

## The Interaction of Gases with Solids

THE last important discussion on adsorption phenomena in Great Britain took place in January 1932 at Oxford, under the auspices of the Faraday Society. At that meeting, the topic which evoked most controversy was that of the activated adsorption of hydrogen on metals and on metallic oxides, that is, on solids particularly active as hydrogenating catalysts. While a great deal of work has been done in the intervening four years, it cannot be said that the matter is at all thoroughly elucidated. Meanwhile, however, several new independent lines of attack have been brought to bear on the varied phenomena encountered in the interaction of gases with solids, which may ultimately lead to more precise views on the question of activated adsorption. On November 21, therefore, Prof. E. K. Rideal opened a discussion at the Chemical Society in order to direct attention to recent work and to focus opinion on a subject still in a state of flux.

Many of our modern ideas on the mechanism of heterogeneous catalysis are based on the pioneering work of Langmuir on the interaction of gases with hot filaments. That the subject is far from exhausted is amply demonstrated by the recent work of Roberts<sup>1</sup> with tungsten. The basis of these experiments is the development of two separate physical methods of studying adsorption. The first arises from the fact that the accommodation coefficient of a neon atom on a tungsten surface is particularly sensitive to the presence of adsorbed films. For example, the accommodation coefficient on a bare surface at 273° K. is 0.08. When the tungsten is covered with a layer of oxygen atoms, the value rises to 0.25. The second method consists in actually measuring the heat of adsorption of gases on a clean tungsten filament by determining the rise in temperature (only 0.01°) which occurs when gas is adsorbed.

One of the most surprising results of the application of these methods is that hydrogen is practically instantaneously adsorbed when it encounters a tungsten surface even at so low a temperature as 83° K. If very small amounts of hydrogen are admitted, the gas is completely adsorbed, the heat of adsorption being about 40 kgm. cal. After sufficient hydrogen has been admitted to cover the tungsten surface, that is, one hydrogen atom to one tungsten atom, there is no further adsorption, and therefore no heating of the filament. That the hydrogen is chemisorbed is proved by the high heat of adsorption and by the fact that the film of hydrogen can only be removed (probably as

atoms) by heating the filament to 700° K. The chemisorption of hydrogen on tungsten therefore proceeds with a very small energy of activation. This is in marked contrast to the considerable energy of activation observed for metallic powders, such as tungsten, nickel and copper. To prevent sintering, these absorbents cannot be outgassed at high temperatures. Hence it may well be that the surface is not free from gas, and that therefore the phenomenon usually observed is really the interaction of hydrogen with a gas-covered metallic surface. It is a matter for further experiment to decide whether this non-activated type of chemisorption on clean surfaces will be observed with metals other than tungsten.

Similar phenomena occur with oxygen and tungsten: the oxygen is immediately adsorbed. From the heat evolved and the energy of dissociation of molecular oxygen, it may be shown that the energy of desorption of an oxygen atom is about 130 kgm. cal., which is in good agreement with Langmuir's value of 160 kgm. cal. derived from the effect of oxygen on the thermionic emission of tungsten. Oxygen atoms go on in pairs, one oxygen atom to one tungsten atom. As this bombardment goes on, a time will come, if the oxygen atoms are immobile, when only single isolated atoms of tungsten are left. It is evident that an oxygen molecule cannot be dissociated on colliding with these isolated atoms. Instead, it is adsorbed as a molecule with a smaller heat of adsorption. Thus at high enough oxygen pressures, the ordinary film of atomic oxygen, necessarily containing gaps, has on top a relatively dilute film of molecules covering about 8 per cent of the surface.

Having obtained conclusive evidence of the nature of adsorbed atomic films, the next question which arises is the rate of migration on the surface of the solid and the rate of penetration into the body of the metal. One ingenious way of following surface migration has been developed by R. C. L. Bosworth<sup>2</sup>. By means of a positive ion gun, a beam of sodium ions is projected on to a negatively charged tungsten strip. The strip is then heated electrically, the sodium atoms migrating. The progress of migration is followed by allowing a spot of light to fall on the sodium-covered tungsten surface, the resultant photo-electric emission at various positions along the strip serving as an indicator of the surface concentration of the sodium atoms. In this way, the rate of migration may be

determined as a function of the temperature and of the surface concentration.

The diffusion of gases through solids is controlled partly by the interaction of the gas with the surface and partly by processes occurring in the body of the solid, both of these in general being specific, for example,  $H_2$ -Pd,  $O_2$ -Ag,  $N_2$ -W. An exception to the rule is the diffusion of hydrogen, helium, neon, argon, nitrogen and oxygen through silica glass<sup>3</sup>. There is no doubt in the case of the inert gases that the forces which the atoms encounter in their passage through silica are purely of the van der Waals' type. In fact, it may be shown by calculation that the energy of activation for the passage of an inert gas atom through a square of similar atoms can attain values commonly associated with chemical reactions, such as 30 kgm. cal. Migration appears to take place through the solid lattice, for the rate is independent of the firing and other treatment of the silica. With oxygen and nitrogen, on the other hand, the rate is very sensitive to surface imperfections, firing and the like, which would point to the diffusion occurring along slip-planes and cracks in the glass.

Much has been written about the usefulness of deuterium as a tool for investigating the mechanism of chemical reactions. Taken along with the ortho-para conversion, the behaviour of deuterium yields important evidence about catalytic hydrogenation and dehydrogenation reactions. For example, if ammonia and ortho deuterium are allowed into contact with an iron catalyst, A. Farkas has found that the rate of conversion of the ortho deuterium is inhibited by the ammonia, and simultaneously there is a slow exchange reaction resulting in the production of deuterammonia. This shows at once that ammonia partially covers the iron surface, that deuterium is dissociated on the portions not covered with the ammonia, and that the rate of exchange is slower than the dissociation of deuterium molecules, the latter reaction therefore not being the rate-determining step.

These few examples suffice to demonstrate that the field of inquiry is an extending one, and that well-defined progress is being made in drawing a more precise picture of the interaction of gases with solids.

H. W. MELVILLE.

<sup>1</sup> *Proc. Roy. Soc., A*, **152**, 445; 1935.

<sup>2</sup> *Proc. Roy. Soc., A*, **150**, 58; 1935.

<sup>3</sup> R. M. Barrer, *J. Chem. Soc.*, 378; 1934.

## Obituary

Mr. F. Escombe

EVERY student and teacher of botany must be familiar with the classic work of Brown and Escombe on the germination of refrigerated seeds; the relative roles of endosperm and embryo in germinating barley; on the static diffusion of gases and liquids in relation to photosynthesis and translocation in plants; the influence of varying amounts of atmospheric carbon dioxide on photosynthesis and plant growth; the interchange of energy between the leaf and its surroundings; the determination of carbon dioxide in the air absorbed by plants, based on the rate of its absorption by a free surface of a solution of caustic alkali; and they will learn with regret of the sudden death of the surviving author of these important researches on October 12. Brown, who was a much older man, died in 1925. Fergusson Escombe, who was only sixty-three years of age, had given up his active career at a comparatively early age owing to ill-health and other circumstances, and thus, though his work will always hold a high place in botanical research, he himself had almost been forgotten, save by a few.

Born in Hampshire in 1872, Escombe went to a preparatory school at Bournemouth and thence to Haileybury for two years. He matriculated in 1892, and later obtained the degree of B.Sc., with honours in botany, at the University of London, from King's College, London. There he won the Carter Gold

Medal and Prize for botany. He studied also at Downton Agricultural College, at Neuenheim College, Heidelberg, and at the Kaiser Wilhelm University at Strassburg. Whilst at the latter, he worked on the chemistry of the cell membranes of lichens and fungi, and published a paper on it in 1896, "Beitrag zur Chemie der Membranen der Flechten und Pilze" (*Hopp.-Seyl. Z. Phys. Chem.*, **22**, 288-306; 1896-97), a preliminary investigation to determine the existence of chitin and cellulose in these groups. This showed his early leaning towards biochemistry.

Shortly afterwards, Escombe went to work with Brown at the Jodrell Laboratory, Kew, on the researches which were published jointly in the Royal Society *Proceedings* and *Philosophical Transactions*, 1897-1905, and which gained for Escombe an established place in botanical science. There is no necessity to summarise these researches—indeed it would be quite impossible except at great length—since they have passed into botanical history and are described in every botanical textbook. They marked, however, a great advance in the state of knowledge then of the essentials of the physiological processes of germination and nutrition. Being reduced to mathematical precision, the results were enunciated so that in some cases they could be stated in formulæ. Special methods and apparatus had to be devised to carry out such delicate experiments, and novel