Techniques for the Kinetic Study of Fast Reactions in Solution

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1 Introduction

Following the earliest investigation in 1850, the rates of chemical reactions in solution were studied by simple methods for many years. The reaction to be studied was initiated by mixing the reagent solutions, and its progress was followed by titrating samples, or carrying out measurements of some physical properties after various time intervals. In this way reactions which last longer than 10 s could have been studied.

In 1866/67 Harcourt and Esson[1] published their classical paper 'on the laws of connexion between the conditions of a chemical change and its amount', and first showed that the rates of reactions can be interpreted in terms of mathematical equations. Since those days a vast number of kinetic investigations has been carried out and has led to the elucidation of the mechanisms of all types of chemical processes.

For a long time there were essentially two time ranges for kinetic investigations. These were the ranges of *chemical kinetics*, the lower limit of which is at about 1 s, and the range of *spectroscopy*, essentially the range between 10^{-10} and 10^{-15} s. This latter range usually does not involve chemical transformations, but gives information on physical processes (*e.g.* electron motion, vibrations, bond stretching, *etc.*). Actual chemical transformation is expected to lie just within the gap extending from 1 to 10^{-10} s. Some time ranges in seconds are given below in Figure 1.

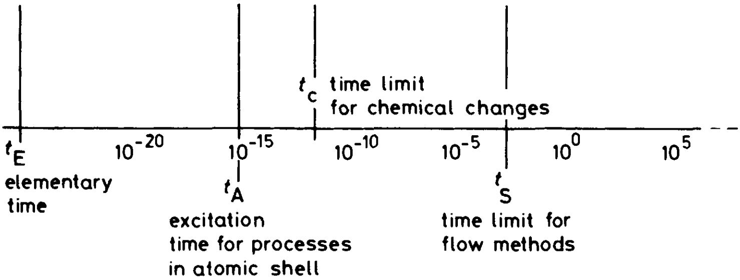

Figure 1 *Time ranges (in seconds)*

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[1] A. V. Harcourt and W. Esson, *Philos. Trans., R. Soc. London*, 1866, **156**, 193: 1867, **157**, 117.

The time range between 1 and 10^{-10} s has been made accessible by a number of new techniques, which enables us to study almost any chemical reaction in solution with half-times between one second and fractions of millimicroseconds.[2] Figure 2 below shows some of the methods available and their time ranges. A whole family of methods for studying fast reactions has been developed over the past 60 years. Much ingenuity has been applied to following the details of chemical reactions on an increasingly short time scale.

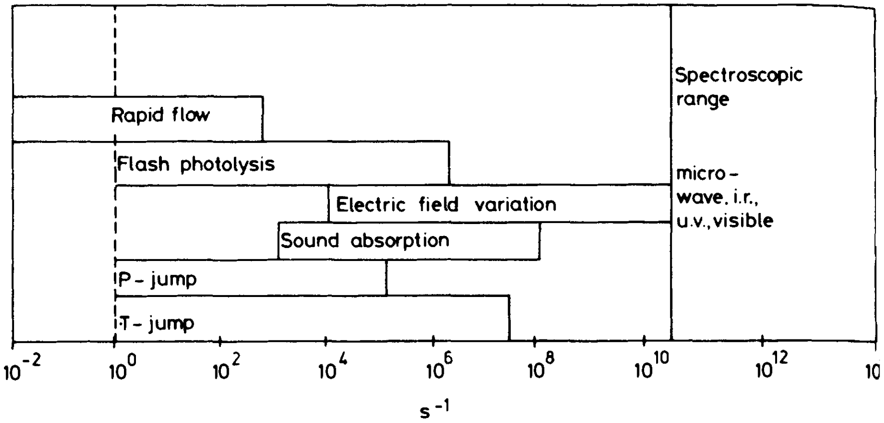

Table 1 *Kinetic methods and time ranges* (*in* s^{-1})

These techniques are specifically adapted to the requirements for recording chemical transformations and utilize conductimetric, polarimetric, spectrophotometric, and fluorimetric detectors depending on which one is most sensitive to the particular reaction. Indirect methods such as n.m.r., e.s.r., electrochemical and photostationary techniques may also provide valuable information.

A. Difficulties in Measuring Fast Reactions.—We generally describe as 'fast' anything that takes place quickly compared to the rate of resolution of our sense perceptions. Since our perceptions are in turn based on chemical processes, these reactions must necessarily be 'fast', indeed 'extremely fast'. The term 'fast reaction' is best applied to reactions that cannot be followed kinetically by conventional methods and which proceed much faster than the time required for mixing and observing.

A chemical reaction is generally started by mixing, for example, two solutions and then measuring the concentration of one or more of the species present at known intervals of time. This type of procedure cannot be used if the start of a reaction is ill defined as when the time of mixing is compatible with or is

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[2] G. G. Hammes, 'Techniques of Chemistry', Vol. VI, Investigation of Rates and Mechanisms of Reactions, Part II, 1974, John Wiley & Sons.

greater than the total time required for the reaction to occur. A similar constraint will apply if the time required to complete a measurement on a reaction mixture is no longer negligible when compared with the duration of the reaction.

There is an upper limit for the rate constant of a chemical reaction. If molecules A and B react, then the process proceeds in two steps. First, A and B must meet in solution. Only after having met can they react with each other. The time of meeting in solution is the time of diffusion of the two partners and is 10^{-12} s. This time cannot be shorter and is also valid for monomolecular reactions. When molecule A decomposes, the time of decomposition is at least 10^{-13} s, *i.e.* the time of vibration of a breaking bond of that molecule.

2 Flow Methods[3-6]

Until 1923 there did not exist any direct, generally applicable method for measuring the velocity of rapid chemical reactions in the liquid phase with half-times of less than about 10 s. In that year, however, Hartridge and Roughton[7] extended the observable time range about 10^4-fold by devising a new method.

If one wants to follow the reaction between species A and B in solution, samples of the two solutions can be let to a mixing chamber, specially designed to achieve rapid mixing, and then passed through an observation tube. The concentration of one or more of the species present can then be detected at various points along the observation tube by spectroscopic means and recorded by some form of high-speed recorders. Other properties of the mixture, such as electrical conductivity, which change during the reaction, can also be measured at different points of the tube. This is called the *continuous-flow* method and is illustrated in Figure 2.

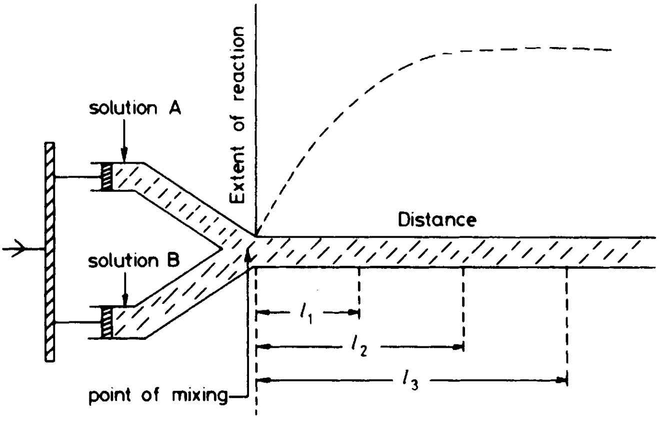

Figure 2 *The continuous-flow method*

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[3] E. F. Caldin in 'Fast Reactions in Solution' 1964, p. 29, Blackwell Scientific Publications.

[4] K. Hiromi, *Kagaku, Zokan* (*Kyoto*), 1979, **80**, 7.

[5] G. Czerlinski and K. Tatti, *J. Biol. Phys.*, 1977, **5**, 184.

[6] New Applications of chemical relaxation spectrometry and other fast reaction methods in solution, W. J. Gettins and E. Wyn-Jones, *NATO Adv. Study Inst. Ser.*, Aberystwyth, 1978, p. 13.

[7] H. Hartridge and F. J. W. Roughton, *Proc. R. Soc. London, Ser. A.*, 1923, **104**, 376.

The flow rate in the tube is known and is approximately 10 ms^{-1}. At distances $l_1 \ldots l_2 \ldots l_3 \ldots$ from mixing chamber a time of $t_n = l_n v^{-1}$ s have passed since mixing took place, where v is the flow velocity. The mixing chamber is specially designed to achieve rapid mixing.

In the *stopped-flow* method,[8] which nowadays is used generally, the flow is suddenly stopped and checked and light absorption measured as a function of time.

The response may be applied to a cathode-ray oscilloscope. With the help of a time base, a curve representing the extent of reaction against time may be displayed on the screen. The time scale extends from a millisecond to several minutes.

Numerous reactions have been investigated by flow-methods, such as the reaction between Fe^{3+} ions and thiocyanate ions,[9] or the dissociation of $Ni(en)_3^{2+}$ in strong acid medium,[10] in proton transfer reactions and enzyme catalysis[3] or in electron transfer reactions,[11-14] and many more.[15-17]

3 Chemical Relaxation Techniques[2,18,19]

A. Introduction.—In 1954 Manfred Eigen reasoned that rate constants could be obtained if a mixture of reactants and products in equilibrium was subjected to a sudden change in external parameters, such as temperature, pressure, electric field strength *etc*. The chemical system could then be monitored by physical means as it underwent equilibration (or 'relaxation') to the new equilibrium state. There is a time lag while the system approaches equilibrium, and this time lag is related to the rate constants of the forward and backward reactions. This basically simple idea provided a new vision into elementary steps of chemical processes and is providing a powerful tool for the detection of fast reactions.

In all relaxation methods the rate of approach to the new equilibrium is exponential as shown in equation (1),

$$\frac{\mathrm{d}\Delta c_i}{\mathrm{d}t} = -\frac{\Delta c_i}{\tau} \qquad (1)$$

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[8] (*a*) Q. H. Gibson, *Discuss. Faraday Soc.*, 1954, No. 17, p. 137.
(*b*) B. Chance, *Rev. Sci. Instrum.*, 1951, **22**, 619.

[9] J. F. Below, jun., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, 1958, **80**, 2961.

[10] Reference 3, p. 51.

[11] C. F. Bernasconi, in 'Relaxation Kinetics', Academic Press, 1976, p. 32.

[12] A. Bakač and J. H. Espenson, *J. Am. Chem. Soc.*, 1981, **103**, 2721.

[13] G. H. Jones, *J. Chem. Res.*, 1981, 228.

[14] J. D. Clemmer, G. K. Hogaboom, and R. Holwerda, *Inorg. Chem.*, 1979, **18**, 2567.

[15] H. Orgino, M. Shimwa, and N. Tanaka, *Inorg. Chem.*, 1979, **18**, 2497.

[16] W. A. Schenk and H. Müller, *Inorg. Chem.*, 1981, **20**, 6.

[17] H. Elias, U. Reiffer, M. Schumann, and K. H. Wannowius, *Inorg Chim. Acta*, 1981, **53**, L. 65.

[18] F. Wilkinson, 'Chemical Kinetics and Reaction Mechanisms', Van Nostrand, 1980.

[19] H. Strehlow and W. Knoche, 'Fundamentals of Chemical Relaxation', 1977, Verlag Chemie, Weinheim.

where Δc_i is the difference in concentration of the *i*-th species between time *t* and infinite time. The relaxation time τ is the characteristic constant for the exponential change. This is illustrated in Figure 3.

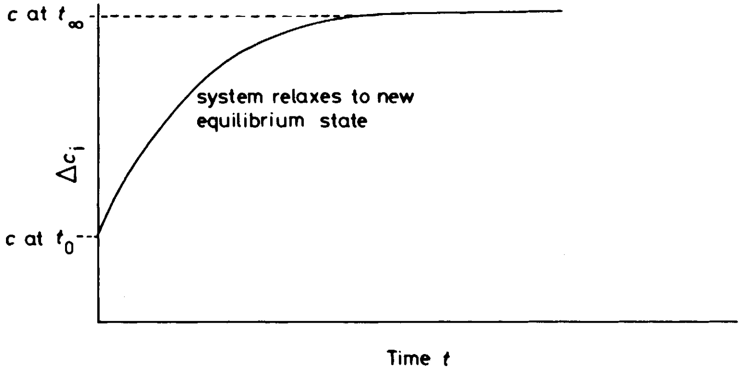

Figure 3 *Relation between time and concentration in relaxation studies*

The graph contains an idealized relaxation curve indicating the variables discussed above. The relaxation time τ is generally taken from a plot of $\ln\Delta c_i$ *versus* time *t*. The relaxation time τ is related in a unique functional way to the rate constants, the equilibrium constant, and to the concentration depending on the reaction mechanisms. In all relaxation studies the rate constants and concentrations are those of the perturbed state.

Provided the displacement of the chemical equilibrium is small enough, the rate of restoration of equilibrium will always follow first-order kinetics, irrespective of the kinetics of the forward and reverse reactions.

The following conditions for relaxation studies are important.

(i) The chemical reaction must take place under constant and defined physical conditions.

(ii) It must be possible to observe the relaxation process separately from other changes in the system.

(iii) Concentrations of the reacting partners must be low in solution.

(iv) The perturbation of the equilibrium state must be sufficiently small, so that all changes can be represented by linear differential equations.

The use of the relaxation methods has widened our kinetic horizons enormously. Many reactions of great importance provided basic information and development of relaxation techniques opened a hitherto inaccessible time range with the measurement of rate of chemical reactions with half-lives of less than a nanosecond ($<10^{-9}$ s). Relaxation rates can be measured for what are probably the fastest of all chemical reactions.[20,21]

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[20] D. W. Oxtoby, *J. Chem. Phys.*, 1981, **74**, 5371.

[21] *Proc. Indian Acad. Sci., Sect. A*, 1978, **44**, 252.

Some of the most spectacular work in the field of fast reactions has concerned biological phenomena.[22,23] Among these are the exact replication of the genetic code by DNA molecules, the action of nerve membranes, enzyme-catalysed biochemical processes in all organisms, the role of chlorophyll in photosynthesis, the interaction of haemoglobin with oxygen in blood, and a variety of aqueous inorganic complex systems. In all relaxation techniques the relaxation time τ has to be determined.[24] When an equilibrium, such as $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ is perturbed, the system adjusts itself to the external parameters. By measuring this adjustment (chemical relaxation) one can obtain information on the evaluation of k_1 and k_{-1}. When $[A_e]$ and $[B_e]$ are the equilibrium concentrations of species A and B the relationship given in equation (2) can be derived.

$$\frac{1}{\tau} = k_1\,([A_e] + [B_e]) + k_{-1} \tag{2}$$

Plotting τ^{-1} against the total concentration $[A_e] + [B_e]$ one obtains k_{-1} from the intercept and k_1 from the slope experimentally.

For pseudo first-order conditions *i.e.* when $[A_e] \gg [B_e]$, equation (3) applies. In the case where $[A_e] = [B_e]$, equation (4) applies.

$$\frac{1}{\tau} = k_1\,[A_e] + k_{-1} \tag{3}$$

$$\left(\frac{1}{\tau}\right)^2 = 4k_1k_{-1}[A_e] + (k_{-1})^2 \tag{4}$$

For other single-step systems:

(*a*) For $2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B : \frac{1}{\tau} = 4k_1\,[A_e] + k_{-1}$

(*b*) For $nA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B : \frac{1}{\tau} = n^2k_1\,[A_e]^{n-1} + k_{-1}$

(*c*) For $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D : \frac{1}{\tau} = k_1\,([A_e] + [B_e]) + k_{-1}\,([C_e] + [D_e])$

(*d*) For $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2C : \frac{1}{\tau} = k_1\,([A_e] + [B_e]) + 4k_{-1}[C_e]$

(*e*) For $A + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C : \frac{1}{\tau} = (k_1 + k_{-1})[C_e]$ (C is a catalyst)

(*f*) For $A + B + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D : \frac{1}{\tau} = k_1\,([A]\,[B_e] + [A_e][C_e] + [B_e][C_e]) + k_{-1}$

In multi-step systems most reaction mechanisms involve several steps and are characterized by more than one relaxation time. If the intermediate states

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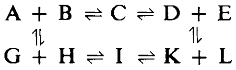
[22] J.-E. Dubois, *Pure Appl. Chem.*, 1978, **50**, 801.
[23] H. Hatano, *Kagaku, Zokan* (*Kyoto*), 1979, **80**, 1.
[24] E. L. King, *J. Chem. Educ.*, 1979, **56**, 580.

accumulate to measurable concentrations, several or all the relaxation times may in fact be observed experimentally. The number of relaxation times is always equal to the number of independent rate equations that can be written for the system. In linear systems, such as $A + B \rightleftharpoons C \rightleftharpoons D \rightleftharpoons E + F$ this number is 3, the number of reaction steps. In cyclic systems, such as the one shown in Scheme 1, this number is smaller than the number of steps. In general the number of relaxation times is always equal to the number of states minus one.

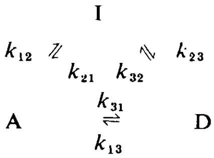


$$\begin{tikzcd} A + B \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, phantom, "\upharpoonleft\downharpoonright"] & C \arrow[r, phantom, "\rightleftharpoons"] & D + E \arrow[d, phantom, "\upharpoonleft\downharpoonright"] \\ G + H \arrow[r, phantom, "\rightleftharpoons"] & I \arrow[r, phantom, "\rightleftharpoons"] & K + L \end{tikzcd}$$

Scheme 1

Two-step systems[11] are among the most frequently encountered multi-step mechanisms in chemistry (see Table 2).

Cyclic reaction schemes are quite common in chemistry. The simplest is the triangle, as shown in Scheme 2. The starting material A forming a product D can react by two competing mechanisms, one being a concerted one-step reaction, the other involving the formation of an intermediate I. Familiar examples are S_N1 *versus* S_N2, or E_1 *versus* E_2.



Scheme 2

For τ_1 a shorter relaxation time than τ_2 and setting

$$\begin{aligned} a_{11} &= k_{12} + k_{13} + k_{21} \\ a_{12} &= k_{21} - k_{31} \\ a_{21} &= k_{23} - k_{13} \\ a_{22} &= k_{23} + k_{31} + k_{32} \end{aligned}$$

we obtain the two relaxation times given in equations (5) and (6). If we assume

$$\frac{1}{\tau_1} = \tfrac{1}{2}(a_{11} + a_{22}) + \{[\tfrac{1}{2}(a_{11} + a_{22})]^2 + a_{12}a_{21} - a_{11}a_{22}\}^{\frac{1}{2}} \tag{5}$$

$$\frac{1}{\tau_2} = \tfrac{1}{2}(a_{11} + a_{22}) - \{[\tfrac{1}{2}(a_{11} + a_{22})]^2 + a_{12}a_{21} - a_{11}a_{22}\}^{\frac{1}{2}} \tag{6}$$

that the k_{12} and k_{13} steps are *bimolecular, i.e.* $A + B \rightleftharpoons D$ and $A + B \rightleftharpoons I$, then we obtain equations (7) and (8) where K_{12} = equilibrium constant for the system $A \rightleftharpoons I$.

$$\frac{1}{\tau_1} = k_{12}([A_e] + [B_e]) + k_{21} \tag{7}$$

$$\frac{1}{\tau_2} = \frac{(k_{23}K_{12} + k_{13})([A_e] + [B_e])}{1 + K_{12}[A_e] + (B_e]} + k_{13} + k_{32} \tag{8}$$

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Table 2 *Two-step systems and their relaxation times*

System	$\frac{1}{\tau_1}$ *(short)*	$\frac{1}{\tau_2}$ *(long)*
$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ $C + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E$ where $k_1([A_e] + [B_e]) + k_{-1} \gg k_2([C_e] + [D_e])$ or k_{-2}	$k_1([A_e] + [B_e]) + k_{-1}$	$k_2[C_e] + k_2[D_e]\frac{k_1([A_e] + [B_e])}{k_1([A_e] + [B_e]) + k_{-1}} + k_{-2}$
$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} k_1 B + C$ $C + D \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E$ where $k_1 + k_{-1}([B_e] + [C_e]) \gg k_2([C_e] + [D_e])$ or k_{-2}	$k_1 + k_{-1}([B_e] + [C_e])$	$k_2\left[[C_e] + [D_e]\frac{k_1 + k_{-1}[C_e]}{k_1 + k_{-1}([B_e] + [C_e])} + k_{-2}\right]$
$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$ where $k_1 + k_{-1} \gg k_2 + k_{-2}$	$k_1 + k_{-1}$	$k_2\frac{k_1}{k_1 + k_{-1}} + k_{-2}$
$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$ (*a*) $k_1([A_e] + [B_e]) + k_{-1} \gg k_2$ or k_{-2}	$k_1([A_e] + [B_e]) + k_{-1}$	$k_2\frac{k_1([A_e] + [B_e])}{k_1([A_e] + [B_e]) + k_{-1}} + k_{-2}$
(*b*) $k_1([A_e] + [B_e])$ or $k_{-1} \ll k_2 + k_{-2}$	$k_2 + k_{-2}$	$k_1([A_e] + [B_e]) + k_{-1}\frac{k_{-2}}{k_2 + k_{-2}}$
$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D + E$ where $k_1([A_e] + [B_e]) + k_{-1} \gg k_2$ or $k_{-2}([D_e] + [C_e])$	$k_1([A_e] + [B_e]) + k_{-1}$	$k_2\frac{k_1([A_e] + [B_e])}{k_1([A_e] + [B_e]) + k_{-1}} + k_{-2}([D_e] + [E_e])$
$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D$ where $k_1 + k_{-1}([B_e] + [C_e]) \gg k_2([B_e] + [C_e])$ or k_{-2}	$k_1 + k_{-1}([B_e] + [C_e])$	$k_2([B_e] + [C_e])\frac{k_1}{k_1 + k_{-1}([B_e] + [C_e])} + k_{-2}$

B. The Temperature-jump Perturbation Method.[2,22,24,25]—Rapid changes in temperature can be brought about in a system in equilibrium by charging a capacitor to a high voltage and then allowing it to discharge through the equilibrium mixture in solution. This discharge current heats the mixture rapidly and the temperature rises a few degrees in microseconds. The instrumentation used for T-jump spectrophotometers is illustrated in Figure 4.

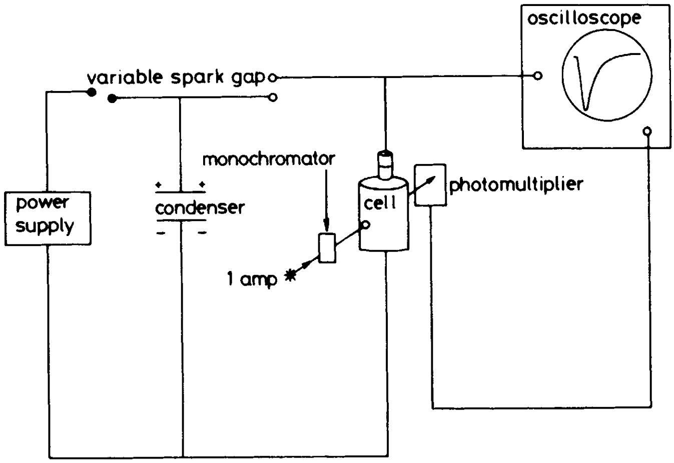

Figure 4 *Instrumental set-up for T-jump measurements*

The sample cell is made of a non-conducting cylindrical plastic chamber equipped with optical observation windows in the side and a pair of electrodes fitted into the ends of the chamber. The high voltage power supply charges the condenser, of some 10^{-8} F, up to 50 kV. When the variable spark gap is fired the condenser (capacitor) is discharged across the cell and the stored electrical energy is converted into Joule's heat. At the same time the scope sweep is triggered.

The temperature-jump is undoubtedly the most versatile and useful of the relaxation methods. Since the vast majority of reaction are temperature dependent, *i.e.* $\Delta H \neq 0$, a variation of equilibrium constant K_e with temperature is to be expected. This dependence is expressed by van't Hoff's equation [equation (9)]. For finite but small changes in K_e, *i.e.* $\Delta K_e \ll Ke$, equation (10)

$$\frac{\partial \ln K_e}{\partial T} = \frac{\Delta H}{RT^2} \tag{9}$$

$$\partial \ln K_e = \frac{\partial K_e}{K_e} \approx \frac{\Delta K_e}{K_e} \tag{10}$$

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[25] T. J. Kemp, *Prog. React. Kinet.*, 1980, **10**, 301.

applies, so that we can re-write equation (9) in the form of equation (11). It is

$$\frac{\Delta K_e}{K_e} = \frac{\Delta H}{RT^2} \cdot \Delta T \tag{11}$$

evident that the relative change in K_e for a given temperature-jump ΔT is proportional to ΔH. The temperature-jump is given by equation (12). Changes

$$\delta T = \frac{U^2 C}{2 c_p \rho V} \tag{12}$$

C is capacitance of condenser (0.1 μF)
U is voltage applied (50kV)
c_p is specific heat of solution
ρ is density of solution
V is volume of solution (2 cm^3)

in colour or transparency of the sample solution to be investigated are monitored by a spectrophotometer and recorded on an oscilloscope. The monochromator emits the wave-length of the maximum absorbance of the species. Changes are recorded on the oscilloscope as a function of time.

There are a few *limitations* to the T-jump method:

(i) Products and reactants of a process to be studied must be in *equilibrium*.

(ii) The reaction system must have an appreciable concentration of *ionic species* present to conduct the discharge current.

(iii) The concentration of species in the system must be *temperature dependent*, *i.e.* $\Delta H \neq 0$.

(iv) *Relaxation times* of less than 10^{-7} s cannot be observed with this technique.

(v) The method can only be applied to reactions in which the *rate* of concentration-change is *slower than the time* required *to heat* solution to new temperature.

The method has an extremely wide range of *applications*. This is particularly as a result of the development work of Leo de Maeyer,[26], G. Czerlinski,[27] and G. G. Hammes.[28] Some well-known applications may be mentioned here:

(i) Proton-transfer reactions:[29,30] The dissociation of water and the recombination of hydrogen and hydroxy-ion are important reactions studied by the T-jump method:

$$2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + OH^-$$

also the base-catalysed proton-transfer in intramolecularly hydrogen bonded naphthylammonium ion.[31]

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[26] Lecture held at the 1968 Meeting of the Optical Society of America, Washington.
[27] G. Czerlinski and M. Eigen, *Z. Elektrochem.*, 1960, **64**, 128.
[28] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, 1962, **84**, 4639.
[29] M. Eigen and L. De Maeyer, *Z. Elektrochem.* 1955, **59**, 986.
[30] G. Ertl and H. Gerischer, *Z. Elektrochem.*, 1961, **65**, 629.
[31] F. Hibbert and H. J. Robbins, *J. Am. Chem. Soc.*, 1978, **100**, 8239.

(ii) Metal complex formation in inorganic- and bio-chemistry, such as the binding of Co^{II} to adenosine 5′-monophosphate,[32] or cations derived from phthalein complexone,[33] or the formation of iron complexes such as $Fe(H_2O)_5Fe(CN)_6$.[34]

(iii) Tautomerizm in organic compounds such as cytosines[35] or keto–enol transformations in heterocyclic compounds.

(iv) Electron-transfer reactions, such as that between ferro- and ferricyanide ions.[36]

(v) Enzyme catalyses in biochemistry and biology have been investigated through temperature-jump methods.[37–39]

(vi) The reaction between oxygen and haemoglobin has also been studied by this method.[40]

Much research has been carried out in order to improve these techniques. A highly sensitive microwave T-jump apparatus has been developed at the University of Paris.[41] Temperature-jumps of 1.5° are achieved in a flow microcell within 1.5 microseconds at a repetition rate of 50 Hz. A nanosecond temperature-jump apparatus for high pressures has been developed at the University of Bochum, which gives an increase of a few degrees within 50 nanoseconds.[42] J. Aubard and co-workers have described a Laser temperature-jump apparatus with highly sensitive and very fast pulsed spectrometric detection.[43] The kinetics of the conformation change of adenylyl 3′ to 5′ adenosine has been studied with a T-jump of 6° within 20 nanoseconds.

C. The Pressure-jump Method.[44–47]—When pressure is changed rapidly and hence adiabatically in a chemical process, the equilibrium constant K_e will change accordingly. Rapid changes in pressure can be brought about by the use of sound waves of certain frequencies.

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[32] A. Pegny and H. Diebler, *J. Phys. Chem.*, 1977, **81**, 1355.

[33] G. Czerlinski and M. Eigen, *Z. Elektrochem.*, 1959, **63**, 652.

[34] J. E. Finholt, *J. Chem. Educ.*, 1968, **45**, 394.

[35] M. Dreyfus, O. Bensaude, G. Dodin, and J. E. Dubois, *J. Am. Chem. Soc.*, 1976, **98**, 6338.

[36] H. Diebler, *Z. Elektrochem.*, 1960, **64**, 128.

[37] *Physiol Chem. Phys.*, 1979, **11**, 537.

[38] G. G. Hammes, *Adv. Inorg. Biochem.*, 1980, **2**, 237.

[39] E. J. del Rosario and G. G. Hammes, *Biochemistry*, 1971, **10**, 716; G. G. Hammes and J. L. Haslam, *ibid.*, 1969, **8**, 1591; G. G. Hammes, *Acc. Chem. Res.*, 1968, **1**, 321; K. Kirschner, E. Gallego, I. Schuster, and D. Goodall, *J. Mol. Biol.*, 1971, **58**, 29.

[40] G. S. Adair, A. V. Bock, and H. Field, jun., *J. Biol. Chem.*, 1925, **63**, 529.

[41] J. Aubard, J. M. Nozeran, P. Levoir, J. J., Meyer, and J. E. Dubois, *Rev. Sci. Instrum.*, 1979, **50**, 52.

[42] *Rev. Sci. Instrum.*, 1979, **50**, 1089.

[43] J. Aubard, J. J. Meyer, and J. E. Dubois, *Chem. Instrum.*, 1977, **8**, 1.

[44] G. Platz and H. Hoffmann, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 491.

[45] R. Van Eldik, *Chemsa*, 1980, **6**, 46.

[46] J. S. Davis and H. Gutfreund, *FEBS Lett.*, 1976, **72**, 199.

[47] H. Strehlow and J. Jen, *Chem. Instrum.*, 1971, **3**, 47.

From thermodynamics:

$$\frac{\partial \ln K_e}{\partial P} = \frac{-\Delta V}{RT} + \frac{\Delta H \alpha T}{RT^2 c_p \rho} \tag{13}$$

ΔV = change in reaction volume
ΔH = change in reaction enthalpy
α = thermal extension coefficient
ρ = density of reaction solution
c_p = specific heat at constant pressure
R = gas constant

Normally, in aqueous solution, the first term on the right side in equation (13) is the major contribution (greater than 90 % of total). The instrumental set-up is shown in Figure 5.

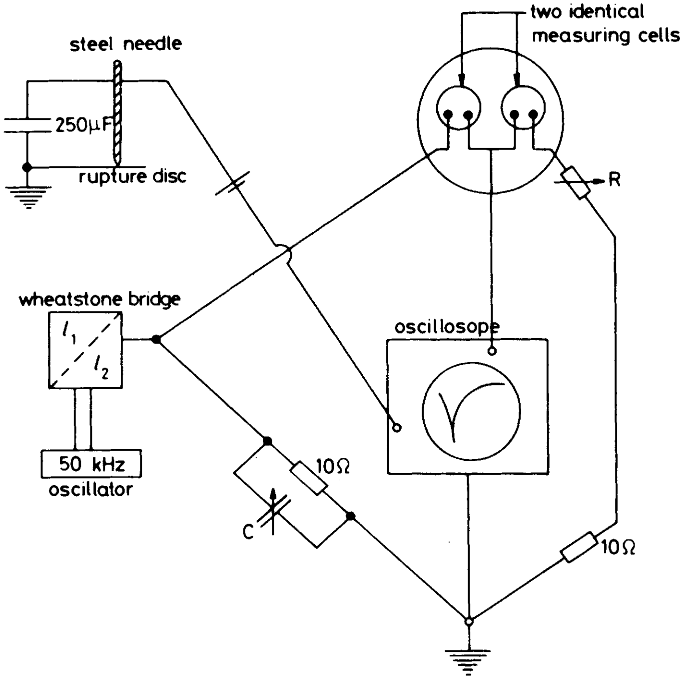

Figure 5 *Instrumental set-up for P-jump measurements*

Two identical conductivity cells are used. One is filled with the test sample, the other with a solution having equal electrical conductivity but showing no relaxation. By comparing the changes in resistance of the two cells, disturbances caused by temperature fluctuation largely cancel. The cells are closed with diaphragms (polyethylene membrane). The Wheatstone bridge is tuned at the ambient pressure of 1 atm. Pressure is increased slowly to ~50 atm until the diaphragms burst spontaneously. The pressure drops to 1 atm within 50 μs.

The fast pressure change generates a voltage peak across a condenser which triggers the oscilloscope. The trace on the screen shows the solution under investigation regaining equilibrium at 1 atm.

Shock-waves have been used in order to perturb the system and shorten the instrument time to 1 μs.

The method has found wide *applications* in the study of the formation of metal complexes,[48–50] the study of biochemical[51–56] and organic[57,58] reactions, and in the study of micelle formation.[59–61]

D. The Electrical-field Jump Method.[2,19,62]—An applied electric field will influence chemical equilibria involving ions, dipoles, and polarizable species. The magnitude of this field required is as high as 100 kV cm^{-1} in liquids of high dielectric constants such as water. The field always induces a shift in the equilibrium towards producing more ions. An electric field applied to a solution of weak electrolyte increases the ion conductivity (first Wien-effect) and the degree of dissociation (second Wien-effect). The former effect must be kept to a minimum, the latter is of importance to our discussion.[31]

The fundamental thermodynamic quantity for the interaction of electric fields with chemical transformation is given in equation (14). This principle is

$$\left(\frac{\partial A}{\partial E}\right)_{T,P} = \Delta m \qquad (14)$$

where A = reaction affinity
E = electric field
and m = electric moment

applied in the electric-field jump method. Whenever a solution of a weak electolyte is subjected to a very large electric field the equilibrium is disturbed and K_e increases as shown in equation (15).

$$\left(\frac{\mathrm{d}\ln K_e}{\mathrm{d}E}\right)_{P,T} = \frac{\Delta M}{RT} \qquad (15)$$

ΔM = change in molar polarization.

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[48] H. Hoffmann and E. Yeager, *Ber. Bunsenges. Phys. Chem.*, 1972, **76**, 491.

[49] H. Strehlow and H. Wendt, *Inorg. Chem.*, 1963, **2**, 6.

[50] G. Macri and S. Petrucci, *Inorg. Chem.*, 1970, **9**, 1009.

[51] K. Heremans and Y. van Nuland, *High Temp.-High Pressures*, 1977, **9**, 539.

[52] H. Kihara and S. Saigo, *Kagaku, Zokan (Kyoto)*, 1979, **80**, 81.

[53] P. B. Chock, F. Eggers, M. Eigen, and R. Winkler, *Biophys. Chem.*, 1977, **6**, 239.

[54] H. R. Halvorson, *Biochemistry*, 1979, **18**, 2480.

[55] D. E. Goldsack, R. E. Hurst, and J. Love, *Anal. Biochem.*, 1969, **28**, 273.

[56] 'Methods in Enzymology', Vol. XVI, Academic Press, 1970.

[57] D. A. Palmer and H. Kelm, *Austr. J. Chem.*, 1977, **30**, 1229.

[58] H. Strehlow and W. Knoche, *Ber. Bunsenges. Phys. Chem.*, 1969, **73**, 427.

[59] H. Hoffmann, W. Ulbricht, and B. Tagesson, *Z. Phys. Chem.*, 1978, **113**, 17.

[60] H. Hoffmann and B. Tagesson, *Z. Phys. Chem.*, 1978, **110**, 113.

[61] H. Hoffmann, R. Nagel, G. Platz, and W. Ulbricht, *Colloid Polym. Sci.*, 1976, **254**, 812; H. Hoffmann and W. Ulbricht, *Z. Phys. Chem.*, 1977, **106**, 167; H. Hoffmann, R. Lang, D. Pavlović, and W. Ulbricht, *Croat. Chem. Acta.*, 1979, **52**, 87.

[62] M. Eigen and J. Schoen, *Z. Elektrochem.*, 1955, **59**, 483.

The change occurs under a certain time-effect. The characteristic magnitude of this time-effect is the relaxation time τ of the system.

The experimental arrangements are virtually identical to those employed for the T-jump measurements,[63] the output from a charged condenser being applied to the electrodes in a similar cell. A specific high-field Wheatstone-bridge arrangement includes the sample cell for the conductiometric detection of the concentration changes. Eigen and De Maeyer,[29,64] suggested electric pulses and detection systems. A high-voltage capacitor was used to generate the field pulse, which triggers an oscilloscope. Measurements were obtained with pulses of 50—150 μs.

There are two methods of measuring the relaxation time τ: (*a*) an amplitude dispersion-method in which single pulses are applied, and (*b*) a relaxation method in which rectangular charge-pulses are applied.

Eigen and co-workers invented and applied this E-jump technique to measure the rate constants for the combination of hydrogen ions with hydroxy-ions (and acetate ions)[62,65,66]

The equilibrium in equation (16) is established very rapidly.[29] However k_{-1},

$$2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3O^+ + OH^- \tag{16}$$

a second-order rate constant for the combination of hydroxonium ions and hydroxide ions has been obtained by this method, *i.e.* 1.4×10^{11} l mol^{-1} s^{-1} at 25 °C. This is the largest second-order rate constant known for a reaction in solution.

The method has been applied in many investigations, all of which show high resistance or low conductivity. Some examples are listed below:

(i) Ion pairing processes.[67,68]

(ii) Protonation and deprotonation reactions.[69]

(iii) The reaction $HgCl^+ + Cl^- \longrightarrow HgCl_2$.[70]

(iv) Many biological processes, *e.g.* the mechanism of binding oxygen to haemoglobin in blood.[71]

(v) The binding of ligands to metal ions, including hydrolysis.[70,72]

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[63] D. T. Rampton, L. P. Holmes, D. L. Cole, R. P. Jensen, and E. M. Eyring, *Rev. Sci. Instrum.*, 1967, **38**, 1637.

[64] 'Techniques in Organic Chemistry' Vol. VIII part 2, Interscience, 1963, p. 895.

[65] M. Eigen, W. Kruse, G. Maass, and L. De Maeyer, *Progr. React. Kinet.*, 1964, **2**, 285.

[66] J. J. Auborn, P. Warrick, jun., and E. M. Eyring, *J. Phys. Chem.*, 1971, **75**, 2488.

[67] A. Persoons and M. Van Beylen, *Pure Appl. Chem.*, 1979, **51**, 887.

[68] Proc. Int. Meet. Soc. Chim. Phys., 1977, p. 345.

[69] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 1.

[70] M. Eigen and E. M. Eyring, *Inorg. Chem.*, 1963, **2**, 636.

[71] T. Yasunaga, H. Takenaka, T. Sano, and Y. Tsuji, in 'Chemical and Biological Applications of Relaxation Spectrometry', Reidel Publ. Co., 1975, Proceedings of a NATO Advanced Study Institute (1974); G. Ilgenfritz and T. M. Schuster, 'Probes of Structure and Function of Macromolecules and Membranes, Vol. II, Academic Press, 1971, Proceedings 5th Colloquium, Johnson Research Foundation, Philadelphia, 1969.

[72] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winkler, *Pure Appl. Chem.*, 1969, **20**, 93; D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, *Inorg. Chem.*, 1969, **8**, 682; L. D. Rich, D. L. Cole, and E. M. Eyring, *J. Phys. Chem.*, 1969, **73**, 713.

(vi) The formation of macrocyclic and open-chain antibiotics.[53]

A new method has been developed for the study of ionic and dipolar equilibria by A. Persoons and co-workers,[73] and this has found application in many kinetic research projects.[74]

E. Ultrasonic Measurements.[2,64,75,76]—So far we have dealt with single discrete perturbations of a chemical system. In ultrasonic measurements we have to do with oscillating perturbations. Sound waves, by means of their incremental pressure and adiabatic temperature oscillations, are able to induce periodical perturbations of a chemical equilibrium. In aqueous solutions the pressure perturbation is most important, in non-aqueous solutions the temperature effect is paramount. Characteristic phase-shift changes occur between the oscillation of pressure or temperature and the position of chemical equilibrium leading to a typical energy absorption or velocity dispersion of the ultrasonic wave, which can at the same time be used as a probe for chemical relaxation. For the small amplitudes of these sinusoidal perturbations the corresponding chemical rate equations can be linearized without significant error.

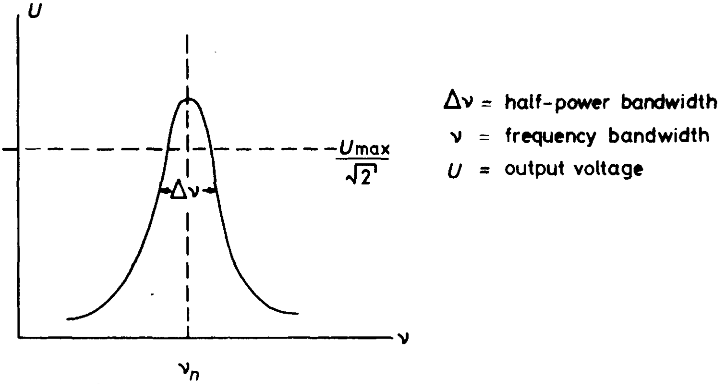

Figure 6 *Relationship between frequency bandwidth and out-put voltage in ultrasonic relaxation measurements*

In the jump methods a recording of the signal on an oscilloscope requires that the time constant T_e of the equipment is smaller than the relaxation time τ, *i.e.* $T_e \ll \tau$. In the case of τ shorter than a few microseconds difficulties arise. Sound-wave absorption techniques can solve this problem. T_e is determined by the frequency bandwith $\Delta\nu$ of the equipment by the relationship shown in equation (17). Also, $\Delta\nu$ is dependent on the signal to noise ratio S/N, where

$$T_e \approx \frac{1}{2\pi\Delta\nu} \tag{17}$$

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[73] A. V. Anisimov and F. G. Miftakhutdinova, *Biophys. J.*, 1979, **24**, 116.

[74] *Int. Symp. Specific Interact. Mol. Ions*, 1976, **2**, 545.

[75] F. Eggers and Th. Funck, *Naturwissenschaften*, 1976, **63**, 280.

[76] M. J. Blandamer, 'Introduction to Chemical Ultrasonics', Academic Press, 1973.

S/N α $(\Delta\nu)^{-\frac{1}{2}}$. For short relaxation times the bandwidth must, therefore, be large in order to make S/N unfavourably small. Frequencies range from 0.1 to 150 MHz corresponding to relaxation times of 2 μs to 1 ns.

The chemical relaxation is observed over many periods of the perturbation. That means the equilibrium concentrations $\bar{c}_i$ change during the measurement, in contrast to the conditions of jump methods. In this case, therefore, $\bar{c}_i$ cannot be used as the reference concentration.

The shift in concentration at any chosen time is given by equation (18):

$$x_i = c_i - c_i^{\mathrm{ref}} \tag{18}$$

and the shift in equilibrium concentration is given by equation (19):

$$\bar{x}_i = \bar{c}_i - \bar{c}_i^{\mathrm{ref}} \tag{19}$$

The rate of change of shift in concentration is then given by equation (20).

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{1}{\tau}(x - \bar{x}) \tag{20}$$

$$\left[\text{Compare with jump-methods: } -\frac{dc}{dt} = \frac{1}{\tau}(c - \bar{c})\right]$$

The sinusoidal pressure change in sound waves have very often been used. This causes a sinusoidal change of the equilibrium concentration c_i and is described by equation (21). Strehlow and Knocke[41] discuss the theory in more detail.

$$\bar{c}_i = c_i^{\mathrm{ref}} + \bar{x}_0 \sin \omega t \quad \text{with} \quad \omega = \frac{1}{\tau} \tag{21}$$

Many different *experimental configurations* have been adopted, such as (i) pulse technique,[77] (ii) ultrasonic interferometer, (iii) reverberation method, *etc.*

The study of sound propagation demands devices for creating sound waves and subsequently for their detection. This is achieved by means of piezoelectrical crystals, which generate an electric signal when subjected to mechanical stress or, conversely, change their shape when an electric field is applied. The sound wave is generated by applying an oscillating electric field of the same frequency. The pressure amplitude of the sound wave is measured as a function of distance *d* in sample solution.

A well-known method of investigation is that suggested by Eggers,[78,79] which has the big advantage that comparatively small volumes of solution are required for the measurements of τ.

Usually a frequency range of 10^3—10^8 cycles per second corresponding to relaxation times of 10^{-4}—10^{-9} s. are covered in all these techniques.[56,78-80]

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[77] M. A. Collins and J. Ross, *J. Chem. Phys.*, 1978, **68**, 3774.

[78] S. Petrucci, *J. Phys. Chem.*, 1967, **71**, 1174.

[79] P. Hemmes and S. Petrucci, *J. Phys. Chem.*, 1968, **72**, 3986.

[80] A. J. Campillo and S. L. Shapiro, *Top. Appl. Phys.*, 1977, **18**, 317.

Some of the *disadvantages* of the ultrasonic technique are:

- (i) Broad-band measurements must be performed, which require several overlapping techniques.
- (ii) Sample cells must be inert against many solvents.
- (iii) There is a lack of commercial, ready-to-use equipment.
- (iv) There are large variations of ultrasonic absorption coefficients with frequency.
- (v) High stability requirements for temperature in the cavity are necessary.

There are many *applications* of this technique, such as:

- (i) Ligand substitution processes in cation complexes.
- (ii) Ion-pair formation and desolvation of ions in aqueous solution of electrolytes.[81,82]
- (iii) Hydrogen bond association processes.[83-85]
- (iv) Proton-transfer reactions or deprotonations, *e.g.*[81,86]

$$H_3O^+ + SO_4^{2-} \longrightarrow HSO_4^- + H_2O$$
$$\text{or } Et_3NH^+ + OH^- \longrightarrow Et_3N + H_2O$$

or in antihistamines.[87]

- (v) Rotational isomerism.[88,89]
- (vi) Helix-coil transition processes.[90,91]
- (vii) Studying properties of ionic hydrate melts.[92]

4 Applications for the Inorganic Chemist[19,93]

In inorganic chemistry, we find many reactions between a positively charged metal ion (M^{n+}) and a negatively charged ligand (X^{m-}) to form a neutral complex. This kind of reaction is frequently described in the literature as very fast.

A metal ion in aqueous solutions is always considered an hydrated ion, $M(H_2O)_m{}^{n+}$. It is surrounded by one or more shells of co-ordinated water molecules. Interactions between metal ion and water molecules (ion–dipole attraction or dipole–dipole repulsion) occur amongst the co-ordination shells of the complex. If the metal ion (M^{n+}) is to combine with another ion of opposite

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[81] G. Kurtze and K. Tamm, *Acustica*, 1953, **3**, 33, *ibid.*, 1954, **4**, 380.

[82] M. Eigen, *Z. Elektrochem.*, 1960, **64**, 115.

[83] J. Rassing, *Adv. Mol. Relaxation Processes*, 1972, **4**, 55.

[84] M. D. Joeston and L. J. Schaad, 'Hydrogen Bonding', M. Dekker Inc. 1974.

[85] G. Allen and E. F. Caldin, *Quart. Rev. Chem. Soc.*, 1957, **11**, 147.

[86] M. Eigen, *Z. Phys. Chem.*, 1954, **1**, 176.

[87] J. Gettins, R. Greenwood, J. Rassing, and E. Wyn-Jones, *J. Chem. Soc., Chem. Commun.*, 1976, 1030.

[88] R. O. Davies and J. Lamb, *Quart. Rev. Chem. Soc.*, 1957, **11**, 147.

[89] J. Lamb, *Z. Elektrochem.*, 1960, **64**, 135.

[90] J. J. Burke, G. G. Hammes, and T. B. Lewis, *J. Chem. Phys.*, 1965, **42**, 3520.

[91] G. G. Hammes and P. B. Roberts, *J. Am. Chem. Soc.*, 1969, **91**, 1812.

[92] R. Carpio, F. Borsay, C. Petravic, and E. Yeager, *J. Chem. Phys.*, 1976, **65**, 29.

[93] M. Eigen, *Angew. Chem.*, 1968, **80**, 892.

charge (X^{m-}), the latter must penetrate the hydration shells, substituting successive water molecules in the different shells. Since water molecules in the inner co-ordination shell are bound most strongly, their substitution will be the slowest step of the process. Relaxation studies on very widely differing metal ions have confirmed this assumption. The stepwise substitution mechanism reveals itself in a relaxation spectrum with several time constants.[94] The inorganic chemist is primarily interested in the substitution in the inner co-ordination sphere, which has been found to be the rate-determining step. All other steps are very fast, *i.e.* 10^{-8} s. Let us consider the reaction of a metal ion (M^{n+}) with a ligand X^-:

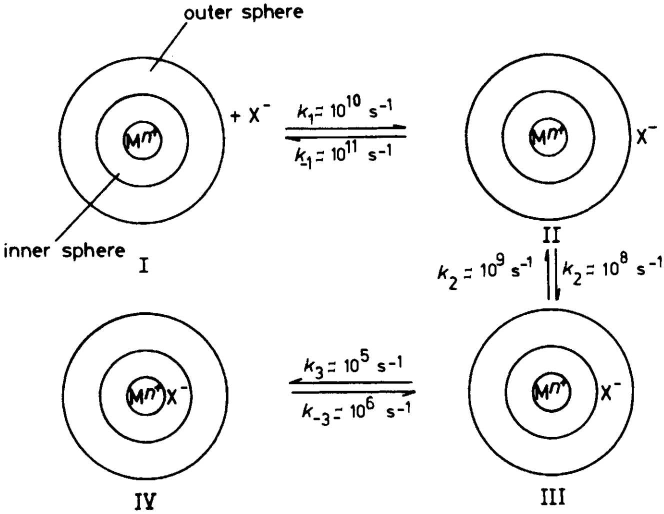

Figure 7 *Substitution of metal ion in inner co-ordination sphere. The rate constants k_3 and k_{-3} control the whole process, which may be of* S

In general, the rate constants are practically independent of the nature of the entering ligand, X^-, and are mostly dependent on the nature, charge, and size of the metal ion, M^{n+}. S_N1 is therefore the predominant process. The smaller the radius and the higher the charge of the metal ion, the more strongly are the H_2O molecules bound, and hence the more slowly does the substitution take place. Most rate constants lie in the range 10^3 to 10^9 s^{-1}. Figure 8 shows the relationship between size of metal ion and rate constant in the substitution of H_2O in non-

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[94] R. G. W. Norrish and B. A. Thrush, *Quart. Rev. Chem. Soc.*, 1956, **10**, 149.

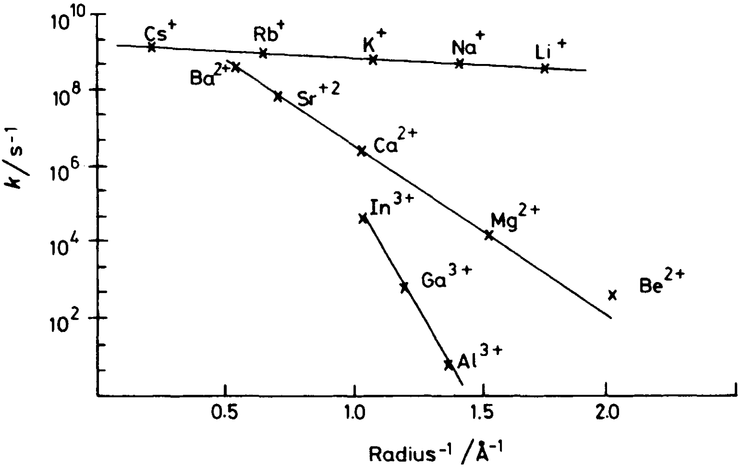

Figure 8 *Relationship between size of metal ion and rate constant in H_2O substitution*

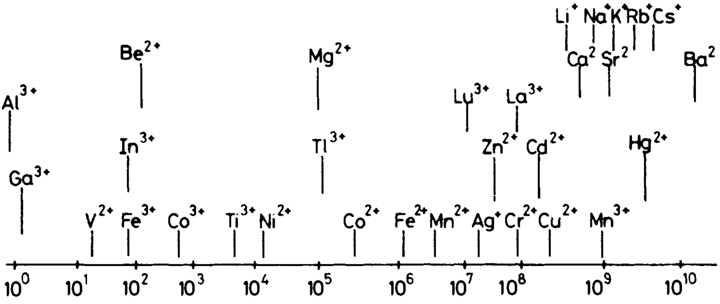

Figure 9 *Rate constants in* H_2O *substitution* (k/s^{-1}). *All rare-earth metal* M^{3+} *ions have k values between* 10^8 *and* 10^7 *from left to right*

transition metals. Ligand substitutions of many transition-metal ions have been studied kinetically. Figure 9 shows a number of rate constants for H_2O-substitition in the inner co-ordination sphere of metal ions. V^{2+} and Ni^{2+} ions have strikingly slow rates of substitution, whereas Cr^{2+} and Cu^{2+} ions are extremely liable to substitution. These two effects may be explained by (*a*) strong crystal and ligand-field stabilization, and (*b*) Jahn–Teller effects (the octahedral structure undergoes distortions).

5 Flash Photolysis[2,94–96]

Flash photolysis is a method whereby a non-equilibrium situation can be created in a reaction system in a short interval of time. It is one of the very few

[95] R. G. W. Norrish and G. Porter, *Discuss. Faraday Soc.*, 1956, No. 17, p. 40, G. Porter and M. W. Windsor, *ibid.*, p. 178.

[96] G. Porter, *Z. Elektrochem.*, 1960, **64**, 59.

methods for preparing and studying high concentrations of electronically excited molecules and radicals. The concentration of intermediates can be directly measured as a function of time, and their physical and chemical properties can be determined.

This technique falls within the category of large perturbations. An intense flash of visible or ultraviolet light over a few micro-seconds is used to initiate a disturbance photochemically. The intensity must be sufficient to produce a change in chemical composition that is measurable, but of short duration compared with that of the ensuing reaction. The time resolution is of the order of a few micro-seconds and could even be pico-seconds by the use of lasers.[97]

The course of a chemical change resulting from the flash is observed by fast photometric techniques. Reactions with half-times down to 10^{-6} s can be observed without difficulty.[18] The following types of change can be studied:

(i) The absorption of light may photolyse a molecule, producing a non-equilibrium state in solution. The reaction proceeds so that equilibrium is re-established. The principle is the same as that of relaxation methods in that a disturbance is initiated by physical means and the return to equilibrium is observed.

(ii) The absorption of light may produce an electronically excited molecule, which in time is deviated and then returns to its original state. Here again the principle is that of relaxation.

(iii) The excited molecules may react with some other molecules, producing permanent changes. The principle here is not relaxation but photochemical initiation of an irreversible reaction. The main difference from ordinary photo-chemistry is that the energy absorption occurs in a very short time and the subsequent fast changes are directly followed.

The *experimental arrangement* can be set up in different ways. Figure 10 shows a typical one.[98]

The factor which determines the fastest reaction that can be studied is the finite duration of the primary flash. The minimum duration of the flash to study half-times of about 10^{-5} s must therefore be about 10 μs. Rate constants that can be determined are about 10^{11} l mol^{-1} s^{-1}.

Only photochemically initiated processes can be studied. The change in the system on absorption of light is generally considerable.

Some *applications* are given below:

(i) Proton-transfer reactions.

(ii) Haemoglobin reactions.[99]

(iii) Photochemically-initiated irreversible reactions.

(iv) Studies of the triplet state.[100]

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[97] U. Schindewolf, *Chem. unserer Zeit*, 1972, **6**, 17.

[98] N. K. Bridge and G. Porter, *Proc. R. Soc. London, Ser. A*, 1954, **244**, 276.

[99] *Kagaku, Zokan* (*Kyoto*), 1979, **80**, 107.

[100] W. Potter and G. Levin, *Photochem. Photobiol.*, 1979, **30**, 225.

(v) Iodine dissociation and recombination: $I_2 + h\nu \rightarrow 2I$

(vi) Reactions of the hydrated electron: $e^- + H_2O \rightarrow H + OH^-$

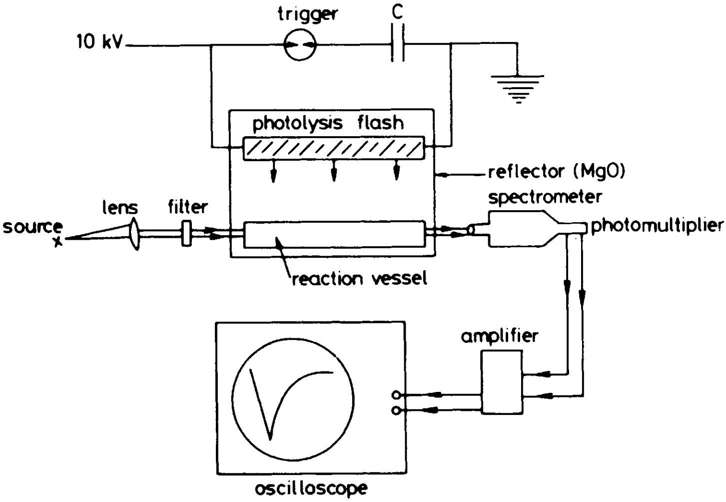

Figure 10 *Instrumental set-up for flash photolysis measurements*

Pulse radiolysis[100,101] can sometimes also be used. It is the analogue of flash photolysis in radiation chemistry. A pulse of high-energy radiation such as X-rays or electrons takes the place of the light flash. *Lasers*[102] have also been introduced, replacing the flash lamps.

6 Electrochemical Methods[2,19]

The electrochemical determination of rate constants requires that at least one of the reactants of the chemical reaction under investigation be coupled to an electrode reaction as in equation (22).

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{+e^-} C \qquad (22)$$

where C is the product of the electrode reaction
A is electroinactive
B is the depolarizer

The rate of the overall process is proportional to the current flowing in the electrochemical system. It depends on the transport of A and B to the electrodes by diffusion and convection. A detailed analysis of the combined diffusion-convection reactions allows the determination of k_1 and k_{-1}. Either the electrode potential U or the current i can be chosen as the parameter forced on to the system. Current or potential is measured as a function of time, or it may be a known function of time.

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[101] P. Wardman, *Rep. Prog. Phys.*, 1978, **41**, 259.
[102] Ref. 18, p. 89.

There are four electrochemical techniques by which rate constants can be determined:

(i) The polarographic method.
(ii) The rotating disc method.
(iii) The potentiostatic method.
(iv) The galvanostatic method.

The *polarographic method*[2,19,103,104] was the first of the many techniques and is well known for the determination of fast chemical reactions. With this method we are able to detect reaction times of about 10^{-8} s. A dropping Hg-electrode is used.

A relationship between the diffusion current and the reaction current is employed for kinetic studies. In the case of an electrode reaction in which a reducible species B accepts an electron at the cathode, as shown in equation (23),

$$B \xrightarrow{+e^-} C \tag{23}$$

we deal with a rapid and irreversible process. Species B which strikes the electrode surface is removed from the system immediately. The current in the cell due to the reduction process is simply proportional to the rate at which species B reaches the surface. The motion of B may be caused either by diffusion, convection, or migration. Migration is avoided by adding KCl. Convection occurs if the solution is heated or stirred. Its effect is small compared to diffusion. *Diffusion* to the surface takes place because B is depleted in the vicinity of the electrode and a concentration gradient therefore builds up around it. This gradient will vary with time as indicated in Figure 11.

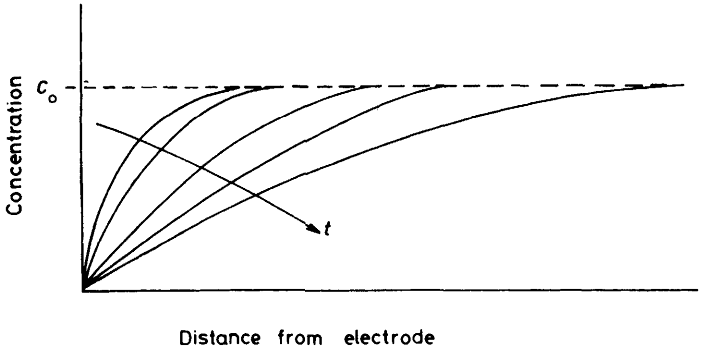

Figure 11 *A plot of concentration against time in the polarogram. The diffusion current which is proportional to the concentration gradient, is initially at a maximum and then falls steadily as the gradient decreases. The gradient can be visualized as confined to a diffusion layer of thickness δ. According to Einstein the displacement x varies with time t,* i.e. $x = 2Dt$ *where D = diffusion coefficient*

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[103] K. Wiesner, *Z. Elektrochem.*, 1943, **49**, 164.
[104] I. M. Kolthoff and J. J. Lingane, 'Polarography', Interscience, Chap. 14, 1952.

According to Fick's law the flux is defined by equation (24):

$$-D\frac{\mathrm{d}c}{\mathrm{d}x} \text{ or } \frac{Dc_0}{\delta} \text{ or } \left(\frac{2D}{t}\right)^{\frac{1}{2}} \tag{24}$$

This flux may be converted to a diffusion current as shown in equation (25):

$$i_{\mathrm{D}} = \left(\frac{2D}{t}\right)^{\frac{1}{2}} FAc_0, \text{ where } A = \text{surface and } F = \text{Faraday} \tag{25}$$

For B participating in a dynamic equilibrium [equation (26)] the rate of arrival

$$\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A} \tag{26}$$

of B at the electrode surface depends both on diffusion and on chemical reaction, and with the equilibrium well to the right and the reverse reaction relatively slow, the current becomes completely under kinetic control. Here we have a reaction layer and not a diffusion layer. An average life time τ for B is the period of time between its formation and its removal in the equilibrium. Species B will diffuse a distance $\mu = (2D\tau)^{\frac{1}{2}}$ during this life-time (Figure 12).

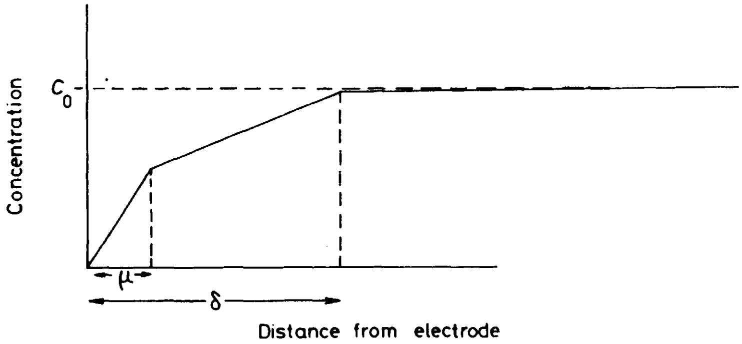

Figure 12 *A plot of concentration against distance from electrode. For* $k_1 \gg k_{-1}$ *the relation between* i_r *and* i_{D} *is given by*:

$$i_r/(i_{\mathrm{D}} - i_r) = C[(k_{-1}t)/K_e]^{\frac{1}{2}} \text{ where } C = \text{constant of unity order}$$

All species B which will be less than the distance μ from the electrode surface (within the reaction layer) will be removed by reduction, whilst those beyond this distance will be transformed back to B before reaching the surface. The current at the electrode is then determined by the rate at which species B are formed in the reaction layer.

Electrochemical measurements may be made in two ways; (i) either holding i or U constant and following the alteration of the other with time; or (ii) creating continuously a 'new' electrode surface to establish a steady-state situation. A time-averaged current is obtained for the applied voltage.

Some of the more important *applications* of the electrochemical method may be mentioned here:

(i) Polarography has been used quite extensively to study the dissociation and recombination of weak acids [equation (27)]:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \tag{27}$$

This technique has produced rate constants which vary from 10^1 to $10^{13}\,l\,mol^{-1}\,s^{-1}$. For extremely fast reactions the reaction layer may well be less than 100 Å thick.[105,106]

(ii) Mutarotation of glucose (and sugars).[107]

(iii) Complex forming reactions.[108–110]

(iv) Redox reactions of transition-metal ions.[111–114]

7 The Fluorescence Method[2,115,116]

Fluorescence techniques for the investigation of rapid chemical processes are concerned with the rates of reaction of photochemically-excited molecules. This is usually carried out by adding a substance which reduces the intensity of fluorescence. The attenuation of fluorescence can be used as a sensitive monitor for the progress of the reaction. The 'quenching' reaction competes with deactivation by other mechanisms that occur. A steady-state is set up, depending on the relative rates of these processes. The resulting fluorescence intensity can be observed without fast-recording apparatus. From the relation between the intensity and concentration of reagent, the rate constant for the reaction can be derived. The method is applicable only to excited molecules and very fast reactions.

Many substances in solution fluoresce when irradiated continuously with ultra-violet light.[117] Examples are anthracene, β-naphthol, and quinine sulphate. Fluorescence occurs because some of the molecules are raised to an electronically excited state, by absorbing quanta of the exciting light, and re-emit light of visible or near-u.v. wavelength as they drop back to the ground state.

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Fluorescence and quenching is outlined in detail in F. Wilkinson's book on pages 268—279.[18]

Relaxation times of the order of 10^{-8} s have so far been determined. There are a number of *applications* of this method:

(i) Rate constants have been determined for various proton-transfers, as illustrated by equations (28) and (29):[118,119]

$$\text{acridine}^*.\text{H}_2\text{O} \rightleftharpoons \text{acridine}^*.\text{H}^+ + \text{OH}^- \qquad (28)$$

$$\text{or } \underset{(\beta\text{-naphthol})}{\text{ROH}^*}.\text{H}_2\text{O} \rightleftharpoons \text{RO}^{*-} + \text{H}_3\text{O}^+ \qquad (29)$$

It has been concluded that the transfer of a proton during these processes is effected in a time much less than the mean life-time of the excited molecules.

(ii) Formation of hydrogen-bonded complexes.[120] 3-Hydroxypyrene and pyridine form a hydrogen-bonded complex [equation (30)]:

$$\text{ROH} + \text{py} \rightleftharpoons \text{ROH.py} \qquad (30)$$

$$\text{ROH}^* + \text{py} \xrightarrow{k_i} \text{ROH}^*.\text{py} \qquad (31)$$

The hydroxypyrene is fluorescent [equation (31)] and k_i may be determined. I/I_0 decreases with increasing concentration.

(iii) Dimerization and self-quenching. Solutions of anthracene in benzene are fluorescent[121] [equation (32)].

$$\text{A} + h\nu \rightarrow \text{A} \rightarrow \text{A}^* + h\nu' \qquad (32)$$

However, they show a marked decrease of fluorescence intensity as the concentration is increased. A stable dimer (dianthracene) is formed photochemically. The reaction scheme was found to be as shown in equation (33):

$$\text{A} + \text{A}^* \rightarrow \text{AA}^* \rightarrow \text{AA} \qquad (33)$$

Excited molecule A* reacts on collision with a ground-state molecule A. Rate constants for dimerization are of the order of 10^{10} l mol^{-1} s^{-1}.

8 Nuclear Magnetic Resonance Techniques[19,,22,123]

A. Introduction.—Nuclear magnetic resonance (n.m.r.) may be exhibited by any compound whose molecule contains a nucleus with a spin. Such nuclei include the proton, the common isotopes of nitrogen and fluorine, and less common isotopes of carbon and oxygen. A spinning nucleus (like a spinning electron)

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has a magnetic moment associated with the axis of the spin, and in a magnetic field it will be aligned somewhat like a bar magnet, with its moment at one definite orientation to the applied field. Nuclei may pass from one orientation to another by applying a second magnetic field, alternating with a particular resonance frequency. When the main field is of the order of 10^4 Gauss, the resonance frequency is in the radio region. The structure of the absorption spectrum and the width of the lines can be determined. These depend on the lifetime of the proton. They are altered whenever the compound undergoes a reaction altering the lifetime. Typical reaction times from 1 s down to 10^{-3} s have been determined. Rate constants may be calculated and values up to 10^{11} l mol^{-1} s^{-1} have been reported.

N.m.r. techniques are discussed in more detail elsewhere,[2,3] including the intensity and structure of absorption bands, line width and shape, and instrumentation used.

B. Nuclear-spin Relaxation and Line-width.—The determination of rates of reaction by n.m.r. methods depends on measurements of *line-shape* and *line-width*. Energy is exchanged between spinning nuclei and their surroundings. A nucleus in the upper spin state can 'relax' to the lower, or *vice versa*. This mechanism is known as *spin-lattice relaxation* and its efficiency can be expressed by relaxation time T_1, which is for most liquids of the order of 1 to 10 s.

A nucleus can also transfer its energy to a similar neighbouring nucleus by a mutual exchange of spin. This is known as *spin–spin relaxation* and its corresponding relaxation time T_2 is also of the order of 1 to 10 s. These relaxation times T_1 and T_2, are commonly measured by the pulse or spin–echo-methods.[124] The mathematical theory of line-width is discussed in E. F. Caldin's book 'Fast reactions in solution', pp. 229—231.[3]

Line-widths are commonly in the region of a few tenths of a cycle per second, and are appreciably larger than $(\pi T_2)^{-1}$. Line-widths are increased by reactions whose relaxation times are comparable with T_2. When a reaction occurs the line-width is increased by $\sigma'\nu = (\pi\tau)^{-1}$ and so becomes $(\pi T_2)^{-1} + (\pi\tau_{\mathrm{HA}})^{-1}$ where τ_{HA} is the mean life-time of the proton in the HA environment that gives rise to the line, and is also the relaxation time for the forward reaction. The line-width may also be expressed in terms of the measured relaxation time T'_2 as $(\pi T_2)^{-1}$.

Hence equation (34):

$$\frac{1}{\tau_{\mathrm{HA}}} = \pi\sigma\nu = \frac{1}{T'_2} - \frac{1}{T_2} \tag{34}$$

where T_2 is the relaxation for nuclear spin and τ_{HA} is the relaxation for the reaction.

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C. Determination of Reaction Rates from N.m.r. Spectra.—Consider the proton exchange in a mixture of HA and HB, illustrated in equation (35):

$$\mathrm{HA} + \mathrm{H'B} \rightleftharpoons \mathrm{H'A} + \mathrm{HB} \tag{35}$$

If there is no interaction, the proton resonance spectrum will show two peaks representing the characteristic chemical shifts of HA and HB. Changes in the n.m.r. spectrum occur as the rate of proton exchange increases. The two lines first broaden and approach each other and then coalesce to a single broad line, which subsequently narrows to a sharp line. For example, the proton resonance spectrum of a mixture of acetylacetone with acetic acid at various temperatures is shown in Figure 13. OH-signals are shown and chemical shifts are given in p.p.m. The initial broadening of each line is due to the shortening of the mean life-times of HA and HB molecules and hence of ^{1}H nuclei in a given environment and spin energy-level as a result of migration of protons. The finite lifetime of the nucleus in a given energy level leads to a finite line-width. Shortening of the lifetime by reaction correspondingly leads to an increase of line-width.

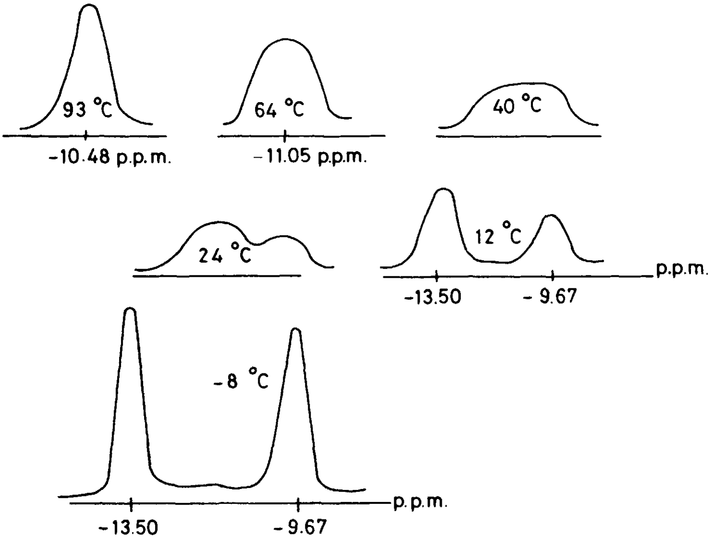

Figure 13 *Proton resonance spectra of acetylacetone at various temperatures*

Theory shows that if the mean lifetime of the proton in a given environment HA is τ_{HA}, broadening $\sigma'\nu$ of the HA line is $(\pi\tau_{\mathrm{HA}})^{-1}$ c.p.s. Hence, if the observed broadening is of the order of 1 c.p.s., the mean lifetime τ is in the region of 0.1 to 1 s. As the exchange rate rises, the protons in the two environments no longer behave as independent systems. Lines approach each other, overlap, and then merge. The increase of width will not continue indefinitely. Separate lines are not observed unless $\tau > \pm (\Delta\nu_0)^{-1}$ where $\Delta\nu_0$ is the frequency difference of the two chemical shifts in absence of exchange. Since $\Delta\nu_0$ is commonly of the order of 100 c.p.s. for proton resonance spectra, coalescence corresponds to a lifetime of $\pm 10^{-2}$ s, and measurements of subsequent narrowing permit estimates of lifetimes down to 10^{-4} s.

The fine-structure due to spin–spin interaction can similarly disappear. The proton resonance in liquid ammonia is a typical example.[125]

The quantitative derivation of rate constants may be obtained from the Bloch equation or its modification[126] shown in equation (36), where ν is the

$$\text{Rate of absorption of energy} \propto \frac{T_2}{1 + 4_\pi{}^2T_2{}^2(\nu_0 - \nu)^2} \tag{36}$$

frequency and ν_0 its resonance value. For maximum absorption $\nu = \nu_0$. The width at half-height is $(\pi T_2)^{-1}$ c.p.s. Thus it is T_2 which primarily determines the natural width of an n.m.r. line.

Line shapes are computed for various τ values and compared with the observed line shapes until a match is obtained. The mean lifetime is related to a first-order rate constant. The mean lifetime of the protons in the HA environment is given by equation (37).

$$\tau_{\mathrm{HA}} = -\frac{[\mathrm{HA}]}{\frac{\mathrm{d}[\mathrm{HA}]}{\mathrm{d}t}} = \frac{1}{k_{\mathrm{HA}}} \tag{37}$$

In general, the quantity measured by the n.m.r. techniques is the mean lifetime τ_A of some particular molecular species. A first-order rate constant is found as $k_A = \tau_A{}^{-1}$. All measurements are made on systems in chemical equilibrium. The equilibrium, however, is not disturbed. The method is especially useful for investigations of symmetrical exchanges. Reactions that are too fast for isotopic methods can be studied. Very detailed information about the mechanism may be obtained since the n.m.r. spectrum identifies directly the atoms that exchange. Values for $\tau\Delta\nu_0$ must be in the region of 10 to 0.01 so that changes in line-shape are noticeable. For nuclei other than the proton, chemical shifts and line-widths are larger, and shorter lifetimes can therefore be determined; lifetimes of about 10^{-7} s have been found with ^{17}O and 10^{-5} s with ^{63}Cu.

The n.m.r. technique has *applications* to a considerable number of reactions, of which a few are mentioned below:

(i) proton transfer:

- (*a*) in alcohols and aqueous alcohols.[127,128]
- (*b*) in liquid ammonia.[129]

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(ii) Inversion of configuration.[130–132]
(iii) Hydration of cations.[133,134]
(iv) Electron transfer reactions.[135–138]
(v) Complex formation reactions.[139,140]
(vi) Exchange processes.[141,142]

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