bath was required was six hours at a temperature of —140°, during which time no readjustment of the apparatus was necessary and a maximum variation of 0.1° was observed. Somewhat less than two liters of liquid air was used. This amount can be greatly reduced since no precautions were taken to heat-insulate the tube between the liquid-air container and the bath. If desired, the thermal regulator can be made more sensitive and the temperature variation reduced to 0.02°.

The above thermostat should prove useful in work where a constant low temperature is desired, such as in the pre-cooling of substances for calorimetric determinations of specific and latent heats and in the standardization of thermometers for low-temperature work.

Acknowledgment is made to the National Research Council of Canada for a Fellowship granted to one of us.

Summary

An automatic, low-temperature thermostat has been described which is cheap and easy to construct. It can be used for any temperature between that of the room and that of liquid air. It remains constant to 0.1° for any desired length of time. It has also been pointed out that the sensitivity can be increased if so desired.

MONTREAL, CANADA

ACTIVITY COEFFICIENTS OF ELECTROLYTES. I. THE LIMITING LAW FOR A TRI-TRIVALENT SALT[1]

BY VICTOR K. LAMER, CECIL V. KING AND CHARLES F. MASON

Introduction

One of the most important generalizations which has been obtained from the theory of the complete dissociation of strong electrolytes involves the principle that as the dilution is increased the laws expressing the thermodynamic behavior of such solutions as a function of concentration become progressively simpler in character, until finally an ideal region of concentration is approached in which this behavior is determined solely by the numbers and valences of the ions involved and not by the specific individual properties of the ions.

As was shown previously,[2] this proposition can be expressed most con-

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[1] An abstract of this paper was presented at the Philadelphia Meeting of the American Chemical Society, September, 1926. Part of the data are given in Dr. Mason's dissertation.

[2] Brönsted and LaMer, THIS JOURNAL, **46**, 555 (1924). The constant α' in our paper is equal to 3/2.3 of the α of Brönsted and LaMer, otherwise the notation is the same.

cisely for chemical purposes in terms of the activity coefficients of the salt or of the ions, namely[3]

$$-\log_{10} f_{(salt)} = \alpha' (-z_1 z_2) \sqrt{\mu} \tag{1}$$

$$-\log_{10} f_{(ion)} = \alpha' z_i^2 \sqrt{\mu} \tag{2}$$

equations which can be obtained on empirical grounds by combining Lewis and Randall's principle of ionic strength with Brönsted's equation for the dependence of the logarithm of the activity coefficient in terms of the valences of the ions and the concentration.

It is a matter of particular interest that the theory of Debye and Hückel not only embraces all of these empirical generalizations by yielding Equations 1 and 2 as limiting laws, but in addition predicts the value of the constant α' solely in terms of natural constants, the absolute temperature T and the dielectric constant of the solution D, which in the limiting case becomes equal to D_0, the value for the pure solvent.[4]

$$\alpha' = 1/2.303 \, [N^2 \epsilon^3 \sqrt{2\pi}/(10 R D_0 T)^{3/2}]$$

If it is true that on dilution all *real* salts actually approach such an ideal range of concentration where their thermodynamic properties are entirely independent of the specific character of the ions, then at any given temperature α' must be a universal constant and presumably should equal the value given by Debye's theory. If, on the other hand, this does not prove to be the case for all strong electrolytes, then the ions exhibiting such behavior must possess specific properties which have not been taken into account in the theory.

Although the experimental work of Brönsted and LaMer[2] gives material support to the Debye theory by yielding a close agreement between the experimental and theoretical values of α' for mixtures of salts involving different combinations of salts, they noted that deviations from Equation 1 which were quite outside possible experimental error were to be observed in their data even in highly dilute solution. These deviations, which become particularly prominent in mixtures of salts of high unsymmetric valence type, are considered in detail in Paper II of this series.[5] The present paper is restricted to a study of a salt of high but symmetrical

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[3] Here z_i represents the valence of an individual ion of the ith kind, while z_1 and z_2 represent, respectively. the valence of a cation and of an anion of a binary salt. It is important to note that the valence of an anion z_2 is considered negative. μ is the ionic strength defined as $1/2 \Sigma c_i z_i^2$, the summation being extended over all ions present in the solution of kinds $1 \ldots i, \ldots . s$. Following Debye and Hückel. c is the molar (not molal) concentration defined as $1000 \, n_i/v$, where v is the volume of the solution and n_i the number of moles of ions of the ith kind; f is the stoichiometric activity coefficient.

[4] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). A more elementary presentation of the fundamental principles involved in the theory has been given by one of us in Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Co.. New York, 1925, pp. 317–334; 339–348; 357–358.

[5] LaMer and Mason, THIS JOURNAL, **49**, 410 (1927).

valence type, which on *a priori* grounds should approximate Debye's picture of ideal ions, and we shall attempt to determine the value of α' more accurately and at higher dilutions than has previously been employed for the purpose by eliminating complicating disturbances as far as possible.

We have chosen to study the tri-trivalent salt luteo ferricyanide, $[Co(NH_3)_6]^{III}[Fe(CN)_6]^{III}$, by the solubility method for a number of reasons. (1) Luteo ferricyanide is a typical strong[6] electrolyte which not only meets the requirement of symmetrical valence type, but according to Werner's theory the NH_3 and CN groups are symmetrically placed about the cobalt and iron atoms. We may, therefore, presume that the distribution of electricity within the respective complex ions is also symmetrical. Further—and this point applies to most salts of the cobaltammine type—according to Werner's theory the coördination numbers of the nuclear atoms are satisfied so that the possibility of chemical interaction with the solvent is minimized, a factor which certainly complicates the case of hydrochloric acid in water. (2) Its solubility in water (0.00003 mole per liter) is comparable to that of silver chloride, and determinations of the activity coefficient may accordingly be carried out to this dilution. (3) The high valence type, $(-z_1z_2) = +9$, increases the accuracy of the determination of α' nine times over that which could be obtained from a study of a uni-univalent salt of corresponding analytical properties. (4) The luteo ion forms one of the components of the salt mixtures which have yielded highly abnormal results in the presence of solvent salts of unsymmetric valence type such as potassium sulfate.[5] (5) Both the luteo and ferricyanide ions are considered very stable in aqueous solution.[7]

Experimental Part

The theory and experimental details of the solubility method of determining activity coefficients have been dealt with at length in the preceding article.[8] Only such differences in experimental technique as were necessary in this investigation will be described.

The apparatus used for preparing the saturated solutions is identical in all essential details with that used previously in the Copenhagen Laboratory, except that the solubility tubes were made of Pyrex and the water-

[6] Lamb and Yngve [*ibid.*, **43**, 2352 (1921)] state that hexammine cobalt hydroxide (luteo hydroxide) and some of the closely related cobaltammines have no parallels among the simple tri-acid inorganic bases as regards solubility and extent of ionization. Potassium ferricyanide shows no hydrolysis and ferricyanic acid is consequently a strong acid. See also Kolthoff, *Z. anorg. Chem.*, **110**, 143 (1920).

[7] Thus Lamb and Larson [*ibid.*, **42**, 2045 (1920)] give $K_c = 2.2 \times 10^{-34}$ as instability constant for the dissociation $[Co(NH_3)_6]^{+++} \rightleftharpoons Co^{+++} + 6NH_3$. For the stability of ferricyanide, see Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, 1911, vol. 1, p. 231.

[8] Ref. 2, pp. 563–569.

bath was maintained at $25° \pm 0.005°$. In some of the preliminary experiments it was found that when the room temperature fell below $25°$, crystals of the saturating salt separated out in the collecting flasks on standing overnight. To prevent this we have surrounded the collecting flasks and the portions of the solubility tubes which project through the floor of the water-bath with an insulating wall and have maintained the temperature in this compartment slightly above $25°$ by means of an electric heater. Four sets of distilling apparatus were used. Three were made of block tin fitted with Hopkins distilling heads and a fourth set was made entirely out of one piece of quartz.

Preparation of Salts

Since the solubility of a high-valence salt like luteo ferricyanide is very sensitive to the presence of minute traces of foreign salts, it is important that its preparation be carried out in very dilute solution to minimize as far as possible any chance that foreign salts might be occluded in the crystal lattice either during the precipitation or subsequent growth of the crystals.

Two methods of preparation were employed. In No. 1 the final salt was prepared by metathesis of potassium ferricyanide with a sample of luteo nitrate made by the iodine method of Biltz.[9] In No. 2 luteo chloride, prepared by a method devised by Professor Kiehl of this Department and kindly furnished us by him, was used, instead of nitrate. The metathetic preparation was essentially identical in both cases and only the details of Preparation 2 will be given.

The luteo chloride was recrystallized thrice by dissolving in water at $25°$ and precipitating by the addition of half its volume of concd. hydrochloric acid. It was freed from acid by washing with a little cold water and finally by repeated washing with alcohol. Seventy-two g. was then dissolved in 8 liters of distilled water and the solution stirred vigorously with a mechanical stirrer; 54 g. of potassium ferricyanide, prepared by two recrystallizations from distilled water, was dissolved in 2 liters of water and the resulting solution allowed to drip slowly, over a period of eight hours, into the luteo chloride solution. By maintaining constant stirring, local excesses of potassium ferricyanide were prevented. After settling overnight, the supernatant liquid was siphoned off and the crystals were washed 10 times by decantation, followed by agitation in pure water for a week to facilitate growth to uniform size.

It is well known from Hulett's work that the solubility of very small crystals (that is, those having a radius of curvature of less than 0.001 mm.) depends upon the size of the crystal, whereas the solubility of larger crystals is independent of the size.

To eliminate the disturbing effect of very small crystals we employed a method of sedimentation. The entire crop of crystals was poured into a tall (100cm.), narrow cylinder filled with water and those crystals which did not settle promptly were siphoned off. The smaller crystals, which could be detected by their lighter yellow color, formed the top of the column of salt which settled to the bottom. The small crystals were

⁹ Biltz, "Laboratory Methods of Inorganic Chemistry," John Wiley and Sons, New York, 1909, p. 176.

sucked off and discarded. By repeating this process about five times it was possible to obtain crops of crystals which appeared to be uncontaminated with smaller crystals, and consequently should be of sensibly identical solubility. In filling the solubility tubes for the saturation experiments, care was also taken that if any small crystals still remained they would be at the top of the column of salt. If any difference in solubility existed which could be due to size of crystals, then the solution saturated with respect to the small crystals would of necessity have to flow through the major portion of the column containing the larger crystals. One of the most important advantages of this method of saturation is that the same column of saturating salt is used in all experiments of a given series.

The salts (potassium nitrate, sodium chloride and magnesium sulfate) used to prepare the solvent solutions were recrystallized twice and carefully dried before being weighed out.

Distillation of Ammonia

Since the quantity of ammonia which is furnished by 400 cc. of a saturated solution of luteo ferricyanide amounts to only one-fiftieth of the amount distilled in the usual Kjeldahl method, it is necessary to use the utmost care in the distillation and titration, if a high degree of accuracy is to be obtained.

The procedure finally adopted for this salt consisted in adding 15 cc. of 20%, C.P. potassium hydroxide solution to a 400cc. aliquot and distilling the ammonia liberated at once through a condenser composed entirely of quartz or of block tin into a receiving flask containing slightly more than an equivalent amount of hydrochloric acid (0.01076 N in Series I and approximately 0.007 N in the separate Series, II, III and IV).

A number of experiments (30 in all) were tried in which 1- or 2-liter aliquots were first evaporated down to a volume of 200 cc. in the presence of 5 cc. of 10% sulfuric acid before adding the alkali to see if it would be possible to increase the accuracy by titrating a larger quantity of ammonia in a smaller volume of distillate. This method did not yield as good checks as did the simpler method of direct distillation of a 400cc. aliquot, and since the values were lower we feared that ammonia was unavoidably lost on long evaporation. A series of time distillations was carried out with ammonium chloride and the various cobaltammine salts to ascertain the length of time for complete decomposition and the optimum conditions of heating in our apparatus in order to make a quantitative distillation and at the same time maintain the final volume of the distillate at a minimum. From the data thus obtained we could ascertain the progress of the distillation of ammonia by knowing the volume of water distilled. If the first stage of the distillation is carried out under a Bunsen flame so low that simmering results, it was found that 95% of the ammonia is carried over in an hour's time, while only 20% of the water has distilled. At the end of one hour's time the flame was increased to full capacity to produce a rapid distillation of water which washed out the last traces

of ammonia remaining in the condenser. By operating in this manner we could determine 0.07 milliequivalent of ammonia in 300 cc. of distillate with a degree of precision which in individual experiments was generally within 0.5%. (See Tables II and III.)

The distillates were titrated to an end-point of P_H 5.2, using buffer solutions containing the same amount of methyl red as indicator for color comparisons. To prevent the effects of carbon dioxide the titrations were carried out immediately after the conclusion of the distillation, using stirring but not shaking. The distilled water used was redistilled over acid potassium permanganate and access of carbon dioxide prevented by the use of soda lime guards on the reagent and wash bottles.

TABLE I

SOLUBILITY RELATIONS OF $[CO(NH_3)_6][Fe(CN)_6]$ AT 25°

Series I. Acid, 0.01076 N HCl. Water blank, 0.46 cc. Preparation No. 1a. Solvent salt KNO_3.

Concn. of added salt, M	No. of final detns.	Acid used, cc. (corr.)	$S \times 10^5$, M	Log S/S_0	$\sqrt{\mu}$	a in Å.
0.0000	2	4.08	2.925	..	0.0162	..
.0005	2	4.46	3.20	.040	.0281	..
.0010	2	5.12	3.67	.099	.0365	..
.0030	5	5.95	4.27	.164	.0582	..
.0050	2	7.47	5.36	.263	.0740	..
.01	1	9.20	6.60	.353	.1029	2.83
.02	2	12.39	8.88	.482	.1442	3.82
.03	2	16.36	11.73	.603	.1762	3.87
.05	2	22.00	15.77	.732	.2268	3.75
.06	1	25.09	17.99	.789	.2482	3.77
.07	2	29.26	20.98	.856	.2681	3.53
.10	2	40.26	28.87	.994	.3203	3.46

Series II. Preparation 2a. Water blank, 0.63 cc. Acid, 0.00735 N HCl. Solvent, water.

(Tube I)	2	12.48	3.058	...	0.0166	
(Tube II)	2	12.51	3.066	...	.0166	
(Tube III)	3	12.43	3.046	...	.0166	
Av.	7	12.47	3.056	...	.0166	
NaCl, Tube I						
0.0005	3	13.79	3.379	0.043	0.0284	
.0010	2	14.39	3.526	.062	.0363	
.0050	1	18.95	4.64	.182	.0736	
.0100	1	26.21	6.42	.322	.1028	
MgSO₄, Tube II						
0.0010	1	26.55	6.506	.327	.0677	
.0050	2	62.20	15.24	.697	.1462	
.0100	2	92.52	22.67	.869	.2050	
BaCl₂, Tube III						
0.0050	2	33.93	8.314	.436	.1255	
K₂SO₄, Tube II						
0.0010	1	25.40	6.224	.308	.0597	

TABLE II

Cc. of 0.007 M HCl to Titrate NH$_3$ from 400cc. Aliquot of $[Co(NH_3)_6][Fe(CN)_6]$

Series III (Preparation 1b)

Date (1926)	Pure water	Date	0.0005 M KNO$_3$, cc. of HCl	Date	0.0010 M KNO$_3$, cc. of HCl	Date	Water blank, cc. of HCl
2/16	10.07	3/8	11.36	3/14	12.26	3/3	0.61
2/16	10.03	3/9	11.35	3/14	12.34		.68
2/17	9.86[b]	3/10	11.29	3/15	12.26	3/5	.45
2/18	9.97	3/11	11.39	3/24	12.24		.42
3/4	10.06			3/24	12.21	3/6	.63
3/4	10.01			3/28	12.27		.68
3/5	10.02					3/12	.43[a]
Av.	10.02	Av.	11.35	Av.	12.26	Av.	.55

Series IV. (Preparation 2b)

	Pure water	Date	0.0005 M	Date	0.0010 M	Date	0.002 M KNO$_3$, cc. of HCl
2/17	9.75	3/8	10.99	3/26	12.19	4/3	13.21
	9.77	3/9	11.04		12.29		13.55
	9.71	3/10	11.00	3/28	12.17	4/4	13.33
2/18	9.72	3/11	11.08		12.27		13.79
3/4	9.74						
3/4	9.74						
3/5	9.52[b]						
Av.	9.74	Av.	11.02	Av.	12.23	Av.	13.47

[a] The water blank recorded for 3/12 contained 0.001 M KNO$_3$.

[b] Omitted from average.

TABLE III

SOLUBILITY RELATIONS OF LUTEO FERRICYANIDE

Series III

Concn. of added KNO$_3$, M	No. of final detns.	$S \times 10^5$, M	Av. dev., %	Log S/S_0	$\sqrt{\mu}$	y[a]
0.0000	6	2.900	0.27	....	0.01616	...
.0005	4	3.308	.27	0.0572	.02825	0.525
.0010	6	3.586	.22	.0922	.03637	.507
.0020	6	4.080	1.5	.1603	.04865	.548

Series IV

0.0000	6	2.814	0.15	....	0.01591	...
.0005	4	3.206	.30	.0566	.02808	0.517
.0010	4	3.577	.42	.1042	.03636	.566
.0020	4	3.959	1.4	.1483	.04854	.509
					Av. =	.528

[a] $y = \log (S/S_0)/[(-z_1 z_2)(\sqrt{\mu} - \sqrt{\mu_0})]$ in this table.

TABLE IV

AVERAGED RESULTS OF SERIES III AND IV (PLOTTED IN FIG. 2)[a]

Concn. of KNO₃, M	No. of detns.	$\sqrt{\mu}$	log S/S_0	$-\log f$	α'	$-\log f$	α'
0.0000	12	0.01603	0.0000	(0.0752)	(0.521)	(0.0727)	(0.504)
.0005	8	.02817	.0569	.1321	.521	.1296	.511
.001	10	.03637	.0982	.1734	.530	.1709	.522
.002	10	.04860	.1543	.2295	.524	.2270	.530
					Av. 0.525		Av. 0.521

[a] The experimental value of the slope of the log S/S_0 plot corresponding to $y = 0.521$ at 0.0005 M KNO₃ was used to extrapolate to infinite dilution in Cols. 5 and 6. In Cols. 7 and 8, the Drude value $y = 0.504$ was used, showing that the change in y has little effect on the average value of α'.

TABLE V

CALCULATIONS OF RESULTS OF BRÖNSTED AND BRUMBAUGH ON THE ACTIVITY COEFFICIENTS OF [Co(NH₃)₆][Co(CN)₆] IN NaCl SOLUTIONS AT 18°

Log f_0 (extrapolated) = 0.049. $\alpha' = 0.496$ (theory), using Equation 3 to determine the value of a.

Concn. of added NaCl, M	Log S/S_0, obs.	Log f, obs.	Devn. of log f from the mean of two series	a in Å. to fit Eq. 3	Log f, calcd. $a = 2.8$ Å., Eq. 3	Diff, log f (calcd.) $-\log f$ (obs.)
0.000	. . .	(0.049)	. . . . .	. .	0.049	. . . . .
.001	0.094	.143	±0.005	5.2	.147	+0.004
.003	.187	.236	± .000	3.6	.239	+ .003
.005	.252	.301	± .006	2.94	.302	+ .001
.010	.357	.406	± .014	3.54	.415	+ .009
.015	.456	.505	± .011	2.29	.496	− .009
.020	.520	.569	± .014	2.54	.563	− .006

Data

The data comprise four separate series of experiments by two observers in which four preparations of saturating salt were used. It will be noted that in spite of the precautions taken in the preparation and subsequent purification of the salts by washing with pure water for periods of time extending up to five months, the values for the solubility in pure water (S_0), although constant in a given series for a period of 17 days when the final values were obtained, nevertheless vary slightly ($< 3\%$) among different preparations.

Fortunately, variation in absolute solubility in different series can have no effect upon the results, for we are concerned primarily with the values of the solubility ratios log S/S_0, which were calculated directly from the number of cubic centimeters of acid consumed in the titration of the ammonia from a constant aliquot obtained from a sample of saturating salt remaining undisturbed in the solubility tubes for the duration of a series.

The data of Series I show that 0.1 M potassium nitrate solution increases the solubility of luteo ferricyanide 100% over its value in pure

water, while even 0.0005 M potassium nitrate produces an increase of 10%. It is clear from Fig. 1 that the curve for log S/S_0, or $-\log f$, which differs only by the constant factor log $f_0 = 0.075$, representing the extrapolation to infinite dilution from 0.00027μ, rapidly approaches and fuses into the straight line (Equation 1) representing the limiting law of Debye and Hückel.

The data of Series III and IV are of higher accuracy than those of Series I and II as indicated by the average deviation from the mean of the individual determinations (Table III, Col. 4). In Col. 7 we give the
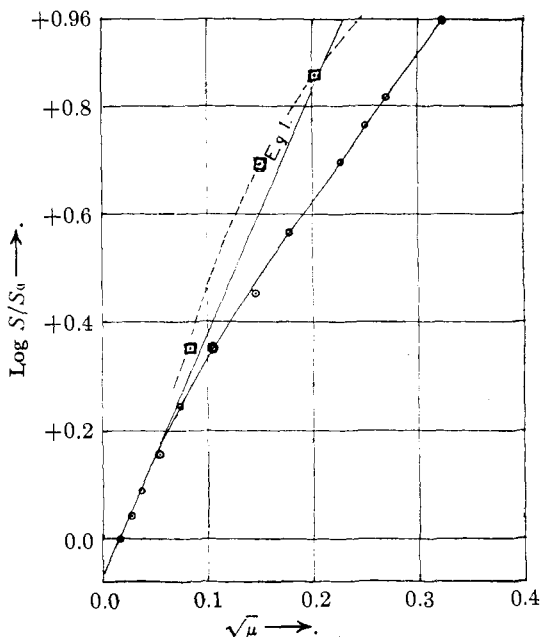

Fig. 1.—$\odot$, solubility effects of KNO$_3$; $\square$, of MgSO$_4$, on [Co(NH$_3$)$_6$] [Fe(CN)$_6$].

value of the slope of the log S/S_0, $\sqrt{\mu}$ curve; namely, $y = \log(S/S_0)/-[(-z_1z_2)(\sqrt{\mu} - \sqrt{\mu_0})]$, when drawn as a straight line through each of the experimental points for Series III and IV. The solubility data for 0.0005 M potassium nitrate solution were determined with particular care, and in our opinion merit more weight than the other data. They yield 0.525 and 0.517, respectively, for y, or an average of 0.521, while the average value of y for all of the data is 0.528.

In order to compare our data with those of others, using salts of different solubilities and at different temperatures, as well as to compute α' in Equation 1, it is necessary to extrapolate the log S/S_0 plot to infinite dilution to determine $-\log f = \log S/S_0 - \log f_0$. Table IV shows that the final

value of α' is affected but very little, whether we extrapolate under the assumption (a) that the experimental slope, $y = 0.521$, is maintained to infinite dilution, or (b) that $y = \alpha' = 0.504$ in this region. Assumption b conforms to Drude's value of $D_0 = 78.77$. Lili Kockel[10] has very recently given $D_0 = 77.81$ at 25°, for whi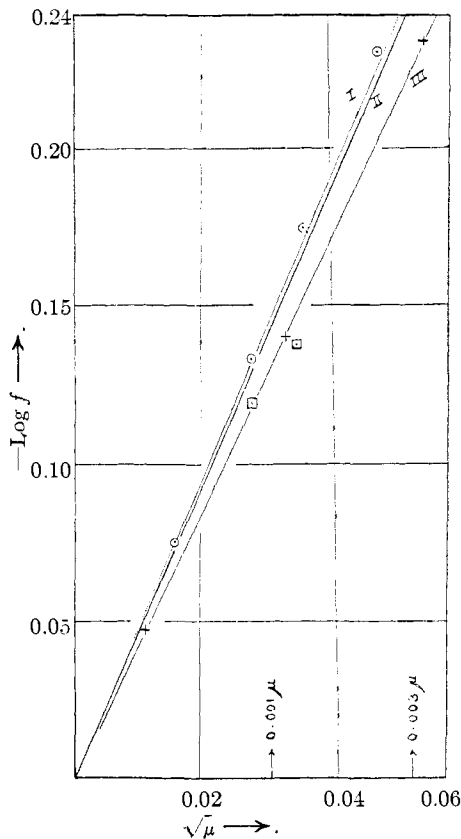ch $\alpha' = 0.514$. Using her value for the extrapolation, we should get results intermediate between Assumptions a and b.

In Fig. 2 we have plotted on a magnified scale the averaged results of Series III and IV in the very dilute region (below 0.003μ), using Assumption a. Curves I and II give the theoretical results of Equation 1 using, respectively, the Kockel and Drude values of D_0. If there were no data available other than our results with potassium nitrate, we could conclude that for a tri-trivalent salt α' agrees with the theoretical value to within 4%, which is of the same order of accuracy for which $(D_0)^{3/2}$ is known, namely, 2%. Since the potassium nitrate data were obtained, Brönsted and Brumbaugh[11] have published results for 18° using sodium chloride as the solvent salt for the closely related saturating salt luteo cobalticyanide ($S_0 =$ 0.000014 M), which differs only in that cobalt replaces iron in the anion. Their averaged data for 0.001, 0.002 and 0.003 M sodium chloride additions fall upon a

Fig. 2.—Curve I, $\alpha' = 0.514$ ($D_0 = 77.81$); Curve II, $\alpha' = 0.504$ ($D_0 = 78.77$); Curve III, $\alpha' = 0.46$. ⊙, KNO$_3$; ⊡, NaCl, on luteo ferricyanide at 25°; +, NaCl on luteo cobalticyanide at 18°.

straight line, yielding a value of $y = \alpha' = 0.46$ (line 3, Fig. 2). The theoretical value (Drude) at 18° is $\alpha' = 0.496$. We have accordingly carried out a few experiments on sodium chloride (Series II) which are plotted as squares in Fig. 2. Although the data of Series II are not of the same high degree of accuracy as those of Series III and IV, they show that detectable

[10] Kockel, *Ann. Physik*, [4] **77**, 417 (1925).

[11] Brönsted and Brumbaugh, THIS JOURNAL, **48**, 2015 (1926).

differences between the effects of potassium nitrate and sodium chloride can still be observed with luteo ferricyanide, even at concentrations as low as 0.001μ, and suggest a lower value of α' when using sodium chloride in this range of concentration.

In Table V we have calculated the values of a (Col. 5) which must be assumed in order to retain the theoretical value of $\alpha' = 0.496$ and at the same time fit their data to the equation of Debye and Hückel where ion size a is taken into account, namely

$$-\log_{10} f = \alpha' \, (-z_1 z_2) \sqrt{\mu} \cdot 1/(1 + 0.327 \, a \sqrt{\mu}) \tag{3}$$

In Col. 6 we have calculated the values of $\log_{10} f$ which would be obtained under the assumption that $a = 2.8$ Å., which happens to be identical with the value of a given by x-ray analysis of sodium chloride crystals. It will be noted that this plausible value fits their data, except for the point $0.003 \, M$, within the limits of error for which the observed value of log f was determined in separate series, but the steady march of the differences makes the agreement of doubtful significance.

Evidently, still more extended and exact data must be obtained in the highly dilute range before the non-variability of α' for different salts can be considered as verified experimentally.

If we rely entirely upon such a simple explanation as that involved in the use of a in Equation 3 to explain all the deviations from the limiting law, we soon encounter further difficulties. Thus our data (Table I, Col. 7) show that above $0.01 \, M$, where a calculation is warranted, the value of a is practically constant and equals 3.7 Å., but in the more dilute range (Series III, IV) the ion size would have to decrease to zero and perhaps become negative. In the case of magnesium sulfate (Fig. 1), a negative value would certainly have to be assumed for a in the neighborhood of 0.01 to 0.04μ. In the following paper we shall communicate very convincing data, involving amongst other ions the sulfates, which would require large negative values of a in highly dilute solution to satisfy Equation 3. The present cases are not the only ones where the simple conception of ion size fails to account for the data in symmetrical mixtures. For example, Schärer,[12] in confirming Equation 3, was obliged to introduce a value of $a = -0.9$ Å. to account for the solubility data of thallous chloride in thallous nitrate. W. P. Baxter's results[13] for potassium sulfate on silver iodate are similar to those for magnesium sulfate (Fig. 1) and would also require negative values in dilute solution. These anomalies, which are to be expected on theoretical grounds when the a value for one or more of the ion pairs falls below a certain limiting value, will be discussed in the next paper.

It should be emphasized that the concordance of the data with the

[12] Schärer, *Physik. Z.*, **25**, 145 (1924).

[13] Baxter, THIS JOURNAL, **48**, 615 (1926).

limiting law for a salt of such high valence type as that of luteo ferricyanide is far more striking and important than are the comparatively minor discrepancies just referred to. The data should be interpreted as substantiating the limiting law and the fundamental postulates upon which it is based, at least in their broader aspects when applied to electrolytes of symmetrical valence type, even though we must grant that α' may be subject to slight variations depending upon the nature of the solvent salts employed at concentrations as low as 0.001μ.

Accepting the Debye-Hückel expression for the electrical *free energy* of the solution, the variation of the dielectric constant with concentration may be calculated directly from the osmotic data in the case of solutions of a single salt composed of two ions.[14] These calculations indicate that in the case of potassium chloride the dielectric constant of the solution becomes about 5% lower than that of pure water at a concentration as low as $0.005\ M$. It is entirely possible that the variations in α' in solubility measurements may be accounted for by a similar variation in the dielectric constant alone, but since such variation in the dielectric constant cannot be computed in ternary mixtures, the question must be left open until direct measurements of the dielectric constants of conducting solutions have been established.

Summary

1. The activity coefficients of a tri-trivalent electrolyte, luteo ferricyanide, S_{H_2O} at $25° = 3 \times 10^{-5}\ M$, have been determined by measuring its solubility in aqueous salt solutions.

2. The results with potassium nitrate and magnesium sulfate conform excellently to the limiting law of Debye and Hückel up to an ionic strength of 0.007μ.

3. The value of the theoretical constant α' was found to be 0.52 for potassium nitrate, while the calculated value is 0.504 or 0.514 when Drude's or Kockel's value of the dielectric constant of pure water is employed.

4. With sodium chloride as solvent salt the value for α' appears, even at 0.001μ, to be somewhat lower than for potassium nitrate. Although this discrepancy may be attributed in the case of sodium chloride to the effect of ionic size, it is doubtful if the simple concept of ionic size as used by Debye and Hückel can account for the deviations from the limiting law even for mixtures of symmetrical valence types in highly dilute solutions, since negative or impossibly small positive values for a would be required in certain cases to satisfy their equations.

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[14] See Gronwall and LaMer [*Science* [N. S.] **64**, 121 (1926)] for a preliminary report of results.