Contribution from the Max-Planck-Institut für physikalische Chemie,
Göttingen, Germany

Fast Ionic Reactions in Solution. IV.
The Formation of the Vanadyl Sulfate Complex in Aqueous Solution

By H. STREHLOW and H. WENDT

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In the first part of this paper an experimental technique is described for the measurement of fast chemical reactions. The position of a chemical equilibrium is shifted suddenly by the application of a pressure change. The relaxation of the concentrations toward the new equilibrium is followed by measuring the conductivity of the solution as a function of time. The pressure jump method[1-6] has been developed to a useful, sensitive, and widely applicable tool for the investigation of fast chemical reactions in solution. Reactions with relaxation times between about 5×10^{-5} and 50 sec. can be studied. Only a few tenths of a cc. of solution are required for the measurement. The accuracy attainable compares favorably with other techniques for the measurement of fast reactions. In the second part of the paper an application of the method is reported. The rate constants of the reaction $VO^{+2} + SO_4^{-2} \rightleftharpoons VOSO_4$ are determined from measured relaxation times, which are of the order of 10^{-3} sec. The thermodynamic stability constant K of the complex has been determined: $K = (3.0 \pm 0.5) \times 10^2\ M^{-1}$ at 25°. The mechanism of the reaction is discussed. From the equilibrium and kinetic measurements the ratio of the concentrations of the inner sphere complex and of the outer sphere complex could be estimated to be about two.

Introduction

Different relaxation techniques have been applied to the measurement of fast chemical reactions. Ultrasonic absorption,[7,8] a temperature jump method,[8-10] and electric field jump techniques have been used.[8,9,11] The pressure jump method[1] is experimentally especially simple. The pressure on a solution is changed suddenly (Fig. 1a) and the position of chemical equilibrium existing in the solution is thereby shifted adiabatically (Fig. 1) according to

$$\left(\frac{\mathrm{d}\ln K_c}{\mathrm{d}p}\right)_S = -\frac{\Delta V}{RT} + \frac{V\alpha_T}{C_P}\frac{\Delta H}{RT} + \beta_S\Delta\nu \qquad (1)^{12}$$

where K_c is the equilibrium constant on the molarity basis, ΔV is the molar change of volume, and ΔH the molar change of enthalpy for the reaction in question. α_T is the thermal coefficient of expansion, C_P the heat capacity at constant pressure for a volume of electrolyte solution V, β_S is the isentropic compressibility, and $\Delta\nu$ is the change in number of moles for the reaction.

The concentrations approach their new equilibrium values exponentially with time (Fig. 1b). The time constant, or relaxation time τ, is a function of the rate constants involved and also may be a function of the concentrations of reacting species. Therefore from the measurement of τ at different concentrations the kinetics of the reaction can be determined.

The relative change in resistance of the solution as a function of time after the pressure jump Δp is given by

$$\frac{\Delta R(t)}{R\Delta p} = r_1 f(t) + r_2 g(t) \qquad (2)$$

The functions $f(t)$ and $g(t)$ depend upon how the pressure has been released. For an exponential pressure decay

$$f(t) = \exp\left(-\frac{t}{\tau_p}\right)$$

$$\text{and } g(t) = \frac{\tau_p \exp\left(-\frac{t}{\tau_p}\right) - \tau\exp\left(-\frac{t}{\tau}\right)}{\tau_p - \tau} \qquad (3a)$$

or for a linear decay of pressure

$$f(t) = \left(1 - \frac{t}{\tau_p}\right)$$

$$\text{and } g(t) = 1 - \frac{t}{\tau_p} + \frac{\tau}{\tau_p}\left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \text{ for } 0 < t < \tau_p \qquad (3b)$$

$$f(t) = 0 \qquad \text{and } g(t) = \exp\left(-\frac{t-\tau_p}{\tau}\right) \qquad \text{for } t > \tau_p$$

τ_p is the time constant of the apparatus. If $\tau >> \tau_p$, which is true except for the fastest reactions measurable by the pressure jump technique, only $g(t)$ is of importance and regardless of the mode of pressure release is given by

$$g(t) = \exp(-t/\tau) \qquad (3c)$$

The amplitude r_2 of the chemical relaxation term in eq. 2 extrapolated to time zero is given by

$$r_2 = \left|\frac{\Delta R}{R\Delta p}\right|_{\text{chem}} = \frac{\Delta\alpha(0)}{\Delta p} = \frac{1-\alpha}{2-\alpha}\left(-\frac{\Delta V}{RT} + \frac{V\alpha_T}{C_P}\frac{\Delta H}{RT} + \beta_S\Delta\nu\right) \qquad (4)$$

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(1) H. Strehlow and M. Becker, *Z. Elektrochem.*, **63**, 457 (1959); see also S. Ljunggren and O. Lamm, *Acta Chem. Scand.*, **12**, 1834 (1958).

(2) B. Behr and H. Wendt, *Z. Elektrochem.*, **66**, 223 (1962).

(3) H. Wendt and H. Strehlow, *ibid.*, **64**, 131 (1960); **66**, 228 (1962).

(4) H. Wendt, *ibid.*, **66**, 235 (1962).

(5) M. Eigen, K. Kustin, and H. Strehlow, *Z. physik. Chem.* (Frankfurt), **31**, 140 (1962).

(6) H. Strehlow, *Z. Elektrochem.*, **66**, 392 (1962).

(7) M. Eigen, G. Kurtze, and K. Tamm, *ibid.*, **57**, 103 (1953); M. Eigen, *Z. physik. Chem.* (Frankfurt), **1**, 134 (1954).

(8) L. de Maeyer, *Z. Elektrochem.*, **64**, 65 (1960); M. Eigen and K. Tamm, *ibid.*, **66**, 93, 107 (1962).

(9) M. Eigen and L. de Maeyer, in "Technique of Organic Chemistry," Vol. VIII, Second Ed., Interscience Publishers, New York, N. Y., in press.

(10) G. Czerlinski and M. Eigen, *Z. Elektrochem.*, **63**, 652 (1959); G. Czerlinski, H. Diebler, and M. Eigen, *Z. physik. Chem.* (Frankfurt), **19**, 246 (1959).

(11) M. Eigen and L. de Maeyer, *Z. Elektrochem.*, **59**, 986 (1955).

(12) In aqueous solutions at 25° a pressure jump of 50 atm. is accompanied by a temperature jump of 0.1°. With ΔV = 30 cm.^{3} mole^{-1}, ΔH = 10 kcal. mole^{-1}, and $\Delta\nu$ = 1, the relative magnitude of the three terms in eq. 1 is about 20:2:1. In non-aqueous systems the last two terms may become much more important.

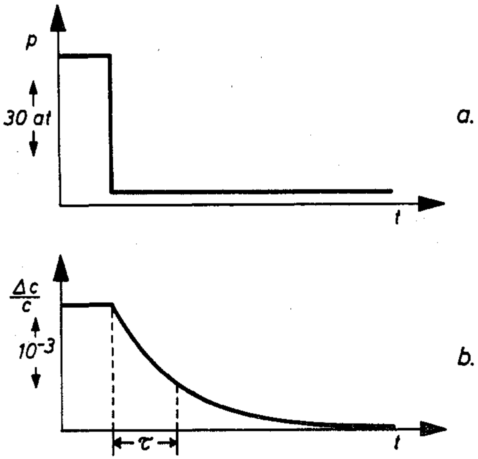

Fig. 1.—Chemical relaxation (1b) after pressure jump (1a) (schematic representation).

α is the degree of dissociation for a reaction of the type

$$AB \rightleftharpoons A + B \qquad (5)$$

An intensive discussion of chemical relaxation has been given by Eigen and de Maeyer.[9]

If there are other electrolytes than the reacting one in the solution $|\Delta R/R\Delta p|_{\text{chem}}$ is given by

$$\left|\frac{\Delta R}{R\Delta p}\right|_{\text{chem}} = \frac{\Delta\alpha}{\left(\alpha + \frac{\Sigma c_i\lambda_i}{c_r\lambda_r}\right)\Delta p} \qquad (6)$$

where c_i and λ_i are the concentrations and conductances, respectively of the non-reacting species; c_r and λ_r those of the reacting electrolyte. $\Delta R/R\Delta p$ therefore may be much smaller in the presence of foreign electrolyte and the sensitivity of the method is seriously reduced. This drawback will be discussed below in more detail.

Another limitation of the technique, which applies to all relaxation methods, is given by the fact that the constant of the disturbed equilibrium (*e.g.*, eq. 5) must not be very small or very great. If $\alpha \approx 1$ according to eq. 4, the amplitude of the effect becomes very small. If, on the other hand, α is small, the sensitivity is seriously reduced by mere traces of non-reacting ions (eq. 6).

According to Fig. 1 the essential parts of the apparatus consist of a device for the production of a very fast pressure jump and of a suitable Wheatstone bridge with an oscilloscope to measure the change of conductivity as a function of time.

Experimental

The Autoclave.—A fast pressure jump can be realized in the autoclave as shown in Fig. 2. Two similar conductivity cells are inside the autoclave. One of the cells is filled with the solution under investigation, the other one with a non-reacting solution; *e.g.*, a solution of KCl with a concentration such that both cells have very nearly the same resistance. In this way, disturbing effects of the change of resistance due to physical effects only largely cancel (see Fig. 5f). The rest of the chamber is filled with a liquid non-miscible with water (kerosene or a more viscous paraffin oil). Lids of soft polyethylene on top of the conductivity cells separate the solution from the kerosene. The reaction chamber is closed by a polyethylene membrane, avoiding any air bubbles. The pressurizing chamber above is connected to a tank of compressed air and is closed by a rupture disk of 0.1 mm. phosphor bronze (critical pressure about 65 atm.). In the actual experiment the rupture disk is punctured at 55–60 atm. by a steel needle as shown in Fig. 3.

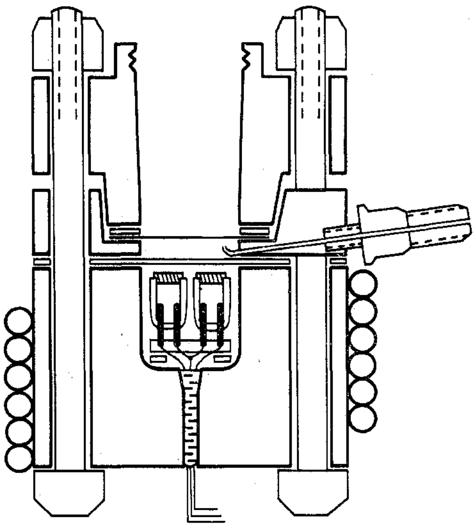

Fig. 2.—The autoclave.

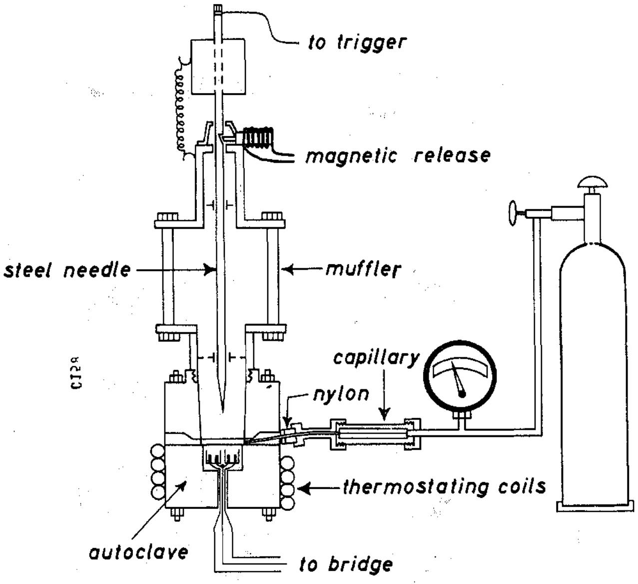

Fig. 3.—The pressure jump apparatus.

The contact of the steel needle with the phosphor bronze closes the trigger circuit and thus triggers a single sweep of the oscilloscope. A muffler made of a tough plastic damps the considerable noise to a tolerable level. A capillary in the lead for the compressed air reduces the rate of flow after the experiment and avoids a heavy shock to the manometer. The autoclave is equipped with copper coils connected to a water thermostat. A thermocouple allows the measurement of the actual temperature inside the autoclave.

The Wheatstone Bridge.—Since only relative changes of the cell resistance are to be measured, the requirements to be fulfilled by the bridge are different from those encountered elsewhere in the setup of impedance bridges. The bridge frequency must of course be greater than the reciprocal of the shortest time constant to be measured (see Fig. 5a and 5b). Either 50 or 100 kc. sec.$^{-1}$ has been used. A bridge as diagrammed in Fig. 4 is satisfactory. The variable resistance R and capacitance C need

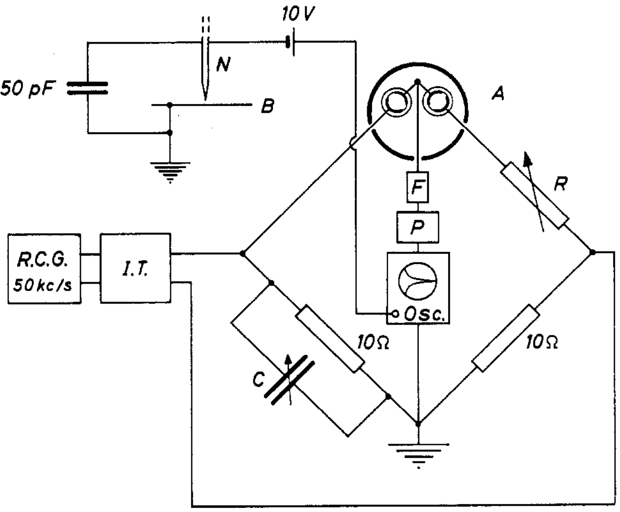

Fig. 4.—The Wheatstone bridge: A, autoclave; R, resistance (0.01 to 10,000 ohms); F, filter; P, preamplifier; Osc., cathode ray oscilloscope; R.C.G., R.-C. oscillator; I.T., impedance transformer; N, steel needle; B, rupture disk.

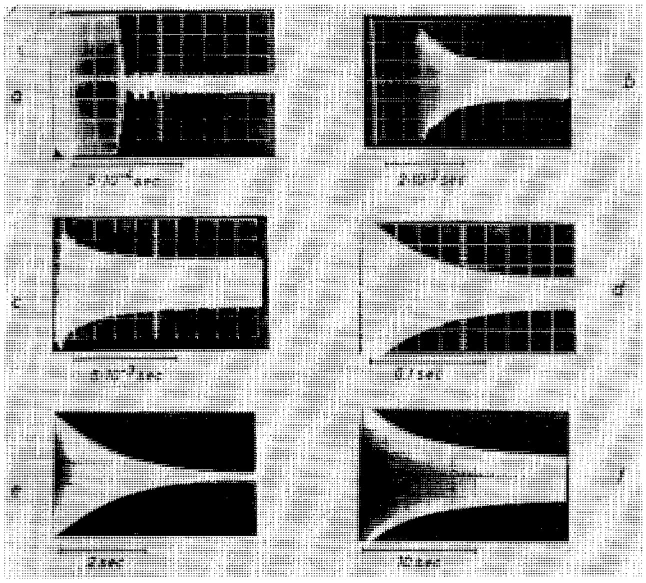

Fig. 5.—Pressure jump oscillograms: (a) 0.1 *M* $MgSO_4$; 2.5 mm. pressure chamber filled with kerosene; linear decay, τ_p = 40 μsec. (oscillator frequency 100 kc. sec.$^{-1}$). (b) Relaxation time for the reaction $VO^{+2} + SO_4^{-2} \rightleftharpoons VOSO_4$: concentration of $VOSO_4$ = 0.1 *M*; pH 2.6; $\tau = 7.0 \times 10^{-4}$ sec. (c) Relaxation time for the reaction[3] $Fe^{+3} + Cl^- \rightleftharpoons FeCl^{+2}$: concentration of $FeCl_3$ = 0.1 *M*, $\tau = 1.6 \times 10^{-3}$ sec. (d) Relaxation time for the reaction[2] $Al^{+3} + SO_4^{-2} \rightleftharpoons AlSO_4^+$: concentration of $Al_2(SO_4)_3$ = 0.05 *M*, $\tau = 5.8 \times 10^{-2}$ sec. (e) Relaxation time for the reaction[5,6] $CH_3COCOOH + H_2O \rightleftharpoons CH_3C(OH)_2COOH$: concentration of pyruvic acid = 0.260 *M*, τ = 1.15 sec. (f) Temperature equilibration after pressure jump.

not be very precise for the reasons mentioned above. To minimize effects of the bridge capacitances to ground at the relatively high frequencies, the resistances of the two equal branches are chosen to be only 10, or at most 100 ohms. Therefore, an impedance transformer (I.T.) is necessary to match the oscillator (R.C.G.) output to the bridge. Since the setup of the bridge is so simple the balancing also depends on the frequency. Therefore, it is important that only one frequency be fed into the bridge; *i.e.*, that the oscillator combined with the impedance transformer be unusually free from overtones. This is only possible for a bridge voltage less than 3 volts. To reject any pickup of 50 c. sec.$^{-1}$ (line) or frequencies > 200 kc. sec.$^{-1}$ (broadcasting and high frequency noise) a filter (F) is inserted between the bridge and the preamplifier (P).[13]

For the measurement of a relaxation time τ a band width for the amplifier plus oscilloscope $\Delta\nu >> 1/\tau$ (for example $\Delta\nu = 10/\tau$) is sufficient to avoid distortion of the recorded signal. To use a band width much greater than this is equivalent to an unnecessary loss in the signal-to-noise ratio. Therefore (P) is a preamplifier with variable band width.[13] A Tektronix Model 535 oscilloscope has been used.

From the instant the steel needle touches the rupture disk a definite time (about 0.5 msec.) elapses before the disk breaks. For very fast reactions, therefore, the delay sweep of the oscilloscope must be used to delay the triggering.

Results and Discussion

The Measurement of Relaxation Times.—In Fig. 5a an oscillogram with a solution of 0.1 *M* $MgSO_4$ is shown. The relaxation time for the reaction $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4$ is less than 1 μsec.,[7] and therefore is too fast to be measured with the pressure jump technique. The oscillogram of Fig. 5a therefore shows only the decrease of pressure with time, $f(t)$; ($\tau << \tau_p$, see eq. 2, 3a, and 3b). The oscillogram is taken with a pressure chamber of 2.5 mm. depth. In the experiment the pressure chamber had been filled with kerosene. The time constant of the nearly linear decay thus obtained is (40 ± 5) μsec. The pressure decay in an air filled 10 mm. pressure chamber is exponential with a time constant of (60 ± 5) μsec. and linear with about the same time constant when the pressure chamber is filled with kerosene.

Figures 5b, 5c, 5d, and 5e show oscillograms for reactions with relaxation times in different time ranges. In general the accuracy attainable increases with increasing relaxation times. For very slow reactions it is important that the solutions in both conductivity cells have as nearly the same temperature coefficient of conductivity as possible. Otherwise the measurement may be disturbed by an exponential temperature change with time inside the autoclave. This process has a reproducible relaxation time of about 6.5 sec. as shown in Fig. 5f.

The Applicability of the Pressure Jump Technique.—The method can be applied in the time range from about 50 μsec. to 50 sec. It is essential that the reaction involves a change in conductivity. However, even reactions between non-ionic species can be measured by this technique if they are followed by faster ones with conductivity changes, *e.g.*, by protolytic reactions. The hydration reaction of pyruvic acid is an example for this type of reaction: The hydrated and the unhydrated acids have different strengths so that the primary slow reaction is followed by a fast establishment of the protolytic equilibrium with a corresponding change in conductivity.

The most serious drawback of the method is the decrease in sensitivity accompanying the addition of non-reacting electrolytes (see eq. 6). Nevertheless we were still able to measure relaxation times with an

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(13) G. B. Miller, *Electronics*, **31**, 79 (1958).

accuracy of ±10% in solutions, 98% of whose conductivity was due to buffer ions and only about 2% to the reacting components. The increase of sensitivity was obtained by using the highest possible bridge voltage (3 volts) and the smallest band width compatible with the relaxation time to be measured. An increase of the applied pressure leads to serious cavitation in the solution and also to an early destruction of the muffler. But a factor of about 2 might be gained for slow reactions using pressure jumps of 100 atm. (For slow reactions with $\tau \geq 2 \times 10^{-3}$ sec., the cavitation bubbles already have disappeared.)

Following the change of concentration not by conductivity but by an optical method, *e.g.*, by absorption spectrophotometry, would avoid the reduction in sensitivity by the addition of non-reacting electrolyte. Since the relative change in concentration by a pressure jump of 50 atm. is rather small, the measurable optical effect would be less favorable than the conductivity effect even in a solution with quite a high buffer concentration, since small concentration differences are measured much more sensitively by conductance than by optical measurements.

The unwanted effect of the extra conductivity resulting from the addition of buffers can be at least reduced by using special buffers with components of low mobility; *e.g.*, the cations of the usual buffers may be replaced by tetraethylammonium ions, etc. An even better solution of the problem would be buffering with suitable amphoteric electrolytes at their isoelectric point. Of course it would have to be shown that these buffer components do not catalyze the reaction under investigation.

Another disturbing effect should be mentioned: Using high sensitivities we found with the 10 mm. pressure chamber a relaxation time of about 10^{-2} sec., which proved to be the escaping time of air from the muffler. This effect can be suppressed by filling the pressure chamber with kerosene.

Investigation of the Formation of the Complex $\mathbf{VOSO_4}$. (a) Kinetic Measurements.—Relaxation measurements in $VOSO_4$ solutions reveal two types of relaxation times of the order of 1 sec. and 10^{-3} sec., respectively (see Fig. 5b). The slow reaction is a hydrolysis process which has not been investigated further. The relaxation time of the faster reaction is only weakly dependent on the $VOSO_4$ concentration and pH. The experimental results are summarized in Fig. 6. Each point is an average of at least five measurements. In analogy to results obtained on similar systems,[2,3,8,9] the observed relaxation times are attributed to the formation of an inner sphere complex according to

$$VO^{+2} + SO_4^{-2} \underset{\text{very fast}}{\overset{K_0}{\rightleftharpoons}} VOH_2OSO_4 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} VOSO_4 \qquad (7)$$

The first step, *i.e.* the formation of the outer sphere complex, is a very fast reaction; thus the equilibrium between the dissociated ions and the outer sphere complex is almost completely established during the measurement. The rate determining step for the over-all reaction is the exchange of a water molecule by a sulfate ion in the first coördination sphere of the vanadyl ion. Neglecting the concentration of hydrogen sulfate ion, the relaxation time for reaction 7 is given by

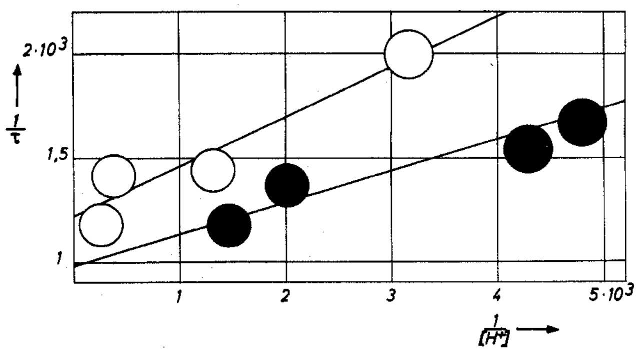

Fig. 6.—Relaxation measurements in aqueous $VOSO_4$ solutions; $1/\tau$ (sec.$^{-1}$) plotted against $1/[H^+](M^{-1})$: ○ 0.1 M $VOSO_4$, $\mu = 0.16$ M; ● 0.01 M $VOSO_4$, $\mu = 0.025$. Temperature 25°; pH adjusted by addition of H_2SO_4 or NaOH. (The diameter of the circles indicates the error in $1/\tau$. $[H^+]$ has been calculated from measured pH values using eq. 12 for the activity correction.)

$$\frac{1}{\tau} = k_{23} \frac{K_0 f_{\pm}^2([VO^{+2}] + [SO_4^{-2}])}{1 + K_0 f_{\pm}^2([VO^{+2}] + [SO_4^{-2}])} + k_{32} \qquad (8)$$

where K_0 is the formation constant of the outer sphere complex

$$K_0 = \frac{[VOH_2OSO_4]}{[VO^{+2}][SO_4^{-2}]f_{\pm}^2} \qquad (9)$$

and $f_{\pm}$ is the mean activity coefficient of the dissociated vanadyl sulfate. $1/\tau$ depends on pH, and the rate constants can be written

$$k_{23} = k_{23}^0 + k_{23}'/[H^+] \text{ and } k_{32} = k_{32}^0 + k_{32}'/[H^+] \qquad (10)$$

Reaction 7 is catalyzed by OH^- ions.[2,3]

The ratio of the slopes for the two curves in Fig. 6 should be equal to the ratio of the formal hydrolysis constants of the vanadyl ion at the two ionic strengths. This ratio has been estimated with eq. 12 and the reliability of the extrapolation in Fig. 6 thus is somewhat increased.

From the known stability constant K (see below)

$$K = \frac{[VOH_2OSO_4] + [VOSO_4]}{[VO^{+2}][SO_4^{-2}]f_{\pm}^2} = (3.0 \pm 0.5)10^2 \, M^{-1} \qquad (11)$$

and the kinetic measurements all equilibrium and rate constants were evaluated as shown in a previous paper.[3] The results are summarized in Table I.

In the two series of measurements ($C_{VOSO_4} = 0.1$ and 0.01, respectively) the ionic strength was not equalized in order to retain a sufficient sensitivity for the measurement of τ in 0.01 M $VOSO_4$ solution (*cf.* previous section). However, some measurements of τ have been made in a solution of 3.6×10^{-2} M $VOSO_4$ with sufficient KNO_3 to raise the ionic strength to 0.16 M. The results are consistent with the data of Table I.

The activity corrections have been made with Davies

TABLE I

EQUILIBRIUM AND RATE CONSTANTS FOR REACTION 7 IN AQUEOUS SOLUTION AT 25° AND DIFFERENT IONIC STRENGTHS

C_{VOSO_4}, M	Ionic strength μ, M	k_{23}^0, sec.$^{-1}$	k_{23}', M sec.$^{-1}$	k_{32}^0, sec.$^{-1}$	k_{32}', M sec.$^{-1}$	$K_0f_\pm^2$, M^{-1}	K_i	$Kf_\pm^2$, M^{-1}
0.1	0.16		1.2×10^{-1}		1.1×10^{-1}	8.3		29
0.01	0.025	1.5×10^3	9.0×10^{-2}	6.0×10^2	9.0×10^{-2}	25	2.5	89
...	0		3.9×10^{-2}		4.0×10^{-2}	86		300

formula[14] (12) assuming an activity coefficient $f_0 = 1$ for

$$-\log f_\pm = 0.5z_+z_-[\sqrt{\mu}/(1 + \sqrt{\mu}) - 0.2\mu] \qquad (12)$$

for the uncharged species. The equilibrium constants K_0 and K_i, which cannot be obtained conveniently by any conventional method, are reliable only within a factor of about two, since the concentration dependence of τ is rather small and the uncertainty due to the activity correction also is considerable. The rate constants are correct to about ±20%. Since the charge distribution around a vanadyl ion in aqueous solution is not spherically symmetrical,[15] the kinetic results cannot be compared with similar substitution reactions of symmetrical ions.[16] The rate of exchange of a water molecule in the inner sphere of a vanadyl ion by a sulfate ion is slower by about two orders of magnitude as compared to the corresponding reaction of magnesium ion, although the stability constants of the two complexes are comparable.[17] From the difference in size of the ions an opposite effect would be expected.

(b) **Estimation of the Stability Constant of $VOSO_4$.**—A value for the stability constant K as defined by eq. 11 is not available in the literature. An exact determination of this constant proved to be rather difficult since the concentrations in unacidified $VOSO_4$ solutions are changed considerably by a slow hydrolysis process.[18]

Different methods have been applied to evaluate K. All measurements indicated that the complex $VO(SO_4)_2^{-2}$ can be neglected at least up to a total concentration of 0.2 M $VOSO_4$ (in contradiction to conclusions of Ducret[19]). Spectrophotometric measurements at 770 and 370 mμ supply only rough values of K due to the small difference in the extinction coefficients of the ion and the complex.[15] Conductivity measurements indicate that K for $VOSO_4$ should be similar to that of $MgSO_4$ ($K_{MgSO_4} = 2 \times 10^2\ M^{-1}$ [17]). The increase of the solubility of Tl_2SO_4 in the presence of $VO(ClO_4)_2$ was measured but the accuracy of the stability constant K thus obtained depends strongly on the stability constants of higher complexes of thallium, which are not well known. By potentiometric titrations of $VO(ClO_4)_2$ with Na_2SO_4 at a lead amalgam electrode[2,20] $K = (2.4 \pm 0.5) \times 10^2\ M^{-1}$ was obtained. This value, however, is too small due to a systematic error, which is the slow oxidation of lead amalgam by VO^{+2} ions. The most successful method for the determination of K was the measurement of the increased solubility of $PbSO_4$ in $VO(ClO_4)_2$ solutions. The concentration of Pb^{+2} was determined polarographically. From these measurements K turned out to be $(3.0 \pm 0.5) \times 10^{-2}$ M^{-1} at 25° and $\mu = 0$. The extrapolation to ionic strength $\mu = 0$ was performed with eq. 12. The other measurements mentioned were consistent with this result.

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[18] F. J. C. Rosotti and H. S. Rosotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

[19] L. P. Ducret, *Ann. Chim.*, **6**, 729 (1951).

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