ACTIVITY COEFFICIENTS OF ELECTROLYTES. II. THE UNSYMMETRIC VALENCE-TYPE EFFECT IN HIGHLY DILUTE SOLUTIONS[1]

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Introduction

In their confirmation of the general applicability of the Debye-Hückel theory and the Lewis and Randall principle of ionic strength to solutions of strong electrolytes, Brönsted and LaMer[3] noted that there was experimental evidence, even at high dilution, which was in conflict with the theory. Since this evidence was restricted primarily to mixtures of highly unsymmetric valence types, they called the anomaly the electric-type effect.

For example, the difficultly soluble tri-univalent salt luteotetranitrodiammino cobaltiate, $[Co(NH_3)_6]^{III} [Co(NO_2)_4(NH_3)_2]_3^I$, exhibits a change of 60% in solubility when passing from 0.01 M magnesium chloride to 0.01 M sodium sulfate, although the total concentration of solvent salt is the same regardless of whether we express the concentration in terms of the molality, the equivalent concentration or the ionic strength. According to the theory the solubility should be sensibly identical in either solvent. It is clearly evident that either these dilute salt solutions possess some highly specific properties or else the valence sequence is of importance in addition to the ionic strength.

It was largely on the basis of experiments of this character that Brönsted had rejected[4] the principle of ionic strength as a complete solution of the problem of activity coefficients of mixtures and substituted for it his principle of specific interaction and of the linear deviation of the activity coefficient.[5]

The principle of Lewis and Randall[6] may be stated as follows: "In dilute

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[1] A preliminary report of this work was read at the Symposium on Strong Electrolytes at the Los Angeles Meeting of the American Chemical Society, August, 1925. A complete report was read at the Philadelphia Meeting, September, 1926.

[2] This paper is constructed from a dissertation submitted by Charles F. Mason to the Faculty of Pure Science of Columbia University in March, 1926, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. More details regarding the experimental data are to be found in the printed dissertation.

[3] Brönsted and LaMer, THIS JOURNAL, 46, 555 (1924). See their Fig. 2, and pages 558 and 573. For a further confirmation of the theory in symmetrical mixtures see Paper I of this series [ibid., 49, 307 (1927)].

[4] Brönsted, ibid., 44, 877 (1922).

[5] Brönsted, ibid., 45, 2898 (1923).

[6] Lewis and Randall, (a) ibid., 43, 1112 (1921); (b) "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 374.

solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." In a consideration of certain of Brönsted's objections they state[7]—"the answer to this interesting argument is again that the rule does not imply that the activity coefficients should be absolutely constant except at infinite dilution, although it implies a rapid approach to this condition as the concentration approaches zero." With the general acceptance of the Debye-Hückel theory[8] it becomes all the more important to subject the question at issue to a more searching experimental and theoretical examination, for the Debye theory in its present form simply reinforces the view of Lewis and Randall that all deviations from the ideal law should vanish rapidly with the concentration.
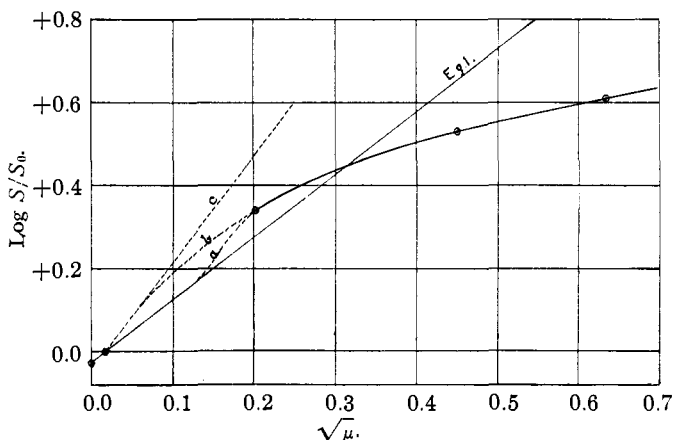

Fig. 1.—Solubility effect of $MgSO_4$ upon $[Co(NH_3)_6][Co(NH_3)_2\text{-}(NO_2)_4]_3$ at $0°$, from Brönsted's data [THIS JOURNAL, **43**, 2265 (1921) (Table XLIV)].

In Fig. 1 we have plotted one of the more representative cases available, and although the data are in reasonably dilute solution it is impossible to state definitely whether the deviations from the limiting law

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

will disappear with sufficient rapidity, as we pass to infinite dilution, to fuse into the ideal Equation 1 as represented by the course of the dotted Curve a in Fig. 1, or whether the data in highly dilute solution will make a discontinuous junction as represented by Curve b. The importance of a definite decision in regard to the course of the curves at very high dilution is evident when we note that a result like that of Curve b furnishes a strong argument for an individual limiting slope for each particular

[7] Ref. 6 b, pp. 368–369.

[8] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). See particularly Debye, *ibid.*, **25**, 97, 203 (1924).

combination of ions. This would demand a fundamental modification in the Debye theory, at least when considering salts of high valence types.

Experimental Part

The experimental method and apparatus employed were identical with those given in the preceding article of this series[9] except that since the salts employed were not as insoluble as luteo ferricyanide and also contained more NH_3 groups, it was possible to obtain much greater experimental accuracy. In the majority of the experiments the accuracy is at least within 0.2% and often within 0.1%. Each determination represents the average of four or more experiments. Preliminary experiments were carried out to satisfy ourselves that the salts used were quantitatively decomposed by the Kjeldahl method. Time distillations were made for each salt as described previously to determine the optimum conditions for distillation which were rigidly adhered to. Little difficulty was noted in reaching a final absolute solubility in pure water. The values given for the solubility in pure water were rechecked at regular intervals and always after the completion of each series of solvent salts and were found to be unchanged. The acid used in titrating the liberated ammonia was 0.01076 N. The same sample of acid was used throughout all of the experiments of this paper so that there is no possibility of error due to variation in titer values. Blank distillations on the distilled water, which included blanks on the chemicals, were run at the regular intervals. Possibility of error from this source is much reduced since the aliquots were only one-fourth to one-half of that of the previous investigation. The burets were calibrated. The temperature was 25 ± 0.003°.

Preparation of Materials

The saturating salts, whose activity coefficients were measured, were the tri-univalent salts (1) luteotetramminodiammino cobaltiate and (2) luteodinitrodiammino-oxalo cobaltiate. Previous work[10] at higher concentrations had led us to suspect that these two salts would exhibit the anomaly referred to. The stability of these salts in solution and their excellent analytical properties make them ideal substances for measurements in highly dilute solution, a point[11] which has previously been discussed in detail.

The luteo cation, $Co(NH_3)_6$, was prepared in the form of the trinitrate by the well-known iodine method as given by Biltz.[12] The anions were prepared in the form of their potassium salts. In the case of the tetra-

[9] LaMer, King and Mason, This Journal, 49, 363 (1927).

[10] Unpublished data by one of us made in connection with the investigation reported in Ref. 3.

[11] Ref. 3, p. 564; Ref. 9, p. 365.

[12] Biltz, "Laboratory Methods of Inorganic Chemistry," English translation by Hall and Blanchard, John Wiley and Sons, New York, 1909, p. 176.

nitrodiammino cobaltiate anion we found that Jörgensen's second method, in which the ammonium salt is prepared,[13] was superior to the method given by Harkins, Hall and Roberts,[14] which is based upon Jörgensen's earlier method, where the potassium salt is formed.

Preparation[15] of K(H₂O)[Co(NH₃)₂(NO₂)₂C₂O₄].—Ten g. of crystallized oxalic acid was dissolved in 50 cc. of water and this solution was added to 100 cc. of a solution containing 20 g. of K[Co(NH₃)₂(NO₂)₄]. After being heated to about 50°, nitrogen dioxide was evolved and a precipitate separated. The latter was removed by filtration and washed with cold water. It was purified by recrystallization from hot water.

Preparation[16] of [Co(NH₃)₆]6H₂O[Co(NH₃)₂(NO₂)₂C₂O₄]₃.—This salt was quantitatively precipitated from an aqueous solution of 160 liters' volume by allowing saturated solutions of [Co(NH₃)₆][NO₃]₃ and K(H₂O)[Co(NH₃)₂(NO₂)₂C₂O₄] to drip simultaneously into 16 liters of distilled water, which was thoroughly agitated by an electric stirrer, while the supernatant liquid was siphoned off and replaced by fresh water ten times during the course of preparation. This procedure facilitated the growth of well-defined crystals, which were necessary for subsequent operations in the investigation.

The final compound was analyzed by decomposing a weighed quantity with sulfuric acid, evaporating to constant weight and weighing the cobalt as cobaltous sulfate.

Anal. Calcd. for $C_6H_{48}O_{30}N_{18}Co_4$: Co, 22.73. Found: 22.62.

Preparation[16a] of [Co(NH₃)₆][Co(NH₃)₂(NO₂)₄]₃.—This salt was quantitatively precipitated from an aqueous solution by adding simultaneously [Co(NH₃)₆][NO₃]₃ and K[Co(NH₃)₂(NO₂)₄] in equivalent quantities to 160 liters of distilled water under conditions identical with those described above.

The average of two determinations showed 23.40% of cobalt; calcd., 23.79%; Jörgensen found 23.39%.

Data

Our new experimental data in highly dilute solutions are given in detail in Tables I and II. For comparison with the Debye-Hückel theory we have plotted the experimental results in terms of the logarithm of the solubility ratio of the saturating salt in pure water and in the corresponding salt solutions in terms of the square root of the ionic strength (Figs. 2 and 3).

The data show, when the saturating salt is of the valence type (3, —1), that solvent salts possessing univalent anions like potassium nitrate and barium chloride conform to the requirements of the Debye-Hückel theory and the Lewis-Randall principle of ionic strength, since the experimental curves, with decreasing ionic strength, rapidly approach and fuse into the straight line as demanded by the limiting Equation 1 which is valid when the ions are separated to such distances that ionic size is of no importance.

[13] Jörgensen, *Z. anorg. Chem.*, **17**, 476 (1898). These directions are also given by Thomas ("Complex Salts," Blackie and Son, Ltd., Glasgow, **1924**, p. 116) and need not be repeated here.

[14] Harkins, Hall and Roberts, THIS JOURNAL, **38**, 2647 (1916).

[15] Jörgensen, *Z. anorg. Chem.*, **11**, 445 (1896).

[16] Jörgensen, (a) *ibid.*, **5**, 179 (1894); (b) Ref. 15, pp. 439, 447.

TABLE I

SOLUBILITY RELATIONS OF $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2C_2O_4]_3$ IN VARIOUS SOLVENTS

Concn. of solvent salt, M	Acid used, cc. (corr.)	Solubility, moles per liter $\times 10^4$	μ	$\sqrt{\mu}$	Log S/S_0	$-$Log f, found	$-$Log f, calcd. (Eq. 1)	Diff.
				Solvent, water				
0.0000	23.06	0.8269	0.0004961	0.02227	....	$+0.0336$	$+0.03373$	....
				Solvent, KNO$_3$				
0.001	24.45	0.8767	0.001526	0.03904	0.0253	0.0587	0.0591	-0.0004
.003	26.44	.9481	.003568	.05973	.0593	.0929	.0905	$+ .0024$
.005	28.12	1.0101	.005606	.07488	.0868	.1204	.1134	$+ .0070$
.010	30.63	1.0984	.01065	.1032	.1232	.1568	.1563	$+ .0005$
.020	34.96	1.2536	.02075	.1440	.1804	.2140	.2181	$- .0041$
.050	44.05	1.5796	.05094	.2257	.2809	.3145	.3419	$- .0274$
.100	55.75	1.9992	.1012	.3180	.3834	.4170	.4817	$- .0647$
				Solvent, K$_2$SO$_4$				
0.0005	28.91	1.0360	0.002121	0.04604	0.0978	0.1314	0.06975	$+0.0617$
.0010	32.63	1.1701	.03702	.06083	.1507	.1843	.09215	$+ .09215$
.0030	41.40	1.4840	.009890	.09945	.2540	.2876	.1506	$+ .1370$
.0050	46.74	1.6760	.01600	.1264	.3068	.3404	.1915	$+ .1489$
.0070	50.97	1.8277	.02209	.1486	.3442	.3778	.2251	$+ .1527$
.0100	56.72	2.0339	.03122	.1767	.3906	.4242	.2677	$+ .1565$
.0200	70.05	2.5120	.06150	.2479	.4825	.5161	.3755	$+ .1406$
.0300	78.17	2.8031	.09168	.3028	.5302	.5638	.4587	$+ .1051$
.0500	93.77	3.3625	.15201	.3898	.6091	.6427	.5905	$+ .0522$
.0700	106.22	3.8090	.21228	.4605	.6633	.6969	.6977	$- .0008$
.1000	121.87	4.3700	.30262	.5500	.7230	.7566	.8333	$- .0767$
				Solvent, MgSO$_4$				
0.0002	26.25	0.941	0.001364	0.03693	0.0561	0.0897	0.05595	$+0.0337$
.0005	28.74	1.030	.002618	.05116	.0953	.1289	.0775	$+ .0513$
.0010	31.91	1.144	.004686	.06845	.1409	.1745	.1037	$+ .0708$
.0030	40.05	1.436	.012861	.1134	.2396	.2732	.1718	$+ .1014$
.0040	42.06	1.508	.016905	.1300	.2606	.2942	.1969	$+ .0973$
.0050	44.64	1.600	.02096	.1447	.2866	.3202	.2192	$+ .1010$
.0070	47.84	1.715	.02903	.1704	.3167	.3503	.2581	$+ .0922$
.0200	62.15	2.228	.08134	.2852	.4304	.4640	.4320	$+ .0320$
.0300	68.02	2.439	.12146	.3484	.4697	.5033	.5278	$- .0245$
.0400	74.37	2.666	.1616	.4020	.5084	.5420	.6090	$- .0670$
.0500	79.42	2.848	.2017	.4492	.5370	.5706	.6805	$- .1099$
.0700	90.30	3.238	.2819	.5308	.5928	.6264	.8041	$- .1777$
				Solvent, BaCl$_2$				
0.0005	24.98	0.8958	0.002037	0.04513	0.0347	0.0683	0.0683	±0.0000
.0010	26.25	.9415	.003564	.05968	.0563	.0899	.0904	$- .0005$
.0030	29.76	1.067	.009640	.09818	.1107	.1443	.1487	$- .0044$
.0050	32.48	1.165	.01569	.1252	.1489	.1825	.1896	$- .0071$
.0100	37.98	1.362	.03081	.1755	.2170	.2506	.2658	$- .0152$
.0200	45.88	1.645	.06098	.2469	.2986	.3322	.3740	$- .0418$
.0400	58.80	2.109	.1212	.3480	.4065	.4401	.5272	$- .0871$
.0500	65.37	2.344	.1514	.3890	.4524	.4860	.5893	$- .1033$
.0600	72.65	2.605	.1815	.4260	.4983	.5319	.6454	$- .1135$
				Solvent, K$_3$Fe(CN)$_6$				
0.001	35.99	1.290	0.006774	0.08230	0.1934	0.2270	0.1247	$+0.1023$
.003	59.17	2.121	.019270	.1388	.4091	.4427	.2103	$+ .2324$
				Solvent, K$_4$Fe(CN)$_6$				
0.0005	50.01	1.793	0.006076	0.07795	0.3362	0.3698	0.1594	$+0.2104$

<div align="center">TABLE II</div>

<div align="center">SOLUBILITY RELATIONS OF $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$</div>

Concn. of solvent salt, M	Acid used, cc. (corr.)	Solubility, moles per liter $\times 10^4$	μ	$\sqrt{\bar{\mu}}$	Log S/S_0	—Log f, found	—Log f, calcd. (Eq. 1)	Diff.
				Solvent, water				
...	11.92	1.651	0.0009906	0.03147	....	0.0320	......	....
				Solvent, K_2SO_4				
0.001	16.62	2.302	0.004381	0.06618	0.1443	0.1763	0.1003	+0.0760
.005	23.62	3.271	.01696	.1302	.2968	.3288	.1972	+ .1316
.010	28.32	3.922	.03235	.1798	.3757	.4077	.2724	+ .1353
.050	46.23	6.403	.1538	.3922	.5886	.6206	.5942	+ .0264
.100	60.07	8.320	.3049	.5522	.7024	.7344	.8366	− .1022
				Solvent, $MgSO_4$				
0.001	16.02	2.218	0.005330	0.07301	0.1283	0.1603	0.1106	+0.0497
.005	22.26	3.083	.02185	.1478	.2732	.3052	.2239	+ .0813
.010	25.68	3.556	.04213	.2052	.3334	.3651	.3108	+ .0543
.050	39.32	5.446	.20326	.4508	.5183	.5503	.6830	− .1327
				Solvent, KNO_3				
0.001	12.41	1.719	0.002031	0.04506	0.0174	0.0494	0.0682	−0.0188
.005	14.27	1.976	.006185	.07864	.0780	.1100	.1191	− .0091
.050	21.95	3.040	.05182	.2277	.2651	.2971	.3450	− .0479
.100	26.98	3.737	.1022	.3197	.3547	.3867	.4843	− .0976
				Solvent, $NaNO_3$				
0.001	12.45	1.724	0.002034	0.04509	0.0187	0.0507	0.0683	−0.0176
.005	14.05	1.946	.006167	.07853	.0713	.1033	.1189	− .0156
				Solvent, $BaCl_2$				
0.001	13.16	1.822	0.004093	0.06397	0.0428	0.0748	0.0969	−0.0221
.003	14.79	2.048	.01023	.1011	.0935	.1255	.1531	− .0276
.010	18.10	2.507	.03150	.1774	.1813	.2133	.2687	− .0554
.020	20.89	2.893	.06173	.2484	.2436	.2756	.3763	− .1007
.030	23.23	3.211	.09193	.3032	.2896	.3216	.4593	− .1377
.050	26.82	3.714	.1522	.3901	.3521	.3841	.5910	− .2069
.100	33.60	4.653	.3028	.5503	.4500	.4820	.8337	− .3510

A quite different state of affairs is manifested when the anion is of a valence higher than unity, as shown by the curves for potassium sulfate, magnesium sulfate, potassium ferricyanide and potassium ferrocyanide. Here highly abnormal results persist down to the lowest concentrations studied; namely, 0.0005μ, corresponding to a solubility of 0.00008 M.

These curves give no evidence whatsoever of fusing into the curve for the limiting law, at least down to these very low concentrations, and we are forced to conclude that the revised statement of Lewis and Randall's principle is not valid in general for mixtures when ions of high and opposite charges are involved. In the case of potassium sulfate a deviation from the limiting law of 100% persists down to 0.0005 M additions (see Table

I), and even greater deviations are manifested on the addition of this amount of ferro- or ferricyanides.

It is of no avail to ascribe these abnormal results to the cobaltammines, for the normal character of the saturating salts is fully established by the data on potassium nitrate and barium chloride as well as by the action of potassium nitrate and chloride on the symmetrical tri-trivalent luteo ferricyanide.[17]

Much more light is thrown upon the character of the deviations from the ideal law when we plot them against the ionic strength as shown in Figs. 4 and 5. In changing from log S/S_0 to —log f we have used the theoretical value for α' in Equation 1 to extrapolate to infinite dilution,
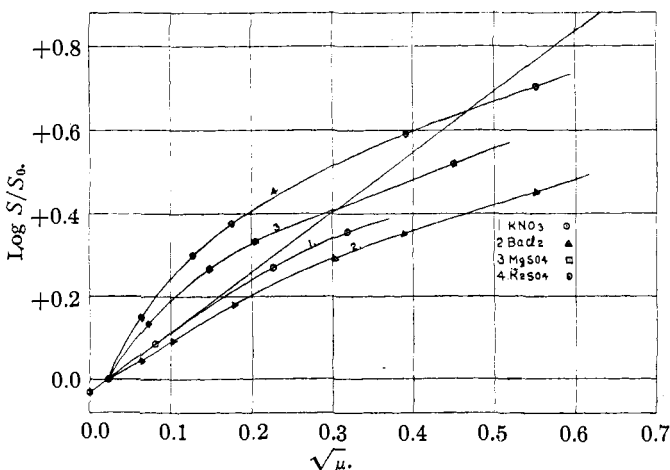
Fig. 2.—Solubility effects of various salts upon $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_4]_3^{I}$ at 25°.

a procedure which is justified by previous work and the present results with potassium nitrate and barium chloride. The value of the extrapolation factor log f_0 is so small in comparison to log S/S_0 that the character of the deviations is unaffected when other values of α' are employed.

According to the Debye-Hückel theory, deviations from Equation 1 are to be expected since ions are not point charges but in a first approximation may be considered as rigid spheres having a uniform distribution of electricity on their effective surfaces. The distance of closest approach of two such ions is measured by their average effective diameter, a_i. The ratio between a and the characteristic distance $1/\kappa$ at which the potential of the ion under consideration has fallen to $1/e$ of its value owing to the atmosphere of surrounding ions is designated as x; that is, $x = a\kappa$, or numerically $x = 0.327 \, a\sqrt{\mu}$, when a is expressed in Ångström units (10^{-8} cm.).

[17] See Ref. 7 for the data. The deviation curves, which are of the normal type, are plotted in Fig. 6.

With the simplification that we can operate with an average effective diameter, Debye and Hückel's expression reduces to

$$-\log_{10} f = \alpha' \, (-z_1 z_2) \sqrt{\mu} \cdot x / (1 + x) \tag{2}$$

Expanding the fraction $1/(1 + x)$ to separate the ideal term we get

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

Combining Equations 1 and 3 yields

$$\text{Deviation} = -\log_{10} f(\text{obs.}) / f(\text{ideal}) = -\alpha' \, (-z_1 z_2) \sqrt{\mu} \cdot x / (1 + x) \tag{4}$$

or, substituting the value of x, we get as the leading terms of the deviation equation

$$\text{Deviation} = -0.165 \, a \, (-z_1 z_2) \, \mu + 0.055 \, a^2 \, (-z_1 z_2) \, \mu^{3/2} + \ldots \tag{5}$$

which depends for a saturating salt of a given valence only upon a and the concentration.[18]
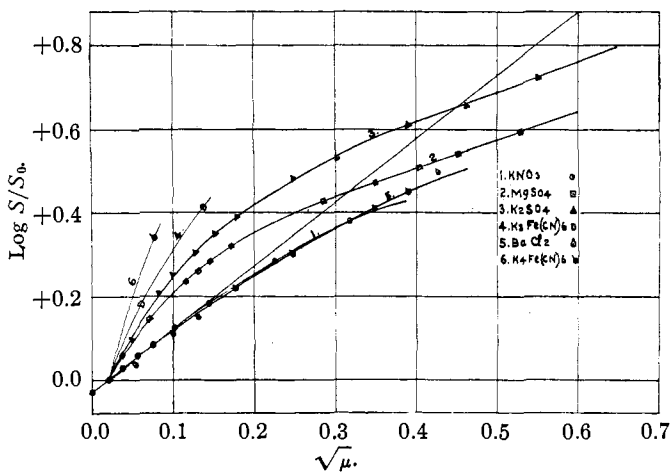
Fig. 3.—Solubility effects of various salts upon $[Co(NH_3)_6]^{III} [Co-(NH_3)_2(NO_2)_2C_2O_4]_3^{I}$ at 25°.

In the case of potassium nitrate and barium chloride, where univalent anions are opposed to the trivalent luteo cation, the deviations are of the general form demanded by Equation 4, that is, the deviations are negative and linear at first, followed by a slow rise as the higher terms of Equations 4 or 5 become effective. This type of curve will be called normal, even though exact concordance with Equation 4 cannot be obtained in all cases. With barium chloride a value of $a = 1.53$ Å. fits as well as could be expected, when we recognize that no account has been taken of possible changes in dielectric constant of the solution with increasing concentration.

In the abnormal curves with the high-valence anions we note that the normal linear nature of the deviation curve emerges at concentrations

[18] See also Eucken, Jette and LaMer, "Fundamentals of Physical Chemistry," McGraw-Hill Book Co., New York, 1925, p. 332.

above 0.05μ, but in the highly dilute region where conditions should be most ideal another factor is operating which displaces the deviation curve
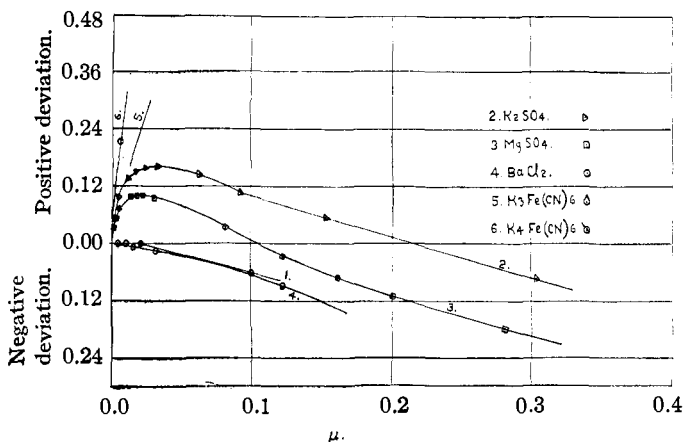
Fig. 4.—Deviation of log f from the ideal Equation 1. Saturating salt $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_2C_2O_4]_3^I$.

in a positive direction. Most significant of all is the almost infinite limiting tangent which the deviation curve exhibits at the lowest concentrations.
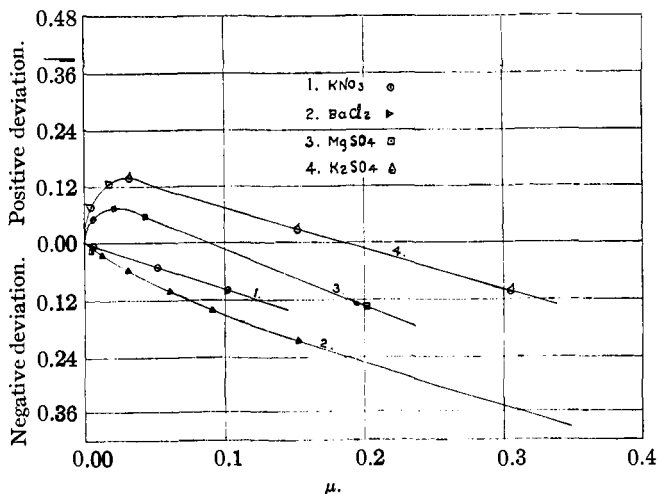
Fig. 5.—Deviation of log f from the ideal Equation 1. Saturating salt $[Co(NH_3)_6]^{III}[Co(NH_3)_2(NO_2)_4]_3^I$.

Any attempt to explain the curves on the basis of ion size as given by Debye and Hückel at once places us in the dilemma of being forced to assume large negative values for a at low concentrations, followed by positive values above 0.1 to 0.2 μ. Similar considerations eliminate

Hückel's assumption[19] of a simple linear deviation of the dielectric constant as an explanation.

We should also point out that the abnormal effects with the sulfates cannot be due to an unobserved precipitation of luteo sulfate. In the experiments with potassium ferrocyanide and ferricyanide we were prohibited from studying the anomaly in higher concentrations for this reason, but luteo sulfate is sufficiently soluble ($0.02\ M$ at $25°$) that at the concentration of luteo ion furnished by the saturating salts, it requires practically $1\ M$ potassium sulfate to produce a precipitate of luteo sulfate. Further, it is difficult to believe that chemical rearrangements have taken place in the complex ions, for this would involve slow reactions, and consequently a progressive change in solubility with time. Instead, we find that a definite solubility value can be promptly established and reproduced at will for each concentration used.

Theoretical Discussion

For simplicity of mathematical development Debye and Hückel were obliged to make certain approximations, the most important of which is the integration of only one term in the expansion of the formula for the density of electricity ρ, namely, that involving the squares of the valences.

The general expression for ρ is

$$\rho = \epsilon \sum_{j=1}^{s} n_j z_j\ e^{-z_j \frac{\epsilon \psi}{kT}} \tag{6}$$

which combined with the Poisson equation

$$\nabla^2 \psi = \frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = -4\pi\ \rho/D \tag{7}$$

forms the basis of the theory.[20] The expansion for ρ yields

$$\rho = \epsilon \sum_{1}^{s} n_j z_j - \frac{\epsilon^2\psi}{kT} \sum_{1}^{s} n_j z_j^2 + \frac{\epsilon^3\psi^2}{2k^2T^2} \sum_{1}^{s} n_j z_j^3 - \ldots \ldots \tag{8}$$

The boundary condition that the solution is electrically neutral eliminates the first term, $\sum n_j z_j = 0$, and leaves the second term involving the ionic strength, which is then introduced into Equation 7, and the latter is integrated to determine $\bar{\psi}$, the potential at the surface of the ion when $r = a$. When the valence types of the salts present are symmetrical, that is, when $z_1 = -z_2$, all terms involving odd values of ν in $\sum_{\nu=1}^{\infty} n_j z_j^\nu$ vanish and Equation 8 reduces to an expansion of the hyperbolic sin $(z_j\epsilon\psi/kT)$, which was the case considered by Debye and Hückel.[21]

[19] Hückel, *Physik. Z.*, **26**, 93 (1925). The question of change in dielectric constant with concentration will be dealt with in detail in the third paper. See Gronwall and LaMer [*Science*, [N. S.] **64**, 121 (1926)] for a preliminary statement of results.

[20] The notation of Debye and Hückel is used throughout.

[21] Dr. T. H. Gronwall and one of us (V. K. L.) have carried out an integration of Equations 6 and 7 by the method of successive approximations. We find that for a

However, when the valences of the cations do not equal those of the respective anions, as is the case in the mixtures studied in this paper, the terms when ν is odd and greater than 2 no longer cancel out. The term in $\sum n_j z_j{}^3$ which assumes positive or negative values, depending upon whether the sum of the cubes of the valences of the cations is greater or less than that of the anions, must accordingly be considered in the next approximation for the solution of Equation 7. Since the anomalies noted in the previous section were usually (but not exclusively) confined to examples where $\sum n_j z_j{}^3$ would be large, we have studied the influence of this term in detail.[22]

Retention of the term in z^3 yields

$$\nabla^2 \psi = \kappa^2 \left(\psi - (\epsilon/2kT)\, q\psi^2 + \ldots\ldots\ldots \right) \qquad \cdot \quad (9)$$

Here, in

$$q = \Sigma n_j z_j{}^3 / \Sigma n_j z_j{}^2 \tag{10}$$

q might be called the unsymmetric ionic-strength ratio; κ has the usual definition.

The solution of this equation for $\bar{\psi}$ when $r = a$, that is, for the potential at the surface of the ion is

$$\bar{\psi} = \frac{e_j}{Da} - \frac{e_j}{Da}\frac{x}{1+x}\left[1 - \frac{\epsilon e_j}{2DkT}\cdot q \cdot \frac{1}{a}\frac{xe^{3x}}{(1+x)^2}\int_x^\infty \frac{e^{-3\xi}}{\xi}\,d\xi \right] \tag{11}$$

which differs from that in the original theory by the term at the right involving q. $e_j = \epsilon z_j$.

The integral may be obtained as a power series in x, the leading term reducing to $x \ln 3x/a$, which vanishes when a is finite and $x \longrightarrow 0$. We may, therefore, state that as we pass to infinite dilution the second approximation for $\bar{\psi}$ will not alter the *limiting* slope of a $-\log f$, $\sqrt{\mu}$ curve, since the electrical free energy F_e and $-\log f$ are calculated in turn from $\bar{\psi}$. That is, we should expect curves like a in Figs. 1 and 6 and not like those marked b. The experimental data show that this requirement is not met, at least down to concentrations as low as 0.0005μ, and we must infer that the deviations which are observed arise, in part at least, from some source other than that of dissymmetry of the valence types. To obtain uni-univalent salt the higher, even-powered terms can affect the potential at the surface of the ion but very little in agreement with the previous statement of Debye and Hückel. This statement must, however, be restricted to ions of normal size; that is, where $a \geqq 3$ Å. Thus, for a 0.1 M aqueous solution of a (1,1) salt we find that the maximum error in $\bar{\psi}$ cannot exceed 8.5, 3.5, 2.4 and 1.3%, when a has the values 1, 2, 3 and 5 Å., respectively. For a 0.01 M solution the corresponding upper bounds are 7.3, 0.56 and 0.42% when $a = 1$, 3 and 5 Å. These calculations show that even in this simple case the error produced by neglecting higher terms becomes of increasing importance as the ion size decreases below 3 Å., and in non-aqueous solutions where D is small may become of greater importance than the first term.

[22] Professor P. Debye, on his visit to the United States in 1925, very kindly worked out this solution of Equation 7 for us. We also wish to thank him for his interest and encouragement in our attempts to interpret the experimental data along these lines.

agreement with our experimental curves it appears necessary to introduce a further physical assumption into the theory.

In order to make numerical comparisons at finite concentrations the expressions for $\log_{10} f$ (salt) and the numerical values of the integrals which arise have been derived and tabulated. The calculations become exceedingly complicated since two terms develop in the expression for $\log_{10} f$, one of which depends upon the dissymmetry of the valence type of the solvent salt and the other upon the combined dissymmetry of the solvent and solute, so that only a summary of results will be given here. The effect of the unsymmetric terms is quite negligible for values of $a > 3$ Å., but increases rapidly as the ion size decreases, and particularly for $a < 1$ Å.
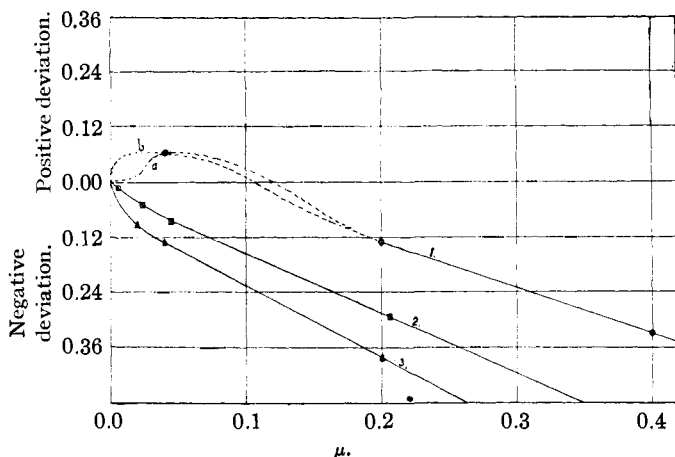

Fig. 6.—Deviation of log f from the ideal Equation 1; data from Brönsted's tables (see Fig. 1). Curve 1, $MgSO_4$ on $[Co(NH_3)_6]$ Co-$(NH_3)_2(NO_2)_4]_3$ (Table XLIV). Curve 2, $MgSO_4$ on $[Co(NH_3)_4$-$C_2O_4]_3$ $[Cr(CNS)_6]$ (Table XLVI). Curve 3, $MgSO_4$ on $[Co(NH_3)_4$-$Cl_2]_3$ $[Fe(CN)_6]$ (Table XLVII). Temp., 0°. The course of the dotted curves is somewhat exaggerated.

For a point charge the correction becomes infinite (!), whereas in the first approximation the activity coefficient remains finite (Eq. 1) when $a \longrightarrow 0$. The sign of the correction depends upon the sign of q which, in turn, depends upon the valence types and relative amounts of saturating and solvent salts. In the particular case of a $(3, -1)$ salt dissolved in a $(1, -2)$ salt the calculations give a correction similar to that demanded by the potassium sulfate data through the use of positive values of a, in the region where the simple theory equation (2) would require very large and absurd negative values. Although correct in sign, the correction curve at high dilution fuses into the limiting law more like Curves a in Figs. 1 and 6 than like the experimental curves (b). Also the average a value neces-

sary to approximate the experimental deviation in dilute solutions proves to be unusually small (about 0.2 Å.).[23]

More convincing evidence that the z^3 term cannot in itself account for the anomaly by the use of a *single a* value is found in the magnesium sulfate data. In the range of concentration where the deviation is greatest, the unsymmetric contribution of the $(3, -1)$ saturating salt to the numerator of q is so completely overshadowed by the increase in the denominator that the term involving q practically vanishes. Many further discrepancies might be cited in support of our general conclusion that a purely formal extension of the Debye theory, which operates with a
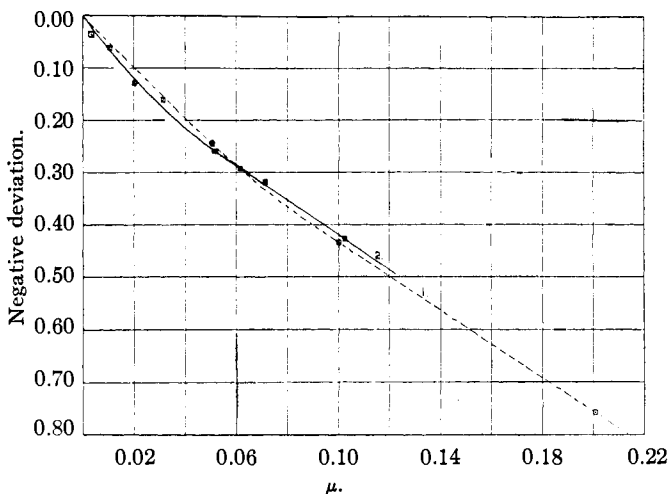

Fig. 7.—Deviation of log f from the ideal Equation 1. Curve 1, KCl; saturating salt [Co(NH₃)₆][Fe(CN)₆]; from Brönsted's Table XLIX (see Fig. 1). Curve 2, KNO₃, from our data.

limited number of terms from Equation 8 and the simplified physical picture of an *average* value of a for ions considered as rigid spheres must necessarily fail to account quantitatively for the effects we have observed. A consideration of all experimental data available indicates that *the anomaly depends more upon the presence of certain high-valence cations, in the present instance the luteo ion, in solution with anions of high valence like the sulfate, than it does upon the dissymmetry of the valence types of the combinations*

[23] Abnormally small a values do not necessarily militate against the theory, for if the charge on one of the high valence ions is near the surface of the ion, either because of natural construction or because of the deforming influence of neighboring ions, the resulting small value of a can completely overshadow the larger values of a in the lower valence ions owing to its greater influence upon the average value.

Better agreement can be obtained by the use of individual a values for each ion, but agreement under such procedure can have little significance until all but one of the a values has been determined by an independent method.

alone. For example, magnesium sulfate gives deviations[24] which are similar in character although much less pronounced than those in Figs. 4 and 5, when it acts upon the symmetrical (3, —3) salt luteo ferricyanide. For an averaged effect of all ions, q and the higher analogous coefficients involving odd powers of z vanish in this (3, —3), (2, —2) case, and the explanation must be sought for in the higher even powers of z. The odd power z terms, however, would not necessarily vanish if we could determine the effect for each combination of ions with its particular a value.
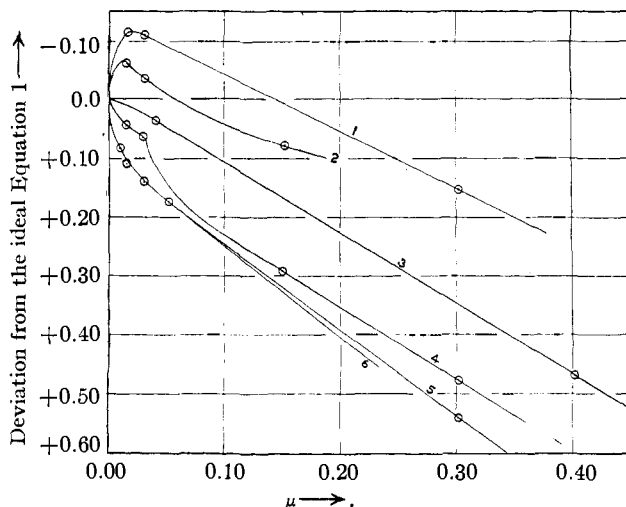

Fig. 8.—Deviations of log f from the ideal Equation 1 for the salt $[Co(NH_3)_5H_2O]^{III}[Cr(NH_3)_2(CNS)_4]_3^{I}$, showing that abnormal deviation curves are also obtained with the aquo pentammine ion in the presence of sulfate and phthalate ions. Solvent salts: 1, K_2 phthalate; 2, Na_2SO_4; 3, $MgSO_4$; 4, $(HCOO)_2Ca$; 5, $MgCl_2$; 6, KCl. Data from Brönsted's Table XLV (see Fig. 1).

When the cation of the saturating salt is of low valence we find that the sulfate ion yields deviation curves of a normal character as shown in Curves 2 and 3 of Fig. 6, even though it is acting upon an unsymmetric (1, —3) type of saturating salt. These data also show that the bivalent magnesium ion does not exhibit the anomaly when present with the Fe- $(CN)_6^{---}$ or $Cr(CNS)_6^{---}$ ions (see below). To show that the abnormal type of deviation curve is not restricted to the luteo ion but is to be observed with other ions, we refer the reader to Fig. 8, where the trivalent cation, aquo-pentammine cobalt, gives the abnormal type with the bivalent sulfate and phthalate anions.

We have considered these results in detail because of their bearing upon

[24] See Ref. 9, Fig. 1.

some recent and important developments by Bjerrum on ion association which have appeared since the present work was completed.[25]

Since it is at present impossible to obtain an exact solution of Equation 7 involving all terms, Bjerrum reaches by an entirely different procedure what he considers an approximate solution of this problem. The probability H that an ion of the ith kind will be present at a distance between r and $r + dr$ from a given ion of the kth kind, when r is small compared to the average distance between ions, is given by

$$H = c_i \cdot 4\pi r^2 e^{\varphi/kT} dr \qquad (12)$$

where c_i is the number of ith ions per cc. and $\varphi = -z_i z_k \epsilon^2/Dr$. When z_i and z_k are zero (uncharged) or of the same sign (Cases 1,2), H is zero when r is zero and H increases steadily as r increases. When z_i and z_k refer to ions of opposite sign (Case 3), H passes through a minimum at

$$r_{\text{min.}} = \epsilon^2 (-z_1 z_2)/2DkT = (-z_1 z_2).3.52 \text{ Å. at } 18° \qquad (13)$$

When $r < r_{\text{min.}}$, H increases very rapidly and becomes infinite as $r \longrightarrow 0$; when $r > r_{\text{min.}}$, the curve for H is higher but parallel to Cases 1 and 2.

Since the work necessary to separate a pair of ions (when at the distance $r_{\text{min.}}$) equals $2kT$, or four times the kinetic energy per degree of freedom, and furthermore increases very rapidly for smaller values of r, Bjerrum utilizes $r_{\text{min.}}$ as the basis for an arbitrary distinction between associated and dissociated (free) ions. The law of mass action is then applied to the association equilibrium by ascribing an activity coefficient of unity to the associated fraction of the total concentration of ions, namely, those separated by a distance less than $r_{\text{min.}}$, while the free ions (those separated by distances greater than $r_{\text{min.}}$) obey the first approximation of the Debye-Hückel theory, namely, Equation 2.

Bjerrum's treatment consequently resolves itself into a more or less arbitrary reduction of the concentration of free ions as a correction to Equation 2. When the combined radii of a pair of univalent ions is greater than 3.52 Å., as is the case for the potassium and chloride ions, the association factor vanishes and Bjerrum's calculations for log f then reduce to those of Debye and Hückel. For a values less than 3.52 Å., the calculated values for log f show deviations which are similar in general character, at least in very dilute solutions, to those obtained by us through a consideration of the higher terms of Equation 8. However, neither our calculations nor Bjerrum's are able to explain the maximum we have observed experimentally in the deviation curves at about 0.05μ, unless we superimpose the assumption that a linear negative deviation due to the salting-out effect is also operating in these solutions. In the particular case of the freezing-point curves for potassium nitrate and potassium iodate, the Debye theory demands values of a which are zero or impossibly small,

[25] Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **7**, 9 (1926); also *Svensk Kem. Tid.*, **38**, 16 (1926).

while Bjerrum is able to obtain excellent agreement on the basis of the ion association which occurs with the small ions, by the use of the more physically plausible values for the single arbitrary parameter $a = 1.57$ and 1.33 Å., respectively. Our calculations also indicate that many of the a values calculated by previous workers will require revision on the basis of the influence of higher terms of Equation 8. In the previous paper we noted that potassium nitrate, when acting upon a $(3, -3)$ saturating salt, would require a zero value for a at high dilutions and there is little reason to doubt that ion association is the cause of the difficulty.

Unfortunately, Bjerrum's methods have not been developed to a point where we can make numerical comparisons with our complicated mixtures. It is sufficient for our purpose to point out that Equation 13 for the upper limit of ion size at which ion association becomes important yields a value of 6×3.52 Å. $= 21$ Å. for a tri-bivalent combination, instead of 3.52 Å. as in the uni-univalent case. The sum of the effective radii of the luteo and sulfate ions can scarcely equal 21 Å., and if they are of normal size a very high degree of association, leading to deviation curves similar in sign to ours for the high dilution, is to be expected.

However, if we invoke this explanation we must point out that it is very surprising that the $(1, -3)$ $(2, -2)$ combinations given in Curves 2 and 3, Fig. 6, are of the normal type. In these cases the magnesium and $Fe(CN)_6^{---}$ or $Cr(CNS)_6^{---}$ ions are involved and according to Bjerrum's theory we should have to ascribe a value to the combined radii of the magnesium and $Fe(CN)_6^{---}$ ions which is considerably greater than for the luteo and sulfate ion pair.

The value of a is determined by that distance at which the attractive forces are exactly counterbalanced by the repulsive forces. The former arise from the net charge on the complex ion and follow the inverse-square law of Coulomb, while the latter are generally considered as falling off at a high (9th) power of the distance. We suggest as a possible explanation for this difference in apparent ion size that the trivalent positive charges on the nuclear atoms of the $Co(NH_3)_6^{+++}$ and $Fe(CN)_6^{---}$ ions are not completely screened off and become effective at molecular distances. Thus, a bivalent sulfate ion would continue to be attracted at close distances by the cobalt atom of the luteo complex with a resulting very small a value, whenever the luteo ion is involved with negative ions. On the other hand, while the net charge on the $Fe(CN)_6^{---}$ ion will attract a magnesium ion, the two cannot approach very closely owing to the repulsive action between the magnesium ion and the ferric nucleus, which would result in a large value of a.

Although exception may be taken to certain of Bjerrum's approximations which he introduces to force numerical solutions, we believe that his idea of ion association amongst the smaller ions furnishes a plausible

explanation of our data and of Brönsted's principle of specific interaction of ions of opposite sign. Further experiments are now in progress to test the applicability of these principles to examples where the present form of the Debye-Hückel theory and the ionic strength fail to do so.

Summary

1.   The activity coefficients of two difficultly soluble ($S_{H_2O} = 0.00016\ M$ and $0.00008\ M$) tri-univalent cobaltammine salts possessing the luteo ion as cation, have been determined by the solubility method in highly dilute solutions with an accuracy within 0.2%.

2.   When the solvent salts (potassium nitrate, barium chloride, sodium nitrate) possess univalent anions, excellent agreement is found with the present form of the Debye-Hückel theory, and their limiting law is confirmed. However, when solvent salts with high-valence anions (for example, potassium sulfate, magnesium sulfate, potassium ferricyanide and ferrocyanide) are used to dissolve the luteo salts, very marked discrepancies (greater than 100% of the calculated values) with the theory and the revised statement of Lewis and Randall's principle of ionic strength persist down to the lowest concentrations studied, namely, 0.0005μ. The experimental curves for the mixtures containing these high-valence cations and anions give no evidence of fusing into the limiting law at low concentrations.

3.   These deviations from the limiting law are essentially linear in respect to ionic strength above 0.05μ, but pass through a maximum in the more highly dilute solutions, showing that another factor is operating which has not been taken into account in the theory. It is believed that the disturbing factor arises from neglect of the higher terms of the Debye-Hückel expression for the density of electricity, which will be most pronounced for high-valence ions of small size and of opposite sign in general agreement with the idea of ion association as developed by Bjerrum.

4.   The expressions of Debye and Hückel have been revised to include the neglected z^3 term in the density of electricity. This extension, which depends upon dissymmetry in the valence types, yields for positive a values a qualitative but not a quantitative agreement in the regions where the simple theory would require impossible negative values. The corrections due to higher terms are highly sensitive to small ion sizes but are negligible for values of a greater than 3 Å. Complete agreement can only be expected when individual a values for each ion combination and the other higher neglected terms have been evaluated.

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