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Fast Complexing Reactions

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I. INTRODUCTION

A division of metal complexes into "inert" and "labile" appeared very early in the development of the chemistry of complex compounds. The "inert" complexes included compounds of tervalent cobalt and chromium, the platinum metals, and certain others. These compounds are characterised by the slowness of their formation and breakdown; it was on these that the various types of isomerism and the important reactions of complexes were studied. Research on the kinetics and the mechanism of changes undergone by these compounds has been especially widely developed during recent years[1].

However, the so called "labile" complexes remained outside the scope of contemporary kinetic methods, and all reactions involving them were described as "instantaneous". There are considerably more "labile" than "inert" complexes, and the kinetics of complex formation thus covered a relatively small proportion of known reactions.

During recent years kinetic methods of investigation have appeared which enable reactions to be studied having a half-life period $t_{1/2}$† of 10^{-9} to 10 s,[2,3] i.e. over a considerably wider range (10^{10}) than for reactions occurring at the customary rates (10–10^4 s). With the appearance of these methods the reactions of the "labile" complexes became accessible to investigation. The first results obtained already show the promise of this branch of chemical kinetics.

Quite a large amount of experimental information has now accumulated on the kinetics of fast reactions. Two symposia have been devoted to these matters, the proceedings of which have been published in special issues of journals[4,5].

† The half-life period is the time during which half the initial concentration of a substance, a deficiency of which has been taken, is used up.

Methods of investigating fast reactions in solution and some of the available experimental information have been discussed in two large monographs[6,7]. There are good reviews of individual aspects of the kinetics of fast reactions[8-10] and reactions involving complex formation[11-15]. However, a sufficiently complete critical review of methods and experimental results on the kinetics of fast complexing reactions in solution is lacking. The present paper is intended to fill this gap.

II. EXPERIMENTAL METHODS OF STUDYING FAST COMPLEXING REACTIONS

All existing methods of investigating fast complexing reactions can be divided into a few large groups—flow methods, relaxation methods with step perturbation, relaxation methods with continuous perturbation, nuclear magnetic resonance (n.m.r.) and electron spin resonance (e.s.r.) methods, and electrochemical methods—which are compared in Table 1.

Table 1. Characteristics of methods for studying fast complex-forming reactions.

Methods	Limits of applicability, (time, s)		Soln.vol. for a kinetic curve
	min.	max.	
Classical methods	10	10^5	0.1—10 ml
Flow methods	10^{-4}	10	0.1 ml — 2 litres
Relaxation methods			
(*a*) step methods	10^{-7}	1	0.1—10 ml
(*b*) ultrasonic absorption	10^{-7}	10^{-4}	0.2—100 litres
Nuclear magnetic resonance	10^{-9}	10^{-1}	0.1—1 ml
Electrochemical methods	10^{-6}	1.0	1 ml

Flow methods, which are widely employed in studying reactions having half-life periods from 0.001 to 10 s, are the simplest from the point of view of apparatus, and are the only methods which enable kinetic curves for the processes to be obtained directly.

1. Flow Methods

The characteristic feature of flow methods is that solutions of the reactants are fed continuously to a special mixer, after which the reaction solution, in the form of a homogeneous, constant-velocity stream, enters an observation tube.

The course of the reaction can be followed firstly by using some physicochemical method to measure the reactant concentrations along the observation tube, in which the flow speed of the reactants is constant throughout the time of the measurements. In this case the distance from the mixer to the point at which the variation in reactant concentrations is recorded is proportional to the time which has elapsed from the start of the reaction to the instant of observation. Secondly, by halting the flow abruptly, we can use a suitable transducer and a rapid-acting device to record the variation in reactant concentrations, after the flow has been stopped, at any point in the observation tube. These two methods of measurement are termed the "constant-flow method" and the "stopped-flow method" respectively.

There are also a few methods which possess elements of both constant-flow and stopped-flow methods. Among these we have arbitrarily included accelerated-flow and quenching methods in the first group, and the method of removable partitions in the second.

The most crucial unit in the flow apparatus is the mixer. The design of the mixer determines the time of mixing of the reactant solutions, which determines the lower time limit of the flow apparatus [16,17], since the time of mixing must be much shorter than the half-life period of the reaction.

Among known designs, relatively simple mixers are most often used, with the solutions fed tangentially, these being employed for the study of reactions in which $t_{1/2} \geqslant 10^{-3}$ s. This is probably the limiting time for such mixers [16,18], since they have a special mixing chamber, preceding the observation tube. The presence of this chamber makes it impossible to define the instant of complete mixing. For the study of more rapid reactions, promise is shown by mixers having more than one channel for introduction of the reactant solutions, the minimum time of mixing being 10^{-4} s. [19]

Kletinik [18], by using a special bellows-type mixer, was able to shorten this time to 5×10^{-5} s. The disadvantage of this mixer is that it is made of metal foil, which may affect the kinetics of the reaction under investigation.

The functioning of the mixer can be tested in several ways [7]. The "chemical" method consists in determining the completeness and time of mixing of the reactant solutions in the mixer by means of a very fast chemical reaction, e.g.

$$H^+ + OH^- \rightleftarrows H_2O, \quad (1)$$

$$I_2 + 2S_2O_3^{2-} \rightleftarrows S_4O_6^{2-} + 2I^-. \quad (2)$$

In the "physical" method liquids differing in refractive index are mixed. In both cases the flow of solution should be homogeneous throughout the length of the observation tube following the mixer. A test method which uses a standard reaction is widely used, and is the most reliable of existing methods. The reaction chosen as standard is very often [6,7]

$$H_2CO_3 \rightleftarrows CO_2 + H_2O. \quad (3)$$

(*a*) Constant-flow methods. With constant-flow apparatus the solution, after leaving the mixer, enters the observation tube at a constant rate. The time t_n (in seconds) required for the liquid to reach a plane n crossing the observation tube is then given by the equation [18]

$$t_n = \frac{l_n}{R} \quad (4)$$

where R (mm s^{-1}) is the flow speed, while l_n (mm) is the distance from the plane of mixing to the point of observation, and the time elapsed after mixing is proportional to the length of the observation tube. With a known flow speed R, it is possible to determine the time from the start of the reaction to the instant of observation at the points n. By measuring the reactant concentration at these points by some physical method, we can obtain the kinetic curve for the given reaction.

The minimum time of reaction which can still be recorded on a constant-flow apparatus will depend on the design of the mixer and the rate of flow in the observation tube, but increasing the flow speed above 10 m s^{-1} may result in cavitation [20].

The solutions can be supplied to the mixer either by gravity feed [21], by means of compressed gas [22-24], or by means of syringes [25].

Among physical methods for recording the variation in concentration in the observation tube, spectrophotometric methods are most often employed [26-30].

In the simplest types of apparatus, light filters are used as monochromators, while the sensors are photocells connected to a measuring instrument, usually a galvanometer [26-30]. Such instruments are usually of low sensitivity and small resolution. The variation in light absorption along the observation tube is recorded from the galvanometer readings, which results in diminished accuracy, increased time of measurement, and hence considerable consumption of the reactant solutions. With the use of monochromators of greater dispersion, flow apparatus having spectrophotometric recording is employed for the study of complicated chemical reactions. Thus with a Beckman spectrophotometer as monochromator it was possible to establish that at least six different processes occurred in the oxidation of sulphurous acid by iodine [32,33].

A double-beam apparatus has been described [34]. The most perfect instrument of this type has been described in Ref. 25. Its distinguishing feature is that the absorption spectra of the test solution at definite points in the observation tube are recorded by means of a monochromator and a photomultiplier, the latter connected to an electronic oscillograph, the screen of which can be photographed with a high-speed cine-camera. If spectrophotometric methods are to be applied, of course, the light absorption of the test solutions must change in the course of the reaction. This somewhat restricts the use of such apparatus.

Great versatility is shown by apparatus having thermometric transducers, which are moved inside the observation tube by means of a special device or—what is not as good—are fixed in the tube, when a certain relation must exist between the size of the transducer and the internal diameter of the tube [17]. The sensitivity of instruments in which the thermocouple current is not amplified is very

low, so that only reactions whose heat of reaction exceeds 20 kcal mole^{-1} can be studied with such apparatus. Their sensitivity can be considerably improved by using thermistors[35-39] or d.c. photoelectric amplifiers[40] as transducers. An apparatus of this type described by Perlmutter-Hayman[41] has enhanced sensitivity, is convenient in operation, and requires a relatively small quantity of reactant solutions.

Reactant concentrations in the observation tube can be determined also from conductivity measurements[18,22-24,42], potentiometrically[43-45], and by the n.m.r. method[46,47]. This last method is very promising for the study of complicated chemical reactions, since it permits the unambiguous identification of many intermediate products and changes occurring in the reactant molecules or ions.

The accelerated-flow and quenching methods can be included in the constant-flow method. In the former[48,49] the transducers are fixed at a certain point in the observation tube, whereas the flow speed changes during observation. Both the variation in the flow speed and that of the reactant concentrations with time are recorded oscillographically. The results can be used to plot a kinetic curve for the process. Considerably less solution is required to determine the kinetic curve in the accelerated-flow method than in the other constant-flow methods.

In the quenching method[50-55] the solution of the reactants, after leaving the mixer and flowing through the observation tube, is rapidly mixed with a "stop solution". Ordinary analytical methods are used to determine, in the reaction mixture "frozen" in this way, the change occurring in the reactant concentrations during the time required for the reactant solution to pass from the first to the second mixer, where this solution is mixed with the "stop solution". This time is governed by the dimensions of the tube and by the flow speed.

The apparatus for the quenching method is very simple, while the reactant concentrations can be determined by ordinary analytical methods (gravimetrically or by titration) with great accuracy. The quenching method is widely used for the study of intermediate products, and also in investigating various exchange reactions.

(*b*) Stopped-flow methods. Whereas about a litre of reactant solution is required to plot the kinetic curve when constant-flow apparatus is used, stopped-flow apparatus requires only a few tenths of a millilitre of the reactant solutions for this purpose, and the whole kinetic curve can be obtained from a single experiment. This considerably facilitates working with expensive, rare reagents, but more complicated apparatus is employed in the stopped-flow method.

In such apparatus[56] the rapid flow of reactant solutions is abruptly halted at a certain instant. At the same instant a recording device, connected to a transducer fixed in the observation tube near the mixer, registers the time variation of the reactant concentrations in the halted stream. The reactant solutions are fed to the mixer and the observation tube from syringes, whose pistons are interconnected and are moved by hand, a spring, or an electric motor.

The stream is halted either by abruptly stopping the syringe pistons or by means of special valves following the observation tube[57,58]. The last method is the most reliable, since it excludes entry of solution into the observation tube after the flow has been stopped, e.g. because of possibly play in the mechanical system feeding the solutions.

In all the forms of apparatus described in the literature the kinetic curve is recorded on an oscillograph, triggered either by means of a special photoelectric device[57] or by electromechanical means. The variation in concentration of the reactant solutions is recorded photoelectrically[57-61]. The most perfect apparatus operating by the stopped-flow method with spectrophotometric recording has been described by DeSa and Gibson[62]. Using a double-beam spectrophotometric arrangement with modulated light flux, these workers considerably improved the sensitivity (to 10^{-3} unit of optical density) and lowered the noise level.

The electrical-conductivity[60] and potentiometric[40-42] methods are seldom used in stopped-flow apparatus. Thermometric transducers are not employed here because of their great inertia. However, fine-wire thermocouples[63], having considerably less inertia, can be used in this type of apparatus.

Among these methods can be included the removable partition method, proposed by Connick and his coworkers[64,65] for studying the kinetics of reactions occurring in very dilute solutions, since in this case long cuvettes can be used for observation. As in the stopped-flow method, the solutions are rapidly mixed and the reaction is followed oscillographically, but the removable-partition method differs greatly in the mode of mixing and the construction of the cuvette for observation by the stopped-flow method.

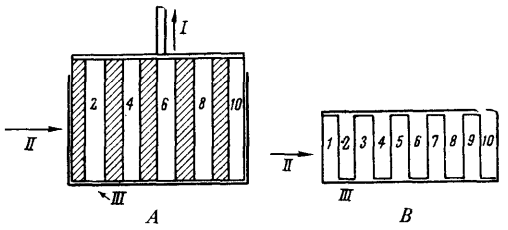


Figure 1. Diagram of cuvette for removable-partition method: *A*) side-view; *B*) plan; *I*) direction of movement of partition by action of spring; *II*) direction of observation; *III*) body of cuvette; *1, 2, 3, 4, ...*) compartments of cuvette.

The cuvette illustrated in Fig. 1 has a movable partition dividing the whole cuvette into a series of compartments (ten in the illustration), with one reactant solution in the even compartments, and the other in the odd compartments. This partition can be removed (upwards in the diagram) by means of a spring, and then the solutions in the isolated compartments will rapidly mix (within 10^{-3} s) and the variation in light absorption of the test solution will be recorded on an oscillograph.

Table 2 gives brief technical characteristics of the types of apparatus designed for the study of fast chemical reactions by flow methods. It is seen that these methods are suitable for reactions having half-reaction times of 10^{-4} to 1 s.

There is little prospect of constructing new mixers and increasing the flow speed to shorten the lower time limit for flow apparatus.

The use of non-aqueous solvents and lowering the temperature of the reactant solutions[66,67] permits the study of reactions which are very fast at 25°C (having rate constants of $\sim 10^6$ M s^{-1}) by existing flow techniques.

A very interesting possibility is the use of magnetic recording instead of photographing oscillograms, which is used to obtain kinetic curves in existing apparatus operating by the stopped-flow method[68].

In the study (by the stopped-flow method) of complicated reactions involving coloured substances, great opportunities are offered by high-speed spectrophotometric instruments, which enable the spectra of substances taking part in processes occurring within 10^{-6} s to be photographed[69].

Table 2. Characteristics of flow methods.

Methods	Limiting time × 10^3, s	Soln. for a kinetic curve, ml	Temp. range, °C	Absorbing layer, mm	Material of mixer	Measurement of concn.
Constant-flow methods	0.1-1		0-50	1-5	glass, plastic, brass	spectrophotometric, conductivity, heat effect
(*a*) Visual readings		500-2000				
(*b*) Automatic recording		6-100				
Accelerated flow	1.0	0.1	10-30	2	plastic	colorimetric
Quenching	10	100	10-50		plastic, glass	any analytical method
Stopped flow	2-5	0.1-1.0	-120 + 40	1-10	glass, plastic	colorimetric, spectrophotometric, potentiometric, conductivity
Removable partitions	15	30	14-30	50	steel	colorimetric

Flow methods (especially the stopped-flow method) are widely used to study the kinetics of fast complexing reactions. Reactions involving the ions of copper[70], iron[71,72], and nickel[73] have been studied in especial detail by these methods.

Among methods for measuring concentrations, the spectrophotometric method has become the most widely used, being the simplest but sufficiently widely applicable and sensitive.

Complex formation is mostly studied in the presence of a large excess of foreign electrolytes, which makes it difficult to use conductivity measurements to determine the reactant concentrations, since existing instruments permit the kinetic curve of a reaction to be recorded only if the change in conductivity occurring during the reaction exceeds 10%. With the use of special amplifiers[74], however, this limit has been lowered to 0.1%, which has enabled the complexing reaction

$$Be^{2+} + HF \rightleftarrows BeF^{+} + H^{+} \qquad (5)$$

to be studied in 0.2 M potassium chloride solution. This opens up wide prospects for the study of various complexing reactions, especially those which are not accompanied by a change in light absorption.

Concluding this survey of flow methods, we must note that these methods can be applied to the study of chemical reactions having $t_{1/2} > 10^{-4}$ s.

Apparatus having a constant flow and electrometric transducers is most simply constructed. For the study of multistage reactions involving coloured substances, more complicated spectrophotometric recording is most often employed, enabling the kinetics of conversion of any of the coloured substances involved in the reaction to be studied directly.

If, however, it is necessary to work with a small consumption of reactants, more complicated apparatus is used, operating by the stopped-flow method, which has the same characteristics as constant-flow instruments, but requires less than 1 ml of reactant solutions for the determination of one kinetic curve.

2. Relaxation Methods

At the present time only relaxation methods permit direct observation of the course of chemical reactions occurring in times less than 10^{-4} s, which considerably facilitates the study of multistage processes of complex formation, such as, for example[75],

$$Co^{2+} + gly \rightleftarrows [Co(gly)]^{+}, \qquad (6)$$

$$[Co(gly)]^{+} + gly^{-} \rightleftarrows [Co(gly)_2], \qquad (7)$$

$$[Co(gly)_2] + gly^{-} \rightleftarrows [Co(gly)_3]^{-}. \qquad (8)$$

(gly = the glycine ion)

A serious limitation of these methods is that they are applicable only to equilibrium processes when the equilibrium has not been displaced too far in the direction of formation of the reaction products.

In relaxation methods a system in a state of dynamic equilibrium is by some means brought out of this equilibrium. After cessation of the disturbing action, a process tending to re-establish the original equilibrium begins in the system. This process is termed relaxation. Relaxation curves are described by the equation

$$I = I_0 e^{-\frac{t}{\tau}}, \qquad (9)$$

where I_0 and I are parameters, which vary linearly with the concentration of an indicator substance, at times t_0 and t respectively, and τ is the relaxation time, which defines the rate of relaxation and is given numerically by the time required for I_0 to change by a factor e. The chemical equilibrium can be disturbed by varying certain physical parameters, such as temperature, pressure, electric field strength, etc.

The relaxation resulting from chemical processes is usually recorded from the variation in the light absorption or the electrical conductivity of the test solution.

With the relaxation time τ known, we can use the mathematical procedure suggested by Eigen[76-79] to calculate the rate constant of the processes under investigation. Thus for a reaction of the type

$$AB \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + B \qquad (10)$$

for example, the relaxation time is given by the equation

$$\tau^{-1} = (k_1 + 2k_{-1}X_e) \qquad (11)$$

where k_1 and k_{-1} are the rate constants of forward and reverse reactions respectively, and X_e is the equilibrium concentration of the species A and B, provided that [A] = [B].

If the equilibrium constant of (10) is unknown, k_1 and k_{-1} can be determined from the dependence of τ on the concentration of the species AB. When the equilibrium constant

is known, the rate constant k_1 is calculated for the same cases by means of the equation‡

$$k_1 = [\tau[A] + [B] + K]^{-1} \quad . \qquad (12)$$

Here [A] and [B] are the equilibrium concentrations of the species A and B, and K is the equilibrium constant corresponding to Eqn. (10). Equation (12) is valid provided that the concentrations [A] and [B] differ at most by a factor of 100. The rate constant k_{-1} for formation of AB is calculated from the equation

$$k_{-1} = \frac{k_1}{K} \quad . \qquad (13)$$

Relaxation methods can be divided into two groups—involving step and continuous perturbation—according to the mode of varying the physical parameters disturbing the chemical equilibrium. The first group includes methods involving abrupt changes in electric field strength, pressure, or temperature, as well as the abrupt change of concentration suggested recently[80].

A. Methods Involving Step Perturbation

(*a*) Temperature-jump method. This method is mostly widely used and widely applicable of the relaxation methods described in the literature. It can be employed for equilibrium reactions which are accompanied by a thermal change. The temperature variation of the equilibrium constant K is given by the equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT} \qquad (14)$$

where T is the temperature and ΔH the heat of reaction. Relaxation curves are recorded oscillographically from the variation in the light absorption or the electrical conductivity of the solutions.

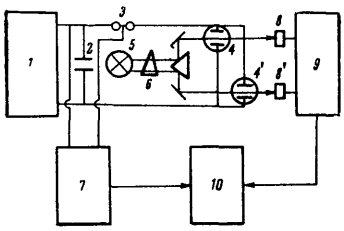


Figure 2. Diagram of apparatus for studying the kinetics of chemical reactions by the temperature-jump method.

For ionic solutions a jump in temperature is achieved by means of a pulse discharge from a capacitor charged to a high voltage[79,81-83]. Fig. 2 shows a simplified diagram of the forms of apparatus used, proposed by Eigen and his collaborators. A high-voltage current source *1* charges the condenser *2* of capacitance 0.1 μF to a voltage at which discharge takes place across the spark gap *3* and through cuvettes containing the test solution *4* and the reference solution *4'*. Platinum electrodes are inserted into the cuvette containing the test solution, of volume 50 ml, in such a way that ~ 1 ml of the test solution lies between them. During the high-voltage discharge, which lasts a few microseconds, the solution between the electrodes is heated by approximately 10 deg. The relaxation curves are recorded by means of a photocolorimetric device consisting of a light source *5*, a monochromator *6*, and photomultipliers *8* and *8'* connected differentially. The amplifier *9* is connected to an electronic oscillograph *10*, triggered by the release device *7*. The rate constant of the processes which occur can be calculated from the variation in optical density of the solution during relaxation[6,7].

It is very important that the duration of the pulses should approximate to the relaxation time. If the duration θ of a pulse differs markedly from the relaxation time of the process under investigation, the error involved in the measurements is considerably increased. The way in which the ratio τ/θ affects the character of the relaxation observed is shown in Fig. 3.

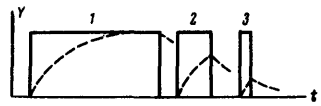


Figure 3. Variation in relaxation signal (broken curve) for periodic pulses (pulse signal represented by full line)—where Y is the magnitude of the signal and t is the time—as a function of the ratio of the duration of the pulse to the relaxation time (θ/τ):
1) 4; *2*) 1; *3*) 0.25.

In apparatus intended for the kinetic study of fast chemical reactions using a temperature jump produced by the discharge of a capacitor (as e.g. in the above apparatus of Eigen's), it is very difficult to vary the duration of the pulse or control its amplitude. An apparatus[84] in which the solution is heated by a powerful high-frequency pulse taken from a magnetron oscillator is free from this defect. This apparatus can be used also to study reactions occurring in non-ionic solutions, where the Eigen method is inapplicable. A periodic temperature-jump apparatus was constructed using repeated high-frequency pulses to heat the test solution[85], which both increased the output of the investigator and improved the reliability of the results, but unfortunately the size of the jump obtainable was small (~ 1 deg).

Equipment combining the flow method with the temperature-jump method is very promising for the study of complicated multistage reactions and also fast irreversible processes[86,87].

(*b*) Electric field-pulse methods. The electrical conductivity of a weak electrolyte increases with increase in the electric field strength. This phenomenon has been termed the Second Wien effect[88]. It is explained by a shift in the equilibrium—weak electrolyte molecule-ion-pairs-free ions—towards formation of free ions.

‡ It would seem that this equation should read

$$k_1 = K\tau^{-1}([A] + [B] + K)^{-1}$$

(Ed. of Translation).

The increase in conductivity is proportional to the applied voltage between 40 and 100 kV cm^{-1}. The total increase may reach 10% of the conductivity in the absence of an electric field. The magnitude of the change is given by the equation[89]

$$\frac{\Delta\lambda}{\lambda_0} \equiv \frac{\lambda_x - \lambda_0}{\lambda_0} = \frac{1-\alpha}{2-\alpha} \cdot b\Delta E \qquad (15)$$

where λ_x and λ_0 are the conductivities of the solution in a field of strength x and in zero field, $\alpha = c_i/c_0$ is the degree of dissociation under the influence of the field, c_i being the concentration of ions formed under the action of the field and c_0 the total concentration of the weak electrolyte, E is the strength of the field, and b is a parameter depending on the mobility of the ions, the absolute dielectric constant, and the temperature.

The electric field–pulse method was first used by Eigen and his coworkers in studying the kinetics of the reaction[76,90-92]

$$H^+ + OH^- \rightleftarrows H_2O. \qquad (16)$$

Relaxation curves are mostly recorded from the variation in conductivity, and the experimental results obtained are processed by the usual methods described previously.

(*c*) Pressure-shock methods. The effect of pressure on the equilibrium constant is represented by the equation[9]

$$\beta = \exp\left[\int_{P_1}^{P_2} (\partial \ln K/\partial P)_s dP\right] = \exp\left[\int_{P_1}^{P_2} \frac{-\Delta V^0 + \Delta H^0 (\partial V/\partial T)_p C_p}{RT} dP\right] \qquad (17)$$

where ΔV^0 and ΔH^0 are the changes in volume and enthalpy, and $\beta = K_2/K_1$, in which K_2 and K_1 are respectively the equilibrium constant at $P = P_2$ and $P = P_1$: a change in pressure thus produces a change in the equilibrium constant, as a consequence of which relaxation processes occur at a rate determined by that of the chemical reactions involved[93-95].

The magnitude of the shift β is 0.004 with $\Delta V^0 = 1$ cm^3 $mole^{-1}$ and a change in pressure from 1 to 100 atm[96]. This shift can be easily recorded by various physicochemical methods.

The types of apparatus used in this method differ both in the way in which the pressure is changed and in the method adopted to measure the reactant concentrations during the relaxation process.

The pressure can be changed by opening a special tap connecting an autoclave to a cylinder containing compressed gas[96]. Since this tap is opened manually, reactions having a half-period exceeding 0.1 s can be studied with such apparatus.

A more modern method of producing a pressure shock[97] consists in rapidly puncturing with a special steel needle a thin steel diaphragm fitted in the system connecting the compressed-gas cylinder with the autoclave containing the test solution. As a result, the pressure in the autoclave drops sharply (within 10^{-5} s). As the workers who have used this method state, reactions can be studied having $t_{1/2} > 10^{-5}$ s.

In all the types of apparatus described, the reactant concentrations are determined either from conductivity measurements or spectrophotometrically.

The great advantage of the pressure shock method is the possibility of studying directly conversions of outer-sphere into inner-sphere complexes and conversely, which is impossible by any other method with the exception of n.m.r.

B. Methods Involving Periodic Perturbation

Fast chemical reactions can be studied not only by pulse methods but also by methods involving a periodic action. Among these, ultrasonic absorption and nuclear magnetic resonance have become the most widely used.

(*a*) Ultrasonic absorption. By means of ultrasonic vibrations it is possible to study chemical reactions whose duration approximates to the period of the sound wave. The frequency dependence of the absorption of sound is influenced by the changes in free energy, entropy, and volume occurring during the reaction, and also by the rates of the chemical reactions taking place in the system[98-101], so that both kinetic and thermodynamic data can be obtained by studying the ultrasonic absorption of the test solution[89,102].

For single-stage reactions the ultrasonic absorption–frequency curve passes through a maximum, the position of which can be used to determine the relaxation time, and from which the reaction rate constant can be calculated by means of Eqns. (11) and (12). With multistage reactions the mathematical processing of the experimental results is considerably more complicated[103,104]. There exists a method of calculation which is applicable only to a two-step process[105,106].

The equipment used in the study of fast chemical reactions by the acoustic method is that usually employed for measuring the velocity and absorption of ultrasound in liquids[60,107,108]. The disadvantages of this method include the relative complexity of the apparatus used, the difficulties of processing the experimental results for complicated reactions, and also the large quantities of solutions necessary for an experiment.

(*b*) Nuclear magnetic resonance. The n.m.r. method is applicable to the kinetic study of chemical reactions occurring at very varied rates. The essence of the method is that, if an atomic nucleus possessing a magnetic moment is placed in a homogeneous magnetic field, its energy levels will be split, and energy quanta may be absorbed or emitted on transition of the nucleus from one split level to another. The magnitude of this splitting will depend on the degree of nuclear screening, which is determined by the nature of the chemical compound formed. Reactions occurring at normal rates can be studied from the time variation in the intensity of the absorption band, while the change in shape of the absorption bands, in particular their broadening, will provide information on the kinetics of reactions which are 50% complete in 10^{-8} s.

Details of the apparatus employed in n.m.r. investigations of fast reactions and of methods of calculating rate constants from experimental results can be found in numerous monographs and reviews on this topic[6,7,104,109-114].

The n.m.r. method has found especially wide use in the study of fast exchange reactions. This requires that the parameters of these n.m.r. absorption bands should be known for the compounds in the absence of exchange. Such data can be obtained, for example, by determining the n.m.r. spectra of the pure compounds. In the case of rapid exchange, the absorption bands of the individual compounds become wider, and at a certain rate they merge into a single broad band, which gradually narrows with increase in the rate of exchange.

The coalescence of absorption bands with rapid exchange can be explained by means of the uncertainty principle,

which in the present case can be written in the form

$$\tau \Delta\nu \approx {}^1/_2\pi , \qquad (18)$$

where $\Delta\nu$ is the distance (in cm^{-1}) between the resonance signals and τ is the shortest time in which these signals still exist separately.

From the shape of the band observed and also its broadening compared with the bands of individual compounds, the rate of exchange can be found [104].

To obtain more accurate data, and also to determine the order of the reactions, the exchange velocity is increased, by altering certain parameters (temperature, catalyst concentration), until the absorption band maxima corresponding to the different chemical shifts coalesce. The rate constant of the reaction is determined from the position and shape of the resulting band, and the order of the reaction is found from the dependence of the broadening $\Delta\nu$ of the band on the variable parameter P. Four cases can be distinguished [115,116] according to the nature of the dependence (Fig. 4).

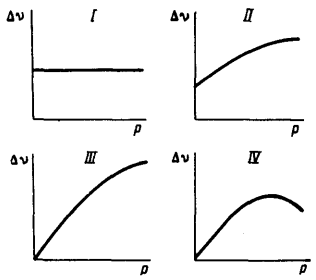


Figure 4. Dependence of $\Delta\nu$ on a parameter P for various types of chemical reactions.

With the type of dependence of $\Delta\nu$ on the parameter P represented by case I (Fig. 4), exchange is very slow. Only "outer-sphere relaxation" occurs, when species in the outer sphere take part in the relaxation process [117]. This type of relationship is observed, for example, with the ethylenediamine complexes of nickel.

In case II the curve obtained does not start from zero, as is possible when first-order and second-order reactions are occurring simultaneously in the system. This relationship can be used to calculate the rate constants of both reactions, as has been done [115] for the glycine complexes of tervalent cobalt and iron.

Case III corresponds to second-order reactions, whereas case IV is observed when variation in the parameter P is accompanied by variation in the concentration of species which make different contributions to the broadening of the absorption band. Case IV is observed with many compounds of bivalent copper [115].

The possibilities of the n.m.r. method in the study of complicated reactions can be considerably extended by using it with flow apparatus [46].

It must be noted that the n.m.r. method is applicable (when the change in shape of absorption bands is used to determine the rate constant) only for the study of very fast reactions of complex formation (having $t_{1/2} < 10^{-4}$ s) in equilibrium systems involving elements whose nuclei have spins differing from zero.

C. Electrochemical Methods

A group of phenomena are known in polarography in which the main electrochemical process of reduction of the depolariser is preceded by chemical reactions occurring in the layer adjacent to the electrode, as a result of which either depolariser is regenerated or it is formed from compounds which are not reduced under the given conditions. As a result of these processes polarographic currents arise which are different in nature from diffusion currents [118], and are termed catalytic or kinetic currents. The magnitude of both catalytic and kinetic currents will depend on many factors, in particular the rate of the chemical reactions associated with the electrochemical process [119,120].

For coupled processes of the type

$$M^{n+} + L \rightleftarrows ML^{n+} , \qquad (19)$$

$$ML^{n+} + me = ML^{(n-m)+} \text{ (on the electrode)} . \qquad (20)$$

Brdička and Wiesner [119] deduced the approximate equation

$$\mu k_1 = \frac{i_{cat}}{nFq10^3 C_M (aC_L - i_{cat})} \qquad (21)$$

linking the strength of the catalytic current with the rate constant k_1 of reaction (19), in which n is the number of electrons involved in the electrochemical process, F is Faraday's constant, q is the mean surface area of the mercury drop, i_{cat} is the maximum catalytic current (in μA), $a = 605nD_L^{1/2}m^{2/3}t^{1/6} \times 10^3$ is the Ilkovič constant, and μ is the thickness of the layer adjacent to the electrode, in which chemical reaction occurs.

For analogous chemical reactions Koutecký [120] linked the rate constant of the chemical reaction with the catalytic (kinetic) current by the more accurate equation

$$\frac{i_{kin}}{i_{diff}} = \frac{0.886\,[(k_1/K)\,t]^{1/2}M}{1+0.886\,[(k_1/K)\,t]^{1/2}M} - \frac{11D^{1/2}m^{-1/3}t^{1/6}(k_1t/K)^{1/2}M^{1/2}}{1+0.14\,(k_1t/K)\,M^2} , \qquad (22)$$

where i_{kin} is the kinetic current, i_{diff} is the diffusion current, $K = k_2/k_1$ is the equilibrium constant of (19), with k_1 the rate constant for formation of the complex ML^{n+} and k_2 the rate constant for dissociation of this complex, m (in mg s^{-1}) is the mercury drop rate, t (s) is the lifetime of a drop,

$$D = (D_M + KD_L)(1 + K) \text{ and } M = (D/D_L)(D_M/D_L)^{1/2}$$

in which D_M and D_L are the diffusion coefficients of the metal ion and the ligand respectively. Equation (22) holds provided that $K \gg 1$ and $(k_1 + k_2)t \gg 1$, i.e. for relatively fast reactions. Tabulated values of the function (22), found by Koutecký and Čižek [121], can be used to calculate the rate constant of reaction (19) from experimental data.

Rate constants of simple chemical reactions of the first and second order can be calculated in a similar manner. If, however, the reaction taking place in the reaction layer is complicated or of order higher than the second, it is difficult to use electrochemical methods to determine the rate constants of fast reactions. Furthermore, the results obtained have poor reproducibility, and require a large excess of the ligand and of foreign substances.

D. Other Methods

Besides the above methods, fast chemical reactions in solution are studied also by concentration relaxation [80],

flash photolysis[122] and radiolysis[123], and pulse conductivity[94]. The rate constants of ultrarapid reactions (having half-conversion periods of 10^{-10}–10^{-11} s) can be calculated from the line broadening in the Raman spectra[124,125]. These methods have not yet become widely used for the study of fast complexing reactions.

III. FAST COMPLEXING REACTIONS

Most cases of complex formation can be regarded as multistage processes, in which the chief part is played by substitution reactions. In aqueous solution all ions are hydrated, so that even with simple electrostatic interaction it is most probable that the formation of complex species involves several stages, for example

$$1.\ M^+aq + L^-aq \rightleftarrows [M^+aq][L^-aq] \quad (23)$$
(formation of ionic association complexes),

$$2.\ [M^+aq][L^-aq] \rightleftarrows [M^+aqL^-] \quad (24)$$
(formation of ion-pairs),

$$3.\ [M^+aqL^-] \rightleftarrows [ML] + aq. \quad (25)$$

It has been shown by various methods that the formation of association (outer-sphere) complexes is controlled by diffusion processes, and has a rate constant of the order of 10^8–10^{10} s^{-1}. In many cases the rate-determining stage is the conversion of outer-sphere complexes into complex compounds containing ligands in the inner sphere (reaction 25); it is more affected than any other stage by the individual characteristics of the interacting species[12].

Substitution reactions involved in the formation of complex compounds can be of two kinds—replacement of one ligand by another or else of one metal ion by another in the complex compound—and in Ingold's proposed classification these types are termed respectively nucleophilic (S_N) and electrophilic (S_E) substitutions. The type of substitution is determined by the starting materials and the final reaction products. Most fast reactions of complex formation which have at present been studied are nucleophilic substitutions (S_N).

1. Rate of Nucleophilic Substitution Reactions

(*a*) Effect of nature of metal ion. The rate of a nucleophilic substitution is influenced by many factors, among the most important of which are the nature of the interacting ligand and the parameters of the central ion—electron configuration, size, and charge.

There is as yet no single reliable method of calculating the rate constants of fast reactions in solution. Existing theories explain only the relative change in rate constant with variation in some parameter. Among such theories those using an electrostatic approach and also the ligand field theory have become most widely known.

The electrostatic approach was first used by Debye[20,126], who applied Stokes' law to ionic reactions of the type

$$H^+ + OH^- \rightleftarrows H_2O$$

and found a relationship between the maximum possible rate constant and the electrostatic characteristics of the reactant species

$$k_{rt} = \frac{4\pi n Z_1 Z_2 e_0^2 (D_1 + D_2)}{10^3 \epsilon k T \left[\exp\left(\frac{Z_1 Z_2 e_0^2}{\epsilon k T \sigma}\right)\right]},$$

where $n = 6.022 \times 10^{23}$ $mole^{-1}$ is Avogadro's number, Z_1 and Z_2 are the charges on the ions (positive and negative integers), $e_0 = 4.80 \times 10^{10}$ $cm^{3/2}$ s^{-1} is the charge of the electron, D_1 and D_2 (in cm^2 s^{-1}) are the diffusion coefficients of the corresponding ions, ϵ is the dielectric constant, $k = 1.38 \times 10^{-16}$ erg deg^{-1} is Boltzmann's constant, T is the temperature on the Kelvin scale, and $\sigma = 7.5 \times 10^{-8}$ cm is the thickness of the reaction layer. This equation holds only for dilute solutions and reactions whose rate is controlled by the diffusion of the reactant ions.

With values of $D_i = 10^{-4}$–10^{-3} cm^2 s^{-1} and $\sigma = 1$–12 Å (i.e. values of these parameters characteristic of ordinary ions) the rate constant of complex formation calculated by means of Eqn. (26) may vary from 10^7 to 10^{10} $mole^{-1}$ s^{-1}. Such rate constants are observed with reactions involving ions of the alkali and alkaline-earth metals as well as certain ions of bivalent metals (Cd^{2+}, Hg^{2+}, Cu^{2+}) (see Tables 7–11, below).

The electrostatic theory can only in certain cases predict the variation in rate constant for a reaction involving ions having a complete electron shell, but it is unable to predict the variation in the rate constant in reactions involving ions of the transition metals. Thus, for example, it cannot explain the great difference in reaction velocities between the ions Fe^{3+} and Cr^{3+}, which have practically the same electrostatic characteristics.

Use of the crystal field and ligand field theory[127–131] for reactions involving transition-metal ions makes it possible in certain cases to calculate the energy characteristics of the initial and a possible transition state. Calculation of these characteristics helps us to foresee qualitative changes in activation energy, and therefore in the rate of complexing reactions involving transition elements.

The energy characteristics of a transition complex are determined mainly by its stereochemistry. To a first approximation the structure of the transition state can be determined from the mechanism of nucleophilic substitution, which may occur either by a unimolecular (S_N1) or by a bimolecular (S_N2) mechanism. In the former case a complex of coordination number 6 is converted into a complex of coordination number 5: i.e. an octahedral configuration passes into a square pyramid or a trigonal bipyramid. In the latter case a complex having the same coordination number is converted into a transition state of coordination number 7, which has the configuration of a pentagonal bipyramid. Which mechanism (S_N1) or (S_N2) is involved in a substitution can be determined from the pressure dependence of the rate constant[1] or from the electrostatic characteristics of the central field.

Table 3. Change in energy (in Dq units) when the initial complex compound passes into the intermediate complex for substitutions involving elements of the first transition period.

Electronic configuration	S_N1 mechanism octahedron → square pyramid		S_N2 mechanism octahedron → pentagonal pyramid		Electronic configuration	S_N1 mechanism octahedron → square pyramid		S_N2 mechanism octahedron → pentagonal pyramid	
	strong field	weak field	strong field	weak field		strong field	weak field	strong field	weak field
d^0	0.00	0.00	0.00	0.00	d^6	4.00	−0.57	8.52	−1.28
d^1	−0.57	−0.57	−1.28	−1.28	d^7	−1.14	1.14	5.34	−2.56
d^2	−1.14	−1.14	−2.56	−2.56	d^8	2.00	2.00	4.26	4.26
d^3	2.00	2.00	4.26	4.26	d^9	−3.14	−3.14	1.07	−1.07
d^4	1.43	3.14	2.98	1.07	d^{10}	0.00	0.00	0.00	0.00
d^5	0.86	−0.57	1.70	0.00					

Table 3, taken from the monograph by Basolo and Pearson[131], gives results of the approximate calculation of the change in energy accompanying the change in configuration

associated with the conversion of an initial complex compound into a transition state. The approximations of the crystal field method were used in the calculation. It is seen that the greatest change in energy is required for ions having d^3, d^6, and d^8 electronic configurations: i.e. reactions involving these ions have a greater activation energy, and should therefore be slower, than reactions involving other ions. This principle is supported by experimental data available in the literature (Table 4).

Table 4. Rate constants for complex formation by elements of the first transition period.

Electronic configuration	Ion	I* k, M^{-1} s^{-1}	II* k, M^{-1} s^{-1}	III* k, M^{-1} s^{-1}
d^0	Ca^{2+}	10^8	$7\cdot10^8$	$2\cdot10^7$
d^5	Mn^{2+}	$2\cdot10^7$	—	10^6
d^6	Fe^{2+}	$3\cdot10^6$	—	$6\cdot10^6$
d^7	Co^{2+}	$33\cdot10^5$	$4\cdot10^4$	10^8
d^8	Ni^{2+}	$3\cdot10^4$	$4\cdot10^3$	10^4
d^9	Cu^{2+}	$3\cdot10^8$	$1\cdot10^6$	10^8
d^{10}	Zn^{2+}	$2\cdot10^8$	$4\cdot10^6$	$3\cdot10^6$

* The reactions are represented by the equations

(I) $[M(H_2\mathring{O})_6] + H_2O \rightleftharpoons [M(H_2O)_6] + H_2\mathring{O}$

(II) $M^{2+} + day \rightleftharpoons [M(day)]^{2+}$

day = 2-*p*-dimethylaminophenylazopyridine

(III) $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$.

More detailed consideration of the dependence of reactivity on the electronic structure of the reactant ions from the viewpoint of crystal field theory suggests that the rate of complex formation should decrease in the sequence of ions having the electronic configurations—$d^5 > d^4 > d^3 > d^6$—for both S_N1 and S_N2 mechanisms. Unfortunately, many postulates were made in this calculation, and there are as yet no reliable experimental data supporting this hypothesis.

Qualitative results can be obtained by considering the influence of the Jahn–Teller effect on the reactivity of complex compounds [130-131]. This effect consists in the distortions arising in a symmetrical non-linear polyatomic molecule having a degenerate electronic state, as a consequence of which distortions the symmetry of the molecule is diminished [132]. Thus in the d^9 system (the Cu^{2+} ion), for example, there is one vacant e_g-orbital, whose axes pass through the central ion and opposite ligands. The absence of an electron in one of the e_g-orbitals diminishes the screening of the central ion, with a consequent increase in the strength of interaction between negatively charged ligands and the central ion, so that the distance between them becomes shorter. Either two or four ligands will move towards the central ion; correspondingly either two short and four long—or four short and two long—bonds appear in an octahedron, and the latter is converted into a bipyramid.

Ligands located farther from a central ion are more reactive, since the mobility of ligands increases with increase in the distortion. Hence the rate of substitution should be considerably smaller with highly symmetrical complexes than in less symmetrical complexes.

The dependence of the Jahn–Teller distortion, arising in an octahedral configuration, on the electronic structure of transition-metal ions of the first series is shown in Table 5. It is seen that the greatest distortion appears with the structures d^4 and d^9, so that complexes of Cr^{2+} and Cu^{2+} should possess the greatest reactivity. This principle is supported by available experimental data (Table 4).

Table 5. Distortion of octahedral complexes of transition metals of the first series (Jahn–Teller effect) [132].

Configuration	Symmetry	Expected distortion due to orbital degeneracy	Configuration	Symmetry	Expected distortion due to orbital degeneracy
d^1	T_{2g}	small	d^6	$5\,T_{2g}$	small
d^2	$3\,T_{1g}$	small	d^7	$4\,T_{1g}$	small
d^3	$4\,A_{2g}$	0	d^8	$3\,A_{2g}$	0
d^4	$5\,E_g$	large	d^9	$2\,E_g$	large
d^5	$6\,A_{1g}$	0			

When the mechanism of substitution in a series of neighbouring elements is examined by the molecular orbital method [133], it is found that the decisive role is played by the change in antibonding effects in the formation of the activated complex, since the remaining characteristics of the complex either do not change or vary monotonically. This principle can be most usefully illustrated by substitution reactions in octahedral complexes of the type ML_6.

In a dissociative mechanism, the activated complex has the composition ML_5 and the configuration of a tetragonal pyramid (symmetry C_{4v}) or a trigonal bipyramid (symmetry D_{3h}). The change in symmetry and the arrangement of the orbitals in these two cases are shown in Fig. 5.

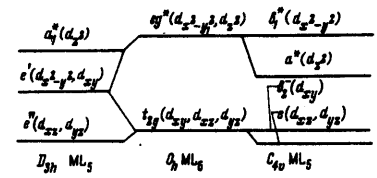


Figure 5. Change in symmetry and arrangement of orbitals for the S_N1 mechanism.

In the formation of ML_5 with the ligands located at the corners of a tetragonal pyramid the non-bonding orbital t_{2g} is converted into the still non-bonding orbitals b_2 and e, while the energy of these orbitals remains fundamentally unchanged. The antibonding orbital e_g is converted into two new antibonding orbitals b_1 and a_1^*, the antibonding effect on the orbitals a_1^* (d_{z^2}) being considerably diminished.

If electrons are present in the e_g^* orbital in a complex, formation of the ML_5 complex should be accompanied by a redistribution of electrons with a gain in energy when they undergo a transition from the orbital e_g^* to the orbital a_1^*. This transition disrupts the monotonic variation in reaction velocity in complexes with metals having d^4, d^5, d^9, and d^{10} configurations (Cr^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Mn^{3+}, etc. complexes), and as a consequence the activation energy is lower, and the rate of substitution reactions higher, for

compounds of these metals than in the case of neighbouring elements. It is probable that substitution by an S_N1 mechanism is typical of compounds of these elements (of the type ML_6).

Similar conclusions can also be reached if the activated complex ML_5 is regarded as a trigonal bipyramid (symmetry D_{3h}). In contrast to the preceding case, substitution in the ML_6 complex of a metal having the electronic structure d^3 (or d^8) should be characterised here by an especially high activation energy, since in these compounds it is necessary to promote one of the electrons from the non-bonding t_{2g} (d_{xy}) orbital to an antibonding orbital e'.

In an associative mechanism (S_N2) the activated complex has the composition ML_7 and the configuration of a pentagonal bipyramid (symmetry D_{5h}) with the characteristic and rearrangement of orbitals shown in Fig. 6. In this case the monotonic change in activation energy (and reaction velocity) breaks down in the complex compounds of metals having the structure d^3 (or d^8) owing to the promotion of one of the electrons from a non-bonding t_{2g} orbital to an antibonding e_2' (d_{xy}) orbital.

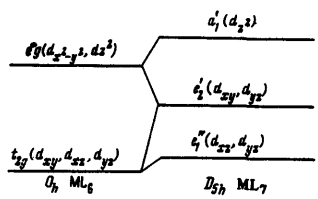


Figure 6. Change in symmetry and arrangement of orbitals for the S_N2 mechanism.

The activation energy is somewhat diminished in the complexes of metals having the configuration $3d^4$ (or $3d^9$), and remains about the same for complexes of metals having the configuration $3d^5$ (or $3d^{10}$) (Table 6).

Table 6. Change in antibonding effect in reactions occurring by S_N1 and S_N2 mechanisms[133].

Electronic structure	σ-Antibonding			π-Antibonding		
	ML_5 (D_{3h})	ML_6 (C_{4v})	ML_7 (D_{5h})	ML_5 (D_{3h})	ML_6 (C_{4v})	ML_7 (D_{5h})
High-spin complexes						
d^1	0.0	0.0	0.0	−0.5	−1.0	+0.5
d^2	0.0	0.0	0.0	−1.0	−2.0	+1.0
d^3	+1.13	0.0	+1.88	−3.5	−2.0	−0.5
d^4	−0.75	−1.0	+0.75	−2.0	−2.0	+2.0
d^5	−1.0	−1.0	+1.0	−2.0	−2.0	+0.5
d^6	−1.0	−1.0	+1.0	−1.5	−3.0	+2.5
d^7	−1.0	−1.0	+1.0	−3.0	−4.0	+3.0
d^8	+0.13	−1.0	+2.88	−5.5	−4.0	+1.5
d^9	−1.75	−2.0	+1.75	−4.0	−4.0	+4.0
Low-spin complexes						
d^3	0.0	0.0	0.0	−1.5	−3.0	+1.5
d^4	0.0	0.0	0.0	−2.0	−4.0	+2.0
d^5	+1.13	0.0	+1.88	−4.0	−4.0	+0.5
d^6	+2.25	0.0	+3.75	−5.5	−4.0	−1.0
d^7	+0.38	−1.0	+2.63	−4.0	−4.0	+1.5
d^8	−1.5	−2.0	+1.5	−4.0	−4.0	+4.0

Experimental results agree well with the variation in rate of substitution by the S_N2 mechanism. Actually, complexes of metals having the electronic configurations d^3 and d^8 react comparatively slowly in substitution reactions, and in this respect differ notably from the complexes of neighbouring metals.

The gradual increase in stability of the complexes with increase in atomic number of the transition metal leads to a gradual increase in the activation energy (decrease in rate) of substitution. This slowing down in the rate becomes especially marked in the complexes of metals having the electronic structures d^3 and d^8 when reactions occur by an S_N2 mechanism, owing to the necessity for promoting one of the electrons to an antibonding orbital. Complexes of metals having d^4, d^5, d^9, and d^{10} configurations, however, are considerably more reactive in an S_N2 and especially in an S_N1 mechanism, because of the transition of one electron from a higher to a lower antibonding orbital.

Unfortunately, none of the available methods enables absolute values to be calculated for the rate constants and activation energies of complex formation. At the best, all existing theories merely explain the relative variation in rate of complex formation in the series of transition elements.

(*b*) Effect of nature of ligand. The rates of many complexing reactions are independent of the nature of the ligands involved. Thus, for example, many doubly charged positive ions (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}) react at approximately the same rate with various ligands (Table 7).

Table 7. Rate constants (in $M^{-1}\,s^{-1}$) for complex formation by the ions Zn^{2+}, Cd^{2+}, Ni^{2+}, and Co^{2+} with various ligands*.

Ligand	Ions			
	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
Br^-	$5.0\cdot10^5$	$1.4\cdot10^9$	—	—
I^-	$5\cdot10^5$	$5\cdot10^9$	—	—
SO_4^{2-}	$3\cdot10^6$	$1\cdot10^7$	—	—
dye	$4\cdot10^6$	$1\cdot10^7$	—	—
CH_3COO^-		$3\cdot10^8$	—	—
imid	—	—	$5\cdot10^3$	$1.3\cdot10^5$
gly^-	—	—	$1.5\cdot10^4$	$4.6\cdot10^5$
$dgly^-$	—	—	$2.1\cdot10^4$	$4.6\cdot10^5$
dye	—	—	$4\cdot10^3$	$4.0\cdot10^4$
SO_4^{2-}	—	—	$1\cdot10^4$	$1\cdot10^4$

* imid = imidazole; gly = glycine; dgly = glycylglycine; dye = 2-*p*-dimethylaminophenylazopyridine.

This can be explained by an S_N1 mechanism for these reactions, in conformity with the equations[134]

$$[M(H_2O)_n] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_{n-1}] + H_2O, \qquad (27)$$

$$[M(H_2O)_{n-1}] + L \xrightarrow{k_3} [M(H_2O)_{n-1}L]. \qquad (28)$$

Using the steady-state method and assuming that the concentration of $[M(H_2O)_{n-1}]$ is considerably less than the concentration of $[M(H_2O)_n]$, we can write

$$\frac{d[M(H_2O)_{n-1}L]}{dt} = \frac{k_1k_3[M(H_2O)_n][L]}{k_2+k_3[L]}, \qquad (29)$$

when $k_3 \gg k_2$ we obtain

$$\frac{d[M(H_2O)_{n-1}L]}{dt} = k_1[M(H_2O)_n]. \qquad (30)$$

It follows from Eqn. (30) that the rate-determining stage in the formation of complex compounds is reaction (27)—the

elimination of water—the rate of complex formation being completely independent of the nature of the ligand [134-136] (Table 7).

For the same reason the rate of addition of each successive ligand in stepwise complex formation is usually lower than or equal to the rate of addition of the preceding ligand. If, however, substitution of a water molecule involves intermediate formation of an outer-sphere complex, and its stability constant exceeds unity, the reverse effect may be observed [137,138].

The rate of complex formation is sharply diminished in reactions with polydentate ligands involved in the formation of chelate compounds. This is probably associated with the multistage character of ring formation [135,136,139].

2. Rate of Dissociation of Complexes

The influence of various factors on the rate of dissociation of complexes has been examined in detail by Wilkins and his collaborators [70,137,138,140-144], who showed that the rate of dissociation is more dependent than is the rate of complex formation on the nature of the ligand. Thus, for example, the rate constants for dissociation of the complexes of bivalent nickel—

$$[Ni(CNS)]^{+} \xrightarrow{k_1} Ni^{2+} + CNS^{-}, \quad (31)$$

$$[Ni(NH_3)]^{2+} \xrightarrow{k_2} Ni^{2+} + NH_3, \quad (32)$$

$$[Ni\,(en)]^{2+} \xrightarrow{k_3} Ni^{2+} + en, \quad (33)$$

—are respectively (in s^{-1}) $k_1 = 100$, $k_2 = 5.8$, and $k_3 = 0.14$, whereas the corresponding rate constants for formation of these complexes are 10^4, 10^4, and 10^6 M^{-1} s^{-1}. With many of the reactions described in the literature, dissociation rate constants are always smaller than formation rate constants for the same complex compounds.

If the rate-determining stage in complex formation is the elimination of water, the rule [142]

$$\Delta \lg k_d \approx -\Delta \lg K_{st} \quad (34)$$

where k_d is the dissociation rate constant of the complex compound and K_{st} is the stepwise stability constant of the same compound, holds for complex compounds having the same central ion and different ligands, as well as for individual stages in a multistage process of complex formation. This rule has been verified on a series of compounds of bivalent nickel [142].

3. Influence of Stereochemical Factors

Hardly any work has been done on the influence of stereochemical factors on the rate of fast complex-forming reactions. Data are available only on the dependence of reaction velocity on the angle of attack for ions having different electronic configurations [12,144,145].

Hammes and Steinfeld [and Kustin et al.] [75,139] have found that the rate of formation of complex compounds by bivalent cobalt, nickel, and manganese is considerably lower with β-alanine than with α-alanine. The explanation given [139] for this difference in rates is that ring formation in the above compounds is a stepwise process, while with β-alanine, owing to steric hindrance, occupation of a vacant place by a water molecule is more rapid than closure of the ring. This type of substitution has been termed sterically controlled substitution.

IV. REACTIONS HAVING AN S_N MECHANISM

1. Reactions involving Elements of Group I

Study of the kinetics of complex formation involving alkali-metal ions has been begun only recently. Investigation of these reactions has been delayed for at least two reasons: reactions of complex formation involving the alkali-metal ions occur very rapidly, and the resulting complexes are not very stable, so that all investigations must be conducted with high concentrations of the ligand, when the effect of foreign ions is very considerable. Available published data on these reactions are listed in Table 8.

Table 8. Rate constants in the replacement of water by various ligands for alkali-metal ions* ($\mu = 0.5$, pH > 11, $T = 20°C$).

Ion	Ligands			
	$Edta^{4-}$	Nta^{3-}	$Imda^{2-}$	Tmp^{3-}
Li^+	$4.8 \cdot 10^7$	$4.7 \cdot 10^7$	$2.5 \cdot 10^8$	$9 \cdot 10^8$
Na^+	$4.7 \cdot 10^7$	$8.8 \cdot 10^7$	$2.5 \cdot 10^8$	$2 \cdot 10^9$
K^+	$7.5 \cdot 10^7$	$1.5 \cdot 10^8$	—	$5 \cdot 10^9$
Rb^+	$1.4 \cdot 10^8$	$2.3 \cdot 10^8$	—	$5 \cdot 10^9$
Cs^+	$2.1 \cdot 10^8$	$3.5 \cdot 10^8$	—	$5 \cdot 10^9$

* Constants (in s^{-1}) obtained by the ultrasonic method [14]. $Edta^{4-}$ = ethylenediaminetetra-acetate; Nta^{3-} = nitrilotriacetate anion; $Imda^{2-}$ = imidazole anion; Tmp^{3-} = trimetaphosphate anion.

Table 8 shows that in all cases the rate of complex formation increases monotonically from lithium to caesium, and the rate constant of these processes, which is very large, varies linearly with the radius of the reactant ions [14]. This indicates that the rate of complex formation involving alkali-metal ions depends mainly on the purely electrostatic intereaction of the reactant ions and is controlled by diffusion, the rate of elimination of water not being the limiting stage.

Only reactions involving compounds of bivalent copper have been relatively well studied among elements of subgroup IB. It is seen from Table 9 that the rate constants for formation of one-coordinate complex compounds of bivalent copper with various ligands vary within a fairly narrow range (10^6–10^8 M^{-1} s^{-1}). Such a large absolute value of the rate constant for the formation of complexes of bivalent copper, in comparison with the rate constants for complex formation by other transition elements of the first series, is usually explained by strong distortions of the octahedral structure of copper compounds resulting from the Jahn–Teller effect [6,129,131].

The absence of an appreciable effect of the nature of the ligands on the rate constant of complex formation by bivalent copper is probably associated with the fact that these reactions occur by an S_N1 mechanism, the rate-determining stage being the elimination of water [13,14].

The literature contains no data on fast complexing reactions involving compounds of silver, gold, or univalent and tervalent copper.

Table 9. Rate constants for the formation and the dissociation of complex compounds of bivalent copper*;

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$[Cu(H_2\overset{*}{O})_6]^{2+} + H_2O \rightleftarrows [Cu(H_2O)_6]^{2+} + H_2\overset{*}{O}$	$3\cdot10^8$	—	25°	n.m.r.	134,146,1
$[Cu(\overset{*}{NH_3})]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)]^{2+} + \overset{*}{NH_3}$	$7\cdot10^6$	--	25°	n.m.r.	148
$[Cu(en)_2(H_2O)_2]^{2+} + en \rightleftarrows [Cu(en)_2(H_2O)_2]^{2+} + en$	—	$2.4\cdot10^7$	27°	n.m.r.	149
$Cu^{2+} + SO_4^{2-} \rightleftarrows [Cu(SO_4)]$	$5\cdot10^7$	10^8	25°	us	150,1
$Cu^{2+} + CH_3COO^- \rightleftarrows [Cu(CH_3COO)]^+$	$4.3\cdot10^8$		25°	n.m.r.	146
$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_4]^{2+}$	$6.6\cdot10^4$	$1.9\cdot10^7$	27°	n.m.r.	115
$[Cu(NH_3)_4]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_5]^{2+}$	$5.7\cdot10^6$	—	27°	n.m.r.	115
$[Cu(NH_3)_5]^{2+} + NH_3 \rightleftarrows [Cu(NH_3)_6]^{2+}$	$6.6\cdot10^4$	—	25°	n.m.r.	152
$Cu^{2+} + en \rightleftarrows [Cu(en)]^{2+}$	115	—	25°	stfl	70
$[Cu(en)]^{2+} + en \rightleftarrows [Cu(en)_2]^{2+}$	433	—	0.15 M HNO_3 25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + Edta^{4-} \rightleftarrows [Cu(Edta)]^{2-}$	370	$1.3\cdot10^9$	0°, $\mu = 0.1$	elch	154,155
$Cu^{2+} + dye \rightleftarrows [Cu(dye)]^{2+}$	—	$1\cdot10^8$	15° 0.1 M KNO_3	tj	146
$[Cu(sarc)]^+ + sarc^- \rightleftarrows [Cu(sarc)_2]$	—	$6\cdot10^5$	27°	n.m.r.	115
$[Cu(dmg)]^+ + dmg^- \rightleftarrows [Cu(dmg)_2]$	—	$1.3\cdot10^4$	27°	n.m.r.	115
$[Cu(gly)]^+ + gly^- \rightleftarrows [Cu(gly)_2]$	—	$8.2\cdot10^6$	27°	n.m.r.	115
$Cu^{2+} + bn \rightleftarrows [Cu(bn)]^{2+}$	4.56	—	25°	stfl	70
$[Cu(bn)]^{2+} + bn \rightleftarrows [Cu(bn)_2]^{2+}$	15.1	—	25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + C\text{-tetraM} \rightleftarrows [Cu(C\text{-tetraM})]^{2+}$	0.42	—	25° 0.15 M HNO_3	stfl	70
$[Cu(C\text{-tetra M})]^{2+} + C\text{-tetra M} \rightleftarrows [Cu(C\text{-tetra M})_2]^{2+}$	0.80	—	25° 0.15 M HNO_3	stfl	70
$Cu^{2+} + terpy \rightleftarrows [Cu(terpy)]^{2+}$		$2\cdot10^7$	5°	stfl	137

* en = ethylenediamine; Edta = ethylenediaminetetra-acetate; dye = 2-*p*-dimethylaminophenylazopyridine; bn = butane-2,3-diamine; gly = glycine; sarc = *N*-methylglycine; dmg = *NN*-dimethylglycine; C-tetraM = 2,3-dimethylbutane-2,3-diamine; n.m.r. = nuclear magnetic resonance method; us = ultrasonic method; stfl = stopped-flow method; elch = electrochemical method; tj = temperature-jump relaxation method.

Table 10. Rate constants for the formation and the dissociation of complex compounds of Group II elements.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$[Be(H_2\overset{*}{O})_n]^{2+} + H_2O \rightleftarrows [Be(H_2O)_n]^{2+} + H_2\overset{*}{O}$	10^2	—		us	14
$[Be(H_2O)SO_4] \rightleftarrows [Be(SO_4)] + H_2O$ **	$1.3\cdot10^3$	$1\cdot10^3$	12° 0,01 0.01–0.2 M $BeSO_4$	tj ps	78,155 156
$[Mg(H_2O)_n]^{2+} + H_2O \rightleftarrows [Mg(H_2O)_n]^{2+} + H_2O$	10^5	—		us	14
$[Mg(H_2O)SO_4] \rightleftarrows [Mg(SO_4)] + H_2O$ **	$8\cdot10^5$	$1\cdot10^5$		tj	78
$Mg^{2+} + SO_4^{2-} \rightleftarrows [Mg(SO_4)]$	$5.52\cdot10^5$ $6.47\cdot10^5$	$8.76\cdot10^7$ $10.3\cdot10^7$	12° 0.003 0.003–0.2 M $MgSO_4$	tj us	78 97,101
$[Mg(H_2O)S_2O_3] \rightleftarrows [Mg(S_2O_3)] + H_2O$**	$1\cdot10^6$	10^5		tj	78
$[Mg(H_2O)CrO_4] \rightleftarrows [MgCrO_4] + H_2O$ **	$1.5\cdot10^6$	10^5		tj	78
$Mg^{2+} + ADP^{3-} \rightleftarrows MgADP^-$	$2.5\cdot10^3$	$3\cdot10^6$	13°	tj	158
$[Ca(H_2\overset{*}{O})_n]^{2+} + H_2O \rightleftarrows [Ca(H_2O)_n]^{2+} + H_2\overset{*}{O}$	10^8	—		us	14
$Mg^{2+} + HT^{3-} \rightleftarrows MgHT^-$	$3.0\cdot10^4$	$3.5\cdot10^6$	pH=9	tj	159
$[Ca(H_2O)CrO_4] \rightleftarrows [Ca(CrO_4)] + H_2O$	$2\cdot10^8$	$2\cdot10^7$		tj	78
$Ca^{2+} + X_o^{2-} \rightleftarrows CaX_o$	—	$7\cdot10^8$		tj	79
$Mg^{2+} + X_o^{2-} \rightleftarrows MgX_o$	—	$1.6\cdot10^6$		tj	79
$[Sr(H_2O)_n]^{2+} + H_2O \rightleftarrows [Sr(H_2O)_n]^{2+} + H_2\overset{*}{O}$	$2\cdot10^8$	—		us	14
$[Ba(H_2O)_n]^{2+} + H_2O \rightleftarrows [Ba(H_2O)_n]^{2+} + H_2\overset{*}{O}$	$2.5\cdot10^8$	—		us	14

** Reactions of conversion of outer-sphere into inner-sphere complexes (k_{form} in s^{-1}).

ADP^{3-} = adenosine 5-diphosphate; HT^{3-} = Tiron [disodium 4,5-dihydroxybenzene-1,3-disulphonate]; X_o = Xylenol Orange; us = ultrasonic method; tj = temperature-jump relaxation method; ps = pressure-shock method.

2. Reactions Involving Elements of Group II

Available published values of the rate constants for the dissociation and the formation of complexes of Group II elements are given in Table 10. The rates of all these reactions, with the exception of those involving beryllium, are determined purely by electrostatic interaction, the elimination of water being the rate-determining stage. It is interesting that the rate of complex formation increases sharply on passing from magnesium to calcium, a fact which has not yet been satisfactorily explained[14].

The relatively small rate constant found with beryllium ions is explained by rapid hydrolysis, as a result of which relatively unreactive species are formed[14,151]. These processes can explain the presence of at least six relaxation times in the relaxation spectrum of beryllium sulphate[151].

Subgroup IIB contains elements whose ions have the configuration d^{10}. In contrast to the alkaline-earth ions, the doubly charged ions of zinc, cadmium, and mercury have an outer d-shell, which may be reflected in their kinetic properties. The comparatively high velocities of reactions involving ions of these elements (Table 11), whose rate constants are approximately equal in magnitude to those of reactions involving elements of the A subgroup, suggest that the mechanism of complex formation is the same in both cases, the rate of the process being determined purely by electrostatic interaction and being limited by diffusion.

3. Reactions Involving Elements of Groups III–VI and Manganese

Preliminary results indicate[14] that complex formation involving V^{2+} ions is abnormally slow, but the ion Cr^{2+} reacts at approximately the same rate as does Cu^{2+}. These data are consistent with the ligand field theory.

Complex formation involving compounds of bivalent manganese is very rapid. Quantitative kinetic data are available for the exchange of water in the inner sphere[111,148] and the formation of sulphate complexes[101] and of complexes with terpyridyl[137] and β-alanine[139]. In most cases the rate constant for the formation of bivalent manganese complexes exceeds $10^6\ M^{-1}\ s^{-1}$.

Fast complexing reactions in which ions of elements in these groups take part in a higher state of oxidation than 3 have not been investigated. Data are available only on the rate of formation of sulphate complexes of aluminium[157] and vanadyl[97] and of dimers of tungsten(VI) and molybdenum(VI).[165]

Few data are available also on reactions involving ions of the rare-earth elements. Eigen[14] assumes that the rate constant for complex formation should be of the order of $10^7\ M^{-1}\ s^{-1}$. This supposition is supported by results for the exchange of ethylenediaminetetra-acetic acid with certain rare-earth ions[166]. For lanthanum this constant is $10^5\ M^{-1}\ s^{-1}$, and it decreases in the sequence—lanthanum, neodymium, dysprosium, ytterbium—in the proportions 7700 : 1200 : 19 : 1.

The temperature-jump method[167] has recently been used to determine the rate constants for the formation and the dissociation of the complexes of lanthanides with murexide,

Table 11. Rate constants of complex formation by elements in Subgroup IIB*.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
$Zn^{2+} + Br^- \rightleftarrows ZnBr^+$	$\leqslant 5\cdot10^8$	$5.0\cdot10^8$	25°	n.m.r.	160
$ZnBr^+ + Br^- \rightleftarrows ZnBr_2$	—	$5.0\cdot10^5$	0.01-5.0 M NaBr	n.m.r.	160
$ZnBr_2 + Br^- \rightleftarrows ZnBr_3^-$	$\geqslant 7\cdot10^6$	$5.0\cdot10^5$	ditto	n.m.r.	160
$ZnBr_3^- + Br^- \rightleftarrows ZnBr_4^{2-}$	$2.0\cdot10^7$	$8\cdot10^7$	»	n.m.r.	160
$Zn^{2+} + I^- \rightleftarrows ZnI^+$	$5\cdot10^4$	$5\cdot10^5$	25° 0.01-5.0 M KI	n.m.r.	160
$ZnI^+ + I^- \rightleftarrows ZnI_2$	—	$5\cdot10^5$	ditto	n.m.r.	160
$ZnI_2 + I^- \rightleftarrows ZnI_3^-$	$\leqslant 5\cdot10^4$	$5\cdot10^5$	»	n.m.r.	160
$ZnI_3^- + I^- \rightleftarrows ZnI_4^{2-}$	$3\cdot10^7$	$7\cdot10^6$	»	n.m.r.	160
$ZnF^+ + F^- \rightleftarrows ZnF_2$		$\tau \geqslant 10^{-4}$		n.m.r.	160
$Zn^{2+} + SO_4^{2-} \rightleftarrows ZnSO_4$	$>10^8$	$3\cdot10^6$	25°	n.m.r.	146
		10^7		tj	78
$Zn^{2+} + CH_3COO^- \rightleftarrows ZnCH_3COO^-$	$3\cdot10^7$	—	25°	n.m.r.	146
$Zn^{2+} +$ dye $\rightleftarrows$ [Zn (dye)]$^{2+}$	—	$4\cdot10^6$	15° 0.1 M KNO_3	tj	146
$Zn^{2+} +$ terpy $\rightleftarrows$ [Zn (terpy)]$^{2+}$	1,1	$1.3\cdot10^6$	25°	stfl	137
$CdCl_3^- + Cl^- \rightleftarrows CdCl_4^{2-}$	$7.6\cdot10^9$	$4\cdot10^9$	25°	us	106
$Cd^{2+} + Br^- \rightleftarrows CdBr^+$	$1.0\cdot10^7$	$1.4\cdot10^7$	25° 0.01-5.0 M NaBr	n.m.r.	160
$CdBr^+ + Br^- \rightleftarrows CdBr_2$	$1.4\cdot10^6$	$1.4\cdot10^8$	ditto	n.m.r.	160
$CdBr_2 + Br^- \rightleftarrows CdBr_3^-$	$7\cdot10^6$	$1.7\cdot10^7$	»	n.m.r.	160
$CdBr_3^- + Br^- \rightleftarrows CdBr_4^{2-}$	$6.0\cdot10^6$	$1.2\cdot10^7$	»	n.m.r.	160
$Cd^{2+} + I^- \rightleftarrows CdI^+$	$\approx 2\cdot10^7$	$\approx 5\cdot10^9$	25° 0.01-5.0 M KI	n.m.r.	160
$CdI_3^- + I^- \rightleftarrows CdI_4^{2-}$	$\approx 2\cdot10^7$	$\approx 5\cdot10^8$	ditto	n.m.r.	160
$Cd^{2+} + SO_4^{2-} \rightleftarrows CdSO_4$	10^8	10^7	0.1 M KNO_3	tj	78
$[Cd(CN)]^+ + CN^- \rightleftarrows [Cd(CN)_2]$	—	$5\cdot10^8$	$\mu = 0.1$	elch	161
$[Cd(CN)_2] + CN^- \rightleftarrows [Cd(CN)]^-$	$2.7\cdot10^8$	$4\cdot10^{11}$	ditto	elch	162
$[Cd(CN)_3]^- + CN^- \rightleftarrows [Cd(CN)_4]^{2-}$	$2\cdot10^4$	$8\cdot10^7$	3 M $NaClO_4$	elch	163
$Cd^{2+} + CH_3COO^- \rightleftarrows [Cd(CH_3COO)]^+$	—	$3\cdot10^8$		n.m.r.	137
$Cd^{2+} +$ dye $\rightleftarrows$ [Cd (dye)]$^{2+}$	—	10^7	15° 0.1 M KNO_3	tj	146
$Cd^{2+} +$ terpy $\rightleftarrows$ [Cd (terpy)]$^{2+}$	25	$3.2\cdot10^6$	25°	stfl	137
$HgCl^+ + Cl^- \rightleftarrows HgCl_2$	$2.5\cdot10^7$	$6.4\cdot10^9$		n.m.r.	160
$HgBr_2 + Br^- \rightleftarrows [HgBr_3]^-$	$2.5\cdot10^7$	$4.6\cdot10^8$	25° 0.01-5.0 M NaBr	n.m.r.	160
$[HgBr_3]^- + Br^- \rightleftarrows [HgBr_4]^{2-}$	—	$5\cdot10^9$	ditto	efp	164

* dye = 2-*p*-dimethylaminophenylazopyridine; terpy = 2,2′,6′,2″-terpyridyl; n.m.r. = nuclear magnetic resonance method; tj = temperature-jump method; efp = electric field-pulse method; elch = electrochemical method; us = ultrasonic method; stfl = stopped-flow method.

and the stopped-flow method to find the dissociation rate constants of the complexes formed by Xylenol Orange with the rare-earth elements of the cerium subgroup[168] (see Table 12). It is possible that, in aqueous solutions of compounds of the rare-earth elements, an equilibrium is established between hydrated forms containing different quantities of water in the inner sphere, and that these forms differ in reactivity[167].

4. Reactions Involving Elements of the Ion Group

Data on fast reactions of complex formation involving elements of this group are the most numerous (Table 13). In most cases the rate of complex formation is limited by the rate of elimination of water from the inner sphere, and is therefore independent of the nature of the ligand.

Two groups of reactions occur with Fe^{3+} ions. The first group comprises reactions in which a ligand reacts directly

Table 12. Rate constants for the reaction $M^{3+} + L^n \rightleftharpoons ML^{3-n}$, where M^{3+} is a lanthanide ion and L^n represents murexide or Zylenol Orange.

L	M^{3+}	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
* Mur	$10^3 k_{diss}$, s^{-1}	32	21	24	8.5	6.5	5.5	4,3
* Mur	$10^7 k_{form}$, $M^{-1}\,s^{-1}$	8.6	9.5	8.6	9.3	9.6	8.2	5.2
X_o	k_{diss}, s^{-1}	152	236	159	116	106	—	95
	M^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
* Mur	$10^3 k_{diss}$, s^{-1}	3.3	2.8	3.3	3.4	5.0	4.3	4.5
Mur	$10^7 k_{form}$, $M^{-1}\,s^{-1}$	3.0	1.7	1.4	1.0	1.1	1.1	1.3

* Mur = murexide, $\mu = 0.1$, $T = 12°C$, pH = 4.0; X_o = Xylenol Orange, $T = 25°C$, pH = 4.90.

with the ions according to the equation

$$Fe^{3+} + X^- \xrightarrow{k_1} FeX^{2+} . \qquad (35)$$

Reactions of the second group occur in conformity with the scheme

$$FeOH^{2+} + HX \xrightarrow{k_1} FeX^{2+} + H_2O \qquad (36)$$

As is evident from Eqn. (35), in the former case k is independent of the hydrogen-ion concentration, whereas the rate constant of reaction (36) is substantially influenced by it. As a rule $k_2 \gg k_1$. In many cases the dissociation of complex compounds of tervalent iron is catalysed by Fe^{2+} ions[72].

The Ni^{2+} ion, which has the electronic configuration d^8 and forms highly symmetrical complex compounds, reacts considerably more slowly than the other transition elements of the first series.

The literature contains no data on fast reactions of complex formation by elements of the platinum group.

V. REACTIONS HAVING AN S_E MECHANISM

Substitution of the central ion in complex compounds has so far been studied mainly on slow or moderately rapid[189-191] reactions in which polydentate ligands take part.

The most interesting of the reactions which have been studied is

$$NiTeta^{2+} + CuEdta^{2-} \rightleftarrows CuTeta^{2+} + NiEdta^{2-} , \qquad (37)$$

where Teta represents triethylenetetra-amine and Edta represents ethylenediaminetetra-acetic acid. This reaction—the first non-redox reaction to be studied—has been shown[192] to have a chain mechanism, which can be represented by the reactions

$$NiTeta^{2+} \rightleftarrows Ni^{2+} + Teta , \qquad (38)$$

$$Teta + CuEdta^{2} \rightleftarrows CuTeta^{2+} + Edta^{4-} , \qquad (39)$$

$$Edta^{4-} + NiTeta^{2+} \rightleftarrows NiEdta^{2-} + Teta , \qquad (40)$$

$$Ni^{2+} + Edta^{4-} \rightleftarrows NiEdta^{2-} . \qquad (41)$$

It is interesting that this reaction is catalysed by small amounts (10^{-6} M) of certain ligands (Teta, Edta), and is inhibited by copper and nickel ions at concentrations of

Table 13. Rate constants of fast complex formation by elements of the iron group.

Reaction	k_{diss}, s^{-1}	k_{form}, $M^{-1}\,s^{-1}$	Conditions	Method	Ref.
1	2	3	4	5	6
$[Fe(H_2O)_n]^{3+} + H_2O \rightleftarrows [Fe(H_2O)_n]^{3+} + H_2O$	$2.4\cdot10^4$	—		n.m.r.	148
$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4$	10^6	$6\cdot10^6$		tj	78
$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$ **	$k_1=1.1$ $k_2=3.4$	$1.9\cdot10^2$	25°; $\mu=3.0$	n.m.r	148
	$k_1=9.4$ $k_2=18$		25°; $\mu=1.0$ Fe^{2+} catalyst	stfl	65,72
$Fe^{3+} + CNS^- \rightleftarrows FeCNS^{2+}$	—	$1.7\cdot10^4$ $k_1=127$ $k_2=20$	20°; $\mu=0.01$	stfl	71,169 170
		132	25°	tj	171
$Fe^{3+} + Br^- \rightleftarrows FeBr^{2+}$	—	20		stfl	172,173
$Fe^{3+} + Fe^- \rightleftarrows FeF^{2+}$		$5.0\cdot10^3$		stfl	172,174
$Fe^{3+} + N_3^- \rightleftarrows FeN_3^{2+}$	—	$1.6\cdot10^5$		stfl	172
$Fe^{3+} + CNS^- \rightleftarrows FeCNS^{2+}$ **	$k_1=0.28$ $k_2=0.016$	—	80% CH_3OH 20% H_2O −45°	stfl	175
$FeOH^{2+} + HCl \rightleftarrows FeCl^{2+} + H_2O$	—	$1.1\cdot10^4$	25°	stfl	158
		18		stfl	65
$FeOH^{2+} + HBr \rightleftarrows FeBr^{2+} + H_2O$	—	$2.7\cdot10^4$		stfl	172,173
$FeOH^{2+} + HF \rightleftarrows FeF^{2+} + H_2O$	—	$3.1\cdot10^3$		stfl	172,174
$FeOH^{2+} + HN_3 \rightleftarrows FeN_3^{2+} + H_2O$	—	$6.8\cdot10^3$		stfl	172
$Fe^{3+} + SO_4^{2-} \rightleftarrows FeSO_4^+$	$6.3\cdot10^4$	$6.4\cdot10^3$	25°; $\mu=0.5$	cfl	176,177
$FeOH^{2+} + HCNS \rightleftarrows FeCNS^{2+} + H_2O$	20.2	$1.0\cdot10^4$		stfl	170,172
$FeOH^{2+} + HSO_4^- \rightleftarrows FeSO_4^+ + H_2O$	—	$3\cdot10^5$		cfl	176
$[Fe(H_2O)OH]^{2+} + Cl^- \rightleftarrows [Fe(H_2O)(OH)Cl]^+$	—	$1.1\cdot10^4$	25°; $\mu=1.0$	stfl	65
$FeOH^{2+} + CNS^- \rightleftarrows [Fe(OH)CNS]^+$	—	$4.2\cdot10^4$	25°	tj	171
$Fe(OH)^{2+} + Fe(OH)^{2+} \rightleftarrows [Fe(OH)_2Fe]^{4+}$	1.0	450	24.5°; $\mu=0.3$	stfl	173,178
$FeCl^{2+} + Fe(OH)^{2+} \rightleftarrows [Fe(OH)ClFe]^{4+}$	—	100	ditto	ps	178
$Fe(OH)^{2+} + FeCNS^{2+} \rightleftarrows [Fe(OH)CNSFe]^{4+}$	—	85	»	ps	178
$FeSO_4^+ + Fe(OH)^{2+} \rightleftarrows [Fe(OH)SO_4Fe]^{3+}$	—	110	ditto	ps	178
$Fe^{3+} + S_2O_3^{2-} \rightleftarrows [Fe(S_2O_3)]^+$				cfl	179
$Fe^{3+} + terpy \rightleftarrows [Fe(terpy)]^{3+}$	$6.3\cdot10^{-8}$	$8.0\cdot10^4$	25°	stfl	137
$[Fe(terpy)]^{3+} + terpy \rightleftarrows [Fe(terpy)_2]^{3+}$	$8.0\cdot10^{-7}$	10^7	5°	stfl	137
$Co^{2+} + SO_4^{2-} \rightleftarrows CoSO_4$	$> 10^7$	10^3		tj	78
		$2\cdot10^5$		n.m.r.	148
$[Co(H_2O)_6]^{2+} + H_2O \rightleftarrows [Co(H_2O)_6]^{2+} + H_2O$	$3.1\cdot10^5$	—		n.m.r.	148,115
$[Co(H_2O)_6]^{2+} + Cl^- \rightleftarrows [Co(H_2O)_5Cl]^{2+} + H_2O$	0.05	2	25°; $\mu=3.0$	stfl	180,181
$[Co(H_2O)_5OH]^{2+} + Cl^- \rightleftarrows [Co(H_2O)_4(OH)Cl]^+ + H_2O$	—	$2\cdot10^2$	25°; $\mu=3.0$	stfl	181
$[Co(NH_3)_5]^{3+} + NH_3 \rightleftarrows [Co(NH_3)_5]^{3+} + NH_3$	$4.7\cdot10^4$	—	25°	n.m.r.	115
$[Co(en)_3]^{3+} + en \rightleftarrows [Co(en)_3]^{3+} + en$	$4.8\cdot10^3$	—	25°	n.m.r.	115
$Co^{2+} + dye \rightleftarrows [Co(dye)]^{2+}$	—	$4.0\cdot10^4$	15°; $\mu=0.1$	tj	146
$Co^{2+} + HT^{3-} \rightleftarrows CoHT^-$	$4.2\cdot10^3$	$4.0\cdot10^6$		tj	159
$Co^{2+} + gly \rightleftarrows [Co(gly)]^+$	10	$4.6\cdot10^5$	25°, $\mu=0.10$, pH 9.0–9.5	tj	75
$[Co(gly)]^+ + gly^- \rightleftarrows [Co(gly)_2]$	360	$4.6\cdot10^5$	ditto	tj	75
$[Co(gly)_2] + gly^- \rightleftarrows [Co(gly)_3]^-$	$3.8\cdot10^2$	$9.0\cdot10^5$	»	tj	75
$Co^{2+} + dgly \rightleftarrows [Co(dgly)]^+$	$4.2\cdot10^2$	$4.6\cdot10^5$	25°, $\mu=0.15$ pH 7.7–8.2	tj	75
$[Co(dgly)]^+ + dgly^- \rightleftarrows [Co(dgly)_2]$	$4.8\cdot10^2$	$9.0\cdot10^5$	ditto	tj	75
$Co^{2+} + imid \rightleftarrows [Co(imid)]^{2+}$	$4.6\cdot10^5$	$1.3\cdot10^5$	25°, $\mu=0.15$, pH 7.1–7.5	tj	75
$[Co(imid)]^{2+} + imid \rightleftarrows [Co(imid)_2]^{2+}$	$9.0\cdot10^4$	$1.1\cdot10^5$	ditto	tj	75
$Co^{2+} + terpy \rightleftarrows [Co(terpy)]^{2+}$	10^{-4}	$2.5\cdot10^4$	25°	stfl	137
$Co^{2+} + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})]^+$	32	$6.0\cdot10^5$	20°, $\mu=0.1$, pH=9.0	tj	139
$[Co(\alpha\text{-alan})]^+ + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})_2]$	280	$8.0\cdot10^5$	ditto	tj	139
$[Co(\alpha\text{-alan})_2] + \alpha\text{-alan}^- \rightleftarrows [Co(\alpha\text{-alan})_3]^-$	$1.6\cdot10^3$	$9.0\cdot10^4$	»	tj	139
$Co^{2+} + \beta\text{-alan}^- \rightleftarrows [Co(\beta\text{-alan})]^+$	7,5	$7.5\cdot10^4$	20°, $\mu=0.1$, pH=8.5	tj	139
$[Co(\beta\text{-alan})]^+ + \beta\text{-alan}^- \rightleftarrows [Co(\beta\text{-alan})_2]$	86	$8.6\cdot10^4$	ditto	tj	139
$[Ni(H_2O)_6]^{2+} + H_2O \rightleftarrows [Ni(H_2O)_6]^{2+} + H_2O$	$3.2\cdot10^4$ $4.4\cdot10^3$	—		n.m.r. n.m.r.	148 115
$Ni^{2+} + CNS^- \rightleftarrows [Ni(CNS)]^+$	10^2	$3.5\cdot10^2$	25°, $\mu=0.5$	stfl	152
				n.m.r.	
		$1.8\cdot10^2$	ditto	elch	182,183
$[Ni(CNS)]^+ + CNS^- \rightleftarrows [Ni(CNS)_2]$	—	$3.8\cdot10^3$		elch	182,183
		$6.3\cdot10^4$		elch	182,183
$[Ni(H_2O)_2(CNS)_4]^{2-} + CNS^- \rightleftarrows [Ni(H_2O)_2(CNS)_4]^{3+} + CNS^-$	$6.9\cdot10^5$	—	25°, $\mu=8.4$	n.m.r.	184

Table 13. (cont'd)

1	2	3	4	5	6
$Ni^{2+} + NH_3 \rightleftarrows [Ni(NH_3)]^{2+}$	6.0	—	25°	n.m.r.	184
	0.011	—	−25°	stfl lt	185 185
$[Ni(NH_3)_5]^{2+} + NH_3 \rightleftarrows [Ni(NH_3)_6]^{2+}$	$6.6\cdot10^4$	—	25°	stfl	185
$[Ni(NH_3)_6]^{2+} + NH_3 \rightleftarrows [Ni(NH_3)_6]^{2+} + NH_3$	$5.6\cdot10^4$ $4.5\cdot10^4$	— $\tau=0.025$	25° −50°	n.m.r. n.m.r. stfl	186 115 187
$Ni^{2+} + en \rightleftarrows [Ni(en)]^{2+}$	0.15	$9\cdot10^6$	25°	stfl	141,142,143
$[Ni(en)]^{2+} + en \rightleftarrows [Ni(en)_2]^{2+}$	5.2	$1.6\cdot10^6$	25°	stfl	141,142,143
$[Ni(en)_2]^{2+} + en \rightleftarrows [Ni(en)_3]^{2+}$	87	$6\cdot10^6$	25°	stfl	141,142,143
$Ni^{2+} + SO_4^{2-} \rightleftarrows [Ni(SO_4)]$	$1.5\cdot10^4$	$1.0\cdot10^4$		n.m.r.	146,148
		$1.0\cdot10^5$		tj	78
$Ni^{2+} + bn \rightleftarrows [Ni(bn)]^{2+}$	0,020		25°	stfl	142,141
$Ni(bn)]^{2+} + bn \rightleftarrows [Ni(bn)_2]^{2+}$	0.26	—	25°	stfl	141,142
$[Ni(bn)_2]^{2+} + bn \rightleftarrows [Ni(bn)_3]^{2+}$	8.25	—	25°	stfl	141,142
$Ni^{2+} + py \rightleftarrows [Ni(py)]^{2+}$	39	$8.1\cdot10^5$	25°, $\mu=0.1$	elch	183
$Ni(py)]^{2+} py \rightleftarrows [Ni(py)_2]^{2+}$	—	$4.4\cdot10^3$	25°, $\mu=1.0$	stfl elch	144 183
$Ni^{2+} + C_2H_4NH \rightleftarrows [Ni(C_2H_4NH)]^{2+}$	5.0	—		stfl	185
$Ni^{2+} + N_2H_4 \rightleftarrows [Ni(N_2H_4)]^{2+}$	3.6			stfl	185
$Ni^{2+} + gly \rightleftarrows [Ni(gly)]^+$	0.024	$1,5\cdot10^4$	25°, $\mu=0.15$, pH 9.0–9.8	tj	75
$[Ni(gly)]^+ + gly^- \rightleftarrows [Ni(gly)_2]$	0.95	$6.0\cdot10^4$	ditto	tj	75
$[Ni(gly)_2] + gly \rightleftarrows [Ni(gly)_3^-]$	10.4	$4.2\cdot10^4$	»	tj	75
$Ni^{2+} + dgly^- \rightleftarrows [Ni(dgly)]^+$	2.6	$2.1\cdot10^4$	25°, $\mu=0.15$, pH 7.7–8.2	tj	75
$[Ni(dgly)]^+ + dgly^- \rightleftarrows [Ni(dgly)_2]$	2.0	$4.0\cdot10^3$	ditto	tj	75
$[Ni(dgly)_2] + dgly^- \rightleftarrows [Ni(dgly)_3]^-$	32	$3.3\cdot10^3$	»	tj	75
Ni^{2+} imid $\rightleftarrows$ [Ni (imid)]$^{2+}$	2.7	$5.0\cdot10^3$	25°, $\mu=0.15$, pH = 7.1	tj	75
$[Ni(imid)]^{2+} + imid \rightleftarrows [Ni(imid)_2]^{2+}$	8.9	$4.3\cdot10^3$	ditto	tj	75
$[Ni(imid)_2]^{2+} + imid \rightleftarrows [Ni(imid)_3]^{2+}$	17	$2.4\cdot10^3$	»	tj	75
$Ni^{2+} + dye \rightleftarrows [Ni(dye)]^{2+}$	—	$4\cdot10^3$		tj	146
$Ni^{2+} + HT^{3-} \rightleftarrows NiHT^-$	$2.8\cdot10^2$	$2.9\cdot10^5$	15°	tj	159
$Ni^{2+} + C_2O_4^{2-} \rightleftarrows NiC_2O_4$	3.6	$7.5\cdot10^4$	25°, $\mu=0.1$	stfl	186
$Ni^{2+} + HC_2O_4^- \rightleftarrows NiC_2O_4 + H^+$ *	$1.5\cdot10^3$	$5\cdot10^3$	ditto	stfl	186
$[Ni(H_2O_6)]^{2+} + Mal^{2-} \rightleftarrows [(H_2O)_4NiMal]$	42	$4.2\cdot10^5$	25°, $\mu=0,0$	ps	188
$Ni^{2+} + terpy \rightleftarrows [Ni(terpy)]^{2+}$	$2.5\cdot10^{-8}$	$1,3\cdot10^3$	25	stfl	137
$[Ni(terpy)]^{2+} + terpy \rightleftarrows [Ni(terpy)]^{2+}$	$1.6\cdot10^{-6}$	$2,0\cdot10^5$	25	stfl	137
$Ni^{2+} + \alpha\text{-alan}^- \rightleftarrows [Ni(\alpha\text{-alan})]^+$	0.022	$2\cdot10^4$	20°, $\mu=0.1$	tj	139
$[Ni(\alpha\text{-alan})]^+ + \alpha\text{-alan}^- \rightleftarrows [Ni(\alpha\text{-alan})_2]$	0.80	$4\cdot10^4$	ditto	tj	139
$Ni^{2+} + \beta\text{-alan}^- \rightleftarrows [Ni(\beta\text{-alan})]^+$	0.23	$1.0\cdot10^4$	»	tj	139
$[Ni(\beta\text{-alan})]^+ + \beta\text{-alan}^- \rightleftarrows [Ni(\beta\text{-alan})_2]$	27	$6.9\cdot10^3$	»	tj	139

* Dimensions $M^{-1}\,s^{-1}$.

Symbols: en = ethylenediamine; dye = 2-*p*-dimethylaminophenylazopyridine; HT^{3-} = Tiron; gly = glycine; dgly = glycylglycine; imid = imidazole; py = pyridine; bn = butane-2,3-diamine; C_2N_4NH = aziridine; N_2H_4 = hydrazine; α-alan = α-alanine; β-alan = β-alanine; terpy = 2,2′,6′,2″-terpyridyl; Mal = malonate.

** $k = k_1 + k_2/[H^+]$.

Methods: cfl = constant flow; stfl = stopped flow; tj = temperature jump; ps = pressure shock; lt = low-temperature method; n.m.r. = nuclear magnetic resonance method; elch = electrochemical method.

10^{-6} M, which may be utilised for the quantitative determination of these substances.

The above facts are worthy of attention, since many reactions of complex formation occurring by an S_E mechanism are probably chain reactions, as Margerum has shown for several processes analogous to reaction (37). [193,194]

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Influence of Intermolecular and Intramolecular Order on the Infrared Absorption Spectra of Polymers

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In the investigation of the vibrational spectra of macromolecular compounds it has been noticed that, when a polymer passes from the amorphous to the crystalline state, new absorption bands appear in the spectrum, or else splitting occurs in bands present in the spectrum of the amorphous substance. With certain polymers it has been established that several bands increase in intensity on passage from the crystalline to the amorphous state. The former group have been termed "crystalline" bands, and the second group "amorphous" bands. The origin of these absorption bands will become clear from a general theoretical examination of the vibrations described by an individual polymer chain and the crystalline unit cell formed by the chains. The method of theoretical examination of the normal vibrations of the crystalline polymer[1-5] is based on the application of group theory and is analogous to the method employed to investigate the vibrations of molecular crystals[6-8]. In a crystalline polymer the potential field of the crystal acts on the molecule in the same way as in molecular crystals. This should lead to a change in the spectrum of the crystalline polymer as compared with the amorphous material. Certain types of vibrations, which are inactive in an individual polymer molecule, may be active in the unit cell of a three-dimensional or one-dimensional crystal, since the symmetry of a molecule in a crystal field is usually lower than the symmetry of a free molecule. This results in a weakening of the selection rules found for an isolated molecule. It must be noted that, if degenerate vibrations occurred in an isolated molecule, the change in selection rules might result in elimination of the degeneracy. The appearance of "crystalline" bands also may be due to a change in the configuration of the molecular chain in the crystal cell of the polymer compared with its configuration in the amorphous state. Consideration of the vibration of an individual molecule in the crystal field is not complete, since it takes no account of the interactions of vibrations between chains in the crystal cell. This can be done in a theoretical investigation of vibrations in the unit cell of a crystal as a whole.

In the spectra of many polymers, transition from the amorphous to the crystalline state is accompanied not only by weakening of the selection rules but also by splitting of the main vibration frequencies. Physically such splitting occurs as a result of the resonance interaction of analogous vibrations undergone by individual chains in the unit cell. If n molecules are contained in the unit cell, as a result of resonance interaction, there will be n vibrations corresponding to each undegenerate vibration of an isolated molecule. The magnitude of the resonance splitting of frequencies will depend on the intermolecular interaction; it may be so small as to be unobservable experimentally. Furthermore, not all components of the resolved band are active in the infrared absorption spectrum.

Considerable interest attaches to study of the vibrational spectra of polymers having a regular chain structure (isotactic and syndiotactic polymers). In several cases these polymers show resonance splitting of the bands associated with interaction between analogous groups located along the polymer chain. Thus polymers having a helical chain structure, for example, show splitting of certain vibrations into two components polarised respectively parallel to the axis of the helix and perpendicular to the plane of the helix[9], and in this case the magnitude of the splitting depends on the type of interaction between the groups involved in the vibrations. In several cases new bands are found—"amorphous" absorption bands—on passing from the crystalline to the amorphous polymer. The appearance of these absorption bands may be caused either by breakdown in the selection rules operating in the crystal or by the existence in the amorphous phase of rotational isomers which are absent in the crystalline phase. The intensity of the "amorphous" bands is usually low. This is probably