Adsorption Concepts in Chemistry

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NO better perspective of the development of our knowledge concerning adsorption at surfaces can be obtained than by contrasting the contents of one of the many monographs published on this subject in recent years with the considered views of Nernst, as expressed in the sixth edition of his famous textbook in theoretical chemistry, which appeared twenty-five years ago. At that time the process of adsorption on surfaces was regarded essentially as due to the formation on the substrate of a dense atmosphere-like layer many molecules thick. Of this concept no vestige remains. Whilst the fundamental qualitative expressions of the more modern views are essentially simpler and more direct than the old, yet the detailed processes are undoubtedly complex and still await complete elucidation.

Two fundamental concepts introduced some twenty years ago, envisaged by the late Sir William Hardy, but most clearly presented and demonstrated by Irving Langmuir, have had the greatest influence in moulding our present views. The two ideas that the forces acting in the process of adsorption are to be recognised as identical with those operative in ordinary chemical processes, and that in molecules, especially in large organic molecules, certain portions are more reactive than others, form the basis of the modern concept of the orientated monolayer as the model of the adsorbed phase.

The reality of the existence of adsorbed materials in the form of orientated monolayers both on solid and liquid surfaces has now been demonstrated by chemical, optical, electrical and thermal methods. More detailed examination has revealed the fact that on liquid surfaces the material in the adsorbed monolayer can, like material in three dimensions, exist in various physical states akin to three dimensional vapours, liquids and solids, and that these phases can be transformed into one another each with its own definite change in free energy of transformation.

Examination of such monolayers on liquid surfaces by means of the Langmuir trough, and by determination of the phase boundary potential, now provides us with some information supplementary to the examination by X-rays as to the configuration of complex molecules like the sterols or proteins. It is also possible to measure the rate of reactions proceedings in these films, for example, such processes as enzyme reactions, chemical reactions involving hydrolysis, oxidation or two dimensional polymerisation. These reactions proceeding in monolayers at fluid interfaces are of great interest, in that not only may they be the prototype of a number of important biological chemical reactions which occur *in vivo*, but they also permit us to alter at will by mere compression or expansion the rate of reaction proceeding in the film, visual evidence of the reality of the factor termed the steric factor in homogeneous reactions.

A much greater variety of phenomena is met with when investigating adsorption at solid surfaces. Two distinct types of adsorptive processes are generally recognised, in one the forces holding the molecule to the surface originate in the mutual polarisation of the molecules and are frequently termed physical or Van der Waals' forces. In suitable circumstances an electronic switch occurs and a chemical reaction takes place between the adsorbed molecule and one or more molecules of the substrate, forming a chemiadsorbed complex. It is customary to consider chemical compounds as belonging to one or other of the extreme types, one where the stability of the compound is due chiefly to the operation of coulomb forces between ions and the other where a bond or a valency force in the form of a pair of electrons is shared between two atoms in a binary compound. We may cite the adsorption of the rare gases on mica, of cæsium on tungsten and oxygen on tungsten as typical representatives of these three types of surface compounds existing in the adsorbed phase.

Whilst the molecules in a distended adsorbed phase on a liquid substrate can move freely over the surface by diffusion, such is not the case on a solid surface, where the adsorbed molecules must migrate *per saltum*, a process termed activated diffusion. Such activated diffusion is not always limited to the surface of the solid, for frequently the process of adsorption is complicated by penetration into the solid through fissures, along slip planes, into large molecular holes, as obtain in the zeolites, or actually into the lattice of the solid itself, and in some cases it is possible to trace the changes in the mode of gas flow inward from simple diffusion to activated diffusion as the fissures change in size and the temperature is varied. As we have noted, the elimination of forces other than Van der Waals' and chemical in adsorption phenomena, does not permit of the assumption of the existence of an atmosphere-like thick adsorption layer, yet thick layers can be built up under suitable conditions by the operation of these short-range forces alone ;

thus relatively thick layers of sodium can be deposited upon tungsten. It is possible that these are not intrinsically stable and may actually aggregate into drops embedded in a monolayer, as occurs when a relatively thick film of oleic acid is deposited on the surface of water. Evidence for the formation of a second layer on the top of a first has often been brought forward, and indeed this phenomenon may be of frequent occurrence ; thus a layer of oxygen molecules may be held on to the top of a layer of oxygen chemi-adsorbed on to tungsten. The second layer is of course 'held' less tightly than the first; in consequence the second layer may be but sparsely populated under conditions when the first is almost complete, and molecules in the second layer may be much more mobile than the atoms or ions in the first. It is indeed due to the surface mobility of the oxygen in this second layer that a tungsten wire becomes coated so rapidly with a chemi-adsorbed layer in oxygen at low pressures. The adsorbed oxygen in the second layer moves over the surface and drops into any vacant hole in the chemi-adsorbed layer beneath.

More recently, evidence has been brought forward that when gases, or more generally, vapours, are adsorbed by the operation of Van der Waals' forces, the adsorbed layer may exist under suitable conditions in more than one state ; thus it is possible to describe phase changes on solid surfaces as due to two dimensional liquefaction or solidification from a two dimensional vapour phase.

Similar phenomena are met with in cases of chemi-adsorption, but here the lateral attractive and repulsive forces between the adsorbed ions or dipoles, and their variation with the changes in the density of population, are great enough both to make a thorough study of the conditions of equilibrium in these two dimensional chemical systems on solid substrates an extremely complicated problem and to render the interpretation of the experimental data difficult.

Adsorption of gases by solids is not always an extremely rapid process but may, over suitable temperature ranges, proceed with measurable speeds. From the influence of temperature on the rate of the process, energies of activation may be calculated. In many cases this slow process, requiring a definite energy of activation, can be ascribed to the slowness of the process of conversion of the Van der Waals' adsorbed molecules into the chemi-adsorbed complex, and for this reason chemisorption is frequently termed activated adsorption, although in a number of cases the process of chemi-adsorption, like many elementary reactions, can proceed with a negligible energy of activation.

A closer analysis of the problem suggests that there are at least three distinct processes where energy barriers may be involved, that is, three different energies of activation may have to be distinguished. These are first, the transition of the Van der Waals' adsorbed molecule to the chemi-adsorbed state ; secondly, the transition of a molecule or atom of the exterior of the solid to a place just inside the solid ; and thirdly, the migration of this molecule farther into the interior.

In many cases where the process of adsorption is proceeding slowly, it is a matter of some difficulty to find out which of these three energy barriers is actually responsible for controlling the speed of the reaction actually being measured.

It seems certain that in many cases, where diatomic gases such as hydrogen, oxygen or nitrogen undergo the process of chemi-adsorption at metallic surfaces, a reaction occurs which is the preliminary stage in a number of heterogeneous catalytic reactions, some of these being of great industrial importance. The resulting chemi-adsorbed complex involves only one atom of the gas undergoing chemi-adsorption. Thus chemi-adsorption involves a process of dissociation of the molecule. The application of the principles of the wave mechanics to the theoretical aspects of this problem suggests that the energies of activation should vary with the spacing or distance apart of the atoms forming the substrate. Whilst the experimental evidence so far produced may be said to support this view, it has not yet been tested in a manner sufficiently rigorous to affirm the correctness of this important theoretical conclusion.

Twenty-five years ago, no distinct ideas as to the mechanism of catalytic reactions at solid surfaces could be said to have been formulated. The chemical view, which postulated the formation of intermediate compounds, could be found side by side with what might be termed a physical view, where it was supposed that the molecules in the condensed atmosphere not only collided more frequently but also the forces opposing reaction were in some mysterious way reduced to smaller magnitudes. At the present time, it may be said that the chemical view has been fully substantiated ; the catalyst provides by chemi-adsorption an alternative chemical path. Surface hydrides, oxides, nitrides, and more complex compounds—for example, such as are formed by chemi-adsorption of olefines on carbon—are known, and their properties have been examined. Much further work is required before the detailed kinetics of these processes can be said to be definitely established, but it is clear that during the last twenty-five years the crops from the field thrown open by Hardy and Langmuir have been good, and bumper harvests may be expected in the future.