EXTENSION TO THE METALLURGY DIVISION OF THE NATIONAL PHYSICAL LABORATORY

THE extension to the Metallurgy Division of the National Physical Laboratory, which was opened by Sir Lawrence Bragg on April 6, has been made necessary by the continuous development of techniques for the examination of the fine structure of metals and by the growth of interest in the properties of materials at very high temperatures. It consists of a two-story building having a total floor area of about 11,700 sq. ft., of which about 5,800 sq. ft. is experimental working space. Its purpose is to accommodate three Sections of the Division—the Ceramics Section, the X-Ray Section and a new Radioactive Tracer Section. Each portion of the building has been designed to meet the requirements of the particular type of work that will be undertaken in it.

The Ceramics Section is on the ground floor and consists of five laboratories and offices, together with a large furnace room. The Section is mainly concerned with the development and production of refractory ware for use under exacting conditions, especially those involving very high temperatures. Facilities are available for crushing, grinding, forming and drying ware, and the furnace room will permit firing on a considerable scale. Space is also available for physico-chemical research and for the needs of specialized experiments and measurements.

Also on the ground floor is a set of rooms for experimental work on the application of radioactive tracer techniques to metallurgical problems. The purpose is to provide a place where these techniques can be applied under suitable conditions to metallic samples, and to assess their value in metallurgical research. The plan underlying the design and equipment of the Section has been to provide facilities for carrying out on metals of all but the highest activity most of the operations normally applied to metals in a research laboratory. The main feature is the foundry, a lofty, well-lit room equipped with melting furnaces, casting equipment, heat-treatment furnaces, a small bar- and sheet-rolling mill and a suitably protected safe for storing active isotopes. Provision has been made to handle active metal in quantities up to about 6 lb. Next to the foundry is a combined workshop and laboratory for metallographic preparations, and next again is a combined chemical and physical laboratory in which chemical analyses and measurements of activity will be carried out. The Section is approached through a semi-sealed door and changing rooms, and is provided with its own air-conditioning system arranged so as to produce a slightly negative pressure. This avoids the possibility of contamination passing to the rest of the building, which is kept at a slightly positive pressure by its own system of air circulation. At selected points in each room, openings to the extract duct are provided, to which extensions to hoods over machines and other equipment may be attached. The rooms are designed to be easily washed down, and have floor ducts and sinks down which all active liquid passes to delay tanks situated under a separate pump house. Separate sinks and drains are provided for non-active liquids (for example, cooling water from pumps, etc.). Warning bells and klaxon alarms are incorporated in the air-conditioning and delay-tank systems to indicate any abnormal feature of their operation.

The upper floor is designed for X-ray diffraction studies of metals and for electron microscopy. The main feature is a single, very large room divided by means of easily removable partitions into a number of cubicles and small laboratories, each of which is intended to contain a single piece of equipment and can be independently darkened. In this way the need of the individual worker to have sole control of his own equipment is combined with adaptability. As a corollary to the use of removable partitions, all services in the Section are carried in a carefully planned system of wall and floor ducts. In addition to the standard services provided throughout the building, there are, in this Section, a circulating system of clean distilled water at 50 lb./sq. in. pressure and 20–25° C. temperature for cooling purposes, and a quiet phase of 230-volt a.c. for apparatus requiring short-term mains stability. Among the pieces of equipment at present installed may be mentioned units primarily intended for standard X-ray techniques, two sets for Geiger–Müller counter work for high-precision measurements of diffraction-line intensities and preferred orientation, one set for work requiring a fine-focus source of radiation, electron microscope and a soft X-ray spectrograph with a recording microphotometer.

In his opening address, Sir Lawrence Bragg referred to the history of the Division, going back to 1901 and to the succession of eminent men who had filled the post of superintendent—Sir Harold Carpenter, Dr. W. Rosenhain, Dr. C. H. Desch, Dr. C. Sykes and, at present, Dr. N. P. Allen. He then went on to say: "I am particularly pleased to be opening the new extension, because all three of its main interests are related to interests of my own. One Section will be devoted to X-ray work, particularly on metals, and I should like to remind you how greatly our country has contributed to this field; in fact, it has been at times almost a British monopoly. Brilliant work on alloys was started by Westgren and Phragmen in Sweden in the early days, but it fell to Owen and Preston here, and to Bradley, who was then with me in Manchester and afterwards came here, to develop the patient study of the structure of alloys which has helped us so much to understand them. Sykes also made contributions to the theory of alloy structure. His experiments and the theories developed by Williams enabled us at Manchester to start the investigations into the order–disorder phenomena, which have exerted a great influence in the study of many other problems of the solid state. The X-ray study of alloys is a rich field to explore, and it is proper that there should be a strong centre of this work at the National Physical Laboratory.

"Another fascinating line which you are to develop here is the application of tracer techniques to problems of metal physics. Metal physics is an extraordinary subject; there is such a vast accumulation of empirical knowledge about the behaviour of metals and so little satisfactory theory behind it. It is an extraordinary position for a subject which has such

immense technological importance. This seems to me to be an ideal activity for the National Physical Laboratory. You will have a special laboratory designed for the purpose and will find by experience how this new technique can be applied. You will be marking a trail which it will be easier for others to follow".

Sir Lawrence then said it must appear he was claiming a finger in every pie; but ceramics are really artificial minerals, and mineral structures have long fascinated X-ray analysts. Minerals are structures of great stability and resistance to change, and these are just the qualities needed for refractories. The juxtaposition of the ceramics and X-ray sections seemed to him completely appropriate, and collaboration between them should be very fruitful. He concluded: "The National Physical Laboratory was founded to keep the country's standards, but it has come to have another function, that of setting standards in experimental investigation. It ought to preserve a judicial and impersonal attitude, contain equipment which is a model of its kind, and be a centre to which one can go for advice, advice which depends upon an impartial review of what is going on all over the country and a readiness to adopt the best ideas whatever their source. With its unique position it has a great part to play in the interchange of ideas and the improvement of standards".

The opening of the main door of the building was performed by Sir Lawrence using a presentation key, made in the Division, of titanium and ornamented with eight other metals, each of which represented some major research or development activity of the Division during the fifty-three years of its existence.

H. A. SLOMAN

UNIMOLECULAR GAS REACTIONS

A MEETING to discuss the theory of gas-phase unimolecular reactions and its applications to specific reactions was held in the Department of Chemistry, University College, London, on December 4. Dr. N. B. Slater (Leeds) opened the discussion by describing his approach to the problem. If it is assumed that a molecule has a few unstable states (r) of high energy which have lifetimes L_r^{-1}, then if p_r is the probability of the rth state, ω the effective collision frequency per molecule and k the rate-constant,

$$k = \sum_r \frac{p_r \omega L_r}{L_r + \omega} \quad . \qquad (1)$$

At high pressures ($\omega \gg L_r$) the majority of energized molecules will be deactivated, and (1) reduces to (2):

$$k = \sum_r p_r L_r. \qquad (2)$$

The reaction-rate is thus the rate at which a molecule possessing at least an energy E_0 attains a critical configuration. The critical configuration may be taken as a large extension of one of the internal co-ordinates of the molecule. Treating the latter as a classical vibrating system, it can be shown[1] that the rate of reaction is given by

$$k = \nu \exp(-E_0/RT), \qquad (3)$$

where

$$\nu^2 = \frac{\sum_i \alpha_i^2 \nu_i^2}{\sum_i \alpha_i^2}, \quad E_0 = \frac{q_0^2 \cdot}{\sum \alpha_i^2} \qquad (4)$$

The ν_i are the vibration frequencies of the molecule and α_i the amplitude factors, both of which are constants of the molecule in question; q_0 is the critical extension of the co-ordinate corresponding to decomposition, and E_0 the activation energy. No attempt is made in the theory to calculate E_0.

At low pressures the rate of dissociation becomes of the same order of magnitude as the rate of de-activation, and so (1) no longer reduces to (2). However, on the basis of the present theory, it is possible to develop from (1) an expression for k/k_∞, the ratio of the rate at any pressure to the limiting rate at high pressure[2]. Calculations have shown that small molecules should show first-order kinetics only at impossibly high pressures, six or more atoms being necessary to give first-order rates below a pressure of one atmosphere. Dr. Slater showed that the rate as given by (3) and (4) is essentially reproduced at high temperatures by a quantal treatment and that these expressions are little altered by taking account of anharmonicity of the vibrations. The relation of the theory under discussion to that of Kassel and to the transition state theory was described.

Dr. A. F. Trotman-Dickenson (Manchester) gave a critical survey of the experimental field. He stated that, in his opinion, only eight decompositions have been reasonably fully investigated over a large range of pressure, which undoubtedly exhibit quasi-unimolecular behaviour: they are nitrous oxide, di-nitrogen tetroxide, nitrogen pentoxide, fluorine oxide, CH_3NNCH_3, C_2H_6, *cyclo*-C_3H_6, and *cyclo*-C_4H_8. The last two decompositions[3] provide the most straightforward examples of the dependence of a unimolecular rate-constant on pressure. The observations could not be explained on the original Hinshelwood–Lindemann theory. But either the Kassel theory or the Slater theory will fit the results for cyclopropane very well, though the latter theory is much to be preferred because no arbitrary parameters are introduced. A table of the relative efficiencies of various inert gases in maintaining the rates of five reactions was shown by Dr. Trotman-Dickenson, from which it can be inferred that 'kinetic theory' collisions between two complex molecules result in an equilibrium distribution of internal energy between the molecules, whereas equilibrium is attained in only one collision in ten of nitrogen with a complex molecule.

The pyrolyses of alkyl chlorides were discussed by Dr. K. E. Howlett (Bedford College, London). Although two mechanisms—unimolecular and radical chain—have been observed, about ten compounds studied have proved to be pure unimolecular. In each case, critical pressure regions exist, and the number of degrees of freedom required to account for these are reasonable[4]. Inert gases, while having no effect upon the high-pressure rates, are capable in various degrees of restoring the low-pressure rate to the high-pressure value. Ethylene has been found to be the most efficient in transferring energy, and helium the least[5]. Further, the efficiencies appear to be of the same order as predicted by the kinetic theory, in marked distinction to the calculations of C. Zener. It is also observed that the range of efficiencies is never very great. Finally, Dr. Howlett reported that Miss A. M. Goodall has found the inhibited decomposition of trichlorethylene to be a homogeneous second-order, non-chain process, in accord with Slater's predictions for small molecules.