SPECIFICITY IN CATALYSIS BY METALS

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Introduction

WE have to consider the factors which can cause variation in activity among different metal catalysts towards a reaction which proceeds on them with an identical mechanism.

In 1921 Langmuir suggested [1] that reaction at a surface would be retarded if the catalyst atoms were too far apart to enter into the necessary dissociation and re-association of reactant molecules. This implies that there is a *geometric* or *lattice spacing factor* in catalysis. The first evidence for it is probably that due to Adkins [2] who in 1922 concluded that in the decomposition of ethyl acetate a larger spacing of catalyst atoms is required for the formation of acetone than for the formation of olefin.

Not all of the features of catalytic specificity can be thus explained, and, in addition, activity must depend on the availability of orbitals in the catalyst for surface bonding. Such factors have been termed *electronic factors*. With the metals two types of electronic factor may operate, one when ionic bonds are formed at the surface, the other when covalent bonds are formed. For ionic layers, Wansbrough-Jones and Rideal [3] suggested in 1929 that the ease of passage of electrons across the surface, that is, the magnitude of the work function, will affect the reaction velocity. Most gases are, however, bound to metal surfaces by covalency, and here the transition metals or the near transition metals of Group IB of the periodic table are the best catalysts. Transition-metal crystals possess an incomplete *d* band, and the electronic factor in these cases is probably connected with this characteristic.

The velocity constant, k, of a catalytic reaction may be expressed as

$$k = A e^{-E/RT} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

with the usual nomenclature. In many cases E is the activation energy of a desorption process, and is given by

$$E = q + E' \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

where q is the heat, and E' the activation energy, of adsorption.

For high activity E must be small, so that E' and q must be small; that is, the adsorption of the reacting species should be weak yet rapid. When chemisorption is fast ($E' \rightarrow 0$), the requirement for high activity becomes a low heat of reactant adsorption. When it is activated, the requirements of low E' and low q may conflict, because metals which adsorb

[1] Langmuir, *Trans. Faraday Soc.*, 1921, **17**, 617.
[2] Adkins, *J. Amer. Chem. Soc.*, 1922, **44**, 2175.
[3] Wansbrough-Jones and Rideal, *Proc. Roy. Soc.*, 1929, A, **123**, 202.

rapidly tend to do so strongly, and those which adsorb weakly tend to do so slowly.

By obtaining experimental values of A and E for different metals in a given reaction some information might be derived as to the factors causing variation in activity.   For example, we shall discuss theoretical evidence that an important effect of the geometric factor is to alter E by altering E'.   Unfortunately, the quantities A and E cannot in general be determined experimentally.   In particular, the ordinary activation energy obtained from the temperature coefficient of velocity at constant gas pressure may be very different from the true energy.[4, 5]   It seems that to measure true energies temperature coefficients must be obtained at *constant adsorbed volume*, and that to attach significance to values of A and E obtained from log k–1/T plots at *constant pressure* is most unsound.

Probably the best way to study specificity is to compare values of k per unit surface area at a typical catalytic temperature.   This is now possible with the use of clean evaporated metal films, for known areas of these may be prepared by controlled evaporation *in vacuo*.[6]

The Geometric Factor

Theoretical Basis.—The activation energies of simple chemical reactions can be calculated [4] from the forces operating between the molecules, and in this way Sherman and Eyring [7] have calculated the energy of activation of hydrogen chemisorption by carbon.   Adsorption was represented by the scheme

$$\begin{array}{ccc} \text{H—H} & & \text{H \quad H} \\ & \rightarrow & \;|\quad| \\ \text{C—C} & & \text{C—C} \end{array}$$
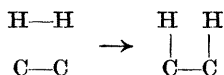
and the usual assumption was made that the electrostatic interaction energy amounted to 10% of the whole.   The C–H bond was assigned an energy of 92 kcal. and it was assumed that in chemisorption a C–C bond was broken the energy of which was 39 kcal.   Since the heat of dissociation of hydrogen is 103 kcal., the molar heat of chemisorption is then $2 \times 92 - 103 - 39 = 42$ kcal., and this is in agreement with experiment.[8]

The important feature of the work is that activation energies were calculated for various distances between carbon atoms.   The results, illustrated in Fig. 1, show that there is a most favourable spacing for adsorption, 3·5 Å, on either side of which the activation energy rises sharply. At very high separations of the carbon atoms, the hydrogen molecule must be effectively dissociated before chemisorption.   Therefore the activation energy of chemisorption is high and approaches the heat of dissociation

[4] Hinshelwood, " The Kinetics of Chemical Change ", Oxford Univ. Press, 1940.

[5] Rideal and Trapnell, *Discuss. Faraday Soc.*, 1950, **8**, 114.

[6] Beeck, Smith, and Wheeler, *Proc. Roy Soc.*, 1940, *A*, **177**, 62.

[7] Sherman and Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 2661.

[8] Barrer, *Proc. Roy. Soc.*, 1935, *A*, **149**, 253 ; *J.*, 1936, 1256.

of the hydrogen molecule.   At very low separations, the activation energy is again high because adsorption is hindered by repulsion forces.   That is, chemisorption being represented as :

$$C^1C^2 + H^1H^2 \longrightarrow C^1H^1 + C^2H^2$$
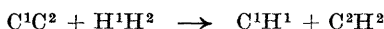
repulsions between the atoms C^1 and H^2 and between C^2 and H^1 are appreciable and raise the activation energy.

The results shown in Fig. 1 agree fairly well with experiment.[8]   On graphite, where the carbon atoms are disposed in flat hexagonal rings, the most favourable distance for chemisorption is on opposite atoms of a
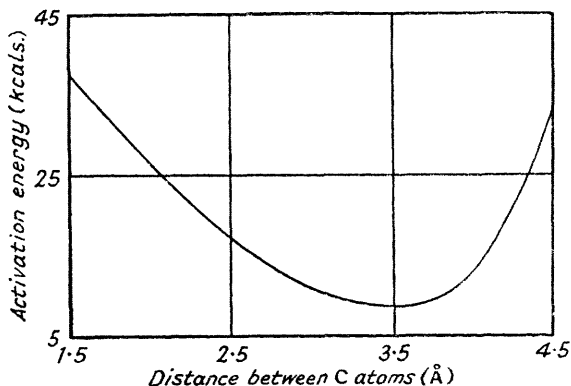

FIG. 1

Chemisorption of hydrogen by carbon.

hexagon where the spacing is 2·84 Å.   The theoretical activation energy, 14 kcal., then agrees moderately well with the experimental value of 22 kcal. On diamond, the corresponding spacing is 2·80 Å, and the theoretical energy, 15 kcal., is very near the experimental value of 14 kcal.

The calculations may therefore be taken as semi-quantitative.   Furthermore, since the activation energy of adsorption enters into that of desorption, we may expect a similar effect in desorption.

The activation energy of a process in which a gas-phase molecule reacts simultaneously with two or more chemisorbed atoms or radicals may similarly be influenced by lattice spacing.   An example is the removal of chemisorbed hydrogen from a surface as ethane by interaction with gaseous ethylene :

$$\begin{array}{ccc} CH_2{=}CH_2 & & CH_3{-}CH_3 \\ H \quad H & \longrightarrow & | \quad | \\ | \quad | & & | \quad | \\ M{-}M & & M{-}M \end{array}$$
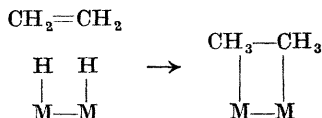
Many metal surfaces, however, enter into chemisorption of simple gases without an energy of activation.   For example, chemisorption of ethylene, acetylene, hydrogen, oxygen, ammonia, and carbon monoxide by the

transition metals is non-activated. In such cases, surface geometry can only affect the quantity E of equation (2) by altering q. Such an effect is probably rare because bond energies are not connected with lattice spacing. However, if the molecule as a whole is adsorbed at more than one point, q may vary with spacing owing to strain ; thus, Twigg and Rideal [9] considered the adsorption of ethylene on nickel by two-point attachment :

$$CH_2{=}CH_2 \qquad\qquad CH_2{-}CH_2$$
$$Ni{-}{-}{-}{-}Ni \quad\rightarrow\quad Ni{-}{-}{-}{-}{-}{-}Ni$$

By taking the Ni–C bond length to be the same as in nickel carbonyl, 1·82 Å, and the C–C bond length from the normal paraffins, 1·54 Å, it is possible to calculate the Ni–C–C valency angle for various lattice spacings. On the 2·47 Å spacing the angle is 105° 4′, and on the 3·50 Å spacing it is 122° 57′. The former angle is very near the tetrahedral angle, 109° 28′, and such strain as is involved may be alleviated by twisting the molecule so that the C–C and Ni–Ni axes lie at a small angle to one another. Adsorption on the 3·50 Å spacing, however, involves considerable strain, and this is only increased by twisting. The heat of adsorption on the 2·47 Å spacing may therefore be somewhat larger than that on the 3·50 Å spacing, and 3·50 Å spacings might as a result be more active in the reactions of ethylene than 2·47 Å spacings.

Similar calculations have been made by Herington [10] for two-point acetylene chemisorption :

$$CH{=}CH$$
$$Ni{-}{-}{-}{-}Ni$$
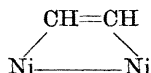
In this case the ideal spacing of nickel atoms proves to be about 3·3 Å, and chemisorption will therefore take place more strongly on 3·50 Å spacings than on 2·47 Å spacings.

A consequence of the theoretical work on lattice spacing is that different crystal planes of the same metal, through exposing different spacings, may differ in catalytic power. For example, the (111) plane of nickel contains only 2·47 Å spacings, while the (110) plane contains both 2·47 and 3·50 Å spacings. By Twigg and Rideal's reasoning this should cause a higher activity of the (110) plane in ethylene hydrogenation, and this actually proves to be the case, as will be seen in the following section.

Experimental Basis.—Early evidence for a geometric factor is due to Balandin,[11] who studied the reactions of six-membered rings at metal surfaces. Typical reactions are the hydrogenation of benzene and dehydrogenation of *cyclo*hexane. In these, the benzene molecule was supposed to lie flat on the surface, and we may picture it as held by six metal–carbon bonds [12] as shown in Fig. 2. In this Figure, catalyst atoms are situated at the intersection of the lighter lines. A certain support for the mechanism

[9] Twigg and Rideal, *Trans. Faraday Soc.*, 1940, **36**, 533.
[10] Herington, *ibid.*, 1940, **37**, 361.
[11] Balandin, *Z. physikal. Chem.*, 1929, **2**, B, 289 ; *ibid.*, 1929, **3**, B, 167.
[12] Trapnell, " Advances in Catalysis ", Academic Press, New York, 1951, vol. 3.

is that neither *cyclo*hexene nor *cyclo*hexadiene has been detected in the products of either reaction.

For such an adsorption to be geometrically possible, the crystal face would have to show hexagonal symmetry, with the spacing lying between
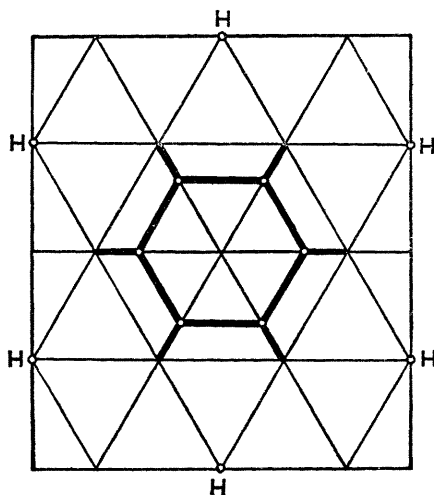

FIG. 2

Chemisorption of cyclohexane.

sharply defined limits. Only (111) planes of face-centred cubic and hexagonal close-packed crystals are suitable, and Balandin claimed that active metals all crystallised in one or other of these habits, and possessed spacings

TABLE 1.   *Structure and atomic radii in Å of some metals*

Body-centred cubic lattices		Face-centred cubic lattices		Close-packed hexagonal lattices	
Mo	1·48	Ce	1·82	Zr	1·61
Ta	1·36	Th	1·80	Mg	1·60
W	1·36	Pb	1·74	Cd	1·48
V	1·30	Ag	1·44	Tı	1·45
Fe	1·29	Au	1·44	*Ru*	1·38
Cr	1·24	Al	1·43	*Os*	1·36
		Pd	1·37	(*Zn*	1·33)
Other lattices		*Pt*	1·35	Be	1 14
		Ir	1·35		
		Rh	1·34		
In	1·62	(*Cu*	1·28)		
Sn	1·40	*Co*	1·26		
Mn	1·24	*Nı*	1·24		

falling between certain limits. Table 1 shows the atomic radii of some common metals, with those active in the dehydrogenation of *cyclo*hexane noted in italics. Copper and zinc, although being geometrically favourable, are inactive because of an unfavourable electronic factor.

The most favourable spacing, on which the MCC valency angle has the tetrahedral value, is some 2·69 Å, close to the mean, 2·61 Å, of the upper and lower limits for activity.

The inactivity of the body-centred cubic metals seems to offer particular support for the theory. The most favourable plane of these metals, the (110) plane, has atoms disposed as isosceles triangles, and the geometry of the most favourable of such planes, that of iron, is readily shown [12] to be less favourable than that of any of the active metals.

Several workers have confirmed the inactivity of these metals. Long, Frazer, and Ott [13] and Emmett and Skau [14] found iron powders to be inactive in benzene hydrogenation, whereas comparable surface areas of cobalt, nickel, and palladium were highly active at similar temperatures.

However, in contrast with these results, Beeck and Ritchie [15] find that iron films are highly active in the hydrogenation of benzene, with the velocity per unit area at room temperatures approaching one half that on nickel.

The cause of the divergence between the results on iron powders and films is not clear, but the activity of the films is inexplicable on the basis of Balandin's hypothesis. Furthermore, recent knowledge suggests that very many metals are inactive in these reactions not because of unfavourable surface geometry but because of an unfavourable electronic factor. For example, silver, cadmium, aluminium, lead, indium, and tin are probably inactive because they are non-transition metals. Thus there may be activity when the geometric factor is unfavourable, and inactivity through electronic causes, so that it is not possible to divide the metals into active and inactive categories simply on the basis of surface geometry. Nevertheless, a further result [15] does show that surface geometry is a factor in deciding the velocity at least of the dehydrogenation of *cyclo*hexane ; this is that non-oriented platinum films show higher activity per unit surface area in the reaction than do oriented films.

With platinum, oriented films preferentially exposing (110) planes may be prepared, and the non-oriented films therefore expose a larger proportion of other planes, in particular of (111) planes. If, as Balandin suggested, reaction proceeds most easily on (111) planes, non-oriented films should be more active per unit area than oriented films. In fact, they are ten times as active.

In the hydrogenation of benzene, however, oriented and non-oriented nickel films have identical activities. Possibly the two reactions differ because chemisorption of *cyclo*hexane is activated whereas that of benzene is non-activated. Since surface geometry alters activation energies of chemisorption,[7] if these participate in the rate equation, surface geometry would operate in the dehydrogenation of *cyclo*hexane but not in the hydrogenation of benzene.

Differences in activity by oriented and non-oriented nickel films are shown towards the hydrogenation of ethylene, the former, which again

[13] Long, Fraser, and Ott, *J. Amer. Chem. Soc.*, 1934, **56**, 1101.
[14] Emmett and Skau, *ibid.*, 1943, **65**, 1029.
[15] Beeck and Ritchie, *Discuss. Faraday Soc.*, 1950, **8**, 159.

expose (110) planes preferentially, being five times more active.[6]   This effect can probably be ascribed to the high activity of the 3·50 Å spacing of the (110) plane, in agreement with the prediction already made on theoretical grounds.

This result led Beeck [16] to attempt to classify the activity of the transition metals in the hydrogenation of ethylene in purely geometric terms. We shall see later that the attempt was unwise because it took no account of electronic factors, but it is convenient to discuss it at this point.   In Fig. 3, the logarithm of the velocity constant of reaction at a particular
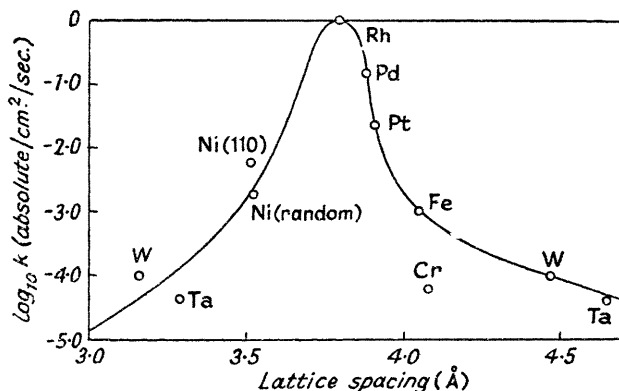

FIG. 3

Activity of transition metals in the hydrogenation of ethylene.

temperature for unit area of a number of metal films is plotted against lattice spacing.   Sometimes it is difficult to know which spacing to choose, as at least two possible spacings present themselves.   In general, the edge length of the fundamental cube has been used, the exceptions being iron and chromium.   With tungsten and tantalum two spacings have been included.   The points for the various metals, with the possible exception of chromium, lie on a smooth curve, suggesting that lattice spacing determines catalyst activity.   The most favourable spacing, 3·75 Å, is that of rhodium.

Similar effects might be expected with the hydrogenation of acetylene. The results [17] are not so complete as for that of ethylene, but at room temperatures iron and tungsten are inactive, and palladium is twenty times and rhodium and platinum are ten times as active as nickel.   The results are similar to those with ethylene, with the difference that the maximum activity has shifted to a longer spacing, namely, from rhodium to palladium. Herington's [10] theoretical considerations predict such an effect.

Electronic Factors

The Influence of d-Band Structure.—(a) *The theory of metals.*   The early theory of metals, associated particularly with Mott and Jones,[18] is

[16] Beeck, *Rev. Mod. Physics*, 1945, **17**, 61.

[17] *Idem, Discuss. Faraday Soc.*, 1950, **8**, 118.

[18] Mott and Jones, " The Theory of Metals and Alloys ", Oxford Univ. Press, 1940.

characterised by two assumptions. The first is that the cohesive forces are due to interaction of the outermost s electrons alone. The second is that the electrons are considered as a whole, without reference to individual atoms. That is, the theory is a collective electron theory, with the electron wave function confined only to the metal crystal, not to the neighbourhood of individual atoms.

The treatment suggests that the electrons in metals retain much of the character which they possess in the isolated atom. Thus it is still possible to talk of s, p, and d electrons in the crystal as in the isolated atom. A difference, however, is that whereas in the isolated atoms the energies of the various spectroscopic states are discrete and single-valued, the energies in the crystal broaden into a band of permitted energies. Thus with nickel, the $3d$ shell of the isolated atom becomes the $3d$ band in the crystal.

The number of electrons per atom in the shells of isolated atoms may differ from the number in the bands of the crystals. For iron and nickel, for example, the configurations of the outer electrons of the atoms are respectively $3d^6 4s^2$ and $3d^8 4s^2$, but in the crystal [18] the band structures are on the average $3d^{7\cdot 8} 4s^{0\cdot 2}$ and $3d^{9\cdot 4} 4s^{0\cdot 6}$. Nevertheless it is the important distinguishing feature of the transition metals that their crystals possess incomplete d bands, in the same way that the isolated atoms possess incomplete d shells.

The newer theory of metals is due to Pauling.[19] In this, the electron wave function is localised round a particular atom or pair of atoms, while cohesion is ascribed to resonance between all possible structures in which the electrons form definite one- or two-electron bonds between atoms in the crystal. In the transition metals, the bonding orbitals are hybrid orbitals of d, s, and p states similar to those found in complex ions.

If, in passing along a transition period, the increase in the number of d electrons merely resulted in an increase in the number of bonding orbitals, the cohesion would increase continuously. This, however, is not found to happen, for, taking the melting point as a convenient index of bond strength, the maximum value always occurs before the end of the transition period in question. This and other evidence led Pauling to conclude that there are three types of d orbital, namely : (i) bonding d orbitals, participating in (dsp) hybrid bonds ; (ii) atomic d orbitals, associated with individual atoms, but not used in bonding ; (iii) metallic d orbitals, participating in electric conduction. In passing along a transition period, the electrons at first primarily enter bonding d orbitals, but after about Group VII, these are full, and the electrons then primarily enter atomic d orbitals. At the end of the period these also are full.

(b) *The importance of* d-*band structure in chemisorption.* The characteristic of the transition metals according to the newer theory is that they possess vacant atomic d orbitals : for the present purposes these correspond largely with the incomplete d band of the older theory. It was then

[19] Pauling, *Phys. Review*, 1938, **54**, 899 ; *Proc. Roy. Soc.*, 1949, *A*, **196**, 343.

suggested by Dowden [20] and independently by Dilke, Maxted, and Eley [21] that the high catalytic activity of the transition metals could be explained if chemisorption involved the metal d band. Thus, in reactions of gases bound to the surface by covalency, non-transition metals would be relatively inactive because there are no d-band vacancies through which covalency could take place.

The first evidence that chemisorption involves the d band (or atomic d orbitals) was provided by Dilke, Maxted, and Eley,[21] who measured the change in magnetic susceptibility of palladium on adsorption of dimethyl sulphide.

Palladium, by virtue of unpaired electrons in the atomic d orbitals, is strongly paramagnetic. If, on adsorption, electrons entered atomic d orbitals, the paramagnetic susceptibility of the surface atoms would be reduced through the pairing of electrons involved, but if surface bonding took place with some other type of orbital, e.g., a (dsp) hybrid orbital employed before adsorption in cohesion, there would be almost no change in susceptibility because the electrons before and after adsorption would be paired. The results are shown in Table 2.

TABLE 2.   *Susceptibility of palladium powders*

Moles $(CH_3)_2S$ per g.-atom of Pd	$100\left(\dfrac{\Delta\chi}{\chi}\right)$	$100\left(\dfrac{\Delta\chi}{\chi}\right)_{Pd}$	$100\left(\dfrac{\Delta\chi}{\chi}\right)_{Calc.}$
0·27	10·1	8·0	13·5
0·23	7·9	6·0	11·5

The second column shows the percentage change on chemisorption of the susceptibility, χ, of the metal plus adsorbed dimethyl sulphide, and the third column the change in the susceptibility of the palladium alone, that is, after subtraction of the calculated diamagnetic susceptibility of the dimethyl sulphide from the total change. The last column gives the decrease in susceptibility calculated on the assumption that the susceptibility of the surface palladium atoms is reduced to zero.

The calculated decrease is larger than the observed decrease, probably because the powder was incompletely freed from initial contamination, so that not all the surface atoms were able to enter into chemisorption. However, the experimental change is of the same order of magnitude as would be expected for bonding with atomic d orbitals, and several orders of magnitude larger than could arise from bonding with any other orbitals.

Evidence for such bonding in the case of hydrogen and ethylene layers has been provided by Beeck,[17] from measurements of the heats of chemisorption of these gases by a number of transition metals. With both these gases, the surface dipole produced on adsorption is small,[22] and this suggests that the surface bond is a covalency.

For covalency with atomic d orbitals, the heat of chemisorption should increase progressively as the number of available orbitals increases. The

[20] Dowden, *Research*, 1948, **1**, 239 ; *J.*, 1950, 242.
[21] Dilke, Maxted, and Eley, *Nature*, 1948, **161**, 804.
[22] Mignolet, *Discuss. Faraday Soc.*, 1950, **8**, 105.

question is whether any quantity is available which is a measure of the number of such orbitals. The quantity suggested by Beeck [17] is Pauling's d character of the metal bond.[19] This is designated δ, and is calculated from the single-bond radius of the metal, R_1, and the number of electrons, z, in the neutral atom outside the inert gas shell. For the metals of the first transition period the relation is

$$R_1 = 1 \cdot 825 - 0 \cdot 043z - (1 \cdot 600 - 0 \cdot 100z)\delta \qquad . \qquad . \quad (3)$$

and similar equations are available for the other periods. Values of δ calculated in this way are shown in Table 3.

TABLE 3. *Percentage* d *characters of the metals*

First transition period	Sc 20	Ti 27	V 35	Cr 39	Mn 40·1	Fe 39·7	Co 39·5	Ni 40·0
Second transition period	Y 19	Zr 31	Nb 39	Mo 43	Tc (46)	Ru 50	Rh 50	Pd 46
Third transition period	Lu 19	Hf 29	Ta 39	W 43	Re 46	Os 49	Ir 49	Pt 44

Equation (3) shows that a low value of R_1, which at constant z indicates strong bonding, is associated with a high value of δ. A large δ thus indicates a large number of bonding d orbitals, and therefore a low availability
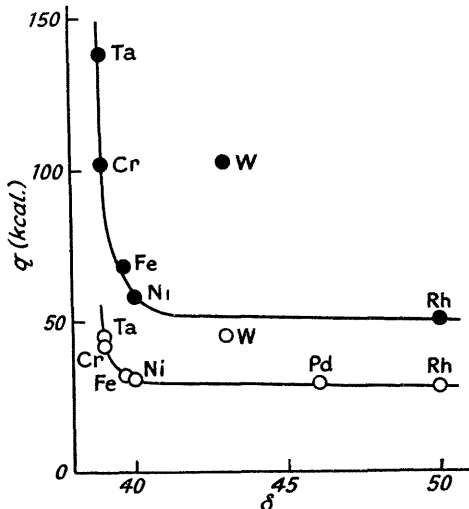

FIG. 4

Heats of chemisorption of hydrogen (open circles) and of ethylene (black circles).

of atomic d orbitals. If these are used in chemisorption the heats of adsorption should decrease continuously as δ increases, and Fig. 4 shows that with the possible exception of tungsten this is the case.

Beeck claimed that tungsten was not in fact exceptional, because his films crystallised in an abnormal face-centred cubic form for which δ would be nearer to 39%. In this case the points for tungsten would lie on the curves. Wahba and Kemball [23] have, however, recently remeasured the heat of hydrogen chemisorption on a body-centred cubic tungsten film, and obtained a value identical with Beeck's.

Trapnell [24] has argued that if the normal rapid chemisorption of simple gases is due to formation of a covalency with the d band, it should be largely confined to the transition metals. In Table 4 are shown data on the activities of some twenty metals between $0°$ and $-183°$ towards the gases nitrogen, hydrogen, carbon monoxide, ethylene, acetylene, and oxygen. These are expressed as " gas chemisorbed " ($+$) or " gas not chemisorbed " ($-$).

TABLE 4.   *The activities of the metals in chemisorption*

| Group | Metals | | | Gases | | | |
		N_2	H_2	CO	C_2H_4	C_2H_2	O_2
A	W, Ta, Mo, Ti, Zr, Fe, Ca, Ba	$+$	$+$	$+$	$+$	$+$	$+$
B	Ni, Pt, Rh, Pd	$-$	$+$	$+$	$+$	$+$	$+$
C	Cu, Al	$-$	$-$	$+$	$+$	$+$	$+$
D	K	$-$	$-$	$-$	$-$	$+$	$+$
E	Zn, Cd, In, Sn, Pb, Ag	$-$	$-$	$-$	$-$	$-$	$+$
F	Au	$-$	$-$	$+$	$+$	$+$	$-$

The metals may be divided into six groups, designated A to F in order of decreasing activity. With few exceptions high activity is associated with transition metals. No transition metal is in the less active groups C, D, E, and F, while the most active groups A and B, with the exception of calcium and barium, contain only transition metals. Also, while calcium and barium are not usually classed as transition metals because their isolated atoms contain no outer electrons in $3d$ and $5d$ states respectively, there is good evidence [25] that in the metal crystals, some electrons are in $3d$ and $5d$ bands. In this case calcium and barium share with the transition metals the property of a partly filled d band.

Chemisorption of nitrogen, hydrogen, carbon monoxide, ethylene, and acetylene was believed to be due to covalency with a d band, for very few non-transition metals chemisorb these gases. The only exceptions are the adsorption of carbon monoxide, ethylene, and acetylene by copper, gold, and aluminium, and of acetylene by potassium.

Of these apparent exceptions, copper and gold immediately succeed transition periods, and although they possess complete d bands, it was shown to be possible [24] for d–s promotions to accompany chemisorption, creating

[23] Wahba and Kemball, *Trans. Faraday Soc.*, 1953, **49**, 1351.
[24] Trapnell, *Proc. Roy. Soc.*, 1953, *A*, **218**, 566.
[25] Manning and Krutter, *Phys. Review*, 1937, **51**, 761.

d-band vacancies and allowing covalency with the d band. Probably, however, the activities of aluminium and potassium are true exceptions to the mechanism.

Chemisorption of nitrogen as atoms does not proceed on all transition metals, for the group B metals do not dissociate nitrogen. These metals contain either one or two vacancies in the d shell of the isolated atom, whereas the group A metals have three or more vacancies, and it is tempting to associate the requirement of three vacancies with the high valency of the nitrogen atom.

Chemisorption of oxygen, which is universal on all metals except gold, cannot on this account proceed by d-band covalency. With the non-transition metals at least the surface bond is probably largely ionic, with electron donation from s and p bands. The failure of gold to chemisorb oxygen may then be due to its possessing exceedingly tightly bound s electrons.

(c) *The importance of* d-*band structure in catalysis.* Since the chemisorption of simple gases other than oxygen involves the d band, and the heat of chemisorption, at least of ethylene and hydrogen, is determined by the Pauling d character, the variation of catalytic activity among metals might also be determined by the d character. A fair number of investigations have been carried out to test this hypothesis. These can be divided into cases where the catalysts were binary alloys of varying composition and cases where the catalysts were pure metals.

Catalysis by binary alloys. Many of the experiments with alloys have used solid solutions of a transition metal and a Group Iʙ metal, notably copper–nickel and palladium–gold solutions. With these, the lattice spacing hardly changes with composition, so that variation of activity from alloy to alloy may be ascribed simply to electronic factors.

In both cases the pure transition metal contains some 0·6 vacancy in the d band per metal atom,[18] but as Group Iʙ metal is added, these vacancies are filled by donation of the single outermost s electrons of the Group Iʙ metal atoms to the d band. Consequently, between 0 and 60 atomic % of Group Iʙ metal, the crystal contains d band vacancies, though in extent linearly diminishing as the percentage of Group Iʙ metal increases, while at 60 atomic % the d band is full, and remains so on further addition.

In cases where the reactants are bound by covalency with the d band, high activity would be expected between 0 and 60 atomic % of Group Iʙ metal, but at 60% chemisorption suddenly becomes far more difficult, and there should be a sudden drop to far lower activity, which should continue at higher percentages.

Such behaviour was found by Couper and Eley [26] in the ortho–para-hydrogen conversion by palladium–gold alloy filaments. The results, plotted as log k against $1/T$, are shown in Fig. 5. At a particular temperature, the activity varies little between 0 and 60 atomic % of gold, while above 60 atomic %, there is a very sharp fall in the value of k.

Further experiments compared the activity of a clean outgassed palladium filament with that of one charged with dissolved hydrogen. Hydrogen,

[26] Couper and Eley, *Discuss. Faraday Soc.*, 1950, **8**, 172.

being held in solution in palladium as protons with donation of electrons from hydrogen to the metal d band, should reduce the catalytic activity. In fact, the activity at 0° was reduced by some three hundred times.

Similar results have been obtained by Dowden and Reynolds,[27] who have used powder or foil catalysts of known surface area. In the hydrogenation of ethylene, and in the decomposition of formic acid and methanol by copper–nickel alloys, the activity per unit area fell sharply as the copper content exceeded 60 atomic %. On binary alloys of iron and nickel, an
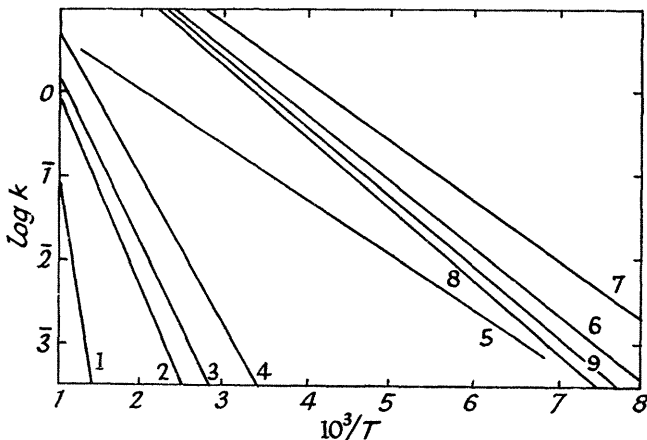

FIG. 5

Ortho–para-hydrogen conversion on Pd–Au *alloys.*

Atomic percentages of palladium · 1, 0 ; 2, 10 ; 3, 20 ; 4, 30 ; 5, 40 ; 6, 55·2 ; 7, 70 ; 8, 90 ; 10, 100%.

extension of the theory suggested that the catalytic activity should rise sharply as the nickel content rose above 80 atomic %, and this proved to be the case in the hydrogenation of styrene.

Further work has been carried out by Schwab,[28] using binary solid solution catalysts with silver as solvent. This work has been interpreted from a somewhat different standpoint, but we may note that alloying with the transition metals palladium and platinum increases the activity in formic acid dehydrogenation quite markedly, while alloying with the electronically similar metals copper and gold causes little change, and alloying with non-transition metals of Groups II, III, and IV of the periodic table causes a considerable fall in activity. This again suggests that high activity is to be associated with systems possessing an incomplete d band.

Catalysis by pure transition metals. Beeck's results [17] on the hydrogenation of ethylene by transition metal films of known area are shown in Fig. 6 plotted as log k against δ, and against the heat of hydrogen chemisorption. With the probable exception of tungsten, a smooth curve may

[27] Dowden and Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184 ; Reynolds, *J.*, 1950, 265.

[28] Schwab, *Trans. Faraday Soc.*, 1946, **42**, 689.

be drawn through the points for all the metals, the catalytic activity increasing continuously with increasing d character, that is, with decreasing heat of chemisorption.

This suggests that d character controls the activity, a result in contradiction with the result claimed earlier by Beeck, that lattice spacing decides the activity. The measurements seem to support both hypotheses equally well. The reason for this in general terms is that the d character is shown by equation (3) to control the lattice spacing. Therefore, in suggesting that lattice spacing controls catalytic activity, we are in fact implying that d character is important.
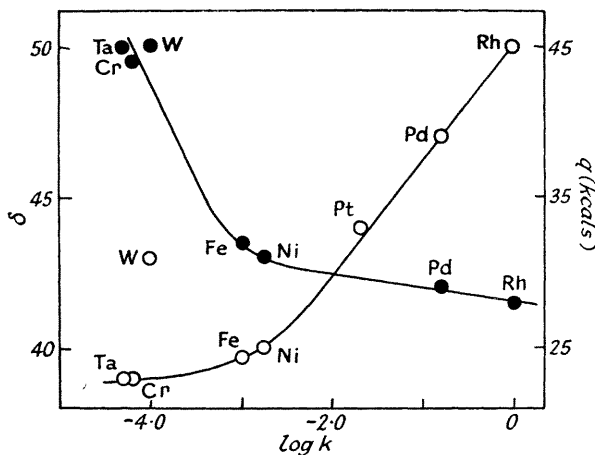

FIG. 6

Hydrogenation of ethylene by transition metals.

● Heats of adsorption.   ○ % d character.

A certain difference of mechanism is however implied in the operation of geometric and electronic factors, and probably the electronic factor is of primary importance. This is indicated by the close parallel between the heats of chemisorption and the catalytic activity shown in Fig. 6. Now the variation among heats is not easily ascribed to surface geometry for this is only possible if the molecule is chemisorbed at two points without dissociation, and this is not the case with hydrogen :
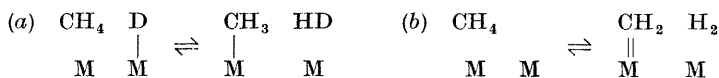
$$2M + H_2 \ \longrightarrow \ 2MH$$

Variation in heats of hydrogen chemisorption must therefore be decided by the availability of atomic d orbitals, and since the catalytic activity follows the heat of chemisorption of hydrogen, the variation in activity is probably due to electronic factors. That is, the hydrogenation of ethylene proceeds most readily on rhodium not because the 3·75 Å spacing is most favourable as regards activation energies, but because the high d character of rhodium enables it to chemisorb the reactants weakly and form a highly reactive surface layer.

A similar conclusion may be drawn from Beeck's results [17] on the hydrogenation of acetylene, although the higher activity of palladium than rhodium, in spite of its possessing a lower d character, must be ascribed to surface geometry.

The last reaction suitable for discussion from the viewpoint of d character is the exchange between methane and deuterium studied at the surfaces of evaporated films of six transition metals by Kemball.[29]

Reaction proceeded by two mechanisms, one resulting in the production of monodeuteromethane, the other responsible for the production of di-, tri-, and tetra-deuteromethane. The two mechanisms may be represented by

$$(a) \quad \begin{array}{cc} CH_4 & D \\ | & | \\ M & M \end{array} \rightleftharpoons \begin{array}{cc} CH_3 & HD \\ | & \\ M & M \end{array} \qquad (b) \quad \begin{array}{cc} CH_4 & \\ | & | \\ M & M \end{array} \rightleftharpoons \begin{array}{cc} CH_2 & H_2 \\ \| & \\ M & M \end{array}$$

where a full line represents chemisorption and a dotted line physical adsorption. For efficient catalysis, rapid adsorption and desorption of methane are required, and equation (2) indicates that for this the heat and activation energy of chemisorption must both be low. The adsorption of methane, unlike the chemisorption of ethylene and acetylene, is activated, and the requirement of a low activation energy may oppose that of a low heat, because the more active adsorbing agents, while giving low activation energies, may give high heats of adsorption.

From Table 3 of Kemball's results it is possible to calculate the velocities of the two processes at the typical reaction temperature $200°$. Values are shown in Table 5, expressed as molecules exchanging per unit area of film per second.

TABLE 5.   *Methane–deuterium exchange at* $200°$

Metal	Ni	Pd	Pt	Rh	W
$\text{Log}_{10}R_a$ . . .	13·3	14·5	14·7	15·2	15 2
$\text{Log}_{10}R_b$ . . .	13·8	12·9	14·6	16·2	14·8

Iron films were found to be quite inactive at $425°$ in both reactions. A possible error of a factor of four in measuring R_a and R_b arises owing to an uncertainty of this magnitude in the surface areas under catalytic conditions. Therefore, for the reaction producing monodeuteromethane the order of activities may be written :

$$\text{Rh,W} > \text{Pt,Pd} > \text{Ni} > \text{Fe}$$
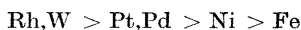
and for the second reaction it is

$$\text{Rh} > \text{W, Pt} > \text{Ni} > \text{Pd} > \text{Fe}$$
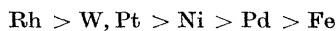
If the factor determining the reaction velocity is the magnitude of the heat of the chemisorption of methane, with rapid reaction due to a low

[29] Kemball, *Proc. Roy. Soc.*, 1951, *A*, **207**, 534 ; 1953, *A*, **217**, 376.

heat following from a high d character, the expected order of activities is :

$$Rh > Pd > Pt > W > Ni > Fe$$

For both reactions there are similarities between this order and the experimental order.   Rhodium in both cases is extremely active, and the relative activities of rhodium, platinum, nickel, and iron follow the order of d characters.   The striking divergences are the high activities of tungsten and the low activity of palladium in the second reaction, and there is no very satisfactory explanation of either of these facts.

The Influence of the Work Function.—The heat of adsorption of a positive ion formed from a neutral atom or molecule may be calculated in the following manner.

(1) From a molecule of adsorbate at an infinite distance from the surface, abstract an electron, and transfer it to the adsorbent.   If the ionisation potential of the molecule is I, and the work function of the adsorbent is ϕ, the energy liberated is $\phi - I$.

(2) With the adsorbent at zero potential, bring the ion to its equilibrium distance r_0 from the surface.   The energy liberated is the work done by the forces of attraction.   The image force of attraction causes a liberation of heat $e^2/4r_0$: there may also be an extra energy q^* arising from short-range interaction.   The total heat is then

$$q = \phi - I + e^2/4r_0 + q^*$$

For adsorption as negative ions

$$q = E^* - \phi + e^2/4r_0 + q^*$$

where E^* is the electron affinity of the adsorbate.   Similar expressions will hold when adsorption involves dissociation.

For the same adsorbate on different surfaces, if r_0 and q^* do not vary greatly, variation of ϕ becomes the main cause of the variation in the heat of chemisorption, and therefore possibly in the velocity of catalytic reaction. Since work functions vary among catalytically active metals by 30 kcal. or more, the effect may clearly be considerable.

The first instance in which it is suggested that the work function controlled the velocity of a surface reaction is due to Wansbrough-Jones and Rideal,[3] who studied the oxidation of nickel, platinum, tungsten, and carbon at temperatures sufficiently high for the oxide to evaporate from the surface as soon as it is formed.   Their conclusion was that the work function controlled the velocity, but is somewhat uncertain as the work functions available at the time are now known to differ from the true values.

Recently, two further attempts have been made to show the importance of work functions in catalytic reactions ; first, Dowden and Reynolds [27] have studied the decomposition of hydrogen peroxide in solution at the surfaces of copper–nickel alloys of varying composition.   The mechanism of reaction, according to Haber and Weiss,[30] involves an initial slow dissociation to a hydroxyl radical and a hydroxyl ion, with an electron transfer

[30] Haber and Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332.

from the catalyst, according to the equation :

$$H_2O + e \longrightarrow OH + OH^-$$
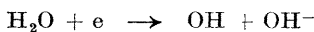
followed by subsequent rapid processes. Since the slow process involves negative-ion formation, its activation energy should increase with increasing work function. The work function of copper is about 4·1 ev, and that of nickel 5·0 ev, and solid solutions of the two should have work functions intermediate between these values. Therefore copper should be the most active catalyst, and alloying with nickel should decrease the activity. This was found to be the case, the specific activity at 60° of a foil containing 30 atomic % of nickel being about one-sixth that of pure copper. This may be contrasted with the result for reactions in covalently bound layers on the same foils where copper is the least active catalyst and alloying with nickel, by producing d-band vacancies, increases the activity.

Secondly, Kemball [31] has suggested that the magnitude of the work function may be a factor in deciding the velocity of ammonia–deuterium exchange at metal surfaces. The mechanism of reaction could not be decided unequivocally from the experiments, but it was shown to be possible on energy grounds for ammonium ions to be formed at the surface.

Exchange might therefore be due to a process such as

$$\begin{array}{ccccc} NH_3D^+ & & & NH_3 & D \\ & \rightleftharpoons & & & | \\ M \quad M & & & M & M \end{array}$$
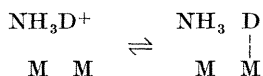
an electron being transferred from the catalyst to the surface complex and back again.
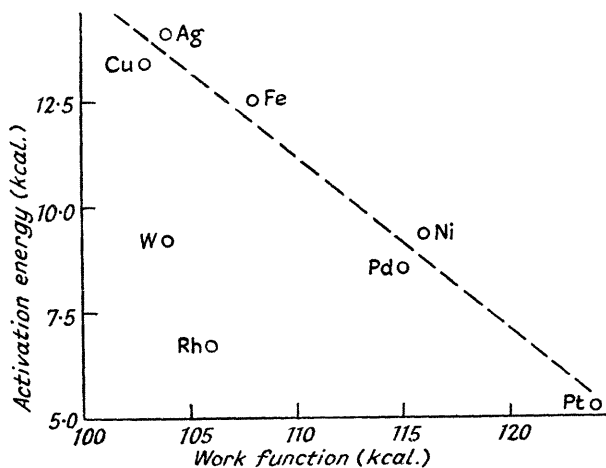

Fig. 7

Ammonia–deuterium exchange.

The results were expressed in terms of the apparent activation energy obtained from the temperature coefficient of velocity at constant pressure,

[31] Kemball, *Proc. Roy. Soc.*, 1952, *A*, **214**, 413.

and an A factor derived from it.   The variation of velocity between metals was found to be localised purely in the apparent activation energy, which may therefore be taken as characteristic of the reaction velocity.

There was no correlation between the energy and lattice spacing and Kemball suggested that the best correlation was with the work function of the metal.   As shown in Fig. 7, there is a general decrease of activation energy with increasing work function, as might be expected if the activation energy of formation of a positive ion controlled the reaction velocity. Of the two points not falling on the line, the work function of rhodium is uncertain, and may be in error.   The work function of tungsten is however known with considerable accuracy.

The work suggests that the work function is important, but an alternative explanation is possible.   The order of activities is $Pt > Rh > Pd > W > Ni > Fe > Cu > Ag$.   This is the order of d characters except that platinum is out of step.   This might be due to a lattice-spacing effect, since platinum has the most dilated lattice of all the transition metals used.

Correlations of catalytic activity with work function are difficult to establish for two reasons.   First, if the work function is important, it will be that of the surface under conditions of catalysis, when the surface is largely covered by gas.   Now the work functions of covered surfaces are frequently 35 kcal. different from those of clean surfaces, and furthermore, the relative order of work functions may be changed by adsorption.   On clean surfaces $\phi_W < \phi_{Ni} < \phi_{Pt}$ but on hydrogen-covered surfaces $\phi_{WH} > \phi_{NiH} > \phi_{PtH}$.[22, 32, 33]

Secondly, work functions may vary by up to 8 kcal. with crystallographic direction on clean surfaces.[34]   This suggests that the main catalytic activity is liable to arise from one crystal face, and strictly the work function of this should be used.

[32] Bosworth, *Proc. Camb. Phil. Soc.*, 1937, **33**, 394.
[33] Oatley, *Proc. Phys. Soc.*, 1939, **51**, 518.
[34] Nichols, *Phys. Review*, 1940, **57**, 297.