QUARTERLY REVIEWS

MECHANISMS OF HYDROGEN CATALYSIS

By D. D. Eley, Ph.D.

(Nash Lecturer in Biophysical Chemistry, University of Bristol)

Introduction.—The building blocks of any theory of catalysis must be facts concerning reaction mechanism and, in particular, the details of reaction paths in a number of simple instances. The work of Rideal and his school, Farkas, Beeck, and others has greatly advanced our knowledge of hydrogenation reactions, and we shall discuss this and other work from this general viewpoint. In the first place, we shall review recent knowledge of chemisorbed films, that is, unimolecular adsorbed films of gases held to the catalyst by forces so strong that they must be chemical in nature, which Langmuir showed to be responsible for surface catalysis.

Chemisorbed Films

Hydrogen.—Because of the production of atomic hydrogen by clean metal surfaces I. Langmuir [1] suggested that the gas was dissociated and held as atoms. If M denotes a surface metal atom,

$$H_2 + 2M \longrightarrow 2MH$$

The very strength with which hydrogen is chemisorbed by metals is in favour of this hypothesis which, however, is not easy to verify exactly, owing to lack of knowledge of surface areas of metals. Working with tungsten wires and assuming a reasonable roughness factor (ratio true : apparent area), J. K. Roberts [2] has verified this to a first approximation. O. Beeck, A. E. Smith, and A. Wheeler [3] have shown that on evaporated films of nickel there is twice as much carbon monoxide chemisorbed as hydrogen and, if we assume single-site adsorption for carbon monoxide

$$CO + M \longrightarrow M{\cdot}CO$$

then the dissociation of hydrogen into atoms is very probable. W. G. Frankenburger [4] has measured surface areas of tungsten powder by the B.E.T. method, and has concluded that one hydrogen atom is adsorbed per tungsten surface atom.

[1] *J. Amer. Chem. Soc.*, 1916, **38**, 1145.

[2] (*a*) *Proc. Roy. Soc.*, 1935, *A*, **152**, 445. (*b*) "Some Problems in Adsorption", Cambridge University Press, London, 1939. [3] *Proc. Roy. Soc.*, 1940, *A*, **177**, 62.

[4] *J. Amer. Chem. Soc.*, 1944, **66**, 1827, 1838.

The theory of chemisorption due to J. E. Lennard-Jones [5] starts from the model of a metal in which electrons move freely through the periodic potential field due to the positive cores of the metal. The effect of an adsorbed atom on the surface of the metal is then to lead to a lowering of the potential energy of the electron in the surface of the metal in its immediate neighbourhood. Thus, we have now two sets of essentially *localised* energy levels for the electron : one on the hydrogen atom and one on the surface of the metal. If the wave functions corresponding to these energy levels overlap we may have the exchange phenomenon with the formation of an electron-pair bond, the second electron for this bond coming from the conduction band of the metal. W. G. Pollard [6] has developed this picture, and considers in general that a two-electron bond will give an unstable charge distribution. Thus, only one electron is available to form a bond to the adsorbed atom. We visualise the bond as covalent, as in H_2^+, where the two levels are nearly equal, or ionic, as in Na^+Cl^-, where the two levels are widely different in energy. Fig. 1 shows the potential energy curve for a hydrogen atom in the neighbourhood of a metal. The curve *aa* refers to the approach of a hydrogen molecule to the metal surface, and is made up of the attractive London dispersion forces and the usual repulsive forces arising from the interaction of closed electron shells. The value *q* corresponds to the heat of van der Waals adsorption, and is about 2 kcals./g.-mol. for hydrogen. Curve *bb* gives the energy of the chemical bond between the hydrogen atom and the metal, or rather, twice this value. *Q* is the heat of chemisorption, usually at least 20 kcals./g.-mol. Where the two curves intersect, a molecule held in the van der Waals layer may pass into a state of chemisorbed atoms, the necessary activation energy being *E*.

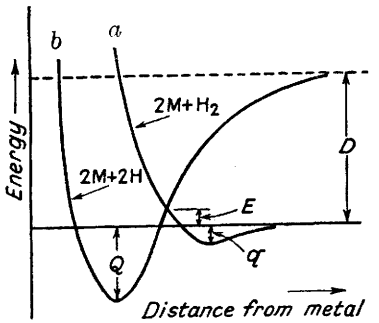


FIG. 1

The potential energy curve for the chemisorption of hydrogen, $2M + H_2 \longrightarrow 2MH$.

H. Eyring and A. Sherman [7] and A. Okamoto, J. Horiuti, and K. Hirota [8] calculate similar potential curves, making use of the Eyring–Polanyi treatment of the London equation for four electrons. Thus for nickel the exchange and coulombic terms in the London equation are obtained by subdividing the Morse curve for NiH obtained from spectroscopic data. Whilst the method is restricted in so far as it regards the surface metal atoms as isolated, it does serve to bring out the possible importance of lattice spacing on the activation energy for chemisorption of hydrogen. Quantitatively the activation energies obtained for hydrogen in general are too high. Nowadays we know from experiment that the activation energy of adsorp-

[5] *Trans. Faraday Soc.*, 1932, **28**, 333.
[6] *Physical Reviews*, 1939, **56**, 324. [7] *J. Amer. Chem. Soc.*, 1932, **45**, 2661.
[8] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 223.

tion of hydrogen on tungsten,[2, 3] nickel, and other metals [3, 11] is close to zero. The activation energies for other gases such as oxygen, nitrogen, carbon monoxide, etc. on these metals must also be small. The rapid chemisorption of the first two gases at liquid-air temperature has been detected by constant potential work [9] and of all three by the poisoning of the para-hydrogen conversion.[10] Until recently many such chemisorptions on metals were believed to possess an appreciable activation energy (" activated adsorptions "), according to the hypothesis of Taylor to account for slow sorption.[12] Whilst this hypothesis may hold for oxides and is not ruled out in principle for any solid, slow adsorption on metals must in many cases be attributable to displacement of impurities [2, 13] or sorption into the solid.[14, 15]

The heat of adsorption of hydrogen on tungsten falls from a value of 45 kcals. for the bare surface to a value of 18 kcals. for the almost full surface. These measurements were made by Roberts [2] by measuring the minute temperature changes associated with chemisorption on fine tungsten wires, and they have been checked by O. Beeck [11] using evaporated films of 10,000 times the area of the wire. Beeck also finds a similar result for nickel.

The powerful adsorption of hydrogen on transition metals is undoubtedly due to the partly empty *d*-band of this metal, which gives rise to a high concentration of empty *d* levels in the surface, much lower in energy than most of the *s*-levels.[16] That the *d*-band in palladium is employed in bonding *dissolved* hydrogen has long been known from magnetic measurements [17] and it seems natural to postulate a similar effect for adsorbed hydrogen. Incidentally, it has been found possible to detect magnetic changes associated with the chemisorption of a monolayer of dimethyl sulphide on palladium,[18] and the method is being extended to hydrogen and other gases.

Hydrogen dissolved in palladium is positively charged, but only weakly so, corresponding to about one-fiftieth of an electronic charge per atom.[19, 20] We may suppose that while the hydrogen atom transfers an electron into the *d*-band of the metal, the proton does, in fact, draw a large cloud of negative electricity around it. Such behaviour is necessary on energetic grounds.[21] On platinum, chemisorbed hydrogen has been found to be positive.[22] On tungsten, the contact potential of hydrogen yields a dipole

[9] R. C. L. Bosworth and E. K. Rideal, *Physica*, 1937, **4**, 925.
[10] D. D. Eley and E. K. Rideal, *Proc. Roy. Soc.*, 1941, *A*, **178**, 429.
[11] O. Beeck, *Physical Reviews*, 1945, **17**, 61.
[12] H. S. Taylor, *J. Amer. Chem. Soc.*, 1931, **53**, 578.
[13] A. J. Allmand and R. Chaplin, *Trans. Faraday Soc.*, 1931, **28**, 223.
[14] A. F. H. Ward, *ibid.*, p. 399.
[15] O. Beeck, A. W. Ritchie, and A. Wheeler, *J. Coll. Sci.*, 1948, **3**, 504.
[16] D. D. Eley, *Research*, 1948, **1**, 304.
[17] N. F. Mott and H. Jones, " Theory of Metals and Alloys ", Oxford, 1936.
[18] M. H. Dilke, D. D. Eley, and E. B. Maxted, *Nature*, 1948, **161**, 804.
[19] A. Coehn and W. Specht, *Z. Physik*, 1930, **62**, 1 ; B. Duhm, *ibid.*, 1935, **94**, 434.
[20] P. H. Emmet and E. Teller, " Twelfth Report of Committee on Catalysis ", p. 77, New York, 1940.
[21] J. Franck, *Nachr. Ges. Wiss. Göttingen*, 1933, **2**, 293.
[22] C. W. Oatley, *Proc. Physical Soc.*, 1939, **51**, 318.

moment $W^+ - H^-$ of 0·4 D., hydrogen being negative.[23] This result has been confirmed by several other workers in Rideal's laboratory. In any event, the dipole is a small one and the bond is essentially non-polar.

Reverting to the decrease of heat of adsorption with fraction of surface covered, the approximately linear relation observed has been attributed to a repulsive potential between nearest neighbours,[2] and the theory for both mobile and immobile chemisorbed atoms fits the experiments equally well.[24] Since the activation energy for surface diffusion of atoms in a monolayer is usually about $\frac{1}{4}$ to $\frac{1}{3}$ of the bond strength of the atoms to the surface, this should be about 20 kcals. for hydrogen on tungsten. Thus we should expect a mobile film at 293° K. and 193° K., but an immobile film at 77° K. From the decrease of heat of chemisorption with surface covered on porous metal films of area approx. 10,000 sq. cm., Beeck [11] has concluded that hydrogen is mobile on nickel and iron at room temperature, but not on iron at 90° K. Where an immobile film is formed by dissociation of gaseous molecules striking a surface, it is a statistical requirement that 8% of the total sites will be " cut-off " as isolated single sites, and be incapable of taking up a hydrogen atom.[2] Roberts suggested that such sites might play a rôle in catalysis.

Other Gases.—Langmuir assumed that oxygen dissociated into atoms on platinum, and this was Roberts's original postulate for oxygen on tungsten.[2] The heat of chemisorption is so high, approx. 150 kcals. for a bare surface, that the oxygen film is almost certainly immobile at room temperature. Such an immobile *atomic* film should possess 8% of holes, and indeed a second film of oxygen has been found to be adsorbed with a heat of 48 kcals. However, the number of molecules in this film, and the change of accommodation coefficient accompanying its removal, are too large for the 8% of holes. If oxygen were adsorbed as *molecules*, then each molecule by its very size would exclude occupation of four adjacent sites on the 110 or 100 planes of tungsten, leading to 50% of gaps, thus allowing a relatively large uptake of gas in the secondary film as described by Roberts.[2b, 25] The W–WO contact potential [9] of − 1·76 v. cannot properly be interpreted in the absence of knowledge concerning the structure of the film. If the film were atomic, the dipole W–O would be 0·66 D., the oxygen being negative. For nickel Beeck [3] has found that at least a double monolayer of oxygen molecules is formed at low pressures, but one suspects that this and other metals may be complicated by formation of surface oxide. There is evidence for surface oxide on nickel catalysing the hydrogen–oxygen reaction.[26] R. Juza and R. Langheim find that the π bond in the O_2 molecule is ruptured on charcoal since on chemisorption the O_2 molecule loses its paramagnetism.[27] It is very likely that the π electrons are used in bonding the molecule to charcoal and also to metals.

Nitrogen is chemisorbed rapidly [9, 10] on tungsten at 90° K., and its

[23] R. C. L. Bosworth, *Proc. Camb. Phil. Soc.*, 1937, **33**, 394.
[24] A. R. Miller and J. K. Roberts, *ibid.*, 1941, **37**, 82. [25] *Ibid.*, 1940, **36**, 53.
[26] D. R. Hughes and D. C. Bevan, *Proc. Roy. Soc.*, 1927, *A*, **117**, 100.
[27] *Z. Elektrochem.*, 1939, **45**, 689.

contact potential is negative, — 1·38 v.[9] On other metals such as iron it may be chemisorbed slowly. Beeck [3] finds that nitrogen is not chemisorbed by nickel at 293° K.,[1] in contrast to hydrogen, carbon monoxide, oxygen, and ethylene.

Ethylene is chemisorbed rapidly by tungsten, as is apparent from its effect in poisoning the para-hydrogen conversion.[16] According to Beeck,[3] at saturation one ethylene molecule occupies four nickel sites, which may be explained by his later observation [11] that on chemisorption on nickel, an ethylene molecule dissociates into an acetylene complex and two hydrogen atoms. The heat of chemisorption for ethylene on nickel falls from 58 kcals. for a bare surface to 25 kcals. for a full (?) surface,[11] but it is stated to be complicated to some extent by a side reaction (hydrogenation of a second ethylene molecule by the chemisorbed hydrogen atoms). So far a value for the contact potential has not been published.

Beeck assumes that each carbon monoxide molecule occupies a single site on nickel.

Mixed Monolayers

Scarcely any work has been done on mixed monolayers as yet. Roberts [2] found that oxygen gas would throw an adsorbed monolayer of hydrogen off a tungsten wire, in agreement with the known difference of 100 kcals. in their heats of chemisorption. Langmuir in his early papers [28] visualised the following two types of bimolecular catalytic reaction.

(1) The two gases compete on more or less equal terms for sites in the chemisorbed monolayer, and adjacent molecules or radicals interact. This mechanism, which we might call the adjacent interaction (A.I.) mechanism has been applied particularly by C. N. Hinshelwood [29] and G. M. Schwab [30] to kinetic data.

(2) Reaction occurs between chemisorbed A and a molecule of B colliding with it from the gas phase or van der Waals layer. This mechanism, which we might call van der Waals–chemisorbed layer interaction (V.C.I.) has been applied recently by E. K. Rideal to certain simple exchange reactions of hydrogen.[31]

It may be difficult to decide between (1) and (2) on kinetic grounds. There seems little reason to doubt the applicability of the A.I. mechanism to many catalytic reactions at high temperatures, where both components give sparse monolayers. One can, however, make some quite general observations for reactions occurring at, say, $T \leqslant 200°$ C. In these circumstances, many pure gases will tend to give full chemisorbed layers, even at very low pressures. Consider two gases A and B, pressures p_A and p_B, heats of chemisorption L_A, L_B (considered independent of surface fraction θ). Then we may suppose that the more strongly adsorbed gas A occupies

[28] I. Langmuir, *Trans. Faraday Soc.*, 1921, **17**, 607.

[29] C. N. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems", 3rd Edn., Oxford, 1933. [30] G. M. Schwab, "Catalysis", London, 1937.

[31] (*a*) *Proc. Camb. Phil. Soc.*, 1938, **35**, 130; (*b*) Sabatier Lecture, *Chem. and Ind.*, 1943, **62**, 735.

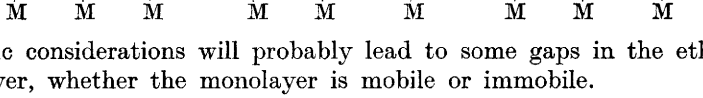
nearly all the surface, that is, $\theta_A \sim 1$, and that θ_B can occupy the surface only by an expenditure of internal energy $L_A - L_B$; since $\theta_A = 1 - \theta_B$,

$$\theta_B/(1 - \theta_B) = p_B e^{(L_A - L_B)/RT}/p_A$$

Suppose we take the case of ethylene and hydrogen on nickel as an example. If we neglect the effect of surface covered on heats of adsorption, and take the L values for the full ($\theta = 1$) single-component monolayers [11] as relevant to the present calculation, for equal pressures of hydrogen and ethylene we find a very small fraction of chemisorbed hydrogen, *viz.*,

$$\frac{\theta_H}{1 - \theta_H} \simeq e^{-10,000/RT} = 10^{-7}(293° \text{ K.})$$

It seems rather unlikely that the A.I. mechanism will hold when the second component has a chemisorbed concentration of only 10^{-7} unless the activation energy for this mechanism is *very much less* than that for a V.C.I. mechanism. Rideal [31] has advanced a quite general reason why the V.C.I. mechanism should have a low activation energy, for the case of monolayers containing "gaps". These gaps are supposed to furnish a particularly strong van der Waals adsorption and to supply a free valency which on general grounds will be expected to lower the inertia of the reaction. Thus for the exchange of deuterium with ethylene,



Steric considerations will probably lead to some gaps in the ethylene monolayer, whether the monolayer is mobile or immobile.

It is, of course, possible that the above considerations might be modified if the A–B repulsions in the monolayer were weaker than the A–A or B–B repulsions (or were even attractions). This might be the case where the two components had opposite dipoles, in which case one would tend to get a higher concentration of hydrogen than that calculated above. C. W. Oatley has made a few observations of this kind.[22] Generally speaking, the electrostatic neighbour interactions will be about 1 kcal., sufficient markedly to modify adsorption concentrations. D. D. Eley and Rideal [10] have related the conversion of para-hydrogen in a partial film of oxygen on tungsten to this concept. Incidentally, the decrease in heat of chemisorption of hydrogen with the surface covered is too large to be only a dipolar effect. It would require a W–H dipole moment of 1·94 D. in comparison with 0·44 D. observed. We would suggest that the difference might be ascribed to a band-nature of the surface orbitals. The first *d*-orbitals taken up will, of course, be lower in energy than those occupied by the last amounts of hydrogen on the surface.

Para-hydrogen Conversion

The para-hydrogen conversion and the related hydrogen deuteride reaction, because of their simplicity, have been subjected to detailed study,

originally by the pioneer workers K. F. Bonhoeffer and A. and L. Farkas, and more recently by the Reviewer and his colleagues. Two mechanisms for the conversion exist, a chemical and a paramagnetic mechanism. Since the latter involves a mere physical twisting of the spins of the hydrogen nuclei, we shall no longer concern ourselves with it. The paramagnetic mechanism may usually be distinguished, since in no case can it give the hydrogen deuteride reaction,

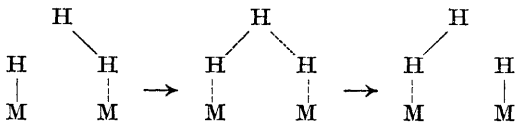
$$H_2 + D_2 \longrightarrow 2HD$$

On the other hand, the evidence is that the conversion of para-hydrogen and hydrogen deuteride goes through a chemical mechanism on the transition metals. The reactions occur with similar rapidity and have the same kinetics (on nickel and on tungsten). The position up to 1935 is set forth in the work by A. Farkas,[32] and more recent work has been discussed by Eley in detail.[33] At present we shall only discuss features of general interest.

In the first place, the mechanism was supposed to involve the dissociation of hydrogen molecules on the surface of the catalyst and the recombination of the atoms to give ortho-molecules.[34]

$$p\text{-}H_2 + 2M \longrightarrow 2MH \longrightarrow 2M + o\text{-}H_2$$

This mechanism was advanced for platinum and other metals, including tungsten, where, however, it was challenged by Roberts,[35] who pointed out that at ordinary temperatures the hydrogen atoms form a saturated, firmly-bound layer and do not recombine at any appreciable rate. Rideal [31a] suggested an exchange mechanism involving hydrogen molecules held over the 8% of gaps assumed to be in the chemisorbed film,



Rideal pointed out that by making use of a free valency in this fashion, one would expect an exchange reaction of low energy. More generally, we can simply write

$$M\text{–}H + p\text{-}H_2 \longrightarrow MH + o\text{-}H_2$$

C. Wagner and K. Hauffe,[36] working with palladium, obtained the rate of recombination of hydrogen atoms from the rate of loss of dissolved hydrogen atoms, measured by electrical resistance changes. This velocity was ten times less than the observed para-hydrogen conversion, so they concluded that the conversion was largely due to some process other than the recombination of atoms, *viz.*, the exchange mechanism above or a paramagnetic conversion.

[32] " Orthohydrogen, Parahydrogen and Heavy Hydrogen ", Cambridge University Press, London, 1935.

[33] Cf. " Advances in Catalysis ", **1**, 157, Academic Press, New York, 1948.

[34] K. F. Bonhoeffer, A. Farkas, and K. W. Rummel, *Z. physikal. Chem.*, 1933, *B*, **21**, 225.

[35] *Trans. Faraday Soc.*, 1939, **35**, 941. [36] *Z. Elektrochem.*, 1939, **45**, 409.

It has been found possible,[37] by working with tungsten films of large area (400 sq. cm.), to pre-adsorb hydrogen and then admit deuterium, measuring directly the exchange reaction,

$$M\text{–}H + D_2 \longrightarrow MD + HD$$

At 193° K. and 293° K. the whole of the chemisorbed hydrogen is exchanged with great rapidity. At 77° K. it is necessary for zero-point energy reasons to follow

$$M\text{–}D + H_2 \longrightarrow MH + HD$$

and one-quarter of the deuterium is exchanged rapidly with a speed comparable with that of the para–ortho conversion. It was considered that a small difference in activation energy, probably due to lattice-spacing effects, slowed down the exchange of the other three-quarters. It was concluded that the conversion reaction involved the exchange mechanism, and A. and L. Farkas [38] came to the same result and conclusion for nickel. At 293° K. on palladium, however, the ratio of rates, conversion : surface exchange, was 15, and for platinum 5. In this case Farkas and Farkas refer to a possible dissociation of hydrogen molecules into atoms *on top* of the chemisorbed film. This type of hypothesis really requires quantum-chemical investigation, since it cannot be justified on the Langmuir surface-valency postulate. There is always, of course, the possibility that the combination mechanism is active on a small number of active spots, not apparent in adsorption investigations.[39] The direct surface exchange work rules this out for nickel and tungsten. Also, whilst we cannot lay too much weight on the experimental data available at present, the A factors found for platinum and palladium correspond to those one would calculate for surface exchange, assuming that the whole surface is active.[40a]

Recent work by A. Couper [40b] in collaboration with the Reviewer makes it unlikely that the exchange mechanism can involve actual empty sites. First, the hydrogen film is probably mobile at approx. room temperature, when the gaps should fill up, but conversion activity remains unchanged. Secondly, a chemisorbed hydrogen film on tungsten at 77° K. treated with hydrogen *atoms*, which should fill the sites, maintains its catalytic activity. However, there seems no reason why the end of the hydrogen molecule should not interact with the metal *between* sites, since the metal electrons are not localised.

Exchange Reactions of Hydrogen Atoms

It will be remembered that J. Horiuti and M. Polanyi [41] discovered that platinum black catalysed the exchange of atoms between deuterium gas and liquid water, whilst A. and L. Farkas and Rideal [42] discovered the exchange between ethylene and deuterium on nickel. Subsequently,

[37] D. D. Eley, *Proc. Roy. Soc.*, 1941, *A*, **178**, 452.
[38] *J. Amer. Chem. Soc.*, 1942, **64**, 1594.
[39] A. Farkas, *Trans. Faraday Soc.*, 1939, **35**, 943.
[40a] D. D. Eley, *ibid.*, 1948, **44**, 216.
[40b] A. Couper and D. D. Eley, unpublished.
[41] *Nature*, 1933, **132**, 819.
[42] A. Farkas, L. Farkas, and E. K. Rideal, *Proc. Roy. Soc.*, 1934, *A*, **146**, 630.

benzene was shown to exchange with deuterium gas,[43] and at higher temperature on active nickel catalysts exchange reactions were obtained with saturated hydrocarbons.[44]

In discussing these exchange reactions it would seem convenient to mention first the general approach adopted by Farkas and Farkas for ordinary hydrides, and later to discuss the special problems of unsaturated hydrocarbons. Much more requires to be done to fix the mechanisms of these reactions, and one can only outline different points of view. Thus A. Farkas [45] assumes that the velocity of para-hydrogen conversion measured in the presence of the hydride RH gives the rate of dissociations of hydrogen molecules on the surface of the catalyst. Thus we have

$$\left.\begin{matrix} H_2 & \rightleftharpoons & H^* + H^* \\ D_2 & \rightleftharpoons & D^* + D^* \end{matrix}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\left.\begin{matrix} RH & \rightleftharpoons & R^* + H^* \\ RD & \rightleftharpoons & R^* + D^* \end{matrix}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We shall in future use an asterisk as above to indicate a postulated valency bond to the catalyst. Thus, where the rate of conversion was found equal to the rate of exchange, the dissociation step (1) was supposed to limit the exchange reaction. Such might be the case for liquid water.[46] In the case where the conversion was more rapid than the exchange, the rate of dissociation or recombination of hydride (2) was supposed to determine the reaction. Thus in the exchange with ammonia,[47] which is of the second type, the exchange is limited by

$$D^* + NH_2^* \longrightarrow NH_2D$$

where the kinetics require NH_2^* to saturate the surface approximately, and D^* to be weakly held. However, there is a possible alternative view of this reaction,[33] an exchange reaction between NH_2^* and D_2 held in a van der Waals layer,

$$NH_2^* + D_2 \longrightarrow NH_2D + D^*$$

The exchange reactions of saturated hydrocarbons are of particular interest in connection with later considerations for unsaturated hydrocarbons. H. S. Taylor and his co-workers [44, 48] have demonstrated an exchange between deuterium on nickel–kieselguhr and methane, ethane, or propane at temperatures of 180°, 110°, and 65° c., respectively. A. and L. Farkas, [49, 50] using platinised platinum foil, have demonstrated exchange reactions of deuterium with *n*-hexane, *cyclo*hexane, propane, and butane. The dehydrogenation equilibrium would, of course, lead to exchange of atoms,

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$$

but this is shown to be much too slow to account for the observed exchange.

[43] J. Horiuti, G. Ogden, and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30,** 663.
[44] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1936, **58,** 1445, 1795.
[45] *Trans. Faraday Soc.*, 1939, **35,** 906.
[46] D. D. Eley and M. Polanyi, *ibid.*, 1936, **32,** 1388.
[47] A. Farkas, *ibid.*, p. 416.
[48] K. Morikawa, N. R. Trenner, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1936, **59,** 1103.
[49] *Trans. Faraday Soc.*, 1939, **35,** 917.
[50] *Ibid.*, 1940, **36,** 522.

All the hydrogen atoms exchange, and the activation energy for butane is 26 kcals. at 30° c., falling to 11 kcals. at 80°, whilst that for propane is 12—9 kcals. However, exchange with the butane is 4—5 times faster than with propane. Again, with *n*-hexane the activation energy is 17 kcals. at 30° c., falling to 9 kcals. in the region 55—124° c. The reactions are of zero order in *n*-hexane and *cyclo*hexane.

Farkas explains his results as above, assuming a dissociative chemisorption,

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n+1}^* + H^*$$

We may regard this as a *weak* chemisorption, since ethane does not inhibit the para-hydrogen conversion;[42] that is, in the presence of H* from hydrogen molecules the above equilibrium is well to the left. However, a high concentration of molecules in the van der Waals layer, such as will be given by the larger hydrocarbon molecules, will lead to a higher concentration of radicals, $C_nH_{2n+1}^*$, and a higher reaction velocity, as shown. For a saturated van der Waals monolayer the activation energy for exchange will be that for the dissociation left to right. The experiments suggest that the true activation energy for this dissociation is approx. 25 kcals. As the temperature is raised, we shall start to desorb molecules from the van der Waals layer, in the order of *increasing* temperature, methane < ethane < propane < butane < hexane. The activation energy will then be $25 - q$, where q is the heat of van der Waals adsorption of the hydrocarbon. For propane we are probably already in the desorption range.

It might be asked if the exchange does not go through a reaction of the type,

$$D^* + C_2H_6 \rightleftharpoons HD + C_2H_5^*$$

However, K. Morikawa, W. S. Benedict, and H. S. Taylor have demonstrated exchange between CH_4 and CD_4 on active nickel catalysts at 184° c. The activation energy is 19 kcals., which they attribute to the energy of desorption of methane, *i.e.*,

$$CH_3^* + D^* \longrightarrow CH_3D$$

Under the same conditions, the methane–deuterium exchange is slower, with an activation energy of 28 kcals. Here they consider that the strongly adsorbed deuterium has displaced the methyl radicals from the surface, and under these conditions the slow process is

$$CH_4 \longrightarrow CH_3^* + H^*$$

in agreement with what has been stated above.

In considering these theories it is remarkable that the chemisorptive rupture of C–H is more difficult than that of H–H, since the bond energy of C–H is only 98·2 compared with 103·2 for H–H.[51] The only explanation possible, since steric effects are probably small, is a low catalyst–carbon bond energy. This is confirmed by the additional observation by Taylor *et al.* that, whilst on nickel ethane exchanges with deuterium at an appreciable rate at 110°, bond scission producing heavy methane only occurs at 40° higher.

$$C_2H_6 + D_2 \longrightarrow 2CH_3D$$

[51] K. S. Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 2140.

So on transition-metal catalysts, the ease of bond rupture is in the order, H–H > C–H > C–C, which is the reverse of their bond energies. There is, however, still some controversy on the carbon-bond energies.

Exchange and Hydrogenation of Unsaturated Compounds

The original papers demonstrated that the hydrogenation of ethylene [42] and benzene [43] on nickel was accompanied by an exchange of atoms,

$$C_2H_4 + D_2 \longrightarrow C_2H_4D_2 \text{ (hydrogenation)}$$
$$C_2H_4 + D_2 \longrightarrow C_2H_3D + HD \text{ (exchange)}$$

We shall at first sketch the original " associative " mechanism of Polanyi and Horiuti [52] for the case of ethylene. This postulates that ethylene is chemisorbed by opening of the double bond,

$$CH_2{=}CH_2 \longrightarrow CH_2{*}{-}CH_2{*}$$

followed by

$$CH_2{*}{-}CH_2{*} + D{*} \longrightarrow CH_2{*}{-}CH_2D \xrightarrow{+D^*} CH_2D{-}CH_2D \text{ (hydrogenation)}$$
$$CH_2{*}{-}CH_2D \xrightarrow{-D} CH_2{*}{-}CH{*}D + D{*} \text{ (exchange)}$$

Half-hydrogenated state

The half-hydrogenated state by gain or loss of a hydrogen atom gives the hydrogenation or exchange reaction respectively. This mechanism then postulates an intimate connection between exchange and hydrogenation.

Farkas [45] postulates that ethylene is chemisorbed by a dissociative mechanism, as for saturated compounds,

$$C_2H_4 \longrightarrow C_2H_3{*} + H{*}$$

exchange following in the previous fashion by recombination of a $C_2H_3{*}$ and a D* to give C_2H_3D.

Polanyi and his co-workers [53, 54] have made numerous experiments with benzene. Here the activation energies for both exchange and hydrogenation are about 10 kcals., suggesting a similar rate-determining process in each case. They find that, while the hydrogenation velocity is of first order in hydrogenation pressure, the exchange reaction is of about half-order, which finds a ready explanation in terms of their mechanism above. For ethylene, however, the activation energy for exchange is much higher than for hydrogenation, which suggests that two different mechanisms are involved in this case. Thus we shall find it convenient to discuss the two reactions separately.

Exchange Reactions

Ethylene.—G. H. Twigg and E. K. Rideal [56] have carefully investigated the exchange with deuterium on an activated nickel wire. At 156° c. the reaction is proportional to the hydrogen and independent of the ethylene

[52] *Trans. Faraday Soc.*, 1934, **30**, 1164.
[53] R. K. Greenhalgh and M. Polanyi, *ibid.*, 1939, **35**, 520.
[54] C. Horrex, R. K. Greenhalgh, and M. Polanyi, *ibid.*, p. 511.
[56] *Proc. Roy. Soc.*, 1939, *A*, **171**, 55.

pressure. The hydrogenation has identical kinetics at this temperature, and the $H_2 + D_2$ reaction is completely inhibited. The observed activation energy is 18·6 kcals., and this falls off with temperature in the same way as for the hydrogenation reaction. Very similar results are reported for platinised foil by A. and L. Farkas,[57] who obtain an activation energy of 22 kcals. The conversion of para-hydrogen is inhibited 5—6 fold by the ethylene, but is not completely stopped, the activation energy being 10 kcals. Twigg and Rideal postulate a modified half-hydrogenated state mechanism,

$$\overset{*}{C}H_2—\overset{*}{C}H_2 + D_2 \longrightarrow \overset{*}{C}H_2—CH_2D + D^* \longrightarrow \overset{*}{C}H_2—\overset{*}{C}HD + HD$$

where the first step determines the velocity. There is evidence that the reaction $D^* + \overset{*}{C}H_2—\overset{*}{C}H_2 \longrightarrow H^* + \overset{*}{C}HD—CH_2^*$, involving chemisorbed deuterium, is very rapid. Farkas postulates the dissociative mechanism, identifying the slowest step as $C_2H_4 \longrightarrow C_2H_3^* + H^*$.

G. K. T. Conn and G. H. Twigg [58] find *no* exchange between ethylene and tetradeuteroethylene and conclude that this must rule out the dissociative mechanism. Farkas,[59] however, believes that this result will hold if the surface combination of H* reduces its surface concentration to zero, in the absence of added hydrogen gas. No test has so far been made for evolved hydrogen from an ethylene-treated nickel surface. Beeck's findings [14] suggest that the amount of chemisorbed hydrogen will be low.

In a further experiment Twigg [60] found that double-bond migration (D.B.M.), but-1-ene → but-2-ene, occurred only in the presence of hydrogen, and that if deuterium were used all the hydrogen atoms in the butene were exchangeable. About twelve butene molecules were isomerised per deuterium atom exchanged, which suggests that the process involves chemisorbed D atoms rather than molecules.

$$\overset{*}{C}H_2—\overset{*}{C}H—CH_2—CH_3 + D^* \rightleftharpoons CH_2D—\overset{*}{C}H—CH_2—CH_3 \rightleftharpoons CH_2D—\overset{*}{C}H—\overset{*}{C}H—CH_3 + H^*$$

A. Farkas's [45] explanation of D.B.M. in terms of his theory is not very convincing.

The main fact that on nickel catalysts ethylene exchanges so much more rapidly with deuterium than does ethane is most strongly in favour of a special mode of adsorption of ethylene.[56] Unfortunately, quantitative comparisons of the two velocities on identical catalysts have not been made and, whilst originally ethane showed only catalytic exchange at approx. 100° c., A. and L. Farkas [50] have now lowered this temperature to 72°. This, however, is still higher than the — 80° at which catalytic ethylene exchange has been detected.

Twigg and Rideal [61] have added some weight to their general conclusions by examining the packing of ethylene molecules on nickel surfaces.

[57] *J. Amer. Chem. Soc.*, 1938, **60**, 22.
[58] *Proc. Roy. Soc.*, 1939, *A*, **171**, 70.
[59] *Trans. Faraday Soc.*, 1939, **35**, 941.
[60] *Proc. Roy. Soc.*, 1941, *A*, **178**, 106.
[61] *Trans. Faraday Soc.*, 1940, **36**, 533.

On this basis they predicted that the bulky methylethylenes would pack badly, leaving space for chemisorbed hydrogen. They managed to detect this by showing the occurrence of the $H_2 + D_2$ reaction in these cases.

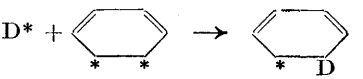
While it is clear that no critical experiment has yet been made, the bulk of the evidence lies in favour of the Twigg–Rideal mechanism.

Beeck's [11] work on hydrogenation raises one further possibility for the exchange reaction. Since no details have been published we cannot give a critical discussion. Beeck's view is that ethylene is chemisorbed on nickel as acetylene plus two hydrogen atoms, the latter being immediately removed by impinging ethylene, as ethane. Thus his view is that the catalyst is *largely* covered by acetylenic complexes, which are *slowly* removed by hydrogen. J. Sheridan's [62] work makes it very certain that the main product of hydrogenation of adsorbed acetylene will be ethylene. Thus, if Beeck is correct in his view of chemisorbed ethylene, the exchange reaction will merely be the deuterogenation of the acetylenic complexes, *viz.*,

$$CH_2{=}CH_2 \longrightarrow \overset{*}{C}H{=}\overset{*}{C}H + 2\overset{*}{H} \text{ (rapid)}$$
$$2H^* + C_2H_4 \longrightarrow C_2H_6 \text{ (rapid)}$$
$$D_2 + \overset{*}{C}H{=}\overset{*}{C}H \longrightarrow CHD{=}CHD \text{ (slow)}$$

This suggestion would fit the kinetics, but until further information is available it can only be regarded as a most tentative suggestion. The main argument against it is that the demonstrated activation energy for hydrogenation of acetylene, *viz.*, 10·9 kcals. on nickel and 12—17 kcals. on platinum,[62] is lower than that for the exchange reaction. But at least, if Beeck should prove correct in his view, a reaction, albeit a secondary one, of this kind leading to exchange must be present.

Benzene.—Benzene is not adsorbed so strongly, or alternatively does not pack so well, on nickel and platinum catalysts. This is shown by the relatively vigorous para-hydrogen conversion which goes on its presence.[46, 54, 63] The activation energy for exchange on both catalysts is about 9 kcals., much lower than for ethylene. Whilst the hydrogenation reaction is always of first order with respect to hydrogen, the exchange is often of one-half [53, 54] or zero order.[63] The half-order effect finds a natural explanation in terms of the original associative mechanism, the step



determining the rate. Because chemisorption of benzene in this way will break the resonance energy, the benzene will be more weakly chemisorbed than ethylene (the difference in heats of adsorption will be approximately the benzene resonance energy minus the butadiene resonance energy, *i.e.*, 35 kcals.). The weak adsorption will allow an ample surface concentration of chemisorbed D*, and so the slow step will not involve D_2 molecules,

[62] *J.*, 1944, 373; 1945, 133, 301, 305, 470.
[63] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1937, **33**, 827.

as with ethylene. This suggestion would bring the exchange reaction into line with H. A. Smith and H. T. Meriwether's observations on the hydrogenation reaction.[64] One would expect that if benzene were chemisorbed by *dissociation* it would be held as strongly as ethylene, also so held. But on platinum the velocity of exchange is sensitive to the benzene pressure,[63] and the surface cannot be anything like saturated, unlike the case with ethylene.

Acetylene.—A. and L. Farkas[65] have investigated the exchange of deuterium and acetylene on platinum. Whilst ethylene reduces the velocity of para-hydrogen conversion on the catalyst by a factor 3, acetylene does so by a factor 15, showing a much stronger adsorption of the latter. The rate of exchange is much less than for ethylene, and is comparable with that for ethane which is very little chemisorbed. In contradiction to Farkas, we should regard these observations as directly against an identical "dissociative" mechanism for acetylene and ethane.

Hydrogenation

Ethylene.—The kinetics of hydrogenation of ethylene has been widely investigated on copper, nickel and other catalysts,[66, 42, 56, 57] and the general picture that emerges is that at 100—150° C. the reaction is of first order with respect to hydrogen and of zero order with respect to ethylene. An excess of ethylene will exert an inhibiting effect. These kinetics have also been found at 0° C. on nickel films,[3] although at these temperatures Twigg[60] has reported a tendency for the reaction to be of fractional order in both gases (*e.g.*, but-1-ene at 50° C., velocity $= \sim p_{H_2}{}^{0\cdot5}.p_{C_2H_4}{}^{0\cdot5}$). At high temperatures, 200° C., it has been known since the work of U. Grassi that the reaction is of first order with respect to both gases. On the transition-metal catalysts, the activation energy is invariably low, 5—10 kcals. for ethylene hydrogenation. A similar value has been reported for copper,[66d] but also a much higher value of 19 kcals.[66g] Beeck[11] reports that for all transition metals, $E = 10{\cdot}7$ kcals. in $k = Ae^{-E/RT}$, and that the variation in activity is due to the A factor, rhodium being most efficient. A well-known feature is the fall-off of activation energy with temperature, reaching zero at 150° for nickel,[66g] but at much higher temperatures for nickel–silicon skeleton catalysts.[66h] H. Zur Strassen has identified this effect with the desorption of ethylene, but Twigg and Rideal[56] prefer the desorption of hydrogen held over gaps in the film, which starts at 100° C. in their view, at which temperature the activation energy for exchange also starts to fall.

[64] *J. Amer. Chem. Soc.*, 1949, **71**, 413. [65] *Ibid.*, 1939, **61**, 3396.

[66] (*a*) U. Grassi, *Il Nuovo Cimento*, 1916, **11**, 147; (*b*) D. M. and W. G. Palmer, *Proc. Roy. Soc.*, 1921, *A*, **99**, 402; (*c*) E. K. Rideal, *J.*, 1922, 309; (*d*) R. N. Pease, *et al.*, *J. Amer. Chem. Soc.*, 1923, **45**, 1196, 2297; 1927, **49**, 2503; (*e*) F. H. Constable, *Z. Elektrochem.*, 1929, **35**, 105; (*f*) C. Schuster, *Z. physikal. Chem.*, 1931, *B*, **14**, 249; *Trans. Faraday Soc.*, 1932, **28**, 406; (*g*) H. Zur Strassen, *Z. physikal. Chem.*, 1934, *A*, **169**, 81; (*h*) G. M. Schwab and H. Zorn, *ibid.*, 1936, *B*, **32**, 169; 1935, *A*, **171**, 421; (*i*) T. Tucholski and E. K. Rideal, *J.*, 1935, 1701; (*j*) G. Rienäcker and E. A. Bommer, *Z. anorg. Chem.*, 1938, **236**, 263; 1939, **242**, 302.

A. Farkas [45] has pointed out that hydrogenation leads to *cis*-compounds whether or not they are thermodynamically stable, and considers that this must involve the simultaneous addition of two hydrogen atoms, or a hydrogen molecule, at one side of the acetylenic or ethylenic bond. R. P. Linstead *et al.*[67] have furnished nine further examples in the hydrogenation of phenanthrene and diphenic acid. R. K. Greenhalgh and M. Polanyi [53] have pointed out that this argument is erroneous and that *cis*-addition will result from the consecutive addition of hydrogen atoms through the half-hydrogenated state.

The other argument advanced for direct addition of a hydrogen molecule, or of two hydrogen atoms simultaneously, is Twigg and Rideal's [56] finding that for ethylene both exchange and hydrogenation are of first order with respect to the hydrogen, and that the activation energy for exchange is always 7—9 kcals. higher than for hydrogenation, for a range of ethylenic compounds. Beeck [11] has recently stated quite new views on the hydrogenation of ethylene on nickel. He points out that since the overall heat of hydrogenation is 32·5 kcals., if we are to secure an energy balance, only the hydrogen can be chemisorbed. Since ethane is not chemisorbed under these conditions, if ethylene were also chemisorbed the heat of reaction must be *at least* 30 + 58 = 88 kcals., far in excess of the allowed value. However, Beeck errs in taking the heats of chemisorption at $\theta = 0$. We are concerned with a largely complete ethylene film, the heat of adsorption being about 25 kcals.

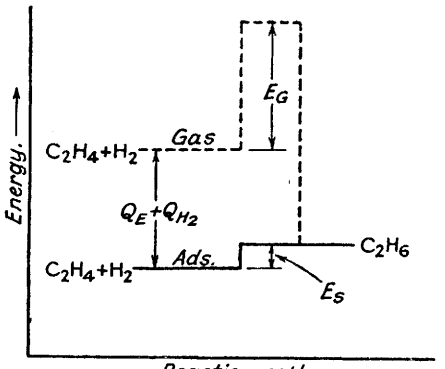


FIG. 2

The energy balance in ethylene hydrogenation. Q_E and Q_H are the heats of chemisorption of ethylene and hydrogen respectively. E_G and E_S are the activation energies for the gaseous and surface reactions. Ethane is assumed to be not chemisorbed.

The heat of chemisorption of hydrogen into this film will certainly not be more than the heat of chemisorption into a full hydrogen film, that is, 15 kcals. If the heat of rearrangement on the surface, that is, the activation energy, is 7·5 kcals., we shall get an energy balance. The point is made clear in Fig. 2. Therefore on thermochemical grounds there is nothing against a reaction between chemisorbed hydrogen and chemisorbed ethylene (Polanyi mechanism) or van der Waals hydrogen molecule plus chemisorbed ethylene (Twigg–Rideal). However, Beeck states briefly the results of two experiments which certainly necessitate a careful reconsideration of these mechanisms : (*a*) a pre-adsorbed ethylene film on nickel, held in his view as acetylenic complexes, is only *slowly* removed by hydrogen ; and (*b*) a pre-

[67] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

adsorbed hydrogen film is very rapidly removed by gaseous ethylene. Beeck's view is that the removal of the acetylenic complexes by hydrogenation leaves a small part of the surface, perhaps one part in 10^6, free to chemisorb hydrogen. The actual ethane formation is then due to a very rapid reaction between colliding ethylene and chemisorbed hydrogen, which he takes to be the mechanism in experiment (*b*) above. The overall hydrogenation velocity, however, is determined by the slow removal of acetylenic complexes. Beeck then argues that the portion of surface covered by hydrogen is proportional to $p_{H_2}/p_{C_2H_4}$ and that the velocity is then proportional to this fraction times the pressure of ethylene, so that

$$\text{velocity} = k.p_{C_2H_4}.p_{H_2}/p_{C_2H_4} = k.p_{H_2}$$

A critical discussion of these interesting conclusions must await the detailed publication of the experimental data. So far this most studied of bimolecular catalytic reactions still evades final solution.

Benzene.—Recent workers [53, 54, 63] employed nickel and platinum catalysts. The reaction is of first order with respect to the hydrogen and, for gaseous benzene,[63] of zero order with respect to the benzene. The activation energy is about 7 kcals., as for ethylene. Smith and Meriwether [64] have pointed out that the resonance energy of benzene must be suppressed on the catalysts, otherwise the activation energy for hydrogenation would be much bigger. This notion, as we have developed it above, is probably the best existing argument for the associative chemisorption of benzene. It is very likely that hydrogenation involves the consecutive addition of two hydrogen atoms, as argued by Greenhalgh and Polanyi, but of course their kinetics do not necessarily rule out addition of a molecule. One may, however, suppose that where chemisorbed hydrogen atoms *can* exist, they will hydrogenate rapidly. Only where the substance is chemisorbed as strongly as ethylene is it really necessary to invoke the direct action of hydrogen molecules.

Smith and Fuzek [68] make the interesting observation that, since furan has an activation energy higher than that of benzene, the slower hydrogenation of benzene must be due to a decreased A factor. This is the second piece of evidence pointing to the importance of A factors in hydrogenation. A careful investigation of the hydrogenation of phenyl-substituted aliphatic acids in solution [69] leads them to the view that the adsorption of hydrogen on the catalyst is a slow process, sterically hindered by the adsorbed substrate. This is not dissimilar to the views of Twigg and Rideal.

Acetylene.—The hydrogenation of this substance [62, 65] is of first order with respect to hydrogen and of zero or negative order with respect to acetylene on the usual catalysts. The reaction is slower and the activation energy is higher than for ethylene. The main product is ethylene, and ethylene has absolutely no effect as a diluent. However, whilst the hydrogenation of acetylene is slower than that of ethylene, so far as one can judge, it would seem to be much faster than Beeck's reaction [11] between hydrogen

[68] H. A. Smith and J. F. Fuzek, *J. Amer. Chem. Soc.*, 1949, **71**, 415.
[69] H. A. Smith, D. M. Alderman, and F. W. Nadig, *ibid.*, 1945, **67**, 272.

and pre-adsorbed ethylene, which would suggest that normally chemisorbed acetylene is different from Beeck's acetylenic complexes.

Conclusion

It will be seen that, in spite of so much work with the probable exception of the para-hydrogen conversion all the hydrogenation mechanisms are at present controversial. It is hoped that this review will help towards their solution. The weight of evidence still lies, in the Reviewer's opinion, in favour of associative chemisorption at the double bond, followed by reaction with chemisorbed hydrogen atoms (for benzene) or hydrogen molecules, where the substance (like ethylene) is so strongly chemisorbed that it displaces the hydrogen atoms.

So far as the basic theory of catalysis goes, two trends of work are apparent. The first, a continuation of the work of A. A. Balandin,[70] seeks to link catalyst activity with the fitting of substrate molecules to lattice spacings. This approach is quite decisively limited at present by our knowledge of reaction paths. Thus the favourable action of the 110 plane of nickel on the hydrogenation of ethylene has been associated with its suitability for chemisorbing, on the one hand, hydrogen [3] and, on the other hand, ethylene.[61]

Recently experimental results have started to appear, linking the electronic band structure of the solid with the activation energy for reaction. In the past, this field of activity has been mainly cultivated by J. E. Nyrop,[71] whose enthusiastic correlations of activity with ionisation have been spoilt, unfortunately, by his misuse of the physical theory.[72] Then G. M. Schwab [73] has demonstrated that the height of the filled electron levels in certain alloys determines their catalytic activity in the dehydrogenation of formic acid. A. Couper and D. D. Eley [74] have demonstrated that filling the partly empty *d*-band of palladium by alloying it with gold destroys its catalytic activity. From their results they argue that the exceptional behaviour of transition metals as catalysts lies in their possession of vacant *d*-orbitals, of low energy and high numerical density. D. A. Dowden and P. W. Reynolds [75] have also discussed correlation between electronic structure and catalyst activity. Work of this kind still calls for a knowledge of reaction paths, but not perhaps so urgently as does the lattice-spacing concept. From the fundamental physical viewpoint, of course, the two approaches are complementary, and the separation is made simply for the benefit of the experimentalist.

[70] *Z. physikal. Chem.*, 1927, *A.*, **126**, 267.

[71] " The Catalytic Action of Surfaces ", London, 1937.

[72] P. H. Emmet and E. Teller, " Twelfth Report of the Committee on Catalysis ", p. 68, New York, 1940.

[73] *Trans. Faraday Soc.*, 1946, **42**, 689.

[74] *Nature* (in the press), and Chemical Society Meeting, London, March 17th, 1949.

[75] Chemical Society Meeting, London, March 17th, 1949.