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# The Electronic Factor in Heterogeneous Catalysis

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## I. INTRODUCTION

The theoretical approach to the subject of surface catalysis was first considered in a series of classical papers by Langmuir (1), who suggested that the adsorbed particles are held to the surface by chemical forces, and applied the theory to interaction of adsorbed species at adjacent adsorption sites on the surface. Langmuir pointed out that steric hindrance effects between molecules might play a prominent part, and the role of the geometric factor in catalysis was greatly emphasized by Balandin and others. The importance of this factor has already been reviewed in this series by Trapnell (2) and Griffiths (3).

As early as 1928, Roginskii and Schul'tz (4) stressed the importance of electronic considerations, and Rideal and Wansbrough-Jones (5) related the work function of metals to the activation energy for their oxidation. Brewer, 1928 (6), Schmidt, 1933 (7), and Nyrop, 1935 (8) proposed that the surface must be capable of effecting ionization of the adsorbed species in some catalytic processes. Lennard-Jones (9) in his

theory of chemisorption on metal surfaces considered the possibility of covalent bond formation due to the pairing of a valence electron of the adsorbed atom and an electron from the conduction band of the metal.

Further developments in the fundamental approach to the electronic structure of catalysts were made possible by the development of the quantum mechanical treatments of solids which followed the work of Sommerfeld, Bloch and others. Similarly, Pauling's resonating valence bond treatment has lent further impetus to consideration of metallic catalysts.

## II. THEORIES OF THE SOLID STATE

### 1. Quantum Mechanical Theory

The molecular orbital treatment of a crystalline solid considers the outer electrons as belonging to the crystal as a whole (10,11). Sommerfeld's early free electron theory of metals neglected the field resulting

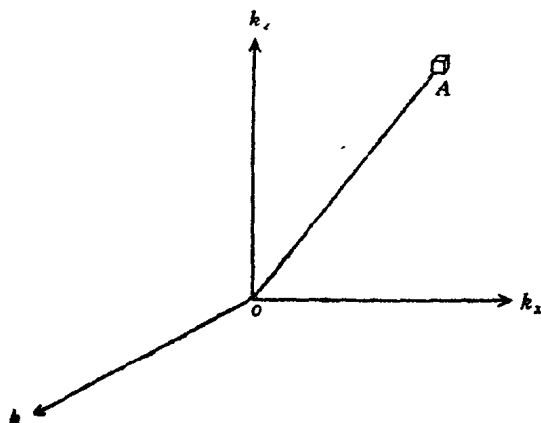


FIG. 1. Momentum diagram.

from the array of metallic nuclei. A great advance was made by Bloch and others who assumed that the electrons move in a field whose periodicity is that of the crystal lattice. The possible energy states for the electrons can be obtained from the solutions of the Schrödinger equation

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - U)\psi = 0 \quad (1)$$

In the consideration of the momentum of a large number of particles restricted to a volume  $V$ , it is often convenient to describe the system by an assembly of points in a momentum diagram (Fig. 1). The length  $OA$  represents the magnitude of momentum of the particle  $A$ , and its direction is  $\vec{OA}$ . The application of Heisenberg's uncertainty principle leads to the

restriction that the momentum of any particle cannot be represented by a point, but must be associated with a volume  $h^3/V$  ( $h$  is Planck's constant). This means effectively that momentum space must be divided into cells of volume  $h^3/V$ , each cell corresponding to an energy state, and from Pauli's Principle each of these states can contain two electrons. Furthermore, the energy of the assembly will be a minimum when the occupied states are clustered about the origin. The wavelength of a free electron is given by  $1/\lambda = mu/h$ . Since the wave number  $k = 2\pi/\lambda$ , it is obvious that a  $k$ -diagram may be constructed in a manner similar to that

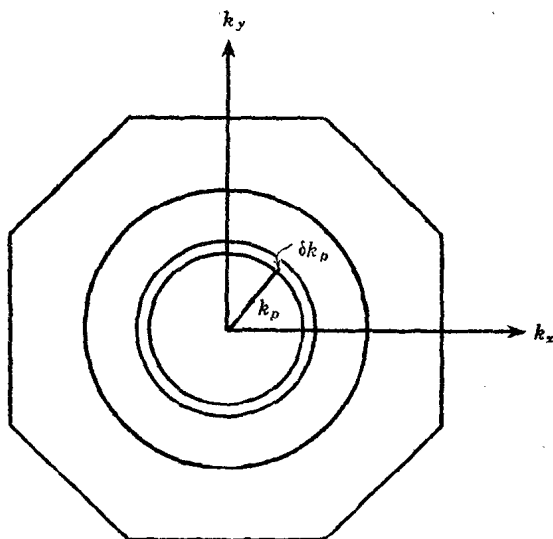


FIG. 2. Brillouin zone for a two dimensional crystal.

used for the momentum diagram. The boundary between occupied and unoccupied states in  $k$ -space is referred to as the Fermi surface. When the periodic field of the lattice is taken into account, the wave number is no longer simply related to the momentum ( $mu$ ). The wave mechanical examination of the equation for the motion of an electron in a periodic field shows that the energy does not vary continuously with the wave number. This means that in any one direction in  $k$ -space, there will arise energy discontinuities as the states are filled. These regions can be represented in the  $k$ -diagram by surfaces; the regions bounded by such surfaces are usually termed Brillouin zones. Figure 2 represents a Brillouin zone for a two-dimensional crystal; in the figure, the Fermi surface is circular and the states are not completely occupied by electrons up to the boundary of the Brillouin zone.

A typical energy distribution curve is represented by Fig. 3. An elec-

tron state, value  $k_p$  in  $k$ -space, will have an energy  $E_p$ . The number of states  $N(E)$  in the energy band  $dE_p$  is related to the volume of the spherical shell, and it can be seen that  $N(E)$  in a range  $dE_p$  will increase with  $E_p$ . The maximum at  $E_2$  occurs at the point where the Fermi surface first touches the Brillouin zone. A rapid decrease of  $N(E)$  then occurs because there are no energy states available for some directions of the wave number  $k$ . If the first and second Brillouin zones do not overlap, on completion of the first band, the next available electron state will involve an increase in energy of  $(E_4 - E_2)$ . If the first and second zones overlap, the addition of electrons will fill the first zone to the point where the

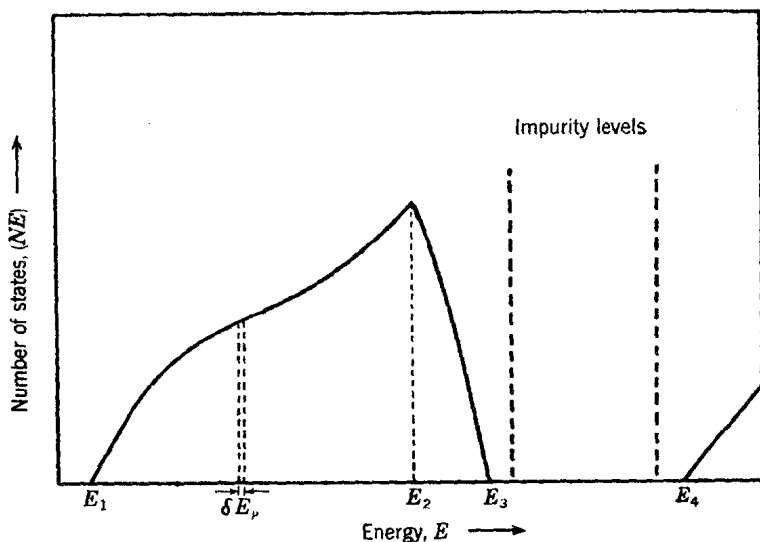


FIG. 3. Typical electron bands.

highest filled states of the first zone have the same energy as the lowest filled states of the second zone. More electrons will then enter the states of both zones. The resulting  $N(E)$  curve has the form shown in Fig. 4.

The effect of an external electric field is to produce an acceleration of the electrons in the direction of the field, and this causes a shift of the Fermi surface. It is a necessary condition for the movement of electrons in the  $k$ -space that there are allowed empty states at the Fermi surface; hence electrical conductivity is dependent on partially filled bands. An insulating crystal is one in which the electron bands are either completely full or completely empty. If the energy gap between a completely filled band and an empty band is small, it is possible that thermal excitation of electrons from the filled to the empty band will result in a conducting crystal. Such substances are usually referred to as intrinsic semiconductors. A much larger class of semiconductors arises from impurities

in the crystal. The introduction of foreign atoms generally creates additional energy levels, and these impurity levels may lie within the energy gap, as shown in Fig. 3. At temperatures above absolute zero there are two possible processes which may occur: either electrons may be thermally excited from the impurity levels to the empty band, or electrons from the filled band may be excited into the impurity levels. In both cases partly occupied bands are produced, and the crystal becomes conducting.

(a) *Alloys*. In the formation of simple alloys, the progressive substitution of one type of metal atom by another type with different valency

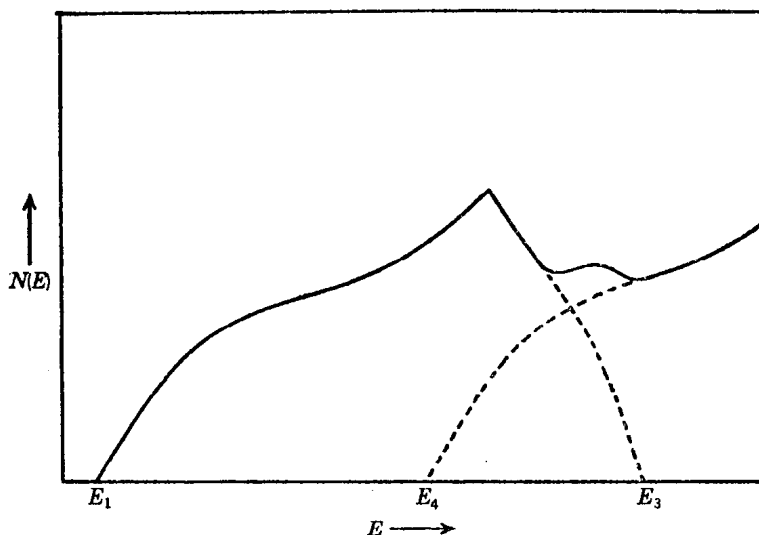


FIG. 4. Overlapping electron bands.

changes the ratio of valence electrons to metal atoms of the crystal. This ratio has been termed the electron concentration. The Fermi level of the solvent metal will be either raised or lowered depending on whether the solute metal has a higher or lower valency. Many properties of alloys can be related to the electron concentration.

Hume-Rothery (12,13) has pointed out that in some alloys the structure of the intermetallic phases are determined by the electron concentration (E.C.). The work of Hume-Rothery and others has shown that the series of changes (i.e.  $\alpha$  phase  $\rightarrow$   $\beta$  phase  $\rightarrow$   $\gamma$  phase  $\rightarrow$   $\epsilon$  phase), which occurs as the composition of an alloy is varied continuously, takes place at electron-atom ratios of  $3/2$ ,  $21/13$ , and  $7/4$ , respectively. The interpretation of these changes in terms of the Brillouin zone theory has been made by H. Jones (14) and can be understood from the  $N(E)$ -curves for typical face centered cubic (a) and body centered cubic (b) structures as



shown in Fig. 5. The alloying of univalent metals, such as copper, silver, and gold, with higher valence elements is considered to be a process in which the solute elements merely serve to increase the electron concentration. The higher the  $N(E)$ -curve, the greater is the number of electrons which may be accommodated in states within the energy range concerned, and hence the lower will be the energy necessary to accommodate a given number of electrons. In Fig. 5 it can be seen that up to the point *A* the face centered cubic structure has the lower energy and will be the stable phase of the alloy. Beyond point *A* the number of states decreases rapidly, and addition of more electrons into the band causes a rapid increase in energy. At some point, the body centered cubic structure

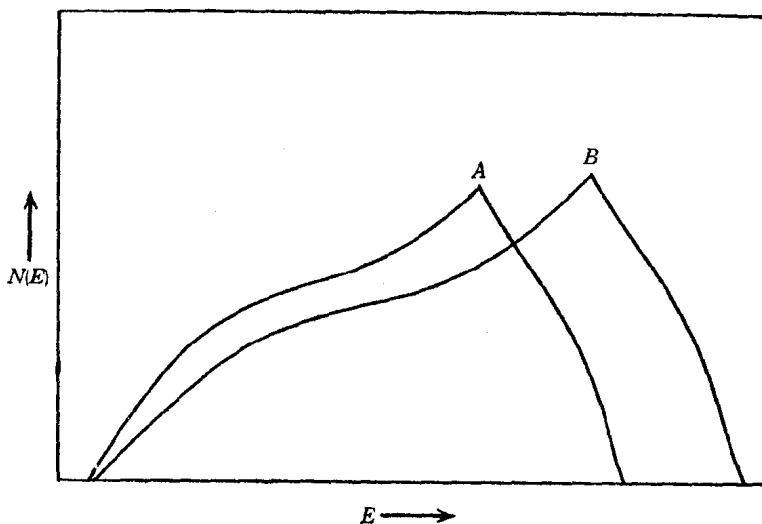


FIG. 5. Interpretation of Hume-Rothery alloys in terms of Brillouin zone theory.

becomes more stable than the face centered cubic structure, since the electron band in the former can accommodate the same number of electrons with a lower energy. H. Jones has calculated the electron-atom ratios corresponding to the maximum  $N(E)$ -peaks for each of the four phases, and has obtained the values  $\alpha = 1.362$ ,  $\beta = 1.480$ ,  $\gamma = 1.538$ . These values for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phases agree quite well with the Hume-Rothery values for the corresponding phase changes.

(b) *Transition Metals.* The transition metals are characterized by ferromagnetism or strong paramagnetism and by their comparatively low electrical conductivity. According to Mott and Jones (10), the outermost electrons are considered to occupy two bands. In the first long period of the periodic table these bands arise from the  $3d$  and  $4s$  atomic states. The broadening of the  $3d$ -band is much less marked than that of the

s-band, since the smaller 3*d*-orbitals overlap to a lesser extent. The broadening process can be seen from Fig. 6(a). The density of states is five per atom in the *d*-band and is one per atom in the s-band. The actual  $N(E)$ -curves for some transitional elements may be complex, but it is more convenient in this discussion to represent the s- and *d*-bands in their general form (Fig. 6(b)). Considering nickel as a typical example, the ten outermost electrons per atom must be shared between the two bands. There is strong evidence that there are 9.4 electrons per atom in the 3*d*-band and 0.6 in the 4*s*-band. The electron bands of copper will not

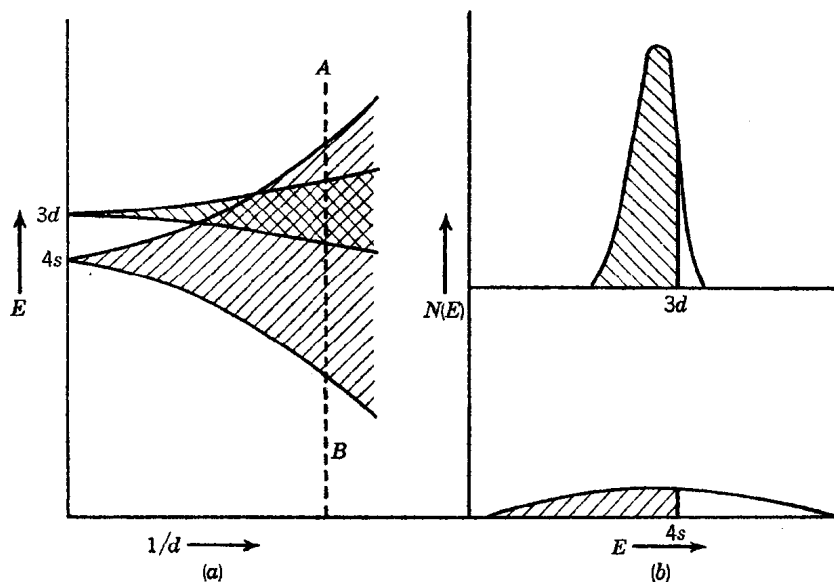


FIG. 6. Electron bands of transition metals.

differ appreciably in energy from those of nickel, but the addition of another electron will completely fill the *d*-band and half fill the s-band, in agreement with its monovalent nature. From this point of view, the ferromagnetism of iron, cobalt, and nickel is almost entirely due to the spins of the *d*-electrons and the saturation magnetization intensity expressed in Bohr magnetons per atom is approximately equal to the number of "holes" in the *d*-band (Fe, 2.2; Co, 1.7; Ni, 0.6). The noninteger number of electrons in the *d*-band can be understood if they are considered as average values for a crystal containing the configurations  $(3d)^{10}$ ,  $(3d)^9$ , and  $(3d)^8$ . Mott and Jones consider that only the  $(3d)^{10}$  and  $(3d)^8$  configurations are important, the two holes in the shell of the  $(3d)^8$ -ion having the same spin. The strong paramagnetism of platinum and palladium, which is probably also due to electron spin, and the physical

properties of their alloys can be explained by this theory if there are about 0.55–0.6 holes in the  $d$ -band.

(c) *Transition Metal Alloys*. The theoretical consideration outlined above readily explains the changes in properties accompanying alloy formation of transition metals with other metals. If we take as an example the Cu–Ni alloys, the replacement of nickel atoms by copper atoms will add extra electrons to the lattice. Since the density of states in the  $d$ -band is much greater than in the  $s$ -band, the added electrons will enter the  $d$ -band until it is filled. As the atomic percentage of copper in the alloy increases, the saturation magnetic moment decreases; extrapolation to zero magnetic moment shows that the  $d$ -band is just full at 60%. The addition of an atom of palladium, zinc, or aluminium will increase the number of electrons in the  $d$ -band by 0, +2, or +3 respectively. Similarly, for the palladium and platinum alloys with copper, silver, and gold, the atomic susceptibility drops as the percentage of solute increases, the susceptibility becoming negligible at a concentration of about 55% of the monovalent metal (10,11). This confirms the assumed number of  $d$ -“holes” in these two metals.

The solution of hydrogen in palladium must be considered as a different type of alloy system, because the hydrogen cannot replace palladium in the lattice structure. The fall in susceptibility to zero at a hydrogen–palladium ratio of 0.55 suggests that all the electrons of the hydrogen atoms enter the  $4d$  palladium levels (11).

## 2. Resonating Valence Bond Theory

Pauling (15–17), in an approach more easily described in language familiar to chemists, considers that metal bonds resemble ordinary covalent bonds, all or most of the outer electrons of the metal atoms taking part in bond formation. He suggests that when the number of possible positions at which bonding can occur is greater than the number of bonds, resonance occurs about the available positions.

This approach explains satisfactorily the decrease in bond length with increasing valency in the sequences of elements  $K \rightarrow Cr$ ,  $Rb \rightarrow Mo$ , and  $Co \rightarrow W$ . The number of electrons available for bond formation in these metals increases with valency, and therefore, according to the resonating valence bond theory, the number of bonds resonating about the available positions increases, resulting in smaller bond lengths.

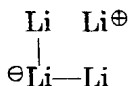
The magnetic properties of these elements also fit into this concept. In metallic vanadium for example (atomic configuration  $3d^3 4s^2$ ), if the  $4s^2$  electrons only were involved in bond formation, the cores of the atoms would have a large dipole moment with the result that ferromagnetism or strong paramagnetism decreasing with increasing temperature should

be exhibited. Contrary to this, vanadium is only weakly paramagnetic, the paramagnetic moment being almost temperature independent. This indicates that all its outer electrons are involved in bond formation. Similarly, all elements in the sequences mentioned above are either diamagnetic or weakly paramagnetic.

Lithium may serve as an example for illustrating the general picture of resonance structures in metals. Pauling points out that it is unlikely that synchronized resonance, i.e. resonance of two bonds simultaneously, of the type:



could give the stabilization necessary to explain the strength of metallic bonding. He shows that a much greater resonance stabilization can be achieved by resonance of one bond involving electron transfer.



According to this concept, the metallic properties are based on the possession by some or all of the atoms in a given metal of a free orbital (the "metallic orbital"), in addition to the orbitals required for bonding and nonbonding electrons, thus permitting uninhibited resonance of valence bonds. For the case of tin, the following scheme illustrates these relationships for three electronic structures (A, B, and C) of this metal:

		3d	4s	4p	
Sn (A) $v = 4$	Kr	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\cdot$	$\cdot \quad \cdot \quad \cdot$	$\uparrow\downarrow$ atomic electrons
(B) $v = 2$	Core	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow$	$\cdot \quad \cdot \quad \circ$	$\bullet$ valence electrons
(C) $v = 0$		$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \quad \circ \quad \circ$	$\circ$ metallic orbitals

} i.e. electrons occupying bonding orbitals

where  $v$  is the valency of the metal atom in each electronic structure. In Sn (A) there is no metallic orbital and therefore no metallic phase; the four electrons are hybridized to give  $sp^3$  tetrahedral bond orbitals. The nonmetallic form of tin, gray tin, does in fact have the diamond tetrahedral structure. Pauling suggests that the metallic form of tin (valency 2.44) consists of Sn (B) resonating with Sn (A), the Sn (B) configuration having the larger statistical weight. The loss in energy due to a decreasing number of bonds is largely compensated by the resonance energy gained.

Although the number of electrons theoretically available for bond formation increases with increasing atomic number in the series, Cr, Mn,

Fe, Co, Ni, the bond length in these metals remains practically the same, indicating about six bonds per atom for all five elements. Pauling suggests, as an additional hypothesis to account for this experimental data, that while some  $3d$ -orbitals may hybridize with  $4s$ - and  $4p$ -orbitals to give bonding orbitals, other  $3d$ -orbitals may be unsuitable for bond formation (atomic orbitals). The ferromagnetic saturation moment of iron, cobalt, and nickel can be attributed to unpaired, nonbonding, electrons in these atomic orbitals. By accepting this hypothesis, the following pictorial representation of the electronic structure of transition metals in the first long period of the periodic table is derived. Iron has a magnetic saturation moment of 2.22 Bohr magnetons. Therefore, of the eight electrons outside the argon core, 5.78 are bonding electrons and 2.22 are unshared electrons in nonbonding orbitals.

*Iron:* Eight electrons outside the argon core.

		$3d$	$4s$	$4p$	
Fe (A) $v = 6$	A	$\uparrow \uparrow \cdot \cdot \cdot$	$\cdot$	$\cdot \cdot \bigcirc$	Magnetic saturation moment 2 Bohr magnetons
Fe (B) $v = 5$	core	$\uparrow \uparrow \uparrow \cdot \cdot$	$\cdot$	$\cdot \cdot \bigcirc$	M.S.M. 3 Bohr magnetons

Both possible valence states contribute in the ratio 78:22, giving iron the necessary magnetic saturation moment of 2.22 magnetons. This concept leads to a valency of 5.78.

*Cobalt:* Nine electrons outside the argon core.

		$3d$	$4s$	$4p$	
Co (A) $v = 6$	A	$\uparrow \uparrow \uparrow \cdot \cdot$	$\cdot$	$\cdot \cdot \cdot$	
Co (B) $v = 6$	core	$\uparrow \downarrow \uparrow \cdot \cdot$	$\cdot$	$\cdot \cdot \bigcirc$	

The saturation moment of 1.71 magnetons indicates resonance between the two forms of electronic states in the ratio 35:65.

*Nickel:* Ten electrons outside the argon core.

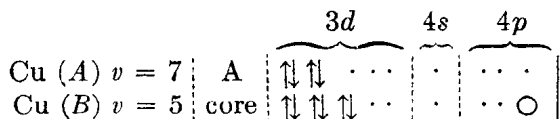
		$3d$	$4s$	$4p$	
Ni (A) $v = 6$	A	$\uparrow \downarrow \uparrow \uparrow \cdot \cdot$	$\cdot$	$\cdot \cdot \cdot$	
Ni (B) $v = 6$	core	$\uparrow \downarrow \uparrow \downarrow \cdot \cdot$	$\cdot$	$\cdot \cdot \bigcirc$	

The saturation moment of 0.6 magnetons corresponds to resonance in the ratio 30:70.

Developing this concept for elements following the transition metals, Pauling employs a system based on two observations in his paper (16): (1) A linear relationship holds between the "single bond" radius and

atomic number for bonds of constant hybrid character. (2) For an element, the single bond radius is approximately linearly dependent on the  $d$ -character of the  $d$ - $s$ - $p$  hybrid bond orbitals. Applying these observations, he is able to postulate a possible valence scheme and electronic structure for the metals of the first ascending branch, copper, zinc, etc.

*Copper:* Eleven electrons outside the argon core.



Metallic copper, on Pauling's hypothesis, involves resonance between structures *A* and *B* in the ratio 25:75, giving a valency of 5.5. Magnetic evidence indicates that platinum and palladium, occupying identical positions to nickel in the second and third long periods, also contain on the average 0.55 to 0.6 unpaired electrons in atomic orbitals. These elements, as well as other metals of the second and third long periods, are treated by Pauling in an identical fashion to the first long period discussed above.

*Percentage d-character:* Considering the electronic structure of metals thus derived, Pauling then calculates the "percentage  $d$ -character" of the metallic bonds, the percentage  $d$ -character being an indication of bond strength. As examples, we have chosen cobalt, nickel and copper (Table I).

TABLE I

*Percentage d-Character of Cobalt, Nickel, and Copper (Pauling Theory) (Brackets Indicate Bonding Orbitals)*

Metal	Outer electrons			Resonance ratio	Percentage $d$ -character
	3d	4s	4p		
Co(A)	$\uparrow \uparrow \uparrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot$	35	$35\%_{100} \times \frac{2}{6} + 65\%_{100} \times \frac{3}{7} = 39.5\%$
Co(B)	$\uparrow\downarrow \uparrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot \circ$	65	
Ni(A)	$\uparrow\downarrow \uparrow \uparrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot$	30	$3\%_{100} \times \frac{2}{6} + 7\%_{100} \times \frac{3}{7} = 40\%$
Ni(B)	$\uparrow\downarrow \uparrow\downarrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot \circ$	70	
Cu(A)	$\uparrow\downarrow \uparrow\downarrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot$	25	$25\%_{100} \times \frac{3}{7} + 75\%_{100} \times \frac{2}{6} = 35.7\%$
Cu(B)	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \cdot \cdot \cdot$	$\cdot \cdot \cdot$	$\cdot \cdot \cdot \circ$	75	

A list of the percentage *d*-characters of the elements in the first, second and third long period is given in Table II.

TABLE II  
*Percentage d-Character and Valency of the Transition Metals, According to Pauling (Proc. Roy. Soc. A196, 343 (1949))*

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Valency	3	4	5	(6,3)	(6,4)	5.78	6	6	5.5
Percentage <i>d</i> -character	20	27	35	39	40.1	39.7	39.5	40.0	36
Element	Y	Zr	Cb	Mo	Tc	Ru	Rb	Pd	
Valency	3	4	5	6	6	6	6	6	
Percentage <i>d</i> -character	19	31	39	43	46	50	50	46	
Element	Lu	Hf	Ta	W	Re	Os	Ir	Pt	
Valency	3	4	5	6	6	6	6	6	
Percentage <i>d</i> -character	19	29	39	43	46	49	49	44	

Whereas Pauling considers that all outer electrons take part in bond formation, Mott and Jones express the view that only the outer *s*-electrons are involved. Pauling was mainly concerned with explaining the properties of the transition metals and the preceding groups (bond lengths and ferromagnetism). The extension of the theory to latter groups is far less satisfactory. For example, on his hypothesis a valency of 5.44 for copper must be assumed. This has no experimental justification. On the other hand the Mott and Jones interpretation is more satisfactory for the elements copper, silver, and gold (one outer *s*-electron, therefore monovalent), but underestimates the part played by the *d*-electrons in the bonding of the transition metals.

The theoretical interpretation of the reactions concerning the earlier transition metals are more easily understood on Pauling's picture. Both the Pauling and the Mott and Jones interpretations can be usefully applied in reactions concerning the later transition elements.

### III. THE NATURE OF THE CHEMISORPTION BOND

It is now generally accepted that chemisorption of one or more of the reactants is essential in heterogeneous catalytic reactions, and a consideration of the nature of the bond between surface and substrate is therefore of decisive importance.

To explain the phenomena of "activated" adsorption, Lennard-Jones (9) in 1935 proposed a scheme for the adsorption of hydrogen on metal

surfaces as represented pictorially by Fig. 7. The transition from van der Waals adsorption to the chemisorbed states requires an energy of activation  $E$ . As recent work (18,19) has shown, there may be cases where adsorption of gases on "clean" surfaces proceeds rapidly with little or no activation energy.

The suggestion of ionic bond formation (6-8) has been strongly criticized by Emmett and Teller (20), and later by Couper and Eley (21), who calculated theoretically that all possible ionization processes are

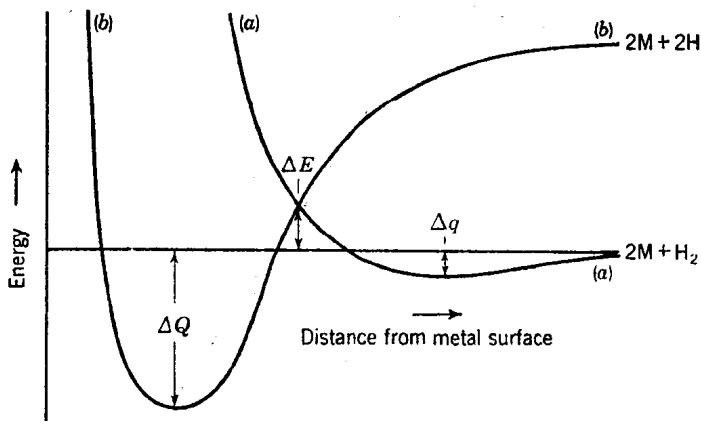


Fig. 7. Potential energy diagram for van der Waals (aa) and chemisorbed hydrogen (bb) [J. E. Lennard Jones, *Trans. Faraday Soc.* **28**, 333 (1932)].  $\Delta Q$  and  $\Delta q$  represent heats of chemisorption and van der Waals adsorption.  $\Delta E$  represents activation energy for chemisorption.

prohibitively endothermic on the surfaces of transition metals. In support of this criticism Eley (22) has pointed out that the experimental values of surface potentials, determined by Bosworth and Rideal (23), Oatley (24), and Mignolet (25), correspond to only a fraction of an electronic charge on a hydrogen atom adsorbed on tungsten and platinum respectively. However his calculation, that the small dipole of 0.4 Debyes for  $W^{3+} - H^{3-}$  corresponds to the transfer of approximately a tenth of an electronic charge, is only applicable if it can be assumed that the  $W \rightarrow H$  dipole is perpendicular to the surface.

Boudart (26) suggests that the presence of the electrical double layer produced by the surface dipoles can account for the observed fall in the heat of adsorption and change in work function as the surface coverage is increased. Furthermore, assuming that the dipole interaction is negligible, as will be the case for small surface coverages, the heat of adsorption and work function changes should be related by the equation

$$\Delta q = \frac{n}{2} \Delta \phi \quad (2)$$



where  $n$  is the number of valence electrons taking part in bond formation,  $\Delta q$  the change in heat of adsorption, and  $\Delta\phi$  is the work function change. Unfortunately only in a few cases is there sufficient data to test this relationship. In Table III the observed decreases in heats of adsorption are listed against the values calculated from the observed work function changes using Equation (2). The agreement is good for the adsorption of hydrogen and nitrogen, but is less satisfactory in the case of oxygen adsorption. It is probable that the large polarizability of oxygen increases the dipole interaction, and this may account for the deviation between the observed and calculated values.

TABLE III

Comparison between Calculated and Observed Heats of Adsorption (Boudart, *J. Am. Chem. Soc.* **74**, 3559 (1952))

		H <sub>2</sub> on W	H <sub>2</sub> on Ni	O <sub>2</sub> on W	N <sub>2</sub> on W	Cs on W
$\Delta q$ (kcal.)	Calculated	12	4	24	15.9	5
$\Delta q$ (kcal.)	Observed	13.5	5	30	15	5.4

The drop in heat of adsorption, and therefore in strength of the bond, will cause an "induced" heterogeneity. Boudart suggests that the presence of "active centers" is not necessarily due to an *a priori* heterogeneity of the surface, but may arise from this induction effect; only a small fraction of the surface will be active at any one time although the whole surface will be involved in catalysis.

Dowden (27) has considered the factors favoring (a) positive ion, (b) negative ion, and (c) covalent bond formation on metal surfaces.

(a) The ratio of the ionized to unionized species in the surface phase is given by (see Figure 8)

$$C_{A^+}/C_A = \frac{f(A^+)}{f(A)} \exp [-(I' + \mu_E^M)/kT] \quad (3)$$

where

$$I' = I + \Delta U^+ \quad (4)$$

and

$$\mu_E^M = -\phi - 1/6\pi^2 k^2 T^2 \left( \frac{d \ln N(E)}{dE} \right)_{E=-\phi} \quad (5)$$

$f(A^+)$ ,  $f(A)$  = partition functions for ionized and neutral particles,

$\mu_E^M$  = thermodynamic potential per metal electron per unit volume,

$I$  = ionization potential of the neutral particle,

$\Delta U^+$  = adsorption energy of the ion,

$\phi$  = electron exit work function.