

In Fig. 2 is shown a plot of x^2 against t/g , as obtained from one of the curves shown in Fig. 1. The slope of the least-square line drawn through these points gave the diffusion coefficient, D' , corresponding to the particular time of measurement (see eq. 4). The closeness of the experimental points to the connecting straight line reveals the consistency of the present method of measurement. The maximum standard deviation in the different sets of data, obtained in the present series of experiments, from which the average values of D' were deduced, was about 0.3%. This may be compared with the corresponding value of 0.1% (from Table I of ref. 1, for $J_m \approx 100$) obtainable by the Gouy method. A typical zero time correction has been illustrated in Fig. 3. From the intercept and slope of the least-square line the value of Δt was obtained as 8 sec., and the extrapolated value of D' to $1/t = 0$ or $D(\bar{C})$ was obtained equal to 5.206×10^{-6} cm.²/sec., with an average deviation from the least-square line, ΔD equal to 0.035%. The values of the diffusion coefficient, $D(\bar{C})$, thus obtained for different mean solute concentrations \bar{C} are shown in Table I.

TABLE I
THE DIFFUSION COEFFICIENT OF SUCROSE AT DIFFERENT CONCENTRATIONS (25°)

\bar{C} , 10 ² g./ml.	ΔC , 10 ⁶ g./ml.	Δt , sec.	$D(\bar{C})$, 10 ⁶ cm. ² /sec.	ΔD , %
1.06	2.12	0	5.219	0.031
2.07	2.20	8	5.206	.035
3.02	2.18	7	5.200	.038
4.07	2.10	15	5.190	.039
5.00	2.02	16	5.188	.019
10.60	2.80	4	5.145	.025

In this table column 3 gives the values of Δt and column 5 gives the values of ΔD as obtained for the respective cases. For the sake of comparison the values of $D(\bar{C})$ were plotted along with the data of Gosting and Morris (25°) and shown in Fig. 4. As the present set of measurements were carried out in a lower concentration range, a test experiment was performed with a mean solute concentration (1.06%) within the range used by Gosting and Morris. It can be seen from Fig. 4 that there is excellent agreement of the present data with those of Gosting and Morris both within and outside the concentration range used by them. The least-square line relating $D(\bar{C})$ with \bar{C} ,

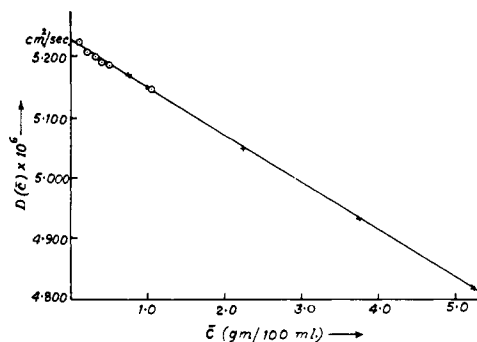


Fig. 4.—Plot of $D(\bar{C})$ against \bar{C} ; \times represents the data of Gosting and Morris, \circ the data of present work.

as obtained from the present data is given by

$$D(\bar{C}) = 5.224(1 - 0.0144\bar{C}) \times 10^{-6} \quad (5)$$

where \bar{C} is given in g./100 cc. The average deviation of the experimental points from the above least-square line was 0.046%. This is to be compared with the corresponding equation obtained by Gosting and Morris

$$D(\bar{C}) = 5.226(1 - 0.0148\bar{C}) \times 10^{-6} \quad (6)$$

with an average deviation of 0.04%. The agreement is thus highly satisfactory and justifies the use of the present technique for the measurement of the diffusion properties of different solutes.

It should be noted, however, that the ΔC values used in the present experiments were appreciably different from those used by Gosting and Morris (25°). This merely points to the fact that the diffusion coefficient of sucrose is independent of the ΔC values.¹ Finally the present set of data when considered along with these of Gosting and Morris and English and Dole lead to the conclusion that the diffusion coefficient of sucrose obeys the same linear relation with the concentration of the solution irrespective of whether it is very dilute or supersaturated.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISC., AND UNIVERSITY OF COLORADO, BOULDER, COLO.]

Equilibrium and Kinetic Studies on the Reaction of Chromium(III) Ion and Chloride Ion in Methanol-Water Solutions^{1,2}

BY RICHARD J. BALTISBERGER AND EDWARD L. KING³

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The formation of inner-sphere chlorochromium(III) ion was studied at 30.0, 43.6, and 60.0° in acidic aqueous methanol solutions from 0 to 70 mole % methanol. The binding of methanol in the first coordination shell of both chromium(III) ion and chlorochromium(III) ion was measured, and this was taken into account in arriving at the equilibrium quotient $Q_1 = [\text{Cr}(\text{OH})_2\text{Cl}^{2+}]_{\text{aH}_2\text{O}} / [\text{Cr}(\text{OH})_2\text{Cl}^{2+}][\text{Cl}^-]$ which ranged at 30.0° from 0.107 in water to 6.2 in 70.6 mole % methanol; the ionic strength was 0.418 *M*. The value of ΔH was 7.4 kcal. mole⁻¹ independent of the solvent composition, and the values of ΔS^\ddagger ranged from 20.0 to 28.1 cal. mole⁻¹ deg.⁻¹ over the range of solvents studied. The rate at which methanol replaces water in the first coordination shell of chromium(III) ion was determined and was found to be very similar to the rate of exchange of water between solvent and the first coordination shell of chromium(III) ion in aqueous solution. The rate at which chloride ion dissociates from chlorochromium(III) ion was found to be approximately 10-fold lower.

Experimental data pertinent to ion association in labile systems in mixed solvents generally yield com-

(1) Based on the Ph.D. Thesis of Richard J. Baltisberger, University of Wisconsin, 1963.

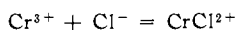
(2) Supported in part under contract AT-(11-1)-1168 between the University of Wisconsin and the U. S. Atomic Energy Commission and in part

posite equilibrium quotients in which concentrations of species with a particular charge but with different

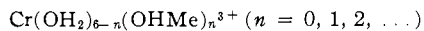
by grant GP-680 to the University of Colorado from the National Science Foundation.

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solvation are summed together. Appropriate studies on inert systems, because of the low reaction rates, allow concentrations of species with different solvation to be obtained, thereby giving a more well-defined picture of such a system. This paper deals with ion association in an inert system, the reaction of chromium(III) ion and chloride ion in acidic aqueous methanol solution of composition 0 to 70 mole % methanol. The chemical equation



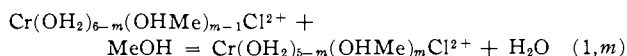
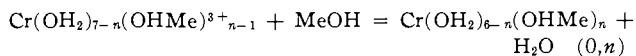
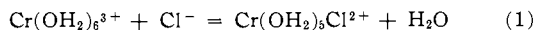
oversimplifies the reaction since Cr^{3+} stands for all of the species



and CrCl^{2+} stands for all of the species.



Therefore, the composite reaction is made up of the independent reactions



involving replacement of ligands in the first coordination sphere of chromium(III). If outer sphere ion-ion interaction is appreciable and is described in terms of ion-pair formation, the situation is complicated still more since the analytical procedure combines ion pairs and species with which they are in rapid equilibrium.

Studies reported in the present paper provide the following as a function of solvent composition: (1) the equilibrium concentration of chromium(III) species of charge 2+ (*i.e.*, $\text{Cr}(\text{OH}_2)_{5-m}(\text{OHMe})_m\text{Cl}^{2+}$) as a function of temperature; (2) the average number of methanol molecules bound per chromium(III) both in species of charge 3+ (*i.e.*, $\text{Cr}(\text{OH}_2)_{6-n}(\text{OHMe})_n^{3+}$) and 2+ (*i.e.*, $\text{Cr}(\text{OH}_2)_{5-m}(\text{OHMe})_m\text{Cl}^{2+}$) as a function of temperature; (3) the rate of replacement of water by methanol in the first coordination shell of chromium(III) ion (*i.e.*, reaction (0,1)) at 30°; and (4) the rates of formation and dissociation of chlorochromium(III) ion at 30°.

The experimental conditions were chosen to keep the concentration of dichlorochromium(III) species very low.

Experimental Details and Results

Reagents.—Doubly distilled water and reagent grade methanol containing less than 0.1% water were used in the preparation of solutions. The second distillation of the water was from alkaline permanganate using a Barnstead still. Methanol was used without further purification.

Lithium perchlorate and sodium perchlorate were recrystallized several times from water after being prepared from perchloric acid and reagent grade carbonates.

Chromium(III) perchlorate was prepared from reagent grade potassium dichromate using hydrogen peroxide as reducing agent in the presence of excess perchloric acid. Recrystallization of the salt from dilute perchloric acid removed most of the potassium perchlorate. Stock solutions of perchloric acid-chromium(III) perchlorate were relatively free of polymeric chromium(III) species as judged from the absorbancy in the ultraviolet region.⁴

Reagent grade hydrochloric acid and perchloric acid were used without further purification.

Analyses.—Acid solutions were analyzed by standard titrimetric procedures. Chromium analyses were performed by conversion of chromium(III) species to chromate ion with alkaline peroxide and measurement of the light absorption at 372 m μ , where the molar absorbancy index of chromate ion is 4815 l. mole⁻¹ cm.⁻¹.⁵ Spectral measurements were made using a Cary Model 14 spectrophotometer. Concentrations of sodium perchlorate and lithium perchlorate solutions were determined

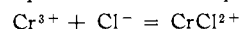
from the acid produced when a measured volume of solution was passed through a Dowex-50 cation-exchange column in the hydrogen ion form. This same procedure was used to evaluate the total normality of chromium(III) perchlorate-perchloric acid solution. The free acid in these solutions was determined by direct titration at 0° after chromium(III) was converted to tris-oxalatochromium(III) ion by heating with a large excess of potassium oxalate.⁶

Separation of chromium(III) species of charge 2+ (*i.e.*, $\text{Cr}(\text{OH}_2)_{5-m}(\text{OHMe})_m\text{Cl}^{2+}$) from equilibrated solutions was made using an ion-exchange procedure carried out at ~0°. Equilibrated solution was poured through a column of Dowex 50-W ion-exchange resin followed by elution with 1 M perchloric acid. Species of charge 2+ are readily eluted by this reagent which does not elute chromium(III) species of charge 3+ at a high enough rate to interfere. At the highest chloride ion concentrations studied in each solvent, where dichloro species of charge 1+ would be most important, elution with 0.15 M perchloric acid preceded elution with 1 M acid. In this way, it was demonstrated that dichloro species were present at negligible concentrations under these most favorable conditions. In most other experiments, elution with 0.15 M acid was omitted, and all chromium species of charge $\leq 2+$ were eluted and considered to be chlorochromium(III) ion, the chromium content of the eluent being determined by the spectrophotometric procedure already described. In the experiments in which elution with 0.15 M perchloric acid was omitted, the eluent containing chlorochromium(III) ion may have contained appreciable solvent methanol. This did not interfere with the chromium analysis as judged by the consistency of these experiments and those involving prior elution with 0.15 M acid.

An ion-exchange procedure also was used to separate species of charge 2+ and 3+ from one another and from solvent methanol in preparation for analysis of these chromium(III) species for bound methanol. Elution with aqueous 0.15 M perchloric acid was continued until all free solvent methanol was removed. Then successive elution by 1.0 M perchloric acid and 3.0 M sulfuric acid gave aqueous solutions containing chromium(III) species of charge 2+ and 3+, respectively, with the only methanol present being that bound in the first coordination shell. Such solutions were analyzed for chromium by the spectrophotometric procedure already described and for methanol by use of cerium(IV)-chromium(VI) at an elevated temperature.⁷ Since chloride ion is oxidized by this procedure, it was removed from chlorochromium(III) ion by precipitation with excess silver nitrate before analysis for methanol. The precipitation was carried out at room temperature in the presence of the oxidizing agent, which increased the apparent rate of dissociation of chloride from chlorochromium(III) ion.

Equilibrium Experiments.—Equilibrium solutions were prepared from stock solutions of known concentrations and density. Therefore, both stoichiometric molarities of solutes and mole fraction solvent composition were known for the equilibrium solutions. The latter quantity designated as Z_{MeOH} (or $Z_{\text{H}_2\text{O}}$) was calculated without taking account of solute species, *i.e.*, $Z_{\text{MeOH}} + Z_{\text{H}_2\text{O}} = 1$. Solutions were sealed in Pyrex tubes, placed in thermostats at 60.00 \pm 0.01, 43.5 \pm 0.1, and 30.00 \pm 0.02°, and heated until equilibrium was established. This was judged from lack of further change in the concentration of chlorochromium(III) ion with time, or for solutions at the two lower temperatures from approach to the same concentration of chlorochromium(III) ion starting from both too high and too low a concentration. In general, solutions were equilibrated for 0.3, 4, and 8 weeks at 60.00, 43.5, and 30.00°, respectively.

Experimental Values of $Q = [\text{CrCl}^{2+}]/(C_{\text{Cr}} - [\text{CrCl}^{2+}])(C_{\text{Cl}} - [\text{CrCl}^{2+}])$.—The sum of concentrations of chlorochromium(III) ions, $\text{Cr}(\text{OH}_2)_{5-m}(\text{OHMe})_m\text{Cl}^{2+}$ ($m = 0, 1, \dots$), was determined by the ion-exchange separation procedure just described coupled with a spectrophotometric analysis for chromium as chromium(VI) in alkaline solution.⁸ This one equilibrium concentration and the stoichiometric composition allowed calculation of an apparent equilibrium quotient for the composite reaction



Values of this quotient

$$Q = \frac{[\text{CrCl}^{2+}]}{(C_{\text{Cr}} - [\text{CrCl}^{2+}])(C_{\text{Cl}} - [\text{CrCl}^{2+}])}$$

in which C_{Cr} and C_{Cl} are the stoichiometric concentrations of chromium(III) ion and chloride ion, respectively, are presented in Table I for experiments at $I = 0.418 M$. The stoichiometric concentration of chromium(III) was ~0.031 M in most experiments but was 0.015 M in some experiments including all of those at $I = 0.194 M$.

In the experiments summarized in Tables I and II, both hydrogen ion concentration and chloride ion concentration vary. If

(4) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

(5) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(6) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(7) J. C. Jayne and E. L. King, forthcoming publication.

TABLE I: EXPERIMENTAL VALUE OF

$$Q = \frac{[\text{CrCl}^{2+}]}{(C_{\text{Cr}} - [\text{CrCl}^{2+}])(C_{\text{Cl}} - [\text{CrCl}^{2+}])}$$

$I = 0.418 M$, $[\text{H}^+] = 0.103 M$, $[\text{Na}^+] = 0.125 M$

Z_{MeOH}^d	No. of expts.	No. of $10^3(C_{\text{Cl}} - [\text{CrCl}^{2+}])$ range of values		Q
		$T = 30.05^\circ$		
0	2	31 ^a -35		0.109 ± 0.001
0.0475	3	5.8-23.3		.147 ± .002
0.128	4	5.8-34.9		.264 ± .001
	1	20.3 ^a		0.265
0.190	4	5.8-34.8		0.382 ± 0.005
0.306	3	5.7-22.9		0.790 ± 0.003
	1	10.1 ^a		0.797
	1	9.0 ^b		0.784
0.391	2	5.6-11.3		1.35
	1	9.9 ^a		1.33
	1	8.9 ^b		1.34
0.505	3	0.95-2.95		2.70 ^c
	1	1.90 ^a		2.60
	1	1.89 ^b		2.84
0.625	3	1.7-5.2		7.73 ± 0.12
	1	1.7 ^a		7.9
	1	1.7 ^b		7.8
0.706	3	0.68-2.12		16.7 ± 0.2
	1	1.37 ^a		16.4
		$T = 43.6^\circ$		
0	2	31 ^a -35		0.1825 ± 0.0005
0.0475	3	11.6-34.9		.251 ± .002
0.128	3	11.6-34.9		.430 ± .003
	1	20.3 ^a		0.427
0.190	3	11.5-34.5		0.653 ± 0.002
0.306	3	5.6-22.5		1.31 ± 0.01
	1	9.9 ^a		1.29
	1	8.9 ^b		1.29
0.391	2	5.5-11		2.33 ± 0.02
	1	9.7 ^a		2.14
	1	8.7 ^b		2.15
0.505	3	0.9-2.81		4.6 ± 0.1
	1	1.8 ^a		4.57
	1	1.8 ^b		4.5
0.625	4	0.73-2.3		13.3 ± 0.2
	1	1.5 ^a		13.1
	1	1.5 ^b		13.1
0.706	3	0.54-1.7		29.7 ± 0.1
	1	1.1 ^a		27.8
		$T = 60.00^\circ$		
0	2	31 ^a -35		0.322 ± 0.005
0.0475	3	11.6-34.7		.445 ± .01
0.128	3	11.5-34.4		.775 ± .004
	1	20.1 ^a		0.741
0.190	3	11.3-34.1		1.12 ± 0.003
0.306	5	5.7-22		2.23 ± 0.03
	1	9.7 ^a		2.18
	1	8.7 ^b		2.16
0.391	4	1.1-16.8		4.13 ± 0.02
	1	9.2 ^a		3.79
	1	8.3 ^b		3.80
0.505	3	0.82-2.55		8.22 ± 0.1
	1	1.6 ^a		8.25
	1	1.7 ^b		8.05
0.625	3	0.6-1.8		24.6 ± 0.6
	1	1.2 ^a		23.2
	1	1.2 ^b		23.2
0.706	3	0.39-0.81		53 ± 1
	1	0.82 ^a		51

^a 0.222 M H⁺, no Na⁺. ^b 0.125 M Li⁺, no Na⁺. ^c An experiment in this series with $C_{\text{Cl}} - [\text{CrCl}^{2+}] = 5.8 \times 10^{-3}$ gave an appreciably higher value of Q (3.20). ^d Z_{MeOH} is the mole fraction of methanol in the solvent, the concentrations of solutes not being taken into account.

TABLE II

$$Q = \frac{[\text{CrCl}^{2+}]}{(C_{\text{Cr}} - [\text{CrCl}^{2+}])(C_{\text{Cl}} - [\text{CrCl}^{2+}])}$$

$[\text{H}^+] = 0.103 M$

Z_{MeOH}	I^a	Q		
		30.05°	43.6°	60.00°
0	0.194	0.135	0.215	0.394
	.959	.086	.154	.260
0.128	.194	.324	.550	.988
	.959	.226	.358	.524
0.306	.194	.960	1.60	3.14
	.959	.511	1.09	1.89

^a Ionic strength maintained with sodium perchlorate.

appreciable acid dissociation of aquomethanolchromium(III) species occurred at the acidities of these experiments, the value of Q would be affected by the ~2-fold change in hydrogen ion concentration. The more relevant of the comparisons which can be made is that between solutions which are 0.232 M hydrogen ion and those which are 0.103 M hydrogen ion-0.125 M lithium ion. There is no appreciable trend in Q with this change in acidity, indicating either that acid dissociation of aquomethanol chromium(III) species is trivial at this acidity or, if not trivial, that acid dissociation of the species of charge 3+ (*i.e.*, $\text{Cr}(\text{OH})_2\text{e}^-$ - $\text{Cr}(\text{OHMe})_n\text{e}^-$) is compensated by acid dissociation of species of charge 2+ (*i.e.*, $\text{Cr}(\text{OH})_2\text{e}^-$ - $\text{Cr}(\text{OHMe})_m\text{e}^-$).

The variation of chloride ion concentration does not have an appreciable effect upon Q . Although this will be interpreted as indicating inappreciable ion pairing of chloride ion and chromium(III) ion, this interpretation is not rigorous. The sum of the concentrations of chloride ion and perchlorate ion is approximately constant in runs at each particular ionic strength, and in addition the variation in perchlorate ion concentration is very small. Therefore, the experimental results are also consistent with appreciable ion pairing of chromium(III) cations with perchlorate ion accompanied by ion pairing of chromium(III) cations and chloride ion of comparable or lower stability.

Experiments run at $I = 0.194$ and $0.959 M$ are summarized in Table II. As expected, association of chromium(III) ion and chloride ion decreases with increase of electrolyte concentration. The sensitivity of Q to electrolyte concentration is very similar in the three solvents studied.

Experimental Values of Methanol Binding by Chromium(III) Ion and Chlorochromium(III) Ion.—Analysis of equilibrated solutions by procedures already described allows evaluation of the average number of methanol molecules bound both by chromium(III) ion, \bar{n}_0 , and by chlorochromium(III) ion, \bar{n}_1 . These data, summarized in Table III, show that the binding of methanol by chlorochromium(III) ion is essentially the same as that by chromium(III) ion.

TABLE III

BINDING OF METHANOL BY CHROMIUM(III) ION (\bar{n}_0) AND CHLOROCHROMIUM(III) ION (\bar{n}_1)

$C_{\text{Cr}} = 3.1 \times 10^{-2} M$, $[\text{H}^+] = 0.103 M$, $I = 0.418 M^a$

Z_{MeOH}	\bar{n}_0			\bar{n}_1		
	30°	43.6°	60°	30°	43.6°	60°
0.190		0.20	0.22			
.306	0.31	.33	.335	0.30	0.31	0.33
.391	.42	.43	.46	.42	.43	.43
.505	.57	.58	.62	.59	.60	.59
.625	.775	.84	.89	.78	.825	.90
.706	.98	1.07	1.14	.98	1.07	1.03

^a Ionic strength maintained with sodium perchlorate.

The Rate of Replacement of Water by Methanol in the First Coordination Shell of Chromium(III).—The binding of methanol by chromium(III) ion in water-methanol solutions containing perchloric acid and chromium(III) perchlorate was followed as a function of time. Experiments were carried out at 30° in solutions of five different compositions ($Z_{\text{MeOH}} = 0.190$ – 0.625). In each experiment the approach of \bar{n} to its equilibrium value was essentially first order. Each

$$\left(1 - \frac{\bar{n}}{\bar{n}_{\text{eq}}}\right) = e^{-kt} \quad (2)$$

experiment involved 5–7 points with reaction being followed 70 to 85% to equilibrium. However, in one

experiment, the approach to equilibrium was followed only to 40%. Values of the rate coefficient defined by eq. 2 are presented in Table IV, which includes a measure of the fit of this equation to the data. This first-order approach to equilibrium defines both rate coefficients of the equation

$$d\bar{n}/dt = k_f(1 - \bar{n}) - k_r\bar{n}$$

with $k = k_f + k_r$ and $k_f = k\bar{n}_{eq}$.

TABLE IV

THE RATE OF REPLACEMENT OF WATER BY METHANOL IN THE FIRST COORDINATION SHELL OF CHROMIUM(III) AT 30°^a

$$[H^+] = 0.103 M, I = 0.418 M$$

Z_{MeOH}	\bar{n}_{eq}	$10^3k, \text{sec.}^{-1}$	Av. diff. ^c	$10^3k_f, \text{sec.}^{-1}$	k_f/k_r
0.19	(0.20) ^b	9.1	0.004	1.8	0.25
306	.31	7.7	.01	2.4	.45
39	.42	6.9	.005	2.9	.73
495	.57	5.6	.007	3.2	1.33
625	.775	4.4	.007	3.4	3.40

^a 0.0308 M Cr(ClO₄)₃, 0.125 M NaClO₄. ^b Calculated using values of Q given in Table VII. ^c Average difference between observed and calculated \bar{n} values in \bar{n} -units.

The Rate of Formation of Chlorochromium(III) Ion.

—When hexaaquochromium(III) ion and chloride ion are brought together in acidic aqueous methanol, a water molecule bonded to chromium(III) ion may be replaced by either chloride ion or methanol. In this type of experiment, formation of chlorochromium(III) ion shows an induction period which is not observed if chromium(III) ion is pre-equilibrated in water-methanol solution before addition of chloride ion. A reasonable interpretation of these observations is that chromium(III) species containing methanol in the first coordination shell react with chloride ion more rapidly than does hexaaquochromium(III) ion. In order to clarify this, experiments were run in particular solvents with varying amounts of hexaaquochromium(III) ion and methanolphentaaquochromium(III) ion. In each solvent, the concentrations of these two species drift to their equilibrium value, but the change is not great during each experiment, and a correction was made using rate coefficients presented in the preceding section. In each experiment the concentration of chlorochromium(III) ion was evaluated 4 or 5 times during a 10-hr. period. The concentrations of chromium(III) ion and chloride ion did not change appreciably during this period, and despite the slowly changing composition of the first coordination shell around chromium(III), the rate was essentially constant during each experiment. Table V presents second-order rate coefficients derived from values of $\Delta[\text{CrCl}^{2+}]/\Delta t$. It was not demonstrated directly in these experiments that the association reaction was first order in chloride ion and first order in chromium(III) ion. However, comparison of the rates of association and dissociation in aqueous solution demonstrates that association in water is second order, and it seems very unlikely that addition of a slight amount of methanol would alter the situation.

The Rate of Dissociation of Chlorochromium(III) Ion.—The rate of dissociation of chlorochromium(III) ion was derived from the approach to equilibrium of acidic solutions containing chromium(III) ion pre-equilibrated in the solvent and chloride ion. Concentration conditions were such that only slight conversion of chromium(III) ion and chloride ion to chlorochromium(III) ion resulted. The concentration of chlorochromium(III) ion, which approached its equilibrium value exponentially, was determined by the combination of ion-exchange and spectrophotometric procedures already described. The exponential approach to

TABLE V

THE RATE OF FORMATION OF CHLOROCHROMIUM(III) ION AT 30°

$$[H^+] = 0.103 M, [Cl^-] = 0.223 M, C_{Cr} = 0.0308 M,$$

$$k_2 \equiv (1/[Cl^-]C_{Cr}) \times (\Delta[\text{CrCl}^{2+}]/\Delta t)$$

Z_{MeOH}	\bar{n}		$10^7 \times k_2$ × moles l. ⁻¹ sec.
	$t = 0$	$t = 10 \text{ hr.}$	
0	0	0	1.6
0.128 ^a	0	0.02	1.7 ^b
	0.47	.37	2.9
	0.63	.49	3.6
0.306 ^c	0	.08	2.2
	0.36	.35	4.9
	.47	.43	5.4 ^d
	.90	.76	9.8

^a $\bar{n}_{eq} = 0.14$. ^b If not constrained to go through origin, the slope of line would give $k_2 = 1.5 \times 10^{-7}$. ^c $\bar{n}_{eq} = 0.31$. ^d If not constrained to go through origin, the slope of line would give $k_2 = 4.6 \times 10^{-7}$.

equilibrium is consistent with the solvation shell around both chromium(III) ion and chlorochromium(III) ion being maintained at approximately their equilibrium values, which probably is the actual situation since the approach to solvation equilibrium by chromium(III) ion is ~10-fold faster than the dissociation of chloride from chlorochromium(III) ion.

With concentrations of solvated chromium(III) ion and chloride ion changing very little in an experiment, the rate law can be written

$$d[\text{CrCl}^{2+}]/dt = A - k_1[\text{CrCl}^{2+}]$$

in which A is the constant rate of formation of chlorochromium(III) ion; this gives

$$2.303 \log \left(1 - \frac{[\text{CrCl}^{2+}]}{[\text{CrCl}^{2+}]_{\infty}} \right) = k_1 t$$

Experiments were followed 75 ± 10% to equilibrium, and values of k_1 were determined graphically. Table VI summarizes experiments of this type; the results

TABLE VI

THE RATE OF DISSOCIATION OF CHLOROCHROMIUM(III) ION

$$T = 30.00, I = 0.418 M, [\text{Cr}(\text{OH}_2)_6^{3+}] + [\text{Cr}(\text{OH}_2)_5(\text{OHMe})^{3+}] \cong 0.031 M$$

Z_{MeOH}	$[H^+]$	$[Cl^-]$	$10^7k_1, \text{sec.}^{-1}$
0	0.103	0.0308	13.5
	.103	.0618	13.8
	.223	.0383	14.3
	.223	.0638	12.6
0.128 ^a	.103	.0205	8.6
	.103	.0957	8.6
	.223	.0454	8.1
0.306 ^b	.103	.0117	8.4
	.103	.0223	7.9
	.103	.0319	6.9
	.223	.0103	8.4

^a In this solvent $\bar{n}_1 \cong \bar{n}_0 = 0.14$. ^b In this solvent $\bar{n}_0 = 0.31$, $\bar{n}_1 = 0.30$.

show the rate of dissociation of chlorochromium(III) ion to be independent of the concentrations of hydrogen ion and chloride ion in the ranges studied: $[H^+] = 0.103$ – $0.223 M$ and $[Cl^-] = 0.01$ – $0.09 M$.

Interpretation of Results

Equilibrium Studies.—The medium effect upon a complex ion formation reaction in a mixed solvent includes the effect of specific interaction of solvent molecules with reaction participants. For the chromium(III)–chloride system, equilibrium quotients for reactions in which methanol replaces water in the first coordination shell of chromium(III) (reactions (0,1), (0,2), (1,1), and (1,2)) appear in the equation relating Q , the apparent equilibrium quotient, and Q_1' , the conventional equilibrium quotient for reaction 1

$$Q_1' = \frac{[\text{Cr}(\text{OH}_2)_6\text{Cl}^{2+}]}{[\text{Cr}(\text{OH}_2)_6^{3+}][\text{Cl}^-]}$$

$$Q_1' = Q \times \frac{(1 + Q_{0,1}r + Q_{0,2}r^2 + \dots)}{(1 + Q_{1,1}r + Q_{1,2}r^2 + \dots)}$$

where r is the ratio $a_{\text{MeOH}}/a_{\text{H}_2\text{O}}$. In derivation of this equation, the ratios of activity coefficients of cationic species of the same charge are assumed to be unity in all solvents.

The \bar{n} data allow calculation of the equilibrium quotients within the limitations imposed by certain assumptions. The equation

$$\bar{n} = \frac{\sum_j Q_{1j} \dots Q_{1j} r^j}{1 + \sum_j Q_{1j} \dots Q_{1j} r^j}$$

is based upon the same assumption regarding activity coefficients of cationic species that was mentioned in the preceding paragraph. In addition, correct use of this equation would involve values of r for the electrolyte-containing solutions being studied. Such data are not available. Since values of \bar{n}_0 and \bar{n}_1 are very similar, the quotient

$$(1 + Q_{0,1}r + Q_{0,2}r^2 + \dots)/(1 + Q_{1,1}r + Q_{1,2}r^2 + \dots)$$

is close to unity, and the estimation of r values is not critical. For this reason the ratio of mole fraction concentrations $Z_{\text{MeOH}}/Z_{\text{H}_2\text{O}}$ have been used for r .⁸ Using the procedure of King and Gallagher,⁹ values of the equilibrium quotients for reactions (0,1), (0,2), (1,1), and (1,2) were derived from the \bar{n} data of Table III; these values are presented in Table VII. Since the maximum observed \bar{n} -values were only slightly greater than unity, the values of $Q_{0,2}$ and $Q_{1,2}$ are very uncertain. Within experimental uncertainty, the factor by which the apparent equilibrium quotient Q is corrected to Q' is unity, and values of Q presented in Tables I and II may be accepted as values of Q_1' .

It is customary to omit the activity of water from equilibrium quotient expressions for reactions involving water as a participant, and this has been done in defining Q_1' . This is justified for a reaction studied in dilute aqueous solution where $a_{\text{H}_2\text{O}} \cong 1.00$, but in more concentrated electrolyte solution or in mixed solvents where $a_{\text{H}_2\text{O}} \neq 1.00$, the activity of water should appear in the equilibrium quotient expression if water appears in the balanced chemical equation. Reaction I involves one water molecule as a specific reaction participant, and the equilibrium quotient Q_1 is more appropriate

$$Q_1 = \frac{[\text{Cr}(\text{OH}_2)_5\text{Cl}^{2+}]a_{\text{H}_2\text{O}}}{[\text{Cr}(\text{OH}_2)_6^{3+}][\text{Cl}^-]}$$

TABLE VII

APPARENT EQUILIBRIUM QUOTIENT VALUES FOR REPLACEMENT OF WATER BY METHANOL IN FIRST COORDINATION SHELL AROUND CHROMIUM(III)

$$[\text{H}^+] = 0.103 M, I = 0.418 M^a$$

t	$Q_{0,1}$	$Q_{0,2}$	$Q_{1,1}$	$Q_{1,2}$
30.0	1.05	0.10	1.08	0.09
43.6	1.05	.10	1.08	.09
60.0	1.08	.13	1.09	.09

^a Ionic strength maintained with sodium perchlorate.

than Q_1' for correlations with temperature and solvent composition or polarity. Values of Q_1 as a function of solvent composition and temperature are summarized in Table VIII.

For each solvent values of the enthalpy and entropy change associated with reaction I were calculated from the temperature dependence of Q_1 . The value of

(8) A more detailed study of solvation of chromium(III) ion in methanol-water solution, including evaluation of the equilibrium quotients $Q_{0,n}$ and discussion of their significance, is described in the forthcoming paper by J. C. Jayne and E. L. King.

(9) E. L. King and P. K. Gallagher, *J. Phys. Chem.*, **63**, 1073 (1959).

TABLE VIII

VALUES OF THE EQUILIBRIUM QUOTIENT $Q_1 = [\text{Cr}(\text{OH}_2)_5\text{Cl}^{2+}]a_{\text{H}_2\text{O}}/[\text{Cr}(\text{OH}_2)_6^{3+}][\text{Cl}^-]^a$, AND THE ASSOCIATED VALUES OF $\Delta S^{\circ b}$

$$I = 0.418 M$$

Z_{MeOH}	30.05°	43.6°	60.00°	$\Delta S^{\circ} \times \text{cal.}^{-1}$ mole deg.
0	0.107	0.180	0.317	20.0
0.0475	.139	.238	.422	20.5
.128	.231	.375	.679	21.5
.190	.316	.540	.928	22.1
.306	.587	.974	1.66	23.1
.391	.902	1.56	2.76	24.2
.505	1.54	2.6	4.7	25.3
.625	3.5	6.1	11.3	27.0
.706	6.2	11	19.8	28.1

^a Experimental values of Q obtained in solutions with $[\text{H}^+] = 0.103 M$ and $[\text{Na}^+] = 0.125 M$ used in evaluation of Q_1 and ΔS° . For the activity of water in the nine solvents studied, the values assumed were 0.985, 0.947, 0.875, 0.829, 0.744, 0.668, 0.572, 0.459, and 0.373, respectively. To obtain these values from smoothed values for the binary solvent system (N. M. Baron and K. H. Mishchenko, *Zh. Obshch. Khim.*, **18**, 2067 (1948); J. B. Ferguson and W. S. Funnell, *J. Phys. Chem.*, **33**, 1 (1929); M. Wrewsky, *Z. physik. Chem.*, **81**, 1 (1912)) the presence of electrolyte was taken into account with Raoult's law. ^b The standard state for water is the pure liquid and that for solutes is the hypothetical ideal 1 M solution of ionic strength 0.418 M.

ΔC_p was assumed to be zero. The values of ΔH for each solvent are equal within experimental uncertainty ($\Delta H = 7.4 \pm 0.5$ kcal./mole); values of ΔS° for each solvent are presented in Table VIII. This value of ΔH is within experimental error of the value 6.6 ± 0.5 kcal./mole obtained for aqueous solution ($I = 5.1 M$) in the calorimetric study of Schug and King.¹⁰

Kinetic Studies.—Methanol may influence rates of the reactions being considered either because it is a specific participant (*e.g.*, in the forward reaction (0,1)) or is part of the first coordination shell of chromium(III) (*e.g.*, in the reverse reaction (0,1)) or because as a solvent component it exerts a "medium" effect. Particularly pertinent to the effect exerted by methanol because of its presence in the first coordination shell of chromium(III) are the rates of reaction of chloride ion and mixtures of hexaaquochromium(III) ion and methanolphentaquochromium(III) ion present in varying proportions; these data are given in Table V. If only species of chromium(III) containing zero and one methanol molecules are present at appreciable concentrations, the apparent second-order rate coefficient k_2 is made up of two terms

$$k_2 = (1 - \bar{n})k_{20} + \bar{n}k_{21}$$

in which k_{20} and k_{21} are the second-order rate coefficients for reaction of chloride ion with hexaaquochromium(III) ion and methanolphentaquochromium(III) ion, respectively. For each solvent studied, values of k_{20} and k_{21} were calculated from the dependence of k_2 upon the average value of \bar{n} during the 10-hr. experiment; these values are: for water, $k_{20} = 1.6 \times 10^{-7}$ l. mole⁻¹ sec.⁻¹; for 12.8 mole % methanol, $k_{20} = 1.5 \times 10^{-7}$ l. mole⁻¹ sec.⁻¹ and $k_{21} = 5.2 \times 10^{-7}$ l. mole⁻¹ sec.⁻¹; and for 30.6 mole % methanol, $k_{20} = 2.4 \times 10^{-7}$ l. mole⁻¹ sec.⁻¹ and $k_{21} = 8.3 \times 10^{-7}$ l. mole⁻¹ sec.⁻¹.¹¹ As expected of rate coefficients for reactions of ions of opposite charge sign, both k_{20} and k_{21} increase with increasing methanol content of the solvent, although the increase is mild. Within the uncertainty of the experiments, the ratio k_{21}/k_{20} has the same value—

(10) K. Schug and E. L. King, *J. Am. Chem. Soc.*, **80**, 1089 (1958).

(11) For the methanol-containing solution with $Z_{\text{MeOH}} = 0.306$, the data point for $\bar{n} = 0.83$ was omitted from the correlation since this mixture of solvated chromium(III) ions undoubtedly contained some dimethanol species.

3.5 in 12.8 and 30.6 mole % methanol. This is the factor by which the reactivity of methanolpentaquo-chromium(III) ion toward chloride ion exceeds that of hexaquo-chromium(III) ion.

In the solvents studied, the pseudo-first-order rate coefficient for dissociation of chlorochromium(III) ion, k_1 , is made up of contributions from species containing zero and one methanol molecule in the first coordination shell. Because equilibration of solvent components between the first coordination shell and the solvent is much faster than replacement of chloride ion in the first coordination shell, solvation equilibrium for chlorochromium(III) ion is essentially maintained as it is formed. Each experimentally determined value of k_1 is, therefore, the sum of contributions from chloropentaquo-chromium(III) ion and chloromethanol-tetraquo-chromium(III) ion present in equilibrium relative proportions

$$k_1 = k_{10}(1 - \bar{n}_1) + \bar{n}_1 k_{11}$$

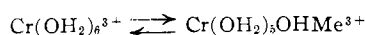
in which k_{10} and k_{11} are the rate coefficients for reaction of the species containing zero and one methanol molecules, respectively. However, unlike the short duration experiments on the formation of chlorochromium(III) ion in which relative amounts of species with different solvation could be varied in each solvent, these long duration experiments involve only one particular mixture of solvated species for each solvent. Further, the pseudo-first-order rate coefficients k_{10} and k_{11} each pertain to a pair of reactions. In reaction of each variety of solvated chlorochromium(III) ion, the dissociating chloride ion may be replaced by either water or methanol. The available data tell nothing about the relative amounts of reaction involving each solvent component. However, dissociation of chloride ion from chloropentaquo-chromium(III) ion in water must involve replacement of chloride ion by water, and the observed value of k_1 for water (1.33×10^{-6} sec.⁻¹) corresponds to this process. If the rate constant for this one process (replacement of chloride in chloropentaquo-chromium(III) ion by water) were proportional to the mole fraction of water, the value of k_1 for $Z_{\text{MeOH}} = 0.128$, which is a sum of terms, could be no smaller than

$$1.33 \times 10^{-6} \times Z_{\text{H}_2\text{O}} \times (1 - \bar{n}_1) =$$

$$1.33 \times 10^{-6} \times 0.872 \times 0.86 = 1.0 \times 10^{-6} \text{ sec.}^{-1}$$

The observed value is 0.84×10^{-6} sec.⁻¹, which indicates that the solvent effect upon the pseudo-first-order rate constant is not adequately taken into account by multiplying it by the mole fraction of the participating solvent component. The comparison also suggests that rate of loss of chloride ion by chloromethanol-tetraquo-chromium(III) ion is not extraordinarily high; if it were even comparable to the rate of loss of chloride ion by chloropentaquo-chromium(III) ion, it would seem unlikely that loss of chloride ion by an equilibrium mixture of solvated chlorochromium(III) ions would be lowered in going from water to a solvent containing 12.8 mole % methanol.

The observed exponential approach to the equilibrium distribution of solvent molecules in the first coordination shell around chromium(III) defines two pseudo-first-order rate coefficients k_f and k_r , values of which are given in Table IV. If inappreciable dimethanol-tetraquo-chromium(III) ion is present in the solution, the rate coefficients k_f and k_r are associated with the reversible transformation



In principle, one should be able to derive a complete rate law including solvent concentration dependences from the solvent dependence of k_f and k_r . Such a

rate law would clarify the mechanism of the reaction. In practice this is rendered difficult by the limited solvent composition range in which only species with zero and one methanol molecule are predominant. Also the inaccessibility of certain terms in the Brønsted activity coefficient factor makes unequivocal evaluation of the reaction order with respect to solvent components difficult. Kinetic studies in mixed solvents rarely settle the question of solvent participation, and the present system is no exception. However, a more rational comparison of the rate coefficients for different solvent mixtures is possible if proportionality is assumed between k_f and Z_{MeOH} and between k_r and $Z_{\text{H}_2\text{O}}$. Alternately, the proportionality can be assumed to involve the activities of the solvent components. Table IX summarizes values of these corrected rate coefficients. Since an appreciable amount of dimethanolchromium(III) ion is present at $Z_{\text{MeOH}} = 0.625$, data from this solvent are omitted. The entries in each row depend upon solvent composition. Because neither formulation

$$d[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]/dt = k_f'[\text{Cr}(\text{OH}_2)_6^{3+}]Z_{\text{MeOH}} - k_r'[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]Z_{\text{H}_2\text{O}}$$

$$d[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]/dt = k_f''[\text{Cr}(\text{OH}_2)_6^{3+}]a_{\text{MeOH}} - k_r''[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]a_{\text{H}_2\text{O}}$$

includes the complete Brønsted activity coefficient factor, the observed solvent dependence of the rate coefficients presented in Table IX does not rule out an SN2 mechanism for this reaction.

TABLE IX

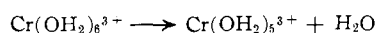
"CORRECTED" VALUES OF RATE COEFFICIENTS FOR THE RATE LAW $d[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]/dt = k_f[\text{Cr}(\text{OH}_2)_6^{3+}] - k_r[\text{Cr}(\text{OH}_2)_5\text{OHMe}^{3+}]$

	Z_{MeOH}			
	0.19	0.306	0.39	0.495
$10^6(k_f/Z_{\text{MeOH}}) \times \text{sec.}$	9.5	7.9	7.4	6.5
$10^6(k_r/Z_{\text{H}_2\text{O}}) \times \text{sec.}$	9.0	7.6	6.6	4.8
$10^6(k_f/a_{\text{MeOH}}) \times \text{sec.}^a$	6.8	6.2	6.3	5.9
$10^6(k_r/a_{\text{H}_2\text{O}}) \times \text{sec.}^b$	8.8	7.1	6.0	4.2

^a The activity values were interpolated from 25° data of N. M. Baron and K. H. Mishchenko, *Zh. Obshch. Khim.*, **18**, 2067 (1948). ^b The activity values are the same as those used in Table VIII.

Relatively uncertain extrapolation of these "corrected" rate coefficients to pure water gives values $k_f/Z_{\text{MeOH}} = 1.1 \times 10^{-6}$ sec.⁻¹ and $k_r/Z_{\text{H}_2\text{O}} = 1.1 \times 10^{-5}$ sec.⁻¹. The first-order rate coefficient for exchange of water with hexaquo-chromium(III) ion at 30° is 3.2×10^{-5} sec.⁻¹.¹² To be compared, these values should be corrected with a statistical correction. The corrected values are $(1/6)(k_f/Z_{\text{MeOH}}) = 1.8 \times 10^{-6}$ sec.⁻¹, $(k_r/Z_{\text{H}_2\text{O}}) = 1.1 \times 10^{-5}$ sec.⁻¹, and $(1/6) \cdot k_{\text{H}_2\text{O}} = 5.3 \times 10^{-6}$ sec.⁻¹, and it is noteworthy that a factor of six encompasses all of the values.

The preceding discussion and calculations are based upon the tacit assumption that displacement of one solvent molecule by another in the first coordination shell of chromium(III) is an SN2 process. One may also attempt to correlate the data with an SN1 mechanism. The correlation is better using the mole fraction scale than the activity scale, although use of the mole fraction scale involves more questionable assumptions regarding the Brønsted activity coefficient factor. Whether mole fraction or activity scales are used for solvent components, the value derived for the rate constant of the reaction



(12) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954) These authors report rate coefficients with the statistical correction already applied; the value given above is uncorrected.

is approximately 7-fold lower than the value derived from the rate of oxygen-18 exchange. Interpreted rigidly, this indicates the exchange of water between solvent and first coordination shell of hexaaquochromium(III) ion *does not occur by a limiting S_N1 mechanism*. However, because of the uncertainty of the assumption regarding the Brønsted activity coefficient factor, this conclusion must be accepted with caution.

Discussion

Specific solvation of metal ions in a complex ion formation reaction in mixed solvents affects the equilibrium if the relative binding of solvent components differs for the metal ion reactant and product. For chromium(III) ion and chlorochromium(III) ion, the tendencies to bind methanol are so nearly the same in the solvent composition range to 70 mole % methanol that the equilibrium quotient in which solvation is taken into account is essentially equal to that in which it is ignored. However, even if the tendency to replace one water molecule with one methanol molecule is the same for chromium(III) ion and chlorochromium(III) ion, the tendency to replace three (or four or five) water molecules with three (or four or five) methanol molecules may differ. Both specific interactions of ligands with one another and the statistical factor lead to this expectation.

The dependence upon solvent composition of Q_1 is remarkably similar to that of the equilibrium constant for association of hydrogen ion and acetate ion,¹³ despite the large difference in charge type, -6 and -2, respectively, being the values of ΔZ^2 . The relative value of Q_1 in solutions of ionic strength 0.418 *M* at 30° with $Z_{\text{MeOH}} = 0, 0.306, \text{ and } 0.706$ are 1, 5.6, and 57, respectively. For the association of hydrogen ion and acetate ion in solutions of zero ionic strength at 25°, the values for the same solvents are 1, 6.2, and 102, respectively. Since participation of water in reaction 1 is specifically taken into account, it should also be taken into account¹⁴ for the reaction $\text{H}_3\text{O}^+ + \text{OAc}^- = \text{HOAc} + \text{H}_2\text{O}$, in which case the relative values of the equilibrium quotient become 1, 4.7, and 41. The relatively high electrolyte concentration in the solutions in which reaction 1 was studied lowers the sensitivity of the equilibrium quotient to solvent polarity, thereby suppressing the expected effect upon charge type.

Resolution of the solvent effect upon reaction 1 into effects upon ΔH and ΔS° is of interest. The enthalpy change accompanying reaction 1 is essentially independent of solvent composition even though the energy of solvation of some electrolytes significantly depends upon solvent composition in methanol-water solutions.¹⁵ For the observation regarding the enthalpy change of reaction 1 to be rationalized, it is necessary only that the solvent dependences of the heats of solution of $(\text{Cr}(\text{OH})_2)_6(\text{ClO}_4)_2\text{Cl}$ and $(\text{Cr}(\text{OH})_2)_6\text{Cl}$ -

$(\text{ClO}_4)_2$ be essentially the same, which is not inconsistent with existing data. The greater extent of reaction with increasing methanol content of the solution is due to the change of ΔS° . The simple rationalization of a positive standard entropy change in an ion-association reaction, namely that solvent molecules gain randomness in the field of the product of lower charge ($\text{Cr}(\text{OH})_2)_6\text{Cl}^{2+}$ in the present example), serves to explain the trend of ΔS° with solvent composition. There is less order in liquid methanol than in liquid water and, therefore, more entropy is gained in methanol-rich solvents when ions of charge 3+ and 1- combine to give an ion of charge 2+. Latimer and Slansky found the sums of partial molal entropies of cation and anion for hydrogen chloride, sodium chloride, potassium chloride, and potassium bromide to be more negative by 24.1, 26.7, 34.6, and 34.2 cal. mole⁻¹ deg.⁻¹, respectively, in methanol than in water.¹⁶ For 69.4-mole % methanol, the corresponding values are 8.3, 15.5, 21.1, and 21.1 cal. mole⁻¹ deg.⁻¹, respectively. These values should be divided by two before comparison with the change of ΔS° of 8.1 cal. mole⁻¹ deg.⁻¹ for reaction 1 in going from water to 70.6 mole % methanol since reaction 1 involves a net decrease of one solute particle and there are two solute particles per mole of the electrolytes studied by Latimer and Slansky. The basis of comparison is at best a little vague, however, since the charge types are different and changes of the partial molal entropies of the binary electrolytes reflect changes in both inner- and outer-sphere interactions with solvent; but for reaction 1 inner-sphere interactions of cationic species with solvent have been fixed.

A point of interest in the kinetics is the effect which methanol in the first coordination shell of chromium(III) has upon the rate of a reaction in which it is displaced and in which it is not displaced. Although rendered somewhat uncertain by questions of medium effects, the conclusion that chloride ion in chloromethanol-tetraaquo-chromium(III) ion is not displaced more rapidly than is chloride ion in chloropentaaquo-chromium(III) ion indicates that the presence of one methanol in the first coordination shell of chromium(III) does not labilize other ligands.

The relative rates of replacement of water by water, water by methanol, and methanol by water in solvent water at 30° are 1, 0.34, and 2.1. The displacement of a bound molecule of methanol is the fastest of these reactions. The observed greater rate of reaction of chloride ion with methanol-pentaaquo-chromium(III) ion than with hexaaquo-chromium(III) ion would seem, therefore, to be due to the fact that *it is the bound methanol molecule which is being displaced in this reaction. Displacement reactions of chromium(III) species solvated with methanol molecules are faster than analogous reactions of hydrated species if it is a methanol molecule which is being displaced.*

(13) T. Shedlovsky and R. L. Kay, *J. Phys. Chem.*, **60**, 151 (1956); A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, *ibid.*, **62**, 856 (1958).

(14) M. Yasuda, *Bull. Chem. Soc. Japan*, **32**, 429 (1959).

(15) W. M. Latimer and C. M. Slansky, *J. Am. Chem. Soc.*, **62**, 2019 (1940).

(16) The standard state used by these authors was the hypothetical ideal 1 molal solution. The molal concentration scale is less appropriate than the molar or mole fraction scales for comparisons of effects of different solvents. Each of these values would be ~ 1.0 cal. mole⁻¹ deg.⁻¹ larger if the hypothetical 1 *M* solution was the standard state of each ion.