Vol. 59 DECEMBER, 1955 No. 12

THE JOURNAL OF PHYSICAL CHEMISTRY

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Published monthly by the American Chemical Society at 20th and Northampton Sts., Easton, Pa.

Entered as second-class matter at the Post Office at Easton, Pennsylvania.

The *Journal of Physical Chemistry* is devoted to the publication of selected symposia in the broad field of physical chemistry and to other contributed papers.

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THE JOURNAL OF PHYSICAL CHEMISTRY

VOL. LIX

1955

EASTON, PA.
MACK PRINTING COMPANY
1955

THE JOURNAL OF
PHYSICAL CHEMISTRY

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VOLUME 59 JANUARY 3, 1956 NUMBER 12

MICELLAR MOLECULAR WEIGHTS OF SOME PARAFFIN CHAIN SALTS BY LIGHT SCATTERING

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Received February 21, 1955

By the use of light scattering methods, the micellar molecular weights have been determined for thirteen normal paraffin chain salts in aqueous solution, alkane sulfonates, alkyl sulfates and alkyl quaternary ammonium salts. The results with 1–1 salts with single paraffin chains form a counter-part to previous results by Debye and co-workers. The necessity for proper screening of electric charge is considered. Some comparisons are made of the influence of uni- and bivalent gegenions.

Introduction

As early as 1913, McBain[1] suggested that soaps in aqueous solution form electrically charged aggregates (micelles). Since then, this concept has had wide application in the study of soaps and other long paraffin chain salts. The first determinations of micellar molecular weights were not made, however, until 1949 by Debye[2, 3] on solutions of alkyl quaternary ammonium salts and amine hydrochlorides. The light scattering technique developed by Debye[4] was used. More recently, Debye and Anacker[5] have employed dissymmetry measurements to determine the shape and molecular weight of the micelles of hexadecyltrimethylammonium bromide in strong electrolyte solutions. Anacker[6] has also studied light scattering by solutions of the "double" paraffin chain salts, octyltrimethylammonium octanesulfonate and octyltrimethylammonium decanesulfonate. Phillips and Mysels[7] have reported on the micellar molecular weight of sodium dodecyl sulfate.

The purpose of the work presented here was to extend previous investigations by making a more general study by light scattering of the micellar molecular weights of several normal paraffin chain salts; alkane sulfonates, alkyl sulfates and alkyl quaternary ammonium salts. The materials included several paraffin chain anions. Heretofore, much more attention has been given to solutions of substances with cationic chains.

Experimental

Materials.—The hydrocarbon chains were unbranched and the polar group in primary position in all instances. For simplicity the prefix *n*- (normal) will be omitted from the names of the salts.

Sodium octane-, decane-, dodecane- and tetradecanesulfonates were prepared by the Strecker reaction.[8] The alkyl bromides were obtained from Halogen Chemicals, Inc., and were subjected to fractional distillation in a column 1.2 meters in length and filled with small, glass helices, which gave a performance equivalent to 19 theoretical plates. The initial and last portions of the distillate were discarded. The refractive indices of the bromides were: octyl, 1.4504; decyl, 1.4536; and dodecyl, 1.4562. These data agree well with the findings of Heston, Hennelly and Smyth.[9]

The alkyl bromide and sodium sulfite were used in the ratio of 1 mole of bromide to 1.2 moles of sulfite, dissolved in 750 ml. of water. This mixture was placed in Pyrex bottles and heated to 110° with occasional shaking. Several days were required for the completion of the reaction which was evidenced by the disappearance of the alkyl bromide phase. The material was then cooled to 0° and filtered on a Büchner funnel to remove excess sodium sulfite, sulfate and bromide. The moist, solid residue was then dried at

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[1] J. W. McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); "Colloid Science," D. C. Heath and Co., San Francisco, Calif., 1950.

[2] P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949).

[3] P. Debye, *J. Phys. Colloid Chem.*, **53**, 1 (1949).

[4] P. Debye, *ibid.*, **51**, 18 (1947).

[5] P. Debye and E. W. Anacker, *ibid.*, **55**, 644 (1951).

[6] E. W. Anacker, *J. Colloid Sci.*, **8**, 402 (1953).

[7] J. N. Phillips and K. J. Mysels, 124th Meeting of Am. Chem. Soc., Chicago, Ill., Sept. 6–11, 1953.

[8] R. M. Reed and H. V. Tartar, *J. Am. Chem. Soc.*, **57**, 570 (1935).

[9] W. M. Heston, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 2071 (1950).

70° and ground to pass through a 40-mesh sieve. This powder was extracted with ethyl ether to remove any alkyl bromide. The extracted residue was dried and recrystallized from water until all bromide ion was removed (usually 2 or 3 recrystallizations). The crystals of sodium octane- and decanesulfonate were easily separated by filtration on a sintered-glass Büchner funnel. The dodecanesulfonate crystallizes in small thin plates which clog the filter; the separation was accomplished satisfactorily by centrifugation. The purified salts were finally dried at 70° *in vacuo* and showed no discoloration when heated to 100° in air.

Sodium dodecyl sulfate was prepared according to the method of Lottermoser and Stoll[10] by the direct reaction of lauryl alcohol with sulfuric acid and subsequent neutralization with sodium hydroxide. The lauryl alcohol was repeatedly fractionally distilled at 4–5 mm. pressure. The fraction used had a quite constant boiling point, 125–126° at 5 mm. The salt obtained by neutralization was further purified by several recrystallizations from alcohol. It was dried *in vacuo* at 70°.

Sodium tetradecanesulfonate was prepared by Reed[8] in this Laboratory.

The preparation of magnesium dodecanesulfonate has been previously described.[11]

Magnesium octane- and decanesulfonate were precipitated by metathesis from the corresponding solutions of sodium alkane sulfonate and magnesium chloride. In each case, approximately 30 g. of sodium alkane sulfonate was dissolved in 125 ml. of water. Then 200 ml. of normal solution of magnesium chloride was added and the resulting mixture warmed gently for a brief time. A small amount of hydrochloric acid was added to bring the solution to *p*H 4 to ensure no precipitation of magnesium hydroxide. The solution was then cooled to room temperature for the decane and to 0° for the octane salt. A large crop of glistening small crystals formed. After standing several hours the crystals were separated by suction filtration on sintered glass and further purified by two recrystallizations from water. A small amount of magnesium chloride was added to the solvent in the first recrystallization.

The salts were dried at 70° *in vacuo* and analyzed for magnesium ion by determining as magnesium pyrophosphate. The samples were first incinerated to a white powder to avoid any interference that might occur due to the presence of the paraffin chain sulfonate ion. The solid residue was then dissolved in hydrochloric acid and the determination carried out in accordance with the procedure given by Kolthoff and Sandell.[12] The results of the analyses were as follows: magnesium octanesulfonate, found 5.91%, theory 5.92%; magnesium decanesulfonate, found 5.06%, theory 5.21%.

Dodecyltrimethylammonium bromide and sulfate were prepared by Voeks as described in the paper which immediately follows.[13]

The sample of didodecyldimethylammonium chloride was furnished through the kindness of Dr. H. J. Harwood, Director of Chemical Research, Armour and Company, Chicago. It was dried at 70° *in vacuo* and used without further purification.

Apparatus and Procedure.—The specific refractive index increments, $(n - n_0)/c$, of the solutions were determined with a differential refractometer[14] at several levels of concentration for each solute; all gave linear relationships above the critical micelle concentration (hereafter designated cmc.).

The turbidities were determined with a photoelectric, light scattering photometer[15] with light of wave length 436 mμ and using the ratio of deflections method for settings at 0 and 90°. As a check, runs were also made in most cases with light of wave length 546 mμ. The solutions were made to volume with freshly distilled water and filtered by pressure through Pyrex, ultrafine sintered-glass filters directly into the optical cells, which were in a closed glass container to avoid dust contamination.

The photometer was checked against the turbidity of colloidal silica[16] solutions (concentration around 0.8% SiO_2) determined by transmittance measurements[17] with a Beckmann spectrophotometer. It was also checked by determining the turbidity of solutions of highly purified sucrose[18] and compared with the values found by Debye,[4] Halwer[19] and Anacker.[6]

The micelles of all the salts were too small to show appreciable dissymmetry in the scattered light.

In all instances, the turbidity due to the solute was obtained by subtracting the turbidity of the solvent alone. In cases where the solubility at room temperature was too small, a higher temperature was chosen to afford convenient working conditions.

Above room temperature, the filtrations were made in a thermostated oven. The readings were carried out by removing the optical cell containing the filtered solution from the oven to the photometer (at room temperature) and reading the galvanometer deflections within approximately 3 minutes; during this period the decrease in temperature was insufficient to modify the turbidities appreciably.

Results and Discussion

General.—The Debye equation[3] $H[(c - c_0)/\tau] = 1/M + 2Bc$ was used to calculate the micellar molecular weights. Here τ is the turbidity in excess of that of the solvent; M is the weight average micellar molecular weight; B, a constant; c, the concentration of the solute; c_0, the cmc.; $H = (32\pi^3 n_0^2/3\lambda^4 N)[(n - n_0)/c]^2$; n and n_0, the refractive indices of solution and solvent, respectively; N, Avogadro's number; and λ, the wave length of light. The reciprocal of the molecular weight was obtained by plotting $H[(c - c_0)/\tau]$ against c and extrapolating to c_0, zero concentration of micelles. To afford better accuracy, the values for c_0 were taken from electrical conductance measurements. The values obtained from plots of turbidity against c agreed very well with those estimated from conductance data. The importance of trustworthy values for c_0 is emphasized. With concentration c near c_0, small errors in the value of the latter give large relative errors in the function $H[(c - c_0)/\tau]$. For the extrapolation, the data should fit closely to a linear relationship.

The molecular weights are for micelles in electrolytic solvents of definite concentration, *viz.*, the cmc. for the particular paraffin chain salt without or with added electrolyte.

The effect of temperature in the range used, 23 to 60°, is not large in solutions of satisfactory ionic strength. Consequently in the time available no systematic study was made of the influence of temperature on micellar size.

The pertinent data are presented in Table I and Figs. 1 to 8. The plots of τ *vs.* c for the uni-univalent (1–1) salts were quite similar to those obtained by others[2, 3] and are omitted to economize space. The values for $H[(c - c_0)/\tau]$ given in the figures are for light at 436 mμ unless otherwise specified. The results with the two wave lengths usually agreed within around 2 to 4%, the higher values being obtained at 546 mμ.

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(14) B. A. Brice and M. Halwer, *J. Optical Soc. Am.*, **41**, 1033 (1951). Constructed by the Phoenix Precision Instrument Co., Philadelphia, Pa.

(15) B. A. Brice, M. Halwer and R. Speiser, *ibid.*, **40**, 768 (1950). Constructed by the Phoenix Precision Instrument Co., Philadelphia, Pa.

(16) Ludox, 30%, kindly furnished by Dr. H. H. Snyder, E. I. du Pont de Nemours and Company, Wilmington, Del.

(17) W. F. Mommaerts, *J. Colloid Sci.*, **7**, 71 (1952).

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(19) M. Halwer, *J. Am. Chem. Soc.*, **70**, 3985 (1948).

TABLE I

LIGHT SCATTERING DATA AND MICELLE MOLECULAR WEIGHTS

Solute	Solvent	Temp., °C.	Cmc. × 10³ g./cc.	N	$\Delta n/\Delta c$	$H \times 10^6$	Micelle mol. wt., M	Aggregation no.
Sodium octanesulfonate, $NaC_8H_{17}SO_3$	Water	23	33.5	155	0.1222	4.04	5500	25.4
Sodium decanesulfonate, $NaC_{10}H_{21}SO_3$	Water	30	9.3	38	.1254	4.26	9900	40
Sodium dodecanesulfonate, $NaC_{12}H_{25}SO_3$	Water	40	3.0	11	.1257	4.28	14700	54
Sodium tetradecanesulfonate, $NaC_{14}H_{29}SO_3$	Water	60	1.0	33	.1300	4.57	24000	80
Sodium decyl sulfate, $NaC_{10}H_{21}SO_4$	Water	23	8.1	31	.1134	3.48	13000	50
Sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$	Water	23	2.3	8	.1208	3.99	20500	71
Sodium tetradecyl sulfate, $NaC_{14}H_{29}SO_4$	0.01 *M* NaCl	23	0.6	1.9	.1200	3.90	43500	138
Dodecyltrimethylammonium bromide, $C_{12}H_{25}$-$(CH_3)_3NBr$	Water	23	4.4	14.4	.1542	6.42	15400	50
Dodecyltrimethylammonium sulfate, $[C_{12}H_{25}$-$(CH_3)_3N]_2SO_4$	Water	23	4.7	16.6	.1500	6.09	17900	65
Magnesium octanesulfonate, $Mg(C_8H_{17}SO_3)_2$	Water	23	22.6	110	.1400	5.3	10400	51
Magnesium decanesulfonate, $Mg(C_{10}H_{21}SO_3)_2$	Water	60	4.67	20	.1360	5.01	24000	103
Magnesium dodecanesulfonate, $Mg(C_{12}H_{25}SO_3)_2$	Water	60	0.86	3.3	.1330	4.78	28500	107
Didodecyldimethylammonium chloride $(C_{12}H_{25})_2$-$(CH_3)_2NCl$	0.003 *M* NaCl	60		10^{-4}	.1220	4.00	43000	206

The heights of the vertical lines at the cmc. in the $H[(c - c_0)/\tau]$ *vs.* c plots represent the value of the reciprocal of the weight average micellar molecular weight.

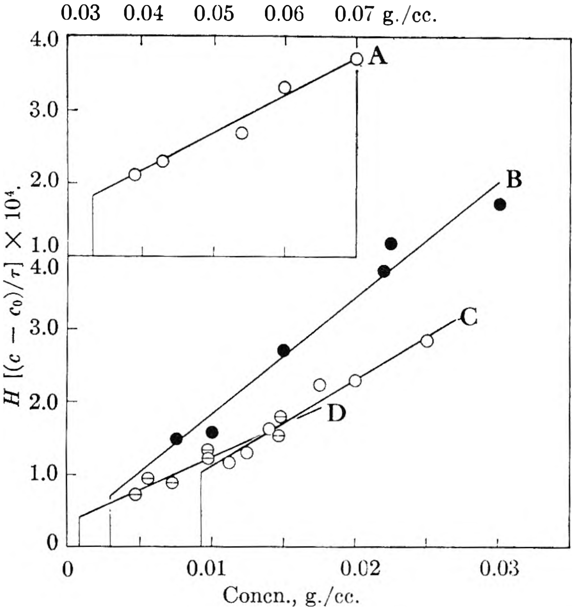

Fig. 1.—Sodium alkane sufonates: A, octanesulfonate; B, dodecanesulfonate; C, decanesulfonate; D, tetradecanesulfonate.

The aggregation number (Table I) is the calculated average number of paraffin chains in the micelle, rounded off to the nearest whole number.

The results for solutions of the uni-univalent (1–1) salts with single hydrocarbon chains form a counterpart to those of Debye and co-workers.[2, 3] For a given chain length and with water as the solvent the molecular weights are of the same order and consequently give similar aggregation numbers. The molecular weight of dodecyltrimethylammonium bromide, 15400 (Table I), is, considering experimental error, identical with 15500, found by Debye. Phillips and Mysels[7] have reported a higher value, 23000, for sodium dodecyl sulfate. In general, the longer the hydrocarbon chain the greater the molecular weight. The turbidity below the cmc. is essentially the same as for the solvent,

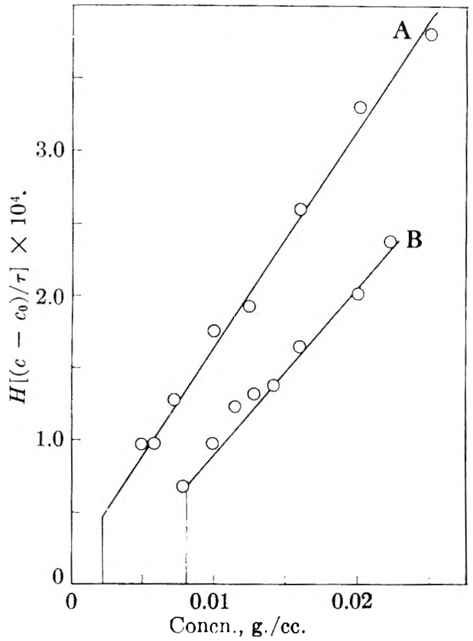

Fig. 2.—Sodium alkyl sulfates: A, dodecyl sulfate; B, decyl sulfate.

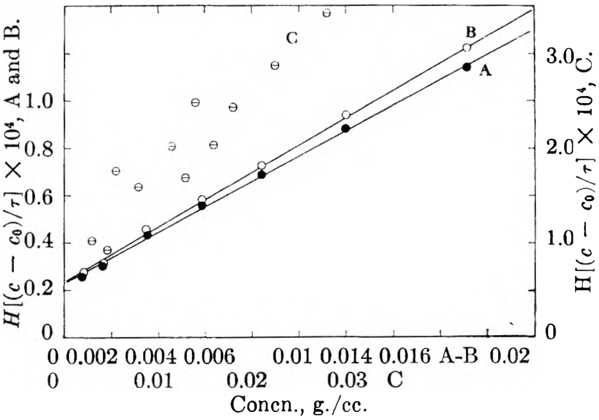

Fig. 3.—Sodium tetradecyl sulfate: A, in 0.01 NaCl; B, in 0.01 NaCl (546 mμ); C, in water.

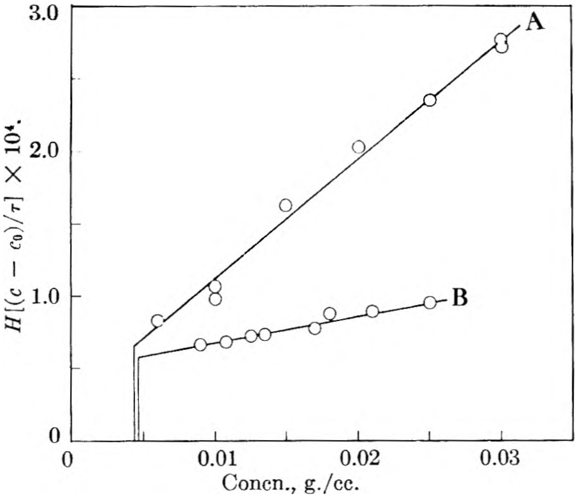

Fig. 4.—A, dodecyltrimethylammonium bromide; B, dodecyltrimethylammonium sulfate.

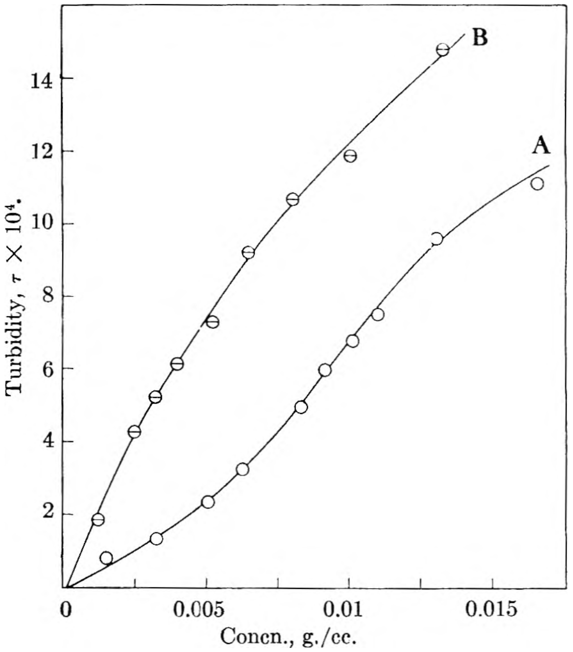

Fig. 5.—Didodecyldimethylammonium chloride: A, in water; B, in 0.003 M NaCl.

especially with longer chains which give lower concentration of the smaller ions, thus showing that the ions are not aggregated in appreciable amounts below the cmc.

The molecular weights of the sodium alkyl sulfates are greater than those of the sodium alkane sulfonates with the same chain length, thus showing large differences in the effects of these closely related polar groups on micellar size.

The Effect of Electric Charge on Micelles.—If the particles bear electric charges there will be restriction of movement and distribution due to electrical effects with a consequent reduction of light scattering. Studies on the scattering of light by solutions of charged colloidal particles have been made by a number of investigators.[20-27] After considering these researches, we have taken a viewpoint analogous to that of Doty and Edsall[24] for proteins to justify the procedure employed to obtain micellar molecular weights. In most solutions the micelles exist in a medium of considerable concentration, the cmc., of smaller positive and negative ions. Around each micelle there is a diffuse ionic ("double") layer containing enough ions of opposite charge to equal the charge on the micelle; in other words, the small ions serve to screen the action of the charges. The scattering due to the small ions can be neglected. The fluctuating species for light scattering is obviously the micelle with its surrounding gegenions. Its net charge is shielded so that at large intermicellar distances there is little net repulsion. However, upon coming together in a collision there is repulsion which can be interpreted as that of an ionic shell of thickness equal to the Debye reciprocal radius added on to the micelle. This screened micelle exists in a medium of nearly constant ionic strength just above the cmc. In this region the micelles with their diffuse ionic layers are present in small concentration (up to 0.015–0.025 g./cc. of solute). It has been shown that the constant B (the interaction constant) is related to the deviation from ideal solution behavior[4, 24] and is made up of both entropy and heat contributions. The slopes, $2B$, of the curves reported herein are positive indicating some repulsive interaction. The effect of the net electric charge in these systems would most likely be to increase the positive value of B. The more positive slopes found, however, do not differ widely in magnitude from those for some non-electrolytes, *e.g.*, polystyrene in benzene[4] and sucrose in water.[19] From the standpoint of Doty and Steiner,[21] one might expect a small curvature in the graphs. However, the experimental data do not reveal appreciable curvature. It is true that at concentrations above those reported, there is a leveling off with smaller slope. Consequently, if the concentration of the smaller ions affords sufficient screening of the electric charge of the micelles, the Debye equation is deemed applicable for the concentrations used and the extrapolation to the cmc. (zero concentration of micelles) gives directly the reciprocal of the weight-average micellar molecular weight at that concentration.

When the concentration of the smaller ions is not sufficient for adequate screening, one obtains a nonlinear relationship analogous to that found by Wall, *et al.*,[25] for polyacrylic acid in solution. They obtained a linear relationship only when the solution was buffered to screen the electric charge effect.

With compounds having longer chain lengths, the smaller cmc.'s may be insufficient to afford satisfactory screening of electric charge. As the solution is diluted toward the cmc. the gegenion atmosphere expands providing poorer shielding and increased

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(21) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **17**, 743 (1949); **20**, 85 (1952).

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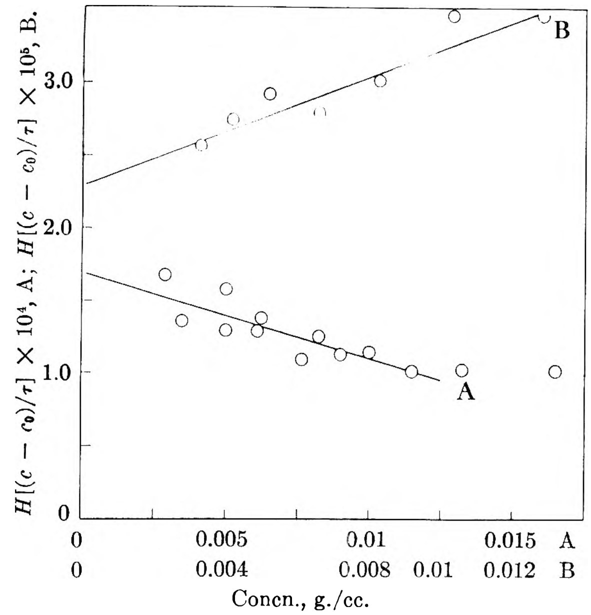

Fig. 6.—Didodecyldimethylammonium chloride: A, in water; B, in 0.003 M NaCl (the cmc. is so small that it has been neglected).

repulsion, thus causing less stability and possible variation in micellar size.

To illustrate, let us consider the $H[(c - c_0)/\tau]$ *vs.* c plots for sodium tetradecanesulfonate, sodium tetradecyl sulfate and didodecyldimethylammonium chloride. For the first, the cmc. is 1.4×10^{-3} g./cc.[28] and at 60° affords a borderline value in concentration for worthy extrapolation to determine molecular weight. It proved difficult to obtain consistent experimental values for the light scattering. The readings were apparently very sensitive to the presence of slight impurities and possibly to temperature changes. The extrapolation appeared to be satisfactory for obtaining the micellar molecular weights, Fig. 1. There may be considerable fortuity, however, in this finding.

The results for solutions of sodium tetradecyl sulfate show strikingly the effect of low cmc. and of added electrolyte. With water alone as the solvent the estimated cmc. at 40° is 0.00052 g./cc. (0.00165 M).[29] The data do not show a linear relationship, Fig. 3, C; there are wide fluctuations. This behavior is attributed to the low concentration of small ions, insufficient to form the double layer requisite to eliminate electric charge repulsions. With 0.01 M NaCl as the solvent and under the same experimental conditions, a very fine linear relationship (Fig. 3, A and B) was obtained for extrapolation; molecular weight, 43800.

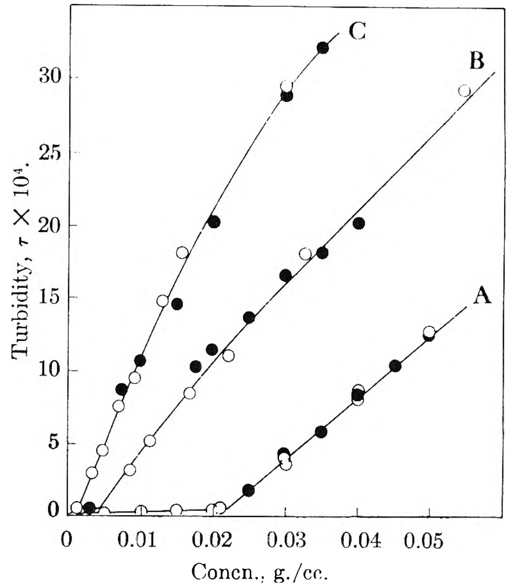

Fig. 7.—Magnesium alkane sulfonates: A, octanesulfonate; B, decanesulfonate; C, dodecanesulfonate.

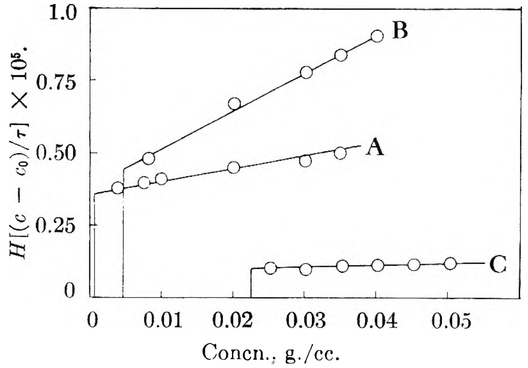

Fig. 8.—Magnesium alkane sulfonates: A, dodecanesulfonate; B, decanesulfonate; C, octanesulfonate.

Solutions of didodecyldimethylammonium chloride afford an outstanding example of the effect of simple ions on the formation and stability of micelles. Ralston and co-workers,[30] from conductance measurements, observed that solutions of this substance gave a maximum in the Λ *vs.* $\sqrt{c}$ plot, thus showing an equivalent conductance exceeding that at infinite dilution. Kraus and co-workers[31] also have obtained similar results with some long paraffin chain salts. With water as the solvent (Fig. 6, A) the data show wider variation the more dilute the solution. The best straight line for concentrations up to 0.011 g./cc. shows a *negative* slope and the extrapolation indicates a molecular weight of 6000. Above this concentration, the slope tends toward zero, corresponding to a molecular weight around 10000. The extrapolation appears to be not justifiable with water alone as the solvent. The concentration of simple ions, 1×10^{-4} M,[30] is inadequate to afford the shielding required for the micellar electric charges. It would seem that as the solution is made more and more dilute with corresponding decrease in ionic strength, micelles of different degrees of complexity exist in equilibrium with one another and with the smaller ions; the smaller the concentration the less complex the micelles. This view is borne out by the τ *vs.* c curve, Fig. 5, which shows an inflection and is not concave downward throughout as is usually the case.

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[31] E. C. Evers, P. P. Grieger and C. A. Kraus, *ibid.*, **68**, 1137 (1948); G. L. Brown, P. P. Grieger, C. Evers and C. A. Kraus, *ibid.*, **69**, 1835 (1947); M. J. McDowell and C. A. Kraus, *ibid.*, **73**, 2171 (1951).

This inflection is deemed to indicate a considerable change in micellar size with change in concentration.

Using 0.003 *M* NaCl as the solvent a more normal behavior with linear relationship prevails (Fig. 6, B). With this small concentration of added electrolyte, sufficient shielding is provided by the simple ions to overcome the effect of the electrostatic repulsions of micellar charges. Considering that there are two C_{12} chains in the cation, the molecular weight, 43800, is in keeping with expectations based upon comparison with the molecular weights of other long chain salts.

Salts with Bivalent Gegenions.—The data afford a limited comparison of the effect of a bivalent gegenion on the number of ions aggregating to form the micelle. The molecular weight of dodecyltrimethylammonium sulfate is 17900, which can hardly be considered as a marked change from that of the bromide, 15400, Fig. 4. The slope for the sulfate is very small compared with that of the bromide.

The τ *vs.* c plots for solutions of magnesium octane-, decane- and dodecanesulfonate are presented in Fig. 7. The data were obtained by two workers, as indicated with the solid and open circles, in different years starting with the same salts but otherwise carrying out the experiments independently about a year apart. The data are in satisfactory agreement. The values for cmc.'s found by light scattering are nearly identical with those determined by electrical conductance measurements.

The micellar molecular weights of the magnesium salts (Fig. 8, Table I) are much larger than those of the corresponding sodium compounds, especially for the decane and dodecane salts; for the dodecane from 28500 to 14700. This change is attributed to the marked influence of the gegenion. Although the cmc.'s are very small, good linear relationships were obtained. This indicates that the magnesium gegenions are quite closely associated with the micelles, thus making the micellar charge much smaller and more easily shielded. This view is attested by the electrical conductance measurements previously made in this Laboratory.[11] The Λ *vs.* $\sqrt{c}$ plots show an exceedingly abrupt drop as the concentration exceeds the cmc. revealing small charge and poor conductance by micelles. Also, the specified conductance plots, L *vs.* c, show much smaller slopes above the cmc. than found for the corresponding sodium salts.[11]

Micelle Structure.—The application of the data given above toward the formulation of a theory of micelle structure will be presented in the fourth paper[32] which follows concurrently.

Acknowledgments.—The authors wish to thank Dr. H. J. Harwood for a helpful conference with him and his co-workers and for the sample of didodecyldimethylammonium chloride. They thank Dr. E. W. Anacker for a very useful conference affording comparisons with closely related work. They also wish to gratefully acknowledge their indebtedness to Dr. E. C. Lingafelter and Dr. G. D. Halsey, Jr., who have given helpful criticisms and suggestions.

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[32] H. V. Tartar, THIS JOURNAL, **59**, 1195 (1955).

THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS OF DODECYLTRIMETHYLAMMONIUM SULFATE AT 25°

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Received February 21, 1955

The electrical conductance has been determined for solutions of dodecyltrimethylammonium sulfate, range 0.420×10^{-2} to 22.86×10^{-2} normal. Comparison is made with solutions of dodecyltrimethylammonium bromide. The results indicate that the sulfate ion has a smaller influence than other bivalent gegenions, which have been studied, toward the aggregation of paraffin chain ions to form micelles.

Introduction

For long it has been recognized that the length of the hydrocarbon chain plays a prominent role in determining the critical concentration for the formation of micelles (hereafter designated cmc.) in aqueous solutions of paraffin chain salts. The value of the cmc. may be taken as an index of the tendency to form micelles; the smaller the cmc. the greater this tendency. Only limited attention has been given, however, to the influence of the gegenions on this critical phenomenon, particularly with ions of different valence.

Lottermoser and Puschel[1] in their study of the solutions of salts of alkyl sulfates found that with the same carbon chain length the bivalent cations (Ca^{++}, Ba^{++}, Mg^{++}, Cu^{++} and Zn^{++}) gave similar values for cmc. which were much less than those with univalent cations (Na^+, K^+ and Ag^+) which were also closely similar.

Samis and Hartley[2] comparing silver and copper dodecyl sulfates, reported a much lower cmc. with the latter in keeping with expectations for the influence of the bivalent gegenion. Working with cetylpyridinium compounds, they found that the cmc. (normality) for the sulfate was slightly greater than that of the bromide which in turn was but little higher than that of the chloride. They also reported that in mixtures of chloride and sulfate, the chloride ion was preferentially adsorbed. These findings for the influence of sulfate ion are quite out of line with the usual expectations for a bivalent gegenion.

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[1] A. Lottermoser and F. Puschel, *Kolloid Z.*, **63**, 175 (1933).

[2] C. S. Samis and G. S. Hartley, *Trans. Faraday Soc.*, **34**, 1288 (1938).

Special emphasis on the marked influence of the gegenion has been made by Grieger and Kraus[3,4] in their study of the electrical conductance of *n*-octadecyltrimethylammonium salts in water solutions (nitrate, bromate, chloride, formate and oxalate). Among the 1–1 salts the ratio of the extremes of the cmc.s was 2:1, formate compared to nitrate. Very striking, indeed, is the fact that with the closely related carboxylic anions, the cmc. of the oxalate is only *one-sixteenth* that of the formate.

In the preceding paper[5] it has been shown that there is a great difference in the micellar molecular weights of the C_{12} salts, dodecyltrimethylammonium sulfate and magnesium dodecane sulfonate, 17900 and 28500 with cmc.s 4.7×10^{-3} and 0.86×10^{-3} g./cc. (17.6×10^{-3} and 3.11×10^{-3} *N*), respectively.

Because of the apparent uniqueness of the influence of the bivalent sulfate ion with paraffin chain salts, measurement has been made of the electrical conductance of solutions of dodecyltrimethylammonium sulfate to afford further pertinent information regarding the influence of the gegenion on micelle formation. The conductance of solutions of the corresponding bromide had been determined previously in this Laboratory.[6]

Experimental

Trimethylamine.—Eastman Kodak Co. white label product was used. A check on its purity was made by fractionally crystallizing the hydrochloride from 95% ethanol. Samples taken from different fractions showed no variation in melting point.

Dodecyl Bromide.—Halogen Chemicals research grade of *n*-dodecyl bromide was purified by fractional distillation at 25 mm. and 160°. The fraction used showed a refractive index of 1.4563 at 25°.

Silver Sulfate.—Analyzed reagent grade product was used without further purification.

Methanol and Acetone.—These were Baker and Adamson reagent quality grade and were used without further purification.

***n*-Dodecyltrimethylammonium Bromide.**—This compound was prepared by passing an excess (10%) of trimethylamine into an alcoholic solution of dodecyl bromide and then refluxing the mixture for approximately one hour. Because of the low boiling point of the amine, 3.5°, a special reflux condenser was used with solid carbon dioxide as the cooling agent. At the completion of the reaction, dry air was passed through the solution to remove the excess trimethylamine. The solution was then evaporated to dryness and the compound recrystallized from acetone to which a few drops of ethanol had been added to increase solubility.

***n*-Dodecyltrimethylammonium Sulfate.**—The preparation of this compound has not been previously reported. Use was made of the double decomposition reaction in aqueous solution between silver sulfate and dodecyltrimethylammonium bromide in equivalent amounts. The silver bromide precipitate was then removed by filtration. Purification of the quaternary sulfate proved difficult. Finally the following procedure was used. The aqueous solution was evaporated to dryness and then heated, for several hours on a steam-heated hot plate, sufficient methanol being added from time to time to dissolve the salt. The purpose of this repeated heating of the solid salt was to remove as much water as possible; a very small amount was sufficient to prevent crystallization. The repeated heating was also necessary for the complete removal of the silver bromide.

When the quaternary sulfate was sufficiently free from water it was dissolved in a boiling solution (dry) containing 20% methanol and 80% acetone. The salt is insoluble in acetone but very soluble in methanol; the ratio of four to one gave a satisfactory solvent for the purpose. (Forty-eight different solvents were tried.) On cooling the boiling, nearly-saturated solution, the salt separated in beautiful white platelets. If sufficient water had not been previously removed a sticky mass was deposited and the material had to be worked over from the beginning. Between crystallizations the solid was subjected to prolonged heating.

Finally, the salt was dissolved in methanol and the insoluble silver salt, which was found to deposit for several recrystallizations, removed by filtration. Acetone was added to the filtrate to give the solvent the desired composition, the mixture heated to boiling and then cooled. With care, five repetitions of crystallizations was sufficient to obtain a salt of the desired purity. Incidentally, it was found that the alcoholic solution of the impure salt showed a faint yellow color. This color was removed by further crystallization. The authors believe that the removal of this yellow color is the best simple criterion of purity.

The salt is markedly hygroscopic. All attempts to obtain an anhydrous product were unsuccessful; even samples spread in thin layers and kept in a desiccator over phosphorus pentoxide continued to lose weight after six months.

Samples of the salt were analyzed for carbon and sulfate ion and the carbon–sulfate ratio calculated. Found: carbon, 53.1, 53.1, 53.6, av. 53.26%; sulfate ion, 14.24, 14.13; av. 14.19. Carbon–sulfate ratio: found, 3.75; theory, 3.745.

Conductance Measurements.—These were made with equipment described in previous papers.[7,8] The temperature was maintained constant to ±0.004°. The calibrated cells were checked frequently against a reference cell. The specific conductance of the water was approximately 2×10^{-6} mho cm.$^{-3}$.

Three stock solutions of *n*-dodecyltrimethylammonium sulfate were prepared by dissolving approximately known quantities of the salt in water to give solutions near the desired concentrations. These were analyzed gravimetrically for sulfate ion according to the procedure given by Kolthoff and Sandell.[9] It was found desirable to digest the barium sulfate precipitates for several days to permit ease of separation by filtration. The results were reproducible to 0.1%.

Other solutions were prepared from the stock solutions by dilution by weight to afford a series of measurements at different concentrations. Three series have been denoted 1, 2 and 3 in Table I.

TABLE I

ELECTRICAL CONDUCTANCE OF SOLUTIONS OF DODECYLTRIMETHYLAMMONIUM SULFATE AT 25°

Series no.	Normality, $N \times 10^{-2}$	Equiv. conductance mho	Series no.	Normality $N \times 10^{-2}$	Equiv. conductance, mho
2	0.4204	94.1	3	3.641	49.81
2	.5885	92.4	3	5.175	40.50
1	.6643	91.9	3	6.550	36.07
2	.7145	91.1	1	6.766	35.73
2	.9612	89.2	3	9.471	31.49
1	1.629	84.8	1	12.39	29.70
2	1.711	82.7	3	13.38	29.36
3	2.480	64.38	1	22.86	29.58
3	2.980	57.01			

Density determinations showed a variation of less than 0.1% over the concentration range of the solutions. This permitted the use of a constant value for density, that of pure water, in making the conversion from moles per thousand grams solution to volume normality.

Before taking the readings, dissolved carbon dioxide was removed by passing nitrogen through the solutions. Before use, the nitrogen was bubbled through sodium hydroxide

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[3] P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 3803 (1948).

[4] P. F. Grieger, *Ann. N. Y. Acad. Sci.*, **51**, 827 (1949).

[5] H. V. Tartar and A. L. M. Lelong, THIS JOURNAL, **59**, 1185 (1955).

[6] A. L. Scott and H. V. Tartar, *J. Am. Chem. Soc.*, **65**, 692 (1943).

[7] V. Sivertz, R. E. Reitmeier and H. V. Tartar, *J. Am. Chem. Soc.*, **62**, 1379 (1940).

[8] A. M. Lelong, *et al.*, *ibid.*, **73**, 5411 (1951).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936.

solution and then through water in a train of wash bottles to ensure saturation. When constance of conductance values was obtained by this procedure, it was assumed that the solvent correction was reduced to negligible magnitude.

The data are presented in Table I and Fig. 1. For comparison, the results obtained by Scott and Tartar[6] for the corresponding bromide are also shown in Fig. 1. The data are believed to be accurate within 0.1%.

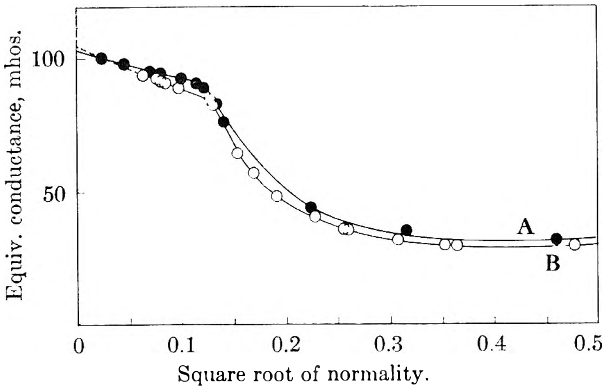

Fig. 1.—Equivalent conductance at 25°: A, dodecyltrimethylammonium bromide; B, dodecyltrimethylammonium sulfate.

In general, it may be said that the two curves are quite similar, especially at concentrations above the breaks. There is no great variation as shown by Lottermoser and Puschel[1] in their comparison of 1–1 and 2–1 salts and by Grieger and Kraus[3] for 1–1 and 1–2 salts. There is no large effect corresponding to that of the change from sodium to magnesium ion in a sulfonate as shown in the preceding paper.[5]

The limiting equivalent conductance of the dodecyltrimethylammonium ion has been reported by several workers.[6,10,11] The value 23.8 mho obtained from these measurements on the sulfate is in good agreement with the value 24.0 mho, obtained from a large-scale plot of Scott and Tartar's[6] data on the bromide. Since both investigations were concerned primarily with the conductance immediately around and above the critical micelle concentration, not all precautions essential for the most precise measurements in the dilute solutions were observed. Furthermore the determinations were not extended into sufficiently dilute solutions to make fully valid an extrapolation to infinite dilution.

Kraus and co-workers,[10,11] however, working with nitrate and bromide, had as a principal objective the determination of the conductances in very dilute solutions. With compounds, the measurements were made with the elaborate care requisite for the maintenance of a constant solvent correction and the accurate determination of its magnitude. The results were 22.4 and 22.3 mho, respectively, showing excellent concordance between values for the two salts. The authors deem these values more reliable than the higher values from the measurements made in this Laboratory.

The limiting slope of the Λ *vs.* $\sqrt{c}$ curve for a 1–2 salt at 25° is 170.8 as calculated using the Onsager equation. The experimental value found here is 147, lower (13.9%) than the theoretical. The value for Λ_0 used in the calculation is 102.2 mho in accordance with McDowell and Kraus.[11] It should be pointed out that the concentrations are somewhat higher than the range in which the Onsager equation holds. The data for the bromide also show a slope somewhat less than the theoretical for a 1–1 salt. The conductances of the bromide solutions agree very closely with the values found by Ralston and co-workers[12,13] and by Kraus and co-workers.[14] On the whole, there appears to be nothing strikingly abnormal in the conductance of the sulfate below the cmc.

It is noteworthy that the cmc. (as normality) for dodecyltrimethylammonium sulfate instead of being lower than that of the bromide is actually *higher* (Fig. 1), 1.64×10^{-2} and 1.44×10^{-2} *N*, respectively. Expressing the cmc.s as molarities the ratio of sulfate to bromide is 1:1.75, within the range for univalent gegenions. This result is in keeping with the findings of Samis and Hartley[2] for cetylpyridinium sulfate. The sulfate ion apparently has a much smaller influence than the other bivalent ions mentioned above toward the aggregation of paraffin chain ions to form micelles. We know that the sulfate ion is highly hydrated in solution and that with this strong binding of water molecules a decrease in entropy will occur. Its partial molal entropy is smaller than for most common oxy-anions.[15] This may have a potent influence on its degree of dissociation from the micelle.

Further comment on the role of the gegenion will be made in the fourth paper[16] which follows concurrently.

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[10] E. Bair and C. A. Kraus, *J. Am. Chem. Soc.*, **72**, 1129 (1951).

[11] M. J. McDowell and C. A. Kraus, *ibid.*, **76**, 2170 (1951).

[12] A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *ibid.*, **64**, 97 (1942).

[13] A. W. Ralston and D. N. Eggenberger, *ibid.*, **70**, 436 (1948).

[14] G. L. Brown, P. F. Grieger and C. A. Kraus, *ibid.*, **71**, 95 (1949).

[15] W. M. Latimer, "Oxidation Potential," Second Edition, Prentice-Hall, Inc., New York, N. Y., 1952.

[16] H. V. Tartar, THIS JOURNAL, **59**, 1195 (1955).

THE MICELLAR RADII OF DODECANESULFONIC ACID AS REVEALED BY DIFFUSION EXPERIMENTS AT 25°

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Received February 21, 1955

The mean diffusion coefficient at 25° has been determined for dodecanesulfonic acid in perchloric acid solutions. The micellar radii have been estimated. After substantially complete "swamping" the radii gradually increase in size with increase in perchloric acid concentration up to the point where a second phase appears.

The work reported here was completed in 1942.[1] Publication has been delayed because additional experiments were contemplated to broaden the scope. The demands of other investigations, however, prevented the consummation of the original plan. The results are presented at this time because they are pertinent to the findings presented in the first and last papers of this group.[2,3]

Experimental

Sodium Dodecanesulfonate and Dodecanesulfonic Acid.—The preparation of the sodium salt has been previously described.[4,5] In addition to purification by repeated recrystallizations from solvent it was converted to the insoluble mercurous salt, thoroughly washed to remove impurities and then reconverted to the sodium salt by metathesis with sodium chloride.

The dodecanesulfonic acid, which is soluble in ether, was easily prepared from the sodium salt by Zuffanti's[6] method. It is a strong acid and its solutions can be titrated directly with sodium hydroxide using phenolphthalein indicator.

Procedure and Equipment.—The mean diffusion coefficient, $\bar{D}$, was determined by measuring the diffusion across a sintered-glass membrane employing the technique developed by previous investigators[7-14] including the use of an added electrolyte with common ion as a "swamping agent" to nullify the influence of electric charge on the movement of the micelle. This added electrolyte produces a substantially complete association of the gegenion with the micelle to form an electrically neutral unit and also lowers the critical micelle concentration to the point where the more rapidly diffusing monomer ion makes a negligible concentration to the total $\bar{D}$.

The diffusion cells were round and made with sintered, Pyrex glass membranes 4.2 cm. diameter and stated by the manufacturer to have a pore size $(2-4) \times 10^4$ Å., (G4). Each cell was made in two parts fitted together with a ground glass joint. The volumes were determined by weighing deaerated distilled water required to fill the cell. The volume of the capillaries of the membrane was estimated by allowing it to fill with water by capillarity. The value so obtained was somewhat large since a film of water invariably formed on the top side. The volume of the capillaries, however, was small and was considered as part of the upper half-cell volume.

The cells were held by heavy rubber bands in individual universal brackets in an air thermostat. The brackets were adjusted to hold the membrane within one degree of level in all directions. The temperature of the thermostat was maintained at 25 ± 0.03° by a mercury–toluene regulator.

Diffusion Measurements.—The upper part of the cell was filled with an aqueous solution of the "swamping" agent, perchloric acid, and of the dodecanesulfonic acid. The lower vessel was filled with the swamping agent in the same concentration as in the upper vessel. The cells were fitted together and kept in the thermostat until 3 to 5% of the diffusing material had entered the lower vessel. The solutions were then removed for analysis. With solutions of the concentrations used special stirring was unnecessary. The mixing to produce uniformity was automatic since the solution of greater concentration was uppermost. The mean diffusion constant was calculated in accordance with the Hartley and Runnicles equation[8]

$$K\bar{D} = \frac{1}{\left(1 + \frac{v'}{v}\right)(t_2 - t_1)} \ln \frac{c_0 + \left(\frac{v'}{v}\right) c_0' - \left(\frac{v'}{v} + 1\right) c_1'}{c_0 + \left(\frac{v'}{v}\right) c_0' - \left(\frac{v'}{v} + 1\right) c_2'}$$

where K is the modified cell constant; $\bar{D}$, the mean diffusion coefficient; $t_2 - t_1$, the diffusion time; V, the volume of the half-cell; c, the concentration of solute in the half-cell. The prime accents refer to the upper half-cell which contained the more concentrated solution.

Each cell was standardized using 0.1 N potassium chloride solution whose diffusion constant was taken to be 1.631 cm.^{2}/day.[9] The cells were also tested for large pores and cracks as suggested by Dawson.[15] Check runs were made in two different cells.

Analysis of Solutions.—The solutions were analyzed by precipitating the dodecanesulfonate ion as the mercurous salt and weighing the precipitate in a Gooch crucible. An aliquot was put in a small beaker, approximately twice the theoretical amount of mercurous mercury reagent (mercurous perchlorate and perchloric acid or mercurous nitrate and nitric acid) was added and the beaker placed on a steam-bath until the precipitate had coagulated. The precipitate was then removed by filtration, washed at room temperature, then washed with alcohol and dried at 70°. Careful checking showed that the weights of the precipitates obtained were invariably lower than the theoretical for mercurous dodecanesulfonate. It was necessary to apply an empirical factor, 1.016, which was determined experimentally and found to be substantially constant over the range of acid concentrations used. With this standardized procedure, the determinations agreed within 0.1%. It is not certain whether the precipitate is low in weight due to solubility or to possible complex compound formation.

Results and Discussion

The radii, r, of the micelles, *assumed to be spherical*, were calculated by the use of the Stokes-Einstein equation, $D = RT/N6\pi\eta r$. Because there may be objections to the applicability of this equation to these systems[3] the values are designated "Equivalent S-E micelle radii." The data are presented in Table I and Fig. 1. The concentrations

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[1] A. Doyle Abbott, Thesis, University of Washington, 1942.

[2] H. V. Tartar and A. L. M. Lelong THIS JOURNAL, **59**, 1185 (1955).

[3] H. V. Tartar, *ibid.*, **59**, 1195 (1955).

[4] K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 539 (1939).

[5] R. M. Reed and H. V. Tartar, *ibid.*, **57**, 570 (1935).

[6] S. Zuffanti, *ibid.*, **62**, 1044 (1940).

[7] J. H. Northrup and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1928).

[8] G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc. (London)*, **168A**, 401 (1938).

[9] J. W. McBain and T. H. Liu, *J. Am. Chem. Soc.*, **53**, 59 (1931).

[10] J. W. McBain and C. R. Dawson, *Proc. Roy. Soc. (London)*, **148A**, 32 (1935).

[11] A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

[12] J. W. Mehl and C. L. A. Schmidt, *Univ. Cal. Publ. Physiol.*, **8**, 165 (1937).

[13] G. S. Hartley and C. Robinson, *Proc. Roy. Soc. (London)*, **134A**, 20 (1931).

[14] J. W. McBain and J. R. Vinograd, *J. Am. Chem. Soc.*, **63**, 2008 (1941).

[15] C. R. Dawson, *ibid.*, **55**, 432 (1933).

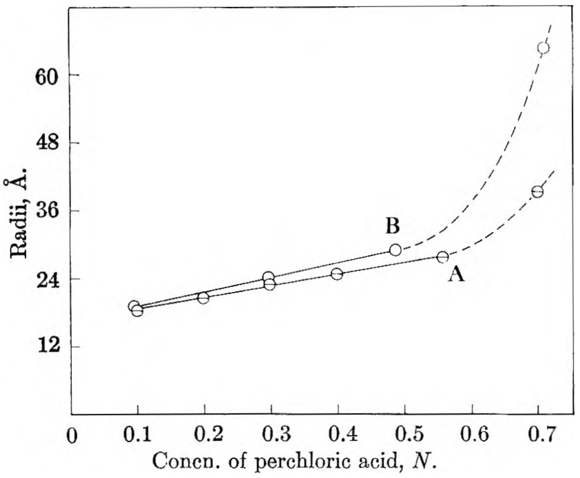

Fig. 1.—Radii of dodecanesulfonic acid: A, 0.025 *N*; B, 0.10 *N*.

given are those at the beginning of the diffusion experiments.

Table I

Diffusion of Dodecanesulfonic Acid at 25°

Concn. of $HClO_4$, *N*	Mean diffusion coefficient *D*, cm.^{2}/day	Equiv. S–E micelle radii, Å.	Concn. of $HClO_4$, *N*	Mean diffusion coefficient *D*, cm.^{2}/day	Equiv. S–E micelle radii, Å.
0.025 *N* Dodecanesulfonic acid			0.10 *N* Dodecanesulfonic acid		
0.10	0.115	18.2	0.0	0.453	
.20	.100	20.7	.0976	.111	18.8
.30	.090	23.2	.2939	.086	24.3
.40	.0839	25.0	.4878	.072	29.1
.56	.0736	28.3	.7123	.029	65[a]
.70	.0529	39.3			

[a] Accurate results were not obtainable at this high concentration.

In addition to the data given, 0.1 *N* dodecanesulfonic acid was diffused into a perchloric acid solution containing the sulfonic acid in concentrations from 0.001 to 0.01 *N*, concentrations above the cmc. under these conditions. The radii calculated from these measurements were essentially the same as those given, thus indicating that diffusion is almost entirely that of the micelles while that of the molecules or ions must be negligible.

Our attention has been called very recently to a possible discrepancy between our value for $\bar{D}$ for the *unswamped* dodecanesulfonic acid, 0.1 *N*, and that of McBain[16]; *viz.*, 0.453 and 0.558, respectively. She determined $\bar{D}$ for the concentration range 0 to 1.16 *N* at 25° and reported a very sharp minimum in the $\bar{D}$ *vs.* concn. curve at 0.0703 *N* ($D = 0.356$). Immediately above this concentration the curve is very steep thus showing a large change in the value of $\bar{D}$ for a small change in concentration. Consequently, this region is hardly suitable for a worthy comparison because of the possible large effect of cumulative errors in the preparation of materials and in the experimental procedure.

In accordance with the theory of diffusion of charged particles, the apparent value of the diffusion constant was found to decrease very rapidly as the concentration of the swamping agent, perchloric acid, was increased from 0 to 0.1 *N*. Thus 0.1 *N* is evidently the concentration required to obtain substantially complete swamping, that is, negligible dissociation of gegenions from the micelle.

At concentrations of perchloric acid from 0.1 to 0.56 *N*, there is a nearly linear relationship between the calculated radii and concentration thus indicating that the micelles gradually become larger with increase in swamping agent. Within this region of concentration of perchloric acid the value of the diffusion constant (and consequently the value of the radius) is independent of the concentrations used of the dodecanesulfonic acid.

Above 0.56 *N* perchloric acid, a second phase appears and the solution becomes opalescent. The value of the diffusion coefficient obtained with such solutions is erratic and not reproducible.

Picturing the molecule of dodecanesulfonic acid as stretched out and using Pauling's values for bond distances in ångströms C—C (using tetrahedral angle), 1.27; CH_3, 2.0; C–S, 1.82; SO_3, 1.51 (radius assumed to be the same as for SO_4); and H, 0.31; the length is 19.6 Å. This compares fairly well with the radius found for the micelle in 0.1 *N* perchloric acid, namely, 18.5 Å., and may be taken to support Hartley's theory of a spherical micelle. At greater concentrations of the swamping agent, however, the radius increases as a linear function of the concentration up to the point of the "salting out" of the new phase. Throughout this region the micelle apparently gradually increases in size and micellar molecular weight with estimated radii becoming too large for the shape to be spherical.[3]

Additional experiments were made with solutions of decanesulfonic acid using hydrochloric acid as the swamping agent. The results were unsatisfactory. The cmc. of the acid is so high that a large amount of swamping agent must be used and even then no sharp break in the micellar radius *vs.* concentration curve occurs to indicate definitely a concentration for substantially complete swamping. The data indicated a gradual change in radius up to 19 Å., in 1.6 *N* hydrochloric acid. This value is greater than for the C_{10} micelle of the Hartley type, 17.0 Å.

Further comments on the results are given in the fourth paper[3] which follows.

Acknowledgment.—The authors are grateful to Mrs. Edith Abbott for helpful counsel and laboratory assistance.

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(16) E. L. McBain, *Proc. Roy. Soc.* (*London*), **A170**, 415 (1939).

A THEORY OF THE STRUCTURE OF THE MICELLES OF NORMAL PARAFFIN CHAIN SALTS IN AQUEOUS SOLUTION

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Received February 21, 1955

The interplay of forces in micelle formation are considered and a theory is presented in which the paraffin portion of the micelle is amorphous ("liquid") and the shape may be spherical or oblate spheroidal. One dimension (semi-axis) is equal to that of the maximum length of the hydrocarbon chain. The shape is dependent upon the micellar molecular weight and the area per polar group on the micellar surface. Data, calculations and discussion are given for the application of the theory.

Introduction

In this Laboratory several investigations have been made over a twenty-year period of solutions of paraffin chain salts. The solutions used were relatively dilute (less than 0.6 N), mobile, optically clear, isotropic liquids. None was sufficiently concentrated to approach the "curd" state with its crystalline type of structure. This paper is addressed to the consideration of the structure of the micelles in this dilute type of solution of normal paraffin chain salts.

The literature is well known to workers in this field and it will suffice simply to cite the most pertinent references proposing lamellar and spherical structures,[1-5] and the cogent objections that have been made to them.[6-9]

The author accepts the idea of a single micellar species for most *n*-paraffin chain salts with a liquid-like hydrocarbon interior.

Theory of Micelle Structure.—In the formulation of this theory important use has been made of some of the ideas set forth by Hartley[2] and by Debye.[5]

The paraffin chain ions dealt with consist of a normal hydrocarbon chain which is attached at one end to a polar, ionic group. In the formation of the micelle two different kinds of energy take part. Energy is liberated by the removal of a number of the hydrocarbon chains from the surrounding water, thus bringing them in contact and decreasing the hydrocarbon–water interface. The chains attract each other. An equally important factor, no doubt, is the strong cohesive forces (hydrogen bonding, etc.) between the water molecules which tend to aggregate and expel the chains from solution. The molecular forces involved in this process are of the short range type commonly designated as van der Waals forces. Simultaneously the electrically charged polar ends are brought closer to each other. This process requires energy when the ionic atmospheres are brought to overlap. Here the forces to overcome are long range electrical (Coulombic) forces. In the formation of the micelle an equilibrium is reached between these opposing forces with the accompanying decrease in free energy. It is the interplay of these short and long range forces which determines the structure of the micelle. The hydrophilic nature of the polar groups keeps the micelles suspended in solution.

We will assume that the interior of the micelles consists of hydrocarbon chains and that the polar groups are spaced on the surface; also that *the chains are in unordered arrangement* and, except for any influence that may come from the spacing of the polar ends, are in a "liquid" state, comparable in density and arrangement to that of the liquid hydrocarbon of like chain length.

The hydrocarbon portion of the micelle cannot have an open space at the center and consequently, *one dimension (semi-axis) does not exceed the maximum (stretched out) length of the hydrocarbon chain.* With this limitation, the simplest geometric form that a micelle may assume having the least area for the volume is that of *a sphere* or of *an oblate spheroid.* The latter has major and minor axes unequal; it is the form obtained by the revolution of an ellipse around its minor axis.[10] When the forces acting reach equilibrium, it is not essential that the micelle be spherical (least surface for the volume). The *shape may vary from spherical depending upon the chain length and the area occupied per polar group on the surface.* With a given chain length, the smaller this area, the greater will be the deviation (oblation). This will be made clear by calculations to be presented later.

The micellar molecular weights and bond distances afford the requisite data for calculating the length of the axes, thereby revealing the general shape of the hydrocarbon interior. Because of the uncertainties of the dimensions of the polar groups it has been deemed best to deal with the dimensions of the hydrocarbon portion because the computations can be made with greater accuracy.

Using this picture of the micelle an illustrative calculation will now be presented using the data for a solution of sodium tetradecyl sulfate in 0.1 M NaCl; just above the cmc. at 23°. We will assume that the hydrocarbon interior has an oblate spheroidal shape with major and minor semi-axes a and b, respectively, and eccentricity e.

To estimate the length of the hydrocarbon chain

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[1] J. W. M Bain, *Trans. Faraday Soc.*, **9**, 99 (1913); "Colloid Science," D. C. Heath and Company, San Francisco, Calif., 1950.

[2] G. S. Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Herman and Cie, Paris, France, 1936.

[3] W. Philippoff, *J. Colloid Sci.*, **5**, 169 (1950). A review.

[4] W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Am. Chem. Soc.*, **68**, 220 (1946).

[5] P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949); THIS JOURNAL, **53**, 1 (1948).

[6] M. L. Corrin, *J. Chem. Phys.*, **16**, 844 (1948).

[7] G. W. Brady, *ibid.*, **19**, 1547 (1951).

[8] E. W. Anacker, *J. Colloid Sci.*, **8**, 402 (1953).

[9] E. Hutchinson, K. E. Manchester and L. Winslow, THIS JOURNAL, **58**, 1124 (1954).

[10] This form, with fixed minor axis, is applicable. With a prolate spheroid (formed by the revolution of an ellipse around its major axis) the ratio of surface to volume is too large.

the bond distances given by Pauling[11] are used: namely, C–C (tetrahedral angle), 1.27 Å.; CH_3, 2.0 Å.; and (C–O)/2, 0.71 Å. For the determination of the volume per mole of the CH_2 group, the densities reported by Egloff[12] for the homologous series octane to tetradecane inclusive are used. From the differences in the molar volumes, the average volume of the CH_2 group is found to be 16.21 cc./mole. The volume obtained for the CH_3 group plus one-half the open space around the chain is 32.63 cc./mole.

We have from geometry the following relationships for an oblate spheroid with major and minor semi-axes a and b, respectively, and eccentricity e: volume $= 4/3\pi a^2 b$; eccentricity $= \sqrt{(a^2 - b^2)/a^2}$ and surface area $= 2\pi a^2 + \pi(b^2/e) \ln (1 + e)/(1 - e)$.

The essential calculations follow immediately.

Micellar mol. wt. = 43500

Mol. wt. of salt = 314.6

No. of hydrocarbon chains in the micelle, aggregation no. $= \frac{43500}{314.6} = 138.3$

Length of the hydrocarbon chain, minor semi-axis, b $= (1.27)13 + 2.00 + 0.71 = 19.22$ Å.

Vol. of the hydrocarbon portion of 1 mole of micelles $= [(16.21)13 + 32.63]138.3 = 33660$ cc.

Vol. of a single micelle $= \frac{33660}{(6.023)10^{23}} = (5.588)10^{-20}$ cc. $= 4/3\pi a^2 b$

$a = \frac{(5.588)10^{-20}}{(4.189)(19.22)^2 10^{-16}} = 26.34$ Å., major semi-axis

Eccentricity, $e = \sqrt{\frac{a^2 - b^2}{a^2}} = \sqrt{\frac{(26.34)^2 - (19.22)^2}{(26.34)^2}} = 0.6839$

Surface area of hydrocarbon portion of the micelle $= 2\pi a^2 + \pi\frac{b^2}{e} \ln \frac{1 + e}{1 - e} = 7177$ Å.^{2}

Surface area per polar group $= \frac{7177}{138.3} = 51.9$ Å.^{2}

The results indicate that the hydrocarbon portion of the micelle is an oblate spheroid with major semi-axis 26.3 Å., and the area per ionic group in the surface is 51.9 Å.^{2}

The reader should bear in mind that the micellar molecular weight is a weight-average value and hence the estimated aggregation number, major semi-axis and surface areas are also average values. The author believes, however, that Debye[5] is correct in his suggestion that the number of the chains in the micelles varies within small limits, say 4 or 5%.

Similar computations have been made for 21 solutions of salts in water alone or with added common-ion electrolyte. The data are recorded in Table I. The micellar molecular weights marked with a superscript a were determined by Debye and co-workers[5]; those with superscript b by Anacker[8]; the others, in this Laboratory.[13] In estimating the chain lengths, some arbitrary choices have been made for the fraction of the bond distance connecting the α carbon atom to the polar group. Using Pauling's[11] values the following distances were chosen: (C–O)/2, 0.71 Å.; (C–S)/2, 0.91 Å.; (C–NH_2)/2, 0.74 Å.; (C–$N(CH_3)_3$)/3, 0.49 Å.

To provide for easy comparison, data were also obtained from calculations made for prolate spheroids having the same volumes and minor semi-axes as the oblate spheroids. The data are given in Table I and marked with an asterisk.*

A spherical shape is ascribed in those instances where the two semi-axes are found to be approximately equal, 1:1; shape S.

With sodium decyl and dodecyl sulfate, tetradecyltrimethylammonium bromide and dodecyltrimethylammonium sulfate, the ratios of the semi-axes and the areas per polar group are so similar that a decision can hardly be made as to whether the shape is oblate spheroidal or prolate spheroidal. Here the variation from a spherical shape is small. It will be noted, however, that the calculated surface areas per micelle are in each instance slightly smaller for the oblate spheroid.

In the other instances of comparison, the surface areas per micelle as well as the areas per polar group are definitely smaller for the oblate spheroids.

Generally, the data show that for a homologous series having a given polar group, the micelles with the shorter chain are more nearly spherical, that is, have a smaller ratio of major to minor axis. The shape of a micelle is shown to vary markedly, however, from that of a sphere, to that of an oblate spheroid with major semi-axis being more than three times that of the minor semi-axis. Variations from 24 to 63 Å.^{2} are obtained for surface areas per polar group.

The conclusion appears justified that the micelles are in more stable form as spheres or as oblate spheroids, as the case may be, to give the smallest ratio of surface to volume, in other words, the form in which the polar groups are brought nearest to each other in the micellar surface. A chain of at least C_8 length is required for the formation of the micelle with polar group occupying a surface area of approximately 60 Å.^{2} Chains of C_{10}, C_{12}, C_{14} lengths would afford relatively great increases in the short range forces opposing the electrical repulsion of the polar groups. Hence in Table I the micellar shapes are given either as spheres, S, or as oblate spheroids, OS.

It is especially noteworthy that with the "double" paraffin chain salt octyltrimethylammonium decane sulfonate, where both ions are in the same micelle with consequent small electric charge, the surface area per polar group is small, 24–36 Å.^{2}, and near that of an insoluble, paraffin chain, condensed film, say of oleic acid on water, and under smaller pressure, ∼ 2 dynes.[14] With 0.178 N potassium chloride as the solvent, the influence of electric charge repulsion is apparently quite completely nullified and hence the polar groups can be brought very close together in the formation of the micelle.

For comparison, the surface areas per polar group

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(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

(12) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1939.

(13) H. V. Tartar and A. L. M. Lelong, THIS JOURNAL, **59**, 1185 (1955).

(14) N. K. Adam, "Physics and Chemistry of Surfaces," 3rd Edition, Oxford University Press, New York, N. Y., 1941.

TABLE I

DATA ON THE SHAPE AND SURFACE AREA OF THE HYDROCARBON PORTION OF THE MICELLES

Paraffin chain salt	Solvent	Micellar mol. wt.	No. of chains/micelle	Minor semi-axis, Å.	Major semi-axis, Å.	Ratio Major semi-axis / minor semi-axis	Micellar surface area, Å.²	Area/polar group, Å.²	Micellar shape S = sphere OS = oblate spheroid
Sodium decyl sulfate, $NaC_{10}H_{21}SO_4$	Water	13000	50	14.24	15.73	1.10	2920	58.4	OS
Sodium decyl sulfate, $NaC_{10}H_{21}SO_4$	Water	13000	50	14.24	17.27*	1.21*	2920*	58.4*	
Sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$	Water	20500	71	16.68	18.86	1.13	4130	58	OS
Sodium dodecyl sulfate, $NaC_{12}H_{25}SO_4$	Water	20500	71	16.68	21.32*	1.28*	4160*	58.5*	
Sodium tetradecyl sulfate, $NaC_{14}H_{29}SO_4$	0.10 *M* NaCl	43500	138	19.22	26.35	1.37	7180	52	OS
Sodium tetradecyl sulfate, $NaC_{14}H_{29}SO_4$	0.10 *M* NaCl	43500	138	19.22	36.11*	1.88*	7520*	54.4*	
Sodium octanesulfonate, $NaC_8H_{17}SO_3$	Water	6000	27.7	11.80	11.63	0.99	1720	62.6	S
Sodium decanesulfonate, $NaC_{10}H_{21}SO_3$	Water	9900	40.5	14.34	14.06	1.02	2520	62.3	S
Sodium dodecanesulfonate, $NaC_{12}H_{25}SO_3$	Water	14700	54	16.60	16.49	0.99	3440	61.8	S
Sodium tetradecanesulfonate, $NaC_{14}H_{29}SO_3$	Water	24000	80	19.42	19.93	1.03	4900	61.3	S
Sodium tetradecanesulfonate, $NaC_{14}H_{29}SO_3$	Water	24000	80	19.42	20.46*	1.05*	4890*	60.0*	S
Decyltrimethylammonium bromide, $C_{10}H_{21}(CH_3)_3NBr$	Water	10200[a]	36.4	13.92	13.6	0.98	2380	65.4	S
Dodecyltrimethylammonium bromide, $C_{12}H_{25}(CH_3)_3NBr$	Water	15500[a]	50.3	16.46	15.98	0.97	3310	65.8	S
Tetradecyltrimethylammonium bromide, $C_{14}H_{29}(CH_3)_3NBr$	Water	23500[a]	75.2	19.00	19.54	1.03	4670	62.1	S
Tetradecyltrimethylammonium bromide, $C_{14}H_{29}(CH_3)_3NBr$	Water	23500[a]	75.2	19.00	20.1*	1.06	4710*	62.6	
Hexadecyltrimethylammonium bromide, $C_{16}H_{33}(CH_3)_3NBr$	0.0130 *M* KBr	61700[a]	169.3	21.78	29.15	1.34	8930	52.7	OS
Hexadecyltrimethylammonium bromide, $C_{13}H_{33}(CH_3)_3NBr$	0.0130 *M* KBr	61700[a]	169.3	21.78	39.01*	1.79	9280*	54.8*	
Dodecyltrimethylammonium sulfate, $[C_{12}H_{25}(CH_3)_3N]_2SO_4$	Water	17900	64.7	16.46	18.13	1.10	3880	60.0	OS
Dodecyltrimethylammonium sulfate, $[C_{12}H_{25}(CH_3)_3N]_2SO_4$	Water	17900	64.7	16.46	19.97*	1.21	3900*	60.3*	
Dodecylamine hydrochloride, $C_{12}H_{26}NH_3Cl$	Water	12300[a]	55.5	16.70	16.64	1.00	3500	63.0	S
Dodecylamine hydrochloride, $C_{12}H_{25}NH_3Cl$	0.01574 *M* NaCl	20500[a]	92.4	16.71	21.50	1.29	4760	51.5	OS
Dodecylamine hydrochloride, $C_{12}H_{25}NH_3Cl$	0.01574 *M* NaCl	20500[a]	92.4	16.71	27.67*	1.66	5120*	55.4*	
Dodecylamine hydrochloride, $C_{12}H_{25}NH_3Cl$	0.04598 *M* NaCl	31400[a]	141.6	16.71	26.6*	1.59	6800	48.0	OS
Dodecylamine hydrochloride, $C_{12}H_{25}NH_3Cl$	0.04598 *M* NaCl	31100	141.6	16.71	42.39*	2.54*	7400*	52.2*	
Magnesium octanesulfonate, $Mg(C_8H_{17}SO_3)_2$	Water	10400	50.6	11.80	16.82	1.43	2870	56.7	OS
Magnesium octanesulfonate, $Mg(C_8H_{17}SO_3)_2$	Water	10400	50.6	11.8	23.93*	2.03	3030*	59.8*	
Magnesium decanesulfonate, $Mg(C_{10}H_{21}SO_3)_2$	Water	24300	104	14.34	22.6	1.58	4940	47.5	OS
Magnesium decanesulfonate, $Mg(C_{10}H_{21}SO_3)_2$	Water	24300	104	14.34	35.82*	2.50	5370*	51.3*	
Magnesium dodecanesulfonate, $Mg(C_{12}H_{25}SO_3)_2$	Water	28600	107	16.88	23.1	1.37	5520	51.5	OS
Magnesium dodecanesulfonate, $Mg(C_{12}H_{25}SO_2)_2$	Water	28600	107	16.88	31.49*	1.87*	5770*	53.7*	
Didodecyldimethylammonium chloride, $(C_{12}H_{25})_2(CH_2)_2NCl$	0.003 *M* NaCl	43600	209	17.00	32.1	1.89	8720	83.6	OS
Didodecyldimethylammonium chloride, $(C_{12}H_{25})_2(CH_2)_2NCl$	0.003 *M* NaCl	43600	209	17.00*	60.56*	3.56*	10470	100*	
Octyltrimethylammonium octanesulfonate, $(C_3H_{17})(CH_3)_3NSO_3C_8H_{17}$	Water	2600[b]	118	11.79	24.1	2.04	4820	40.8	OS
Octyltrimethylammonium octanesulfonate, $(C_8H_{17})(CH_3)_3NSO_3C_8H_{17}$	Water	2600[b]	118	11.79	49.2*	4.17*	5870*	49.6*	
Octyltrimethylammonium decanesulfonate, $(C_8H_{17})(CH_3)_3NSO_3C_{10}H_{21}$	Water	89700[b]	456	14.33	47.4	3.31	16700	36.6	OS
Octyltrimethylammonium decanesulfonate, $(C_8H_{17})(CH_3)_3NSO_3C_{10}H_{21}$	Water	89700[b]	456	14.33	157*	10.96*	22250*	48.8*	
Octyltrimethylammonium decanesulfonate, $(C_8H_{17})(CH_3)_3NSO_3C_{10}H_{21}$	0.178 *M* KCl	138000[b]	701	14.33	58.8	4.09	16900	24.1	OS
Octyltrimethylammonium decanesulfonate, $(C_8H_{17})(CH_3)_3NSO_3C_{10}H_{21}$	0.178 *M* KCl	138000[b]	701	14.33	241.7*	16.9*	34200*	48.8*	

were calculated for hypothetical spherical micelles with radii equal to the length of the hydrocarbon chains. Even numbered carbon atom chains were used, C_8 to C_{16}. The areas found increased slightly with chain length; from C_8, 61.8 Å.^{2} to C_{16}, 62.6 Å.^{2}. The data show that with the increase of $2CH_2$ groups per chain, the polar groups on spherical micelles would not occupy an area less than approximately 62 Å.^{2}.

The size of the areas per polar group reported in Table I indicates that the surface of the micelle is similar to that of a liquid-expanded film[14]; besides the space-occupied by the water-soluble polar group there is also a hydrocarbon–water (solution) interface. The spacing of the polar groups on the micellar surface may not be strictly uniform and depend somewhat on increase in charge density in spots due to the dissociation of the gegenion.

The thickness of the ionic atmosphere of the polar group becomes an important factor in determining the shape of the micelle. In its formation these groups are brought together with the consequent overlapping (and repulsion) of the ionic atmospheres. Although the concentration of the smaller ions is too great in most instances for the quantitative application of the Debye–Hückel theory, nevertheless the approximate results obtained by its use will serve the purpose in hand. The thickness of the ionic atmosphere is $1/K$; for a uni-univalent ion the thicknesses at three molarities are: 0.001 M, 96 Å.; 0.01 N, 30 Å.; and 0.1 M, 9.6 Å. For a bi-univalent salt the corresponding thicknesses are 56, 19 and 5.6 Å., respectively. The thickness decreases with the ionic strength of the solution; the greater the ionic strength the closer the polar groups can be brought together before overlapping occurs. For the sodium alkane sulfonates at the cmc. the thickness of the ionic atmospheres are estimated to be: C_8, 7.6 Å.; C_{10}, 15.6 Å.; and C_{12}, 30 Å. Also assuming that the ionic atmospheres are spherical the area of equatorial planes are: C_8, 181 Å.^{2}; C_{10}, 765 Å.^{2} and C_{12}, 2800 Å.^{2}. These data indicate that to have an area around 60 Å.^{2} per polar group there must be considerable overlapping and distortion of ionic atmospheres before equilibrium is reached between the short and long range forces in the formation of the micelle.

When an electrolyte with common ion is added to the solution there is an increase in the micellar molecular weight; that is, a greater number of chains are brought together. There are evidently two major contributing factors: (1) the decrease in the dissociation of the gegenion from the micelle with corresponding decrease in surface electric charge and (2) the thickness of the ionic atmosphere is reduced with greater screening of electric charge. Thus the polar groups can be brought closer together with less energy. The cmc. is decreased and a larger micelle is formed. This view is well illustrated by the results for dodecylamine hydrochloride (Table I) where the molecular weights have the variation 12300, 20500 and 31400, with per areas polar group 63, 51.5 and 48 Å.^{2}, respectively.

No satisfactory solution is available at present for the problem of determining the potential function for a sphere or oblate spheroid of electricity of a given charge density which is immersed in a solution of an electrolyte.[5,15,16] Only rough approximations can be made. For a surface charge of one electron per 60 Å.^{2}, the potential certainly exceeds 20 millivolts. Estimations indicate that it will be several times this value. Under this condition, the Debye–Hückel potential function is not quantitatively applicable. The ion of like charge to the micelle is so strongly repelled at the surface that its concentration is very small. This seems to account for the experimental findings that foreign simple ions of the same sign as the micellar ion have but small influence and the principle of ionic strength does not hold.[5,17]

The theory presented here seems inapplicable in some rare cases given in the literature where the size and the stability of the micelle apparently show wide variations with small concentrations of the salt. The cmc. is indefinite. This finding is obtained with salts which have a very long chain, C_{18}, or two fairly long chains, say $2C_{12}$, and consequently have small solubilities. Ralston, *et al.*,[18] and Kraus, *et al.*,[19] have reported results on equivalent conductance measurements on solutions of such salts which give a maximum in the Λ *vs.* $\sqrt{c}$ plot thus revealing an equivalent conductance exceeding that at infinite dilution. Light scattering data with appropriate comments have been given in the first paper preceding[20] on solutions of one of these salts, didodecyldimethylammonium chloride. Insufficient data are available to warrant any statement outside the realm of conjecture as to the size and arrangement of the ion aggregates. It appears that only a few ions may be assembled at the lowest concentrations and that micelles of increasing complexity exist in equilibrium with the smaller ions as the concentration is increased to the point where micelles of greater uniformity and stability are produced.

For solutions of paraffin chain salts, the theory presented here places a severe limitation on the interpretation of the data from the determination of the diffusion coefficient, D, by diffusion across a sintered-glass membrane using an added electrolyte with common ion as the "swamping agent."[21] The values obtained for the coefficient are, no doubt, satisfactory for the experimental systems employed. The size of the micelle, however, varies with the concentration of the swamping agent and may not be spherical, a requisite for the application of the Stokes–Einstein equation for the calculation of the micellar radius. The data given in the preceding paper[22] on the diffusion of dodecanesulfonic

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acid show that at concentrations of perchloric acid (swamping agent) above 0.1 M, the calculated micellar radii become larger with increasing concentration of this acid. A change of this kind is in accordance with the theory. In this region, the shape of micelles changes from spherical to oblate spheroidal, the oblateness becoming greatest at the concentration where "salting out" begins. The radii estimated by the use of the Stokes–Einstein equation are valid where the micelles are spherical (or nearly so). With oblate spheroidal micelles the error involved would seem to become larger as the difference between the lengths of the axes increases. So far as the author is aware there is no method available for evaluating the magnitude of this possible error. It would appear that with the oblateness occurring here, the values obtained for the radii might approximate an average of the major and minor semi-axes. Even with this limitation, however, the results obtained[22] are judged worthy of published record. The data are from an experimental procedure entirely independent of light scattering for revealing the approximate size of the micelles and that they increase in size with added electrolyte.

No theory of the micelle is complete which does not give due consideration to the role of the gegenion. Unfortunately, worthy data for making comparisons are meager. The properties of these smaller ions in solution differ widely. One cannot expect any simple relationship such as that between cmc. and the number of carbon atoms in the chain attached to a given polar group.[23] Various factors must influence the dissociation of the gegenion from the micellar surface. The valence (charge) evidently plays a prominent role. The results from the second paper[24] presented above show that there must be other factors, however, which are of great significance. The decrease in the free energy of solution varies widely. The binding of water molecules to an ion will occur with a decrease in entropy. The partial molal entropies of various ions can be correlated with their respective degrees of hydration. Further experimental data are required for estimating the influence of the different factors on the part played by the gegenion in micelle formation and structure.

The author realizes the incompleteness and possible inaccuracies in the formulation of the theory presented above. More investigations are necessary for working out the details. As given here, however, it seems to serve much better than previous ones for explaining the various properties of the solutions considered: electrical conductance, transference, e.m.f., solubilization, change of cmc. with chain length, effect of added electrolytes, equilibria of micelles with smaller ions, etc.

Acknowledgment.—The author desires to express his thanks to Professors E. C. Lingafelter and G. D. Halsey, Jr., and to Doctors A. L. M. Lelong, A. D. Abbott and J. F. Voeks who have read the manuscript and given helpful criticisms and suggestions.

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CATALYSIS BY ION-EXCHANGE RESINS: ACETONE–IODINE REACTION

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Received April 20, 1955

The kinetics of the acetone-iodine reaction catalyzed by cross-linked sulfonated polystyrene based cation-exchange resins have been studied, using a procedure which gives reproducible results. The reaction rate has been studied as a function of concentration of acetone, concentration of resin, particle size and degree of cross-linking and the results are discussed.

The cation-exchange resins in the hydrogen form and the anion-exchange resins in the hydroxyl form behave as catalysts for a variety of acid–base catalyzed reactions.[1] In addition to the interesting possibilities of practical applications, catalysis by ion-exchange resins is also of theoretical interest as the homogeneous system is changed to the heterogeneous system and their comparative studies should be of interest. Such available kinetic studies include sucrose inversion,[2] ester hydrolysis[3] and esterification reactions.[4] In this paper results for acetone–iodine reaction, catalyzed by monofunctional cross-linked polystyrene based sulfonic acid type cation-exchange resins, Nalcite HCR (National Aluminate) and Amberlite IR-112 (Rohm and Haas) are briefly summarized. Presumably, the two resins differ only in the degree of cross-linking, that is, the nominal divinylbenzene content, this being about 10% for the former (which is same as Dowex-50[5]) and about 4.5% for the latter.[3c]

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(3) (a) N. L. Smith and N. R. Amundson, *ibid.*, **43**, 2156 (1951); E. Mariani, *Ann. Chim. Appl.*, **39**, 717 (1949); E. Mariani and F. Baldass, *Ricerca. Sci.*, **20**, 32 (1950). (b) G. G. Thomas and C. W. Davies, *Nature*, **159**, 372 (1947); C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, 1607 (1952). (c) V. C. Haskell and L. P. Hammett, *J. Am. Chem. Soc.*, **71**, 1284 (1949); S. A. Bernhard and L. P. Hammett, *ibid.*, **75**, 1788, 5834 (1953); S. A. Bernhard, E. Garfield and L. P. Hammett, *ibid.*, **76**, 991 (1954); P. Riesz and L. P. Hammett, *ibid.*, **76**, 992 (1954).

(4) C. L. Levesque and A. M. Craig, *Ind. Eng. Chem.*, **40**, 966 (1948); D. I. Saletan, Univ. Microfilm No. 3549, Ann Arbor, Mich., 1950; Dissertation Abst., 1952, Vol. 12, 275.

(5) H. P. Gregor, *et al.*, *J. Colloid Sci.*, **6**, 248 (1951); **7**, 511 (1952); J. I. Bregman, *Ann. N. Y. Acad. Sci.*, **57**, 125 (1953).

Experimental

Resins.—The resins were thoroughly washed, conditioned with three cycles of regeneration (with 10% C.P. hydrochloric acid) and exhaustion (with 5% C.P. sodium chloride) and finally regenerated with a very large excess of hydrochloric acid (A.R.), washed free of acid, air-dried, sieved and the fractions stored in glass stoppered containers. Their capacity, by determining limiting exchange with normal barium chloride solution, and moisture, by heating to constant weight at 105° (±2) were estimated.[6] The capacity for both type of catalysts was 5.12 meq. per g. oven-dry resin. The sieve openings were checked with a travelling microscope at several places, randomly taken, and the average values for different sieves were 920, 500, 390, 250 and 178 μ, respectively, and the average particle diameter for the fractions was therefore taken as 710, 445, 320 and 214 μ, respectively.

Aqueous Iodine Solution.—Aqueous iodine (without potassium iodide) solution was used for the acetone–iodine reaction. It was prepared by shaking washed iodine (B.D.H. resublimed) with distilled water and the filtered solution was stored in the dark in a glass stoppered Pyrex container. Fresh stock solutions were prepared as required. The strength of the aqueous iodine solution was obtained by a procedure as given by the following example: solution A, standard sodium thiosulfate (A.R.) solution, checked against standard bromate–bromide solution, 0.02416 *N*; solution B, standard iodine solution (in potassium iodide), 0.0151 *N*. Four iodine flasks were taken: flask A, 10 cc. of solution A; flask B, 100 cc. of distilled water; flask C, 10 cc. of solution A and 100 cc. of distilled water; flask D, 10 cc. of solution A and 100 cc. of aqueous iodine solution. Freshly prepared starch solution (1%) was added to each flask and then titrated to practically the same shade with solution B. The values of titer required for flasks A, B, C and D were 16.00, 0.30, 16.30 and 2.10 cc., respectively. From these values, the calculated strength of the aqueous iodine solution is 10.72×10^{-4} *M*. This procedure gave reproducible results and the values were obtained at least in duplicate.

Acetone.—A.R. acetone was dried over anhydrous calcium chloride and potassium carbonate[7] and fractionally distilled. The middle fraction (about one-third of the volume) was stored in a glass stoppered colored container for this work.

*p*H measurements were made with Beckman *p*H meter and conductivity measurements with a Leeds and Northrup conductivity bridge. The conductivity cell (capacity about 10 cc.) with a ground glass stopper was kept in the same thermostat in which the runs were carried out. The thermostat temperature was 30.1°. This was checked with a Beckmann thermometer (0.01°) calibrated by the Meteorological Office, Poona. The variation in the thermostat temperature was within 0.02°.

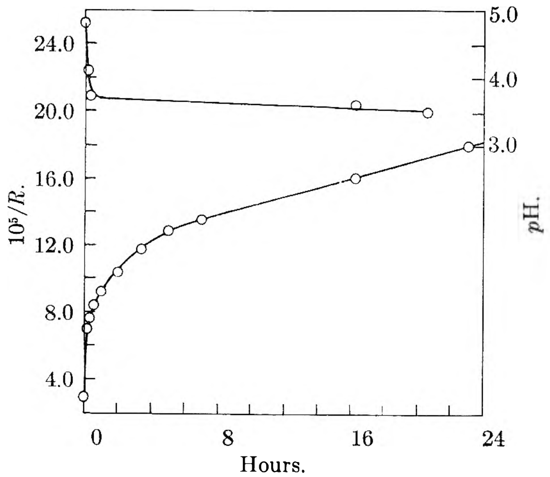

Fig. 1.—Variation of *R* (bottom curve) and *p*H (top curve) with time, *t*, when the catalyst Nalcite HCR was stirred with aqueous iodine solution; average particle diameter *a*, 710 μ; temperature, 30.1°; volume of aqueous iodine solution 450 cc.; *B*, 37.90 (the meq. replaceable hydrogen ions in the catalyst per liter of solution); stirring r.p.m. ~1050.

The runs (reactions) were carried out in a 500-cc. three-neck flask (Pyrex, with standard joints), using the stirred bath technique. The central neck carried a worm shaped Pyrex stirrer with mercury seal and was operated with a $^1/_{30}$ h.p. Kestner motor, regulated with a variac. The readings of the variac were calibrated by measuring the r.p.m. with a speedometer. The value of r.p.m. for the runs was ~1050. Samples (10 cc.) were withdrawn at different times, noted with a stopwatch, and the resistance *R* was measured. The volume of the solution in the flask was always initially 450 cc. and not more than five samples were withdrawn during one run. The required number of readings were obtained by repeating the run as required. The following further symbols are used: *B*, the milliequivalents of replaceable hydrogen ions in the catalyst (resin)/liter of solution; *a*, the average particle diameter of the catalyst (resin); $[I_2]_i$, the concentration of aqueous iodine solution; $[I_2]_e$, the concentration of same aqueous iodine solution after stirring at r.p.m. ~ 1050, with catalyst (resin) for 17 hours, at 30.1°; *R*, the measured resistance of the solution sample (10 cc.) at 30.1°; R_∞, the measured resistance *R*, when it did not change further with time (usually taken after 2 to 3 times the expected time for complete reaction); t_F, the calculated time for complete reaction; *n*, % decrease in iodine concentration $= 100\{1 - [I_2]_e/[I_2]_i\}$.

Preliminary Work.—The variation of *R* and *p*H was studied when the catalyst was stirred with distilled water. The values decreased in the first few minutes and then further change was relatively very slow and decreasing with time. Thus, when catalyst *B*, 37.90 meq./l., was stirred with distilled water, *p*H at $t = 0$ was 5.90, and at $t = 21$ hours was 4.90.

Similar studies were made when the catalyst was stirred with aqueous iodine solution. An example is given by Fig. 1. For Fig. 1, $[I_2]_i$ and $[I_2]_e$, the concentrations of iodine when $t = 0$ and 17 hours were 10.74×10^{-4} *M* and 8.270×10^{-4} *M*, respectively. Hence $n = 23.0$. The value of *n*, when the same run was carried out without resin, was 6.6. Hence *n* corrected for blank = 16.4. The change in concentration of iodine from $t = 17$ to $t = 23$ hours was negligible. In the above as well as in further work blanks were carried out for each run.

When an aqueous iodine solution with hydrochloric acid (4 to 40×10^{-3} *M*) was similarly stirred for 17 hours at 30.1°, the value of *n*, corrected for blank, was nil.

The capacity of the resin after experiments (as illustrated by Figs. 1 and 2) was estimated by washing the resin carefully with distilled water and following the procedure as given before. The capacity in all such cases was practically the same (within 0.02 meq./g. oven-dry resin) and hence the capacity of the resin was regarded as unaffected during the rate experiments.

Kinetics of the Resin-catalyzed Acetone–Iodine Reaction.—On the basis of preliminary work the rate measurements of the resin-catalyzed reaction were made as given by the following example: temperature, 30.1°; $10^4 \times [I_2]_i$, 8.945 *M*; volume of solution, 450 cc.; catalyst, Nalcite HCR; a, 710 μ; stirring rate ~ 1050 r.p.m.; (i) aqueous iodine solution stirred for 17 hours, $n = 6.6$; (ii) aqueous iodine solution and catalyst, $B = 16.84$, stirred for 17 hours; $[I_2]_e$, 7.625×10^{-4} *M*; hence *n*, corrected for blank, 8.3; (iii) aqueous iodine solution and catalyst stirred for 17 hours as in (ii). Then the stirrer was stopped, a known quantity of acetone (5.976×10^{-2} *M*) was added, the stopwatch started and the stirrer restarted. Samples (10 cc.) were pipetted out at known times (by stopping the stirrer for a few seconds) and *R* measured. The value of R_∞, measured at least in triplicate, was the measured value of *R* when it did not change further with time (taken after about two to three times the expected time for complete reaction.) The run was repeated twice.[1a] For a zero-order reaction the plot of *x*, where *x* is the iodine used against time *t*, is linear. The concentration of iodine used in the reaction is same as the concentration of HI formed. Since the concentration of HI is very low (~ 10^{-3} *M*), it may be considered to be completely ionized and the conductivity of the (reaction) solution may be taken to be proportional to the concentration of HI formed. Hence, for the zero-order

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(6) S. L. Bafna, *et al.*, *J. Ind. Chem. Soc.*, **29**, 611, 187 (1952); *J. Sci. Ind. Research*, **11B**, 134 (1952).

(7) I. F. Dippy, H. O. Jenkins and J. E. Page, *J. Chem. Soc.*, 1391 (1939); V. Gold, *Trans. Faraday Soc.*, **44**, 606 (1947).

TABLE I

EFFECT OF VARIATION OF ACETONE CONCENTRATION ON THE RESIN-CATALYZED ACETONE–IODINE REACTION

Temp., 30.1°; volume of soln. 450 cc. B, 16.84; r.p.m. (stirring) ~1050; n is corrected for blank.

a denotes the average particle diameter, n, the fraction, $100\{1 - [I_2]_e/[I_2]_i\}$; $[I_2]_e$, the concentration of iodine when stirred with catalyst for 17 hours, B, the meq. of replaceable hydrogen ions in the resin/liter, and t_F the calculated time for complete reaction.

Resin→	Nalcite HCR.						Amberlite, IR-112	
a, μ→	710		445		320		710	
n, %→	8.3		8.1		8.0		13.0	
10^2 [Acetone], M	10^4 $[I_2]_e$, M	$t_F/60$, sec.	10^4 $[I_2]_e$, M	$t_F/60$, sec.	10^4 $[I_2]_e$, M	$t_F/60$, sec.	10^4 $[I_2]_e$, M	$t_F/60$, sec.
0.747	7.625	802	7.805	790	9.310	925	7.610	912
1.494	7.625	420	8.555	450	9.755	486	7.610	456
2.241	7.625	297	8.555	311	9.310	311	7.610	304
2.988	7.625	234	7.805	220	9.755	254	7.610	228
5.976	7.625	137	7.805	121	9.755	136	7.610	120
8.964	7.625	99	7.805	86	9.310	91	7.610	83
11.95	7.625	78	7.805	66	9.755	75.5	7.610	64

TABLE II

EFFECT OF VARIATION OF RESIN CONCENTRATION ON THE RESIN-CATALYZED ACETONE–IODINE REACTION

Temp., 30.1°; volume of the soln. 450 cc.; 10^2 [Acetone], 5.976 M/l.; r.p.m. (stirring) ~1050; n is corrected for blank; resin, Nalcite HCR. (The symbols have the meaning given before.) a denotes the average particle diameter, n, the fraction $100\{1 - [I_2]_e/[I_2]_i\}$; $[I_2]_e$, the concentration of iodine when stirred with catalyst for 17 hours, B, the meq. of replaceable hydrogen ions in the resin/liter, and t_F the calculated time for complete reaction.

a, μ		710			445			320			214	
B	10^4 $[I_2]_e$, M	n, %	$t_F/60$, sec.	10^4 $[I_2]_e$, M	n, %	$t_F/60$, sec.	10^4 $[I_2]_e$, M	n, %	$t_F/60$, sec.	10^4 $[I_2]_e$, M	n, %	$t_F/60$, sec.
2.104	8.121	1.3	854	9.875	1.4	1000	10.58	1.0	1056	8.250	1.0	825
4.209	10.30	2.4	570	9.770	2.4	572	10.73	2.2	536	8.340	2.2	416
6.313	10.19	3.4	390	9.695	3.4	353	10.69	3.1	356	...	...	...
8.418	7.475	4.3	228	9.695	4.0	270	8.555	4.0	222.5	8.160	4.0	203
16.84	7.625	8.3	137	9.075	8.1	140	8.180	8.0	115	7.830	8.1	100
25.25	7.475	11.6	95	7.140	11.8	78	9.755	11.4	96	...	...	...
33.68	7.170	14.9	72	8.285	15.0	72	7.505	15.0	56.5	...	...	...

law, the plot of $1/R$ against t should be linear. In Fig. 2, $1/R$ is plotted against t. The plot is linear in the beginning, but later on the slope decreases as t increases. Hence, the order of the reaction with respect to iodine is zero for the resin-catalyzed reaction, but the rate falls off at the latter part of the reaction.[3b] From the linear plot (Fig. 2) the value of t_F corresponding to $1/R_\infty$ was read. Then the velocity coefficient k is given from

$$k = \frac{x}{t[\text{Resin}][\text{Acetone}]} = \frac{[I_2]_e}{t_F[\text{Resin}][\text{Acetone}]} = 9.22$$

The values obtained by this procedure were reproducible within ±1% for higher concentrations and within ±0.5% for lower concentrations. A study of the effect of the rate of stirring indicated that the rate of the reaction was not affected above r.p.m. ~ 500 by a further increase in the rate of stirring.

Results and Discussion

Tables I and II give the data for the effect of variation of the concentration of acetone and catalyst (resin), respectively, on acetone–iodine reaction. Table II also gives the dependence of n on catalyst concentration. The values of k calculated from these data are plotted in Fig. 3 against [Acetone] and [Resin].

The results given above indicate that when the resin is contacted with aqueous iodine solution (Fig. 1 and Table II), the pH of the solution falls and the concentration of iodine is decreased. A possible explanation may be the small sorption of the weak acid HIO (due to slight hydrolysis of I_2) by the resin.[8]

For the homogeneous strong acid-catalyzed acetone–iodine reaction, the value of the velocity coefficient k_H, obtained from

$$k_H = \frac{k_0}{[\text{Acetone}][\text{Catalyst}]}$$

where $k_0 = x/t$ is independent of the concentration of the acid catalyst and acetone. Essentially,

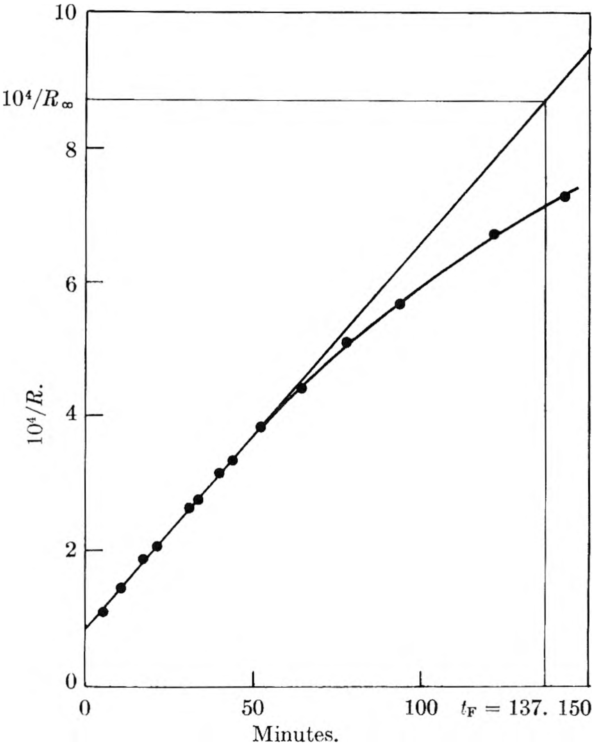

Fig. 2.—Plot of $1/R$ against time t, where R is the measured resistance of a 10-cc. sample of the reaction mixture.

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(8) C. W. Davies and G. G. Thomas, *J. Chem. Soc.*, 2694 (1951).

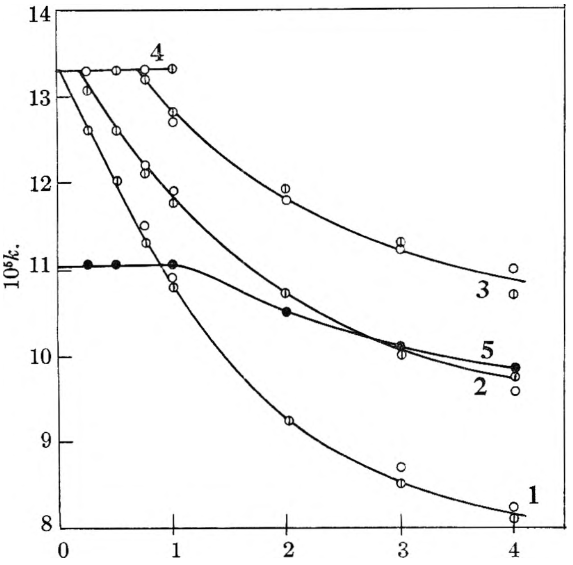

Fig. 3.—Variation of velocity coefficient k with [Resin] or [Acetone]: 1, a = 710 μ; Nalcite HCR, 2, a = 445 μ; 3, a = 320 μ; 4, a = 214 μ; Amberlite IR-112; 5, a = 710 μ; ⦶, acetone concn. varied, keeping resin concn. constant = 16.84 meq./l.; ○, resin concn. varied, keeping acetone concn. constant = 5.976 × 10^{-2} m./l. B denotes meq. of replaceable hydrogen ions in the catalyst per liter of solution.

the same equation may be regarded to hold for the resin (strong acid)-catalyzed reaction also, taking into consideration (a) the effect of diffusion[3b] in the resin phase and (b) the activity coefficient f for the catalyst (resin), it being treated as a concentrated electrolyte solution.[9] The reason for considering f is that the rate-controlling step could occur only on or within the resin particle. The velocity coefficient k for the resin-catalyzed reaction may then be given by

$$k = k_{\rm H}rf$$

where r is a factor introduced to take care of the diffusion effect, its limiting values being obviously 0 and 1. The values of rf can be calculated from this relation. The value of $k_{\rm H}$ is taken as 5.13 × 10^{-5} for 30.1°. It is calculated from the data of Rice and Kilpatrick[10] for the HCl catalyzed reaction by plotting log $k_{\rm H}$ against $1/T$ where T is the absolute temperature.

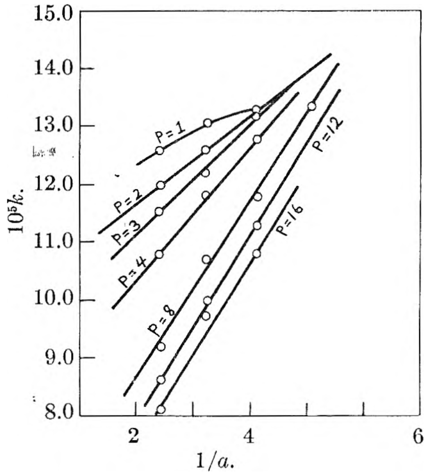

Fig. 4.—Plots of k (average values from Fig. 3) against reciprocal of average particle diameter: $P = 10^4$[Acetone]·[Resin]/1.257.

The data of Tables I and II indicate that the value of k (and hence r) decreases as the concentration or the particle diameter is increased.[3] However, by sufficiently decreasing the concentration and particle diameter or the degree of cross-linking, the value of k becomes *independent* of the concentration of the catalyst or acetone, as is true for homogeneous catalysis. Also, the values of k for a catalyst of lower cross-linking are less than those for a catalyst of higher cross-linking for lower concentrations, and the reverse is true for higher concentrations (Fig. 3). The plots of average values of k, from Fig. 3, for Nalcite HCR, against $1/a$ are linear (except for the lowest concentration) and are given in Fig. 4.

The limiting value of k and hence of rf when the concentration approaches zero (Fig. 3), is independent of the particle diameter a. Since the maximum value of r is unity, from these limiting values the calculated values of f are 2.59 for Nalcite HCR and 2.15 for Amberlite IR-112.

The work summarized above was carried out as part of the research programme of National Chemical Laboratory of India, Poona, and is published with the permission of the Director. The author wishes to acknowledge his grateful thanks to the Director, Professor G. I. Finch, F.R.S., for his interest and encouragement. The author also wishes to thank Dr. A. B. Biswas, Assistant Director, Physical Chemistry Division, for helpful comments.

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(9) E. Glueckauf, *Proc. Roy. Soc. (London)*, **214A**, 207 (1952); J. W. Duncan, *ibid.*, 344 (1952); H. Jenny, This Journal, **36**, 2217 (1932).

(10) F. O. Rice and C. S. Kilpatrick, *J. Am. Chem. Soc.*, **45**, 1412 (1923), (Table VI).

THE THERMODYNAMICS OF CHELATE FORMATION. I. EXPERIMENTAL DETERMINATION OF ENTHALPIES AND ENTROPIES IN DIAMINE-METAL ION SYSTEMS

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Received May 13, 1955

This is the first report of a series of investigations to determine the origin of the so-called "chelate effect," *i.e.*, the superior stability of chelate complexes *vs.* non-chelated complexes and of small chelate rings *vs.* larger ones. Enthalpy and entropy data for the formation of ethylenediamine and trimethylenediamine complexes of Cd, Cu and Ni were determined from the formation constants measured at 0 and 49.1°. These and other previously published data are evaluated and correlated, and it is concluded that the "chelate effect" is primarily an entropy effect in these systems. Precautions necessary to obtain accurate results by this method are discussed and it is concluded that meaningful results are obtained although the direct calorimetric measurement of ΔH is probably inherently capable of greater accuracy. It is suggested that the entropy effect may not be entirely the result of differences in entropy of ring closure on formation of the chelate.

I. Introduction

There has been much interest recently in the effect of chelate rings upon the stability of coördination complexes.[1,2] It is by now fairly well established that generally, among complexes containing a given metal ion, a chelated complex, particularly one containing a five-membered ring, is more stable than a similar non-chelated complex, usually by one to two *pK* units. Among the chelated complexes, the stability generally decreases with increasing ring size. Both these "chelate effects" have been established not only on the basis of such kinetic evidence as ease of isolation, but also from the equilibria governing complex formation.

The chelate effect in amine complexes was first studied carefully by Bjerrum,[3] who compared the stabilities of ethylenediamine complexes with the stabilities of similar ammonia complexes. Bjerrum made extensive measurements of the equilibria at room temperature, and a few measurements at other temperatures to provide values of ΔH. However, lack of sufficient data and the intrinsic differences between the coördination bonds by ammonia and by amines, prevented Bjerrum from reaching definite conclusions as to the relative roles of enthalpy and entropy in the chelate effect. Fragmentary data[4-6] describing enthalpy and entropy changes accompanying chelation involving amines have more recently appeared, but as yet no comprehensive study has been made of the systematic variations of these thermodynamic quantities in a simple series of complexing systems.

In this series of papers we shall describe the results of enthalpy and entropy measurements in diamine systems, first among systems showing a normal chelate effect and, in a subsequent publication, in systems involving silver(I), in which quite different results arise due to the 180° angle between its coördination bonds.[7] The present paper presents enthalpies and entropies of formation of chelates of cadmium, copper and nickel with ethylenediamine (en) and trimethylenediamine (tn), obtained from equilibrium measurements over a temperature range. The experimental method is carefully described and evaluated, and the results are correlated with those of earlier investigations. In the second paper of the series, theoretical studies of the thermodynamic changes accompanying ring closure, as well as additional thermodynamic data for the diamines in aqueous solution, are employed to elucidate the origin of the enthalpy and entropy changes accompanying both chelation and noncyclic complex formation.

Experimental

Reagents.—All cations used were introduced as perchlorates, to avoid extraneous anion complexing. Exactly 0.05 *M* cupric perchlorate solution was prepared by dissolving a weighed amount of CuO (dried several hours at 130°) in a 10% excess of Mallinckrodt AR perchloric acid. The solution was then carefully fumed several times to remove excess acid, and diluted to volume. The *p*H of this solution was ~5. Cadmium perchlorate, ~0.05 *M*, was prepared by dissolving in an excess of perchloric acid a weighed stick of high purity cadmium metal kindly supplied by Prof. J. J. Lingane. A small amount of nitric acid was added to hasten dissolution. After all the metal had dissolved, the solution was taken to fumes several times to remove nitric acid and excess perchloric acid. The solution was then diluted to volume and found to have a *p*H of ~5. Nickel perchlorate, ~0.05 *M*, was prepared from nickel nitrate by fuming with perchloric acid as described above. The solution was then diluted to volume and standardized by precipitation of nickel from aliquots using dimethylglyoxime. The *p*H of the final solution was ~6. An approximately 0.05 *M* solution of barium perchlorate, for use in the base constant determinations, was prepared by carefully neutralizing a slurry of barium hydroxide with dilute perchloric acid to a final *p*H of ~7. This operation was carried out under nitrogen to exclude carbon dioxide. A small amount of 0.1 *M* sodium perchlorate was prepared in a similar manner.

A solution of approximately 0.15 *M* perchloric acid was prepared from Mallinckrodt AR perchloric acid and standardized against red mercuric oxide. Approximately 1.3 *M* solutions of ethylenediamine (en) and trimethylenediamine (tn) were used. Eastman Kodak Co. 75% ethylenediamine was distilled through a 20-plate column and the fraction boiling at 115–117° collected. A rough standardization was made on this distillate and a suitable aliquot taken and diluted to volume. Reagent quality trimethylenediamine was purchased from L. Light and Co., Ltd., England, in the form of the hydrochloride. This was treated with a twofold excess of sodium hydroxide and the amine distilled off through a short column, the fraction boiling at 134–136° being collected, roughly assayed, and diluted to volume. The exact molarity of each amine solution was determined in the course of the base constant determinations.

[1] H. Irving, R. S. P. Williams, D. S. Ferrett and A. E. Williams, *J. Chem. Soc.*, 3494 (1954).

[2] G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2344 (1952).

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[4] M. Calvin and R. H. Bailes, *J. Am. Chem. Soc.*, **68**, 953 (1946).

[5] C. G. Spike and R. W. Parry, *ibid.*, **75**, 2726 (1953).

[6] (a) F. Basolo and R. K. Murmann, *ibid.*, **74**, 5243 (1952); ( ) **76**, 211 (1954).

[7] G. Schwarzenbach, *Helv. Chim. Acta*, **36**, 23 (1953).

Apparatus.—The titrations were carried out in a 200-ml. round-bottomed flask to which four additional necks had been added, two for the electrodes, one as a nitrogen inlet, and one to admit the tip of a 10-ml. microburet, which was especially lengthened to project beneath the surface of the liquid. The large center neck of the flask was lengthened and used to clamp it in place and to admit the shaft of a rotary stirrer. Measurements at 49.1 and 25.5° were made with the flask immersed in a constant temperature bath controlled to ±0.05°. The liquid in the flask was placed about 1.5 inches below the surface of the water in the bath, and the entire bath was covered with a "transite" sheet to ensure thermal equilibrium in the solution. Measurements at 0° were made by immersing the flask in an ice-slush bath contained in a large dewar vessel. In early runs, the temperatures of solutions to be titrated were checked after various equilibration periods until a minimum time requirement of the order of 15 minutes was established. Thereafter, periods of 20–30 minutes were allowed for temperature equilibration.

Hydrogen ion activity was determined with a Beckman model G *p*H meter equipped with a calomel reference electrode (1170) and a model 1190–75 glass electrode. This glass electrode is a special purpose model for accurate measurement in basic solution; it is also quite accurate in acid solution with shortened lifetime. In order to obtain reproducible *p*H meter readings it was necessary to ground carefully the bath heater and the stirring motor shell, and to insert a grounded platinum wire into the solution under study.

Measurement of *p*H.—The most critical portion of the entire experimental procedure is the determination of hydrogen ion activity in the metal–amine systems. As may be seen from the equations used in calculating results, a systematic error in the values of the logarithms of the complex formation constants results from an equal systematic error in determining the *p*H. It is therefore necessary to relate accurately the true *p*H of the solutions with the readings of the *p*H meter, particularly when making measurements at temperatures far from those for which the instrument was primarily designed. Previous workers generally have not commented upon the method used to convert *p*H meter readings to actual *p*H values when working far from the 20–30° range. Preliminary studies indicated that the temperature compensator of the *p*H meter did not sufficiently accurately convert electrode potentials to *p*H readings at temperatures other than 25°, so that it proved advantageous in the present work to use the *p*H meter as a potential measuring device, and to account explicitly for the temperature of the solutions with the aid of the Nernst equation. Accordingly, one may write

$$p\mathrm{H}' = A(T) + (T/298)p\mathrm{H} \qquad (1)$$

where *p*H′ is the "apparent *p*H" read from the meter when the temperature compensator is set at 25°, *p*H is the true *p*H of the solution, which is at a temperature T°, K., and $A(T)$ is a (temperature dependent) empirical constant. The constant A was found to be somewhat variable, in the sense that it must be redetermined before (and also, as a check on constancy over the period of measurement, after) each titration. Included in A are the effects of the temperature dependence of the standard potentials of the glass electrode and calomel reference electrode, *p*H of the buffer solution within the glass electrode, and of the zero of potential of the *p*H meter potentiometric circuit.

On the basis of the foregoing considerations, the following procedure was used to determine *p*H. Buffer solutions supplied by the Beckman Instrument Co., Inc., were used. The temperature compensator of the meter was set at 25° and left there permanently. The zero adjustment of the meter was first set using *p*H 7 buffer at 25°. The electrodes were then immersed in a sample of *p*H 7 buffer held at the temperature to be used in the following series of measurements. After equilibrium had been reached the meter was read. The electrodes were then transferred to a solution of *p*H 10 or *p*H 4 buffer (depending upon whether the base constants or complex formation constants were to be measured, since the *p*H range for the former is mainly > 7 and for the latter, mainly < 7) and the meter again read. From the reading of each buffer at temperature T, together with the *p*H of the buffer at that temperature as quoted by the manufacturer, the constant $A(T)$ in eq. 1 was evaluated. Consistency among buffers to within 0.01 *p*H unit was always obtained. The electrodes were then rinsed and placed in the flask containing the solution to be measured, which had been equilibrated for 20–30 minutes in the bath. After allowing about 10 more minutes for final equilibration of the electrodes, the titration was begun. At the conclusion of the titration, the value of A was again determined using one or another of the buffers. This value of A was found always to agree within 0.01 unit with the prior value for runs at 49.1°. However, variations of 0.01–0.03 unit were found in runs at ice temperature. When the two values of A differed, the average of the pre- and post-run values was used.

Determination of Titration Curves.—The flask was charged with approximately 50 ml. of perchloric acid, about 25 ml. of the appropriate metal perchlorate solution and sufficient water to make a total volume of approximately 97 ml. The exact volume of each solution added was accurately measured from a buret. The 10-ml. buret, filled with amine solution, was mounted with the tip below the surface of the liquid in the flask. The quantities used result in an ionic strength of 0.15 ± 0.01, with the total concentration of divalent cation the same for all titrations. When determining base constants, barium perchlorate replaced the chelated divalent cation. Magnesium ion has been used by some workers for this purpose, but was rejected here as unsuitable since Bjerrum has shown that magnesium binds amines appreciably, whereas barium ion does not.[3] The titration flask was slowly swept with dry nitrogen throughout each run. In the determination of base constants of the amines, it was necessary to add, in addition to the listed reagents, a small amount of $NaClO_4$ between titration of the first and second dissociations, to allow for a change in ionic strength not occurring in the titration of the chelating systems.

The titrant amine solution was added in small increments and the *p*H read after each addition. Readings always became constant within a few seconds and, as occasional checks revealed, remained so for at least 0.5 hour. Each titration curve was run in duplicate, or, if necessary to secure two runs in close agreement, in triplicate. The measure of agreement may be seen in Fig. 1.

Calculation of Formation and Base Constants.—Base constants $K_{\mathrm{b}}^{(n)}$ were defined as

$$K_{\mathrm{b}}^{(n)} = \frac{\{\mathrm{H}^+\}\,(\mathrm{BH}_{n-1}{}^{+(n-1)})}{(\mathrm{BH}_n{}^{+n})} \qquad (2)$$

where $(\mathrm{BH}_n{}^{+n})$ represents the concentration of $\mathrm{BH}_n{}^{+n}$, B refers to the amine, and $\{\mathrm{H}^+\}$ represents the activity of hydrogen ion. These "mixed" equilibrium constants are convenient to compute from the data, as $\{\mathrm{H}^+\}$ is measured and the $(\mathrm{BH}_n{}^{+n})$ are obtained from stoichiometric quantities. In calculating the $(\mathrm{BH}_n{}^{+n})$, the difference between $\{\mathrm{H}^+\}$ and (H^+) causes no difficulty as in the region of interest the free hydrogen ion is always an insignificant proportion of the total amount added.

Values of the base constants measured in this research are listed in Table I.

The complex formation constants were defined in the form

$$k_n = \frac{(\mathrm{MB}_n{}^{++})}{(\mathrm{MB}_{n-1}{}^{++})(\mathrm{B})} \qquad (3)$$

where M represents the metal ion. It is convenient to compute the k_n by first utilizing the base constants and stoichiometry to obtain for each point of the titration curve values of (B) and of $\bar{n}$, the average number of amine molecules bound to each metal ion. The base constants appear in such combinations with $\{\mathrm{H}^+\}$ that use of eq. 2 together with the measured $\{\mathrm{H}^+\}$ leads to the concentration constants (3) without a knowledge of the activity coefficients except in regions where the free hydrogen ion is an appreciable fraction of the stoichiometric amount added. Fortunately, the *p*H rises quite rapidly, and no consideration need be given this matter except in the earliest part of the formation curve, where *p*H values are low and the concentration of free hydrogen ion is then comparable to the total amount. When the *concentration* of hydrogen ion is accurately obtained from the measured $\{\mathrm{H}^+\}$, the curves approach $\bar{n} = 0$ as $(\mathrm{B}) \rightarrow 0$, whereas without this adjustment, meaningless negative values of $\bar{n}$ would be obtained.

From plots of $\bar{n}$ against *p*B, as in Fig. 1, the k_n were calculated by standard methods. The values obtained in this research are listed in Tables II and III, together with the estimated errors in these quantities. Only directly determined constants are listed in these tables; interpolated values at 25° appear in Tables IV and V.

TABLE I

BASE CONSTANTS OF ETHYLENEDIAMINE AND TRIMETHYLENEDIAMINE[a]

	$pK_b^{(1)}$			$pK_b^{(2)}$		
Temp., °C.	49.1	0	25.5	49.1	0	25.5
en	9.40	10.80	10.07	6.66	7.86	7.23
tn	9.95	11.50	...	8.21	9.69	...

[a] The estimated maximum error is ±0.02, the average error is believed to be ±0.01. The $K_b^{(n)}$ are defined in eq. 2. Values are at ionic strength 0.15.

TABLE II

METAL–DIAMINE COMPLEX FORMATION CONSTANTS AT 0°[a]

Metal ion	n in k_n	$\log_{10}k_n$ en	$\log_{10}k_n$ tn
Cu^{++}	1	11.45 ± 0.05	10.52 ± 0.03
	2	9.83 ± .01	7.94 ± .04
Cd^{++}	1	5.85 ± .03	4.97 ± .04
	2	4.72 ± .04	3.34 ± .04
Ni^{++}	1	7.88 ± .01	6.98 ± .03
	2	6.70 ± .01	4.93 ± .05
	3	4.78 ± .08	1.90 ± .10

[a] The k_n are defined in eq. 3. "en" represents ethylenediamine; "tn," trimethylenediamine. Values are in concentration units at ionic strength 0.15.

TABLE III

METAL–DIAMINE COMPLEX FORMATION CONSTANT AT 49.1°[a]

Metal ion	n in k_n	$\log_{10}k_n$ en	$\log_{10}k_n$ tn
Cu^{++}	1	10.01 ± 0.04	9.00 ± 0.03
	2	8.46 ± .03	6.45 ± .03
Cd^{++}	1	5.21 ± .02	4.33 ± .02
	2	4.20 ± .03	2.81 ± .02
Ni^{++}	1	6.92 ± .03	5.91 ± .01
	2	5.75 ± .04	3.93 ± .01
	3	3.90 ± .08	1.2 ± .12

[a] The k_n are defined in eq. 3. "en" represents ethylenediamine; "tn," trimethylenediamine. Values are in concentration units at ionic strength 0.15.

Results

From the values of the complex formation constants as determined in this study at 0 and 49.1° interpolated values of the equilibrium constants and thermodynamic functions for formation of the chelate complexes at 25° were computed. Reduction of the primary experimental data required use of the base constants of ethylenediamine and trimethylenediamine, which were also determined at 0 and 49.1° under conditions paralleling those obtaining for the complex formation measurements. All interpolations were made assuming $\Delta H°$ to be constant over the temperature range used. Previous studies[5,6a] have shown that this assumption is valid. The final results for the metal ammine complex formation constants at 25° are presented in Tables IV and V, with errors consistent with those associated with the primary data in Tables I–III. In the last columns of Tables IV and V are some values of equilibrium constants actually determined at 25.5° to spot check the accuracy of the interpolations. The agreement is seen to be good.

At this point we may profitably consider such data as have been previously reported. To our knowledge, no other study of the complete set of thermodynamic functions for formation of trimethylenediamine complexes has been published. However, for ethylenediamine complexes of nickel, copper, cadmium, some results obtained both by the method used here and by direct calorimetric measurement of ΔH have appeared.

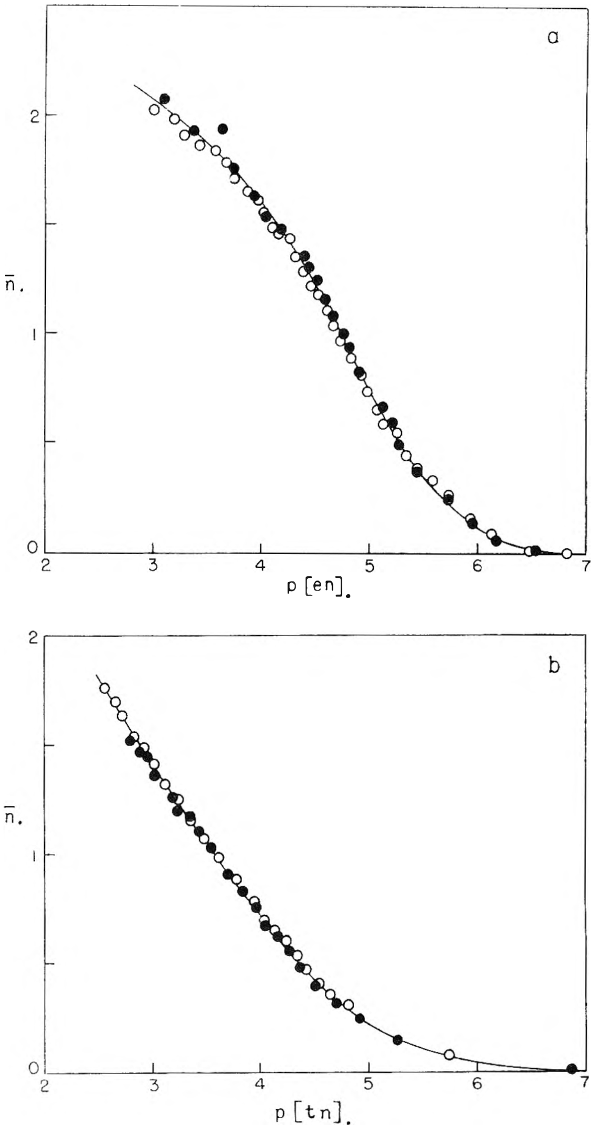

Fig. 1.—Formation curves for cadmium complexes of ethylenediamine (a) and trimethylenediamine (b) at 49.1°.

Calvin and Bailes[4] have stated that for the reaction

$$Ni^{++}(aq) + 3en(aq) = Ni(en)_3^{++}(aq)$$

$\Delta H° = -25$ kcal. and $\Delta S° = +2$ cal./deg. These values were determined from the temperature dependence of the equilibrium constant, but unfortunately, no specifications of temperature intervals, ionic strength, other experimental details, or error were made by these authors. From Table VI, however, it may be seen that we have found, for the same reaction, $\Delta H° = -23 \pm 2$ kcal. and $\Delta S° = 7 \pm 7$ e.u. In the absence of further information with regard to Calvin and Bailes' work, the agreement may be considered satisfactory.

Basolo and Murmann[6] have published enthalpy and entropy values for formation of nickel and

TABLE IV

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC FUNCTIONS OF FORMATION OF ETHYLENEDIAMINE COMPLEXES AT 25°[a]

Metal ion	n in k^n	Interpolated values $\Delta F°$, kcal.	$\Delta H°$, kcal.	$T\Delta S°$, kcal.	$\Delta S°$, cal./deg.	$\text{Log}_{10}k_n$	Measured (25.5°) $\log_{10}k_n$
Cu^{++}	1	−14.6 ± 0.1	−11.9 ± 0.6	2.7 ± 0.6	9.0 ± 2.5	10.67 ± 0.04	10.61 ± 0.02
	2	−12.4 ± .05	−11.3 ± .3	1.1 ± .3	3.7 ± 1.0	9.10 ± .02	9.12 ± .02
Cd^{++}	1	− 7.52 ± .03	− 5.3 ± .4	2.2 ± .4	7.4 ± 1.1	5.51 ± .02	
	2	− 6.06 ± .04	− 4.3 ± .5	1.8 ± .5	6.0 ± 1.5	4.44 ± .03	
Ni^{++}	1	−10.03 ± .05	− 7.9 ± .3	3.1 ± .3	10.4 ± 1.0	7.35 ± .03	
	2	− 8.42 ± .05	− 7.8 ± .5	0.6 ± .5	2.0 ± 1.5	6.17 ± .03	
	3	− 5.8 ± .1	− 7.2 ± 1.3	−1.4 ± .4	−4.7 ± 4.7	4.31 ± .08	

[a] The k_n are defined in eq. 3. Values are for ionic strength 0.15. Standard state for thermodynamic functions, hypothetical 1 molal solution with ionic strength 0.15.

TABLE V

EQUILIBRIUM CONSTANTS AND THERMODYNAMIC FUNCTIONS OF FORMATION OF TRIMETHYLENEDIAMINE COMPLEXES AT 25°[a]

Metal ion	n in k_n	$\Delta F°$, kcal.	$\Delta H°$, kcal.	$T\Delta S°$, kcal.	$\Delta S°$, cal./deg.	$\log_{10}k_n$
Cu^{++}	1	−13.20 ± 0.02	−12.5 ± 0.5	0.7 ± 0.5	2.3 ± 1.7	9.68 ± 0.03
	2	− 9.71 ± .04	−12.3 ± .5	−2.6 ± .5	−8.7 ± 1.7	7.12 ± .03
Cd^{++}	1	− 6.30 ± .04	− 5.3 ± .5	1.0 ± .5	3.4 ± 1.7	4.62 ± .03
	2	− 4.16 ± .04	− 4.4 ± .5	−0.2 ± .5	− 0.6 ± 1.7	3.05 ± .03
Ni^{++}	1	− 8.72 ± .02	− 8.8 ± .3	−0.1 ± .3	− 0.3 ± 1.0	6.39 ± .02
	2	− 5.97 ± .05	− 8.2 ± .5	−2.2 ± .5	− 7.4 ± 1.7	4.38 ± .03
	3	− 2.0 ± .2	− 6 ± 1.5	−4 ± 1.7	−13 ± 6	1.5 ± .11

[a] The k_n are defined in eq. 3. Values are for ionic strength 0.15. Standard state for thermodynamic functions, hypothetical 1 molal solution with ionic strength 0.15.

copper chelates with a number of N-substituted derivatives of ethylenediamine as well as with en itself. In their first paper,[6a] these quantities were determined from the temperature dependence of potentiometrically measured formation constants, but in the second,[6b] the enthalpies were measured calorimetrically. We find that the results of Basolo and Murmann which are based on calorimetrically determined values of ΔH are in substantial agreement with this study, whereas the results from their first paper are in very serious disagreement both with their later work and with our present results. They have remarked upon the discrepancy between their two sets of results, but did not suggest any explanation. An inspection of the base constants for ethylenediamine which were used in the potentiometric work of Basolo and Murmann, however, reveals a probable source of error in that investigation.

To further clarify the situation we examined some recently determined values of the base constants of ethylenediamine, converted by us for purposes of comparison to the form given in eq. 2 at 25.0°. Our own data, at 0, 25.5 and 49.1°, are consistent with constant values of $\Delta H°$ for both dissociations in that temperature range and yield dissociation constants at ionic strengths 0.15: $pK_b^{(1)} = 10.06 \pm 0.02$, $pK_b^{(2)} = 7.22 \pm 0.02$. Data of Everett and Pinsent and of Schwarzenbach,[8] reported by the authors entirely in terms of concentrations, have been adjusted to constants involving hydrogen ion activity by assuming that the activity coefficient of hydrogen ion in a solution of ionic strength 0.10 is ~0.77 and, in a solution of ionic strength 0.15, about 0.80.[9] Data were adjusted from 20 to 25° when necessary using the temperature dependences found in this study (which incidentally agree within error with those found by Everett and Pinsent).

The data of Everett and Pinsent are from what is doubtless the most accurate study which has been reported and we believe that even with such error as may have been introduced in conversion to hydrogen ion activity, their figures at ionic strength 0.15 (10.04, 7.20) are accurate to one or two hundredths of a pK_b unit. It is seen that their work is in excellent agreement with the results of the present study. The data of Schwarzenbach at ionic strength 0.10 (9.94, 7.15) are perhaps slightly low, but in the same general range. It is clear, however, that the base constants of Basolo and Murmann at ionic strength 0.55 (10.18, 7.47) are high, particularly the value of $pK_b^{(2)}$. To show that this is not due to differences in ionic strength among the various investigations, we also examined values reported by Bjerrum at very high ionic strengths. Bjerrum reported,[3] at ionic strength 1.5, pK_b's of 10.05 and 7.31, and at ionic strength 1.8, values of 10.08 and 7.34. The change with ionic strength is evidently far too small to account for Basolo and Murmann's results.

Recalculation of some of Basolo and Murmann's data, using appropriate base constants, was found to result in reasonable agreement with their other data and the results of the present study. Professor Basolo[10] has agreed that his pK_b values at 25° seem

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(8) D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc.* (*London*), **215A**, 417 (1952).

(9) (a) See, for example, W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 354. (b) Irving and Griffiths' table of base constants (*J. Chem. Soc.*, 215 (1954)) for en and other diamines makes no distinction between those involving hydrogen ion activity and those completely in terms of concentration.

(10) F. Basolo, private communication.

high and that this is the probable source of error.

A set of values of thermodynamic quantities for the formation of nickel and copper complexes of ethylenediamine has been reported by Irving.[11] These results diverge irreconcilably from those obtained in this study and from those obtained by Basolo and Murmann using calorimetrically determined values of ΔH, and appear to be in error.

We believe that the results of the present study indicate that when due precautions are taken, it is possible to derive reliable values of $\Delta H°$ and $\Delta S°$ from measurements of the temperature dependence of the complex formation constants. These precautions have been discussed explicitly in the Experimental section. Although somewhat more accurate results can probably be obtained by independent calorimetric measurement of ΔH, the present method appears to be highly satisfactory unless results of the highest accuracy are required.

Discussion

It is now possible to determine the contributions of enthalpy and entropy to the chelate effect describing stability differences among chelated rings of different sizes. Although the data of this work characterize only diamine complexes, the conclusions to be reached may not be irrelevant to the wider class of chelates whose qualitative behavior has been found to be similar. Proceeding, we inquire about the thermodynamic quantities associated with the reaction

$$M(\mathrm{en})^{++}(\mathrm{aq}) + \mathrm{tn}(\mathrm{aq}) = M(\mathrm{tn})^{++}(\mathrm{aq}) + \mathrm{en}(\mathrm{aq}) \quad \text{(I)}$$

For simplicity, we consider only the formation of the 1:1 complex. The values of $\Delta F°$, $\Delta H°$ and $\Delta S°$ for this reaction, where M is nickel, copper and cadmium, are presented in Table VI. These results indicate that the six-membered ring (tn complex) is slightly favored by enthalpy, by about 0–1.0 kcal.

TABLE VI

THERMODYNAMICS OF REACTION

$\mathrm{M(en)^{++}(aq) + tn(aq) = M(tn)^{++}(aq) + en(aq)}$ AT 25° AND IONIC STRENGTH 0.15[a]

M	$\Delta F°$, kcal.	$\Delta H°$, kcal.	$T\Delta S°$, kcal.	$\Delta S°$, cal./deg.
Cu	$+1.4 \pm 0.2$	-0.6	-2 ± 1	-7 ± 4
Cd	$+1.2 \pm .1$	0.0 ± 1.0	-1 ± 1	-4 ± 3
Ni	$+1.3 \pm .1$	$-0.9 + 0.6$	-3.2 ± 0.6	-11 ± 2

[a] "en" represents ethylenediamine; "tn," trimethylenediamine. Standard state for thermodynamic functions hypothetical 1 molal solution with ionic strength 0.15.

It may be of interest to compare reaction (I) with an analogous cyclization reaction among saturated hydrocarbons

$$\overline{\mathrm{CH_2(CH_2)_3C}}\mathrm{H_2} + n\text{-}\mathrm{C_6H_{14}} = \overline{\mathrm{CH_2(CH_2)_4C}}\mathrm{H_2} + n\text{-}\mathrm{C_5H_{12}} \quad \text{(II)}$$

For reaction (II) in the gas phase at 25°, $\Delta H° = -6$ kcal.[12] As has been pointed out by Spitzer and Huffman,[13] the enthalpy difference in (II) can be semi-quantitatively accounted for in terms of hydrogen–hydrogen repulsions, which are more important in the five-membered ring than in the favorable conformation assumed by a six-membered ring. It is not surprising that $\Delta H°$ has a larger negative value for reaction (II) than for (I), since in the diamine chelates the absence of hydrogen atoms bonded to the metal materially reduces the number of hydrogen–hydrogen repulsions. Furthermore, the increased size of the metal ion over a carbon atom makes the stereochemistry of the chelates not exactly equivalent to alicyclic rings of the same number of links. In fact, the six-membered chelate ring might be expected to have a relatively higher enthalpy due to distortion away from a sterically ideal structure, whereas the five-membered chelate ring is altered to make its stereochemistry more similar to the more stable six-membered alicyclic ring, with a concomitantly reduced enthalpy. The above considerations suggest that the enthalpy change in reaction (I) is reasonable, and the small value of that enthalpy change indicates that the chelate effect influencing (I) is primarily an entropy effect.

Recently, Spike and Parry[5] have reported a study designed to determine the contributions of enthalpy and entropy to the chelate effect describing the enhanced stability of chelates relative to corresponding non-chelated complexes. They considered the reaction

$$\mathrm{Cd(H_2NCH_3)_2^{++}(aq) + en(aq) = Cd(en)^{++}(aq) + 2CH_3NH_2(aq)} \quad \text{(III)}$$

and found that $\Delta H° = \sim 0$, and $\Delta S° = \sim 4.7$ e.u. Unfortunately, it is necessary to work at very high ionic strength in order to study methylamine systems (Spike and Parry used 2 molar solutions of the appropriate ammonium ions) and the relation of measured values of $\Delta H°$ and $\Delta S°$ to the true thermodynamic values is less certain than might be desired. However, reactions such as (I) or (III) involve no changes in the number of ions of any charge, so that deviations from the limiting properties at high dilution would not be expected to be serious. Therefore, we believe the values obtained by Spike and Parry to be at least qualitatively significant, and together with the results of the present study indicate that, at least for amine systems, both types of chelate effect reflect differences in entropy rather than enthalpy.

Entropy differences were originally suggested as the cause of the chelate effect by Schwarzenbach,[2] on the basis of the assumption that the enthalpies of coördination of various "homologous" ligands would be nearly the same. However, he was unable by means of a very naive calculation to explain the differences in the entropies of chelate rings of different sizes. Irving, Williams, Ferrett and Williams[1] have, however, assumed that the failure of Schwarzenbach's calculation implied that the chelate effect does not result from entropy differences after all, and that enthalpy differences must be responsible. As our present results show,

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[11] H. Irving, unpublished results, taken from summary of a talk given in 1951 on "The Stability of Coördination Compounds in Aqueous Solution and the Varying Strength of Metal–Ligand Bonds," quoted by Basolo and Murmann, reference 6a.

[12] Computed from heats of formation given by E. J. Prosen and F. D. Rossini, *Bur. Standards J. Research*, **34**, 267 (1945), and by E. J. Prosen, W. H. Johnson and F. D. Rossini *ibid.*, **37**, 51 (1946).

[13] R. Spitzer and H. M. Huffman, *J. Am. Chem. Soc.*, **69**, 211 (1947).

Schwarzenbach's original assumption, that the chelate effect is primarily the result of entropy differences, is in fact quite correct. However, in order to calculate these entropy differences, one must consider the amines themselves, as well as the complex ions. If one assumes, as Schwarzenbach tacitly does, that the entropies of the amines in solution contribute equally in the free amines and in the complex, the entropy contribution to the chelate effect is just that associated with the closure of the rings of different sizes. On the other hand, if either amine involved in a metathetical reaction such as (I) deviates abnormally in its entropy of solution, it is quite possible that additional contributions will be made to the entropy change of the reaction.

It is apparent that further progress in understanding the chelate effect requires both additional knowledge concerning the thermodynamic properties of the amines and more refined consideration of the entropies of ring closure. We have therefore carried out a calculation of the statistical factors in the closing of 5-, 6-, 7- and 8-membered rings, using a Monte Carlo method on a digital computer. We are also investigating the thermodynamic properties of various amines in aqueous solution. The results of this work, which will be published shortly, should throw considerably more light on the origin of the entropy effect whose existence has now been demonstrated.

Acknowledgments.—We are indebted to the General Electric Company for financial support through a Swope Fellowship to F.A.C. We should like to thank Dr. Arnold Hartley for placing at our disposal his very considerable knowledge of analytical techniques.

THE EQUILIBRIA IN ACIDIC SOLUTIONS OF CHROMIUM(III) ION AND THIOCYANATE ION[1-3]

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Received May 18, 1955

Values of the equilibrium quotient $K_1 = (Cr(OH_2)_5NCS^{++})/(Cr(OH_2)_6^{+++})(SCN^-)$ as a function of the electrolyte concentration have been determined from spectrophotometric measurements at six temperatures in the range 30.0 to 94.6°. Extrapolation with the aid of an equation of the form of the Debye–Hückel equation has allowed the evaluation of the equilibrium constant K_1°. These values supplemented by kinetically determined values at 14.0, 25.1 and 30.0° lead to the values $\Delta H^\circ = 70(T - 328.7)$ cal. and $K_1^\circ = 1.00 \times 10^3$ at 328.7 °K, the temperature at which K_1° has a minimum value. Values of $K_7 = (H^+)(Cr(OH_2)_5OH^{++})/(Cr(OH_2)_6^{+++})$ have been determined over the range of temperature 46.2–94.6°. The values of $\Delta H_7 = 9.4$ kcal. and $\Delta S_7 = 14.1$ e.u. (at $\Gamma = 0.068$) have been obtained. A possible rationalization of the significant difference between these values and those for the analogous iron(III) reaction is a change in the coördination number of iron(III) which may occur with acid dissociation. Measurements of the influence of chromium(III) perchlorate upon the iron(III)–thiocyanate complex ion equilibrium lead to an approximate value of 1.0 for the equilibrium quotient for the "outer-sphere" association of $Cr(OH_2)_6^{+++}$ and SCN^- at $\Gamma = 1.2$. The probable reason for the lower stability of outer-sphere complexes involving aquometal ions compared to those involving ammine complexes is discussed.

The initial motivation behind the present study was the desire to obtain values of the equilibrium constant for a complex ion formation reaction over a wide range of temperature. Such data, which allow the evaluation of ΔH° and ΔS° for the reaction, are an aid in the elucidation of the factors which influence complex ion stability.[5] In view of the large value of ΔC_p associated with the ionization of weak acids in aqueous solution,[6,7] one might reasonably expect a detectable value of ΔC_p for the association reaction of a metal ion and an anion. The study of a complex ion equilibrium in an *inert* system[8] offers certain advantages when compared to a *labile* system.[8] In a *labile* system the experimental measurements must be made at the equilibration temperature. If the rate of equilibration in the *inert* system is low enough, the measurements can all be made at room temperature even though equilibrium was established at some other temperature. In the present spectrophotometric study, it was not necessary either to make the assumption that the molar absorbancy indices[9] of the individual species are independent of the temperature, or to determine the values as a function of the temperature; all of the measurements were made at the same temperature (25.0°). In addition, the molar absorbancy indices of the *inert* complexes can be evaluated independently since it is generally possible to prepare a solution containing but a single complex.

Chosen for study was the chromium(III)–thiocyanate system which has been the subject of an

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[1] Taken in part from the Ph.D. Thesis of Clarence Postmus, University of Wisconsin, 1954.

[2] Supported in part by grants from the U. S. Atomic Energy Commission and the Research Committee of the Graduate School, University of Wisconsin.

[3] Presented before the 127th National Meeting of the American Chemical Society at Cincinnati, Ohio, April 4, 1955.

[4] U. S. Rubber Company Fellow, 1953–1954; present address, Argonne National Laboratory.

[5] (a) J. W. Cobble, *J. Chem. Phys.*, **21**, 1446 (1953); (b) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953); (c) E. L. King, *J. Chem. Ed.*, **30**, 71 (1953); (d) W. M. Latimer and W. L. Jolly, *J. Am. Chem. Soc.*, **75**, 1548 (1953); (e) R. E. Connick and M.-S. Tsao, *ibid.*, **76**, 5311 (1954); (f) R. J. P. Williams, THIS JOURNAL, **58**, 121 (1954).

[6] K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).

[7] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 508–516.

[8] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[9] In this paper, the nomenclature recommended in National Bureau of Standards Letter Circular No. 857 is adopted. The definitions and symbols are included in Table I.

extensive investigation by N. Bjerrum,[10] and which has been studied more recently by Poulsen, Bjerrum and Poulsen.[11] In N. Bjerrum's work,[10] it was shown that complex ions containing one to six thiocyanate ions per chromium(III) existed in solution. By limiting consideration in the present work to solutions in which the concentration of hydrogen ion is moderately high (>2 × 10^{-3} molar) and in which chromium(III) is in large excess, the only equilibria which are important are

$$Cr(OH_2)_6{}^{+++} + SCN^- \rightleftarrows Cr(OH_2)_5NCS^{++} + H_2O \quad \text{(Reaction 1)}$$

$$Cr(OH_2)_6{}^{+++} \rightleftarrows Cr(OH_2)_5OH^{++} + H^+ \quad \text{(Reaction 7)}$$

The fact that *other* species

$$Cr(OH_2)_{6-n}(NCS)_n{}^{+3-n}\ (n > 1),$$
$$Cr(OH_2)_{6-m}(OH)_m{}^{+3-m}\ (m > 1),$$

and

$$Cr_p(OH_2)_q(OH)_r{}^{+3p-r}\ (p > 1)$$

can be neglected has been demonstrated experimentally. The experimentally measured quantities are the absorbancy of the equilibrated solutions at 292 mμ where the absorbancy index of $CrNCS^{++}$ has a maximum value, which is very large in comparison to that of Cr^{+++},[12] and the absorbancies at 458 and 480 mμ of the equilibrated solution to which iron(III) was added. The latter measurements yield the concentration of thiocyanate ion which is not in *inert* combination with chromium(III). These quantities and the original stoichiometric composition of the solution allow the evaluation of a quantity, K_m, defined by the equation

$$K_m \equiv \frac{A_{292}/(a_{CrNCS^{++}}b)}{\{(Cr^{III}) - A_{292}/(a_{CrNCS^{++}}b)\}(SCN^-)} \qquad (1)$$

which involves symbols defined in Table I. If the only important chromium(III) species in the solution are Cr^{+++} and $CrNCS^{++}$, K_m is equal to K_1. Variations in the equilibrium values of K_m which result from a variation in the stoichiometric composition of the solution indicate (1) a *medium* effect upon K_1, and/or, (2) the importance of species other than Cr^{+++} and $CrNCS^{++}$.

It was desired to vary the electrolyte concentration in order to extrapolate the experimentally determined values of K_1 to zero electrolyte concentration and thus obtain $K_1°$, the thermodynamic equilibrium constant for reaction 1. The low electrolyte concentrations desired can be attained only if the acidity is decreased to the point where reaction 7 becomes important. Under such conditions, the value of K_m is a function of the hydrogen ion concentration

$$K_m = \frac{(CrNCS^{++})}{\{(Cr^{III}) - (CrNCS^{++})\}(SCN^-)} = \frac{(CrNCS^{++})}{\{(Cr^{+++}) + (CrOH^{++})\}(SCN^-)} = \frac{K_1(H^+)}{K_7 + (H^+)} \qquad (2)$$

Values of K_7 are obtained from the variation in K_m with the concentration of hydrogen ion. It is to be noted that these values of K_7 correspond to the temperature at which equilibrium is established. The fact that equilibrium in reaction 7 is rapidly established and shifts when the reaction mixture is quenched is not a matter of concern. At the elevated temperature, the formation of $CrOH^{++}$ has lowered the amount of chromium(III) available for complexing by thiocyanate and thus has influenced the value of K_m; the extent of this influence is determined by the concentration of hydrogen ion and the value of K_7 *at the equilibration temperature.*

TABLE I

DEFINITIONS AND SYMBOLS[12]

(X) = molar concn. of the species X
(Cr^{III}) = sum of the concn. of all chromium(III) species
A_λ (the absorbancy) = $\log I_0/I$ at wave length λ
a_x (the molar absorbancy index of the species X) = $A_x/(X)b$ where A_x is the absorbancy due to species X and b is the cell length

$$K_n = \frac{(Cr(NCS)_n{}^{+3-n})}{(Cr^{+++})(SCN^-)^n} \qquad n = 1 - 6$$

$$K_7 = \frac{(CrOH^{++})(H^+)}{(Cr^{+++})} \qquad K_{FeNCS^{++}} = \frac{(FeNCS^{++})}{(Fe^{+++})(SCN^-)}$$

$$K_{01} = \frac{(Cr(OH_2)_6\cdot SCN^{++})}{(Cr(OH_2)_6{}^{+++})(SCN^-)}$$

$$\Gamma \text{ (the ional concentration)} = \sum_{\text{all ions}} (X)Z_x{}^2$$

where Z_x is the charge on species X.

Experimental Methods

Reagents.—All solutions were prepared using doubly distilled water, the second distillation being from an alkaline permanganate solution using either a Pyrex glass or Barnstead still.

Hexaaquochromium(III) perchlorate was prepared by reducing reagent grade chromium trioxide with a slight excess of reagent grade formic acid in the presence of excess perchloric acid. The chromium(III) perchlorate was recrystallized twice from dilute perchloric acid and then was dissolved in perchloric acid solution. The acidity of the solution was determined by a method suggested by the work of Blaedel and Panos[13] on the determination of the acidity of aluminum(III) solutions; this method has been summarized elsewhere.[14] The chromium concentration was determined spectrophotometrically after oxidation to chromium(VI) by peroxide in alkaline solution. Reagent grade sodium thiocyanate was crystallized two times from water. The stock solution, which was stored at 0°, was standardized against a silver nitrate solution of known concentration. Lanthanum perchlorate was prepared in two ways: (1) the fuming almost to dryness of twice recrystallized lanthanum chloride with perchloric acid, and (2) the solution of lanthanum oxide in insufficient perchloric acid, the oxide having resulted from the ignition of precipitated lanthanum oxalate. Lithium perchlorate and sodium perchlorate were recrystallized once, while barium perchlorate was recrystallized twice. Stock solutions were analyzed by gravimetric techniques.

Spectrophotometric Measurements.—All spectrophotometric measurements were made with a Beckman DU spectrophotometer at 25.0° using, except on a few occasions, one cm. cells. The temperature control was ±0.2° during most of the measurements reported in this paper.

Determination of Absorbancy Indices of Chromium(III) Complexes.—Each of the complex ions $CrNCS^{++}$ and $Cr(NCS)_2{}^+$ was obtained free of thiocyanate ion and other chromium(III) species by ion exchange techniques.[15] The molar absorbancy indices of these species at 292 mμ are 2.90

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[10] N. Bjerrum, *Z. anorg. allgem. Chem.*, **118**, 131 (1921); **119**, 39, 51, 179 (1921).

[11] K. G. Poulsen, J. Bjerrum and I. Poulsen, *Acta Chem. Scand.*, **8**, 921 (1954); this work was cited in the paper by J. Bjerrum and K. G. Poulsen, *Nature*, **169**, 463 (1952).

[12] In general, chromium(III) species will be represented without showing water molecules of the first coördination sphere. The formulas of the complexes are written in a way which implies bonding between chromium(III) and nitrogen (*i.e.*, isothiocyanato complexes); no evidence regarding this point was obtained in the present study.

[13] W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

[14] E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

[15] E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952).

$\times 10^3$ and 5.99×10^3, respectively. At this wave length, the molar absorbancy index of hexaaquochromium(III) ion is 0.7, definitely negligible compared to the values for the complexes. (The percentage of the two geometrical isomers of the dithiocyanato complex which are present in solution is not known. The weighted average molar absorbancy index which is obtained here is probably close to the value which corresponds to equilibrated solutions since the elution procedure used in obtaining the ion(s) of charge +1 was not designed to separate the isomeric ions of that charge.[16]) These values of the absorbancy indices of chromium(III) complexes depend, of course, upon the chromium analyses which were carried out by first converting the chromium to chromate ion with alkali and hydrogen peroxide. The absorbancy of such a solution was determined at 372 mμ, a maximum in the chromate spectrum. The molar absorbancy index using a slit width of 0.10–0.15 mm. (equivalent to 1.0–1.4 mμ) was found to have the value 4.89×10^3 from measurements upon ten dilutions of two different standard solutions of potassium dichromate in sodium hydroxide solutions.[17] This value was found to be independent of the concentration of chromate ion and hydroxide ion over the concentration ranges studied, 2×10^{-5} to 10^{-4} molar and 0.01 to 0.20 molar, respectively.

Experimental Procedure.—Solutions of the desired stoichiometric compositions were prepared and sealed in Pyrex test-tubes. These were placed in a darkened constant temperature bath which was regulated to within ±0.05°. For analysis, cooled, and therefore quenched, aliquots of the solution were diluted to a definite volume. One of these was measured *versus* a water blank at 292 mμ. Another aliquot, to which iron(III) nitrate and perchloric acid had been added, was measured at 458 and 480 mμ, wave lengths at which $FeNCS^{++}$ absorbs strongly, against a blank containing the same amount of equilibrated solution but which contained no iron(III).

The iron(III) concentration was high (0.010 *M*) compared to the total concentration of unbound thiocyanate ($<6 \times 10^{-4}$ *M*) and thus was uninfluenced by the extent to which $FeNCS^{++}$ forms. The concentration of hydrogen ion was never lower than 0.10 *M*, thus making the formation of $FeOH^{++}$ negligible. The increment of absorbancy per unit concentration of thiocyanate ion was established for each medium studied using solutions with known concentrations of thiocyanate ion. The absorbancy measurements were made within 10 minutes after adding the iron(III) solution. This made negligible any changes in absorbancy due to the oxidation–reduction reaction which involves iron(III) and thiocyanate ions.[18]

In general, the value of the concentration of uncombined thiocyanate ion obtained spectrophotometrically agreed well with that calculated by subtracting the concentration of $CrNCS^{++}$ from the stoichiometric concentration of sodium thiocyanate. However, at the higher temperatures and at the higher acidities some thiocyanate ion disappears. The greatest loss of thiocyanate was 9% of that uncombined with chromium(III) while in most (~93%) solutions it was less than 2%. As long as the side reactions proceed slowly compared to the reaction forming $CrNCS^{++}$, the value of the concentration of thiocyanate ion obtained using iron(III) is the value required for substitution into the equation for K_m. The decomposition products do not appear to interfere with the spectrophotometric measurements since in the experiment in which 9% of the thiocyanate ion disappeared, the value of K_m changed by less than 2% during the time period in which the decomposition of thiocyanate increased from 5 to 9%.

The reproducibility of duplicate equilibrium runs was within approximately 1% in the value of K_m.

The Influence of Hexaaquochromium(III) Ion on the Equilibrium: $Fe^{+++} + SCN^- \rightleftarrows FeNCS^{++}$.—The apparent absorbancy index of thiocyanate ion in the presence of iron(III) depends upon the electrolyte concentration since the value of the equilibrium quotient for the reaction

$$Fe^{+++} + SCN^- \rightleftarrows FeNCS^{++}$$

depends upon the electrolyte concentration and since the iron(III) concentration employed was not sufficiently high to convert thiocyanate ion predominantly to $FeNCS^{++}$. In one series of experiments, on solutions containing 0.01 *M* iron(III) nitrate, 10^{-4} *M* sodium thiocyanate and 0.10 *M* perchloric acid, the ional concentration was varied over the range 0.32 to 0.7 by the addition of sodium perchlorate, barium perchlorate *or* chromium(III) perchlorate. Over this range of electrolyte concentration, the absorbancy of the solutions at 458 and 480 mμ changed by approximately 30%; the absorbancy values were the same for solutions of the same ional concentration containing the three different added salts. This is an interesting observation in view of the recent studies which demonstrate the existence of "ion-pairs" or "outer-sphere" complex ions involving cobalt(III) and chromium(III).[5b,19] If one assumes that ion-pair formation effects are absent in the sodium perchlorate and barium perchlorate solutions and that these data place an upper limit on the extent of association of thiocyanate ion and hexaaquochromium(III) ion of 5%, one calculates the value 1.7 as an upper limit for K_{01}, the equilibrium quotient for the formation of ion-pairs. In order to establish this limit more certainly, a similar series of experiments was performed to investigate the influence of sodium perchlorate and chromium(III) perchlorate upon the absorbancy at 458 mμ of a solution containing 5.0×10^{-4} *M* iron(III) nitrate, 5.0×10^{-4} *M* sodium thiocyanate and 0.10 *M* perchloric acid. These data, used in conjunction with the molar absorbancy index of $FeNCS^{++}$ at 460 mμ,[18] with no correction being made for the 2 mμ difference in wave length, allow the calculation of the equilibrium quotient $K_{FeSCN^{++}}$. The results are presented in Fig. 1 which includes the value obtained by Betts and Dainton.[18] Only at the highest concentration of chromium(III), 0.10 *M*, does an effect appear which suggests ion-pair formation. If one attributes all of the difference between the apparent values of $K_{FeNCS^{++}}$ in the sodium perchlorate and chromium(III) perchlorate solution to the formation of the ion-pair $Cr(OH_2)_6 \cdot SCN^{++}$, one calculates a value of $1._0$ for K_{01} at $\Gamma = 1.2$. That hexaaquochromium(III) ion and thiocyanate ion do form "outer-sphere" complexes is also suggested by the observations by Evans and Nancollas[5b] on the interaction of $Co(NH_3)_6^{+++}$ and N_3^- and by Adamson and Wilkins[19c] on the interaction of $Co(NH_3)_5(OH_2)^{+++}$ or $Cr(NH_3)_5(OH_2)^{+++}$ and SCN^-. Light absorption measurements in the ultraviolet region of the spectrum would undoubtedly reveal the presence of such species.[20] The approximate value for K_{01} established in the measurements already discussed, while not sufficiently low to rule out the presence of an appreciable amount of $Cr(OH_2)_6 \cdot SCN^{++}$, indicates that the presence of such species would not influence the calculated value of K_1°.

The Establishment of Equilibrium.—The time required to establish equilibrium was determined in experiments run at concentration conditions which set an upper limit for the required time in the equilibration experiments. Such experiments at 94.6, 84.8, 73.7 and 63.6° consisted of comparing the measured value of K_m as a function of time for two solutions of the same stoichiometric composition, one of which had an initial value of K_m of zero and the other of which had an initial value of K_m in excess of the equilibrium value. The determination of the time required for equilibration at 30.0 and 46.2° was similar to that employed at the other temperatures except that the initial K_m values were closer to the equilibrium values. As examples, the times of equilibration for a solution of the composition 9.9×10^{-4} *M* chromium(III) perchlorate, 4.2×10^{-4} molar sodium thiocyanate and 0.010 *M* perchloric acid were 7 days, 1 day, and 2 hours at 63.6, 73.7 and 94.6°. The solutions used in the equilibrium studies at 30.0° were kept

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[16] E. L. King and R. R. Walters, *J. Am. Chem. Soc.*, **74**, 4471 (1952).

[17] This is to be compared with the value 4.83×10^3 which has been interpolated from the data of G. W. Haupt (*J. Research Natl. Bur. Standards*, **48**, 414 (1952)). H. S. Gates and K. Schug in this Laboratory have obtained the value 4.81×10^3 using the same Beckman instrument now equipped with a photomultiplier unit which makes possible the use of narrower slit widths (~0.03 mm. which is equivalent to 0.4 mμ) (H. M. Haendler, *J. Opt. Soc. Am.*, **38**, 417 (1948)).

[18] R. H. Betts and F. S. Dainton, *J. Am. Chem. Soc.*, **75**, 5721 (1953).

[19] (a) H. Taube and F. A. Posey, *ibid.*, **75**, 1463 (1953); (b) R. E. Connick and M.-S. Tsao, paper no. 9 presented before the Div. of Physical and Inorganic Chem., Los Angeles, Calif., March 15, 1953; (c) A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954). (References to earlier papers in this field are to be found in references 5b and 19a.)

[20] It has been learned that R. A. Plane of Cornell University is carrying out such experiments.

in the thermostat for 1.5 years after first having been brought part of the way to equilibrium at a higher temperature.

The Stability of $Cr(NCS)_2^+$.—The value of K_1 is most conveniently obtained from measurements upon solutions which do not contain an appreciable concentration of $Cr(NCS)_2^+$ and higher complexes. Such complexes are more important the higher the concentration of thiocyanate ion. It can be shown that

$$K_m \cong \frac{K_1 + (5.99/2.90)K_2(SCN^-)}{1 + K_7/(H^+)}$$

in solutions containing relatively low concentrations of $Cr(NCS)_2^+$. The coefficient 5.99/2.90 is the ratio of the molar absorbancy indices of $Cr(NCS)_2^+$ and $CrNCS^{++}$ at 292 mμ, the wave length at which the measurements were made. At 84.8°, the values of K_m at $\Gamma = 0.048$, $(H^+) = 1.04 \times 10^{-2}$ are 371, 374, 379, 376 and 384 at $(SCN^-) = 2.7, 3.4, 4.2, 5.6$ and 7.1×10^{-4} *M*, respectively. At this same temperature at $\Gamma = 0.075$, $(H^+) = 1.08 \times 10^{-2}$, the values of K_m are 320, 318, 321, 325 and 349 at $(SCN^-) = 2.0, 3.1, 4.1, 5.2$ and 11.1×10^{-4}, respectively.

Evaluation of the data of the first mentioned series of experiments leads to a value of K_2 of $\sim 9 \times 10^3$ which corresponds to 1.5% of the complexed chromium(III) being present as $Cr(NCS)_2^+$ at 6.5×10^{-4} *M* thiocyanate ion. The point at the highest concentration of thiocyanate in the second series of experiments shows a trend which can be reasonably attributed to the presence of $Cr(NCS)_2^+$. Practically all of the data used in the evaluation of K_1 were obtained in experiments in which the uncombined thiocyanate was present at concentrations lower than 6×10^{-4} *M*. In the treatment of the data to yield K_1, no allowance was made for the presence of $Cr(NCS)_2^+$, which was present in most of the solutions to an extent of less than 1% of the concentration of $CrNCS^{++}$.

The Question of Polymeric Chromium(III) Species.—In acidic solutions containing a metal ion of charge +3 or larger, there is the possibility of the metal ion being present as polymeric species containing more than one metal ion.[21] Such is true for chromium(III)[22] and it was of interest, therefore, to learn whether such species were present in the solutions being studied in the current work. Two approaches, spectrophotometric measurements upon chromium(III) perchlorate solutions and a study of the influence of the concentration of chromium(III) upon the value of K_m, were used to elucidate this question.

It was observed that 0.0132 *M* perchloric acid solutions of chromium(III) perchlorate (concentration range 10^{-3} to 5×10^{-2} *M*) which had been heated at 74° for 50 hours and then measured one to ten hours after cooling did not obey Beer's law in the wave length region 400–640 mμ. The deviation was not large (a 4–12% increase in the absorbancy index of chromium(III) with the increase in chromium(III) concentration over the whole concentration range stated above) but it does appear to be real. The molar absorbancy index values of chromium(III) in a solution which was similarly heated but which had the composition 5.0×10^{-2} *M* chromium(III) perchlorate–1.0 *M* perchloric acid were essentially equal to the values obtained from the solution of lower acidity and the *lowest* chromium(III) concentration. That the extent of polymer formation is diminished in the one molar perchloric acid solution compared to 0.013 *M* perchloric acid is to be expected, since the predominant monomeric chromium(III) species has a +3 charge and all polymeric species involving oxide or hydroxide bridging have a charge of less than +3/chromium(III) atom. These data *do not* prove that a measurable fraction of the chromium(III) is present as polymeric species in the medium of lower acidity and high chromium(III) concentration but only that a measurable fraction of the light absorption is due to such species. The data of Poulsen, Bjerrum and Poulsen[11] suggest that the extent to which polymeric species form in 0.02 *M* perchloric acid–0.02 *M* chromium(III) perchlorate upon heating at 75° is *very slight*.

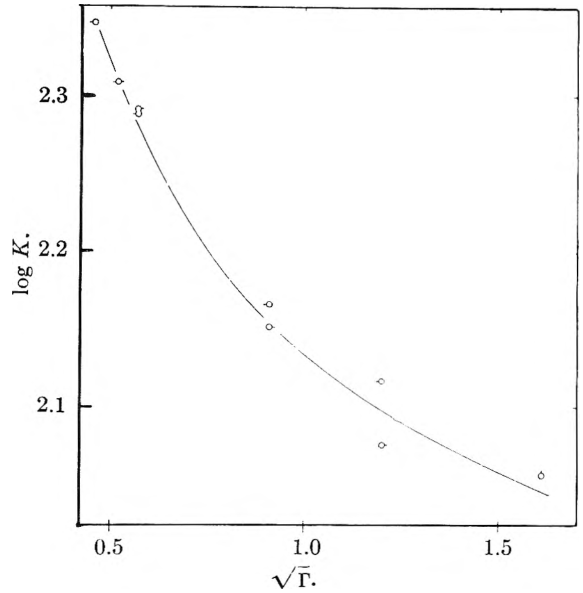

Fig. 1.—The logarithm of the equilibrium quotient for the reaction: $Fe^{+++} + SCN^- = FeNCS^{++}$ as a function of the electrolyte concentration: -o, in the presence of sodium perchlorate; o-, in the presence of chromium(III) perchlorate; ȯ, from the work of Betts and Dainton[18] (added electrolyte is sodium perchlorate).

An experimental approach which is more to the point than the spectrophotometric measurements is the measurement of K_m as a function of the chromium(III) concentration. The extent of polymer formation will increase with an increase in the metal ion concentration if a continuous series of polymers forms or if a single polymer forms in the concentration range in which the monomer is the predominant species. The medium was maintained essentially constant as the concentration of chromium(III) changed by using lanthanum(III) perchlorate keeping both the ional concentration and the electrolyte normality constant.[23] The results of this series of experiments are presented in Table II.

TABLE II

K_m AS A FUNCTION OF THE CHROMIUM(III) CONCENTRATION

$T = 73.7°$, $\Gamma = 1.23$, $(H^+) = 1.32 \times 10^{-2}$,[a] $(SCN^-) = 3.5 - 5.2 \times 10^{-4}$, $\{(Cr^{+++})^b + (La^{+++})\} = 0.100$.

$(Cr(ClO_4)_3) \times 10^3$	$(Cr^{+++})^b \times 10^3$	K_m	$(Cr(ClO_4)_3) \times 10^3$	$(Cr^{+++})^b \times 10^3$	K_m
0.99	0.89	102	9.88	8.76	109
2.47	2.22	104	24.7	22.4	109
4.94	4.47	105	49.4	44.2	108

[a] In calculating the concentration of hydrogen ion, account is taken of that liberated in the formation of $CrOH^{++}$. [b] In calculating the concentration of hexaaquochromium(III) ion, account is taken of formation of $CrNCS^{++}$ and $CrOH^{++}$.

In the design of these experiments, use was made of the approximate values of K_7 and K_1 which were already known; it was possible, therefore, to adjust the stoichiometric composition of the solutions such that both the hydrogen ion concentration and the sum of the concentrations of hexaaquochromium(III) ion (not total chromium(III)) and lanthanum(III) ion were constant. The observed trend in

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(21) (a) F. Graner and L. G. Sillen, *Acta Chem. Scand.*, **1**, 631 (1947); (b) L. J. Heidt and M. E. Smith, *J. Am. Chem. Soc.*, **70**, 2476 (1948); (c) R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951); (d) E. L. King and M. L. Pandow, *ibid.*, **74**, 1966 (1952); (e) B. O. A. Hedstrom, *Arkiv Kemi*, **6**, 1 (1953); (f) M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **100**, 85 (1953); **101**, 39 (1954); (g) K. A. Kraus and R. W. Holmberg, THIS JOURNAL, **58**, 325 (1954); (h) L. G. Sillen, *Acta Chem. Scand.*, **8**, 299, 318, 1607 (1954); (i) R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955); (j) L. N. Mulay and P. W. Selwood, *ibid.*, **77**, 2693 (1955).

(22) (a) N. Bjerrum and C. Faurholt, *Z. physik. Chem.*, **130**, 584 (1927); (b) H. T. Hall and H. Eyring, *J. Am. Chem. Soc.*, **72**, 782 (1950).

(23) It is probable that $Cr(NH_3)_6^{+++}$ or $Co(NH_3)_6^{+++}$ would have been better stand-ins for $Cr(OH_2)_6^{+++}$ in maintaining a constant medium.

K_m with an increase in the concentration of chromium(III) is slight and in the opposite direction from that which would be produced by the existence of polymeric chromium(III) species. The assumption that lanthanum(III) does not form a mixed polymeric species with chromium(III) seems reasonable in view of the low acidity of aquolanthanum(III) ion.

While these experiments at 73.7° were the only ones designed to elucidate possible polymerization, other data are relevant in this connection. In experiments at other temperatures, the values of K_1 obtained at two different chromium(III) concentrations (4.9×10^{-3} and 9.9×10^{-2} M) and comparable values of the ional concentration fall on the same straight line correlating K_1 and Γ (see Fig. 2 for the data at 94.6°). It is reasonable, therefore, to assume that polymeric species are not present in appreciable amounts in any of the solutions studied in this work.

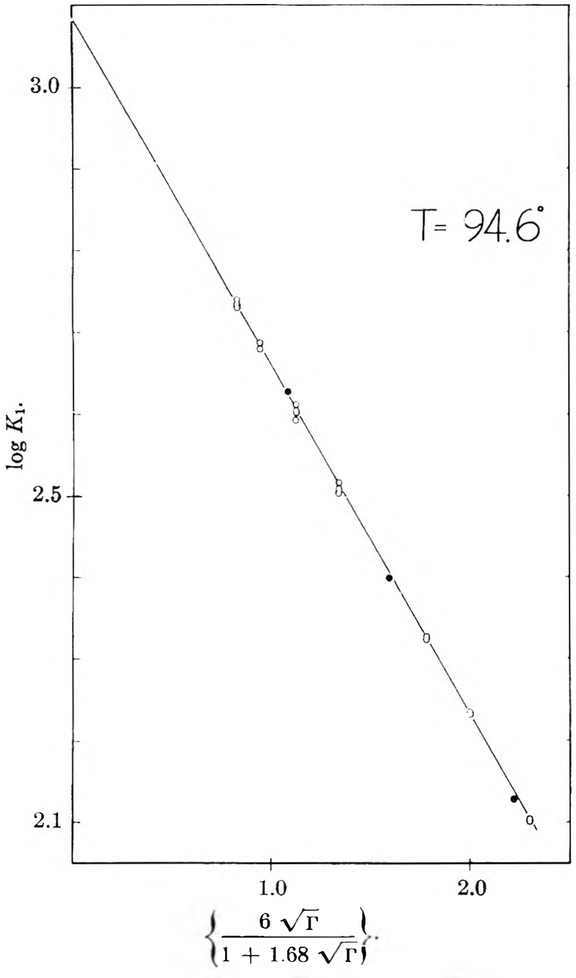

Fig. 2.—Log K_1 *versus* $6\sqrt{\Gamma}/(1 + 1.68\sqrt{\Gamma})$. The data are for 94.6°. The slope of this line has the required value for this temperature, $B = 0.4258$. The solid points are for experiments with a chromium(III) concentration as much as 10–20 fold lower than in experiments for adjacent points.

The Evaluation of K_7.—If $CrOH^{++}$ is the only chromium(III) species containing hydroxide ion which is of importance in the solutions, the dependence of K_m upon the concentration of hydrogen ion is that given by equation 2. Experiments designed to evaluate K_7 have involved measurements upon solutions of varying concentration of hydrogen ion. It was desired that *medium effects* associated with these composition changes be kept as small as possible; to accomplish this, the ional concentration was maintained constant with lithium perchlorate; the basis for making this choice has been outlined previously.[24] Since the concentration of the other electrolytes (chromium(III) perchlorate, sodium thiocyanate and, in some of the series, lanthanum perchlorate) were constant in a particular series, the assumption that the relevant activity coefficients were approximately constant seems justified. The compositions of the solutions which were studied are summarized in Table III.

Table III

Composition of Solutions Studied in Order to Evaluate K_7

Γ	0.068	0.232	0.966
No. of solutions[a]	8–9	8–9	11–12
$(Cr(ClO_4)_3) \times 10^3$	2.47	2.47	4.94
$(NaSCN) \times 10^4$	6.30	6.34	8.40
$(La(ClO_4)_3) \times 10^2$	...	...	5.84
$[(HClO_4) + (LiClO_4)]$	0.0200	0.100	0.100
$(HClO_4) \times 10^3$ range at			
94.6°	3.0–20.0	2.0–100	3.0–100
84.8°	3.0–20.0	2.5–100	2.0–100
73.7°	2.0–20.0	2.0–100	2.0–100
63.6°	2.0–20.0	1.0– 50	2.0– 50
46.2°	2.0–10.0	1.0– 50	...

[a] The number of solutions studied was not the same at each temperature.

A method of successive approximations was used to calculate consistent values of K_7, (H^+), $(CrOH^{++})$ and K_1 for each solution (*i.e.*, each measured value of K_m). (Because of the occurrence of reaction 7, the concentration of hydrogen ion in many of the solutions was significantly greater than the concentration of perchloric acid.) A summary of the results of these calculations is presented in Table IV.

Table IV

Summary of the Values of K_1 and K_7 Obtained in Studies of Solutions of Varying Acidity

T, °C.	Γ	Obsd. K_m range	K_1	$K_7 \times 10^3$	Av. % dev.[b]	Calcd. $K_7 \times 10^3$[c]
94.6	0.068	231–364	423[a]	3.35	0.4	3.21
	.232	130–243	251[a]	2.98	1.1	2.90
	.966	90–131	137[a]	2.43	0.9	2.33
84.8	0.068	248–355	400	2.36	0.3	2.26
	.232	145–225	231	2.00	0.8	2.04
	.966	91–130	134	1.65	0.7	1.64
73.7	0.068	249–352	378	1.45	0.5	1.48
	.232	156–232	234	1.36	0.5	1.34
	.966	98–130	130	0.98	0.8	1.08
63.6	0.068	274–352	364	0.84_5	0.7	0.98
	.232	158–228	231	0.85_2	0.8	0.89
	.966	107–131	136	0.78	0.6	0.72
46.2	0.068	329–376	397	0.50	0.4	0.46
	.232	190–244	243	0.42	0.4	0.41

[a] These are the three points plotted as solid circles in Fig. 2. Since these points arise from experiments in which the chromium(III) concentration is much lower than in the other experiments shown in this figure, the agreement is evidence against significant polymer formation. [b] This is the average per cent. deviation between the observed value of K_m and that calculated using the listed K_1 and K_7. [c] Calculated using ΔH_7 and ΔS_7 values listed in text.

The dependence of the value of K_7 upon the electrolyte concentration is less pronounced than is observed for the equilibrium quotient for the corresponding iron(III) reaction.[21] This small change of ΔF_7 (~200 cal.) over the electrolyte concentration studied suggests an even smaller change of ΔH_7 (~100 cal. in the opposite direction)[25] with electro-

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[24] J. Y. P. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6181 (1953).

[25] At 25°, the ratio of the limiting slopes in ΔF *versus* $\sqrt{\Gamma}$ and ΔH *versus* $\sqrt{\Gamma}$ is −1.93: H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, Chap. 5.

lyte concentration. It seems reasonable, therefore, to treat all of the data in order to obtain a single value of ΔH_7 independent of electrolyte concentration and temperature. This has been done by considering the ratio of K_7 values at successive temperatures and leads to a value of 9.4 kcal. for ΔH_7 (an uncertainty of 0.4 kcal. is estimated). With this value of ΔH_7, it is possible to calculate the value of ΔS_7 corresponding to each value of K_7. The calculated values of ΔS_7 at each of the three Γ values have been averaged; they are 14.1, 13.9 and 13.5 e.u. at $\Gamma = 0.068$, 0.232 and 0.966, respectively. The 14 different values of K_7 calculated using these 4 parameters are presented in the last column of Table IV. The average percentage difference between these values and the experimental values is 4.8%. Calculated values in closer agreement with the observed values would have been obtained if ΔH_7 had not been assumed to be independent of temperature. The values of ΔH_7 calculated from the K_7 ratios at the successive temperature intervals show the trend expected for a positive value of ΔC_p for reaction 7.[26] Since the over-all agreement between the observed and calculated values of K_7 is as good as the data justify, it does not seem worthwhile to introduce the additional parameter, ΔC_p for reaction 7.

The Evaluation of $K_1°$.—Measurements of K_m have been made as a function of the electrolyte concentration at six temperatures between 30 and 94.6°. A summary of the concentration conditions is given in Table V which includes the value of $K_7/(H^+)$ for the solutions of each series at the extreme temperatures, thus indicating the magnitude of the correction which was applied to K_m in obtaining K_1. The values of K_7 used in the calculation of K_1 by equation 2 were interpolated or extrapolated in plots of the calculated values of log K_7 *versus* $\sqrt{\Gamma}$, the calculated values of K_7 being those presented in Table IV. The uncertainty in the calculated values of K_1 arising from the estimated uncertainty in the values of K_7 is calculated to be less than 1%.

It is possible to correlate the variation of K_1 with electrolyte concentration by an equation of the form of the Debye–Hückel equation

$$\log K_1 = \log K_1° + \frac{\Delta(Z^2)B\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \qquad (3)$$

with two adjustable parameters $K_1°$ and A.[27] The coefficient of $\sqrt{\Gamma}$ in the numerator is determined by the ΔZ^2 value for the reaction (−6 in the present case) and the temperature.[28] In the Debye–Hückel equation for the activity coefficient of an electrolyte, the coefficient of $\sqrt{\Gamma}$ in the denominator, A, is equal to $(35.57\ a)/(DT)^{1/2}$, where D is the dielectric constant and a is the distance of closest approach of the two ions of the electrolyte. The values of a calculated from the values of the parameter A lose some significance when used in connection with as complex a mixture as is here under consideration and, further, the assumptions behind the derivation of the equation in this form are probably not valid at the high values of Γ which are included in these experiments. The fact is, however, that the values of K_1 are consistent with this equation.

TABLE V

SUMMARY OF THE CONCENTRATION CONDITIONS EMPLOYED IN THE EVALUATION OF K_1[a]

Γ[b]	$(Cr(ClO_4)_3) \times 10^3$	$(NaSCN) \times 10^4$ range	Value of $K_7/(H^+)$ 30.0°	94.6°
0.032	0.99	4.0– 7.4	. . .	0.33
.048	2.47	5.0–10.6	0.021	.31
.076	4.94	5.0–12.7	.021	.29
.13	9.9	10.0–25.0	.020	.26
.36	29.6	12.5–37.5	.018	.19
.59	49.4	25.0–50.7	.016	.15
1.19	98.8	34.0–62.5	.010	.10

[a] The concentration of perchloric acid was 0.010 *M* in all series except that at the highest concentration of chromium(III) where it was 0.015 *M*. The concentration of hydrogen ion was larger than these values because of the occurrence of reaction 7. [b] These are approximate values. The actual value of Γ was not the same at the several temperatures due to the extent to which reaction 7 occurred.

TABLE VI

THE EVALUATION OF $K_1°$ AT VARIOUS TEMPERATURES

T (°C.)	No. of points	Best A	$a \times 10^8$ (cm.)	$K_1° \times 10^{-3}$ Exp.	Eq. 4	Eq. 5
94.6	23	1.68[a]	6.80[a]	1.24[a]	1.27	1.25
84.8	29	1.65	6.77	1.15	1.14	1.14
73.7	22	1.64	6.80	1.06	1.05	1.06
63.6	21	1.64	6.85	1.04	1.01	1.02
46.2	23	1.615	6.87	1.03	1.02	1.02
30.0	19	1.60	6.86	1.10	1.14	1.13
30.0				1.12[b]	1.14	1.13
25.1				1.23[b]	1.20	1.19
14.0				1.38[b]	1.39	1.41

[a] The values recorded for 94.6° are those resulting from the calculation which took into account the change of volume of the solution with temperature. [b] Determined by kinetic means (reference 31).

The "best" values of $K_1°$, A and the associated values of a are given in Table VI. To obtain these values successive assumed values of A were used to evaluate $K_1°$ from the values of K_1 calculated from the measured values of K_m. That value of A which gives the smallest average difference between the calculated individual values of $K_1°$ and the average of the calculated values of $K_1°$ is chosen as the best value. Figure 2 shows the values of K_1 at 94.6° as a function of Γ.

It might still be argued that the value of the parameter $K_1°$ of equation 3 is not equal to the value of K_1 at zero electrolyte concentration since the extrapolation is from an electrolyte concentration ($\Gamma \leqq 0.032$) in excess of values at which very marked deviations of certain activity coefficient factors from the Debye–Hückel limiting law are observed.[29] Many of these examples are ones in which outer-sphere complexing undoubtedly accounts for the specificity (*e.g.*, the anomalous influence of sodium sulfate upon the rate coefficient for the reaction[29b]: $Co(NH_3)_5Br^{++} + OH^- \rightarrow$). It has already been pointed out that ion-pair formation is not important in the present studies in those solutions which have the most influence over the extrapolated value of $K_1°$. In connection with the use of equation 3, it is of interest to note that the quenching of the fluorescence of the quinine cation of charge plus two by bromide ion in the presence of sodium perchlorate, magnesium perchlorate and lanthanum perchlorate exhibits an electrolyte effect consistent with this equation; while the values of A for the three salts differ, the extrapolated values of $k°$ are essentially the same.[30] It seems reasonable, therefore, to

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[26] In view of the value of ΔC_p for reaction 1 (to be presented later), it would be surprising if the analogous association reaction

$$Cr(OH_2)_6^{+++} + OH^- \rightleftarrows Cr(OH_2)_5OH^{++} + H_2O \quad \text{(Reaction 7')}$$

did not have a comparable value of ΔC_p. The value of ΔC_p for reaction 7 is, of course, less positive than the value of ΔC_p for reaction 7′ by the value of ΔC_p for the association of hydrogen ion and hydroxide ion (+46.5 e.u.)

[27] In the correlation of the mean activity coefficient of an electrolyte with the electrolyte concentration in the concentration range comparable with the upper limits studied here, a linear concentration term is generally added to the right hand side of equation 3. The equation of the same form as equation 3 does, however, give a reasonable fit to the experimental values of the mean activity coefficients of certain electrolytes. At a concentration of 0.1 *M*, the activity coefficient of sodium chloride is within 0.2% of the value calculated using an equation of the form of equation 3. (A. S. Brown and D. A. MacInnes, *J. Am. Chem. Soc.*, **57**, 1356 (1935).) A corresponding comparison for hydrochloric acid yields a 1% difference at 0.10 *M* (T. Shedlovsky and D. A. MacInnes, *ibid.*, **58**, 1970 (1936)), while for potassium chloride the difference is but 0.7% at 0.5 *M* and 3% at 1.0 *M* (T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937)) and for calcium chloride a difference of 1.6% is observed at 0.1 *M*.

[28] Values of the Debye–Hückel limiting slope, here designated as *B*, as a function of temperature are to be found in the reference cited in footnote 25.

[29] (a) V. K. LaMer and C. M. Mason, *J. Am. Chem. Soc.*, **49**, 410 (1927). (b) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[30] W. E. Harty and G. K. Rollefson, *J. Am. Chem. Soc.*, **76**, 4811 (1954).

equate the parameter $K_1°$ of equation 3 and the thermodynamic equilibrium constant for reaction 1.

Considering the total of 137 experiments in which the equilibrium was studied directly, the maximum per cent. difference between an *observed* value of K_1 (*i.e.*, a value calculated from the observed value of K_m and an interpolated or extrapolated value of K_7) and a value calculated using equation 3 with the parameters appropriate for that temperature was 3.1% and the average difference was 1%.

Included in Table VI are values of $K_1°$ obtained at 30.0, 25.1 and 14.0° by a study of the kinetics of the forward and reverse of reaction 1.[31]

The Choice of a Concentration Scale.—It has proven most convenient to prepare the solutions on a volume concentration basis at room temperature and, as has already been mentioned, the measurements have been made at 25.0°. The volume concentrations are different at each equilibration temperature, however. The error in $K_1°$ arising from this simplification has been investigated using the data obtained at 94.6°, where the error would be largest. In this calculation, the expansion of the solutions in being raised in temperature by 70° was assumed to be the same as for pure water (an increase of 3.7%). The calculated values of K_1 were 3.7% higher and the values of Γ were 3.7% lower on the corrected basis. In the extrapolation to zero electrolyte concentration, these two errors partially cancel one another and it is found that the corrected value of $K_1°$ is 2.6% higher. The best value of A, the coefficient of in the denominator is 1.68, essentially equal to the value, 1.69, obtained in the uncorrected calculation. This correction has not been made at the lower temperatures where it would be smaller.

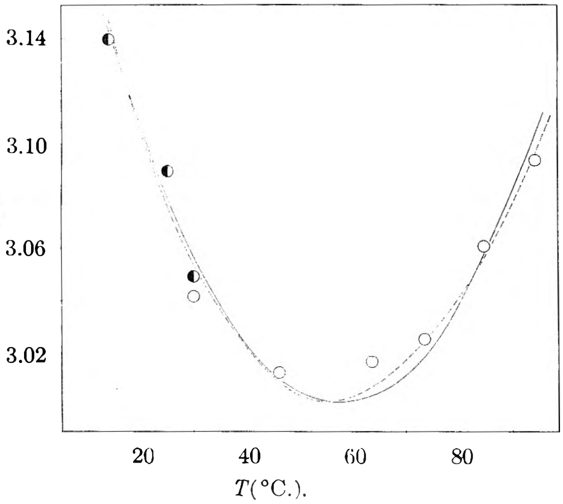

Fig. 3.—Log $K_1°$ *versus* T. The shaded points are from kinetic experiments.[31] The lines shown are calculated using equations 4′ (——) and 5′ (- - - - -).

Discussion of Results

The Temperature Coefficient of $K_1°$.—The values of $K_1°$, an *association constant*, go through a *minimum* indicating that the value of $\Delta C_p°$ for reaction 1 is positive; the reaction is endothermic at high temperatures and exothermic at low temperatures. This behavior has long been recognized for weak acids, the *dissociation constants* going through a *maximum*. Two three-parameter equations, widely used in the correlation of the weak acid dissociation constants and the temperature, have been used in the present study; these equations are

$$\log K_1° = \log K_{1\theta}° + p(T - \theta)^2 \qquad (4)^{32}$$

and

$$\log K_1° = \log K_1° + \frac{\Delta C_p°}{R}\left\{\log\frac{T}{\theta} + \frac{\theta}{2.303}\left(\frac{1}{T} - \frac{1}{\theta}\right)\right\} \qquad (5)^{6}$$

where θ is the absolute temperature at which $K_1°$ has its minimum value. Equation 4 is an empirical equation and equation 5 is derived on the assumption that $\Delta C_p°$ is independent of the temperature. The values of the sets of three parameters have been determined by the method of averages using the $K_1°$ values of Table VI.[33] Using such values of the parameters, one calculates values of $K_1°$ which have an average difference of 1.9% (equation 4) and 1.5% (equation 5) from the observed values. Both the experimental points and the calculated curves are presented in Fig. 3. The calculated values of log $K_{1\theta}°$ and θ are 3.0014 and 330.7° for equation 4 and 3.0005 and 328.7° for equation 5. The value of p in equation 4 is 7.5×10^{-5}; this value is to be compared with the value $p = 5 \times 10^{-5}$ which fits the experimental values of most acid dissociation constants very well[32]; for boric acid a value of $p = 8 \times 10^{-5}$ is a better choice.[34] The calculated value of $\Delta C_p°$ is +70 cal. deg.$^{-1}$. While considerably in excess of the value of ~40 cal. deg.$^{-1}$ observed for the reaction in which hydrogen ion associates with an anion,[6] the value is probably a reasonable one in view of the greater charge of one of the reactant ions in the chromium(III)–thiocyanate reaction. This value of $\Delta C_p°$ is related to the partial molal heat capacities of the electrolytes and the heat capacity of water

$$\Delta C_p° = C_p°(H_2O) + \bar{C}_p°\,(M^{II}\,(ClO_4)_2) - \bar{C}_p°\,(M^{III}\,(SCN)(ClO_4)_2)$$

where M^{II} stands for $Cr(OH_2)_5NCS^{++}$ and M^{III} stands for $Cr(OH_2)_6^{+++}$. Since $\bar{C}_p°$ for water is 18 cal. mole^{-1} deg.$^{-1}$, the value of $\bar{C}_p°(M^{II}(ClO_4)_2) - \bar{C}_p°(M^{III}(SCN)(ClO_4)_2) = 52$ cal. mole^{-1} deg.$^{-1}$. That this quantity is positive is not surprising in view of the trend of $\bar{C}_p°$ with charge type observed for certain electrolytes.[35]

The values of $\Delta H_1°$ and $\Delta S_1°$ at 25.0° calculated using equation 5 are −2.13 kcal. and 6.9 e.u., respectively. The value of ΔH_1^0 becomes 0.70 kcal. more positive for each 10° increase in temperature. The increment in $\Delta S°$ with temperature, which is proportional to the change in the logarithm of T, is ~+2.4 e.u. per 10° increase in temperature at 25° and is ~+1.9 e.u. per 10° increase at 95°. The value of $\Delta S°$ at 95.0° is +21.7 e.u. This increase in $\Delta S°$ with an increase of temperature, which is related to the value of $\Delta C_p°(\partial\Delta S°/\partial T = \Delta C_p^0/T)$ may be described as a consequence of the greater freedom which the *liberated* solvent mole-

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(31) C. Postmus and E. L. King, THIS JOURNAL, **59**, 1216 (1955).

(32) H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.*, **56**, 1050 (1934).

(33) For fitting equations 4 and 5 to the data, they have been rewritten as

$$\log K_1° = A + BT + CT^2 \qquad (4')$$

and

$$\log K_1° = \alpha + \beta T^{-1} + \gamma \log T \qquad (5')$$

The values of the parameters for equations 4′ and 5′ are $A = 11.1586$, $B = -0.049328$ and $C = 7.4567 \times 10^{-5}$, and $\alpha = -100.7825$, $\beta = 5019.17$ and $\gamma = 35.17$.

(34) (a) H. S. Harned and B. B. Owen, *Chem. Revs.*, **25**, 50 (1939); (b) R. W. Gurney, "Ionic Processes in Solution," McGraw–Hill Book Co., New York, N. Y., 1953, pp. 122–125.

(35) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 245–246.

cules stand to gain upon escaping from the field of the ions at higher temperatures. If the effect were exclusively this, the change of $\Delta S°$ with temperature corresponds to ~4 water molecules being set free per conversion of the two ions $Cr(OH_2)_6^{+++}$ and SCN^- into one ion $Cr(OH_2)_5NCS^{++}$. Only one of these water molecules is explicitly shown in the equation.

A comparison of the value of $\Delta S_1°$ at 25.0° with the ΔS values for the association of various trivalent cations and univalent anions[36] is of interest. In Table VII, are summarized such values.[37] It is seen that the values of ΔS are much more positive for the association of iron(III) and the monatomic anions than for the association of iron(III) or chromium(III) and the triatomic anions. One factor which may be responsible for this is the lower hydration of the polyatomic anions in which the one unit of charge is more diffuse; in addition, the polyatomic anions lose some rotational freedom in becoming associated with the cation. The observed difference in the ΔS values is probably too large to be explained by these factors alone. It is possible that the formation of the iron(III)-halide complexes is accompanied by a decrease in coördination number as suggested by Taube.[38] (The coördination number of four for iron(III) is observed in solid compounds of the formulas $MFeCl_4$ ($M = NH_4$, K, Cs) and this coördination number persists in ether solutions of $MFeCl_4$ and in solutions of iron(III) chloride in concentrated hydrochloric acid[39a,b].) A reaction

$$Fe(OH_2)_6^{+++} + X^- \rightleftharpoons Fe(OH_2)_3X^{++} + 3H_2O$$

would be expected to have an abnormally positive value of ΔS. Thus, the iron(III) complexes with azide and thiocyanate ion are assumed to form from hexaaquoiron(III) ion with no change in the coördination number for iron(III) while the halide complexes form in a reaction which involves a decrease in the coördination number for iron(III). While the first thiocyanate complexes of iron(III) and chromium(III) have very similar stabilities, the complex $FeCl^{++}$ is between 10- and 100-fold more stable than $CrCl^{++}$ (undoubtedly $Cr(OH_2)_5Cl^{++}$). A comparison of the ΔS values for the formation of AlF^{++} and FeF^{++} also suggests the change of coördination number for iron(III), it being reasonable that no change in coördination number occurs with the formation of AlF^{++} since complexes containing six fluoride ions per aluminum(III) are known.[5d,40] A change in coördination number for the central metal ion with the substitution of a more polarizable anion for a coördinated water molecule will clearly influence the stability of the complex. The varying tendencies for metal ions to exhibit more than one coördination number is intimately connected with the orbitals available for the formation of bonds, a subject which deserves and is now getting considerable attention.[8,41]

TABLE VII

ΔS VALUES FOR THE ASSOCIATION OF TRIVALENT CATIONS AND UNIVALENT ANIONS

$$M^{+3} + X^- = MX^{+2}$$

M^{+3}	X^-	ΔS_{298}
Cr^{+++}	SCN^-	+6.9
Fe^{+++}	SCN^-	+8[18]
Fe^{+++}	N_3^-	+5[36b]
Fe^{+++}	Br^-	+23[36a]
Fe^{+++}	Cl^-	+35[36a]
Fe^{+++}	F^-	+49[36b]
Al^{+++}	F^-	+32[5d]

The Acid Dissociation of Hexaquochromium(III) Ion.—The values of K_7 reported by earlier workers are comparable with the values reported here. N. Bjerrum[42] has reported the value of K_7 to be 0.2×10^{-4} and 0.9×10^{-4} at 0 and 25°, respectively. Although these values are lower than the values reported in this paper, their temperature dependence leads to a value of ΔH_7 of 9.6 kcal., in remarkable agreement with the value of 9.4 kcal. reported here.[43] The values 1.58×10^{-4} (a value relatively independent of electrolyte concentration) at 25°[44] and 7.6×10^{-5} (a value interpolated for $\Gamma = 0.068$) at 15°[45] have also been reported for K_7. Using the values of ΔH_7 and ΔS_7 (for $\Gamma = 0.068$) obtained in the present work, one calculates values of K_7 of 1.5×10^{-4} and 9×10^{-5} for 25.0 and 15.0°, respectively.

A comparison of the thermodynamic quantities for acid dissociation of hexaaquochromium(III) ion and aquoiron(III) ion (presumably hexaaquoiron(III) ion) is of interest. The values of ΔH and ΔS for the iron(III) reaction analogous to reaction 7 are +12.5 kcal. and +30 e.u., respectively.[36,46] Hexaaquoiron(III) ion has an acid dissociation constant which is approximately tenfold larger than that of hexaaquochromium(III) ion despite the fact that the iron(III) reaction is more endothermic.[47,48] The more positive value of ΔS for the iron-

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(36) (a) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942); (b) N. Uri, *Chem. Revs.*, **50**, 391 (1952).

(37) Since the values of ΔS for the iron(III) reactions depend, in general, upon the assumption that the molar absorbancy indices of individual species are independent of temperature, they are subject to some uncertainty.

(38) H. Taube, THIS JOURNAL, **58**, 528 (1954).

(39) (a) H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952); (b) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(40) C. Brosset and J. Orring, *Svensk Kem. Tid.*, **55**, 101 (1943).

(41) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954).

(42) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

(43) The value of ΔH_7 calculated from the standard heats of formation of $Cr(OH_2)_6^{+++}$ and $Cr(OH_2)_5OH^{++}$ as reported in Circular 500 of the National Bureau of Standards, is quite different, 14.3 kcal.; this value is almost certainly in error.

(44) A. B. Lamb and G. R. Fonda, *J. Am. Chem. Soc.*, **43**, 1155 (1921).

(45) J. N. Brönsted and C. V. King, *Z. physik Chem.*, **130**, 699 (1927).

(46) W. C. Bray and A. V. Hershey, *J. Am. Chem. Soc.*, **56**, 1889 (1934).

(47) There is an uncertainty in the value of ΔH (and therefore ΔS) for the iron(III) reaction because of the dimerization to form $Fe_2(OH)_2^{++++}$.[21e,i,j] While this species was present at relatively low concentrations in the solutions studied by Rabinowitch and Stockmayer,[36a] it could contribute significantly to the light absorption and, therefore, to the temperature coefficient of the light absorption which was taken as a measure of ΔH. The value of ΔH obtained by Rabinowitch and Stockmayer agrees well with the value obtained by Bray and Hershey[46] using data obtained by an entirely different experimental method from solutions which in no case contained more than 7% of the iron(III) as the dimeric species and in general contained much less than this. (This calculation has been made using the dimerization equilibrium quotient presented by Hedstrom.[21e])

(48) (NOTE ADDED IN PROOF)—In the paper by L. G. Hepler, J. W. Kury and Z. Z. Hugus (THIS JOURNAL, **58**, 26 (1954)) are cited values of the acid dissociation quotient for aquoiron(III) ion at 15°, 25° and

(III) reaction, which finds no simple explanation if the iron(III) reaction were exactly analogous to reaction 7, may be explained in the same terms as employed in the last section; a decrease in coördination number upon acid dissociation

$$Fe(OH_2)_6^{+++} = Fe(OH_2)_3OH^{++} + H^+ + 2H_2O$$

rationalizes both the more positive value of ΔH and the more positive value of ΔS for the iron(III) reaction.

The Stability of Outer-sphere Complexes.—It appears that "outer-sphere" complexes of hexaaquochromium(III) ion and a particular anion are considerably less stable than are corresponding "outer-sphere" complexes of hexaammine-cobalt-(III) ion. Extrapolating various measured association quotients to zero electrolyte concentration by equation 3 using the same a value as was valid for K_1, one finds $K_{01}°$ values at 25°: $Cr(OH_2)_6{\cdot}SCN^{++}$, 7; $Cr(OH_2)_6{\cdot}Cl^{++}$, 13[19b]; $Co(NH_3)_6{\cdot}N_3^{++}$, 58[5b]; and $Co(NH_3)_6{\cdot}Cl^{++}$, 210.[5b] The greater acidity of water compared to ammonia might lead one to expect the peripheral hydrogens in the aquocation to be more positive than in the amine complex and thus attract anions more strongly. Such is not the case. The probable explanation for this is to be found in a consideration of the structures of these species in more detail than simply consideration of the positive nature of the individual hydrogen atoms. While the periphery of the amine complex consists of eighteen hydrogen atoms, all positive in nature, the periphery of the hexaaquocation consists of 12 hydrogen atoms, all positive, *and* six regions of high electron density, the six unshared electron pairs. An anion is, therefore, much less strongly attracted by the aquocation since it cannot be in close proximity to the positive hydrogen atoms without at the same time being close to a localization of negative charge.

35° in solutions of $\Gamma = 1.00$ determined by R. E. Connick, *et al.* The value of ΔH obtained from these measurements is +8.8 kcal, a value decidedly lower than earlier values.[36,46] The value of ΔS obtained from this value of ΔH and the equilibrium quotient value at 25° is 17 e.u. This value corresponds more nearly to the value of ΔS_7 and thus there may be little necessity for finding an explanation of the difference between the iron(III) and chromium(III) reactions.

THE RATE LAW FOR THE FORWARD AND REVERSE OF THE REACTION $Cr(OH_2)_6^{+++} + SCN^- = Cr(OH_2)_5NCS^{++} + H_2O$[1-3]

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Received May 18, 1955

Although the reaction $Cr(OH_2)_6^{+++} + SCN^- \rightleftarrows Cr(OH_2)_5NCS^{++} + H_2O$ proceeds very slowly at room temperature, it is possible to evaluate the rates of both the forward and reverse reactions during the few tenths of a per cent. of reaction. Such is possible using spectrophotometric measurements because $CrNCS^{++}$ is very opaque compared to Cr^{+++} in the ultraviolet and $FeNCS^{++}$, which rapidly forms with free SCN^-, is very opaque compared to Cr^{+++} and $CrNCS^{++}$ in the visible region of the spectrum. Measurements upon the forward reaction demonstrate that the rate law is $d(CrNCS^{++})/dt = (Cr^{+++})(SCN^-)\{k_1 + k_2(H^+)^{-1} + k_3(H^+)^{-2}\}$. The combination of this with the equation for the net reaction leads to the rate law for the reverse reaction $+d(SCN^-)/dt = (CrNCS^{++})\{k_{-1} + k_{-2}(H^+)^{-1} + k_{-3}(H^+)^{-2}\}$ which was confirmed by the direct measurements to the extent of a demonstration of first-order dependence upon $CrNCS^{++}$ and the evaluation of k_{-1}. The rate law terms $k_2(Cr^{+++})(SCN^-)(H^+)^{-1}$ and $k_3(Cr^{+++})(SCN^-)(H^+)^{-2}$ correspond to reaction paths with activated complexes containing one and two hydroxide ions. The activated complexes which involve one and two hydroxide ions are more important than are the chromium(III) species containing one and two hydroxide ions despite the less favorable electrostatic attraction between the reactants in these paths. The first-order dependence of the reaction rate upon the thiocyanate ion concentration *does not* rule out reaction mechanisms with activated complexes with coördination number six. Measurements of the rate of the forward and reverse reactions at 14.0, 25.1 and 30.0° allow the evaluation of the equilibrium quotient for the reaction at these temperatures.

In the preceding paper,[5] the equilibrium quotient for the reaction

$$Cr(OH_2)_6^{+++} + SCN^- = Cr(OH_2)_5NCS^{++} + H_2O \quad \text{(Reaction 1)}$$

has been determined as a function of the electrolyte concentration at six temperatures in the range 30.0–94.6°. In the present paper, the results of kinetic studies upon this reaction at three temperatures in the range 14.0–30.0° will be presented. Both the forward and reverse reactions have been studied. The studies had two purposes; it was desired to: (a) establish the rate law which yields the composition of the activated complex(es), and (b) calculate the value of the equilibrium constant for reaction 1 from the rate constants for the forward and reverse reactions. This provides a mutual check of the rate and direct equilibrium studies at 30°, where both types of data were obtained and, in addition, extends the temperature range over which values of $K_1°$, the equilibrium constant for reaction 1, are known to temperatures at which the direct equilibration requires extraordinary amounts of time.

The system has proved an ideal one to study in spite of the very low rate of reaction because an accurate evaluation of the rates of both the forward and reverse reactions can be obtained while the respective reactions are proceeding less than 1% toward equilibrium. This makes it possible to perform the experiments in a reasonable time while

[1] Taken in part from the Ph.D. Thesis of Clarence Postmus, University of Wisconsin, 1954.

[2] Supported in part by grants from the U. S. Atomic Energy Commission and the Research Committee of the Graduate School, University of Wisconsin.

[3] Presented before the 127th National Meeting of the American Chemical Society at Cincinnati, Ohio, April 4, 1955.

[4] U. S. Rubber Company Fellow, 1953–1954; present address, Argonne National Laboratory, Lemont, Illinois.

[5] C. Postmus and E. L. King, THIS JOURNAL, 59, 1208 (1955).

realizing experimental conditions which make the rate of the opposing reaction negligible.

Measurements upon solutions in which the forward reaction is occurring demonstrate that the rate law is[6]

$$\frac{d(\mathrm{CrNCS^{++}})}{dt} = (\mathrm{Cr^{+++}})(\mathrm{SCN^-})\{k_1 + k_2(\mathrm{H^+})^{-1} + k_3(\mathrm{H^+})^{-2}\} \quad (1)$$

The combination of this with the equation for the net reaction leads to the rate law for the reverse reaction

$$+\frac{d(\mathrm{SCN^-})}{dt} = (\mathrm{CrNCS^{++}})\{k_{-1} + k_{-2}(\mathrm{H^+})^{-1} + k_{-3}(\mathrm{H^+})^{-2}\} \quad (2)$$

which was confirmed experimentally to the extent of showing a first-order dependence of the rate upon $\mathrm{CrNCS^{++}}$. The measurements of the reverse rate were carried out at acidities which allowed the evaluation of k_{-1} but did not allow the evaluation of k_{-2} and k_{-3}.

Experimental

Equipment and Reagents.—In general, the equipment and reagents were the same as used in the equilibrium measurements.[5] There were, however, some changes which will be described.

Since the rate of the forward reaction was, in some cases, followed by using a particular portion of solution in the spectrophotometer cell which was kept in the cell housing throughout the run, more precise temperature control of the cell housing was needed than in the equilibrium studies. Installation of a more efficient pump with which to circulate the thermostat water through the cell holder resulted in temperature control to ±0.01° which is comparable to the control in the thermostat.

In the study of the reverse reaction, solutions containing $\mathrm{CrNCS^{++}}$ at a concentration greater than corresponds to equilibrium were required. One of the simplest ways of realizing such a solution was the dilution of a concentrated solution in which the equilibrium in reaction 1 had been established. It was found, however, that the rate of appearance of thiocyanate ion in such a solution was too high (see discussion below) and it was concluded that the side reactions which are responsible for the disappearance of thiocyanate[5] in the equilibration produces a substance which catalyzes the reaction. Ion-exchange techniques which have been used to produce relatively small amounts of the separated complexes[5,7] have proved effective in the preparation of relatively large batches of perchloric acid solutions of $\mathrm{CrNCS^{++}}$. Use of the light colored cation exchange resin Dowex 50-W has proved advantageous; one can readily see what is occurring since the chromium(III) species are purple in color. The complex $\mathrm{Cr(NCS)_2^+}$ was removed by washing of the column with 0.15 *M* perchloric acid prior to the elution of $\mathrm{CrNCS^{++}}$ with 1.0 *M* perchloric acid. This washing also removed the interfering decomposition products since the rate coefficient k_{-1} of the rate law for the reverse reaction of $\mathrm{CrNCS^{++}}$ which was prepared in this manner had a lower value; this lower value of k_{-1}, when coupled with the rate coefficient k_1 of the rate law for the forward reaction, yielded a value of the equilibrium quotient which was in agreement with the directly determined value.[5] (This seems a reasonable criterion for the validity of the rate measurements.)

Details of Experimental Procedure.—In the study of the forward reaction, solutions containing chromium(III) perchlorate, sodium thiocyanate and perchloric acid were prepared from the appropriate stock solutions. A solution was placed in 2, 5 or 10 cm. cylindrical type cell and the absorbancy was measured as a function of time in the Beckman Model DU Spectrophotometer. An extremely small change in the concentration of $\mathrm{CrNCS^{++}}$ can be measured by evaluating the absorbancy of the solution at 292 mμ where $\mathrm{CrNCS^{++}}$ has a molar absorbancy index of 2.90×10^3. At this wave length, hexaaquochromium(III) ion and thiocyanate ion are essentially transparent. Thus, in a solution with a concentration of hexaaquochromium(III) ion of 0.01 *M*, 0.1% conversion of this to $\mathrm{CrNCS^{++}}$ results in a change in absorbancy of 0.29 (per ten cm. of light path), making such measurements with a ten cm. cell yield rather precise data during a small extent of reaction. Because the extent of reaction is so low (<1%), a plot of absorbancy *versus* time gives a straight line. The slope of the line is proportional to the rate of appearance of $\mathrm{CrNCS^{++}}$, $\{\Delta(\mathrm{CrNCS^{++}})/\Delta \text{ time}\}$.

In the study of the reverse reaction, measurements of very low concentrations of thiocyanate ion in the presence of relatively large concentrations of $\mathrm{CrNCS^{++}}$ in aliquots of the reaction mixture were made by the same method as was used in determining the concentration of thiocyanate ion in the study of the equilibrium.[5] At the iron(III) concentration employed (0.010 *M*), a change in absorbancy of 0.10 (per ten cm. of light path) corresponds to an increase in the concentration of thiocyanate ion of 3×10^{-6} molar; this makes possible an accurate evaluation of the rate during the aquation of less than 1% of the $\mathrm{CrNCS^{++}}$ which is present. Thus, the reverse reaction rate can also be determined under conditions which lead to a constant rate in each experiment.

In the runs at 14.0°, the aliquots of reaction mixture were allowed to warm up to room temperature and measured as before. A standardized procedure was used such that the measurements were made at the same interval of time after removal of each aliquot from the 14.0° thermostat. Thus, the change of the absorbancy per unit time is that which corresponds to 14.0°. The slopes of the lines for the 14.0° runs were determined by the method of averages while in the other cases the best straight line was drawn after visual inspection.

The Rate Law of the Forward Reaction.—Extensive measurements at 25.1° in media with Γ[8] = 0.600 have been made for the purpose of establishing the rate law. A summary of the concentration conditions employed is given in Table I including the calculated quantities which demonstrate that the reaction is first order in hexaaquochromium(III) ion and first order in thiocyanate ion. Actually, the scattering of the values of $\{Rate/(\mathrm{Cr^{+++}})(\mathrm{SCN^-})\}$ at each particular acidity is not random. The orders of the reaction with respect to both hexaaquochromium(III) ion and thiocyanate ion which best fit the data are slightly greater than first, with the deviation from first-order dependence being largest at the lowest acidities. The deviation from unity of the order with respect to either reactant is in the opposite direction from that which would arise if an outer-sphere complex (*i.e.*, an ion-pair) involving hexaaquochromium(III) ion and thiocyanate ion formed to an appreciable extent. (This argument assumes that the activated complex contains one chromium(III) and one thiocyanate over the entire concentration range.) The cause of the slight deviation of the order from unity may be due to the occurrence of the relatively slow side reaction which has been shown to produce catalysts for the reaction. In addition, medium changes necessarily occur as the concentrations are varied at constant ional concentration.

The increase in the value of $\{Rate/(\mathrm{Cr^{+++}})(\mathrm{SCN^-})\}$ with a decrease in acidity is due to the presence of a term or terms in the rate law which involve the hydrogen ion concentration raised to a negative power. In order to describe the dependence of the rate upon the concentration of hydrogen ion, it is necessary to use the three term rate law given as equation 1. Values of the rate coefficients which yield calculated values of $\{Rate/(\mathrm{Cr^{+++}})(\mathrm{SCN^-})\}$ in close agreement with the average values observed at each acidity are

$$k_1 = 1.92 \times 10^{-6} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$
$$k_2 = 7.2 \times 10^{-9} \text{ sec.}^{-1}$$
$$k_3 = 4.2 \times 10^{-12} \text{ mole l.}^{-1} \text{ sec.}^{-1}$$

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[6] As was true in the preceding paper, the water molecules in the first coördination sphere of chromium(III) species will generally not be shown. A formula in parentheses stands for the molar concentration of the indicated species. The *k*'s of the rate equations, which are valid for a particular medium under consideration, will be called *rate coefficients;* the term *rate constant,* which will be designated by a zero superscript (*i.e.*, k^0), will be reserved for the values extrapolated to infinite dilution.

[7] E. L. King and E. B. Dismukes, *J. Am. Chem. Soc.*, **74**, 1674 (1952).

[8] Γ, the ional concentration, is defined $\Gamma = \Sigma C_i Z_i^2$, where C_i is the molar concentration of an ion and Z_i, its charge. This quantity differs from μ, the ionic strength, by the factor 2 as well as by the concentration scale used.

TABLE I

EXPERIMENTS AT 25.1° USED IN ESTABLISHMENT OF THE FORM OF THE RATE LAW[a]

$\Gamma = 0.600^{b}$; $(HClO_4) + (LiClO_4) = 0.100$.

(H^+) × 10^2	Range of concn. $(Cr(ClO_4)_3)$ × 10^3	$(NaSCN)$ × 10^3	No. of exp.	$\frac{Rate}{(Cr^{+++})(SCN^-)}$ × $10^{6\,c}$ Range of values	Av.	Av. % dev.[d]	Calcd.[e]
10.0	6.0–24.0	1.04–52	5	1.95–2.08	2.02	1.9	1.99
1.02	1.2–24.0	1.04–52	6	2.65–2.78	2.69	1.8	2.67
0.298	6.0	7.3	1	4.75	4.75	...	4.81
.200	9.6	1.04–105	3	6.45–6.73	6.61	1.7	6.58
.150	6.0	1.04–105	3	8.23–9.45	8.80	7.9	8.6
.100	1.2–3.6	1.04–105	5	12.6–15.3	14.0	7.0	13.3

[a] In the calculation of the concentrations of Cr^{+++} and H^+, account is taken of the chromium(III) which is present as $CrOH^{++}$. [b] Sodium perchlorate added to give this ional concentration. [c] The units of rate are moles $l.^{-1}$ $sec.^{-1}$. [d] This is the average % deviation of the individual values from the average value. [e] Calculated using the values of k_1, k_2 and k_3 given in the text.

The average difference between the average values of $\{Rate/Cr^{+++})(SCN^-)\}$ observed at each acidity and the calculated value using these parameters is 1.8%; the calculated values are also presented in Table I.

The Evaluation of k_1 and k_2 as a Function of the Electrolyte Concentration at 25.1°.—A detailed study of the rate of the forward reaction as a function of the electrolyte concentration has been made at 25.1°. Measurements at five different concentrations of hydrogen ion allow the accurate evaluation of k_1 and k_2 and an estimate of k_3 to be made at each of seven electrolyte concentrations. Four of the acidities ($(H^+) = 0.0200$, 0.0100, 0.00667 and 0.00500 M) were high enough to make the terms involving k_1 and k_2 of dominant importance. A lower acidity ($(H^+) = 0.00150\ M$) was studied at each electrolyte concentration in order to correct the rate observed at the higher acidities for a small contribution by the path corresponding to the term $\{k_3(Cr^{+++})(SCN^-)(H^+)^{-2}\}$ in the rate law. From 2–5% of the observed rate at the next higher acidity (0.00500 M hydrogen ion) can be attributed to this path. A plot of $\{Rate/(Cr^{+++})(SCN^-) - k_3(H^+)^{-2}\}$ *versus* $1/(H^+)$ gives a straight line, the slope of which is k_2 and the intercept of which is k_1; an example of such a plot is given in Fig. 1. An approximation method was used to obtain a consistent set of values of the rate coefficients k_1, k_2 and k_3. In Table II are given the values of k_1 and k_2 as well as a summary of the concentration conditions existing at each electrolyte concentration.

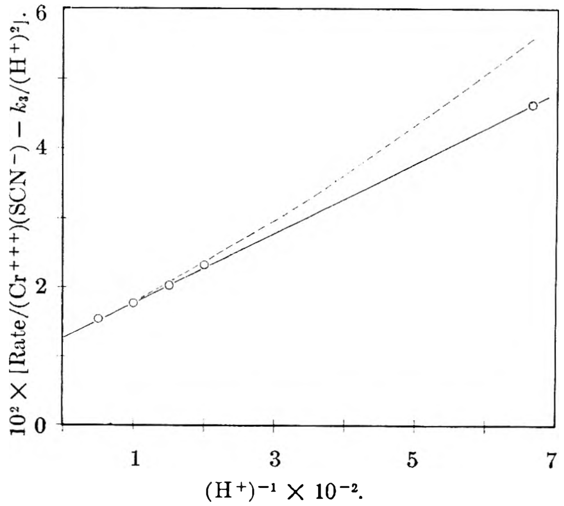

Fig. 1.—The results of a series of experiments at 25.1°, $\Gamma = 0.16$. The experimental values of Rate/(Cr^{+++})-(SCN^-) uncorrected by the term $k_3(H^+)^2$ fall on the dashed line. The circles and the solid line correspond to the final approximation yielding values of k_1 and k_2 presented in Table II. (The unit of time in the values of R and k_3 is hours.)

TABLE II

THE EVALUATION OF k_1 AND k_2 AS A FUNCTION OF THE ELECTROLYTE CONCENTRATION

$T = 25.1°$, $(HClO_4) + (LiClO_4) = 0.0200\ M$

Γ	Concn. (in moles/l.) $(Cr(ClO_4)_3)$ × 10^3	$(NaSCN)$ × 10^3	$(NaClO_4)$	Rate coefficients[a, b] k_1 × 10^6	k_2 × 10^8
0.0702	1.20	7.97	...	4.28	1.96
.110	4.20	9.96	...	3.86	1.84
.160	6.00	9.96	0.014	3.53	1.41
.210	6.00	9.96	.039	3.17	1.30
.375	6.00	9.96	.122	2.42	0.98
.640	6.00	9.96	.254	2.08	0.645
1.00	6.00	9.96	.435	1.79	0.54

[a] The units for the rate coefficients are k_1, l. $moles^{-1}$ $sec.^{-1}$; k_2, $sec.^{-1}$. [b] The range of values of k_3 is 3.1–7.2 × 10^{-12} moles $l.^{-1}$ $sec.^{-1}$.

In view of the success which was realized in relating the equilibrium quotient values and the ional concentration by means of an equation of the form of the Debye–Hückel equation (equation 3 of reference 5), a similar equation

$$\log k = \log k° + \frac{\Delta(Z^2)B\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \qquad (3)$$

has been used in correlating the rate coefficients with electrolyte concentration. In using this equation for the correlation of the rate coefficients with electrolyte concentration, one assumes the Brönsted rate expression to be valid. In this equation, $\Delta(Z^2)$ pertains to the over-all conversion of the reactants which appear in the rate equation into the activated complexes. Such over-all conversions for the two paths presently of concern are

$$Cr(OH_2)_6{}^{+++} + SCN^- = \{Cr(OH_2)_{6\pm n}\cdot SCN^{++}\}^{\ddagger} \mp nH_2O$$

and

$$Cr(OH_2)_6{}^{+++} + SCN^- = \{Cr(OH_2)_{5\pm m}(OH)\cdot SCN^{+}\}^{\ddagger} + H^+ \mp mH_2O$$

for which the $\Delta(Z^2)$ values are −6 and −8, respectively. It is to be noted that *no assumptions regarding mechanism are made* in the calculation of $\Delta(Z^2)$; *the kinetic salt effect is determined by the rate law and not by the mechanism.*[9] Two parameters, k^0, the rate constant (*i.e.*, the rate coefficient extrapolated to zero electrolyte concentration) and A are used in fitting the equation to the data. In selecting the value of $k°_1$, a method analogous to that used in the equilibrium studies[5] is suitable. It was found that a value of A of 1.75 gave the lowest average difference (2.2%) between the seven individual values of $k°_1$ and the average value of $k°_1$. This average difference is lower than that associated with any other value of A including $A = 1.59$ which led to an average difference of 3.5%. The comparison with the fit obtained using $A = 1.59$ is worthy of note since this is the A value which would be expected to correlate K_1 as f(Γ) at 25.1°.[5] In Fig. 2 are shown plotted the observed values of log k_1 *versus* the function of the ional concentration {6

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[9] I. Weil and J. C. Morris, *J. Am. Chem. Soc.*, **71**, 1664 (1949).

$(0.358)\sqrt{\Gamma}/(1 + A\sqrt{\Gamma})\}$ for both values of A, 1.75 and 1.59. The average $k°_1$ values using A = 1.75 and 1.59 are 1.08×10^{-5} and 1.16×10^{-5} l. mole^{-1} sec.$^{-1}$, respectively. The fact that different values of A give the best correlation of K_1 and k_1 with Γ may be due to the fact that different electrolytes are the principal contributors to the ional concentration in the two cases.[10] It must be noted, however, that K_1 has approximately the same value at a particular value of the ional concentration whether the principal electrolyte is chromium(III) perchlorate or sodium perchlorate.[5] In view of these mild contradictions, an average of the two values, 1.12×10^{-5} l. mole^{-1} sec^{-1}, is selected as the "best" value for $k_1°$.

Because of the relatively larger uncertainty in the values of k_2, the evaluation of $k°_2$ is correspondingly less certain. The results can be summarized by reporting the average values of $k°_2$ arising from different assumed values of A and the associated average difference between the seven calculated values of $k°_2$ and the average value. These quantities, in the order A, $k°_2$ (in sec.$^{-1}$) and the average difference (in %), are: 1.75, 6.55×10^{-9}, 6.8%; 1.59, 7.14×10^{-9}, 5.3%; 1.45, 7.72×10^{-9}, 5.2%; and 1.30, 8.5×10^{-9}, 6.6%. The corresponding calculations at A = 1.90 and 1.15 lead to $k°_2$ values with decided trends. It appears that the "best" value of $k°_2$ is between 7.1×10^{-9} and 7.7×10^{-9} sec.$^{-1}$. The plot of log k_2 *versus* $\{8\ (0.358)\sqrt{\Gamma}/(1 + 1.59\sqrt{\Gamma})\}$ is also present in Fig. 2. The electrolyte concentration dependences of k_1 and k_2 are seen to be consistent with the Brönsted-Debye and Hückel equation.

The Evaluation of the Rate Constants as a Function of Temperature.—At both 14.0 and 30.0°, single series of experiments in which the hydrogen ion concentration was varied were run at $\Gamma = 0.160$. These series of experiments, which were like those described in the preceding section, allowed the evaluation of k_1, k_2 and k_3. The evaluation of $k°_1$ is possible using the values of k_1 obtained at the single electrolyte concentration studied if one is willing to assume that a, the "distance of closest approach," is independent of temperature; this has been shown to be approximately true in the equilibrium studies.[5] A summary of the experimentally determined values of k_1 and k_2 at $\Gamma = 0.160$ and the calculated values of $k°_1$ are given in Table III.

TABLE III

VALUES OF k_1 AND k_2 AS A FUNCTION OF TEMPERATURE

	Path I Rate = $k_1(Cr^{+++})(SCN^-)$ $\Gamma = 0.160$	 $\Gamma = 0.000^c$	Path II Rate = $k_2(Cr^{+++})$ $(SCN^-)(H^+)^{-1}$ $\Gamma = 0.160$
k^a at 14.0°	6.3×10^{-7}	2.02×10^{-6}	1.72×10^{-9}
25.1°	3.53×10^{-6}	1.12×10^{-5}	1.41×10^{-8}
30.0°	6.7×10^{-6}	2.21×10^{-5}	3.64×10^{-8}
E (kcal.)	25.7	26.0	32.8
$(PZ)^b$	2.32×10^{13}	1.28×10^{14}	1.66×10^{16}

[a] The units of k_1 and k_2 are l. mole^{-1} sec.$^{-1}$, and sec.$^{-1}$, respectively. [b] The values of PZ are defined by the equation $k = PZe^{-E/RT}$; the dimensions of PZ are the same as those given in (a) for k. [c] The values of $k°$ listed are the average of two values, the value calculated using a = 6.83 Å. (which is calculated from A = 1.59 at 25.1°) and the value calculated using a = 7.53 Å. (which is calculated from Å. = 1.75 at 25.1°).

The values of $k°_1$ and k_1 and k_2 at $\Gamma = 0.160$ at the three temperatures have been treated by the method of least squares to yield experimental energies of activation $E°_1$, E_1 and E_2 defined by the equation $\ln k = \ln PZ + E/RT$. These experimental energies of activation correspond to the process of conversion of the reactants which appear in the rate equation (*i.e.*, $Cr(OH_2)_6^{+++}$ and SCN^-), into the activated complexes; $Cr(OH_2)_{6\pm n}\cdot SCN^{++}$ and $Cr(OH_2)_{5\pm m}(OH)\cdot SCN^+$, and are not uniquely identifiable as being associated with a single kinetic step.

The values of k_3, for which little accuracy can be claimed, are worth mentioning, however. At $\Gamma = 0.160$, the values of k_3 at 14.0, 25.1 and 30.0° are 1.3×10^{-13}, 5.8×10^{-12} and 1.8×10^{-11} molel .$^{-1}$ sec.$^{-1}$, respectively. These values lead to an experimental activation energy of 54 kcal. for the path corresponding to the term $k_3(Cr^{+++})(SCN^-)\cdot(H^+)^{-2}$ and a value of 1.9×10^{28} mole l.$^{-1}$ sec.$^{-1}$ for PZ.

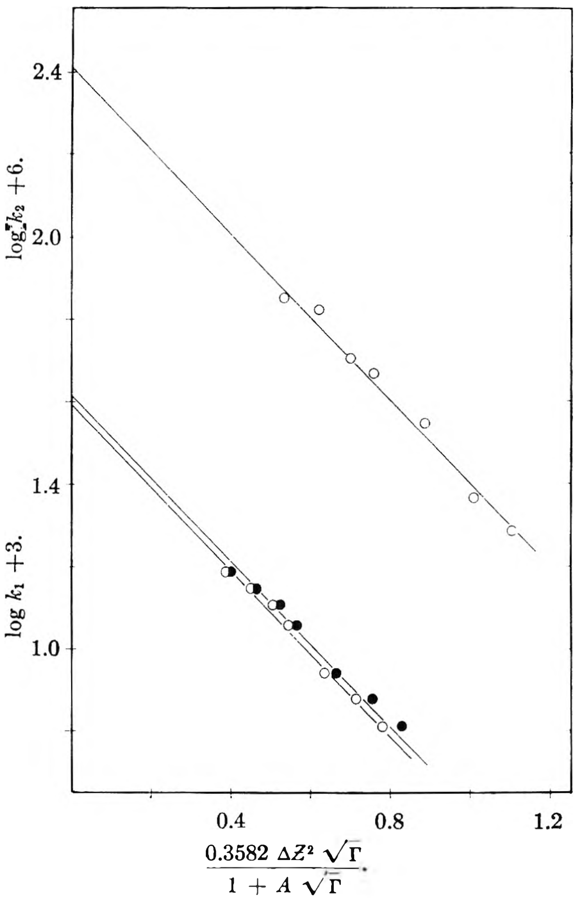

Fig. 2.—The dependence of k_1 and k_2 upon the electrolyte concentration (25.1°). For k_2, $\Delta Z^2 = -8$, A = 1.59. For k_1, $\Delta Z^2 = -6$, (○) A = 1.75, (●) A = 1.59. (The unit of time in the values of k_1 and k_2 is hours.)

Using the values of PZ and E reported in Table III and in the preceding paragraph, one calculates values of $k°_1$, k_1 ($\Gamma = 0.16$), k_2 ($\Gamma = 0.16$) and k_3 ($\Gamma = 0.16$) at the three temperatures which agree with the observed values with average differences of 2.5, 2.6, 2.1 and 15%, respectively.

The Rate of the Reverse Reaction.—The rate of appearance of thiocyanate ion has been followed in eight solutions which initially contained $Cr(OH_2)_5NCS^{++}$ as the only chromium(III)—or thiocyanate-containing species. In these solutions, the reaction which occurs is

$$H_2O + Cr(OH_2)_5NCS^{++} = Cr(OH_2)_6^{+++} + SCN^- \quad \text{(Reaction 1, reverse)}$$

The data presented in Table IV demonstrate that (1) the reaction is first order in $CrNCS^{++}$, (2) the rate of the reaction is independent of the concentration of hydrogen ion for $(H^+) > 0.05$, and (3) the reaction rate shows no significant electrolyte effect. The rate law for the reverse reaction is

$$\frac{d(SCN^-)}{dt} = k_r(CrNCS^{++}) \qquad (4)$$

A comparison of this rate law with that expected (equation 2) identifies k_r as k_{-1} of the more complete rate law. The terms involving k_{-2} and k_{-3} were not detected because the acidities of the solutions which were studied were too high.

A reaction of this type, with ΔZ^2 of activation equal to zero, would be expected to have but a slight electrolyte effect and it appears to be so small, in fact, that the rate coefficient k_{-1} observed at these finite electrolyte concentrations can be equated to $k°_{-1}$, the corresponding rate constant at zero electrolyte concentration.

The treatment of the values of $k°_{-1}$ as a function of the temperature by the method of least squares leads to an ex-

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[10] W. E. Harty and G. K. Rollefson, *J. Am. Chem. Soc.*, **76**, 4811 (1954).

TABLE IV

THE RATE OF THE REVERSE REACTION

T (°C.)	Γ	(CrNCS^{++}) × 10^3	(HClO$_4$)	(MClO$_4$)	% aquation[c]	$\left\{\frac{\Delta(\text{SCN}^-)}{\Delta t}\right\}^d$ × 10^{11}	k_r[e] × 10^9
14.0	0.53	14.4	0.25	...	0.07	2.14	1.47
	2.0	14.4	1.0	...	.07	2.08	1.45
25.1	0.32	3.17	0.050	0.100[a]	.16	2.94	9.30[f]
	0.32	3.17	.150	...	.15	2.84	8.95
	0.34	6.35	.150	...	.14	5.80	9.10
	0.67	6.35	.150	0.168[b]	.09	5.83	9.20
	1.0[illegible]	6.35	.150	0.335[b]	.12	5.83	9.18
30.0	0.32	3.17	.150	...	.20	6.23	19.7

[a] LiClO$_4$. [b] NaClO$_4$. [c] This is the % aquation occurring during the duration of an experiment. Between six and nine points were taken per experiment. [d] $\Delta(\text{SCN}^-)/\Delta t$ in moles l.$^{-1}$ sec.$^{-1}$ [e] k_r in sec.$^{-1}$ [f] At this acidity, a calculated 7.7% of the reaction is going by the path with the activated complex containing one hydroxide ion.

perimental activation energy $E°_{-1}$ of 28.1 kcal. and a PZ value of 3.78×10^{12} sec.$^{-1}$. The values of $k°_{-1}$ calculated using these values of $E°_{-1}$ and PZ agree with the observed values with an average difference of 0.2%.

Discussion

The dependence of the rate of the forward reaction upon the concentration of hydrogen ion requires a three-term rate law, equation 1. Each term corresponds to an independent reaction path and the form of each term indicates the composition of the activated complex for the reaction *via* that path. The three activated complexes for reaction 1 have zero, one, and two hydrogen ions *fewer* than has chromium(III) in that form, the concentration of which appears in the rate equation, $Cr(OH_2)_6^{+++}$. Thus, the activated complexes have the compositions represented by the formulas

$$Cr(OH_2)_{6\pm n}SCN^{++},\ Cr(OH_2)_{5\pm m}(OH)SCN^{+} \text{ and } Cr(OH_3)_{4\pm p}(OH)_2SCN$$

The rate law goes no further than this in establishing the mechanism of the reaction. The uncertainty in the number of water molecules in the activated complexes is a consequence of the impossibility of establishing the order of the reaction with respect to the solvent, water, which is at approximately constant activity. The formation of the activated complexes containing hydroxide ion (*i.e.*, containing fewer hydrogen ions than $Cr(OH_2)_6^{+++}$) undoubtedly occurs as the result of the acid dissociation reactions

$$Cr(OH_2)_6^{+++} \rightleftarrows Cr(OH_2)_5OH^{++} + H^+ \quad \text{(Reaction 7)}$$

and

$$Cr(OH_2)_5OH^{++} \rightleftarrows Cr(CH_2)_4(OH)_2^{+} + H^+ \quad \text{(Reaction 8)}$$

which precede the rate-determining steps. From the values of k_1, k_2 and k_3, one can calculate the fraction of the reaction going by each of the reaction paths as a function of the acidity. Such values are summarized in Table V. For comparison, the fraction of the chromium(III) which is present as $Cr(OH_2)_5OH^{++}$ is presented in the footnote; the fraction present as $Cr(OH_2)_4(OH)_2^{+}$ is assumed to be negligible. It is seen that the *activated complexes* involving one and two hydroxide ions are of much greater importance than are the *species* which contain one and two hydroxide ions. The reaction system, thus, goes out of its way to react by the paths involving activated complexes with one and two hydroxide ions despite the less favorable electrostatic interaction in such paths. That the same is true for the reaction of chromium(III) and chloride ion follows from the rate law which has been found for the aquation of $Cr(OH_2)_4Cl_2^{+}$.[11]

TABLE V

PERCENTAGE CONTRIBUTION BY THE THREE PATHS TO THE TOTAL REACTION RATE[a]

$T = 25.1°$; $\Gamma = 0.600$.

	(H$^+$)		
Activated complex	0.10	0.010	0.0010
$Cr(OH_2)_{6\pm n}\cdot SCN^{++}$	96.4	71.5	14.4
$Cr(OH_2)_{5\pm m}(OH)\cdot SCN^{+}$	3.6	27.0	54.3
$Cr(OH_2)_{4\pm p}(OH)_2\cdot SCN$	...	1.5	31.3

[a] For comparison, the fraction of the chromium(III) not associated with thiocyanate which is present as CrOH^{++} is 0.1, 1.4 and 14% at 0.10, 0.010 and 0.0010 molar hydrogen ion.

The rationalization of the greater importance of the path with an activated complex containing one hydroxide ion compared to the path with activated complex containing no hydroxide ions and, for that matter, the details of the mechanism corresponding to either path do not follow in a simple way from the present kinetic data. It is worthwhile, however, to outline the two probable mechanisms and discuss the relevance of the present data to settling the question of mechanism. The two possible classes of mechanisms are those with activated complexes of coördination number *seven* for chromium(III) and those with activated complexes of coördination number *six*[12a,b]; the first of these is the S$_N$2 mechanism while the second, although resembling an S$_N$1 mechanism, is not really an S$_N$1 mechanism since the rate-determining step is *not* the unimolecular step. For the present reaction, these are as follows.

Activated Complex of Coördination Number 7 (S$_N$2 mechanism):

$$Cr(OH_2)_{6-j}(OH)_j^{+3-j} + SCN^- \rightleftarrows Cr(OH_2)_{5-j}(OH)_jNCS^{+2-j} + H_2O$$

Activated Complex of Coordination Number 6:

$$Cr(OH_2)_{6-j}(OH)_j^{+3-j} \rightleftarrows Cr(OH_2)_{5-j}(OH)_j^{+3-j} + H_2O$$

$$Cr(OH_2)_{5-j}(OH)_j^{+3-j} + SCN^- \rightleftarrows Cr(OH_2)_{5-j}(OH)_jNCS^{+2-j}$$

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(11) (a) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); (b) R. E. Hamm and C. M. Shull, *J. Am. Chem. Soc.*, **73**, 1240 (1951).

(12) (a) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951); (b) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

The first-order dependence of the reaction rate upon the concentration of thiocyanate ion is consistent with both mechanisms. Such is the case for the second mechanism if thiocyanate ion (at the concentrations studied) *does not* compete effectively with water for the pentacoördinated chromium(III) intermediate. Since the first step of the second mechanism is a path for oxygen exchange between solvent water and coördinated water, it cannot be assumed to occur more rapidly than corresponds to the low observed rate of oxygen exchange.[12a,13a,b] No such assumption is necessary for this system; if both thiocyanate complex formation and oxygen exchange occur exclusively by paths with activated complexes with coördination number six, it can be calculated that thiocyanate ion at the highest concentration studied reacts with the pentacoördinated chromium(III) about 4% as fast as does water. Thus equilibrium in the first step of the second mechanism is not appreciably disturbed by the occurrence of the second step. The second step is rate determining and the reaction is very close to first order in thiocyanate ion. The possibility of settling the question of mechanism by carrying out experiments at higher concentrations of thiocyanate ion,[14] where the order of the reaction with respect to thiocyanate ion would be first and zero for the first and second mechanisms, respectively, is rendered remote by the probable existence of hexaaquochromium(III) ion—thiocyanate ion "outer-sphere" complexes.[5] In addition, the primary kinetic salt effect works against making thiocyanate ion a lively competitor with water for the cationic pentacoördinated chromium(III) intermediate. The rate coefficient for the reaction of ions of unlike charge is decreased by an increase in the electrolyte concentration while the rate coefficient for the reaction of water and the cationic species is relatively uninfluenced by the increase in the salt concentration.

Some details of the mechanism may be revealed by the values of the parameters of the absolute rate theory.[15] The value of the entropy of activation for the reverse reaction, $\Delta S^{\ddagger}_{-1}$, is calculated to be -3.0 e.u. (assuming κ, the transmission coefficient, to be unity). This value suggests the S_N2 path, for it is approximately equal to the value of the entropy change which would result from the binding of one water molecule.[16] The determination of the number of water molecules in the activated complex (to the nearest *one* water molecule) from the value of $\Delta S^{\ddagger}$ is a risky business, however, in view of the small entropy change for each water molecule bound (3.0 e.u. suggested by Powell[16]).[17]

If the thermodynamic quantities for reaction 7, ΔH_7 and ΔS_7, are subtracted from the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ associated with k_2, one obtains the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the conversion of $Cr(OH_2)_5OH^{++}$ and SCN^- into the activated complexed $\{Cr(OH_2)_{5 \pm m}(OH)\cdot SCN^+\}^{\ddagger}$. A comparison of these values with the values for the conversion of $Cr(OH_2)_6^{+++}$ and SCN^- into the activated complex $\{Cr(OH_2)_{6 \pm n}\cdot SCN^{++}\}^{\ddagger}$ is of interest. These values at $\Gamma = 0.160$ for path I are $\Delta H^{\ddagger} = 25.1$ kcal. and $\Delta S^{\ddagger} = +0.7$ e.u. while for path II (with reaction 7 subtracted out), they are $\Delta H^{\ddagger} = 22.8$ kcal. and $\Delta S^{\ddagger} = -0.6$ e.u. In the absence of definite evidence regarding the coördination number of chromium(III) in the activated complexes for these reaction paths, the reason for the lower value of $\Delta H^{\ddagger}$ for the path involving an inverse hydrogen ion concentration dependence cannot be uniquely assigned.

A value of $\Delta S^{\ddagger}$ for the reaction under consideration has frequently been cited[15,18] as supporting a general relationship between the value of $\Delta S^{\ddagger}$ and the product of the charges on the reacting ions. The value of $\Delta S^{\ddagger}$ so cited is ~30 e.u., and is obtained from the temperature coefficient of the reaction evaluated by N. Bjerrum[19]; as has been recently pointed out,[20] these measurements were not intended to be subjected to so quantitative an interpretation. In fact, the experimental conditions used by N. Bjerrum (hexaaquochromium(III) ion was the only acid present) were such as to make important the terms in the rate law with an inverse hydrogen ion dependence. The temperature coefficient obtained from these data is not, therefore, to be associated with k_1; further, it is not a true weighted average of the temperature coefficients of the several k's (k_1, k_2 and k_3) since the hydrogen ion concentration changes with temperature in solutions of such a composition.

The coupling of the rate constants k°_1 and $k^{\circ 1}_{-1}$ for the forward and reverse reactions by the same path, that with the activated complex $Cr(OH_2)_{6 \pm n}$ SCN^{++}, leads to values for the equilibrium constant K°_1: $K^{\circ}_1 = k^{\circ}_1/k^{\circ}_{-1}$. The values so calculated are: 1.38×10^3, 1.23×10^3 and 1.12×10^3 at 14.0, 25.1 and 30.0°, respectively. The correlation of these equilibrium constant values with those obtained directly is presented in the previous paper.[5]

Acknowledgment.—The authors wish to express appreciation for the financial support already cited,[2,4] and, in addition, wish to acknowledge a number of interesting discussions with Professor Henry Taube regarding the subject of this and the preceding paper.[5]

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[13] (a) R. A. Plane and H. Taube, THIS JOURNAL, **56**, 33 (1952); (b) J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

[14] F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *ibid.*, **76**, 3079 (1954).

[15] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, Chapter VIII.

[16] R. E. Powell, THIS JOURNAL, **58**, 528 (1954).

[17] It is to be noted that the values of $\Delta S^{\ddagger}$ for the aquation of $Cr(NH_3)_5NCS^{++}$ and $Co(NH_3)_5NCS^{++}$ are -13 and -14 e.u., respectively (these values are calculated from the data of A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954)). Such figures, which are difficult to explain on the basis of either of the mechanisms, do not suggest any difference in mechanism for the aquation of these two complexes. Adamson and Wilkins have suggested that $Cr(NH_3)_5NCS^{++}$ aquates *via* a S_N2 path and $Co(NH_3)_5NCS^{++}$ aquates *via* a S_N1 path. The basis for this suggestion is the difference in the influence of thiocyanate ion on the two reactions; the rate coefficient for aquation of the cobalt complex is expressible as $k_1 = k_1' + k_1''(SCN^-)$ while the rate coefficient for the aquation of the chromium(III) complex is not a function of the thiocyanate ion concentration. While the data do demonstrate that a reaction path is important for the aquation of the cobalt complex which is not as important for the chromium complex, it cannot, because of this, be asserted that the thiocyanate concentration-independent paths for the aquation of the two complexes correspond to different mechanisms.

[18] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 132.

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PRESSURE–TEMPERATURE–COMPOSITION STUDIES OF SOME RARE EARTH/HYDROGEN SYSTEMS[1]

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Received July 1, 1955

Pressure–temperature–composition data are presented for the lanthanum–, cerium–, praseodymium- and neodymium-hydrogen systems in the ranges $T = 150$ to 800°, $p = 0.01$ to 400 mm. It is concluded that La, Ce, Pr and Nd all behave similarly with hydrogen, exhibiting two solid phases, metal and a hydride phase, for compositions between M and MH_2, and a single solid hydride phase for compositions between MH_2 and approximately MH_3. (M = La, Ce, Pr or Nd.) In the latter range, composition is dependent on temperature and pressure. The heats of formation of the MH_2 hydride phases, as obtained from the pressure–temperature measurements are: LaH_2, 49.7; CeH_2, 33.9; PrH_2, 47.8 and NdH_2, 44.8, kcal. per mole of H_2. The equations for the dependence of decomposition pressure on temperature are: for LaH_2: $\log_{10} p = 10.758 - 10858/T$; for CeH_2: $\log_{10} p = 7.708 - 7417/T$; for PrH_2: $\log_{10} p = 10.229 - 10446/T$; for NdH_2: $\log_{10} p = 9.370 - 9796/T$, pressures in mm. of mercury, temperatures in degrees Kelvin. The heats and equations are actually for the process xM (sat. with H_2) + H_2 = $x MH_2$ (sat. with metal). The saturation solubilities vary with temperature.

Introduction

The occlusion of hydrogen by metals of the rare earth group has been known since about 1900, when Matignon[2] first noted that hydrogen was taken up by Ce, La, Pr, Nd and Sm to form solid products. The most extensive work in the field has been done by Sieverts and co-workers, who collected pressure–temperature–composition (*P–T–C*) data for La and Ce,[3,4,6] and for Nd and Pr.[5] Heats of formation for various rare earth hydrides were also determined[6–8] by solution calorimetry. All this work was done with impure metals or sometimes with alloys. Complete *P–C* isotherms for lower hydrogen contents, where we have found plateaus to occur, were not always obtained by Sieverts, *et al.*, although for Ce and for La mischmetall, they obtained isotherms 800° which agree with our 800° isotherm for Ce.

More recently, Viallard[9] and Viallard and Jaszczyn[10] have observed compositions for La deuteride close to LaD_3, and for cerium deuteride between $CeD_{2.2}$ and $CeD_{2.8}$. Viallard[11] has concluded that probably there are compounds CeH_2, CeD_2 and LaH_3, but he has made no systematic study of the *P–T–C* behaviors. Viallard[12] has also made gadolinium hydride and claims that, upon heating Gd in hydrogen to about 220°, Gd_2H_3 is obtained, which becomes GdH_2 upon cooling.

Several authors have discussed the rare earth/hydrogen systems and have attempted to classify the hydride phases. Chief among them are Emeleus and Anderson,[13] D. P. Smith,[14] and T. Moeller.[15] On the basis of the high heats of formation, Emeleus and Anderson conclude that the rare earth hydrides are similar in character to such ionic hydrides as CaH_2. Smith disagrees with this conclusion and indicates a similarity with the Pd–H system. Moeller considers the lanthanide hydrides as having alloy-like character as well as possessing some characteristics of saline compounds. Hurd[16] has discussed the rare earth hydrides briefly, but prefers not to attempt a classification until a definition of the term "hydride" has been agreed on.

This report presents pressure–temperature–composition data obtained on the La–H, Ce–H, Pr–H and Nd–H systems. These investigations were started with the idea of finding out how much similarity exists between the rare earth/hydrogen systems and the plutonium/hydrogen system. They were continued because these systems are interesting in themselves.

The data for the various systems were obtained at different times and with different apparatus. Consequently, information is more extensive on some of the systems than on others and the information on none of them can be considered complete. The data from all the systems taken as a whole show a great deal of self-consistency, however, and it is felt that the behavior of each individual system is quite well understood.

In addition to the determination of pressure–temperature–composition data, metallographic studies, X-ray diffraction studies and neutron diffraction studies were made. The metallographic studies are reported here. The X-ray diffraction and neutron diffraction studies are reported in another paper.[17]

Experimental

The apparatus used for La and Pr was like that employed by Mulford and Sturdy[18] in an investigation of Pu–H equilibria. The apparatus used for Ce and the apparatus used for Nd were much the same except for minor differences in design. In general, all three consisted of a silica sample bulb, a mercury manometer or McLeod gage for measuring hydrogen pressure over the sample, a device for measuring the quantity of hydrogen put into or

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[1] Work done under the auspices of the Atomic Energy Commission. This paper was presented at the 127th National Meeting of the American Chemical Society.

[2] C. Matignon, *Compt. rend.*, **131**, 891 (1900).

[3] A. Sieverts and G. Muller-Goldegg, *Z. anorg. allgem. Chem.*, **131**, 65 (1923).

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[5] A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, **150**, 261 (1926).

[6] A. Sieverts and A. Gotta, *ibid.*, **172**, 1 (1928).

[7] A. Sieverts and A. Gotta, *Z. Elektrochem.*, **32**, 105 (1926).

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[9] R. Viallard, *Compt. rend.*, **221**, 144 (1945).

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[11] R. Viallard, *Ann. chim.*, **20**, 1 (1945).

[12] R. Viallard, *Compt. rend.*, **219**, 417 (1944).

[13] H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," second edition, D. Van Nostrand, New York, N. Y., 1938, p. 292.

[14] D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, 1948, pp. 178 ff.

[15] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, p. 407.

[16] D. T. Hurd, "An Introduction to the Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 172 ff.

[17] C. E. Holley, R. N. R. Mulford, F. H. Ellinger, W. C. Koehler and W. H. Zachariasen, *J. Phys. Chem.*, **59**, 1226 (1955).

[18] R. N. R. Mulford and G. E. Sturdy, *J. Am. Chem. Soc.*, **77**, 3449 (1955).

removed from the sample bulb, a source of pure hydrogen, and a controlled furnace surrounding the sample bulb.

Regardless of the apparatus used, the *P–T–C* data were all obtained in the same way, by measuring the pressure of hydrogen in equilibrium with the solid sample at various temperatures in a closed, constant-volume system. Knowledge of the volume occupied by the gas phase made possible calculation of the quantity of hydrogen present as gas, taking into account the fact that part of the gas was at room temperature and part at furnace temperature. Subtraction of the gas-phase hydrogen from the total in the bulb gave the quantity of hydrogen in the solid. The over-all composition of the solid was then computed from the weight of metal present.

Temperatures and pressures were measured to within about ±1%, and solid compositions are believed to be accurate to about ±0.02 atom-ratio units.

The hydrogen was generated from uranium hydride. This procedure gives very pure hydrogen if proper precautions are exercised. Mass spectrometric analysis of such hydrogen has shown the major impurity to be 0.02% nitrogen, with other impurities undetectable.

The rare earth metals used were obtained through the courtesy of Dr. F. H. Spedding of the Institute for Atomic Research at Ames, Iowa. Analysis showed the following impurities in weight per cent.; only the La and Nd were analyzed for C, N, and O. Nd: 0.04 Fe, 0.004 C, 0.21 O, 0.06 N, 0.02 Na; Pr: 0.4 Mg, 0.05 Ca; Ce: 0.1 Mg, 0.1 Si, 0.02 Fe, 0.01 Pb, 0.01 Ca; La: 0.005 Mg, 0.005 Na, 0.006 C, 0.0075 N, 0.061 O, 0.005 Ca.

The La described above was used only for the *P–T–C* measurements of Fig. 7. The La used for X-ray and metallographic samples came from commercial sources and was much less pure.

The isotherms were constructed by taking all the pressures observed for the desired temperature and calculating the appropriate compositions. The direct data were plotted as pressure *vs.* temperature to facilitate interpolation for the composition ranges from MH_2 to MH_3, M representing a rare earth metal. For composition ranges M to MH_2, the pressures are constant at constant temperature, and plots of $\log p$ *vs.* $1/T$ were used to enable straight-line interpolation between observed points. Small interpolations were necessary because it was not possible to set the furnace controller to arrive at the exact isotherm temperatures, and pressures usually were obtained at temperatures slightly higher or lower than desired.

All the points on the pressure–temperature curves were obtained by holding the sample at various constant temperatures until pressures that did not vary with time were observed, and the curves were obtained by approaching the constant temperatures both from above and from below. If the curve obtained with decreasing temperature did not coincide with that obtained with increasing temperature, the data were discarded as not representing equilibrium. This criterion does not guarantee that the systems were at true equilibrium,[19] but it at least provides a check on the reproducibility of a point as approached from different directions.

Results

A number of La–H samples of different compositions were examined metallographically and by X-ray methods. It was clear from the results that the phase behavior of the La–H system was the same as for Ce, Pr and Nd; and thus only the plateau pressures for LaH_2 at three compositions in the two solid-phase range were measured. The plateau pressures observed are plotted in Fig. 8. The three compositions were $LaH_{0.49}$, $LaH_{0.97}$ and $LaH_{1.46}$.

The isotherms as derived from *P–T* plots of the direct data in the composition range M to MH_2 are shown in Figs. 1, 2 and 3, and the isotherms for higher hydrogen contents are shown in Figs. 4, 5 and 6.

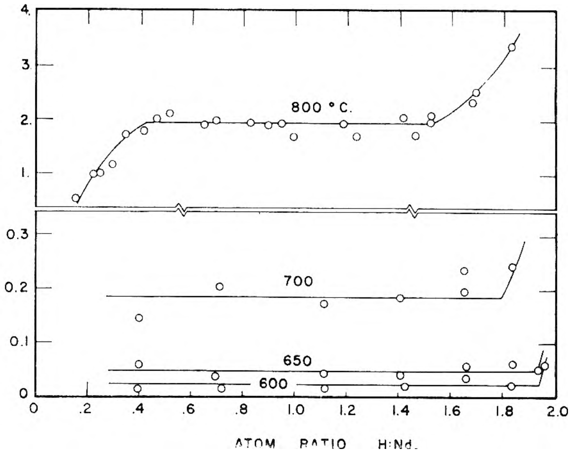

Fig. 1.—Pressure–solid composition isotherms for neodymium–hydrogen.

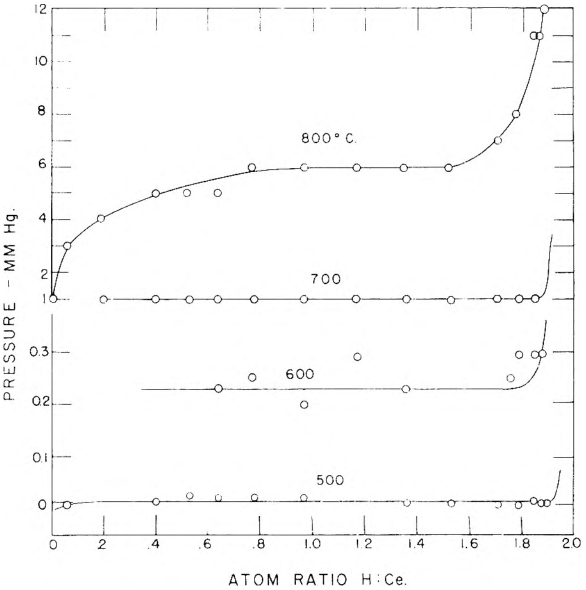

Fig. 2.—Pressure–solid composition isotherms for cerium–hydrogen.

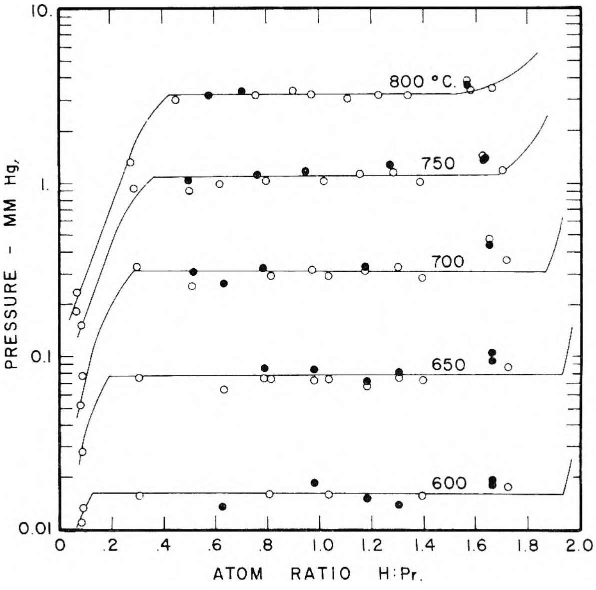

Fig. 3.—Pressure–solid composition isotherms for praseodymium–hydrogen.

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[19] A situation is conceivable where the curves for ascending and descending temperature would coincide, although the system would not be at equilibrium.

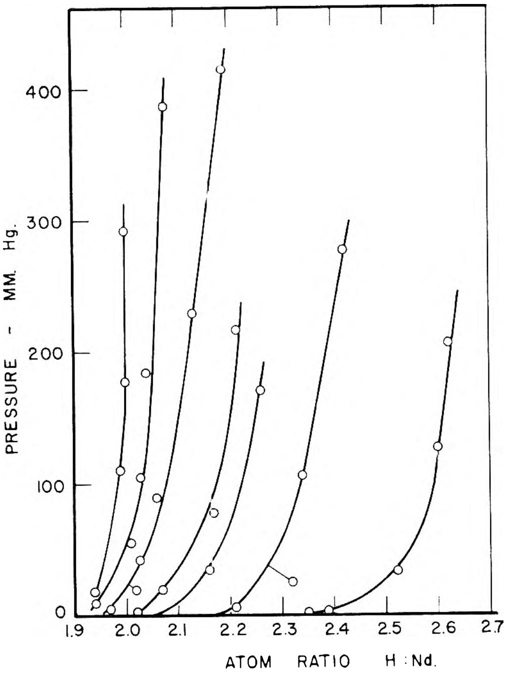

Fig. 4.—Pressure–solid composition isotherms for neodymium–hydrogen.

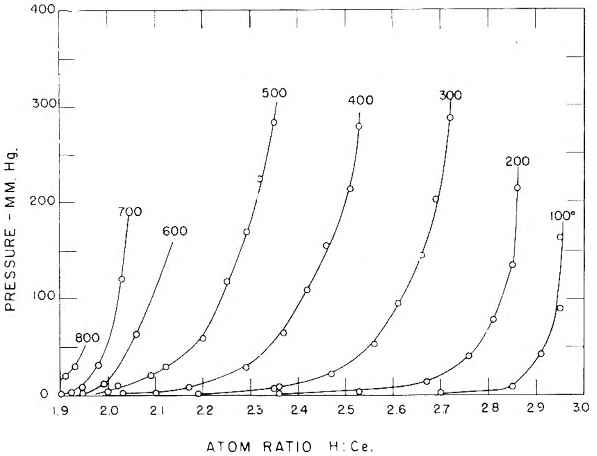

Fig. 5.—Pressure–solid composition isotherms for cerium–hydrogen.

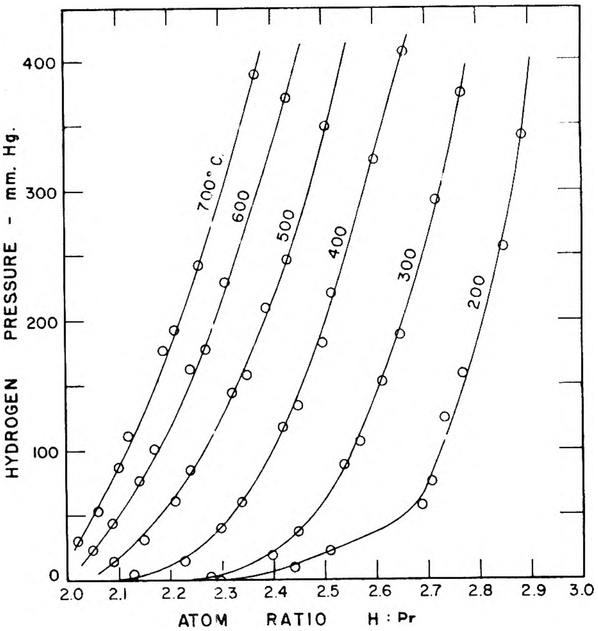

Fig. 6.—Pressure–solid composition isotherms for praseodymium–hydrogen.

The hydrides investigated were all metallic in appearance and ranged from gray to black in color, depending on the composition. Usually the metal cracked or flaked as hydrogen was absorbed, so that the hydrides were obtained in the form of irregular brittle flakes, easily crushed in a mortar. Some of the previous workers have reported that reaction commences between the metal and hydrogen at some specific temperature, but we have observed that, although higher temperatures certainly facilitate starting the reaction, it will begin at almost any temperature if enough time is allowed. Once started, the heat evolved raises the temperature of the metal, and the reaction velocity increases. The hydrides containing more hydrogen than MH_2 are usually pyrophoric when exposed to air, but not always. Any handling of the hydrides must be done under an inert atmosphere to avoid oxidation. The hydrides react with water and with acid, to liberate hydrogen.

A single attempt was made to dissolve cerium hydride of composition $CeH_{2.1}$ in liquid ammonia at $-30°$, but the hydride appeared to be insoluble.

A sample of cerium hydride was prepared by slow cooling under a hydrogen pressure of 1300 p.s.i. X-Ray examination showed only cubic hydride. This result is believed to indicate that the cerium–hydrogen system does not contain any hydrides other than the cubic.

Metallography.—Numerous samples of La with different amounts of occluded hydrogen were examined by standard metallographic techniques. In general, in the two phase composition range, the hydride phase was observed to occur as a fairly coarse, rounded structure. In some samples, hydride also formed as a shell surrounding the metal. As the over all sample composition approached LaH_2, less and less metal phase was visible, until at about $LaH_{1.95}$ no metal could be found.

Discussion

Application of the phase rule to explain the form of the isotherms for the various systems shows that two solid phases coexist in the composition ranges where a constant-pressure plateau occurs. For portions of the isotherms where there is no plateau, a single homogeneous solid phase exists. At the low-hydrogen end of the composition scale, the isotherms indicate solid solubility of hydrogen in the metal, and the limits of solid solubility, or the hydrogen content at which a hydride phase commences to separate, are the intersections of the curved part of the isotherm with the plateau. These limits vary with temperature, as can be seen from the figures. At the other end of the plateaus, a single solid hydride is present. The intersections of the plateaus with the curved portions of the isotherms at this end give composition values which are the lower homogeneity limits of the hydride phase. These limits are below $MH_{2.00}$ at the higher temperatures, but approach $MH_{2.00}$ as the temperature decreases.

Isotherms in the MH_2 to MH_3 range show the presence of a single homogeneous solid phase. The phase consists of the MH_2 structure with the additional hydrogen in interstitial solid solution.[17]

A generalized phase diagram, such as Fig. 7, may be inferred from the isotherm data to illustrate more clearly the phase relationships in the rare earth metal/hydrogen systems. The points plotted are derived from the various isotherms where the ends of the plateaus are best defined. The exact numerical values for the points vary slightly from system to system, but the general behaviors are all the same. Referring to Fig. 7, the region labeled "M" is the bivariant region of a single solid phase, the metal containing hydrogen in solution. The "M + H" region is univariant and contains two solid phases, hydride and metal saturated with hydrogen. The "H" region is bivariant, containing hydride having hydrogen in solid solution. The left-hand portion of the diagram must be more complicated than is indicated, because most of the metals involved undergo transformations, and doubtless the presence of dissolved hydrogen affects both the transformation temperatures and the melting points. Although data are not available to construct this part of the diagram in detail, the boundary shown does represent the limit of solid solubility of hydrogen in all the metals so far as it has been observed.

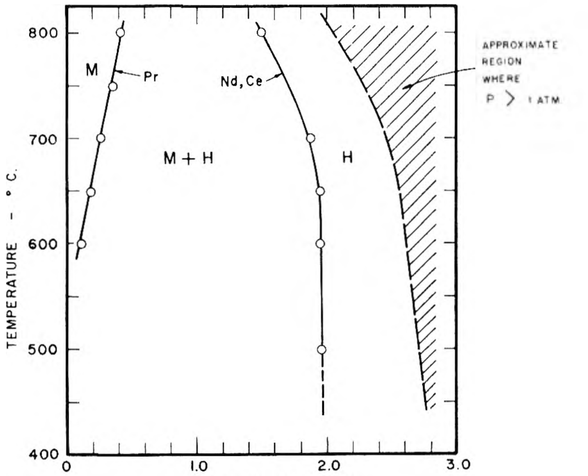

Fig. 7.—Generalized phase diagram for the systems La–, Ce–, Pr–Nd–hydrogen.

It is necessary to note in connection with Fig. 7 that this type of diagram does not represent pressure (*i.e.*, equilibrium hydrogen pressure). The phase boundaries shown are projections of phase boundaries that actually lie on a three-dimensional *P–C–T* surface, and hence are skew curves. Thus there is a definite and different pressure associated with every different point on any phase boundary, and it is not correct to say that Fig. 7 is an isobaric section.

The data available do not show whether the solid-solution equilibrium continues all the way up to a composition of MH_3. Compositions close to MH_3, of the order of $MH_{2.95}$, are usually obtainable by slow cooling in a hydrogen atmosphere, but the temperatures at which the solid phase reaches $MH_{2.96}$ are so low that equilibrium is not achieved. From the shapes of the isotherms, it may be anticipated that, in order to observe compositions close to MH_3 at temperatures where equilibrium can be reached, hydrogen pressures well above one atmosphere would be necessary.

Figure 7 thus represents the phase relationships for hydrogen with La, Ce, Pr and Nd. The subsequent X-ray and neutron diffraction paper[17] contains a description of the crystal structures of the hydride phases.

Hysteresis in the isotherms was not observed for the cerium data of Figs. 2 and 5. The points for these isotherms were obtained by both addition and removal of hydrogen from the system, and the isotherm pressures for addition corresponded to those for removal. The data for the other metals were obtained by addition of hydrogen only, and any true hysteresis would not have been detected.

Plotting plateau pressures on a logarithmic scale *vs.* reciprocal absolute temperature shows that the points fall on a straight line for each system, as indicated in Fig. 8. Application of the van't Hoff isochore yields, from the slopes of the lines, differential heats of occlusion for one mole of hydrogen in the two-phase solid. The heats obtained from the slopes of the least-square lines are listed in Table I, together with the calorimetric heats of formation given by Sieverts and Gotta.[5–7] Our values of ΔH may be considered to be the heats of formation of the hydrides according to the equation

$$2/x\text{M} + \text{H}_2 = 2/x\text{MH}_x$$

where the value of x depends on temperature, x being 2, or very close to 2, when the temperature is

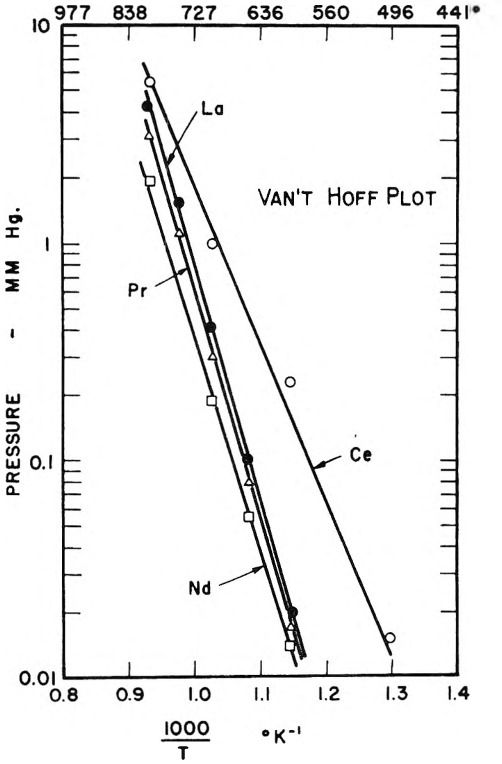

Fig. 8.—Plot of log plateau pressure *vs.* reciprocal temperature for dihydride phases.

low, but becoming less than 2 as the temperature increases. The "M" represents metal which is saturated with hydrogen in solid solution. Since the lines in Fig. 8 are straight, the ΔH's do not change with composition or temperature within the accuracy of the measurements, and thus the numbers in column 3 of Table I may be regarded as the heats of formation of one mole of the "ideal" MH_2 phase formed from the metal and gaseous hydrogen. No strict comparison with Sieverts and Gotta's calorimetric data is possible, because Sieverts and Gotta's data were obtained for compositions other than MH_2 and do not represent differential heats of occlusion. The calorimetric data should, however, be close to ours, and general agreement is evident from the table.

TABLE I

HEATS OF FORMATION OF DIHYDRIDES[a]

	Calorimetric ΔH (kcal./mole H_2)	Differential ΔH (kcal./mole H_2)
La	-40.09 ($LaH_{2.76}$)	-49.7 ± 0.1
Ce	-42.26 ($CeH_{2.69}$)	-33.9 ± 0.9
Pr	-39.52 ($PrH_{2.85}$)	-47.8 ± 0.2
Nd	...	-44.8 ± 0.8

[a] Errors listed are the probable errors as computed from the deviations of the experimental points from the least-square lines.

Equations for the variation of decomposition pressure with temperature of the MH_2 phases may be obtained by fitting expressions of the form, $\log p = A - B/T$, to the available points of Fig. 8 by least-square methods. The equations so obtained are

$$\text{for La, } \log_{10} p = (10.758 \pm 0.001) - (10858 \pm 23)/T$$
$$\text{for Nd, } \log_{10} p = (9.370 \pm 0.179) - (9796 \pm 171)/T$$
$$\text{for Pr, } \log_{10} p = (10.229 \pm 0.048) - (10446 \pm 46)/T$$
$$\text{for Ce, } \log_{10} p = (7.708 \pm 0.226) - (7417 \pm 190)/T$$

Temperatures are in degrees Kelvin, pressures in mm. of mercury. The limits of error indicated are the probable errors as calculated from the deviations of the data from the fitted curves.

Acknowledgments.—The authors wish to thank Miss Gladys E. Sturdy, who made many of the measurements, O. R. Simi, W. H. Smiley and E. Van Kooten for the analyses of the metals, and E. M. Cramer for the metallography.

THE CRYSTAL STRUCTURE OF SOME RARE EARTH HYDRIDES[1,2]

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Received July 1, 1955

La, Ce, Pr, Nd and Sm form an isomorphous series of hydrides of composition MH_2 to $MH_{<3}$. X-Ray and neutron diffraction data have shown that the MH_2 hydrides have the fluorite-type structure and that the additional hydrogen in the $MH_{>2}$ compositions is statistically distributed in the octahedral interstices of the fluorite structure. The unit cube of the hydride contracts as it takes up hydrogen.

Introduction

Structural investigations of the rare earth hydrides have hitherto been confined mostly to lanthanum hydride. A. Rossi[4] found lanthanum hydride and cerium hydride to be face-centered cubic with $a_0 = 5.62$ to 5.70 Å. and $a_0 = 5.61$ Å., respectively. He noted in the case of lanthanum hydride that the unit cell appeared to contract with increase of hydrogen content. More recently Dreyfus-Alain[5a] and Dreyfus-Alain and R. Viallard[5b] have reported the cubic structure for lanthanum hydride with $a_0 = 5.650$ to 5.695 Å., the variation in the unit cell size depending on the hydrogen pressure at which the hydrides were formed.

The phase relationships of some of the rare earth metal–hydrogen systems as deduced from their pressure–temperature–composition behavior have been reported by Mulford and Holley.[6] The results may be briefly described by stating that an intermediate phase of limiting formula MH_2 is formed and that this intermediate phase will take hydrogen into solid solution in the composition range between MH_2 and MH_3 to form a single homogeneous phase whose exact composition is pressure and temperature dependent. The systems are thus seen to be alloy-like in character. The present paper gives the results of X-ray and neutron diffraction experiments on the various phases in the systems and provides descriptions of the structures of the phases. The MH_2 phase is found to have the fluorite-type structure, and as the hydrogen content increases from MH_2 to MH_3, the additional hydrogen atoms go into the octahedral interstices, so that, in the composition range between MH_2 and MH_3, interstitial solid solution of hydrogen in the MH_2 phase occurs.

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) Presented before the Division of Physical and Inorganic Chemistry, 127th Meeting, A.C.S., Cincinnati, Ohio, April 7, 1955.

(3) Consultant to Los Alamos Scientific Laboratory.

(4) A. Rossi, *Nature*, **133**, 174 (1934).

(5) (a) B. Dreyfus-Alain, *Compt. rend.*, **235**, 540, 1295 (1952); **236**, 1265 (1953); (b) B. Dreyfus-Alain and R. Viallard, *ibid.*, **237**, 806 (1953).

(6) R. N. R. Mulford and C. E. Holley, Jr., THIS JOURNAL, **59**, 1222 (1955).

There appears to be no particular correlation between the metal structure and the MH_2 structures in general; although, for some of the metals, the structural arrangement of the metal atoms in the MH_2 phase corresponds to the structure of the metal.

Experimental

For the most part, the hydride samples used in the present X-ray and neutron diffraction work were prepared in conjunction with the pressure–temperature–composition studies of the various metal–hydrogen systems described by Mulford and Holley.[6] The compositions containing hydrogen in excess of $MH_{2.6}$ were satisfactory for phase identification but were unreliable for determining the lattice constant *vs.* composition relationships because the diffraction patterns showed weak and diffuse high angle lines difficult to measure. This is believed caused by two effects: (1) because of the low temperature necessary to keep hydrogen in solid solution at attainable pressures, homogeneity was apparently not always achieved in attempts to prepare samples with high hydrogen contents, and (2) the low temperatures resulted in the hydride phase having presumably a very small crystal size. Attempts were made to increase the size of the hydride crystallites and to produce homogeneity in the hydrides of high hydrogen content by heat-treating the samples for long periods of time in sealed vitreous silica capillary tubes. This was not successful because the samples apparently lost hydrogen during the heat treatment. However, heat treatment was used in some cases for improving the X-ray powder patterns of metal plus hydride mixtures; even though some hydrogen was lost, the two phase equilibrium was not changed.

The X-ray diffraction photographs were taken with a Norelco 114.6 mm. diameter camera using filtered Cu K-radiation. The powder specimens were prepared in a helium atmosphere by placing the crushed hydrides in vitreous silica capillary tubes which were then sealed.

X-Ray Diffraction Results.—The investigation of the hydrides was begun on a series of cerium hydride preparations with various hydrogen contents from $CeH_{1.0}$ to about $CeH_{2.7}$. It was found that the samples containing less hydrogen than is required by the formula CeH_2 were composed of metal and hydride, and that samples of hydrogen content corresponding to CeH_2 and above were composed of only the hydride phase. The powder patterns show that the metal atoms of cerium hydride are arranged on a face-centered cubic lattice and that there are four metal atoms in the unit cell in the positions (0 0 0), ($\frac{1}{2}$ $\frac{1}{2}$ 0), ($\frac{1}{2}$ 0 $\frac{1}{2}$), (0 $\frac{1}{2}$ $\frac{1}{2}$). The unit cell dimension, a_0 = 5.581 ± 0.001 Å. for the composition CeH_2, decreases gradually with increase of hydrogen content, reaching a value of a_0 = 5.540 ± 0.003 Å. at $CeH_{2.47}$.

Subsequent examination of hydride preparations of La, Pr and Nd obtained during the course of the *P–T–C* studies showed these hydrides to be isomorphous with cerium hydride. In the case of Sm, the *P–T–C* behavior is not known. A small sample of Sm was observed to absorb about two atoms of hydrogen per Sm atom, and an attempted preparation of Sm metal contained a large proportion of Sm hydride which after heating at 200° for 260 hr. in a sealed capillary tube gave the X-ray data presented.

The unit cell dimension of each hydride having the composition MH_2 is shown in Table I together with its calculated density. The extent of the contraction of the unit cell with increase of hydrogen content above MH_2 may be seen in Fig. 1.

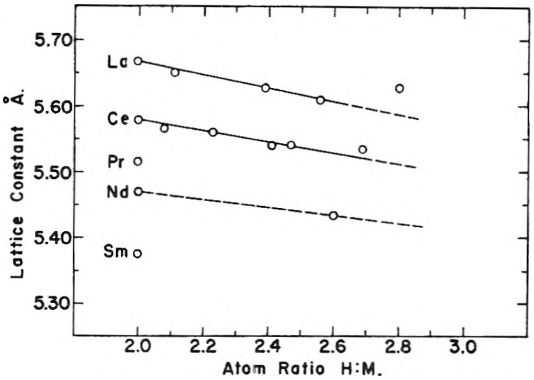

Fig. 1.—Variation of lattice constant with composition.

Neutron Diffraction Results.—In order to locate the positions of the hydrogen atoms in the structure, neutron diffraction data were obtained from a sample of cerium hydride and from a sample of cerium deuteride. The neutron diffraction apparatus and method have been described by Wollan and Shull.[7] The neutron wave lengths used were λ = 1.03 Å. for the hydride sample and λ = 1.163 Å. for the deuteride sample. The neutron scattering powers for the elements involved are given as

$$f_{Ce} = 0.46 \times 10^{-12} \text{ cm.}$$
$$f_D = 0.65 \times 10^{-12} \text{ cm.}$$
$$f_H = -0.378 \times 10^{-12} \text{ cm.}$$

The following conclusions can be reached as regards the two samples.

TABLE I

LATTICE CONSTANT AND X-RAY DENSITY OF THE DIHYDRIDES

Compd.	Lattice constant (Å.)	X-Ray density (g./cm.³)
LaH_2	5.667 ± 0.001	5.14
CeH_2	5.581 ± .001	5.43
PrH_2	5.517 ± .001	5.65
NdH_2	5.470 ± .001	5.94
SmH_2	5.376 ± .003	6.52

CeH_2.—The fluorite type of structure for this composition was postulated. The values $|F|/n$ where $|F|$ is the structure factor per unit cell and n is the number of molecules per unit cell calculated on this basis may be compared with the observed values below. They are considered to furnish conclusive proof of the correctness of this structure.

hkl	$\|F\|/n$ Obsd.	$\|F\|/n$ Calcd.
111	0.58	0.46
200	1.23	1.22
220	∼0.10	0.30

$CeD_{2.43}$, a_0 = 5.530 Å.—For this sample the observed values of $|F|/n$ for the (111) and (200) reflections are smaller than expected for the fluorite type of structure. However, it is well known that the fluorite structure can have interstitial anions. This is observed for instance in yttrofluorite, CaF_2-YF_3.[8,9] It is generally supposed that the additional

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[7] E. O. Wollan and C. G. Shull, *Phys. Rev.*, **73**, 830 (1948).

[8] V. M. Goldschmidt, *Geochem. Verteilungsgesetze*, **VII**, 88 (1926).

[9] E. Zintl and A. Udgard, *Z. anorg. angew. Chem.*, **240**, 150 (1939).

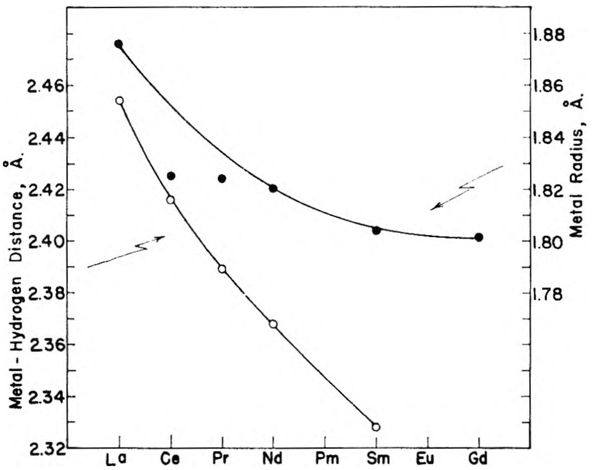

Fig. 2.—Metal–hydrogen distances and metallic radii.

anions are distributed at random over the holes at $(\frac{1}{2}\,0\,0)$, $(0\,\frac{1}{2}\,0)$, $(0\,0\,\frac{1}{2})$, $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$.

In the case of $CeD_{2.48}$ the suggested atomic positions are

$$\begin{aligned}&4\ \mathrm{Ce\ in}\ (0\,0\,0),\ (\tfrac{1}{2}\,\tfrac{1}{2}\,0),\ (\tfrac{1}{2}\,0\,\tfrac{1}{2}),\ (0\,\tfrac{1}{2}\,\tfrac{1}{2})\\&8\ \mathrm{D\ in}\ \pm(\tfrac{1}{4}\,\tfrac{1}{4}\,\tfrac{1}{4}),\ (\tfrac{1}{4}\,\tfrac{3}{4}\,\tfrac{3}{4}),\ (\tfrac{3}{4}\,\tfrac{1}{4}\,\tfrac{3}{4}),\ (\tfrac{3}{4}\,\tfrac{3}{4}\,\tfrac{1}{4})\\&1.9\ \mathrm{D\ in}\ (\tfrac{1}{2}\,0\,0),\ (0\,\tfrac{1}{2}\,0),\ (0\,0\,\tfrac{1}{2}),\ (\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})\end{aligned}$$

The neutron intensities calculated for this structure compare favorably with the observed.

	$\lvert F\rvert/n$	
hkl	Obsd.	Calcd.
111	0.175	0.15
200	0.368	0.53
220	1.95	2.07

In this structure each metal atom has eight deuterium neighbors at 2.40 Å. and about three more at 2.77 Å.

Discussion of the Structures.—The metal–metal separation in the MH_2 hydrides is so much larger than in the corresponding metals that the main cohesive energy must be attributed to the metal–hydrogen bonds. It is reasonable to suppose that two valence electrons of each metal atom participate in the M–H bond formation in the MH_2 compounds, and that the metallic character of these substances is due to the presence of additional valence electrons. Other compounds of 4f and 5f elements showing metallic character and a subnormal valence of two are the monoxides and monosulfides.[10]

The observed M–H distances and the metallic radii of the metals concerned are shown in Table II and in Fig. 2. The metallic radii of cerium and praseodymium lie considerably below the smooth curve connecting the radii of the typically trivalent 4f elements. Pauling[11] has taken this to mean that in cerium and praseodymium metal there are slightly more than three valence electrons, his suggested values being 3.2 valence electrons for cerium and 3.1 valence electrons for praseodymium. It is seen in Fig. 2 that the observed M–H distances do lie on a smooth curve, thus suggesting that in the MH_2 hydrides exactly 3.0 valence electrons should be assigned to all the 4f elements involved.

Again referring to Fig. 2 it is seen that the M–H distances decrease faster with increasing atomic number than do the metallic radii. Thus, a constant hydrogen radius cannot be obtained if one assumes the observed M–H distance to be the sum of the covalent radii of metal and hydrogen.

TABLE II

INTERATOMIC DISTANCES, METAL AND HYDROGEN RADII (Å.)

Compd.	M–8H	Metal radius (12 co-ordin.)	Metal radius (8 co-ordin.)	Hydrogen radius (tetrahedral configuration)
LaH_2	2.454	1.876[a]	1.823	0.631
CeH_2	2.416	1.825[a]	1.799	.617
PrH_2	2.389	1.824[b]	1.780	.609
NdH_2	2.368	1.820[a]	1.767	.601
SmH_2	2.328	1.804[a]	1.751	.577

[a] Values from measurements at Los Alamos Scientific Laboratory. [b] Pauling's value.

The values for the tetrahedral hydrogen radius deduced from the observations are shown in Table II. For cerium and praseodymium the radii taken from the smooth curve of Fig. 2 were used instead of the actually observed values. A value of 0.053 Å. was assumed for the contraction in radius in going from twelve to eight coördination. The hydrogen tetrahedral radius of 0.58 to 0.63 Å. is intermediate between the values of 0.55 Å. in ZrH and 0.67 Å. in ThH_2 following from the structures deduced by Rundle, Shull and Wollan.[12] However, all of these values are much higher than the tetrahedral radius of 0.45 Å. for hydrogen according to Pauling.

Acknowledgment.—The authors are grateful to Marion Gibbs for measuring the diffraction films, and to E. I. Onstott for the samarium metal samples.

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(10) "National Nuclear Energy Series," IV-14A, Chapter 18, McGraw-Hill Book Co., New York, N. Y., 1954.

(11) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(12) R. E. Rundle, C. G. Shull and E. O. Wollan, *Acta Cryst.*, **5**, 22 (1952).

THERMAL DIFFUSION IN LIQUID METALS[1]

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Received July 22, 1955

Thermal diffusion measurements have been made on a series of liquid metal mixtures. The results are totally consistent with a previously presented theory. The separations depend on the "activation energy density" $\Delta U^{\ddagger}/V$ of the components. It is also shown that the quantity $X(\partial\mu/\partial X)$ in the denominator is important for quantitative prediction of the separation. Results also are presented and discussed for three ternary mixtures.

In recent papers[2] we have discussed theories of thermal diffusion in liquids and their application to data on binary organic mixtures. The two theories presented differed in their interpretation of the "net heat of transport," a quantity which appears in the theory of thermodynamics of irreversible processes.

The thermal diffusion separation in a binary mixture can be discussed in terms of the thermal diffusion ratio α defined (for the steady state) by

$$\ln\left(\frac{X_1}{1-X_1}\right)_{\mathrm{H}}\left(\frac{1-X_1}{X_1}\right)_{\mathrm{C}} = \alpha \ln \frac{T_{\mathrm{H}}}{T_{\mathrm{C}}} \qquad (1)$$

where

X_1 = mole fraction component 1
T = temperature

The subscripts H and C refer to the hot and cold walls, or chambers, of a single stage system. Our previous papers give for α the relationship

$$\alpha = \frac{M_1\bar{V}_2 + M_2\bar{V}_1}{2M}\left(\frac{\Delta\bar{U}_2^{\ddagger}}{\bar{V}_2} - \frac{\Delta\bar{U}_1^{\ddagger}}{V_1}\right)\frac{1}{X\,\dfrac{\partial\mu}{\partial X}} \qquad (2)$$

where

$\bar{V}_{\mathrm{i}}$ = partial molar vol. of component i
M_{i} = mol. wt. of component i
μ_{i} = chemical potential of component i

The quantity $\Delta\bar{U}_{\mathrm{i}}^{\ddagger}$ is an energy quantity associated with motion of component i out of a given region. Previously[2a] we presented an interpretation of this quantity in terms of a fraction of the latent heat. In reference 2b we discussed it in terms of the partial molar activation energy of component i in the mixture. The latter concept seems more reasonable and gives better agreement with the theory for organic mixtures, but the difference is not clear, since, as Eyring[3] has shown, the ratio of latent heat to activation energy is substantially constant (3 to 4)/1 for most organic liquids.

The liquid metals supply a very good test of these theories since the simple relationship discussed above does not apply, as can be seen in Table I.

TABLE I

Metal	T, °C.	ΔHvap. / $\Delta H^{\ddagger}$	Metal	T, °C.	ΔHvap. / $\Delta H^{\ddagger}$
Tin	295	58.5	Mercury	295	23.3
Cadmium	295	17.7	Gallium	295	69.9
Lead	295	16.0	Bismuth	295	36.0
Zinc	375	9.6			

Thermal diffusion measurements have been made for a series of binary liquid metal mixtures containing 50 mole % of each component. The gallium, cadmium, zinc, tin, lead and bismuth were A. D. Mackay's purest. The mercury was redistilled stock.

The cell consisted of a ceramic tube $^1/_2$-inch long, $^1/_8$-inch i.d. and $^3/_8$-inch o.d. The bottom was sealed with a thin copper disk fastened on with sauereisen. A thermocouple was silver-soldered to the disk. The cell was filled with the molten alloy to be studied and a second couple was inserted at the top. The alloy was then solidified and the top sealed with sauereisen.

The temperature gradient was imposed by means of a tubular core electric heater. By varying the current and the position in the core, almost any mean temperature and ΔT could be attained. The samples were run at a ΔT of 50° and at the mean temperatures shown in Table II.

By successive runs it was shown that 12 hours was usually ample for the steady state to be established. All runs reported were at least 24 hours. At the end of the run the cell was quickly lowered into ice-water to ensure instantaneous solidification. The metal slug was removed and cut into five pieces which were weighed and analyzed by standard titrimetric methods.[4] All systems except the lead-bismuth contained tin, for which we analyzed. In the lead-bismuth system the latter component was measured.

The results are shown in Table II. Each point is the average of at least three runs, and the average deviation is less than 5% from the mean.

The activation energies were obtained from viscosity data[5] using Eyring's[3] equation

$$\eta = \frac{hN_0}{V}\exp\frac{\Delta F^{\ddagger}}{RT} \qquad (3)$$

$$R\left(\frac{\partial \ln \eta V}{\partial\, 1/T}\right)_{\mathrm{P}} = \Delta H^{\ddagger} \cong \Delta U^{\ddagger} \qquad (3')$$

where

η = viscosity
V = molar volume
h = Planck's constant
N_0 = Avogadro's number
R = gas constant
$\Delta F^{\ddagger}$ = activation free energy
$\Delta H^{\ddagger}$ = activation enthalpy
$\Delta U^{\ddagger}$ = activation energy

Where available, the measured values of $X_1(\partial\mu/\partial X)$ were used. Otherwise the ideal solution value RT was assumed. It was necessary to use the molar volumes and activation energies of the pure components as partial molar quantities were not available.

For mixtures where activity data were available the predicted value checks experiment quite well. There is a slight discrepancy for the case of tin-bismuth, but there were only three viscosity points available and these indicated that $\Delta H^{\ddagger}$ varied significantly with temperature, but the exact value was hard to determine.

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[1] This work was supported in part by the A.E.C.

[2] (a) E. L. Doughtery, Jr., and H. G. Drickamer, *J. Chem. Phys.*, **23**, 295 (1955); (b) THIS JOURNAL, **59**, 443 (1955).

[3] S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[4] N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. I, D. Van Nostrand Co., New York, N. Y., 1939.

[5] "Liquid Metals Handbook," U. S. Govt. Printing Office, 2nd Ed., 1952.

TABLE II

System[a]		$T_{av.}$, °C.	α_{exp}[b]	$\alpha_{calcd.}$	$\Delta V_1^{\ddagger}$	$\Delta U_2^{\ddagger}$	V_1	V_2	$X \frac{\partial\mu}{\partial X}$
I	(1) (2) Sn–Bi	295	0.10	−0.15	1.30	1.40	17.1	20.8	1028
II	(1) (2) Sn–Cd	295	0.35	0.325	1.30	1.27	17.1	14.0	707
III	(1) (2) Sn–Zn	375	4.10	4.14	1.45	2.90	17.3	9.4	365
IVa	(1) (2) Sn–Pb	295	1.90	1.09	1.30	2.81	17.1	19.5	1130 = RT
IVb	(1) (2) Sn–Pb	450	0.83	0.46	1.46	2.32	17.4	19.7	1440 = RT
V	(1) (2) Sn–Ga	295	0.18	0.12	1.30	1.01	17.1	11.8	1130 = RT
VI	(1) (2) Sn–Hg	295	−0.51	−0.54	1.30	0.61	17.1	15.6	1130 = RT
VII	(1) (2) Bi–Pb	295	1.13	0.64	1.40	2.28	20.8	19.5	1560

[a] Activity data for systems I, III and VII were obtained from F. J. Dunkerly and G. J. Mills, "Thermodynamics in Physical Metallurgy," American Society for Metals, 1949, pp. 57, 53 and 64, respectively. Activity data for system II were obtained from N. W. Taylor, *J. Am. Chem. Soc.*, **45**, 2865 (1923). [b] A positive α indicates component (1) concentrates at the hot wall.

No solution data were available for tin–lead. The predicted values are low, but there is probably a positive heat of mixing which would reduce the denominator and give better agreement with experiment. The activation energy of lead varies with temperature but there were sufficient data to establish it well. It is interesting to note that the correct temperature dependence for α is predicted.

It is significant to note that the molar volumes vary by a factor of 2. Thus we have strong evidence that it is the activation energy density, and not the activation energy which controls the separation.

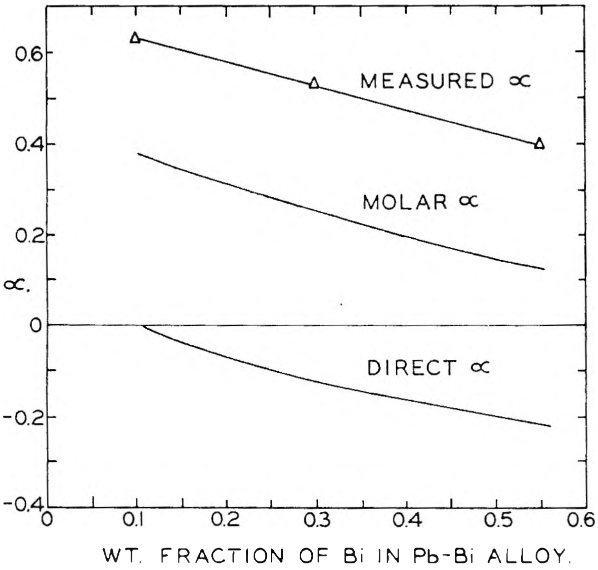

Fig. 1.—Comparison of the equilibrium ratios (α) for the ternary Sn–Bi–Pb systems predicted using both the molar average activation energy for viscous flow and the directly determined activation energy of the Pb–Bi alloy.

Ballay[6] has studied several liquid metal systems using a large tube a cm. in diameter and several cm. long. For lead–tin and cadmium–tin he obtained separations of the same sign and magnitude as ours but somewhat smaller. For zinc–tin his separation was considerably smaller. A large diameter tube is much more susceptible to convection, particularly in a system like zinc–tin where the density difference between components is very small. We attribute the differences to this possibility.

A general treatment of ternary systems is quite complex,[7] but for ideal solutions it simplifies considerably.[2a] In this case one can study the distribution of one component and treat the remainder of the mixture as if it were a single component having averaged physical properties. The question which arises is how to average the activation energies to get that of the "pseudo component." We have studied three ternary mixtures each containing 50 mole % tin and varying fractions of lead and bismuth. The activation energies for the pure components and for the binary lead–bismuth mixture were available.[8] Figure 1 shows the measured values of α, the values calculated using the measured activation energy for the binary mixture, "direct α," and the values using for the "pseudo component" $\Delta U^{\ddagger} = X_1 \Delta U_{10}^{\ddagger} + X_2 \Delta U_{20}^{\ddagger}$.

The latter procedure is apparently preferable, although the non-ideality of the mixture may be an important factor.

F. R. Winter would like to acknowledge assistance from the Standard Oil Company of Ohio Fellowship.

[6] C. R. Ballay, *Acad. Sci. Paris*, **183**, 603 (1926); *Rev. Metallurgie*, **25**, 427 (1928).

[7] S. R. de Groot, "Thermodynamics of Irrev. Processes," Interscience Pub., New York, N. Y., 1950.

[8] AEC Cont. At(30-1)-844, Progress Rept. No. 3, J. L. Everhard and E. L. Van Nuis, Amer. Ref. and Smelting Co., Barber, New Jersey.

NOTES

FREEZING POINT DIAGRAMS OF SOME SYSTEMS CONTAINING TNT

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Received July 5, 1955

In the course of a study of the physical properties of 2,4,6-trinitrotoluene (TNT) data are being acquired on a number of binary systems containing TNT. Freezing point data on three of these systems, TNT–2,4-dinitromesitylene, TNT–3-nitro-2-iodotoluene and TNT–*p*-dibromobenzene are presented here. These systems do not appear to have been investigated previously.

The TNT used in these studies had a vacuum melting point of 80.9°. The 2,4-dinitromesitylene was Eastman Kodak Co. material with a melting point of 87.5°. The 3-nitro-2-iodotoluene was Eastman Kodak Co., material melting at 64°. The *p*-dibromobenzene was Eastman Kodak Co. material which melted at 88°.

The apparatus used in these investigations has been described elsewhere.[1] Three-gram samples were used and temperatures were determined with 10% rhodium–platinum thermocouples. Supercooling of the melts was minimized by withdrawing small portions of the melt on a platinum ribbon, allowing the material to solidify and returning it to the melt.

The system TNT–2,4-dinitromesitylene was found to form an equimolar compound which melted at 58°. Two eutectics, one containing 43.5 mole % of dinitromesitylene and melting at 51°, the other containing 56 mole % of dinitromesitylene and melting at 57°, were found. Data for this system are presented in Fig. 1.

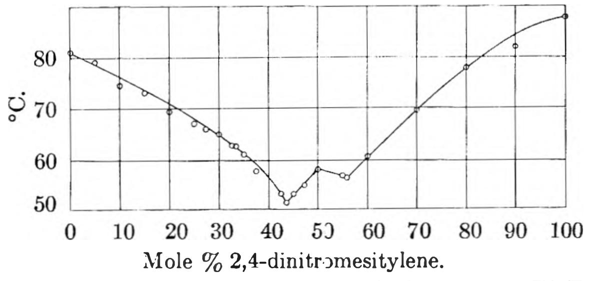

Fig. 1.—Freezing point diagram of the system TNT-2,4-dinitromesitylene

The system TNT–3-nitro-2-iodotoluene is found to form one compound containing 66.6 mole % 3-nitro-2-iodotoluene which melts at 48°. A eutectic containing 59 mole % of 3-nitro-2-iodotoluene, melting at 35°, and a eutectic containing 72 mole % 3-nitro-2-iodotoluene, melting at 40°, are found. Data for this system are presented in Fig. 2.

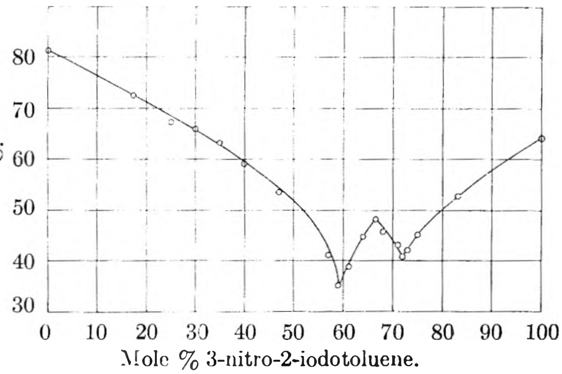

Fig. 2.—Freezing point diagram of the system TNT-3-nitro-2-iodotoluene.

The system TNT–*p*-dibromobenzene forms a single eutectic containing 33.5 mole % *p*-dibromobenzene. This eutectic melts at 61°. Data for this system are presented in Fig. 3.

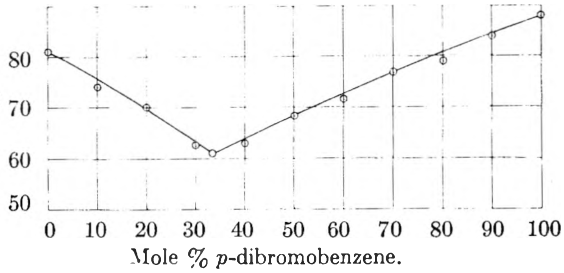

Fig. 3.—Freezing point diagram of the system TNT–*p*-dibromobenzene.

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[1] L. A. Burkardt, D. W. Moore and W. S. McEwan, *Rev. Sci. Inst.*, **40**, 461 (1953).

GASEOUS METAL NITRIDES. I. THEORETICAL DISSOCIATION ENERGIES FOR DIATOMIC NITRIDES[1]

By John L. Margrave and Prasom Sthapitanonda

Received July 25, 1955

There are presently available data on nearly 400 gaseous diatomic molecules, including more than 125 gaseous halides, and over 60 gaseous oxides. Surprisingly enough, only thirteen gaseous diatomic nitrides are known: AsN, BN, CN, IN, NBr, NH, ND, NO, NO^+, NS, PN, SbN and SiN.[2] There are no known gaseous nitrides of the "active" or transition metals.

This observation arouses considerable interest since (1) nitrogen is a highly electronegative element and (2) many solid metal nitrides are known. It would appear that the binding energies of diatomic nitrides should be comparable with those of oxides, or at least sulfides or hydrides, which are well known. In view of the success of an ionic model for treating gaseous halides and hydrides of group I, II and III metals,[3] and of the fact that this

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[1] Presented at the 127th Meeting of the American Chemical Society in Cincinnati, Ohio, on April 7, 1955.

[2] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

[3] (a) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951); (b) W. A. Klemperer and J. L. Margrave, *ibid.*, **20**, 527 (1952); (c) J. L. Margrave, This Journal, **58**, 258 (1954).

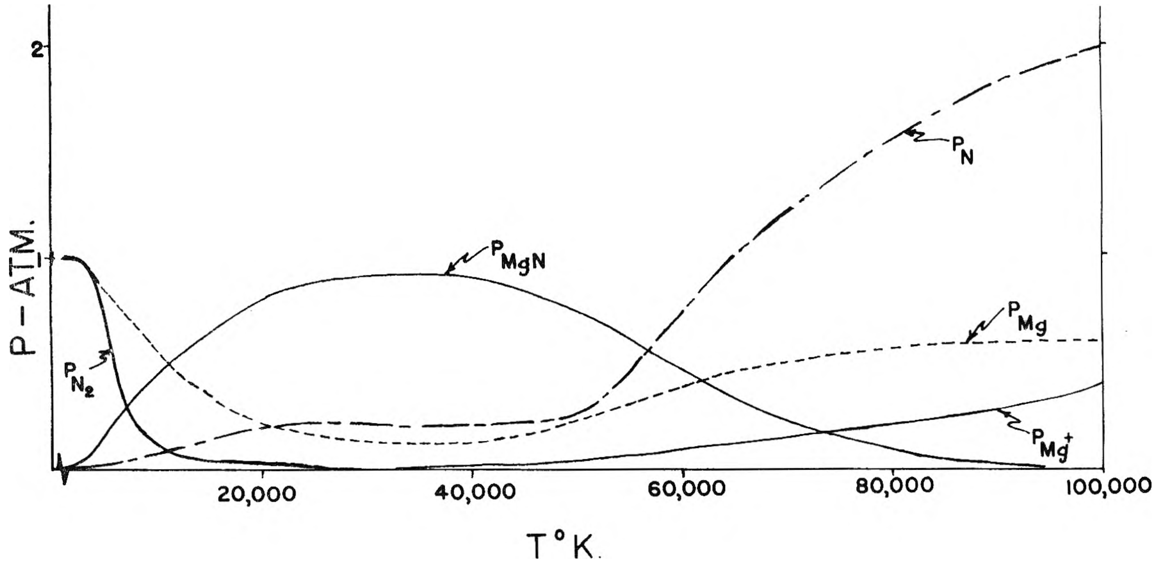

Fig. 1.—Species in the Mg–N system.
$P_{Mg} + P_{MgN} = 1$ atm. $P_{N_2} + {}^1/_2P_N + {}^1/_2P_{MgN} = 1$ atm. (T ≥ 4000°K.).

same approach gives binding energies to ±10% for diatomic oxides,[4] it appears that an ionic model for gaseous diatomic nitrides is at least a good first approximation.

The ionic binding energy U_g^0 is assumed to be given approximately by e^2/r where e is the electronic charge and r is the equilibrium internuclear distance. This can be related to the dissociation energy of the MN(g) molecule to neutral atoms by

$$D(\text{MN}) = U_g^0 - I + E$$

where I is the first ionization potential of M and E is the electron affinity of nitrogen. Values for I have been taken from Moore[5] and Latimer,[6] and E has been taken as 26 kcal./mole.[7] The equilibrium internuclear distances may be estimated by an ionic-radius approach like that used previously. For N^-, the radius lies in the range 0.70 to 1.08 Å. from considering the BN distance, the isoelectronic O atom, and the radii for O^-, O^-, F and F^-.

In Table I are presented values for the dissociation energies of the gaseous diatomic nitrides of group I, II and III metals for both $r_{N^-} = 1.08$ Å. and $r_{N^-} = 0.70$ Å. The higher stability, of course, goes with the smaller r_{N^-}. With these dissociation energies one may make approximate calculations concerning diatomic nitrides in gaseous systems at high temperatures. In general such calculations indicate that no gaseous diatomic nitrides are likely to be very important below 3500–4000° K. At higher temperatures, where N_2 dissociation is appreciable, gaseous nitrides should exist. An indication of the possible importance of gaseous nitrides at very high temperatures is given in Fig. 1. It would appear that gaseous nitride spectra might very well be observed in light from stars in which nitrogen and metals are present at 10,000–100,000° K.

TABLE I

DISSOCIATION ENERGIES OF GASEOUS DIATOMIC NITRIDES

Gaseous nitride	D(MN) (kcal./mole)	Gaseous nitride	D(MN) (kcal./mole)
LiN	111–178	SrN	53–87
NaN	84–124	BaN	57–89
KN	79–111	BN	93–203
RbN	70–96	AlN	82–137
CsN	72–97	GaN	72–121
BeN	64–167	InN	70–116
MgN	45–101	TlN	52–92
CaN	52–92		

This research was in part conducted under contract No. AF 33(616)-338 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

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(4) (a) L. Brewer and J. L. Margrave, THIS JOURNAL, **59**, 421 (1955); (b) J. L. Margrave, unpublished calculations, 1955.

(5) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Washington 25, D. C., Circular 467, Vol. I (1949), and Vol. II (1952).

(6) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(7) J. L. Margrave, *J. Chem. Phys.*, **22**, 1937 (1954).

COMMUNICATION TO THE EDITOR

FORCE-AREA PROPERTIES OF FILMS OF POLYFLUOROQUATERNARY AMMONIUM COMPOUNDS ON HYDROCARBON LIQUID SUBSTRATES[1]

Sir:

Recently we have described an all-Teflon film balance which makes it possible to observe directly the existence of insoluble surface films on organic liquid substrates and to characterize such films by their mechanical properties.[2] With it we have studied the surface-active properties of a variety of fluorocarbon derivatives at the cetane/air, mineral oil/air and diethyl diisopropyl benzene/air interfaces. The polyfluoroquaternary ammonium compounds recently described by Ahlbrecht and Blake[3] have exhibited some unusual and interesting film properties. These results can be exemplified by the behavior on mineral oil of an insoluble film of $F(CF_2)_7CONH(CH_2)_3N(CH_3)_3I$.

When the oil substrate used had been freed previously from trace polar impurities, the film (spread from isopropyl alcohol) was rigid and its reproducible F-A curve had a limiting area of 18 Å.^{2}/molecule. This is approximately half of the cross-sectional area of the fluorinated paraffin chain, which according to Arrington and Patterson[4] is 29 Å.^{2} and from our measurements of a Stuart-Briegleib molecular model[5] is 27 Å.^{2}. Although such a small experimental limiting area could have resulted from loss of film molecules to the substrate by solubility or by incomplete spreading, these possibilities were eliminated by appropriate experiments. Thus, it must be concluded that this highly reproducible film was thicker than one molecule.

When the white mineral oil substrate had not been freed of trace polar impurities, the limiting area of the F-A curve obtained shortly after spreading the film and allowing the isopropyl alcohol to evaporate was only slightly greater than that on the purified substrate. But several hours afterwards the limiting area had increased, and it continued to increase until a reproducible maximum of 45 Å.^{2}/molecule was reached in two days. Since this limiting area exceeds the cross-sectional area of the oriented polar molecule, it was concluded that the final film was a monolayer.

Thus molecules of an impurity in the mineral oil substrate can react with the molecules of the fluorinated film to cause a transition from a bimolecular to a monomolecular film. The same behavior was observed with two related polyfluoroquaternary ammonium compounds on hydrocarbon substrates except that initially the films were over two molecules thick.

Subsequent experiments showed that organic peroxides produced in such hydrocarbon oils by oxidation in the atmosphere, or by the addition to the purified oils of a known peroxide, caused these adsorbed films to behave in essentially the same way. Further work is being done to determine the mechanism of interaction of peroxides in organic substrates with these fluorinated quaternary ammonium iodides and also the structure of the complexes formed. These results will be reported more fully subsequently.

It has been reported recently[6] that these polyfluoroquaternary ammonium compounds form films on the surfaces of volatile organic liquids like gasoline and Stoddard Solvent which greatly inhibit evaporation. Our results indicate that in the absence of peroxides such films were more than one molecule thick and probably were insoluble and rigid at low film pressures.

It appears that the surface-active properties of such polar compounds at the oil/air interface can be used to follow the development of peroxides with aging in animal, vegetable and mineral oils. Also, these results demonstrate that careful purification of the organic substrate is required in studies of the adsorption of such polar compounds at the organic liquid/air interface.

NAVAL RESEARCH LABORATORY A. H. ELLISON
WASHINGTON 25, D. C. W. A. ZISMAN

RECEIVED OCTOBER 24, 1955

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[1] Taken from a thesis submitted by A. H. Ellison to the Graduate School of Georgetown University in partial fulfillment of the requirements for the Ph.D. degree.

[2] A. H. Ellison and W. A. Zisman, submitted to THIS JOURNAL.

[3] A. H. Ahlbrecht and G. B. Blake, "Quaternary Ammonium Compounds from Fluorinated Acids," presented at the American Chemical Society Meeting, New York, N. Y., September 11-17, 1954.

[4] C. H. Arrington, Jr., and G. D. Patterson, THIS JOURNAL, **57**, 247 (1953).

[5] *Chem. Eng. News*, **32**, 2534 (1954).

[6] G. B. Blake, A. H. Ahlbrecht and H. G. Bryce, "Perfluoroalkyl Surface Active Agents for Hydrocarbon Systems," preprints of papers presented to the Petroleum Division of the American Chemical Society at the Fall Meeting, New York, N. Y., September 11-17, 1954.

ADDITIONS AND CORRECTIONS

VOL. 58, 1954

George Scatchard and R. G. Breckenridge. Isotonic Solutions. II. The Chemical Potential of Water in Aqueous Solutions of Potassium and Sodium Phosphates and Arsenates at 25°.

Page 596. In the heading the initials of Breckenridge should be R. G.

Page 600. Equation 10 should read

$$B = \Sigma_i c_i b_i/c + \Sigma_{ij} c_i c_j b_{ij}/2\nu c \tag{10}$$

To the definitions below it, may be added

$$\nu = \Sigma_i \nu_i c_i/c \text{ and } \nu_i = m_i/c_i = 1/|z_i|$$

The more usual definition for an electrolyte with ions *i* and *j* is to multiply our ν_i and ν_j by the least common multiple of $|z_i|$ and $|z_j|$, which makes ν_i depend upon the associated ion. Equation 13 should read

$$(\ln \gamma_{34}''')_{34}/c = 2B_{34}$$

The left-hand side of equation 15 should read

$$\nu_{34}(\ln \gamma_{34}''')/c$$

and should be followed by the definitions

$$x_i = c_i/c \text{ for a cation, } y_j = c_j/c \text{ for an anion}$$

Page 601, 602. It was Güntelberg[15] who explicitly assumed that every b_i is zero.

Page 602. Since ϕ''', etc., were limited to the linear terms, another superscript should be used to indicate the application to more concentrated solutions and the assumption of the first equation in this section.—GEORGE SCATCHARD.

Rex Neihof. The Preparation and Properties of Strong Acid Type Collodion-Base Membranes.

Page 922. In col. 2, lines 10 and 11, for "meq." read "micro eq."—REX NEIHOF.

VOL. 59, 1955

Herman E. Ries, Jr., and Wayne A. Kimball. Monolayer Structure as Revealed by Electron Microscopy.

Page 95. In the caption of Fig. 1, for "−15" read "15".

R. J. Tykodi. On First Order Transitions in Adsorption Systems.

Page 383. At the end of col. 2, for "University Park, Pennsylvania," read "State College, Pennsylvania."

Martin L. Black. The Ionization Constants of the Pyridine Monocarboxylic Acids. A Reinterpretation.

Page 671. In Fig. 1 legend for "Top" read "Bottom," and in Fig. 2 legend, for "Bottom" read "Top."—MARTIN L. BLACK.

L. I. Grossweiner. Photochemical Production of Hydrogen Peroxide Catalyzed by Mercuric Sulfide.

Page 742. In footnote (4) for "J. A. Ghormley" read "C. J. Hochanadel."

Page 744. In col. 1, second line below equation (2), for "k_1/k_2" read "k_2/k_1." In equation (3) insert a bracket after "$\log_e$." In the line below equation (4) for "to" read "of."

Page 745. In col. 1, line 27, for "maximum" read "minimum." In col. 2, line 17, for "axis" read "*c*-axis."

Page 746. In col. 1, line 6, for "ν^1" read "ν^0."—L. I. Grossweiner.

O. Johnson. Acidity and Polymerization Activity of Solid Acid Catalysts.

Page 827. In col. 2, line 8 should read "The straight line has the slope $2.3(a + 1/b)$." In Table III the polymerization rates in the last column should be (A) 0.07, (B) 0.30, (C) 0.48, (D) 0.60, (E) 0.75, (F) 2 ± 2.0, (G) 0.8 ± 0.2. These changes are a consequence of plotting x/t *vs.* $1/t \log_{10} a/(a - x)$ instead of $1/t \log_e a/(a - x)$. The values of *k* in Table VI should be all multiplied by 250 for the same reason. All catalysts studied except (F) and (G) gave *b* values of 1 and slopes very nearly $2.3a$; thus *k* values were obtained for F and G by assuming the same kinetics and drawing a line of slope $2.3a$ through the experimental points. Since the *k* values are increased by a constant factor the linear relation between acidity and polymerization rate is unchanged except that the rate for catalyst F is too uncertain to include. I am indebted to Dr. J. R. Schaefgen for calling the above error to my attention.—OLIVER JOHNSON.

Harvey T. Kennedy, Edward O. Burja and Robert S. Boykin. An Investigation of the Effects of Wettability on the Recovery of Oil by Water Flooding.

Page 869. In Fig. 2 the abscissa numbers should be placed one square to the left in each case. In the first footnote, for "Recovery" read "Resources." The "Discussion" shown here is applicable to the next paper, pp. 870 ff.

Author Index to Volume LIX, 1955

Subject Index to Volume LIX, 1955

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