Russian Chemical Reviews

October 1984

Translated from *Uspekhi Khimii*, 53, 1601-1624 (1984)

U.D.C. 541.12.036+541.49

The Temperature Jump Method and Its Application in the Study of Complex Formation

V.I.Pogonin and A.K.Chibisov

The present state of the apparatus used in the temperature jump method (methods for rapid heating, recording concentration changes, and collecting and processing experimental data) has been described. The formal kinetics of chemical relaxation on complex formation (relaxation times and amplitudes) have been examined. The mechanisms of complex formation by metal ions with various ligands, based on data obtained by the temperature jump method, have been discussed.
The bibliography contains 118 references.

CONTENTS

I.	Introduction	929
II.	The temperature jump method	929
III.	The kinetics of chemical relaxation on complex formation	932
IV.	The use of the temperature jump method to study complex formation	937

I. INTRODUCTION

In the last twenty years, considerable progress has been made in the study of fast reactions, due primarily to the development of methods for studying them.[1,2] With the development of pulse, relaxation, flow, electrochemical, radiofrequency spectroscopic, and other methods,[2] it has now become possible to study intermediate short-lived products (excited molecules and complexes, ions, radicals, etc.), and also to study the kinetics and mechanism of reactions taking place in times of down to 10^{-14} s.

Among chemical relaxation methods, which are widely and successfully used to study the kinetics of reversible reactions in which equilibrium is established rapidly, an important place is occupied by the temperature jump method. The relative simplicity of the method makes it widely accessible for the study of redox and protolytic reactions, complex formation, enzyme reactions, hydrolysis, etc.

The present review examines the temperature jump method and its application in the study of complex formation in solution. The latest experimental techniques are described, and the formal kinetics of chemical relaxation on complex formation are examined. There is practically no information on these topics in the Soviet literature.

As an illustration of the application of the temperature jump method in the study of fast reactions, the process of complex formation by metal ions with various ligands is examined (the last review in this field was published in 1968 [3]).

II. THE TEMPERATURE JUMP METHOD

The temperature jump method is based on the temperature dependence of the equilibrium constant of a reaction. In accordance with the Van't Hoff isobar equation, the change in the equilibrium constant produced by change in temperature

is revealed by a corresponding change in the equilibrium concentrations of the reagents and reaction products. If the temperature of a system in equilibrium is increased rapidly (temperature jump), a relaxation process involving the establishment of new equilibrium concentrations begins to take place in the system. The rate of this process and the magnitude of the change in concentration are determined by the properties of the system being studied. Various methods for rapidly increasing the temperature, and methods for recording the concentration changes and for processing the experimental data, are examined below.

1. Methods for Rapidly Increasing the Temperature

The internal energy of a system is determined by the sum of the translational, rotational, vibrational, and electronic energies. Each of the components of the internal energy can be expressed in terms of the distribution of the populations of the corresponding levels and determines the corresponding temperature of the system: translational, rotational, vibrational, and electronic, which are equal to one another at thermodynamic equilibrium. An increase in one of these temperatures is brought about by a selective change in the distribution of the populations of the corresponding energy levels, but as a result of rapid internal relaxation and exchange of energy between the molecules in the liquid phase, temperature equilibrium is re-established in a time of <1 ns.[4]

Thus the temperature of a system can be increased rapidly and effectively by introducing energy in any of the above forms into the system. Thus different methods are available for rapidly increasing the temperature: a) Joule heating and a heat-exchange temperature jump (excitation as a result of a change in the rate of translational movement of the molecules); b) microwave heating (rotational excitation); c) laser temperature jump (vibrational excitation); and d) pulse ultraviolet irradiation (electronic excitation).

Joule heating is the simplest and most widely encountered method for obtaining a temperature jump. The heating is brought about by the discharge of a high-voltage condenser through the electrolyte solution. The discharge is usually controlled by a discharger or thyratron. The use of Joule heating makes it possible to obtain a temperature jump of 3–10 K in 1–10 μs in a system with a volume of 0.1–25 ml.[2] Decreasing the heating time is a technically difficult problem. A temperature jump apparatus has been described,[5] which can heat 0.2 ml of solution through 3 K in 300 ns by using a low-induction condenser, gas-filled dischargers of the "krytron" type, and a specially designed cell. A coaxial line, matched with the cell, is also used as condenser, to obtain a temperature jump of 10 K in 50 ns.[6] Decrease in the length of the coaxial line, and suppression of stray effects of electro-luminescence and electrodichroism, produced in solutions at electric field intensities greater than 60 kV cm^{-1}, made it possible to decrease the heating time to 10 ns.[7]

The heat-exchange temperature jump method uses two water-baths, kept at different constant temperatures.[8] The temperature jump can be made fairly large, and both heating and cooling of the system being studied are possible. The heat-exchange temperature jump method makes it possible to study relaxation processes with times of 0.5 s or more.

The temperature jump method is usually employed to study systems in equilibrium at normal atmospheric pressure. Temperature jump apparatus with Joule heating, in which the cell design makes it possible to study chemical relaxations at a pressure of up to 3×10^8 Pa, have also been described.[9–11]

Microwave heating, or heating as a result of the dielectric relaxation of a liquid, is achieved by using a pulse superhigh-frequency (SHF) generator. For water, as for most polar solvents, the maximum absorption of microwave energy takes place at ~10 GHz. Apparatus with SHF heating[12–15] usually employs magnetrons, operating under pulse conditions with an output energy of up to 0.5 J; the solution is heated through 0.2–2 K in 0.25–5 μs.

Rapid heating of a solution can be achieved by the absorption of the light pulse of, for example, a neodymium or ruby laser (laser temperature jump), for which the wavelength of the radiation is 1.06 μm or 0.694 μm respectively. For most solvents, however, the absorption at these wavelengths is extremely small, so that it is impossible to obtain a significant temperature jump. Thus when a neodymium laser operating under free lasing conditions[16,17] or under modulated Q conditions,[18,19] was used, the temperature jump for aqueous solutions was ≤ 0.6 K. A temperature jump of more than 1 K using a neodymium laser with modulated Q is prevented both by the plasma produced when the powerful laser radiation is focussed and by the two-photon processes excited in the system being studied.[20]

One method for increasing the efficiency of laser heating is by introducing into the system substances (absorbers) which strongly absorb the laser radiation. These substances should be chemically inert with respect to the solvent and the system being studied, should be transparent in the range of the spectrum where the changes in absorption are being recorded, and should effectively transform the absorbed light energy into heat during the laser pulse.[16] The absorbers proposed for use with a ruby laser include copper nitrate and Naphthol Green B for aqueous solutions,[16,21] and also vanadyl phthalocyanine for aprotic solvents.[22] The temperature jump achieved by this method was 2–5 K. The heating time was determined by the duration of the laser pulse and amounted to 300–500 μs. The heating time cannot be decreased using a laser with modulated Q, because of the bleaching of the absorber at high laser energy densities.

A temperature jump of 3–10 K has been obtained using lasers with modulated Q by employing Raman neodymium lasers. The radiation of the neodymium laser, operating under modulated Q conditions, is transformed into radiation of longer wavelength by passing through an appropriate Raman medium. A laser temperature jump apparatus using liquid nitrogen ($\lambda_{rad} = 1.41$ μm) as Raman medium has been described.[23–29] In this case, 0.1 ml of aqueous solution was heated through 5–9 K in 30 ns. A laser temperature jump apparatus using gaseous hydrogen ($\lambda_{rad} = 1.89$ μm) at a pressure of 8×10^6 Pa as Raman medium has been described.[30–32] The temperature jump was 2–3 K in 18–50 ns. The use of hydrogen does not require cryogenic techniques, as in the case of liquid nitrogen. 24 different media for Raman lasers, and also a laser temperature jump apparatus using liquid nitrogen, with subnanosecond resolution (heating time 180 ps), have been described.[33] The possible use of excimer lasers to achieve a temperature jump has been examined.[24] An iodine laser ($\lambda_{rad} = 1.315$ μm)[34–36] and a neodymium laser operating at 1.32–1.36 μm without additional transformation[37] have also been described.

The use of laser heating also makes it possible to study relaxation processes at pressures of up to $(2–3) \times 10^8$ Pa.[16,17]

Pulse ultraviolet lamps, whose radiation is readily absorbed by solvent molecules, can also be used to heat solutions rapidly. A spiral pulse ultraviolet lamp, through which a condenser with a capacity of 10 μF, charged to a voltage of 15 kV, is discharged, has been described.[38] In temperature

jump apparatus with ultraviolet irradiation, an aqueous solution has been heated through 1 K in 5 μs.

The characteristics of different methods for obtaining a temperature jump are compared in Table 1.

2. Methods for Recording Changes in Concentration

The most convenient and widely used method for recording the changes in the concentrations of the reagents or reaction products is the spectrophotometric method. In this method, a light beam (usually monochromatic) is passed through the cell containing the solution being heated, and falls on a photoreceiver (for example a photomultiplier instrument), whose output is transferred to an oscillograph, which records the change with time in the transmission in the cell. Methods for supplying the photomultiplier instrument, and the amplifiers and integrating and differentiating filters used in fast-action absorption spectrophotometry, have been described in detail.[2,39]

When an equilibrium between reagents and reaction products is displaced, their concentrations change by an amount Δc_i, leading to a change in the optical density of the system D in accordance with the Lambert–Beer law:

$$\Delta D = \sum_i \varepsilon_i \Delta c_i l$$

where ε_i is the molar absorptivity of the absorbing species, and l the optical path length of the cell. If $\Delta D \ll D$, the relative change in the light intensity is given by

$$\frac{\Delta I}{I_0} = -2.304 \frac{\Delta D}{D} \cdot D \cdot 10^{-D}$$

Differentiating this expression with respect to D and assuming that the ratio $\Delta D/D$ is constant gives the value of the optical density $D = 0.434$ corresponding to the maximum change in intensity ΔI. The maximum signal/noise (S/N) ratio for a system in which particles of only one kind absorb is observed at $D = 0.868$.[40] These conclusions apply to systems whose composition is fixed. For systems with varying composition, usually studied by the temperature jump method, the calculation of the optimum values of the S/N ratio is extremely complicated. The calculation has been carried out using a computer for the single-stage protolytic reaction of Methyl Orange (pH indicator).[41] The calculation showed that the conditions under which the highest values of the intensity of the photometric signal and the S/N ratio are reached depend on the absorption by the particles $\varepsilon_i l$, the pH of the solution, and the analytical concentration of the reagent. The optimum value of the optical density is approximately half that given in Ref. 40.

The sensitivity limit of a temperature jump apparatus with spectrophotometric recording is usually 10^{-3}–10^{-4} optical density units, and is determined by the S/N ratio. This ratio in turn depends on the transmission band Δf of the recording scheme, the quantum efficiency of the photo-receiver, and the intensity of the probing light source. The transmission band is usually controlled during the experiment by integrating and differentiating filters, and is kept in the following range:

$$(3-10)\,\tau_f^{-1} > \Delta f > (0.1-0.3)\,\tau_s^{-1}$$

where τ_f and τ_s are the relaxation times of the fastest and slowest of the processes being studied. The photo-receiver is usually a photomultiplier, for which the quantum yield of the photo-cathode is 1–30%. A silicon photo-diode, combined with a low-noise amplifier, has been used.[42] This apparatus makes it possible to record changes in absorption in the range 1 μs–5 ms with a better S/N ratio than a photomultiplier.

The S/N ratio can be increased by increasing the brightness of the probing light source. Increasing the brightness of a halogen lamp by a factor of ~5 with an increase in the supply voltage from 12 V (nominal conditions) to 16 V (forced conditions) in a time of 300 ms has been proposed.[43] Xenon arc lamps are usually supplied from stabilised current sources; by applying rectangular pulses of increased current with a duration reaching 1 ms, it is possible to obtain an increase in the brightness of the lamp by a factor of 50–700 in the blue and ultraviolet ranges of the spectrum.[44–46] This method makes it possible to improve the S/N ratio by a factor of $(I_f/I_{st})^{1/2}$, where I_f and I_{st} are the intensities of the emission from the lamp under forced and stationary conditions respectively. With pulse supply of the probing lamp, it is necessary to use special active schemes to compensate automatically the constant component of the output current of the photomultiplier[47] or a high-frequency passive filters.[48]

Table 1. Comparison of methods for obtaining a temperature jump.

Heating method	τ_h, s	ΔT, K	V_{min}, ml	Solvent requirements	Possibility of using conductometric recording	Possibility of operating under frequency conditions with accumulation and averaging	Possibility of application to heterogeneous systems	Technical simplicity of heating apparatus	Notes
Joule	10^{-8}–10^{-5}	5–10	0.1–10	polar, ionic strength 0.05–0.5 M	no	no	no	simple, particularly for the range 10^{-6}–1 s	side reactions with electrolysis products and the salts added to create the required ionic strength are possible
SHF	10^{-6}	0.2–2	0.07–0.2	polar, any ionic strength	yes	yes	yes	complex	—
Laser	10^{-8}–10^{-11}	2–9	0.01–0.1	none	yes	yes	yes	complex, particularly when liquid N_2 is used as the Raman medium	requires a laser with wavelength in the range of infrared absorption by the solvent; cavitation is possible; heating is non-uniform
Ultraviolet	$5 \cdot 10^{-6}$	5	5	none	yes	—	—	simple	simultaneous photochemical reactions are possible

Notes: τ_h = heating time; V_{min} = minimum solution volume.

In temperature jump apparatus with spectrophotometric recording, the reaction cell is usually illuminated by a monochromatic light beam, and this makes it possible to record the relaxation process at only one wavelength in one experiment. A series of experiments is necessary to record the spectrum of relaxation amplitudes. An apparatus using a polychromator has been described,[49] which makes it possible to record the kinetic curves at several wave-lengths simultaneously. The output from the polychromator passes to 10–30 photo-electronic multipliers, connected to digital memory blocks, in which the information is recorded simultaneously in the course of one experiment. A similar apparatus using a dissector instead of a set of photomultipliers has been described.[50] Spectrophotometric recording has a high selectivity, and this is of considerable importance in the study of multi-equilibrium systems.

Conductometric recording is used in addition to spectrophotometric recording in the temperature jump method. In conductometric recording, two planar inert electrodes (usually of platinum or gold), to which a probing voltage is applied, are placed in the reaction cell. Slow relaxation processes are observed using a constant current,[51] and fast processes using rectangular current pulses,[52] which makes it possible to decrease the polarisation effects at the electrodes. Best results are obtained, however, using a varying probing voltage; in this case, a high-frequency Wheatstone bridge is used to increase the sensitivity. The bridge is supplied from the generator of a variable (usually sinusoidal) voltage with a frequency of from 100 kHz to 10 MHz, and a narrow-band amplifier and oscillograph are connected to its diagonals. On temperature perturbation of the reaction system, the bridge is unbalanced: the change in the amplitude of the high-frequency voltage reflects the relaxation process.

Conductometric recording is used with microwave heating,[12–14] optical heating using lasers,[16,18] and pulse ultraviolet lamps.[38] Conductometric recording has a higher sensitivity (reaching 0.001%) than spectrophotometric recording, and, other conditions being equal, it makes it possible to obtain a better S/N ratio.[52]

Recording changes in fluorescence can be an extremely effective method for observing chemical relaxation in the temperature jump method. A temperature jump method with Joule heating, using recording of the changes in concentration both from the absorption and from the intensity of the fluorescence, has been described.[53] The cell had four optical windows, two of which were used for the spectrophotometric recording, and the other two were used to record both the polarised and the non-polarised fluorescence emission. An apparatus of this kind can also be used to record changes in the light scattering.

3. The Collection and Processing of the Experimental Data

In the general case, the kinetic curve obtained in temperature jump experiments represents the sum of several exponents:

$$S(t) = \sum_i A_i \, e^{-t/\tau_i}$$

where A_i and τ_i are the initial amplitude and time of the relaxation of the ith equilibrium. The traditional method for processing the kinetic curves involves photographing the curve on the oscillograph screen and then transforming it to a semilogarithmic scale. If the relaxation process is characterised by a single relaxation time, the transformed line is strictly linear. If there is a set of relaxation times, the transformed line is a curve. In this case, graphical separation of the terms included in the sum $S(t)$ is possible with the condition that the values of τ_i differ by factors of not less than 2–3.

The question of the accuracy of the graphical separation of two or more exponential curves has been discussed.[54,55]

Since the graphical procedure described above is extremely laborious, other methods have been proposed for determining relaxation times. Thus a method has been proposed[56] for processing a kinetic curve characterised by a single relaxation time. The photographic image of the curve is projected on to the screen of an oscillograph, and an exponentially damping voltage, produced by means of an RC-circuit, is supplied to the oscillograph input. The values of R and C are varied to achieve superposition of the curves and hence find the relaxation time $\tau = RC$. A scheme has been proposed,[57] in which the voltage from the output of the temperature jump apparatus is applied to the input Y of the oscillograph, and the voltage from the generator of the exponentially quenching voltage is applied to the input X. When the parameters are equal, a Lissajou figure in the form of a straight line is observed on the oscillograph screen. The uncertainty of the determination of the relaxation time by the two methods is 10%.

A widely encountered method for collecting and processing the experimental data involves the use of a computer. The signal being studied is transformed into digital form by means of an analogue–digital transformer and recorded in the memory of the computer, which processes the kinetic curve using special programs. A method involving the use of a digital oscillograph connected to a mini-computer has been described.[58] With a large number of breakdown points (up to 4000), the subsequent mathematical treatment to a large extent makes it possible to avoid periodic and random noise in the signal, to improve considerably the signal/noise ratio, and to determine the parameters of the relaxation process with a high accuracy.

Digital recording readily makes it possible to accumulate and average the signals from a large number (N) of repeat experiments, leading to an increase in the S/N ratio by a factor of $(N)^{1/2}$. This method, combined with preliminary analogue integration of the signal,[59] makes it possible to increase the accuracy of the processing of the experimental data. Accumulation and averaging of the signal are particularly easily carried out in apparatus with microwave[12,14,15] and laser[37] heating, since the excitation sources used in these methods operate under frequency conditions. Using accumulation of the data, it has been possible to achieve a sensitivity of 0.01% in the microsecond time range and of 0.1% in the nanosecond range.

The digital information is usually processed by the least-squares method for non-linear curves, and various methods for doing this on a computer have been described.[60–62]

III. THE KINETICS OF CHEMICAL RELAXATION ON COMPLEX FORMATION

In the general case, complex formation between metal ions $M^{m+}(aq)$ and a ligand $L^{n-}(aq)$ is a multi-stage reversible reaction:

$$M^{m+}(aq) + L^{n-}(aq) \rightleftharpoons \rightleftharpoons ML^{(m-n)+} \qquad (1)$$

If the equilibrium constants of the reactions (1) depend on temperature, heating displaces the equilibrium. If the system is in equilibrium at an initial temperature T_1, then a rapid change (jump) in temperature by δT leads to the production of non-equilibrium conditions. The time taken to reach the new equilibrium state corresponding to the final temperature

T_2 (the relaxation time τ) in general depends on the rate constants of the stages of reaction (1) and on the equilibrium concentrations of the reagents. The change in the equilibrium concentrations of the reagents (the relaxation amplitude), reached at the moment when the new equilibrium state is established, depends on the magnitude and sign of the enthalpy changes of the separate stages of the reaction, and also on the equilibrium constants and the equilibrium concentrations of the reagents. Expressions for the relaxation times and relaxation amplitudes in complex formation reactions with different degrees of complexity are given below.[63,64]

1. Relaxation Time and Relaxation Amplitudes in a Single-Stage Reaction

In the simplest case, complex formation can be represented as a single-stage reversible reaction:

$$M^{m+}(aq) + L^{n-}(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML^{(m-n)+} \qquad (2)$$

The expression for the relaxation time is obtained from the equation describing the kinetics of the reaction after the temperature jump (or after any other short-lived perturbation of the system, leading to displacement of its equilibrium).[63] The expression for the rate of reaction (2)†

$$-d[M]/dt = k_{12}[M][L] - k_{21}[ML]$$

written in terms of the equilibrium (at the final temperature) concentrations $[\bar{M}]$, $[\bar{L}]$, and $[\overline{ML}]$ and in terms of the small changes in the concentrations $\delta[M]$, $\delta[L]$, and $\delta[ML]$, due to the displacement of the equilibrium, has the form:

$$-\frac{d[\bar{M}]}{dt} - \frac{d\,\delta[M]}{dt} = k_{12}[\bar{M}][\bar{L}] - k_{21}[\overline{ML}] + k_{12}\delta[M][\bar{L}] + k_{12}\delta[L][\bar{M}] + k_{12}\delta[M]\delta[L] - k_{21}\delta[ML] \qquad (3)$$

For small deviations from the equilibrium position, it is possible to neglect the term $k_{12}\delta[M]\delta[L]$ in Eqn.(3). The material balance equation

$$\delta[M] + \delta[ML] = 0;\ \delta[L] + \delta[ML] = 0 \qquad (4)$$

gives

$$-\frac{d\,\delta[M]}{dt} = k_{12}([\bar{M}] + [\bar{L}])\,\delta[M] + k_{21}\delta[M] \qquad (5)$$

Thus the expression for the relaxation time has the form

$$\tau = \{k_{12}([\bar{M}] + [\bar{L}]) + k_{21}\}^{-1} \qquad (6)$$

The values of the rate constants k_{12} and k_{21} of the forward and back reactions are found from the graphical plot of τ^{-1} against $[\bar{M}] + [\bar{L}]$. Since the values of $[\bar{M}] + [\bar{L}]$ are usually unknown, k_{12} and k_{21} are determined by the widely used technique in which one of the reagents, for example L, is taken in excess. In this case

$$\tau^{-1} = k_{12}[L]_0 + k_{21} \qquad (7)$$

where $[L]_0$ is the initial concentration of the ligand, and $[L]_0 \gg [M]_0$.

To find k_{12} and k_{21}, it is also convenient to use the expression

$$\tau^{-2} = k_{12}^2([M]_0 - [L]_0)^2 + 2k_{12}k_{21}([M]_0 + [L]_0) + k_{21}^2 \qquad (8)$$

obtained from Eqn.(6). In this case, the values $k_{12}k_{21}$ are found from the graphical plot of τ^{-2} against $[M]_0 + [L]_0$ for a fixed value of the difference $[M]_0 - [L]_0$. In the particular case where $[M]_0 = [L]_0$, expression (8) is simplified to

$$\tau^{-2} = 4k_{12}k_{21}[M]_0 + k_{21}^2 \qquad (9)$$

and when $[L]_0 \gg [M]_0$ it becomes Eqn.(7).

Eqn.(6) leads to an important conclusion about the conditions for achieving the extremal value of τ (τ resonance). Expressing the equilibrium concentrations $[\bar{M}]$ and $[\bar{L}]$ in terms of the initial concentrations $[M]_0$ and $[L]_0$ and the equilibrium constant $K = k_{12}/k_{21}$ and using Eqn.(6) gives

$$\tau k_{12} = \{([M]_0 - [L]_0 + K^{-1})^2 + 4K^{-1}[L]_0\}^{-1/2} \qquad (10)$$

From Eqn.(10) it follows that τk_{12} has a maximum value for $[M]_0 = [L]_0$ (Fig.1):

$$\tau_{max} k_{12} = (K^{-2} + K^{-1}[L]_0)^{-1/2} \qquad (11)$$

Eqn.(11) can also be obtained from Eqn.(9), which is simplified when $K^{-1} \ll [M]_0$, $[L]_0$ (for a strongly bonded complex)

$$\tau_{max} k_{12} = \frac{1}{2}\left(\frac{K}{[L]_0}\right)^{1/2}$$

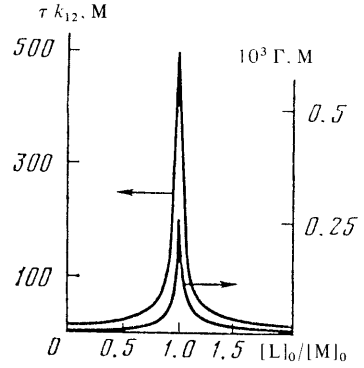


Figure 1. Resonance of τ and Γ for a strongly bonded complex, $K = 10^5$ litre mole^{-1}; $[M]_0 = 0.1$ M.[63]

The relationship between the relaxation amplitude and the parameters of reaction (2) can be established as follows. From the expression for the equilibrium constant

$$K = [\overline{ML}]/[\bar{M}][\bar{L}] \qquad (12)$$

it follows that

$$\frac{\delta K}{K} = \frac{\delta[ML]}{[\overline{ML}]} - \frac{\delta[M]}{[\bar{M}]} - \frac{\delta[L]}{[\bar{L}]} \qquad (13)$$

The material balance equation (4) and Eqn.(13) gives:

$$\frac{\delta K}{K} = \delta[ML]\left(\frac{1}{[\bar{M}]} + \frac{1}{[\bar{L}]} + \frac{1}{[\overline{ML}]}\right)$$

On the other hand, the Van't Hoff isobar equation

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$$

gives:

$$\frac{\delta K}{K} = \frac{\Delta H}{RT^2}\delta T$$

Thus the relaxation amplitude is given by the expression

† For simplicity, the indices $m+$, $n-$ and $(m-n)+$ for M, L, and ML are omitted.

$$\delta[ML] = \Gamma \frac{\Delta H}{RT^2} \delta T \qquad (14)$$

where $\Gamma = (1/[\bar{M}] + 1/[\bar{L}] + 1/[\overline{ML}])^{-1}$ is the transfer function of reaction (2).

Thus the change in the concentration of the complex (or the reagents) is directly proportional to the product of the enthalpy of the reaction, the change in temperature as a result of heating, and the value of the transfer function. The values of the relaxation amplitudes are important for finding the change in the enthalpy of the reaction. It follows from Eqn.(14) that the enthalpy of the reaction can be determined from direct measurements of $\delta[ML]$ (or $\delta[M]$, $\delta[L]$, the quantity δT, and the value of Γ.

A knowledge of the value of Γ is of considerable importance for finding the optimum conditions for measuring the relaxation amplitude. Using Eqn.(12), it is possible to write the expression for Γ as:

$$\Gamma = \frac{K[\bar{M}][\bar{L}]}{1 + K([\bar{M}] + [\bar{L}])} \qquad (15)$$

In the particular case where $[\bar{M}] = [\bar{L}]$, Eqn.(15) becomes

$$\Gamma = \frac{K[\bar{M}]^2}{1 + 2K[\bar{M}]} \qquad (16)$$

Introducing the parameter $\alpha = [\bar{M}]/[M]_0$ gives from Eqn.(16)

$$\Gamma = \frac{\alpha(1-\alpha)}{2-\alpha}[M]_0$$

from which the maximum value of $\Gamma/[M]_0 = 0.173$ for $\alpha = 0.586$.

The transfer function Γ can be expressed in terms of the initial concentrations $[M]_0$ and $[L]_0$. For this purpose, the expression for Γ is written in the form:

$$\Gamma = \frac{[\overline{ML}]K^{-1}}{[\bar{M}] + [\bar{L}] + K^{-1}}$$

obtained from Eqns.(12) and (15). Expressing $[\overline{ML}]$ in terms of $[M]_0$, $[L]_0$ and K gives:

$$\Gamma = \frac{1}{2K} \cdot \frac{[M]_0 + [L]_0 + K^{-1}}{\{([M]_0 - [L]_0)^2 + 2K^{-1}([M]_0 + [L]_0) + K^{-2}\}^{1/2}} - 1 \qquad (17)$$

Particular cases give the following results:

1) for $[M]_0 \gg [L]_0$

$$\Gamma = \frac{1}{2K}[([M]_0 + K^{-1})^{1/2} - 1] \qquad (18)$$

2) for $[M]_0 = [L]_0 \neq K^{-1}$

$$\Gamma = \frac{1}{2K}\left[\frac{2[M]_0 + K^{-1}}{(4K^{-1}[M]_0 + K^{-2})^{1/2}} - 1\right] \qquad (19)$$

3) for $[M]_0 = [L]_0 = K^{-1}$

$$\Gamma = 0.6K^{-1} \qquad (20)$$

Eqns.(18)–(20) can be used to calculate Γ, which is necessary to find ΔH for the reaction.

It is of interest to examine the case where a strongly bonded complex is formed, $[M]_0 + [L]_0 \gg K^{-1}$; in this case, from Eqn. (17):

$$\Gamma = \frac{1}{2K}\left(\frac{[M]_0 + [L]_0}{[([M]_0 - [L]_0)^2 + 2K^{-1}([M]_0 + [L]_0)]^{1/2}} - 1\right)$$

If the initial concentrations are equal, $[M]_0 = [L]_0$ (resonance of Γ), it follows that:

$$\Gamma \simeq {}^1/_2([M]_0/K)^{1/2}$$

It is obvious that the value of Γ for $[M]_0 = [L]_0$ is much greater than the limiting values of Γ for $[M]_0 \gg [L]_0$ or $[L]_0 \gg [M]_0$, that is for a given value of $[M]_0$ the plot of Γ against $[L]_0/[M]_0$ passes through a maximum, which is reached at $[L]_0/[M]_0 = 1$ (see Fig.1).

2. Relaxation Times and Relaxation Amplitudes in Two-Stage Reactions

A two-stage reaction (for example the formation of a unidentate complex) is described by the equation:

$$\underset{(I)}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(II)}{M^{m+}(aq)L^{n-}} \overset{k_{23}}{\underset{k_{32}}{\rightleftharpoons}} \underset{(III)}{ML^{(m-n)+}} \qquad (21)$$

where $M^{m+}(aq)L^{n-}$ and $ML^{(m-n)+}$ are the outer-sphere and inner-sphere complexes. Stage (I) → (II) involves the loss of a water molecule from the hydration layer of the ligand, whereas stage (II) → (III) involves the loss of a water molecule from the hydration layer of the metal cation.

An approach to the derivation of an expression for the relaxation times in the case where the rates of reactions (I) ⇌ (II) and (II) ⇌ (III) are close to one another[63] is examined below. For small departures from the equilibrium position, the rate of reaction (21) is described by the system of equations #:

$$\begin{cases} -\dfrac{d\,\delta[M]}{dt} = k_{12}\delta[M]([\bar{M}] + [\bar{L}]) - k_{21}\delta[M(aq)L] \\ \dfrac{d\,\delta[ML]}{dt} = k_{23}\delta[M(aq)L] - k_{32}\delta[ML] \end{cases}$$

which with allowance for the material balance equation

$$\delta[M] + \delta[M(aq)L] + \delta[ML] = 0 \qquad (22)$$

becomes

$$\begin{cases} \dfrac{d\,\delta[M]}{dt} + \{k_{12}([\bar{M}] + [\bar{L}]) + k_{21}\}\delta[M] + k_{21}\delta[ML] = 0 \\ \dfrac{d\,\delta[ML]}{dt} + k_{23}\delta[M] + (k_{23} + k_{32})\delta[ML] = 0 \end{cases} \qquad (23)$$

The solution of this system of differential equations has the form:

$$\begin{cases} \delta[M] = \delta[M]^0 e^{-t/\tau} \\ \delta[ML] = \delta[ML]^0 e^{-t/\tau} \end{cases} \qquad (24)$$

Substituting Eqns.(24) in Eqns.(23) gives the relaxation times τ_1 and τ_2, $\tau_1 < \tau_2$, in the form:

$$\tau_1^{-1} = \frac{1}{2}\{\Sigma k + [(\Sigma k)^2 - 4\pi k]^{1/2}\} \qquad (25)$$

$$\tau_2^{-1} = \frac{1}{2}\{\Sigma k - [(\Sigma k)^2 - 4\pi k]^{1/2}\} \qquad (26)$$

where

$$\Sigma k = \tau_1^{-1} + \tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21} + k_{23} + k_{32}$$
$$\Pi k = \tau_1^{-1}\tau_2^{-1} = k_{12}(k_{23} + k_{32})([\bar{M}] + [\bar{L}]) + k_{21}k_{32}$$

The values of the rate constants of reaction (21) are found graphically from the linear dependence of the sum $\tau_1^{-1} + \tau_2^{-1}$ on $([\bar{M}] + [\bar{L}])$ and the linear dependence of the product $\tau_1^{-1}\tau_2^{-1}$ on $([\bar{M}] + [\bar{L}])$.

It is important to examine the expressions for τ_1^{-1} and τ_2^{-1} for the following particular cases:

1) $k_{12}([\bar{M}] + [\bar{L}] + k_{21} \gg k_{23}, k_{32}$,
that is reaction (I) ⇌ (II) is more rapid than reaction (II) ⇌ (III) In this case the expression for the relaxation times have the form

$$\tau_1^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21}$$
$$\tau_2^{-1} = k_{23}\frac{K_1([\bar{M}] + [\bar{L}])}{1 + K_1([\bar{M}] + [\bar{L}])} + k_{32}$$

where $K_1 = k_{12}/k_{21}$;

2) $k_{21} + k_{23} \gg k_{12}([\bar{M}] + [\bar{L}])$, k_{32},
that is the state of the complex M(aq)L can be regarded as

For simplicity, the indices $m+$, $n-$, and $(m-n)+$ for M, L, and ML are omitted.

stationary. In this case,

$$\tau_1^{-1} = k_{21} + k_{23}$$
$$\tau_2^{-1} = \frac{k_{12}k_{23}([\bar{M}] + [\bar{L}])}{k_{21} + k_{23}} + \frac{k_{21}k_{32}}{k_{21} + k_{23}} \quad (27)$$

Eqn.(27) can also be obtained by the method of stationary concentrations. It is simplified in the limiting cases where $k_{21} << k_{23}$ and $k_{21} >> k_{23}$. For $k_{21} << k_{23}$, that is when the formation of the inner-sphere complex ML is more rapid than the dissociation of the outer-sphere complex M(aq)L to the solvated ions,

$$\tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + \frac{k_{21}k_{32}}{k_{23}}$$

In the opposite situation, when $k_{21} >> k_{23}$, Eqn.(27) becomes

$$\tau_2^{-1} = k_{23}K_1([\bar{M}] + [\bar{L}]) + k_{32}$$

3) $k_{23} + k_{32} >> k_{12}([\bar{M}] + [\bar{L}])$, k_{21}, that is reaction (II) ⇌ (III) is more rapid than reaction (I) ⇌ (II). In this case,

$$\tau_1^{-1} = k_{23} + k_{32}$$
$$\tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21}k_{32}/(k_{23} + k_{32})$$

Table 2 gives expressions for the relaxation times in two-stage reactions taking place by different mechanisms. Thus the reaction

$$\begin{cases} LH^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} L + H^+ \\ L + M \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \end{cases} \quad (A)$$

corresponds to the typical case of complex formation involving a ligand L present in equilibrium with the protonated form LH^+. In the reaction

$$\begin{cases} L' \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} L \\ L + M \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \end{cases} \quad (B)$$

the ligand is the reactive tautomer L, present in equilibrium with the tautomer L′ which does not form complexes. In the reaction

$$\begin{cases} M + L_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML_1 \\ ML_1 + L_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML_1L_2 \end{cases} \quad (C)$$

successive addition of the two ligands L_1 and L_2 takes place.

It is convenient to examine the expressions for the relaxation amplitudes for the example of the two-stage reaction (21) with the condition that there is an excess concentration of one of the reagents, for example the ligand ($[L]_0 >> [M]_0$).[63] In this case, from the expressions for the equilibrium constants, defined as

$$K_1 = \frac{k_{21}}{k_{12}[L]_0} = \frac{[\bar{M}]}{[\overline{M(aq)L}]}; \quad K_2 = \frac{k_{23}}{k_{32}} = \frac{[\overline{ML}]}{[\overline{M(aq)L}]}$$

it follows that the maximum changes in the concentrations $\delta[M]^0$ and $\delta[ML]^0$ can be written as

$$\delta[M]^0 = K_1\delta[M(aq)L]^0 + \delta K_1[\overline{M(aq)L}] \quad (28)$$

$$\delta[ML]^0 = K_2\delta[M(aq)L]^0 + \delta K_2[\overline{M(aq)L}] \quad (29)$$

The material balance equation (22) and Eqns.(28) and (29) give the following expressions for the relaxation amplitudes

$$\delta[M]^0 = [\bar{M}]\frac{(1+K_2)\cdot\delta K_1/K_1 - K_2\cdot\delta K_2/K_2}{1+K_1+K_2} \quad (30)$$

$$\delta[ML]^0 = [\overline{ML}]\frac{(1+K_1)\cdot\delta K_2/K_2 - K_1\cdot\delta K_1/K_1}{1+K_1+K_2} \quad (31)$$

$$\delta[M(aq)L]^0 = -[\overline{M(aq)L}]\frac{K_1\cdot\delta K_1/K_1 + K_2\cdot\delta K_2/K_2}{1+K_1+K_2} \quad (32)$$

Since the relative changes in the equilibrium constants K_1 and K_2 are proportional to the enthalpies of the reactions

$$\delta K_1/K_1 = (\Delta H_1/RT^2)\delta T, \ \delta K_2/K_2 = (\Delta H_2/RT^2)\delta T$$

where ΔH_1 and ΔH_2 are the enthalpies of reactions (II) ⇌ (I) and (II) ⇌ (III), it follows that the expressions for the relaxation amplitudes (30)–(32) represent essentially the dependence of these amplitudes on the enthalpies ΔH_1 and ΔH_2.

Table 2. Expressions for the relaxation times for the two-stage reactions (A)–(C) for different relationships between the rate constants of the separate stages; $K_1 = k_{12}/k_{21}$, $K_2 = k_{32}/k_{23}$.

Reaction	Conditions	τ_1^{-1}	τ_2^{-1}
(A)	$k_{12} + k_{21}([\bar{L}] + [\bar{H}^+]) \gg k_{23}([\bar{L}] + [\bar{M}]), k_{32}$	$k_{12} + k_{21}([\bar{L}] + [\bar{H}^+])$	$k_{23}\left([\bar{L}] + [\bar{M}]\frac{K_1 + [\bar{L}]}{K_1 + [\bar{L}] + [\bar{H}^+]}\right) + k_{32}$
	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32} \gg k_{12}, k_{21}([\bar{L}] + [\bar{H}^+])$	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32}$	$k_{12} + k_{21} \times \left([\bar{L}] + [\bar{H}^+]\frac{K_2 + [\bar{L}]}{K_2 + [\bar{L}] + [\bar{M}]}\right)$
(B)	$k_{12} + k_{21} \gg k_{23}([\bar{L}] + [\bar{M}]), k_{32}$	$k_{12} + k_{21}$	$k_{23}\left([\bar{L}] + \frac{K_1[\bar{M}]}{1 + K_1}\right) + k_{32}$
	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32} \gg k_{12}, k_{21}$	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32}$	$k_{12} + k_{21}\frac{K_2 + [\bar{L}]}{K_2 + [\bar{L}] + [\bar{M}]}$
(C)	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21} \gg k_{23}([\overline{ML_1}] + [\bar{L}_2]), k_{32}$	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21}$	$k_{23}\left([\overline{ML_1}] + [\bar{L}_2] \times \frac{K_1[\bar{M}] + K_1[\bar{L}_1]}{1 + K_1([\bar{M}] + [\bar{L}])}\right) + k_{32}$
	$k_{23}([\overline{ML_1}] + [\bar{L}_2]) + k_{32} \gg k_{12}([\bar{M}] + [\bar{L}_1]), k_{21}$	$k_{23}([\overline{ML_1}] + [\bar{L}_2]) + k_{32}$	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21}\frac{K_2 + [\overline{ML_1}]}{K_2 + [\overline{ML_1}] + [\bar{L}_2]}$

In particular, if complex formation is conjugated with the protonation of the ligand, then for a definite value of the ratio $\Delta H_1/\Delta H_2$, a change in the sign of the relaxation amplitudes (a bicipital phenomenon[65–67]) with change in the pH of the medium is possible.

Thus the following reaction can be considered:

$$\begin{matrix} M + L \overset{\Delta H_1}{\rightleftharpoons} ML \\ L + H^+ \overset{\Delta H_2}{\rightleftharpoons} LH^+ \end{matrix} \quad (33)$$

Assuming that the stage involving the protonation of the ligand L is more rapid than the stage involving the formation of the complex ML, and also that complex formation takes place in an excess concentration of the metal, $[M]_0 >> [L]_0$, it follows that the relaxation amplitudes $\delta[H^+]^0$, $\delta[L]^0$, and $\delta[ML]^0$ can be expressed as follows in terms of the transfer function Γ of reaction (33), where $\Gamma^{-1} = [\bar{L}]^{-1} + [\bar{H}^+]^{-1} +$

$[\overline{LH^+}]^{-1}$, and the enthalpies ΔH_1 and ΔH_2:

$$-\delta[H^+]^0 = \Gamma \frac{\Delta H_2}{RT^2}\delta T$$
$$\frac{\delta[ML]^0}{[\overline{ML}]} - \frac{\delta[L]^0}{[\overline{L}]} = \frac{\Delta H_1}{RT^2}\delta T$$

The material balance equation

$$\delta[L]+\delta[ML]+\delta[LH^+]=0$$

gives

$$\delta[ML]^0 = \frac{[\overline{L}][\overline{ML}]}{[\overline{L}]+[\overline{ML}]}\left(\Delta H_1 - \frac{\Delta H_2}{1+\beta}\right)\frac{\delta T}{RT^2} \quad (34)$$

where

$$\beta = \frac{1}{K[\overline{H^+}]} + \frac{[\overline{L}]}{[\overline{H^+}]}, \quad K = [\overline{LH^+}]/[\overline{L}][\overline{H^+}] \quad (35)$$

It follows from Eqns.(34) and (35) that if $\Delta H_2/\Delta H_1 > 1$, then the relaxation amplitude $\delta[ML]^0$ changes sign when

$$[\overline{H^+}] = \frac{K^{-1}+[\overline{L}]}{\Delta H_2/\Delta H_1 - 1}$$

Eqns.(30)–(32) represent the total changes in the concentrations of M, ML, and M(aq)L in reaction (21). Expressions are given below for the relaxation amplitudes in the stages (I) ⇌ (II) (provisionally taken as fast, subscript A) and (II) ⇌ (III) (provisionally taken as slow, subscript B) of reaction (21):

$$\delta[M]^0_A = [\overline{M}]\frac{1}{1+K_1}\cdot\frac{\delta K_1}{K_1}$$
$$\delta[M(aq)L]^0_A = -[\overline{M(aq)L}]\frac{K_1}{1+K_1}\frac{\delta K_1}{K_1}$$
$$\delta[M]^0_B = [\overline{M}]\frac{K_2(K_1\cdot\delta K_1/K_1 - \delta K_2/K_2 - K_1\cdot\delta K_2/K_2)}{(1+K_1)(1+K_1+K_2)} \quad (36)$$

$$\delta[M(aq)L]^0_B = [\overline{M(aq)L}]\frac{K_2(K_1\cdot\delta K_1/K_1 - \delta K_2/K_2 - K_1\cdot\delta K_2/K_2)}{(1+K_1)(1+K_1+K_2)} \quad (37)$$

The amplitude $\delta[ML]^0_B = \delta[ML]^0$ is given by Eqn.(31).

It follows from Eqns.(31), (36), and (37) that to observe stage (II) ⇌ (III) by the temperature jump method it is not necessary that the enthalpy of this stage have a finite value ($\Delta H_2 \sim \delta K_2/K_2 \neq 0$). It follows from Eqn.(31) that for $\Delta H_2 = 0$,

$$\delta[ML]^0 = -[\overline{ML}]\frac{K_1\cdot\delta K_1/K_1}{1+K_1+K_2}$$

that is the relaxation amplitude $\delta[ML]^0$ is determined essentially by the enthalpy ΔH_1 of the stage (I) ⇌ (II). This feature is of considerable practical importance; small relaxation amplitudes can be increased considerably by selecting a stage (I) ⇌ (II) with a high rate of establishment of equilibrium and a high enthalpy value.

3. Relaxation Times in Multi-Stage Reactions

In the general case, the kinetics of multi-stage reactions involving $n+1$ states can be described by a system of n linear differential equations[63]

$$\frac{d[x_i]}{dt} + \sum_{j=1}^{n} a_{ij}[x_j] = 0, \text{ where } i, j = 1, 2, \ldots, n \quad (38)$$

Here, $[x_j] = \delta[c_j] = [c_j] - [\bar{c}_j]$ is the change in the concentration of the jth state for a small displacement of the equilibrium, and a_{ij} is a parameter which depends on the rate constants and the equilibrium concentrations of the states of the multi-stage reaction.

The solution of the system of equations (38) is a set of n exponents of the form:

$$[x_i] = \sum_{j=1}^{n}[x_i]^0_j e^{-t/\tau_j}, \text{ where } i, j = 1, 2, \ldots, n \quad (39)$$

The relaxation times (relaxation spectrum) are found by solving the system of algebraic equations obtained by substituting Eqn.(39) in Eqn.(38).

The most general example of a reaction involving more than two stages is the three-stage reaction of complex formation with a bidentate ligand:

$$\underset{(IV)}{M^{m+}(aq)} + L^{n-}(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(V)}{M^{m+}(aq)L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(VI)}{ML^{(m-n)+}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{(VII)}{M{=}L^{(m-n)+}} \quad (40)$$

which compared with reaction (21) includes the additional stage (VI) ⇌ (VII) involving the formation of the bidentate complex $M{=}L^{(m-n)+}$, associated with the loss of a second water molecule from the hydration layer of the metal cation. In accordance with the scheme for the solution of Eqns.(38) and (39), the three values of the relaxation times characterising the three-stage reaction (40) are the roots of the cubic equation

$$(1/\tau)^3 + A_1(1/\tau)^2 - A_2(1/\tau) + A_3 = 0$$

where

$$A_1 = k_{12}([\overline{M}]+[\overline{L}]) + k_{21} + k_{23} + k_{32} + k_{34} + k_{43}$$
$$A_2 = (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{23}+k_{32}) + (k_{23}+k_{32})(k_{34}+k_{43}) + (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{34}+k_{43}) - k_{21}k_{23} - k_{32}k_{34}$$
$$A_3 = (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{23}+k_{32})(k_{34}+k_{43}) - (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))k_{32}k_{34} - (k_{34}+k_{43})k_{21}k_{23}$$

The corresponding concentration dependence of the relaxation times τ_1, τ_2, and τ_3, obtained experimentally, and the relationships

$$A_1 = \tau_1^{-1} + \tau_2^{-1} + \tau_3^{-1}$$
$$A_2 = \tau_1^{-1}\tau_2^{-1} + \tau_1^{-1}\tau_3^{-1} + \tau_2^{-1}\tau_3^{-1}$$
$$A_3 = \tau_1^{-1}\tau_2^{-1}\tau_3^{-1}$$

can now be used to determine the values of all six rate constants of reaction (40).

In complex formation, the stages of the reaction often differ considerably in the rates at which equilibrium is established. In this case, the analysis of the relaxation spectrum is much easier. Table 3 gives expressions for three relaxation times, corresponding to fast, medium, and slow stages in the reaction.

A frequently encountered particular case is complex formation (A) (R.p.1612) not accompanied by spectral changes. The kinetics of the establishment of equilibrium can then be followed using an acid–base indicator added to the system. The set of coupled equilibria is represented by the scheme:[2]

$$\underset{(VIII)}{M} + \underset{(IX)}{L} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML$$
$$H^+ + L \rightleftharpoons LH^+$$
$$H^+ + Ind \rightleftharpoons Ind\,H^+$$

If the formation of ML is slow compared with the rapid protonation of the ligand L and the indicator Ind, the establishment of equilibrium (VIII) ⇌ (IX) after the temperature jump is followed from the change in the colour of the indicator. The relaxation time is given by the expression

$$\tau^{-1} = k_{12}\left(\frac{[\overline{M}]}{1+\gamma} + [\overline{L}]\right) + k_{21}$$

where

$$\gamma = \frac{[\bar{H}^+]}{K_{LH^+} + \chi[\bar{L}]}; \quad \chi = \frac{K_{IndH^+} + [\bar{H}^+]}{K_{IndH^+} + [\bar{H}^+] + [\bar{Ind}]};$$
$$K_{LH^+} = [\bar{H}^+][\bar{L}]/[\bar{L}\bar{H}^+]; \quad K_{IndH^+} = [\bar{H}^+][Ind]/[\bar{Ind}\,\bar{H}^+]$$

If the values of K_{LH^+} and K_{IndH^+} are known, the value of γ can be calculated for any value of the pH of the solution, and this in turn makes it possible to determine graphically the values of k_{12} and k_{21} from the experimentally determined value of τ.

Table 3. Expressions for the relaxation times in the system

$$M(aq) + L(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M(aq)\,L \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} M\text{-}L$$

for different ratios of the reaction rate constants*.

Conditions	τ_1^{-1} (fast stage)	τ_2^{-1} (medium stage)	τ_3^{-1} (slow stage)
$k_{12}([\bar{M}]+[\bar{L}])$, $k_{21} \gtrsim k_{23}$, $k_{32} \gtrsim k_{34}$, k_{43}	$k_{12}([\bar{M}]+[\bar{L}])+k_{21}$	$k_{23}\frac{K_1([\bar{M}]+[\bar{L}])}{1+K_1([\bar{M}]+[\bar{L}])}+k_{32}$	$k_{34}\frac{K_1([\bar{M}]+[\bar{L}])K_2}{1+K_1([\bar{M}]+[\bar{L}])(1+K_2)}+k_{43}$
$k_{12}([\bar{M}]+[\bar{L}])$, k_{21}, k_{23}, $k_{32} \gtrsim k_{34}$, k_{43}	see Eqn. (25)	see Eqn. (26)	$k_{34}\frac{K_1([\bar{M}]+[\bar{L}])K_2}{1+K_1([\bar{M}]+[\bar{L}])(1+K_2)}+k_{43}$
$k_{12}([\bar{M}]+[\bar{L}])$, k_{21}, k_{34}, $k_{43} \gtrsim k_{23}$, k_{32}	$k_{12}([\bar{M}]+[\bar{L}])+k_{34}$	$k_{34}+k_{43}$	$k_{23}\frac{K_1([\bar{M}]+[\bar{L}])}{1+K_1([\bar{M}]+[\bar{L}])}+k_{32}\frac{1}{1+K_3}$

* $K_1 = k_{12}/k_{21}$, $K_2 = k_{23}/k_{32}$, $K_3 = k_{34}/k_{43}$.

IV. THE APPLICATION OF THE TEMPERATURE JUMP METHOD IN THE STUDY OF COMPLEX FORMATION

Studies of the kinetics of complex formation carried out in the early stages of the development of the chemistry of complex compounds made possible an arbitrary division into inert and labile complexes.[68,69] For inert complexes, substitution takes place in minutes or longer, whereas for labile complexes the half-reaction time is much less than one second.[69] A very large number of labile complexes, formed by the ions of the alkali, alkaline earth, and transition metals with various inorganic and organic ligands, are now known.[3,70–77] The study of labile complexes has become possible only with the development of methods for studying fast reactions, in particular the temperature jump method.

A large number of studies have been devoted to complex formation between a hydrated metal ion $M^{m+}(aq)$ and a unidentate ligand $L^{n-}(aq)$. The most general scheme for a reaction of this kind is given below:[63–64]

$$\underset{(X)}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(XI)}{M^{m+}(aq)\,(aq)\,L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(XII)}{M^{m+}(aq)\,L^{n-}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{(XIII)}{ML^{(m-n)+}} \quad (41)$$

The initially solvated (hydrated) ions of the metal and the ligand, as a result of diffusion, form an encounter complex (XI), or an ion pair, in which the ions are separated from one another by not more than two monolayers of solvent molecules. The stage of ion pair formation is diffusion controlled, and therefore very fast. The rate constant k_{12} of the diffusion approach of the ions can be calculated from the expression[64,78]

$$k_{12} = \frac{4\pi Na}{1000}(D_+ + D_-)\left(\frac{\alpha}{e^\alpha - 1}\right)$$
$$\alpha = \frac{mne_0^2}{\varepsilon akT}\left(\frac{1}{1+\varkappa a}\right)$$
$$\varkappa = \left(\frac{8\pi e_0^2 NI}{1000\varepsilon kT}\right)^{1/2}$$

where D_+ and D_- are the diffusion coefficients of the cation and the anion, N Avogadro's number, a the distance of closest approach in the encounter complex; e_0 the charge of the electron, ε the dielectric constant of the medium, I the ionic strength, and k the Boltzmann constant.

The value of k_{12} for an encounter complex, for example with the 1:1 composition and $a = 0.7$ nm in an aqueous solution at $I = 0.01$ and 25 °C, is 1.1×10^{10} litre mole^{-1} s^{-1}.

The rate constant k_{21} for the diffusion separation of an encounter complex is given by the expression:[78,79]

$$k_{21} = \frac{3(D_+ + D_-)}{a^2}\frac{\alpha e^\alpha}{e^\alpha - 1}$$

The value of k_{21} for the same conditions is 6×10^9 s^{-1}.

The next stage (XI) ⇌ (XII) reflects the formation of the outer-sphere complex (XII), in which two ions are separated by only one monolayer of solvent molecules. Since the interaction between the ligand anion and the water molecule is weaker than that between the metal cation and the water molecule, the formation of the outer-sphere complex is accompanied by the loss of a water molecule from the hydration layer of the ligand. The stage (XI) ⇌ (XII) is also fast (k_{23}, $k_{32} \cong 10^8$–10^9 s^{-1}). The temperature jump method cannot distinguish stages (X) ⇌ (XI) and (XI) ⇌ (XII). Their existence follows from ultrasonic absorption data; three relaxation processes have been established for aqueous solutions of $CoSO_4$, $NiSO_4$, and $ZnSO_4$.[80]

The final stage (XII) ⇌ (XIII), that is the replacement of a water molecule from the inner coordination sphere of the metal ion by a molecule (ion) of the ligand, is the slowest stage, and gives the inner-sphere complex (XIII). Thus the stage (XII) ⇌ (XIII) is the limiting stage, and this makes it possible to simplify the reaction scheme (41) to the form given by scheme (21). The applicability of scheme (21) is confirmed by the experimental detection of two relaxation times. Thus the slow relaxation time is given by the expression

$$\tau^{-1} = K_1 k_{23}\frac{[\bar{M}]+[\bar{L}]}{1+K_1([\bar{M}]+[\bar{L}])} + k_{32}$$

which can be used to find the value of k_{32} and the product $K_1.k_{23}$. The values of the product $K_1.k_{23}$ obtained in this way for complex formation by Ni^{2+} with various unidentate ligands ($CH_3PO_4^{2-}$, CH_3COO^-, NCS^-, F^-, HF, NH_3, C_5H_5N, etc.) have been published.[73] If K_1 is known, the rate constant for the formation of the inner-sphere complex k_{23} can also be determined.

The equilibrium constant K_1 can be estimated from the expression[81,82]

$$K_1 = \frac{4\pi Na^3}{3000}e^{-\alpha} \quad (42)$$

For some reactions, independent estimates of the values of K_1 have been obtained from spectral, polarometric, NMR, and EPR measurements.[69,74,83] These estimates show fairly good agreement with the values calculated from Eqn. (42) (see

Table 4), if it is assumed that $a = 4-5$ Å, as in the estimation of the distance of the closest approach in an encounter complex.[74]

Table 4. Values of the equilibrium constant K_1 for the formation of the outer-sphere complex in the system $M(aq)^{m+} + L(aq)^{n-}$.

System	K_1, litre mole^{-1}	
	calculation	experiment
$Ni(H_2O)_6^{2+} + CH_3PO_4^{2-}$	14 [69]	4 (Refs. 84, 85)
$Ni(H_2O)_6^{2+} + NH_3$	0.15 [69]	0.15 (Ref. 69)
$Ni(H_2O)_6^{2+} + CH_3COO^-$	3 [73]	—
$Ni(H_2O)_6^{2+} + C_5H_5N$	0.15 [73]	—
$Cr(H_2O)_6^{3+} + Cl^-$	13 [75]	—

Thus the temperature jump method and other methods for studying fast reactions can be used to find the values of the rate constants for the formation and dissociation of an inner-sphere complex.

1. Complex Formation With Unidentate Ligands

The extensive experimental material obtained in the study of the mechanism of fast reactions of complex formation has made it possible to separate the metals studied into three groups, depending on the magnitude of the rate constant of the inner-sphere replacement of a water molecule for different metal aquo-ions.[72] Fig. 2 gives characteristic values of the rate constants for this reaction. The first group consists of the alkali and alkaline earth metals (Ca^{2+}, Sr^{2+}, and Ba^{2+}). For the ions of these metals, the value of the rate constant for the exchange of coordinated water is greater than 10^7 s^{-1}.[86] In this case the limiting stage of the reaction is the attack by the ligand, and the observed reaction rate constant for complex formation is close to the diffusion value.

Table 5 gives the values of the rate constant of the replacement of coordinated water for the aquo-ions of the alkali metals, and shows that the rate of replacement depends on the nature of the ligand. The difference in the rates of substitution observed in each series can be explained simply by the difference in the electrostatic potentials (that is the charge/size ratios) of the metal ions.

The ions Zn^{2+}, Cd^{2+}, and Hg^{2+} react at the same high rates as Ca^{2+} (Fig. 2), but the rates do not depend significantly on the nature of the ligand. Thus for example for the Zn^{2+} ion the rate constant k_{23} for the replacement of water by SO_4^{2-} is 3×10^7 s^{-1},[87,88] and is close to the value 3.2×10^7 s^{-1} corresponding to complex formation by Zn^{2+} with oxalic acid.[71]

The second group contains the ions Fe^{3+}, Al^{3+}, and Be^{2+}, for which the rate of the exchange of a water molecule from the inner coordination sphere of the metal ion is lower than the rate of hydrolysis. The following mechanism of complex formation has been proposed for these ions. After the formation of the outer-sphere complex, hydrolysis takes place, followed by the formation of the inner-sphere complex, involving attack by a protonated ligand molecule:[78]

$$Fe^{3+}(aq) + L^-(aq) \rightleftharpoons (H_2O)_5Fe^{3+}(H_2O)L^- \rightleftharpoons$$
$$\rightleftharpoons (H_2O)_5FeOH^{2+}HL \rightleftharpoons (H_2O)_5FeL^{2+} + H_2O$$

According to this mechanism, the rate of complex formation depends on the nature of the ligand, and in particular on its basic strength. The mechanism of complex formation by Fe^{3+} with various ligands has been confirmed by the pressure jump method[89] and other methods for studying fast reactions.[90–92]

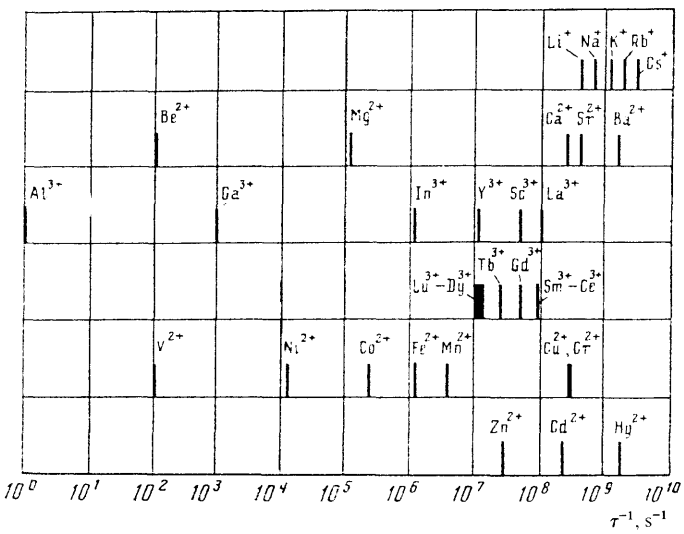


Figure 2. Characteristic rate constants (s^{-1}) of the inner-sphere replacement of a water molecule for various aquo-ions.[72]

Table 5. Values of the rate constants (10^{-7} τ^{-1}, s^{-1}) of substitution for alkali metal ions in water.[78]

Cation	$EDTA^{4-}$	NTA^{3-}	IDA^{2-}
Li^+	4.8	4.7	25
Na^+	4.7	8.8	25
K^+	7.5	15	—
Rb^+	14	23	—
Cs^+	21	35	—

Notation: NTA = nitrilotriacetate, IDA = iminodiacetate.

The third group consists of the ions of transition metals, and also metals of the main sub-groups of the periodic system, for which the rate constant for the exchange of coordinated water is less than 10^7 s^{-1}. A primary characteristic of these ions is that the rate constant for complex formation k_{eff} is practically independent of the nature of the ligand. Table 6 gives the values of k_{eff} obtained by the temperature jump method. A more complete summary of k_{eff} values obtained by other methods for studying fast reactions has been published.[74] The fact that k_{eff} is independent of the nature of the ligand is related to the fact that the limiting stage of the reaction is the removal of water molecules from the inner coordination sphere of the metal ion. The values of k_{eff} obtained experimentally and the values of K_1 calculated from Eqn. (42) can be used to determine k_{23}. For example, for complex formation by Ni^{2+} with CH_3COO^-, NH_3, and C_5H_5N,

$k_{23} = 3 \times 10^4$ s^{-1}.[73] On the other hand, the value of k_{23} practically coincides with the value of the rate constant for the exchange of coordinated water in metal aquo-ions.[74]

Table 6. Values of the rate constant k_{eff} for complex formation.

Metal ion	Ligand	lg k_{eff}, litre mole^{-1}s^{-1}	Refs.
Mg^{2+}	4,5-dihydroxybenzene-1,3-disulphonic acid	6.5	[93]
Mg^{2+}	8-quinolinol	5.5	[94]
V^{2+}	SCN^-	1.2	[95]
Fe^{2+}	SO_4^{2-}	3.6	[96]
Fe^{3+}	$Fe(CN)_6^{3-}$	3.2	[97]
Co^{2+}	SO_4^{2-}	5.3	[96]
Co^{2+}	NH_3	5.0	[98]
Co^{2+}	L-carnosine	5.6	[99]
Co^{2+}	α-alanine	5.8	[100]
Co^{2+}	β-alanine	4.8	[100]
Co^{2+}	4,5-dihydroxybenzene-1,3-disulphonic acid	6.0—6.6	[93]
Ni^{2+}	NH_3	3.2	[98]
Ni^{2+}	α-alanine	4.3	[100]
Ni^{2+}	α-aminobutyrate	4.0	[101]
Ni^{2+}	Murexide	3.5	[102]
$Ni(en)^{2+}$	NH_3	4.1	[103]
Cu^{2+}	L-carnosine	6.5	[104]
Cu^{2+}	Murexide	7.7	[105]
Zn^{2+}	Murexide	6.9	[105]
Cd^{2+}	pyridine-2-azodimethylaniline	7	[106]
Cd^{2+}	Murexide	8.1	[102]

Thus the results of kinetic measurements carried out chiefly by the temperature jump method, together with thermodynamic data (entropy and enthalpy of activation),[107] indicate that complex formation takes place by a dissociative mutual exchange mechanism (*Id* mechanism).[69,76] A large number of kinetic measurements have shown that the rate constant k_{23} depends markedly on the size and charge of the cation and other factors.[72] On the whole, the rate of replacement is lower, the greater the charge of the ion and the smaller its size. For example, the rate of complex formation by $Mg^{2+}(aq)$ with CrO_4^{2-}, ATP^{4-}, and ADP^{3-} is lower by 10^2—10^3 than that for $Ca^{2+}(aq)$.[72]

2. Complex Formation With Bidentate Ligands

The mechanism of complex formation by metal ions with bidentate ligands on the whole is analogous to the mechanism examined above for unidentate ligands. For bidentate ligands there is an additional stage of ring closure. The reaction scheme is given below:

$$\underset{\text{(XIV)}}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{(XV)}}{M^{m+}(aq)L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{(XVI)}}{M{-}L^{(m-n)+}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{\text{(XVII)}}{M{=}L^{(m-n)+}}$$

where the stages (XV) ⇌ (XVI) and (XVI) ⇌ (XVII) describe the formation of unidentate and bidentate inner-sphere complexes respectively. The last stage involves the replacement of a second water molecule from the inner coordination sphere of the metal ion and closure of the ring.

In complex formation involving a bidentate ligand, two cases are possible: 1) ring closure takes place at a higher rate than the formation of the encounter complex from the unidentate complex, that is $k_{34} \gg k_{32}$; this case corresponds to "normal" substitution;[73,100] 2) the stage of ring closure is slower, and is therefore the limiting stage in complex formation. These substitution reactions belong to the class of "sterically controlled" reactions.[100] The study of complex formation involving bidentate ligands by the temperature jump method has made it possible to observe two stages (two values of the relaxation time), corresponding to the replacement of two water molecules. Table 7 gives the values of the rate constants for different stages of complex formation by Ni^{2+} with various bidentate ligands.

Table 7. Rate constants for complex formation by Ni^{2+}.[73,108]

Aquo-ion	Ligand	K_1k_{23}, litre mole^{-1}s^{-1}	k_{32}, s^{-1}	k_{34}, s^{-1}	k_{43}, s^{-1}
$Ni(H_2O)_6^{2+}$	diaminoethylene	$4.0 \cdot 10^5$	$4.5 \cdot 10$	$9 \cdot 10^2$	$1.4 \cdot 10^{-1}$
$Ni(H_2O)_6^{2+}$	bipyridyl	$1.5 \cdot 10^3$	$4.5 \cdot 10$	$3 \cdot 10^3$	$3.4 \cdot 10^{-3}$
$Ni(H_2O)_6^{2+}$	maleate	$8.5 \cdot 10^5$	$3.5 \cdot 10^3$	$4.5 \cdot 10^3$	$1 \cdot 10^2$
$Ni(en)_2(H_2O)_6^{2+}$	diaminoethylene	$5.5 \cdot 10^6$	$1.2 \cdot 10^5$	$2.2 \cdot 10^5$	$8.7 \cdot 10$
$Ni(H_2O)_6^{2+}$	pyridine-2-azodimethyl-aniline	$1.5 \cdot 10^3$	$1.4 \cdot 10^4$	$2.9 \cdot 10^4$	$3 \cdot 10^{-1}$

An experimental criterion for distinguishing "normal" and "sterically controlled" substitution reactions is the magnitude of the volume of activation $\Delta V^{\neq}$.[109] Values of $\Delta V^{\neq}$ equal to 5—8 cm^3 mole^{-1} indicate that the reaction is a "normal" substitution reaction. For "sterically controlled" reactions, the values of $\Delta V^{\neq}$ are ~3 cm^3 mole^{-1}. The values of $\Delta V^{\neq}$ for complex formation by $Ni^{II}L$ with pyridine-2-azodimethylaniline (PAA) have been determined.[110] The measurements were made by the laser temperature jump method at pressures of up to 3 kbar. The reaction took place by the "normal" substitution mechanism when the ligand L was nitrilotriacetate, ethylenediaminediacetate, and diethylene-triamine, and by the "sterically controlled" reaction mechanism when L was 2,2',2''-triaminotriethylamine and triethylene-tetramine. The volumes of activation have also been determined for the reactions of Co^{II}, Cu^{II} and Zn^{II} with NH_3, PAA, glycinate, and Murexide.[77] In all cases the values of $\Delta V^{\neq}$ were positive, as is characteristic of the exchange-dissociative mechanism of complex formation.[17,109,111]

Convincing evidence in support of the "normal" substitution mechanism was obtained by complex formation by Ni^{2+} with PAA.[108,112] The laser photo-excitation method made it possible to observe directly the fast stage of five-membered ring closure.

In complex formation by Ni^{II} and Co^{II} with α-alanine, the limiting stage is the loss of the first water molecule from the inner coordination sphere of the metal ion, whereas for complex formation with β-alanine, the limiting stage is the ring closure.[113] The stage of ring closure probably also limits the rate of complex formation by the lanthanides of the cerium sub-group with the dye Xylenol Orange.[114] The values of the reaction rate constants given in Ref.114 are appreciably lower than the rate constants for the exchange of water in lanthanide ions.[74] It is suggested that the low rate of formation of the chelate compound compared with the rate of formation of the unidentate inner-sphere complex is related to the difficulty of the formation of six- and seven-membered chelate compounds.

Complex formation in micellar solutions has been studied.[115,116] For the reaction of Ni^{II} with PAA in the presence of sodium dodecylsulphate, the maximum reaction rate is achieved close to the critical micelle concentration, and the reaction takes place by an Id mechanism.

The ions of transition metals and other multivalent cations can form complexes with more than one ligand. On the whole, the rate of complex formation by a metal with a second and subsequent ligands is greater than that with the first ligand. Since the ligands are generally stronger electron donors than the water molecule, it follows that on complex formation with the first ligand, the effective charge of the metal cation is decreased, and the radius increases, and there is an overall increase in the exchange rate.[74]

The study of the kinetics of complex formation in non-aqueous media has established that reactions with unidentate ligands take place by an *Id* mechanism. For bidentate ligands, the organic solvent has a specific influence,[107] in that complex formation is either slower or faster than normal substitution in aqueous solutions. The study of the role of the solvent has shown that for bidentate ligands, for which in the case of the normal substitution reaction in water the relationship $k_{eff} = K_1k_{23}$ applies, the ratio k_{eff}/K_1k_{23} deviates considerably from unity. This deviation is due to the influence of the solvent on all three stages of complex formation represented by scheme (43). The nature of the solvent influences the stability of the outer-sphere complex and the orientation of the ligand in the outer sphere.[77] These factors are also influenced by ion–dipole interaction and the formation of H-bonds.[117] For example, the mechanism of the formation of $BeSO_4$ in a water–dimethyl sulphoxide mixture is much more complex than that in aqueous solution,[118] as indicated by the experimental observation of five values of the relaxation times.

---o0o---

Thus the temperature jump method has proved to be extremely promising for the study of the kinetics and mechanism of complex formation. The further development of experimental technique should create the conditions for the development of this method and its extensive introduction in the study of various types of chemical transformation, and the temperature jump method will occupy an important place among other physical methods for studying fast reactions.

REFERENCES

1. E.F.Caldin, "Fast Reactions in Solution" (Translated into Russian), Izd.Mir, Moscow, 1966.
2. G.G.Hammes, "Methods of Studying Fast Reactions" (Translated into Russian), Izd.Mir, Moscow, 1977.
3. L.I.Budarin and K.B.Yatsimirskii, Uspekhi Khim., 1968, **37**, 469 [Russian Chemical Reviews, 1968(3)].
4. D.M.Goodall and R.C.Greenhow, Chem.Phys.Letters, 1971, **9**, 583.
5. R.M.Reich and J.R.Sutter, Anal.Chem., 1977, **49**, 1081.
6. H.W.Hoffman, Pribory dlya Nauchn.Issled., 1971, **42**(11), 85.
7. D.Perschke, Pribory dlya Nauchn.Issled., 1976, **47** (11), 47.
8. F.M.Pohl, in "Chemical Relaxation in Molecular Biology", Springer, Berlin, 1977, p.282.
9. A.D.Yu, M.D.Waissbluth, and R.A.Grieger, Pribory dlya Nauchn.Issled., 1973, **44**(9), 248.
10. A.Jost, Ber.Bunsenges.Phys.Chem., 1974, **78**, 300.
11. R.Doss, R.Van Eldik, and H.Kelm, Pribory dlya Nauchn.Issled., 1982, **53**(10), 87.
12. P.Brumm and H.Rüppel, Z.Naturforsch., 1967, **22b**, 980.
13. K.J.Ivin, J.J.McGarvey, and E.L.Simmons, Trans. Faraday Soc., 1971, **67**, 97.
14. Y.Egozy and S.Weiss, J.Phys., E, Sci.Instrum., 1976, **9**, p.366.
15. J.Aubard, J.M.Nozeran, P.Levoir, J.J.Meyer, and J.E.Dubois, Pribory dlya Nauchn.Issled., 1979, **50**(1), 60.
16. E.F.Caldin, M.W.Grant, B.B.Hasinoff, and P.A. Tregloan, J.Phys.,E, Sci.Instrum., 1973, **6**, p.349.
17. E.F.Caldin, M.W.Grant, and B.B.Hasinoff, J.Chem. Soc., Faraday Trans.I, 1972, **68**, 2247.
18. H.Kaffer, Ber.Bunsenges.Phys.Chem., 1971, **75**, 1245.
19. T.Yasunaga, S.Harada, and K.Tamura, in "Chemical and Biological Applications of Relaxation Spectrometry", Reidel, Dordrecht, 1975, p.277.
20. J.T.Knudtson and E.M.Eyring, Ann.Rev.Phys.Chem., 1974, **25**, 255.
21. B.B.Hasinoff, Canad.J.Chem., 1979, **57**, 77.
22. J.E.Crooks and B.H.Robinson, Trans.Faraday Soc., 1970, **66**, 1436.
23. D.H.Turner, G.W.Flynn, N.Sutin, and J.V.Beitz, J.Amer.Chem.Soc., 1972, **94**, 1554.
24. G.W.Flynn and N.Sutin, in "Chemical and Biochemical Applications of Lasers, Acad.Press, New York, 1974, p.309.
25. T.G.Dewey and D.H.Turner, Adv.Mol.Relaxation and Interact.Processes, 1978, **13**, 331.
26. M.M.Farrow, N.Purdie, A.L.Cummings, W.Hermann (Jr.), and E.M.Eyring, in "Chemical and Biological Applications of Relaxation Spectrometry", Reidel, Dordrecht, 1975, p.69.
27. J.Aubard, J.J.Meyer, and J.E.Dubois, Chem. Instrum., 1977, **8**, 1.
28. J.Aubard, in "Protons and Ions Involved in Fast Dynamic Phenomena", Elsevier, Amsterdam, 1978, p.191.
29. J.Aubard, J.J.Meyer, J.M.Nozeran, and P.Levoir, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.41.
30. S.Ameen, Pribory Dlya Nauchn.Issled., 1975, **46**(9), 68.
31. S.Ameen and L.De Maeyer, J.Amer.Chem.Soc., 1975, **97**, 1590.
32. W.Inaoka, S.Harada, and T.Yasunaga, Bull.Chem. Soc.Japan, 1978, **51**, 1701.
33. C.Reiss, in "Lasers in Physical Chemistry and Biophysics", Elsevier, Amsterdam, 1975, p.239.
34. J.F.Holzwarth, A.Schmidt, H.Wolff, and R.Volk, J.Phys.Chem., 1977, **81**, 2300.
35. W.Frisch, A.Schmidt, J.F.Holzwarth, and R.Volk, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.61.
36. J.F.Holzwarth, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.47.
37. I.Giannini, in "Chemical and Biological Applications of Relaxation Spectrometry", Reidel, Dordrecht, 1975, p.53.
38. H.Strehlow and S.Kalarickal, Ber.Bunsenges.Phys. Chem., 1966, **70**, 169.
39. J.P.Keene, E.D.Black, and E.Hayon, Pribory dlya Nauchn.Issled., 1969, **40**(3), 70.
40. M.Eigen and L.De Maeyer, in "Technique of Organic Chemistry", Vol.8, Wiley, New York, 1963, p.895.
41. J.Muirhead-Gould and J.E.Stuehr, J.Phys.Chem., 1975, **79**, 2461.

42. J.A.Van Best and P.Mathis, Photochem.Photobiol., 1980, **31**, 89.
43. S.Claesson, B.Finnström, and J.E.Hunt, Chem. Scripta, 1975, **8**, 197.
44. L.H.Luthjens, Pribory dlya Nauchn.Issled., 1973, **44**(11), 114.
45. J.J.Meyer and J.Aubard, Pribory dlya Nauchn. Issled., 1977, **48**(6), 122.
46. B.W.Hodgson and J.P.Keene, Pribory dlya Nauchn. Issled., 1972, **43**(3), 135.
47. J.Keen, Int.J.Radiat.Phys.Chem., 1973, **5**, 463.
48. L.H.Luthjens and A.M.Schmidt, Pribory dlya Nauchn.Issled., 1973, **44**(5), 33.
49. P.Suppan, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.151.
50. A.N.Mogilevskii, V.A.Slavnyi, E.A.Afanas'ev, P.N.Astaf'ev, A.I.Subochev, P.N.Shishmanov, S.T.Kovachev, N.S.Koralov, and N.G.Uzunov, Nauchn.Pribory, 1975(7), 53.
51. G.Beck, Int.J.Radiat.Phys.Chem., 1969, 1, 361.
52. J.Lilie, J.Amer.Chem.Soc., 1979, **101**, 4417.
53. R.Rigler, C.R.Rabl, and T.M.Jouin, Pribory dlya Nauchn.Issled., 1974, **45**(4), 117.
54. G.M.Fleck, in "Chemical Reaction Mechanisms", Holt Rinehart, New York, 1971, p.66.
55. H.Strehlow and J.Jen, Chem.Instrum., 1971, **3**, 47.
56. J.E.Crooks, M.S.Zetter, and P.A.Tregloan, J.Phys., E, Sci., Instrum., 1970, **3**, 73.
57. F.Eggers, Nature, 1971, **229**, 89.
58. U.Strahm, R.C.Patel, and E.Matijevic, Talanta, 1980, **27**, 853.
59. M.Krizan and H.Strehlow, Chem.Instrum., 1973–1974 **5**, 99.
60. R.D.Dyson and I.Isenberg, Biochemistry, 1971, **10**, 3233.
61. L.M.Schwartz and R.I.Gelb, Anal.Chem., 1978, **50**, 1592.
62. L.M.Schwartz, Anal.Chem., 1981, **53**, 206.
63. C.F.Bernasconi, "Relaxation Kinetics", Acad.Press, New York, 1976.
64. H.Strehlow and W.Knoche, "Fundamentals of Chemical Relaxation", Verlag Chemie, Weinheim, 1977.
65. R.W.Taylor and D.B.Rorabacher, J.Phys.Chem., 1972, **76**, 452.
66. D.E.Tallman, G.Graf, T.J.McNeese and M.M.Wilson, J.Amer.Chem.Soc., 1975, **97**, 173.
67. V.I.Pogonin, E.A.Likhonina, S.B.Savvin, and A.K.Chibisov, Teor.Eksper.Khim., 1982, **18**, 507.
68. H.Taube, Chem.Rev., 1952, 50, 69.
69. R.G.Wilkins, "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Alleyn and Bacon, Boston, 1976, p.181.
70. M.Eigen, Pure Appl.Chem., 1963, **6**, 97.
71. M.Eigen, and R.G.Wilkins, in "Mechanisms of Inorganic Reactions, Adv.Chem.Ser.", 1965(49), p.55.
72. H.Diebler, M.Eigen, G.Ilgenfritz, G.Maass, and R.Winkler, Pure Appl.Chem., 1969, **20**, 93.
73. R.G.Wilkins, Acc.Chem.Res., 1970, **3**, 408.
74. D.J.Hewkin and R.H.Prince, Coordin.Chem.Rev., 1970, **5**, 45.
75. C.H.Langford, in "Ionic Interactions", Vol.2, Acad. Press, New York, 1971, p.2.
76. M.L.Tobe, "Inorganic Reaction Mechanisms" (Translated into Russian), Izd.Mir, Moscow, 1975.
77. E.F.Caldin, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.301.
78. S.Petrucci, in "Ionic Interactions", Vol.2, Acad. Press, New York, 1971, p.40.
79. M.Eigen, W.Kruse, G.Maass, and L.De Maeyer, in "Progress in Reaction Kinetics", Vol.2, Pergamon Press, Oxford, 1964, p.285.
80. K.Fritsch, C.J.Montrose, J.L.Hunter, and J.F.Dill, J.Chem.Phys., 1970, **52**, 2242.
81. R.M.Fuoss, J.Amer.Chem.Soc., 1958, **80**, 5059.
82. M.Eigen, Z.phys.Chem., 1954, **1**, 176.
83. S.Petrucci, in "Ionic Interactions", Vol.1, Acad. Press, New York, 1971, p.118.
84. R.G.Pearson and P.Ellgen, Inorg.Chem., 1967, **6**, 1379.
85. H.Brintzinger and G.G.Hammes, Inorg.Chem., 1966. **5**, 1286.
86. M.Eigen and G.Maass, Z.phys.Chem., 1966, **49**, 163.
87. F.Fittipaldi and S.Petrucci, J.Phys.Chem., 1967, **71**, 3414.
88. P.Hemmes, F.Fittipaldi, and S.Petrucci, Acustica, 1969, **21**, 228.
89. H.Wendt and H.Z.Strehlow, Elektrochem., 1962, **66**, 228.
90. D.Seewald and N.Sutin, Inorg.Chem., 1963, **2**, 643.
91. E.Moorhead and N.Sutin, Inorg.Chem., 1966, **5**, 1866.
92. D.W.Carlyle and J.H.Espenson, Inorg.Chem., 1967, **6**, 1370.
93. K.Kustin and K.O.Watkins, Inorg.Chem., 1964, **3**, 1706.
94. D.N.Hague and M.Eigen, Trans.Faraday Soc., 1966, **62**, 1236.
95. R.W.Kruse and D.Thusius, Inorg.Chem., 1968, **7**, 464.
96. F.P.Cavasino, J.Phys.Chem., 1968, **72**, 1378.
97. D.L.Singleton and J.H.Swinehart, Inorg.Chem., 1967, **6**, 1536.
98. D.B.Rorabacher, Inorg.Chem., 1966, **5**, 1891.
99. K.Kustin and R.F.Pasternack, J.Amer.Chem.Soc., 1968, **90**, 2805.
100. K.Kustin, R.F.Pasternack and E.M.Weinstock, J.Amer.Chem.Soc., 1966, **88**, 4610.
101. A.Kowalak, K.Kustin, R.F.Pasternack and S.Petrucci, J.Amer.Chem.Soc., 1967, **89**, 3126.
102. G.Geier, Helv.Chem.Acta, 1968, **51**, p.97.
103. D.W.Margerum and H.M.Rosen, J.Amer.Chem.Soc., 1967, **89**, 1088.
104. R.F.Pasternack and K.Kustin, J.Amer.Chem.Soc., 1968, **90**, 2295.
105. A.Bewick and P.M.Robertson, Trans.Faraday Soc., 1967, 63, 678.
106. R.G.Wilkins, Inorg.Chem., 1964, **3**, 520.
107. J.F.Coetzee, in "Protons and Ions Involved in Fast Dynamic Phenomena", Elsevier, Amsterdam, 1978, p.77.
108. B.H.Robinson and N.C.White, J.Chem.Soc., Faraday Trans. I, 1978, **74**, 2625.
109. M.W.Grant, J.Chem.Soc., Faraday Trans. I, 1973, **69**, 560.
110. M.W.Grant and C.J.Wilson, Faraday Trans. I, 1976, 72, 1362.
111. A.Jost, Ber.Bunsenges.phys.Chem., 1975, **79**, 850.
112. R.C.Greenwood, B.H.Robinson, and N.S.White, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.321.
113. E.M.Eyring and B.C.Bennion, Ann.Rev.Phys.Chem., 1968, **19**, 129.
114. K.B.Yatsimirskii and L.I.Budarin, Dokl.Akad.Nauk SSSR, 1968, **180**, 1383.

115. V.C.Reinsborough and B.H.Robinson, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.275.
116. P.D.I.Fletcher and B.H.Robinson, in "Techniques and Applications of Fast Reactions in Solution", Reidel, Dordrecht, 1979, p.283.
117. T.Takahashi and T.Koiso, Bull.Chem.Soc.Japan, 1980, **53**, 3400.
118. D.H.Devia and H.Strehlow, in "Techniques and Applications of Fast Reactions in Solution, Reidel, Dordrecht, 1979, p.329.

Vernadskii Institute of
Geochemistry and Analytical
Chemistry, Moscow.