JOURNAL OF CATALYSIS 2, 259–273 (1963)

Parahydrogen Conversion on the First Transition Series

D. D. ELEY AND D. SHOOTER

From the Chemistry Department, University of Nottingham

Received January 24, 1963

The effect of pressure on the reaction velocity has revealed a new phenomenon, in which zero, or negative reaction order changes over to a fractional or first order reaction at higher pressures. This was found for Mn, Fe, Co, Ni at 90°K, and Co at 293°K. The mechanisms suggested are hydrogen atom recombination in a saturated layer, probably accompanied by hydrogen poisoning at low pressures and hydrogen molecule–atom exchange in a partly filled "second layer" at higher pressures. The reactions on Cr at 90°K, and Cr, Fe, and Ni at 293°K are simple zero order, and Mn, 293°K, Zn, 368°K, fractional and first order, respectively. Hydrogen-deuterium equilibration goes at comparable rates with the conversion, for Ti, V, Cr, and Ni; there is evidence for Ni that this holds down to 77°K. Attempts to estimate the rate of the paramagnetic conversion at 90°K using the Wigner equation confirm the dominance of the chemical mechanisms for all metals except Zn, where the mechanism is probably paramagnetic. A correlation between reaction velocity and sublimation energy for the range of metals at 293°K is associated with a mechanism of recombination of H atoms held on sites of minimum bond energy. The low frequency of these sites for body-centered cubic metals gives a frequency factor of 10^{16} molecules cm^{-2} sec^{-1} compared with 10^{19} for close-packed metals. A lower activation energy is found for bcc metals and is associated with a greater interaction energy between adsorbed atoms, in its turn associated with the broad character of the *d* band in this group of metals.

INTRODUCTION

Catalytic activity in the transition metals is associated with the presence of holes in the *d* band, as a result of studies on palladium-gold and copper-nickel alloys (*1, 2*). Holes in the *d* band seem to favor a low activation energy in hydrogen reactions, including dehydrogenation (*3*), and a high activation energy in carbon monoxide oxidation (*4*). It is natural to extend this study to the whole first transition series, titanium to zinc, for which results are available only for the oxides (*5*). There is the added complication that numbers of the series show changes in lattice structure as well as in electronic *d* band, but some insight is now available into the theoretical aspects (*6, 7*). In the first place a study was made of the parahydrogen conversion activity at 293°K on evaporated films of the whole series of metals. The results obtained (*8*) were closely parallel to those obtained for hydrogen atom recombination on metal foils (*9*) and will be further considered in this paper, which presents in addition a detailed discussion of activation energies and pressure dependencies, and studies on hydrogen–deuterium equilibration.

In discussing the results we shall refer by Roman numerals to four well-known mechanisms:

Paramagnetic, Bonhoeffer, Farkas and Rummel (*10*)

$$pH_2 + P \rightarrow P..pH_2 \rightarrow P + oH_2 \qquad \text{I}$$

Chemical, Bonhoeffer and Farkas (*11*)

$$pH_2 + M.M \rightarrow MH.MH \rightarrow M.M + oH_2 \qquad \text{II}$$

Chemical, Rideal (*12*)

$$pH_2 + MH.M \rightarrow MHM..pH_2 \rightarrow M.MH + oH_2 \qquad \text{IIIa}$$

Chemical, Eley (*13, 1*)

$$pH_2 + MH \rightarrow MH..pH_2 \rightarrow MH + oH_2 \quad \text{IIIb}$$

Here P denotes a paramagnetic center, M an unoccupied surface metal site, M–H chemisorbed hydrogen, M..pH_2, a hydrogen molecule physically adsorbed on a bare site, and M–H..pH_2 a hydrogen "molecule" adsorbed over, or on the same site as chemisorbed hydrogen.

Boreskov and Vassilevitch (*14*) have suggested a modification of IIIa in which adsorption–desorption of molecules occurs on a small fraction of active sites, but H-atom exchange may occur over the whole surface.

EXPERIMENTAL

The vacuum system was similar to that described by Eley and Rideal (*15*). The reaction space consisted of a cylindrical reaction vessel, cold trap, and mercury cutoff in series, connected to a gas preparation and storage system, a micro-Pirani gauge, and two mercury diffusion pumps plus an oil pump in series. The cylindrical reaction vessel contained an axial tungsten wire, round which the catalyst wire was wrapped preparatory to evaporation. The two exceptions to this procedure are noted below. The reaction system was baked out for 48 hr at 400°C, the wire being electrically heated in the final stages. The cold trap was then immersed in liquid oxygen, the reaction vessel cooled and immersed in cold water, and the metal film evaporated. The evaporation procedure followed that used by Trapnell (*16*), and in particular manganese was electroplated onto the tungsten wire, and chromium was evaporated as chips from a tungsten spiral.

Hydrogen was purified by passage through a heated palladium thimble, and parahydrogen prepared by using a charcoal catalyst cooled to the triple point of nitrogen (*17*).

The reaction velocity was studied at a standard pressure of 1.2 mm Hg over a wide range of temperature above 77°K. Temperatures below 273°K were obtained using a simplified earlier version of a recently described cryostat (*18*). Pressure dependencies were studied in many cases, and also the hydrogen–deuterium equilibration reaction.

RESULTS

Velocity Constants and Activation Energy, 293°K

The notation is that of Couper and Eley (*19*), the experimental first order constant being defined as

$$k_e(\text{min}^{-1}) = \frac{1}{t} \ln \frac{x_0 - x_{eq}}{x_t - x_{eq}}$$

where the fractions of parahydrogen, x_0 at zero time, x_t at time t minutes, and x_{eq} at equilibrium, are taken from the resistance values of the appropriate samples in the micro-Pirani gauge. If n is the number of hydrogen molecules in the reaction volume, and A the area of the metal film catalyst, the absolute velocity is

$$k_m(\text{molecules cm}^{-2}\ \text{sec}^{-1}) = nk_e/60A$$

We have calculated k_m values under the standard conditions and 1.2 mm pressure and with the reaction vessel (therefore catalyst) at 293°K. The apparent volume of the reaction space was calibrated with the reaction vessel at 293°K and the trap at 90°K. It was usually in the range 300–340 cc.

Apparent activation energies E were derived from the Arrhenius equation,

$$k_e = B_e e^{-E/RT}$$

or

$$k_m = B_m e^{-E/RT}$$

where

$$B_m = nB_e/60A$$

In some cases E was not constant over the wide temperature ranges studied, and values listed refer to 293°K and allow a comparison between different metals.

In general, the metal films were about 1–2 mg in weight, with geometrical areas of about 40 cm², and it was assumed in calculating k_m that their surface areas were equal to their geometric areas. The films were all laid down at room temperature and not heated very much above it. A study of the results of Anderson and Baker (*20*) for nickel films and Porter and Tompkins (*21*) for iron films suggests 1 mg films for these metals should have true areas of 100 and 200 cm², respectively, so the appropriate roughness factor for our films is 4 ± 1, which might be expected to hold for the series Ti to Ni inclusive. If future work should confirm this supposition, it will be necessary to correct our k_m and B_m values by dividing them by this factor 4. Except for the case of zinc films, no decrease in activity attributable to sintering was observed during the measurements, which favors the idea of a low roughness factor for all our films. Results for k_m, E, and B_m at 293°K are summarized in Table 1. The temperature coefficient plots are in Fig. 1.

Mott and Stevens (*6*) classified the transition metals into groups A and B on the basis of differences in crystal structure which they associated with differences in electronic band structure. Mott's latest view (*7*) is that the group A, fcc or close-

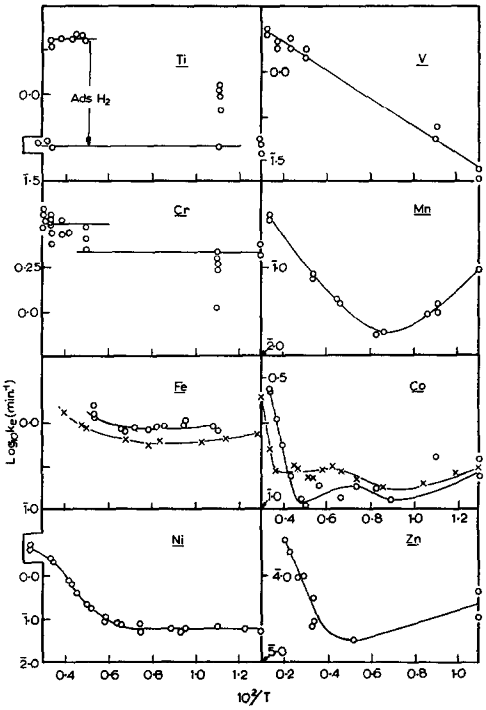

Fig. 1. Arrhenius plots for the parahydrogen conversion at 1.2 mm. The crosses are due to J. C. T. Fowell. V, Mn, and Co have the same values of abcissa.

TABLE 1

Arrhenius Constants at 293°K, and 1.2 mm Hg

Group	Metal film	k_m (molecules cm⁻² sec⁻¹)	E (kcal mole⁻¹)	B_m (molecules cm⁻² sec⁻¹)
B	Ti(+2.28H)	2.32×10^{16}	0.0	2.32×10^{16}
	V(+0.75H)	1.47×10^{16}	0.37	2.67×10^{16}
	Cr	1.39×10^{16}	0.0	1.39×10^{16}
	Mn	1.66×10^{15}	1.5	2.10×10^{16}
	Fe (1)	1.42×10^{16}	0.0	1.42×10^{16}
	Fe (2)[a]	1.21×10^{16}	0.36	5.18×10^{16}
A	Co (1)	1.85×10^{16}	4.2	2.95×10^{19}
	Co (2)	1.18×10^{16}	4.6	2.96×10^{19}
	Co (3)[a]	7.3×10^{15}	5.78	1.54×10^{20}
	Ni	1.67×10^{16}	3.5	0.80×10^{19}
	Cu[b]	7.56×10^{12}	8.5	1.65×10^{19}
	Zn (1)	3.70×10^{10}	3.3	1.20×10^{13}
	Zn (2)	6.10×10^{10}	3.1	1.26×10^{13}
	Zn (3)	4.50×10^{10}	3.0	1.38×10^{13}

[a] J. C. T. Fowell (*22*).

[b] D. D. Eley and D. R. Rossington (*23*).

packed metals have a narrow 3*d* band structure, while the group B bcc metals have a broad 3*d* band. It will be seen from Table 1 that the metals in group B are those with low activation energy and frequency factor, and group A those with high activation energy and frequency factor.

Hydrogen Adsorption and Hydrogen Poisoning

Of the group B metals, iron, chromium, and manganese show practically no absorption of hydrogen into the bulk of the metal at room temperature, but titanium and vanadium show a very strong absorption. The titanium film was found to instantaneously absorb 2.28 H atoms per Ti atom in the film, changing from a bright smooth surface to a matt appearance in the process. The vanadium film instantaneously absorbed 0.75 atoms H per V atom in the film. The results recorded in Table 1 are for films of titanium and vanadium containing this absorbed hydrogen and the catalytic activities are at least as high as for iron and chromium which absorb no hydrogen. However, in the case of titanium, if the film is left overnight in hydrogen at room temperature there is a fourfold loss of activity (cf. Fig. 1), the original activity being recoverable on pumping at room temperature for 5 hr. It would, therefore, appear that the two modes of hydrogen absorption, instantaneous and slow, are different in character. The slow adsorption which leads to a reversible poisoning effect is probably analogous to the observed earlier in palladium (*1*).

In the case of group A metals, the cobalt (1) (Table 2) film after a number of runs was baked out at 400°C, which resulted in a marked decrease of activity. E increased to 5.8 kcal mole^{-1}, but since B_m remained constant the effect was not due to sintering, but could possibly be attributed to hydrogen poisoning, as a result of hydrogen diffusion inwards in the baking process. In the case of nickel, some hydrogen sorption occurred above room temperature with a drop in catalytic activity, but it was not discovered whether the effect was reversible.

The Low-Temperature Conversion

The conversion of normal to parahydrogen was followed at the temperatures 77° and 90°K, and the films of manganese, zinc, and possibly cobalt, were found to show a definite negative activation energy in this range (cf. Fig. 1). For these particular metals we list k_m and E in Table 2.

TABLE 2

PARA-ORTHO CONVERSION AT 90°K

Metal film	k_m (molecules cm^{-2} sec^{-1})	E (kcal mole^{-1})
Mn(1)	5.8×10^{14}	−0.97
Mn(2)	2.9×10^{14}	−0.92
Co(1)	3.6×10^{15}	−1.09
Co(2)	4.8×10^{15}	(−0.24)
Co(3)	3.9×10^{15}	(−0.38)
Zn(3)	8.2×10^{11}	(−0.32)

Since in these cases the surface coverage must be less than one, the B_m values are certain to be complex and involve surface concentrations; they are, therefore, omitted.

The Pressure Dependency of the Conversion

Although in the past a number of pressure dependencies have been found to accurately fit the Langmuir isotherm, e.g., copper films (*23*) and tungsten wires (*19*), much of the present data is more complex. We have, therefore, presented it first in terms of a plot of log $k_e p$ (where $k_e p$ is proportional to k_m) against log p, the slope of which gives the order of reaction n in the Freundlich isotherm.

$$k_e p = \text{const. } p^n$$

The data are plotted in Figs. 2a and 2b, and values of n are given in Table 3.

For four metals at 90°K, and 1.0 mm pressure, the order is negative, becoming positive at 10 mm pressure. While the actual changes in $k_e p$ are small, the effect is clearly distinguishable from the simple zero order case of chromium. The behavior of all metals at 293°K is conventional except for the case of cobalt.

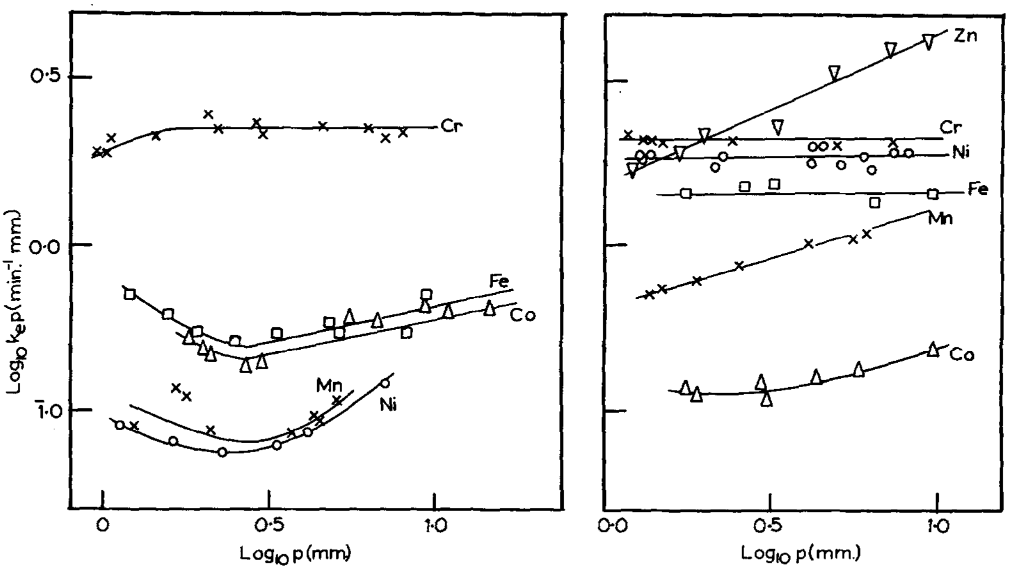

FIG. 2. Pressure dependencies as Freundlich plots for the conversion, (a) at 90°K, (b) at 293°K. (Zn at 368°K.)

TABLE 3
APPARENT ORDER OF REACTION, n

Metal	293°K		90°K	
	1 mm	10 mm	1 mm	10 mm
Cr	0	0	0	0
Mn	0.6	0.6	−0.5	+1.0
Fe[a]	0	0	−0.9	+0.7
Co[a]	0	0.6	−1.2[a]	+0.7
Ni	0	0	−0.5	+1
	368°K			
Zn	1.0	1.0	—	—

[a] J. C. T. Fowell (*22*).

Hydrogen–Deuterium Equilibration

Results are available for titanium, vanadium, chromium, and nickel in Fig. 3, and Table 4. Unfortunately, in the absence of mass spectrometric analysis, measurements could not be extended below 195°K. The negative temperature coefficient observed for titanium is probably an artifact due to evolution of occluded hydrogen. The k_e values of the parahydrogen conversion taken from Fig. 1 have been shown in Fig. 3 by dotted lines and the equilibration rate is seen to equal the conversion rate for vanadium at all temperatures, and for nickel at lower temperatures, and to be two or three times slower in the other cases. Either result would point to identical mechanisms, since such differences in rate may easily arise from differences in zero point energy from hydrogen and deuterium.

TABLE 4
EQUILIBRATION AT 293°K AND 1.2 MM

Metal film	k_m (molecules cm^{-2} sec^{-1})	E (kcal mole^{-1})	B_m (molecules cm^{-2} sec^{-1})
Ti	(1.3×10^{16})	0.0	(1.3×10^{16})
V	1.4×10^{16}	0.92	6.7×10^{16}
Cr	7.5×10^{15}	0.33	2.2×10^{16}
Ni	1.2×10^{16}	2.44	8.9×10^{17}

DISCUSSION

Activation Energies and Frequency Factors at 293°K

When the order of the reaction is specified by the coefficient n of the Freundlich isotherm, it has been found (*24*) that the apparent activation energy E and true activation energy E_t are related to the heat of adsorption q by

$$E = E_t - qn$$

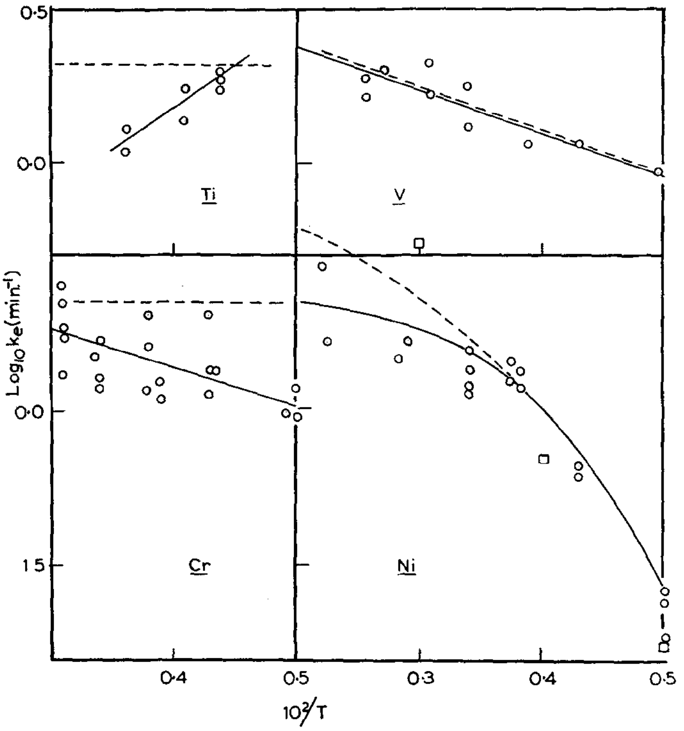

FIG. 3. Arrhenius plots for $H_2 + D_2 \rightarrow 2HD$, at 1.2 mm. Ti and V; Cr and Ni have same values of ordinates. The dotted lines denote parahydrogen conversion data. The three squares for Ni are H_2, D_2 data for Ni–SiO_2. (Schuit and van Reijen.)

Now it may be shown that where Langmuir and Freundlich isotherms coincide, the surface coverage θ is $\theta = 1 - n$ (*13*). Also, for the general case of Langmuir adsorption where $\theta = bp/(1 + bp)$ with $b = b_0 \exp(q/RT)$, it follows that (*25*)

$$E = E_t - q(1 - \theta)$$

The latter equation is an extension of Hinshelwood's well known relation (*26*).

Referring to Table 3, the order $n = 0$ holds for the metals chromium, iron, cobalt, and nickel, all of which strongly chemisorb hydrogen (*16*, *27*), and a similar result is to be expected for titanium and vanadium, which also fall into this class of strong adsorbers.

For manganese, $n = 0.6$ corresponds to $\theta = 0.4$. The hydrogen uptake measurements for manganese (*28*) point to a value of $\theta \approx 0.1$ at 293°K and 1×10^{-2} mm, so that at 10 mm pressure a value of $\theta = 0.4$, is not unreasonable. The heat of adsorption is 17 kcal mole^{-1} (*28*) so we estimate a true activation energy $E_t = 1.5 + 0.4$ (17) $=$ 8.3 kcal mole^{-1}, and the true B_m becomes 2.5×10^{22} molecules cm^{-2} sec^{-1}. For copper the apparent E and B_m values in Table 1 correspond to the true values $E_t = 13$ kcal mole^{-1} and $B_m = 3.83 \times 10^{21}$ molecules cm^{-2} sec^{-1} [i.e. $(5.6 \times 10^6$ sec$^{-1}) \times (0.68 \times 10^{15}$ molecules cm$^{-2})$], derived from the effect and temperature on the Langmuir isotherms (*23*). Similar corrections are applicable to the data for zinc where $n = 1.0$ over the whole pressure range.

Theoretical Kinetics

Let there be f sites per cm^2, surface fraction covered θ_H for H atoms, θ_{H_2} for H_2 molecules, both in the chemisorbed layer, and θ_{VW} for H_2 molecules in the van der Waals' layer. We shall need to distinguish a second layer adsorption of hydrogen molecules, stretched molecules or atoms in mechanism IIIb by θ_{II}. For simplicity we assume Langmuir-type adsorption, with adsorption coefficients b_H, b_{H_2}, and b_{VW}, and as previously (*23*) relate k_m in molecules cm^2 sec^{-1} to $(k_o + k_p)$, sec^{-1} the sum of the ortho → para and para → ortho transitions per site per sec (*17*).

In fact, while Langmuir adsorption holds strictly for the almost bare surfaces, it also, as Wang showed (*29*), holds approximately for the almost saturated surfaces with repulsive interactions between adsorbed atoms, i.e., for the coverages $\theta_H \rightarrow 1$. In the latter case $b = b_0 \exp{(q - ZV)/RT}$ where ZV is the interaction energy term. All our cases except Mn fall into one or other of these two classes.

Mechanism I, The Paramagnetic Mechanism

Wigner (*30*) expressed the transition probability per site per collision as $W_{01} \cdot G(T)$, and Ashmead, Eley, and Rudham (*31*) applied this to calculate k_m for a paramagnetic surface of n_0 magnetic sites per cm^2, each with magnetic moment μ Bohr magnetons, with a separation r_s between hydrogen molecule and magnetic site,

$$k_m = \theta n_0 \nu W_{01} G(T)$$

Here θ is the fraction of magnetic sites covered with hydrogen molecules, ν the vibration frequency of the hydrogen molecule against the surface site, and $G(T) =$ 0.210 for 77°K, 0.254 for 90°K.

$$W_{01} = 1.177 \times 10^{-9}(\mu^2/r_s^6 T),$$

where μ is in Bohr magnetons, r_s in Å, and T in °K. If we assume a total of 10^{15} sites per cm^2, a fraction F_a being magnetic sites ($n_0 = F_a \ 10^{15}$) and $\nu = 4.5 \times 10^{11}$ sec^{-1} (*32*),

$$k_m = 1.49 \times 10^{15}(\mu^2/r_s^6) \cdot F_a\theta \text{ molecules cm}^{-2} \text{ sec}^{-1} \text{ at } 90°\text{K}$$

For neodymium oxide, conversion occurred at 90°K on a small fraction of *saturated* sites, under conditions where the van der Waals' layer was very dilute (*31*). With an estimated $n_0\theta = 5 \times 10^{12}$, the ratio k_m (obs) : k_m (calc) = 100, which, since this conversion must be purely paramagnetic, forms a reference figure for the transition metal films.

If in the above equation the only effect of temperature is to decrease the coverage of hydrogen molecules θ, as assumed by Bonhoeffer *et al.* (*11*).

$$E = RT^2 \frac{d \ln k_m}{dt} = RT^2 \frac{d \ln \theta}{dT}$$
$$= RT^2 \frac{d \ln}{dT} \left(\frac{bp}{1 + bp} \right)$$

$$\therefore \text{ (ref. 27)} \quad E = -q(1 - \theta)$$

For neodymium oxide (*31*) and gold (*32*) where conversion occurs on a small number of saturated sites, we may have the heat of adsorption on the sites q greater than the heat of van der Waals' adsorption and $\theta \sim 1$. The nature of these special sites is still unknown. But in general one would first assume $F_a = 1$ and θ and q appropriate to van der Waals' adsorption.

Mechanism II

If we write this as the rate of recombination of chemisorbed H atoms held on separate equivalent sites,

$$k_m = f(k_o + k_p)\theta_H^2$$
$$= f(k_o + k_p) \left(\frac{\sqrt{bp}}{1 + \sqrt{bp}} \right)^2$$

Since $k_m = k_e pV/60\ AkT$

$$\frac{1}{k_e} = \frac{V}{60AkTf(k_o + k_p)} \cdot \left(\frac{1}{b} + \sqrt{\frac{p}{b}} + p \right)$$

In the one well-investigated case of this mechanism, pH$_2$ on a copper film, it was observed by Eley and Rossington (*23*) that $1/k_e$ is linear with p. Ward observed a similar result for hydrogen uptake on a copper powder, as noted by Trapnell (*27*). Normally, at $p < 10$ mm we expect the $\sqrt{p}$ term to be dominant, and where, at these low pressures we find the p term is dominant we must suppose either that the conversion occurs on "site-pairs," or that hydrogen molecules may dissociate on single sites. In this case

$$\frac{1}{k_e} = \frac{V}{60AkTf(k_o + k_p)} \cdot \left(\frac{1}{b} + p \right)$$

Observations of hydrogen chemisorption suggest that all the metals examined here, excepting manganese, copper, and zinc have a complete monolayer of H atoms at 293°K and 1 mm pressure (*16, 27*), and in this case the reaction is predicted to be zero order. In terms of the above equations k_m or $k_e p$ will be independent of pressure, and a plot of $1/k_e$ vs. p will be a straight line effectively passing through the origin. The data of Fig. 2b are replotted according to the Langmuir isotherm in Fig. 4. The deviations for cobalt at 4 mm point to a second mechanism setting in at this pressure, probably one involving hydrogen molecules in a second, partly covered layer.

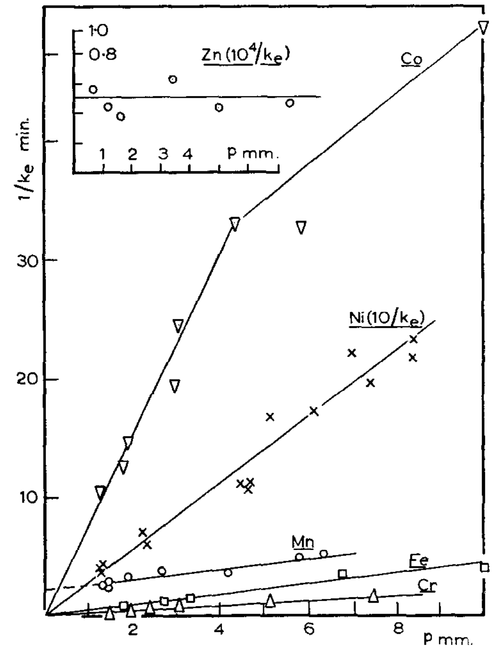

FIG. 4. Pressure dependencies as Langmuir plots, for the conversion at 293°K. (Data of Fig. 2b.)

Mechanism IIIa

This assumes a competition between H atoms and H_2 molecules for sites in the chemisorbed layer. Thus

$$k_m = f(k_o + k_p)\theta_{H_2} \cdot \theta_H = f(k_o + k_p)\left[\frac{b_{H_2} p b_H^{1/2} p^{1/2}}{(1 + b_H^{1/2} p^{1/2} + b_{H_2} p)^2}\right]$$

For the conditions usual on transition metals where $\theta_H \to 1$, $b_H^{1/2} p^{1/2} \gg 1 + b_{H_2} p$

$$k_m = f(k_o + k_p)(b_{H_2}/b_H^{1/2})p^{1/2}$$

i.e.,

$$\frac{1}{k_e} = \frac{V}{60AkTf(k_o + k_p)} \cdot \frac{b_H^{1/2}}{b_{H_2}} p^{1/2}$$

The same result was found by Boreskov for his modified mechanism IIIa, assuming the rate of desorption determines the rate of conversion, $k_m \propto \theta_{H_2}$ (*14*).

Mechanism IIIb

This assumes H_2 molecules in a second layer, reacting with an underlying layer of chemisorbed H atoms. Since appreciable second layer coverages are found, van der Waals' forces must be augmented in some fashion, as discussed later, and we write the fractional coverage θ_{II} rather than θ_{VW}.

$$k_m = f(k_o + k_p)\theta_H\theta_{II} = f(k_o + k_p)\left(\frac{b_H^{1/2} p^{1/2}}{1 + b_H^{1/2} p^{1/2}} \cdot \frac{b_{II} p}{1 + b_{II} p}\right)$$

For transition metals where $\theta_H \to 1$

$$k_m = f(k_o + k_p)\left(\frac{b_{II} p}{1 + b_{II} p}\right)$$

i.e.,

$$\frac{1}{k_e} = \frac{V}{60AkTf(k_o + k_p)} \cdot \left(\frac{1}{b_{II}} + p\right)$$

If we use a Freundlich isotherm instead of a Langmuir isotherm then

$$k_m = f(k_o + k_p)kp^n \qquad (n = 0 \text{ to } 1)$$

It is expected at room temperature that $\theta_{II} \to 0$, so that $b_{II} p \ll 1$ and the reaction will be first order ($n = 1$). There is adsorption evidence for a considerable second layer coverage for transition metals at 90°K, so at this temperature we may expect to find reaction orders of less than 1.

Present Results Compared with Earlier Data

A. and L. Farkas (*33*) found $n = 0.65$ for the conversion on a nickel film at

293°K, 10^{-2} to 1 mm. However, their catalyst was probably partially poisoned since it was 85 times less active than our film, which may explain the difference in order from our results.

The close similarity in rate of the conversion and equilibrium reactions found here for nickel confirms those previously observed on a nickel tube by Fajans (*34*), for the temperatures around 373°K. The low activity of Fajan's catalyst probably indicates adventitious poisoning of its surface. Schuit and van Reijen (*35*) have examined the equilibration reaction down to 77°K on nickel-silica catalysts and their log k_e vs. T^{-1} graph exactly corresponds with that given for the conversion on a nickel film in Fig. 1. The absolute rates per unit area are estimated to be closely similar for supported catalyst and evaporated nickel film.

Schuit and van Reijen (*35*) list hydrogen–deuterium equilibration rates for four metals supported on silica, as values of $N_g \lambda/N_s$. Here λ is the usual first order rate constant (our k_e), N_g the number of hydrogen atoms in the gas phase, and N_s the number of sites on the catalyst. Basing N_s for all four metals on the value for nickel of 1.54×10^{15} sites per cm² (*36*) we derive $k_e = 0.173 \, (N_g\lambda/N_s)$ and apply this to the data in their Fig. 34. There is a further factor of 4.45×10^{15} to convert k_e to k_m, or B_e to B_m. We find that for nickel there is a close agreement between the data on the supported catalyst and the film, even to the extent of the curve flattening out from 140° to 77°K with a rate one-third that found for the conversion reaction (Fig. 1). Therefore, we conclude the conversion on nickel at 77°K goes predominantly through a chemical mechanism. At 293°K supported nickel gives for hydrogen–deuterium $E = 3.26$ kcal mole^{-1} and $B_m = 0.21 \times 10^{19}$ which agrees with the figures for the conversion on the film in Table 1. For supported copper at 293°K, $E = 6.1$ and $B_m = 2.4 \times 10^{19}$, which also agrees with conversion on a copper film. For supported iron at 293°K, $E = 6.1$ and $B_m = 2.4 \times 10^{19}$ as for copper, but in grave disagreement with our two independent values for iron films. For supported cobalt the hydrogen–deuterium reaction had $E = 1.34$ and $B_m = 9.7 \times 10^{16}$ which disagrees with the two independent values for conversion on films in Table 1 and Fig. 1. The hydrogen–deuterium reaction rate on supported cobalt fell away continuously with decrease of temperature until at 78°K, it was ten times slower than the conversion rate on the film. We, so far, have no data on iron films, but Kummer and Emmett (*37*) found a ratio of conversion to equilibration rates of between 50 and 167 for a singly promoted iron catalyst at 78°K.

Perhaps the simplest and safest conclusion at present is that on all these metals at 78°K conversion and equilibration go through the same chemical mechanism. The ratio of rates for cobalt and nickel could easily arise from differences in activation energy due to zero point energy differences in M—H and M—D bonds. Thus a difference in activation energy of 1 kcal mole^{-1}, quite possible from this source, would give rise to a ratio of conversion:equilibration rates of 660 at 78°K. While such differences are not found for nickel (or earlier for tungsten) they can arise in principle and prevent us from ascribing the observed ratio to a strong paramagnetic conversion on cobalt and iron. Further work is in progress.

Conversion Mechanisms at 90°K

A negative temperature coefficient below 293°K, as for manganese and zinc in Fig. 1, has usually been indicative of paramagnetic conversion for the reason given earlier. Although cobalt shows more complex behavior, there is an indication of similar behavior for this metal, cf. Table 2. Although zinc is diamagnetic in bulk, its surface may well be paramagnetic as in the case of charcoal (*10*) and gold (*32*). For zinc, the paramagnetic centers are most likely dangling valencies, i.e., free electrons at special sites such as steps or dislocations, and we shall assume a similar situation to that found for gold (*32*), but while for zinc this may be $F_a = 0.01$, $\theta = 1$, for the transition metals each site will be paramagnetic, $F_a = 1$, but the coverage will be that appropriate to the van der Waals' layer, which might be 0.01 at 90°K. We, therefore, have calculated velocities by

$$k_m\ (\text{calc}) = 1.49 \times 10^{15}(\mu^2/r_s^6) \cdot 0.01$$

taking $r_s = 2.5$ Å (the sum of the metallic and H_2 radii). Because of the presence of chemisorbed hydrogen r_s may well be larger than 2.5 Å so k_m (calc) is an upper value. The results are shown in Table 5.

TABLE 5

Observed and Calculated Paramagnetic Conversion, 90°K

Metal	μ (B.M.)	k_m (calc)	k_m (obs)	k_m(obs)/k_m(calc)
Mn	1.1	7.3×10^{10}	5.8×10^{14}	7.9×10^{3}
Fe	2.22	3.0×10^{11}	1.3×10^{16}	4.3×10^{4}
Co	1.71	1.8×10^{11}	3.6×10^{15}	2.0×10^{4}
Ni	0.61	2.2×10^{10}	1.0×10^{15}	4.5×10^{4}
Zn	(1.73)	1.8×10^{11}	8.2×10^{11}	4.6

It should be remembered that a careful comparison of observed and calculated rates for Nd_2O_3 gave rise to a ratio of 100 in a case where the number of sites could be estimated and the conversion was certainly paramagnetic (*31*). Even so, the discrepancies for Mn, Fe, Co, and Ni are so large that it seems fairly certain the conversion at 90°K is chemical rather than paramagnetic in character. This merely reinforces what is already certain for Ni from the H_2,D_2 study.

The conversion on zinc at 90°K seems quite definitely paramagnetic in character since the ratio k_m(obs)/k_m (calc) is certainly well within the error of our calculation. In fact, it is not possible to visualize any chemical activation of hydrogen by so uncatalytic a metal as zinc at 90°K.

It seems clear that for vanadium the conversion at 77°K, with a positive temperature coefficient, will occur by the chemical mechanism. Further experiments will be necessary with H_2, D_2 at 77°K to decide the matter for Ti and Cr.

The available pressure dependencies at 90°K show a complex behavior for all metals except chromium. Hickmott (*38*) has shown that there are two kinds of adsorbed hydrogen on a tungsten surface, type β which corresponds to one chemisorbed H atom per tungsten site, and the much more weakly held type α, which is molecular hydrogen. At 10^{-5} mm and 77°K there are 6.2×10^{14} molecules cm^{-2} in the β state (heat of chemisorption 15 kcal mole^{-1}) and 6.0×10^{13} molecules cm^{-2} in the α state. Since there are approximately 1.2×10^{15} sites cm^{-2} assuming a roughness factor of unity for the tungsten surface, these surface concentrations correspond to $\theta_H = 1$ for the H atoms and $\theta_{II} = 0.13$ for the H_2 molecules. If it is permissible to extrapolate the log–log isotherms, we should expect $\theta_{II} = 0.38$ at 1 mm hydrogen pressure. At 194°K and 10^{-5} mm pressure we still expect $\theta_H \approx 1$ for the β state, but θ_{II} for the α state will approximate to zero. Gomer, Wortman, and Lundy (*39*), and Couper *et al.* (*32*) concluded that mechanisms II and III were both operative for tungsten but that mechanism III was dominant below 198°K and mechanism II above this temperature. Hickmott supports this view, pointing out that mechanism II can operate over the whole range from 373 to 77°K but would be most important above 200°K. We, therefore, suggest that at low temperatures such as 90°K we shall first expect mechanism II with a zero order pressure dependency, passing over at higher pressures to IIIa or IIIb occurring in a partly filled (second) monolayer, with a pressure dependency between zero and first order. Referring to Fig. 2a we therefore suppose that mechanism III is not operative on Cr, but may be operative on Fe, Co, Mn, and Ni. At lower pressures on these last four metals there are definite indications of a negative order which may be due to (a) a steep decrease in sticking probability at $\theta_H \rightarrow 1$ or (b) a poisoning of the catalyst by dissolved hydrogen occupying empty *d* orbitals otherwise available for surface bonding.

The negative temperature coefficient found for Mn at 90°K may be associated with desorption of hydrogen molecules from a second layer, slowing down mechanism IIIb (not the paramagnetic mechanism). The rate goes through a minimum since a considerable temperature rise is then necessary before the chemisorbed H-atom concentration increases to give an appreciable rate for mechanism II. We suppose the hydrogen molecules for IIIb are held on empty *d* orbitals, and for vanadium these will all be filled by electrons from dissolved hydrogen. If only mechanism II is then left active for V, this would explain the straight line observed for the temperature coefficient.

The problem of a zero order conversion followed by a first (or positive fractional) order reaction at higher pressures was first found for the paramagnetic conversion on gold at 90°K (*32*). What was once a unique result now emerges in an even more complex form for the chemical mechanism. It is in complete contrast to the prediction for a single Langmuir mechanism of a first order reaction tending to a zero order reaction at higher pressures. It is possible that mechanism II may be operative on one set of sites A and mechanism III on another set of sites B, as visualized by Mignolet (*40*) and Sachtler and Dorgelo (*41*). According to these authors the hydrogen on the A sites is negative, and that on the B sites positively charged. Two hydrogen atoms on an AB pair of sites form a stretched hydrogen molecule, and this may constitute the van der Waals' layer of mechanism IIIb and give an order between 0 and 1 as observed. In the absence of an accurate half order pressure dependency, we are inclined to rule out IIIa at present.

Mechanisms at 293°K

We may safely assume at this temperature that the surface coverage of second layer hydrogen θ_{II}, Hickmott's α hydrogen, is very small, at least at 10 mm pressure. We may therefore ignore mechanism III, and concentrate on the behavior of mechanism II, recombination of hydrogen atoms, in the primary layer, Hickmott's β hydrogen. It follows from Fig. 2b that this primary monolayer is saturated for chromium, iron, nickel, and cobalt, where the order is clearly zero (for the last metal at low pressures only). The onset of a reaction order of 0.6 for cobalt at 4 mm pressure suggests the setting in of mechanism IIIb due to a population of the second layer with hydrogen molecules at

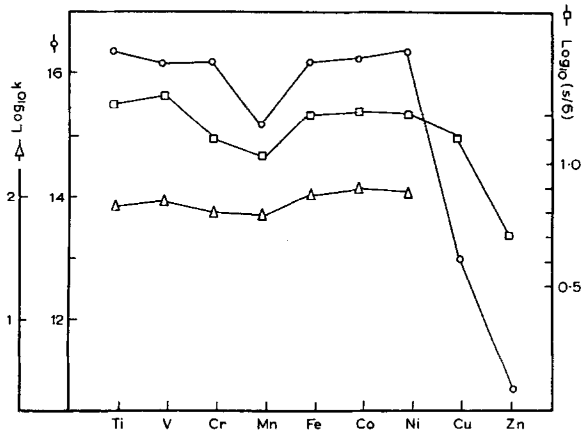

FIG. 5. Catalytic activity and atomic number, $k = k_m$ for the conversion (units 12–16) and relative activity for Nakada's data on H atom recombination (units 1–2). The right-hand ordinate is a log plot of one-sixth the sublimation energy of the metal, in kcal mole^{-1}.

increased pressure. The conversion on manganese denotes the operation of mechanism II in a primary layer of coverage $\theta_H = 0.4$, with a similar conclusion for zinc but with $\theta_H \rightarrow 0$. For manganese and zinc the apparent activation energy for this conversion should be that for the chemisorption process. The chemisorption activation energy for manganese is 1 kcal mole^{-1} (*28*), which agrees with the value in Table 1.

The above conclusions are also demonstrated very clearly by the Langmuir isotherm plots in Fig. 4. The zero order metals show good straight lines through the origin, while manganese and zinc show the expected definite intercepts on the $1/k_e$ axis. The change of mechanism on cobalt at 4 mm pressure is also shown.

Catalytic Activity and Electronic Structure

The k_m values at 293°K are plotted in Fig. 5 as a function of atomic number together with Nakada's data (*9*) for H-atom recombination on foils. There is a clearly marked minimum for manganese which we may assume, since it is found for both films and foils, to be free from uncertainties due to surface area variations. Of the various metallic properties, the only close parallel is that with the sublimation energy of the metal (*8*) and this is shown in Fig. 5. Treating the metal–hydrogen bond as a covalent bond, involving the normal (*dsp*) metal orbitals, and extending an earlier treatment (*42, 43*) for heat of adsorption $q(\theta)$

$$q(\theta) = 2E(\text{M–H}) - E(\text{H–H})$$
$$= E(\text{M–M}) + 46(X_M - X_H)^2$$

where the usual procedure is to approximate the energy of the metal–metal bond E(M–M) as one-sixth of the sublimation energy S.

The electronegativity of the metal *surface* $X_M = 0.355\phi_m$, where ϕ_m is its work function (*44*) and $X_H = 2.1$.

In the past this equation has been used, with values of X_m or ϕ_m for the clean metal surface averaged over the exposed lattice planes, to derive the heat of adsorption for the bare surface $q(\theta = 0)$. However, it may be extended to calculate $q(\theta = 0)$ values for the different lattice planes should appropriate ϕ_m values be known. In general for a given metal ϕ_m is highest for the most close-packed planes, e.g. for tungsten it varies from 4.39 ev for the (111) plane to 5.53 ev for the (011) plane (*45*). Also the effect of chemisorbed hydrogen is to give a negative film, raising ϕ_m with increased coverage by 0.3 to 0.5 ev (*46*). Therefore, as a metal surface is covered with hydrogen the effect of these two factors, lattice plane and negative film, will be to cause ϕ_m to rise and $q(\theta)$ to fall, until $\phi_m = 5.9$ ev, corresponding to $X_M = X_H = 2.1$. At this coverage there will be found a minimum value for the heat of chemisorption on the particular metal, given by

$$q(\text{min}) = E(\text{M–M}) = S/6$$

The hydrogen in this film will be predominantly covalent in character with zero ionic component.

Therefore, the results of Fig. 5 may be understood in terms of mechanism II, with a rate-determining activation free energy related to the heat of desorption of hydrogen in a nearly full layer on the most close-packed lattice planes available.

The activation energies and frequency factors offer a more complex problem, the group B bcc metals with the exception of manganese having $E \sim 0$ kcal mole^{-1}, $B_m \sim 10^{16}$ molecules cm^{-2} sec^{-1}, while the group A close-packed metals have $E \sim 4$ to 8, $B_m \sim 10^{19}$.

Considering first the case of manganese, this has a heat of adsorption for hydrogen only half the value for the other bcc metals (*44*). Referring to Fig. 6, if we only have to consider the potential energy curve of covalently bound H atoms held on *dsp* orbitals, $2M_{dsp}$–H, crossing a van der Waals adsorption curve 2M . . . H_2, then a decrease in heat of desorption should give rise to a decrease in the activation energy for desorption, whereas for manganese, the reverse was observed. We, therefore, invoke the presence of an intermediate state, H atoms held on atomic *d* orbitals of the

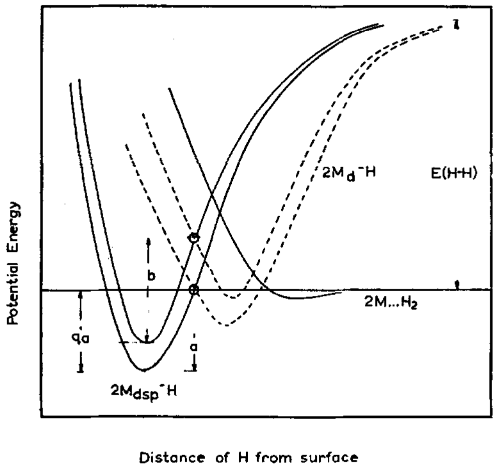

FIG. 6. Lennard-Jones curves for chemisorption of hydrogen on metal *d* and *dsp* orbitals. $2M_d$–H, is an intermediary in mechanism II. On going from bcc metal with a high heat of adsorption q_a to one with a lower value, the M_{dsp}–H and M^d–H curves both rise so the activation energy increases from a to b.

metal M_d–H, as suggested by Gundry and Tompkins (*47*). To explain the observed increase in *E* from Fe to Mn then it is necessary to assume an even greater shift in the energy of the intermediate M_d–H, than the initial M_{dsp}–H, giving the increase in *E* from a to b as shown in Fig. 6. This explanation then ascribes a special role as intermediates to the atomic *d* orbitals in bcc metals. In the modern picture of a broad hybridized *d* band with two peaks separated by a minimum, the *dsp* and *d* orbitals may correspond to levels at the bottom and top of the band, respectively.

The zero activation energy for desorption on bcc metals is reconcilable with the saturated adsorbed layer on the surface (zero order reaction), because the observed activation energy is simply that at $\theta_H \rightarrow 1$. It is, of course, very much less than the value at zero coverage, due to the presence of repulsive interactions (*48*, *49*). The possibility of such a system obeying the Langmuir isotherm over a restricted range of high coverages near $\theta_H = 1$ has already been mentioned.

Since it appears the reaction proceeds preferentially on the most close-packed planes, and these are relatively infrequent for bcc metals, we may expect the relatively low frequency factor observed.

We may compare the group A metals with the group B metals in terms of Takaishi's observation (*50*), that the q/θ curve for the A metals falls less steeply than for the B metals, so that we may expect the values at complete coverage to be $q_{\text{group A}}$ $(\theta = 1) > q_{\text{group B}}$ $(\theta = 1)$. The difference is attributed to the basic difference in orbitals involved, the A metals with narrow 3*d* band having orbitals interacting less with those on neighboring atoms, than the B metals with their broad 3*d* band based on highly interacting orbitals. The situation now is just the reverse of that discussed for manganese. It receives a natural explanation in that for the group A metals with narrow 3*d* bands the M_{dsp} and M_d orbitals will be much closer in energy and barely distinguishable. In this case there will be no intermediate state to lower the activation energy for desorption, which will, therefore, be larger than that found for the group B metals.

Since there will be a greater frequency of close-packed planes for the close-packed group A metals, the larger frequency factor of 10^{19} may be understood.

The frequency factors for evaporated films found here are all less than those found earlier for the same metals in the form of wires (*32*). This confirms our earlier conclusions for copper, silver, and gold (*23*) and emphasizes that the frequency factors are influenced by structural considerations, presumably the presence of defects, or dislocations in the catalytic surface.

The operation of mechanism IIIb on nickel and the other metals at 90°K involves a coverage θ_H of H_2 molecules, presumably held on metallic *d* orbitals (*51*) rather than as the separated atoms of Fig. 6. This absorbed molecular hydrogen may possibly be that called type C by Emmett (*52*) and the matter has recently been extensively discussed by Bond (*53*). It is undoubtedly a form of weak chemisorption, the nature of which is still not clear.

Since the reaction on zinc is first order, its true activation energy will be $3.2 + q$, where q is the, at present unknown, heat of adsorption, and the B_m factor will be greater than the apparent value of 10^{13}. When this true B_m is known it will be interesting to estimate the number of chemically active sites and compare it with the number of paramagnetic sites. The sites may possibly be dislocations.

ACKNOWLEDGMENTS

The authors wish to thank the D.S.I.R. for a studentship, Dr. Fowell for data on iron and cobalt, and the referees for some helpful comments on van der Waals adsorption.

REFERENCES

1. COUPER, A., AND ELEY, D. D., *Discussions Faraday Soc.* **8**, 172 (1950).
2. DOWDEN, D. A., AND REYNOLDS, P. W., *Discussions Faraday Soc.* **8**, 184 (1950).
3. ELEY, D. D., AND LUETIC, P., *Trans. Faraday Soc.* **53**, 1483 (1957).
4. DAGLISH, A. G., AND ELEY, D. D., *in* "Actes du Deuxième Congress International de Catalyse," Vol. 1, p. 1615. Éditions Technip, Paris, 1960.
5. DOWDEN, D. A., MACKENZIE, N., AND TRAPNELL, B. M. W., *Proc. Roy. Soc.* **A237**, 245 (1957).
6. MOTT, N. F., AND STEVENS, K. W. H., *Phil. Mag.* **2**, 1364 (1957).
7. MOTT, N. F., *Repts. Progr. Phys.* **25**, 218 (1962).
8. ELEY, D. D., AND SHOOTER, D., *Proc. Chem. Soc.*, p. 315 (1959).
9. NAKADA, K., *Bull. Chem. Soc. Japan* **32**, 809 (1959).
10. BONHOEFFER, K. F., FARKAS, A., AND RUMMEL, K. W., *Z. Phys. Chem.* **B21**, 225 (1933).
11. BONHOEFFER, K. F., AND FARKAS, A., *Trans. Faraday Soc.* **28**, 242 (1932).
12. RIDEAL, E. K., *Proc. Cambridge Phil. Soc.* **35**, 130 (1939).
13. ELEY, D. D., *Trans. Faraday Soc.* **44**, 216 (1948).
14. BORESKOV, G. K., AND VASSILEVITCH, A. A., "Actes du Deuxième Congress International de Catalyse," Vol. 1, p. 1095. Éditions Technip, Paris, 1960.
15. ELEY, D. D., AND RIDEAL, E. K., *Proc. Roy. Soc.* **A178**, 452 (1941).
16. TRAPNELL, B. M. W., *Proc. Roy. Soc.* **A218**, 566 (1953).
17. FARKAS, A., "Orthohydrogen, Parahydrogen and Heavy Hydrogen." Cambridge Univ. Press, London and New York, 1935.
18. ASHMEAD, D. R., AND RUDHAM, R., *Chem. and Ind.*, p. 401 (1962).
19. COUPER, A., AND ELEY, D. D., *Proc. Roy. Soc.* **A211**, 544 (1952).
20. ANDERSON, J. R., AND BAKER, B. G., *J. Phys. Chem.* **66**, 482 (1962).
21. PORTER, A. S., AND TOMPKINS, F. C., *Proc. Roy. Soc.* **A217**, 544 (1953).
22. FOWELL, J. C. T., personal communication (1962).
23. ELEY, D. D., AND ROSSINGTON, D. R., *in* "Chemisorption" (W. E. Garner, ed., Keele Conference), p. 137. Butterworths, London, 1957.
24. SANDLER, Y. L., *J. Chem. Phys.* **21**, 2243 (1953).
25. ELEY, D. D., *Nature* **194**, 1076 (1962).
26. HINSHELWOOD, C. N., "The Kinetics of Chemical Change," Chap. 8. Oxford Univ. Press, London and New York, 1940.
27. TRAPNELL, B. M. W., "Chemisorption." Butterworths, London, 1954.
28. TRAPNELL, B. M. W., GREENHALGH, E., AND HAYWARD, D. O., *J. Phys. Chem.* **61**, 1254 (1957).
29. WANG, J. S., *Proc. Roy. Soc.* **A161**, 127 (1937).
30. WIGNER, E., *Z. Phys. Chem.* **B23**, 28 (1933).
31. ASHMEAD, D. R., ELEY, D. D., AND RUDHAM, R., *Trans. Faraday Soc.* **59**, 207 (1963).
32. COUPER, A., ELEY, D. D., HULATT, M. J., AND ROSSINGTON, D. R., *Bull. soc. chim. Belges.* **67**, 343 (1958).
33. FARKAS, A., AND FARKAS, L., *J. Am. Chem. Soc.* **64**, 1594 (1942).
34. FAJANS, E., *Z. Physik. Chem.* **B28**, 239 (1935).
35. SCHUIT, G. C. A., AND VAN REIJEN, L. L., *Adv. in Catalysis* **9**, 242 (1958).
36. KLEMPERER, D. F., AND STONE, F. S., *Proc. Roy. Soc.* **A243**, 375 (1957).
37. KUMMER, J. T., AND EMMETT, P. H., *J. Phys. Chem.* **56**, 258 (1952).
38. HICKMOTT, T. W., *J. Chem. Phys.* **32**, 810 (1960).
39. GOMER, R., WORTMAN, R., AND LUNDY, R., *J. Chem. Phys.* **26**, 1147 (1957).
40. MIGNOLET, J. C. P., *Bull. soc. chim. Belges.* **67**, 343 (1958).
41. SACHTLER, W. M. H., AND DORGELO, G. J. H., *in* "Fourth Intern. Conf. on Electron Microscopy" (1958), Vol. 1, p. 51. Springer, Berlin, 1960.
42. ELEY, D. D., *Discussions Faraday Soc.* **8**, 34 (1950).
43. ELEY, D. D., "Catalysis and the Chemical

Bond." Univ. of Notre Dame Press, Notre Dame, Indiana, 1954.

44. Stevenson, D. P., *J. Chem. Phys.* **23,** 207 (1955).

45. Suhrmann, R., *Adv. in Catalysis* **7,** 303 (1955).

46. Culver, R. V., and Tompkins, F. C., *Adv. in Catalysis* **11,** 67 (1959).

47. Gundry, P. M., and Tompkins, F. C., *Trans. Faraday Soc.* **52,** 1609 (1956).

48. Rideal, E. K., and Trapnell, B. M. W., *Discussions Faraday Soc.* **8,** 114 (1956).

49. Trapnell, B. M. W., *Proc. Roy. Soc.* **A206,** 39 (1951).

50. Takaishi, T., *Z. physik. Chem. N.F. (Frankfurt)* **14,** 164 (1958).

51. Dowden, D. A., *in* "Chemisorption" (W. E. Garner, ed., Keele Conference), p. 3. Butterworths, London, 1957.

52. Emmett, P. H., and Harkness, R. W., *J. Am. Chem. Soc.* **57,** 1631 (1935).

53. Bond, G. C., "Catalysis by Metals," p. 109. Academic Press, New York, 1962.