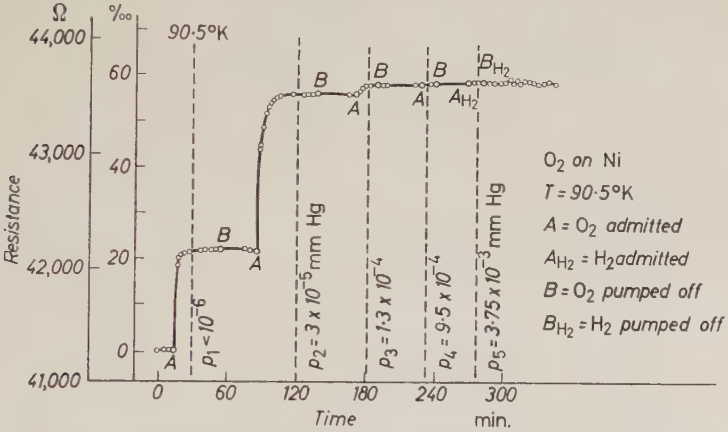

Figure 6. Resistance increase of a transparent nickel film on the adsorption of oxygen at $T = 90$°K. (Suhrmann, R., and Schulz, K., *Z. phys. Chem., N.F.*, 1 (1954) 69.)

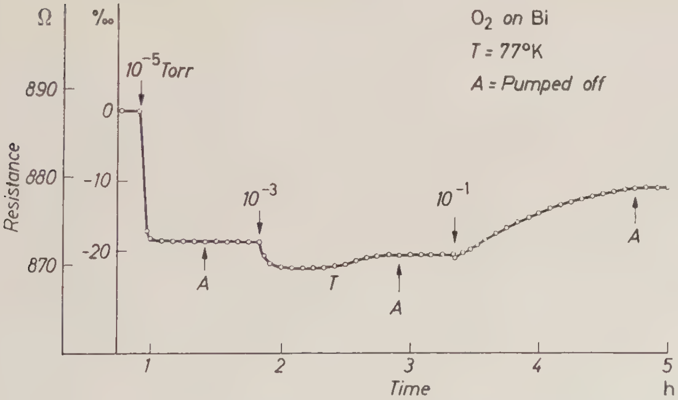

Figure 7. Change of the resistance of a transparent bismuth film on the adsorption of oxygen at $T = 77$°K. (Suhrmann, R., and Keune, H., *Z. Electrochem.*, 60 (1956) 898.)

the film resistance suddenly *decreases* by 19 per mille (*Figure 7*). At such a low temperature and low pressure the oxygen molecules are adsorbed without decomposition, forming the preliminary stage of O_2^+ ions[8]. They deliver electrons to the metal surface so that the resistance decreases. The adsorbing spots are those with the highest electron affinity. At 10^{-3} mm Hg they are nearly all covered for only a gradual decrease of the resistance is observed, and after some minutes, at *T* in *Figure 7*, the resistance change slowly changes sign. At 10^{-1} mm Hg, after a first small decrease, the resistance slowly increases by up to 10 per mille. Besides the spots with high electron affinity there exist some spots which easily give up electrons. If the former are filled, the molecules migrate to the latter where they take up electrons and dissociate[9].

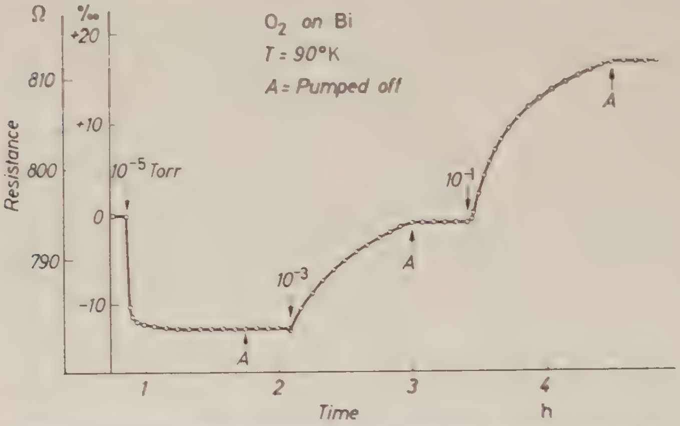

Figure 8. Change of the resistance of a transparent bismuth film on the adsorption of oxygen at $T = 90$°K. (Suhrmann, R., and Keune, H., *Z. Elektrochem.*, 60 (1956) 898.)

If this explanation proves right, the initial decrease of the resistance at low pressure of oxygen must be smaller at a higher temperature and the subsequent increase must be more pronounced at higher pressures. *Figure 8* shows this expectation to be fulfilled at 90°K. At 293°K (*Figure 9*) even as low a pressure as 10^{-5} mm Hg increases the resistance, and at 10^{-3} and 10^{-1} mm Hg the resistance increase reaches very high values. The weak minimum after the sudden increase and the decrease on pumping off may be explained by the recombination of atoms to molecules.

The slow increase of the resistance at 10^{-1} mm Hg and 90°K or 195°K caused by the migration of adsorbed oxygen molecules to spots of low electron affinity can be represented very well by an exponential function. The temperature dependence of its velocity constant gives an activation energy of 180 cal/mol.

If the bismuth film is not heated to room temperature after evaporation at 90°K, it is quasi-liquid[10] and has a higher electric conductivity than when crystallized by heating it to room temperature. The quasi-liquid film has a higher electron concentration than the tempered film and electrons are therefore given up more easily to the adsorbed oxygen molecules. As can be seen in *Figure 10*, the polarization of the O_2 molecules on such a film is insignificant

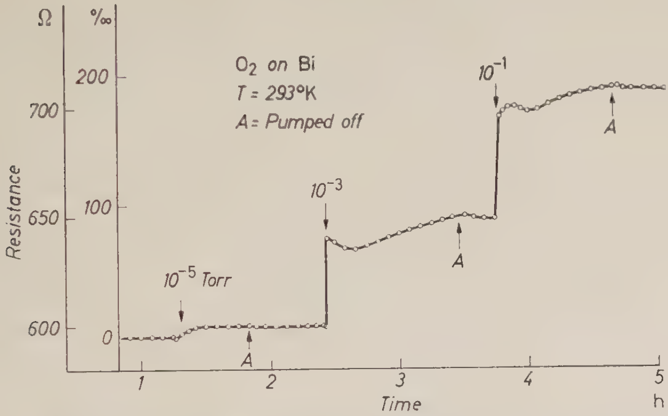

Figure 9. Change of the resistance of a transparent bismuth film on the adsorption of oxygen at $T = 293°$ K. (Suhrmann, R., and Keune, H., *Z. Elektrochem.*, 60 (1956) 898.)

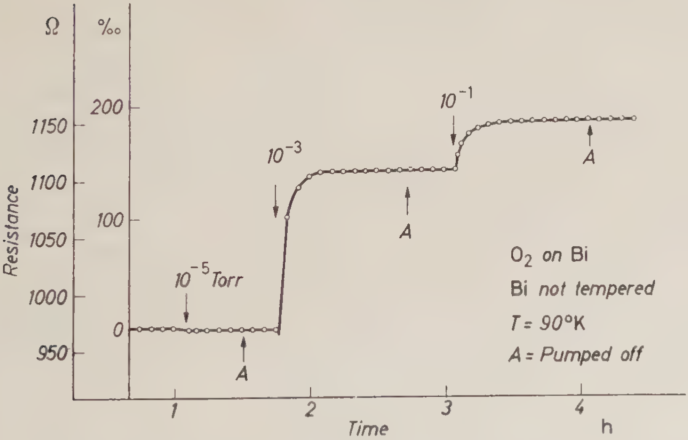

Figure 10. Change of the resistance of a transparent, not tempered bismuth film on the adsorption of oxygen at $T = 90°$K. (Suhrmann, R., and Keune, H., *Z. Elektrochem.*, 60 (1956) 898.)

also at 90°K and the resistance already increases markedly at 10^{-3} mm Hg because the O_2 molecules decompose into atoms at once.

HYDROGEN ON NICKEL AND BISMUTH

In order to understand the interaction between hydrogen and nickel we must pay attention first to the difference between the work functions of the ordered and disordered nickel film and second to the dissociation of hydrogen into atoms, protons, and electrons

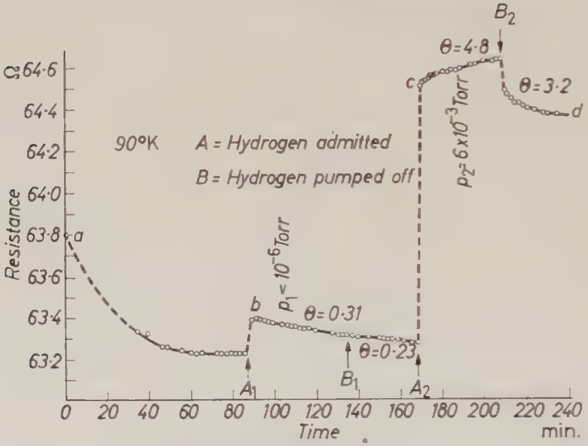

Figure 11. Resistance increase of a transparent, not tempered nickel film on the adsorption of hydrogen at $T = 90°K$. (Suhrmann, R., and Schulz, K., *Naturwissenschaften*, 42 (1955) 340.)

$$H_2 \rightleftarrows 2H \rightleftarrows 2H^+ + 2\ominus$$

The work function of the disordered nickel film condensed and kept at 90°K is smaller by 0·45 volts than that of the same film in the ordered stage, i.e. when heated to room temperature[11]. The surface of the disordered film has, apart from the spots with small work function, some crystalline spots with the higher work function observed on ordered films. At these spots the H_2 molecules dissociate into atoms which migrate to the neighbouring spots with small work function. There they take up electrons and increase the electric resistance, as shown in *Figure 11*[12]. The decrease of the resistance before the introduction of hydrogen is caused by weak crystallization occurring already at the low temperature. The hydrogen adsorbed at the higher pressure of 10^{-3} mm Hg can be partly pumped off. The negative film formed by the H atoms on the nickel surface raises the work function.

On the surface of an ordered nickel film there are many spots with high work function so that the decomposition of the H_2 molecules is not terminated by the formation of H atoms but leads furthermore to the formation of electrons and protons. The protons

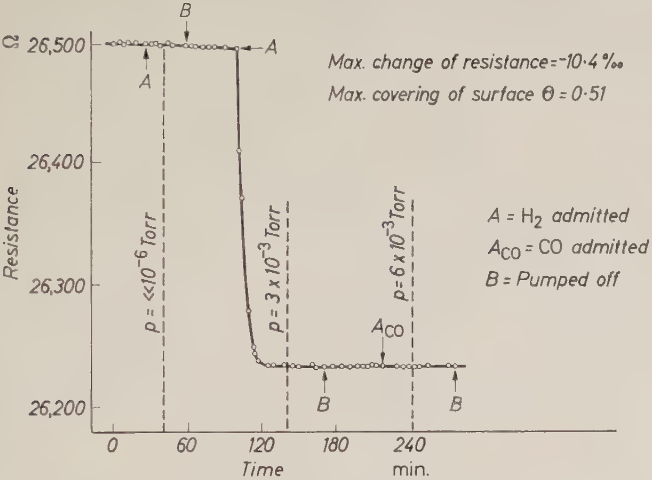

Figure 12. Resistance decrease of a transparent, tempered nickel film on the adsorption of hydrogen at $T = 90°K$. (Suhrmann, R., and Schulz, K., *Z. phys. Chem. N.F.*, 1 (1954) 69.)

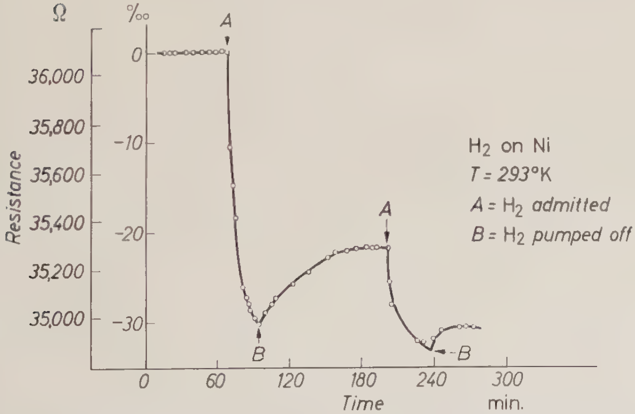

Figure 13. Resistance decrease of a transparent, tempered nickel film on the adsorption of hydrogen at $T = 293°K$. (Suhrmann, R., and Schulz, K., *Z. phys. Chem. N.F.*, 1 (1954) 69.)

bind electrons to the outer surface so that the work function is increased; the electrons decrease the resistance, as *Figures 12* and *13* show[4]. At 90°K, the dissociation products of the molecules remain on the surface, but at room temperature they penetrate into the film; the resistance decreases therefore not as rapidly now as at 90°K. But at 293°K, much more hydrogen is adsorbed and, on pumping off, part of it recombines to molecules which leave the surface. The resistance therefore, increases again.

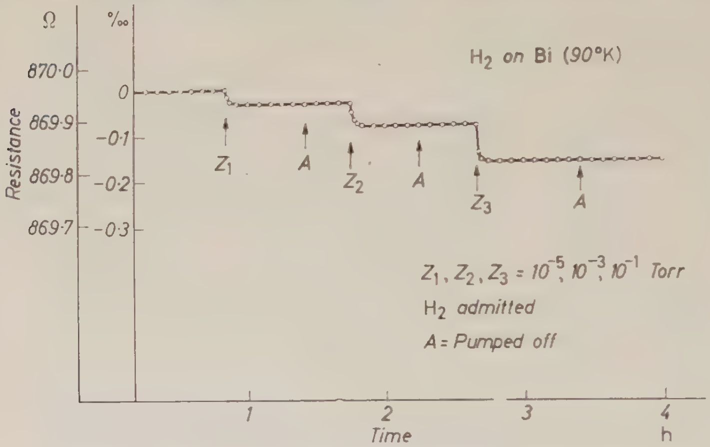

Figure 14. Resistance decrease of a transparent bismuth film on the adsorption of hydrogen at $T = 90°K$. (Keune, Dissertation, Braunschweig, 1956.)

The behaviour of hydrogen on a *bismuth* film is much simpler. Because of the low work function (0·65 volts less than that of a nickel surface) and of the electronic configuration of bismuth, adsorbed hydrogen molecules apparently do not dissociate into atoms, or protons, and electrons, as the resistance decreases only by 0·2 per mille at 90°K (*Figure 14*) and by 0·1 per mille at 293°K, because at 293°K the electron concentration is not as small as at 90°K. The hydrogen is most probably polarized, forming the preliminary stage of H_2^+ ions.

The results sketched in this paper show that the electron affinity of a metal surface is determined not only by its work function but also by its electronic configuration.

The author wishes to thank the 'Deutsche Forschungsgemeinschaft' and the 'Verband der Chemischen Industrie' for financial assistance which made these investigations possible.

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3.4

THE CHARGE TRANSFER IN PHYSICAL FILMS ON METALS

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SUMMARY

It is shown on semi-intuitive grounds that the double layer at the surface of a metal must be positive (positive charges outwards).

Physical films of non-polar particles on metals exhibit positive surface potentials. The experimental evidence is reviewed and the interpretation in terms of donor-acceptor interaction is discussed.

THE DOUBLE LAYER AT BARE METAL SURFACES

It is appropriate, before examining the effect of films on the work function, to try to get a good idea of the structure of the double layer at bare metal surfaces. This problem has been approached in a number of theoretical studies using a model in which the positive charge is uniformly distributed. It is generally accepted [1,2,3,4] that the double layer is negative (negative charges outside) and, for instance, Bardeen[2] has obtained values of −0·4 and −1·0 V in the case of sodium. The model has led to good results for many applications, and it was natural to use it in the treatment of the double layer.

It would seem, however, that the model is inadequate in this case. The reason is very simple. The double layer originates from a small lack of symmetry in the distribution of the charges. It is a differential effect which cannot be studied with too rough approximations. In real surfaces, the electron cloud projects further out than do the nuclei. This effect alone would result in a negative double layer as in the case of the model, but there is a contribution of opposite sign from the other side of the electron cloud. For instance, in the case of a solid composed of spherical atoms up to the surface the compensation is perfect and, accordingly, there is no double layer.

In the model, a step-shaped distribution of positive charge is arbitrarily assumed at the start. Then, applying more or less refined treatments, a corresponding distribution of negative charge is derived. The two densities must be equal except perhaps near the step and it is found, quite normally, that the angles are rounded off in the electronic distribution. No compensation is then possible and the negative sign is thus seen to result from an arbitrary feature of the model. Another approach is therefore desirable.

Let us start from a more rigorous treatment of simpler systems. Consider the density ψ^2 in the ground state of H_2^+, using the LCAO approximation at first†. It is seen that in comparison with the densities ψ_A^2 and ψ_B^2 in the free atoms, the density ψ^2 in the molecular orbital exhibits a displacement towards the centre of the molecule. A similar displacement is present in the hydrogen molecule where two electrons occupy the σ 1s orbital and, accordingly, the H_2 molecule must possess a quadrupole moment

$$+\,- \qquad -\,+$$

This conclusion is confirmed by more accurate calculations based on the James-Coolidge[5] wave functions and by experiment[6]. The displacement is in the opposite direction in the antibonding orbital σ^* 1s, but the latter is vacant in the ground state of H_2. Now, it is felt that the situation met in H_2^+ and in H_2 denotes a general tendency of the electron cloud to concentrate between nuclei, i.e. in regions of low electrostatic field.

In more complicated systems, there are additional ways for concentration, such as changes in occupation or in hybridization, and it is believed that the possibilities are actually used to some extent. These views directly lead to the conclusion that the electron cloud at the surface of metals and of some other solids must be shifted and that, accordingly, these surfaces are the seat of a positive double layer‡. Further, there must also occur a displacement from the hills to the valleys of the surface, resulting in a certain smoothing of the surface. Such effects may be expected on simple current views, considering that the electrons at the surface will rather desert the outer orbitals corresponding to the so-called free valencies and participate in bond formation between the surface atoms.

The above argument is admittedly too intuitive, but it is probable that theorists will give a more satisfactory justification. As will

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† *See*, for instance, figures 4·4 and 4·5 in Coulson's book, *Valence*.

‡ Clearly, the argument implies that the orbital quadrupole moment of all diatomic molecules A_2 should have the same sign. This conclusion may well have been reached previously by other authors. It would be interesting to know whether the suggestion is borne out by existing evidence.

appear below, there is also some experimental evidence in favour of a positive double layer.

Owing to its orientation, the double layer facilitates the exit of electrons. The double layer is responsible for a part in the difference between the ionization energy of the free atoms and the work function of the solid.

THE CHARGE TRANSFER IN PHYSICAL ADSORPTION

The measurement and interpretation of the surface potential (S.P.) of films has been the subject of a large number of studies. However, until recently, the physical films of non-polar particles has been much neglected. This is not due to a lack of interest in these films or to technical difficulties but, apparently, to a widespread belief that their S.P.'s must be negligible. Noteworthy, however, is the clear recognition by Frost[7] that polarization of the adsorbate by the double layer of the surface can give rise to a surface potential.

Table I. SURFACE POTENTIALS OF SOME PHYSICAL FILMS (V)

K Xe	(0)[a]	HgXe	+0·23	WXe	+1·1
CaXe	(0)[a]	HgO_2	+0·03[b]	(WO)Xe	+0·3[c]
TiXe	+0·84	$HgCH_4$	+0·16[b]	(WO)Xe	+0·12[d]
CrXe	+0·95	HgC_2H_6	+0·23	$(WO)O_2$	+0·08[c]
FeXe	+0·66	HgC_2H_4	+0·27	$(WO)O_2$	+0·035[d]
NiXe	+0·85	HgC_2H_2	+0·21	CuN_2	+0·45[b]
CuXe	+0·67	NiC_2H_6	+0·77	$CuCH_4$	+0·14[b]
ZnXe	+0·21	NiC_2H_4	+0·88	CuC_2H_6	+0·69
SeXe	+0·1	NiC_6H_6	+1·3	CuC_2H_4	+1·2

[a] Under saturated vapour pressure, but existence of film not ascertained.
[b] Incomplete films.
[c] On incomplete WO film having a S.P. of −1·3 V.
[d] On nearly complete WO film having a S.P. of −1·91 V.

The data are taken from references [9, 10, 11, 12]. Some values have been obtained in experiments of an exploratory character and may be somewhat inaccurate—say ± 10 per cent. The gas was admitted to the surface cooled at −190°C or −196°C.

When not otherwise specified, the values refer to approximately complete films.

In trying to understand the nature of the positive adsorption of hydrogen on nickel, the author was led to suspect[8] that the physical films of non-polar particles might possess notable S.P.'s, and the adsorption of xenon on a bare nickel surface was therefore investigated when the NiXe film was found to exhibit a S.P. as high as +0·85 V[9]. Since then, a large number of physical films, on bare as well as on covered surfaces, have been examined and each time a positive S.P. has been found[10,11,12]. Some typical results are given in *Table I.* In the case of WXe and HgXe, concordant results were obtained with the condenser method and with the thermionic method[11]. Recently, SUHRMANN[13], using the photoelectric method, has also found a notable positive effect for a film of xenon on a contaminated nickel surface. The effect is therefore real.

Inspection of *Table I* leads to some remarks*:

1. The S.P.'s are of the same order of magnitude as those of chemical films.

2. The S.P.'s are all positive. Films of molecular oxygen on bare Hg and on an incomplete WO film are no exception, in spite of the electronegative character of the adsorbate. We may consider with little risk of error that a film with a negative S.P. is necessarily chemical in nature. This criterion was first derived from a much narrower experimental basis[9].

3. Although W and Hg have nearly the same work function, the S.P.'s of WXe and HgXe differ by a factor of 5.

4. In column 1 are given the S.P.s of a series of xenon films on elements of the 4th period of the periodic chart. Although incomplete, the data give some indications as to the influence of the chemical nature of the solid. Noteworthy is the high flat maximum between Ti and Cu. The smaller differences in this range are real, as far as the writer can judge. Thus there seems to be an absolute maximum at Cr (or V) and a secondary one at Ni (or Co).

The positive effect has received three different interpretations in terms of induced polarization[9], charge transfer of the donor-acceptor type[10], and surface defects[13]. It seems that the latter explanation given by Suhrmann is inadequate and it is proposed here to deal only with the two former interpretations.

The interpretation of induced polarization given first[9] was based for simplicity on the model of a plane double layer, i.e. one in which the equipotential surfaces are planes. With such a double layer, the adatoms lie necessarily within the electron cloud of the surface, which is inacceptable. Alternately, the inducting double layer may be pictured as an array of parallel dipoles. The field then reaches beyond the electron cloud of the surface atoms and an adatom lying on the latter will be polarized. However, other difficulties arise because the sign of the field changes periodically along the surface. The sign of the S.P. therefore depends on whether the adatoms are situated on top or between the surface dipoles. The positive sign would require the adatoms to be on the top, assuming the double layer to be positive. Further, the surface potentials of polyatomic molecules should be small since, generally,

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* Positive effects due to a molecular adsorption of hydrogen have also been found. Values are not included in the table because the matter raises problems which fall outside the scope of this article.

there is no good fit with the surface. These features are not compatible with the experimental data. Thus polarization of the adatoms by the electric field of the double layer must be ruled out as the cause of the observed effect.

According to the second interpretation[10], the positive effect is due to an interaction of the donor acceptor type. A complex between a donor (*D*) and an acceptor (*A*) must generally possess an electric moment even though the constituents are non-polar. This has been established by FAIRBROTHER[14] in the case of $C_6H_6.I_2$. Transposing these ideas into the field of adsorption, one may anticipate that some non-polar molecules will form *DA* complexes with metal surfaces and give rise to surface potentials. SACHTLER[15] has recognized this possibility. His results on adsorbates possessing π electrons, particularly PtC_6H_6, confirm this view. The explanation also applies to the films NiC_2H_4 and NiC_2H_2 studied previously[9] and to NiC_6H_6.

It is tempting to generalize the explanation of *DA* interaction to all the films, but a difficulty arises immediately for it is then necessary to consider Xe, CH_4, C_2H_6, and even O_2 as donors, which is rather unusual. The objection is especially strong in the case of the HgO_2 film, for the O_2 molecule has an electro-affinity somewhat greater than 6 eV while mercury has a work function of about 4·5 eV. On the basis of electronegativity, the film should therefore be negative. In an attempt to avoid this difficulty which already arose, though less strikingly, in the case of the xenon films, the author suggested[10] that the overlap conditions are determining and pointed out that these are more favourable for the positive than for the negative ions.

The justification does not hold in the case of the O_2 molecule, however, since the same $\pi_g 2p$ is involved for the ions of both signs. It rather appears that the objection is not relevant. The electro-affinity was introduced from a consideration of chemical bonds. A similar quantity is needed in the field of *DA* interaction, but it cannot be taken for granted that the electro-affinity is suitable. The electro-affinity, defined as the mean of the ionization energy (I) and of the electron affinity (E), apparently places equal importance on I and E. In fact, however, E has little influence, since it is generally much smaller than I, frequently by a factor of 10 or more with molecules. In view of this feature, it is clear that the difference in electronegativities cannot be the controlling factor* in the *DA* interaction where the acceptor has at least as much importance as the donor.

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* Such a difference as $\left(\frac{\varphi}{I} - \frac{E}{\varphi}\right)$ would be more suitable. It leads to a correct sign.

It may be argued here that metals with work functions of the order of 4 eV are comparable with the most electronegative atoms as regards electronegativity and that, accordingly, these metals must be outstanding acceptors. On this view, HgXe, has a much lower S.P. than has WXe because the surface orbitals are less suited for overlap. This is going too far. The work function refers to inner orbitals and gives no sure indication as to the stability of the surface orbitals available for *DA* interaction.

It is well known that transition metals possess *d*-orbitals of low energy. They must be good acceptors and, therefore, give rise to high S.P.'s. This is precisely what is found experimentally. Further, it might be anticipated that in the films of the first column of *Table I*, a drop in S.P. should occur between NiXe and CuXe when the *d*-band is filled. Actually, a strong drop occurs, but between CuXe and ZnXe. In the author's opinion, this means that the *d*-orbitals at the copper surface are not completely filled. The difference in occupation between the surface and the interior is not surprising from the point of view of the first section. Indeed, the anomaly may be taken as an experimental indication of the positive sign of the double layer at a copper surface. On the whole, the data of *Table I* reveal a parallelism between the S.P.'s and the cohesion of the substrate—as measured, for instance, by the sublimation energy. For instance, among the xenon films, it is that on tungsten which has the greatest S.P. From an intuitive point of view, the parallelism is not unexpected, for the strength of the free valencies at the surface must be in proportion to the strength of the bonds within.

The positive double layer in physical films is, in a way, a continuation of the double layer at the surface of the bare metal. It cannot be said that the latter is the cause of the former. Rather, both are effects of the same tendency of the electron cloud to move towards regions of lower potentials according to the laws of quantum mechanics. The weakness of the hypothesis of induced polarization lies not so much in the description of the positive effect as a polarization than in the neglect of the forces other than electrostatic.

In conclusion of this discussion, it is considered that there is no serious obstacle* to the interpretation of the positive effect as a *DA* charge transfer and, further, the general character of the positive effect is taken as direct experimental proof of the general occurrence of *DA* interactions between adsorbates and substrates.

These views are in harmony with those which have emerged from a growing body of evidence in the field of molecular complexes,

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* Incidentally, the transfer of a small fraction of an electron—or of an electron pair on a small distance—is sufficient to account for the highest S.P.'s observed.

especially those of MULLIKEN[17]. In his general theory of the *DA* interaction, Mulliken stressed the general character of the charge-transfer forces which he states, 'may be of comparable importance to London's dispersion forces in accounting for van der Waals' attraction', and he pointed out that these, 'may also be important in adsorption'.

It is perhaps in S.P. studies that the *DA* interaction or, using Mulliken's terminology, the no-bond charge transfer is most apparent, but it has other important effects. For instance, the transfer forces bring a notable contribution to the heat of adsorption and thereby increase the stability of the molecular adsorptions.

I am very grateful to Professor L. D'Or for his continued interest and encouragement. I am much indebted to the 'Fonds National de la Recherche Scientifique' for a mandat d'associé and to the 'Union Minière du Haut Katanga' for financial assistance to our laboratory.

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3.5

CHEMISORPTION AND CATALYSIS ON METALS OF GROUP VIII

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SUMMARY

Recent research in heterogeneous catalysis has particularly emphasized the importance of the role played by the solid catalyst, and, for metals, certain electronic and geometrical requirements for efficient catalysis have been recognized. Chemisorption processes are inevitably involved in all surface reactions; thus, while weakly chemisorbed species react readily, strongly held entities act as catalyst poisons. In attempting to elucidate the mechanisms involved in hydrogenation, correlations have been sought between the reaction parameters E *and* A, *the strengths of adsorption of the reactants, and the physical properties of the metals employed as catalysts. Such correlations have sometimes been found and are helpful, but in other cases the position is much less clear.*

As an alternative to measuring rates of reaction, the redistribution between deuterium and hydrogen in hydrocarbon radicals during hydrogenation has been studied and has yielded information of relevance to chemisorption. Deuterated propanes arising from the reaction of cyclo*propane with deuterium and from the exchange between propane and deuterium over* Rh, Pd, Ir, *and Pt catalysts have been analysed in a mass-spectrometer; the resulting distributions are more characteristic of the metal than of the hydrocarbon, and can be interpreted in terms of two statistical redistributions of pools of hydrogen and deuterium atoms, in one of which the deuterium content is very high* (>95 *per cent*)*. The parameters of the distributions have been successfully correlated with the physical properties of the metals; the application of such studies to chemisorption problems is developed.*

CHEMISORPTION AND CATALYTIC ACTIVITY

Research in heterogeneous catalysis in the past decade has emphasized the importance of the role played by the solid catalyst. The catalytic efficiency of metals in hydrogenation-type reactions varies very widely, and the variations have been interpreted in terms of geometric and electronic factors; the greater relevance of the latter has now been recognized. Metals must possess vacant *d*-orbitals to enable the necessary chemisorption to take place, and if the *d*-orbitals are filled, as in the case of the Group IB metals, little catalytic activity results.

It is, however, doubtful whether the geometric factor is distinguishable from the electronic factor, since changes in electronic constitution are always accompanied by changes in geometric structure. Thus, for example, as the *d*-level is filled in passing along each of the Transition Series, the decrease in metallic radius reflects the increase in the percentage *d*-character of the metallic bonds (δ) and the decrease in the number of vacant *d*-orbitals[1]. It is also known that the work function of tungsten (a typical 'electronic' property) varies considerably from one crystal face to another, that is, as the geometric arrangement of the surface atoms is altered[2].

There is, furthermore, a marked difference between both the chemical and physical properties of the metals of the first Transition Series and those of the second and third. This results largely from the close similarity between the metallic radii in the second and third Series, which is due to the lanthanide contraction: the effect of electronic structure on crystal geometry is again apparent. A corresponding difference between their catalytic properties has also been found, and this underlines the connection between catalytic, chemical, and physical phenomena.

There is good evidence that the chemisorption of hydrogen and of hydrocarbons on metals of the Transition Series involves covalent bonding between the adsorbate and the vacant *d*-orbitals of the metals[3]. Hence strengths of adsorption of hydrogen and ethylene should, and do, increase with the number of such orbitals per atom, or decrease with increasing δ[4]. However, the hydrogen heats at zero surface coverage for metals in the second and third triads of Group VIII are all within error equal[5], thus indicating little dependence of initial heat of adsorption on δ in the range 44–50 per cent.

An inverse relationship between adsorption strength and catalytic activity is to be expected, and is indeed especially clear in the case of ethylene hydrogenation, where the heats of adsorption of both reactants show similar trends[4]; for example, log k increases roughly linearly with the quantity $(\Delta H_{ads}(H_2) - 25)^{-1}$. The linear relationship between log k and the product of the metallic valency and $\delta (V\delta)$ was pointed out by SCHUIT in 1950[6]; this implies some relationship between $V\delta$ and heats of adsorption. It is, however, worth noting that for most of the metals used by BEECK[4] the activation energy (E) was constant, and hence the Schuit plot is really one of log (frequency factor) versus $V\delta$. However, for tungsten and tantalum, the activation energies were much lower than for the other metals, and they would not be expected to fall on the line unless a precise compensation effect between E and the frequency factor (A) were operating. Extension of the linear relationship to metals other than those of Group VIII may therefore be misleading.

Other attempts to correlate activation energies or frequency factors for a given reaction with the physical properties of a variety of catalytic metals have met with less success[7,8]. This is probably because apparent activation energies bear little relation to true ones unless the heats of adsorption of both reactants are always the same, in which case they will differ by a fixed amount. It appears that correlations between physical properties of metals and reaction parameters are more likely to succeed for systems where E is constant and A varies, rather than the reverse: if, however, there is a compensation effect, a relationship between rates at a fixed temperature and physical properties might be expected to hold.

For example, the rates of the processes in the methane-deuterium exchange at 200°C have been calculated by TRAPNELL[9] from KEMBALL's[7] results, and there is a reasonably linear relationship between log R_a (CH_3D production) and δ for the Group VIII metals, and also between log R_b (multiple exchange) and δ, although in the latter case the activity of palladium is much lower than expected. Similar plots for the ethane-deuterium exchange reaction[8] show a linear increase of log R at 150°C with δ for the Group VIII metals, with the activity of palladium again low. The values of log R at 150°C for the other metals increase roughly linearly with $V\delta$, the slope of the line being about the same as for the Group VIII metals when similarly plotted.

The order of activity for propane-deuterium exchange on pumice-supported catalysts is

$$\mathrm{Rh} > \mathrm{Ir} > \mathrm{Pt} > \mathrm{Pd}$$

and the order is the same for the addition of hydrogen or deuterium to *cyclo*propane[10]; nickel is less active than palladium in this reaction[11]. In both these systems, the activation energies are constant at about 17 kcal and 9 kcal, respectively. The low activity of palladium in most of these reactions is probably attributable to the poisoning action of dissolved hydrogen or deuterium[12]: apart from this, there is a distinct tendency for increased activity to accompany an increase in the percentage *d*-character of the metallic bond. This tendency is observed in spite of the apparent lack of dependence of initial heats of hydrogen chemisorption on δ previously noted, and can only be due either to the dependence of the heat of chemisorption of the hydrocarbon on δ, or to dependence of heats of adsorption on δ at full surface coverage. There is little information available on either of these points.

THE APPLICATION OF ISOTOPIC-EXCHANGE STUDIES TO CHEMISORPTION PROBLEMS

In view of the uncertainties which are associated with the measurement and interpretation of absolute rates of surface reactions, it is desirable to look for other quantities which may be related to the catalytic efficiency of metals and hence to chemisorption activity and the physical properties of metals. The interaction of adsorbed hydrocarbon radicals with adsorbed deuterium results in hydrocarbon molecules which contain various numbers of deuterium atoms. The manner in which the deuterium is distributed under non-equilibrium conditions can throw light on the individual steps involved in the reaction. In a comprehensive investigation of the ethane-deuterium reaction, ANDERSON and KEMBALL[8] have found it necessary to suppose that two mechanisms are occurring; in mechanism A the adsorbed ethyl radicals are extensively exchanged before desorption, whereas in mechanism B the degree of exchange is much smaller. If the mean deuterium content of the products from mechanism A is δ_A, and if x_A is the fraction of the total exchange which proceeds through this mechanism, x_A shows a general tendency to increase with increasing δ, and a fairly smooth relation exists between δ_A and δ (*Figure 1*), although tungsten is anomalous in both cases. The value of δ_A measures the efficiency of the multiple-exchange process, and a method is therefore available for the 'internal' measurement of catalytic activity, that is, without reference to rates of reaction. For the metals of Group VIII, δ_A is proportional to log R at 150°C (*Figure 2*); the plot of δ_A versus the log of the relative rates of ethylene hydrogenation[4] is also linear, and chromium lies on the line (*Figure 3*), but tungsten is anomalous in both cases.

In the reaction between olefines and deuterium, saturated hydrocarbons containing more than two deuterium atoms are produced, and the yield of any species $C_nH_{2n+2-x}D_x$ decreases with increasing values of x. In many cases, the plot of log (yield of

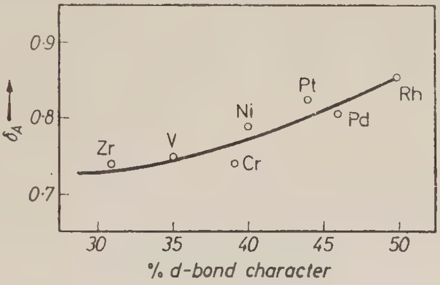


Figure 1. The dependence of δ_A for ethane exchange on the percentage *d*-bond character of metals (δ).

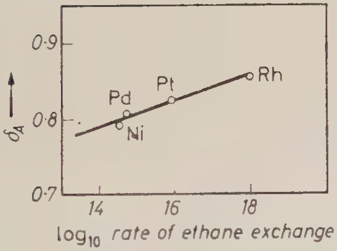


Figure 2. The dependence of δ_A for ethane exchange on the log of the rate of ethane exchange at 150°C for various metals.

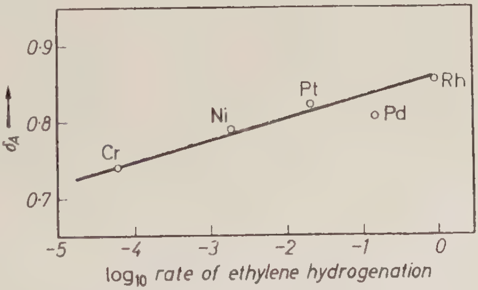


Figure 3. The dependence of δ_A for ethane exchange on the log of the relative rate of ethylene hydrogenation for various metals.

$C_nH_{2n+2-x}D_x$) versus x is linear[13], and the reciprocal of the slope of this line, σ, is defined by

$$\sigma = \frac{\text{yield of } C_nH_{2n+1-x}D_{x+1}}{\text{yield of } C_nH_{2n+2-x}D_x}$$

where x is greater than one (or in some cases greater than two) and less than $2n + 2$. High values of σ therefore imply efficient exchange between deuterium and the adsorbed hydrocarbon radicals which are intermediates in the addition process: a relationship may therefore be expected between σ and the average deuterium content of exchanged saturated hydrocarbons for various metals. The available results are shown in *Figure 4*, where σ is plotted against the average deuterium content of exchanged ethanes[8]. Values of σ are those derived from Kemball's[14] results on the ethylene-deuterium reaction over evaporated films of rhodium, nickel, and tungsten at −100°C, and the other values are from work with supported palladium at 50°C using propylene[15], with supported platinum at temperatures greater than 0°C[13], and supported nickel at −50°C[16]. Two smooth curves are obtained, the points for the supported metals lying a little above those for evaporated films; the difference may be due either to the different nature of the catalysts or to the different temperatures employed. Smooth relationships also exist between σ and percentage *d*-bond character. These observations may form the basis for another method for the internal measurement of catalytic activity.

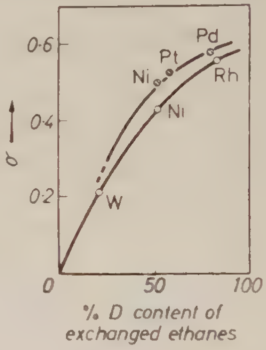


Figure 4. The dependence of σ for the ethylene (propylene)-deuterium reaction on the average deuterium content of exchanged ethanes. Open circles: evaporated films; hatched circles: supported metals.

THE INTERACTION OF ADSORBED C_3 RADICALS WITH DEUTERIUM

The results of a recent investigation may now be discussed with a view to finding out what further correlations are possible between metallic properties, chemisorption, and the parameters describing the distribution of deuterium in molecules which have undergone exchange at a catalyst surface. Pumice-supported rhodium, palladium, iridium, and platinum catalysts have been used; these are the four face-centred cubic metals with the highest values of δ, and for which, therefore, maximum catalytic activity was to be expected. The study of the behaviour of iridium was of particular interest, since no rate or exchange measurements appeared to have been made with this metal.

The reaction of *cyclo*propane and of propane with deuterium has been examined over each catalyst in turn through an extended temperature range; a large excess (generally about 60-fold) of deuterium was necessary to dilute the HD formed by the exchange processes, and so minimize its further reaction. The condensible products were analysed mass-spectrometrically; unreacted *cyclo*propane, into which small amounts of deuterium had sometimes been introduced by a subsidiary exchange process, was often removed by chemical separation before the analysis was performed. The formation of HD was almost always sufficient to cause a change in the shape of the propane distribution after a very few percent reaction; reactions were therefore restricted to less than about 20 per cent conversion wherever possible, and extrapolation procedures employed to obtain initial distributions.

Table I. OBSERVED AND CALCULATED PROPANE DISTRIBUTIONS FROM THE REACTION OF *CYCLO*PROPANE WITH DEUTERIUM OVER Pd AT 125°C

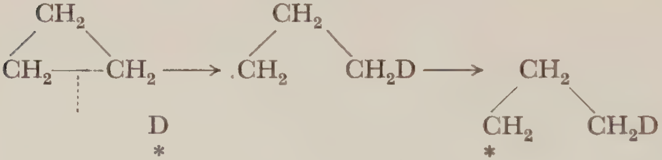
	Propane composition in percentages							
	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
observed	0·6	4·1	3·0	4·0	2·9	3·6	17·1	64·7
calculated	0·4	4·2	3·1	3·8	3·2	3·4	17·2	64·7

The observed initial distributions could generally be described in terms of two random distributions (A and B) of pools of hydrogen and deuterium atoms whose deuterium contents were respectively δ_A and δ_B. With *cyclo*propane, some direct addition also occurred, and with propane a third random distribution of very low deuterium content was usually required to describe the results. ΣA (or B) is the fraction which distribution A (or B) is of the whole. Hereafter it will generally be sufficient simply to record some values of the parameters, since the observed distributions can be closely reproduced with their aid (*see Table I*).

A detailed study was first made of the interaction of *cyclo*propane with deuterium on the palladium catalyst, to see whether the same duality of behaviour existed as was previously observed with platinum[17]. It was found that the observed distributions were essentially independent of temperature and of partial pressure variation; a typical initial distribution is given in *Table I*, together with a distribution calculated from the following parameters: ΣA, 0·835; δ_A, 0·968; ΣB, 0·138; δ_B, 0·50; and 2·7 per cent direct addition. Over 80 per cent of the propanes are almost completely deuterated.

Experiments on the exchange reaction between propane and deuterium over palladium were then performed, and the initial distributions were similar in respect of their values of δ_A and δ_B, but differed from the results for *cyclo*propane in that ΣA and ΣB were temperature dependent. *Figure 5* shows the dependence of $\Sigma A/(\Sigma A + \Sigma B)$ on temperature for both reactants.

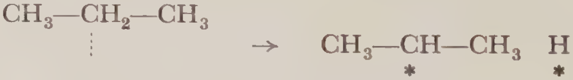
It is believed[17] that the reaction between *cyclo*propane and deuterium is initiated as follows:



(1a)

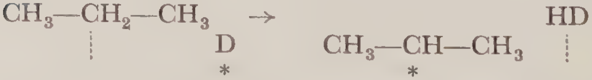
$$\xrightarrow{+\mathrm{D}} \mathrm{C_3H_6D_2} \qquad (1b)$$

Mechanism (1b) is termed a direct-addition process. Propane probably adsorbs either as



$$\mathrm{CH_3{-}\underset{\vdots}{CH_2}{-}CH_3} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}CH_3}\quad \underset{*}{\mathrm{H}} \qquad (2)$$

or as



$$\mathrm{CH_3{-}\underset{\vdots}{CH_2}{-}CH_3}\quad \underset{*}{\mathrm{D}} \rightarrow \mathrm{CH_3{-}\underset{*}{CH}{-}CH_3}\quad \overset{\mathrm{HD}}{\vdots} \qquad (3)$$

Now the temperature dependence of $\Sigma A/(\Sigma A + \Sigma B)$ for propane implies that E_A is not equal to E_B for this molecule, and following the suggestion[8] that mechanisms A and B proceed on different crystal faces, it seems likely that the activation energies will be different for different crystal faces only if the slow step has a geometric requirement, and will be equal if there is no such requirement. Mechanism (1) is therefore the probable slow step in the *cyclo*propane system, and the two-site mechanism (2) in the propane system.

Since both *cyclo*propane and propane yield deuterated propanes distributed so that at least δ_A and δ_B are the same in each case, the normal- and *iso*-propyl radicals assumed to be formed in the respective initiating steps must be indistinguishable and hence freely interconvertible. It is therefore highly likely that adsorbed

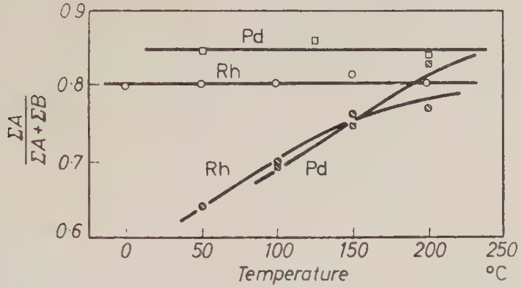
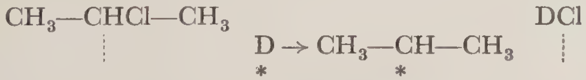


Figure 5. The dependence of $\Sigma A/(\Sigma A + \Sigma B)$ on temperature for the reaction of *cyclo*propane and of propane with deuterium over palladium and rhodium catalysts. Squares: Pd; circles: Rh; open points: *cyclo*propane; hatched points: propane.

propylene is the intermediate, and that multiple exchange proceeds through the equilibrium

$$\text{adsorbed } iso\text{-propyl} \rightleftharpoons \text{adsorbed propylene} + \text{H,D} \rightleftharpoons \text{adsorbed } n\text{-propyl}$$

a deuterium atom being gained almost every time a radical is formed from the olefine. To confirm this hypothesis, *n*- and *iso*-propyl chlorides were reduced with deuterium over the palladium catalyst at 100°C: these substances must necessarily afford *n*- and *iso*-propyl radicals on adsorption. The propane distributions were very similar and much like those obtained with *cyclo*propane: the high values of $\Sigma A/(\Sigma A + \Sigma B)$ suggest the absence of any geometric requirement in the slow step which is hence presumably, for example,


$$\underset{\vdots}{CH_3\text{—}CHCl\text{—}CH_3}\qquad \underset{*}{D} \rightarrow CH_3\text{—}\underset{*}{CH}\text{—}CH_3\ \ \underset{\vdots}{DCl} \qquad (4)$$

Results very similar to those for palladium were obtained in experiments performed with *cyclo*propane and propane over the rhodium catalyst: values of δ_A were, however, slightly higher, and the quantity $\Sigma A/(\Sigma A + \Sigma B)$ for propane was again temperature dependent (*see also Figure 5*). Similar experiments with the iridium catalyst showed that this quantity was the same for both reactants, and decreased slowly with increasing temperature (*Figure 6*); the average value of δ_A was 0·979, independent of temperature.

Some further experiments were carried out over a platinum catalyst to supplement the previous work on *cyclo*propane[17]. The values of $\Sigma A/(\Sigma A + \Sigma B)$ both for this reactant and for propane are shown in *Figure 6*, together with those derived from the earlier work. The essential identity of the distributions given by both reactants now invalidates the mechanism formerly proposed to account for multiple exchange. It has also been established that δ_A is temperature dependent over this metal, rising from about 0·90 at 0°C to 0·955 at 250°C: this latter value is taken to be the one characteristic of the metal.

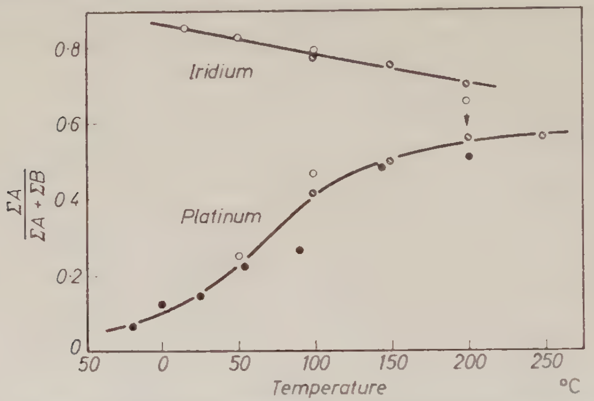


Figure 6. The dependence of $\Sigma A/(\Sigma A + \Sigma B)$ on temperature for platinum and iridium and for both reactants. Open circles: *cyclo*propane; hatched circles: propane; full circles: *cyclo*propane, reference 17.

A comparison of the behaviour of the four metals is instructive. Over rhodium, palladium, and iridium, 77–85 per cent of the propanes formed from *cyclo*propane have been exchanged to the extent of about 97–98 per cent; these figures should be increased by about 0·8 per cent to allow for the original hydrogen content of the deuterium. Over platinum at 250°C, about 56 per cent of the exchanged propanes contain about 95 per cent deuterium. The values of δ_A for C_3 radicals fall with decreasing δ or increasing metallic radius, except that the value for iridium is slightly greater than that for rhodium (*Table II*); assuming a relationship between δ_A and activity (*Figures 2* and *3*), the high activity of iridium already noted receives confirmation.

The C_3 system behaves quite analogously to the ethane system[8] (although δ_A values are much higher), notwithstanding the difference in the types of catalyst used. It is interesting to note that anomalous behaviour with platinum has been found both by Anderson and Kemball and by ourselves; their value of x_A in ethane exchange is 0·46 independent of temperature, whereas our value is 0·56 at 250°C, and both of these values are much lower than the corresponding ones for rhodium, palladium, and iridium. The temperature dependences of δ_A and ΣA over platinum and of ΣA over iridium imply a geometric requirement in the slow step; the only explanation which suggests itself is that desorption rather than adsorption steps are rate-controlling for these metals. These results in general demonstrate an unexpected closer similarity of behaviour between horizontal pairs than between vertical pairs of metals.

Table II. VALUES OF δ_A, PERCENTAGE *d*-BOND CHARACTER AND METALLIC RADIUS FOR SOME METALS OF GROUP VIII

Metal	δ_a	*Percentage d-bond character*	*Metallic radius*
rhodium	0·975	50	1·34
iridium	0·979	49	1·36
palladium	0·968	46	1·37
platinum	0·954	44	1·39

CONCLUSION

This work demonstrates that exchange processes between propyl radicals and deuterium proceed efficiently on the surface of rhodium, palladium, iridium, and platinum, and that the high degree of exchange is related to their high catalytic activity. Significant differences are shown to exist between metals whose initial heats of hydrogen chemisorption are within error equal. From a careful analysis of the results, deductions can be made concerning probable mechanisms of adsorption. The part played by surface geometry and the associated electronic factor in determining the catalytic efficiency of different crystal faces is, however, far from clear: it appears that different faces of nickel have different activities in ethane exchange[8], but the relation of this finding to BEECK's work[4] on activities in ethylene hydrogenation is puzzling, and remains to be explained. One of the most urgent needs in catalysis and chemisorption studies is the measurement of further activities and heats of adsorption on oriented films or, better, on specific faces of single crystals: only in this way will the influence of surface geometry be unequivocally established. Our knowledge of the detailed relations between reactants and catalyst on a molecular scale remains meagre, although an instructive approach has been made by WINFIELD[18].

A fuller account of this work will be submitted for publication in due course.

We are grateful to the University of Leeds for awarding us, respectively, an I.C.I. Research Fellowship (during part of the work) and a University grant.

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3.6

THE PARAHYDROGEN CONVERSION ON COPPER, SILVER, AND GOLD

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SUMMARY

The parahydrogen conversion has been investigated for the metals copper, silver, and gold in the form of wires, evaporated films, and foils. A detailed investigation of the effect of pressure on the reaction velocity was carried out on a copper film, at a series of temperatures. The results support the view that the reaction is unimolecular, and involves the chemisorption of hydrogen on copper with a heat of 8 *kcal/mole. The true activation energy of the conversion,* 13 *kcal/mole, is equated to the activation energy for desorption, a Bonhoeffer-Farkas mechanism probably being operative. The entropies of adsorption and of activation are* —26 *E.U. and* —29 *E.U., respectively, and these values are discussed. The apparent activation energies E are* 5·5 *to* 6 *kcal/mole for* Au, 7·2 *to* 8·6 *for* Ag, *and* 6·7 *to* 10·7 *for* Cu, *irrespective of the form of the catalyst, and the apparent frequency factors B^0 lie in the order foil $<$ film $<$ wire. For a given type of specimen, e.g. wires, there is a linear relation between log B^0 and E including the data on all three metals. This is interpreted as a relation of energy and entropy type, involving adsorption or activation of the hydrogen molecule on the surface, or both.*

INTRODUCTION

It is well known that copper shows a negligible chemisorption of hydrogen at room temperature. This has been found for reduced oxide powders[1], and for evaporated films of metal[2,3]. A similar conclusion was reached for evaporated films of silver and gold[3]. Reduced oxide powders[4,5] of copper actually show an activated adsorption, which only becomes appreciable at temperatures above 300°C[5]. A particularly sensitive test for chemisorption is given by the parahydrogen conversion or hydrogen-deuterium exchange reactions. Copper[6,7] and silver powders[8], copper foils[9], and gold wires and foils[10] are known to show a slight activity for the conversion, and experiments with alloys of these metals with transition metals[9,10] led Couper and Eley[10] to the conclusion that Group 1B metals were poor catalysts because they did not possess holes in the *d*-band. Mikovsky, Boudart, and Taylor[11] found the following activation energies for the hydrogen-deuterium reaction on foils, 23·1 kcal/mole for Cu, 16·5 for Ag, and 13·9 for Au. The activation energies for the conversion reaction are 12·4 and approximately 11 for Cu[9,12] and 17·5 for Au[10], and the differences between these values and those for the hydrogen-deuterium reaction suggest the need for a further study. Couper and Eley[10] have noted how the activation energy for the conversion on Au foil varied with temperature, and we may derive the following figures from Couper's thesis[13], —1·8 kcal at —183°C, 0 at —130°C, 5·2 over 50–230°C, becoming constant at 17·5 kcal above 300°C. Such behaviour was first observed by Bonhoeffer, Farkas, and Rummel[7] for carbon, copper, and other powders, and attributed to the change-over from a paramagnetic to what is conveniently called a chemical mechanism. There is always the possibility of more than one chemical mechanism operative at high temperatures[10]. In this work we have in the first place measured apparent activation energies E for the metals as foils, wires, and films, paying due attention to effects of temperature and pressure on the value of E. In the second place in one favourable instance we have been able to arrive at values of the true activation energy E_t for the catalytic reaction, together with the heat of adsorption of the molecules on the catalyst.

The two chemical mechanisms usually considered for the parahydrogen conversion are

$$pH_2 + 2M \rightarrow 2MH \rightarrow 2M + oH_2 \qquad \text{(I)}$$

and

$$pH_2 + HM \rightarrow MH_3 \rightarrow MH + oH_2 \qquad \text{(II)}$$

Couper and Eley[10], while supporting the exchange mechanism (II) for palladium, with its virtually complete chemisorbed MH layer, favoured the dissociative mechanism[14] (I) for Au, passing over to a mechanism involving the desorption of H atoms (III) at temperatures around 800°K.

$$AuH \rightarrow Au + H, \qquad H + pH_2 \rightarrow oH_2 + H \qquad \text{(III)}$$

The activation energy will be expected to be about 50 kcal/mole for reaction (III) which involves rupture of an Au—H bond (cf. Bryce[15]). On the other hand, Mikovsky and co-workers took the view that mechanism (II) was likely for the Group 1B metals, while the Bonhoeffer-Farkas mechanism (I) was likely for the transition metals.

EXPERIMENTAL METHOD

The apparatus was the same as that used in earlier work[10,16]. A cylindrical reaction vessel of 160 c.c. volume contained the catalyst or evaporation wire, sealed down its axis. It was connected to the usual vacuum line, storage vessels, etc., via a liquid air trap and mercury cut-off. Analyses were made with a micro-Pirani gauge. The reaction vessel was first baked for 48 hours at 450–500°C. The catalyst wires, length 12 cm, 42 SWG, were cleaned by an electrodeless discharge in 1 mm hydrogen[10]. In a typical experiment the walls of the vessel were kept at room temperature T_V, and the wire heated electrically and its temperature T determined from its resistance. In forming an evaporated film on the walls of the vessel, a 50 cm length of the wire concerned was wrapped around an axial tungsten wire of 0·15 mm diameter which was heated electrically. Such films were only used as catalysts for a period of 48 hours to avoid contamination, and the whole vessel was heated by an electric furnace, controlled by an electronic thermoregulator[17]. The catalyst foils, 10 cm square, were chemically cleaned, rolled into cylinders for insertion in the vessel, and reduced in hydrogen at 450–500°C before use as catalysts.

The wires and foils were supplied by Johnson and Matthey Ltd. with stated purities, Cu and Ag $>$ 99·999 per cent and Au $>$ 99·99 per cent. The Cu and Au wires were checked for spectrographic purity in our own laboratory.

RESULTS

Apparent Activation Energies

If $C_o(C_t)$ denotes the concentration of parahydrogen in excess of its equilibrium value at time zero (t), it was found as usual that the conversion at constant pressure obeyed the first order law with a constant k_e,

$$k_e = \frac{1}{t} \ln \frac{C_o}{C_t}, \text{ min.}^{-1} \qquad (1)$$

The effect of temperature on k_e at $p = 1{\cdot}2$ mm follows the Arrhenius equation

$$k_e = B\, e^{-E/RT} \qquad (2)$$

examples being shown in *Figures 1* (wires), *2* (films), and *3* (foils).

Here E is the *apparent* activation energy and B the *apparent* frequency factor. The silver and gold films were only *partly* sintered as a result of laying them down on the reaction walls at 20°C. This is brought out by an irreversible decrease in activity on heating these two films to a sufficiently high temperature, the effect being shown by the dotted lines in *Figure 2*. The copper films may have been

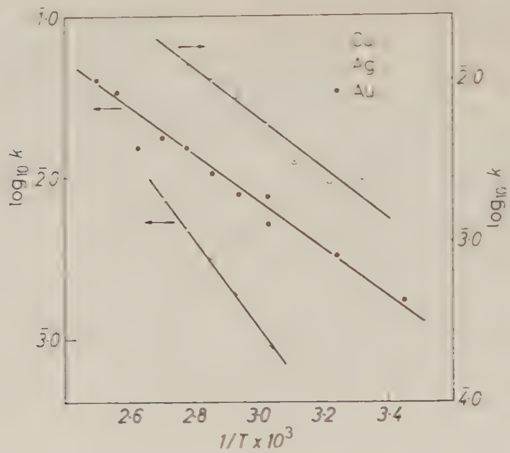

Figure 1. Arrhenius plots for wires.

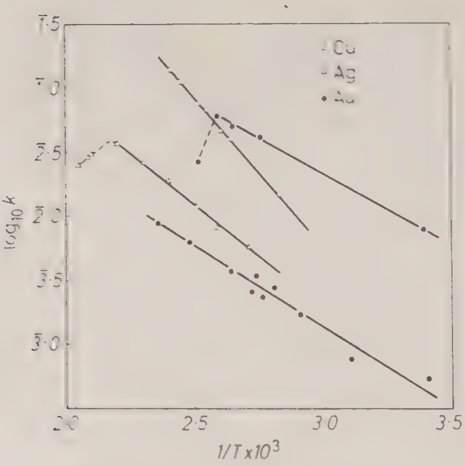

Figure 2. Arrhenius plots for films.

completely sintered in the lay-down process, as suggested by ALLEN and MITCHELL[2].

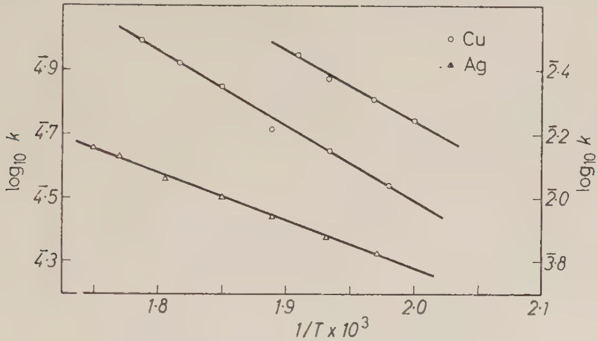

Figure 3. Arrhenius plots for foils.

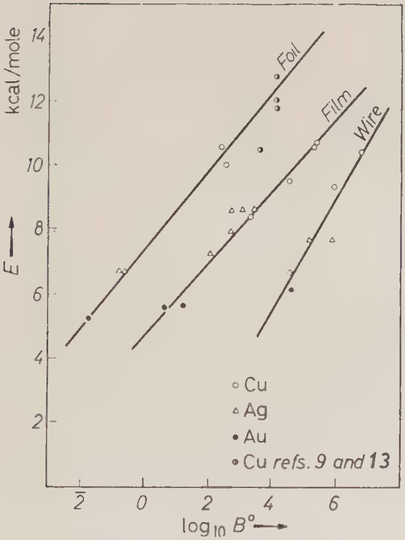

Figure 4. The logarithmic relation between apparent activation energy E and apparent frequency factor B^0 for foils, wires, and films.

The apparent frequency factor corrected for volume and catalyst area B^0, in cm min^{-1} is calculated by

$$B^0 = \frac{BV}{A}$$

Complete results for E and B^0 are given in *Table I*, and are represented in *Figure 4*.

Table I. APPARENT ACTIVATION ENERGIES AND APPARENT FREQUENCY FACTORS, AT $p = 1{\cdot}2$ mm Hg

Catalyst		*Activation energy* kcal/mole	*Temp. range* °C	$\log_{10} B_0$
Cu	Wire	10·4	20–80	6·7
	Wire	9·3	20–80	5·9
	Wire	6·7	0–80	4·55
	Foil	10·0	100–300	2·49
		10·6	100–300	2·37
	Film *A*	10·6	80–150	5·25
		9·5	80–150	4·49
	Film *B*	8·5*	100–180	3.40
	Film *C*	10·7	80–140	5·36
Ag	Wire	7·7	40–100	5·2
	Wire	7·7	40–80	5·9
	Foil	6·74	190–300	$\bar{1}{\cdot}25$
	Film *A*	7·2	120–180	2·04
	Film *C*	8·65	90–170	3·48
	Film *D*	8·6	100–165	3·01
		7·95	100–165	2·71
		8·6	205–260	2·77
Au	Wire	6·06	10–130	4·6
	Foil	5·2†	50–230	$\bar{2}{\cdot}26$
	Film *A*	5·6	0–170	1·24
	Film *B*	5·56	40–280	0·62

* Calculated from pressure-dependency results at 1·2 mm (*Figure 5*).
† Calculated from unpublished results by COUPER[13].

The True Activation Energy for Copper Film B

If we assume the reaction in the adsorbed layer is first order in H_2 molecules (and this includes the case of recombination of 2H atoms in a chemisorbed layer, or the reaction between an H_2 molecule in a van der Waal's layer and a *saturated* film of chemisorbed atoms), then the experimental first-order constant is[10,18]

$$k_e = \frac{AfkT_V}{V}(k_0 + k_p)\frac{\sigma}{p} \tag{3}$$

Here A is the catalyst area (cm^2), f the number of sites/cm^2, T_V the temperature of the vessel of volume V, p the hydrogen pressure, and σ the fractional coverage in the adsorbed layer. $k_p(k_0)$ is the unimolecular constant for the change para → ortho (ortho → para). Results so far obtained suggest σ may be approximated by the Langmuir isotherm[10,19,20]

$$\sigma = bp/(1 + bp)$$

so

$$1/k_e = \frac{V}{AfkT_V(k_0 + k_p)}\left(\frac{1}{b} + p\right) \tag{4}$$

Earlier work showed this relation to hold for W, Pd–Au, and Pt wires, and here it was found to hold for an Ag foil and a Cu film. In the case of the Cu film *B*, a series of isotherms have been obtained at different temperatures, as shown in *Figure 5*. These isotherms have been used to calculate values of $(k_0 + k_p)$, given in *Figure 6a* in min^{-1}, and b, given in *Figure 6b* in mm Hg^{-1}, at a series of six temperatures.

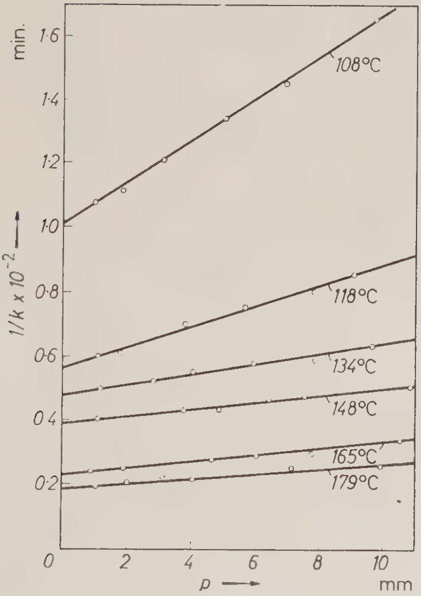

Figure 5. Reaction velocity isotherms for an evaporated copper film.

Considering first *Figure 6a*, for the four points below 148°C we have an approximately linear plot, as expected for the Arrhenius equation, which may be expressed as

$$\frac{(k_0 + k_p)}{60}, \sec^{-1} = B_t\, e^{-E_t/RT} = \frac{ekT}{h}\, e^{\Delta S^{\ddagger}/R}\, e^{-E_t/RT} \qquad (5)$$

The derived quantities are $E_t = 13$ kcal/mole and $B_t = 5{\cdot}6 \times 10^6$ sec^{-1}, and lead to a value for the entropy of activation of the molecule in the adsorbed layer, per mole, of $\Delta S^{\ddagger} = -29$ E.U.

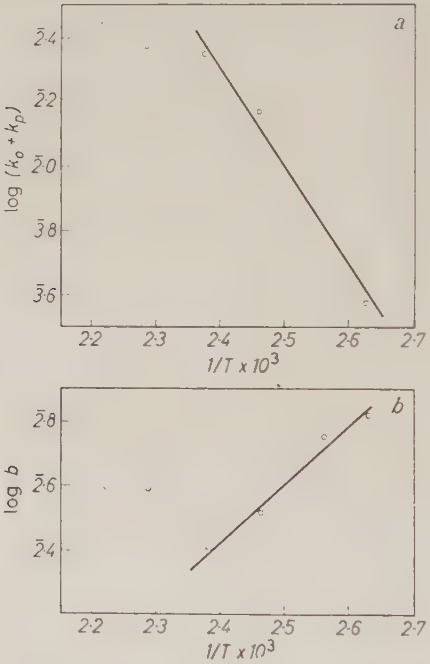

Figure 6. *a*. The true activation-energy plot for an evaporated copper film.

b. The plot to give the heat of adsorption of H_2 molecules on an evaporated copper film.

As is well known, Langmuir expressed *b* as the ratio of condensation rate : evaporation rate and showed how its temperature coefficient was determined by the heat of adsorption. It was later expressed by Fowler in terms of the statistical treatment of a localized monolayer[21], but for the present purpose a thermodynamic presentation[22] is preferable. If we take as standard states the gas of $p = 1$ mm Hg, and a surface coverage of $\sigma = 0{\cdot}5$ in the monolayer, the functions[22] are

$$\Delta G^{\circ}_{\text{ads}} = -RT \ln b, \qquad \Delta H^{\circ}_{\text{ads}} = RT^2 \frac{d \ln b}{dT} \tag{6}$$

$$\Delta S^{\circ}_{\text{ads}} = \{\Delta H^{\circ}_{\text{ads}} - \Delta G^{\circ}_{\text{ads}}\}/T$$

We derive

$$\Delta H^{\circ}_{\text{ads}} = -8{\cdot}0 \text{ kcal/mole}, \qquad \Delta S^{\circ}_{\text{ads}} = -26 \text{ E.U.}$$

DISCUSSION

Mechanism of the Conversion

It is possible to reach certain conclusions for copper film B. The heat of adsorption of 8·0 kcal/mole agrees with figures of 9 measured for a powder[4] and 14 calculated for the surface process I of dissociative adsorption[23].

$$\text{H}_2 + 2\text{Cu} \rightleftharpoons 2\text{Cu} - \text{H}$$

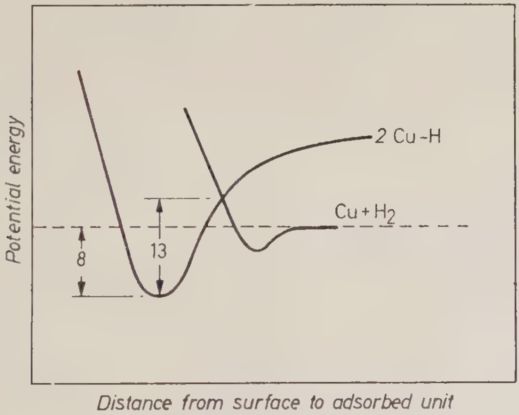

Figure 7. Lennard-Jones curves for the copper-hydrogen system.

Since the surface coverage is small, the parahydrogen conversion rate may be put equal to the rate of adsorption (or desorption) of hydrogen molecules, so that the true activation energy of $E_t = 13$ kcal/mole must be the true activation energy for desorption. It is a matter of interest that E_t is close to the value for activated adsorption on a powder, 14·1, attributed by WARD[4] to a surface-diffusion process. The assignment of values is shown in the Lennard-Jones diagram, *Figure 7*.

The apparent activation energy of the conversion may be derived from equation (3) (through equation (8), *see* later), to be (for $\sigma \ll 1$)

$$E = 2RT + E_t + \Delta H^\circ_{\text{ads}} = 6{\cdot}7 \text{ kcal}$$

This applies over 100°–148°C, and the discrepancy with the value of 8·5 kcal in *Table I* resides in the fact that the latter is derived from the best line fitting points over 100°–180°C.

The only previous entropy calculation for the pH_2 conversion is an estimate of $\Delta S^{\ddagger} = -21$ E.U. for tungsten[16]. This value was based on a questionable extrapolation of B^0 to a saturated film. The present data for copper film B allow us to make a complete analysis for this particular system. Thus we may compare the observed $\Delta S^\circ_{\text{ads}}$ of -26 E.U. with values calculated by TRAPNELL[24] for a film of H_2 on W. These values are $-17{\cdot}6$ E.U. for a mobile and $-26{\cdot}5$ E.U. for an immobile film, for standard states of 1 atmosphere pressure and $\sigma = 0{\cdot}8$. To correct to our standard state we subtract a further $R \ln 760$, i.e. 13·2 E.U., giving $-30{\cdot}8$ E.U. and $-39{\cdot}7$ E.U., and neglect the small difference due to correcting σ to 0·5. We may further calculate that the entropy of an H atom film possessing two-dimensional mobility at $\sigma = 0{\cdot}5$ is 10·5 E.U. per gram atom of adsorbed atoms leading to an entropy of dissociative adsorption per mole of H_2 molecules of $-23{\cdot}5$ E.U. We are thus led to conclude that the molecules in the film are mobile, and since the film is actually an atomic film the atoms are mobile. This result would have been expected since surface diffusion will presumably occur more rapidly than desorption, and therefore more rapidly than the parahydrogen conversion observed.

The observed $\Delta S^{\ddagger} = -29$ E.U. for the unimolecular reaction in the adsorbed layer is a much larger negative value than is ever observed in gas reactions. If two atoms, mobile in the two-dimensional film, are localized in the transition state, the above figures suggest $\Delta S^{\ddagger} = -21$ E.U. The difference of -8 E.U. is too small to merit detailed discussion, but might arise from a removal of entropy from neighbouring Cu atoms in the surface. Alternatively, we might argue that only a fraction of sites $e^{-8/1{\cdot}98}$ are active in the conversion.

A type (II) mechanism may also give rise to large negative $\Delta S^{\ddagger}$ values, especially if both a mobile H_2 molecule and a mobile H atom are brought together in an immobile activated complex, as would be expected to be the case for a Group 1B metal. However, it appears that mechanism (II) must be definitely ruled out for copper film B, since it would require a molecularity of 1·5, whereas the pressure dependency of *Figure 5* points clearly to a molecularity of 1·0. For this reason we cannot accept the view of MIKOVSKY, BOUDART, and

TAYLOR[11] that mechanism (II) applies to the Group 1B metals.

THE LOG $B^0 - E$ RELATION

The results in *Table I* and *Figure 4* show:

1. The apparent activation energy for a given metal is the same roughly for foil, wire, and film, namely 5·6 kcal/mole for Au, 7·9 kcal/mole for Ag, and 9·6 kcal/mole for Cu. This order, Au < Ag < Cu was also found by MIKOVSKY, BOUDART, and TAYLOR[11] for the HD reaction, but their activation energies were twice those given here and only a part of this difference can be ascribable to an isotope effect. Since there is reason to believe the activation energies increase with temperature, the main difference may be due to the higher temperature range used by Mikovsky, Boudart, and Taylor.

2. For a given metal, the apparent frequency factor B^0 increases in the order foil < film < wire.

3. The results for all three metals lie close to a single straight line for a given form of catalyst, viz.

$$\begin{aligned} \text{wires } E(\text{kcal}) &= 1{\cdot}8 \log_{10} B^0 - 1{\cdot}25 \\ \text{films } E &= 1{\cdot}1 \log_{10} B^0 + 5{\cdot}0 \\ \text{foils } E &= 1{\cdot}2 \log_{10} B^0 + 7{\cdot}5 \end{aligned}$$

Result 3 may be compared with the relation for a series of clean tungsten wires found earlier[19]

$$E = 0{\cdot}6 \log_{10} B^0 - 1$$

A 'normal' B^0 value for hydrogen molecules colliding to give an 'immobile' activated complex is about 10^5 cm min^{-1},[19] the exact value varying somewhat with temperature.

TRUE AND GEOMETRIC AREAS

It is unlikely that the B^0 factors are in error due to an omission of a roughness factor (true area : geometric area), since it is known that this factor is usually not far from unity for wires, which have here been aged above the sintering temperature. Considering the other catalysts, there is a good deal of evidence that films of Cu, Ag, and Au deposited on glass at room temperature have a roughness factor near to unity[2,25,26], and we may certainly expect a factor of unity for the foils.

THEORETICAL ASPECTS

O. W. RICHARDSON found a relationship of this type to hold for thermionic emission, the effective emission constant changing with apparent work function in this way, when a surface was progressively covered with adsorbed gas[27]. Richardson's result has been discussed by De Boer[28] and Herring and Nichols[29], who show it will arise even for a uniform surface wherever the true activation energy depends on the temperature. The pioneer investigations of Constable[30], further developed by Schwab[31], showed that a log $B^0 - E$ relation can arise for a given catalyst heated to various temperatures in the course of preparation, if the effect of heating is to change the distribution function for 'active spots' on a non-uniform surface. Other discussions are due to Storch[32] and Couper and Eley[19], the latter authors supporting the view that the relation is essentially one between energy and entropy of activation of the substrate on a predominantly uniform surface, a view which gains support from the similar cases available in homogeneous kinetics and equilibria. Cremer[33], in a recent review of the subject, introduces a new suggestion that the log $B^0 - E$ relation may arise in certain cases from electron tunnelling from substrate to catalyst. Sosnovsky[34] found a log $B^0 - E$ relation for formic acid decomposition on various crystal faces of Ag single crystals. The relative frequency of crystal planes is an uncontrolled variable in the present work, which may help to give rise to the relationships of *Figure 4*. A log $B^0 - E$ relation also holds for the formic acid decomposition on a range of alloys of varying electron concentration[35], and also for the deuterium-methane exchange on five transition metals where it was attributed to the effect of an energy-entropy relation for the adsorption of an inhibiting gas[36]. We shall now discuss the three main theories in detail.

The Effect of a Temperature-Variable Activation Energy. If, in fact, the true activation energy and frequency factors are functions of temperature, so that

$$k_e = B^0(T)\, e^{-E(T)/RT}$$

then the apparent values are

$$\ln B^0 = \ln B^0(T) + \left(\frac{T \mathrm{d} \ln B^0(T)}{\mathrm{d}T} - \frac{1}{R}\frac{\mathrm{d}E(T)}{\mathrm{d}T}\right)$$

$$E = E(T) + RT\left(\frac{T \mathrm{d} \ln B^0(T)}{\mathrm{d}T} - \frac{1}{R}\frac{\mathrm{d}E(T)}{\mathrm{d}T}\right)$$

and

$$E = 2{\cdot}303\, RT \log_{10} B^0 + \{E(T) - 2{\cdot}303\, RT \log_{10} B(T)\} \quad (7)$$

If the term in braces may be assumed to be constant, then a straight line results for E vs. log B^0, the slope of which should be $2{\cdot}303\, RT$, which gives the following values to compare with the observed slopes in brackets. T is taken as the average temperature for the series.

Wires $T \sim 358°\text{K}$ $\quad 2{\cdot}303\ RT = 1{\cdot}64$ kcal (1·8)
Films $423°\text{K}$ $\quad 2{\cdot}303\ RT = 1{\cdot}94$ kcal (1·1)
Foils $473°\text{K}$ $\quad 2{\cdot}303\ RT = 2{\cdot}16$ kcal (1·2)
W wires[19] $142°\text{K}$ $\quad 2{\cdot}303\ RT = 0{\cdot}65$ kcal (0·6)

While it seems reasonable to assume the term in brackets is constant for a single metal, and thus to explain say the earlier results for W wires, it merely shifts the problem one stage further back in the present instance where the relation holds for three metals.

The Distribution of Sites Theory. The Constable-Schwab theory (*see also*, LAIDLER[37]) essentially considers a distribution of lattice spacings around a most favourable value, with the breadth of the distribution $h = 1/R\theta$ where θ is the temperature at which the catalyst is prepared. This leads to

$$E = 2{\cdot}303\ R\theta \log_{10} B^0 + \text{const.}$$

and to fit the above results we require θ values of 393°K (wires), 240°K (films), and 262°K (foils), which are not related to the temperatures used in practice in the pretreatment of these particular catalysts. For W wires $\theta = 142°\text{K}$ and the wires were actually aged at 2500°K. It seems probable that this theory is restricted to the case of reduced oxide powders, for which it was originally developed.

The Entropy of Activation Theory. Eley and Couper suggested that the $E - \log B^0$ line for a series of tungsten wires was to be explained in terms of a relationship between the energy and entropy of activation for the reaction. Using equation (5) for k_e, assuming a fractional coverage $\sigma = bp \ll 1$, as is usually the case for $p = 1{\cdot}2$ mm, and inserting conversion factors for k_e min^{-1}, b(mm Hg)$^{-1}$,

$$k_e \frac{V}{A}, \text{cm min}^{-1} = \frac{60}{1{\cdot}33 \times 10^3} fkT(k_0 + k_p) \,.\, b$$

It follows that

$$B^0\, \mathrm{e}^{-E/RT} = \frac{60\, fkT}{1{\cdot}33 \times 10^3} \cdot \frac{ekT}{h}\, \mathrm{e}^{\frac{(\Delta S^\circ_{\text{ads}} + \Delta S^\ddagger)}{R}}\, \mathrm{e}^{\frac{-(E_t + \Delta H^\circ_{\text{ads}})}{RT}} \tag{8}$$

It may be seen that low values of B^0 might arise if only certain sites were active leading to a low f value. Since copper film B with a log B^0 of 3·40 has $\Delta S^\ddagger = -29$ E.U., it is clear that the entropy term for an Au foil, with log $B^0 = \bar{2}{\cdot}26$, must be even more negative, if f is to have a similar value to that taken for Cu of $1{\cdot}37 \times 10^{15}$ sites cm^{-2} (an average for 110 and 100 planes). However, there seems no reason to assume the cleaning process used with the foils is inefficient, and it would be very improbable that the foils, including these used by the other authors, are all poisoned so as to yield the log $B^0 - E$ relation with a slope similar to that observed for films and wires. It therefore seems probable that the log $B^0 - E$ relation arises fundamentally from a relation between the terms on the right-hand side, ΔS and ΔH, either for adsorption or activation or both simultaneously. Such relations were first advanced by EVANS and POLANYI[39] and are now well known both for adsorption [40], and for activation processes, at least in solution[41]. In the present instance $\log_{10} B^0$ varies from $\bar{2}$ to 6, and since $\log_{10} B^0$ values on tungsten wires have been observed up to 10, the total range over variation known to date is 12. The 'normal' log B^0 value[19] has been taken as 5, and we are left with a variation in entropy of ± 32 E.U. on each side of the 'normal' value. Interpreted in this way, the present results would require the entropy term to be sensitive to surface structure, but how this varies between the foils, wires, and films cannot be decided at present. The range of ΔS is so large that it seems necessary to invoke entropy change in more than two atoms in forming the activated complex, which brings us once again to the idea of a coupling of surface atoms of the metal. The actual mechanism will vary from the type (I) occurring with dilute films of mobile H atoms on Group 1B metals to the type (II) mechanism for tungsten, where the WH monolayer is immobile at the temperature of measurement[42].

Since a temperature-variable activation energy can explain the slope of the $E - \log B^0$ line for W wires and may be applicable to other single metals, it is worth noting its basic connection with the energy-entropy model, in so far as a small value of $-\Delta S^\ddagger$ gives a relatively rapid reaction, occurring at a low temperature, and therefore gives rise to a small slope for the $E - \log B^0$ line.

The authors express their thanks to the D.S.I.R. for the award of a grant to D.R.R., and a grant for purchase of catalysts to D.D.E.

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3.7

KINETICS OF SORPTION OF HYDROGEN AND CARBON MONOXIDE BY IRON AND NICKEL FILMS

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SUMMARY

A more extensive investigation of the kinetics of sorption of hydrogen and carbon monoxide on nickel films has largely confirmed the previous result obtained with these gases on iron films. However, some new facts suggest that the previous theory of activated surface diffusion requires modification. There is little doubt, for the conditions of presintering used in this and in the previous work with iron films, that the slow process is a surface phenomenon. However, introducing an intermediate chemisorbed state as a necessary precursor to the final state of lowest potential energy, it is not essential to postulate a non-uniform surface of the adsorbent to explain the kinetics, although at higher coverages it requires the heat of adsorption to fall linearly with coverage over a small range. The Elovich equation follows as a necessary consequence and the redistribution of 'sites' following certain conditions of thermal cycling can be simply interpreted.

INTRODUCTION

The rate of sorption of hydrogen and carbon monoxide by evaporated iron films in the temperature range 78°–140°K, following 'instantaneous' adsorption to about 70 per cent coverage, was found by Porter and Tompkins[1] to follow the Elovich equation[2],

$$\mathrm{d}q/\mathrm{d}t = a \exp(-bq) \qquad (1)$$

q is the amount sorbed at constant pressure p, and a, b are constants at a particular temperature. The following experimental results led these authors to conclude that the rate process was a surface phenomenon:

1. A 20-fold reduction in the surface area per unit mass (by increasing the presintering temperature from 78° to 638°K) gave

only a 40 per cent increase in the ratio of amount of 'instantaneous' sorption to that of slow sorption.

2. The b-value for films presintered at different temperatures varied inversely with the surface area at constant temperature, i.e. $(bq_1)_T = \text{constant}$, where q_1 is the total amount sorbed at 273°K and 0·1 mm pressure.

3. Almost instantaneous and complete (>95 per cent) desorption was effected by exposure of a hydrogen-covered film at 78°K to 10^{-3} mm pressure of mercury vapour, although at least 20 per cent of the total amount of hydrogen on the film was taken up in the slow process.

The conclusion, however, is at variance with that of BEECK *et al.*[3], who concluded that the slow uptake of hydrogen by nickel films was absorption into the bulk metal. A re-examination of this system has therefore been undertaken.

For hydrogen on nickel films, presintered at different temperatures in the range 78°–333°K, with a consequent 15-fold variation in the surface/bulk ratio, we find only a 37 per cent variation in the ratio of amount of fast to slow sorption using the method of Porter and Tompkins; the conclusion has also been confirmed in this temperature range of presintering using Beeck's 'isobaric' method. Furthermore, the b-value increased with presintering such that $(bq_1)_T$ was constant. Finally, fairly rapid and almost complete desorption of a hydrogen-covered film by mercury vapour was possible. Similar results were also obtained with carbon monoxide as sorbate. For the above conditions of presintering, we conclude, therefore, that the rate process for hydrogen and for carbon monoxide is a surface phenomenon.

VARIATION OF b WITH THERMAL CYCLING

A particularly significant result from the viewpoint of formulating any mechanism of the rate process was that the b-values for the iron + hydrogen system, although substantially the same for different films presintered at the same temperature, could be greatly increased by suitable thermal treatment of the hydrogen-cover film. Thus a b-value was first obtained for hydrogen at 10^{-3} mm pressure at 90°K on a clean film; then, *without* evacuation, the temperature was raised to 273°K and finally lowered to 90°K, when all the gas in the gas phase was found to have been sorbed. A further dose of hydrogen was admitted and the b-value then obtained was markedly higher, e.g. in one run the original value of 530 increased to 2680. Repetition of the temperature cycle gave a b-value of >6000. It was therefore stated that 'the kinetic data appear to exclude any mechanism depending solely on lateral repulsions of adatoms or the production of a surface electrical double-layer on a uniform surface . . . the concept of the non-uniform surface seems essential'.

We have, therefore, extended our measurements to hydrogen on nickel films and obtained parallel results; in one run, for example, the original *b*-value of 1440 increased to 9700, and on further repetition to 21,000. Carbon monoxide on both metals gave similar results.

However, with a view to examining this phenomenon in more detail, more extensive measurements were made on nickel with hydrogen as sorbate. Thus

1. A *b*-value was obtained at 90°K as before on a clean film and evacuation was immediately commenced as the temperature was raised from 90°K to 273°K. The film was then isolated from the pumps, the temperature lowered to 90°K, and a further dose of hydrogen admitted. The new *b*-value (1500) was substantially the same as the original one (1435) and repetition of the thermal cycle *with* evacuation gave 1550. The constancy of *b* under these conditions was confirmed with carbon monoxide, *and* for both gases on iron films.
2. A film, which had undergone a thermal cycle *without* evacuation and therefore had an abnormally high value for *b*, gave the normal 'clean-film' value if then subjected to a cycle *with* evacuation; similarly, the film at the end of the treatment 1 above, gave a much higher *b*-value after subjection to a thermal cycle without evacuation.
3. Increased *b*-values were obtained by pumping the film for short periods during the warming-up period, or by pumping *only* for short periods at lower temperatures (195°K) during the cycle.
4. The magnitude of *b* did not depend specifically on the amount of gas removed by desorption but on the conditions employed in the thermal cycle.

These more extensive results confirm the previous conclusion that the distribution of adsorption sites available for further adsorption could be varied under suitable conditions, but some aspects of the previous theory now require modification.

THE ACTIVATED SURFACE MIGRATION THEORY[1]

In that theory, the slow process was attributed to an activated diffusion over a non-uniform surface from sites of low to high adsorption potential, and it was shown that a linear relationship between the activation energy (E_M) for migration to a site and the adsorption potential (H_A) might be anticipated. The Elovich equation followed as a consequence of the linear increase of E_M as the diffusion front moved to sites of higher adsorption potential.

Warming and cooling without evacuation caused the further movement of the front by vacation of lower potential sites and a greater filling-up of the high potential sites. The higher *b*-values then obtained with a new dose of hydrogen was due to E_M rising more sharply with increasing amount sorbed q. It was essential to this theory that the high-potential sites were not filled by adsorption direct from the gas phase by reason of the higher activation energy for the transition from the van der Waals' layer to the chemisorbed layer. It follows that in the slow take-up those sites associated both with a high E_M value and also a high H_A value were filled up.

The limitation of this theory is that the high adsorption sites are the last to be filled in the slow process but, in addition, are also the last to be vacated on desorption; consequently, no matter whether the thermal cycle is effected with or without evacuation, the subsequent *b*-value should always be greater than the original magnitude.

Much of the difficulty of re-formulating a mechanism could be obviated if the act of adsorption was the rate-determining process. Now for hydrogen on iron, the rate (r_S) was proportional to p^x, where x in five experiments was 0·45, 0·44, 0·60, 0·63, 0·47 (mean 0·52); for carbon monoxide, three results gave $x \sim 1$. If it is accepted that $r_S \propto p^{1/2}$ for hydrogen, then both for an immobile layer in which adatoms remain on adjacent sites and for a mobile layer in which one or both atoms move to a more distant site, the primary act of adsorption cannot be rate-determining. Indeed, only a process involving adatoms such that sites are made available for further adsorption, as in the activated-migration theory, remains. It was, therefore, of some importance to determine x as precisely as possible for the nickel system. Greater accuracy has been obtained by applying desorption corrections and a mean of eleven values gave $x = 0{\cdot}51 \pm 0{\cdot}2$ for hydrogen. With CO, the mean x-value was 0·65 for nickel, and when corrections for the finite desorption rates were applied to the previous results for the adsorption of CO on iron, we obtained 0·85. We are therefore convinced that the rate for hydrogen varies as $p^{1/2}$ and that the x-value is substantially different from unity for carbon monoxide.

MECHANISM OF THE SLOW PROCESS

When the metal film is exposed to hydrogen or carbon monoxide, molecular van der Waals' adsorption takes place. Since the pressures used are low (10^{-3} mm or less) and the heat of van der Waals' adsorption of hydrogen molecules is small, the isotherm over this pressure range is confined to the Henry-law region, i.e.

$$[H_2] \propto ap \qquad (2)$$

where $[H_2]$ is the number of hydrogen molecules per unit area of the film. For carbon monoxide, however, the heat of adsorption is usually 5–10 times greater than for hydrogen; the isotherm will therefore probably be fitted by a Freundlich type equation, i.e.

$$[CO] = kp^x \tag{3}$$

where $x = 0{\cdot}65$ for Ni films and k = constant at a particular temperature. We now assume that the final chemisorbed state C_f is attained only by passing through an initial chemisorbed state C_i of

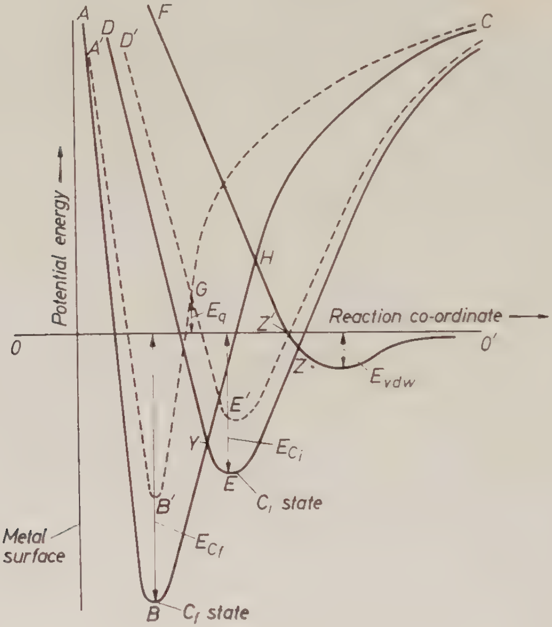

Figure 1.

higher potential energy. This possibility was pointed out in 1950 by Dowden[4] for metals such as iron and nickel which have holes in the d-band. He envisaged certain surface metal atoms having a lifetime in charged states as multiple-charged positive ions so that electrons from the sorbate tend to enter at one of these 'ionized' levels. Such states are therefore important kinetically, although from the equilibrium viewpoint the process corresponds to the entry of the electron at the Fermi level. It must be emphasized that from our present considerations it is unimportant to distinguish between complete donation of an electron or the formation of a covalent bond with some ionicity. DOWDEN[5] has further suggested that the C_i state could involve solely *d*-orbitals, and that the bonding might go over to stronger hybridized bonds of the *dsp*-type in the C_f state—this involves readjustment of the surface hybridized metal-to-sorbate bonding plus differently hybridized metal-to-metal bonding to obtain the minimum free energy of the 'surface' complex.

The potential-energy diagram is shown in *Figure 1*; this is based on the familiar Lennard-Jones plot but includes the additional curve DEC for the C_i state. It is evident that $E_{C_f} > E_{C_i} > E_{v.d.W}$ where E is an enthalpy of adsorption, and the slopes decrease such that $AB > DE > FZ$.

For hydrogen, adsorption in state C_i is dissociative, and we can define an equilibrium constant K_1 such that

$$K_1 = [\mathrm{H}_{C_i}]^2/[\mathrm{H}_2] \tag{4}$$

where $[\mathrm{H}_{C_i}]$ = the number of hydrogen atoms per unit area of the film in the chemisorbed state C_i. Combining with equation (2),

$$K = kK_1 = [\mathrm{H}_{C_i}]^2/p = \text{constant} \exp\left(-\Delta F'/RT\right) \tag{5}$$

where $\Delta F'$ is the free-energy difference per mole for hydrogen adsorption in the C_i state and in the van der Waals layer. Hence, for hydrogen

$$[\mathrm{H}_{C_i}] = \text{constant}\, p^{1/2} \exp\left(-\Delta F'/2RT\right) \tag{6}$$

and for CO, where adsorption in the C_i state is nondissociative, using equation (3),

$$[\mathrm{CO}_{C_i}] = \text{constant}\, p^{x} \exp\left(-\Delta F''/RT\right) \tag{7}$$

where $x = 0{\cdot}85$ for iron films and $0{\cdot}65$ for nickel.

It is now postulated that the process

$$[\mathrm{H}_{C_i}] \rightarrow [\mathrm{H}_{C_f}]$$

is a unimolecular one involving transformation (rehybridization) of the hydrogen atoms to a state of lower potential energy. Referring to the full curves of *Figure 1* for a clean metal, it is evident that no enthalpy of activation is required to proceed from the van der Waals layer through C_i to C_f, the final chemisorbed state, provided that the transmission coefficients at the intersections Y and Z approach unity. However, the measured heat of chemisorption decreases with amount sorbed (q); consequently after an amount q' has been taken up, the potential-energy curve changes from ABC, DEC to $A'B'C'$, $D'E'C'$ and when the point of intersection G is raised above OO′, the transformation C_i to C_f requires an enthalpy of activation $E(q)$ which increases with increase of q. As soon as the free energy of activation $E'(q)$ reaches 500 cal/mole or more, the transference from C_i to C_f becomes slow compared with the rate of adsorption from, and desorption to, the van der Waals layer so that the equilibrium, equation (3), is rapidly set up at the commencement of the slow process and remains substantially the same throughout. At the same time E' remains a constant distance below OO′. The rate r_s is therefore given by

$$r_s = \text{constant}\, p^{1/2} \exp(-\Delta F'/2RT) \exp(-E'(q)/RT) \qquad (8)$$

where we require $E'(q)$ as an explicit function of q.

Now our rate measurements extend, at most, over 5–10 per cent variation in coverage, and the heat of adsorption decreases linearly with q over this range (∼85–95 per cent coverage). Consequently, provided the relevant sections BG, DG of the curves are reasonably straight, $E(q)$, the enthalpy of activation, increases linearly with q. It is reasonable to assume that $E'(q)$, the free energy of activation, varies in a similar manner. Hence, writing

$$E'(q) = c(q - q_0) \qquad (9)$$

where q_0 is the value of q when G reaches OO′,

$$r_s = \text{constant}\, p^{1/2} \exp(-cq/RT) \qquad (10)$$

for hydrogen, which, with $b = c/RT$, and $a = \text{constant}\, p^{1/2}$, is the Elovich equation (1).

For carbon monoxide on iron

$$r_s = \text{constant}\, p^{0\cdot 85} \exp(-c'q/RT) \qquad (11)$$

The constancy of b-values following a thermal cycle with evacuation is consistent with the above mechanisms. For example, for the iron + hydrogen system at 85 per cent coverage, the heat of desorption (H_D) from C_f is the sum of the heat of adsorption ∼18 kcal/mole,[6] and the activation energy ∼3 kcal/mole,[1] i.e. 21 kcal/mole; at 50 per cent coverage, $H_D = 26 + 0$ kcal/mole. At 25°C, the initial rate of desorption of adatoms is 1 in 10^{-3} sec^{-1} falling to 1 in 10^{-6} sec^{-1} at 50 per cent coverage if a perfect vacuum is maintained. Thus, after the 16 h evacuation, we find 20 per cent of the sorbed hydrogen is desorbed. Adding further gas at 90°K causes a rapid filling-up of the van der Waals and C_i layers to their relevant equilibrium value and the rate process becomes measurable when G rises above OO′. The b-value will thus be the same as that obtained on the clean film.

The condition of the adsorbed film is, however, altered by raising the temperature without evacuation. The original rate before increasing the temperature on the clean film was allowed to become negligibly slow at 90°K, i.e., $E'(q)$ was comparatively large. At the higher temperatures, this $E'(q)$ value can be easily acquired, and more gas enters the C_f state; $E'(q)$ therefore becomes prohibitively high for transition into C_f at 90°K. On admitting hydrogen at 90°K, gas only enters the van der Waals and C_i layers. The rate is initially rapid, but with increase of q the potential energy curve $D'E'C$ is raised, and the slow rate becomes measurable when Z' rises above OO′. The number of C_i sites per unit area is comparatively small (cf. the rapid fall of adsorption heats as θ approaches unity) so that the gradient $\mathrm{d}\,E(q)/\mathrm{d}q$ is much higher, therefore the b-value is greater.

Repetition of the cycle without evacuation gives very high b-values (21,000 for nickel), and we believe this represents the rate of molecular diffusion of the gas to the more inaccessible surfaces of the film and the attainment of thermal equilibrium of the gas at 306°K with the films at 90°K.

Table I

T°K	b (mmoles/g)$^{-1}$	bT
78	1220	$9{\cdot}5 \times 10^4$
90	1140	$10{\cdot}3 \times 10^4$
147·5	680	$10{\cdot}1 \times 10^4$
177	590	$10{\cdot}4 \times 10^4$
195	570	$11{\cdot}1 \times 10^4$
	mean	$10{\cdot}3 \times 10^4$

As a measure of confirmation of the present interpretation, three relationships should be valid and all are experimentally accessible.

1. From equation (9),

$$b = c/RT, \quad \text{where } c \text{ is} \quad \mathrm{d}E'(q)/\mathrm{d}Q$$

c is expected to be temperature-independent for a particular film, i.e. the product bT should be constant. We have, therefore, obtained b-values for hydrogen on a nickel film presintered at 300°K which, for every determination, has been previously evaluated for $1\frac{1}{2}$h at 300°K to attain a constant coverage. *Table I* shows that the relationship is experimentally realized.

For carbon monoxide, a similar constancy is found with a mean value of bT of $14{\cdot}6 \times 10^4$, the higher magnitude reflecting the more rapid fall of heat of adsorption with coverage for carbon monoxide than for hydrogen.

2. Increase of presintering temperature causes a reduction in surface areas but, at least for $\theta = 0{\cdot}7$ and higher, the variation of the heat of adsorption with q is the same. Since b is expressed in terms of q, the b-value should (at constant temperature) increase proportionally to the decrease in surface area as measured by the q_1-values, i.e.

$$(bq_1)_T = \text{constant}$$

The results in *Table II* for the iron + hydrogen system confirm this for a 70-fold increase in b. Similar results were obtained with nickel films.

Table II

b (mmoles/g)$^{-1}$	q_1 (mmoles, 273°K, 0·1 mm pressure)	bq_1
85	0·80	68
500	0·15	75
750	0·11	84
3450	0·018	62
5830	0·011	64
	mean	71

3. $E(q)$ should increase linearly with q for $q > q_0$. For the iron + hydrogen system Porter and Tompkins find that

$$E(q) = 470q - 61 \text{ in kcal/mole}$$

where q is in mmoles/g Fe.

A similar relationship has also been obtained using nickel films.

The previous theory[1] had therefore correctly stated the requirements of the mechanism to account for the kinetics of the slow process, but the model used cannot explain the additional experimental results, in particular, the constant b-values obtained after thermal cycling with evacuation. The present interpretation obviates this difficulty and, instead of requiring the movement of a chemisorbed adatom to a new site of higher adsorption, it shows that a transition of the adatom at the original site to a different chemisorbed state of lower potential energy can adequately account for all the results. The concept of the non-uniform surface is therefore not essential provided, as is normally found, the heat of adsorption falls appreciably and linearly with coverage θ over a small range at the higher θ-values.

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3.8

THE BOMBARDMENT OF SURFACES BY POSITIVE IONS

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SUMMARY

Observations on the adsorption of positive ions with energies up to 5000 eV *on to the surfaces of nickel, tungsten, aluminium, and molybdenum are described. The work has been carried out under high-vacuum conditions with a mass-spectrometer, so that it has been possible to follow the slow desorption of one gas against a large background of some other gas. Measurements have been limited to helium, neon, argon, krypton, hydrogen, nitrogen, oxygen, and carbon dioxide. Metal targets have been bombarded with positive ions of these gases at known energy for fixed times. In subsequent heating, gas has been recovered from the target, showing it to have been held at the surface or inside the metal as either ions or neutral molecules. The maximum quantity of gas that can be taken up increases with increasing ion energy to a maximum of approximately that required to form a complete surface layer one atom in depth. Temperatures of the order of* 700–800°K *are required to remove the adsorbed gas, thus showing binding energies much higher than for physical adsorption, especially for the inert gases. It has also been noticed that the ions can dislodge, and take the place of any molecules already adsorbed at the surface.*

INTRODUCTION

This work was initiated and has been carried out chiefly as a high-vacuum problem, where the disappearance of molecules from the gas phase in an electrical discharge is of great practical importance. These experiments were designed in order to determine the fraction of gas taken up at metal electrodes and the influence of the discharge voltage and current upon the adsorption mechanism. The experiments have all been carried out in a high-vacuum chamber, a mass-spectrometer being used for all pressure measurements. Thus it has been possible to isolate one small component in a complex gas mixture, and also, possible errors due to gas contamination have been eliminated.

The results obtained are interesting in that they show physical adsorption of the inert gases at metal surfaces with a high heat of desorption, the molecules being held tightly at temperatures up to 700°K. They are important as they show that the technique of surface preparation by bombardment with positive ions of the inert gases, for example the work of OATLEY[1] and EGGLETON and TOMPKINS[2], does not in fact produce a perfect result.

APPARATUS

The vacuum pumping system shown diagrammatically in *Figure 1* consists of two oil-diffusion pumps in cascade with a small single-stage rotary pump, a solid carbon dioxide vapour trap being placed between the experimental tube and the diffusion pumps. The gas composition and pressure in the experimental tube were controlled by passing gas from a two litre reservoir vessel through a porous plug into the main vacuum system, the pressure in the manifold being approximately proportional to that in the reservoir, 10^{-5} mm of mercury in the manifold corresponding to a reservoir pressure of the order of a few mm of mercury.

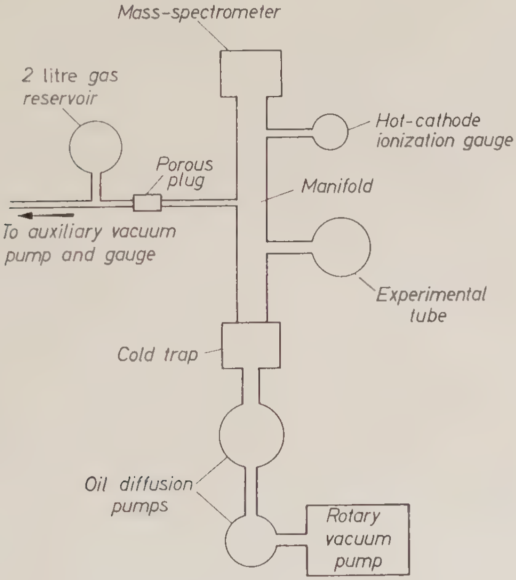

Figure 1. Schematic diagram of apparatus.

A 90° deflexion mass-spectrometer with a Nier-type source and fixed magnetic field was used throughout this work. This instrument resolved up to mass 90 and, with an automatically stabilized high-voltage supply and a high gain d.c. amplifier, proved capable of partial-pressure measurements of less than 10^{-10} mm of mercury. The spectrometer tube connected directly to the pumping manifold without intermediate valves or constrictions. An ordinary hot cathode ionization gauge was included in the vacuum system to measure the total pressure, the pumping speed at the manifold and also for calibrating the mass-spectrometer. (The pumping speed for any gas could be obtained by measuring the increase in pressure in the manifold due to a known flow of gas through the porous plug, the gas flow being calculated from an observation of the rate of fall of pressure in the reservoir. By definition, the pumping speed of the manifold is given by the ratio (gas throughout)/(gas partial pressure).)

The mass-spectrometer and the connecting pipe work could be baked to 100°C and the glass bulb of the experimental tube to 400°C. A radio-frequency induction heater enabled the gauge electrodes to be heated to about 1000°C. After 100 hours pumping with the mass-spectrometer tube and the gauge envelope baked continuously, the residual gases were found, as expected, to consist largely of water and hydrogen vapours. Water vapour, the largest of the residuals, was of the order of 10^{-8} mm of mercury. The residual spectrum was similar to that reported by BLEARS[3] for an almost identical vacuum system, the total pressure being a factor two or three times greater in the present work, probably because of the rather less stringent pumping cycle.

The positive ions were produced in the experimental tube by either a cold- or hot-cathode discharge. With the cold-cathode discharge tube, using a magnetic field to increase the electron-path lengths, ion current densities of the order of 10 to 100 μA/cm^2 were obtained at the disc cathodes 1 cm diameter for a gas pressure of 10^{-5} mm of mercury. (This discharge tube was, in fact, a Penning-type high-vacuum gauge[4].) In the alternative hot-cathode discharge, the ions were collected at an auxiliary anode in the form of a thin wire held at some potential negative to the cathode. In this case, ion current densities of the order of 1 μA/cm^2 were obtained at a pressure of 10^{-5} mm of mercury. (This tube corresponded closely to a Bayard-Alpert type ionization gauge[5].) The cold-cathode tube had the advantage of a high current density but the measurement of ion energies and densities was much more difficult than in the case of the hot-cathode discharge. Further, it was not easy to control or measure accurately the temperature of the rather large experimental surfaces in the cold-cathode tube.

EXPERIMENTAL PROCEDURE AND RESULTS

The following procedure was observed to measure the ion adsorption. After a low pressure had been obtained in the vacuum system, a particular gas was fed into the experimental tube through the porous plug and the discharge run for a given time, the total number of ions sticking the target being measured. The test gas was then pumped from the system. Finally, the target was heated and any gas driven off measured by means of the mass-spectrometer. The mass-spectrometer pressure measurements were multiplied by the effective pumping speed at the target and integrated over the whole period of the desorption to give the total quantity of gas evolved. Thus the observations were made of gas desorption after take up, rather than of the actual gas taken up.

Table I. NUMBER OF MOLECULES RECOVERED FROM TARGET AND NUMBER REQUIRED TO FORM A COMPLETE SURFACE LAYER

Gas	*Maximum number of molecules adsorbed* $\times 10^{-16}$	*Number of molecules to form a surface layer* $\times 10^{-16}$
Helium	10	4·7
Neon	4	3·3
Argon	2·3	1·7
Krypton	0·17	1·3
Nitrogen	2·18	1·7
Oxygen	1·0	1·6

Gas was recovered readily at a temperature of 700 to 800°K in the case of the hot-cathode tube, the calculated heat of desorption being of the order of 50 kcal/mole. (Lower temperatures for rapid desorption were observed for the cold-cathode tube, but here measurements were less reliable.) The total quantity of gas taken up (or, more accurately, the total recovered) was a function of the energy and the total number of ions striking the target. The results obtained for all the target materials, nickel, tungsten, molybdenum, and aluminium were essentially the same. *Table I* shows how, for the inert gases, the total quantity of gas recovered decreases with increasing molecular weight. In this table the number of molecules required to form a simple surface layer (roughness factor unity) is given to form a basis of reference. A complete set of results for argon on tungsten is given in *Figure 2*. Results for all other gases showed the same general characteristics. Before commencing each experiment, the target surface was carefully cleaned by heating to the highest practical temperature for 10 minutes at the ultimate pressure of the system (with tungsten, for example, the heating was at over 2500°K). There was, however, no measurable change in the results when this cleaning procedure was not observed.

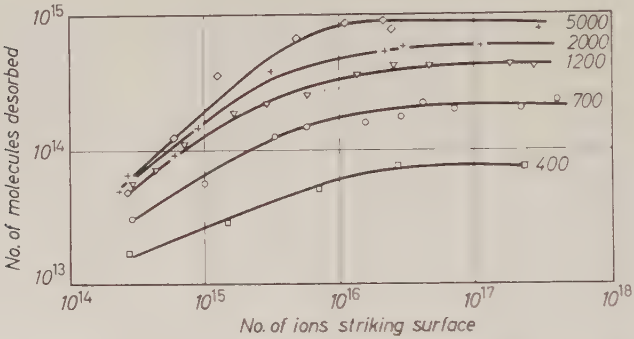

Figure 2. Number of argon molecules recovered from a tungsten surface of area 0·5 cm^2 as a function of the number of positive ions striking the target in the previous discharge. The values of ion energy in eV are marked on each curve.

In another series of experiments, the adsorbed gas was removed by a further ion bombardment. Again sorption was first achieved by running the discharge in a particular gas for a given time. Then, after switching off the discharge and removing the gas sample from the vacuum system, the molecules taken up by the discharge tube were recovered by restarting the discharge in another gas. The desorption rate, observed by means of the mass-spectrometer, rose to a maximum immediately after restarting the discharge, and then fell off exponentially to zero in a period of from 20 to 60 minutes. If, after some minutes operation in the second gas, the gas composition in the discharge was changed, either to the original or some other gas, molecules of the second gas were immediately recovered. This desorption by the discharge was observed for all the gases used in these experiments. Although the desorption rate depended upon the discharge current, the total quantity of gas recovered was independent of this current. Typical desorption characteristics of argon in a nitrogen discharge plotted in *Figure 3* illustrate the general shape of all characteristics, and in particular show that, with the reduced discharge current, desorption takes place at a reduced rate but for a longer time.

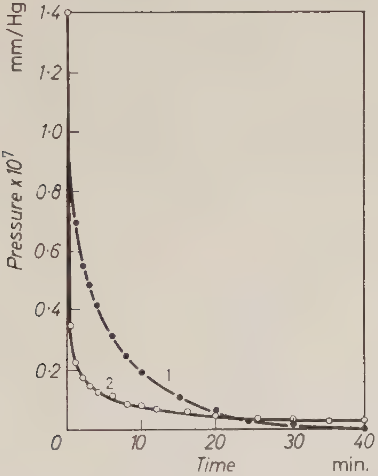

Figure 3. Desorption of argon in a nitrogen discharge. Previous sorption of argon was in a discharge of 100 μA for 20 min. Discharge current in nitrogen—Curve 1: 100 μA; Curve 2: 15 μA.

DISCUSSION AND CONCLUSIONS

It is clear that with energies of over a few hundred electron volts there is appreciable ion adsorption even with the inert gases. The phenomenon must be physical rather than chemical as there are no effective differences between widely different gases such as nitrogen, neon, and oxygen. The ions are probably neutralized on arrival at the metal surface and, by virtue of their kinetic energy, penetrate a few atom layers deep into the bulk metal[8]. They must be held in the lattice at room temperature, but at 700 to 800°K become free to move. Most arrive at the surface where they can be desorbed very quickly. (This is borne out by the fact that no further gas was ever recovered even by baking up to the fusion point of the target, over 3000°K for tungsten.)

It is apparent that positive-ion bombardment with the inert gases does not, as Oatley assumes[1], result in a perfectly clean surface. The previous adsorbed layers are to some extent replaced by molecules of the inert gases which, even though they may not be actually on the surface, probably affect its nature. It is only by heating the target for a few minutes to 800°K that it can be freed from the inert gas molecules.

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3

DISCUSSION

Chairman: D. D. ELEY

E. R. S. WINTER: I note that Dr. Mignolet stressed that his films were physically adsorbed. Was he able to desorb the gases, recover the original contact potential for the clean metal and put the film back to yield the same value as before? It appears to me that ability to do this at the temperature of the original adsorption would be a fair criterion of physical adsorption here.

J. C. P. MIGNOLET: Some fairly volatile films such as $HgCH_4$ and CuN_2 may be pumped out completely at −196°C. Others, such as the xenon films, require a warming-up. With such films as NiC_2H_4 and NiC_6H_6 which react upon warming-up, reversibility is difficult to establish. As regards NiC_2H_4, I may point out that the film prepared and kept at −196°C can be displaced by CO with the help of a small warming-up.

In recent years, evidence has accumulated[1] showing that molecular hydrogen is adsorbed much more strongly than was before thought possible. The evidence is especially compelling in the case of the $Pt + H_2$ system[2], where the molecular adsorption may be demonstrated by measurements of adsorbed quantities. The estimated heats of adsorption for $(WH)H_2$ and $(PtH)H_2$ are about 9 and 15 kcal/mole, respectively. Having accepted the stability of the molecular adsorptions in these cases, we must be prepared to accept the consequences.

The molecular adsorption is able to compete with the atomic adsorption in some concentrated films. This then gives rise to a special mode of adsorption consisting in the replacement of atoms by molecules. This substitutional adsorption is an activated process. A saturated mixed film appears to be over-stoichiometric in comparison with a complete atomic film. When the substitutional adsorption is prevailing, an increase in pressure reduces the concentration of atoms to the benefit of the molecules.

Space is lacking for discussing the application of these remarks, but I should like to express my feeling that these are not sufficiently taken into account in many interpretations. For instance, some of the slow sorptions observed with initially clean surfaces may be accounted for very simply and reasonably on the basis of an activated substitutional adsorption. In another direction, it may be recalled that the pressure dependence of the rate provides a means for choosing between the Bonhoeffer-Farkas and that of Rideal in the range of conditions where substitutional adsorption is operating. An increase of the rate with pressure rules out the former mechanism.

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W. E. Garner: A clear-cut distinction between physical or van der Waals adsorption and chemisorption does not appear to be practicable at the present time. The one type appears to grade gradually into the other. A high heat of chemisorption is indicative of chemisorption but it is possible to obtain moderately high heats from van der Waals adsorption, or solution processes, if at the same time there is a lattice rearrangement. The changes occurring in the adsorbent that accompany the adsorption are in part responsible for the difficulties in distinguishing between the two types of adsorption. Also charge-transfer bonds of the Mulliken type complicate the issue.

B. A. Pethica: I would like to refer to recent work by Koenig and Lange on the thermodynamics of the contact potential. Koenig has made a thorough examination of the processes involved in the measurement of contact potentials (*C.I.T.C.E. Proc.*, 1951, p. 299). The contact potential, as usually measured, is the potential applied on a suitable potentiometer such that there is no field gradient between two pieces of metal *in vacuo*. Koenig prefers to call this the compensation potential. The contact potential, properly speaking, is precisely the difference between the volta potentials of the metals when no external potential is applied on the potentiometer. In the original theory of the measurement of contact potentials, the assumption was made by Lorentz, Kelvin and Bridgmann that the contact potential is the same as the compensation potential. This is equivalent to saying that the electron work function does not vary with the charge on the phases being considered. Koenig points out that the Lorentz–Kelvin–Bridgmann assumption has not really been tested, and until it has been tested thoroughly, it is best to be cautious about calling compensation potentials contact potentials. A number of corollaries follow from Koenig's analysis of compensation and contact potentials. The dropping of the Lorentz–Kelvin–Bridgmann assumption means that the classic law concerning the equipotential surface on a conductor need not necessarily be correct. In conversation with Prof. Lange, he made an interesting observation on the assigning of the potential changes due to adsorbed dipoles, and I hope I represent his views correctly. Consider two massive pieces of metal, connected by a piece of the same metal. In Lange's notation, suppose the two pieces of metal to have inner potentials ϕ_1, ϕ_2, surface potentials χ_1, χ_2, and outer potentials relative to infinity ψ_1, ψ_2. For the clean pieces *in vacuo* the respective ϕ, χ and ψ are equal. Suppose that a layer of dipoles is now adsorbed onto piece 1 only, and let a unit charge be brought inside 1 by two routes. Passing through the surface of 1 the electrostatic work is $\phi_1 = \psi_1 + \chi_1$. Passing through the surface of 2 the electrostatic work is $\phi_1 = \psi_2 + \chi_2 + (\phi_1 - \phi_2)$. There seems to be no reason *thermodynamically* for supposing that $\phi_1 = \phi_2$. For a massive metal, it is obvious that a row of dipoles will not alter the interior of the phase very much, but for a very thin film in which charge transfer and electron shifts can occur (cf. Prof. Suhrmann's paper), we cannot assume $\phi_1 = \phi_2$. In measuring contact potentials of thin films, it is therefore possible that the potential changes may be assigned to ϕ as well as χ. This bears immediately on the calculation of the energies involved, and can be particularly serious with semiconductors in which thick charged double layers may penetrate deeply into the bulk phase.

J. H. DE BOER: Physical adsorption of many gases, including CO, N_2, and hydrocarbons, on charcoal leads to the formation of dipole layers (positive double layer) in the same sense as found by Dr. Mignolet. An extensive study (thesis of Dr. Kruyer), has shown that all these gases behave as two-dimensional gases; the molecules move over the surface and they rotate freely. There is a strong repulsion between the adsorbed molecules, which can be described by a mutual dipole repulsion. This conception leads together with the van der Waals (dispersion) forces, to the right order of magnitude for the heat of adsorption, while the dipole moments are of the same order of magnitude as those found by Mignolet. There is, in my opinion, no need to describe these effects by the conception of a charge-transfer. The 'normal' polarization of the physically bound molecules by the electron field of the metal (here, charcoal) is sufficient.

A. S. PORTER: Comparative measurements on a series of metal films, as suggested by Dr. Trapnell, will certainly be valuable, but the interpretation may be complicated by variations in surface heterogeneity produced by impurities or by a particular ageing treatment. Gaseous impurities are the most troublesome, but their importance can be estimated by the study of films prepared in the presence of known additions. The degree of sintering under specified conditions must be treated ultimately as a property of the metal and related to its electronic character. Until adequate means are available to do this, a simpler correlation between electronic character and surface phenomena might be obtained by ageing films of each metal at a temperature related to the melting point, or which gives a definite surface area per unit weight (measured by physical adsorption). Care would be needed to avoid differential contamination during ageing.

J. PRITCHARD: Dr. Pethica has recalled the possible difference between the true contact potential and the compensation potential difference measured in the Kelvin method and its modifications. It is worth considering whether this is of importance in actual determinations of the surface potentials of adsorbed gases on metals. In the diode method this compensation potential difference is found to be constant over a range of retarding and accelerating fields. While diode characteristics before and after adsorption on the anode may deviate from parallelism outside this range, it is usually possible to ascribe this to edge or end effects. Thus it seems unlikely that the variation of work function with moderate surface charge density is experimentally important. This is supported by the early work of Glasoe who showed that the difference of the photoelectric work functions of a nickel and an iron surface equalled the contact potential difference measured by the Kelvin method. Similarly, the recent work of Mitchell and of Mignolet shows very good agreement between contact-potential differences measured by the Kelvin method and thermionic methods.

Some further justification for the desirability of adopting some standard for the thermal pre-treatment of evaporated metal films for adsorption studies as advocated by Dr. Porter is provided by measurement of the changes of work function on sintering metal films. I have found that the work function of copper films deposited at −183 C increases by 0·3 EV on sintering to room temperature. This is accompanied by a change in the maximum surface potential obtainable with atomic hydrogen at −183°C or −78°C. The effects are reproducible and do not seem to be due to contamination. A similar effect is found for silver, though ageing at the temperature of deposition is accompanied by a decrease of work function as noted by Farnsworth. In the latter case the effects have been shown by Farnsworth to be due to relief of strain in the film.

Dr. Pethica has suggested that the effect of surface charging on the work function may be more important in the case of evaporated films consisting of small crystallites. Using the diode method, I have found the characteristics with unsintered purple silver films (∼1 micron thick) deposited at −183°C and the same films after sintering at 25°C to be quite parallel. Similar results were obtained with copper and gold. Thus, over a range of particle size, of about 50 A to probably about 1000 A the effect if present, must remain constant.

M. W. Roberts: Recent adsorption studies that Professor Sykes and I have carried out at Swansea have furnished some interesting results with reduced nickel oxide.

It has been generally accepted that metal powder and metal film surfaces differ markedly in their adsorption characteristics. Nickel oxide reduced by previous investigators[1] has been relatively inactive to hydrogen chemisorption. Little adsorption has occurred at low temperatures and the main uptake has required many hours to come to completion at room temperature.

However, it has been shown that using stringent vacuum conditions, carefully purified hydrogen, and long times of reduction (100 hours) at 450–500°C that the properties usually associated with powder surfaces gradually disappear, giving way finally to adsorption characteristics almost identical with those associated with nickel films[2].

Some of the properties we observed for thoroughly reduced nickel powder were as follows:

1. 80 per cent of the surface chemisorbed hydrogen at a very fast rate at liquid oxygen temperature and an equilibrium pressure of approximately 10^{-4} mm. The surface area was assessed by the B.E.T. method from the physisorption of krypton.
2. There was an overall desorption of 10 per cent of the gas chemisorbed at −183°C on warming to room temperature. Maximum adsorption, however, occurred at 'card-ice' temperature.
3. The ratio of the 'slow' to 'fast' adsorption at −183°C was 0·24 which is in good agreement with Tompkins' values for H_2 on iron and nickel films[3].
4. Oxygen was shown to be responsible for the slow activated adsorptions associated with reduced powders. A thoroughly reduced nickel surface showed no slow activated processes at room temperature or above.
5. Heats of adsorption determined from high-temperature isotherm data gave values ranging from 27 kcal mole^{-1} at $\sigma = 0$ to 21 kcal mole^{-1} at

$\sigma = 0{\cdot}5$. The criterion for coverage was again the physisorption of krypton at −183°C.

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D. J. C. Yates: As Professor de Boer was mentioning the degree of freedom of adsorbed molecules, I thought that some recent work which Dr. N. Sheppard and I have been doing at Cambridge (Colloid Science Department), on the infra-red spectrum of adsorbed methane may be of interest. Infra-red spectroscopy is a technique which may give direct evidence of the mobility of adsorbed molecules, in contrast with the more indirect methods used previously.

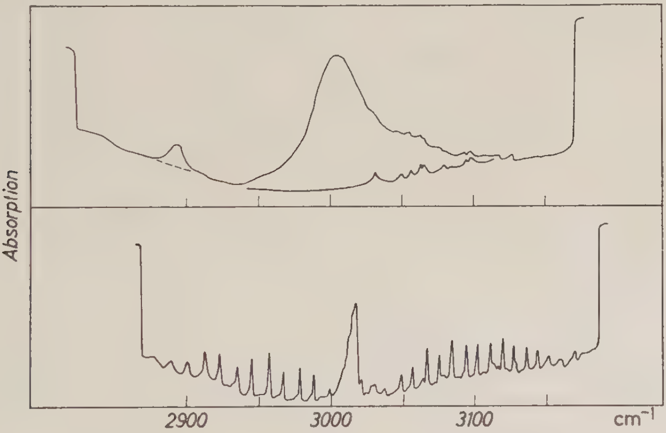

Figure 1

When a molecule rotates freely in the gas phase its vibrational infra-red frequencies will be modulated by rotation giving rise to extra lines on both sides of the main band. In the lower half of *Figure 1*, the rotational lines for the ν_3CH stretching frequency of methane in the gas phase are shown using a diffraction grating spectrometer. With the prism instruments usually used in infra-red spectroscopy, this rotational fine structure would not be resolved. The upper half of the figure shows the band observed when methane is adsorbed on porous glass (of surface area about 180 square metres per gram) at 90°K with a coverage of 0·08 of a monolayer. It will be seen immediately that no fine structure is resolved, although the resolving power used is the same as that for the gaseous methane. This shows that completely free rotation is not present in the adsorbed state. However, it remains possible that the rotation is sufficiently free so that the overall band contour will reflect rotational motion even if the individual lines are not resolved. On this assumption, we have calculated the shape of the adsorption band to be expected if the adsorbed molecules are (a) rotating freely about one axis, or (b) rotating freely about all three axes. The observed shape is not consistent with (b), but is consistent with assumption (a), i.e. rotation about a single axis, presumably perpendicular to the surface. Another band appears in the spectrum of adsorbed methane, which is forbidden in the gaseous and liquid states. The relative widths of the allowed and forbidden bands of adsorbed methane can also be explained on the assumption that free rotation is present about a single axis. The detailed results on which the above conclusions are based are in course of publication.

B. M. W. Trapnell: Mr. Greenhalgh and I were unable to detect any chemisorption of H_2 and CO on Bi films by volumetric methods under identical conditions to those used by Professor Suhrmann. The resistance method is thus more sensitive.

It would be interesting to know whether the resistance method reveals small amounts of chemisorption on other *sp* metals such as Zn, Cd, In, Sn, Pb, and Ag which by volumetric methods appear inactive towards N_2, H_2, CO, and C_2H_9. It would also be valuable to have data on the Au/O_2 system.

F. S. Stone: Professor Suhrmann has suggested that the fall in resistance observed when oxygen is admitted to bismuth at 77°K can be attributed to the formation of O_2^+. This is indeed so, but our general experience with metals and semiconductors would suggest that the formation of such an ion under these conditions is unlikely. Oxygen is invariably chemisorbed as a negative ion. It may be possible to resolve this apparent anomaly by bearing in mind that, if the semiconductivity of the thin bismuth films is genuinely intrinsic, positive holes as well as electrons will be contributing to the conductivity. Although chemisorption of oxygen as a negative ion will increase resistance if conducting electrons are captured, there will be a *decrease* in resistance if oxygen anions are produced with positive-hole formation. The latter may be the preferred process at 77°K. The recovery phenomenon observed at 90°K may then be associated with the slow recombination of holes and electrons after chemisorption.

E. R. S. Winter: Dr. Leck's observations of the penetration of argon and other gases below the surface of metals subjected to positive-ion bombardment have considerable interest to chemists in view of the similar techniques often used to clean metal films and wires. Has he any similar work to report on hydrogen?

J. H. Leck: Yes, we made investigations with hydrogen, and also with oxygen and nitrogen. With hydrogen, things are difficult because there is a lot of glass in the system, and hydrogen tends to behave peculiarly. To a first approximation, effects due to hydrogen are very similar to those found with argon. Hydrogen is taken up in amount equivalent to the formation of about one surface layer at voltages of 1000 or above. A set of curves, as obtained with argon, cannot be given, because secondary effects spoil the results.

G. C. A. SCHUIT: With regard to the relation between log k (ethylene hydrogenation) and the product of Pauling's metal valency and per cent d-character: I agree with Dr. Bond that W and Ta are different from the other metals as concerns activation energy and 'frequency factor'. However, since log k is connected with the difference in free energy between initial state and transition state it appears the most significant factor, the more so since we do not know in this case how to account for the peculiar constancy in E and the variation in log A.

I do not believe, however, that the relation in itself is very fruitful. Although Pauling's concept is very valuable, I feel some doubt as to the numerical values of both valency and per cent $-d$.

With regard to the relation between log B and E, I would like to ask whether there is some connection between the actual values of log B or E and the temperature. In other words—do we find the high values of log B and E at the higher or at the lower temperatures?

D. D. ELEY: There does not appear to be any general relation between the temperature and the log $B^0 - E$ relation. In the complete version of our paper we have examined how far the slope of the log $B^0 - E$ relation is given by 2·303 RT, when T is the average temperature of the catalyst in the reaction series. This seems to hold for the Group 1B wires, and also for data on tungsten wires obtained in an earlier paper cited, but not for the films and foils.

J. C. P. MIGNOLET (*Communicated*): Recently, in developing the interpretation of my empirical relationship[1], I failed* to notice the similarity with Professor de Boer's early views[2,3,4]. In apologising for this regrettable oversight I should make it clear, however, that there is no question of using de Boer and Veenemans' formula[3]

$$\lambda_a = Q_i - I + \varepsilon\varphi_\theta$$

in the case of the hydrogen films which I considered. Indeed, even in the case of WCs, the term $\varepsilon\varphi_\theta$ does not account for the fall in heat of adsorption for $\theta > 0{\cdot}02$. The authors recognized[4] that the double layer extends beyond the adatoms and pointed out that Q_i must increase with θ. After 20 years, one still admires de Boer and Veeneman's logical and ingenious treatment, but one is no longer satisfied† because, really, the variation of Q_i with θ—which the authors did not evaluate—deprives the work-function effect of most of its significance. In this respect, Langmuir's treatment[5], which recognizes at the start that only part of the double layer is effective, is perhaps preferable‡.

* Probably because I have always been reluctant to follow de Boer and Langmuir in some of their interpretations and all the more so to extend the picture of ions held by image forces to other films, e.g. H-films.

† And I should think that Professor de Boer is not either.

‡ But still open to criticism because it neglects the energy of depolarization.

In my paper, I could not escape the conclusion that the electrostatic forces are unable to account for the whole of the interaction energy. This led me to an interpretation which has one essential point in common with de Boer's early views. Since then, I have realized how silly I was in considering the dipoles MH as due to the shift of only one electron. Clearly, in a covalent bond, the two electrons equally contribute to the dipole moment. The structural factor required by the experimental data is ½ instead of 1. This entails a revision of the interpretation. I hope to be able soon to discuss the matter in detail.

As regards the cause of the fall in the heat of adsorption, I do not quite share Professor de Boer's opinion, at least as expressed in his conclusion. I think that the building up of the double layer—or rather the charge in the double layer—is the fundamental cause. It has two effects, viz. the change in work function and the fall in the heat of adsorption. The connection between the two effects involves a structural factor which is the main source of our difficulties.

Finally, I may perhaps point out that, about 80 years ago, Kelvin already understood that the formation of a double layer requires an energy[6], and gave a relation formally equivalent to de Boer's work-function term and to my empirical relationship.

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D. A. Dowden: In reference to Dr. Porter's comments, the ease with which metals such as copper, silver, and gold sinter raises a fundamental question. Thus, films of nickel sintered to the same area per unit weight as those of copper may yet retain more 'defects' per unit area of surface due to the smaller diffusion coefficients in the *d*-metal. If chemisorption requires these defects, as in nucleation, then it can be argued that differences in activity arise from this source and not solely from valency differences *per se*. While the concentration of such defects in well sintered films must be relatively small, it seems to be a point requiring experimental work.

One could sympathize with Dr. Trapnell's efforts to simplify our problems by supposing that surface atoms may bear a strong resemblance to free atoms, but I question whether this is helpful in the long run. Because of the almost linear relationship between atomic number and the energy of the Fermi surface in metals (regardless of the model upon which the calculation is based) the two are interchangeable in correlations and $E_{\text{max.}}$ is hardly a characteristic of the free atom.

J. M. Thomas: Dr. Porter's remarks draw attention to the radiant heat emitted from a filament during the production of an evaporated film. The operation of a heat-transfer factor will influence the sintering, and therefore the adsorptive capacity, of the metal and hence complicate the conclusions deduced from the adsorptive properties of a set of metal films. It has been suggested[1] that this factor, because it varies from investigation to investigation, is the probable cause for the discrepancies in the literature among adsorptive capacities.

Another factor likely to be of importance when the behaviour of different films are examined, and which is likely to vary from experiment to experiment, is the structure of the surface on which the film is deposited. TOLANSKY[2], with the aid of multiple-beam interferometry, has shown that an evaporated film contours the micro-topography of the substrate, height changes as small as 10 Å being significant.

In view of this it appears profitable to consider, for future work, the use of fire-polishing, or some suitable process, so as to obtain glass and silica surfaces smooth in molecular dimensions[3].

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SECTION 4

CHEMISORPTION ON SEMICONDUCTORS

Chairman: F. S. STONE

4.1

CHEMISORPTION ON SEMICONDUCTORS

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During the last ten years the ‘electronic factor’ has become established as an important concept in chemisorption, and the present Symposium provides a timely opportunity to enquire to what extent individual chemisorption behaviour is characterized absolutely by the mere choice of solid type (viz. metal, semiconductor, or insulator). In developing this theme for the case of chemisorption on semiconductors, it is convenient to begin by reviewing briefly the main theoretical approach. We shall follow this by a discussion of the experimental material and conclude with some remarks about the general features which emerge from a correlation of experimental studies on semiconductors.

The general picture of chemisorption at the interface between a semiconductor and a gas is illustrated in *Figure 1* for an *n*-type semiconductor, a *p*-type semiconductor, and an intrinsic semiconductor. respectively. Let us first consider the *n*-type semiconductor. Electron transfer is possible from the conduction band to a vacant level of the physically adsorbed molecule M, converting M to M^-. The energy liberated is $E - \phi$, where E is the electron affinity of M and ϕ is the work function of the semiconductor. The source of the electron is effectively a donor centre near the surface of the semiconductor. At the surface of the *p*-type semiconductor, M may donate an electron to the valence band, becoming M^+. The heat of adsorption is now $\phi - I$, where I is the ionization energy of M. We may note that in both cases the act of chemisorption depletes the semiconductor of carriers and therefore leads to a decrease in its conductivity. We may therefore refer to these cases generally as constituting *depletive chemisorption*. For the intrinsic semiconductor, both possibilities exist; it follows that there is a mechanism here whereby the presence of an adsorbed layer allows the electrons received from the conduction band to be returned to the valence band. It is well known in germanium physics that adsorbed gases can be very effective in promoting ‘surface recombination’ of holes and electrons[1]. Effects of this kind may be expected for any semiconductors in which the gap between the valence and conduction bands is small (e.g. α-Sn, InSb). However, for the majority of oxide and sulphide semiconductors, which are our principal concern in this short review, the energy gap between the bands is sufficiently large to preclude any significant contribution from intrinsic behaviour below about 500°C.

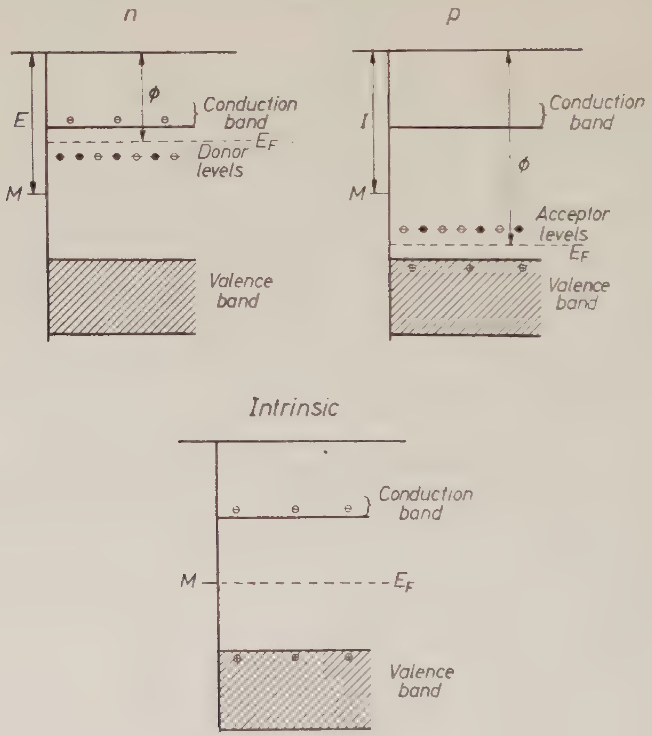

Figure 1.

With *n*- and *p*-type semiconductors, the process of electron transfer during depletive chemisorption cannot occur indefinitely. As more and more donor centres are emptied of electrons (or, for the *p*-type case, as acceptor centres are filled), a space charge builds up in the boundary layer and a potential barrier develops opposing further transfer (*Figure 2*)[2–8]. Equilibrium is attained when the potential energy of electrons in the semiconductor (represented by E_F, the Fermi level) becomes equal to the potential energy of electrons in the adsorbate (represented by the height of the level at M). The analogy here is with the Schottky model of rectification at a metal–semiconductor contact[9]. Using this model[2,3,4], it may be shown that the above condition of equilibrium leads to the relation

$$N_f = \left[\frac{\kappa}{2\pi e} n_0 V_f\right]^{1/2} \tag{1}$$

where N_f is the number of molecules adsorbed at equilibrium, κ is the dielectric constant, n_0 the concentration of impurity centres in the semiconductor and V_f the height of the potential barrier. In practical terms, this equation implies that chemisorption should cease at very low coverages[8]. The heat of adsorption should fall as the coverage rises, the form of the dependence being parabolic ($\Delta Q = A + BN^2$)[2,4]. Temperature should be virtually without effect on the equilibrium until intrinsic behaviour becomes appreciable. Finally, any agency (e.g. irradiation) which modifies the Fermi level of the semiconductor may be expected to modify the adsorption equilibrium accordingly.

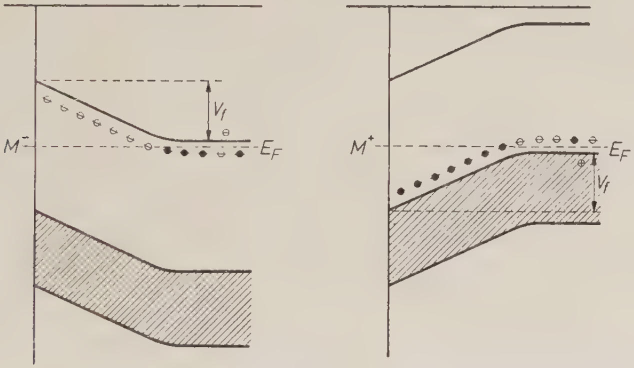

Figure 2.

It is interesting to enquire at this stage how far the model outlined above is supported by experimental observations on chemisorption. Taking as a criterion for depletive chemisorption an observed decrease in conductivity in the presence of adsorbed gas, established examples are as follows: O_2 on ZnO[10], O_2 on n-type Ge[11], O_2 on n-type PbS[12], O_2 on n-type Ag_2S[13], CO and H_2 on Cu_2O[14]. As expected, the electron-acceptor gas oxygen has to be associated with an n-type conductor, whilst the reducing gases H_2 and CO require a p-type conductor. Information concerning equilibrium coverages is rather fragmentary, but there are definite indications that they are, in fact, low. Thus, at 20°C, ~5 per cent coverage has been found for H_2 on Cu_2O[15], 1 per cent for CO on NiO and 3–6 per cent for CO on CoO[16]. However, true equilibrium in the sense of equation (1) may not be reached in these cases, for as the potential barrier of *Figure 2* develops, so the *rate* of electron transfer becomes progressively smaller[4] and may halt the adsorption prematurely. Since the rate of transfer increases with temperature[4], this provides a mechanism whereby coverage can increase with increasing temperature, even though equation (1) itself allows virtually no temperature dependence. Such a phenomenon, of course, is familiar as Taylor's 'activated adsorption'. The problem of these false equilibria has been specifically discussed for the case of oxygen on zinc oxide[17]. Very few heats have been reported for cases of depletive chemisorption; moreover, in view of the small limiting coverages, measurement of the dependence upon coverage becomes difficult. It has been shown, however, that for CO on CoO the heat of adsorption certainly falls rapidly[16]. A parabolic dependence of heat of adsorption upon coverage has recently been claimed for the case of CO_2 on zinc oxide at 450–500°C[7]. Although conductivity measurements are lacking, this is likely to be an example of depletive chemisorption and as such is in line with the theory. It is significant that, despite a high heat of 48 kcal/mole, the limiting coverage in this case was below 1 per cent. There is a real need for more experimental data on coverages and heats in depletive chemisorption. As far as the existing results go, however, the agreement with the simple theoretical model is encouraging.

The type of chemisorption reviewed above is peculiar to semiconducting systems and has been discussed in some detail in the present context for that reason. It is important to realize, however, that numerous established cases of chemisorption on semiconductors do not come into this category. Among these are some which have been studied in detail, e.g. the chemisorption of oxygen on the *p*-type oxides Cu_2O, NiO, and CoO, and the chemisorption of hydrogen on zinc oxide. For the majority, conductivity measurements show that they are accompanied by an *increase* in the number of carriers in the surface of the semiconductor. It would appear that, in the model of *Figure 1*, the donor or acceptor levels of *M* must now lie outside the gap, being either above the conduction band or below the top of the valence band. This situation, therefore, is analogous to that which prevails for chemisorption on metals and insulators. Due to the very high level density in the allowed bands, the limitation on equilibrium coverage found in depletive chemisorption no longer applies. This is certainly borne out in practice; high coverages have been reported in all the special examples cited above. It is likely that polarization phenomena and covalent bonding play a large part in determining the characteristics of chemisorption of this type. As regards heats of absorption, concerning which there is still much theoretical speculation[10], the two cases most fully studied on semiconductors, viz. O_2 on Cu_2O and O_2 on CoO, show an initial fall followed by very little dependence of heat of adsorption upon coverage[16].

The chemisorption of hydrogen on zinc oxide calls for special mention. Although calorimetric measurements of the heat of adsorption are lacking, this system has been extensively studied from a number of points of view and the behaviour observed illustrates certain general aspects of chemisorption on semiconductors. Below 100–120°C, hydrogen is readily chemisorbed on zinc oxide, probably with a low heat of adsorption. On raising the temperature above 120°, TAYLOR and LIANG observed that hydrogen is first desorbed and then slowly re-adsorbed[19]. They concluded that different adsorption centres are involved in the high-temperature chemisorption. The distinction between the two kinds of chemisorption has recently been sharply accentuated by the work of KUBOKAWA and TOYAMA[20]. These authors noted that, below 110°, hydrogen chemisorption was without appreciable effect on the conductivity of zinc oxide. Above this temperature, however, the adsorption was always accompanied by a substantial increase in conductivity. There is no unique interpretation of this behaviour at the present time. One possibility which may be envisaged is that hydrogen atoms are entering interstitially into the surface layers of the zinc oxide lattice during chemisorption, and that above 120° these are able to act as donor centres by virtue of dissociation into protons and electrons. The equilibrium which such a dissociation involves will be affected by the concentration of quasi-free electrons already prevailing in the zinc oxide. It is therefore of particular interest that the adsorption of hydrogen on zinc oxide containing altervalent additives has now been investigated[21]. It is found that for lithium-containing ZnO, in which the concentration of quasi-free electrons is low, the quantity of chemisorbed hydrogen at 200°C is considerably greater than for the highly-conducting gallium-containing oxide. The notion of interstitially bound hydrogen is also in accord with the fact that hydrogen can be desorbed as such at all but the highest temperatures. The more conventional interpretation of the behaviour supposes that, in contrast to the chemisorption in the lower range of temperature, the high-temperature form represents some kind of chemical combination with the oxygen ions of the zinc oxide lattice. Thus the reaction

$$2O^{2-} + H_2 \rightarrow 2OH^- + 2e$$

yielding electrons to the oxide may be readily visualized, and there is little doubt but that this reaction takes place at sufficiently high temperatures. This idea has now been developed by MORRISON[17], who actually anticipated the result obtained by KUBOKAWA and TOYAMA[20]. Morrison proposed that zinc oxide surfaces evacuated below 500°C contain residual *adsorbed* oxygen, some of which is present in the form of O^-_{ads}, some as O^{2-}_{ads}. Chemisorption of hydrogen at low temperatures was then considered as interaction with O^-_{ads} (no electrons being liberated), while chemisorption at high temperatures is considered as interaction with O^{2-}_{ads} lying at a higher level of energy, analogous to the reaction above.

There is ample evidence to support the concept of chemical combination with lattice oxygen (or sulphur) during chemisorption on oxide and sulphide semiconductors. The main studies have been concerned with the chemisorption of carbon monoxide, so extensively investigated by GARNER[22]. This particular problem is currently being tackled by calorimetric methods[16], by isotope exchange[23], and by infra-red absorption studies of the chemisorbed species[24]. It is apparent that, under many conditions, the combination is sufficiently strong to preclude the desorption of carbon monoxide as such, the gaseous product obtained being carbon dioxide. WINTER[23] has shown, however, that this is not an inevitable consequence of complex formation. He concludes from his isotope-exchange work that reversible dissociation of a CO_3 entity can take place on cuprous oxide. This bears appropriately upon the interpretation of the chemisorption of hydrogen on zinc oxide discussed above. Chemisorbed complexes with lattice oxygen may be stable up to high temperatures, a property which may sometimes bear adversely upon their behaviour as catalysts. CO_3 formation on nickel oxide is a specific case where, because of the formation of a tightly bound complex, the activity in heterogeneous catalysis does not run parallel with activity in chemisorption[16]. Interaction with lattice anions is also prominent in chemisorption on sulphides; the practice of sensitizing lead sulphide detectors by heating in oxygen necessitates the binding of chemisorbed oxygen in the form of stable sulphur–oxygen surface complexes[25].

In considering the complexes which reducing gases form with compound semiconductors, it is interesting to speculate whether a reversible form of chemisorption is not always a prerequisite. In this respect, the property of semiconductors to exhibit depletive chemisorption takes on a new significance. As far as studies with carbon monoxide and hydrogen on oxides and with oxygen on sulphides are concerned, the existence of reversible chemisorption can invariably be revealed if the studies are made at sufficiently low temperatures. The transition giving irreversible complex formation requires an activation energy. Although this may be concerned entirely with the promotion and redistribution of electrons, one may expect that in the general case some movement of the adsorbed ion or atom into a new position will be necessary. Lattice defects in the solid surface may therefore exert a controlling influence upon the transition.

The role of ionic processes in chemisorption on semiconductors is often of equal importance to that of pure electronic effects. Apart from one of the earlier papers of VOLKENSTEIN[26], however, the part played by lattice defects *per se* has been very much ignored in the theoretical treatments. There are a number of cases where ionic factors primarily determine the pattern of behaviour. On cuprous oxide and cobalt oxide, for example, oxygen is chemisorbed in excess of a monolayer at room temperature; the incorporation probably arises from the movement of cations into the interstices of the adsorbed layer, cation vacancies being formed in the surface layers of the oxide[16]. Secondly, interstitial sites may be used in chemisorption; the possibility of interstitial hydrogen in zinc oxide has already been mentioned, and an authenticated case of an interstitially accommodated species is that of oxygen chemisorbed on uranium dioxide[27]. Thirdly, we may recall the effect of temperature upon lattice defects in respect of both generation and propagation: the mobility which results is manifest at the surface well below the Tammann temperature. The activity of refractory oxides such as MgO and TiO_2 towards oxygen exchange at fairly low temperatures[23,28] is a direct consequence of the operation of this factor.

It is evident from the preceding paragraphs that our main knowledge of chemisorption on semiconductors stems from studies on metallic oxides and sulphides. With a few exceptions[5,10,29,30], work in this field on elemental semiconductors has received very little attention. However, in view of the elegant techniques which are now available for the preparation of single crystals of pure germanium and silicon and for the measurement of their electrical properties, specific investigations of the behaviour of these semiconductors in chemisorption would be most valuable. Studies of adsorption isobars and heats of adsorption on these crystals will nevertheless require the development of new techniques. But as far as the study of pure electronic effects (i.e. without complications from ionic factors) in semiconductor chemisorption is concerned, work on germanium crystals offers particularly challenging opportunities. In this connexion, the work of LAW and his collaborators[29] is especially noteworthy. Interest in the more general aspects of chemisorption on oxide and sulphide semiconductors must still remain, however, if only because of their established application in heterogeneous catalysis.

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4.2

STUDIES OF CHEMISORPTION ON OXIDES USING ^{18}O

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SUMMARY

The kinetics of the exchange of ^{18}O *between* O_2 *gas and the surface of (mainly) semiconducting oxides are reviewed and discussed and some new data presented. The exchange of oxygen between* CO, CO_2, *and a* Cu_2O *surface is appreciable at low temperatures; earlier work on* Cu_2O *is reviewed and data on* ZnO *presented. On the latter oxide,* CO_2 *suffers exchange with* $E = 0$ *between* 20 *and* 280°C; *the exchange of* CO *has* $E = 14{\cdot}5$ kcal mole^{-1} *between* 208 *and* 280°C *and the isosteric heat of adsorption is* 9·0 kcal mole^{-1} *between* −20 *and* 20°C. *Preliminary experiments on the exchange of* CO *and* CO_2 *with other oxides are mentioned. It is concluded, in agreement with earlier workers, that in many cases* CO *can be chemisorbed in two ways, only that operating at higher temperatures leading to oxygen exchange, which, however, occurs in general at lower temperatures than has hitherto been thought, and with no reduction of the oxide.*

The application of these techniques to studies of the mechanism of the catalysed decomposition of N_2O *and of the* CO–O_2 *reaction is briefly discussed. The* N_2O *decomposition on* NiO *and mixed* NiO–*metal oxide preparations proceeds on a small fraction of the surface sites, with oxygen from the lattice participating and appearing in the oxygen gas formed: the proportion of active sites increases with increasing temperature. Similar results are presented for the* CO–O_2 *reaction. The two reactions occur on different sites on* NiO. N_2O *is reversibly chemisorbed on* NiO.

Comparisons are made of the extent of the exchangeable oxide surface, determined with O_2, CO, *and* CO_2 *and the area calculated from the* B.E.T. (N_2) *isotherms at* −196°C: *reasonable agreement is found.*

It is concluded that the oxide surfaces possess intrinsic heterogeneity and that this non-uniformity is modified by electronic changes during chemisorption.

INTRODUCTION

Current theories of chemisorption and of catalysis on oxides discuss the electronic factor in some detail, but in general treat the ionic oxide lattice as a rigid structure. This assumption is often true at around room temperature and below (although even here certain highly active preparations, such as Cu/Cu_2O prepared by the method of GARNER, STONE and TILEY[1], show considerable lability of oxygen), but at higher temperatures isotopic studies reveal ready transfer of oxygen between the solid and chemisorbed gases. The primary purpose of this paper is not to attempt to develop new theoretical conceptions, but to present and review some of the experimental evidence showing the way in which lattice oxygen itself takes part in the chemisorption step and often in catalytic reactions involving oxygen-containing gases. Such lability has been inferred, particularly by Garner and co-workers from their studies of heats of adsorption and semi-conductivity changes during chemisorption.

The first work showing by means of ^{18}O the lability of surface oxygen in oxides was that of the Japanese workers, MORITA and TITANI, starting in 1938, who showed, mainly by flow methods, that the surface oxygen of a number of oxides was readily exchangeable with either gaseous oxygen or water vapour, and also that oxygen exchange between oxygen gas and water vapour was catalyzed by these oxides. However, the method used was perforce somewhat crude and involved the use of relatively large amounts of water, or oxygen for subsequent conversion to water, for density determinations; it was not, therefore, possible for them to study the initial reactions in the surface layer: similar remarks apply to the work of ALAN and LAUDER[2] and to the Russian work in this field, for instance KARPACHEVA and ROZEN[3,4] and VASILEV, ELOVICH, and MARGOLIS[5].

The technique and general procedure used in the present work and the interpretation of the isotopic-exchange kinetics have been given elsewhere, together with more detailed accounts and discussion of much of the work (WINTER *et al.*[6–13]).

CHEMISORPTION AND ISOTOPIC EXCHANGE OF OXYGEN

The process of oxygen adsorption/desorption and isotopic exchange on an oxide surface may be written in the following fashion, where $^{18}O_2$ or ^{18}O represents a species enriched in ^{18}O.

$$^{18}O_2 \rightleftharpoons {}^{18}O_{2(ads)} \tag{1}$$

$$^{18}O_{2(ads)} \rightleftharpoons 2{}^{18}O_{(ads)} \tag{2}$$

$$2e^-_{(s)} + 2{}^{18}O_{(ads)} \rightleftharpoons 2{}^{18}O^-_{(ads)} \tag{3}$$

$$2e^-_{(s)} + 2{}^{18}O^-_{(ads)} \rightleftharpoons 2{}^{18}O^{2-}_{(ads)} \tag{4}$$

$$2{}^{18}O^{2-}_{(ads)} + 2{}^{16}O^{2-}_{(s)} \rightleftharpoons 2{}^{16}O^{2-}_{(ads)} + 2{}^{18}O^{2-}_{(s)} \tag{5}$$

Where equation (5) may be trivial if, as is possible, $O^{2-}_{(ads)}$ is indistinguishable from $O^{2-}_{(s)}$. In addition, there may be rate-limiting processes associated with the migration of adsorbed species or solid defects in the surface layers. Not all of these steps may occur, or be separable, on all oxides. Step (1) is the physical adsorption of oxygen; (2) is unlikely to occur by itself, since it would be strongly endothermic due to the energy required to break the oxygen—oxygen bond, and it must therefore be combined with (3), or with (3) and the subsequent steps together in particular cases, the electron affinity of oxygen providing part of the energy needed. The electrons e_s^- are donated by the solid lattice: when electron sharing between the solid and the adsorbed gas occurs, changes in electrical conductivity of the oxide are detectable, and detailed studies of these changes throw light on this part of the process (c.f. GARNER, GRAY, and STONE[14]; GARNER, STONE and TILEY[1]; GRAY and DARBY[15]; BEVAN and ANDERSON[16]). Other methods of following particular stages of the process include measurements of magnetic susceptibility. Similarly, the overall rate of adsorption (or desorption) of the gas may be directly measured by the usual methods.

Equations (2)–(5) above may be rewritten, using the symbolism proposed by REES[17], in a manner which emphasizes the part played by the solid. Thus for a *p*-type oxide, e.g. NiO,

$$\tfrac{1}{2}{}^{18}O_{2(\mathrm{ads})} + \square_s^- + \square_s^+ \rightleftharpoons ({}^{18}O \mid \square_s^-) + \square_s^+ \tag{2'}$$

$$({}^{18}O \mid \square_s^-) + \square_s^+ \rightleftharpoons ({}^{18}O^- \mid \square_s^-) + (p \mid \square_s^+) \tag{3'}$$

$$({}^{18}O^- \mid \square_s^-) + (p \mid \square_s^+) \rightleftharpoons ({}^{18}O^{2-} \mid \square_s^-) + (2p \mid \square_s^+) \tag{4'}$$

or for an *n*-type conductor, e.g. ZnO, assuming the participation of interstitial zinc:

$$\tfrac{1}{2}{}^{18}O_{2(\mathrm{ads})} + \square_s^- + \square_s^+ + (e_2 \mid Zn^{2+} \mid \Delta) \rightleftharpoons \Delta + (Zn^{2+} \mid \square_s^+) + ({}^{18}O^{2-} \mid \square_s^-)$$

Isotopic exchange then depends on the reversal of (4′), or its equivalent, involving neighbouring $^{16}O^{2-}$ ions from the original oxide lattice, according to (5).

The work on the isotopic exchange of gaseous oxygen with oxide surfaces reviewed here comprises:

1. Studies of the overall exchange reaction, using usually normal oxides and gas containing 1·0–15·0 atom per cent ^{18}O excess.
2. Studies of the equilibration reaction

$$^{16}O_2 + {}^{18}O_2 \rightleftharpoons 2\,{}^{16}O^{18}O$$

using a 1:1 mixture of normal oxygen and oxygen containing 30 per cent ^{18}O.

3. Miscellaneous complementary experiments including measurements of semiconductivity and of the rates of adsorption and desorption of oxygen.

The conclusions so far reached may be summarized by reference to *Figures 1–4.*

Figure 1. ZnO[10]. Along *A'AB*: adsorption-desorption, involving dissociation. In this temperature range pellets of ZnO, outgassed at higher temperatures, show a change of conductivity on exposure to oxygen and we, therefore, suggest that here we are following reactions (2) and (3) above. Along *C'CA D*: surface migration of oxygen, presumably as $O^-_{(ads)}$. Along *K'C K*: the exchange reaction proper, probably effectively reaction (4).

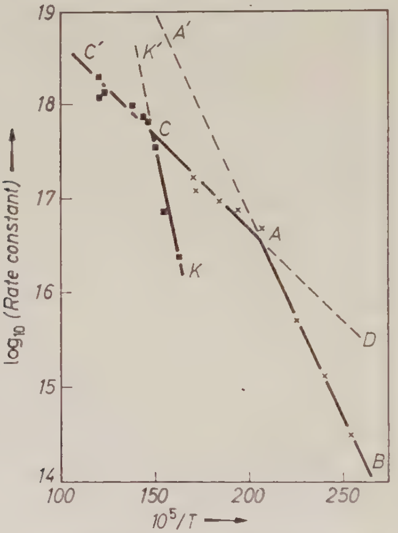

Figure 1. ZnO, outgassed for *c.* 16 hours at 630°. ×: equilibration; ■: exchange.

Figure 2. MgO[10]. Along *F'F G*: dissociative adsorption/desorption. The electrical conductivity of MgO pellets is too small to detect any change of semiconductivity with change of oxygen pressure at these temperatures, but one imagines that reactions (2) and (3) are involved. Nevertheless, it is curious that, if this is the case, these reactions occur much more readily, at say 230°C, on MgO which is virtually an insulator than on the semiconducting ZnO, even allowing for a twelve-fold difference in surface area. *J'I J* represents the true exchange reaction (4).

Figure 3. NiO, Cr_2O_3, and Fe_2O_3[13]. In all three cases the lines of steepest slope represent the dissociative adsorption-desorption of oxygen: this has been confirmed by independent measurements of the rates of oxygen adsorption at constant pressures and various temperatures and coverages. Evidently here either reaction (4) occurs more readily than (2) and (3) or the act of dissociative adsorption involves a direct change from O_2 (ads) to $2O^{2-}$. The

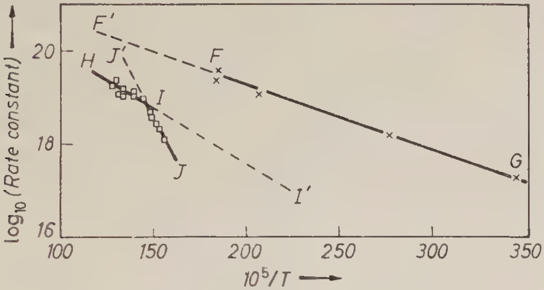

Figure 2. MgO, outgassed *c.* 16 hours at 540°.
×: equilibration; □: exchange.

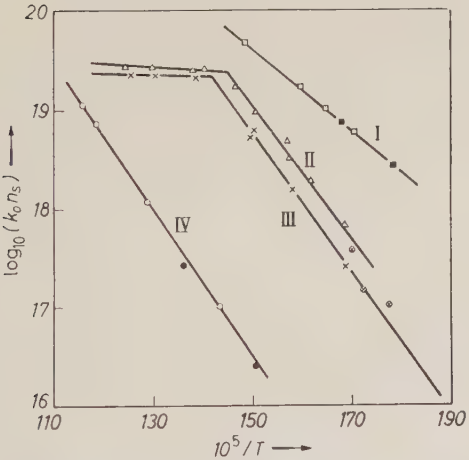

Figure 3. Exchange and equilibration experiments.
□ ■: exchange and equilibration on Fe_2O_3, outgassed at 450°; $P_{O_2} = 5{\cdot}7$ cm.
△: exchange on Cr_2O_3 (*A*), outgassed at various temperatures between 385° and 520°; $P_{O_2} = 6{\cdot}5$ cm.
× ⊗: exchange and equilibration on Cr_2O_3 (*B*), outgassed at 630°; $P_{O_2} = 6$ cm.
○ ●: exchange and equilibration on NiO, outgassed at 605°; $P_{O_2} = 6$ cm.

conditions, of course, need not be the same on all three oxides. These results indicate that adsorption/desorption of oxygen on a NiO surface saturated with oxygen occurs with $E \approx 34$ kcal mole^{-1}. GRAY and DARBY (loc. cit.), from semiconductivity studies on NiO films at much lower pressures, find $E \approx 32$ kcal mole^{-1} for the overall adsorption reaction. The line of practically zero slope, for Cr_2O_3, must represent the diffusion of either adsorbed oxygen or of surface defects promoting adsorption or exchange.

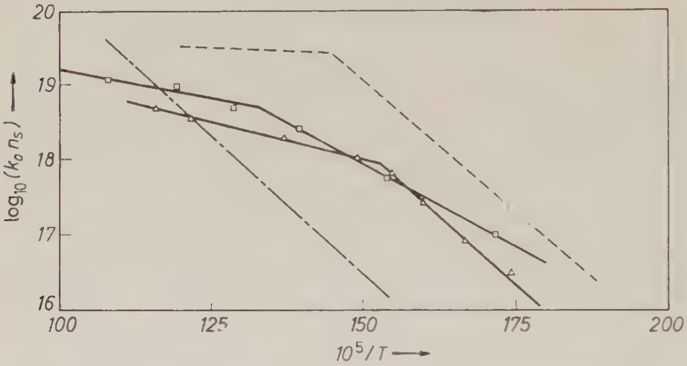

Figure 4. Exchange and equilibration experiments.
— · — · — : NiO (cf. *Figure 3*); — — — — : Cr_2O_3 (cf. *Figure 3*);
☐ : NiO + 0·01 M per cent Cr_2O_3; △ : NiO + 0·01 M per cent Li_2O.

Figure 4. NiO with admixtures of various foreign oxides. All these catalysts show the same type of behaviour as Cr_2O_3, and similar remarks apply. Over the temperature range 300–500°C the reactivities of these materials fall between Cr_2O_3 and pure NiO. It is worth noting that a study of the N_2O-decomposition on these same catalysts (WINTER, unpublished data) has given activation energies identical with those reported here for the adsorption/desorption of oxygen, as shown in *Table I*. This provides confirmation of the

Table 1

Oxide	E (kcal mole^{-1})	
	^{18}O *exchange*	N_2O *decomposition*
NiO	35 ± 2	34 ± 2
NiO + Li_2O*	35 ± 3	36 ± 3
NiO + Cr_2O_3*	16 ± 2	18 ± 2

* 0·01 molar per cent.

findings of WAGNER, HAUFFE *et al.*[18], that in many cases the desorption of oxygen is the rate-determining step in the catalytic reaction.

EXCHANGE REACTIONS OF CO AND CO_2 WITH Cu_2O AND ZnO

Cu_2O

These gases readily exchange their oxygen with that of the Cu_2O lattice surface at around room temperature; formation of CO_2 during the exchange of CO is negligible: $E \approx 4(CO_2)$ and $10(CO)$ kcal mole^{-1}. The results have been discussed elsewhere[12]: the mechanism suggested is (c.f. GARNER[19])

$$CO + 2(O^{2-} \mid \square_s^-) \rightleftharpoons (CO_3^{2-} \mid \square_s^-)(e_2 \mid \square_s^-) \tag{6}$$

$$CO_2 + (O^{2-} \mid \square_s^-) \rightleftharpoons (CO_3^{2-} \mid \square_s^-) \tag{7}$$

There is some disagreement between the results of this work and the conclusions drawn by GARNER *et al.* (loc. cit.) from their calorimetric and semiconductivity studies. The latter do not expect lattice oxygen to take part in the chemisorption process below about 50°C. In order to extend and confirm our findings, we have recently re-examined the matter using a somewhat different technique, a fresh preparation of Cu_2O, and lower temperatures.

The Cu/Cu_2O was prepared as before from hot ammoniacal $CuSO_4$ solution and hydrazine, washed, dried, and alternately oxidized and reduced three times before finally oxidizing (with normal oxygen) and outgassing for 24 hours at 180°C. The solid was cooled to -20 ± 2°C and sufficient CO added to give a residual pressure of $1{\cdot}28 \times 10^{-1}$ mm: after 66 minutes a sample of gas was collected over 100 minutes by means of a Puddington diffusion pump (PUDDINGTON[20]), analysed by the mass-spectrometer, and quantitatively returned to the adsorption system. The original CO contained 63·2 per cent ^{13}C with ^{18}O unequally distributed between ^{12}C and ^{13}C; the ^{18}O content calculated from masses 28 and 30 was 12·4 per cent and from masses 29 and 31, 1·33 per cent. The recovered sample showed no dilution of ^{13}C, but the ^{18}O was almost completely redistributed between the two isotopes, the figures now being 4·52 per cent (28/30) and 3·65 per cent (29/31); the overall ^{18}O content of the gas was originally 5·4 per cent and finally 3·9 per cent so that appreciable exchange with oxygen from the Cu_2O had occurred. Slightly less than an equal volume of normal CO was added, giving a residual pressure of 1·59 mm, and after 110 minutes a further sample of gas was collected (over 13 minutes only) and analyzed. This sample had 31·9 per cent ^{13}C and the oxygen was equally distributed between the two isotopes.

Successive samples were collected over the next 16 hours and showed slowly increasing ^{13}C content; viz. 32·3 per cent, 33·1 per cent and 34·5 per cent, the latter figure being the same as that found for the CO_2 liberated when the oxide was later regenerated with excess O_2 at 180°C. The overall recovery of ^{12}C and ^{13}C was not accurately determined but was well over 90 per cent.

A similar experiment was performed with the oxide at —78°C. The enriched CO was left for 4 hours in contact with the catalyst, at a residual pressure of $1{\cdot}04 \times 10^{-2}$ mm and a sample collected over 24 hours. This had the original ^{13}C content and $^{18}O = 4{\cdot}65$ per cent (28/30) and 2·92 per cent (29/31); oxygen exchange with the surface had occurred. The sample was returned to the system and normal CO added, giving a final pressure of 4·84 mm. A sample taken over 10 hours, commencing 22 hours after the adsorption, showed further oxygen exchange with the surface and about 30 per cent ^{13}C indicating almost completely uniform distribution of ^{13}C between the gaseous and adsorbed phase. The formation of CO_2 during these experiments was negligible.

After outgassing at 180°C and reactivation of the surface twice with excess O_2, followed each time by outgassing for 24 hours at 180°C, the sample was cooled to —78°C and CO_2 containing 1·152 per cent ^{18}O added to give a residual pressure of 1·02 mm. A sample collected over 2 hours commencing 24 hours after the adsorption had 0·839 per cent ^{18}O, showing appreciable exchange with oxygen from the Cu_2O.

Table II

Sample	*Gas*	$n_s \times 10^{-19}$ *	$\log_{10} (k_0 n_s)$ *	$10^5/T$
ZnO	CO_2	1·76	18·696	187·6
		1·32	18·654	196·8
		1·25	18·612	207·9
		1·58	18·699	225·8
		1·30	18·625	341·3
	CO	2·77	18·453	185·0
		2·19	18·265	187·6
		1·69	17·913	196·0
		1·16	17·725	207·9

* $(k_0 \; n_s)$ in atoms min.$^{-1}$ g^{-1}; n_s in atoms g^{-1}; n_s calculated from B.E.T. (N_2) area $\approx 4 \times 10^{19}$ atoms g^{-1}.

These experiments confirm and extend our earlier work and demonstrate considerable lability both in the adsorbed layer and between that and the gas phase at low temperatures. They may be compared with those of WEBB and EISCHENS[21] showing similar effects in the chemisorption of CO on iron.

ZnO

Chemisorption of both gases occurs readily on this oxide (c.f. GARNER and MAGGS[22], GARNER and VEAL[23], GARNER[24]); we have studied the exchange of ^{18}O between gas and surface and find $E = 14{\cdot}5$ (CO) and 0 (CO_2) kcals mole^{-1}, at pressures of 3–6 cm and over the temperature range 208–280°C (CO) and 20–280°C (CO_2) (*see Table II*). The formation of CO_2 during the exchange reactions of CO was negligible. The very ready exchange of CO_2 is not surprising since the pressure of CO_2 over pure $ZnCO_3$ is about $7{\cdot}6 \times 10^{-1}$ mm at 33°C and 7·6 mm at 93°C (*Contributions to the Data on Theoretical Metallurgy IV*, U.S. Bureau of Mines, Bulletin 384, 1935); the exchange of CO_2 may be written as for the case of Cu_2O, equation (7), and that of CO in a similar fashion to equation (6).

$$CO + 2(O^{2-} \mid \square_s^-) + \Delta + (Zn^{2+} \mid \square_s^+)$$
$$\rightleftharpoons (CO_3^{2-} \mid \square_s^-)(e_2 \mid Zn^{2+} \mid \Delta) + \square_s^- + \square_s^+ \qquad (8)$$

These equations do not indicate any great difference of view from that of Garner *et al.* The isotopic technique has, however, demonstrated that mixing of oxygen between gas and surface and between adsorbed species can occur at lower temperatures than had been thought: it also provides quantitative information of the extent and kinetics of the exchange.

Earlier work has shown that CO can be chemisorbed in two ways on ZnO—described by GARNER[19], as reversible and irreversible—the former occurring around room temperature with a heat at high coverage of about 13 kcals mole^{-1} (GARNER, MAGGS, loc. cit.), and we have confirmed this for our preparation, finding $\Delta H = 9{\cdot}0$ kcal mole^{-1} between 250 and 293°K. No unsaturation of the surface towards oxygen was produced in this case (GARNER and VEAL, loc. cit.), and we found that isotopic exchange at room temperature was exceedingly slow; it may be noted that the extrapolated rate constant is about $1{\cdot}9 \times 10^{13}$ atom g^{-1} min.$^{-1}$ at 17°C. Clearly, at this temperature, chemisorption does not involve equation (8) to any significant extent. It may well be that, as suggested by GARNER[24], the adsorption involves two sets of sites—possibly CO is adsorbed at room temperature upon zinc ions as a positively-charged complex as has been suggested for H_2 on oxides (GARNER, loc. cit.). This picture is rendered more plausible by the adsorption isobar of CO on our ZnO, shown in *Figure 5*; it is seen that the lower temperature chemisorption (with $\Delta H = 14{\cdot}7$ kcal mole^{-1}) rapidly decreases, the minimum being found at about 150°C. Above this temperature the quantity adsorbed increases with temperature: this second type of chemisorption is associated with hysteresis and occurs over the temperature range in which ^{18}O exchange is readily measurable.

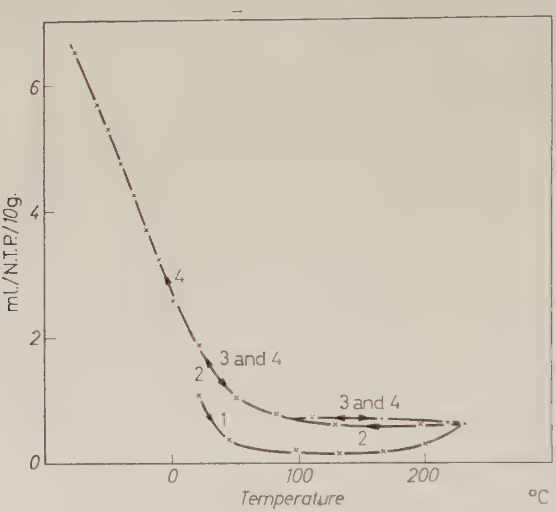

Figure 5. Isobar of CO at 3·67 cm. on ZnO.

EXCHANGE REACTIONS OF CO AND CO_2 WITH NiO, Cr_2O_3, MgO AND Fe_2O_3

Detailed examinations of these systems have not yet been made; preliminary experiments were performed to find at what temperatures exchange is detectable in order to see if the isotopic method could be used to determine the mechanism of the CO–O_2 reaction catalysed by these oxides. In the cases of MgO and Fe_2O_3, exchange occurs only at temperatures around those at which the catalytic reaction is first readily measurable, but this is not so for NiO and Cr_2O_3 where the CO-oxidation proceeds at much lower temperatures than ^{18}O exchange.

Since chemisorption of CO occurs on NiO at room temperature and below, whereas isotopic exchange requires higher temperatures, similar remarks to those of the last paragraph of the last section probably apply here. It may be remarked, however, that the case of NiO is not so well defined as there is some disagreement in the literature on this system; c.f. DELL and STONE[25], TEICHNER and MORRISON[26].

APPLICATION TO CATALYTIC REACTIONS

We have used our knowledge of the reactive surface obtained from these isotopic-exchange reactions to determine approximately the fraction of the surface sites active in certain catalytic reactions, e.g. the decomposition of N_2O and the oxidation of CO by O_2. In this work the oxide surface was first enriched by a higher-temperature exchange reaction with oxygen and then outgassed and cooled to the temperature of the catalytic reaction. The reactant gas was added and the ^{18}O content of reactant and product was followed[12]. It was, of course, necessary to ensure by parallel experiments (*see* the last section), that neither reactant nor product alone undergoes oxygen exchange with the surface at the temperature and pressure of the catalytic reaction. From this work it transpires that in many cases only a small proportion of the surface oxygen is active in catalytic reactions, as shown in *Table III.* We assume that only those sites are active which yield their ^{18}O to the product gas (O_2 or CO_2, respectively). It is interesting to note that from these results one can calculate approximately the order of reactivity of these active sites and it turns out to be extraordinarily low even in cases where the overall catalytic reaction under the

Table III

Oxide	*Gas*	*Temp.*	*x* *
NiO	N_2O	275 330	3·25 5·31
NiO + Li_2O †	N_2O	227 330	6·9 21·4
NiO + Cr_2O_3 †	N_2O	255 288	4·8 5·2
NiO	CO + O_2	49 112 151 211	0·34 0·93 1·46 2·28
Cr_2O_3	CO + O_2	44 91 155	2·05 1·52 2·05

* x = per cent of surface oxygen taking part in the catalytic reaction.
† 0·01 molar per cent.

conditions used might by other criteria be regarded as fairly fast. Thus, considering an experiment upon the decomposition of N_2O upon NiO at 275°C, it was found that the $3{\cdot}8 \times 10^{18}$ of reactive sites per gram decomposed on an average one molecule of N_2O every 20 minutes. A further interesting observation made possible by the isotopic technique is that catalysts such as NiO which are active both in the CO oxidation and in the N_2O decomposition utilize *different* reactive sites for the two reactions; thus these two reactions can be performed alternately upon NiO^{18}, and by measuring the ^{18}O in the product in each case one can show by stoichiometry that two different sets of sites are involved and that these sets are progressively stripped of ^{18}O.

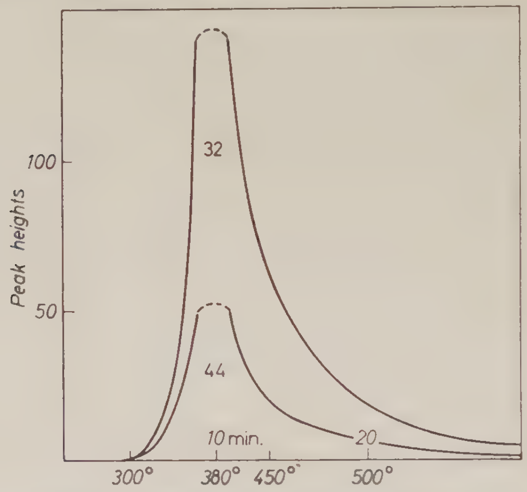

Figure 6. Desorption of chemisorbed O_2 and N_2O from NiO on heating.

The per cent x, of the total surface n_s (*see* below) which takes part in a catalytic reaction by releasing ^{18}O into the product gas often increases with increasing temperature, as shown by *Table III.* In such cases the activation energy for increase of x with temperature is low, of the order of 2–4 kcal, which is of the same magnitude as the increase of n_s with temperature found during exchange reaction with gaseous oxygen at higher temperatures.

An interesting observation made during studies of the N_2O decomposition was that N_2O is (reversibly) chemisorbed on NiO during the catalytic reaction and that this can be detected at temperatures around those at which appreciable decomposition occurs. This is illustrated by *Figure 6*; similar observations have been made on various NiO preparations, such as those shown in *Figure 4*, and, though with more difficulty, on Cr_2O_3. This result was communicated to Dr. Stone and I understand that he has since been able to measure the heat of chemisorption of N_2O on CoO at room temperature. *Figure 6* was obtained by exposing the catalyst to several cm of N_2O for 20 min. (by which time under the conditions used $\sim$10 per cent of the N_2O had decomposed), pumping out rapidly to $\sim 10^{-3}$ mm, isolating the reaction system from the pump, and connecting directly with the ionization region of the mass-spectrometer without the intervention of the normal capillary leak. The temperature of the reaction vessel was then rapidly raised, and the peaks due to O_2 and N_2O measured with the results shown.

These findings have obvious applications to the mechanism of these catalytic reactions: for instance it seems clear that the currently accepted mechanism for the N_2O decomposition

$$N_2O + e^- \text{ (from catalyst)} = N_2 + O^-$$

$$O^- = \tfrac{1}{2}O_2 + e^- \text{ (to catalyst)}$$

or

$$O^- + N_2O = N_2 + O_2 + e^- \text{ (to catalyst)}$$

(Stone[27] and Hauffe[18]) is incorrect since the surface oxygen plays an essential part in the reaction. This has been confirmed by detailed isotopic and kinetic studies of this reaction on various catalysts (Winter, unpublished data).

NATURE AND EXTENT OF THE OXIDE SURFACE

The isotopic-exchange experiments, performed in a closed system with virtually no change of reactant concentration during the course of the reaction, readily yield figures for the number of surface oxygen atoms (ions) per g of oxide undergoing exchange with the gas phase. We call this n_s:

$$n_s = \frac{n_g}{w}\left(\frac{\alpha_0 - \alpha_\infty}{\alpha_\infty - \beta_0}\right) \tag{9}$$

where n_g = number of atoms of oxygen in the volume of gas used.

w = weight of oxide in grams.

α_0, α_∞ = ^{18}O content of the gas at the beginning and end of the reaction.

β_0 = ^{18}O content of the solid surface at the beginning of the reaction.

(The assumption is made that $\beta_\infty = \alpha_\infty$ (Winter[6]).)

n_s Values obtained from relatively high temperature experiments involving exchange with gaseous oxygen, although showing some scatter, in most cases increase with increasing temperature. The apparent activation energy in all cases so far studied lies between 0 and about 8 kcal: n_s values obtained in the 400 to 600°C temperature range show a distinct parallelism with the surface areas found by application of the B.E.T. method to low-temperature nitrogen isotherms (*Table IV*). As is shown by the observations on MgO, the onset of sintering is clearly detectable by a rapid fall in the extent of the exchangeable surface. There seems little doubt from these results that the B.E.T. method, in spite of its poor theoretical basis, provides a close approximation to the true oxide surface.

Table IV

Oxide	*Temp.*	$n_s \times 10^{-20}$	
		from exch.	*from* B.E.T.
Cr_2O_3 (*A*)	380–600	1·8	3·0
Cr_2O_3 (*B*)	320–522	0·8	1·4
NiO	486–570	~1·0	0·70
Fe_2O_3	300–400	~6·5	5·0
MgO	370–507	~5·0	6·0
	866*	0·286	1·88
	748*	1·72	3·67
	640*	3·02	3·31
	600*	4·00	3·44
	540*	4·53	3·86
	510*	6·97	6·15
ZnO	380–580	~1·0	~0·40
(with CO_2)	20–240	~0·15	~0·40
(with CO)	208–268	~0·20	~0·40

* Outgassing temperature; exchange reaction at 460°C.

Exchange reactions using CO and CO_2, *Table IV*, show a similar order for the reactive surface, although these experiments have usually been conducted at lower temperatures than those with oxygen. It is possible that these two gases would show some penetration of the surface on raising the temperature, and indeed reproducible measurements of adsorption isotherms of CO on ZnO at 160°C and upwards proved impossible because of hysteresis and slow approach to equilibrium: this was in spite of treatment (between experiments) with ~5 cm O_2 at 510°C for 24 hours followed by 18 hours outgassing at this temperature (*see also Figure 5*).

As discussed in the first section, in detailed studies of the kinetics of the exchange reactions with oxygen gas it was in many cases found that the kinetics showed a change in mechanism somewhere in the 400–500°C region, the activation energy changing from 20–40 kcal (lower temperatures) to 0–8 kcal at temperatures above the inflection point. Parallel studies of the adsorption of oxygen showed that under reaction conditions even upon *p*-type oxides and upon Cr_2O_3 the surface coverage with oxygen is small, ranging from 1–15 per cent; upon *n*-type oxides and MgO the saturation coverage is very much less, usually below 0·1 per cent. Similarly, the coverage of ZnO by CO is small (~3 per cent) during the isotopic exchange of oxygen in this system. Nevertheless, in all cases, fairly rapid isotopic exchange takes place between the gas phase and virtually the whole of the surface layer of the oxide, so that either the defects promoting chemisorption migrate about the surface, or the chemisorbed gases themselves migrate so that effectively all the surface suffers isotopic exchange.

These observations suggest we are dealing with non-uniform oxide surfaces: this heterogeneity is almost certainly caused by edges, corners, and dislocations and by the presence in the immediate sub-surface layers of lattice defects: the specificity of a few fixed sites on NiO surfaces for certain catalytic reactions illustrates the heterogeneity very well. There is, of course, much earlier evidence for the existence of heterogeneity in systems similar to those studied here, for instance the high initial heats of adsorption of H_2 and CO on ZnO/Cr_2O_3 catalysts (GARNER and KINGMAN[28]), and similar observations by BEEBE and DOWDEN[29] on Cr_2O_3. Heterogeneity is also undoubtedly induced by the electronic changes involved in the chemisorption process, and this is the basis of the theoretical treatments of HAUFFE[18], WEISZ[30], and AIGRAIN and DUGAS[31], who however assume an initially uniform surface, as does DOWDEN[32]. It may be that such theories can be adapted in something like their present form to the relatively small number of highly active surface sites involved in the original act of chemisorption, but in view of the specificity and rarity of these sites it is probable that important geometric factors are concerned which may often obscure theoretical relationships.

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4.3

CHEMISORPTION ON CUPROUS, NICKEL, AND COBALTOUS OXIDES

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Cuprous, nickel, and cobaltous oxides are among the most active of catalysts for the oxidation of carbon monoxide, each oxide being able to effect the conversion at room temperature. These oxides also are all *p*-type semiconductors, containing a stoichiometric excess of oxygen. One of the interesting problems in heterogeneous catalysis at the present time is to decide to what extent these properties (and other parallels of this kind) may be directly related. The catalytic activity is conceivably related to the semiconducting property *per se*, by virtue of favoured electron-transfer processes at the gas/solid interface. It may equally arise from the specific ability of the oxides to release and absorb oxygen, as manifested by their oxygen excess. These questions cannot be answered effectively until a large body of experimental data has been accumulated. The present paper contributes by making a detailed comparison of the properties of the above oxides, both in the chemisorption of the individual gases concerned and in their promotion of the various steps which lead to the union of carbon monoxide and oxygen in the adsorbed phase. The main emphasis is on calorimetric measurements. Isolated accounts of the calorimetric work at Bristol on cuprous oxide[1] and nickel oxide[2] have already been published; the studies on these oxides are now reviewed in the light of new work on cobaltous oxide.

EXPERIMENTAL METHOD

The adsorption studies have been made on thin films of the oxide (*c.* 100 Å in thickness) formed by oxidation of the parent metal. Copper metal was prepared by reduction of an aqueous suspension of $Cu(OH)_2$ with an excess of hydrazine. Nickel and cobalt were prepared by thermal decomposition *in vacuo* of nickel oxalate and cobalt formate, respectively. For calorimetric studies the metal samples were incorporated in calorimeters of the Garner-Veal type[3] and after reduction with hydrogen the oxide film was produced *in situ*. Cu_2O, NiO, and CoO films were formed by controlled oxidation at temperatures up to 150°, 300°, and 200°, respectively.

Surface areas were obtained by B.E.T. measurements with krypton at −183°. Monolayer coverages of chemisorbed gases are calculated from the measured surface areas and the number of adsorption sites per sq. cm[1].

THE ADSORPTION OF OXYGEN

CUPROUS OXIDE

Oxygen is readily adsorbed by cuprous oxide over a wide range of temperature and pressure. The main feature of the adsorption is that it proceeds beyond a monolayer, indicating that some kind of incorporation of oxygen in the oxide is taking place. The kinetics of this reaction have been studied in considerable detail[1,4]. The first part of the adsorption process has been shown to obey the relationship for activated dissociated chemisorption

$$\frac{d\theta}{dt} = kp(1 - \theta)^2 \exp(-E/RT) \tag{1}$$

the coverage θ being set equal to unity for the calculated monolayer value (*q.v.*). The activation energy E is 7 kcal/mole. Beyond the monolayer, the rate of chemisorption accurately obeys the Roginsky-Zeldovich[5] equation, the integrated form of which is

$$q = k \log(\tau + \tau_0) - k \log \tau_0 \tag{2}$$

The heat of adsorption has been measured for coverages up to 50 per cent (*Table I*). Each heat corresponds to a small range in coverage, as indicated. The heat is independent of film thickness in the range 16–170 Å.

Table I

Coverage θ per cent	0–4	0–5	5–8	0–11	11–17	47–50
Molar heat of adsorption (kcal)	62	61	57	55	52	54

No oxygen can be desorbed at room temperature. As the temperature of the adsorbed film is raised, any oxygen which is not desorbed is used in further oxidation of the underlying copper. The activity of the surface towards adsorption of gases can be fully and reproducibly restored by heating the surface to 200° for 16–20 hours. In terms of the stabilization of intrinsic heterogeneity (a necessary requirement for studies of kinetics of chemisorption), this ability to regain the equivalent surface by such a gentle treatment has obvious advantages.

NICKEL OXIDE

Unlike cuprous oxide, the extent of adsorption of oxygen on NiO is limited by the inability to clear the surface of previously adsorbed oxygen. The volume adsorbed is critically dependent on the 'baking-out' procedure[2]. After heating *in vacuo* at 380°, the total uptake of oxygen at 20° and 0·5 mm corresponded to only 8–10 per cent of a monolayer. Rapid adsorption was observed, but no formal studies of kinetics have been undertaken in our laboratory. We refer later, however, to some measurements of rates at high pressures made by ENGELL and HAUFFE[6].

The integral heat of adsorption over the coverage range quoted above was found to be 43 kcal/mole. In a subsequent experiment, the admitted charge of gas was divided into two increments. A heat of 54 ± 4 kcal/mole was recorded for the first increment and 20 kcal/mole for the second. These values are in marked contrast to the constancy found with cuprous oxide. The rapid fall in heat with a total obtainable coverage of < 10 per cent indicates that the measurements were made on an almost covered surface.

COBALT OXIDE*

Cobalt oxide behaves similarly to cuprous oxide. The adsorption at 20° and 0·5 mm proceeds to a monolayer and beyond. The dependence of the heat of adsorption upon coverage has been investigated over the range $\theta = 0$ to $\theta = 1{\cdot}4$. The usual procedure of making a large number of small increments in coverage was adopted, heats being measured for appropriate increments. The main calorimetric results are shown in *Figure 1*. Experimental difficulties arising from non-selective adsorption in the calorimeter rendered individual heats below $\theta = 0{\cdot}3$ liable to error, and the broken lines between $\theta = 0$ and $\theta = 0{\cdot}3$ are average values for the integral heat over this range. Attention is drawn to the sudden decrease in heat in the neighbourhood of the calculated monolayer value. Comparison with the NiO results strengthens the interpretation that the measurements in that case were made on an almost covered surface.

Measurements of the rate of chemisorption qualify the calorimetric results. In *Figure 2* are shown results of two uninterrupted adsorptions on cobalt oxide, plotted according to equation (2). Pressure was not kept constant during these experiments, and we

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* A detailed account of this and succeeding work on cobalt oxide will be published elsewhere[7].

therefore do not wish to attach absolute significance to the adherence to equation (2). In the absence of a more detailed investigation,

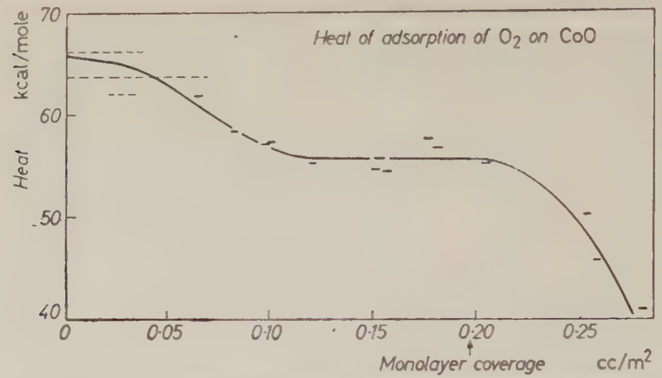

Figure 1. The heat of adsorption of oxygen on cobalt oxide as a function of coverage. The thick horizontal lines show the average heat over an increment, whose coverage increase is represented by the length of the line.

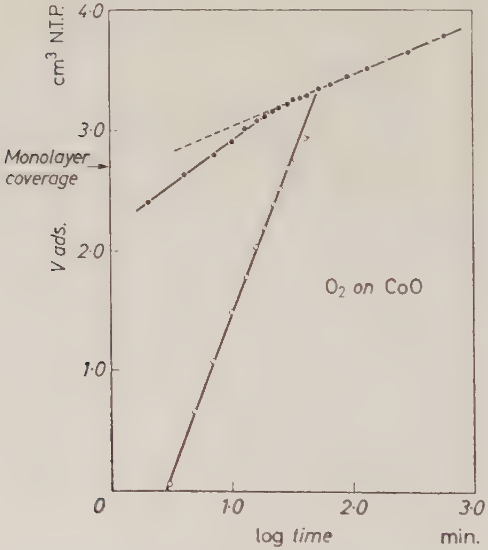

Figure 2. Rate of adsorption of oxygen on cobalt oxide.
○: initial pressure 2·0 mm; ●: initial pressure 4·8 mm.

however, the plots of *Figure 2* have the significance of detecting two different kinetic stages. It is suggested that the change in slope at a value near the monolayer is due to the reaction of incorporation (discussed below) becoming the rate-controlling process. Curves of the same form have been obtained by ENGELL and HAUFFE[6] in the course of their investigations on nickel oxide at high pressures.

DISCUSSION OF OXYGEN RESULTS

The results on each oxide support the thesis that oxygen is chemisorbed in the form of a negative ion. The vacant level or levels offered by adsorbed oxygen on these oxides must accordingly lie opposite the valence band of the oxide[8]. The unlimited supply of electrons in the valence band assures that, other things being equal, complete surface coverage of adsorbed gas can be achieved. Where the coverage proceeds to a monolayer (Cu_2O and CoO), we note that the heat of chemisorption shows very little variation with coverage. This suggests that the height of the Fermi level relative to some arbitrary zero is not being appreciably affected by the chemisorption.

Chemisorption of oxygen on these oxides, however, is too complex a process to be dismissed in terms of electron transfer alone. It is necessary to explain, for instance, why chemisorption can proceed readily *beyond* a monolayer. Accommodation of oxygen in interstitial sites[9] is ruled out for these oxides on steric grounds, but an understanding of the behaviour may be obtained in terms of the relative ease with which cation vacancies can be formed at the surface[1]. It is well known that the stoichiometric excess of oxygen characteristic of Cu_2O, NiO, and CoO arises from the presence of cation vacancies. At high temperatures the concentration of vacancies is in thermodynamic equilibrium with gaseous oxygen; an increase in oxygen pressure is immediately reflected in the formation of cation vacancies at the surface followed by diffusion of these vacancies into the oxide. The diffusion into the bulk of the oxide, however, possesses a high activation energy and at low temperatures vacancies effectively become 'frozen in'. At the surface, on the other hand, the mobility at low temperatures will be much greater and it is suggested that, provided oxygen is being supplied, formation of vacancies can still persist at room temperature. The net effect is that oxygen is incorporated into the lattice. Clearly, the process cannot proceed indefinitely since, with bulk diffusion frozen, a negative space charge develops in the surface layers. The consequent decay of the rate of uptake with increasing amount incorporated is reflected in the adherence of the kinetics to equation (2). A rise in temperature releases the restriction on bulk diffusion of vacancies. Thus baking-out of the adsorbent converts any residual adsorbed oxygen to oxide and renders the vacancy concentration homogeneous by solution of the appropriate number of metal ions at the metal/oxide interface. A replica of the original surface is thereby regenerated. It is apparent, however, that with nickel oxide it is not possible to clean the surface in this way below 400°.

The reactions during the chemisorption of oxygen may therefore be summarized as follows:

$$O_2 \text{ (gas)} \rightleftharpoons O_2 \text{ (ads)} \tag{3a}$$

$$O_2 \text{ (ads)} \rightleftharpoons 2O \text{ (ads)} \tag{3b}$$

$$O \text{ (ads)} + e \rightleftharpoons O^- \text{ (ads)} \tag{3c}$$

$$O^- \text{ (ads)} + e \rightleftharpoons O^{2-} \text{ (ads)} \tag{3d}$$

$$O^{2-} \text{ (ads)} \rightleftharpoons Cu^+O^{2-}Cu^+ + 2\square(Cu^+) \tag{3e}$$

(or its analogue for NiO, CoO)

Together with a possible reaction involving the formation of O_2^- ions, reactions (3c) and (3d) are the electron-transfer steps which give rise to positive holes in the valence band. Release of these holes then produces the observed changes in conductivity. For Cu_2O and NiO, detailed studies of the rate of change of conductivity have been made at Bristol by Gray and his co-workers[10]. The conductivity change begins as a second-order process and later becomes first order, suggesting that the first three reactions above may be combined to give

$$O_2 + 2e \rightleftharpoons 2O^- \tag{4}$$

followed by (3d), possibly at another location on the surface. Reaction (3e) is the reaction of incorporation discussed above, which necessitates the movement of cations into the interstices of the adsorbed layer. If underlying metal is absent, treatment of the oxide at high temperature completely reverses the course of reactions (3a)–(3e). The presence of metal beneath the oxide restricts this reversibility by competing with reaction (3e) for cation vacancies (*q.v.*). If the gas phase is evacuated after the uptake has reached saturation, a considerable proportion of the oxygen remains as a reactive species, possibly O^-. The reaction of this adsorbed oxygen with CO and CO_2 is discussed on p. 211 *et seq.*

ADSORPTION OF CARBON MONOXIDE AND CARBON DIOXIDE

In this section we discuss the adsorption of CO and CO_2 on surfaces which have been baked out *in vacuo*. These are referred to later as 'evacuated surfaces'.

ADSORPTION OF CO

With cuprous oxide, equilibrium was reached at 30 per cent coverage during studies at room temperature and low pressure

(0·2 mm)[1]. About one-third of the volume adsorbed could be desorbed as carbon monoxide at room temperature. The variation of Q with θ is shown in *Table II*. At higher pressures, higher equilibrium coverages were observed[11].

Table II

Coverage θ per cent	0–9	9–20	24–27
Molar heat of adsorption Q (kcal)	20·8	19·0	18·1

Only small amounts of CO were adsorbed on the nickel oxide films, limiting values being less than 1·5 per cent coverage at 0·5 mm[2]. For this reason only integral heats of adsorption could be measured. The heat of adsorption was 26 kcal/mole at 20°C, and the uptake was partly reversible at this temperature.

With CoO, the equilibrium coverages were slightly higher. The variation of Q with θ is shown in *Table III*.

Table III

Coverage θ per cent	0–0·6	0·6–1·5	2·5–3·3
Molar heat of adsorption Q (kcal)	21·5	16·5	14·1

3 per cent coverage was observed at 25° and 0·1 mm; 6 per cent at 25° and 1 mm pressure. The majority of the adsorbed gas could be desorbed as CO by pumping at room temperature. In one experiment, specifically designed to investigate desorption, 65 per cent of the gas was so desorbed.

For each oxide, the equilibrium coverage increases on lowering the temperature, but decreases again on returning to room temperature. This observation is in accord with the low heats which have been measured. The rate of adsorption in all cases is so rapid that no studies of kinetics could be made.

Any interpretation of the results on CO adsorption must take into account the part played by chemical combination with lattice oxygen[12]. In general, we may suppose that CO will chemisorb on both the cations and the anions, the various oxides exhibiting some selectivity towards the two chemisorbed forms. WINTER[13] has shown, however, that combination with oxygen does not necessarily imply irreversible chemisorption (i.e. desorption only as CO_2).

On the nickel oxide, where the observed coverage was only about 1 per cent, it appears unlikely that the oxide ions are, in fact, much involved; the chemisorption seems a true example of 'depletive chemisorption' (*see* STONE[8]). Exchange studies support this conclusion. If desired, however, nickel oxide can be prepared in a much more active form[14]. Thus, unsintered oxide, prepared by decomposition of the carbonate at 250°, adsorbs CO to 24 per cent coverage at room temperature[15]. We do not consider this result to be at variance with that of DELL and STONE[2] (*q.v.*); we suggest that the more disordered the material, the greater the lability of the oxygen ions and their contribution in CO adsorption*. Furthermore, as we have seen, pressure strongly influences coverage of CO on the oxides at room temperature, in agreement with the magnitude of the heats measured.

Table IV

	A	*B*	*C*
Coverage range (per cent)	0–1·4	1·4–3·1	5·0–5·7
Molar heat of adsorption (kcal)	21·1	22·9	13·1

The anions of sintered cuprous oxide are more labile than those of the corresponding nickel oxide surface[13], and, accordingly, their participation in CO adsorption is reflected in the high coverage of 30 per cent. Cobalt oxide is intermediate in behaviour. The coverage is lower than with Cu_2O and the degree of reversibility higher. These results, taken together with the rapid fall in heat of adsorption with coverage, suggest a proportionately larger contribution from depletive chemisorption, in the case of cobalt oxide.

ADSORPTION OF CO_2

No appreciable adsorption of CO_2 occurs on evacuated cuprous oxide. With NiO and CoO, however, the adsorption was appreciable at 0·5 mm and 20°. A heat of adsorption of 28 ± 2 kcal/mole and a limiting coverage of about 10 per cent were found for nickel oxide. For cobalt oxide, the calorimetric data are given in *Table IV*.

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* The lability of Teichner and Morrison's oxide is demonstrated by the fact that on heating *in vacuo* at 210°, nickel is nucleated. We do not, however, incline to the view which they have advanced that Dell and Stone's oxide had disproportionated, in spite of the heat treatment at 400°. The heat of adsorption of oxygen on NiO observed by Dell and Stone is much too low to be accounted for by adsorption on nickel metal[15]. There is, in fact, good agreement between the respective values for oxygen chemisorption in the two studies: TEICHNER and MORRISON report 10 per cent, DELL and STONE 8–10 per cent.

Increments *A* and *B* could not be desorbed at 25°C. Increment *C*, however, could be totally desorbed under these conditions. The relationship between heat of adsorption and reversibility is very clearly emphasized.

INTERACTION OF CARBON MONOXIDE AND CARBON DIOXIDE WITH OXYGEN

The heat of adsorption of oxygen on the oxides is greatly enhanced if presorbed CO or CO_2 is present; equally, the heat of adsorption of CO and CO_2 is enhanced if presorbed oxygen is present on the surface. This is clear evidence for chemical interaction between the adsorbed gases at room temperature. The effect has been studied in detail and the main results are summarized in *Table V*. Figures refer to molar heats of adsorption and values in brackets are for surfaces which were not saturated with oxygen before adsorption of CO.

Table V

	CO *adsorption*		CO_2 *adsorption*		O_2 *adsorption*		
	evacuated surface	*presorbed oxygen*	*evacuated surface*	*presorbed oxygen*	*evacuated surface*	*presorbed* CO	*presorbed* CO_2
Cu_2O	20	49	—	21	55	100	—
NiO	26	88 ± 2 (70 ± 1)	28 ± 2	37 ± 2	43 (54)	100 ± 2	71 ± 2
CoO	20 ± 1	52 (49)	22 ± 1	22 ± 1	59 (60)	95 ± 2	74 ± 3

The point which immediately arises is whether it is possible to account for these thermal changes in terms of a single adsorption complex. The initial work on Cu_2O[1] and NiO[2] has shown that all calorimetric results are consistent with the idea of a single complex with the formula CO_3. This work is now presented together with new results on cobalt oxide in *Table VI*. The results show that the heats of formation of the complex from carbon monoxide and oxygen on the different oxides are as follows: Cu_2O, 114 ± 6 kcal; NiO, 127 ± 4 kcal and CoO, 116 ± 5 kcal.

Table VI

I. *Reaction of oxygen with adsorbed carbon monoxide*

	Cu_2O	NiO	CoO	
$CO\,(g) \rightarrow CO\,(ads)$	20	26	20	kcal
$CO\,(ads) + O_2\,(g) \rightarrow$ Complex	100	100	95	kcal
$CO\,(g) + O_2\,(g) \rightarrow$ Complex	120	126	115	kcal

II. *Reaction of carbon monoxide with oxygen-saturated surface*

	Cu_2O	NiO	CoO	
$O_2\,(g) \rightarrow 2O\,(ads)$	55	43	59	kcal
$2O\,(ads) + CO\,(g) \rightarrow$ Complex	49	88	52	kcal
$CO\,(g) + O_2\,(g) \rightarrow$ Complex	104	131	111	kcal

III. *Reaction of carbon monoxide with oxygenated surface, but not saturated*

	Cu_2O	NiO	CoO	
$O_2\,(g) \rightarrow 2O\,(ads)$	—	54	60	kcal
$2O\,(ads) + CO\,(g) \rightarrow$ Complex	—	70	49	kcal
$CO\,(g) + O_2\,(g) \rightarrow$ Complex	—	124	109	kcal

IV. *Reaction of carbon dioxide with oxygen-saturated surface*

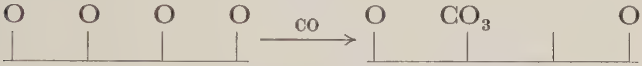
	Cu_2O	NiO	CoO	
$CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g)$	68	68	68	kcal
$\frac{1}{2}O_2\,(g) \rightarrow O\,(ads)$	28	22	30	kcal
$O\,(ads) + CO_2\,(g) \rightarrow$ Complex	21	37	22	kcal
$CO\,(g) + O_2\,(g) \rightarrow$ Complex	117	127	120	kcal

V. *Reaction of oxygen with adsorbed carbon dioxide*

	Cu_2O	NiO	CoO	
$CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g)$	68	68	68	kcal
$CO_2\,(g) \rightarrow CO_2\,(ads)$	—	28	22	kcal
$CO_2\,(ads) + \frac{1}{2}O_2\,(g) \rightarrow$ Complex	—	35	37	kcal
$CO\,(g) + O_2\,(g) \rightarrow$ Complex	—	131	127	kcal

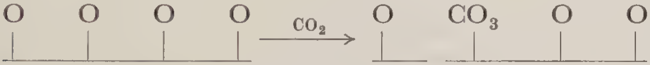
With NiO and CoO it was observed that complex formation from the reaction of carbon monoxide with an oxygen-saturated surface *released sites for further oxygen adsorption.* Oxygen subsequently adsorbed on these sites gave a heat which was in good agreement with the value for a complex free surface. Similar processes probably occur on Cu_2O, but the corresponding experiment was not performed. By contrast, *no adsorption sites were released* after the formation of the complex from CO_2 and an oxygen-saturated surface. This is to be expected if the formula of the complex is CO_3, occupying one site, as the following diagram illustrates.

I. *Adsorption of* CO *on an oxygenated surface*



Oxygen can be adsorbed after the complex has formed.

II. *Adsorption of* CO_2 *on an oxygenated surface*



No oxygen can be adsorbed after the complex has formed.

The calorimetric data give valuable information about the likelihood of catalytic reaction of gaseous CO and oxygen occurring via the surface complex. The enthalpy change in the decomposition of the complex by excess carbon monoxide will be as in *Table VII.*

Table VII

	Cu_2O	NiO	CoO
$CO\ (g) + O_2\ (g) \rightarrow CO_3\ (ads)$	−114	−127	−116
$CO\ (g) \rightarrow CO\ (ads)$	− 20	− 26	− 20
$2CO\ (g) + O_2\ (g) \rightarrow 2CO_2\ (g)$	−135	−135	−135
$CO\ (ads) + CO_3\ (ads) \rightarrow 2CO_2\ (g)$	−1	+18	+1

On nickel oxide, the decomposition reaction is endothermic to the extent of 18 kcal, but on Cu_2O and CoO the enthalpy change is favourable for reaction. These predictions are entirely in line with the observed facts, for with nickel oxide, the complex was found to be stable in the presence of excess CO. With cuprous oxide and cobalt oxide, on the other hand, it was found that the complex was readily decomposed to carbon dioxide in the presence of excess carbon monoxide. We may conclude that, during the

CO-oxidation at 20° on Cu_2O and CoO, a mechanism involving complex formation is very plausible. On nickel oxide, however, complex formation will poison the surface for reaction between CO and oxygen, and the reaction must therefore proceed by another path. Specific studies on the catalytic reaction enable us to amplify these statements. We have observed an activation energy of 2 kcal/mole for the oxidation of CO on both CoO and NiO; the rate constant per square metre, however, is $89{\cdot}5 \times 10^{-4}$ min.^{-1} for CoO at 20° and $5{\cdot}81 \times 10^{-4}$ min.^{-1} for NiO at 20°. Assuming that entropy factors are similar, this supports the view[2] that the NiO reaction is proceeding on only a small fraction of the available sites. This has also been confirmed by WINTER[13].

The results which have been presented in this section have so far been discussed solely in terms of interactions occurring between adsorbed species. We have attempted to show on this basis that the concept of a CO_3 complex renders a great deal of experimental material self-consistent. It is evident, however, that there is also some interaction with lattice oxide ions (*q.v.*). No direct information on this point was available at the time when the concept of complex formation was first proposed. Thus, although GARNER, STONE and TILEY[1] visualized the possibility of the CO-oxidation on cuprous oxide proceeding via an extraction reaction involving the removal of lattice oxygen above 70°, they did not anticipate that it would be effective at 20°. Using the isotope-exchange method, however, WINTER[13] has now established that lattice oxygen can, in fact, be removed from cuprous oxide at room temperature and below. The extraction reaction is therefore a possibility at room temperature, although it may be restricted to a very small number of sites. Winter's results are more in line with a CO_3 entity which already at low temperatures involves lattice oxygen in the sense of Garner's carbonate ions[12].

CHEMISORPTION AND DECOMPOSITION OF NITROUS OXIDE

Attempts to adsorb nitrous oxide on the oxides at low pressure (~0·5 mm.) and room temperature always led to the slow evolution of heat and the production of a small amount of chemisorbed oxygen. When allowance was made for the heat of formation of N_2O, good agreement was obtained between the observed heat and the heat of adsorption of oxygen as measured directly. This is illustrated in *Table VIII*.

If, however, the pressure is increased, reversible chemisorption of nitrous oxide may be demonstrated. This has been observed with cobalt oxide. N_2O was decomposed in the calorimeter until the rate became negligible, and was then evacuated to remove residual nitrogen. N_2O was then readmitted at a pressure of 4·13 mm. The gas was instantaneously chemisorbed to a coverage of approximately 0·8 per cent with a heat of 13 kcal/mole (25°). Complete desorption could be effected by evacuation at 25°. Winter[17] has recently observed reversible chemisorption of nitrous oxide on nickel oxide using the mass-spectrometer. Hole-conducting oxides are by far the best catalysts for nitrous oxide decomposition[18]; it is interesting to speculate to what extent the low-temperature threshold of their activity is extended by virtue of this weak form of chemisorption.

Table VIII

Oxide	*Molar heat of decomposition of* N_2O (kcal)	*Calculated equivalent heat of adsorption of oxygen** (kcal/mole)	*Experimental heat of adsorption of oxygen* · (kcal/mole)
NiO	46	52	54
CoO	50	60	65

* $N_2O\ (g) \rightarrow N_2\ (g) + \frac{1}{2}O_2\ (g)$ $\Delta H = -20$ kcal/mole
$N_2O\ (g) \rightarrow N_2\ (g) + O\ (\text{ads})$ $\Delta H = -46$ (NiO) or -50 (CoO) kcal/mole
$\frac{1}{2}O_2\ (g) \rightarrow O\ (\text{ads})$ $\Delta H = -26$ (NiO) or -30 (CoO) kcal/mole

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4.4

THE SURFACE CHEMISTRY OF URANIUM AND THORIUM OXIDES

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SUMMARY

An account is given of many of the reactions of oxygen, carbon monoxide, and hydrogen with uranium dioxide and thorium dioxide and solid solutions of these two oxides. Carbon monoxide is adsorbed on both uranium and thorium sites at low temperatures, while oxygen is adsorbed only on uranium sites, one molecule reacting with one surface uranium atom. Hydrogen is chemisorbed on oxygen sites at high temperatures, and carbon is deposited from carbon monoxide at high temperatures and high pressures.

SCOPE OF WORK REVIEWED

We wish to review in this paper the studies we have made at Harwell of the reactions of oxygen, carbon monoxide, and hydrogen with the surfaces of the isomorphous dioxides of uranium and thorium. Most of the results of the measurements of adsorption isotherms have already been published[1]; we shall also discuss in a preliminary way some measurements of heats of adsorption, which will shortly be published by one of us[2].

The main features of the reactions studied are summarized in *Table I.* The type of reaction occurring in the temperature range listed in column 3 is shown in column 4, and the maximum amounts of gas reacting in the various temperature ranges are shown in column 5 as a fraction or multiple of Vm, the amount of oxygen necessary to form a physically-adsorbed monolayer at —183°, which is a measure of the surface area of the specimens used. Heats of adsorption are given in column 6; the values for oxygen were directly measured, those for carbon monoxide were estimated from rates of desorption and the value for hydrogen was calculated from adsorption isotherms. The heat evolved during bulk oxidation of

UO_2 above 100° was estimated from the heats of formation of UO_2 and $UO_{2\cdot25}$ given by BREWER[3].

Oxygen enters interstitial positions in the uranium dioxide lattice during oxidation at 100° to 180°, and also during the different process that occurs around room temperature; no abrupt phase changes occur at these temperatures, the x-ray patterns showing only a small, apparently continuous contraction of the unit cell.

Table I

Gas	*Solid*	*Temperature*	*Reaction*	*Gas reacting* (V) *Vm*	*Heat evolved* kcal/mole
O_2	UO_2	−195 to −183	Chemisorption	0·3–0·6	55–10
		−138 to 50	Oxidation of ~40 Å depth	⩽2·2	—
		100 to 180	Oxidation to $UO_{2.4}$		(88)
O_2	ThO_2	−183	(Chemisorption)	0·03	—
CO	UO_2	−183 to 20	Chemisorption	0·7–0·8	(20–4)
		275	Chemisorption(?)	0·08	—
		>500	Carbon deposition	~2·0	—
	ThO_2	−183 to 20	Chemisorption	0·78	(20–4)
		>500	Carbon deposition	—	—
H_2	UO_2	−183	Chemisorption(?)	~0·3	—
		20	—	0	
		>400	Chemisorption	1·0–1·6	~35
	ThO_2	600 to 700	Chemisorption	~1·0	—

Uranium dioxide is a *p*-type semiconductor, and the conductivity decreases as the oxygen content decreases[4]; this observation is not inconsistent with the incorporation of excess oxygen in interstitial positions, since U^{iv} ions in the crystal lattice lose electrons in the process, becoming U^{v} or U^{vi}. Solid solutions of UO_2 in ThO_2 show the same oxidation behaviour[5].

Two lines of evidence suggest that the reaction with oxygen at −183° is confined to the surface. If uranium dioxide is exposed at −183° to an excess of oxygen, adsorption of the amount shown in *Table I*, in addition to physical adsorption, is rapid and complete in seconds or minutes; the temperature has to be raised 40° before the start of a second, slow, time-dependent absorption can be observed. Secondly, the absorption at −183° causes a decrease in density of the order of magnitude to be expected for the formation of a layer of oxygen ions on the outside of a UO_2 particle[6], while the oxidation reactions at higher temperatures are accompanied by an increase of density as oxygen enters the UO_2 lattice.

The results in the fifth column of *Table I* show the high surface coverages attained in most surface reactions of these oxides. It should be emphasized that this characteristic is qualitatively, and even semi-quantitatively, independent of the mode of preparation of the oxide and of the particle size of the preparation. Similar surface coverages have been observed for a given reaction on uranium dioxide powders prepared by reduction of higher oxides with hydrogen or carbon monoxide at temperatures from 450° to 700° and on samples prepared by crushing pellets that have been sintered at 2000° in vacuum; surface areas have ranged from 0·2 to 11 m^2/g.

PREPARATION OF REPRODUCIBLE SURFACES

The ease with which uranium dioxide will oxidize at low temperatures renders reduction necessary before every adsorption experiment. This was usually carried out by passing small volumes of hydrogen or carbon monoxide over the oxide at temperatures between 500° and 700° and pressures of about 0·1 atm. until the quantities of water or carbon dioxide that could be frozen out of the reducing gas were negligible. Uranium dioxide so prepared is as closely stoichiometric as our analytical methods can measure; the stability of UO_2 in high pressures of hydrogen at 1100°C has been demonstrated[7], though GRONVOLD[8] has reported reduction to $UO_{1\cdot 99}$ at 1000°.

In view of the activated adsorption of hydrogen on uranium dioxide at these temperatures and of the occurrence of a slow disproportionation reaction when carbon monoxide is passed over either oxide under certain conditions[9], we must discuss whether or not it is possible to obtain a clean oxide surface by reduction with these gases. The heat of desorption of hydrogen, equal to the sum of the activation energy for adsorption and the heat of adsorption, is roughly 70 kcal/mole; desorption should therefore be fairly rapid above 700°C. The deposition of carbon from carbon monoxide is very slow unless the pressure is high, about one atm., and unless continuous flow conditions are maintained. The results of combustion analysis show that little or no hydrogen remained on the surface after reduction in the ordinary way and pumping at 800°C, and also that the carbon deposited by reductions with carbon monoxide in the manner described above amounted to no more than 5 per cent of surface coverage.

The effects of gross contamination by hydrogen and carbon on oxygen adsorption at −183° are illustrated in *Table II*. Oxygen chemisorption on seven different preparations reduced in such a way that the surfaces should have been free of hydrogen and of carbon amounted to between 0·52 and 0·64 of *Vm*, *Vm* being, as before, the amount of oxygen in a physically-adsorbed monolayer at −183°, as determined by the B.E.T. equation; only in two cases were lower values found. Adsorption of ~1·0 *Vm* of hydrogen lowered the oxygen chemisorption in two cases from 0·56 *Vm* to 0·46 *Vm*. The oxygen adsorption at −183° was an approximately linear function of the carbon coverage of the surface, falling to nearly zero as the surface was completely poisoned. Extrapolation to zero carbon content yielded oxygen coverages of 0·56 *Vm* and 0·62 *Vm* on a clean surface, using two different preparations. The heat of adsorption of oxygen at low coverage was independent of the presence of some carbon, which is some confirmation that oxygen is chemisorbed at −183° only on a clean oxide surface.

Table II. OXYGEN ADSORPTION ON URANIUM DIOXIDE AT −183°

Condition of surface	$Vm(O_2)$ c.c./g	$\frac{V}{Vm}$
Reduction with CO, ~10 cm, for 30 min.	0·05–0·40	0·52–0·66
After chemisorption of 0·34 c.c./g H_2	0·35	0·47
After chemisorption of 0·42 c.c./g H_2	0·33	0·44
H_2 removed at 740°	0·33	0·56
Carbon on surface = 0·027 mg/g	0·40	0·50
Carbon on surface = 0·43 mg/g	0·41	0·33
Carbon on surface = 0·73 mg/g	0·37	0·12

The results presented here can therefore be regarded as characteristic of clean surfaces of uranium dioxide. Surfaces of thoria were prepared in the same way, viz. treated with a few cm of carbon monoxide at about 700° for times of between 10 and 30 minutes.

ADSORPTION ON METAL SITES

Oxygen is chemisorbed on uranium dioxide to a large extent at −183°, covering a large fraction of the available surface, while surfaces of thoria reduced in the same way chemisorb very little oxygen. It seems clear that oxygen is adsorbed on donor centres, and that the surface uranium ions, but not thorium ions, can donate the necessary electrons. This remains true when uranium ions are dispersed amongst thorium ions. The amount of oxygen chemisorbed on surfaces of solid solutions of uranium dioxide and thorium dioxide was a linear function of the uranium content, at least down to 15 mole per cent UO_2 (*see Figure 1*); the surfaces were prepared by crushing sintered compacts, so as to expose internal surfaces in which uranium and thorium ions were randomly distributed on the metal sub-lattice. The one result we have to date on UO_2–Y_2O_3

solid solutions, which contain anionic vacancies, indicates that oxygen adsorption at —183° proceeds to the same extent as on a UO_2–ThO_2 solid solution having the same UO_2 content, in which the anionic sub-lattice is complete; the adsorption at this temperature seems to be determined by the metal ions only.

The results reported so far were all obtained by the subtraction of an adsorption isotherm characteristic of the physical adsorption of oxygen at —183° from an isotherm determined on a reduced surface; the pressures of oxygen actually in equilibrium with the chemisorbed gas only would be immeasurably small at —183°. The physical adsorption was usually determined after pumping off at —78°.

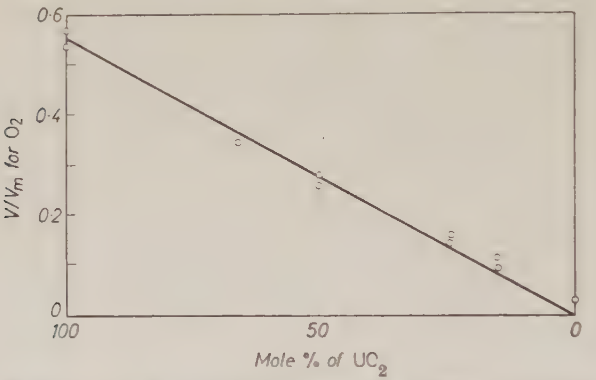

Figure 1. The chemisorption of oxygen at —183°C on solid solutions of uranium and thorium dioxides. (Reproduced from the *J. chem. Soc.* (1954) 3338, by permission of the editor.)

The total amount reported as 'chemisorbed' at —183° therefore includes all oxygen adsorbed with a heat of adsorption too high to permit of removal by pumping at —78° in the apparatus used, and is to that extent arbitrary. Measurements of differential heats of adsorption of oxygen on UO_2 at —183° have shown that the initial heat on a bare surface is always 55 ± 2 kcal/mole and that this always falls regularly as the surface is covered; the shape of the differential heat v. coverage curve is somewhat different on samples of very different particle size, but the differential heat has fallen to 10 — 12 kcal/mole by the time the chemisorption limit, as determined from isotherm experiments, is reached. It is significant that heats higher than those characteristic of physical adsorption (3–5 kcal/mole) are occasionally, though not always, observed at higher surface coverages.

The chemisorption of carbon monoxide at low temperatures is very similar on both uranium dioxide and thorium dioxide, in complete contrast to the behaviour of oxygen. The surface coverage quoted at −183°, 0·8 *Vm*, is the amount adsorbed at low pressures, and equal to the amount that could not be removed by prolonged pumping at −183°. The surface coverage fell to 0·5 *Vm* at −78° and 0·1 *Vm* at 23°, at pressures of about 10 cm. It is clear that the amounts reported as chemisorbed at −183° include some gas adsorbed with a heat not much more than that corresponding to physical adsorption, and that the heat of adsorption falls regularly as the surface is covered. Adsorption of 0·8 *Vm* of carbon monoxide at −183° inhibits almost completely the subsequent chemisorption of oxygen, and also markedly lowers the physical adsorption of oxygen; moreover, adsorption of more carbon monoxide follows a curious adsorption isotherm, as if 'second-layer' rather than 'first-layer' physical adsorption was being followed. These characteristics, together with the high surface coverage and the order of magnitude of the heats of adsorption, are all strongly reminescent of the low-temperature chemisorption of carbon monoxide on other oxides such as ZnO, Cu_2O, NiO, which have been reported by the Bristol school. They consider that such adsorption occurs on metal sites, and they have shown that it is accompanied by electron donation from the gas to the oxide[10]. If the analogy holds, we have an example here of U and Th sites acting as electron acceptors, in which role they are clearly closely similar; it is the inability of Th ions to act as donor centres which is so marked.

We have some evidence that may support the hypothesis that both oxygen and carbon monoxide are adsorbed on the same sites on uranium dioxide at −183°. Not only does carbon monoxide adsorption block the adsorption of oxygen, oxygen adsorption lowers the subsequent adsorption of carbon monoxide and, furthermore, does so molecule for molecule. The quantities of carbon monoxide chemisorbed on two samples of uranium dioxide before and after the adsorption at −183°, of amounts of oxygen lower than the chemisorption limit for oxygen are shown in *Table III*.

Table III

Oxygen adsorbed at	−183° (c.c.)	0	0·136;	0	0·074
Carbon monoxide adsorbed at	−183° (c.c.)	0·470	0·328;	0·268	0·190
Total gas adsorbed	(c.c.)	0·470	0·464;	0·268	0·264

The total amount of gas adsorbed, oxygen plus carbon monoxide, remained nearly the same in each case. A similar result is obtained when oxygen is chemisorbed to the limit possible at −183° before carbon monoxide adsorption, as long as a correction is made for the small amount of oxygen lost from surface sites during the pumping at room temperature which preceded carbon monoxide adsorption.

These results, and the result that oxygen chemisorption on UO_2–ThO_2 solid solutions is proportional to the U content, both suggest that the primary act of chemisorption consists in the interaction of one oxygen molecule with one uranium site.

Quantitatively, there would seem to be enough room on the surface for this simple model to be true. The cleavage planes of single crystals of thoria are the (111) planes. If these are the outermost planes of the uranium dioxide preparations, the area occupied by every U surface ion is 13 $Å^2$. Referred to the area of a nitrogen molecule, 16·4 $Å^2$, as standard, we then find for these preparations the number of U surface sites per physically-adsorbed oxygen molecule is about 1·3. V/Vm values of 0·6 for oxygen, and 0·8 for carbon monoxide, at −183°, would then mean that about 45 per cent of the surface U ions react with an oxygen molecule and that about 60 per cent are occupied by carbon monoxide at −183°. This is quite consistent with the form of the isotherms observed, although, of course, such comparisons cannot be regarded as certain, since the oxide particles are probably not perfect crystals bounded by one set of planes and the areas of molecules of physically adsorbed gases are not accurately known. Nevertheless, it remains true that the chemisorption reactions considered are characteristic of the whole surface, and are not dependent upon special 'active' sites.

ADSORPTION ON OXYGEN SITES

We should mention here that the activated adsorption of hydrogen, which occurs at measurable rates at temperatures greater than 500°, seems similar to the high-temperature adsorption of hydrogen on other oxides, such as ZnO[11]. Adsorption of large quantities of hydrogen by UO_2 had only a small effect on the subsequent adsorption of oxygen at −183°, and this is compatible with the hydrogen being adsorbed on oxygen sites, as has been assumed by other authors[12]. The high activation energy (~35 kcal/mole) suggests that the process is dissociative and, if it is, the surface coverages attained are very high, more than 1 H atom/surface oxygen calculated on the basis set out above. This circumstance, and the slowly increasing adsorption found in some temperature-cycling experiments, suggest that either hydrogen is adsorbed in two ways, or that some hydrogen may be soluble in the lattice. The question cannot be regarded as settled yet; more data is needed. Recent results indicate that hydrogen is adsorbed in much the same manner on ThO_2 in the same temperature range.

OXYGEN ADSORPTION

It appears then that adsorption processes on these oxides are similar to those on other oxides, except for the low-temperature adsorption of oxygen by uranium dioxide, which seems to have unique features. One more piece of recent experimental evidence on this reaction must be mentioned. In the presence of an excess of oxygen, at a few cm pressure, the chemisorption at −183° is rapid. However, the rates at which heat is evolved when oxygen is added in small increments show that, under these conditions, chemisorption is slow after an appreciable fraction of the surface has been occupied; heat corresponding to physical adsorption is liberated as soon as an increment of oxygen is added to a partially oxidized surface, but the subsequent evolution of heat is slow; the conversion of physically adsorbed molecules to the chemisorbed state becomes progressively more difficult as the surface is covered.

The surface reactions of uranium dioxide may be compared with those of the lower oxides of other transition metals; the best comparison is with those oxides that are stable under highly reducing conditions and where a higher oxide is stable at low temperatures—e.g. the lower oxides of Mn, V, Cr, Mo, W. The most complete data are available for adsorption on Cr_2O_3. The heat of adsorption of O_2 at −183° was measured by BEEBE and DOWDEN[13] as 22–30 kcal/mole; there was some mutual interference between oxygen and carbon monoxide adsorption and their sample adsorbed ~5 c.c./g at a residual pressure of a few mm. The monolayer volume can be roughly calculated as 17 c.c./g from some measurements they made of argon adsorption, and therefore oxygen coverage was ~0·3 *Vm*. A slow evolution of heat was observed, which the authors considered might have been due to a slow migration of physically adsorbed gas over the surface. While a similar explanation may hold in our case, it seems rather less likely to apply to experiments with well-crystalline adsorbents than to adsorbents such as an 'unglowed' Cr_2O_3 with the very high specific surface of about 60 m^2/g.

Our data indicate that one oxygen molecule reacts with one surface U atom, and that the surface of a reduced uranium dioxide is similar in other reactions to that of thorium dioxide. The oxygen adsorption is then probably accompanied by the oxidation of U^{iv} to U^{v} or U^{vi}. It is possible that the transfer of electrons to the adsorbed oxygen becomes progressively more difficult as the surface coverage increases, and this could lead to an explanation both of the falling heat of adsorption and of the slow chemisorption. We do not at present know how many electrons are transferred to the absorbate, nor whether the oxygen molecule is dissociated in the act of adsorption or not. However, there is evidence that oxygen can penetrate below the surface layers at temperatures above —130°, and this would seem to demand that at least some dissociation occurs at these temperatures.

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4.5

THE ANTIFERROMAGNETIC PROPERTIES OF CHROMIUM SESQUIOXIDE AND THEIR RELATION TO THE FORMATION OF BENZENE RING COMPOUNDS

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SUMMARY

α-Cr_2O_3 *is antiferromagnetic, showing a tendency for the resultant spin of the three unpaired* 3d-*electrons on the chromic ion to be aligned antiparallel to the resultant spins on its nearest chromic ion neighbours. This tendency is complete below about* 60°, *leading to the formation of a spin superlattice, detectable by neutron diffraction, and it is shown that the magnetic susceptibility above this temperature indicates the persistence of statistical short-range order of spins at least up to about* 400°. *It is shown that chromium ions of opposite spin attract one another, leading to observable effects on the unit-cell dimensions in the crystal, both on the axial ratio of the hexagonal unit cell and on the volume per oxygen atom. The significance of these effects is discussed and compared with the values found in isomorphous crystalline oxides, whence it is shown that* V_2O_3 *also shows strong attractive antiferromagnetic coupling between the unpaired electrons on neighbouring cations, reflected also in its magnetic properties and probable ordering of spins. Corresponding symptoms of antiferromagnetic coupling in the amorphous oxides and the solid solutions in* α-Al_2O_3 *are discussed. The crystal unit-cell dimensions of the dioxides isomorphous with rutile* (TiO_2) *are similarly analysed, and it is found that* MoO_2 *and* WO_2 *show similar strong attractive antiferromagnetic coupling. Since* Cr_2O_3, V_2O_3, *and* MoO_2 *are the main commercial catalysts for dehydrogenation and cyclization, it is suggested that antiferromagnetic interaction is related to catalytic activity. Comparison is made with the behaviour of ferromagnetic catalysts, a tentative mechanism is proposed, and some of the implications in chemisorption and catalysis are examined.*

INTRODUCTION

In previous discussions of chemisorption, attention has been directed to geometrical and electronic factors. Some evidence is now presented to show that the coupling of unpaired electrons on neighbouring surface ions may be an additional factor influencing the nature and stability of chemisorbed molecules. The behaviour of chromia-alumina ring-closing catalysts is discussed from this point of view.

The physical properties of some coprecipitated Al_2O_3–Cr_2O_3 catalysts have been examined in these laboratories[1,2] and related to their catalytic activity[3] for the conversion of *n*-heptane to toluene, by dehydrogenation and ring-closure. The activation energy of the conversion was close to that of *n*-type semiconduction in the catalysts, but the activity bore no direct relation to the number of conducting centres.

This work has been extended to the determination of the activity of the catalysts for conversion of methyl*cyclo*hexane to toluene[4] by dehydrogenation only, and to their examination by x-ray diffraction[5]. Except for pure chromia, the catalysts were shown to be amorphous in the high-area active state, but although they were coprecipitated, they were highly inhomogeneous. High activity for ring-closure was associated with chromia-rich segregates richest in Cr_2O_3, while this factor was less important for dehydrogenation only. It was concluded that the geometrical requirements for ring-closure were more stringent than those for dehydrogenation alone.

Herington and Rideal[6] have shown that dehydrogenation and ring-closure are initiated by a two-point dehydrogenation and chemisorption of an olefine which then rapidly converts to an aromatic. The above findings suggest that for ring-closure a larger group of surface Cr ions is required to complete the ring-closure of adsorbed olefine than to complete the dehydrogenation of a naphthene. Balandin first suggested that a six-point adsorption was involved in ring-closure and dehydrogenation to form aromatic hydrocarbons, but the high activity of amorphous Cr_2O_3 for this reaction[7] was considered to be evidence against such a mechanism since it was thought not to exhibit a suitable hexagonal array of surface Cr ions. The probable existence of such an array is demonstrated below, from the structure of crystalline α-Cr_2O_3. It is also shown that the oxide ring-closing catalysts are antiferromagnets with strong quasi-covalent bonding between the metal ions, and a contribution from this factor to their catalytic activity is suggested.

CRYSTAL STRUCTURE OF α-Cr_2O_3

Crystalline α-Cr_2O_3 is isomorphous with α-Fe_2O_3 and α-Al_2O_3, whose structures were determined by Pauling and Hendricks[8].

The structure follows from packing together spherical ions as closely as possible, with cations in octahedral intersitices between oxygen ions. Electrostatic repulsions between ions of like sign cause both oxygen ions and cations to be distributed as uniformly as possible through space.

Figure 1 shows a typical layer of ions in α-Cr_2O_3. Close-packed layers of oxygen ions are stacked in hexagonal close-packed array . . . *ABABABA* . . .. Octahedral interstices form layers midway between those of oxygen ions; layers of octahedral positions are themselves in close-packed configuration, offset from neighbouring oxygen-ion layers forming a sequence . . . *AcBcAcBcAcBcA* . . . in which small letters indicate cations. The layers of octahedral positions, being all in the *c* position, superpose and there are as many such positions as oxygen ions. However, from the formula Cr_2O_3, one-third of the positions are vacant, and these are distributed equally in each layer and as far apart as possible, leading to the hexagonal layout of cations in *Figure 1.*

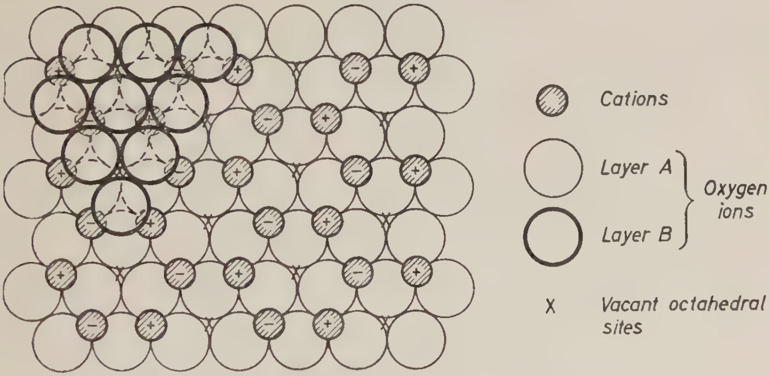


Figure 1. Ideal packing of ions on the basal plane in chromium sesquioxide (not to scale).

It can be seen that in any layer there are three equivalent sets of octahedral positions, ⊕ ⊖ and ×, of which one set is vacant (× in *Figure 1*). The choice follows a sequence in successive layers in order to keep vacancies in neighbouring layers as far apart as possible, leading to the final representation

$$\ldots A\tfrac{2}{3}c_1B\tfrac{2}{3}c_2A\tfrac{2}{3}c_3B\tfrac{2}{3}c_1A\tfrac{2}{3}c_2B\tfrac{2}{3}c_3A \ldots$$

for the structure, where $\tfrac{2}{3}$ refers to the degree of filling of a layer and the subscript to the sequence of choices of vacant positions.

The same influence of electrostatic repulsions between cations leads to a similar array of cations in face-centred cubic close-packed oxygen ions, as in θ-Al_2O_3,[9] represented as

$$\ldots A\tfrac{2}{3}cB\tfrac{2}{3}aC\tfrac{2}{3}bA\tfrac{2}{3}cB\tfrac{2}{3}aC\tfrac{2}{3}bA \ldots$$

with the same cation layers as in *Figure 1.* θ-Al_2O_3 is the most crystalline form of gamma alumina obtained from alumina gel, and is preceded by the less crystalline form η-Al_2O_3 obtained directly by dehydration of poorly crystallized bohmite $Al_2O_3 . H_2O$.

The amorphous catalysts gave diffraction patterns with MoKα radiation with broad diffuse bands indicating an apparent crystal size of about 20 Å,[5] while surface-area and density measurements indicated a particle size of about 80 Å. The crystal structure was therefore irregular but from the resemblance of the diffraction patterns to that of η-Al_2O_3 they contained essentially close-packed oxygen ions and octahedrally coordinated cations, rather than the defect spinel structure of γ-Cr_2O_3 made hydrothermally[10].

It follows from the structure of crystalline α-Cr_2O_3 that a hexagonal array of Cr ions arises from their electrostatic repulsions, and such an array is inherently likely on the oxide surface. The same arguments apply to the amorphous materials, and are consistent with the diffraction evidence above, so that the activity of chromia-alumina ring-closing catalysts may be related to a six-point mechanism in which, after initial two-point adsorption, the remaining four Cr ions in a hexagon serve to orientate the adsorbed olefine into a suitable position for ring-closure.

CATION REPULSIONS IN α-Cr_2O_3

The ideal structure described in the second section for α-Cr_2O_3 does not distribute the Cr ions entirely uniformly through space. Each cation has three close neighbours in the same layer, and one in a neighbouring layer at only 80 per cent of the separation of those in the same layer. *Figure 2a* shows such a closest pair of cations with associated oxygen ions, drawn in the ideal configuration. Immediately above and below the outer oxygen ions are vacant octahedral positions. Repulsion between cations towards the vacant positions allows the equatorial oxygen ions to converge and the upper and lower triplets to diverge and close over the cations, thus decreasing the overall height of the group, as shown in *Figure 2b.* That repulsions between cations are responsible is shown by the fact that they lie nearer to the upper and lower, than to the equatorial, triplets of oxygen ions. The hexagonal unit cell of α-Cr_2O_3 has its *c*-axis perpendicular to the cation layers so that the effect of the distortion is to decrease the axial ratio c/a from its ideal value, 2·828, for the undistorted packing.

The arrangement of cations in space is illustrated in *Figure 3a*, showing portions of four successive cation layers and omitting intervening oxygen ions. They can be seen to form a rhombohedral array with a centring ion (*Figure 3b*) and the effect of

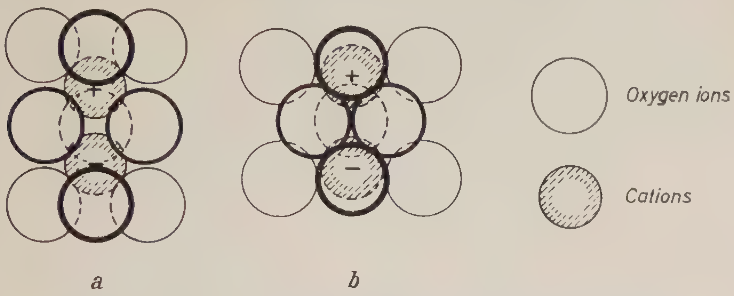


Figure 2. Distortion of R_2X_9 group as in chromium sesquioxide.
a. Ideal regular configuration.
b. Distorted configuration.

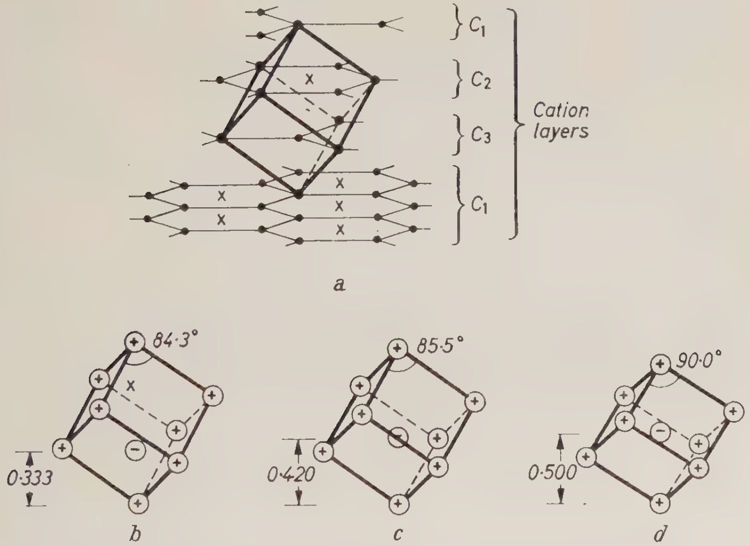


Figure 3. Relation of cation positions in chromium sesquioxide to a body-centred cubic arrangement.
a. Cation layers in ideal configuration.
b. Centred rhombohedral cell in ideal configuration.
c. Observed rhombohedral cell in Cr_2O_3.
d. Body-centred cubic cell.

distortion is to bring the actual arrangement (*Figure 3c*) nearer to a true body-centred cubic array (*Figure 3d*). The final structure then represents a compromise between that for uniform packing of oxygen ions and that for a uniform distribution of cations through space, with the hexagonal axial ratio of the unit cell as an index of the state of compromise.

Structural data for the three oxides are given in *Table I* together with ideal data for the two limiting structures. v_0 is the volume per oxygen ion and is a measure of the scale of the structure. It can be shown that v_0 is related to the cation–oxygen separation, d, as

Table I. STRUCTURAL DATA FOR CORUNDUM-TYPE OXIDES

Structure	*Volume per oxygen ion* v_0—$(kX)^3$	*Axial ratio* c/a	*Structure parameters*		
			Oxygen ions x	*Cations* u	k
Ideal Packing		2·828	−0·083	0·167	1·00
Al_2O_3 [8]	14·070	2·730	−0·053	0·145	$0{\cdot}99_6$
Fe_2O_3 [8]	16·647	2·730	−0·055	0·145	$0{\cdot}99_8$
Cr_2O_3 [17]	15·984	2·742	−0·042	0·145	$0{\cdot}99_9$
BCC cations		2·450	<0·000	0·125	1·02

$$\tfrac{1}{2}v_0 = (kd)^3$$

where k is a constant, unity for the ideal packing and lying between 0·99 and 1·02 for all combinations of c/a, u, and x, corresponding to cation repulsions, between the limits in *Table I*. Distortion is therefore accomplished with only a small volume change. Values of k for the data shown for the three oxides are also given in the table.

COMPARISON OF OXIDES

Instead of the individual unit-cell dimensions, v_0 and c/a may be used to describe the scale and distortion of the crystal structure of chromia. It may be compared with the other oxides isomorphous with it, as in *Figure 4*. $v_0^{1/3}$ is related to the Goldschmidt ionic radii[11] of the cations in the upper diagram, on which is drawn the theoretical relation above, for an oxygen ion radius 1·35 Å, and $k = 1$. Limits for $k = 0{\cdot}99$ and 1·02 are also shown. Cr_2O_3, Rh_2O_3, and possibly V_2O_3 all have anomalously short cation–oxygen separations.

In the lower diagram c/a is related to $v_0^{1/3}$. For the diamagnetic oxides Al_2O_3, Ga_2O_3, the departure from ideal packing increases, i.e. c/a decreases, as $v_0^{1/3}$ increases. From *Figure 2* this trend is expected since larger cations, by forcing oxygen ions further apart, allow them to respond more to cation repulsions. The normal trend between c/a and $v_0^{1/3}$ is drawn from data for Al_2O_3–Ga_2O_3 solid solutions[12]. The same trend is shown by dilute Al_2O_3–Cr_2O_3[13] and Al_2O_3–Fe_2O_3[14] solid solutions, departing from it at higher concentrations when there is a higher proportion of closest neighbouring Cr or Fe ions. Higher values of c/a than expected imply that the electrostatic repulsion between paramagnetic ions is less than that for diamagnetics, or that there is an attractive force between the paramagnetic ions, counteracting their repulsions. Cr_2O_3, Rh_2O_3, and V_2O_3 show this attractive force as well as the short cation-oxygen separation, and it also occurs in Fe_2O_3, but not in Ti_2O_3, which is also weakly paramagnetic.

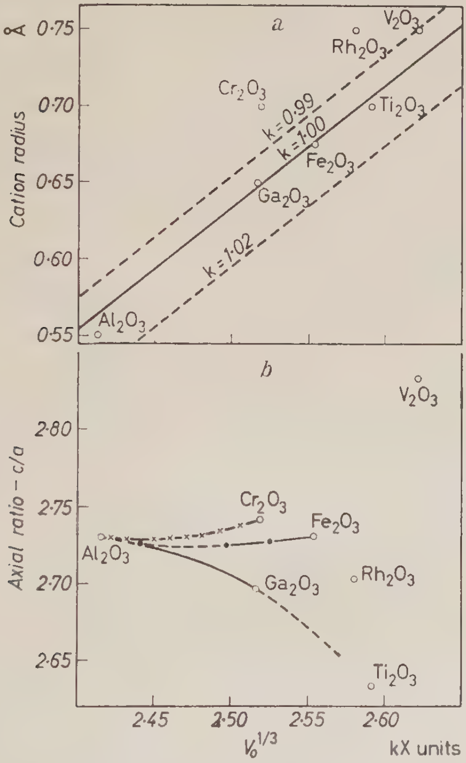


Figure 4. Comparison of unit-cell dimensions of corundum-type oxides.

The rutile-type dioxides contain hexagonal close-packed oxygen ions, with half the octahedral positions filled, and their distortion from ideal packing by cation repulsions follows the same principles as in chromia, etc.[15]. In the tetragonal unit cell the cations lie at the corners and centre, with the c spacing their shortest distance of approach. Distortion of the packing by electrostatic repulsions therefore increases c/a, while the same relation holds between r_0 and the cation-oxygen separation as for chromia. Data for these oxides are plotted in *Figure 5*, where it can be seen that MoO_2 and WO_2 are outstanding for their short cation–oxygen separation and small distortion from the ideal packing, as compared with the diamagnetic dioxides TiO_2, etc. MAGNELI has shown[16] that their structure actually departs slightly from a true tetragonal unit cell owing to a tendency for Mo or W ions to associate in closely spaced pairs, rather than the evenly spaced rows of cations in rutile.

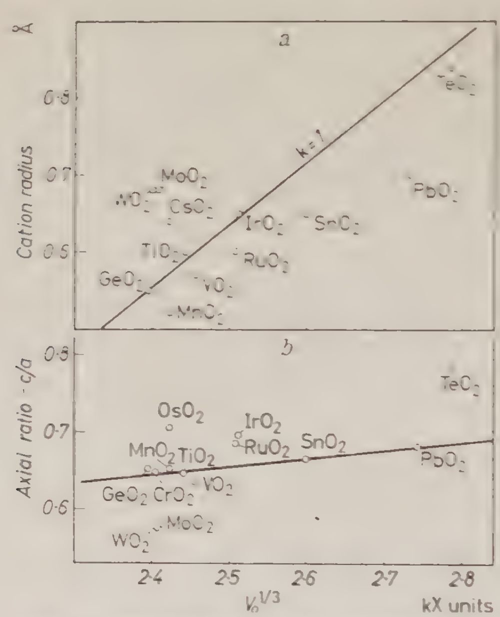


Figure 5. Comparison of unit-cell dimensions of rutile-type dioxides.

MAGNETIC TRANSFORMATIONS IN α-Cr_2O_3

The magnetic properties of Cr_2O_3 indicate the origin of the intercation attractions shown by its crystal structure. Below 60°C it is antiferromagnetic, with the resultant spins of unpaired $3d$-electrons on neighbouring Cr ions coupled antiparallel, so that ⊕ and ⊖ ions in *Figures 1–3* have opposed spins[17]. Greenwald[18] has studied the variation of the unit-cell dimensions of α-Cr_2O_3 on heating through the antiferromagnetic transformation and her revised results, recalculated in terms of v_0 and c/a, are shown in *Figure 6*. The ordering of spins at low temperatures causes an increase in c/a and decrease in v_0, and accounts for about one-fifth of the total departure of chromia at room temperature from the ideal relations in *Figure 4*.

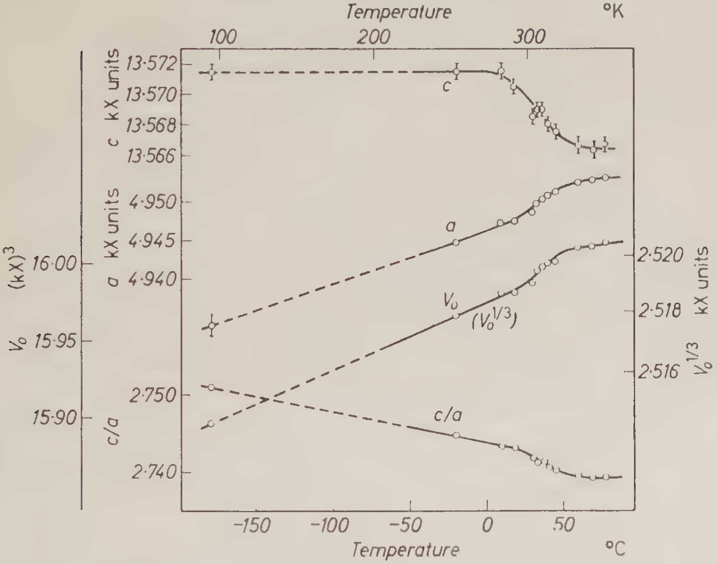


Figure 6. Variation of unit-cell dimensions of Cr_2O_3 near its antiferromagnetic transition.

Immediately above 60°C, chromia is not a true paramagnet since its Curie-Weiss atomic moment is anomalously high (*Figure 7*), although paramagnetic-resonance studies[19] show that, in fact, the Cr ions in α-Cr_2O_3 have the normal spin-only moment, 3·87 BM, at this temperature. The Curie-Weiss atomic moment decreases to near the normal spin-only value at high temperatures. According to Honda and Soné[20], this occurs fairly sharply just above 400°C, although somewhat lower temperatures are found by other workers. The explanation of the high apparent atomic moment between 60° and 400°C is given theoretically by Li[21], who finds that a short-range order of spins should persist above the antiferromagnetic transformation temperature, disappearing at higher temperatures. From the crystallographic data for α-Cr_2O_3, this short-range order is accompanied by a short cation-oxygen separation and attractive force between the cations.

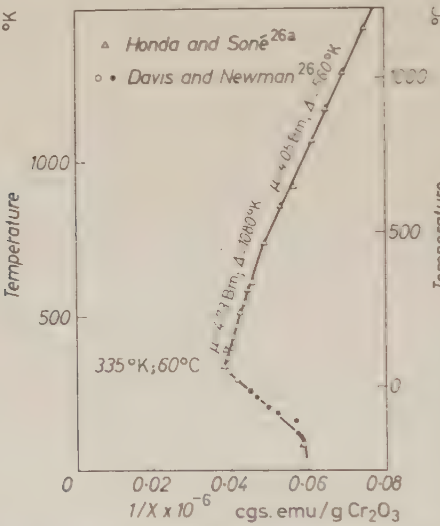


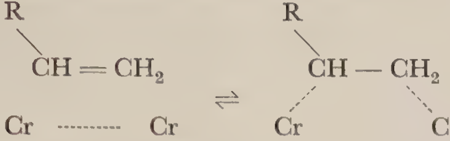
Figure 7. Variation of magnetic susceptibility of Cr_2O_3 with temperature.

Amorphous Cr_2O_3 shows an anomalously low Curie-Weiss atomic moment for Cr ions, 3·24 BM. The same effect is found in polynuclear complex ions and implies some degree of covalent bonding between the paramagnetic ions.

MAGNETIC COUPLING AND CATALYSIS

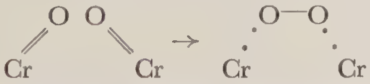
The oxides selected previously as showing strong interaction forces, show similar magnetic symptoms of cation interaction so far as is known. Ti_2O_3 is weakly antiferromagnetic at low temperatures, but shows no short-range order effects[22]. Those stable to reduction, Cr_2O_3, V_2O_3, MoO_2, and WO_2, are the main oxide dehydrogenation and ring-closing catalysts, either alone or supported on alumina. A relation between their antiferromagnetism and catalytic activity is suggested.

The forces between cations in chromia have the attributes of covalent bonding, attractive antiparallel coupling of unpaired electrons. The tendency of spins to couple antiparallel contributes to weak chemisorption and easy desorption of olefines, usually explained in terms of interatomic distances alone



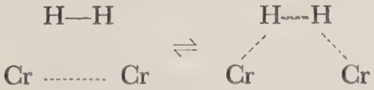
In a ferromagnet the corresponding effect of parallel coupling of spins would be to encourage desorption in biradical form. Nickel is well known to promote cracking and polymerization when used for dehydrogenation of hydrocarbons. Both chromia and nickel are used for dehydrogenations above their Curie temperatures, so that a contribution from magnetic coupling applies to the desorption step only.

There has been little work on the correlation of magnetic coupling with catalytic activity. Hedvall has studied the variation of activity of nickel with temperature for a number of reactions and found that many show a sharp inflection in the variation at the Curie temperature of nickel. For chromia, WINTER[23] has shown that in the exchange of O_2^{18} with chromia, the adsorption-desorption step is rate-controlling at temperatures below 420°C, while the exchange reaction is the slowest step above this temperature. A possible magnetic interpretation is that the O_2 molecule, having a pair of antibonding electrons, is less easily formed by atom recombination, and desorbed, while the Cr ions on which the atoms are adsorbed tend to be coupled antiparallel.



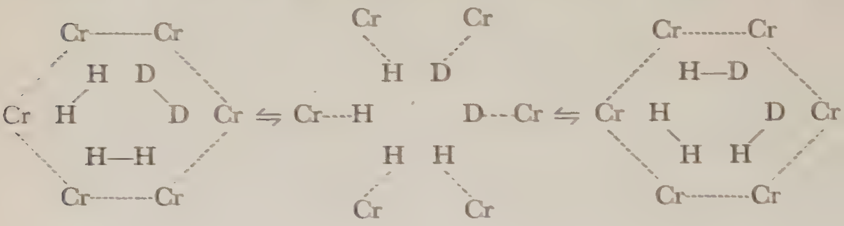
In the presence of hydrogen, a similar inflection at 420°C occurs in the variation of *n*-type semiconduction with temperature in chromia[2]. Above 420°C the activation energy is 34 kcal, but below this temperature it falls to a much lower value, suggesting that weakly adsorbed hydrogen can then participate in the production of conducting centres. The high temperature activation energy of semiconduction is, curiously, the same as that for adsorption-desorption of oxygen below 420°C, although chromia is then a *p*-type semiconductor with activation energy 14 kcal.

On the magnetic interpretation, the effect of coupling between Cr ions is to allow interaction with a hydrogen molecule of the kind



WELLER and VOLTZ[24] showed that chromia readily catalyses H_2–D_2 exchange at low temperatures, provided that it is reduced and evacuated at 500°C first. Strongly chemisorbed hydrogen therefore shields Cr ions and Voltz and Weller showed that such hydrogen does not participate in the exchange, which therefore does not involve an atomic mechanism.

The hexagonal array of surface Cr ions on chromia, with unpaired electrons coupled antiparallel, shows a strong resemblance to that of active carbon. A possible mechanism of exchange on chromia is of the kind



SURFACE GEOMETRY, SEMICONDUCTION, AND MAGNETIC COUPLING

The above observations suggest that surface geometry, semiconduction, and magnetic coupling are closely related to each other and to catalytic activity in chromia. Two-point chemisorption is usually considered as governed by the distance between surface ions—magnetic coupling is suggested as a contributory factor. Magnetic coupling appears to influence the rate of catalytic reactions on surface paramagnetic ions, and influence electron transfers which occur in semiconduction with weakly chemisorbed molecules. Coupling may, indeed, directly affect semiconduction characteristics, as in V_2O_3.[25]

Six-point mechanisms for hydrogenation of aromatics and dehydrogenations and ring-closures have been advanced. The low activity of bulk iron for hydrogenation of benzene has been related to its geometrically unfavourable *BCC* structure. Bulk MoO_2 is also geometrically unfavourable for a six-point mechanism, and is inactive for ring-closures even at temperatures where it is not reduced to the metal[6], whereas on a gamma alumina surface, where it is active, hexagonal arrays of Mo ions are inherently likely for the same reasons as in amorphous Cr_2O_3.

It has also been shown[3] that the activation energy for ring-closure on chromia alumina catalysts is closely related to that for their *n*-type semiconduction.

The contribution of a magnetic factor to dehydrogenation and ring-closure reactions can be seen from *Figure 1*, in which antiparallel coupling of Cr ions in hexagonal arrays offers six-point sites for the weak chemisorption of aromatics of the same spin-symmetry as the aromatic sextet of electrons in benzene, and therefore this factor tends to encourage the formation of aromatic character in hydrocarbons and the easy desorption of the aromatic hydrocarbons produced, while the converse is the case for ferromagnets such as nickel.

Thanks are due to W. E. Armstrong and J. Newman for help in the experimental work leading to this, and to J. D. F. Marsh and Dr. R. H. Griffith for helpful and stimulating discussion. This paper is published by permission of the Gas Council.

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4

DISCUSSION

Chairman: F. S. Stone

On Paper 4.1

P. T. Landsberg: The rate laws which have been put forward on the basis of the boundary-layer theory of chemisorption[1] are

$$\mathrm{d}q/\mathrm{d}t = A(q) \exp(-\alpha q), \qquad \alpha \equiv 4\pi e^2 a/\varepsilon kT \tag{1}$$

and

$$\mathrm{d}q/\mathrm{d}t = B \exp[-\alpha(q + q^2/2an)] \tag{2}$$

Here q is the number of atoms chemisorbed per unit area, and is regarded as a function of the time, n is the number of impurity centres per cm^3, and a is a certain distance of atomic dimensions. kT has its usual significance and ε is the dielectric constant of the semiconductor. If the process of chemisorption uses up electrons, then equation (1) applies to p-type, equation (2) to n-type, semiconductors. If the chemisorption process frees electrons, the situation is reversed, and equation (1) applies to n-type, (2) to p-type, semiconductors. B is a constant, but A depends on q in a fairly complicated manner. It is to be emphasized that neither law can be regarded as strictly equivalent to the frequently observed logarithmic ('Elovich-type') rate law

$$bq = \log[(t + t_0)/t_0]$$

or, equivalently,

$$\mathrm{d}q/\mathrm{d}t = C \exp(-bq) \tag{3}$$

for which alternative models have been proposed[2]. Observations which satisfy (3) can therefore not necessarily be used to support the barrier-layer theory in the form (1) or (2).

Some of the assumptions involved in the deduction of equations (1) and (2) may be questioned, and reconsideration of this matter in the light of the analogous barrier-layer theory of rectification[3] leads to the following conclusion. If chemisorption uses up current carriers (electrons in an n-type semiconductor, holes in a p-type semiconductor), and if eq_0 be the space charge per unit area of the barrier at the beginning of the experiment, then, in a first approximation,

$$\mathrm{d}q/\mathrm{d}t = C \exp[-b'(q_0 + q)^2], \qquad b' \equiv 2\pi e^2/\varepsilon nkT \tag{4}$$

This assumes that the rate-controlling factor is the diffusion of current carriers over the potential-energy hump created in the semiconductor due to the extraction of current carriers by the chemisorbed atoms. Note that equation (4) yields a law of the form of equation (3) if $q \ll q_0$. However, in general one will aim at conditions in which the experiment is started with a negligible number of chemisorbed atoms at the surface of the semiconductor, i.e. $q_0 \ll q$. Of the two limiting cases

$$dq/dt = C' \exp(-2b'q_0q) \qquad (q_0 \gg q) \tag{5}$$

$$dq/dt = C \exp(-b'q^2) \qquad (q \gg q_0) \tag{6}$$

of equation (4), equation (6) is therefore the more likely one.

The questions which are raised by these considerations are:

1. For a given semiconductor, what is the difference between the rate of chemisorption on an *n*-type, as against a *p*-type, specimen?
2. Given a semiconductor, and its conductivity type, what is the difference between the rate of a chemisorption process which uses up electrons, as against one which frees electrons?
3. Is there any evidence in favour of a rate law equation (4)?

Experimentally verified answers to these questions will clearly decide if the barrier-layer theory of chemisorption is tenable, and, if it is, in what direction it has to be developed.

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P. White: It may be of interest to give a brief account of an experimental study which we have recently made of the interaction of oxygen with an evacuated layer of lead selenide, arrangements having been made to measure the resistance of the layer at any time.

The layer of lead selenide was evaporated in vacuum on to a glass substrate maintained at −195°. The lead selenide prepared in this manner was found by thermo-e.m.f. measurements to possess *p*-type conductivity. After measuring its resistance and surface area, the layer was warmed to −78°, and then its resistance and surface area measured at −195°. This cycle of operations was repeated, the final temperature being raised by successive steps to 200°C. It was found that the resistance at any one temperature decreased as the final temperature increased; since also the surface area decreased it seems that the resistance is due in part to resistance between crystallites.

Volumetric measurements were made of adsorption of oxygen on a previously heat-treated, evacuated lead selenide evaporated layer at temperatures ranging from −195° to 200°. Above 200°, no measurements were possible due to decomposition of the lead selenide. At temperatures up to 25°, the conductivity of the layer changed only very slightly on adsorption of oxygen. As the temperature increased from −195° to 25°, the amount adsorbed at constant pressure decreased. Between 100° and 200°, however, on adsorption of oxygen, the resistance changed rapidly. At 200° the resistance increased at a rate proportional to the initial pressure, reached a maximum independent of initial pressure, and then decreased at a constant rate. At this temperature the amount which had disappeared when the resistance of the layer was a maximum, was independent of initial pressure. Analysis of rates of resistance change and rates of oxygen adsorption indicates that at this temperature the oxygen first diffuses into the lattice, and then when a definite amount of gas has dissolved, an amount independent of initial pressure, the remaining oxygen builds up as an adsorbed layer on the surface. The rate of formation of this adsorbed layer is given by

$$\frac{dv}{dt} = \frac{t}{v}$$

where v is the volume of gas adsorbed at time t.

D. A. DOWDEN: Morrison's model for two kinds of chemisorption of hydrogen, mentioned by Dr. Stone, requires bonding with chemisorbed oxygen and this may well be correct for strongly bonded hydrogen. On the other hand, the poisoning of hydrogen reactions for example hydrogen–deuterium exchange and *iso*propanol dehydrogenations by oxygen and oxygenated species does suggest, eschewing further hypotheses, that this is unlikely for the hydrogen chemisorption involved in catalysis. Then if Morrison's picture is valid there may be yet a third type of chemisorption involving bonding to zinc species.

Professor de Boer suggested in the thirties that the active centres could be considered to be zinc atoms. Formation of anion vacancies or interstitial zinc ions at the surface leads to entities rather like electron-deficient triatomic zinc molecules, and it may well be these which bond the 'active' hydrogen. Then a moderately simple molecular-orbital treatment should give enlightening results.

On Paper 4.2

R. A. W. HILL: Does Dr. Winter find that in the oxygen (O^{18}) exchange reactions he has studied, the activation energy changes always to a lower value at the higher temperatures?

E. R. S. WINTER: Yes, where a change is observed it is in this direction.

L. E. J. ROBERTS: Does the amount of O^{18} appearing in the gas phase indicate that the exchange is with the surface layers only, or does exchange with oxygen of the bulk lattice take place at the temperature studied? Are there clearly two rate-determining processes occurring at different temperatures even though the reaction is confined to the surface layer?

E. R. S. WINTER: (a) All the reactions discussed in this paper appear to be confined to the surface layer only. See reference 6 and also HOUGHTON and WINTER, *Nature*, 164 (1949) 1130; WINTER, *Disc. Faraday Soc.*, 8 (1950) 231.

(b) Yes the results shown in *Figures 1–4* indicate this quite clearly.

On Paper 4.3

D. A. DOWDEN: Does the oxygen adsorbed in the second layer possess any characteristics which can be related to the electronic configuration of the cations?

F. S. STONE: The close similarity between cuprous oxide and cobaltous oxide in respect of the post-monolayer uptake suggests that one must look for the interpretation of this phenomenon rather in terms of their lattice defect structure than in terms of actual electronic configuration of the cations. Nevertheless, in addition to lattice expansion, the adsorption requires the formation of Cu^{2+} (or Co^{3+}) ions in the matrix of Cu^{+} (or Co^{2+}) ions and, in this sense, the increasing difficulty of electron transfer giving O^{-} or O^{2-} is probably the main factor bringing the uptake to a standstill.

L. E. J. ROBERTS: The reaction of UO_2 with oxygen around room temperature certainly involves much more than monolayer adsorption; it is probable that the outermost adsorbed layer remains substantially complete, as it is at −183°, and that the additional oxygen penetrates 40 or 50 Å below the surface[1]. This cannot happen by the same mechanism which controls the diffusion process above 100°, since the thermal energy at room temperature and below is insufficient to provide the activation energy required, which is about 20 kcal/mole. It may be that the strong field set up between the negative chemisorbed species and the compensating positive charges in the interior of the crystal aid the diffusion of oxygen ions into the outer layers of the crystals.

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On Paper 4.4

D. A. DOWDEN: I have recently re-examined the results of my pre-war work with Professor R. A. BEEBE[1] on chromia in the quest for evidence upon the several types of chemisorption. Using the argon isotherms given at that time to calculate surface areas, it is now certain that the phenomena referred to by Dr. Roberts were all surface adsorptions and that they are quite similar to those found for UO_2.

At the same time we found a little evidence for what might be called autocatalytic adsorption, for which some tantalizing fragments of evidence can be found scattered elsewhere in the literature.

It was noticeable with carbon monoxide, oxygen, and nitrogen that if a run was interrupted for an abnormally long time (e.g. overnight) after the last increment of adsorbed gas had reached the strongly bound state, then the slow process of transition from the weakly adsorbed state to the strongly bound state did not occur in the next admission. Only the weak adsorption was found; yet the next increment always yielded the transition. It seems that a small portion of the adsorbed gas nucleates the subsequent processes.

Similar autocatalytic effects are found elsewhere[2,3].

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L. E. J. Roberts: There is some evidence of an 'autocatalytic' effect in the adsorption of oxygen by UO_2. After 50 per cent coverage there is a distinct time lag between the evolution of the heat corresponding to physical adsorption and the start of the chemisorption itself. However, we have not observed any difference in the rate of evolution of heat due to interrupting the runs by waiting overnight; the specimens were always kept at −183° overnight.

We have not considered the adsorption at −183° to occur on any particular sites since the surface coverages are so high and surface mobility at −183° is probably low.

M. W. Roberts: The adsorption of nitrogen on calcium films, which Dr. Tompkins and I have been studying, shows a similar phenomenon to that mentioned by Mr. Dowden. The second and successive doses of gas were adsorbed at a faster rate and to lower pressures than the initial one. It may be that the initially adsorbed nitrogen forms a surface nitride into which the successive doses of nitrogen were incorporated.

W. E. Garner: With reference to autocatalytic processes on surfaces, it is possible that the process of adsorption occurs in two stages: (1) the chemisorption of gas molecules on surface sites, followed by (2) a rearrangement of the valencies in the solid around the site. As a result of the latter, new active sites are produced.

G. C. Bond: Cases of autocatalytic chemisorption have been treated by Taylor and Thon[1], who suggest that the adsorption of one species may create sites for further adsorption. The mechanism by which this may occur is not clear, but it represents an interpretation of autocatalytic effects in chemisorption phenomena.

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F. S. Stone: I think one should not lose sight of the fact that the heat of adsorption itself may set in motion a process of regeneration of sites. Localized thermal effects may easily change the spectrum of defects at the surface. Some general consequences of thermal disorder on adsorption, including mechanism, have been discussed by Volkenstein.

D. A. Dowden: The suggestion by Dr. Roberts that one oxygen molecule reacts with one surface uranium atom is in line with the fact that extremely dilute solutions of vanadium species in potassium pyrosulphate are active in sulphur dioxide oxidation under conditions where it seems almost certain that only one vanadium atom is effective in the activation of the oxygen molecule.

Similar models have recently been proposed for enzyme systems using singly and doubly bonded π-complexes with oxygen.

D. J. E. Ingram: (*Communicated*). Mr Dowden has made reference to the work on adsorption by enzyme systems. A brief summary of our results on haemoglobin may be of interest. The main object of the investigation of such compounds by electron resonance has been to elucidate the way in which the central iron atom is bound to the radicals on the sixth coordination point. The ease with which the bond with this radical can be made and broken, in such cases as in the uptake of oxygen, is of particular interest and detailed information on the orbitals involved in the bonding should be very valuable. As a result of our initial measurements[1] it appears that both the oxygen and NO molecules are held in position with their interatomic axis parallel to the haem planes[2] instead of perpendicular to them, as had been previously supposed. This would seem to fit in with the general idea of a type of reversible chemisorption rather than the formation of a stable chemical bond. It is hoped that further studies by electron-resonance techniques will add more detail to this picture.

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D. D. Eley: Mr. Dowden has referred to the possibility of one metal atom making two surface bonds. This hypothesis ('multivalent-site hypothesis') is one that we have frequently used in discussing activated complexes in hydrogen reactions, since it arose out of work carried out with Dr. Couper on Pd–Au alloys. In transition metal surfaces, depending on the lattice plane, there will be two to five crystallographic positions above an atom, and one may conclude that if steric conditions allow, two to five adsorbed atoms might be held by half-bonds, or one to two-and-a-half electron pair bonds might be made[1,2]. This is using the ordinary *dsp*-orbitals, and in addition the atomic *d*-orbital is available, at least for activated complexes.

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D. A. Dowden: It is not possible to say whether a loose chemisorption, or an activated complex, using orbitals mainly of *d*-character, can occur on a metal site already holding adsorbates by strong bonds. It is, however, quite analogous to the use of a seventh orbital in the formation of the activated complex in the $S_{N}2$ reactions of octahedral inorganic complexes. Taube's work[1,2] suggests that in some cases this also requires the use of empty *d*-orbitals.

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On Paper 4.5

D. A. Dowden: It seems to me that Dr. Davis's paper is singularly close to the point. In my paper I have given similar structures, but involving H^{+}

between two metal species. Then, rather as in the magnetic oxides, one might expect the nature of the bonding to depend upon the electronic configuration of the cations. Such a 'mixed-bond' effect illustrates the shortcomings of purely ionic models and similar crystal-field theory plus molecular-orbital treatments can be given to the bonding of the proton and of carbon monoxide.

D. D. Eley: Has Mr. Dowden considered the various terms contributing to the energy of his postulated structure $M^- \ldots H_2^+ - M$? The ionization potential of H_2 is 16·2 eV, and using the image approximation for a bulk metal, the E is $+9{\cdot}88$ eV[1] for

$$H_2 + W \qquad H^+ \ldots W^-$$

I should have thought the antiferromagnetic interactions were not of the order of $-9{\cdot}88$ eV required to make this structure thermoneutral. (I would add that similar difficulties with respect to energy would appear to face the bond–no bond charge-transfer mechanisms.)

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D. A. Dowden: Evidence existing in the literature suggests that weak chemisorption should have heats lying between 0 and 10 kcal mole^{-1}. While it is true that the ionization potential of H_2 is *c.* 15 eV, only detailed calculation can yield the compensating terms on the credit side.

SECTION 5

CHEMISORPTION ON CARBON

Chairman: W. F. K. WYNNE-JONES

5.1

CHEMISORPTION OF OXYGEN ON CARBON

H. Harker, H. Marsh, and W. F. K. Wynne-Jones
King's College, Newcastle-upon-Tyne

SUMMARY

Adsorption by carbon has been extensively studied on account of the ease of preparation of material of high surface area. Studies of the adsorption of inert gases have shown that one can obtain a wide variety of 'pore' sizes, and Dubinin, by correlation of the results of adsorption and electron-microscope studies, has obtained a 'pore' distribution for active charcoal.

The carbons commonly used for adsorption studies are mainly non-crystalline, giving very diffuse X-ray patterns indicating the presence of small graphitic crystallites, and are usually far from pure carbon. They are usually prepared at temperatures below 1500°C *and consequently contain appreciable amounts of hydrogen, as well as other impurities. It has been shown by Steenberg and others that low-temperature carbons are usually acidic. Attempts are now being made to prepare active carbons of more defined chemical composition.*

When oxidizing gases are used, chemisorption invariably occurs and some reaction takes place, as well as the firm retention of gas on the carbon.

The work of Gulbransen and Andrew has shown that, during reaction with carbon dioxide, graphite always retains oxygen which is difficult to remove: similar results are obtained with other carbons and also in the reaction with sulphur.

INTRODUCTION

It is well known that carbon will chemisorb oxygen above 0°C and that the oxygen can only be recovered as a mixture of oxides of carbon[1]. The nature of the chemisorbed oxygen, which is usually called the surface-oxide complex, is incompletely understood. Most gases containing oxygen (e.g. CO_2, CO, O_2, and N_2O)[4,5,12] can produce surface oxide on carbons at elevated temperatures, but the study is complicated by the simultaneous production of reaction products in the gas phase. The nature of the surface oxide cannot be deduced readily from a knowledge of the surface of the carbon because of the lack of a precise understanding of the carbon structure, which is usually described as consisting of small graphitic layer-planes bonded to various amounts of disordered material[6]. There is also the possibility that some of the oxygen of this surface oxide is chemically bonded to hydrogen since many of the 'amorphous' carbons which form surface oxide are prepared by carbonizing hydrogenous organic materials, e.g. cellulose and sucrose.

However, it is well known that this complex shows a range of thermal stability, oxygen chemisorbed at 0°C producing oxides of carbon over the whole range of temperature up to 900°C[2], and that it can be reduced by hydrogen and carbon monoxide[3]. Considerations show that it is reasonable to assume that the oxygen will be most strongly chemisorbed on carbon atoms at the edges of the layer planes because it is here that chemical unsaturation can occur.

This paper describes an examination of the formation of surface oxide over a range of temperature.

SURFACE ACIDITY OF CARBONS

Most amorphous carbons contain significant amounts of hydrogen. When oxygen is chemisorbed on to the surface of such a carbon a variety of groupings would be possible, including phenolic, carboxylic, ether, ketonic, and aldehydic groups. Phenolic and carboxylic groups would be expected to confer acid properties to the surface. Surface acidity has been detected on a variety of carbons by STEENBURG[8] and other workers. VILLARS[9] has produced evidence for the existence of phenolic, ketonic, and ether linkages by reacting a Grignard reagent with carbon blacks.

In the present investigation the acidity was measured by reaction with sodium hydroxide solutions. A weighed (1 g) sample of the carbon was shaken up with 20 ml of standard sodium hydroxide for 24 hours followed by duplicate back-titrations of NaOH in the centrifuged supernatant solution. Bromo-thymol blue was used as indicator and precautions were taken to exclude carbon dioxide.

The preliminary experiments showed that a period of 24 hours was sufficient to establish equilibrium between the 'surface' and the solution. Measurements of the 'take-up' of sodium hydroxide (at a given concentration) could be duplicated to within 10μ equiv./g of carbon. The quantity of alkali taken up by the carbon was found to increase regularly with increasing alkalinity of the supernatant solution (*see Figure 1*). Separate experiments showed that the acidity of a 'neutralized' surface could be completely regenerated by washing six times successively with 50 ml of distilled water (*see Table I*).

The 'take-up' of alkali appears to be due to specific acid groups on the surface since a single sample of carbon (in this case coconut charcoal) can vary widely in acidity after oxidation for short times, which would not be expected to cause great changes in surface area.

Table I

Carbon	NaOH *taken up from from* N/50 *solution* (microequivalents/g)	*Repeat experiment after washing sample*
Cellulose 400° char.	207	226
Cellulose 1000° char.	52	58
Oxidized coconut charcoal	235	255

These facts indicate a reversible neutralization reaction

$$\mathrm{RH} + \mathrm{NaOH} \rightleftharpoons \mathrm{RNa} + \mathrm{H_2O}$$

If the forward and reverse reactions are both first order with concentration, the isotherm (e.g. *Figure 1*) should be represented by a Langmuir equation

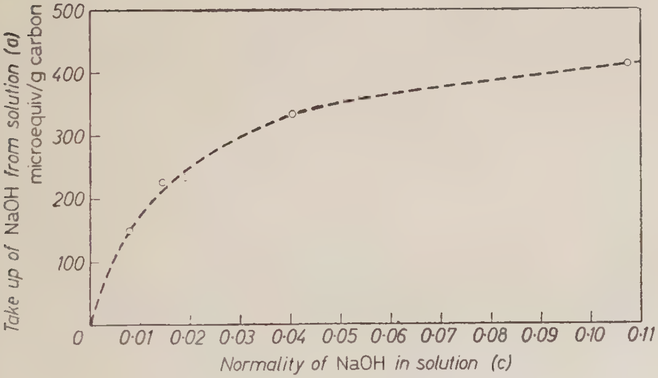


Figure 1. Reaction of oxidized coconut charcoal with sodium hydroxide solutions.

$$\frac{c}{a} = \frac{1}{KA} + \frac{c}{A}$$

where

C = equilibrium concentration of sodium hydroxide
a = number of neutralized acid groups
A = total number of acid groups on the surface
K = the equilibrium constant

A typical Langmuir plot is shown in *Figure 2*. The acidity (A) of the carbon was deduced from the slope.

The acidities, determined by this method, for a coconut charcoal heated in air to various weight losses are shown in *Figure 3*. It is

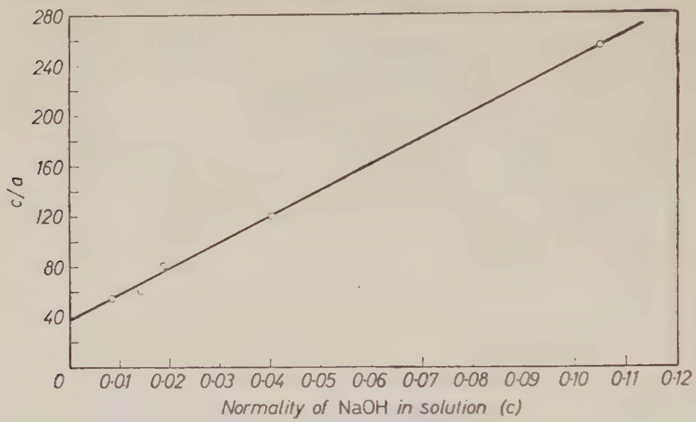


Figure 2. Langmuir plot for oxidized coconut charcoal.

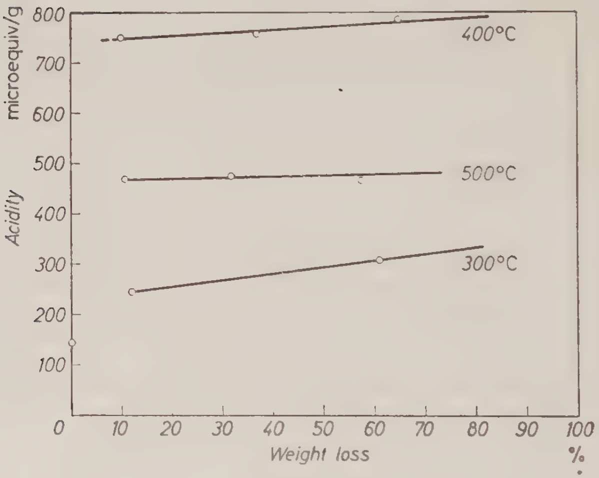


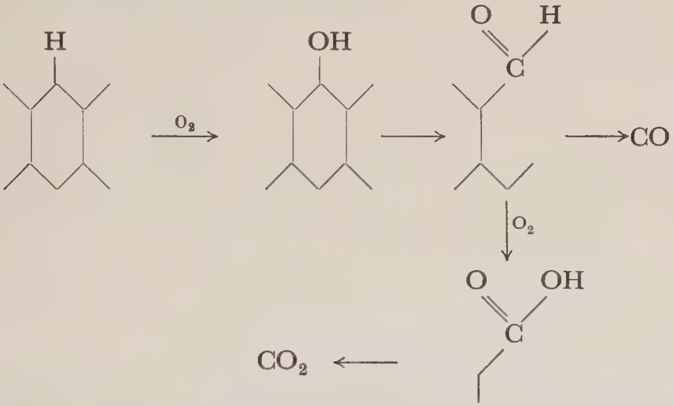
Figure 3. Acidity of coconut charcoal heated in air.

clear from these experiments that the optimum temperature for the formation of acid groups is about 400°C.

A sample of coconut charcoal of acidity 450 μ equiv./g (after heating in air at 400°C) lost its acidity completely after heating for 24 hours in vacuum at 400°C.

Though the nature of the acid groups on carbons is not yet established, it seems likely in view of the above experiments that they contain both oxygen and hydrogen and could be either phenolic or carboxylic in character. Since they are formed in air at 400°C and decomposed in vacuum at the same temperature, the possibility arises that they function as reaction intermediates in the oxidation of carbon at these temperatures.

It has hitherto been difficult to account for the production of carbon dioxide from oxide layers on carbon at temperatures less than 500°C. On the assumption that the acidity is due to carboxyl groups which can decarboxylate, an explanation is immediately forthcoming from some such scheme as:



A similar scheme has been shown to account for the production of carbon dioxide in the low temperature combustion of hydrocarbons by Bone[10]. Some carbon monoxide could presumably arise from direct decomposition of the aldehyde groups.

Sato and Akamatu[1] have shown that the addition of various inorganic compounds to amorphous carbons can increase the adsorption of oxygen at room temperature by a large factor. The presence of such compounds can also markedly increase the rate of reaction of carbon with oxidizing gases such as carbon dioxide and oxygen. The two effects are probably related.

In an investigation (to be published) of the reaction at 300–500°C between oxygen and amorphous carbon admixed with alkali metal carbonates, the results suggest that the salt functions in this case by ion-exchanging with the 'acid oxide' on the surface. Some of the metal atoms thus become attached to the carbon in surface 'salt' groups. The magnitude of the effect appears to be connected with the polarity of such surface 'salt' groups formed, because the order of catalytic activity for a series of alkali metal carbonates is Cs > Rb > K > Na > Li.

A comprehensive theory of the chemisorption of oxygen on carbon surfaces would have to account for the effect of such polar groups.

THE CHEMISORPTION OF OXYGEN UPON CARBON FROM CARBON MONOXIDE ABOVE 500°C

During the reactions of carbon dioxide and carbon monoxide with carbon at temperatures above 500°C, oxygen is chemisorbed upon the carbon surface. The mechanism of formation and properties of this surface oxide have been studied quite extensively when examining the mechanisms of gasification reactions[11–17], one conclusion being that adsorption of carbon monoxide can occur.

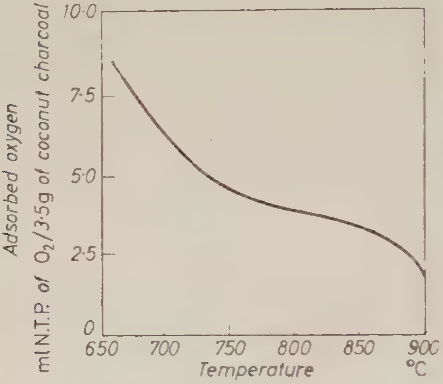


Figure 4. Variation of amounts of surface oxide with varying temperature when CO_2 reacts with coconut charcoal, previously outgassed at 900°C in vacuum. Volume of reaction vessel 250 ml.

As previously mentioned, the mechanism of formation of surface oxide when carbon reacts with gases containing oxygen is rendered obscure by other simultaneously occurring reactions. Although adsorption of carbon monoxide at temperatures above 500°C has been accepted for many years, no direct experimental evidence has been available to confirm this. Analysis of the published data shows that when surface oxide is formed from carbon monoxide in the presence of carbon, the possibility that other reactions can occur has not been excluded. For example, BARRER[17] does not publish subsequent gas-analysis data, so that the pressure reduction measured by him is perhaps due to CO_2 production.

Work carried out in these laboratories has shown that when CO_2 or CO, in the presence of various carbons, reacts to establish the C—CO_2—CO equilibrium state, surface oxide is always formed. Data, presented in *Figure 4*, show the variation of amounts of surface oxide with temperature when CO_2 reacts with a coconut charcoal (previously outgassed at 900°C in vacuum) to give a final equilibrium pressure of 1 atm. It has been established that the rates of the CO_2—C, and CO—C reactions, including the formation of surface oxide, are very sensitive to the amounts of inorganic impurities which may be present[18,19]. Further, the formation of surface oxide from carbon monoxide, using pure and impure graphite and coconut charcoal, has been studied at temperatures of 800°C with previous outgassing at 900°C in vacuum. The pure carbons contained only several parts per million of inorganic material, whereas the impure materials contained about 1 per cent of added inorganic material, such as ferric citrate or sodium carbonate. The results of these experiments show that if, during the reaction of carbon monoxide with carbon, no carbon dioxide is formed, then no surface oxide is produced. Evidently the carbon monoxide was not adsorbed by these pure carbons.

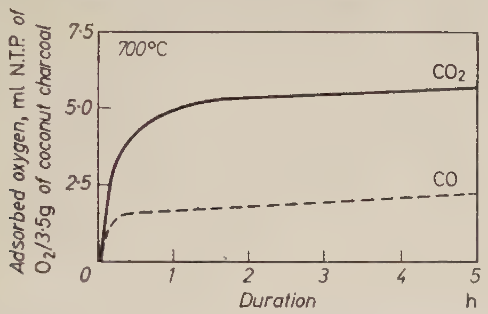


Figure 5. Formation of surface oxide from CO_2 and CO.

This evidence rather suggests that the surface oxide is formed from carbon dioxide, which is itself produced by decomposition of the carbon monoxide, the reaction sequence being as follows:

$$2CO \rightarrow C + CO_2$$

$$CO_2 + C \rightarrow CO + C(O) \text{ stable surface oxide}$$

Experiments carried out by us, over the temperature range 650–900°C, using a coconut charcoal outgassed at 900°C, showed that surface oxide was formed much more quickly from carbon dioxide than from carbon monoxide (*see Figure 5*). Also, if carbon monoxide reacts with impure coconut charcoals outgassed in vacuum at 900° and 700°C, respectively, carbon dioxide was produced much more rapidly in the latter case (see *Figure 6*).

The reaction of the secondary carbon dioxide with the carbon surface appears to be retarded by the surface oxide already present.

There remains the possibility that carbon monoxide can be adsorbed upon certain carbon sites created during the course of the reaction of the carbon dioxide with the carbon. This view is not supported, however, by experimental evidence obtained by workers using ^{14}C.[20,21] In experiments involving the use of ^{14}CO, the amount of ^{14}C deposited upon the carbon surface was attributable to decomposition and not adsorption of carbon monoxide. One may conclude by pointing out that evidence has been brought forward which suggests that during gasification reactions at temperatures above 500°C, adsorption of carbon monoxide by carbons plays no significant part in the reactions which occur, the surface oxide being formed by reaction of carbon dioxide with the carbon.

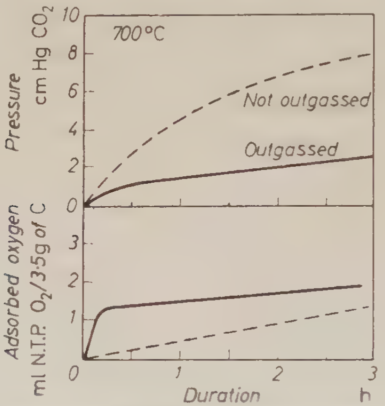


Figure 6. Formation of CO_2 from CO and impure coconut charcoals, outgassed at 900° and 700°C.

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5.2

ELECTRON RESONANCE STUDIES ON CARBON ADSORPTION

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SUMMARY

Recent measurements using the new technique of electron resonance have shown that all carbons formed below 650°C *contain a large number of stabilized unpaired electrons. The mechanism producing these appears to be some form of bond breakage round the edge of the condensed carbon rings, and this is confirmed by the very marked change which occurs in the energy states of the unpaired electrons when oxygen is adsorbed. The most striking feature of these effects is their complete reversibility, since the original signal can be restored by simply pumping off the oxygen. It would appear that there are two different effects corresponding to two different types of interaction of the oxygen with the carbon surface, one involving no short-range forces, the other seeming to require a pairing of electrons and formation of some type of bond.*

Further investigations have shown that the carbon surface can be 'shielded' from the oxygen attack by the adsorption of various liquids, and these results, together with others on the effect of heat treatment, suggest possible mechanisms for the interactions taking place over the carbon surface. An interesting correlation is also obtained from measurements on the electron concentrations during the milling and vulcanization of rubbers with carbon blacks.

Before describing the results in detail, a summary is given of the basic theory and technique of electron resonance as applied to chemical problems, so that the advantages and limitations of this kind of investigation can be appreciated.

INTRODUCTION

The discovery[1] of a high concentration of unpaired electrons, or free radicals, in low-temperature carbons has opened up a new method for studying the surface state of such systems, and a detailed investigation of the different factors affecting the radical concentration and energy states promises to throw fresh light on the nature of some of the adsorption interactions. Since the method of electron resonance, which is used to study these effects, is relatively new, a brief outline of the basic theory and experimental technique is given first so that the nature of the measurements can be clearly understood. This is followed by a summary of the initial measurements on free-radical concentrations in carbons, from which the mechanism of radical formation is shown to be associated with the breaking of peripheral bonds of the condensed carbon rings. One of the most striking results in this connection is the interaction between gaseous oxygen and the radical centres[2], and this effect can be used directly as a probe to investigate the state of the carbon surface. This is particularly useful in adsorption studies, and the second section of the experimental results describes a series of experiments in which the effect of adsorbed liquids is studied in this way. Although these measurements are only of a preliminary nature, it would appear that certain conclusions can already be drawn about some of the interactions occurring across the carbon surface.

EXPERIMENTAL TECHNIQUE

It is possible to detect and investigate free radicals by electron resonance because the unpaired electrons possess non-compensated magnetic moments. In the absence of any applied magnetic field all the electrons will have the same energy, irrespective of the orientations of their magnetic moments, but if a magnetic field is applied across the specimen the moments will align themselves either parallel or anti-parallel to the field, and two energy levels will thus be formed. The separation between these two levels will depend on the magnitude of the applied magnetic field and is equal to $g\beta H$ where g is the 'spectroscopic-splitting factor', normally called the 'g value' and equal to 2·0023 for a completely free spin; β is the Bohr magneton.

This splitting of the energy levels by the applied magnetic field is illustrated in *Figure 1*, and it can be seen that if radiation of frequency ν, such that $h\nu = g\beta H$, is now fed to the sample, an absorption of the radiation will occur as electrons are raised from the bottom to the top level. Stimulated emission will also be produced as electrons fall from the excited state to the ground level, but since the number in the excited state is less than that in the ground level, a net absorption of the radiation occurs. It is evident that the net absorption will increase with increasing energy difference between the two levels and decreasing temperature of the specimen, as both of these conditions will produce a higher proportion of electrons in the ground state. It is for this reason that electron-resonance measurements are normally made at microwave frequencies, and often at low temperatures if the highest sensitivity is required.

A block diagram of a typical electron-resonance spectroscope as used for free-radical investigations at room temperature is shown in *Figure 2.* The specimen to be studied is placed in a cavity resonator, which serves to concentrate the microwave radiation, and this is placed between the poles of the electromagnet as shown. The detection and display system is arranged so that the absorption spectrum can be directly presented on an oscilloscope screen[3], or, alternatively, traced out on a pen-recorder.

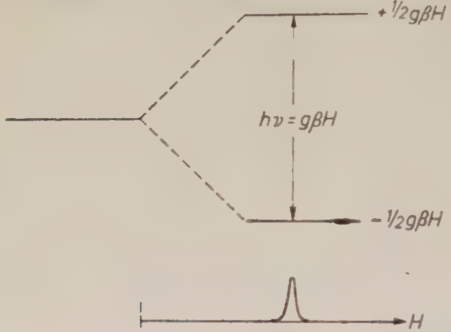

Figure 1. Electron resonance. Resonance condition:—

$$h\nu = g\beta H$$

$$\therefore \quad \nu = 2{\cdot}8 \,.\, 10^6 \,.\, H \text{ for free electron}$$

i.e. at 10,000 gauss

$$\nu = 28{,}000 \text{ Mc/s.}$$

There are three features of the spectrum which are of interest so far as the derivation of chemical information is concerned. First, the '*g* value' corresponding to the centre of the absorption line, this being calculated directly from the field-frequency ratio required for resonance. Any deviation of this value for the 2·0023 of a free spin indicates an admixture of orbital momentum and hence some interaction and binding with other atomic orbits. Secondly, the width of the absorption line can give information on the nature of interactions present in the specimen. The two major contributions to this are normally 'spin-spin' interaction and 'spin-lattice' interaction. The former is due to the random fields produced by the moments of neighbouring spins, and can be reduced by dilution with a diamagnetic material, while the latter is a broadening process produced by the thermal motion or vibrations of the specimen as a whole, and can be reduced by lowering the temperature. The third feature of interest in the spectrum is the occurrence of hyperfine structure, which arises from the interactions of the unpaired electron with any nuclear magnetic moments which are included in its orbit. A detailed analysis of the hyperfine pattern associated with a free-radical resonance can often give very considerable information on the spacing and orientation of different groups within the molecule[4]. Unfortunately C^{12} has no nuclear moment, and hence no hyperfine splitting of the spectrum is produced by the carbon nuclei.

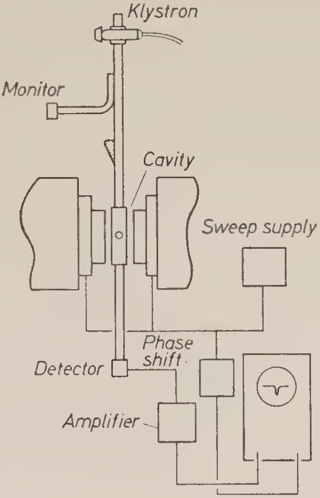

Figure 2. Room-temperature resonance apparatus.

For the particular case of the carbon resonance there are, therefore, only two parameters associated with the absorption line which vary with the condition of the carbon and can thus be quantitatively studied, i.e.

1. The integrated intensity of the absorption line, which gives the total concentration of free radicals in the sample.
2. The width of the line, any variation in this indicating a change in the interactions across the carbon surface.

INITIAL MEASUREMENTS ON THE VARIATION OF FREE RADICAL CONCENTRATION

The first series of measurements[5] undertaken on the free-radical concentration in low-temperature carbons was the variation of signal intensity with increasing carbon content. The results are summarized in *Figure 3*, where the number of unpaired electrons per g, determined from the integrated adsorption, is plotted against the percentage carbon content of a series of different coals. It is seen that the curve rises steeply between 85 and 94 per cent carbon content, and then falls even more steeply to zero once the 95 per cent point has been passed. It would appear that the only type of mechanism that can explain this kind of variation is one involving bond breakage round the periphery of the condensed carbon rings. Thus, if the growth of radical concentration in the 85 to 93 per cent carbon range is compared with x-ray measurements[6] on the same samples, it is found that the radical concentration

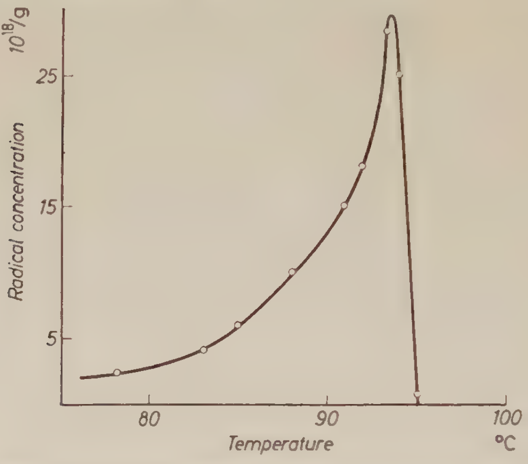

Figure 3. Variation of radical concentration with carbon content.

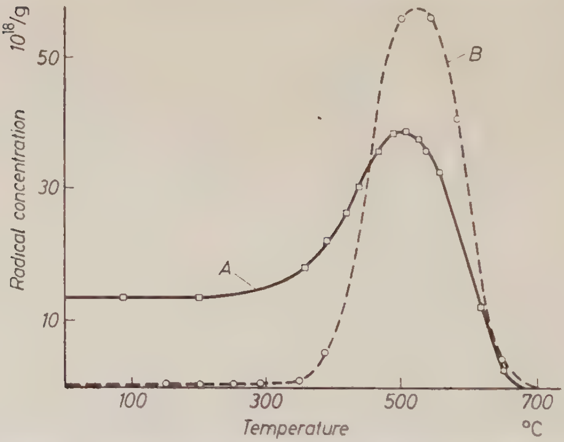

Figure 4. Variation of free-radical signal with temperature of carbonization. A: coal samples; B: oil residues.

is rising rapidly just when the individual benzene rings are beginning to cluster and form large systems. A reasonable quantitative correlation[7] can, in fact, be made over this range between the radical concentration and the number of peripheral carbon atoms, assuming that the rings pack in the most compact form. This, therefore, suggests that, in the formation of large condensed ring structures, some of the edge bonds may be left unsaturated and the highly resonant nature of the ring system will stabilize the unpaired electrons so formed. As soon as the carbon content becomes so high that the condensed rings start joining to form large graphitic sheets, the proportion of edge bonds will begin to drop, however, and the rapid fall in free-radical concentration in the meta-anthracites is attributed to this partial graphitization.

A similar kind of variation is found when the free-radical concentration is plotted against temperature of carbonization. Typical results are shown in *Figure 4* for the carbonization in air of (*A*) coal and (*B*) oil. The coal carbonization was carried out by B.C.U.R.A. Leatherhead, each sample being held at the stated temperature for two hours, and the oil samples were supplied by Shell Research Ltd., being the residues left after distillation at the given temperature. The rapid growth of the free-radical signal at a temperature of about 550°C can be clearly seen in both cases, and it is just at this temperature that most of the volatile matter is driven off[8]. This again supports the hypothesis that the free-radical formation takes place as the original structure is disintegrating and the carbons are joining to form condensed ring systems.

Further confirmation that the radicals are formed by edge-bond breakage, rather than localized in the centre of the ring systems, is obtained from the 'oxygen effect' which occurs in all normal low-temperature carbons when formed above 600°C. If such specimens are investigated at atmospheric pressure no, or very little, signal is discernible, but if the samples are carbonized *in vacuo* instead of in air an intense absorption line is still obtained which decays on admission of oxygen to the sample[2]. The most striking feature of this oxygen effect is its reversibility, in that the height of the free-radical absorption peak can be varied in either direction by just adjusting the pressure of the oxygen above the sample. More detailed investigations[9], described in the next section, show that this oxygen effect appears to occur in two distinct ways, but the initial measurements were sufficient to demonstrate that the unpaired electrons associated with the free radicals were near enough to the carbon surface to interact strongly with gaseous oxygen admitted to the samples.

It has been suggested[10] that a form of triplet excitation may have been responsible for the unpaired electrons, but the normal variation of the signal intensity with temperature appears to rule this out. The observed g value of $2{\cdot}003 \pm 0{\cdot}001$ also indicates very little orbital admixture, and hence suggests a non-localized orbit for the unpaired electron, resonating round the ring structure.

It therefore seems evident from the initial measurements on various carbons that these radicals are formed when the original structure disintegrates and the carbon atoms start joining to give condensed ring systems, which possess unsaturated bonds and associated resonance-stabilized unpaired electrons around the periphery. The marked change in the signal on admission of oxygen confirms this idea, and can also be used as a probe to investigate any changes occurring over the carbon surface.

THE STUDY OF ADSORPTION PROCESSES

Since the free radicals present in the low temperature carbons are located round the edge of the condensed ring systems, it seemed likely that adsorption processes which affect the carbon surface might well interact with the radical centres as well. A series of different experiments have therefore been carried out to see if this was in fact so, and from the preliminary results discussed below it is found that very definite changes are produced in some cases.

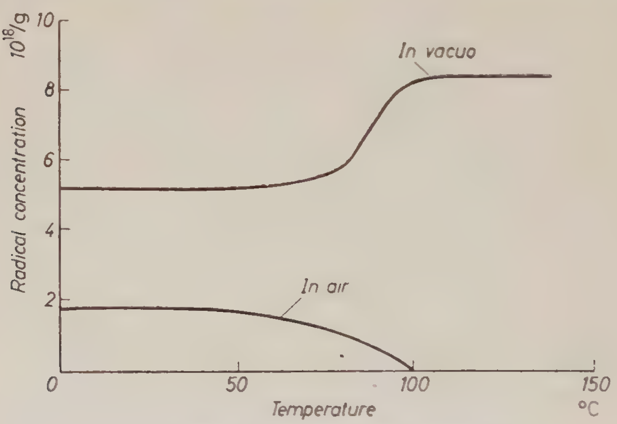

Figure 5. Variation with heating.

The first effect studied was that of water vapour adsorbed on the carbon surface. Finely ground samples of activated wood charcoal were used for the adsorbing carbon in this series of experiments, and the results were found to be generally true for all types of fine ground 'activated carbons' that were tested. These samples will absorb water vapour to a considerable extent if left in the air, and in the first measurements the samples were slowly heated through 100°C to study the radical concentration as the water vapour was driven off. The results are summarized in *Figure 5*, and it can be seen that if the samples are heated in air, then the height of the resonance absorption line decreases, slowly at first, and then more rapidly as the 100°C temperature is approached. All these measurements were made while the sample was being heated *in situ* in the cavity resonator, and the complete heat treatment took several hours. (It should also be noted that it is the peak height of the absorption signal that is plotted in these graphs, and the radical concentration is calculated assuming a constant line width of 8 gauss. The variation of this line width and the effect that this has on the total radical concentration is discussed in more detail later when the different oxygen effects are considered.)

The decay of the free-radical signal as the temperature rises to 100°C suggests that the water vapour has a 'shielding effect' on the radical centres and prevents the atmospheric oxygen interacting with them. When the water vapour is driven off, however, the radical sites are left open for oxygen attack and the signal therefore broadens and decays in the normal manner[2]. This hypothesis is confirmed by the measurements on samples heated *in vacuo* which are also summarized in *Figure 5*. No diminution is now found as the 100°C is reached, in fact a slight increase is actually obtained which may be due to further bond breakage as the water vapour is driven off. If, however, oxygen is admitted to the sample, once it has been heated over 100°C, the absorption signal will rapidly decay until it becomes too broad to detect, showing that the oxygen can now interact with all the radical centres.

This hypothesis of 'radical shielding' by the absorbed water vapour is also supported by further experiments with other liquids. If any liquid such as benzene, toluene, or *cyclo*hexane is added to a carbon which has been heated in air above 100°C, then the free-radical peak is found to rise from zero to exactly the same value as is obtained by pumping off the oxygen (i.e. rises from zero up to the top curve in *Figure 5*). It would therefore appear that these liquids can enter the carbon structure, displace the adsorbed oxygen, and remove the signal broadening. The ability of the liquid, not only to shield from the oxygen, but also to displace it, can be shown very directly in the case of water vapour by leaving an oxygen-poisoned carbon exposed to the air for a few days, when it gradually recovers the narrow absorption line, showing that the radical centres are no longer interacting with the gaseous oxygen. This recovery will not take place, however, if the sample is left for the same time in a desiccator, and is thus unable to adsorb any water vapour.

In order to explain this action, some type of mechanism must be postulated which enables the radical centres to attract and coordinate more strongly with liquids than with gaseous oxygen. It was at first thought that the polar charge of the OH group might be responsible, but this was ruled out when the same effect was obtained with non-polar solvents. The other possible mechanism appears to be a form of capillary action in the very small pores of the activated carbon. Very strong forces might then be brought into being which would tend to hold any liquid present at the expense of the gaseous oxygen.

The general idea of a shielding process is also supported by the results of some experiments on the milling of rubbers. The carbon blacks used in reinforcing rubbers are made in the 650°C to 900°C region and will normally show no free-radical signal when they themselves are placed in the electron-resonance apparatus. The natural rubber itself also gives no signal, but when the rubber and black are milled together a relatively large absorption signal is observed. This, therefore, suggests that milling with a long chain polymer has the same effect in removing the oxygen interaction as the action of the liquid adsorbate or actual evacuation of the sample.

THE OXYGEN EFFECTS

Since the effect of oxygen on the radical absorption signal forms such a useful probe for studying the carbon surface, a more detailed investigation of this effect was undertaken to try and elucidate the actual interaction between the radical centres and the oxygen molecules. The preliminary measurements[2,11] had shown that the absorption line not only decreased in peak height as the oxygen was admitted, but also broadened at the same time. This suggests that the total concentration of free radicals may be constant (as determined by the integrated area under the absorption curve), and that the interaction with the oxygen just broadens the energy states. Quantitative analysis of this broadening shows that this is not the complete picture, however, as the integrated absorption does drop in value initially as oxygen is admitted and only reaches a more or less constant value as the higher pressures are reached. The amount of radical concentration that is actually destroyed varies with the heat treatment of the carbon, being very small in those formed at high temperatures, but quite appreciable in those made at 550°C or below. Thus, in carbons made at 890°C, Singer and Spry[12] find that during the decay of the signal the integrated absorption remains nearly constant and the shape of the line is Lorentzian, these two facts suggesting that the interaction with the oxygen is similar to a collision process in which the thermal motion of the gaseous molecules broadens the energy states of the unpaired electrons; whereas in the case of chars made at 500°C there is sometimes a loss of 30 per cent of the integrated absorption before a constant value is obtained. These measurements, therefore, suggest that the oxygen is interacting with the carbon surface in two different ways:

1. By a purely physical process whereby its thermal motion is shared with that of the unpaired electrons.
2. By some mechanism in which the spins of the oxygen can actually pair with those of the carbon, via spin-spin interaction, if not in actual bond formation.

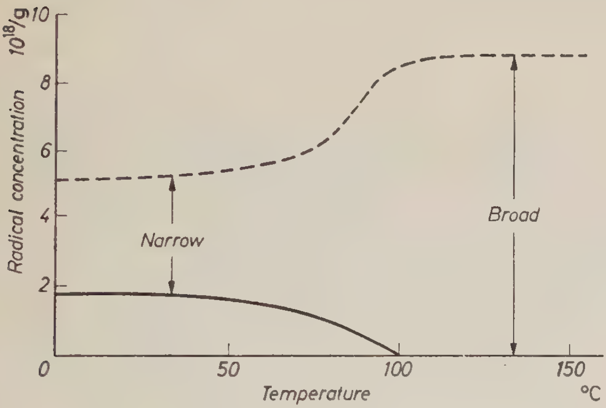

Figure 6. Oxygen effects.

The existence of these two distinct oxygen effects can be seen clearly if the activated charcoals described before are studied. These results are illustrated in *Figures* 6 and 7. If the oxygen effect is observed on the charcoals which have been heated above 100°C, then the normal type of decay is obtained in which the line broadens as it decreases in height, the integrated absorption reaching a constant value at the higher pressures. A series of photographs showing this is shown at the top of *Figure* 7 (the somewhat pointed shape of the absorption in the later stages is probably due to the finite time taken by the oxygen to diffuse into the carbon pores, and thus the signal corresponds to a summation of absorption signals corresponding to different pressures). If, however, the oxygen effect is studied for the activated carbons before they have been heated to 100°C, an entirely different decay of the signal is obtained, in which the line width stays exactly the same as the height of the signal decreases. This is illustrated in *Figure 6* and in the series of photographs at the bottom of *Figure* 7. Another set of results that confirm the existence of two separate effects are those obtained from the milled-rubber samples. If the rubbers are milled with a high-temperature black, only one broadish line is obtained, but if milled with a lower-temperature black two absorption lines are obtained, a narrow line superimposed on a broad one. It would seem that the extremely fine grinding and severe milling of these samples eliminates any effects not due to the nature of the carbons themselves.

There thus seems to be definite evidence that although the main interaction with oxygen in the higher temperature carbons is of a purely physical nature, there is also another interaction, more noticeable in the lower-temperature carbons, in which an actual pairing of spins occurs. It is not yet clear whether this implies that two different kinds of radical species are formed which interact with oxygen differently, or whether it is the immediate surroundings of the radical centres that mainly determine the interaction mechanism. The decay of the signal can be brought about by any other paramagnetic species that can be brought into close contact with the carbon surface, such as nitric oxide gas or salts of paramagnetic atoms in solution, e.g. ferric chloride, manganese and chromic sulphates, and the like. It is interesting that the 'shielding

Figure 7. Decay of signal on admission of oxygen. Top: high-temperature carbon showing broadening. Bottom: low-temperature carbon showing constant width.

effect' of the liquid in the latter case is no longer able to protect the radical centres as the interacting unpaired spins are in the solvent and able to reach close to the carbon surface.

CONCLUSION

It can be seen that much yet remains to be done in elucidating the exact nature of the interaction of various adsorbents with the free radicals present over the carbon surface. These preliminary measurements do indicate some of the general features, however, and suggest that although one of the main interactions with gaseous oxygen is more of a physical process, there is another mechanism in which electron-spin sharing appears to be a necessity and thus might rightly come under the title of 'chemisorption'.

The use of these effects as a probe to study the carbon surface and its interaction with other adsorbents may well prove very helpful in general adsorption studies, and the main contribution of the initial results reported in this paper is probably that of illustrating the possibilities of these new techniques.

We would like to acknowledge the financial help and supply of samples afforded by both Shell Research Ltd. and B.C.U.R.A., Leatherhead.

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5.3

THE INFLUENCE OF ATMOSPHERE ON THE FRICTION OF GRAPHITE

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SUMMARY

The friction of graphite in air and in vacuum is discussed. It is suggested that the increase in friction observed after heating in vacuum is caused by the loss of chemisorbed materials from the surface of graphite crystallites, leaving free bonds available to increase the adhesion between them.

The low friction of graphite in air has been thought to be an inherent property of the material caused by its lamellar structure, the position of weakness being in the plane of the lamellae. However it has been demonstrated[1,2] that the friction and wear of graphite increase in vacuum, showing that sorbed gases and vapours have an effect. Some experiments have been carried out in Dr. Bowden's laboratory on the effect of atmosphere on the friction of graphite and hard gas carbon at slow sliding speeds. It was found that simply outgassing at room temperature had little effect on the friction, but when the materials were outgassed at 800°C and then cooled to room temperature the friction increased considerably (*see Figure 1*). On first admitting oxygen to the hard carbon the friction fell along the top curve, indicated by the single arrow. If the gas was then pumped away at room temperature the friction rose along the lower curve, but the friction could not be increased to the value obtained immediately after outgassing at 800°C. This curve was then reversible as indicated by the double arrows. The highest friction value could only be obtained by outgassing at the elevated temperature once again. It was found that graphite behaved in exactly the same way, but with lower friction at all stages, and also that the friction of clean graphite in oxygen was indistinguishable from the friction in water vapour.

Experiments were also carried out in an atmosphere of bromine, which can form intercalation compounds with graphite, but even so the friction was only reduced slightly below the value obtained in air.

The fact that the high friction of graphite obtained on outgassing at elevated temperatures could not be restored by simply pumping off oxygen at room temperature suggests that a proportion of the oxygen was held more firmly than the remainder. Also, an appreciable time was required for the friction to fall by its full extent on admitting the gas, which suggests that it diffused into the body of the material and had some effect other than masking the surfaces immediately in contact.

The tracks left when graphite was rubbed on silver in vacuum at elevated temperatures, and in air, have been examined by electron diffraction. In the track formed in air the graphite was oriented so that the crystallites had their cleavage planes parallel to the surface of the metal, whereas the graphite rubbed on in vacuum appeared to have no preferred orientation.

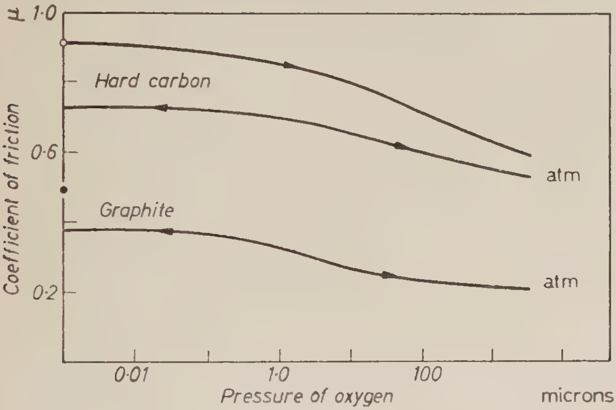

Figure 1.

The increase in friction after heating in vacuum could be explained by supposing that gases are removed from between the carbon sheets of the graphite lattice, causing an increase in the cohesion between them. However, this would probably necessitate a change in the interlayer spacing which, as far as is known, has not been observed. Also, although there are only comparatively weak binding forces between the carbon atoms of adjacent planes, the large number of atoms in each plane will cause the cohesion between them to be considerable even in air. This view is supported by the fact that the planes can only be separated by 'peeling' in air; thus the bonds are broken singly rather than all at the same time. A better explanation appears to be that on evacuation chemisorbed materials are lost from the surface of separate crystallites, rather than from the internal cleavage planes, leaving free bonds available to increase the adhesion between neighbouring crystallites. In air the chemisorbed materials cause the adhesion between the plate-like crystallites to be relatively weak, and on rubbing allows them to become oriented in the most favourable position.

Thanks are due to Dr. F. P. Bowden and to Mr. R. F. Deacon for valuable discussions.

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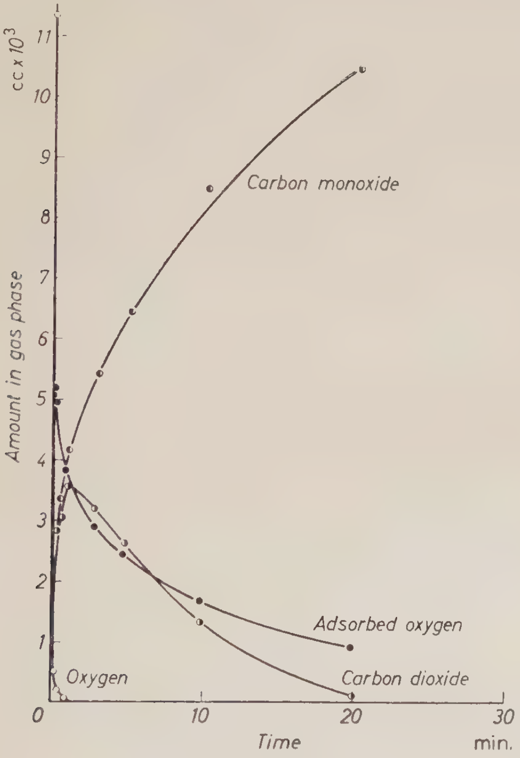
5

DISCUSSION

Chairman: W. F. K. WYNNE-JONES

On Paper 5.1

P. WHITE: Some results obtained recently in a series of experiments on the oxidation of different types of carbon show a formal similarity to the CO_2–C reaction described by Dr. Harker. The graph shown here refers to the oxidation, at 600°C, of 0·25 g of diamond, which was outgassed before



Oxidation of diamond at 600°C.

reaction at 1000°C for approximately 30 hours. A pressure of 10^{-2} mm of oxygen was admitted to the reaction vessel and, in a series of experiments, the contents of the gas phase analyzed at different times after the admission of oxygen. In the first $1\frac{1}{2}$ minutes gaseous oxygen disappeared completely, adsorbed oxygen appeared very quickly, and gaseous carbon monoxide and gaseous carbon dioxide formed at approximately equal rates. It is interesting to note that the maximum in the carbon dioxide curve seems to occur at a time when gaseous oxygen disappears. It seems, therefore, that at this temperature gaseous oxygen reacts with either (a) a carbon surface or (b) with adsorbed oxygen to give gaseous CO and gaseous CO_2 which is subsequently reduced to carbon monoxide in a manner similar to that suggested by Dr. Harker.

On Paper 5.2

R. F. DEACON: I should like to ask Dr. Ingram whether his results on milled carbon-rubber systems are unambiguous. AYREY *et al.*[1] have reported the production of free radicals when milling rubber, and presumably breaking the carbon particles will also produce radicals, both of which types may have similar g values.

REFERENCE

1. AYREY, MOORE, and WATSON, W. F., *J. Polym. Sci.*, 19 (1956) 1.

D. J. E. INGRAM: We have looked for free radicals in masticated rubbers, and those milled by themselves and with carbon black. No signal has been observed which can be definitely attributed to the rubbers, but this is not surprising as we have not, as yet, been able to exclude air from the sample for the whole of the time. It is true that PIKE and WATSON[1] have demonstrated the existence of radicals in rubbers masticated under nitrogen, but they also found that this radical concentration decayed immediately on admission of oxygen. We imagine that this is what has happened in our case, and therefore provisionally interpret the signals obtained from our samples milled in air as due to the reinforcing carbons.

REFERENCE

1. PIKE, M., and WATSON, W. F., *J. Polym. Sci.*, 9 (1952) 229.

B. DAILEY: Is it possible to use the paramagnetic-resonance technique to determine the presence of H in the carbons? Why does one not see a resonance from the paramagnetic O_2?

D. J. E. INGRAM: The additional information that can be obtained from resolved hyperfine structure in an electron-resonance spectra is often very considerable[1]. So far, however, no hyperfine structure has been observed with the carbon absorption lines, although we suspect that some contribution to the width may be due to unresolved hyperfine structure from the hydrogen atoms. We are hoping to investigate this further by using a much more homogeneous magnetic field, and this may then enable an accurate determination to be made of both the details of the electron orbit and the aromatic hydrogen content of the sample.

In regard to the electron-resonance spectra from gaseous oxygen itself, this does exist, of course, but can only be observed at very low pressures because of the large collision broadening. Even then most of the lines occur at higher fields[2] than that of the free-spin value, and hence they never overlap to confuse the spectrum due to the carbon samples.

We have investigated the effect of admitting other gases to the evacuated carbon samples and find no change with hydrogen, nitrogen, or argon. The broadening of the resonance line due to the collision process is not to be expected unless the incoming gas also has a magnetic moment, however, and this is confirmed by the fact that nitric oxide does have a similar effect to oxygen.

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D. D. Eley: Some experiments I carried out in Professor Polanyi's laboratory (1935–37)[1] get a new significance from Dr. Ingram's interesting work. If one sublimes say 100 mg of phthalocyanine (or copper phthalocyanine) in high vacuum, at 500°C, one obtains a film of phthalocyanine (or CuPC) which shows hardly any catalytic activity. There is left, however, a small residue, perhaps 1 mg of unsublimable, and presumably partially carbonized, residue. This contains hydrogen of constitution which gives a rapid exchange with D_2 (at say 200°C):

$$\text{residue} - H + D_2 \rightarrow \text{residue} - D + HD$$

There is also a strong surface paramagnetism, since we found a very active conversion of $pH_2 \rightarrow oH_2$ at 90°K, with a negative temperature coefficient characteristic of the paramagnetic conversion.

Clearly these results receive a ready explanation in terms of the free electrons, demonstrated by Ingram (by electron resonance), in such systems, and they also show that these electrons may be active in hydrogen catalysis.

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W. E. Garner: The heat of adsorption of oxygen on amorphous carbon decreases rapidly with coverage from 90 kcal/mol O_2. There is a plateau on the curve which indicates that there are at least two kinds of oxygen chemisorption. One of these may occur on the periphery of the ring structure and the other on the plane surfaces.

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