

graduates. There are four main laboratories, two for physical work and two for chemical. Other rooms, such as a spectrographic room, balance room, dark room, workshop and store, are provided for special purposes. The laboratory accommodation and equipment offer facilities, on the chemical side, for work on the analysis of sea-water, particularly of trace elements by spectrophotometric methods, and on the composition of marine sediments. On the physical side, there are facilities for developing and testing apparatus for measuring, for example, the temperature and electrical conductivity of sea-water, and the velocity and turbulent fluctuations of currents.

At right angles to the single-storey wing, parallel to the main wing, there is a two-storey block containing, at one end, staff rooms and a combined library and chartroom for oceanography. The remainder of this block is occupied by the Sub-Department of Numerical Analysis, which possesses, in addition to rooms for its staff, others which house an electronic computer and its ancillary equipment, and a mathematical laboratory.

The building was designed to cater for the estimated number of science and engineering students, and the appropriate staff, likely to study mathematics in one or more of its aspects, or oceanography, within a total student community of 5,000. The erection of the building had scarcely been begun, however, when, under the stimulus of revised estimates of national requirements, the University agreed to plan its development on the basis of an ultimate student population of about 7,000. Large as it appears to be, therefore, the building will probably not be big enough to meet the demands likely to be made on it towards the end of the 'sixties.

The research carried out by the staff and graduate students of the Department of Pure Mathematics (Prof. A. G. Walker), the Department of Applied Mathematics (Prof. L. Rosenhead), with its Sub-

Department of Mathematical Statistics (R. L. Plackett, reader in mathematical statistics), and its Sub-Department of Numerical Analysis (Dr. A. Young, reader in numerical analysis), and the Department of Oceanography (Prof. K. F. Bowden) covers a very wide range. The work that is going on in oceanography has been mentioned earlier; in pure mathematics research interests include classical analysis, group theory, algebraic and differential geometry and topology; and in applied mathematics work is being done on fluid motion, acoustics, quantum theory, nuclear physics, theoretical chemistry, astronomy, geophysics, numerical analysis and mathematical statistics.

The facilities of this well-co-ordinated group of teachers and research workers will be increased within the next few years when, with the aid of the grant recently promised by the University Grants Committee, an English Electric *KDF9* Computer will be obtained to replace the existing *Deuce* of the Computer Laboratory, which was bought with funds provided by local industrialists and the University Council.

The University skyline at the top of Brownlow Hill is changing significantly—new buildings for physics, chemistry and veterinary science have been erected; still more buildings are going up for chemistry—and the foundations of engineering buildings as well as those of an extension of the Students' Union are now being laid. Within this complex of building activity the white-walled Mathematics and Oceanography Building stands out as something rather different and aloof; but the building will, we hope, serve as a university focus of mathematical thinking, teaching and research, and a centre from which mathematical service will flow to the University as a whole—as well as a place where important work on oceanography will be carried out.

L. ROSENHEAD

OXIDATION PROCESSES IN CHEMICAL MANUFACTURE

THE two-day symposium on "Oxidation Processes in Chemical Manufacture" organized by the London Section of the Society of Chemical Industry, was held in the William Beveridge Hall of the University of London during September 28–29, and attracted an audience of some 250 scientists from industry and the universities—with many overseas members.

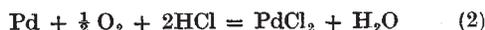
The remarkable development in industrial oxidation processes over the past decade is perhaps best illustrated by the fact that while six comparatively new processes were discussed in some detail by the speakers, an equal number were mentioned only in passing. Among the latter were the direct oxidation of ethylene to ethylene oxide, the oxidation of propylene to acrolein, the subsequent oxidation of acrolein to glycerol, the direct oxidation of propylene in the presence of ammonia to acrylonitrile, and the production of hydrogen peroxide by the peroxidation of isopropyl alcohol. The processes chosen for discussion were the direct oxidation of ethylene to acetaldehyde, the vapour phase oxidation of acetaldehyde to peracetic acid, the uses of hydrogen peroxide in industrial oxidations with particular reference to epoxide formation, recent developments in the oxida-

tion of aromatic hydrocarbons and the recovery of chlorine by oxidation of hydrogen chloride. Theoretical work on liquid-phase oxidation of organic compounds, vapour-phase oxidation of hydrocarbons and liquid phase oxidation catalysed by soluble metal salts was also discussed.

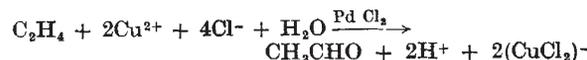
The direct oxidation of ethylene to acetaldehyde in the presence of a palladium chloride-copper chloride catalyst was described by Dr. Smidt (Consortium für Elektrochemische Industrie G.m.b.H.) as a single-stage reaction possibly applicable to other olefines. The mechanism of the reaction in the case of ethylene involves the formation of a complex between ethylene and palladium chloride. The resulting complex decomposes to give acetaldehyde, the palladium metal being precipitated. Since the decomposition of the complex is inhibited by acids, it is suggested that the first step in the reaction is the addition of a hydroxyl ion to the complex-bound olefine. In the second stage the π electron pair of the olefine passes over completely to the palladium with simultaneous migration of an hydride ion from carbon 1 to carbon 2. A double bond is then formed between carbon atom 1 and the oxygen of the hydroxyl group with expulsion of proton. On this hypothesis the oxygen required for the oxidation

of the olefine is supplied by the water, and only the oxygen atom from the water passes over to the olefine during the reaction, all four hydrogen atoms originally present in the ethylene remaining in the aldehyde. This is in contrast to the suggested mechanism discussed by Moiseev and co-workers. Unpublished work of Dr. Kreckeler of Farbwerke Hoechst has, however, shown that decomposition of the dinuclear ethylene-palladium chloride complex by heavy-water yields acetaldehyde which does not show any deuteration in mass spectrographic examination.

The commercial development of the reaction to a continuous process required the precipitated palladium metal to be re-oxidized after reaction 1:



The addition of cupric chloride enables the second step of the process to be carried out since cupric chloride readily oxidizes the finely divided palladium and the cuprous chloride so formed is quickly re-oxidized to the cupric state. The overall reaction may then be written:



the cuprous chloride being reoxidized by air.

In the commercial process, as outlined by Dr. Smidt, ethylene reacts with the catalyst solution, under moderate pressure and medium temperatures, in a flow reactor to 99 per cent conversion. After releasing the pressure of the catalyst solution the acetaldehyde formed distills off (the reaction heat being sufficient to accomplish this), and the reduced catalyst solution is pumped to the oxidation reactor when it is regenerated by air and returns to the ethylene reactor. Further details of this elegant process will be awaited with great interest.

The development of a commercial process for the manufacture of peracetic acid by the vapour phase oxidation of acetaldehyde was described by J. A. John and F. J. Weymouth, of Courtaulds, Ltd., and British Celanese. The major problem associated with this development was the explosion hazard associated with the concentration of peracetic acid. Experimental work established that concentrations of peracetic acid in acetic acid below 40 per cent peracetic acid were stable and that in the vapour phase excess acetaldehyde reduced the hazard to safe conditions. Three pilot plants, each of increasing capacity, had been successfully operated and the process was now considered suitable for commercial exploitation. The major industrial usage of peracetic acid developed in recent years is as an epoxidizing agent for the production of epoxy soya bean oil, epoxy tall oil esters, dicyclopentadiene dioxide and the diepoxide from vinyl cyclohexene.

The production of hydrogen peroxide by the barium process or by electrolytic methods has been virtually replaced in Britain by the method based on the cyclic oxidation and reduction of 2-ethyl-anthraquinol. The development of an alternative method of production by direct oxidation of isopropylalcohol in the United States will lead to increased availability of this material. T. D. Manly, of Laporte Chemicals, Ltd. gave an account of the wide variety of industrially important chemical processes using hydrogen peroxide. Supplied in tank-car quantities stabilized against chance impurities the modern product can

be used at all strengths under many different conditions without suffering detectable loss by decomposition.

The recent developments in the production of a variety of chemicals using aromatic hydrocarbons from petroleum or coal tar were outlined by R. Landau and R. W. Simon. The processes discussed included the manufacture of phthalic anhydride from naphthalene or *ortho*-xylene, maleic anhydride from benzene—or from butene although a direct comparison of these two processes was not given—liquid-phase oxidation of mixed xylenes to yield isophthalic, phthalic, terephthalic acids and the recently announced oxidation of pseudocumene to give trimellitic anhydride. Brief mention was also made of the many processes now available for the production of phenol from benzene and of newer processes using cyclohexane and cyclohexanol obtained by hydrogenation of benzene and phenol respectively, for the production of adipic acid.

An account of recent developments in the oxidative recovery of chlorine from hydrochloric acid by W. F. Engel, S. Muller and M. J. Wade of the Shell Laboratory, Amsterdam, introduced an inorganic oxidation process—the Deacon process—into the discussion. The increasing amounts of by-product hydrochloric acid produced in conjunction with the manufacture of chlorinated organic compounds coupled with the probability of an increase in the price of chlorine as the demand for chlorine increases beyond the so-called caustic-chlorine balance—has stimulated development of processes for the recovery of chlorine from the acid. Three such processes have been announced recently, the De Nova electrolysis of hydrochloric acid operated by Monsanto, the oxidation by mixed nitric/sulphuric acid developed by the Institut Français de Pétrole and the modified Deacon process described by Shell. Several companies have suggested the use of a fluidized-bed technique using modified cupric chloride catalysts. The Shell process employs a modified cupric chloride catalyst supported on silica in a fluidized bed at temperatures between 350° and 360° C. using air or oxygen. Conversions of 76–77 per cent per pass are claimed. On the figures presented the economics of the process are attractive.

Theoretical aspects of oxidation process were reviewed in three papers. Liquid-phase oxidation by molecular oxygen was reviewed by G. H. Twigg with particular reference to the oxidation of hydrocarbons and the reactions involved in the oxidation of cumene to phenol and acetone. The extension of the general reaction mechanism to oxidation of aldehydes, ketones, alcohols and olefines while generally accepted does not entirely satisfy, and further work in this field is desirable. Recent work on the oxidation of binary mixtures is likely to be of considerable theoretical interest. The gaseous oxidation of organic compounds was discussed by C. F. Cullis with particular reference to the effects of temperature, pressure, surface catalysis and mixture composition on the course of oxidation of a particular starting material. Investigations such as those reported on the vapour-phase oxidation of acetaldehyde to peracetic acid indicate that by careful choice of reaction conditions the reaction may be controlled to give, as final products, compounds which normally would occur only as intermediates in a more general oxidation. It is, however, doubtful if the knowledge of low-temperature vapour-phase oxidation processes is sufficiently advanced to enable prediction of reaction conditions in particular cases to be made on the basis of generalized theory.

The oxidation of organic compounds by metal ions and complexes was reviewed by H. R. Bacon with particular reference to complexes of silver and copper. Recent work using argentic piccolinates to catalyse the oxidation of primary and secondary amines has indicated that the effectiveness of the metal ion may be modified by the nature of the ligand. Comparison of reactions catalysed by cobalt, silver and copper complexes may lead to a better understanding of the reaction mechanism.

The conference concluded with a general discussion of the relative merits of fluidized-bed versus fixed-bed reactors for oxidation reactions. For those reactions, such as the modified Deacon process, in which thermal balance is readily achieved, the fluidized process is preferable. In reactions liable to rapid heat evolution, leading to possible explosion hazard, fixed-bed reactors may be preferred although sufficient data on the successful application of the fluidized technique to such reactions are not yet available. F. MORTON

FAST REACTIONS IN PHYSICAL CHEMISTRY

THE first of the triennial Cambridge Physical Chemistry Summer Schools was held in August 1947 but the sequence was broken after 1956 by a gap of five years.

Each school has been organized by Prof. R. G. W. Norrish and his colleagues in the Department of Physical Chemistry in Cambridge and this year Dr. A. B. Callear and Dr. B. P. Levitt acted as organizers. The topics were selected to form a composite pattern of ideas related to current researches in the Department. Certain lecturers belonged to the Department; others were guest lecturers.

The intention has always been to correlate facts and notions within the pattern chosen, to stimulate discussion, to invite, even to provoke, in a friendly way controversy, rather than to instruct by presenting the facts, figures and theory as finished uninspiring blocks of knowledge which could well be posted in cyclostyled form. The pattern for the 1961 School was "The Study of Fast Reactions".

Dr. T. M. Sugden (Cambridge) dealt effectively with the recent developments in the collision and transition state theories, a matter of constant concern with so many chemists in industry and college alike. In his energetic, elusively 'off the cuff' manner, he analysed the processes of energy exchange with special reference to fast reactions, unimolecular decomposition of polyatomic molecules and the recombination of atoms. It may be well imagined that there was much animated discussion during the half-hour coffee-break.

Dr. Sugden described the photometric investigation of flames. He referred to experimental techniques for the measurements of H-atom, O-atom and OH— group concentrations in flames. Significances of the method included the determination of bond strengths in molecules such as $M-Cl$, $M = Mn$, Ni , etc. Trends into the future were not neglected. In another talk, Dr. Sugden dealt with chemical reactions in the upper atmosphere. Methods of investigation of temperature, density, pressure, and composition gradients and the reactions occurring in different strata are bound to attract quickly growing interest in coming years.

Reactions in shock waves were discussed by Dr. A. G. Gaydon (Imperial College of Science and Technology), who outlined experimental methods of observing the emission spectra and temperatures of shock-heated gases. Vibrational relaxation times of nitrogen and carbon monoxide, and the measurement of dissociation-rates of oxygen, hydrogen and carbon dioxide were other points of lively interest to the non-expert as well as to the expert listener. In another lecture, Dr. Gaydon discussed the advantages of low-pressure flames for the study of reaction zones,

referring to the identification of reactive intermediates by emission spectra of flames, to the measurement of temperature by study of rotational structure of bands, the reversal of spectral lines and to reactions in hydrocarbon flames.

Chain reactions in gases, especially those leading to the ignition of gases, were discussed by Dr. P. G. Ashmore (Cambridge), who has taken part in a number of previous Schools. Theories of ignition limits and of induction periods were discussed with reference to non-branching and branching chain reactions.

Ultra-violet spectroscopy and fluorescence was dealt with by Dr. A. B. Callear (Cambridge), who opened with a helpful reminder on the use of term symbols and mode of coupling of angular momenta in atoms. Information on spin-orbit relaxation can be gained from examination of the quenching of the fluorescence of sodium and mercury. Rate of vibrational relaxation of electronically excited I_2 , S_2 and NO was referred to.

Evidence for ions in flames was presented by Dr. D. R. Jenkins (Cambridge), who outlined experimental methods for the determination of distribution of ions by means of Langmuir probes, microwave and radio-wave attenuation and mass spectroscopy.

Relaxation in liquids was the title of a lecture by Prof. J. Lamb (Imperial College of Science and Technology), who outlined the fundamental theory of acoustic relaxation to what must have been many new attentive ears. The potentialities of the method were amply illustrated in a very convincing way.

Techniques for the measurements of fast reactions in solution were considered by Dr. R. H. Prince (Cambridge), who gave a lucid survey of mechanism and reactivity revealed by a study of fast reactions in solution. Substitution reactions in organometallic and co-ordination compounds; redox reactions, rapid isotope exchange were mentioned in particular.

Kinetics of fast reactions in solution was the title of the lecture by Dr. E. A. Moelwyn-Hughes (Cambridge), who, in his inimitable and stimulating way, brought freshness to the ever-difficult problems of rate data and transition-state characteristics. Interpretation of rate data as a function of temperature, certain limitations of the transition state formulation and the derivation of equations used in the interpretation of relaxation of ionic equilibria were critically commented on.

The lecture on fast electrode reactions by Dr. G. C. Barker (Atomic Energy Research Establishment, Harwell) was a very helpful contribution. He considered the theoretical basis of the measurement of rapid redox reactions which occur at the electrolyte/electrode interface and remarked in useful detail on