56. *Heterogeneous Catalysis. Part I. Theoretical Basis.**

By D. A. Dowden.

In heterogeneous catalysis the rate of reaction is controlled by the formation of a chemisorbed complex which may be bound to the solid surface by ionic or covalent bonds.

If the rate is limited by the formation of a positive ion at a metal surface, the process is most favoured and fastest when the ionisation potential of the metal atom and the metal work function are both large, and when the gradient of electron level density with electron energy at the Fermi surface is large and positive. Formation of negative ions is optimum with small metal ionisation potentials and work functions but with an electron level density gradient which is large and negative.

Covalent bonding is treated qualitatively using Pauling's newer concept of transitional metal valencies, and the electron band theory, with the result that bonding appears most favoured and fastest on metals possessing vacant " atomic " *d*-orbitals, or a large density of electron levels close to the Fermi surface.

Activity in multiple-bond hydrogenation is associated with the " holes " in transitional metal *d*-bands, and falls to a very low value at those alloy or inter-metallic compound compositions where the " holes " are just full. These principles are applied to many catalytic phenomena, *e.g.*, poisoning.

Analogous ideas are applied to semi-conducting catalysts where activity is associated with the electron levels and lattice defects arising from impurity centres or non-stoicheiometry.

It is suggested that insulator catalysts, *e.g.*, γ-Al_2O_3, function through a proton-exchange mechanism which is particularly easy at cation defects.

1. Introduction.

War-time exigencies in industry yielded a variety of novel catalysts selected almost wholly by empirical methods and revealed our almost total ignorance of the precise rôle of the solid in heterogeneous catalysis.

In 1943 a survey of the relevant literature, including patents, showed either a complexity wherein one could not " see the wood for the trees " or kinetic studies for the most part uncorrelated with the electronic and geometric characteristics of the catalyst lattice. Separate small researches with limited objectives gave a pattern of results, broadly interpretable according to the " active centre " concept and its several models, but not at that time picturing details of importance for industrial catalyst design.

With the advent of the quantum theory of the covalent bond and transition state treatment of the activated complex, the active centre came to be portrayed as one surface atom, or a group of such atoms, possessing a unique configuration and orientation relative to certain substrate parameters. As long as such a centre could be represented by a portion of a normal lattice plane, the model was useful, but when special nuclei were postulated, having properties not simply related to those of the catalyst crystallite bulk, its heuristic value was severely limited.

Chemisorption of one or more of the reactants at an active region appeared as the first requisite of a solid catalyst in any heterogeneous reaction, chemisorption of the activated complex of the rate-controlling step determining the overall reaction rate. The bonding of the chemisorbed species with the surface might be, in the extreme, ionic or covalent.

A re-assessment of the catalytic problem then falls naturally into three parts: (*a*) a description of the chemisorbed particles, (*b*) a description of the active regions, and (*c*) the interactions in the group of particles plus regions.

The kinetics of homogeneous catalysis have been considerably advanced in recent years by the introduction of entities such as the free radical and the radical ions, and by the use of the Lewis viewpoint on generalised acid–base catalysis. Broad analogies, drawn between homogeneous acid-catalysed reactions and similar heterogeneous processes at the surface of some cation-defective oxide insulators containing protons, encourage the view that the same intermediate particles are active in both. Less well-defined relations suggest identical species at the surface of metals and semi-conductors (Bremner, *Research*, 1948, **1**, 281).

The electron shifts resulting in radical and ion formation reveal the catalyst crystallite as an electron source or sink and, in the presence of hydrogen-containing materials, as a potential proton reservoir. Lennard-Jones (*Trans. Faraday Soc.*, 1932, **28**, 333), Schmidt (*Chem. Reviews*, 1933, **12**, 363), and Nyrop (" The Catalytic Action of Surfaces," London, 1937) were aware of some of the implications of the former rôle. The binding electrons will be found in electronic levels and the chemisorbed particles in geometric sites which together minimise the free energy of activation and make the overall free-energy change a maximum for the bonding process.

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The electron-band concept of solids and the classical ionic-lattice theory, together, provide a reasonably adequate qualitative description of the significant electron and ion energy levels in the principal solid types while detailed application of conventional physical techniques to crystals and glasses has rapidly increased the number of known macroscopic and microscopic lattice defects.

It seemed therefore in 1943 that a definite correlation must exist between the electronic structure of solids and their catalytic activity; in fact a number of useful working rules were derived. Unfortunately it was not possible to commence experiments directed to the verification of these until 1946 (the data in the literature were equivocal). Recent publications concerning the catalytic activity of pure metals and alloys in hydrogenation and dehydrogenation reactions, and related observations on the catalytic, adsorptive, etc., properties of pure and so-called " mixed " oxides, imply a growing awareness of such relations. A partial statement of the situation has been published by Schwab (*Trans. Faraday Soc.*, 1946, **42**, 689) and Garner (*J.*, 1947, 1239).

This paper describes some present ideas on the subject as an interim report on a unitary theory of catalysis (Dowden, *Research*, 1948, **1**, 239).

2. THE GEOMETRY OF THE CATALYST PARTICLE.

All bulk catalysts are aggregates of an entity which is taken to be a crystallite in normally crystalline materials (*e.g.*, metals) but a glassy or gel-like particle in amorphous catalysts derived from glass-forming constituents. These ultimate particles are the units affecting catalysis and possess, it is assumed, the following additional characteristics : (i) The volume properties and the surface properties (per unit surface) are identical with those of the massive material. (ii) Defective and ordered or disordered states, when present in the virgin catalyst lattice, exist unmodified right up to the solid–gas interface unless tending to equilibrate with the gas phase. (iii) Single-phase multicomponent catalysts, macroscopically homogeneous, have no excess or deficiency of any component in the surface at equilibrium. Thus, in an equilibrium copper–nickel solid solution, there is no copper enrichment at the surface. (iv) The particles are bounded by essentially plane surfaces.

It should be noted that (i) probably fails below some small particle size while (ii) may not be exactly true even at equilibrium in view of the asymmetry at the surface.

At temperatures above absolute zero, in addition to vibratory heat motion, a small fraction of the lattice ions are displaced from their lattice positions to yield Frenkel and Schottky defects (see section 10). Catalysts prepared below the Tammann temperature ($\frac{1}{2}$ × m. p. in °K.) may have a concentration of such defects considerably in excess of the equilibrium value.

3. SPECIFIC AREA OF THE SOLID.

The catalysed reaction proceeds at a gas–solid interface so that its rate must be a direct function of the specific area (area per unit weight) of the catalyst. Diffusion may limit effective reaction to a fraction of the total surface, but if the available area remains proportional to the total then activity per unit catalyst weight is proportional to specific area; this has been demonstrated experimentally (*e.g.*, Siller, *J. Amer. Chem. Soc.*, 1943, **65**, 431).

Catalyst modification can alter both specific area and activity per unit area (specific activity), and the two must be evaluated separately. The factors controlling development or maintenance of a given specific area are usually less critical and better known than those affecting specific activity; they will not be discussed further.

4. SPECIFIC ACTIVITY.

Activity per unit area, a function of catalyst composition and state, is independent of specific area within the approximations of section 2.

When the system is chosen so that volume and surface diffusion steps are very fast a catalytic reaction can be formally presented as (i) chemisorption of one or more reactants, (ii) reactions in the total adsorbate plus surface complex, and (iii) desorption of the products.

In the stationary state the overall reaction rate (V_S) is that of the slowest step.

$$V_S = k \times (A)^m \times (B)^n \times \ldots . \qquad (1)$$

where letters in parentheses represent surface or volume concentrations of those species yielding the activated complex.

The rate constant k equals

$$K \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp. [- \Delta F^*/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$K \frac{\boldsymbol{k}T}{\boldsymbol{h}} \exp. [- \Delta U^*/\boldsymbol{k}T + \Delta S^*/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

K is the transmission coefficient, ΔF^*, ΔU^*, ΔS^* are the Helmholtz free energy, intrinsic energy, and entropy of formation, respectively, of the complex. $\boldsymbol{k}$ is the Boltzmann constant and $\boldsymbol{h}$ is Planck's constant.

Ideally the reaction mechanism can be defined and ΔF^* evaluated at the slowest step. In practice the trends in ΔF^* at the likely controlling steps must be predicted from semi-empirical rules.

(a) *Chemisorption*.—When adsorption or desorption is the limiting process the Lennard-Jones (*loc. cit.*) free-energy diagram illustrating activated adsorption is informative (see Fig. 1, where only electronic entropy contributions are included).

FIG. 1.

Free energy changes in the sorbed state. Only electronic entropy changes included. Positive ion formation.

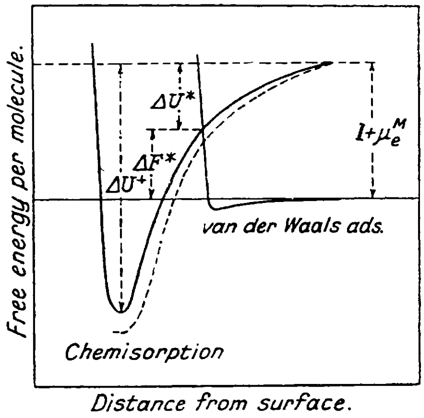
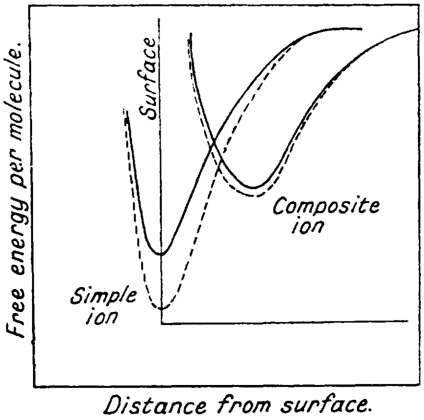


FIG. 2.

Free energy changes for a reaction in the adsorbed state.



The van der Waals adsorption free energies of a substrate are generally small, their differences still less at similar sites on a series of catalyst surfaces, so that the free energy of activation depends chiefly on the contour of the chemisorption curve, the value of the chemisorption free energy, and the distance between the two minima. On catalysts of the same solid type, if the change in force law is small, ΔF^* decreases as the chemisorption free energy increases or when the distance between the equilibrium van der Waals and chemisorption positions diminishes. Active centres must therefore be associated with adsorption sites, the geometry of which requires the minimum movement of the mass centre of the particle during the transition, consistent with a maximum chemisorption free energy. Desorption free energy of activation, being the sum of ΔF^* and the chemisorption free energy, can be made smaller only by modifications simultaneously minimising both the chemisorption free energy and the distance between equilibrium positions. These conclusions are independent of the nature of the bond with the surface (cf. Ogg and Polanyi, *Trans. Faraday Soc.*, **1935**, **31**, 1375).

(b) *Reactions in the Adsorbate*.—Generalisation is more difficult when reaction between adsorbed species provides the rate-controlling step, as the participants may be molecules, radicals, or ions. Nevertheless a sufficiently detailed analysis of a reaction mechanism usually reveals a unimolecular or bimolecular process as the slowest step. For example :

$$\mathrm{ROH} + \mathrm{H}^+ \longrightarrow \mathrm{ROH_2}^+$$

or

$$\mathrm{ROH_2}^+ \longrightarrow \mathrm{R}^+ + \mathrm{H_2O}$$

or

$$\mathrm{R}^+ \longrightarrow \text{Olefin} + \mathrm{H}^+$$

Where the neutral molecules are physically adsorbed, the ions are held by Coulomb forces, and each ion is partitioned between the surface and a neutral molecule at the surface (Fig. 2).

Arguments, similar to those of section (*a*), suggest that the activation free energy will be lowered as the equilibrium positions are brought closer together. Catalyst changes must move the curves in the same direction parallel to the ordinate, when the forces are purely ionic and the ions of one sign, but, the radius of the composite ion being greater, the changes will there be less than for the simple ion of smaller radius (the small ion is more correctly taken to be embedded in the catalyst surface). According to this model therefore, the activation free energies for composite or simple ion formation are lowered by decreasing or increasing, respectively, the adsorption free energy of the simple ion; active centres can be defined as sites which minimise the separation of the ions and change the adsorption free energy of the smaller ion to its lowest or highest level.

When the intermediates are adsorbed radicals (as possibly at metal surfaces), the situation can be described similarly, but free energy changes cannot be easily discussed even on simple bases.

In subsequent sections consideration will be given to those factors affecting the free energy and geometry of adsorption, since these are paramount in predicting activity trends over " homologous " series of catalysts.

5. ELECTRON TRANSFER AT SURFACES.

Recent studies of the electrical properties of solid–fluid interfaces emphasise the existence of electron-transfer and exchange phenomena between surface and sorbate, whereby neutral molecules can yield one or more adsorbed ions (positive and negative) or radicals, depending on the electronegativities of the surface and the molecular fragments (Seitz, *J. Appl. Physics*, **1937**, **8**, 246).

Spontaneous production of a surface dipole on adsorption happens when a normally full electron level lies above a normally empty level. If the donating level lies below the acceptor level then an activation energy is required.

There are at least five pre-requisites of electron-transfer changes :

(i) The free energy change of the overall process must be negative.

(ii) At the position of van der Waals adsorption the normally full substrate levels (minimum ionisation potential I) or empty levels (maximum electron affinity E) must be brought close to the normally empty or full levels, respectively, of the catalyst crystallite.

(iii) Either (*a*) the discrete electron levels of the isolated sorbate species must broaden as the surface is approached so that the minimum ionisation potential of the sorbate is decreased and its maximum electron affinity increased, or (*b*) the levels may remain discrete even at the surface, but I and E change as in (*a*).

(iv) The catalyst crystallite must possess vacant or occupied levels capable of accepting or donating electrons to form the activated complex [another aspect of (ii)].

(v) The potential barrier separating the crystal levels and the sorbate levels, when it exists, must be permeable to electrons.

Level broadening occurs when I and E are less that the inner potential of the crystal, providing that the corresponding levels interact with a quasi-continuous band of levels in the solid.

The inner potentials of metals range from 7·3 ev. (K) to 16 ev. (Ni) and seem to fall, as far as they have been measured, between 12 ev. and 16 ev. midway in a long period (Fowler, "Statistical Mechanics," 2nd Edn., Cambridge, 1936, p. 355). In semi-conductors and insulators similar magnitudes appear (O'Bryan and Skinner, *Proc. Roy. Soc.*, 1940, *A*, **176**, 229).

Remembering that measured values of the inner potential are only average values for the crystal, and noting the effect of electrical image forces in reducing ionisation potentials, it is reasonable to assume that the inner potentials of the transitional elements, and of other compounds of catalytic interest, are always greater than the ionisation potentials of normal sorbates.

In typical metals the volume electron levels lying above the inner potential are always quasi-continuous, except for narrow forbidden regions confined to certain directions in some lattices, *e.g.*, those of bivalent metals. Insulators differ in having a wide region of forbidden energy levels lying between the top of the full band and the bottom of the empty band; sorbate levels cannot interact with this forbidden region. Semi-conductors have more or less localised and discrete, full or empty levels in this energy gap. Interaction between sorbate levels and these semi-conductor levels depends on the energy, and density in energy and volume of the latter.

Juxtaposition of the relevant levels, according to (ii), is exact when the radius, ionisation potential, and electron affinity of the adsorbed particle are equal to those of a lattice atom or ion. In saturated molecules the first two characteristics are larger, and the third smaller than those of metal atoms, so that the required adjustment of levels can occur, if at all, only in special positions. Analogous remarks can be made of ionic lattices.

At absolute zero the energy levels of a metal crystal are full up to the Fermi surface of energy $-\phi$ (ϕ = metal electron work function). All levels above this are empty but above 0° K. the cut-off becomes diffuse due to thermal energy. Both vacant and full levels may correspond to eigen-functions of *s*, *p*, *d*, or mixed character.

Bound surface states of various origin may exist. These comprise levels corresponding to crossing of atomic levels (Shockley, *Phys. Review*, 1939, **56**, 317), to variation in Madelung potential at the surface (Mott, " Electronic Processes in Ionic Crystals," Oxford, 1940, p. 86), and to the presence of the sorbate (Lennard-Jones, *loc. cit.*; Pollard, *Phys. Review*, 1939, **56**, **324**). Such states lying above the Fermi surface will be empty, those lying below will be full and in metals, because of transitions between the surface and volume levels, need not be considered in detail. In semi-conductors and insulators, on the other hand, surface levels where they arise may be of considerable interest.

FIG. 3.

Energy of an electron in the potential field of the metal and the substrate positive ion.

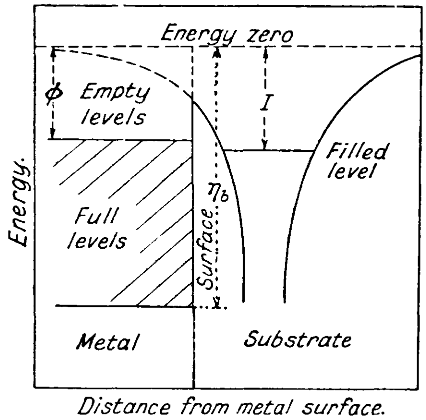
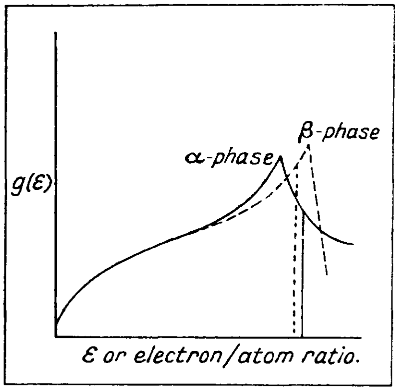


FIG. 4.

Electron level density in Hume-Rothery alloys.



Now that the general conditions leading to electron movement have been sketched, some special cases will be treated for various solid types on the assumption that the above conditions hold.

6. METALS.

In metal crystals the lattice electron affinity equals the lattice ionisation potential and the electron exit work function.

(i) *Positive-ion Formation.*—Positive ions are formed by transferring an electron from the highest occupied level ($-I$) of the absorbed species to the lowest unoccupied lattice level ($-\phi \simeq \mu_e^M$) when $I^1 \leqslant \phi$ (Fig. 3).

(a) *Equilibrium.* If the sorbate at the surface is considered to be a surface phase, the electrons of which are in equilibrium with those of the metal phase through a dilute electron gas, then the ratio of ionised species in the surface phase is given by

$$ {}^{c}A^{+}/{}^{c}A = \frac{\mathrm{f}(A^{+})}{\mathrm{f}(A)} \exp. [-(I^1 + \mu_e^M)/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4) $$

where

$$ I^1 = I + \Delta U^{+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5) $$

and

$$ \mu_e^M = -\phi - 1/6\pi^2\boldsymbol{k}^2T^2(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6) $$

(see Fowler and Guggenheim, " Statistical Thermodynamics," Cambridge, 1939, p. 472). f(A^+) and f(A) represent partition functions for the ionised and neutral particles respectively, $\mu_e^M = (\partial F_e^N/\partial N)_V$ equals the thermodynamic potential per metal electron per unit volume, I is the ionisation potential of the neutral particle, ΔU^+ the adsorption energy of the ion (always negative, corresponding value for the neutral particle $\simeq 0$), $g(\varepsilon)$ the density in energy of electron levels per unit volume, and ε the metal electron energy.

The entropy change per added electron in the metal corresponding to μ_e^M is

$$(\partial S/\partial N)_V = 1/3\pi^2\boldsymbol{k}^2T(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and can be neglected as in some thermionic work except when $(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi}$ is large.

The electron exit work function (ϕ) is known accurately only for a few pure metals, so that it will be useful to note that it is defined by the approximate relation

$$N \simeq \int_{-\eta_b}^{-\phi} 2g(\varepsilon)\ \mathrm{d}(\varepsilon) . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

N is the number of electrons per unit volume of metal and $-\eta_b$ the energy at the bottom of the electron band.

Other things being equal, $|\phi|$ increases as $g(\varepsilon)$ increases.

The ionised electron need not enter the crystal at the Fermi energy level. For instance, in metals having holes in the d-band, surface atoms will have a certain lifetime in charged states corresponding to singly- or multiply-charged positive ions, and the donated electron will tend to enter one of these " ionised " levels. However, the Pauli principle ensures that this process from the equilibrium standpoint is equivalent to the addition of an electron at the Fermi level. Gurney (*Phys. Review*, 1935, **47**, 479) has indicated that the ionisation potential of the metal atom, rather than the work function of the metal crystal, is the better parameter to use in the treatment of ionisation at surfaces. ${}^0A^+/{}^0A$ is a maximum for a given sorbate when I^1 is a minimum and $|\mu_e^M|$ a maximum.

(b) *Geometry of the " active centre."* In a given system $|\Delta U^+|$ is a maximum (and I^1 a minimum) when the ion has acquired the greatest number of lattice atom nearest neighbours. In this state the ion takes up a position interstitially at the surface, or as near as possible to a vacant surface lattice point.

From another viewpoint, since level breadth increases exponentially as the distance between the absorbate and the surface atoms decreases, I will be a minimum when the neutral adsorbate is itself in equilibrium at a lattice defect.

Obviously such sites are most likely to exist on catalyst planes of least packing density, *e.g.*, (111) of α-iron and (110) of nickel, or at a point in the surface plane from which an atom is missing. At these centres minimum movement of mass centre occurs between the physically and chemisorbed states contributing to a minimum activation free energy; the values of parameters giving most favourable equilibrium give also the greatest ionisation velocity.

The continuity with older work on the relative energies of surface lattice points of various co-ordination number and with the more recent ideas of lattice dislocations is obvious (Mott and Nabarro, " The Strength of Solids," Physical Society, London, 1948, p. 1).

(c) *Rate.* The free energy of activation depends on the value of ΔU^+ for the system in the activated state. Reference to section 4(a) shows that it is a reasonable approximation to put the adsorption energy of the ionic activated complex proportional to ΔU^+, *i.e.* $\Delta U^* = a\Delta U^+$ where a is a constant <1.

Then

$$\Delta F^* \propto I + \mu_e^M - a\Delta U^+ \quad \text{or} \quad \Delta F^* = b(I + \mu_e^M - a\Delta U^+) \quad . \quad . \quad . \quad . \quad (9)$$

where b is a constant and ΔU^+ now refers to the value of the ionic adsorption energy.

The corresponding entropy of activation

$$\Delta S^* \propto T(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and for k^+, the rate constant for ionisation, we have

$$k^+ = K^+ \exp . [-b(I^* + \mu_e^M)/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $I^* = I - a\Delta U^+$ and $K^+ =$ a transmission factor.

The value of each parameter depends on the condition of the surface, that is to say whether it is bare, in unstable condition as in the induction period, or in a stationary state.

Over a " homologous " series of metals such as a series of solid solutions, and using a given sorbate, ΔU^+, ϕ and $g(-\phi)$ vary.

(d) *Factors affecting* ΔU^+ *and* I^*. In this formal presentation, the magnitude of the ionisation potential at the surface depends wholly on ΔU^+ when the forces binding the ion are taken to be purely coulombic; ΔU^+ increases as the ion gets closer to its lattice nearest neighbours. Generally the adsorbed ion diameter (D) exceeds that of the lattice atoms (d), and ΔU^+, at a vacant lattice point or interstitially, increases with increasing d since the molecule and ion can merge more closely with the metal. If ΔU^+ varies linearly with ion-surface distance, then $\Delta U^+ \propto \mathrm{f}(d)$, where a simple model shows that fractional changes in d (when $D > d$) produce corresponding changes in the adion equilibrium distance smaller by a factor of ~ 10. Metal atom diameters, in any long period between groups 5 and 2 (*e.g.*, vanadium through nickel to zinc), show a maximum variation between successive members of 10% and an average variation of 3%; between iron and copper the maximum variation between successive members is 3·2%, between ruthenium and silver 5·1%, and between osmium and gold 4·4%. This is also the order of the change in radius of both the vacant sites in the surface planes of greatest packing density, and the interstices in the planes of least packing density, when the lattices are of the same type. Change of crystal type causes abrupt radius differences in the interstices, such as the increase in interstice radius by *ca.* 15% at the transition from the body-centred cubic to the face-centred cubic metals (iron to cobalt, molybdenum to rhodium, tungsten to iridium), and a much larger increment when hexagonal close packing occurs (zinc, ruthenium, cadmium, rhenium, osmium). It will be assumed therefore that varying d from catalyst to catalyst has negligible effect upon ΔU^+ when the metals are near neighbours and no change in lattice type is apparent. This is particularly true of the series iron, cobalt, nickel, and copper in their face-centred cubic forms.

If the linearity between ΔU^+ and ion-surface distance in the critical range is not a good approximation, then atomic diameter in the catalyst will have a somewhat larger influence on ΔU^+ than suggested above. The purely coulombic conditions are most likely to be satisfied when the ion has an inert gas structure, and when overlap is small; generally this is not so and ΔU^+ will be augmented by exchange forces of the kind described below.

Ionisation need not be simple but may produce a number of positive ions so that I must be replaced by a quantity representing a sum of dissociation energies and ionisation potentials and ΔU^+ by a sum of adsorption energies.

(e) *The electron exit work function.* The work functions of metals and alloys are largely inaccurate or unknown, but available data indicate a trend in each long period to a flat maximum in group 8, probably at nickel, palladium, and platinum where the peak in electron level density at the Fermi surface also appears.

When ϕ is not known, as in alloy systems, it cannot be calculated since it is a sum of lattice inner potential, electron kinetic energy, and intrinsic surface dipole, none of which can be estimated to the required accuracy. Generally ϕ is greatest when $g(-\phi)$ is as large as possible, which is equivalent to taking electron kinetic energy as the dominant term in the sum. Thus in alloy systems where increasing electron to atom ratio shifts the Fermi surface to regions of smaller $g(-\phi)$, it will be assumed that the rate of decrease of ϕ is larger. Certainly the rate of increase of maximum electron kinetic energy per added electron is greatly increased in such regions, *e.g.*, at the composition where a d-band becomes full or where a Hume-Rothery alloy changes phase.

In a metal crystal ϕ depends upon the indices of the surface plane and changes with lattice type; lattices and faces of densest packing seem to possess work functions slightly greater than the rest by a few tenths of an electron-volt.

The positive dipole produced at the surface by the adsorbed ions reduces ϕ until the electron transfer ceases when only a fraction of the surface is covered with ions. Clearly electropositive contaminants decrease ϕ and the equilibrium surface concentration of ions as well as the rate of ion formation; electronegative species have the opposite effect.

(f) *Electron level density.* The density of electron levels at the Fermi surface, $g(-\phi)$, attains maxima in group 8 at nickel and perhaps palladium and platinum, falling to much lower values in their alloys with copper, silver, and gold respectively, at approximately the equiatomic composition. Similar rapid changes in level density occur at the phase boundaries of Hume-Rothery alloys. Again the data are not sufficiently accurate for our purposes since they provide only average value of $(\delta \log_e g(\varepsilon)/\delta\varepsilon)_{\varepsilon=-\phi}$ over fairly wide ranges of composition whereas $(\mathrm{d} \log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi}$ is required at a special composition.

A large positive value of the gradient implies an appreciable positive entropy contribution and a fall in the activation free energy; a large negative value for this parameter has the opposite effect.

While the simple band scheme provides a qualitative picture of these variables, it breaks down if pushed too far and data are too scanty to yield adequate corrections at the present time.

(g) *Change of adsorbate.* When the catalyst remains unchanged but the adsorbate varies, both I and ΔU^{+} are affected. The ionisation potential of the electron removed from the adsorbate is greater or smaller depending on its bonding or non-bonding character and the environment in the molecule (Price, *Chem. Reviews*, 1947, **41**, 257). In a homologous series of molecules of increasing molecular weight, I decreases and the molecule diameter or length increases as the series is ascended. These parameters are not necessarily identical with those of the earlier considerations since in complex molecules only the smaller groupings can be accommodated at an active centre. Thus in $C_nH_{2n+1}{\cdot}OH$ adsorption the appropriate radius might be that of OH and the ionisation potential that of the non-bonding oxygen electrons; alternatively the radius of CH_3 or covalently-bound H, and the ionisation potential of the C–H bond, might be appropriate. When the reactant possesses non-localised electrons or electrons which can be excited to low lying non-localised orbitals, the relevant ionisation potential is that of the molecule as a whole. Evidently in large molecules ionisation can occur at one or more groups corresponding to multiple attachment to the surface with all its geometrical consequences. Whether the ionised electron is bonding or non-bonding the resulting ion is often unstable, as the results of mass spectroscopy often indicate (Hipple, Fox, and Condon, *Phys. Review*, 1946, 347).

Summarising, it appears that positive-ion formation is most favoured and fastest on metals and alloys possessing the following properties: large electron exit work function, large positive value of $(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)$ at the Fermi surface, crystallisation such that planes of least dense packing are exposed to the gas phase or such that other more densely packed planes have a high concentration of vacant sites and controlled quantities of electronegative additives.

(ii) *Negative-ion Formation.*—A negative ion is formed by removal of an electron from the highest occupied level $-\phi \simeq \mu_e^M$ of the crystallite to the lowest unoccupied level ($-E$ = electron affinity at the surface) of the adsorbed species.

This process is the converse of that given for positive-ion formation and the fraction of ionised species in the surface phase:

$$ {}^{c}B^{-}/{}^{c}B = \frac{f(B^{-})}{f(B)} \exp.\,[-(E' - \mu_e^M)/kT] \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where

$$E' = E + \Delta U^{+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

E is the electron affinity of the isolated substrate and ΔU^{-} the adsorption energy of the anion, both being negative in the cases of interest.

The argument now runs much as before. Owing to the large polarisability of the negative ion there is a small image effect increasing the electron affinity at large distances from the surface, but the big increment comes into play only when the adsorbate approaches an active centre defined exactly as for positive-ion formation. A chief point of difference is the relatively large size of the anion which reduces the coulombic contributions to ΔU^{-} and suggests that only strongly electronegative particles form negative adions in the absence of overlap forces. The free energy of activation for ionisation is again

$$\Delta F^{*} \propto E + c\Delta U^{-} - \mu_e^M \text{ or } \Delta F^{*} = d(E + c\Delta U^{-} - \mu_e^M), \text{ where } c \text{ and } d = \text{constants} \quad . \quad (14)$$

and the corresponding entropy

$$\Delta S^{*} \propto -T(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The rate constant for ionisation is

$$k^{-} = K^{-} \exp.\,[-d(E + c\Delta U^{-} - \mu_e^M)/kT] \quad . \quad . \quad . \quad . \quad . \quad (16)$$

The electron affinity E is unknown for most particles; the best values and the largest are available for oxygen, sulphur, and the halogens.

Negative-ion formation is fastest and most favoured on metals and alloys possessing the following properties: low electron exit work function, large negative value of $(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)$ at the Fermi surface, all electronegative contaminants excluded, controlled quantities of electropositive additives.

(iii) *Covalent Bonding.*—Electron exchange affecting bonding through the resultant resonance energy yields two conveniently distinguishable bond types : the metallic bond, where the bonding electrons are more or less mobile, and the covalent bond, where they are localised between the bound atoms to give a directed bond. These and intermediate bond types can arise in chemisorption.

The ratio of the work function to the first ionisation potential is about 0·5 for most elements, and atoms of metal may be deposited from the vapour on to the metal surface to form a chemisorbed layer which is an extension of the metal crystal. In the same way atoms of zinc, phosphorus, arsenic, hydrogen, and nitrogen, having first ionisation potentials between 9 and 15 ev. form solid solutions or metallic compounds with some of iron, copper, nickel, and palladium ($\phi = 4{\cdot}5$—5 ev.). The intermediate chemisorbed state cannot differ markedly from the equivalent two-dimensional solid solution, and will possess bond character of the same kind as the bulk solution, modified by the asymmetry at the interface. Similarly a gas such as carbon monoxide forms a surface complex in which the bond approximates to that in the metal carbonyls. Morris and Selwood (*J. Amer. Chem. Soc.*, **1943**, **65**, 2245) observed magnetic changes on poisoning a metallic nickel catalyst with mercury, lead, and carbon monoxide, which parallel those expected on formation of solid solutions or nickel carbonyl, and support such a correspondence. Most radicals and unsaturated molecules have ionisation potentials in the above range or smaller, and homopolar bonding is expected.

Electron exchange to cause covalent bonding occurs between levels of the catalyst–substrate complex of comparable energy; moreover, since a condition of resonance is that the extreme neutral and ionic forms must involve only small displacements of the nuclei, the geometric properties already given for an active centre are optimum here also. Other things being equal, the adsorption free energy will be proportional to the adsorption energy of the radical or molecule, *i.e.*, to the additional resonance energy of the system.

(a) *Metallic bonding.* If interactions of substrate levels with all metal levels are considered qualitatively, in a molecular-orbital approximation where the metal volume levels remain mainly unaffected, it appears that a number of electrons equal to the loosely bound (" valency ") electrons of the substrate, must be promoted to the lowest, unfilled, essentially metallic level of the complex. These anti-bonding electrons must therefore be accommodated at the Fermi surface and this will be accomplished most easily when the difference in energy between the metal work function and the substrate ionisation potential at the surface is a minimum and when the energy density of levels at the Fermi surface is large (compare a copper or zinc atom alloying with a nickel surface). A physically absorbed, large saturated molecule, at a plane surface without defects, possesses a large ionisation potential and $I - \phi \sim 10$ ev. Homopolar-bond formation on closer approach can result only when the energy gained by the depression of the bonding levels exceeds that required to put electrons in the anti-bonding levels. Interaction produces a symmetrical divergence of bonding and anti-bonding orbitals about the unperturbed substrate levels, but since the metal levels are initially full at this energy no appreciable energy can be gained, certainly not 10 ev., and no bond can be formed. Bonding on this basis is possible only for initial levels close to the Fermi surface where the anti-bonding levels may be largely empty. The process is equivalent to the elevation of a metal electron, from a filled level near the substrate level, to the Fermi surface followed by interaction between the substrate level and the now unfilled metal level (Lennard-Jones, *loc. cit.*).

By analogy with solid solution effects, chemisorption is easiest when the substrate ionisation potential is less than or equal to approximately twice the catalyst work function. The limiting ionisation potential may be smaller or larger than this when the covalent radius of curvature of the intruding electron distribution is larger or smaller respectively than that of the metal atoms. Chemisorption of saturated molecules with I greater than this limit is possible only in special positions (active centres), as already described. Dissociation of the molecule into radicals of smaller I and possibly smaller radius (*e.g.*, hydrogen atoms) is a much more likely event. Saturated molecules (*e.g.*, H_2) and " unsaturated " molecules such as carbon monoxide, carbon dioxide, nitrogen, etc., because of their small covalent radius or that of the atoms into which they may split, can merge more into the metal and behave as though of lower ionisation potential than the same molecules *in vacuo*.

If the catalyst crystallite is sufficiently large for the filling of its electron levels to remain essentially undisturbed by the chemisorption, then the addition of the anti-bonding electrons at the Fermi surface introduces an electronic entropy contribution which has the same dependence on the gradient of electron level density as given for ionic bonding.

(b) *Localised bonding.* The localised bond properties follow most simply from Pauling's recently formulated valencies for the transitional series of metals (*Phys. Review*, **1938**, **54**, 899;

Proc. Roy. Soc., 1949, *A*, **196**, 343) if electron pairing in chemisorption occurs both in the unfilled "atomic " orbitals (maximum number 2·48 per atom), and in the unused fraction of surface " bonding " orbitals (maximum number 6 per atom). The number of ligands of the surface atoms is less than that for a bulk atom by a factor of $\sim \frac{1}{2}$ and the geometry is asymmetric, so that the surface orbitals need not have the same character or distribution as those in the interior. Magnetic data (Selwood, *loc. cit.*; Dilke, Eley, and Maxted, *Nature*, 1948, **161**, 804) seem to show that the " atomic " orbitals are occupied by the electrons of chemisorbed species, although what probably happens is a rehybridisation of orbitals on the surface atoms to give the strongest bond with the substrate *s*-, *sp*-, or *p*-orbitals, while maintaining maximum metal-atom-to-metal-atom cohesion. Since *dsp*-orbital strength increases with *d*-content, one may expect strong bonds to be formed most easily where almost pure *d*-orbitals (" atomic orbitals ") already exist, unused in metal–metal bonds. This means that covalent-bond formation should be favoured and fast on metals with unfilled " atomic orbitals." However it does not follow that bond strength must increase with increasing number of these vacant orbitals (estimated for interior atoms), because there will be modifying surface effects and energy limitations.

Taking the localised bond and the band models together suggests that the strongest covalent bonding of a substrate would result when the density of *d*-levels is largest compared with that of the *s*-, *p*-levels at the Fermi surface. This maximum in *d*-level density occurs close to pure nickel and its congeners in the transitional series. Copper and zinc can form bonds of comparable strength only after formation of an excited state requiring considerable energy input; actual bonds in chemisorption will therefore be weak.

(c) *Surface states* (Lennard-Jones, *loc. cit.*). At sufficiently small distances between the adsorbed particle and the metal surface, the superposition of the potential well of the particle on the potential step at the metal–gas interface produces a potential well just inside the metal, the depth of which depends on the metal–particle distance. Below a critical well depth surface states exist, which may be occupied by a substrate electron to form a one-electron bond (Pollard, *Phys. Review*, 1939, **56**, 324); pairing with a second electron from the metal is considered improbable.

This model for covalent bonding in chemisorption does not explain the decreased paramagnetism or ferromagnetism observed during chemisorption on some metals, or the apparent dependence of catalytic properties on conditions at the metal Fermi surface. Adsorption by this mechanism may occur alongside the types already treated especially when the metal conduction band is narrow.

Summarising these conclusions on covalent bond formation, it appears that the process of chemisorption is most favoured and fastest at surfaces having the following characteristics: large electronic work function, large value of $g(-\phi)$, large positive $(\mathrm{d}\log_e g(\varepsilon)/\mathrm{d}\varepsilon)_{\varepsilon=-\phi}$ and presence at the surface of " atomic " orbitals in the Pauling sense.

(iv) *Real Bonds*.—Real bonds are formed by van der Waals, coulombic, and exchange forces acting together, all of which depend on the electronic structure of the solid, whether the adsorbate is molecule, radical, ion, atom, or activated complex. It is impossible to estimate the strength or rate of formation of a mixed bond by simple methods, and even in the case of the pure-bond types the models involving formal ionisation potentials, electron affinities, and work functions are not very satisfying. The problem deserves a thorough quantum-mechanical analysis which might eliminate a number of the hypotheses introduced above.

Apparently however positive-ion and covalent-bond formation have a similar dependence on the properties at the Fermi surface. Thus, when the rate-controlling step involves donation of an electron to the catalyst with exchange, or involves the surface concentration of a particle formed by such a process, then activity improves with increasing work function, level density, positive density gradient, or *d*-content of the bonding orbitals. There will be values of $|\phi - I'|$ and $|E' - \phi|$ at which the ionic contribution to the bond begins to predominate.

The reaction of saturated molecules or molecules of high ionisation potential is most likely to proceed, where possible, by mechanisms of the kind $C_2H_6 + H^+ \longrightarrow C_2H_5^+ + H_2$ or $C_2H_6 + H \longrightarrow C_2H_5 + H_2$ where the inert molecule is physically adsorbed (see Rideal, *Proc. Camb. Phil. Soc.*, 1939, **35**, 130) rather than by direct chemisorption with bond fission.

In reactions of low activation energy (~5 kcals. per mole) the variation of van der Waals free energy of adsorption with electronic structure, hitherto neglected, must be taken into account.

7. THE SPECIFIC ACTIVITY.

The foregoing analysis of simplified models suggested a special configuration for the active centre, while electronic-band theory and valency theory led to optimum values for the electron energy and level density at the Fermi surface. In particular when electron donation to the catalyst is involved at the rate-controlling step, " holes " in a *d*-band fulfil the electronic requirements and the free energy of activation at an active centre is a minimum. On the other hand if the rate-controlling step involves the positive ion as a reactant its concentration is a maximum under the same conditions. So far the electronic characteristics at an active centre have been taken equal to the average for the whole crystal, but, viewed from the atomic rather than the band standpoint, the holes in the *d*-band of a *d*-metal appear at lattice points as ions of short life. Mott and Jones (" Properties of Metals and Alloys," Oxford, 1940, pp. 192, 224) have inferred from magnetic data for pure nickel that either a pair of holes (Ni^{2+}) or none (Ni) are the preferred structures at a lattice point, but specific heat results fix the number at one (Ni^+; Mott, *Proc. Physical Soc.*, 1949, **62**, 416). In alloys having a constituent not normally possessing holes in its *d*-bands, *e.g.*, copper, zinc, or aluminium (" *s,p*-metals ") in nickel, the probabilities of a hole appearing at an *s,p*-atom or at a *d*-atom are not the same. Niessen (*Physica*, 1939, **7**, 1011) considered that the holes appear mainly in the *d* atoms except in copper–nickel and nickel–zinc alloys where the distribution is random. At present the problem remains unsolved.

In our ignorance a number of possibilities need examination. The model involves a binary alloy system of uniform crystal size when the surface is essentially bare and electron donation to the crystal is rate-controlling.

(a) *Holes Randomly Distributed and All Available.*—When the crystals are small the total number of holes may be available for reaction, since the tunnel effect should render interior holes accessible up to *ca.* 40 A. from the surface when the barrier is small.

The rate of reaction per unit is then

$$\propto \frac{nn_{\mathrm{d}}^{1}}{A} \exp. [-b(I^* + \mu_{\mathrm{e}}^{x})/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where n is the number of atoms in the crystal, n_{d}^{1} the number of holes per atom in the *d*-band at temperature T° K. and *s,p*-metal atomic fraction x. μ_{e}^{x} is the thermodynamic potential per metal electron per unit volume in the alloy crystal and A its surface area.

(b) *Groups of* n *Holes, randomly distributed, Available only at the Surface.*—Although the tunnel effect enables an electron of suitable energy to reach all holes, the electrons considered here are not initially in the right state. The ionisation of the adsorbed species will be dependent on the powerful Coulomb field of the transient positive ion, and its effect upon the potential barrier will decline rapidly as the hole recedes from the surface due to the perfect shielding by the mobile electrons. The chance of finding a hole at a surface atom is proportional to the concentration of holes in the crystal and to the ratio of surface atoms (n_{a}) to the rest (n_{r}), *i.e.*, $\propto n_{\mathrm{d}}^{1}n_{\mathrm{a}}/n_{\mathrm{r}}$, or if the holes move in groups of y the chance of finding such a group in the surface becomes $\propto n_{\mathrm{d}}^{1}n_{\mathrm{a}}/n_{\mathrm{r}}y$ and the rate of reaction per unit area

$$\propto \frac{n_{\mathrm{d}}^{1}n_{\mathrm{a}}}{n_{\mathrm{r}}yA} \exp. [- b(I^* + \mu_{\mathrm{e}}^{x})/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

(c) *As* (b) *but the Holes appear only at* d-*Atoms.*—The above equation must be multiplied by the atomic fraction of *d*-atoms giving a rate

$$\propto \frac{n_{\mathrm{d}}^{1}n_{\mathrm{a}}}{n_{\mathrm{r}}yA} (1 - x) \exp. [- b(I^* + \mu_{\mathrm{e}}^{x})/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In all the above examples the activity of an active complex has been put equal to the average for an active centre.

n_{d}^{1} is itself a function of the alloy composition and for simplicity will be put $\simeq n_{0\mathrm{d}}^{1}$ the corresponding value at 0° K., when for a binary alloy of a *d*-metal and an *s,p*-metal $n_{0\mathrm{d}}^{1} = (1 - x)n_{0\mathrm{d}} - x(n_{0\mathrm{s}} - {}_{\mathrm{d}}n_{0\mathrm{s}}) = (1 - x)n_{0\mathrm{d}} - xn_{\mathrm{s}}$. $n_{0\mathrm{d}}$ and ${}_{\mathrm{d}}n_{0\mathrm{s}}$ refer to the *d*-metal and are respectively the number of holes in the *d*-band and the number of *s,p*-electrons per atom. $n_{0\mathrm{s}}$ is the number of *s,p*-electrons per atom of *s,p*-metal and x is the atomic fraction of *s,p*-metal. At a critical composition (x^*), $n_{0\mathrm{d}}^{1}$ becomes zero and the alloy activity can be considered in two parts corresponding to alloys having holes and those having none. If we use the (*b*) approximation and take first the *d*-metal-rich side of the critical composition, the total activity of unit area includes that of active centres with holes and active centres without holes. The activity of centres without holes is the same as that at the critical composition.

The rate of reaction at composition $x < x^*$ is then

$$\propto \frac{Z}{A}\left\{\frac{n_d^1 n_a}{n_r y}\,\text{exp.}\,[-\,b(I^* + \mu_e^x)/\boldsymbol{k}T] + \left(1 - \frac{n_d^1 n_a}{n_r y}\right)\text{exp.}\,[-\,b(I^* + \mu_s^{x^*})/\boldsymbol{k}T]\right\} \quad . \quad (20)$$

where Z is the fraction of the surface occupied by active centres. In the range of composition where there are no holes ($x > x^*$) the rate

$$\propto \frac{Zna}{A}\,\text{exp.}\,[-\,b(I^* + \mu_e^x)/\boldsymbol{k}T] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Since the activity term corresponding to holes in the *d*-band is such as to give a large activity, this must fall rapidly to a small value or zero (depending on the exponential containing x^*) at the critical composition.

At temperatures above 0° K. there is a transference of electrons from the *d*-band to the *s,p*-band in alloys such as copper–nickel (Wohlfarth, *Proc. Physical Soc.*, 1948, **60**, 360; *Proc. Roy. Soc.*, 1949, *A*, **195**, 434) so that $n_d^1 > n_{0d}^1$ and the sharp drop of n_{0d}^1 to zero at the composition x^* is replaced by a more gradual approach of n_d^1 to zero at a slightly different critical composition $x_1^* > x^*$. When the reaction is such that the holes in the *d*-band are very active and the filled band is effectively inactive, then the activity of the *s,p*-metal-rich alloys at $x > x^*$ will be very sensitive to small variations in n_d^1 brought about the thermal activation. Under these conditions

$$n_d^1 \propto \text{exp.}\,(-\,\Delta\varepsilon/\boldsymbol{k}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where $\Delta\varepsilon$ is the difference in energy between the top of the *d*-band and the Fermi surface (Mott, *Phil. Mag.*, 1936, **22**, 287; Wohlfarth, *loc. cit.*).

Over alloys where the holes appear only at *d*-atoms, the initial decline in activity with increasing x is much more rapid than that given above, but reaches zero at the same value of x. Similar results obtain regardless of the valency of the *s,p*-metal in solid solution and the activity falls more quickly to zero at a smaller x^* with increasing Δn_s since $\partial n_{0d}^1/\partial x = -\Delta n_s$.

Relevant data on the alloys of *d*-metals amongst themselves are scanty and not always reconcilable with simple band theory. Here it will be assumed that the same general principles apply. In alloys containing no *d*-metal, *e.g.*, α-brass, the two metals appear to have a common *s,p*-band and the electronic structure of an active centre will be taken, in a first approximation, to be independent of nearest neighbour atom type.

The fact that vacant electron sites appear at specific atoms suggests the link between the electronic-structure effect in catalyses and the current purely geometric interpretations.

(d) *Retardation by Reactants and Products.*—The reaction rate trends given above may be said to be typical of the metal and not of the general class of catalyst–sorbate complexes. They hold for processes proceeding in a stationary state on a sparsely populated surface, or for the induction period of a reaction involving surface coverage by chemisorbed reactants or products. In a stationary state where some chemisorbed species covers an appreciable fraction of the surface, the rate-controlling step may proceed on the bare surface or it may involve the removal of the chemisorbed material itself; both situations are normally treated by the methods initiated by Langmuir. However, where the chemisorption of the retarding species involves increase of the electron : atom ratio of the crystal it affects the whole surface by reducing n_d^1 or by raising the electron energy in *s,p*-metals. In coherent catalyst crystallites of normal size the drop in activity from this cause should be small. On the other hand, when the rate-controlling step involves an attack on the retarding layer itself, the local concentration of electrons or holes at its periphery will tend to be larger or smaller respectively than in the crystal bulk, and the reaction rate may be slower than expected. That is to say the strongly chemisorbed molecules function in the same way as *s,p*-metal, and displace the rapid onset of activity in *d*-metal alloys to values of x lower than x^*, or in *s,p*-metal alloys produce a lowered activity corresponding to a higher electron : atom ration than actually present in the bare alloy.

All the foregoing major conclusions are reversed in an obvious manner when negative-ion formation is the rate-controlling step.

8. PURE METAL AND ALLOY CATALYSTS.

In this section the rules laid down will be applied to some real catalysts. A metallic catalyst is defined as one which *in situ* in its quasi-stationary state contains metal as a separate phase regardless of form or manner of support. When there is more than one metallic constituent the resulting alloys are assumed to be homogeneous, while in the presence of several metallic phases the total activity is taken to be a linear function of the percentage weight, specific activity, and specific area of each phase.

Metallic catalysts of industrial interest have almost-full or just-filled 3*d*-, 4*d*-, and 5*d*-bands, and our discussion shows that their activity must vary rapidly with composition in that range. The variation in physical properties is well known (Mott and Jones, *loc. cit.*). Less well known are the hydrogen solubility studies of Sieverts *et al.* (*Z. anorg. Chem.*, 1915, **92**, 329) in the silver–, gold–, and copper–palladium systems, where the solubility at low temperatures (10—100° c.) falls rapidly from the high value in palladium to almost zero at the equiatomic composition. There exist, also, less well defined properties which change with the filling of *d*-band holes and are probably associated phenomena, *e.g.*, the rate of oxidation (Pilling and Bedworth, *Ind. Eng. Chem.*, 1925, **17**, 372) and sulphuric acid attack (Irmann, *Abhandl. Inst. Metall., Aachen*, 1916, **1**, 39) on the copper–nickel alloys, the diffusion of nickel in copper (Johnson, *Metals Tech.*, Tech. Publ. No. 2007, 1946), etc. See also Uhlig (*Trans. Electrochem. Soc.*, 1944, **85**, 307) on corrosion.

(i) *Transitional Metals.*—Only the metals from chromium to zinc will be considered but the reasoning applies equally to the remaining members of the period and to the other long periods.

Calculation (Krutter, *Phys. Review*, 1935, **48**, 664; Manning, *ibid.*, 1943, **63**, 190) shows that the density of electron levels, $g(-\phi)$, increases steadily from chromium to iron. The low-temperature electronic specific-heat data of Keesom and Kurrelmeyer (*Physica*, 1940, **7**, 1003) indicate a flat in $g(-\phi)$ extending from α-iron to β-cobalt, a sharp rise between the solid solution 85 : 15 nickel–iron and pure nickel, and a rapid fall between the nickel–copper solid solutions containing 40% and 20% of nickel. Since the best recorded electron work functions may vary by as much as 0·5 ev. for a given metal only the trends in each period will be noted. There appears to be a relatively rapid increase of work function between the metals of group 5A and 8, followed by a constant or slowly increasing value up to nickel, palladium, or platinum in each period and a rapid fall to copper, zinc, etc. (Reimann, " Thermionic Emission," Chapman and Hall, London, 1934; Herring and Nichols, *Rev. Mod. Physics*, 1949, **21**, 187). Parallel changes occur in the inner potential, where it is known, and in the reciprocal of the metal interatomic distances. If the effects of increasing electron : atom ratio from copper to zinc are observed in the properties of the corresponding solid solutions (intermetallic compounds also in the copper–zinc alloys), the above trends show discontinuities at phase boundaries, and changes of slope where the gradient of $g(\varepsilon)$ undergoes rapid change.

(a) *Rate controlled by positive-ion formation.* There will be a gradual increase in activity from chromium to cobalt, onset of high activity between the alloy 85 : 15 nickel–iron and pure nickel, and a sharp maximum either at pure nickel or in dilute solid solutions of iron and cobalt in nickel. Beyond nickel the activity drops almost linearly to a very low value at 40 : 60 nickel–copper (depending on the temperature and the reaction) and then decreases slowly still further to zinc.

A number of additional effects operate but it is difficult to estimate their magnitudes or to superpose them upon the general curve. Thus, according to Pauling and Ewing (*ibid.*, 1948, **20**, 112) the electron : atom ratios of both α- and β-manganese correspond to full or almost full Brillouin zones, and therefore their activities should be less than expected on simple interpolation between the activities of body central cubic chromium and α-iron [see section 8 (iii)]. In addition, the alloys and elements between pure nickel and 40 : 60 nickel–copper are ferromagnetic at those temperatures where the free metals are normally used as catalysts. This implies [section 8 (v)] the presence below the Curie temperature of an inhibiting effect, decreasing in the series cobalt, iron, and nickel, which must be included in the total assessment of activity.

(b) *Rate controlled by negative-ion formation.* The activity trend is the opposite of that discussed in (a) while the secondary variations can obviously be treated similarly.

(c) *Rate controlled by covalent-bond formation.* The table shows how the valency orbitals are occupied in the various elements according to Pauling (*Proc. Roy. Soc.*, 1949, *A*, **196**, 343).

Transitional-metal Orbitals (Pauling).

Orbital type.	Cr.	Mn.	Fe.	Co.	Ni.	Cu.	Zn.
Bonding (max. 6) filled	3·6	4·6	5·6	6	6	5·5	4·5
Atomic (max. 3) not full	0·22	1·22	2·2	1·7	0·6	Nil	Nil

The total number of singly occupied " atomic " orbitals reaches a maximum value at the alloy of approximate composition iron 77% and cobalt 23%, and falls to zero at an alloy containing nickel 40% and copper 60%. Therefore up to this latter composition *d*-orbitals are readily available at the surface to form strong bonds, but at higher electron : atom ratios only a fraction of the " bonding " orbitals, which are themselves decreasing in number, can be used. The activity changes must parallel these given under (a) and similar filled-zone and ferromagnetic effects will be apparent.

(ii) *Alloys of* d-*Metals with* s,p-*Metals and Metalloids.*—As an element with loosely held valency electrons is added in solid solution to a transitional element with holes in the *d*-band, the decrease in activity, when positive-ion or covalent-bond formation is rate-controlling, parallels the decline in the number of holes per atom in the *d*-band of the alloy. The rate of decrease depends upon Δn_s (cf. section 7), and is larger the higher the valency of the solute *s,p*-metal. Only in a number of simple cases can the band theory be used to predict in detail the characteristics at the Fermi surface of the alloys, and in more complex alloys recourse should be had to the physical (particularly magnetic) data themselves.

In the alloy composition range where $g(-\phi)$ begins to drop rapidly, the activation energy ($\propto I^* + \mu_e^m$) of the substrate reaction begins to increase because the rise of Fermi energy per added electron increases; the electronic contribution to the entropy of activation ($\propto dg(\varepsilon)/d\varepsilon$ at $\varepsilon = -\phi$) falls. This phenomenon occurs because of the extensive overlapping of energy levels in solids. Homogeneous reactions correspond largely to transitions between potential surfaces, in which the energy level density, and therefore also the entropy and the entropy factor, always increase with increasing energy and hence with activation energy.

The activity–composition relation holds whether the composition corresponds to an intermetallic compound or to a solid solution, and whether the range of solid solution is wide as in nickel–copper alloys, narrow as in tin–iron, very limited (iron–copper), or scarcely different from the chemisorption of the *s,p*-metal. Hydrogen, boron, carbon, nitrogen, phosphorus, and the metalloids function in the same way as the *s,p*-metals, but possible failure of the band theory when applied to their alloys and compounds suggests caution in fixing the effective valency at the normal chemical value. The effect of hydrogen in deactivating palladium (Beeck, U.S.P. 2,223,777) must be explained on this basis and the much disputed rôle of " bulk " carbide in the Fischer–Tropsch processes appears, at the least, to be that of a diluent.

When negative-ion formation is rate-controlling the activity changes are the converse of those given above.

(iii) *Hume-Rothery Alloys.*—Jones (*Proc. Roy. Soc.*, 1934, *A*, **144**, 225) has pointed out that the phase changes occur at special electron : atom ratios, when the Fermi surface can be reduced in energy because of the greater density of electron levels available at the Fermi surface in the new phase. Sharp changes in activity must be expected at the phase boundaries associated with the electronic readjustments and with the different geometry. The geometric contribution cannot be estimated but the electronic effects follow from the theory.

Consider the brasses, beginning at pure copper and adding zinc. At pure copper the first Brillouin zone is half full, but addition of zinc in solid solution increases the electron : atom ratio, the energy of the Fermi surface and the electron-level density [at first $g(\varepsilon) \propto \varepsilon^{\frac{1}{2}}$]. The gradient of level density, $dg(\varepsilon)/d\varepsilon$, is positive but its numerical value is small compared with that at the critical composition in the copper–nickel alloys. As the Fermi surface approaches and touches the zone boundary, $g(\varepsilon)$ increases more rapidly to a sharp peak and then falls off rapidly, so that the face-centred cubic structure has a decreasing value of $g(\varepsilon)$ and becomes unstable with respect to the body-centred cubic structure which possesses a large increasing value of $g(\varepsilon)$ at the same electron : atom ratio. The α-phase therefore rearranges to yield the β-phase, in which the level density at the Fermi surface increases, the gradient of level density changes from large negative to large positive, and the energy of the Fermi surface decreases (Fig. 4).

A similar description can be given of the changes at the boundaries of the β-phase with the γ-phase and of the γ-phase with the ε-phase.

(a) *Rate controlled by positive-ion formation.* The free energy of activation must increase up to the composition where the Fermi surface touches the zone boundary because the energy of activation increases with increase of Fermi energy and the electronic contribution to the entropy of activation is small but positive. [The gradient of $g(\varepsilon)$ must be very large to make an appreciable entropy contribution since it appears in the latter as $d \log_e g(\varepsilon)/d\varepsilon$.] Further increase of electron : atom ratio pushes the Fermi surface up to the peak in $g(\varepsilon)$, and this will be accompanied by a flattening of the rising activation free energy curve owing to a diminution in the rate of increase of the Fermi energy per added electron and to the increasing electronic entropy effect. As the Fermi surface passes under the peak of $g(\varepsilon)$ the situation is similar to that in the nickel–copper alloys, at the critical composition when the *d*-band is filling up, and a rapid increase in the free energy of activation results. However in the new phase the electronic characteristics are similar to (not identical with) those in the old phase at the composition where $g(\varepsilon)$ is just rising to its peak. Thus at the boundary of the new phase the free energy of activation is considerably lower than that at the electron-rich edge of the old phase. This activity pattern repeats itself in each new phase as long as the structure is controlled by electron : atom ratio. In the intermediate regions of mixed phases a linear relation holds between the activities of the old and new boundaries (see Schwab, *loc. cit.*).

It is worth noting that in a given phase the activity variations between crystal faces of different Miller index will be most pronounced around the maximum in $g(\varepsilon)$.

When negative-ion formation is rate-controlling the trends are the converse of those given above.

(b) *Rate controlled by covalent-bond formation.* Pauling's valencies lead one to suppose a gradual decrease of activity from copper to zinc through the brasses, but with oscillations about this average line corresponding to the phase changes. Band theory gives the same results as in (a).

(iv) *Order and Disorder in Alloys.*—Pauling and Ewing (*loc. cit.*) suggest that ordering in β-alloys may be affected by electron filling of Brillouin zones and this leads to conclusions on activity changes during ordering and disordering similar to those considered in subsection (iii). The state corresponding to a filled zone, or one filled to just past the peak in $g(\varepsilon)$, should have the lowest activity in the absence of dominating geometric factors.

(v) *Magneto-catalytic Effect.*—Hedvall's observations (see *Chem. Reviews*, **1934**, **15**, 139; *J. Physical Chem.*, 1942, **46**, 841; " Handbuch der Katalyse," edited by Schwab, Springer, Vienna, Vol. VI, p. 578) on activity changes as catalyst temperatures pass through the Curie point receive in part a very natural explanation according to this theory. Cardwell (*Phys. Review*, **1949**, **67**, 125) has produced evidence of a small increase in the work function of pure nickel as its temperature increases through a region including the Curie point, and this together with the accompanying disorientation of the metal-electron spins indicates a change in catalytic activity. In a ferromagnetic metal at absolute zero all d-band holes are of one spin only and the energy required to uncouple an electron spin is $\sim \boldsymbol{k}\theta_c$ where θ_c is the Curie temperature in °K. Addition of electrons to the metal (or formation of a covalent bond) near 0°K. with the lowest activation energy can occur only for electrons of one kind of spin, and in the absence of any orienting effect of the metal-electron–substrate-electron exchange energies this implies the reduction of the entropy factor by one half. Rising temperature uncouples an increasing number of spins so that the entropy factor increases and the rate constant contains a factor $(1 + \exp. - \theta_c/T)$. Above θ_c spins of both kinds can be paired in the d-band and the entropy contribution from this factor is a maximum; at the same time terms containing $\boldsymbol{k}\theta_c$ drop out of the activation energy. Now in real polycrystalline metals the saturation magnetisation seldom falls to zero sharply at a specific temperature but " tails " to zero slowly over a finite temperature range (Gerlach, *Z. Elektrochem.*, **1939**, **45**, 151). Over this range the entropy factor increases and the activation energy decreases in the manner described, whether positive-ion, covalent-bond, or negative-ion formation is rate-controlling; this is the magneto-catalytic effect.

If the effect noted by Cardwell (*loc. cit.*) is general, then this change in work function is an additional factor; it decreases the activation energy of reactions controlled by positive ions and increases the activation energy where negative ions are dominant.

Practically the effect can best be demonstrated on alloys of low Curie point where side reactions interfere least, but these are the catalysts where the effect will be a minimum. At higher temperatures side reactions (*e.g.*, carbide formation) confuse the issue, and the reaction between hydrogen and deuterium seems most suited to this study.

(vi) *Poisons.*—Three mechanisms of catalyst poisoning must be recognised although they are not entirely independent of each other.

(a) *Change of electron work function* (cf. Nyrop, *op. cit.*). Addition of strongly electropositive substances lowers the work function and poisons reactions proceeding *via* a positive ion at the slowest step, whereas strongly electronegative reagents poison the corresponding anion-controlled processes by raising the work function. Beyond a certain range of work function both types will poison reactions involving covalently bonded intermediates.

The rate of change of work function with surface concentration of poison is greatest when the concentration is small. Since the work function appears in the rate equation as an exponential, it can be seen that this model accounts quite well for those poisoning effects which have been used as evidence for the " non-uniform " surface. According to this view, even a uniformly active surface must exhibit a proportionally greater fall in activity on chemisorption of the first traces of poison than for the later portions.

(b) *Electron-level effects.* Multivalent elements with easily removable valency electrons, *e.g.*, mercury, lead, arsenic, antimony, tin, bismuth, etc., poison by forming surface alloys with metals having *d*-band holes, whereby the holes or orbitals are blocked with electrons. The poisoning effect is greater the larger the valency, other things being equal [cf. section (ii)]. In the Hume-Rothery-type alloys of metals without *d*-band holes, the effect of these added substances may be that of deactivation caused by a rapid rise of the Fermi energy per poisoning atom, or of activation when sufficient of the poison is added to precipitate a localised phase change with drop in free energy of activation [cf. section (iii)]. These remarks are true for reactions involving positive-ion or covalent-bond formation at the slowest step; the converse is true in an obvious way for anion formation.

A dipole must be expected at the surface under these conditions which will have an additional effect according to (a).

(c) *Steric effects.* Both (a) and (b) imply occupancy of active centres and surface coverage with all its geometric consequences.

(vii) *Special Metallic Catalysts.*—The earlier sections have described the properties of catalysts which are obviously metallic. There are other catalysts which behave as metals although the situation is more complex; two types and their possible mode of action will be described.

(a) *Reducible metal oxide plus "irreducible oxides."* Under reducing conditions, as in hydrogenation, the easily reducible metal oxide yields small metal crystals in a matrix of unreduced mixed oxides (*e.g.*, Cu in CuO.ZnO and in $CuCr_2O_4$), or the metal crystallites carry the unreduced oxides as inclusions and adhesions (*e.g.*, promoted-iron ammonia catalysts). At the same time, owing to the possibility of alloy formation between the reduced metal and the metal of the "irreducible" oxide, the free energy of that reaction is available to assist the reduction of the intransigent oxide. This holds even though the extent of alloy formation at equilibrium amounts to scarcely more than the chemisorption of the second metal. Thus with CuO.ZnO, small crystals of brass appear and the activity of copper is diminished; or in $CuCr_2O_4$ there may be a very small concentration of chromium dissolved in copper with production of holes in the copper *d*-band and an enhancement of activity. (Such catalysts are used at moderately high temperatures.)

"Alkalisation" of metal catalysts with alkali-metal compounds, such as the carbonates and hydroxides, is a common device in hydrogenations such as ammonia synthesis. Since the reactions take place at metal surfaces it seems that the function of the electro-positive metal must be to adjust the metal work function (see Brewer, *J. Amer. Chem. Soc.*, 1931, **53**, 74; 1932, **55**, 1888; *Phys. Review*, 1931, **38**, 401), the free alkali metal being supplied by a mechanism similar to that above.

(b) *"Irreducible" oxides.* In our approximation, only the oxides of beryllium, magnesium, boron, aluminium, and silicon are considered to be irreducible. Other oxides such as zinc oxide, are known to be defective in oxygen and to be excess semi-conductors even at considerable partial pressures of oxygen. At high pressures of hydrogen or carbon monoxide this reduction will be increased, although thermodynamic data show that no bulk metal phase can separate at ordinary temperatures ($<1000°$ c.). It seems possible that the metal atoms may form what amounts to a "dilute metal" in the oxide lattice, or they may separate into some essentially metallic surface phase, so that the catalysed reaction proceeds at a metal surface. When the oxygen-defective oxide is metallic its behaviour can be described by the principles of this section, and when it is a semi-conductor by those of following sections.

9. REACTION EXAMPLES.

Unfortunately there are no known reaction mechanisms in heterogeneous catalysis, and the application of the theory to given reactions can follow only the most general lines. As far as the scanty data go, hydrogen generally reduces the work function of group 8 metals (de Boer, "Electron Emission and Adsorption Phenomena," Cambridge, 1935, p. 149), which suggests that protons exist at the surface and that hydrogenation ought therefore to provide examples of mechanisms involving positive ions. In the same way surface reactions with oxygen or the hydroxyl ion should provide examples of anion-controlled reactions.

(a) *Hydrogen Addition at Multiple Bonds.*—Suppose that saturation of multiple bonds proceeds *via* one of the following steps which is rate-controlling (H_2, R, and RH_2 physically adsorbed; R is, *e.g.*, an olefin; the rest chemisorbed) :

$$\begin{aligned} \tfrac{1}{2}H_2 &\rightharpoonup H^+ + e \\ R &\rightharpoonup R^+ + e \\ R + H^+ &\rightharpoonup RH^+ \\ R^+ + H &\rightharpoonup RH^+ \\ RH^+ + H_2 &\rightharpoonup RH_2 + H^+, \text{ etc.} \end{aligned}$$

$$\begin{aligned} \tfrac{1}{2}H_2 &\rightharpoonup H \\ R + H &\rightharpoonup RH \\ RH + H_2 &\rightharpoonup RH_2 + H \end{aligned}$$

The rate in the ionic mechanism is either that of the formation of a positive ion, or is proportional to the stationary concentration of a positive ion. The rates and concentrations depend upon the number and characteristics of holes in the *d*-band of a transitional metal as already described (section 7) and hydrogenation activity must fall to a low value as the holes are filled. Similar behaviour is to be expected if the intermediates are covalently bonded. The results of Rienäcker on the hydrogenation of ethylene (*Z. anorg. Chem.*, 1939, **242**, 302; 1943, **251**, 60) and cinnamic acid (*J. pr. Chem.*, 1941, **158**, 95), although not clear-cut, are in general accord with this picture.

(b) *Hydrogenolysis of Bonds.*—Bremner (*Research*, 1948, **1**, 281) has attributed the large effects in the hydrogenolysis of esters to a " protonolysis," and similar steps can be postulated for some alcohols, *e.g.*, $ROH + H^+ \longrightarrow R^+ + H_2O$ (rate-controlling), followed by $R^+ + H_2 \longrightarrow RH + H^+$. The reaction rate then depends on the surface concentration of protons, and the process may be slowed down or stopped by " alkalisation " [section 8 (vii)] which reduces the stationary work function of the metal surface. Components of acidic function such as alumina and silica may act by controlling the alkali-metal concentration through equilibria equivalent to $Na_2O + Al_2O_3 \longrightarrow Na_2Al_2O_4$, etc., and it should be possible to adjust the work function of the composite surface over a wide range (see Brewer, *loc. cit.*).

Conversely hydrogenolysis should be promoted by small concentrations of electronegative reactants such as hydrogen sulphide, provided that the surface coverage is so small that complete blocking of active centres does not occur.

(c) *Anions in Copper–Nickel Alloy Oxidation.*—A class of reaction where negative ions certainly participate is the oxidation of metals, and it is interesting to note that Pilling and Bedworth (*loc. cit.*) found large changes in rate between 20% and 70% of nickel in copper–nickel alloy oxidation at high temperatures (850—1000° c.). The oxidation rate is fairly constant up to between 30 and 40% of nickel at 850° and 900°, but then begins to fall off rapidly and approaches a much lower limiting value at 60—80% of nickel, depending on the temperature.

It may be significant that this decrease in reaction velocity begins close to the composition where the *d*-band of the alloys starts to empty and suggests that the rate-controlling step in this region involves the passage of electrons from the metal Fermi surface to oxygen to form the corresponding anions.

(d) *Electron Transfer in Hydrogen Peroxide Decomposition.*—Weiss (*Trans. Faraday Soc.*, 1935, **31**, 1547) in a continuation of earlier studies on the catalysed decomposition of hydrogen peroxide (Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332) suggests that with metal catalysts the rate-controlling step is $H_2O_2 +$ metal electron $\longrightarrow OH^- + OH$. The theory predicts therefore that over copper–nickel alloys the decomposition rate will be fastest on copper and copper-rich alloys, falling to a lower value as the *d*-band begins to empty in the neighbourhood of 40% of nickel. This applies at hydrogen-ion concentrations where the alloys are not attacked, and on bare metal surfaces where the oxide film is not thick enough to prevent the electron transfer.

10. SEMI-CONDUCTORS.

Many solid catalysts employed in reactions involving reducing and oxidising gases have some metallic characteristics or are semi-conductors *in situ* in the stationary state. This is qualitatively apparent in the radical colour changes undergone by " irreducible " oxides and sulphides on activation or in use, to yield black, lustrous, or highly coloured contact masses. It is significant also that these semi-conductors are much less active, for instance in hydrogenation, than metals at the same low temperatures and are not nearly so sensitive to poisoning by sulphur and its compounds.

Unfortunately these oxide and sulphide catalysts are amorphous in the most active forms and their structure can only be guessed, whereas metal catalysts are often recognisably crystalline by ordinary techniques. The bonding of the chemisorbed species at the semi-conductor surface must nevertheless follow the same principles as with metals, but the electronic characteristics are considerably different and the already complex substrate reactions are augmented by others in the solid. A convenient classification of catalysts follows that devised for the discussion of the electrical properties, namely as intrinsic, normal, and abnormal semi-conductors (see Mott and Gurney, " Electronic Processes in Ionic Crystals," Oxford, 1940; Seitz, " Modern Theory of Solids," McGraw Hill, New York and London, 1940). The last two kinds arise most simply under hydrogenating and oxidising conditions respectively, while many oxides and sulphides can exist in both forms depending upon the partial pressure of the electronegative element in the gas phase. In the following discussion the oxide and sulphide stoicheiometric lattices are assumed to be purely ionic; covalent and van der Waals contributions to the inter-ionic forces are neglected without, it is believed, detracting from the validity of the results which can in any case be only of a general character. If greater detail is required, then the basic ideas must be applied to special systems along the lines followed by Mott and Littleton (*Trans. Faraday. Soc.*, 1938, **34**, 485), Seitz (*Rev. Mod. Physics*, 1946, **18**, 384), and Wright (*Proc. Physical Soc.*, 1948, **60**, 13) in studies on the solid alkali and silver halides and group 2 oxides.

(i) *Positive-ion Formation.*—Production of positive ions during chemisorption at the surface occurs, as in metals, by transfer of an electron from the filled substrate level of highest energy to the empty crystal level of lowest energy. Appropriate thermodynamic potentials for the electrons in a semi-conductor are used (see Fowler, " Statistical Mechanics," Cambridge, 1936) and conclusions are formed analogous to those found for metals. Only an outline of principles and inferences is given in the succeeding sections.

(a) *Intrinsic semi-conductors* (Fig. 5). One may suppose that few catalysts function by a purely intrinsic mechanism, but it is useful to discuss this type first because it forms a basis, small modifications of which lead to the other catalyst types.

FIG. 5.

Electron levels in an insulator or intrinsic semi-conductor (idealized).

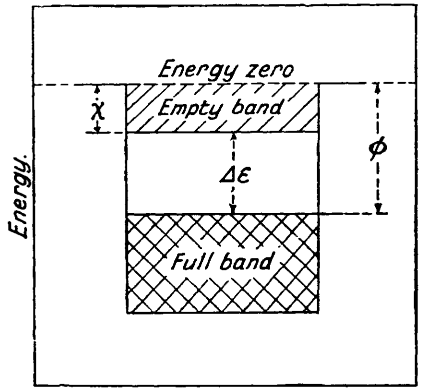
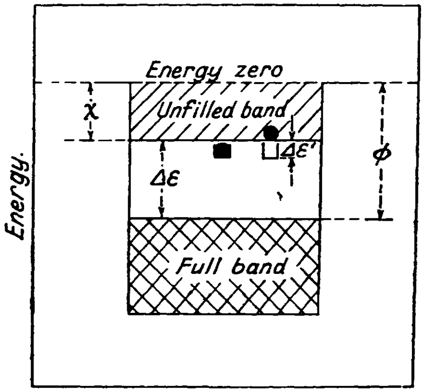


FIG. 6.

Electron levels in a normal semi-conductor (idealized).



In these solids the top (energy $= -\phi$) of the filled electron band is separated from the bottom (energy $= -\chi$) of the empty band by a forbidden energy region $\Delta\varepsilon \sim \boldsymbol{k}T$, and the formation of holes in the filled band by thermal activation of electrons to empty levels is not dependent on non-stoicheiometry or impurities. At any absolute temperature T, the concentration of holes at the top of the filled band and of electrons in the empty band is $\propto$ exp. $[-\Delta\varepsilon/2\boldsymbol{k}T]$. The holes, which may be in the filled band of the cation or anion whichever lies higher, are the acceptor levels of lowest energy, while the electrons promoted to the empty band lie in the donor levels of highest energy; both holes and electrons are mobile and can appear at the surface. For a given substrate the energy of activation for positive-ion formation is readily shown to be $\propto (I^* - \phi + \Delta\varepsilon/2)$ where I^*, equal to $I + \Delta U^*$, is the ionisation potential of the activated complex and the activation energy decreases as ϕ increases and $\Delta\varepsilon$ decreases. When the catalyst lattice is ionic, $\phi = A_a\boldsymbol{e}^2/a + E_a - \omega_h$, $-\chi = A_c\boldsymbol{e}^2/a - I_c - \omega_e$ (see Mott and Gurney, *op. cit.*) where A_a and A_c are the Madelung potentials at anion and cation sites respectively, ω_h the polarisation energy around the electron hole, ω_e that around the excess electron, E_a is the least energy required to remove an electron from the anion *in vacuo*, I_c is the energy gained on adding an electron to the cation *in vacuo*, $\boldsymbol{e}$ is the electronic charge, and a the unit cell parameter. Therefore, $\phi - \chi = \Delta\varepsilon = (A_a + A_c)\boldsymbol{e}^2/a + E_a - I_c - \omega_h - \omega_e$, and in binary compounds, where anion and cation exert the same electrovalence, $\phi - \frac{1}{2}\Delta\varepsilon \simeq (E_a + I_a)/2$ if polarisation effects are neglected. Thus on the assumption that the anion-filled band lies higher than that of the cation, the activation energy decreases as E_a and I_c increase. The full expression for $\Delta\varepsilon$ shows how it depends on the Madelung potentials and reveals that $\Delta\varepsilon$ is smaller in the surface plane owing to the reduced values of A_a and A_c in that region.

Among the catalysts of bivalent metals the effect should be apparent in cupric, mercuric, nickel, and zinc oxides where the atoms have the highest second ionisation potentials in the periodic table, and particularly in the corresponding sulphides because of the smaller negative value of the S^- electron affinity compared to that of O^-. Unfortunately these metals are multivalent or reducible and the intrinsic phenomena are masked by others, described below, arising from non-stoicheiometry; the ionic oxides having a very small potential variability of composition are insulators because of the large values of $\Delta\varepsilon$. The discussion indicates that the intrinsic semi-conductors of most use will be almost metallic in properties, and these are found amongst the metalloids and intermetallic compounds having ionic character. Their catalytic properties follow most readily by extending the arguments used for the Hume-Rothery alloys to compounds where the full and empty bands are separated by a small energy gap in all lattice directions. In this way the electronic entropy factor can be reintroduced and shown up in its dependence on $dg(\varepsilon)/d\varepsilon$, for semi-conductors and insulators, as for metals.

The value of the activation energy depends also upon ΔU^* and therefore on ΔU^+ which has its largest value when the substrate positive ion is adsorbed over a vacant cation point in the surface lattice. The significance of this factor will be remarked in the next section concerning a more important type of semi-conductor.

(b) *Normal semi-conductors* (Fig. 6). Here the energy bands are similar to those in intrinsic semi-conductors, but the localised occupied electron level occurs close to the bottom of the empty band and separated from it by an energy $\Delta\varepsilon'$. The number of empty localised levels in a given volume at temperature T is proportional to both the volume and energy densities of levels and to exp. $[-\Delta\varepsilon'/2\boldsymbol{k}T]$; these are the acceptor levels of lowest energy. Although the promoted electrons can migrate to the surface, the emptied levels are unable to do so, and only centres in or near to the surface are of interest in catalysis.

For a given adsorbate yielding a positive ion, the activation energy for chemisorption is now $\propto (I^* - \phi + \Delta\varepsilon - \Delta\varepsilon'/2)$ and this is minimised by the conditions noted under (a) but with additional parameters affecting $\Delta\varepsilon'$. The localised levels may be due to impurities or to a small excess of the lattice metal. Amongst oxide and sulphide non-stoicheiometric semi-conductors of the type found under reducing conditions, $\Delta\varepsilon'$ is very small (see particularly Fritsch, *Ann. Physik*, 1935, **22**, 375, the extensive review by Meyer, *Z. Elektrochem.*, 1944, **50**, 274, and Mott and Gurney, *op. cit.*) so that the probability of substrate ionisation by electron donation to these vacated localised levels is even less than that at the surface of an intrinsic semi-conductor having the same values of ϕ and $\Delta\varepsilon$.

The loss of electronegative constituent to give the reduced lattice is accompanied by displacement of metal atoms into interstitial positions (Frenkel, *Z. Physik*, 1926, **35**, 652) or by formation of anion defects (de Boer, *Proc. Physical Soc.*, 1937, **49**, extra part, 59; cf. Schriel, *Z. anorg. Chem.*, 1937, **231**, 313); neither model possesses cation vacancies to adsorb positive ions. Thus electron level energy, cation adsorption energy, and active centre requirements for positive ion formation apparently cannot be met in simple, normal semi-conductors of the zinc oxide type at the conductivity centres. However if substrate ions are formed by donation of electrons to the unreduced lattice cations, or to anion defects (producing F-centres), the activation energies may become reasonable. Consider a stoicheiometric zinc oxide crystallite containing its equilibrium quantity of intrinsic Schottky defects (Schottky, *Z. physikal. Chem.*, 1935, *B*, **29**, 335); cation and anion vacancies occur in equal but small concentration. Hydrogen might react with the lattice in several ways : it may yield hydroxyl ions, Zn^+, and zinc metal, or form Zn^+ or F centres (Mott and Gurney, *op. cit.*) with the protons adsorbed at cation defects, etc.

The proton is of course most strongly adsorbed as OH^- or when situated at a cation vacancy, but may be adsorbed with a sufficient energy at other general positions bridging anions by virtue of the powerful polarisation it produces. Substrates yielding larger positive ions require cation vacancies and, as already indicated, these are present only in small concentration in the stoicheiometric crystal and are still fewer in the reduced, semi-conducting state.

Positive-ion-forming processes can be encouraged, other things being equal, only by maintaining or increasing the concentration of cation vacancies by cutting down the extent of lattice reduction in the equilibrium state, or by adding or forming an irreducible ionic compound in which the cation defect is large and permanent. These modifications are affected simultaneously by " supporting " the semi-conducting oxide upon, or combining it as a solid solution or compound with, an irreducible oxide possessing the incomplete spinel lattice, *e.g.*, γ-Al_2O_3 (Verwey, *J. Chem. Physics*, 1935, **3**, 592) and possibly amorphous Cr_2O_3 (cf. Visser, *Chem. Weekblad*, 1946, **42**, 127); other suitable cation-defective reagents include the amorphous glass-like oxides such as silica and the mixed alumina–silica oxides where the network-modifying positions are empty (see section **11** on insulators).

Small amounts of sulphur cannot have a drastic effect on these lattices, and such lattices are not poisoned as are metal lattices by traces of this element. On the other hand alkali-metal ions and the like, which block cation defects, will function as poisons in reactions controlled by the rate of formation of a positive ion or by the surface concentration of a positive ion.

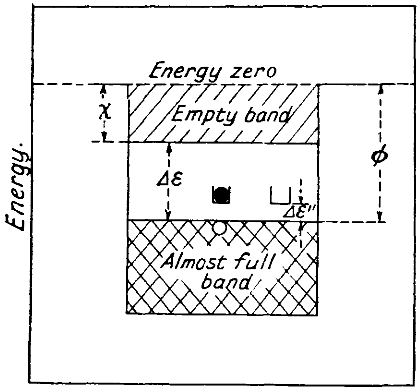
(c) *Abnormal semi-conductors* (Fig. 7). Abnormal or oxidation semi-conductors have in the forbidden region an empty localised electron level close to the top of the full band and separated from it by a small energy increment $\Delta\varepsilon''$. The number of holes per unit volume in the top of the full band at any temperature T is proportional to the volume and energy level densities and to exp. $[-\Delta\varepsilon''/2\boldsymbol{k}T]$, and these are the acceptor levels of lowest energy. Here the empty localised levels, existing through non-stoicheiometry or impurities, are immobile and only those at or close to the surface can function directly as acceptor levels. The holes in the full band are mobile and can migrate to the surface.

The activation energy for positive-ion formation is now $\propto (I^* - \phi + \Delta\varepsilon''/2)$ and is a minimum for a given substrate when ϕ is a maximum and $\Delta\varepsilon''$ is a minimum. For oxide and sulphide catalysts where conductivity ensues from a big excess of the electronegative constituent, $\Delta\varepsilon''$ is usually small compared to $\Delta\varepsilon$ (*e.g.*, Cu_2O; Juse and Kurtschatow, *Physikal. Z. Sovietunion*, 1933, **2**, 453; Mott and Gurney, *loc. cit.*) so that the activation energy is approximately $(I^* - \phi)$ and, other things being equal, this class of semi-conductor is most likely to induce positive-ion formation. The incorporation of excess of oxide or sulphide into the lattice requires an increase in the positive charge at a number of cations and the omission of cations from a number of other lattice points according to $M^+(s) + \frac{1}{2}X_2(g) \longrightarrow M^{2+}(s) + X^-(s) + h^+$. The cation vacancies ($h^+$) in the surface are the active centres at which ΔU^+ will be greatest and I^* a minimum.

While such non-stoicheiometric semi-conductors may be formed from appropriately chosen catalysts in oxidation reactions, they are not likely to be present in the reducing atmospheres of reactions involving hydrogen and hydrocarbons. Under the latter conditions one might choose an irreducible basis oxide and support upon it a second multivalent metal oxide so that the " valence induction " effect (Selwood *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 883, 2145, 2271; Report of the Pittsburgh International Conference on Surface Reactions, 1948, p. 49) stabilises to some degree the oxidised state of the supported oxide. At least the basis oxide should possess stable cation defects, and the supported oxide also if possible.

FIG. 7.

Electron levels in an abnormal semi-conductor (idealized).



(ii) *Negative-ion Formation.*—Negative-ion formation is most easy and fastest for a given substrate when the electrons in the catalyst are loosely held. On intrinsic semi-conductors this means when both ϕ and $\Delta\varepsilon$ are small. Subsection (i,b) (p. 260) indicates that normal semi-conductors should form negative ions readily since the electrons in the localised levels are situated relatively high in energy and are raised to the conductivity band, where they are comparatively free, with only a small energy input. Moreover there are anion vacancies to act as active centres and to increase the value of the anion adsorption energy.

Lattices which become abnormally semi-conducting in an oxidising atmosphere will affect substrate negative-ion formation by a process converse to that for positive-ion production at normal semi-conductor surfaces [see (i,b)]. Just as the latter reaction is more favoured in equilibrium and accelerated by the presence of structures with extensive stable cation defects, so should the former be assisted by stable extensively-anion-defective compounds. Not many representatives of this last kind are known at present but mention should be made of the compounds of bismuth oxide, Bi_2O_3, with lead, cadmium, and alkaline-earth oxides (Sillén and Aurivillois, *Z. Krist.*, 1939, **101**, 483; Sillén and Sillén, *Z. physikal. Chem.*, 1941, *B*, **49**, 27; Aurivillois, *Arkiv Kemi, Min., Geol.*, 1943, **16**, *A*, No. 17).

(iii) *Covalent-bond Formation.*—Covalent bonding in chemisorption must follow rules fundamentally similar to those given for metals, but there exists in the more complex oxides and sulphides considerable variation on that comparatively simple theme. Thus in addition to the simple bonding, arising for instance from use of the empty orbitals at the top of an almost full anion band in an abnormal semi-conductor to form single electron bonds, there are chemisorptions of the type $CO_2(g) + O^{2-}(s) \longrightarrow CO_3^{2-}(s)$ studied by Garner (*J.*, 1947, 1239).

11. INSULATORS.

As already suggested in section 10 (i,a), electron-transfer processes are not expected at ordinary catalyst temperatures on insulators, except to a minor extent at mechanical and intrinsic defects. The ionic insulator catalysts include chiefly the solid oxides and halides of the lower elements of groups 3, 4, and 5 of the periodic table. As a class they bring about reactions such as dehydration, isomerisation, polymerisation, cracking, etc., a most striking feature of which is the analogy with the corresponding homogeneous processes catalysed by strong acids, aluminium halides, and so on, increasingly described by carbonium- and oxonium-ion mechanisms in current literature (Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274; Ciapetta, *Ind. Eng. Chem.*, 1945, **37**, 1210; Schmerling, *J. Amer. Chem. Soc.*, 1944, **66**, 1422; 1945, **67**, 1438, 1778; 1946, **68**, 275; Oblad and Gorin, *Ind. Eng. Chem.*, 1946, **38**, 822; Gorin, Kuhn, and Miles, *ibid.*, p. 795; Oblad, Messenger, and Brown, *ibid.*, 1947, **39**, 1462; Hansford, *ibid.*, p. 849; Bremner, *Research*, 1948, **1**, 281). It is significant in this respect that the oxide catalysts are of low activity in hydrocarbon reactions if their small water content is further reduced (see Hansford, *loc. cit.*) and if the water is looked upon as a source of protons. When pure these oxides are very poor hydrogenation, dehydrogenation, and oxidation catalysts. They are invariably colourless, as expected, and are notable glass-formers and ion exchangers; alkali-metal ions are strong poisons (Clark, Graham, and Winter, *J. Amer. Chem. Soc.*, 1925, **47**, 2748; U.S.P. 2,333,903; cf. Bremner, *loc. cit.*). Unfortunately the majority of the catalysts are amorphous with unknown lattice structures; except for active γ-alumina which has the defective spinel lattice (Verwey, *J. Chem. Physics*, 1935, **3**, 592) and related catalysts, they will be assumed to have glass-like skeletons (Zachariasen, *J. Amer. Chem. Soc.*, 1932, **54**, 3841; Hägg, *J. Chem. Physics*, 1935, **3**, 42; Weyl, *J Soc. Glass Tech.*, 1943, **27**, 133) from which the normal network-modifying ions are absent, the resulting cation vacancies and some anion bridge positions being occupied by protons.

γ-Alumina appears to occupy a unique position in the study of insulator catalysts since a number of workers confirm that activity is attributable to γ-Al_2O_3 which changes to α-Al_2O_3 at elevated temperatures (cf. Visser, *Chem. Weekblad*, 1946, **42**, 127; B.P. 571,352, 572,110; Feachem and Swallow, *J.*, 1948, 267; Fricke, Niermann, and Feichtner, *Ber.*, 1937, **70**, 2318) and they have associated activity with cation vacancies in general terms. In the following theory the properties of γ-alumina are taken to provide the clue to insulator activity which, it is asserted, arises principally from cation vacancies and possibly to a lesser extent from anion vacancies.

If carbonium- and oxonium-ion mechanisms are accepted as roughly correct for the characteristic reactions, they should be fastest at surfaces capable of forming and retaining carbonium ions through proton addition or exchange. Active surfaces must be those with cation defects, and the defects are the active centres since they possess the closest approximation to the geometry suggested in earlier sections. The free energy of chemisorption of a positive ion at a cation defect will increase as the electrostatic potential at a cation lattice point increases. In defective lattices, such as the defective spinel or a glass, it is usually assumed that the cations are distributed statistically over all the interstices of suitable radius. Although this is not likely to be an exact description at all temperatures, it does indicate that cation defects in the surface may have only a moderate life at a given lattice point. Now let the lattice contain a little water accommodated as hydroxyl groups, where the hydrogen may form hydrogen bonds with adjacent anions, then periodically, as a nearest neighbour cation site becomes empty, a proton will occupy the vacancy. At the lattice surface a cation defect has lost at least one of its anion nearest neighbours, and the deficit is made up by a substrate molecule held by polarisation forces somewhat larger than simple van der Waals forces. A proton, adjacent to the surface cation defect, now distributes itself amongst the cation point, nearest neighbour anions, and the substrate molecule according to their respective proton affinities in the solid and adsorbed phases. Thus a chemisorbed carbonium ion of definite life is formed directly from a sorbed olefinic reactant and will isomerise to the carbonium ion of greatest resonance energy (isomerisation), add to an adjacent physically adsorbed molecule (polymerisation), or to benzene and saturated hydrocarbons (alkylation), and so on. Similarly the oxonium ions derived from alcohols form carbonium ions with loss of water, and olefins are produced as the proton returns to a defect from the carbonium ion.

At low temperatures, when the mobility of the lattice cations is small, the life of surface cation defects is long, and the life of the corresponding chemisorbed complex will be controlled almost solely by the proton affinities already mentioned. On rise of temperature, cation vacancies have a much shorter existence, and the history of the chemisorbed complex will be affected by the intrusion of metal cations and the increased chance of the close approach of another defect. As a lattice cation moves into a vacancy the proton switches *via* the surrounding anions (forming OH^-) to the lattice vacancy in its new position, the net result being that the proton tends to follow the vacancy. In the presence of sufficient water, therefore, every defect possesses at least one associated proton : hydrous γ-alumina must contain at least 2·2% of its weight as water for this to be true. Occupation by a metal cation of a surface vacancy, chemisorbing the proton–substrate complex, results in the proton following the vacancy away from, or along, the surface by the mechanism described. It may happen however that the proton remains with the substrate as a positive ion and returns to a surface vacancy at some point other than that of its origin. The effect in the case of hydrocarbon residue is that of a charge migration along the chain. High temperatures increase cation mobilities exponentially and therefore shorten the life of cation defects ; at the same time the decreased equilibrium water concentration reduces the fraction of vacancies containing associated protons. Under these conditions direct scission of a substrate into a positive ion chemisorbed at a vacancy and a negative ion held by polarisation forces is increasingly probable (cf. Eyring, Hulbert, and Harman, *Ind. Eng. Chem.*, 1943, **35**, 511).

The activity of all solid insulator catalysts whether oxides or halides can be interpreted on this basis although there is no evidence as yet for the presence of cation defects in the well-known pure-halide catalysts. Activity and specificity with a given substrate depend on the surface density of cation vacancies, the electrostatic potentials at the vacancies, and their nearest neighbour anions, and the fraction of vacancies containing protons. For different substrates the effective variables are the proton affinities and the radii of molecules and fragments. Even though these parameters are not independent, it is convenient for classification to consider them separately.

(i) *Cation-vacancy Density.*—The density of cation defects should be adjustable along the lines used by Koch and Wagner (*Z. physikal. Chem.*, 1937, **38**, *B*, 295) in their studies on the silver halides. If we confine our remarks to the oxides (although they are of general applicability), this requires the solid solution of a metal oxide of high valency in the lattice of one of lower valency. The extent of such solid solution is usually small, but in the amorphous oxides it may be appreciably larger owing to the metastability implied in their glassy structures, because of the very extended surfaces where geometric restrictions will be less than in the bulk, and because of the cross-linking by hydrogen bonds. This process of cation replacement requires that a number of cations of lower valency should be omitted from the lattice ; the resulting vacancies are the active centres.

Alternatively, the solute may contain an anion of lower charge than the oxygen ion, and the fluoride ion is almost ideal in that it has almost the same radius as O^{2-} and OH^-. Addition of, say, aluminium fluoride in solid solution to aluminium oxide might result in the dropping of some Al^{3+} from the lattice with creation of active vacancies. Even in favourable circumstances it is unlikely that solid solution can be pursued indefinitely : it will eventually result in the lattice breaking down into two or more solid solutions or compounds (cf. Anderson, *Proc. Roy. Soc.*, 1946, *A*, **185**, 69) some or all of which may retain cation defects. The vast number of possibilities of cation defect in compounds is too large to be covered in a discussion of this kind and recourse should be had to reviews such as those of Laves (*Z. Krist.*, 1930, **73**, 202), Strock (*Z. Krist.*, 1936, **93**, 285), Anderson (*Ann. Reports*, 1946, **43**, 104), and Wells (*Quart. Reviews*, 1948, **2**, 185).

Catalyst poisons include all those agents which occupy surface cation vacancies irreversibly, *e.g.*, alkali-metal ions introduced during preparation of γ-Al_2O_3, alumina–silica gels, etc. Generally all ions which take up " network-modifying " positions in glasses should be poisons, and those taking up " network-forming " positions should be mild promoters or deactivators depending on the reaction. Many ions can take up both sorts of position (see Weyl, *loc. cit.*), but with the present lack of understanding of catalyst preparation processes it is impossible to foretell the distribution of a particular ion in a freshly prepared catalyst (cf. Plank and Drake, *J. Colloid Sci.*, 1947, **2**, 399, 413). More empirically, it can be seen that all oxides the radius ratio (cation : anion) of which is less than 0·414 are glass-formers (Kuan-Han Sun and Silverman, *J. Amer. Ceram. Soc.*, 1942, **25**, 97) and should possess maximum activity; pure oxides outside the group BeO, B_2O_3, SiO_2, P_2O_5, and perhaps GeO_2 will possess much smaller activity on this basis. Network-formers include such oxides as Al_2O_3, TiO_2, ZrO_2, ThO_2 SnO_2, ZnO, and maybe As_2O_5, which presumably enter the network of polyhedra in the catalyst gels as in glasses ; the pure oxides (except Al_2O_3) will be less active than the glass-forming group because the tendency to random linking of polyhedra, and therefore the concentrations of cation defects is less. Other reasons will be given in the next section. Similar conclusions hold for the fluorides, or mixed lattices in which some oxygen ions have been replaced by fluorine ions; beryllium fluoride as a glass-former also yields somewhat unstable gels and is a typical borderline case. Fluorine ions however cause weakening of the polyhedra networks (Weyl, *loc. cit.*) so that fluorine-containing catalysts will be unstable compared to those containing only oxygen ions and will tend to crystallise and lose hydrofluoric acid with loss of both protons and cation vacancies at higher temperatures. Temperature stability can be improved by addition of sufficient alkali-metal or alkaline-earth oxides to stabilise the network or the defective spinel (*e.g.*, " β-alumina," Beevers *et al.*, *Z. Krist.*, 1936, **95**, 472; 1937, **97**, 59; B.P. 571,352, 572,110); such incorporations must be made in the catalyst bulk and not merely at the surface, with inevitable reduction of the number of cation vacancies. Moreover at higher temperatures ThO_2, SnO_2, ZnO, and to a lesser extent TiO_2 and ZrO_2, are reducible either completely (SnO_2), or in the semi-conductor sense (TiO_2, ZrO_2, ThO_2) and cause unwanted side-reactions which may be hindered by increasing the partial pressure of water vapour in the stationary state.

(ii) *Electrostatic Potential at a Vacancy.*—The proton affinity of an active centre is fixed, in the absence of covalent binding, by the proton affinity of the anion *in vacuo* and the electrostatic potential at the cation and anion sites. The calculations of Verwey and Heilmann (*J. Chem. Physics*, 1947, **15**, 174; 1948, **16**, 1091) show that the Madelung potential at the tetrahedral interstices is almost twice as great as that at the octahedral interstices in some spinel structures. In defective spinel lattices containing traces of water this situation can hardly be affected and the two sorts of cation vacancy will have different proton affinities with protons preferring the empty tetrahedral interstices. Thermal motion, gross structural defects, and the like will spread these proton levels out into narrow bands without displacing them appreciably. In the less crystalline glasses and " gels " a given cation defect will have a definite co-ordination number, but different defects may have co-ordination numbers varying slightly about the average, so that in the amorphous catalyst the proton affinity of the surface will vary over a wider range than at a crystal surface. Following Verwey and Heilmann (*loc. cit.*), it appears that tervalent and quadrivalent ions, in accordance with electrostatic rules, prefer octahedral interstices, while some tervalent ions such as Fe^{3+}, In^{3+}, and Ga^{3+}, along with a few bivalent ions (Zn^{2+}, Cd^{2+}), prefer tetrahedral interstices. This should provide in the defective γ-spinel structure a method for controlling the availability of the two types of vacancy; for instance, in a process deemed to require a vacancy of low proton affinity, as perhaps in a hydrocarbon reaction, the tetrahedral interstices might be blocked. Extension to amorphous catalysts is essentially simple but lack of data enforces again the use of approximations based on the properties of the relevant ions in the glasses, ion exchangers, etc.

Replacement of one or more vacancy nearest neighbour cations by one of higher charge reduces the negative potential at the vacancy and also its proton affinity. The rules affecting such substitutions have been noted above, and the possibilities depend on the co-ordination number of the site concerned. In the same way replacement of a nearest neighbour anion by one of lower charge also reduces the vacancy proton affinity. The same effects will occur regardless of the structure containing the vacancies and permit, ideally, variation of the lattice proton affinity over a wide range when polarisation is taken into account; in fact geometric restrictions arise, as mentioned in (i) (p. 263). Hansford (*loc. cit.*) and more recently Weiss (*J.*, 1948, 2164) have used Pauling's concept of electrostatic bond strength (see " The Nature of the Chemical Bond," Cornell, 1942, p. 386) to give a qualitative account of changes in the lattice " acidity," but the picture provides no model for the active centre and could be made quantitative only along lines similar to those suggested above.

Generally, increasing cation radius reduces the proton affinity at a vacancy in the pure lattice and may be another factor in the decline of catalytic activity of this kind as groups 2, 3, 4, and 5 of the periodic table are ascended.

(iii) *Proton Density.*—On the foregoing grounds ionic reaction mechanisms require protons. At low temperatures retained structural water is sufficient, but at high temperatures a partial pressure of water in the gaseous reactants may be required. Conversely, in hydrations in the liquid-phase or at high pressure, the catalyst may lose activity owing to complete hydration of the lattice with disappearance of all defects and change of lattice. The proton concentration can be raised by ion exchange with acids, by incorporating strong acids into the lattice, or by adding gaseous hydrogen to the reactants and a metal or semi-conductor to the solid phase. The last method would require a standard of control beyond that available at present.

Poisons include all substances of high proton affinity which compete with the substrate for protons and yield strongly chemisorbed positive ions (Bremner, *loc. cit.*). In the same way, molecules possessing a large affinity for carbonium ions (*e.g.*, benzene) are catalyst poisons.

Analogous reasoning leads to the conclusion that, under suitable conditions, anion-defective lattices, or lattices able to sustain an anion defect, should catalyse processes involving anion intermediates. The chief difficulty is that the known anion-defective structures (see Sillen *et al.*, *loc. cit.*; Zintl *et al.*, *Z. anorg. Chem.*, 1939, **240**, 145, 150; 1939, **242**, 79; Croatto *et al.*, *Gazzetta*, 1943, **73**, 257; 1948, **78**, 83, 95) are crystalline and not easily prepared with a large specific area.

12. CONCLUSIONS.

Ideally, the path of reaction should be predicted from the contours on an energy surface drawn to represent the change in total energy with variation of all the independent parameters. This problem is too complex to be solved at the present time, and interest has to be centred on the alteration of the total energy with variation in single parameters or small groups of parameters, called factors.

Thus we have the " geometric factor " (Ballandin, *Z. physikal. Chem.*, 1929, *B*, **2**, 289; 1929, *B*, **3**, 167; *Acta Physicochim. U.R.S.S.*, 1941, **14**, 223; Beeck, *Review Mod. Physics*, 1945, **17**, 61; also a recent review by Griffiths in " Recent Advances in Catalysis," Vol. I, p. 91, Academic Press, Inc., New York) and the " electronic structure " factor (Roginsky and Schultz, *Z. physikal. Chem.*, 1928, *A*, **138**, 21; Russell, *Nature*, 1926, **117**, 47). These factors are obviously not independent and, from the point of view of convenience in practical application, that one is preferred which shows the sharpest change with variation in catalyst activity. The preferred factor is undoubtedly that of electronic structure inasmuch as it can be related to physical measurements such as magnetic susceptibility, electrical conductivity and related phenomena, dielectric constants, etc., even when the crystal parameters are unknown or the catalyst amorphous.

The semi-empirical theories advanced in the earlier sections have been used in our laboratories at Billingham since 1943 and have permitted, it is thought, a closer insight into methods of catalyst preparation and action than was obtainable on a purely geometric basis. These studies are being continued in order to strengthen the relatively weak theoretical bases, to provide a quantitative approach, and particularly to derive experimental support for the many deductions from theory. This continuation includes not only experiments in limited systems of high purity and exact definition, but also the amassing of empirical data over wider, more ambiguous systems where the pattern of results points with more generality, although less clarity, to the desired conclusion.

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