Homogeneous Catalysis.

In previous discussions held by the Faraday Society, the influence of surfaces and of light on the velocity of chemical actions has been reviewed, and it was with the object of obtaining a summary of the present position in respect to homogeneous reactions that a further discussion was held at Cambridge on Sept. 28 and 29.

The application of the term catalytic to any reaction occurring in homogeneous phases has been considered by some to be unsuitable, but provided that the original definition of Berzelius is not considered to be too broad for practical purposes, there is really little objection to this title. Our knowledge of the mechanism of many gas reactions has been made more complete chiefly by the work of Bodenstein and Hinshelwood; even the famous case of nitrogen pentoxide, which has defied the attacks of many investigators, has just been solved by Bodenstein, the pioneer in gas reaction technique. Yet, as the recent work of Kistiakowsky on the decomposition of hydrogen iodide reveals, it cannot be said that all is known as to the mechanism of these apparently simple reactions, what molecular target area or what activation by collision really is. No less than seven of the communications, including those of Drs. Bäckström, Christiansen, Dhar, Hinshelwood, Mardles, and Polanyi, were to a great extent devoted to what is undoubtedly one of the centres of interest at the present time, namely, the mechanism of chain reactions, and Messrs. Egerton, Garner, and Moureu took part in the discussion. These are of peculiar interest, in that they include a number of cases of reactions which proceed at great but measurable speed in a sort of no man's land between ordinary chemical reactions and explosions.

In general, a chain reaction, as indicated by its name, consists of a reaction of such a type that when one molecule of the reactants suffers reaction, it causes others to react. The number of molecules induced to react, that is, the chain length, may vary with the reaction from two or three molecules to several millions. Some investigators insist that there are in reality two problems to be solved, how a chain starts and how a chain is propagated. Others emphasise the importance of the propagation and believe that ordinary kinetic collision suffices to set a chain in action.

There are at least three different views as to the nature of the chain mechanism in these reactions; it is indeed possible that there are reactions conforming to each type. Historically, the oldest view is that of Nernst, in which an atom mechanism is postulated. This process can be visualised most readily by the following equations applicable to the combination of hydrogen and chlorine:

$$(1)\ Cl + H_2 \longrightarrow HCl + H$$
$$(2)\ H + Cl_2 \longrightarrow HCl + Cl.$$

Provided a chain has once started, it will on this view terminate when the atoms which form the chain links are fixed by some atom accepter.

A second mechanism is that first advanced by Christiansen, in which it is suggested that the product of combination, containing as it does at the moment of formation both the original energy of activation and that resulting from combination, can excite a fresh molecule of one of the reactants. This suggestion has been applied by Bäckström, especially to the oxidation of benzaldehyde, and by Hinshelwood to the oxygen-hydrogen combination. It may be represented by the following equations:

$$(1)\ A + O'_2 \longrightarrow AO'_2$$
$$(2)\ AO'_2 + O_2 \longrightarrow AO_2 + O'_2$$

It is worthy of note that inhibitors in these reactions which have been examined so exhaustively by Moureu and his co-workers frequently undergo oxidation themselves, suggesting that the breaking of the chain is effected by a reaction involving either the species AO'_2 or O'_2; likewise that these reactions occur not only in the gas phase, but also in solutions where numerous collisions with solvent molecules must take place between each chain link, if collision, and not radiation be the mechanism of propagation.

Finally, there exists the hypothesis of Semenoff, in which it is postulated that reaction centres are formed; these diffuse through the reacting system and act as initiators of chemical reaction until destroyed by chemical reaction or adsorption on the surface of the vessel. Some investigators believe that ions, which are possibly always formed in small quantities, especially in these reactions, are to be identified with the reaction centres of Semenoff. Many of those reactions increase rapidly in speed after a period of induction, and it is a necessary consequence that the chains must branch or that the concentration of reaction centres must increase during the reaction. A chemical formulation of this action may be made by postulating a dissociation of one of the reactants; for example:

$$A + O \longrightarrow AO'$$
$$AO' + O_2 \longrightarrow AO + 2O.$$

In this case each single molecule of active product AO' produces two oxygen atoms, giving rise to two fresh reactive molecules.

It was a pity that the limitations of time did not permit of a more adequate discussion of these reactions so that a serious attempt might have been made to reconcile the somewhat divergent opinions expressed.

The second part of the meeting was devoted to discussion of the mechanism of homogeneous catalysis in solution, and with the exception of an interesting paper by Prof. Boeseken in which he developed his well-known views on the application of the theory of molecular 'dislocation' to homogeneous reactions and cited an interesting application in the effect of catalysts on the polymerisation of acetaldehyde, the session was almost entirely confined to the question of the mechanism of reactions accelerated by hydrogen ions. In the discussion on this subject it was clear that the interest of the various investigators was directed to two different aspects of the problem. Some were clearly interested rather in the mechanism of the reaction, that is, the nature of the reacting complex and how it reacts, whilst others were more interested in the formal relationship between concentrations and reaction velocity. Both of these aspects are of course, to a certain extent, interdependent.

The investigations of Kendall on complex formation in ester–water, ester–acid, and acid–water systems may be said to be representative of the first group of investigations; we may include the views of Lapworth, Goldschmidt, and of F. O. Rice on the nature of the complexes formed by the hydrogen ion in aqueous and alcoholic media. The mechanism of the changes taking place in the action of mutarotation, where a sugar hydrogen ion complex is involved, has been elaborated by Brönsted and by Lowry. Emphasis is laid upon the amphoteric character of esters and sugars by Euler, but as observed by Brönsted, it is difficult to decide which are reactants and which products in a reversible system which can be denoted by the equation

$$G^- + H_2O \rightleftarrows HG + OH^-$$

where HG represents the sugar undergoing change.

The second group of investigations includes those in which attempts have been made to deduce the mechanism of these reactions from investigations on the formal relationship between concentrations and reaction velocity. The abnormal effects of strong acids as well as the effects of the addition of non-electrolytes have long been known and different interpretations of the accelerating effects have been advanced from time to time. In this discussion the summaries presented by Drs. Brönsted and Dawson respectively may be said to have been representative of the difference in point of view.

According to Dawson, the catalytic effect of an acid in aqueous solution may well be ascribed to the sum total of a number of several effects, those due to the acid and its components and of the medium. We may represent the velocity of such a reaction by an equation of the following type:

$$v = R_1H^+ + R_2\overset{-}{A} + R_3OH^- + R_4HA + R_5H_2O.$$

In this equation $R_1 \ldots R_5$ represent the specific activities of the various catalytic reactants. In order to justify such an equation it is necessary to evaluate with accuracy the actual concentrations of the reactants; this is, in the case of electrolytes, no easy matter.

The view advanced by Brönsted and by Bjerrum is based upon the hypothesis of the existence of a quasi-complex or very unstable combination between reactants and catalyst and in mass equilibrium with them, the rate of change of this complex being so slow that the mass equilibrium is always established. This hypothesis leads to a very simple formulation of the reaction velocity:

$$v = kA \,.\, B \,.\, \frac{f_A f_B}{f_{AB}},$$

where f_A, f_B, f_{AB} are the activity coefficients of the reactants and complex. Whilst the theoretical evaluation of the relationship between the values of the activity coefficients and the concentrations in the case of electrolytes has not yet been completely solved, in spite of the progress achieved by Milner, Debye, and Hückel, yet their experimental determination by a number of methods does not present serious difficulties.

Brönsted and his co-workers have presented a number of investigations in which this formulation of the reaction velocity has been shown to be justified, and in the case of weak acid and salt mixtures the differentiation between primary and secondary kinetic salt effects is clearly exemplified, although the contribution by Harned and Akerlof demonstrated the complexity of the changes introduced when strong salt solutions are employed. The termination of the second day's discussion likewise proved too abrupt for either of the protagonists to make many converts to their views.

ERIC K. RIDEAL.

New Buildings at the University of Leeds.

AN important stage in the ambitious but urgently necessary development scheme of the University of Leeds was reached on Tuesday, Oct. 2, when the foundation-stone of the new buildings was laid by Her Grace the Duchess of Devonshire.

After the ceremony, honorary degrees were conferred upon Her Grace The Duchess of Devonshire; Sir Albert Ernest Bain, chairman of the Finance Committee of the University; Mr. Alexander Campbell, chairman of the House and Estates Committee of the University; Mr. Morton Latham, Master of the Clothworkers' Company, 1912–13, and chairman of the Trusts and General Superintendence Committee of the Company, 1915–28.

The Mining Block is the first of the new buildings to be erected under the scheme for the enlargement of the University, which was designed by Messrs. Lanchester, Lucas, and Lodge, the winners of the architectural competition. The Department stands at the extreme north of the University's site and forms the right wing of the new University front as seen from Woodhouse Lane. Towards the cost of this building the Yorkshire Coal Owners' Association has contributed £25,000, and the Miners' Welfare Committee, £10,000. In accordance with a decision reached by the University authorities after very careful consideration, the front of this building, as well as the other buildings, will be of Portland stone. The back elevation will be of a good local brick with stone dressings. The building is 158 feet long. The general width of the building is 44 feet, but the central portion stands farther back in the form of a single storey glass-roofed shed which is capable of easy modification should the necessity arise owing to the development of the work of the Department. In common with the other buildings in the scheme, the block will have a flat roof, and the height of the parapet above ground level is 46 feet.

The work of construction is in the hands of Messrs. William Airey and Son (Leeds), Ltd. The building is in three main floors with a partial basement. In the basement a gallery is being built the full length of the building, especially designed for carrying out experiments in mine ventilation and similar problems. The ground floor accommodates the main laboratory, machinery room, crushing shed, and subsidiary rooms for stores and other purposes. The first floor houses laboratories for research, gas analysis, photometry, and general assay work, together with rooms for the staff. The second floor is devoted to the lecture theatre, drawing office, museum, and staff rooms.

The building will be heated by hot water, unconcealed panels being used partly in the ceilings and partly on the walls instead of the ordinary type of radiator. The department will be equipped with the most up-to-date apparatus and machinery designed to give students a complete scientific training before entry into this important branch of industry.

Cotton Growing in the Sudan.

THE Sudan Government, in collaboration with the Empire Cotton Growing Corporation, has issued the "Report for 1926–27 of Agricultural Work in the Sudan," in which the programmes of work for the following season are included. The Gezira Research Farm, which was established in 1918 in connexion with the irrigation project, comprises an area of more than 400 acres and possesses well-equipped laboratories. Considerable progress has been made during the year in bringing the farm up-to-date, and the establishment of two more stations where similar problems could be tested under different conditions is now suggested.

Cotton is the principal crop dealt with. In the chemical section the salt content, salt and moisture movement, and nitrate content of soils in relation to plant growth, are under investigation. The beneficial effect of heavy applications of gypsum on the permeability of Gezira soil is most marked, the uptake, penetration, and distribution of water being greatly improved; further work on this important question is in progress.

On the botanical side, the effect of climate and other factors such as time of planting on growth, is being