

A century of solution chemistry

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Abstract - The first Nobel prize in chemistry, awarded to van't Hoff, was partly for his work in solution chemistry. His great success in chemistry was due to his imaginative approach to problems, and to his genius for combining experimental and theoretical studies in the most effective manner. In August, 1890, N.A. Menshutkin published an important study on solvent effects on reaction rates, and the considerable extensions of this type of investigation, carried out over many decades, have greatly enriched our understanding of solution chemistry. Over the last century our ideas have been revolutionized by the quantum theory and quantum mechanics. Even more important has been the development of new experimental techniques, such as relaxation methods, nuclear magnetic resonance, ultrasonics, and flash photolysis, allowing us to explore the fastest of physical and chemical processes, such as those occurring in solutions.

INTRODUCTION

In 1901, eighty-nine years ago, the first Nobel prizes were awarded, and the award in chemistry was given partly for work on solution chemistry, the subject of this symposium. The recipient, the great Dutch scientist J.H. van't Hoff, not only made outstanding contributions to the science of chemistry: he also, in my opinion, did more than anyone else to provide a firm foundation to modern chemistry by convincing others of the importance of introducing physical methods into chemistry. We now take it for granted that this is the best approach, but in van't Hoff's time the application of mathematics and physics into chemistry was regarded with great suspicion.

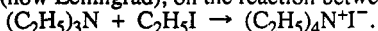
What was the secret of van't Hoff's success? It was not that he was a great experimentalist or a great theoretician; in these areas he was not much above average. His success sprang, I think, from the fact that his approach to scientific problems was much more imaginative than was common at the time; his inaugural lecture at the University of Amsterdam was entitled "Imagination in Science". Also, van't Hoff always preserved a delicate balance between experiment and theory, formulating his theories with the idea of interpreting the experimental results, and conducting his own experiments with the specific purpose of testing his theories. As a result he developed thermodynamics in a very practical way, and until the 1930s it was his system of thermodynamics that exerted the greatest influence on the development of chemistry. In this respect van't Hoff was in marked contrast to that great American genius Willard Gibbs whose system of thermodynamics exerted little influence until it had been interpreted much later by such men as G.N. Lewis and E.A. Guggenheim. van't Hoff took the chemical equilibrium constant as the starting point of his thermodynamics, and made much reference to experimental results. By contrast Gibbs, although dealing with chemical equilibrium, never mentioned an equilibrium constant - he had perhaps never heard of it - and rarely referred to experimental results.

Besides maintaining this fine balance between theory and experiment, van't Hoff had a very broad knowledge of much of science. This is illustrated by the fact that in his first academic appointment he was responsible for the teaching of organic and inorganic chemistry, crystallography, mineralogy, geology, paleontology, animal physiology and plant physiology. His work for the Ph.D. degree, which he obtained at the age of 22, was a rather mundane piece of research in organic chemistry. Two months before he completed it in 1874 he had published privately his now famous memoir on the tetrahedral carbon atom. This memoir gave rise to much controversy - the organic chemist Hermann Kolbe in a particularly vitriolic attack described it as 'akin to witchcraft' - and van't Hoff shrewdly kept this work out of his Ph.D. thesis, realizing that it would probably do him more harm than good. Subsequently van't Hoff worked entirely in the new field of physical chemistry, but always made good use of his knowledge of practical chemistry. From all accounts he was a man of unusually fine character, modest, kind and generous in every way, and as a result he exerted a wide influence. If anyone was the ideal scientist, it was van't Hoff. For many years I have had his portrait in my study, and I was pleased to learn that Arrhenius had his portrait prominently displayed in his home.

I think that we can have the satisfaction of knowing that van't Hoff would have approved entirely of this symposium, which has brought together workers in so many different fields, and has combined together the experimental and theoretical approaches to problems of inherently great complexity. To deal with them we must have a wide knowledge of chemistry and of much of physics. Happily gone are the days when chemists were antagonistic towards introducing physical methods into their subject. It is hard now to believe that this hostility persisted well into the present century. In the 1920s the professor of chemistry at Oxford, W.H. Perkin, Jr. - the son of the more famous Perkin of aniline fame - was fond of remarking that "physical chemistry is all very well, but of course it doesn't apply to organic compounds". He was one of the last of the diehards, and his successor Sir Robert Robinson had a very different approach. I remember vividly attending Robinson's lectures on organic chemistry in 1935. He began with a very lucid account of his electronic theories of organic reactivity, and then applied them in detail to his own researches on the structures of morphine, strychnine and the anthocyanins. Fortunately, during the last half century, chemists have been freed from any reluctance to make use of physics and mathematics, and have realized that it is essential to do so if any progress is to be made.

MENSCHUTKIN REACTIONS

When I chose the title "A Century of Solution Chemistry" I thought I was using the word century in an approximate sense - perhaps with an uncertainty of 5 per cent or so, which is good enough for a kineticist. However, I soon found that I was being more precise than I deserved to be, since a paper that I had decided to use for the beginning of my story was in fact published in August, 1890, just a hundred years ago this month. This is the paper (ref. 1) of the Russian physical chemist Nikolai Alexandrovich Menschutkin of the University of St. Petersburg (now Leningrad), on the reaction between ethyl iodide and triethylamine in a variety of solvents:



He found, for example, that at 100°C the reaction in acetophenone proceeds over seven hundred times as fast as it does in hexane solution. The importance of this work is that it countered the conclusion that some people were drawing from van't Hoff's analysis of the osmotic pressures of solutions, which were the same pressures that a solute would exert if it were in the gas phase at the same concentration. This result seemed to suggest that solvents did no more than fill up the space between solute molecules. Menschutkin's work showed that at least for some solvents this conclusion was far from correct.

van't Hoff himself was quick to appreciate the significance of Menschutkin's results, and within a few years he was demonstrating, in his lectures at the University of Berlin (ref. 2) a correlation between the rate of a Menschutkin reaction and the dielectric constant of the solvent. He also pointed out that there is no correlation with the viscosity of the solvent, which we can now understand since the reaction is not diffusion controlled.

When Menschutkin did this work the Arrhenius equation had only recently been proposed (ref. 3) and it was by no means generally accepted for another twenty-five years. Menschutkin therefore measured no activation energies, but in 1931 the German chemists Grimm, Ruf and Wolff (ref. 4) measured a number of activation energies for Menschutkin reactions, and they also extended the range of solvents. They found, for example, that at 100°C the triethylamine-ethyl-iodide reaction proceeds over 2700 times as fast in nitrobenzene as in benzene. Their temperature-dependence studies showed that the variations in rates are not entirely determined by the variations in activation energies. Their results, in fact, initiated the important studies of compensation and correlation effects that are still investigated actively today.

A little before this work, in 1930, Henry Eyring and Farrington Daniels, at the University of Wisconsin, had made important studies of another reaction, the decomposition of nitrogen pentoxide in various solvents (ref. 5). They found that certain solvents, such as carbon tetrachloride, had little effect on the kinetics, whereas others (e.g. nitric acid) had a very marked effect.

I must admit to a special interest in the reactions between tertiary amines and alkyl iodides - conveniently called Menschutkin reactions - since my first research, carried out in 1937 with C.N. Hinshelwood, was on such reactions in various solvents, including benzene and nitrobenzene. The laboratory in which we worked was a converted college bathroom, and the equipment in it was very primitive. We had to construct our own thermostats, and the reactions were caused to occur in sealed soft-glass bulbs, the extent of reaction being determined by titration. Having this converted bathroom as his research laboratory was something of a rise in the world for Hinshelwood, as previously he had worked in a converted college lavatory in which the toilet fittings were still clearly visible. This building was once visited by the distinguished German kineticist Max Bodenstein, who remarked to Hinshelwood "Ihr Institut ist doch schrecklich". Hinshelwood was not surprised at being told that the building was quite dreadful, but was amused to hear it referred to as an Institute. Hinshelwood's 1956 Nobel prize was largely for his work on the explosive reaction between hydrogen and oxygen, carried out in that converted lavatory. In those earlier times much research in chemistry had to be carried out under such primitive conditions.

Hinshelwood's interest in reactions in solution (ref. 6) began with the arrival in his laboratory, in 1930, of E.A. Moelwyn-Hughes, who had a long and distinguished career in that field. One of the things that Hinshelwood and Moelwyn-Hughes did was to try to study a Menschutkin reaction in the gas phase, in order to compare the behaviour with that in various solvents. The reactions, however, would not occur in the gas phase, but instead went on the walls of the vessel. Obviously a solvent, or a surface, is required to stabilize the polar intermediates and products of these reactions. During the 1930s other important work on the kinetic effects of solvents was carried out, notably by E.D. Hughes and C.K. Ingold (ref. 7). Much of that work has been of lasting value in that it provided a conceptual framework by means of which a practical chemist can make qualitative predictions of the effects of different kinds of solvents on the rates of reactions.

TRANSITION-STATE THEORY

In 1935 there came an important clarification of the whole problem of reaction rates in the form of what is now called transition-state theory, developed independently by Henry Eyring (ref. 8) at Princeton and by M.G. Evans and Michael Polanyi (ref. 9) at the University of Manchester. The importance of this theory is not so much that it allows us to calculate reaction rates; this it does in principle, but there are formidable practical difficulties especially for reactions of any complexity and more especially for reactions in solution. More important is the fact that transition-state theory presents us with an intellectual framework which greatly aids us in understanding the general principles of reaction rates, including the effects of solvents.

According to the theory, the effect of a solvent on the rate of a reaction depends on the difference between its effect on the initial reactants and on the activated complex or transition state. The problem of understanding the effect of solvents on rates is therefore very closely related to that of understanding the thermodynamic properties of solutions.

THEORIES OF SOLUTION

In developing any chemical theory we are faced with a fundamental dilemma. We can formulate a theory of great simplicity, knowing that the model we have chosen is by no means realistic, and that the conclusions we draw from it are necessarily somewhat uncertain. We can then introduce modifications of various kinds into the theory, or can adopt a radically different and more complicated model. The trouble is that the treatment usually becomes much more difficult, and perhaps impossible, to carry out. We are then forced to introduce approximations into our more complicated model, but who is to say which approximations are most acceptable? Sometimes we are forced in the end to admit that the simple treatment was actually the most useful, and almost always the simple model is the one that is most helpful to the practical chemist in leading to qualitative predictions.

Theories of ionic solutions in water provide us with a good example of this. Ninety-six years ago a remarkable paper was published by Drude and Nernst (ref. 10) in which they treated the electrostriction of water which they regarded as a dielectric continuum. A later continuum theory was that of Max Born, who considered the hydration of gaseous ions (ref. 11). Although these treatments are still useful to us for some qualitative purposes and as first approximations, they are obviously not entirely satisfactory. For one thing, water is not in reality continuous. More important, the assumption of a constant dielectric constant that is made in these theories is far from the truth, since because of the intense electric field in the neighbourhood of an ion the dielectric constant is greatly reduced. Calculations of the thermodynamics of hydration with this taken into account have been made (ref. 12). The results are better than obtained from Born's assumption of a constant dielectric constant, but the improvement has been obtained only at the cost of much more labour. Perhaps the greatest value of the improved treatment is that it shows that in considering problems such as the formation of ion pairs in solution we should recognize that the effective dielectric constant is much less than the bulk dielectric constant.

Instead of considering water to be continuous we can treat it as having a molecular structure, but then at once the difficulties become very much greater. H.S. Frank (ref. 13) constructed a useful treatment of this type by considering a layer of water molecules surrounding an ion, the rest of the water being treated as a continuum. Calculations have been made along these lines (ref. 14) but are rather laborious and do not lead to any significant improvement over the continuum model.

In reviewing a century of solution chemistry we have to recognize that two great scientific revolutions have occurred during that period. The first is the quantum theory, born 90 years ago this coming December, and all its refinements, including quantum mechanics. The second, about which I will speak later, is the extraordinary development of technology.

The quantum theory completely revolutionized our thinking, and allowed us to understand certain matters that were quite incomprehensible previously, particularly the energies of atoms and molecules and their spectra. At the same time we must recognize that the new quantum mechanics did not have the overwhelming effect on chemical research that some theoretical physicists predicted. Dirac, for example, believed at one time that with the introduction of quantum mechanics all chemical problems were solved, since everything could be done by setting up and solving the appropriate quantum mechanical equations; there would be no need for further experimental work.

In fact, things have not worked out that way. Quantum mechanics is useful for dealing with individual molecules provided they are not too large, but when we come to solution chemistry the difficulties are overwhelming. Suppose that we consider a system composed of 10^{20} elementary particles, such as a tiny drop of liquid. The number of interactions between these particles is roughly 10^{20} raised to the power of 10^{20} , which is not only greater than the capacity of all the computers in the world, it is greater than the estimated number of particles in the universe! It is true that some of these interactions are very weak, but there is an enormous number of these weak interactions. We are facing the problem mentioned earlier, that to deal with a problem on the basis of a sophisticated theory we are forced to make many approximations, and it is hard to know which to make. In this connection I should mention also the usefulness of computer simulations, such as those described by Professor Diederich in his paper at this Symposium.

Chemists must obviously continue to base their science on an experimental approach and on simple approximate theories, and it seems likely that this will always be the case. Professor Klibanov's conclusions, in his paper at this Symposium, about the behaviour of enzymes in various solvents could hardly have been arrived at from purely quantum-mechanical theory, and the same is surely true of Professor Lu's work on the behaviour of supercritical solvents and of Professor Zitic's conclusions from her electroanalytical studies.

SOME MODERN TECHNIQUES IN SOLUTION CHEMISTRY

The impact on chemistry of new experimental techniques has been even greater than that of quantum mechanics. Prior to World War II everything had to be done with the simplest of apparatus, and there was little change from the 1870s when van't Hoff did his earliest experiments until the 1940s. Many of the techniques now invaluable for investigating solutions are a direct result of scientific effort during World War II. During a war, governments perforce are more willing than at other times to finance scientific research in an adequate way. Among the techniques important in solution chemistry are lasers, which through masers were a product of wartime research on radar detection. Underwater research during the war led to a great development in ultrasonics, now valuable for the study of some of the processes occurring in solutions. Nuclear magnetic resonance (NMR) spectroscopy was a by-product of radio and radar work done during the war. Work on flash photolysis was a direct result of the work during the war on photographing missiles in flight, and the later developments in flash photolysis depended on the use of lasers.

All of these techniques are valuable for the study of the various chemical and physical processes that occur in solution and are too fast for conventional techniques. Figure 1 may help us to appreciate the range of speeds of various processes and the techniques available for measuring them. The abscissa relates to the half lives or relaxation times of the processes, and the upper part of the diagram shows the approximate ranges for particular types of process. The diagram also indicates the corresponding spectral region. This is useful since for vibrations and rotations the frequencies of the processes themselves are in the same domains as the corresponding regions of the electromagnetic spectrum.

Modern spectroscopic techniques provide a powerful means of investigating solutions, and there are several examples of their use at this Symposium. Professor Barthel's paper, for example, is concerned with investigations in the microwave region. Professor Yamaguchi has probed various types of ionic solutions by X-ray and neutron diffraction, and by X-ray absorption. It is interesting to recall that the first convincing evidence that strong electrolytes are completely dissociated in aqueous solution was provided by spectroscopy. That great Danish chemist Niels Bjerrum examined aqueous solutions of chromium salts over a wide concentration range, and found a constancy in light absorption, leading him to conclude that there was no variation in their degree of dissociation. When Bjerrum first presented his evidence in 1909 at a meeting in London (ref. 15), Arrhenius took the paper as a personal affront and refused to discuss it. Until his death in 1927 Arrhenius always refused to believe that salts are completely dissociated in water (ref. 16).

Until the 1950s there was no way of measuring half lives of less than about 10^{-2} s. Eigen's relaxation techniques (ref. 17) could be used for faster chemical processes, and the ultrasonic and NMR techniques have also been extremely useful. For the fastest of physical processes, however, the only methods available are the flash photolysis techniques in which modern lasers are used.

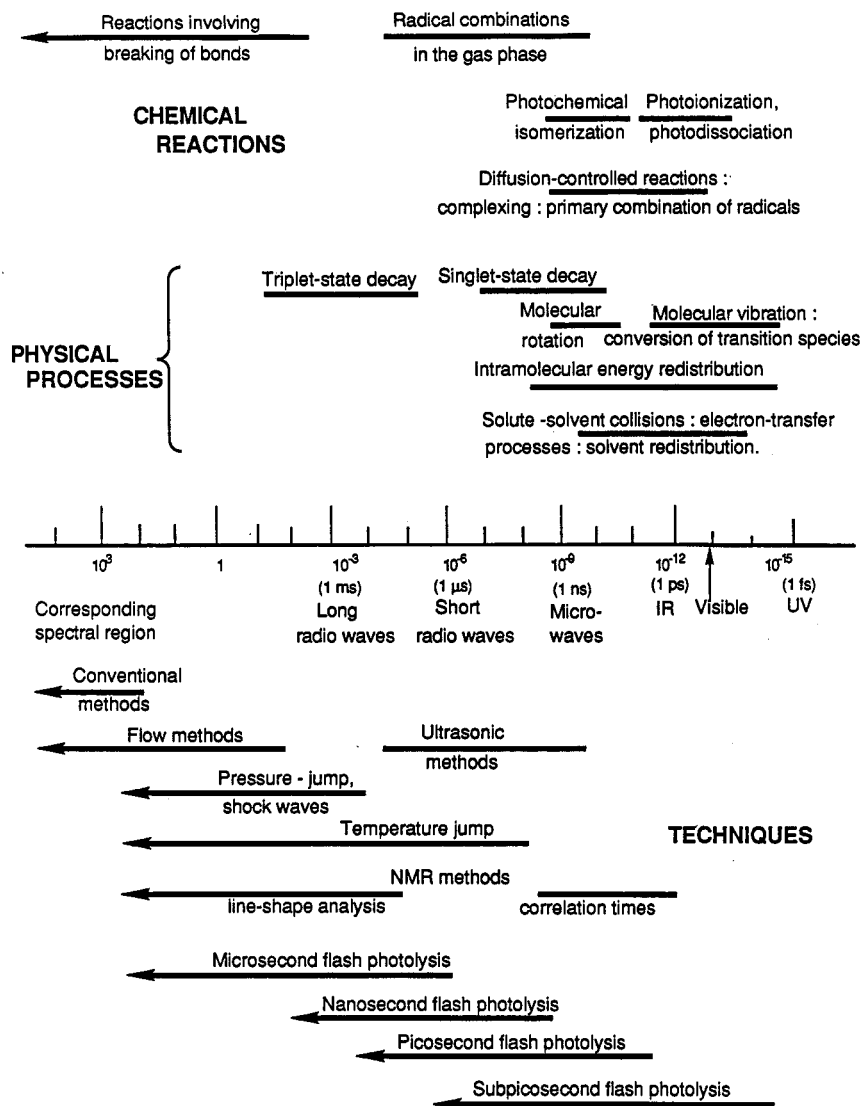


Figure 1 The range of half lives or relaxation times for some chemical and physical processes, and the ranges of times available to various experimental techniques.

The ultrasonic techniques have not yet been exploited as much as they could be, and we are fortunate at this Symposium to have Professor Edward Eyring's contribution in which the technique is applied to the formation of complexes in solution. The ultrasonic technique is often said to have begun with the work at Harvard of G.W. Pierce (ref. 18), who in 1925 produced high-frequency sound by means of a piezo-electric device, and made accurate measurements of its velocity in air and carbon dioxide. The first suggestion that sound might be used for studying dynamical processes was, however, made as early as 1910 by Nernst (ref. 19) who tried unsuccessfully to determine the rate of dimerization of nitrogen dioxide, NO_2 , by measuring the sound dispersion. The first to obtain evidence for a dynamical process from experiments with sound were K.F. Herzfeld and F.O. Rice (ref. 20), who analysed the data of others including Pierce, and were able to interpret some of the results in terms of an exchange of energy between translational and internal modes.

However, the application of the technique to the study of dynamical processes developed very slowly, and required stimulation from technical advances during World War II. In 1959 Herzfeld and Litovitz (ref. 21) wrote an authoritative book on ultrasonic waves and this led to further work in this area. Since then useful kinetic information has been provided by ultrasonic methods, particularly interesting work having been done on proton transfer, conformational changes, and ion association (ref. 22). As seen from Figure 1, the technique is useful for processes occurring in the microsecond and nanosecond ranges.

Another technique that in recent years has been applied to rapid chemical and physical processes is nuclear magnetic resonance (NMR) spectroscopy. Nuclear magnetic resonance was discovered independently and almost simultaneously in 1946 by two groups of workers, E.M. Purcell and his colleagues (ref. 23) at the Massachusetts Institute of Technology Radiation Laboratory, and Felix Bloch and his colleagues (ref. 24) who did their work partly at the Radio Research Laboratory at Harvard and partly at Stanford University. Their discoveries were a by-product of wartime research, and it is interesting that although for a time the two groups were working within 4 kilometres of each other, they were unaware of each other's work partly as a result of wartime secrecy. Purcell and Bloch shared the 1952 Nobel prize for physics.

NMR spectroscopy rapidly developed into an important and widely-used laboratory technique. It became evident that linewidths in NMR spectra are related to the dynamics of relaxation processes, and the analysis of linewidths has now provided valuable information about processes having relaxation times of 10^{-5} s and higher (ref. 25). Dr. D.G. Cox, who is presenting a paper at this Symposium, has made much use of this procedure. A more recent technique, involving correlation times, allows one to study processes occurring in times of 10^{-8} s to 10^{-12} s (ref. 26). As seen from Figure 1, the ultrasonic method and the two NMR methods together cover a wide range of times.

Similar investigations to those done with NMR can be done by electron paramagnetic resonance (EPR) spectroscopy, but this technique is limited to paramagnetic species such as free radicals.

A technique that over the past forty years has developed in a remarkable way is flash photolysis, and it has contributed greatly to our knowledge of solutions. This technique was first developed at Cambridge University by G. Porter and R.G.W. Norrish (ref. 27), their first paper on the subject appearing in 1949, with details in 1950. For this work they were awarded Nobel prizes in 1967, together with Manfred Eigen who had developed the relaxation techniques (ref. 17). Subsequent to the work of Porter and Norrish, flash photolysis equipment was built and used by G. Herzberg and D.A. Ramsay (ref. 28) here in Ottawa, and by N.R. Davidson (ref. 29) at the California Institute of Technology in Pasadena.

In Porter's earliest experiments at Cambridge, in 1948, the duration of his flashes was about a millisecond, 10^{-3} s, and it is a remarkable fact that during the next four decades the duration of the flash was reduced by eleven powers of ten, to about 10^{-14} s, or 10 femtoseconds, which was achieved in 1986 by C.V. Shank at the AT&T Bell Telephone Laboratories. This improvement has had particularly important consequences for solution chemistry.

In 1966, a year before he received his Nobel prize, Porter and his colleagues (ref. 30) developed a highly efficient laser flash system capable of dealing with processes occurring in the nanosecond (10^{-9} s) range. This enabled him to study many additional chemical processes, such as the radiative decay of species in singlet excited states, both in the gas phase and in solution.

A flash of a nanosecond duration is adequate for the study of most purely chemical processes, by which is meant processes in which there is a change in chemical identity. Accompanying chemical processes, however, there are always processes of a purely physical nature, such as energy redistributions and solvent reorganization, and the chemist must obviously be interested in these. Such physical processes commonly occur in the picosecond range.

During the 1970s, following further improvements in laser technology, shorter flashes were achieved, particularly in the Bell Telephone Laboratories by Charles V. Shank, Peter M. Renzepis, and others (ref. 31). Many processes have now been studied with flashes of a picosecond duration. For example, Porter and his colleagues (ref. 32) at the Royal Institution made a study of a process that is commonly shown in photochemical demonstrations, the reaction between the purple dye thionine and ferrous ions in aqueous solution. The half life of this photochemical process, of the order of picoseconds, was determined by a flash of about a picosecond duration.

During the last decade, largely due again to the efforts of Shank and his colleagues (ref. 31), it has become possible to achieve flashes of even shorter duration, of only a few femtoseconds (10^{-15} s). We should note that the uncertainty principle now imposes a limitation on what can be done. According to the uncertainty principle for energy, the product of the uncertainty in time and that in energy is approximately equal to Planck's constant:

$$\Delta t \Delta E \cong h.$$

It follows that if the flash duration is 10^{-15} s, the uncertainty in energy is about 6.6×10^{-19} J, which is equivalent to 400 kJ mol^{-1} ; this is greater than the energy of most chemical bonds. Since uncertainty in energy is reflected in uncertainty in the spectroscopic information needed for knowing what occurs after the flash, it follows that further

reduction in flash duration will not provide any useful information. We have thus achieved the limit for the study of fast reactions; if faster processes do occur they are beyond the reach of experiment.

Much has already been done by the use of flashes of a few femtoseconds duration. For example, transition species are species in elementary reactions that lie between the reactants and products, and spectroscopic evidence for them was first obtained in 1980 by John Polanyi at the University of Toronto. They are now being actively investigated by the use of flashes of a few femtoseconds duration particularly by Philip R. Brooks (ref. 33) at Rice University and by Ahmed H. Zewail (ref. 34) at the California Institute of Technology.

Dynamic processes in liquids and solutions are also being investigated with the use of these extremely short flashes. The behaviour of solvation clusters, and the development of vibrations when a reaction occurs in solution, have been investigated in this way. Such work has been carried out over the past few years by Geraldine Kenney-Wallace (ref. 35) at the University of Toronto. At this Symposium we are to hear from Professor Simon an account of his work in this area of research.

Since solution chemistry comprises a large fraction of the whole of chemistry, it required considerable temerity on my part - some would say recklessness - to try to cover a century of it in 35 minutes. What I have tried to do is to give a highly impressionistic view of one or two aspects of the subject. I hope that I have not been impressionistic in the manner of so many modern artists, whose work seems to have no relation to reality; instead I have tried to give a true impression of a small but important part of the landscape. Many of the topics that I have had to omit entirely will be dealt with during the next few days at this Symposium.

Acknowledgement I thank Professor C. Detellier, the chairman of the local organizing committee for this Symposium, for inviting me to present this lecture. I am grateful to him and to Professor Margaret H. Back for valuable suggestions and discussions.

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