HOKKAIDO UNIVERSITY

Instructions for use

ON THE HYDROGEN-DEUTERIUM
EXCHANGE REACTION

By

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Since 1935 when A. FARKAS published his book entitled "Orthohydrogen, Parahydrogen and Heavy Hydrogen" (C. U. P. 1935) numerous investigations have been carried out on a variety of catalytic surfaces and these have given rise to a number of suggestions in respect to the molecular mechanisms involved in o. p. H_2, D_2 and the HD reactions. These have been discussed in detail in recent papers, especially by D. D. ELEY and P. R. NORTON (Disc. Faraday Society, **41**, 120, 1966) and by G. M. SCHWAB and E. KILLMANN (Z. Phys. Chem., N. F., **24**, 119, 1960). Apart from the paramagnetic molecular conversion investigated by WIGNER and shown by ELEY to be of more frequent occurrence than was at first suspected, and which is not applicable to the hydrogen deuterium exchange, there is as yet no unanimity regarding this latter reaction. SCHWAB, basing his view on the asymmetry of the reaction velocity curve in respect to the partial pressures of the hydrogen and deuterium, considers that molecular exchange, *e. g.*, $MH_2 + MD_2 \rightleftharpoons 2MHD$ gives the best interpretation of the experimental data, whilst ELEY concludes that atoms are involved, both a Bonhoeffer-Farkas and a Rideal mechanism being operational at the surface of a nickel catalyst, in addition to an unexpected paramagnetic contribution to the o. p. H_2 and o. p. D_2 conversions. It is of some interest to examine the possibilities inherent in these so-called atoms reactions in more detail, since neither the original Bonhoeffer-Farkas nor the Rideal mechanisms really postulate the participation of free atoms, and indeed it is possible to view them both from the same mechanistic point of view.
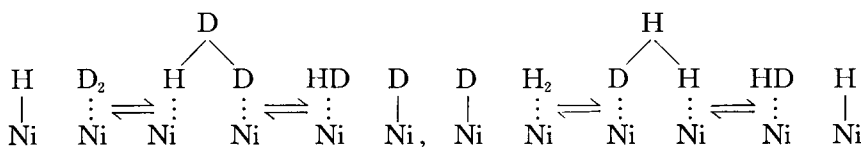
In gas reactions the break-down of the activated transition complex is associated with a replacement of some of the ordered vibrations by less ordered transitions and rotations, and the extent of pooling of the energy or the number of squared terms involved and its effect on the A and E terms of the Arrhenius equation $k = nAe^{-E/RT}$ have been investigated by KASSEL, RICE and

many others. It is possible, as postulated by LAIDLER and EYRING, to regard a surface complex in a similar manner. Here we have to deal in the first place with chemisorption or charge transfer bonds between substrate and reactant, and physically adsorbed molecular interaction between them due to the dispersive forces.

The basis of the Rideal mechanism is that since the breaking of a chemical bond involves the formation of a free ion or radical the energy necessarily involved must be much greater than that for the cleavage of a 'physical' bond and in consequence in surface reactions the evaporation or desorption of a chemisorbed species causing the formation of free reaction sites occurs only under extreme conditions. When the surface is catalytically active the catalytic process must involve some mechanism by which this evaporation or desorption of the product is made possible such as by the exchange of the chemisorption bond for a physical one. Since the pooling of energy in a transition complex is possible we can construct models in which this 'bond' exchange process can be carried out.

There are a variety of catalytic reactions of the type $A + B \rightleftharpoons C$ for which suitable models of the transition complex can be constructed. For the exchange reaction on nickel the simplest reaction mechanism can be formulated

$$
\begin{array}{ccccc}
 & & D & & H \\
 & & /\backslash & & /\backslash \\
H & D_2 & H\quad D & HD & D \quad D \quad H_2 \quad D\quad H \quad HD \quad H \\
| & \vdots \rightleftharpoons \vdots & \vdots \rightleftharpoons \vdots & | \quad | \quad \vdots \rightleftharpoons \vdots \quad \vdots \rightleftharpoons \vdots \quad | \\
Ni & Ni \quad Ni & Ni \quad Ni & Ni, \; Ni \quad Ni \quad Ni \quad Ni \quad Ni \quad Ni
\end{array}
$$

where the symbols — and ⋯ designate chemi- and physical adsorption respectively. If these equilibria be established on the surface then the evaporation of the three species H_2, D_2 and HD in the ratios demanded by equilibrium in the reaction $H_2 + D_2 \rightleftharpoons 2HD$ at the temperature of the surface is ensured as well as the condensation of the reactants to initially physically adsorbed states. For such a mechanism to be operative it is necessary that the interconversion of the physically and chemi-sorption 'bonds' should be possible and that the distances between the reactants should be within the Balandin limits which can ensure interaction between neighbouring hydrogen and deuterium atoms.
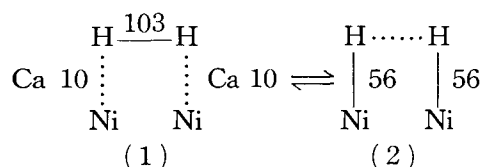
When depicted in this manner we note that chemisorbed atoms are apparently involved. It has, however, an advantage over the usual presentation of the Bonhoeffer-Farkas mechanism, *viz.*,

$$
\begin{array}{ccccccc}
H_2 & H & D_2 & D & H & D & HD \\
\vdots & | & \vdots & | & | & | & \\
Ni \rightleftharpoons 2Ni & & Ni \longrightarrow 2Ni & & Ni & Ni \rightleftharpoons Ni & Ni
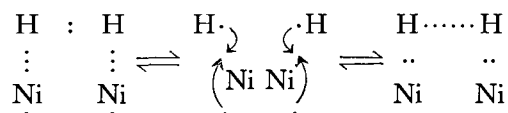\end{array}
$$

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in that no chemisorptive bonds have to be broken and is consequently more favourable energetically, but it does imply that a single chemisorbed atom with a neighbouring site on which a molecule can be adsorbed within the Balandin limits may serve as a catalytic centre, such as on glass or alumino-silicate surfaces.

On an extended catalytic surface we have to ensure the presence both of chemisorbed atoms as well as of physically adsorbed molecules. Chemisorption of hydrogen, or the conversion of physically adsorbed molecular hydrogen into the chemisorbed state, proceeds on catalytically active metals with no sensible energy of activation. Taking the bond energies $D(H_2) \sim 103$ kcal/mole, $D(NiH)$ ~ 56 kcal/mole, $D(Ni \cdots H_2)$ 20–4 kcal/mole, at $\theta = 0$ to $\theta = 1$ respectively we can express the transition forms in terms of change in the bond energies

$$
\begin{array}{ccc}
& \mathrm{H}\!\overset{103}{\rule{1.5em}{0.4pt}}\!\mathrm{H} & \mathrm{H}\cdots\cdots\mathrm{H} \\
\mathrm{Ca}\ 10\ \vdots \qquad \vdots\ \mathrm{Ca}\ 10 & \rightleftharpoons & \Big|\ 56 \quad \Big|\ 56 \\
\mathrm{Ni} \qquad \mathrm{Ni} & & \mathrm{Ni} \qquad \mathrm{Ni} \\
(\,1\,) & & (\,2\,)
\end{array}
$$

In (1), molecular evaporation can take place whilst in (2) the hydrogen is in the form of quasi-atoms but there is still interaction energy between them although this may be small. At high temperatures only, can the strong NiH be broken and atoms evaporated. These forms can be represented by electron distributions

$$
\begin{array}{ccc}
\mathrm{H}\ :\ \mathrm{H} & \mathrm{H}\cdot_{\displaystyle)} \quad {}_{\displaystyle (}\cdot\mathrm{H} & \mathrm{H}\cdots\cdots\mathrm{H} \\
\vdots \qquad \vdots \quad \rightleftharpoons & \big(\mathrm{Ni}\ \mathrm{Ni}\big) \quad \rightleftharpoons & \cdot\cdot \qquad \cdot\cdot \\
\mathrm{Ni} \qquad \mathrm{Ni} & & \mathrm{Ni} \qquad \mathrm{Ni} \\
\cdot \qquad \cdot & \cdot \qquad \cdot &
\end{array}
$$

The covalent NiH bond is thus formed from one electron from the hydrogen and one from an unpaired electron in the metal and has a dipole $Ni^+ : H^-$ as determined by the change in phase boundary potential. That an electron in the metal formerly "free" is now localised at the NiH bond, is confirmed by the fact that films of the metal suffer a loss in electrical conductivity when hydrogen is admitted to the surface. This intraconversion of (1) and (2) forms the real basis of the Bonhoeffer-Farkas mechanism and any single molecule may suffer a number of transitions from the physical to the chemisorbed state and *vice versa* during its life time on the surface, this time being the sum of the times spent in the two states. The reaction (2)→(1) may proceed with a relatively small energy of activation on the assumption that the transition complex consists of two sites and a molecule or two juxtaposed hydrogen atoms and that there is always interaction between the latter, the exothermic

transfer of an electron from the metal to the covalent NiH bond being compensated for by the simultaneous endothermic transfer of one from the HH bond. On a fully covered surface of hydrogen and deuterium on a lattice, any one hydrogen atom can interact with four neighbours *e.g.*, 2 hydrogens and 2 deuterium atoms, the amount of interaction energy involved being dependent on the lattice spacing within the Balandin limits and the electron density of the catalyst. The latent heat of molecular evaporation of any pair as a molecule is consequently less for a fully covered surface where any one hydrogen can react with four neighbours than it is for one sparsely covered, ΔH falling off from 20 to 4 kcal/mole as θ rises from 0 to 1. Likewise the higher the electron density at the catalyst adsorbate bonds the more readily will the necessary fission of the covalent H:H bond be achieved. This effect is apparent in semi-conducting hydrogenating catalysts such as zinc oxide where the energy of activation for hydrogenation may be varied from 25 to 6.3 kcal/mole on changing the P, n characteristics by doping with such ions as Ga^{+++} or Li^+. With the catalytic oxides, such as V_2O_3 or Ti_2O_3, the active sites are those where two metallic ions are in close proximity and electrons released in the cation cation bonding can interact (with adsorbed hydrogen) as the temperature is raised to form covalent linkages and thus permit the exchange reaction. In chromium oxide the inter metal ionic binding is already weak at low temperatures and this oxide is consequently already active. At the same time the reverse process, *i.e.* the electron transfer from the covalent adsorbed hydrogen to the interionic bond, can also proceed at a high rate with elevation of the temperature and the expected increase in rate of desorption of adsorbed hydrogen has been experimentally observed. We note in addition that since there is always a sensible equilibrium pressure of hydrogen necessary to maintain a definite surface coverage even for chemisorbed gas and that the postulated mechanism involves chemisorbed molecules undergoing transformation into physically adsorbed molecules which can then evaporate, the maximum rate for the HD reaction could be calculated from the conditions of dynamic equilibrium.
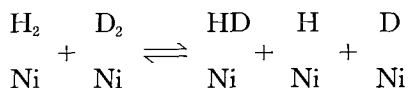
Any single atom pair can during its lifetime as a physically adsorbed molecule either evaporate or migrate over the surface; atom migration owing to the stronger interaction with the substrate only taking place at higher temperatures. On metals the energy required to raise a chemisorbed atom to the lowest migratory level in the periodic potential field at the surface is some one third of the energy required to bring about evaporation or complete detachment, whilst on composite surfaces, such as catalytic oxides, evaporation and recondensation may be necessary. We note that the exchange mechanism

involves two molecules to form the transition complex

$$\text{H} \cdots\cdots \text{H} \cdots\cdots \text{D} \cdots\cdots \text{D}$$
$$| \qquad | \qquad | \qquad |$$
$$\text{Ni} \quad \text{Ni} \quad \text{Ni} \quad \text{Ni}$$
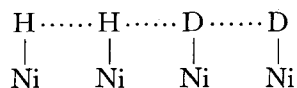
which after evaporation leaves a two-site gap which can again be filled from the gas phase, corresponding to a molecular mechanism, *e.g.*

$$\begin{array}{ccccccccc} \text{H}_2 & & \text{D}_2 & & \text{HD} & & \text{H} & & \text{D} \\ & + & & \rightleftharpoons & & + & & + & \\ \text{Ni} & & \text{Ni} & & \text{Ni} & & \text{Ni} & & \text{Ni} \end{array}$$

On increase of the gas pressure and lowering the temperature the surface coverage increases and the number of isolated single sites is augmented; even when the surface is completely filled with a non mobile two-site reactant there will be some 9% of single sites left v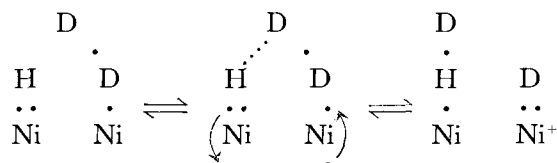acant. These vacant single sites can be filled from the gas phase by molecular hydrogen $\begin{smallmatrix} \text{H} \\ \text{H} \\ \text{Ni} \end{smallmatrix}$. There is but little evidence to support the view that this form of adsorbed molecular hydrogen can exist in a chemisorbed form. It must have a smaller heat of adsorption and require higher pressures to maintain surface coverage. Infra red absorption measurements and the phase boundary potential change suggests that it is a polarised physically adsorbed molecule $\begin{smallmatrix} \text{H}^+ \\ \text{H}^- \\ \text{Ni}^+ \end{smallmatrix}$ rather than a complex containing one electron bonded hydrogen $\begin{smallmatrix} \text{H} \\ \text{H} \\ \text{Ni} \end{smallmatrix}$. From the point of view of electron transfer, however, it is simpler to view it as such. The interaction of such a polarised molecule with a chemisorbed atom may be represented as follows

$$\begin{array}{ccccccccc} & & \text{D} & & & \text{D} & & \text{D} & \\ & & \cdot & & & \cdot\cdots\cdot & & \cdot & \\ \text{H} & & \text{D} & & \text{H} & \text{D} & & \text{H} & \text{D} \\ \cdot\cdot & & \cdot & \rightleftharpoons & \cdot\cdot & \cdot & \rightleftharpoons & \cdot & \cdot\cdot \\ \text{Ni} & & \text{Ni} & & (\text{Ni} & \text{Ni}) & & \text{Ni} & \text{Ni}^+ \end{array}$$
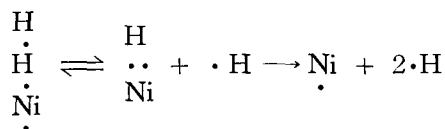
Evidently the electron transfers and their accompanying thermal changes in the respective bond energies are self-compensating to a much greater extent than in the conversion of a two-site chemisorbed molecule to the physically adsorbed form, and we should expect a much smaller energy of activation.

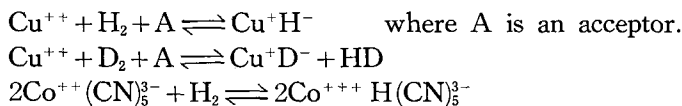The view that such a form of single site metal-molecular hydrogen complex

can exist receives support from many directions. When the criterion of molecular reversibility and the principle of detailed balancing are applied to the dissociation of hydrogen on a hot wire it is found that two processes can lead to atom formation. The one usually considered is the case where a molecule impinges on the wire, undergoes surface dissociation into chemisorbed atoms which subsequently evaporate independently of one another. The other process possible is when a molecule on impingement on the wire one atom only is retained by the wire, the other becoming free. The retained atom can subsequently evaporate as such, or, if struck by another atom may evaporate as a molecule. In the first case the rate of atom production $\alpha P_{H_2}^{\frac{1}{2}}$ until θ approaches unity. In the second case whilst proportionality obtains at low pressures the rate also approaches $P_{H_2}^{\frac{1}{2}}$ as θ approaches unity. Early experiments in 1935 on a tungsten wire at P *ca.* $1.25 \cdot 10^{-2}$ mmHg suggested that even at $1400°$ K $\theta \sim 0.6$ and the second method of atom production had become the more important one. If this be the case a reaction of the type

$$\begin{matrix} H \\ \cdot \\ H \\ \cdot \\ Ni \\ \cdot \end{matrix} \quad \rightleftharpoons \quad \begin{matrix} H \\ \cdot\cdot \\ Ni \end{matrix} + \cdot H \longrightarrow Ni + 2 \cdot H$$

can take place.

An analogous process is observed in the 'activation' of hydrogen by metallic ions and by organo metallic compounds with suitable ligands. HALPERN cites many cases of both homolytic and heterolytic splitting of molecular hydrogen such as

$$Cu^{++} + H_2 + A \rightleftharpoons Cu^+ H^- \qquad \text{where A is an acceptor.}$$
$$Cu^{++} + D_2 + A \rightleftharpoons Cu^+ D^- + HD$$
$$2Co^{++}(CN)_5^{3-} + H_2 \rightleftharpoons 2Co^{+++} H(CN)_5^{3-}$$

Both the o. p. as well as the exchange reaction can be catalysed by these substances. Rough calculations suggest that $D(Cu^+H^-)$ is comparable with the isoelectronic NiH, where D(NiH) is *ca.* 56 kcal/mole. Both ELEY (Trans. Faraday Soc., **60**, 1157, 1964) and TAMARU and his coworkers (*e.g.* Trans. Faraday Soc., **63**, 1215, 1967) have shown that the HD reaction can take place readily on phthalocyanine derivatives and that two Rideal mechanisms are involved, *viz.* $D_2 + HX \rightleftharpoons HD + DX$, $D_2 + H_2X \rightleftharpoons D_2X + DH$. They advance arguments for the presence of two sites, $_1X$, $_2X$ for the chemisorbed forms. These are situated at the center and periphery of the phthalocyanine ring. The reactivity of each species depends upon the degree of electronegativity induced in the chemisorbed hydrogen by the donor. The central hydrogen

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atom Cu^+H^- for a copper phthalocyanine is more electronegative than the peripheral bonded hydrogen but the electronegativity of both the chemisorbed as well as the bonded hydrogen can be augmented to a very marked extent by the addition of electron donors, *e.g.*, metallic sodium and marked increase in the catalytic activities for both reactions, especially those of the peripheral hydrogen, results.

It would appear that two HD reactions can take place on a metal catalyst both of the Rideal type, one in which two molecules of gas and the other in which a chemisorbed atom and a molecule are involved. The kinetics of these possible processes should thus conform to SCHWAB's molecular and Rideal mechanisms, the former preponderating at low pressures.