millions must now be present from small numbers set free in the past two or three years. *C. vittiger* has also been released at various places.

Of the internal-feeding caterpillars, one species, *Melitara junctolineella*, has been readily acclimatised; about a million have been liberated, and it is now firmly established in several localities. These caterpillars are solitary in habit, and tunnel within the joints or pads of prickly-pear. A related insect is *Melitara prodenialis*, but the caterpillars are social in habit, a number feeding together within the pear pads; recently this species has been set free in the Westwood district, and promises to be especially useful as a pear destroyer.

One of the most recent of the Board's importations has been strikingly successful in so far as rapid increase is concerned. This insect is *Cactoblastis cactorum*, a

social caterpillar allied to the *Melitaras*. Less than three thousand larvæ arrived from Argentine in May 1925, but the increase has been so great that in February and March 1926, nine months later, sufficient stocks had been raised to warrant the release of two and a half millions throughout the pear areas. These caterpillars are voracious feeders, and should the increase in the field be sustained at one-half the rate experienced in the cages, great destruction of pear should be brought about.

Many other insects are being bred and acclimatised, and the Board is continuing the introduction of new forms, believing that the control of prickly-pear by biological means can only be brought about by the combined attack of a variety of insects operating on the different parts of the plant.

Chemical and Physical Action at Surfaces.¹

By Dr. ERIC K. RIDEAL.

THE subject of colloid chemistry is intimately associated with the properties and peculiarities of interfaces, of which those formed by liquids and solids are the most important. The difficulties met with in an exact study of reactions taking place in colloidal systems are greatly enhanced by their dispersity, and in addition the application of thermodynamic methods to the treatment of the two-dimensional interfacial phases becomes a problem of great complexity when these phases are subdivided and not plane but curved. For these reasons the increasing attention which is being devoted to surface phenomena is a development to be welcomed. As the late Lord Rayleigh first indicated, the properties of oil films on water studied by Miss Pockels give us valuable information on molecular magnitudes, a view which has been emphasised and amply confirmed by the able experiments of numerous investigators, notably Devaux, Langmuir and Adam.

An examination of the process of spreading of oil films and their conditions of equilibrium presents several features which can be compared with phenomena occurring in three-dimensional systems. If a crystal of myristic acid be placed upon the surface of water a process of surface solution occurs, molecules are torn off the edge of the crystal in contact with the water by hydration of their polar or hydrophilic groups and float on the surface as a two-dimensional vapour. This process of surface solution continues until the vapour attains, as measured by the fall in surface tension of the water, the critical 'vapour pressure' value necessary for conversion into a two-dimensional liquid, the so-called expanded film of Adam. The liquid undergoes further two-dimensional compression by continued surface solution from the crystal, and if the temperature be sufficiently low, the expanded film is converted into a condensed film which may be liquid or solid. If the temperature be high, no formation of a condensed film occurs but the film remains in the expanded state. Compression does not proceed indefinitely, for the substance possesses but a finite surface solubility at a constant temperature and a saturation equilibrium is attained.

Both the rate of spread, which in the case of a rapidly spreading acid, such as oleic acid, rarely exceeds a linear speed of 25 cm. per second, as well as the progress of surface saturation and the transformation of the two-dimensional vapour into the expanded and condensed states, can readily be followed by observing the changes in surface tension at different points on the water when a cylinder of the acid is plunged below the surface. In the case of the spreading of solid acids, the rate of surface solution is so slow that no pressure gradient exists in the expanding film, but for acids which spread quickly molecules go into solution so rapidly that those already on the surface are actually pushed out by those entering, causing a local lowering of the surface tension.

For the long-chain fatty acids the molecular adhesion by the hydrocarbon tails is so great that these two-dimensional films, even at high temperatures, are analogous to vapours rather than gases. Substances which can exist in a state equivalent to two-dimensional gases on a water surface over the ordinary experimental temperature range must possess chains less than eleven carbon atoms long; these are appreciably soluble in water and their surface concentrations must be calculated by means of the Gibbs Thomson equation. It is found that if the force-area curves calculated in this manner for substances such as the short-chain fatty acids or alcohols on the surface of water, or at interfaces such as benzene-water or mercury-water, be plotted, they reproduce in all respects the pressure volume curves obtained by Amagat for gases at high pressures.

Not only can we examine the behaviour of matter in its various states in this two-dimensional system, but a knowledge of the variation of the equilibrium pressures with the temperature, and the application of the Clapeyron equation, also yields values for the latent heats of 'spreading' of these substances. We may note in addition that the potential difference existing at the boundary between a homogeneous aqueous phase and its vapour is profoundly modified by the presence of such films. From a knowledge of the surface concentration and the change in potential effected by the presence of the film, the change in electric moment caused by the introduction of one molecule of the fatty

¹ Based upon two lectures delivered at the Royal Institution on February 2 and 9.

acid into the surface phase may be determined. If these be calculated for a number of organic substances, many interesting results are obtained: thus the electric moment of the fatty acids appears to reside entirely in the carboxyl group and is of a value equivalent to that produced by separating a proton and an electron to a distance of 0.06 Å.U. The moment of the alcoholic hydroxyl group is some twenty per cent. smaller. Very considerable changes in electric moment are caused by the introduction of the halogens or amino groups in place of hydrogen. Careful analysis of these changes may throw some light on the vexed question of polarity, which appears to be of some importance in organic chemistry.

The experimental examination of the behaviour of gases and vapours at solid surfaces is a much more difficult problem, for whereas a liquid surface is a surface of equipotential, it is almost impossible to obtain solid surfaces uniform in surface energy. Calculations from the compressibility of cubic heteropolar crystals, such as rock salt, of the surface energies of various planes, have been made by Born and more recently by Jones; the data, although admittedly only approximate in character, indicate enormous variations from face to face. Microscopic examination of the process of crystal growth, solution and etching, likewise support this conception of a variation in the forces of adhesion to crystal facets and edges. The change from a super-cooled liquid to a crystal may be regarded as resulting in a diminution in the potential energy of the surface as well as of the material in the interior.

These speculations lead us to the idea that the surface of a metal prepared, say, by the reduction of the oxide at low temperatures, is not a regular and uniform, if somewhat undulatory, checker board of equipotential points, but consists of portions of minute crystal edges, planes and corners in addition to numerous skeletal chains of atoms awaiting the opportunities provided by thermal agitation for slipping into a more compact crystal lattice. Both the interatomic distance, as well as the number and variety of atoms around one particular atom, affect the field of force which contributes to the adhesional potential energy of the surface. By a process of summation we may regard the surface as containing patches of varying activity on which substances are adsorbed but not with equal facility. Adsorption on a very active patch is associated with a large heat evolution and presumably also with a large decrease in the free energy of the system, and the patch may become saturated with gas before the less active patches are more than sparsely covered. This conception of a variation in the 'availability' of a surface, as an explanation for the experimental data indicating different saturation maxima for various gases and vapours, cannot, however, be considered a general one, for we find that many vapours, and possibly some gases, especially when near their critical points, may be adsorbed in layers more than one molecule thick. A difference in the amounts of two vapours adsorbed at saturation may be interpreted as due to a difference in film thickness.

Whilst the first or unimolecular layer is held on extremely firmly, the decrease in free energy resulting in building up the subsequent layers is but small;

their formation may be regarded as due to an increase in the molecular cohesion of a molecule resulting on adsorption rather than a direct attraction of the surface for a molecule some distance away. As a convenient analogy we may cite the example of a weak magnet holding a string of iron filings. A second filing may be attached to the free end of one already hanging from the magnet, but if the first one be removed a filing will not be drawn towards the magnet from the position originally occupied by the second.

In catalytic actions also which appear to be limited in action to the primary adsorbed film, we find that those portions which are unstable and readily adsorb gases are also catalytically active. Since the measure of the catalytic efficiency of a metal is the rate of reaction, it is clear that a relatively large area of the active surface is required. A variation in the closeness of packing, as well as an introduction of foreign elements, frequently alters the rate of reaction. There appear to be at least three different types of such active surfaces on carefully prepared nickel: on one all hydrogenation reactions, including saturation of ring compounds, may be performed; on a less active area, simple double bonds undergo hydrogenation but not ring compounds; and a third area facilitates only the reduction of nitro groups. In the case of carbon containing both iron and nitrogen, there exists a large area, inactive catalytically, for the oxidation of oxalic acid; but in addition there exist areas of active carbon, active carbon-nitrogen, active carbon-nitrogen-iron and active carbon-iron complexes; these all possess different specific surface activities and different temperature coefficients for the reaction velocities. Since the products of reaction must leave the surface before new reactants can approach, it is possible that there is an upper as well as a lower limit to the strength of field on the surface which is most desirable for an efficient catalyst.

There has been a great deal of speculation, founded upon little experimental work, as to the nature of the union between substrate and adsorbate and the mechanism by which some of these complexes are rendered active. That complex organic molecules are attached by particular groups, usually the polar or lyophilic group, to metals and oxides can be demonstrated in a number of cases; the union, however, is not so intimate as in a true chemical compound of the heteropolar type, for a ready distinction in ease of reduction is to be noted in the case of films of copper or nickel oxide and films of oxygen adsorbed on the metals. Again, a few interesting observations scattered in the literature would lead us to conclude that there exists an intimate connexion between the catalytic activity of a metal and those electrons in the metal capable of being ejected in thermionic emission. Hydrogen and oxygen, it is stated, commence to combine rapidly on a platinum wire which has been heated to such a temperature that the rate of thermionic emission becomes sensible; also a tungsten wire poisoned with a suitable impurity neither effects catalysis nor emits thermions. Finally, the investigations of Richardson on the possibility of different rates of thermionic emission from different parts of a metal surface are suggestive in connexion with the concept of areas of different activities.

Whilst our present knowledge of the mode of adsorption and type of binding is very incomplete, our information on the mechanism of activation is still scantier. It is in many cases difficult to obtain a measure of the true energy of activation, not only on account of the possible variation in stability of these adsorption compounds with the nature of the surface, but also because the velocity of the reaction, from the variation of which with the temperature these energies are obtained, may be determined by some other factor than the excitation of the reactant. Apart from these additional complexities, the fundamental problem of the mechanism of molecular activation in simple uni-

and possibly also in the case of bimolecular gas reactions, cannot be said to have received a successful solution.

Almost a decade has passed since Langmuir published his most stimulating paper on surface action, which did much to renew interest in this field. An enormous volume of experimental work has been accomplished during this time and the complexities of the subject have undoubtedly increased. In spite of this it is as full of interest as it was in the time of Faraday, and whilst many of the problems unsolved then await solution now, our knowledge of the processes occurring at surfaces still continues to increase.

Obituary.

PROF. W. J. LEWIS, F.R.S.

THE sudden and unexpected death of Prof. W. J. Lewis deprives mineralogy of a well-known personality. He passed away peacefully in his sleep in the afternoon of April 16 at the house of his sister, Mrs. G. T. Pilcher, at Godalming, Surrey. William James Lewis, the second son of the Rev. John Lewis, was born at Llanwyddelan in Montgomeryshire on January 16, 1847, and was educated at Llanrwst Grammar School. Entering Jesus College, Oxford, as a scholar in 1865, he took first classes in Mathematical Moderations in 1867, in Mathematical Finals in 1868, and in Natural Science in 1869. He gained the Senior Mathematical Scholarship in 1871, and was elected a Fellow of Oriel College in 1872. Not being married, he held this fellowship until his death, and the funeral service was conducted in the chapel of Oriel College.

For a time (1870-71) Lewis was an assistant master at Cheltenham College, and in 1875 he became an assistant in the Mineralogical Department of the British Museum, which at that time was under the keepership of Prof. Story-Maskelyne in the old building at Bloomsbury. On account of his health he retired from this position in 1877, and was succeeded by Sir Lazarus Fletcher. At that time Lewis was ordered abroad and given only a year to live; but in spite of that he reached his eightieth year. He took the opportunity of joining two solar eclipse expeditions, making observations on the polarisation of the corona.

Lewis had studied crystallography under Prof. W. H. Miller at Cambridge in 1874, and in 1879 during Miller's illness he acted as his deputy. He took the Cambridge M.A. degree by incorporation in 1880, and since then had lived in rooms in Trinity College. In 1881 he was appointed professor of mineralogy in succession to Miller, who had held office since 1832. Between them they had thus held the chair for ninety-four years; and it seems to have been Lewis's ambition to beat the record created by Adam Sedgwick and McKenny Hughes, who had sat tightly in the Cambridge chair of geology for ninety-nine years. Fortunately, under the new regulations, this state of affairs cannot be repeated. The professorship of mineralogy, founded in 1808, had previously been held by E. D. Clarke, the botanist J. S. Henslow, and the celebrated William Whewell, Master of Trinity, and it has been closely connected with the development of the sciences of mineralogy and crystallography. The Millerian system of notation now in general use for the planes of crystals

was conceived by Whewell and elaborated by Miller; and the crystallographic constants still accepted for many mineral-species were first published by Miller in his classical treatise on mineralogy. The Cambridge collection of minerals contains much material of historical value and interest, and it has been considerably added to by Lewis, notably by the acquisition of the Carne and the Wiltshire collections.

Lewis encouraged many more students than in the old days, and mineralogy soon became a popular Tripos subject taken in conjunction with geology. He was not a prolific author, the list of his original papers being limited to twenty-one titles, many of them only short notes. The earliest, in 1875, on the crystallography of some organic compounds, were published in the *Journal of the Chemical Society*, and others on the crystallography of various minerals (glauco-dote, miargyrite, stephanite, albite, etc.) appeared in the *Philosophical Magazine* (and reprinted as the *Proceedings of the Crystallogological Society*), the *Proceedings of the Cambridge Philosophical Society*, and the *Mineralogical Magazine*; some of them being also translated into German in the *Zeitschrift für Krystallographie und Mineralogie*. Lewis delighted in the intricacies and difficulties presented by twinned crystals, and in devising geometrical methods for dealing with the rhombohedral system of crystals. In later years the material described had been collected by himself during his many trips to the Binnenthal and other mineral localities in Switzerland. In 1919, at the age of seventy-two years, when alone in the Lengenbach quarry, he had the misfortune to slip and break his leg. There he lay in the snow all night, and in the morning he found a piece of wood to bind as a splint, thus enabling him to crawl out and fortunately attract attention.

The most important work written by Lewis was his "Treatise on Crystallography," published in 1899 in the series of Cambridge Manuals. In the preparation of this book he spared no pains, and it remains the best text-book on geometrical crystallography. He also wrote in 1913 a history of the parish of North Wraxhall in Wiltshire, which included a life of his friend Francis Harrison, the late rector.

Lewis acted as secretary of the Crystallogological Society from its foundation in 1876 until its amalgamation with the Mineralogical Society in 1883, and was librarian of the Mineralogical Society since 1890 and president in 1909-12. He joined the Chemical Society