

CHEMISORPTION  
AND  
CATALYSIS

# CHEMISORPTION AND CATALYSIS

*Proceedings of a conference organized by the Institute of Petroleum and held  
at the Mount Royal Hotel, London W.1, 29-30 October 1970*

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# Opening Address

By H. POWELL

(Chairman, Hydrocarbon Research Group, Institute of Petroleum)

ON behalf of the Institute of Petroleum and the organizing committee, I am very happy to welcome you to this symposium and I would like to extend a particular welcome to those from overseas.

I feel it would not be inappropriate for me to say something about the Hydrocarbon Research Group. It has been in existence for over 26 years and its prime function is to give financial support to academic research of interest to its member companies, of which there are at present nine. These are BP, Burmah, Esso, The Gas Council, ICI, Mobil, Monsanto Chemicals, National Coal Board, and Shell. Its funds are derived from equal annual subscriptions from the member companies. It operates through three specialist panels—the Spectroscopic, Mass Spectrometry, and Hydrocarbon Chemistry Panels. Panel meetings are held three times a year, at which specialist representatives of the member companies and leaders of the academic research teams receiving support meet to discuss the results of the work supported.

As many of you will know, the Hydrocarbon Research Group has held many conferences and symposia over the years but these have invariably been arranged by a particular panel of the Group. This symposium is unique in that it involves all three panels. This is, indeed, not surprising when one considers the scope of the work covered by the programme, and in fact the chairmen of the three sessions are the chairmen of the three panels.

This symposium is a result of the work of the Hydrocarbon Research Group in that nearly all the papers presented cover either work supported at universities by the Group through its three constituent panels, or come from the research laboratories of member companies of the Group.

The programme gives a representative cross-section of work related to the problems of heterogeneous catalysis, the importance of which in industry today is such that it has been estimated that over 90 per cent of all new chemical processes introduced in recent years have been based on catalysts. These problems range from a careful study of the kinetics of a host of different catalytic reactions under varying conditions of temperature and pressure, using the most modern and refined analytical techniques such as gas chromatography and mass spectrometry, to fundamental questions of the nature of the interaction between gases and solid surfaces. In the latter case various spectroscopic techniques have proved of enormous help, infra-red spectroscopy being of proven value since its general adoption 15 years ago. Two, much newer techniques, Laser-Raman and Auger electron spectroscopy, are also covered in the Symposium and so too is Low Energy Electron Diffraction.

A feature of the symposium is the way in which studies carried out in universities for the advancement of knowledge fit in with the more fundamental work

carried out by a number of industrial laboratories. The problems which arise on the plant sometimes seem to be quite unrelated to those under study here; problems of catalyst stability and life, of heat and mass transfer which may require more attention in the long run than the original formulation of a suitable catalyst. One of the ways whereby "feedback" between such industrial problems and the research into the elements of fundamental catalysis carried out in universities can be brought about is by having workers in industry who, by virtue of their own advanced studies, can talk on equal terms with their academic counterparts, but who are also in close contact with their colleagues who have to operate plant, which is based on existing scientific knowledge. This is where the discussions at the panel meetings are of considerable benefit.

I do not propose to take up any more of your time. I feel sure that the papers to be presented will stimulate considerable discussion on the various topics covered, and I hope that at the end of the symposium you will all feel that your attendance has been well worthwhile.

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# Metal Electrons in Chemisorption and Catalysis

By D. A. DOWDEN

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## INTRODUCTION

THE specific activity of solid catalysts is dependent upon the intrinsic properties of asymmetrical surface complexes, the formation and behaviour of which are regulated by the rules which apply in homogeneous chemistry. The catalytic efficacy of solids conforms to patterns which are clearly related to the periodicities of Mendeleef's table of the elements and thus, in modern terms, to the electronic states of the participating structures. Current research is concerned to elaborate and to investigate these relationships, both empirically and fundamentally, in order to uncover new phenomena and to evolve more effective theories.

The characteristic activity of the conductors is seen in the catalysis of reactions such as hydrogenation-dehydrogenation, carbon-carbon bond fission, and oxidation. Excepting situations in which a reactant is very electronegative, the mechanisms on metals seem to involve homolytic dissociation and bound radicals. Especially notable among the catalytic properties of the conducting solids is the resemblance between the activity patterns for the reactions of hydrogen over the metals, oxides, and sulphides of the first long period (Fig 1). As the relative inertness, in some situations, of half-full and full *d*-shells has been known for many years, this is a strong indication of the importance, directly or indirectly, of electronic configuration and symmetry in surface chemistry. The significance of such concepts has only recently begun to make an impact on research into the adsorptive and catalytic properties of solid solutions of transitional metal ions, where modern techniques make possible more detailed descriptions of surface states.

A comparable account of the surface of metals cannot yet be given despite the great advances which have been made in the understanding of surface geometry. The purpose of this paper is to outline the original theory of the electronic factor in catalysis by transitional metals and to bring it up to date.

## THE ELECTRONIC FACTOR IN SURFACE CHEMISTRY

The first theory,<sup>1-4</sup> now over 20 years old, relied greatly upon the simple band theory of metals,<sup>5,6</sup> and upon Pauling's unsynchronized resonating-bond theory.<sup>7</sup> The existing data for the most part concerned the surface properties of solids which had not been well-characterized by modern standards even in the bulk. Although the evidence was imprecise, some qualitative support existed in the overall trends of activity; the results of more pointed research were soon available.<sup>3</sup>



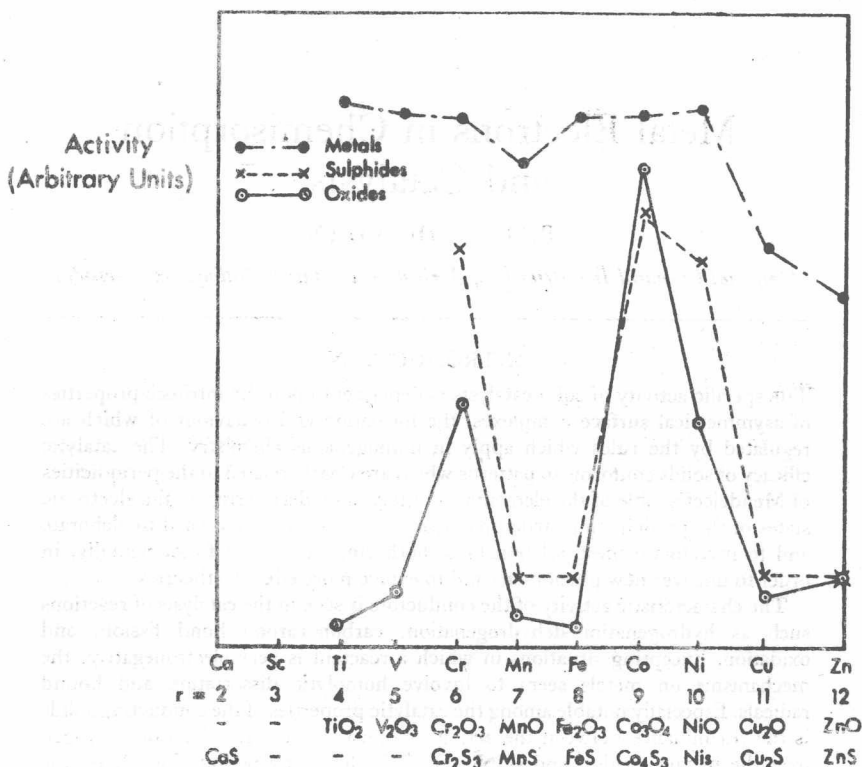


FIG 1. The activity of transition metals and compounds.

### The Electronic Structure of Metals

As the free atoms, with their discrete energy levels,  $s$ ,  $p$ ,  $d$ , etc., condense to form a crystal, the levels interact and broaden at the observed interatomic distance to form overlapping bands. The electrons of the metal are thus confined to a potential box in molecular orbitals which are akin to free-atom wave-functions near the nuclei but to free-electron waves elsewhere. Only the electrons in excess of the inert-gas configurations are considered (or counted in electron/atom ratios,  $r$ ) and at 0° K these occupy the levels in pairs up to the Fermi level ( $E_M$ ), so that the properties of the solid are dependent upon the energy-density of levels,  $n(E)$ , as a function of energy ( $E$ ), and upon the extent to which the levels are filled (Fig 2).

According to the rigid-band model, there exists, for metals of the same crystal structure in each long period, a "standard" curve of  $n(E)$  v.  $E$  because the  $d$  bands and the  $s, p$  bands maintain fixed relative positions. Then addition to the potential box of the number of electrons appropriate to each element gives  $E_M$  and the corresponding  $n(E_M)$  can be read from the curve. Theory and experiment indicated a sharp drop in the density of levels at  $r \sim 10.5$  in each long period, especially in the FCC series of binary solid solutions formed between

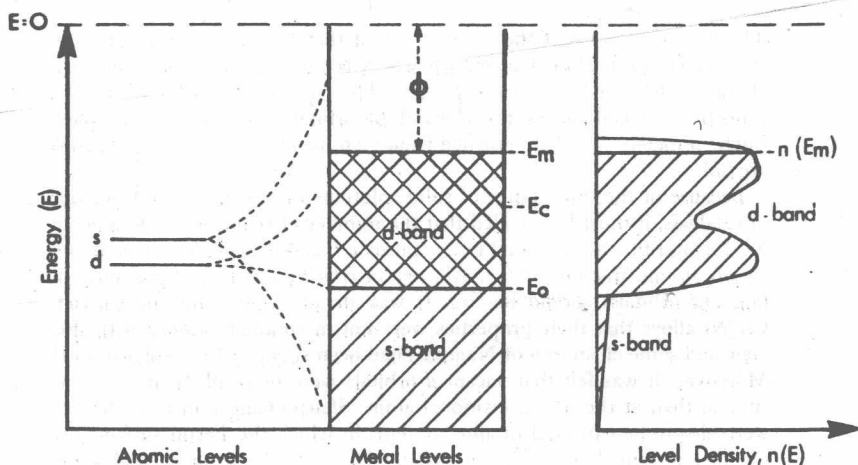


FIG 2. Levels in atoms and metals (diagrammatic).

Ni, Pd, or Pt and Cu, Ag, or Au. There was also the suggestion of a minimum in the middle of the long periods so that the density of levels curve was often represented as twin-peaked, although calculations using the Wigner-Seitz cellular method<sup>6</sup> had indicated other subsidiary peaks.

Pauling's chemical-bond model<sup>7</sup> ascribed the bonding in the transitional metals to the hybrid orbitals formed from the five *d* orbitals, one *s* orbital, and three *p* orbitals (as in inorganic complexes); using magnetic and crystal data, electrons were assigned to the orbitals, which were divided into three sets:

"Atomic", essentially *d* orbitals, primarily responsible for the magnetic properties but not for cohesion.

"Bonding", *dsp* orbitals of varying *d* content giving cohesion by resonance of electron-pair bonds between neighbouring atoms. The number of electrons per atom in these orbitals gave the metallic valency.

"Metallic", essentially *sp* orbitals; a fraction of these is empty to permit unsynchronized resonance of the bonds.

Pauling's description is related to earlier<sup>8</sup> and later<sup>9</sup> crystal field explanations of band-splitting in metals but recent work indicates that this effect is small. However, the system did emphasize the importance of hybridization, localized levels, the division into bonding and non-bonding orbitals, and the spatial properties of orbitals; it also suggested a sharp fall of level density at Mn.<sup>10</sup>

The following points are important:

1. Quantum chemistry teaches that the interaction between orbitals is critically dependent upon their energy. Originally, neither the work-functions ( $\phi$ ) of the metals nor the positions of the electron bands with respect to  $E_M$  were known accurately and there was a corresponding deficiency in the data on the ionization potentials of molecules and radicals.
2. Even at high temperatures, the only unpaired electrons are those with  $E \simeq E_M$ .

3. The rate of increase of the total energy of the system per added electron is inversely proportional to  $n(E_M)$ , which is much greater for levels of  $d$  character than for those of  $s$  or  $p$  types. The position of  $E_M$  for the typical transitional metal leaves the  $d$  band ( $d$  orbitals) only partly occupied. Such " $d$  metals" are distinguished from " $s, p$  metals" in which the  $d$  bands are full.

Because of the importance of solid solutions in the theory and practice of catalysis, it must be recalled that the number of holes in the  $d$ -bands of Ni, Pd, and Pt was estimated to be approx 0.6 and that in alloys containing  $\geq 0.6$  atomic fraction of Cu, Ag, or Au (the "critical" composition) all holes ( $d$  orbitals) should be full. It was already known for the Cu-rich Cu-Ni alloys that their properties were not in complete accord with this view and some clustering of Ni atoms had been suggested in explanation.<sup>11</sup> Moreover, it was felt that vacant  $d$  orbitals were more likely at the transitional than at the non-transitional atom. Sharp changes in level density were also to be expected in alloy systems in which the Fermi surface just touched a zone boundary, *e.g.* in the Hume-Rothery alloys and some sigma phases.

4. The gradient of level density,  $\partial n(E)/\partial E_M$ , also affects the ease of electron addition (positive slope). This conclusion was reached intuitively, although  $\partial[\log_e n(E)]/\partial E_M$  is proportional to the electronic entropy of the metal; Friedel<sup>12</sup> subsequently demonstrated this kind of effect in the shielding of the cores of polyvalent solutes in dilute alloys.

The inadequacies of the simple model were well recognized and workers were recommended always to refer to the physical properties of metals and alloys where these were known.

### THE ELECTRONIC FACTOR IN CATALYSIS

If the limiting step of a reaction involves simply the transfer of single electrons between the metal and a reactant, then the previous section suggests the properties required of the metal: to favour positive ion formation,  $\phi$  and  $n(E_M)$  must be large and  $\partial n(E_M)/\partial E$  positive, but for negative ions the reverse is required.

Co-valent bond formation, between metal surfaces and saturated or odd-electron species, also requires electrons to be placed at  $E_M$  because the highest occupied levels of the adsorbates lie adjacent to or below the filled levels of the metal; the desired properties are like those giving positive ions.

The most marked changes in  $n(E_M)$ , unaccompanied by phase change, occur in the solid solutions noted above and these were subsequently closely investigated. It was assumed that the degree of order, the atomic fractions, and the concentration of  $d$ -band holes were the same in the surface as in the bulk.

Pauling's model yielded similar conclusions but with additional features, such as the effect of the bonding and anti- or non-bonding electrons of the metal on the strength of chemisorption and the possibility of multiple chemisorption states.<sup>13</sup> Further details will be alluded to in the discussion of more recent data.

Electronic structure controls, through the Aufbau principle, all the properties of atoms and ensembles of atoms, so that many correlations of surface properties with physical properties (themselves dependent upon  $n(E_M)$ , etc.), are possible and have been recognized.

## EXPERIMENTAL RESULTS

The PdAg and PdAu alloys provide the best approximations to the model, because it is fairly clear<sup>14</sup> that the  $4d$ -band of Pd is full at all atomic fractions  $\leq 0.4$  Pd and that the alloys show little sign of short-range clustering.<sup>15</sup> NiCu alloys give evidence of clustering or even of phase change.<sup>16</sup>

### Chemisorption

The accommodation of energy at surfaces is difficult to determine but data exist for the series of PtCu alloys, showing<sup>17</sup> for ethane that the transfer of vibrational energy decreases monotonically as the  $5d$ -band is filled.

Most molecules are chemisorbed extensively (coverage,  $\theta$ ,  $\sim 1$ ) strongly and swiftly by the transitional metals of groups 4 to 8 but much less so by the metals of groups 1B and 2B.

Chemisorbed hydrogen could not be detected on the Au-rich alloys of the PdAu series containing more than 55–60 per cent Au and a similar trend has been found for PtCu alloys;<sup>18–20</sup> manganese chemisorbs hydrogen only very weakly (heat,  $\nabla H \sim 15$  k cal mole<sup>-1</sup>).<sup>21, 22</sup> If the heats of adsorption of hydrogen and ethylene are normalized to unity at nickel and plotted against the difference between  $E_M$  and the average electronic energy for each transitional metal, then they lie on one curve showing<sup>13</sup> a rise to the left of group 8 and a fall to its right.

It is now well known that a given crystal face can sustain adsorbates in more than one chemisorbed state sometimes corresponding to different simple, ordered surface arrays, such as those visualized by early workers.  $\Delta H(\theta)$  always decreases with increasing  $\theta$  and the strongly-bound complexes are often associated with a negative surface dipole, as was to be expected from the simple theory.<sup>2</sup>

### Absorption

Interstitial solutions and compounds with H, B, C, N, O, etc., are similar in bonding to, and may affect, chemisorption at apical, bridging, and interstitial surface sites. The heats of formation decrease with increasing  $r$ , but sharp changes in the properties are often found for values of  $r$  between 5 and 7 (especially for H, C, and N) and at  $r \sim 10.6$  for H.

In the second long period it has been shown that the heats of solution of hydrogen (and oxygen) fall abruptly in alloys (Ti–Nb, Ti–Mo) with  $r \geq 5.6$ , where  $n(E_M)$  decreases rapidly and the bonding orbitals are becoming full.<sup>23, 24</sup> In group 8 palladium combines exothermally with molecular hydrogen to form a solid solution ( $\alpha$ ) and a hydride ( $\beta$ ), containing H atoms in octahedral interstices, with a limiting composition  $\sim \text{PdH}_{0.6-0.7}$ , where the magnetic properties suggest that the  $4d$ -band is just full.<sup>25</sup> The solubility in the substitutional PdM alloys ( $M = \text{Cu, Ag, Au}$ ) also decreases to small values near the composition  $\text{PdM}_{0.6}$  (full  $d$ -band) after passing through a maximum near  $\text{PdM}_{0.25}$ ; these characteristics have been associated with electronic effects and lattice strain as the  $4d$ -band fills and the lattice expands.<sup>24</sup>

For some nitrides ( $\text{Mn}_4\text{N}$ ,  $\text{Fe}_4\text{N}$ ,  $\text{Fe}_3\text{NiN}$ ) and carbides, modern techniques have demonstrated that the interstitial atoms share electrons (3 for N, 2 for C) with their octahedrally disposed metal neighbours<sup>27</sup> and suggest that the instability of nickel nitride is associated with the inability to accommodate the electrons in the  $e_g(\text{Ni})$  orbitals.<sup>28</sup>

### Catalysis

The determination of the variations of activity in a series of alloys is complicated by the difficulties encountered in obtaining truly homogeneous series of solid solutions of the same crystalline texture, without clustering or surface segregation. The *d*-metals possess much greater intrinsic activity than *s,p*-metals in all the reactions of hydrogen and of hydrocarbons, including oxidation.

The trend of activity with *r* illustrated in Fig 1 is frequently found. The rates of hydrogenation of ethylene and propylene and of the H<sub>2</sub>-D<sub>2</sub> exchange over the palladium-hydrogen alloys also decrease with increasing H/Pd ratio approaching zero (H<sub>2</sub>-D<sub>2</sub>) at the critical compositions.<sup>29</sup> The activation energies are usually higher for compositions rich in *s,p*-metal, although examples of the reverse are known,<sup>30</sup> and the transition from low to high values may be gradual or stepped, but with a change of slope at or near the critical composition. Little has been done with single crystal solid-solutions apart from a significant result with carbon monoxide disproportionation over the Ni-Cu series<sup>31</sup>; only the (110) face has activity but this falls monotonically from pure nickel to the critical composition.

It is noteworthy that high activity for nitrogen hydrogenation first appears in the iron sub-group at the edge of the region of stable nitrides.

Overall, it appears that the bulk and surface properties of metals depend upon common factors which produce the similar patterns of behaviour and activity. The interatomic distance in metals and alloys of the same structure cannot alone account for the large differences, so that the significance of "electronic structure" must be examined in greater detail.

### SURFACE STATES ON METALS

The surface atoms have ground and excited states which are related to those of interior atoms; the problem is to specify the electronic configurations at the surface.

### The Geometry

Most types of defect have been observed at the atomic scale but little can be predicted concerning their concentration or distribution. The surfaces of clean crystals  $\geq 100$  Å in size usually have the expected geometry and are therefore taken to be atomically smooth and to have the structure appropriate to the lattice and the plane. Adsorbed species may lie outside the surface plane (above or bridging metal atoms), within the plane at an open interstitial site, or below the plane. This progression represents solution for the atoms H, C, and N but molecules and radicals cannot bond to atoms in penultimate planes, except perhaps for those of low density, *e.g.* FCC (110), BCC (100).

### The Orbitals

Current theories indicate that the interior molecular orbitals of the transitional metals are constructed principally from an *s* orbital and the five, degenerate, even, *d*-orbitals of the constituent atoms. In fields of cubic symmetry, the *d*-orbitals split into two groups labelled *e<sub>g</sub>* ( $= d_{z^2}, d_{x^2-y^2}$ ) and *t<sub>2g</sub>* ( $= d_{xy}, d_{yz}, d_{zx}$ ) which are directed respectively towards the face-centres and (after hybridization) the corners of a cube. In BCC metals, where *e<sub>g</sub>* overlaps only with

next-nearest neighbours, a simple model suggests that  $e_g$  orbitals may be more localized and higher in energy, on average, than  $t_{2g}$ , which form a wide band. Many workers have used the especially suitable even orbitals ( $s$ ,  $d$ ,  $ds$ ,  $d^2sp^3$ ) for qualitative interpretations of bonding and frequent attempts have been made to justify the division into localized (quasi-atomic) and de-localized orbitals, but opinion now favours the itinerant electron of the modern band theory.<sup>32</sup>

Calculation and experiment confirm that a narrow (4–6 eV)  $d$ -band is overlapped by a wide  $s$ -band; that in the typical transitional metal  $n(E_M)$  is large (but much smaller in Cu, Ag, and Au) and that  $n(E)$  for the  $d$ -band of cubic metals has, broadly, a twin-peaked structure. The unpaired magnetic electrons are in  $d$ -like orbitals at  $E_M$  and in FCC metals, such as nickel, have marked  $t_{2g}$  character, so that the spin density tends to be highest along the body diagonals.<sup>33</sup> FCC cobalt may have slightly more electrons in  $e_g$  orbitals, but in BCC iron the bonding and anti-bonding states seem to be slightly  $t_{2g}$  and  $e_g$ , respectively, in character.

Surface atoms will adjust their bonds to minimize the surface energy and the use of given bonding capacity among fewer neighbours implies an increased pair-wise bond strength of about 10 per cent.<sup>34</sup> There may, therefore, be some re-hybridization, as by the formation of odd hybrids with  $p$ -orbitals directed inwards ( $p_z d_{z^2}$ ) or laterally ( $d_{sp^2}$ ); an associated reconstruction of virgin surfaces remains in doubt, but there is a small weakening and extension of bonds perpendicular to the surface.<sup>35</sup> The  $p$  levels of the atoms lie appreciably (3–4 eV) above  $d$  and  $s$ , so the extent of admixture will be small and seems to favour the in-plane bonds.

### The Energy of Surface States

Fig 3 gives a rough indication of the energy of interior states for some metals and alloys.<sup>36</sup> At the surface, some narrowing of the bands may occur because of fewer neighbours. A localized  $3d$  state at a nickel surface would lie approx 1.5 eV below  $E_M$ <sup>32</sup> at the centroid ( $E_c$ ) of the band system.

### Occupation of the Surface Orbitals

The electronic state of the surface atoms depends upon the energy of the orbitals with respect to  $E_M$  and to the "spreading" and "smoothing" invoked to account for the variation of  $\phi$  between crystal faces.<sup>37</sup> In spreading, the electrons move into the outward directed orbitals,  $d_{z^2}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $p_z$  on (001) but this is counteracted in smoothing by the occupation of laterally-directed orbitals ( $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $p_x$ ,  $p_y$ ) so that the number and distribution of  $d$ -band holes may not be the same as in the interior.

In the ferromagnetic metals, the saturation magnetization is a measure of the number of holes in the  $d$ -band and the Curie point is a sensitive index of the interatomic forces coupling unpaired species on adjacent atoms. Neither of these decreases significantly in small crystals (diameter,  $D$ ) until  $D \leq 20$ –40 Å,<sup>38</sup> where about half the atoms are in the surface and the X-ray, K-adsorption edges begin to differ from those for massive metal. Also, the dissociative chemisorption of hydrogen on nickel reduces the saturation magnetization by 0.5–0.72  $\mu_B$  per adatom, approximately as found for solution in bulk nickel, but the decrement is less for  $D < 40$  Å.<sup>39</sup>

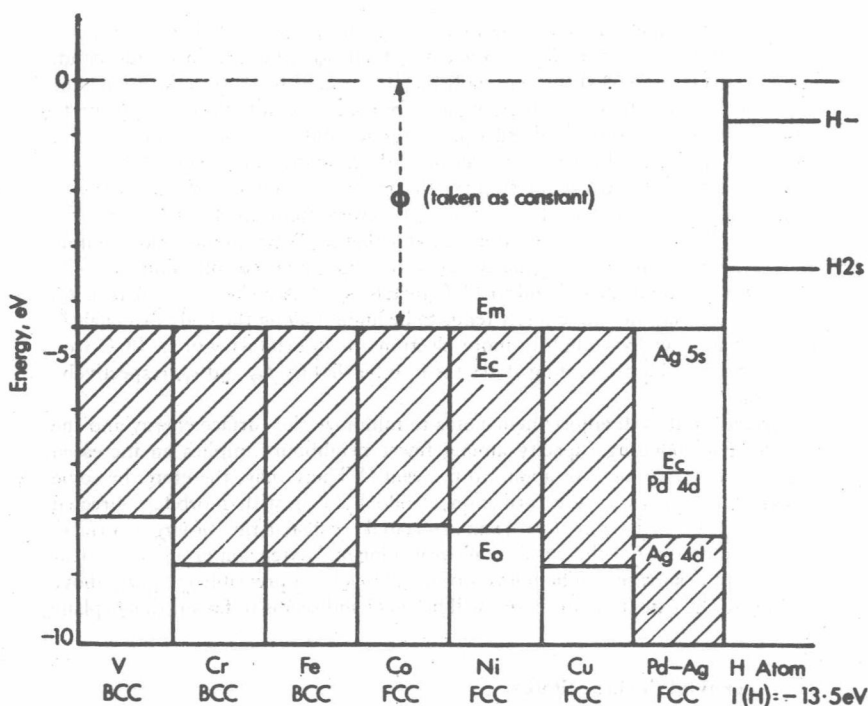


FIG 3. Band positions in metals.

The electronic configuration at the surface appears to differ but slightly from that of the interior if the crystals are not too small.

### ELECTRONIC EFFECTS IN SOLUTION

Because some kinds of chemisorption are akin to solution, it is appropriate to consider the progression of states as a solute atom moves towards the surface. The interaction of the solute with the solvent can be treated as a perturbation of the band system of the metal by the potential due to the foreign atom; it leads either to the separation of a localized level from the band, the establishment of a virtual state, or both, as shown by Friedel.<sup>12</sup> Alternatively, the interaction can be seen as the deployment of specific orbitals on individual atoms to form molecular orbitals.<sup>9</sup>

#### Screening Effects

A hydrogen atom, for example, is ionized, the proton introduced into an interstice, and the electron into the Fermi surface. The electron will remain near the proton and Friedel showed for solid solutions how the screening of the excess charge ( $Z = 1$ ) depends upon the properties of the metal and the impurity.

The character of the bond, as in all bonding, depends upon the energy of the valency electrons of the partners, given by the ionization potential ( $I$ ) and the electron affinity ( $E'$ ) for the solute and by the energy of the bottom of the band

( $E_0 = E_m + \phi$ ) for the metal. There are then three kinds of screening according to whether  $E' < E_0 < I$  (one bound electron forming a neutral species), or  $E_0 \ll E'$  (two bound electrons — a negative ion), or  $E_0 > I$  (screened by mobile electrons displaced locally within the band). The third case is common and much depends upon the radius within which the charge is screened. The following results are relevant:

1. The screening radius ( $R_0$ ) at very small concentrations depends in a first approximation only upon  $n(E_M)$  and is, therefore, much larger for  $sp$  than for  $d$  metals. At higher concentrations, solutes should interact when their screening charges overlap, as in copper, iron, and nickel at  $R_0 \approx 4.7$ ,  $1.7$ , and  $1.1$  Å, respectively.

If  $R_0$  is greater than the radius of the atomic sphere, solutes in  $sp$ -metals with  $Z > 0$  yield a small fraction of their excess electrons to adjacent atoms of the solvent and the subsequent charges give rise to an electrostatic interaction which may cause short-range ordering. Generally, there is repulsion between species having  $Z$  of the same sign and attraction for opposite signs. In ferromagnetic metals, the overlapping electrons enter the band of electrons of one spin and high  $n(E_M)$ , so altering the saturation magnetization.

2. In a better approximation, these conclusions are modified only slightly;  $R_0$  now depends upon  $Z$ ,  $n(E_M)$ , and  $\partial n(E)/\partial E_M$ ; screening is concentrated close to the impurity but with a smaller, long-range component of electron density. In metals with  $\partial n(E)/\partial E_M > 0$ , the electrons are more strongly displaced for  $Z > 0$ , increasingly so for increasing  $Z$ , and  $R_0$  is somewhat smaller, whereas the reverse is true for  $\partial n(E)/\partial E_M < 0$ . In  $d$ -metals  $n(E_M)$  is large but  $R_0$  can be large for  $Z > 0$ ; in metals with less than one hole in the  $d$ -band (e.g. Ni, Pd, Pt), where  $R_0$  is greater than the atomic radius, solutes with  $Z = 1$  (H, Cu, Ag, Au) must interact at small concentrations. Consequently, interstitial hydrogen adjacent to a substitutional atom in  $d$ -metal alloys will be in a region of incomplete screening and will be repelled by substituents with  $Z > 0$ , but attracted if  $Z < 0$ .<sup>40</sup> It is evident, in the absence of significant size effects, that marked changes in solubility, heats of solution, and even structure should occur at values of  $r$  where large changes of  $n(E_M)$  and  $\partial n(E)/\partial E_M$  occur.

### Orbital Descriptions

Hydrogen, carbon, nitrogen, and oxygen atoms are found in the octahedral interstices of their solutions and compounds with transitional metals. The valency orbitals ( $s$  for hydrogen,  $p$  for the rest) are overlapped by the  $e_g$  orbitals of the metal atoms giving rise to bonding and anti-bonding molecular orbitals.<sup>28</sup> Situations are favoured in which the bonding orbitals can accommodate the metal  $e_g$  electrons and the valency electrons of the interstitials.

### CHEMISORPTION

Extension of the theory to chemisorption has been suggested and Grimley<sup>41</sup> has shown that effects similar to those found for solutes should exist, but it becomes necessary to distinguish between the several types of chemisorption (Fig 4).



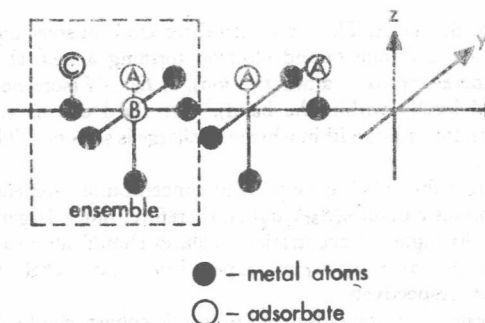


FIG 4. Adsorption sites on (001) FCC.

### Interstitial

The analogy with solution is appropriate only for type B adsorption, in which small adatoms reside at open interstices or where the lobe of an orbital of a radical or molecule can overlap such a site. Consequently, in a rough approximation, the results for solutes may be applied directly to adsorbates and, in the absence of size effects which should be somewhat less important in the surface interstices, it appears that pronounced changes in chemisorption occur when  $n(E_M)$  and  $\partial n(E)/\partial E_M$  become small and the gradient changes sign, in accord with the observed patterns of activity. Unfortunately, neither of these properties is accurately or widely known throughout the periodic table, so that attention is paid to their well-known, broader variations rather than to the multiplicity of maxima found in theoretical calculations of  $n(E_M)$ . Major changes in  $n(E_M)$  are found between group 8 and group 1B and near-groups 6 and 7 (although differences exist here between the long periods). Theoretical and experimental evidence has been given for a small energy gap or  $n(E_M)$  minimum near  $E_M$  in chromium<sup>42</sup> and for a deeper minimum at  $E_M$  in  $\alpha$  and  $\gamma$ -manganese, where it also separates the bonding from the anti-bonding states.<sup>45</sup> Thus the small heat of chemisorption of hydrogen in manganese can be understood. In the second long period, the amount and the strength of B hydrogen chemisorption should depend upon  $r$ , just as does the solubility.<sup>44</sup> In the third long period, a relative minimum should exist near W and Re.

The other implications will not be developed here, as they follow directly from the above, but it is evident that dissolved hydrogen in palladium must inhibit the chemisorption of species with similar properties. Also, the chemisorption of nitrogen as atoms ( $Z = 3$ ) occurs only on metals where an appreciable number of atoms can have three holes in the  $d$ -band (e.g. Fe), just as proposed in the original theory.

### Apical

The analogy with solutions is weak for chemisorptions of types A and C, in which the adsorbate centres lie outside the envelope of the surface atoms. A molecular orbital approach is more practical; the bonds may be single- or multi-centred and of  $\sigma$ ,  $\pi$ ,  $\delta$ , etc., types.<sup>45</sup>

A hydrogen atom, atop a metal atom (type C) overlaps negligibly with other