ADSORPTION AND HETEROGENEOUS CATALYSIS*

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WE now recognize two forms of adsorption: that in which the dispersive forces alone are operative —the so-called van der Waals or physical adsorption —and adsorption in which an electron switch has taken place between adsorbent and adsorbate—chemi-sorption. It is important to obtain criteria for distinguishing between these two forms so that we can identify the type or types involved in any particular case of heterogeneous catalysis.

The literature concerning adsorption is very voluminous, and we may refer to Brunauer's recent volume on physical adsorption to get an idea of its magnitude and extent. Here we merely observe that if we are to obtain a complete picture of such adsorption, more attention will have to be paid to the forces operative with different and definite substrates. A commencement has already been made, but we require more systematic investigation of the adsorption of polarizable and non-polarizable adsorbents on substrates which are respectively ionic, covalent and metallic in lattice structure. One may cite as an example of the former the adsorption of the rare gases on one hand, and of iodine on the other, on crystalline potassium chloride, whereby the theoretical treatment can be examined in the light of experimental data. As an example of the latter, we may mention the experimental work on the adsorption of vapours at the surface of liquid mercury, which reveals the shortcomings of the various theoretical expressions which have been derived for such interactions with metallic surfaces.

Apart from the complications introduced by the fact that the adsorbing surface is scarcely ever uniform, it is by no means improbable that many cases of physical adsorption on what is believed to be a metallic substrate may well be taking place on the top of a chemi-sorbed monolayer such, for example, as hydrogen on tungsten, on which there is already a chemi-sorbed monolayer of gas such as tungsten oxide or tungsten hydride. The slow uptake of gas which results on the admission of a gas to a bulb containing finely divided reduced metal, or other solid, may be due to the formation of a chemi-sorbed layer on its surface, or to a process of solution and diffusion into the interior of the solid. The data derived from a study of the kinetics of such processes have been interpreted on a basis both of 'activated' adsorption and of 'activated' diffusion. It is clearly important to be able to distinguish between these two different processes, since either of them might prove to be the controlling reaction in a case of heterogeneous catalysis. Valuable information may be obtained by studying the processes on surfaces freshly prepared *in vacuo*. So far, tungsten wire and mirrors of other metals deposited by thermal evaporation have been employed.

Different physical methods are available for examining the surface properties of a wire or a mirror. Thus the accommodation coefficient for a gas, the heat change, the thermionic and photo-electric properties all provide information on the presence or absence and, indeed, on the structure also of chemi-sorbed monolayers.

Such experiments reveal the fact that many cases of slow uptake of gas, which had been attributed to the chemi-sorptive process, possessing a definite and large energy of activation, were in reality due to other causes; for example, solution or displacement of one surface layer by another, since the chemi-sorptive process proceeded on the clean metal surface without any appreciable energy of activation.

While there may be some doubt in particular cases as to the exact magnitude of the energy of activation involved, it is relatively small compared to the bond-strengths of the ordinary diatomic gases which undergo dissociation on chemi-sorption. The metal-electron substrate must act in a manner analogous to a free radical. That an electron switch has taken place during chemi-sorption is revealed by the strong dipole character of the chemi-sorbed complex; for example,

$$\overset{-}{W}\,\overset{+}{CS} \text{ or } \overset{+}{W}\,\overset{-}{O},\; \overset{+}{W}\,\overset{-}{H}.$$
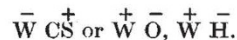
In several cases, for example, oxygen and ethylene, the reacting electron is probably the π-electron of the adsorbate; whereas many catalytic metals, for example, those in the transition group, have a narrow d-band overlapped by a broad s-band of electron-levels, and it is possibly an electron-level in this band which is involved. While a number of experiments have been carried out to determine the thickness of metal required for the emergence of 'metallic' characteristics, the great experimental difficulties involved in maintaining the substrate, in the effects of surface tension, in formation and preservation of a thin continuum in lattice form, have so far hindered progress in this direction. It is possible that further advances in our knowledge of the nature of the chemi-sorbed complex may come through physical examination of such systems, for example, the determination of specific heats of surface films, of the dielectric constant and para- or dia-magnetic susceptibilities. Experimentally, such investigations are proving to be within the compass of modern technique.

One of the most important problems connected with adsorptive phenomena is that concerning surface mobility. Under what conditions are adsorbed layers, held by dispersive forces and chemi-adsorbed layers respectively, mobile over the surface? The surface field is an undulating periodic one, and movement from one site to another may involve evaporation and recondensation, or movement over a potential hill. The adatom or adion may be raised into a migratory level. Here it may be free to move all over the surface, or may be limited to flight in one line only. It may move only into the next trough, or have a relatively long range of flight. We can develop equations to satisfy each of these conditions, but the experimental evidence so far is too inexact and too scanty to make any decision.

In the case of the alkali metals on tungsten, the data favour the view that the ion in the migratory level is restricted to a linear path and can traverse several tungsten atoms before terminating its flight. The growth of crystals from the vapour phase and the migration of organic molecules and metallic atoms

over glass surfaces provide further evidence for lateral mobility. Such evidence as is available at present suggests that lateral mobility of physically adsorbed molecules, but not of the chemi-sorbed species, can occur within the range of temperature at which the catalytic reactions occur. We cannot, however, eliminate the possibility of some mobility even in the chemi-sorbed species.

Several hypotheses concerning surface catalysis involve the concept of two-dimensional gas reactions. The experimental evidence available suggests that in surface reactions chemi-sorbed reactants, and not physically adsorbed reactants, are involved; thus the question of mobility becomes one of great importance. Apart from the fact that this mobility for the chemi-sorbed species appears to be non-existent or extremely limited, we must note that the adatoms have dipole moments, and as a result strong repulsive fields exist between them. It is interesting to compare this repulsive or spreading pressure of a film of adatoms where the pressure is due to a free two-dimensional gas, that is, one which obeys the formal relationship

$$F = \sigma KT,$$

where σ is the surface density of adatoms, with the pressure due to a free two-dimensional array of dipoles, that is,

$$F^1 = 4 \cdot 51 \; \mu^2 \; \sigma^{5/2},$$

where μ is the dipole moment. At values of $\sigma = 0 \cdot 8 \times 10^{14}/\text{cm}^2$ and $4 \cdot 6 \times 10^{14}/\text{cm}^2$, the values of F and F^1 are for formic acid on mercury 14 and 52 dynes/cm. for F, and for potassium on tungsten $26 \cdot 0$ and 307 dynes/cm. for F^1 respectively. The value of the dipole moment μ likewise changes as we alter the surface density of the film, due to mutual interaction.

Examination of the heats of adsorption gives us some indication as to the extent of mutual interaction which is repulsive in the chemi-sorbed layer, as well as on the mobility of the film. It is interesting to note that, in the physically adsorbed layer, below the critical temperatures attractive forces appear to predominate; for example, in the condensation of metallic and other vapours on glass.

In the chemi-sorption of a diatomic gas such as hydrogen on the surface of a metallic lattice, the molecule undergoes dissociation to form a pair of metallic hydride molecules. If the film·be immobile during the process of filling up the lattice, some eight per cent of the lattice points will be léft isolated as singlets. These singlets may play an important part in heterogeneous catalysis. Two of the simplest cases of heterogeneous catalysis are the ortho-para conversion of hydrogen or deuterium and the exchange reaction between hydrogen and deuterium at the surface of non-paramagnetic metals. The reactions proceed smoothly at quite low temperatures with small but definite energies of activation. In the cases which have been examined, the metal is covered with a chemi-sorbed layer of hydride broken only by the gaps already referred to. The formal kinetics of the reaction and reference to the corresponding homogeneous reactions preclude the possibility of the reaction proceeding by a two-dimensional bimolecular gas reaction in a mobile physically adsorbed phase on the top of the chemi-sorbed atomic or hydride layer. One of the current views is that the reaction proceeds by interaction of two neighbouring adsorbed hydrogen adatoms with subsequent evaporation of the newly formed molecule.

In view of the repulsive forces which we have shown to be operative and the great heat of adsorption even in a closely packed film, it is clear that many difficulties have still to be overcome before this hypothesis as to the mode of action can be freely accepted.

An alternative proposal involving an interaction between a physically adsorbed molecule situated over one of the vacant sites, and a neighbouring chemi-sorbed adatom to form a transition complex, presents us with a mechanism involving exchange of valence forces rather than rupture of any primary bonds, and goes far to overcome the difficulties associated with the other two proposed mechanisms. Many of the heterogeneous catalytic reactions can be readily interpreted by means of such a mode of action, but experimental re-examination of some of the catalytic exchange reactions is necessary before an unequivocable decision is possible.

The mechanism proposed, it will be seen, involves what is, in fact, the half-hydrogenated state which in the catalytic chemistry of the hydrocarbons has proved such a useful concept. The hypothesis of vacant sites inaccessible to particular reactants suggests their accessibility to other species, and provides us with an explanation of the broken linear character of the curves connecting poisoning with catalytic activity, an explanation alternative to a series of patches of different activity. Dissociation in chemi-sorption involves not only an electron switch, but also the problem of interatomic spacing; the relation of both these factors to the energetics of surface action provides yet another field of inquiry as yet almost unexplored. Provisional theoretical examination of the effects of surface spacing on the activation energy have not taken the electron distribution in the substrate into consideration; while attempts to evaluate energies of activation by examination of metals which form a continuous series of solid solutions and thus provide a gradual change in the mean lattice spacing, require a more detailed examination of the composition of the Gibbs surface layer and its dimensions before we can draw justifiable conclusions.

THE MAIN GEOMAGNETIC FIELD

THE main geomagnetic field and its secular variation were the subject of a Geophysical Discussion held at the Royal Astronomical Society on February 27. The largely attended meeting, at which the Astronomer Royal was chairman, was addressed by Dr. E. C. Bullard, of the Department of Geodesy and Geophysics, Cambridge (who is shortly to take up the post of head of the Department of Physics in the University of Toronto), Dr. J. McG. Bruckshaw, in charge of the sub-department of applied geophysics at the Imperial College of Science and Technology, London, Mr. D. W. Bishopp, director of the Geological Survey of Eire, and Mr. S. K. Runcorn, of the Physics Department in the University of Manchester.

Dr. Bullard outlined a new theory of the secular magnetic variation. He first recalled the main character of this variation, as exemplified by the longest series of observations, for London, which suggests a cycle of change of magnetic direction, of which about three-quarters has been completed in four centuries. Other places, however, show variations that suggest shorter periods. The accumulated data discredit the