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ELECTRONIC CONFIGURATIONS AND HETEROGENEOUS CATALYSIS

By

D. A. DOWDEN^{*)}

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1. Introduction

The typical catalytic system is not in thermodynamic equilibrium, but it may be treated as though in a stationary state; it comprises a solid, the solid surface and ambient fluid reactants.

To properly understand and to advance our knowledge of catalysis by solids requires a broad grounding in the whole of chemistry and the sciences of the solid state as well as in the most recent of appropriate physical techniques.

Despite our inability to describe with certainty the details (on the atomic scale) of the mechanism of any heterogeneous process, or to calculate its absolute rate, yet, as chemists we are undeterred—this is after all a feature common to all chemistry.

The history of the development of the Periodic Table of the elements, and the many examples of the different ways in which the classification has been used, teaches us to look for patterns of behaviour which we believe to depend ultimately upon the electronic structure of the atoms and ions in the solid. Information on the structure of molecules, illuminated by molecular orbital and other theories of quantum chemistry, allows us to consolidate the empirical data on the reactivities of adsorbate molecules into forms suitable for extrapolation and prediction.

When we move then to the more detailed description of heterogeneous catalysis it will be presumed that the similarities with homogeneous catalysis are not accidental and that the principles to be applied are the same. We shall start from the viewpoint that the rules are essentially the same as in homogeneous chemistry modified only by the more common occurrence of cooperative effects and of asymmetry in the complexes chemisorbed on the solid surface.

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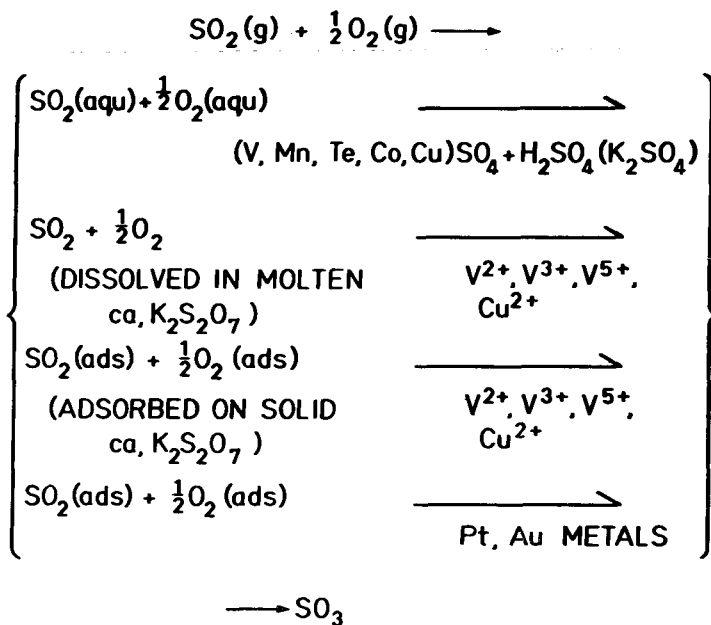
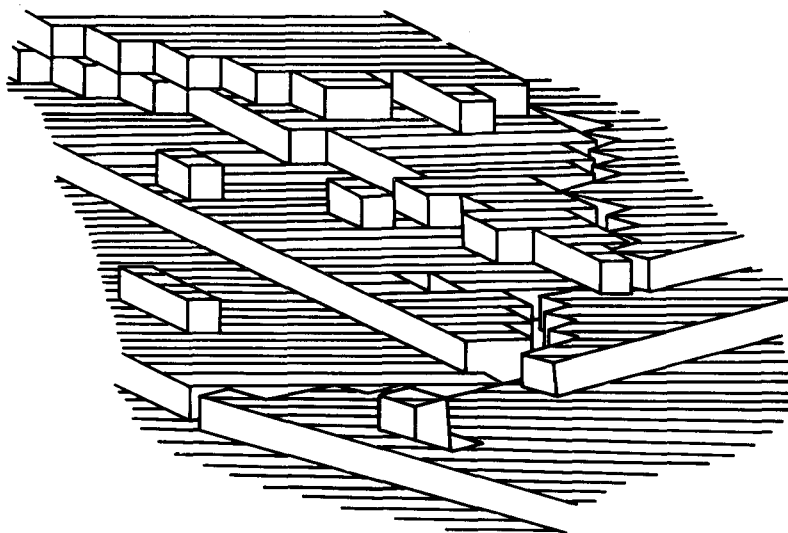
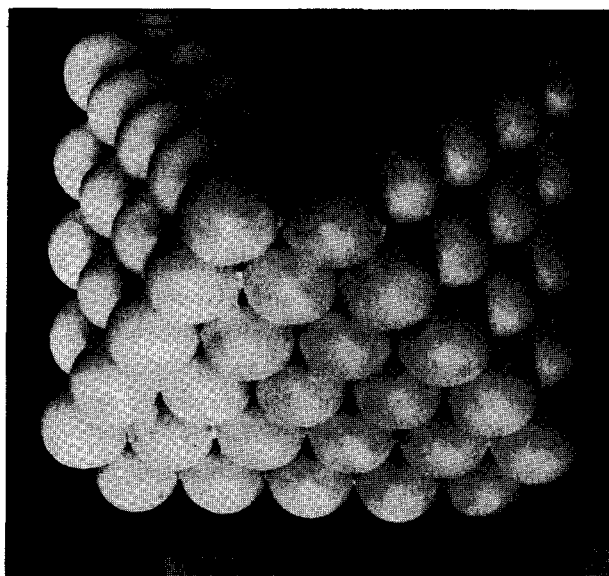
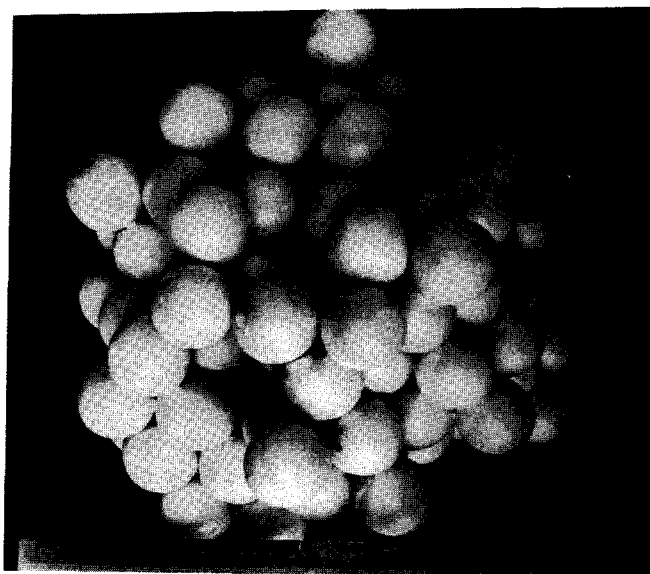
Fig. 1. The oxidation of SO_2 to SO_3 over various catalysts.

Fig. 2.

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(a)



(b)

Fig. 3.

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A catalytic progression of the type shown in the first slide (Fig. 1) concerning the oxidation of sulphur dioxide to sulphur trioxide indicates that homogeneous and heterogeneous catalysis in a specific system can be similar if not the same.

2. The Intrinsic Activity of Solid Surfaces

The intrinsic activity of a solid surface depends upon its physical conformation and upon the chemistry of its constituents, Fig. 2 depicts the defects which can occur at the interface; Fig. 4 and 5 show a classification of elements and compounds on the broad basis of physical properties.

Point defects, line defects, and ensembles of these, are represented in Fig. 2 but the contribution of these to catalyst activity is not yet properly understood; we expect it to be different for different reactions. Certainly edges and corners may be important in small crystals but Fig. 3 shows that for very rough crystals the ordinary models of defects in the surface lose their meaning. The figure reproduces a model of a face-centred cubic lattice grown regularly and one grown more or less randomly.

The classification of solids is not intended to be complete, only to display the more extreme types and to give representative examples. Thus the division into ionic and covalent lattices is never sharp and the charge on lattice species seems seldom to be as large as the formal charge.

The physical and chemical properties of the surface are not truly independent. Thus the non-stoichiometry of oxides such as nickelous oxide and zinc oxide (Fig. 6) is known to be associated with cation vacancies and interstitials and the homologous series of oxides related to TiO_2 , MoO_3 , and WO_3 (studied by MAGNELI and his co-workers in SWEDEN) possess lattices with regular dislocations.

In metals such as copper it is suspected that dislocations bring the top of the filled 3d-bands closer to the FERMISurface; that is to say, transitions of the kind $\text{Cu}(3d^{10} 4s) \rightarrow \text{Cu}(3d^9 4s^2)$ become more easy.

2.1 Elements

Among the elements certain characteristic differences can be observed in their catalytic activities. Here of course I refer only to elements which do not transform during the reaction:—

- (a) Metals appear to be more active than non-metals.

For example in reactions involving the activation of the hydrogen molecule-chemisorption at 90°K , the hydrogenation of unsaturated molecules, hydrogen-

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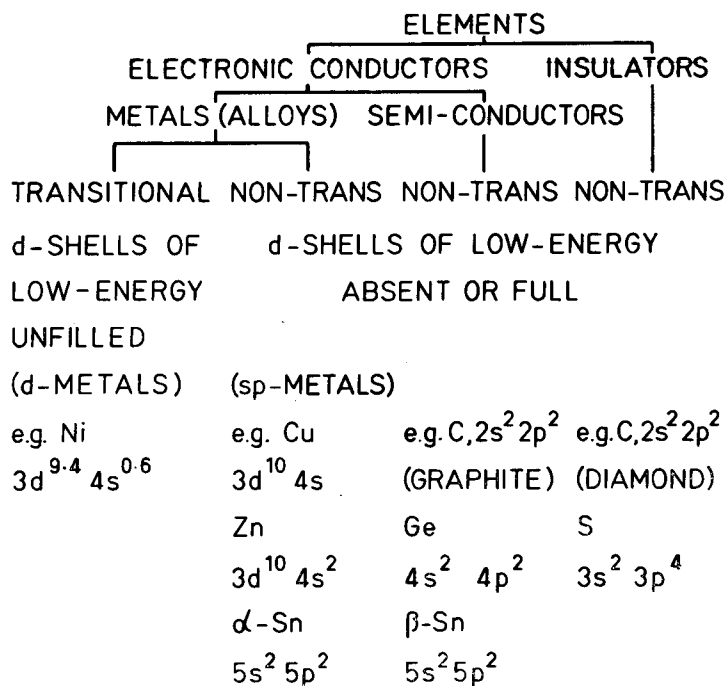


Fig. 4. Classification of solid types-elements.

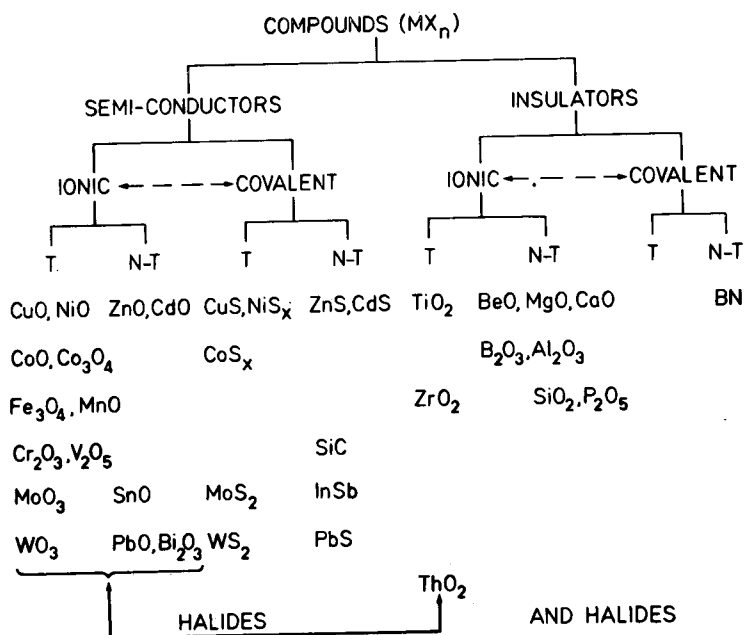


Fig. 5. Classification of solid types-compounds.

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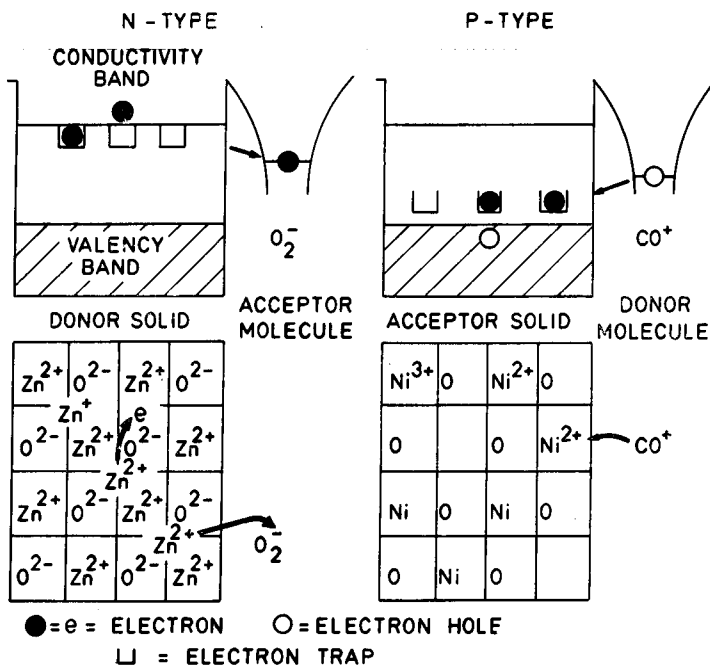


Fig. 6. Non-Stoichiometry & lattice defects.

olysis (the splitting of bonds with addition of hydrogen to the fragments) and oxidation with molecular oxygen.

Thus, lead will catalyse the hydrogenolysis of long chain esters and the hydrogenation of nitrobenzene to aniline; carbon has not been found to catalyse these reactions.

(b) Transitional metals are more active than non-transitional metals.

Nickel, palladium and platinum will chemisorb hydrogen and catalyse the hydrogen-deuterium exchange reaction at 80°K; copper, silver, gold, zinc, tin, lead, *etc.* are not effective.

An extension of this statement, to say that metals (such as copper) having electronic configuration close to those of the transitional metals are more active than the typical non-transitional metals (sodium, calcium), is probably true. The electronic configuration of the metal determines its cohesive energy, which in turn affects the melting point and the mobility of the lattice atoms. The transitional metals usually possess high melting points and can be prepared and maintained in the form of small, possibly defective, crystallites whereas the typical non-transitional element sinters quickly. Thus a proper comparison of

their intrinsic activities has never been made.

2.2 The Compounds

Table 5 does not show the correct stoichiometry of the semi-conductors. The composition of the oxide and sulphide catalysts depends upon the partial pressures of the reactants and the reaction conditions. For example, in some oxidation reactions nickelous oxide contains more oxygen than corresponds to its formula and vanadium pentoxide is reduced to an oxide having the composition $V_{12}O_{26}$. Some of these semi-conductors may be near-metallic.

The most noteworthy features are, first, the marked difference in properties between the conductor oxides and the insulator oxides and second the great activity of the solids containing transitional metals.

3. Insulators

The lattices are held together by forces which range from the wholly covalent, as in diamond, to the wholly ionic as in magnesium oxide.

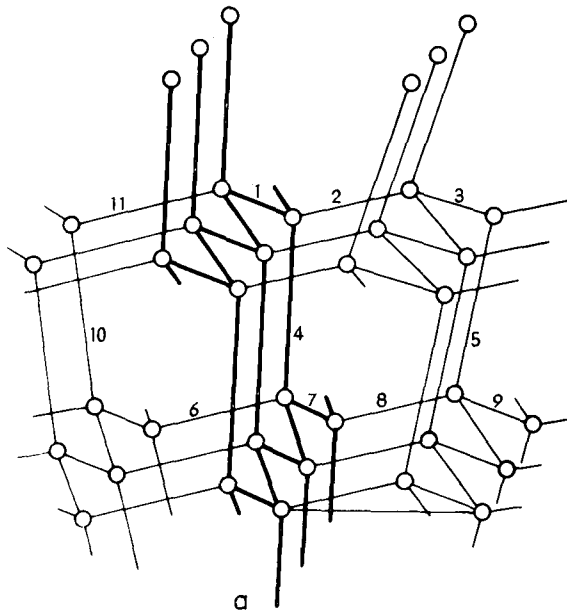
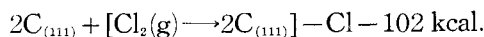
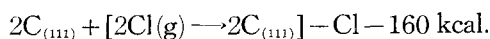
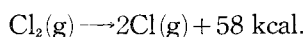


Fig. 7.

3.1 Carbon-Diamond

FARNSWORTH and MARSH have shown by slow-electron diffraction that the surfaces of diamond are only slightly distorted from the structures expected from the cleavage of the carbon tetrahedra. All exposed planes contain carbon atoms bound to either three nearest neighbours, as in (111) or two, as in (001) (Fig. 7). The empty 3d orbitals lie so high in energy that only electrons in 2s and 2p orbitals contribute to the binding (sp^2) of the interior.

On the (111) surface the electronic configuration of the carbon atom must lie between sp^3 and $2s2p^3$ or $2s^2 2p^2$. The observed slight distortion, whereby the exposed carbon atoms sink inwards only a little, suggests that the configuration is close to sp^3 . Therefore, there is one broken sp^3 -band projecting outwards from each carbon atom in the surface and the surface is a giant free radical. The distance between each such carbon atom is 2.52 Å; this is to be compared with carbon-carbon distance of 1.54 and 1.4 Å in paraffinic and aromatic hydrocarbons respectively. There can be little pi-interaction between these free valencies, and they should form bonds with adsorbates which are approximately equal in strength to those formed by tertiary carbon atoms in hydrocarbon chemistry. Chemisorption should be easy when the interatomic distance in the adsorbate molecule is close to 2.52 Å, the atoms of the molecule are monovalent and the reaction is exothermic. For example the chemisorption of the halogens:—



The greater difference between the interatomic distance in molecular hydrogen (0.74 Å) and that between the carbon atoms of the surface (2.52 Å) suggests a slower chemisorption although the calculated heat (a. 76 kcal. mole⁻¹) is high.

Because of the negligible steric hindrance between nearestneighbour carbon-hydrogen bonds and the small dipole of the C-H bond, the heat of chemisorption should not fall off rapidly with coverage. Also, the activation energy for diffusion should be high and the surface would not be expected to populate rapidly from a few active centres.

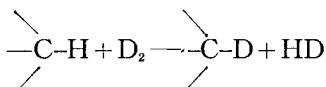
Catalysis of the hydrogen-deuterium exchange by the regular (111) surface at low temperatures would not be expected for the following reasons:

- (i) the dissociative mechanism of BONHOEFFER-FARKAS would require a prohibitively high activation energy for desorption; it would be not less than

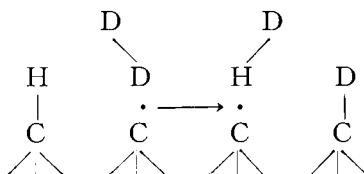
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the heat of chemisorption.

(ii) the associative mechanism (RIDEAL-ELEY)



has no available low-lying unfilled electron-levels to lower the energy of the activated complex except at special sites:—

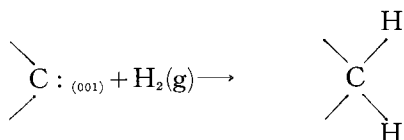


The high heats suggest that the number of such sites will be small because of the high coverages.

The properties of the saturated valencies in the 'good' (111) surface must be similar to those of the corresponding tertiary paraffin derivatives.

On (001) the most probable valencies are based upon the configuration $2s^2 2p^2$ (divalent carbon, with a lone pair of electrons), because of the excitation energy required to reach the sp^3 valency state. The properties of these atoms will be similar to those of the carbon atoms in carbenes but in the bent, excited state.

Concerning the hydrogen-deuterium exchange on the good (001) surface, the conclusions are quite similar to those on (111); although the activation energy for chemisorption:—



should be smaller (because the reaction is at one centre, there must be a contribution from the valency state excitation).

The presence of defects in the surfaces does not change the picture much in this approximation. A vacancy in the top layer (111) produces three new free valencies in the penultimate layer. A vacancy in the penultimate layer of the (111) plane produces carbon atoms in the same configuration as in (001).

A line defect may have more effect, for instance an emergent 60° edge dislocation, in simple form, on the (111) plane. HASEN (Fig. 8) has shown that the bonds immediately opposite the extra half-plane suffer great strain and

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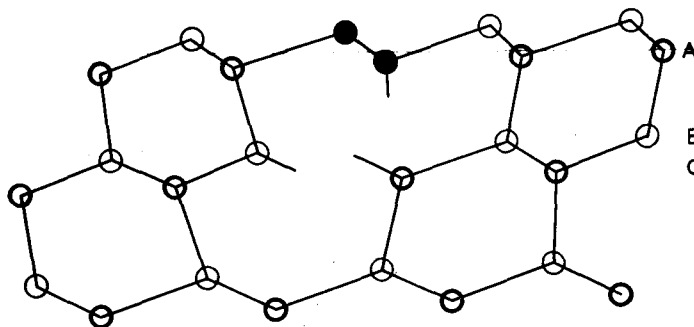


Fig. 8. Defect in Diamond (HASSEN).

should break more easily; under these conditions it is possible that hydrogen-deuterium exchange could occur by the dissociative mechanism because the compression of the C-H bonds must lead to small heats of chemisorption.

These properties of diamond suggest that the surface chemistry of this form of carbon should be similar to the organic chemistry of the aliphatic series.

3.2 Acid-Base Catalysts

The insulating oxides, in their hydrous forms, function best as acidic or basic catalysts; they have much less activity than conductors in oxidation and reduction reactions, involving molecular hydrogen and molecular oxygen. The distinction is not always sharp; it is less sharp at higher temperatures or under conditions which cause the insulators to become semi-conductors.

Chemistry teaches that all active solids are acidic or basic to some degree but the typical base is an alkaline earth oxide and the typical acid a congener of boric oxide, silica or phosphoric pentoxide in groups 3 to 5 of the periodic table. The constituent ions all possess closed electron shells.

There is general agreement that these catalysts behave similarly to conventional acids and bases but whether by mechanism involving protons (BRÖNSTED) or electron-pairs (LEWIS) is not always certain. Also the geometry of the active centre is in doubt.

3.2.1 Acids

The best known oxides of acidic function are alumina, alumina-silica, magnesia-silica and phosphates such as AlPO_4 ; they usually contain a small residue of structural or added water (taken to be evidence for protonic acidity) and strongly chemisorb bases which are thus catalyst poisons. The processes illustrated in Fig. 9 for the dehydration of t-butanol show the kinship with

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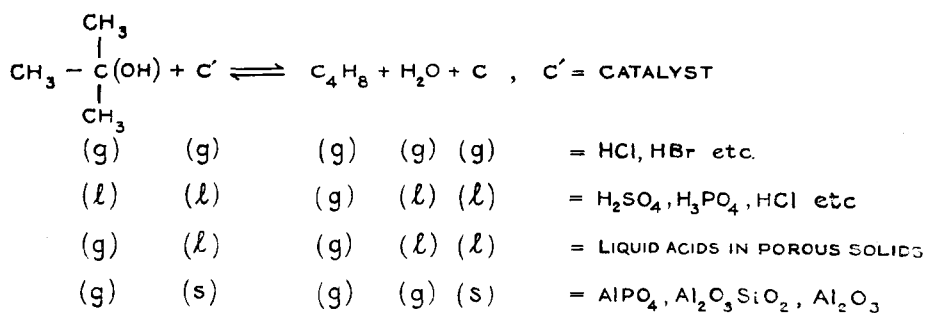
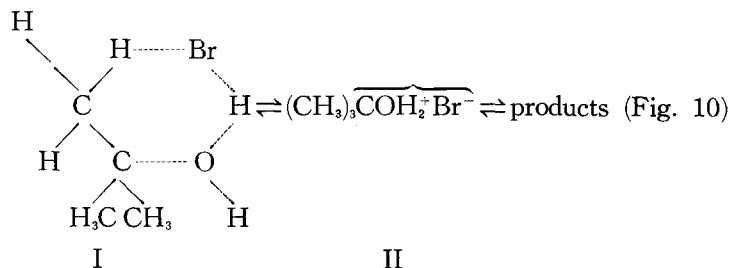


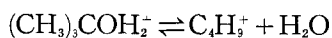
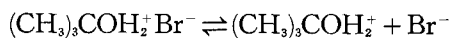
Fig. 9.

other protonic acids in different phases.

In the gas phase the activated transition state seems to lie between I and II (MACCOLL)



but in polar solvents the ion pair dissociates:—



III

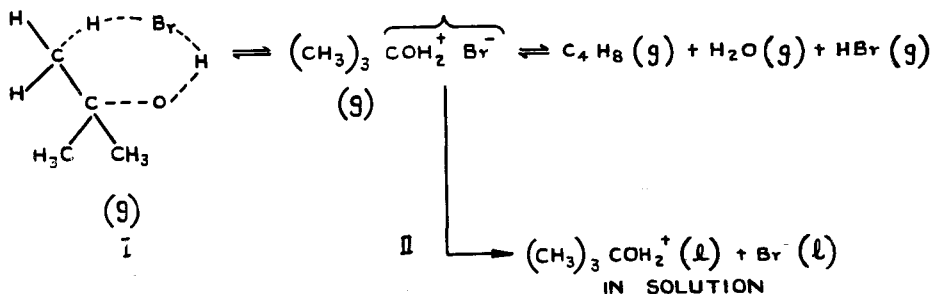


Fig. 10.

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The isomerisation, alkylation, polymerisation, and cracking reactions of hydrocarbons appear to proceed through intermediates resembling carbonium ions (III). Electrostatic forces contribute to the binding energy of the ion in the gas phase, to its solvation energy in solution and to its chemisorption on acidic oxides: similar progressions can be devised to illustrate the relation between FRIEDEL-CRAFT catalysts and acidic oxides.

If water is carefully excluded from the system the acidic solids show some hydrogenation-dehydrogenation and oxidation activity.

3.2.2 Bases

Little is known about the basic oxides operating under conditions where a liquid phase, and consequently classical dissolved bases, are absent. They chemisorb acids, such as phenol, more strongly than bases and catalyse reactions like the aldol condensation in the gas phase. It is especially significant that magnesium oxide is a good catalyst for the transfer of hydrogen between chemisorbed molecules-except of course molecular hydrogen.

The basic oxides dehydrogenate alcohols; they do not have dehydrating activity unless specially prepared.

3.2.3 Specific Examples

The mechanism of catalysis by the insulator oxides is best discussed by means of examples. I shall begin with an oxide of simple structure.

3.2.3.1 Magnesium Oxide

Magnesia (MgO) has the simple sodium chloride structure and maintains a stoichiometric lattice, with a negligible tendency to lose oxygen even up to the highest temperatures. MITOFF and others have shown that the electrical conductivity of almost pure magnesia depends upon impurities but that in very pure single crystals the conductivity around 1,000°C is largely ionic; there is some doubt about the occurrence of electronic conductivity in the lattice even at 1,500°C.

The lattice is ionic and contains very few F-centres. The surfaces are formed from truncated octahedra corresponding to the sixfold co-ordination of the ions of the interior; for example the (001) surface comprises cations lying at the centres of the bases of square pyramids. There may be some deformation of the surface polyhedra whereby the oxygen anions move outward and the magnesium cations move in by small amounts.

Because the lattice is ionic and the ions have closed shells with small tendency to change their valency, and because the number of intrinsic F centres is small, the reactions catalysed by magnesia will be heterolytic in character.

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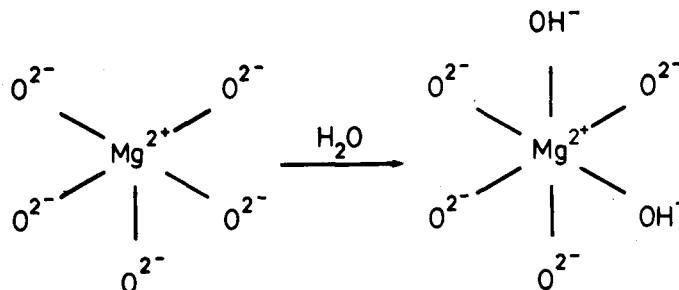


Fig. 11.

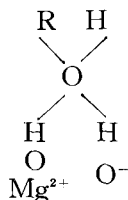
In support of this we observe that magnesium oxide chemisorbs only very small amounts of hydrogen and oxygen at moderate temperatures and a pressure of one atmosphere. However it chemisorbs water and hydrogen sulphide. Infra-red and nuclear resonance investigations of this chemisorption demonstrate unequivocally that it occurs with the hydroxide or hydrosulphide anion above the magnesium cation and the proton attached to the oxygen anion in the surface to give a second hydroxyl ion. For example in the (001) surface of magnesia the situation is as shown in Figure 11.

The corresponding polarisation of $\text{H}_2(\text{H}^{\delta+}-\text{H}^{\delta-})$ or $\text{O}_2(\text{O}^{\delta+}-\text{O}^{\delta-})$ is not sufficient to make these molecules reactive. If it does occur it must be at a few special sites only. This mechanism may be generalised to include the chemisorption of all heteropolar molecules.

The magnesium oxide surface without defects comprises therefore bare cations and anions and two kinds of hydroxyl ion; one hydroxyl ion lies *in* the surface and is more strongly held than the hydroxyl ion *above* the surface.

An alcohol must then be chemisorbed on the clean surface as shown in Fig. 12, and dehydrogenation results. This process should occur to some extent on all ionic surfaces.

The alcohol is probably weakly held by hydrogen bonds on the surface covered by hydroxyl groups:—



The proton affinity of the surface is so large that oxonium and carbonium ions are not formed; then dehydration by a WHITMORE mechanism does not take place.

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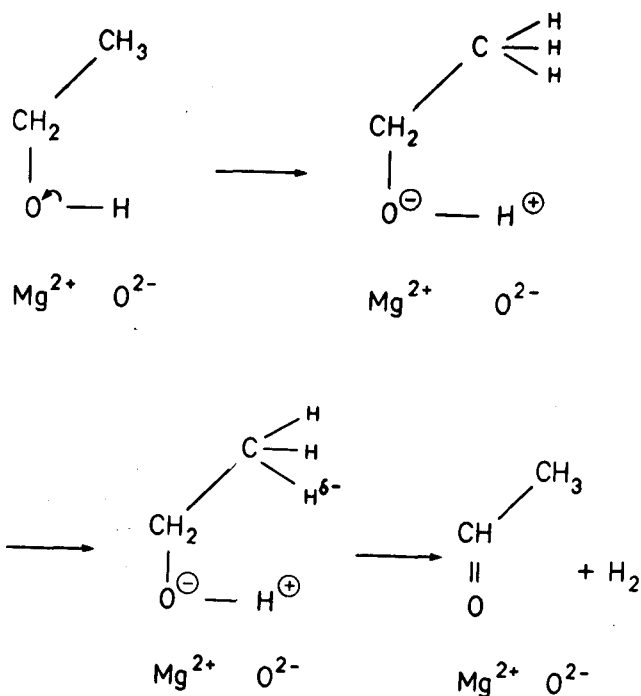


Fig. 12.

However a synchronous 'switch' mechanism could occur at special sites (EUCKEN-WICKEN TURKVITCH-SCHWAB) (Fig. 13), and might account for dehydration by some samples of magnesium oxide.

Electrically neutral molecules with lone electron pairs (such as ammonia)

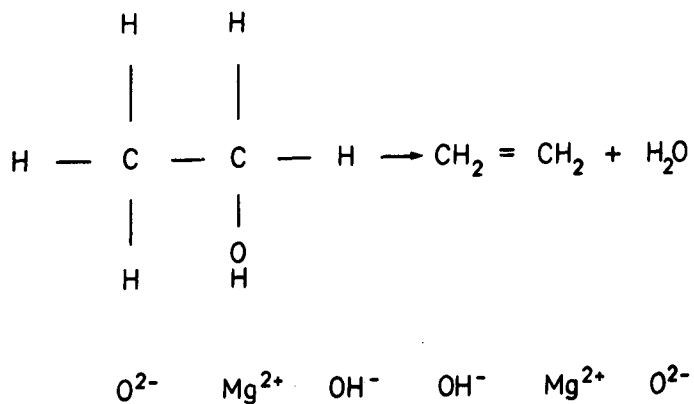


Fig. 13.

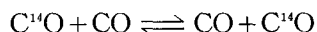
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are held by relatively weak polarisation forces (shown by MALINOWSKI and co-workers) on the clean surface and by hydrogen bonds on the hydroxylated surface.

This is in reasonable accord with the known chemistry of the complexes of magnesium and is attributable mainly to electrostatic interactions.

Oxidation and reduction processes involving electron transfer with the oxide surface are associated with lattice defects and with adventitious transitional metal impurities. English workers at HARWELL have shown that F-centres (*i.e.* anion vacancies trapping one electron) are responsible for the formation of the negative molecular oxygen ion (O_2^-) in irradiated magnesium oxide. LUMFORD in America has demonstrated that hydrogen-deuterium exchange by irradiated magnesium oxide is due to V_1 centres, *i.e.* an electron-hole trapped at an oxygen ion adjacent to a cation vacancy.

These and similar centres may be associated with the decomposition of nitrous oxide and the homomolecular exchange of carbon monoxide:—



These abnormal states of the oxide lattice can be introduced by irradiation or they can be produced by the reacting gases themselves. For example an oxygen ion under compression at a dislocation in the surface will be preferentially reduced by hydrogen.

Magnesium oxide catalysts are frequently prepared by calcining the precipitated hydroxide. In this case it is worth noting that the decomposition of crystalline magnesium hydroxide (brucite) is known to produce intermediate phases which give x-ray DEBYE patterns similar to those of a spinel with the possible composition $Mg_{24}O_{16}(OH)_{16}$, requiring some magnesium ions to pass into tetrahedral positions. The consequent faults in the stacking of the planes may well be the cause of the defects in the completely dehydrated lattice.

Beryllium oxide can be discussed similarly so as to bring out the marked difference between it and diamond—both having the same geometric structure.

3.2.3.2 Alumina

Alumina is similarly an electronic insulator with an ionic lattice. However the ionic potential of the aluminium ion (the square of the formal charge on the ion divided by its radius— $(ze)^2/r$) is much greater than that of the magnesium ion. As a consequence the aluminium ion is a network-former in glasses, and amorphous or disordered crystal forms of alumina are more common. The Al^{3+} ion prefers tetrahedral or octahedral interstices and the bare surface must expose aluminium ions in truncated tetrahedra and octahedra.

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Conventional tests of acidity show that the surface of active alumina is more acidic than basic; this accords with the type of reaction which it catalyses. Alumina which has been heated at high temperatures, near 1000°C, is almost anhydrous and causes the dehydrogenation of alcohols instead of dehydration.

The contention that the acids of the surface are BRONSTED acids found early support in the observation that the activity of the catalyst in some reactions (*e.g.* dehydration) is dependent upon a small water content. Alternatively the acidic centres could be LEWIS acids with water functioning as a cocatalyst. Currently it appears that at sufficiently low temperatures an alumina surface carries complexes which resemble hydrated BRONSTED acids; these lose

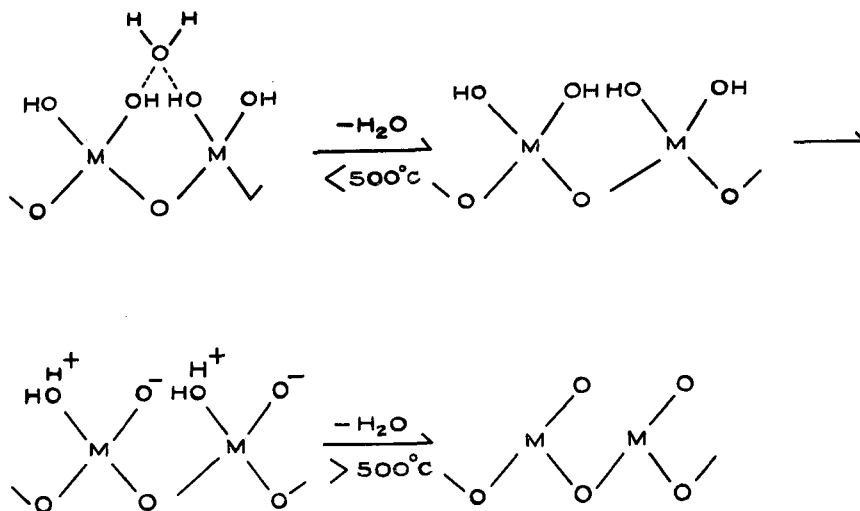


Fig. 14.

some water at moderate temperatures and are finally dehydrated to LEWIS acids at higher temperature (500°C). This is shown diagrammatically in Fig. 14, due to MCIVER, the reaction proceeds to the right with increasing temperature; the complexes probably co-exist (but at different sites,) except under extreme conditions.

Gamma-alumina is an active form of alumina made by dehydrating boehmite (α -AlOOH) at moderate temperatures. Electron diffraction and x-ray diffraction studies by SAALFELD have shown that its structure is based upon a cubic stacking of oxygen ions with the layer-sequence ABC...ABC..., containing aluminium ions in octahedral holes. COWLEY suggested that stacking faults in the layer-sequence can bring aluminium ions abnormally close together and can result

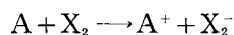
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in vacant aluminium sites; the vacancies can be arranged to give the gamma-alumina lattice. Because the lattice contains a small amount of water DE BOER has described it as similar to a hydrogen spinel ($[H_{0.5}Al_{0.5}]Al_2O_4$).

The surface complexes which are formed and the mechanisms which operate are like those described for magnesium oxide but in alumina the electrostatic potentials are such that the oxide is more acidic. LEWIS acid centres seem to predominate and acidity arises from the more powerful electron-acceptor properties of the aluminium ion.

Irradiation and other energetic treatments cause the formation of electron-acceptor or electron-donor centres which increase the activity of alumina in oxidation and reduction reactions.

Dielectrics such as alumina can also function like polar solvents; they can thus induce electron transfer reactions:—



when the low ionisation potential of A and the high electronegativity of X_2 is assisted by the attractive electrostatic field at the surface. A may thus be a polycyclic, condensed-ring aromatic and X_2 may be the oxygen molecule.

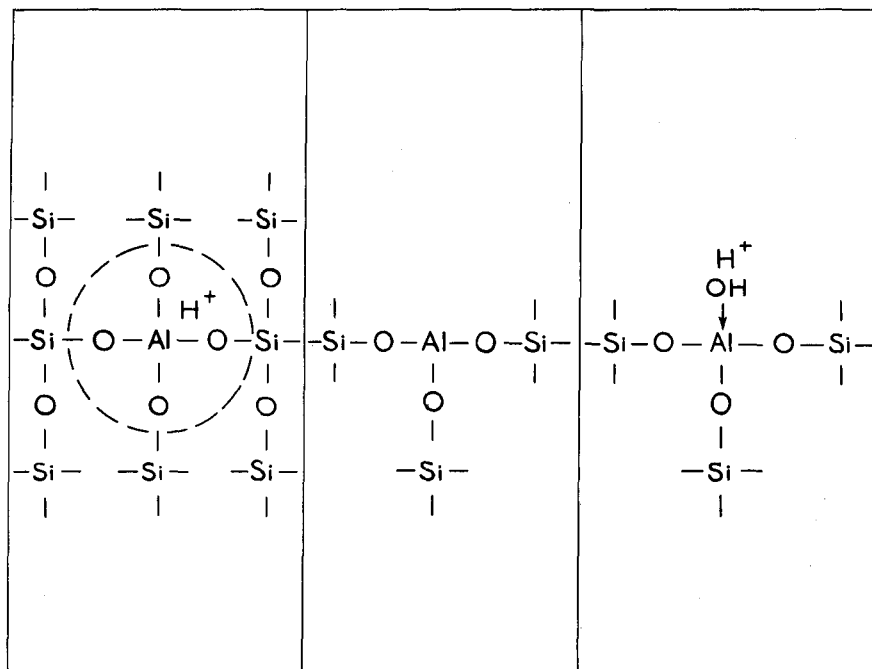


Fig. 15.

Again these stabilising electrostatic potentials are increased by the presence of defects in the surface lattice or by the presence of irreducible ions of different valency.

3.2.3.3 Silica-alumina

The complexes formed at the surface of silica-alumina catalysts, and the catalytic properties of the surface, are similar to those of pure alumina but more acidic. Essentially this arises because of the substitution of Al^{3+} for Si^{4+} in the silica network and the presence of a proton to preserve electroneutrality; the ions are irreducible under ordinary conditions, so that electroneutrality cannot be achieved by change of valency. One can hardly say more about this than BASILA, KANTNER and RHEE who have decided in favour of a model for the acid site which is the exact analogue of the homogeneous FRIEDEL-CRAFT system with a polar co-catalyst. They suggest that all of the primary acid sites on silica-alumina are LEWIS acids centred on aluminium atoms in the surface and that BRONSTED activity is caused by a second-order interaction between the reactant molecule held in the LEWIS site and a nearby hydroxyl group (Fig. 15).

3.3 General Conclusions—Insulators

- (i) The properties of covalent insulators are those to be expected from non-ionic solids utilising sp^3 orbitals.
- (ii) The ionic insulators induce heterolytic reactions without change in valency but they preserve electroneutrality by change in co-ordination number and by moving protons about. Untypical reactions are caused by energetic processes which change valencies and move electrons about.

As dielectrics they assist electron-transfer reactions between reactants when water is absent; this effect increases with the polarisation and hence with the charge on the metal ion and with increase in the number of charged lattice defects.

4. Semi-conductors

It is an easy transition, conceptually, from the atypical properties of insulators with defects of an electronic character to the typical properties of semi-conductors in which electronic defects are present in large concentrations.

4.1 Elements

The semi-conducting elements (graphite, silicon, germanium, *etc.*) differ

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from diamond in that their surfaces tend to self-saturation and, in the heavier elements, to the use of d-orbitals (silicon). We do not have time to discuss these in detail, only to bring out the main features.

4.1.1 Graphite

These remarks apply to some extent to carbon black. Clean pure carbons are very poor catalysts for hydrogen-deuterium exchange and for the oxidation of gaseous reactants. Electron-microscope examination of the oxidation of graphite shows that activity is confined to the edges of the basal layers and to defects within the layers. In the basal planes the geometric and electronic configuration of the carbon atoms is essentially that found in other aromatic systems; carbon-carbon sigma bonds are formed from sp^2 hybrids together with delocalised electrons in pi-bonds formed from p_z -orbitals. The figure (Fig. 16)

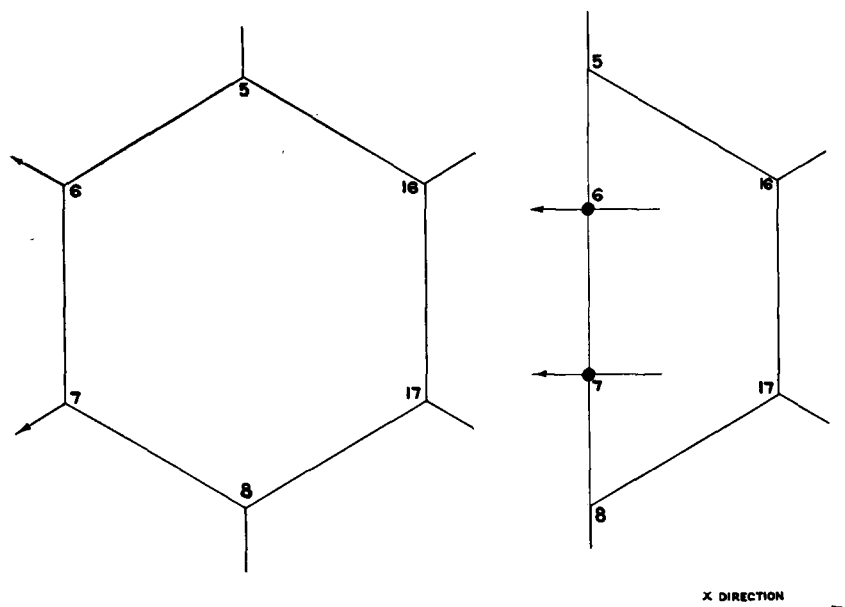


Fig. 16. Modified valencies at the surface of graphite.

shows the self-saturation which occurs according to COULSON. Isolated atoms at the apices of exposed rings alter their configuration as for carbon atoms on the (001) planes of diamond. Atoms along the edges of the hexagons possess either unpaired spins or there is distortion to give an acetylenic bond stabilised by about $40 \text{ kcal. mole}^{-1}$. In either case we can interpret the activity of graphite in the same way as was done for diamond. Here however, the approximate

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corresponding form of organic chemistry is aromatic.

4.1.2 Silicon and Germanium

These semi-conducting elements crystallise in the same structure as diamond or graphite.

There is however a marked difference in surface structure; unlike diamond the surfaces achieve self-saturation by considerable deformation, or reconstruction, of the surface geometry. The energy of the silicon-hydrogen bond is $76 \text{ kcal. mole}^{-1}$, quite sufficient for the chemisorption of hydrogen; but hydrogen is not chemisorbed and this may be due to the extra energy required to restore the silicon surface to the undistorted diamond-type structure.

4.2 Compounds

After a short look at the III-V semi-conductors we shall pass to the compounds of the greatest interest in catalysis.

4.2.1 III-V Semi-conductors

Crystals of substances such as indium antimonide (AB Fig. 17) have the sphalerite structure and possess a polar axis perpendicular to (111) planes.

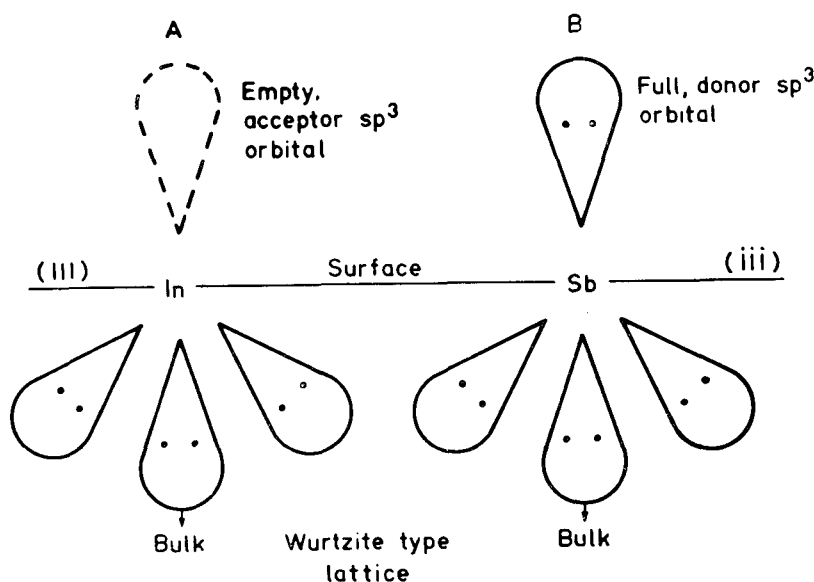


Fig. 17.

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There is evidence that such faces expose on the (111) plane only atoms of A (indium) and on ($\bar{1}\bar{1}\bar{1}$) only atoms of B (antimony). Then the atoms of both surfaces are in a tetrahedral configuration with the outward pointing orbital empty on the A atom (*i.e.* electron accepting) but full on the B atom (*i.e.* electron donating). GATOS has shown that there is some chemical evidence for this.

4.2.2 Oxides

Here the patterns of activity and the stoichiometry of the solid depend upon the reactant gases.

4.2.2.1 Reactions of Hydrogen

These include hydrogen exchanges, dehydrogenations, disproportionations, hydrogenolysis, *etc.*

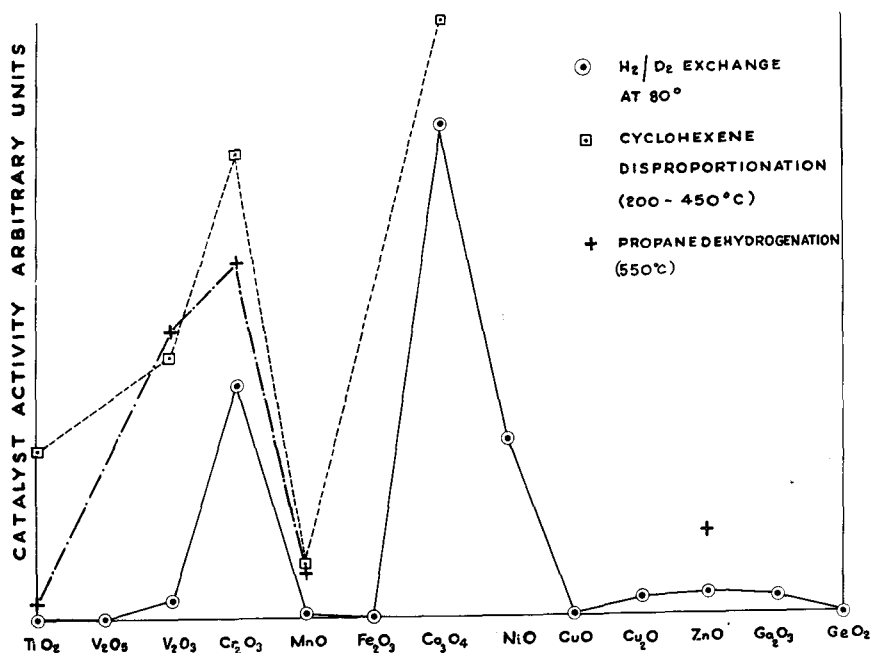


Fig. 18 shows the intrinsic activity, *i.e.* the activity per unit area, of some microcrystalline oxides of the first long period in

- (a) Hydrogen-deuterium exchange at 90°K (the same twin peaked curve is also found at 293°K)

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(b) Propane dehydrogenation at 600°C
and (c) Cyclohexene disproportionation at 200–500°C. (STEINER *et al*)

BALANDIN and his co-workers have found a maximum in the activation energies for the dehydrogenation of cyclohexane and isopropanol at manganous oxide. KRYLOV has claimed similar twin peaked patterns of activity in the recombination of oxygen and hydrogen atoms, the homomolecular exchange of oxygen and many other processes. TAYLOR and WILLIAMSON showed as long ago as 1931 that manganous oxide does not chemisorb hydrogen at 0°C but takes up small amounts of gas at temperatures above 184°C. Chromia chemisorbs hydrogen at 90°K (BEEBE and DOWDEN).

The chlorides of the metals do not exhibit this pattern of behaviour; BRENNAN in unpublished work has noticed that there is no activity until the chlorides decompose.

The activity of the oxides of the metals of group 8 cannot be determined in reducing reactions at high temperatures because of the reduction of the oxides to metals during the course of the reaction.

4.2.2.2 The Hydrogen-Deuterium Exchange

In this pattern of activity it is particularly noticeable that there exists no direct correlation with the type of semiconductivity possessed by the oxide.

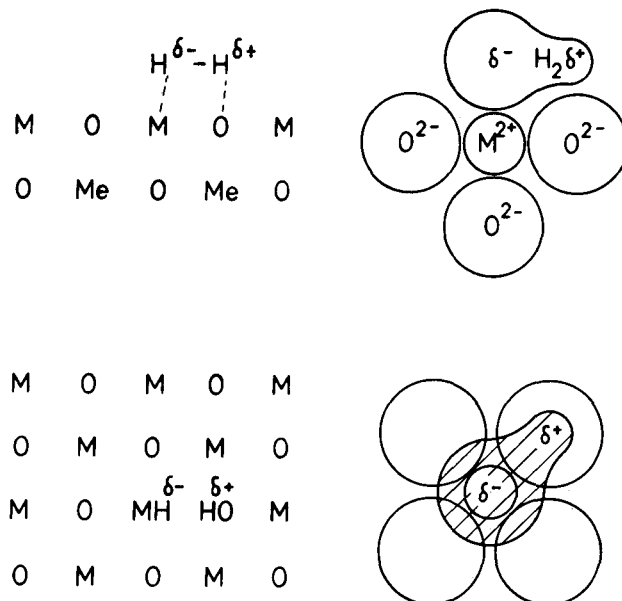


Fig. 19. Chemisorption of Hydrogen on oxides.

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For example compare MnO with ZnO and Fe_2O_3 with Cr_2O_3 . The most significant relationship is the association of low activity with empty, half-full or full 3d-shells; this led us to seek for an explanation based in crystal and ligand-field theory. A second reason for looking for such a theory lay in the inadequacy of simple electron donor-acceptor models in the interpretation of the more complex reactions.

Let us return to the model of the surface of oxides having the sodium chloride structure, such as was used in the earlier remarks on magnesium oxide. Then the ions on the (001) surface will tend to chemisorb and polarise the hydrogen molecule in such a way as to restore the co-ordination to six and to return the symmetry to octahedral. Therefore, if the electronic configuration of the cation is $d^1, d^2, d^3, d^4, d^6, d^7, d^8$, or d^9 there will be crystal field stabilisation effects both on the clean surface (co-ordination number 5, symmetry square pyramidal) and on the surface carrying chemisorbed hydrogen (co-ordination number 6, symmetry, near octahedral). These can be roughly estimated using the model shown in the Fig. 19. The crystal field splitting for the progression from the square pyramidal configuration to the approximately octahedral configuration is given in the next figure (Fig. 20) where the relative

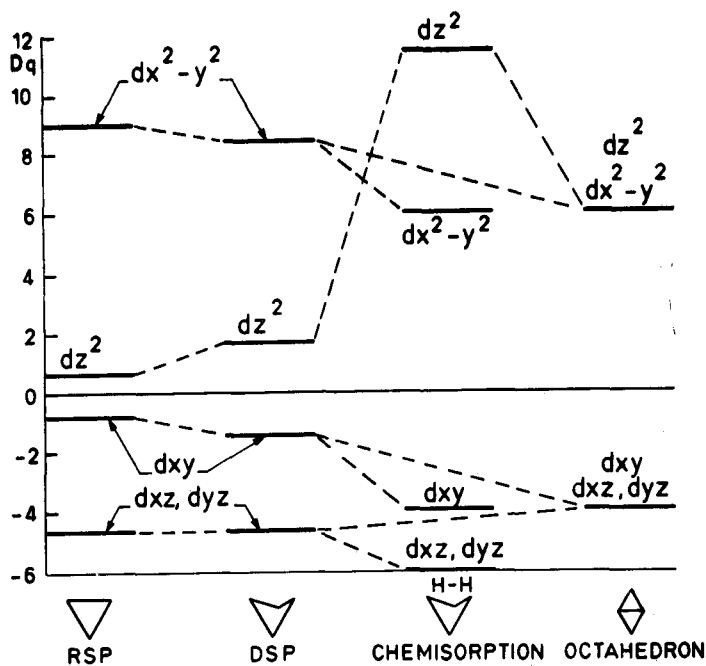


Fig. 20. d Orbital energy levels for various CO ordinations.

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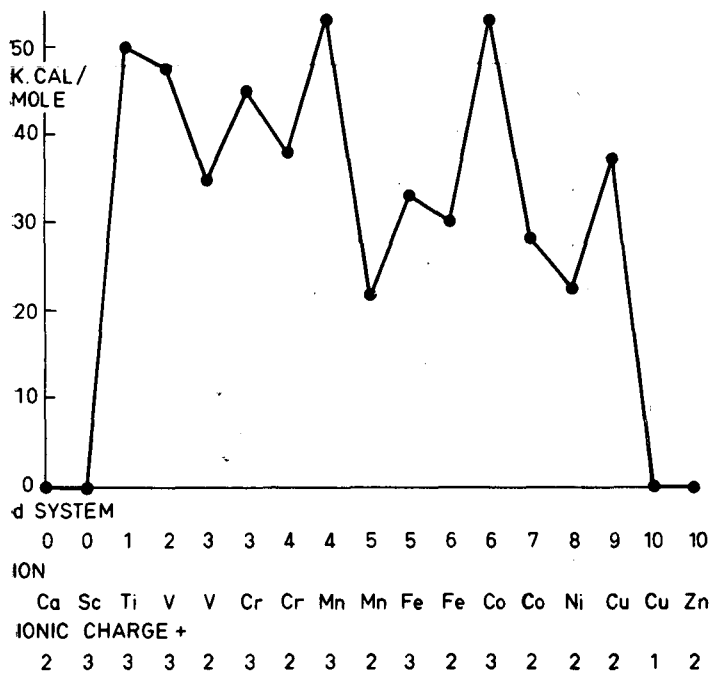


Fig. 21. Values of Dq for transition ions.

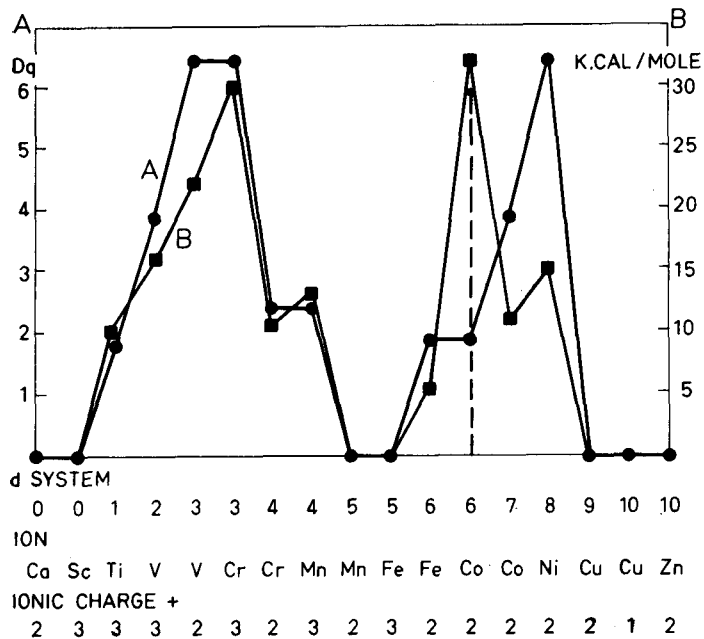


Fig. 22. Crystal field contribution to chemisorption energies for $H^{\beta}-H^{\beta+}$ on NiO.

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energies of the separate orbitals are given in units of Dq , the crystal field splitting parameter. Values of $10 Dq$ taken from the literature on the optical spectra of these same ions in solution, or in octahedral co-ordination in solids are also given (Fig. 21). If the proper number of d-electrons for each ion is placed in these energy levels in the weak field approximation (by HUND's rule) then one can make a very rough estimate of the crystal field contribution to the chemisorption energy (Fig. 22). Only for the ion Co^{3+} in the Co_3O_4 lattice has the strong field approximation been employed: the magnetic properties of this solid (COSSEE) indicate a strong field situation.

There is a strong correlation between this calculated crystal-field contribution and the pattern of activity of the oxides in hydrogen-deuterium exchange. This effect can best be seen if oxides of the same crystal structure are compared, *e.g.*



and NiO, MgO, MnO

Notice that reduction of the metal ion to a lower valency does not occur in this model. If reduction is introduced, *e.g.* $Cr^{3+}O^{2-} \rightarrow Cr^{2+}H \cdot HO^-$ the calculations become so complicated that a worthwhile conclusion cannot be drawn.

There are many criticisms of this interpretation, for example:—

- (i) we do not know the true charges on the ions of the lattice. This is in part corrected by the use of empirical values of Dq .
 - (ii) the effective radii and the charges on the polarised hydrogen molecule have been varied only over a range of likely values and a reasonably consistent set chosen. This is arbitrary.
 - (iii) the model is perhaps not realistic. No account is taken of covalent bonds, although hydride complexes such as $Cr^{2+}-H$ may well be formed.
- and finally
- (iv) it is now known that the simple crystal field theory is quite unable to give a correct calculation of the sign and the magnitude of Dq in inorganic complexes.

Further progress in this direction requires complete molecular orbital calculations.

For all these reasons we have not taken this type of calculation further. Mr. WELLS and I did consider the situation at the end of an emergent edge-dislocation on the (001) face of the sodium chloride structure. Fig. 23 reveals that this centre resembles a binuclear complex with a metal-metal bond. However its marked asymmetry destroys the twin-peaked pattern found for the more symmetrical centres.

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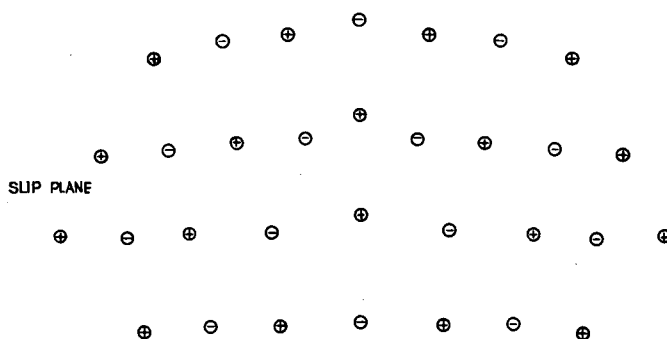


Fig. 23. Edge dislocation for slip on a plane.
(Na⁺Cl⁻)

Clearly therefore if catalysts are tested in metastable states in which the lattice is so distorted that it contains cations in abnormal co-ordinations the twin-peaked pattern may itself be distorted or may not appear at all. In particular transitional metal oxides which possess metal-metal bonds in the regular lattice should possess abnormal catalytic activity. F. S. STONE has found such an example in the sesquioxides of titanium and vanadium which crystallise with the rhombohedral corundum lattice. Here there is some tendency for the cations to group in pairs with cation-cation interaction between adjacent ions. As the spins uncouple at the anti-ferromagnetic CURIE point, activity in hydrogen-deuterium exchange increases.

This effect may be expected to occur often among transitional oxides, *e.g.* MoO₂ and the homologous series of oxides found by MAGNELI, where dislocations forming regular lattice sequences are common.

4.2.2.3 Dehydrogenation of Hydrocarbons

BURWELL has reported exchanges of deuterium with saturated hydrocarbons over chromium sesquioxide (Cr₂O₃) which suggest that the dissociation RH→R+H occurs. If we replace H-H of our earlier model by R-H then we can find a similar correlation with the activity pattern for the dehydrogenation of propane.

The formation of this bound radical is an important first stage in many reactions involving the breakdown of hydrocarbons. The process of dehydrogenation may then be written down as in the figure. Here we required the intervention of a pi-complex and the reversal of an insertion reaction (Fig. 24). We shall see later that the electronic configurations which are effective in dehydrogenation may also be effective in forming pi-complexes.

Electron spin resonance experiments with chromia-alumina dehydrogenation

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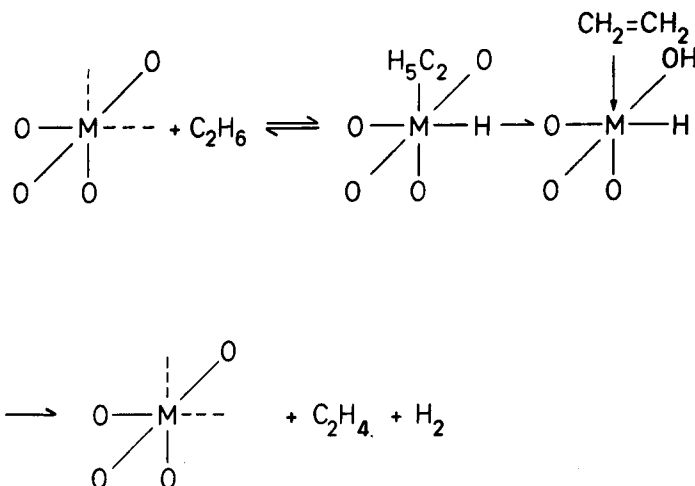


Fig. 24. Dehydrogenation and hydrogenation of ethane.

catalysts by Dutch and RUSSIAN workers have received slightly different interpretations. The consensus of opinion however is that the surface complexes involve Cr^{2+} or Cr^{3+} ions or both.

4.2.2.4 The Disproportionation of Cyclohexene

This is a more complicated reaction than dehydrogenation but STEINER finds that the rate controlling step is nevertheless most likely to be the breaking of the carbon-hydrogen bond. Then the activity pattern should again be twin-peaked—as it is.

4.2.2.5 The Polymerisation of Olefines

It is now well-known that supported oxides of chromium and molybdenum, containing the elements in the state M^{5+} , are effective in the polymerisation of alpha olefines at moderate pressures and temperatures. We gave an interpretation of this reaction in 1960 which is quite similar to that developed in great detail by COSSEE for the ZIEGLER-NATTA polymerisation. It is based on an insertion mechanism (Fig. 25) and employs as an active centre Cr^{5+} or Mo^{5+} in octahedral or tetrahedral co-ordination. The olefine displaces adsorbed water and is itself chemisorbed as a pi-complex. A small amount of hydrogen is formed by dehydrogenation, is chemisorbed and reacts to form an alkyl radical or an alkyl radical may be introduced from a metal alkyl. The polymerisation then proceeds as shown.

The active centre is a site in the surface produced by the loss of two

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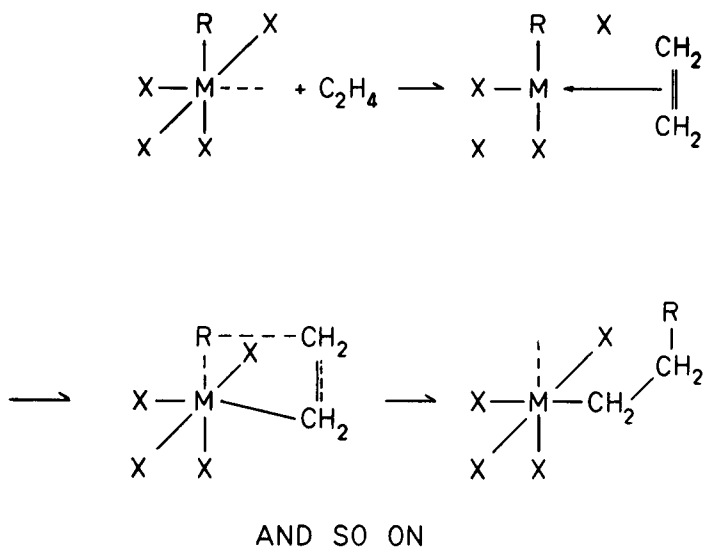


Fig. 25. The ZIEGLER-NATTA reaction by insertion.

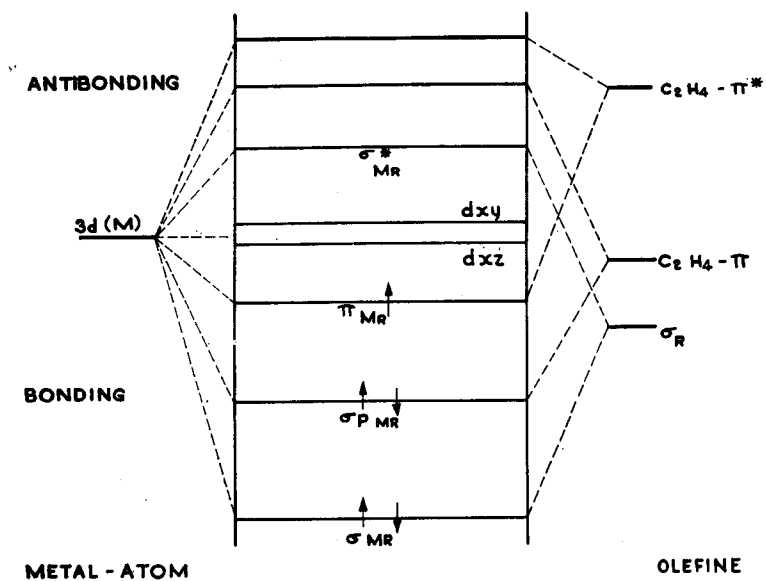


Fig. 26. Energy levels in COSSEE's complex.

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ligands from the co-ordination shell of a surface cation. This loss of oxygen, or oxygen and water, may be more easy at some kinds of lattice defect. The molecular orbital diagram will look something like that given in the Fig. 26. This interpretation requires that ions having the configuration d^1 , d^1 , d^2 and d^3 should be active: oxides having the configuration d^1 seem to be the most effective.

Similarly in many other reactions in which olefines and allylic residues participate, when these electronic configurations occur, pi-complexes may be present as important intermediates, *e.g.* in dehydrogenations, dehydrations and oxidations.

4.2.2.6 The Reactions of Oxygen

The reactions which have been investigated include :

- (i) the homo-molecular exchange of oxygen
- (ii) the decomposition of nitrous oxide
- (iii) the oxidation of carbon monoxide
- (iv) the oxidation of many hydrocarbons

In every example the transitional metal oxides are more active than the non-transitional oxides and among the transitional metal oxides the P-type semi-

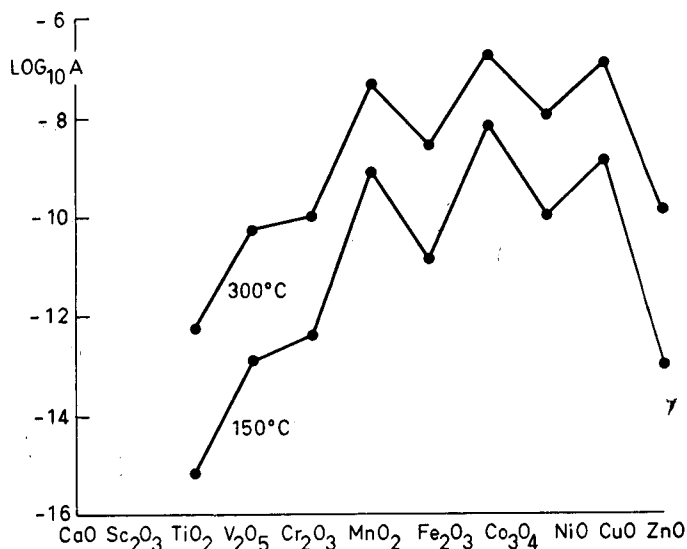


Fig. 27. Activity of oxides in hydrogen oxidation (BORESKOV)

A = Activity in moles H_2 $hr^{-1} cm^{-2}$ in the reaction
 $H_2 + 1/2O_2 \rightarrow H_2O$

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conductors are more active than the N-type (Fig. 27). In the oxidation of hydrocarbons, catalysts formed from N-type oxides of transitional metals are more selective than those formed from P-type oxides. Fig. 28 shows the marked resemblance to catalysis by complexes in homogeneous solution.

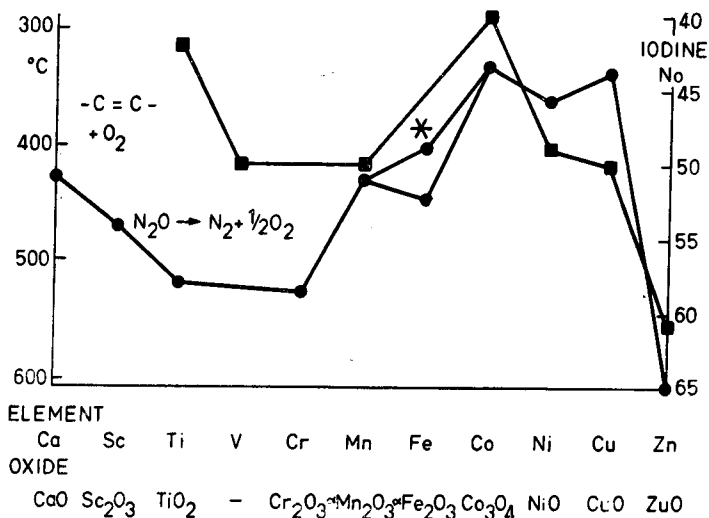


Fig. 28. Activity of metal oxides and cations in reactions involving oxygen.

- Activity of metal cations in oxidation of oleic acid (Iodine number) (SKELLON)
- Activity of 'Specpure' metal oxides in the decomposition of nitrous oxide (Arbitrary units) (DOWDEN & WELLS)

In their normal valency states the P-type semi-conducting oxides are confined to the oxides of the metals to the right of vanadium, *i.e.* Mn, Co, Ni and Cu (MnO, FeO, CoO, NiO, Cu₂O). Vanadium pentoxide, chromium sesquioxide, chromic trioxide and titanium dioxide are most readily classed as N-type semiconductors. I do not propose to treat this complicated topic further in this lecture.

4. 2. 2. 7 Sulphides

The next figure (Fig. 29) shows that a twin-peaked pattern of activity exists also for the hydrogenolysis of carbon disulphide over the sulphides of the first long period. In the solid sulphides the phases are more numerous and the structures more complex than those of the oxides but it seems that similar principles must apply.

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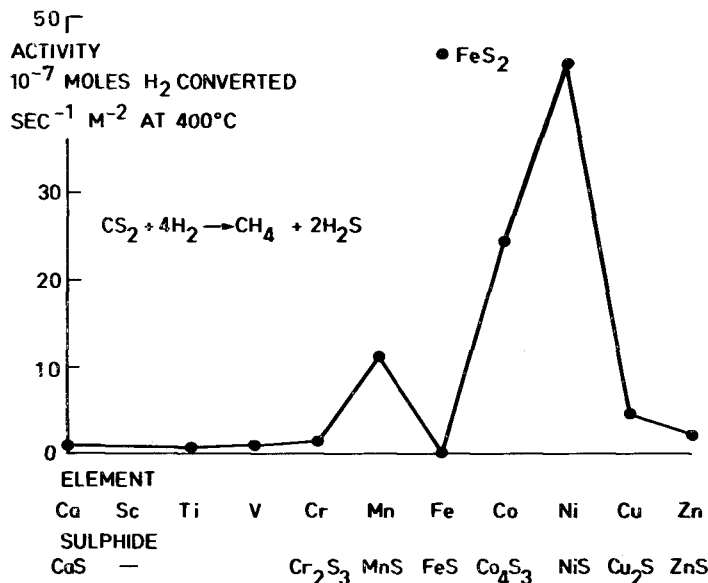


Fig. 29. Activity of metal sulphides in the hydrogenolysis of carbon disulphide.

(DOWDEN, FISH & WELLS)

4.2.2.8 Halides

The halides tend to have layer lattices and to expose metal ions only at the edges of the layers. Hydrogen-deuterium exchange occurs only as the halides undergo thermal decomposition.

On the other hand the ZIEGLER-NATTA polymerisation of alpha-olefines is well known and requires the same electron-configuration as has already been noted for the oxides.

5. Metals

Twenty years have passed since it was first suggested that an intimate correlation existed between the catalytic activity of metals and their electronic structure as interpreted by simple band theory. This correlation may be summarised as follows:—

- (i) the activity of metals is greatest, with few exception, when the metal contains unfilled, electron-levels of high density, *i.e.* density in energy, states per electron volt per cm³ at the FERMI surface (Fig. 30). Normally such high densities are attained only in transitional metals. This theory was based upon the concepts, then used in the discussion of alloys, that

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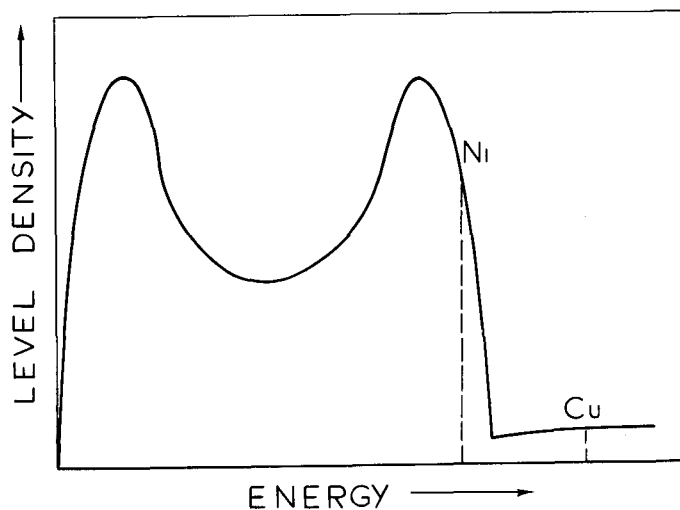


Fig. 30.

the change in total energy per absorbed surface complex, stable or activated, would be a minimum when the energy level density was high and increasing with energy (Fig. 30).

- (ii) Marked changes in energy level density with composition would be associated with marked changes in catalytic activity. Because these changes also, according to the HUME-ROTHERY rules and the MOTT-JONES theory, induce crystallographic transformations, the correlation will be interrupted by variations due to geometric factors. There were three situations where these marked changes in level density occurred:
 - (a) as the 3d, 4d and 5d bands were filled in alloys between Ni, Pd, Pt and Cu, Ag, Au
 - (b) close to the phase boundaries in the HUME-ROTHERY alloys
 - (c) at any filled zone structure, *e.g.* manganese in the first long period (PAULING)

The first two were readily demonstrated but only recently ELEY and SHOOTER have found a minimum in the catalytic activity for hydrogen-deuterium exchange at manganese. The Fig. 31 shows the activity of evaporated films against electron to atom ratio. The solubility and the heats of solution of oxygen and hydrogen for some metals and alloys of the first and second long periods show similar variations.

At all times it is important to understand that the theory of the electronic factor in catalysis is not a theory of the electronic configuration of alloys. Stress

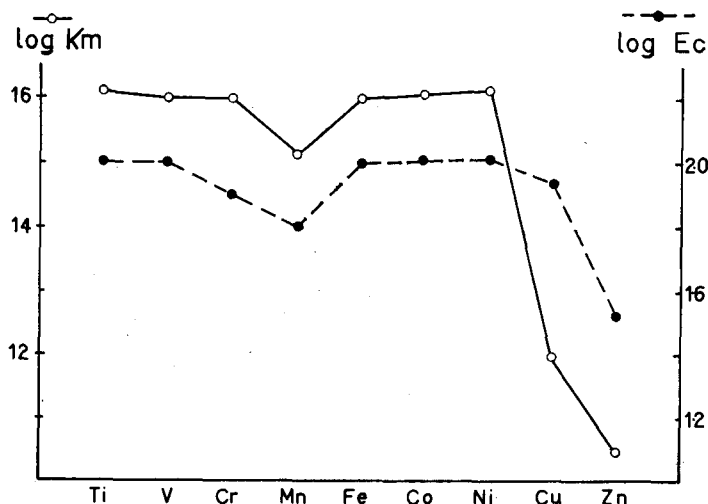
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Fig. 31. Variation of the velocity constant and cohesive energy (Sublimation energy) with atomic number.

was always laid upon the fact that simple band theory of metals and alloys was inadequate to explain many of their physical properties and that recourse must always be made to the experimental properties of the metals themselves as determined by experiment.

5.1. Alloys between Ni, Pd, Pt and Cu, Ag and Au

There are now many examples of the marked change in activity which occurs in these binary alloys as the d-band becomes full (Fig. 32, 33). However here I am more concerned with the many departures from the expected pattern.

5.1.1 Excess Activity in the Cu, Ag and Au-rich phases

I am not concerned with alloys which are not homogeneous in composition because of deficiencies in preparation. But there is well-documented work, in which the alloys should be homogeneous, where there remains appreciable activity beyond the composition at which the saturation magnetisation indicates that the d-band is full. This is particularly true of the Ni-Cu alloys at higher temperatures.

In my early work I pointed out that in the Ni-Cu alloys, a marked fall in activity at the alloy composition at which the saturation magnetisation falls to zero is only strictly to be expected at low temperatures. At higher temperatures, according to WOHLFARTH, there must be some transfer of electrons from the d-band to the s-band; then according to my model, under these

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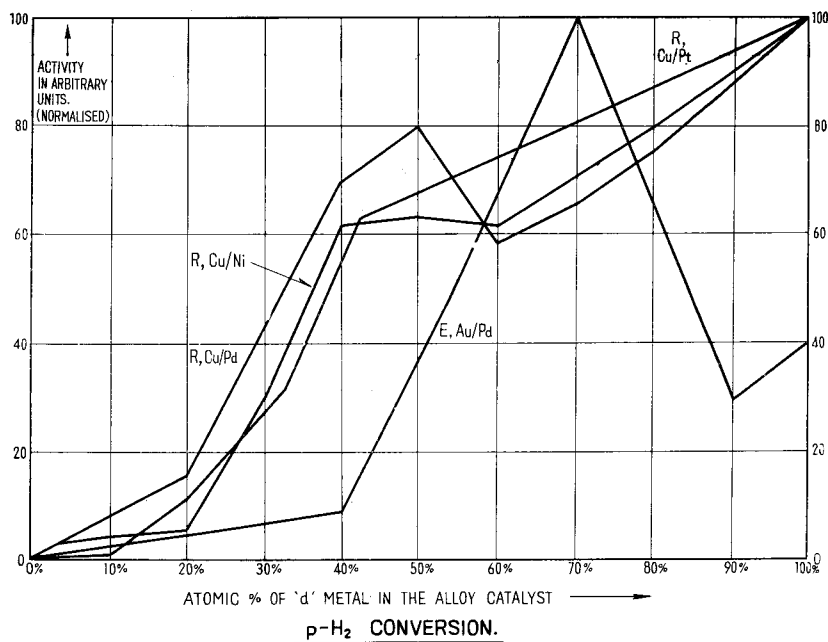
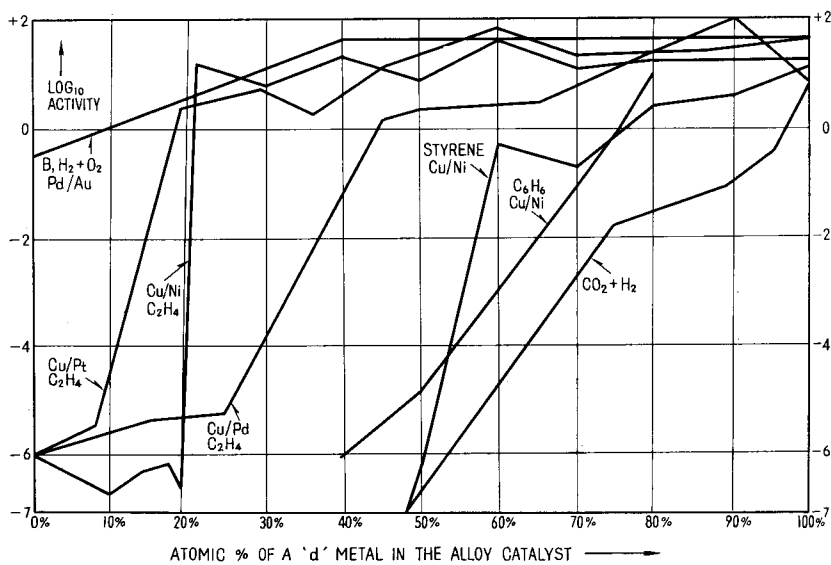
Fig. 32. $p\text{-H}_2$ Conversion.

Fig. 33. Hydrogenation.

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conditions, activity should persist into the copper-rich alloys. This effect should not be large; thus it should not extend the high activity beyond *ca.* 0.7 atomic fraction of copper.

KEESOM and KURRELMEYER found that the electronic specific heat of the Ni-Cu alloys remained high beyond the alloy composition at which the saturation magnetisation fell to zero. Similarly physicists found that beyond this composition there remained a strong, field-dependent paramagnetism rather than the expected diamagnetism. SMOLUCHOWSKI and GOLDMAN attributed this to clustering of nickel atoms—a nickel atom having a small preference for a nickel nearest-neighbour rather than a copper nearest-neighbour. This complication then requires that activity remains unexpectedly high as long as the clusters persist.

SACHTLER has very recently produced evidence that under some conditions a miscibility gap may appear in the Ni-Cu and Pd-Au systems. We can imagine that this phase separation is accelerated when the crystals are small and when the system Ni-Cu-H is maintained at moderate temperatures for long periods of time—as when mixed oxides are reduced.

5.1.2 Excess Activity in the Ni, Pd, Pt-rich phases

There are some examples where the addition of Cu to Ni first increases the activity before it begins to fall as the composition of the alloy approaches the critical composition.

Here I exclude changes in intrinsic activity which are only apparent. This can occur because of inexact corrections for the surface areas of the alloys which are much higher on the Ni-rich side than the Cu-rich side. This is due to the fact that NiO and CuO form solid solutions up to *ca.* 35 moles % CuO and that reduction of these leads to much smaller crystal sizes than reduction of the immiscible compositions. Also nickel oxide containing copper is more easily reduced than pure nickel oxide.

The increase in activity with added copper in nickel or gold in palladium parallels the observed increase in the solubility of hydrogen which occurs at low or moderate temperatures. This has recently been ascribed to the decrease in the cohesive energy of the alloys which makes the insertion of hydrogen more easy. If the hydrogen atoms are chemisorbed at interstitial surface sites a similar explanation is possible here.

5.2 Recent Empirical Models

The study of the band theory of metals is a proper exercise for the physicist but it presents problems for the chemist. For example how is one

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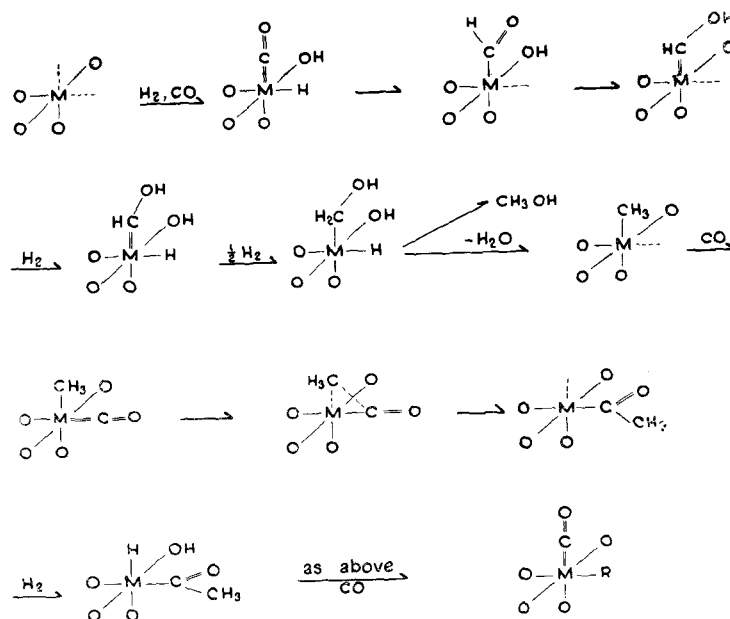


Fig. 34. Hydrolytic polymerisation of carbon monoxide.

to proceed from this mechanism (Fig. 34) for the FISCHER-TROPSH synthesis to a consideration of the complexes found at metal surfaces.

For these reasons some recent empirical models of metals repay investigation.

5.2.1 Metal Surfaces

The results of electron-emission and field-ion-emission microscopy show that the surfaces of the refractory metals present arrays of atoms just as had been expected by the early crystallographers. Low-energy electron-diffraction provides confirmatory evidence of surface structure and its re-arrangement during chemisorption. The infra-red spectra of adsorbed species and the conclusions of flash-desorption studies reveal the presence of different chemisorbed states for a given molecule (H_2 , CO and N_2) and indicate that the bonds (*e.g.* of CO) are not very different from those found elsewhere in chemistry. Finally the alteration of magnetic and electrical properties shows that some perturbation of the metal-metal bonds occurs in chemisorption.

Thus we can affirm that the surface complexes will be those which are indicated by general chemical principles:

- (i) use atomic orbitals or combinations of orbital appropriate to the symmetry about the surface atom and the adsorbate

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- (ii) the surface orbitals employed in chemisorption must match with the best for the interior
- (iii) use the best available empirical model for the interior orbitals

We next assume that the valencies of the clean surface are not very different from those of interior atoms. The reasons for this are as follows:

- (i) the counting of broken bonds appears to give a good account of the measured surface energies of copper, silver and gold
- (ii) the saturation magnetisation of particles as small as 21 Å (cobalt), 15 Å (iron) and 20 Å (nickel) is, within experimental error, the same as that of massive metal
- (iii) the CURIE point of small nickel particles (20 Å) extrapolates almost to the value for massive nickel
- (iv) the x-ray absorption edges of platinum particles only deviate from those for massive platinum when the particle size drops below 15 Å.

How are the d, s and p orbitals of the transitional metal atoms employed in the bulk?

In accord with a number of recent semi-empirical models it will be supposed that binding in the interior is largely by the resonance of even orbitals

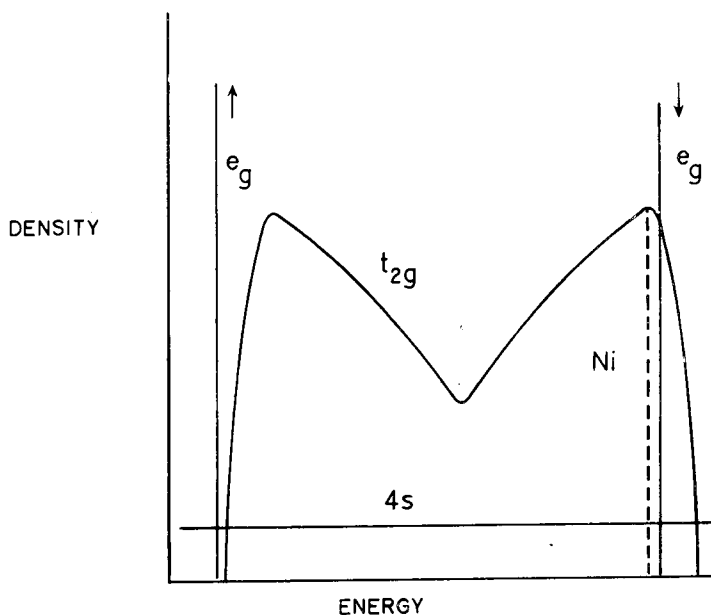


Fig. 35. Energy level Densities in nickel.
(GOODENOUGH)

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(simple or hybridised) among nearest-neighbours. Then there are two classes of orbitals—localised, accommodating the unpaired electrons which contribute the magnetic properties and bonding, non-localised, overlapping, which cause cohesion.

The specific model which I use is that given by GOODENOUGH (Fig. 35) which is extreme in that the electrons are sharply divided into localised and non-localised groups.

5.2.1.1 Face-centred Cubic Metals

In the Al structure cubic symmetry requires that the coordinate axes be directed towards next nearest (nn) neighbours (Fig. 36). For Ni and Co this

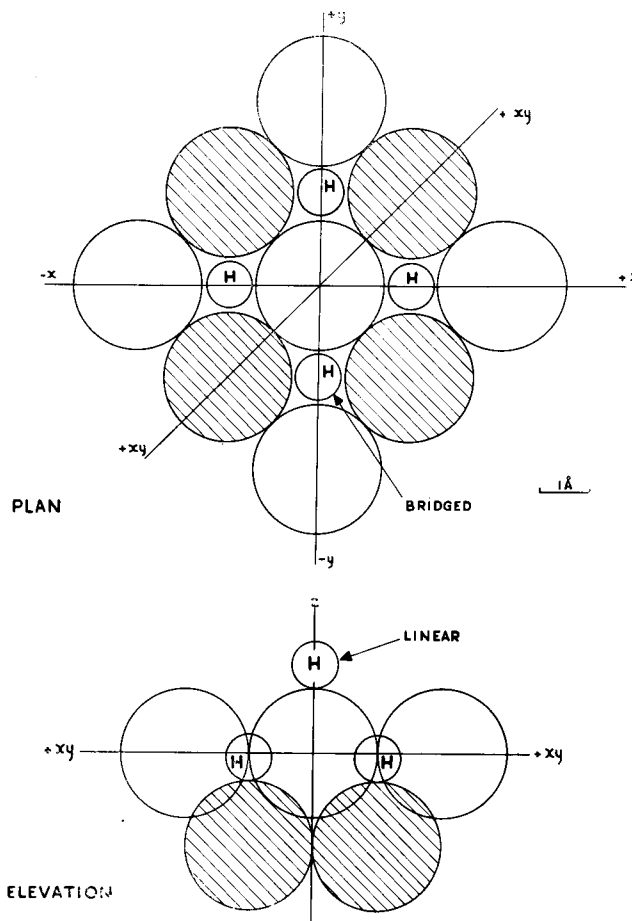


Fig. 36.

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implies that the collective t_{2g} (d_{xy} , d_{xz} , d_{yz}) electrons occupy a metallic band which overlaps localised (d_{z^2} , $d_{x^2-y^2}$) electrons in two e_g levels arising from intra-atomic exchange-splitting (Fig. 37); the wide sp-band contains not more than one electron and the resulting structure resembles that proposed in other theories.

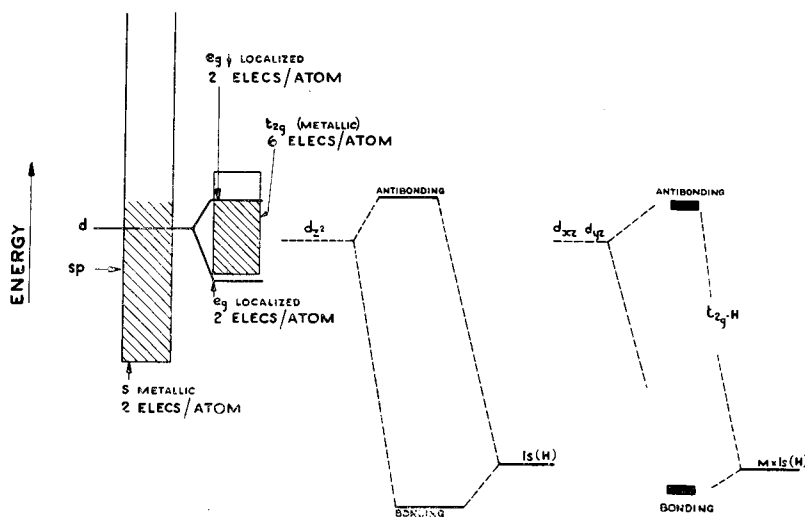


Fig. 37.

With the z -axis perpendicular to the (001) face (Fig. 36) then the lobes of $d_{x^2-y^2}$ are directed towards nn-neighbours lying on the x and y axes in the surface, and half of the lobes of each of d_{xz} and d_{yz} projects outwards towards the site of the missing nearest (n-) neighbours. There are four kinds of site to participate in bonding, three in linear arrangements involving the d_{z^2} orbital (above and below the surface atoms and in the incomplected octahedral interstices above the exposed n-neighbour atoms in the penultimate layer) and one bridging arrangement using d_{xz} and d_{yz} (near the missing n-neighbour sites). There are no sites of trigonal symmetry.

5.2.2. Nickel

Ten electrons are just sufficient to fill the 3d-band but consistency with experimental data is achieved by placing 0.55 electrons peratom in the sp-band and arranging 0.55 holes 0.41 t_{2g} , 0.14 e_g) in the d-levels.

According to the model d_{z^2} is almost completely localised; in the surface this would be accentuated by outward movement of the surface atoms. Thus bonding with d_{z^2} can be considered as involving no interaction with that using

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t_2 ; there may be some small hybridisation with s and p_z but for illustrative purposes this will be neglected. On the approach of a hydrogen atom (ionization potential 13.5 e.v.) along the z -axis a localised bonding orbital will emerge below 13.5 e.v. and an antibonding orbital at a higher level, probably just above the work function of nickel (4–5 e.v.). To form a two-electron bond 0.86 electrons must be removed from the e_p orbitals and placed at the FERMI surface, in s and d bands in proportion to their density of states (for Ni, 0.74 e in t_2 , 0.12 e in s). The change in saturation magnetisation then lies between $-0.88 \mu_B$ and $-1.29 \mu_B$ (μ_B = the BOHR magneton) per H atom depending upon the polarisation of the spins in t_2 ; this decrease is greater than observed but it can be made smaller by reasonable devices. The change in electron concentration at the Ni atom is -0.86 , therefore the 0.86 electrons displaced into the bands must remain in the vicinity of the adsorbed atom; the situation is similar to that occurring near a solute of higher valency than the solvent. Following FRIEDEL one can suppose that repulsive effects arise (depending upon the density and the gradient of the density of energy levels), as well as dipolar and conductivity phenomena. In the absence of steric effects the d_{z^2} -H bonds will form with about the same strength on all surfaces.

In the bridging positions multicentre orbitals may be formed using the gerade d_{zz} , d_{yz} orbitals of the metal. A hydrogen atom overlaps four lobes ($4 \times \frac{1}{4} t_2$) *i. e.* one orbital, at an isolated interstitial C_{4v} site to give one bonding and one anti-bonding level. Again 0.8 electrons must be displaced to the FERMI level, with results similar to those discussed above. There are many surface cells of this type each having bonding and anti-bonding surface states which may overlap. It seems reasonable to link these with the strong negative, A-type bonding distinguished by EISCHENS on platinum and associated with chemisorption heats calculated by the ELEY-STEVENSON method.

This approach has been extended, in a similar approximation, to the sigma and pi-bonding of atomic nitrogen and molecular CO, O₂, N₂, N₂H₂, C₂H₄, C₆H₆ *etc.* Although at this stage completely descriptive and very sensitive to the model it does indicate how bonding can depend upon local symmetry and energy-level densities; it also suggests the possible existence of unsuspected types of chemisorption and the reasons for variations in chemisorption and catalysis across the long periods.

Metals are very different in their properties from halides and oxides but fundamentally the same chemical principles appear to apply.