

INSTITUT INTERNATIONAL DE CHIMIE

fondé par Ernest Solvay

DOUZIEME CONSEIL DE CHIMIE

tenu à l'Université Libre de Bruxelles

du 5 au 10 novembre 1962

**TRANSFERT D'ENERGIE**  
**DANS LES GAZ**



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# CHEMICAL KINETICS

by A.R. UBBELOHDE \*

Studies of rates of chemical change comprise one of the main branches of chemistry. Progressive refinements and extensions have depended in the main on progressive improvements in methods for detecting and analysing chemical change. Observation of nature in terms of chemical change is in its origins as old as man himself. Cleopatra watched the rate of dissolution of her famous pearl in vinegar, and every schoolboy has observed the rate of melting of ice in the sun. But in order to reduce such general observations to precise quantitative terms, methods of chemical analysis of sufficient accuracy had first to be developed. A long history shows that analysis was one of the earliest branches of chemistry to be taught as a science. For example, the Fuggers supported a school for analysts in Augsburg as early as 1500, in connection with their mining operations.

To be of use for measuring rates of change, methods of analysing the chemical make-up of a system must be as far as possible instantaneous. In practice this means that they must involve a time interval much smaller than the total duration of the rate process to be measured. We are familiar with this condition in measuring other rates of change. In order to time the boiling of an egg at all accurately, for example, each separate grain of sand in the sand glass must fall in a time interval very short relative to the total duration of the operation.

About 100 years ago, chemists began to use methods of analysis sufficiently rapid to determine rates of change. At first, the chemical

\* Cet exposé a été fait à l'occasion de la réunion extraordinaire du Conseil de Chimie en présence de Sa Majesté le roi Baudouin, le vendredi 9 novembre 1962.

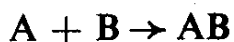
This lecture was held at the special session of the « Conseil de Chimie » in the presence of His Majesty King Baudouin, on Friday 9 November 1962.

reactions studied were simple and quite slow. A favourite example involved the combination of alcohols with acids to form esters, a process which is of such dominant importance in the maturing of fruit and wine. In the present century, with the advent of more accurate knowledge about the structure of molecules, the subject of chemical kinetics has diverged into two main branches, whose methods and disciplines have separated progressively. One great branch of kinetics deals with rates of chemical change in what are known as condensed states of matter, which include liquids and especially solids. In such materials the atoms and molecules are tightly packed together, and the movements which lead to chemical rearrangements are under strong "social" or co-operative influence from neighbours. We all know from watching crowds of people, or the more disciplined displacements of a company of soldiers, that in such condensed systems hindrances to movement from nearest neighbours are of decisive importance. So it is in the chemical kinetics of condensed systems. Transformations of major technical importance such as the setting of cement, the development of a photographic image in grains of silver salts, or the conversion of carbon into diamond, illustrate to what extent profound scientific researches on kinetics of chemical change in condensed states of matter are also of very considerable economic interest.

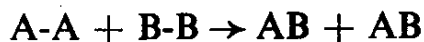
Compared with reaction-rate studies in solids, physicists and chemists have made considerably greater advances in the second main branch of chemical kinetics, in reactions in gases (dilute solutions behave similarly). One reason is that rates of chemical change in gases can be interpreted theoretically, in relatively simple terms. What happens in the encounter or collision between two molecules can be isolated from all the rest, because in a gas at ordinary pressures the average separation between molecules is many times as great as the size of the molecules themselves. Thus, they can collide and interact in pairs, without any crowding or disturbance from neighbours. Anyone who reflects on the difference between human relationships "à deux" and what is possible in a crowd, will realise that even for simple molecules isolated collisions in the gas phase involve more distinctive interactions, than under the molecular crowding in condensed states of matter.

Studies of chemical reactions in gases were at first directed towards

extremely simple examples of chemical change. These included the pairing of two atoms into a molecule



and the redistribution of atomic partners in the encounter between a pair of molecules



Rate measurements soon led to a kinetic molecular theory for reactions conforming to these simple patterns. Quite early in the study of gaseous chemical reactions it was observed that many of them increase in rate very steeply as the temperature of the environment is increased. Following Arrhenius, this striking observation is interpreted on the basis that molecules must collect energy considerably in excess of the average, in order that a gaseous collision may be chemically fruitful.

Much modern research has explored the nature of the so-called "activation energy" required for chemical reaction. Understanding of its significance has been closely linked with the application of Quantum Theory to molecules. Three general comments can serve to indicate some of the most striking lines of advance : —

The first comment is concerned with chain reactions, or chain activation. In the simplest case collisions between a pair of atoms or molecules in the gas lead to isolated chemical reaction. Provided sufficient activation energy is available, rearrangement of chemical linkages takes place during the collision; new chemical species separate and any excess (or deficit) of energy above the average is rapidly distributed over other gaseous molecules in subsequent collisions. For example, physical chemists have frequently examined the collision between molecules of hydrogen and of iodine. By rearrangement of atomic partners these give a new molecule, hydrogen iodide, if sufficient activation energy is available, and that is all. But in a chain reaction, one or more products of a chemically fruitful collision *remain active* and can immediately enter into a succession of similarly fruitful encounters. The most easily demonstrated examples of chain reactions involve a free atom as one of the collision partners. Thus an atom of hydrogen colliding with a molecule of chlorine gives rise to a stable molecule of hydrogen chloride, together with an atom of chlorine which can immediately attack another molecule of hydrogen without requiring fresh activation. The succession of such reactions does not cease until the atoms are trapped or removed in some way. Concepts of chain-linked chemical reactions have proved highly



significant for the understanding of explosions, and have also influenced the development of nuclear reactions in atom bombs and nuclear power stations.

A second striking line of advance in kinetics refers to the chemical reactions associated with biological processes. At present study of these is relatively less developed; but there is reason to believe that the preparation needed by a molecule to ensure successful reaction in an encounter often requires its passage into a special configuration of low probability instead of just the collection of large amounts of activation energy. Chemists describe this special feature in the critical requirements for reaction, in terms of an entropy factor in addition to the better known energy factor. Related concepts are of great importance in general problems of the catalysis of chemical reactions.

The third line of advance in the study of chemical kinetics refers to processes of energy transfer in gaseous collisions. At this 12th Solvay Conference, chemists from all over the world are engaged in discussing new attacks on this extremely fundamental aspect of what happens when two molecules collide in a gas. Its importance has been realised ever since Arrhenius first coined the term "activation energy". But analytical methods for observing rates of energy uptake by individual chemical molecules have become sufficiently rapid to be meaningful, only quite recently. In our discussions at Brussels this week we are particularly concerned with the rate of transfer of internal energy of molecules, for which characteristic time intervals range from  $10^{-5}$  to  $10^{-9}$  seconds, or even shorter. These time intervals can now be dealt with quite confidently, using modern spectroscopic techniques together with the most recent inventions of electronics. I will end by giving only one illustration out of many. It has been established that any molecule of ethylene in gaseous collisions with similar molecules transfers its vibrational energy only once in about three thousand opportunities. This reluctance of ethylene molecules to change their vibrational state can be reduced by catalysts, till about one collision in twenty-five is successful. Theoretical interpretations of these and other striking discoveries about the conditions for energy transfer between molecules are rapidly being developed. Such advances provide an essential foundation to existing knowledge about rates of chemical change. When it is remembered that hundreds of thousands of tons of ethylene are used every year in the high polymer and petrochemical industry, it is easy to show how close are the links between the most abstract advances in science, and the economic welfare of a nation.

# SOME PROBLEMS IN ENERGY EXCHANGE RELATED TO CHEMICAL KINETICS

by O.K. RICE

Chemical reactions are in practically all cases the results of energy exchange processes. Certain reactions are the direct result of intermolecular energy exchange in a single collision. These are the recombination of atoms in the presence of a third body, the dissociation of diatomic molecules, and the dissociation of more complicated molecules at a very low pressure. In unimolecular reactions at high pressures the rate-determining step is intramolecular transfer of energy to some particular bond in the molecule. Of course, the rate of activation, which determines the rate of reaction at low pressures, is in all cases connected with the transfer of energy between molecules. In polyatomic molecules this is a very complicated process, since all kinds of interchanges of vibrational, translational, and rotational energy may occur. The dissociation of diatomic molecules activated by rare-gas atoms involves only exchange of translational energy with vibrational or rotational energy, but the situation is complicated by the fact that the vibrations are highly anharmonic. The relaxation of the lower, more nearly harmonic vibration states, is also very important as a process which must occur on the way to reaction. There is a reasonably well-developed theory for the exchange of vibrational and translational energy, which is fundamental to the whole subject, and which is the first topic with which we shall deal. There are, of course, other types of reaction in which interesting energy-transfer problems arise. In view of limitations of space and time, we shall confine ourselves to the ones specifically mentioned above.