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STUDIES ON SOLUBILITY. III. THE SOLUBILITY OF METAL AMMONIA SALTS IN SALT SOLUTIONS.

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Introduction.

In two previous papers[1,2] one of the writers has given views on the treatment of solubility equilibria, involved when salt solutions are employed as solvents for salts. To illustrate the scope of these views a few results were communicated from an extensive series of experimental determinations on solubility, dealing mainly with solubility of metal ammonia salts in solutions of other salts. In this and later articles a more complete statement of the data procured and of additional experiments will be given.

The employment of metal ammonia salts is specially fitting for the purpose of studying the laws of solubility. They are in general really strong electrolytes, and for the most part not liable to hydrolysis of any kind. On account of the great number of cations and anions belonging to this group the number of salts it contains is extremely high. The solubility is usually small, and salts of a solubility between 0.01 and 0.0001 molal,

[1] Brönsted, THIS JOURNAL, 42, 761 (1920).
[2] Ibid., 42, 1448 (1920).

the most convenient range of concentration for the theoretical and experimental treatment, can be prepared easily, abundantly and usually in a very pure state. Finally, and this point is not to be undervalued, the determinations of solubility can for all compounds of this type be carried out uniformly, namely by decomposing with alkali, with or without addition of reducing substances such as stannous chloride, by simply estimating the ammonia liberated by adsorption in sulfuric acid, using methyl red as an indicator.

A number of the salts employed for our investigations have been described before in the publications of the leading authors in this domain, S. M. Jörgensen and A. Werner. A good many, however, have been produced for the first time by us. As in all such cases the constituent ions were well known, we have confined ourselves to an analysis of their ammonia and water contents. In order to secure the high purity which was essential, the whole sample of each salt was stirred repeatedly with fresh portions of water till a constant solubility was found. The salt was considered pure when this constant value agreed with that found when using only a small quantity of salt for solution.
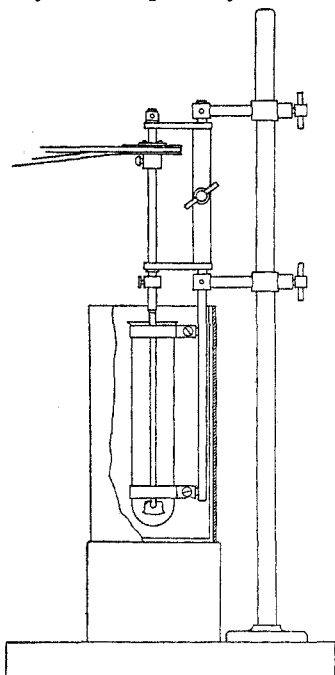

Fig. 1.

The temperatures of the experiments were 0° and 20°. Determinations were made on a number of salts at both temperatures, whereby the important figures for the temperature coefficient, to be considered later, have been obtained. The praseo salts are the most unstable within the range of compounds employed and could not be studied at 20°; but other salts are also transformed in solution and so give solubility values, which slowly increase with the time, especially at 20°. As the velocity of solution for a metal ammonia salt is generally rather high such slow transformations were usually no hindrance in our determinations.

The determinations at 20° were carried out in an ordinary thermostat, regulating to within ±0.01°. The apparatus employed for the measurements at 0° is shown in Fig. 1. When saturation had taken place a known volume of the saturated solution was sucked out through a small cotton plug, and the determination of the concentration made as described above.

In judging the accuracy reached by our measurements we must distinguish between relative and absolute exactness. When a series of ex-

periments is carried out with the same sample of salt using the same acid for estimation and working under the best conditions obtainable, the possible relative error in the determinations will hardly reach some tenths of a per cent., and the possible absolute error 1%. Especially in that part of our data which was first obtained and most of which appears in the first part of the tables following the accuracy is probably considerably lower.

In carrying out these determinations we were valuably assisted by cand. polyt. Max Möller, and cand. polyt. E. Smith-Jensen to whom the writers wish to express their best thanks. We likewise wish to express our indebtedness to Carlsbergfonden for subsidizing the work.

I. Solubility of Metal Ammonia Salts in Water.

We shall first give a survey of the metal ammonia ions, and others, constituting the salts employed in our determination. The names, formulas and valences of the ions used, are given below.

Ion.	Formula and Valence.
Luteo cobaltic or hexammine cobaltic	$[Co(NH_3)_6]^{+++}$
Roseo cobaltic or aquo-pentammine cobaltic	$[Co(NH_3)_5H_2O]^{+++}$
Tri-ethylene-diamine cobaltic	$[Co(C_2H_4N_2H_4)_3]^{+++}$
Chloro-pentammine cobaltic	$[Co(NH_3)_5Cl]^{++}$
Chloro-pentammine chromic	$[Cr(NH_3)_5Cl]^{++}$
Chloro-pentammine rhodium	$[Rh(NH_3)_5Cl]^{++}$
Chloro-aquo-tetrammine cobaltic	$[Co(NH_3)_4(H_2O)\ Cl]^{++}$
Bromo-pentammine cobaltic	$[Co(NH_3)_5Br]^{++}$
Xantho cobaltic or nitro-pentammine cobaltic	$[Co(NH_3)_5NO_2]^{++}$
Thiocyanato-pentammine cobaltic	$[Co(NH_3)_5CNS]^{++}$
Praseo cobaltic or dichloro-tetrammine cobaltic	$[Co(NH_3)_4Cl_2]^{+}$
Croceo cobaltic or dinitro-tetrammine cobaltic (trans)	$[Co(NH_3)_4(NO_2)_2]^{+}$
Flavo cobaltic or dinitro-tetrammine cobaltic (cis)	$[Co(NH_3)_4(NO_2)_2]^{+}$
Oxalo-tetrammine cobaltic	$[Co(NH_3)_4C_2O_4]^{+}$
Carbonato-tetrammine cobaltic	$[Co(NH_3)_4CO_3]^{+}$
Sulfato-pentammine cobaltic	$[Co(NH_3)_5SO_4]^{+}$
Tetranitro-diammine cobaltiate	$[Co(NH_3)_2(NO_2)_4]^{-}$
Tetrathiocyanato-diammine chromiate	$[Cr(NH_3)_2(CNS)_4]^{-}$
Oxalo-dinitro-diammine cobaltiate	$[Co(NH_3)_2(C_2O_4)\ (NO_2)_2]^{-}$
Dioxalo-diammine cobaltiate	$[Co(NH_3)_2(C_2O_4)_2]^{-}$
Dioxalo-triammine cobaltiate	$[Co(NH_3)_3(C_2O_4)_2]^{-}$
Hexathiocyanato chromiate	$[Cr(CNS)_6]^{---}$
Hexacyano ferriate	$[Fe(CN)_6]^{---}$
Hexacyano cobaltiate	$[Co(CN)_6]^{---}$
Trioxalo cobaltiate	$[Co(C_2O_4)_3]^{---}$

The following table records the solubilities of salts formed by these and more usual cations and anions, using pure water as solvent.

In all cases when not otherwise especially indicated, the figures for solubilities and concentrations mean molal concentrations; for luteo sulfate, for example, the number of molecules of $[Co(NH_3)_6]_2(SO_4)_3$ in one liter of the solution. The abscissas of the figures are in equivalents of added salt per liter.

TABLE I.—SOLUBILITY OF METAL AMMONIA SALTS IN WATER.

I. Salts Containing a Univalent Cation.

	0°.	20°.	$S_{20°}/S_{0°}$.
Cesium tetranitro-diammine cobaltiate..............	0.00531	0.01720	3.24
Cesium tetrathiocyanato-diammine chromate.........	0.000790	0.00258	3.26
Potassium tetranitro-diammine cobaltiate.............	0.0240		
Silver tetranitro-diammine cobaltiate................	0.000772	0.00210	2.72
Silver oxalo-dinitro-diammine cobaltiate..............	0.00278	0.00822	2.96
Thallous tetranitro-diammine cobaltiate..............	0.00251	0.00789	3.14
Thallous oxalo-dinitro-diammine cobaltiate............	0.00420	0.00977	2.34
Tetramethylammonium-tetranitro-diammine cobaltiate.	0.00749	0.0197	2.63
Carbonato-tetrammine-cobaltic-tetrathiocyanato cobaltic sulfate.....................................		0.07	
Carbonato-tetrammine-cobaltic-tetrathiocyanato cobaltic chromiate, β.................................	0.00185	0.00555	3.00
Carbonato-tetrammine-cobaltic-tetranitro-diammine cobaltiate.......................................	0.00366	0.0124	3.42
Croceo bromide....................................	0.012		
chloride...................................	0.0222	0.043	1.95
dioxalo-diammine cobaltiate..................	0.000066		
dioxalo-triammine cobaltiate..................	0.00059		
hexachloro-platinate.........................	0.00233		
nitrate, α.................................	0.00546	0.01483	2.71
nitrate, β.................................	0.00494	0.01298	2.62
perchlorate................................	0.0124	0.0290	2.34
picrate β..................................		0.00704	
selenate...................................		0.0092	
sulfate....................................	0.00096	0.00411	4.17
tetrachloro-aurate..........................		0.017	
tetranitro-diammine cobaltiate................	0.000096	0.000355	3.70
tetrathiocyanato-diammine chromate........	0.000057	0.000143	3.11
Flavo tetranitro-diammine cobaltiate...............	0.000949	0.0033	3.46
tetrathiocyanato-diammine chromiate, α........	0.000322	0.00100	3.11
tetrathiocyanato-diammine chromiate, β.......		0.00073	
chloride....................		0.034	
Oxalo-tetrammine-cobaltic hexathiocyanato chromiate...	0.00053		
nitrate..................	0.0066	0.018	2.73
perchlorate...............	0.0051	0.0140	2.74
tetranitro-diammine cobal-...			
tiate...................	0.00103		
trioxalo cobaltiate	0.00083		
Praseo bromide...................................	0.00632		
chlorate...................................	0.0180		
chloride...................................	0.0141		
dioxalo-diammine cobaltiate..................	0.000171		
hexacyano ferriate..........................	0.000121		
iodate.....................................	0.00441		

	0°.	20°.	$S_{20°}/S_{0°}$.
nitrate	0.00383		
picrate	0.00021		
thiocyanate	0.00289		
Sulfato-pentammine cobaltic nitrate		0.026	

II. Salts Containing a Bivalent Cation.

	0°.	20°.	$S_{20°}/S_{0°}$.
Magnesium dinitro-oxalo-diammine cobaltiate	0.00348		
Bromo-pentammine cobaltic bromide	0.00275		
chloride	0.00542	0.011	2.0
nitrate	0.0	0.010	
Bromo-pentammine rhodium chloride		0.015	
Chloro-aquo-tetrammine cobaltic chloride	0.057	0.11	1.9
Chloro-pentammine chromium	0.000660		
Chloro-pentammine chromium chloride	0.0149	0.030	2.0
nitrate		0.055	
oxalate	0.00125		
cobaltic bromide	0.00725		
chloride	0.00914	0.018	2.0
iodate	0.00200		
hexachloro-platinate	0.000091		
nitrate		0.046	
oxalate	0.00036		
sulfate		0.029	
tetranitro-cobaltiate	0.0001731	0.000637	3.1
rhodium chloride	0.00945	0.020	2.1
Thiocyanato-pentammine chromium chloride		0.040	
cobaltic chloride		0.039	
chromate	0.00107		
iodate		0.00505	
sulfate		0.0290	
Xantho chloride		0.11	
chromate	0.000258	0.000547	2.12
nitrate	0.0170	0.038	2.2
oxalate	0.000161	0.000432	2.68
tetranitro-diammine cobaltiate	0.00031	0.00099	3.2
tetrathiocyanato-diammine chromate	0.000392	0.001284	3.27

III. Salts Containing a Trivalent Cation.

	0°.	20°.	$S_{20°}/S_{0°}$.
Luteo cobaltic chloride		0.26	
chloride sulfate	0.01055		
hexacyano chromiate	0.000028		
cobaltiate	0.000007	0.000016	2.3
ferriate	0.000009	0.000022	2.4
iodate	0.00181	0.00458	2.53
nitrate	0.0202	0.052	2.6
sulfate	0.0090	0.020	2.2
tetranitro cobaltiate	0.000043		
trioxalo cobaltiate	0.000019		
Roseo cobaltic hexacyano ferriate	0.000172		
sulfate		0.016	
tetrathiocyanato-diammine chromiate	0.00006		

II. Uni-univalent Salts in Uni-univalent Solvents.

With most of the uni-univalent salts specified in the foregoing section, determinations have been carried out using as solvents salt solutions of various concentrations.   In a previous paper the following equation was found to indicate the change in solubility with the concentration, based

$$\log \frac{s}{s_0} = a(\sqrt[3]{c_t} - \sqrt[3]{s_0})$$

on the assumption of Noyes and Falk[3] of the equality of the activity coefficients and the validity of the expression for the lowering of the freezing point.

The experimental results are given in the following tables.   The value of the coefficient a, which may be calculated according to the above equation for each concentration of the solvent $c = c_t - s$ is also given in the tables to show the validity of the underlying assumptions.

The first data are those of certain praseo cobaltic salts.   As mentioned above, the praseo salts are rather unstable in aqueous solutions, owing to the progress of the reaction

$$[Co(NH_3)_4Cl_2]^+ + H_2O \longrightarrow [Co(NH_3)_4H_2O\ Cl]^{++} + Cl^-,$$

easily observable through the change in color of the solution from green to red.   This reaction takes place rapidly at 20°, and constant figures are therefore not to be obtained at this temperature.   At 0°, when the time of stirring varies, no appreciable change in solubility is observed within 5 to 10 minutes.   As the salts dissolve very quickly, reliable results can be obtained at this temperature.   The figures at least will be mutually comparable even when the absolute values may be somewhat more uncertain here than in most other cases.

TABLE   II.—PRASEO THIOCYANATE. $(Co(NH_3)_4Cl_2)CNS.$ $s_0 = 0.00289.$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$	Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$
KOOCH	0.01	300	1.038	(0.175)	NaCl	0.02	313	1.108	0.309
	0.03	321	1.111	0.255		0.05	332	1.173	0.295
	0.05	331	1.146	0.252		0.1	353	1.247	0.292
	0.1	345	1.194	0.235					0.30
	0.2	374	1.294	(0.251)					
	0.5	409	1.415	(0.231)	KClO₃	0.02	318	1.124	0.353
	1.0	439	1.519	(0.211)		0.05	339	1.198	0.333
				0.25		0.1	365	1.288	0.335
KCl	0.02	314	1.110	0.314					0.34
	0.05	336	1.187	0.317					
	0.1	358	1.265	0.311	NaClO₃	0.02	316	1.115	0.329
	0.2	389	1.375	0.313		0.05	337	1.191	0.323
				0.31		0.1	361	1.274	0.320
									0.32

[3] Noyes and Falk, THIS JOURNAL, **32**, 1011 (1910); **33**, 1436 (1911); **34**, 454, 458 (1912).

For the calculation of s/s_0 in the last four solvents the value $s_0 =$ 0.00283 was used as found in this series of experiments. The value of a for sodium chlorate becomes a little greater than that given in the previous paper (0.30).

TABLE III.—PRASEO NITRATE. $(Co(NH_3)_4Cl_2)NO_3$. $s_0 = 0.00383$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.	Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.005	395	1.031	(0.262)	NaCl	0.005	395	1.032	(0.262)
	0.01	409	1.068	0.335		0.01	405	1.057	0.286
	0.05	455	1.188	0.336		0.05	449	1.173	0.310
	0.1	487	1.272	0.331		0.1	480	1.253	0.311
	0.2	533	1.392	(0.331)					0.30
	0.5	635	1.658	(0.343)	HCl	0.005	404	1.055	(0.447)
	1.0	760	1.984	(0.352)		0.01	410	1.070	0.348
				0.33		0.05	447	1.167	0.301
						0.1	474	1.238	0.294
KCl	0.005	399	1.042	0.345					0.31
	0.01	408	1.065	0.323					
	0.03	434	1.133	0.322					
	0.05	458	1.196	0.349	$NaC_6H_5SO_3$	0.005	394	1.029	(0.241)
	0.1	496	1.295	0.356		0.01	404	1.055	0.274
				0.34		0.05	445	1.162	0.293
						0.1	477	1.245	0.303
						0.2	519	1.355	0 305
									0.29

Experiments were also made with praseo nitrate in potassium and sodium chlorate solutions, but the increase in solubility is here much smaller than in the case of other solvents. Moreover the values were found to decrease with increasing time of stirring. Some special reaction must here evidently take place.

Inspection of the data in Tables II and III shows that the solubility of the two salts concerned increases with increasing concentration of the solvent, in all cases in close analogy to what has been stated in the previous article. The values of a for any solvent show a marked agreement and approximation to the value $1/3$. For the calculation of the mean of the values of a, the solutions stronger than 0.1 molal, for which the solubility equation at any rate does not hold good, and the most diluted ones, in which the experimental error has too great influence, have been excluded. In these and subsequent tables $t = 0°$, except when otherwise indicated.

With praseo bromide in addition to salt solutions both acetic acid and the three-chloro-acetic acids have been used. The incomplete dissociation of these acids is very markedly proved in the values of s/s_0 and a. While for all salt solvents the calculated normal values of a are in the neighborhood of 0.3, using these acids we find that increasing concentration is accompanied by a rapid decrease in this coefficient. This phenomenon is extremely pronounced with the weak acetic acid, but also the substituted

acid and even the trisubstituted acid show similar behavior. This indicates that not even trichloro-acetic acid is a really strong electrolyte.

TABLE IV.—PRASEO IODATE. $(Co(NH_3)_4Cl_2)IO_3$.

$s_0 = 0.00441$.

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$
KCl	0.02	487	1.104	0.337
	0.05	525	1.191	0.349
	0.1	571	1.295	0.363
				0.35
NaCl	0.02	486	1.102	0.330
	0.05	524	1.188	0.345
	0.1	568	1.288	0.356
				0.34
KClO₃	0.02	491	1.113	0.364
	0.05	531	1.204	0.372
	0.1	579	1.313	0.383
				0.37
NaClO₃	0.02	491	1.113	0.364
	0.05	528	1.197	0.360
	0.1	576	1.306	0.375
				0.37

TABLE V.—PRASEO PICRATE. $(Co(NH_3)_4Cl_2)C_6H_2N_3O_7$.

$s_0 = 0.000212$.

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$
KCl	0.02	25.7	1.215	0.396
	0.05	27.4	1.292	0.360
	0.1	29.5	1.392	0.354
	0.2	33.5	1.580	(0.378)
	0.5	41.8	1.972	(0.401)
	1.0	53.6	2.528	(0.428)
				0.37
NaCl	0.02	25.3	1.193	0.360
	0.05	26.6	1.255	0.318
	0.1	28.5	1.347	0.319
	0.2	30.1	1.420	(0.290)
	0.5	33.8	1.594	(0.274)
	1.0	41.4	1.953	(0.309)
				0.33

TABLE VI.—PRASEO BROMIDE. $(Co(NH_3)_4Cl_2)Br.$ $s_0 = 0.00632$.

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$	Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$	$a.$
KOOCH	0.02	678	1.073	0.267	CCl₃COOH	0.02	681	1.078	0.283
	0.05	720	1.139	0.283		0.05	703	1.112	0.231
	0.1	752	1.190	0.260		0.1	731	1.157	0.218
	0.2	805	1.274	(0.258)		0.2	752	1.190	0.186
				0.27					
KOOCCCl₃	0.02	683	1.081	0.294	CHCl₂COOH	0.02	677	1.071	0.261
	0.05	719	1.138	0.279		0.05	702	1.111	0.228
	0.1	755	1.185	0.266		0.1	723	1.144	0.201
	0.2	802	1.269	(0.254)		0.2	740	1.171	0.168
				0.28					
KOOCCHCl₂	0.02	689	1.090	0.327	CH₂ClCOOH	0.02	656	1.038	0.143
	0.05	725	1.147	0.297		0.05	673	1.065	0.137
	0.1	763	1.207	0.281		0.1	677	1.071	0.103
	0.2	811	1.283	(0.266)		0.2	685	1.084	0.086
				0.30					
KOOCCH₂Cl	0.02	687	1.087	0.316	CH₃COOH	0.02	638	1.010	0.036
	0.05	726	1.149	0.300		0.05	642	1.016	0.034
	0.1	764	1.209	0.283		0.1	641	1.014	0.021
	0.2	818	1.295	0.275		0.2	636	1.006	0.007
				0.29					

The croceo cobaltic salts are rather stable in solution and give as a rule easily reproducible values for their solubilities. Some of the figures for croceo nitrate stated below have been communicated in an earlier paper,[4] where the existence of two modifications, an α- (unstable) and a β-modification (stable), was indicated.

TABLE VII.—β-CROCEO NITRATE.

$(Co(NH_3)_4(NO_2)_2)NO_3$.

$s_0 = 0.00494$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.02	536	1.086	0.290
	0.05	575	1.164	0.311
	0.1	621	1.258	0.328
	0.2	693	1.404	0.350
				0.32
KSCN	0.02	546	1.107	0.355
	0.05	596	1.208	0.387
	0.1	663	1.344	0.422
				0.38
KOH	0.02	553	1.120	
	0.05	405	0.820	
	0.1	311	0.630	

TABLE VIII.—β-CROCEO NITRATE.

$t = 20°$. $s_0 = 0.01298$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.05	1467	1.130	0.320
	0.1	1570	1.210	0.329
	0.2	1713	1.320	(0.329)
	0.5	2035	1.568	(0.343)
				0.32
CCl_3COOH	0.2	1547	1.190	(0.207)
	0.387	1601	1.234	(0.181)

We find again constant values for a when potassium formate is used as a solvent, while potassium thiocyanate gives increasing values. Special attention should be called to the behavior of potassium hydroxide as solvent. We find here an increase in the solubility only with the most diluted solution. At higher concentrations it falls very markedly, indicating a specific effect of the solvent. To explain the phenomenon we imagined the possibility of a separation of croceo hydroxide in the solid state. On adding a solution of molal sodium hydroxide to a solution of croceo nitrate or croceo chloride, we indeed observed the appearance of a crystalline precipitation of a sparingly soluble compound. This proved, however, to be croceo carbonate, and does not appear when using pure solutions. As solubility measurements are carried out with an hydroxide entirely free from carbon dioxide, the explanation of the phenomenon is not to be found here. It may be due to a special reaction between the solvent and the saturating salt, or it may be looked upon as a peculiarity of the solvent, manifesting itself through an exceedingly great "salting out" effect. Of course, merely using this expression does not explain the phenomenon. However, it is sufficient to place it in that great field of phenomena which are of deep significance in connection with the theory of solubility and with which we will deal more thoroughly in subsequent articles.

[4] *Meddel. K. Vetenskapsakad. Nobelinst.*, **5**, 25 (1919).

When using potassium and sodium chloride solutions as solvents, other peculiarities were noted. The increase in solubility of croceo nitrate is found to be much less than otherwise, for example with 0.1 N solutions at 0° for potassium chloride, 1.16; and for sodium chloride, 1.14. This phenomenon was also studied by using mixed nitrate and chloride solutions as solvent and will be discussed more thoroughly when the question of such mixed solvents is taken up.

TABLE IX.—CROCEO TETRANITRO-DIAMMINE COBALTIATE. $(Co(NH_3)_4-(NO_2)_2)(Co(NH_3)_2(NO_2)_4)$.

$s_0 = 0.000096$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.05	11.9	1.24	0.287
	0.1	12.8	1.33	0.297
	0.2	13.9	1.45	(0.249)
	0.5	17.5	1.82	(0.346)
				0.29
KCl	0.05	12.4	1.29	0.341
	0.1	13.2	1.38	0.332
	0.2	14.9	1.55	(0.354)
	0.5	20.2	2.10	(0.431)
				0.34

TABLE X.—CROCEO PERCHLORATE. $(Co(NH_3)_4(NO_2)_2)ClO_4$.

$s_0 = 0.01239$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.05	1423	1.148	0.356
	0.1	1566	1.264	0.398
				0.38
NaOOCH	0.05	1362	1.099	0.246
	0.1	1420	1.146	0.233
				0.24
KOOCCCl₃	0.1	1562	1.261	0.393
				0.39
CCl₃COOH	0.1	1398	1.128	0.207

TABLE XI.—CROCEO DIOXALO-TRIAMMINE COBALTIATE. $(Co(NH_3)_4(NO_2)_2)-(Co(NH_3)_3(C_2O_4)_2)$.

$s_0 = 0.000593$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.1	89.5	1.509	0.468
	1.0	233	3.93	(0.648)
				0.47
KCl	0.02	70.3	1.186	0.388
	0.05	79.0	1.332	0.435
	0.1	91.7	1.546	0.496
	1.0	334	5.633	(0.818)
				0.44

TABLE XII.—CROCEO CHLORIDE. $(Co(NH_3)_4(NO_2)_2)Cl$

$s_0 = 0.0222$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.02	2310	1.043	0.261
	0.05	2400	1.084	0.252
	0.1	2520	1.136	0.253
				0.26

TABLE XIII.—OXALO-TETRAMMINE COBALTIC NITRATE. $(Co(NH_3)_4C_2O_4)NO_3$.

$s_0 = 0.00658$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KCl	0.02	736	1.119	0.429
	0.05	803	1.220	0.433
	0.1	905	1.375	0.477
				0.43

The figures in Tables IX, X and XI show values of a which are rather variable when the concentration changes. This is especially noteworthy

in the instance of the dioxalo-triammine cobaltiate. The rise in solubility is here much greater than usual.

In Table XII are given the figures obtained with croceo chloride, the most soluble of the croceo salts employed.

Further measurements were carried out with oxalo-tetrammine cobaltic salts. These are stable in solution, but it is more difficult to produce them in a quite pure state than the croceo salts. The data given in Tables XIII, XIV, XV and XVI will therefore scarcely possess the same degree of accuracy.

TABLE XIV.—OXALO-TETRAMMINE COBALTIC TETRANITRO-DIAMMINE COBALTIATE. $(Co(NH_3)_4C_2O_4)$-$(Co(NH_3)_2(NO_2)_4)$.

$s_0 = 0.00103.$

Solvent.	c.	$s \times 10^5$.	s/s₀.	a.
KOOCH	0.02	112	1.09	0.214
	0.05	121	1.18	0.261
	0.1	132	1.28	0.297
				0.26
NaOOCH	0.02	111	1.08	0.194
	0.05	120	1.17	0.245
	0.1	128	1.25	0.265
				0.24
KCl	0.02	115	1.12	0.275
	0.05	123	1.20	0.291
	0.1	137	1.33	0.340
				0.30
NaCl	0.02	114.5	1.12	0.27
	0.05	123	1.20	0.290
	0.1	137	1.33	0.339
				0.30
KNO₃	0.02	116	1.13	0.297
	0.05	126	1.22	0.324
	0.1	141	1.37	0.373
				0.33

TABLE XV.—OXALO-TETRAMMINE COBALTIC PERCHLORATE. $(Co(NH_3)_4C_2O_4)ClO_4$.

$s_0 = 0.00508.$

Solvent.	c.	$s \times 10^4$.	s/s₀.	a.
KOOCH	0.05	616	1.21	0.395
	0.1	679	1.34	0.417
	0.2	796	1.57	(0.464)
				0.40
NaOOCH	0.05	596	1.17	0.330
	0.1	640	1.26	0.332
	0.2	718	1.41	(0.357)
				0.33
KCl	0.05	634	1.25	0.456
	0.1	712	1.40	0.484
				0.47
NaCl	0.05	614	1.21	0.388
	0.1	684	1.35	0.426
				0.41
KOOCCCl₃	0.1	677	1.33	0.44
	0.2	781	1.54	(0.444)
				0.44
CCl₃COOH	0.1	607	1.11	0.256
	0.2	638	1.26	(0.236)
				0.26

Thallous tetranitro-diammine cobaltiate, with which salt a series of measurements was also carried out, showed surprisingly small increases in the solubility, as indicated in Table XVII. The small solubilities in potassium salt solutions are probably due to the formation of a solid mixture of thallous and potassium tetranitro-diammine cobaltiate.

TABLE XVI.—OXALO-TETRAMMINE COBALTIC PERCHLORATE. $t = 20°$. $s_0 = 0.0140$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOH	0.02	1603	1.143	0.652
	0.05	1814	1.287	0.670
	0.1	1808	1.290	0.443

TABLE XVII.—THALLOUS TETRANITRO-DIAMMINE COBALTIATE. $(Co(NH_3)_2(NO_2)_4)Tl$.

$$s_0 = 0.00259.$$

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.	Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
KOOCH	0.02	273	1.053	0.153	KClO$_3$	0.02	274	1.055	0.159
	0.05	285	1.097	0.169		0.05	287	1.108	0.188
	0.1	287	1.108	0.135		0.1	298	1.150	0.184
	0.15	283	1.093	0.095					0.18
	0.2	277	1.067	0.063					
					KNO$_3$	0.02	278	1.072	0.206
						0.05	294	1.134	0.230
						0.1	308	1.187	0.224
									0.22

In the following table are collected all the a values found with various solutes and solvents according to the preceding figures given above.

TABLE XVIII.—THE a VALUES AT 0°.

Solvent. → Salt.	KOOCH.	NaOOCH.	KCl.	NaCl.	KNO$_3$.	KClO$_3$.	NaClO$_3$.	KOOCCl$_3$.	KSCN.	NaSO$_4$C$_6$H$_5$.	HCl.
Praseo thiocyanate....	0.25		0.31	0.30		0.34	0.32				
nitrate.........	0.33		0.34	0.30						0.29	0.31
iodate.........			0.35	0.34		0.37	0.37				
picrate........			0.37	0.33							
bromide.......	0.27							0.28			
Croceo nitrate.........	0.32								0.38		
tetranitro co-baltiate......	0.29		0.34								
perchlorate....	0.38	0.24							0.39		
oxalo-triammine cobaltiate....	0.47										
chloride........	0.26										
Oxalo-tetrammine co-baltic nitrate...				0.43							
tetranitro co-baltiate......	0.26	0.24	0.30	0.30	0.33						
perchlorate.....	0.40	0.33	0.47	0.41				0.41			

The mean value of all these figures is $a = 0.31$, which is in accordance with the a-value derived from the freezing-point measurements as shown in the previous paper.   Inspection of Table XVIII and the foregoing tables shows, however, that we cannot count upon constant a values, even if one salt is considered in connection with different solvents, or what was

more probable, when one solvent is considered in connection with different salts. There is, however, an important regularity to which attention must be called. When a solvent proves of greater dissolving power in one instance, it seems to prove so in all. We see, for example, that potassium salts have a greater dissolving effect than sodium salts, chlorates than chlorides, and these again than formates, etc. With a single exception, that of praseo nitrate in potassium formate solution, the sequence of solvent power for all of the salts for which sufficient data have been procured, is as follows: potassium chlorate, sodium chlorate, potassium chloride, sodium chloride, potassium formate, sodium formate.

This sequence is observed not only with uni-univalent salts, with which we are dealing, but also with salts of other types, and especially when non-electrolytes are considered. We shall in a later paper deal more in detail with this fact, which is of high importance for our conception of electrolytic solution. The sequence also, as far as reliable data are available, is coincident with that obtained by ranging the salts according to their freezing-point lowering. Of all salts employed, potassium nitrate showed the slightest lowering of the freezing point and at the same time produced the greatest increase in solubility. From both of these facts we infer that the activity coefficients of univalent ions have smaller values here than in the other solvents employed. Sodium formate on the other hand shows large values for the freezing-point lowering and correspondingly less solvent power than the other salts. At any rate these are phenomena to be duly regarded as derived from a rigid relation between osmotic and activity properties of solutions.

It cannot, however, be denied, that really constant a values are not obtained in most cases, even with very sparingly soluble salts. We can imagine that the incompleteness of our hypothesis is the reason for such deviations. It is true that the secondary electric effect spoken of in the previous paper may influence the activity to a considerable extent, even with univalent ions. On the other hand the cube root expression of Noyes and Falk,[3] underlying our calculation of the a values, certainly gives no exact representation of the freezing-point curves, as illustrated in a recent publication of G. N. Lewis and G. A. Linhart,[5] and many discrepancies may be due to this fact.

The equation found by Lewis and Linhart, claimed by them to be of universal validity, is

$$\log \left(n\lambda - \frac{\theta}{c} \right) = \alpha \log c + \log \beta, \tag{1}$$

where n is the number of ions formed by one mol of salt on complete dissociation, λ the theoretical molecular freezing-point lowering (1.858°), θ

[5] Lewis and Linhart, THIS JOURNAL, **41**, 1951 (1919).

the lowering found, c the concentration and α and β constants. The equation may also be written,

$$\Delta = \Delta_0 - \beta c^{\alpha}, \qquad (2)$$

where Δ and Δ_0 indicate the molal lowering observed and calculated, respectively.

In the first two columns of Table XIX are given the values of α and β for a number of salts calculated by Lewis.

TABLE XIX.

	α.	β.		α.	β.
KCl	0.535	1.223	K_2SO_4	0.374	3.187
NaCl	0.535	1.223	$BaCl_2$	0.364	2.660
KIO_3	0.442	1.196	$CoCl_2$	0.362	2.456
$NaIO_3$	0.442	1.196	Mean	0.37	2.7
Mean	0.49	1.21	$MgSO_4$	0.293	3.404
			$CdSO_4$	0.325	4.421
			Mean	0.31	3.9

In the last two columns we have added the mean values of α and β. According to these figures it seems that the α-values decrease, and the β-values increase, by increasing valences of the ions.

The term $\gamma = \dfrac{x}{c}$, called by Lewis the thermodynamic or corrected degree of dissociation, is the same as the activity coefficient f used throughout the previously mentioned papers. Equation 17 in Lewis' paper expressing the relationship between activity coefficient and concentration is easily reached by introducing the osmotic coefficient,

$$\varphi = \frac{\Delta}{\Delta_0}, \qquad (3)$$

and the relation between this and the activity coefficient,

$$c\,\frac{d\ln f}{dc} = c\,\frac{d\varphi}{dc} - (1 - \varphi). \qquad (4)$$

Substituting here from Equation 2

$$\varphi = 1 - \frac{\beta c^{\alpha}}{\Delta_0},$$

and hence,

$$\frac{d\varphi}{dc} = -\frac{\beta}{\Delta_0}\,\alpha\,c^{\alpha-1}.$$

We then find,

$$\ln f = -\frac{\beta(1 + \alpha)}{\Delta_0\,\alpha}\cdot c^{\alpha} \qquad (5)$$

which is identical with Equation 17 of Lewis and Linhart.

In the case of saturation of a binary salt in a binary hetero-ionic solvent we have, when s indicates the solubility,

$$sf = \text{Const.}$$

or

$$\log s = \frac{\beta(1 + \alpha)\ c^\alpha}{2.303\ \Delta_0\ \alpha} + \text{const.} \tag{6}$$

Introducing for the solubility in pure water,

$$\log s_0 = \frac{\beta(1 + \alpha)\ s_0^\alpha}{2.303\ \Delta_0\ \alpha} + \text{const.,}$$

and putting

$$\frac{\beta(1 + \alpha)}{2.303\ \Delta_0\ \alpha} = L \tag{7}$$

we obtain

$$\log \frac{s}{s_0} = L.c^\alpha \tag{8}$$

Inserting in (7) and (8) the values of α and β for potassium chloride we find,

$$\log \frac{s}{s_0} = 0.41\ c^{\ 0.535}; \tag{8a}$$

and for potassium iodate,

$$\log \frac{s}{s_0} = 0.456\ c^{\ 0.442}; \tag{8b}$$

and for magnesium sulfate,

$$\log \frac{s}{s_0} = 1.76\ c^{\ 0.293.} \tag{8c}$$

Using the formula given by Noyes and Falk for the freezing-point lowering we have found as shown in the foregoing paper

$$\log \frac{s}{s_0} = a\ c^{\ b} \tag{9}$$

where a and b are constants, an expression of the same form as that reached by means of the equation of Lewis. There is however a considerable difference between the constants in the two formulas. While in the case of uni-univalent salts L and α both have values in the neighborhood of 0.4–0.5, a and b are both equal to $1/3$. For magnesium sulfate the difference lies in the same direction. It is remarkable however that the solubility curve of xantho chromate in magnesium sulfate calculated in

the foregoing paper according to Formula 9, gives a rather close agreement with (8c) since we have here,

$$L = 1.76 \qquad\qquad a = 1.80$$
$$\alpha = 0.293 \qquad\qquad b = 0.333.$$

III. Uni-univalent Salts in Solvents of Other Types.

A small number of experiments has been made to find the influence of the type of the solvent upon the solubility of uni-univalent salts. The results of these experiments are given in the following tables.

TABLE XX.—PRASEO THIOCYANATE IN MAGNESIUM SULFATE AT $t = 0$.

c.	$s \times 10^5$.	s/s_0.
0	289	
0.02	340	1.11
0.05	358	1.19
0.1	379	1.27
0.2	400	1.38

TABLE XXI.—OXALO-TETRAMMINE COBALTIC PERCHLORATE IN MAGNESIUM SULFATE, $t = 0$.

c.	$s \times 10^5$.	s/s_0.
0	510	
0.05	739	1.45
0.1	823	1.61

TABLE XXII.—CROCEO NITRATE IN SODIUM OXALATE, $t = 0$.

c.	$s. \times 10^5$.	s/s_0.
0	494	
0.02	572	1.154
0.05	621	1.256
0.1	678	1.370

TABLE XXIII.—CESIUM TETRATHIO-CYANATO-DIAMMINE CHROMIATE. $(Cr(NH_3)_2(SCN)_4)Cs$.
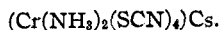
Solvent.	c.	$s \times 10^5$.	s/s_0.
NaOOCH	1	83.1	1.05
NaNO$_3$	1	136.5	1.73
Mg(NO$_3$)$_2$	0.5	135.6	1.72
MgSO$_4$	0.5	97.6	1.22
H$_2$O		78.9	

TABLE XXIV.—CESIUM TETRANITRO-DIAMMINE COBALTIATE. $(Co(NH_3)_2(NO_2)_4)Cs$.
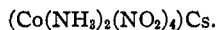
Solvent.	c.	$s \times 10^5$.	s/s_0.
NaOOCH	1	785	1.47
NaNO$_3$	1	1268	2.38
Mg(NO$_3$)$_2$	0.5	1113	2.09
MgSO$_4$	0.5	815	1.54
H$_2$O		532	

Comparing the data from these tables with those found for the same salts in uni-univalent solvents, we find that as a rule the solubility is mainly governed by the equivalent concentrations of the solvent, independent of its type. A solution of magnesium sulfate or of sodium oxalate dissolves just as much as a solution of a uni-univalent salt of the same equivalent concentration. The agreement between the figures is at any rate probably sufficient for establishing this rule as general, the deviations being of the same order of magnitude as found when uni-univalent solvents are mutually compared.

The values from Tables XXIII and XXIV show great diversity owing to the high concentration of the solvent employed, whereby the secondary effects are greatly increased. However, no systematic distinction between solvents of different types can be observed in these cases, either.

Because of the character of the systems no a values can be calculated here.

IV. Bi-bivalent Salts in Bi-bivalent Solvents.

Six systems of this type have been examined. The results are given in the tables below.

TABLE XXV.—ISOTHIOCYANATO-PENT-AMMINE COBALTIC CHROMATE.

$(Co(NH_3)_5NCS)CrO_4$. $s_0 = 0.001074$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.02	224	2.086	1.79
	0.05	329	3.07	1.78
	0.1	455	4.23	1.70
	0.2	673	6.26	(1.63)
	0.5	1150	10.72	(1.48)
	1.0	1770	16.48	(1.35)
				1.76

TABLE XXVI.—CHLORO-PENTAMMINE CO-BALTIC HEXACHLOROPLATINATE.

$(Co(NH_3)_5Cl)PtCl_6$. $s_0 = 0.000091$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.05	28.2	3.10	1.51
	0.1	48.3	5.31	1.73
				1.62

TABLE XXVII.—XANTHO CHROMATE.

$(Co(NH_3)_5NO_2)CrO_4$. $s_0 = 0.000258$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.02	62	2.40	1.81
	0.05	90.8	3.52	1.79
	0.1	123.7	4.80	1.69
	0.2	180.4	6.99	(1.61)
	1.0	512.0	19.84	(1.38)
				1.76

TABLE XXVIII.—XANTHO OXALATE.

$(Co(NH_3)_5NO_2)C_2O_4$. $s_0 = 0.0001614$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.02	131	8.11	4.08
	0.05	183	11.3	3.31
	0.1	310	19.1	3.09
	0.2	445	27.6	(2.69)
	1.0	1026	63.6	(1.90)
				3.5

TABLE XXIX.—CHLORO-PENTAMMINE COBALTIC OXALATE. $(Co(NH_3)_5Cl)C_2O_4$.

$s_0 = 0.000359$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.02	238	6.63	3.90
	0.05	354	9.87	3.25
	0.1	608	16.9	3.05
	0.2	1150	32.0	(2.87)
	0.5	2040	56.8	(2.39)
	1.0	2930	81.6	(2.04)
				3.4

TABLE XXX.—CHLORO-PENTAMMINE CHROMIC OXALATE. $(Cr(NH_3)_5Cl)C_2O_4$.

$s_0 = 0.001250$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	a.
MgSO$_4$	0.02	596	4.77	3.60
	0.05	1014	8.11	3.20
	0.1	1706	13.65	2.98
	0.2	2640	21.10	(2.64)
	0.5	4580	36.6	(2.20)
	1.0	7070	56.6	(1.92)
				3.3

The a values are calculated according to the same equation as used in uni-univalent salts,

$$\log \frac{s}{s_0} = a \left(\sqrt[3]{c_t} - \sqrt[3]{s_0} \right).$$

For all the c and s calculations molal concentrations are used. The average a values of the first three systems, 1.71, is somewhat more than four times the a values for uni-univalent systems, corresponding to curves that rise much more precipitously than in the case of uni-univalent systems.

Using equivalent concentrations instead of molal concentrations in the equation we find $a = 1.38 = 4 \times 0.34$, instead of $a = 1.71$.

The three oxalates afford a very much higher increase in solubility than the other bi-bivalent salts, and correspondingly higher a values, about 3.4.

V. Bi-bivalent Salts in Solvents of Other Types.

Bi-bivalent salts have also been determined by employing uni-uni- and uni-bivalent solvents. The results are given in Tables XXXI-XXXVI.

TABLE XXXI.—CHLORO-PENTAMMINE COBALTIC HEXACHLOROPLATINATE. $(Co(NH_3)_5Cl)PtCl_6$. $s_0 = 0.000092$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.02	13.7	1.49
	0.1	26.8	2.91
	0.15	32.7	3.55

TABLE XXXII.—CHLORO-PENTAMMINE COBALTIC OXALATE. $(Co(NH_3)_5Cl)C_2O_4$. $s_0 = 0.000359$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.02	35.9	1.47
	0.05	52.8	1.99
	0.1	71.5	2.61
	0.15	93.5	3.04
KOOCH	0.1	84.9	2.37
	0.2	111.3	3.10
	0.5	171.5	4.78
	1.0	242.4	6.76

TABLE XXXIII.—XANTHO OXALATE. $(Co(NH_3)_5NO_2)C_2O_4$. $s_0 = 0.0001614$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KOOCH	0.02	27.2	1.68
	0.05	35.6	2.20
	0.1	45.5	2.82
	0.2	61.2	3.79
	0.5	96.7	5.99
	1.0	127.7	7.91
KCl	0.02	28.0	1.73
	0.05	38.2	2.36
	0.1	48.7	3.01
	0.2	70.5	4.37
	0.5	121.2	7.50
	1.0	201.1	12.4

TABLE XXXIV.—CHLORO-PENTAMMINE CHROMIC OXALATE. $(Cr(NH_3)_5Cl)C_2O_4$. $s_0 = 0.00111$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KOOCH	0.02	150	1.34
	0.05	194	1.75
	0.1	254	2.29
	0.2	331	2.98
	0.5	475	4.27
	1.0	555	5.00

TABLE XXXV.—ISOTHIOCYANATO-PENTAMMINE COBALTIC CHROMATE. $(Co NH_3)_5SCN)CrO_4$. $s_0 = 0.00107$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KOOCH	0.02	140.2	1.31
	0.05	162.8	1.52
	0.1	189.9	1.77
NaOOCH	0.02	137.7	1.29
	0.05	157.0	1.47
	0.1	183.5	1.71

A glance at these tables and the tables in the foregoing section shows first, much more precipitous curves than found with uni-univalent solvents; second, that the rule of the equal action of equivalent normal solutions, found to hold for uni-univalent solutes, does not hold when the solute contains bivalent ions. It is evident, as appears in Fig. 2 representing the curves of solubility of xantho chromate, that a solution of a bi-bivalent

TABLE XXXVI.—XANTHO CHROMATE.　(Co(NH$_3$)$_5$NO$_2$)CrO$_4$.　s_0 = 0.000258.

Solvent.	c.	$s \times 10^5$.	s/s_0.	Solvent.	c.	$s \times 10^5$.	s/s_0.
KOOCH	0.02	36.1	1.40	KCl	0.02	37.1	1.44
	0.05	48.0	1.86		0.05	52.0	2.02
	0.1	63.6	2.47		0.1	69.0	2.68
	0.2	81.6	3.17		0.2	88.7	3.45
	0.5	121.2	4.70	KClO$_3$	0.02	33.2	1.28
	1.0	178.7	6.93		0.05	42.1	1.63
NaOOCH	0.02	32.3	1.25		0.1	57.0	2.21
	0.05	41.0	1.59	NaClO$_3$	0.02	31.8	1.23
	0.1	55.8	2.16		0.05	41.7	1.61
	0.2	74.6	2.89		0.1	56.1	2.17
	0.5	113.1	4.38	KNO$_3$	0.02	34.5	1.34
	1.0	172.9	6.70		0.05	44.4	1.72
NaCl	0.05	41.5	1.61		0.1	58.8	2.28
	0.1	56.5	2.19	NaNO$_3$	0.02	34.4	1.33
	0.2	78.5	3.04		0.05	44.2	1.71
					0.1	57.7	2.24

salt, such as magnesium sulfate, dissolves considerably more of the bi-bivalent solute than does an equally strong solution of a uni-univalent salt, such as potassium formate or sodium chloride. From this we can
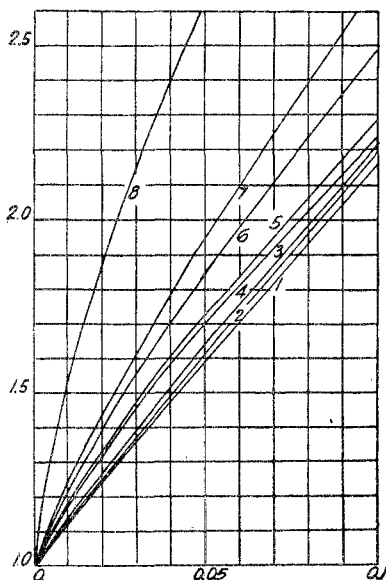
Fig. 2.—Solubility ratio s/s_0 for xantho chromate in (1) NaOOCH and NaClO$_3$, (2) NaCl, (3) KClO$_3$, (4) NaNO$_3$, (5) KNO$_3$, (6) KOOCH, (7) KCl, (8) MgSO$_4$. The abscissa indicates here and in all other diagrams equivalent concentration of the solvent.
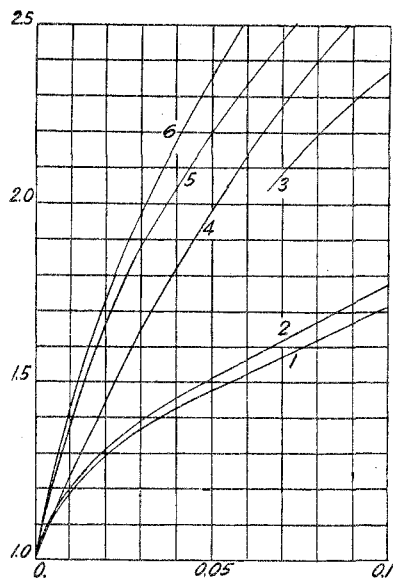
Fig. 3.—Solubility ratio s/s_0 (1) Iso-thiocyanate chromate in NaOOCH, (2) Iso-thiocyanate chromate in KOOCH, (3) Pentammine oxalate in KOOCH, (4) Pentammine oxalate in KCl, (5) xantho oxalate in KOOCH, (6) xantho oxalate in KCl.

draw the conclusion that in an equal equivalent concentration of the solvent the activity coefficient of a univalent ion present in the solution is influenced to a smaller extent than is the activity coefficient of a bivalent ion. The significance of this conclusion will be clearer when considering solutes composed of ions of different valences. This is treated in the following section.

VI. Uni-bivalent Salts in Solvents of Various Types.

The first measurements were carried out with uni-univalent solvents alone. The data are as follows.

TABLE XXXVII.—BROMO-PENTAMMINE COBALTIC BROMIDE. $(Co(NH_3)_5Br)Br_2$.

$s_0 = 0.00275$.

Solvent.	c.	$s \times 10^5$.	s/s_0.	Solvent.	c.	$s \times 10^5$.	s/s_0.
NaOOCH	0.02	315	1.14	KOOCCCl₃	0.1	388	1.41
	0.05	351	1.28		0.2	444	1.62
	0.1	393	1.43	CCl₃COOH	0.1	372	1.35
	0.2	442	1.61		0.2	411	1.49
	0.5	527	1.91	KClO₃	0.02	323	1.17
	1.0	593	2.16		0.05	371	1.34
KOOCH	0.02	323	1.16		0.1	425	1.54
	0.05	357	1.30	NaClO₃	0.02	323	1.17
	0.1	397	1.46		0.05	369	1.34
	0.2	455	1.65		0.1	420	1.53
	0.5	549	1.98				
	1.0	648	2.36				

TABLE XXXVIII.—BROMO-PENTAMMINE COBALTIC CHLORIDE. $(Co(NH_3)_5Br)Cl_2$.

$s_0 = 0.00542$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KClO₃	0.05	699	1.29
	0.1	792	1.47
NaClO₃	0.05	694	1.28
	0.1	791	1.47
	1.0	1511	2.79

TABLE XL.—CHLORO-PENTAMMINE COBALTIC CHLORIDE. $(Co(NH_3)_5Cl)Cl_2$.

$s_0 = 0.0091$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KOH	0.02	1090	1.20
	0.05	1320	1.45
	0.1	1310	1.44

TABLE XXXIX.—THIOCYANATO-PENTAMMINE COBALTIC IODATE. $(Co(NH_3)_5CNS)(IO_3)_2$. $s_0 = 0.00204$.

Solvent.	c	$s \times 10^5$.	s/s_0.
NaOOCH	0.02	230	1.13
	0.05	268	1.31
	0.1	312	1.53
	0.2	367	1.80
	0.5	488	2.39
	1.0	635	3.11
KOH	0.02	286	1.40
	0.05	324	1.59
	0.1	323	1.58

TABLE XLI.—XANTHO NITRATE. $(Co(NH_3)_5NO_2)(NO_3)_2$. $s_0 = 0.0170$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.01	1784	1.05
	0.02	1858	1.09
KOOCCHCl₂	0.02	1840	1.09
	0.05	2010	1.18
	0.1	2150	1.26
MgCl₂	0.01	1850	1.09
Na₂SO₄	0.01	1970	1.16
	0.02	2210	1.30
	0.05	2720	1.60
	0.1	3360	1.97

The data represented in Figs. 4 and 5 show a somewhat stronger increase with increasing concentration of the solvent than in the case of uni-univalent salts. Otherwise the curve is almost the same, particularly as to the order of the various solvents with regard to dissolving power.

Fig. 4.—Solubility ratio of bromo-pentammine bromide in (1) KOOCCCl₃, (2) NaOOCH, (3) KOOCH, (4) NaClO₃, (5) KClO₃.

Three other salt determinations were carried out using solvents of higher types. The results from these are given in Tables XLI–XLIII and in Figs. 6, 7 and 8.

In describing the phenomena appearing in these systems it is necessary to make a sharp distinction between two cases of interaction of uni-bivalent salts. In the first of these the two salts are electrically isotypic, as for example chloro-pentammine bromide and calcium formate [Co(NH₃)₅ Cl]Br₂ and Ca(OO-CH)₂; and in the other they are electrically heterotypic, as for example croceo sulfate and magnesium chloride, [Co(NH₃)₄(N-O₂)₂]₂ SO₄ and MgCl₂. When a uni-bivalent isotypic solvent is employed, the solubility of the salt does not increase any more than when a uni-univalent one is employed. Potassium dichloro-acetate and calcium formate dissolve chloro-pentammine cobaltic bromide to nearly the same extent. Sodium oxalate and potassium chloride dissolve equal amounts of croceo sulfate. On the other hand using an electrically heterotypic solvent we find much greater solubilities, nearly the same as when bi-bivalent solvents are employed.

Fig. 5.—Solubility ratio of bromo-pentammine chloride in (1) NaClO₃, (2) KClO₃, and of thiocyanate pentammine iodate in (3) NaOOCH.

From these results and those previously given we are justified in concluding that the activity of an ion is affected similarly by ions of the same sign, only when the equivalent concentration of the acting ions is the same. If the dissolved ion is uni-univalent the action of ions of the opposite sign will likewise depend chiefly upon the equivalent concentration. In the case of dissolved ions of higher valence than unity, the

Fig. 6.—Solubility of xantho nitrate in (1) KOOCHCl₂, (2) Na₂SO₄.

effect of the ion of opposite sign will increase with increasing valence. In all cases the activity of an ion depends much more upon the nature

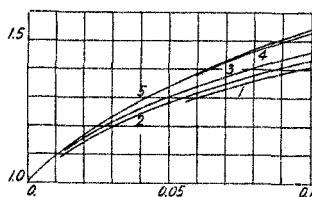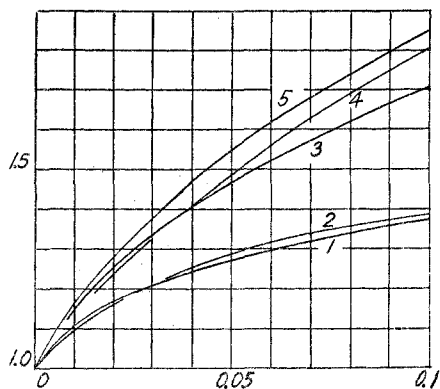Fig. 7.—Solubility ratio of chloro-pentam-mine bromide in (1) Ca(OOCH)₂, (2) KOO-CCH-Cl₂, (3) MgSO₄, (4) Na₂SO₄, (5) (KOO-C)₂C₆H₄.
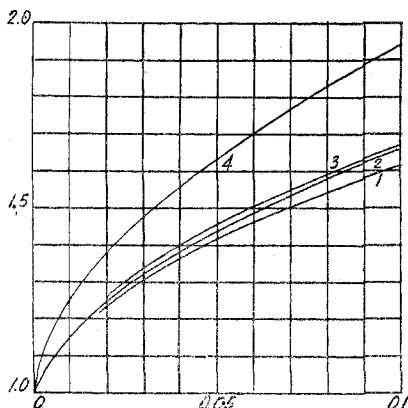
Fig. 8.—Solubility ratio of croceo sul-fate in (1) KOOCCHCl₂, (2) KCl, (3) Na₂-C₂O₄, (4) MgCl₂.

of the ions of the opposite sign than on that of the ions of the same sign, a point of view of importance in the general conception of salt solutions.

TABLE XLII.—CHLORO-PENTAMMINE COBALTIC BROMIDE. (Co(NH₃)₅Cl)Br₂.

$s_0 = 0.00725.$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$
KOOCCHCl₂	0.01	774	1.07
	0.05	938	1.29
	0.075	980	1.35
	0.1	1016	1.39
Ca(OOCH)₂	0.01	815	1.12
	0.02	900	1.24
	0.04	979	1.35
	0.05	997	1.38
(KOOC)₂C₆H₄	0.01	932	1.29
	0.02	1073	1.48
	0.05	1340	1.85
	0.1	1604	2.21
Na₂SO₄	0.01	903	1.24
	0.02	1040	1.42
	0.05	1312	1.81
MgSO₄	0.01	916	1.26
	0.02	1027	1.40
	0.05	1245	1.72

TABLE XLIII.—CROCEO SULFATE. (Co(NH₃)₄(NO₂)₂)₂SO₄. $s_0 = 0.00096.$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$
KCl	0.01	111.5	1.16
	0.02	119.9	1.25
	0.05	138.5	1.44
	0.1	161.2	1.67
KOOCCHCl₂	0.02	118.9	1.24
	0.05	136.6	1.42
	0.1	155.8	1.62
MgCl₂	0.01	132.6	1.38
	0.02	150.0	1.56
	0.05	185.5	1.95
	0.1	223.5	2.32
Na₂C₂O₄	0.01	122.2	1.26
	0.025	140.7	1.46
	0.05	161.0	1.67
	0.1	189.1	1.97

VII. Uni-trivalent Salts in Solvents of Various Types.

The following results were obtained.

TABLE XLIV.—LUTEO TETRANITRO-DIAMMINE COBALTIATE. $(Co(NH_3)_6)$-$(Co(NH_3)_2(NO_2)_4)_3$. $s_0 = 0.000043$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.01	5.23	1.22
	0.05	7.56	1.76
	0.1	9.60	2.23
$MgCl_2$	0.01	6.36	1.48
	0.05	9.41	2.18
	0.1	11.40	2.65
$Ca(OOCH)_2$	0.01	6.05	1.41
	0.05	8.93	2.08
	0.1	10.20	2.37
Na_2SO_4	0.01	10.1	2.35
	0.05	15.6	3.63
$(KOOC)_2C_6H_4$	0.01	11.0	2.56
	0.05	18.2	4.23
$MgSO_4$	0.01	9.48	2.20
	0.05	14.4	3.35
	0.1	17.3	4.02

TABLE XLV.—AQUO-PENTAMMINE COBALTIC TETRATHIOCYANATO-DIAMMINE CHROMIATE. $(Co(NH_3)_5H_2O)(Cr(NH_3)_2(CNS)_4)_3$. $s_0 = 0.0000663$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.01	7.32	1.10
	0.05	9.05	1.36
	0.1	10.24	1.54
$MgCl_2$	0.005	7.41	1.11
	0.01	8.12	1.22
	0.1	11.84	1.77
$Ca(OOCH)_2$	0.005	8.61	1.29
	0.01	9.76	1.46
	0.05	12.0	1.80
	0.1	13.6	2.04
Na_2SO_4	0.005	11.0	1.65
	0.01	12.6	1.86
	0.05	19.8	2.98
$(KOOC)_2C_6H_4$	0.005	12.3	1.85
	0.01	14.1	2.12
	0.1	27.2	4.08
$MgSO_4$	0.01	11.5	1.72
	0.1	18.6	2.79

TABLE XLVI.—OXALO-TETRAMMINE COBALTIC HEXATHIOCYANATO CHROMIATE. $(Co(NH_3)_4C_2O_4)_3(Cr(CNS)_6)$. $s_0 = 0.000532$.

Solvent.	c.	$s \times 10^5$.	s/s_0.
NaCl	0.001	54.9	1.03
	0.005	58.6	1.10
	0.01	62.7	1.18
	0.05	79.7	1.50
$MgCl_2$	0.001	57.7	1.09
	0.005	66.6	1.25
	0.01	72.8	1.37
	0.05	95.4	1.79
$Ca(OOCH)_2$	0.001	57.5	1.08
	0.005	66.5	1.25
	0.01	72.9	1.37
	0.05	95.4	1.79
Na_2SO_4	0.001	57.5	1.08
	0.005	67.8	1.27
	0.01	77.0	1.45
	0.05	117.7	2.21
$MgSO_4$	0.001	58.6	1.10
	0.005	68.7	1.29
	0.01	76.6	1.44
	0.05	110.0	2.07

TABLE XLVII.—PRASEO HEXACYANO FERRIATE. $(Co(NH_3)_4Cl_2)_3(Fe(CN)_6)$. $s_0 = 0.000121$.

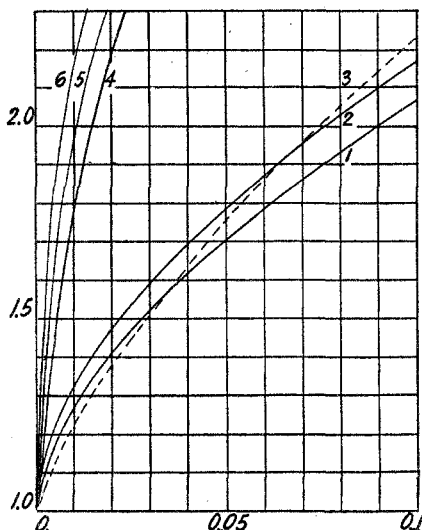| Solvent.	c.	$s \times 10^5$.	s/s_0.
KCl	0.01	13.9	1.15
	0.05	19.3	1.60
	0.1	23.3	1.93
$MgCl_2$	0.005	15.7	1.30
	0.01	17.1	1.41
	0.05	23.1	1.91
	0.1	26.1	2.16
$Ca(OOCH)_2$	0.01	16.8	1.39
	0.05	23.0	1.91
	0.1	26.3	2.18
Na_2SO_4	0.005	13.8	1.14
	0.01	15.8	1.30
	0.05	22.2	1.84
	0.1	26.5	2.19
$(KOOC)_2C_6H_4$	0.005	14.4	1.19
	0.01	16.0	1.32
	0.05	22.7	1.88
	0.1	28.2	2.33
$MgSO_4$	0.005	14.9	1.23
	0.01	16.7	1.38
	0.05	22.2	1.84
	0.1	25.1	2.08

Fig. 9.—Solubility ratio of luteo tetra-nitro cobalitate in (1) Ca(OOCH)$_2$, (2) MgCl$_2$, (3) KCl, (4) MgSO$_4$, (5) Na$_2$SO$_4$, (6) (KOOC)$_2$C$_6$H$_4$.
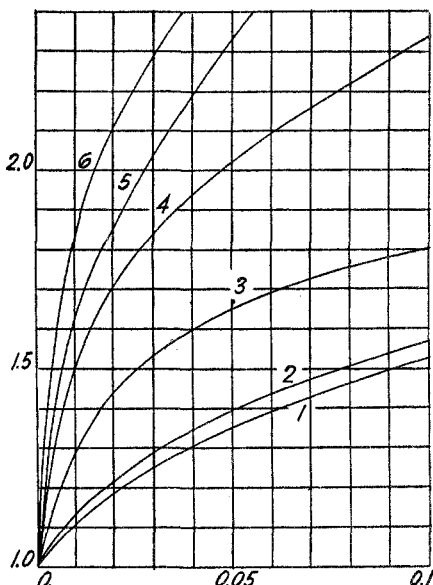

Fig. 10.—Solubility ratio of aquo-pentammine tetrathiocyanate chromiate in (1) KClf (2) MgCl$_2$, (3) Ca(OOCH)$_2$, (4) MgSO$_4$, (5) Na$_2$SO$_4$, (6) (KOOC)$_2$ C$_6$H$_4$.
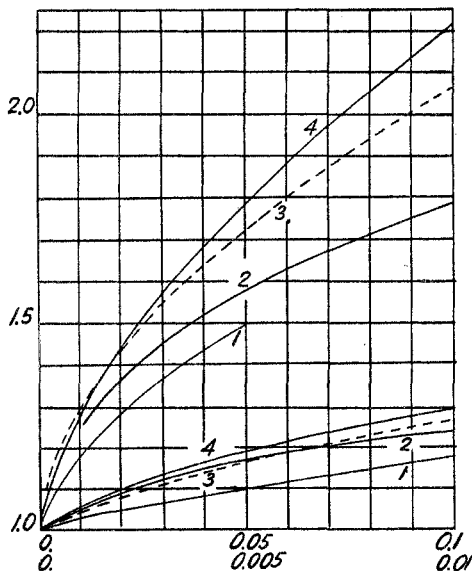

Fig. 11.—Solubility ratio of oxalo-hexa-thio-cyanato chromiate in (1) NaCl, (2) MgCl$_2$ and Ca(OOCH)$_2$, (3) Na$_2$SO$_4$, (4) MgSO$_4$.
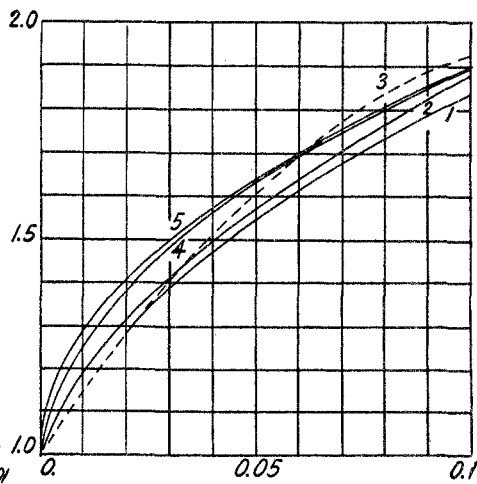

Fig. 12.—Soludility ratio of praseo hexacyano ferriate in (1) Na$_2$SO$_4$, (2) (KOOC)$_2$C$_6$H$_4$, (3) KCl, (4) Ca(OOCH)$_2$, (5) MgCl$_2$.

The curves are shown in Figs. 9, 10, 11 and 12. In the case of luteo-tetranitro-diammine cobaltiate we encounter the same effect of the electric type of solute and solvent as in the case of uni-bivalent salts, but to a still more marked degree. When the solvent contains bivalent anions the solubility is increased very much more than when it contains bivalent cations, in accordance with the principle developed in the foregoing section.

Roseo-tetrathiocyanato chromiate exhibits the same behavior towards solvents of different electrical type. Here, however, the individual influence of the solvents proves to be more marked. Only the curves for magnesium chloride and potassium chloride are nearly coincident.

The diagrams for the two salts with trivalent anions show this less conspicuously. The greater dissolving power of the bivalent cation as compared to the bivalent anion is still noticeable but only in the most diluted solutions. With rising concentration the individual nature of the solvent seems to play a considerable part in the action, obscuring to a certain degree the pure primary electrical effect. The diagram of praseo-hexacyano ferriate is particularly difficult to account for from the point of view adopted here. On account of the instability of the saturating salt the data are probably not very reliable.

VIII. Tri-trivalent Salts in Solvents of Various Types.

TABLE XLVIII.—LUTEO HEXACYANO COBALTIATE. $(Co(NH_3)_6)(Co(CN)_6)$.

$s_0 = 0.0000070.$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$
KCl	0.05	3.79	5.4
	0.1	6.50	9.3
	0.2	12.46	17.8
	0.5	34.7	49.6
	0.75	56.2	80.3
	1.0	81.3	116
	2.0	207	296
NaCl	0.1	6.02	8.6
	1.0	60.2	86
NaOOCH	0.2	12.16	12.4
	0.5	26.32	26.8
	1.0	48.82	49.8
KOOCH	0.2	13.77	14.0
	0.5	34.02	34.7
	1.0	71.35	72.8
MgSO4	0.05	24.3	22.7
	0.1	39.0	39.8
	1.0	277	282

TABLE XLIX.—LUTEO HEXACYANO FERRIATE. $(CO(NH_3)_6)(Fe(CN)_6)$.

$s_0 = 0.0000098.$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$
KCl	0.05	5.34	5.4
	0.1	9.11	9.3
	0.2	17.24	17.3
	0.5	46.2	47.2
	0.75	75.1	76.5
	1.0	107.9	110
	2.0	272	277
NaCl	0.1	8.31	8.5
	1.0	79.1	81

TABLE L.—LUTEO TRIOXALO COBALTIATE. $(Co(NH_3)_6)(Co(C_2O_4)_3)$.

$s_0 = 0.000019$

Solvent.	$c.$	$s \times 10^5.$	$s/s_0.$
NaCl	0.05	10.14	5.3
	0.1	17.8	9.4
	0.2	34.8	18.3
	0.5	100.8	53.1
	1.0	245	129

In this series the increase in solubility is very much higher than in the foregoing, as shown in Table XLVIII–L, and the accompanying diagram.
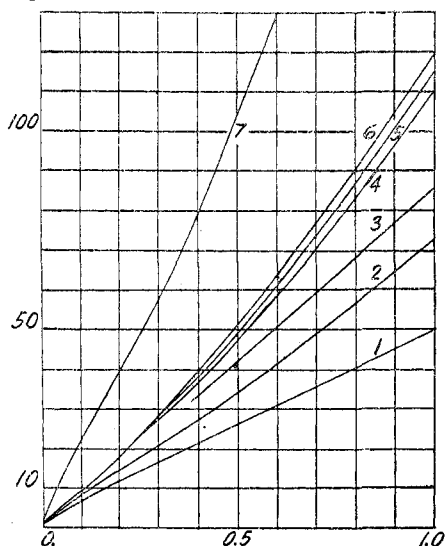

Fig. 13.—Solubility ratio of luteo hexacyano cobaltiate in (1) NaOOCH, (2) KOOCH, (3) NaCl, (5) KCl, (7) MgSO₄, and of luteo hexacyano ferriate in (4) KCl, and of luteo trioxalo cobaltiate in (6) NaCl.

The curves for luteo-hexacyano cobaltiate and ferriate exhibit a remarkable concordance, and the absolute solubilities are also very nearly the same.[7]

Also the shape of the solubility curve of the trioxalo cobaltiate shows a close agreement with that of the cyanides. The first mentioned curve is however steeper, showing that the activity of the trioxalo cobaltiate ion is lessened by the solvent more than is the activity of the two others.

A saturated solution of luteo hexacyano cobaltiate in 3 N potassium chloride solution gives on dilution with water to 0.5 N in a short time a precipitate of the solid luteo salt, indicating that the solubility increases more than in proportion to the increase in the concentration of potassium chloride.

Magnesium sulfate again gives sharply rising solubility curves for tri-

[6] An attempt was made to determine the solubility of luteo-trioxalo cobaltiate in KCl solution as well. While with NaCl as solvent, green solutions are obtained, the color of which is due to the CoOx₃⁻⁻⁻ ion, KCl gives yellow solutions evidently not containing the complex ion. The phenomenon is explained by assuming the existence of the double salt: K₃[Co(NH₃)₆][Co(C₂O₄)₃]₂, 6H₂O described by S. P. L. Sörensen ("Studier over Koboltidoxalater," Copenhagen, 1899, p. 71). As no corresponding sodium double salt is formed under the same condition and the potassium salt is very sparingly soluble, this peculiar reaction probably could be used for the separation of the two alkali metals.

[7] The agreement in properties of salts of the ions Co(CN)₆⁻⁻⁻ and Fe(CN)₆⁻⁻⁻ are well-known. It is probable, however, that a careful scrutiny will show much more concordance than hitherto assumed. According to Werner's theory, we have in both cases in octahedral arrangement of CN groups around a central Co or Fe atom. Just as with the nucleus in isotopic atoms, the central atom in these groups is shielded from reaction with outside atoms or groups if the distances between the central atom and the coördinated groups are the same. The figures for the specific weight of K₃Fe-(CN)₆ and K₃Co(ON)₆ prove that this holds very approximately, the distances in the Fe compound exceeding those in the Co compound by less than 2%.

trivalent salts. In 0.1 M solution the solubility of luteo-hexacyano cobaltiate is 40 times as great as in pure water.

In accordance with the theoretical shape of the solubility curves for tri-trivalent salts shown in the first paper of this series, all the curves for these salts are more like straight lines than those found with salts of lower types. That the individual nature of the solvent is here found to be much more pronounced than in the case of uni-univalent salts is likewise in agreement with the theory requiring changes in s/s_0, which for the same percentage change in the coefficient a, are greater in proportion to the absolute value of a.

IX. General Remarks.

In the first paper of this series the expression

$$\log \frac{s}{s_0} = a \left(\sqrt[3]{c_t} - \sqrt[3]{s_0} \right)$$

was chosen to cover approximately the solubility changes of salts in hetero-ionic solvents up to about 0.1 N solution, a being here a constant, which in uni-univalent salt systems has a value of about $1/_3$. The experimental material in salt systems of the same type used in the present paper agrees approximately with the established equation, and an equation of the same structure seems to hold in the case of bivalent salt systems as well. However the individual behavior of the salt employed is more pronounced in the more developed material now at hand, and tends to obscure any numerical regularity in salt systems of promiscuous type. On the basis of the above experiments the following qualitative rules may be formulated. *The influence of the solvent increases with the increasing valence of the ion of the solvent salt, which in the case of the tri-bivalent salts leads to an enormous increase of solubility, even on the addition of solvents of very low concentration. When both the dissolved and dissolving ions are of the higher valence, the effect of the sign of the electric charge is very marked, producing the highest solubility values when the polyvalent ions of solvent and solute are of different sign.*

As already indicated in the first paper, the reason for the appearance of individuality in the solubility curves must be sought partly in the hydration of the solvent and the solute, and partly in the fact that in these ions we are dealing not with mass as points, but with particles of different sizes bearing a number of electric charges of opposite signs, the algebraic sum of which gives the net charge or valence of the ion.

It is probable that this influence of size of ion, especially in the field of metal ammonia salts considered in this paper, on account of the rather complicated molecular structure of these salts will in many cases prove to be of considerable magnitude.

Since the theory of solubility as here developed, showing the dependence of solubility on the solvent, is really nothing but a theory of solutions, the proper way of attacking the problem, when its complicated nature has been thus manifested, will be a more detailed systematic examination of single cases of equilibrium, rather than the broad consideration of an elaborate mass of material, such as is given in the present paper. The knowledge now available as to the general behavior of salts as saturating substances in salt solution is, however, of great value in such a closer study of single cases. The conclusive results achievable from experiments in this direction will be the subject matter of the next article in this series.

COPENHAGEN, DENMARK.

THE CRYSTAL STRUCTURE OF AMMONIUM CHLOROPLATINATE.

BY RALPH W. G. WYCKOFF AND EUGEN POSNJAK.

Received June 24, 1921.

Introduction.—This study of the crystal structure of ammonium chloroplatinate is intended primarily to furnish an illustration of the application of that method of studying the structures of crystals which arises from the use of the theory of space groups.[1] At the same time it will show the possibilities and more especially the present limitations in the study of any but the very simplest of structures.

Outline of the Determination.—The study of the arrangement of the atoms in this crystal will be carried out through the following main steps: (1) a consideration of the X-ray reflection spectrum from some important crystal face, in order to determine the absolute dimensions of the unit cell and to indicate the number of chemical molecules to be associated with it; (2) a description, with the aid of the results of (1), the crystallographic data, and the theory of space groups, of all of the ways in which it is possible for the atoms of ammonium chloroplatinate to be arranged; (3) the obtaining of diffraction data suitable for distinguishing between these various possible structures and the determination of the correct one to represent the arrangement of the atoms within the crystals of this salt.

The Specimens.—The crystals that were employed for this investigation are clear octahedrons 2 to 3 mm. on their largest diameters. They were sufficiently small so that the Laue photographs, to be described later, were prepared by passing the X-rays through the entire crystal without

[1] P. Niggli, "Geometrische Krystallographie des Discontinuums," Leipzig, 1919; Ralph W. G. Wyckoff, *Am. J. Sci.*, **1**, 127 (1921) and earlier papers.