to lead to satisfactory agreement with the mixture rule. When large departures are observed, as in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^-, NO_3^-, some specific effect is probably present and its cause may be due to slightly incomplete dissociation of one of the salts present. Outside of these exceptional cases, the regularities which we have just discussed hold whether the salts have a common ion or not.

The application of the mixture rule to solutions of a given molality rather than to solutions of a given molar concentration has been quite customary. We have found that the departures between measured and calculated conductivities are of the same order of magnitude in both scales of concentration.

Summary

1. The densities and the conductivities of nine pairs of alkali halides and nitrates have been measured at a total concentration of one-molal.

2. The mixture rule has been found to be more nearly correct when the component salts have conductivities which differ but slightly.

3. Attention has been called to the wide discrepancies between measured and calculated conductivities in the case of solutions containing simultaneously the ions Na^+, K^+, Cl^- and NO_3^-.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 3, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conductivities of Concentrated Binary Mixtures of Electrolytes with a Common Anion and at Least One Ion of Charge Two

BY PIERRE VAN RYSSELBERGHE, S. W. GRINNELL AND J. M. CARLSON

Introduction

In the foregoing paper, Van Rysselberghe and Nutting[1] have shown, in general agreement with previous results of Stearn and of Ruby and Kawai,[2] that mixtures of 1-1 salts exhibit but small departures from the mixture rule, with the exception of mixtures containing simultaneously the Na^+, K^+, Cl^- and NO_3^- ions for which the departure is sometimes larger than 2 conductivity units. The results seem to show that there is a rough parallelism between the maximum departure from the mixture rule observed for a series of mixtures of a given total concentration and the difference between the conductivities of the pure salts at this same concentration.

In the case of mixtures containing ions of higher valence Smith and Gortner[3] observed departures as large as 7 conductivity units on a Λ of about 120 at concentrations as low as 0.01 N. In the present investigation we have studied mixtures for which extreme departures from the mixture rule were observed (cadmium halides + potassium halides) and others for which large departures were expected but were actually found to be small (magnesium chloride + alkali halides). Other cases are of an intermediate type. Some of these mixtures have been studied previously in a less systematic manner from the point of view of complex ion formation. This older literature is reviewed in various monographs such as that of Walden.[4] The interpretation given by the various authors is based upon the Arrhenius theory and should be carefully revised.

Experimental

The method followed in the present work is essentially the same as that used by Van Rysselberghe and Nutting.[1] Solutions were prepared on a volume concentration basis by means of calibrated glassware. The salts used were of the highest possible purity (Baker C. P. Analyzed, Merck reagent analyzed, Kahlbaum für Analyse). Several of these salts, however, are very hygroscopic, others decompose upon drying at temperatures above 120° and, although all the usual precautions were taken, the accuracy is in several cases less than ±0.5% on the absolute value of the conductivity. Mixtures were prepared by mixing solutions of the pure salts. Conductivities of the pure salts were measured several times, each time with a freshly prepared solution, and were found to be at least as accurate as the data available in "I. C. T." or in the Landolt-Börnstein-Roth Tables. The temperature was in all cases 25 ± 0.02°. In Table I we give the measured specific conductivity, the measured equivalent conductivity, the equivalent conductivity as deduced from the mixture

---

[1] Van Rysselberghe and Nutting, THIS JOURNAL, **59**, 333 (1937).

[2] Stearn, *ibid.*, **44**, 670 (1922); Ruby and Kawai, *ibid.*, **48**, 1119 (1926).

[3] Smith and Gortner, *J. Phys. Chem.*, **37**, 79 (1933).

[4] Walden, "Das Leitvermögen der Lösungen," in "Handbuch der allgemeinen Chemie," Akademische Verlagsgesellschaft, Leipzig, Vol. IV, Part II, 1924, pp. 257-262.

rule and the difference ΔΛ between measured and calculated conductivities for a series of mixtures of cadmium iodide and potassium iodide. Several of these mixtures correspond to the composition $CdI_2 \cdot KI$ for which data were so far not available. Conductivities of mixtures corresponding to the composition $CdI_2 \cdot 2KI$ are given in the literature.

TABLE I

CONDUCTIVITIES OF MIXTURES OF CdI_2 AND KI AT 25°

Composition Equivalents per liter CdI_2	KI	Specific conductivity	Equivalent conductivity measured	Equivalent conductivity calculated	ΔΛ
1.0	0	0.01781	17.81		
1.0	0.1	.02442	22.20	26.3	− 4.1
1.0	.2	.03132	26.10	33.6	− 7.5
1.0	.3	.03834	29.53	39.6	−10.1
1.0	.5	.05289	35.26	49.1	−13.8
1.0	.8	.07677	42.65	59.0	−16.4
1.0	1.0	.09419	47.09	64.0	−16.9
1.0	1.5	.14413	57.65	71.7	−14.1
1.0	2.0	.19365	64.55	76.0	−11.5
1.0	3.0	.28422	71.05	79.0	− 7.9
1.0	4.0	.35998	72.00	76.1	− 4.1
0.2	0.1	.01423	47.42	58.3	−10.9
.6	.3	.03477	38.63	51.7	−13.1
1.0	.5	.05289	35.26	49.1	−13.8
1.6	.8	.07645	31.85	46.0	−14.2
2.0	1.0	.09001	30.00	43.8	−13.8
0.2	1.0	.11528	96.07	100.5	− 4.4
.4	1.0	.11179	79.85	87.6	− 7.7
1.0	1.0	.09419	47.09	64.0	−16.9
2.0	1.0	.09001	30.00	43.8	−13.8

In order to follow the trend of ΔΛ in each series, the data for three mixtures ($1\ CdI_2 + 0.5\ KI$, $1 + 1$, $2 + 1$) are given twice in the table. The conductivities of the pure salts, used in the calculated Λ's, were taken from smooth curves obtained by plotting all the data available in the literature.

In Table II we give the conductivities of eight groups of mixtures arranged in series corresponding to the same total equivalent concentration. We represent by x and $1 - x$ the fractions of the total equivalent concentration corresponding to salts 1 and 2, salt 1 being the first in the title of the series. Some of the data given for the CdI_2 + KI mixtures were obtained from curves drawn by means of the data of Table I.

TABLE II

CONDUCTIVITIES OF CONCENTRATED MIXTURES AT 25°

Composition x	$1 - x$	Specific conductivity	Equivalent conductivity Measured	Equivalent conductivity Calculated	−ΔΛ
	1.1	0.5 N mixtures of CdI_2 + KI			
1	0		21.4		
2/3	1/3		43.8	54.8	11.0
1/2	1/2		56.8	71.5	14.7
1/4	3/4	0.04355	87.10	96.6	9.5
0	1	.06083	121.66		
	1.2	1 N mixtures of CdI_2 + KI			
1	0	0.01781	17.81		
11/12	1/12	.02230	22.30	26.12	3.82
2/3	1/3		38.0	51.02	13.0
1/2	1/2		51.6	67.64	16.0
1/4	3/4		83.5	92.56	9.1
1/8	7/8	.10001	100.01	104.98	4.97
0	1	.11746	117.46		
	1.3	2 N mixtures of CdI_2 + KI			
1	0	0.02835	14.18		
2/3	1/3		33.2	47.4	14.2
1/2	1/2	.09419	47.1	63.9	16.8
0	1	.2274	113.7		
	2.1	1 N mixtures of $CdBr_2$ + KBr			
1	0	0.02109	21.09		
5/6	1/6	.03396	33.96	37.08	3.12
2/3	1/3	.04606	46.06	53.06	7.00
1/2	1/2	.05930	59.30	69.05	9.75
1/3	2/3	.07620	76.20	85.03	8.83
0	1	.11701	117.01		
	2.2	2 N mixtures of $CdBr_2$ + KBr			
1	0	0.02909	14.54		
5/6	1/6	.05195	25.97	30.58	4.61
2/3	1/3	.07109	35.54	46.61	11.07
1/2	1/2	.10114	50.57	62.64	12.07
1/3	2/3	.13601	68.00	78.68	10.68
0	1	.2215	110.75		
	3.1	1 N mixtures of $CdCl_2$ + KCl			
1	0	0.02264	22.64		
5/6	1/6	.03417	34.17	35.86	1.69
2/3	1/3	.04739	47.39	52.40	5.01
1/2	1/2	.06161	61.61	67.27	5.66
1/3	2/3	.07717	77.17	82.15	4.98
1/6	5/6	.09444	94.44	97.02	2.58
0	1	.11190	111.90		
	3.2	2 N mixtures of $CdCl_2$ + KCl			
1	0	0.02820	14.10		
5/6	1/6	.04903	24.51	29.34	4.83
2/3	1/3	.07453	37.26	44.58	7.32
1/2	1/2	.10329	51.64	59.81	8.17
1/3	2/3	.13601	68.00	75.05	7.05
1/6	5/6	.17292	86.46	90.29	3.83
0	1	.21106	105.53		
	4.1	1 N mixtures of ZnI_2 + KI			
1	0	0.07823	78.23		
2/3	1/3	.09007	90.07	91.30	1.23
1/2	1/2	.09637	96.37	97.84	1.47
1/3	2/3	.10362	103.62	104.37	0.75
1/6	5/6	.11097	110.97	110.92	−0.05
0	1	.11746	117.46		
	4.2	2 N mixtures of ZnI_2 + KI			
1	0	0.12333	61.66		
2/3	1/3	.15422	77.11	78.62	1.51
1/2	1/2	.16986	84.93	87.10	2.17
1/3	2/3	.18743	93.71	95.57	2.86
1/6	5/6	.20644	103.22	104.06	0.84
1	0	.22507	112.53		

TABLE II (*Concluded*)

Composition x	$1-x$	Specific conductivity	Equivalent conductivity Measured	Calculated	$-\Delta\Lambda$
4.3 4 N mixtures of ZnI$_2$ + KI					
1	0	0.11814	29.55		
5/6	1/6	.1519	37.97	41.34	3.37
2/3	1/3	.1872	46.80	53.16	6.36
1/2	1/2	.2326	58.15	64.99	6.84
1/3	2/3	.2807	70.17	76.81	6.64
1/6	5/6	.3343	83.57	88.62	5.05
0	1	.4018	100.45		
4.4 6 N mixtures of ZnI$_2$ + KI					
1	0	0.0833	13.88		
5/6	1/6	.1229	20.48	25.18	4.70
2/3	1/3	.1691	28.18	36.48	8.30
1/2	1/2	.2367	39.45	47.78	8.33
1/3	2/3	.3093	51.55	59.08	7.53
1/6	5/6	.4079	67.98	70.38	2.40
0	1	.4901	81.68		
5.1 1 N mixtures of CdSO$_4$ + K$_2$SO$_4$					
1	0	0.02852	28.52		
5/6	1/6	.03510	35.10	37.40	2.30
2/3	1/3	.04328	43.28	46.27	2.99
1/2	1/2	.05185	51.85	55.15	3.30
1/3	2/3	.06108	61.08	64.03	2.95
1/6	5/6	.07104	71.04	72.90	1.86
0	1	.08178	81.78		
6.1 2 N mixtures of CdSO$_4$ + MgSO$_4$					
1	0	0.04350	21.75		
5/6	1/6	.04462	22.31	22.31	0.00
2/3	1/3	.04575	22.87	22.86	− .01
1/2	1/2	.04691	23.45	23.42	− .03
1/3	2/3	.04791	23.95	23.97	.02
1/6	5/6	.04903	24.51	24.53	.02
0	1	.05018	25.09		
6.2 4 N mixtures of CdSO$_4$ + MgSO$_4$					
1	0	0.05486	13.71		
5/6	1/6	.05527	13.82	13.78	−0.04
2/3	1/3	.05589	13.97	13.86	− .11
1/2	1/2	.05621	14.05	13.99	− .06
1/3	2/3	.05661	14.15	14.01	− .14
1/6	5/6	.05684	14.21	14.08	− .13
0	1	.05711	14.28		
7.1 1 N mixtures of MgCl$_2$ + NaCl					
1	0	0.07177	71.77		
5/6	1/6	.07390	73.90	74.13	0.23
2/3	1/3	.07628	76.28	76.56	.28
1/2	1/2	.07869	78.69	79.02	.33
1/3	2/3	.08091	80.91	81.42	.51
1/6	5/6	.08357	83.57	83.85	.28
0	1	.08628	86.28		
7.2 2 N mixtures of MgCl$_2$ + NaCl					
1	0	0.11714	58.57		
5/6	1/6	.12230	61.15	61.30	0.15
2/3	1/3	.12749	63.74	64.03	.27
1/2	1/2	.13319	66.59	66.75	.16
1/3	2/3	.13857	69.28	69.48	.20
1/6	5/6	.14422	72.11	72.21	.10
0	1	.14986	74.93		
7.3 4 N mixtures of MgCl$_2$ + NaCl					
1	0	0.15935	39.84		
5/6	1/6	.17011	42.53	42.66	0.13
2/3	1/3	.18102	45.25	45.89	.64
1/2	1/2	.19276	48.19	48.76	.57
1/3	2/3	.20484	51.21	51.94	.73
1/6	5/6	.21732	54.33	54.96	.63
0	1	.23077	57.69		
7.4 5 N mixtures of MgCl$_2$ + NaCl					
1	0	0.16187	32.37		
5/6	1/6	.17462	34.92	35.28	0.36
2/3	1/3	.18822	37.64	38.18	.54
1/2	1/2	.20219	40.44	41.09	.65
1/3	2/3	.21686	43.37	43.99	.62
1/6	5/6	.23287	46.57	46.90	.33
0	1	.24906	49.81		
8.1 5 N mixtures of MgCl$_2$ + LiCl					
1	0	0.16187	32.37		
5/6	1/6	.16603	33.21	33.25	0.04
2/3	1/3	.17008	34.02	34.13	.11
1/2	1/2	.17456	34.91	35.01	.10
1/3	2/3	.17894	35.79	35.89	.10
1/6	5/6	.18352	36.70	36.77	.07
0	1	.18823	37.65		
8.2 9 N mixtures of MgCl$_2$ + LiCl					
1	0	0.10386	11.54		
5/6	1/6	.11120	12.36	12.44	0.08
2/3	1/3	.11864	13.18	13.34	.16
1/2	1/2	.12538	13.93	14.23	.30
1/3	2/3	.13448	14.94	15.13	.19
1/6	5/6	.14337	15.93	16.03	.10
0	1	.15236	16.93		

Discussion

If we classify the various groups of mixtures studied in the present paper according to the difference between the conductivities of the pure salts, we obtain Table III in which are given, for each type of mixture, this difference, λ, and the maximum departure from the mixture rule for the series, $\Delta\Lambda$.

If we except a few irregularities and make allowances for the experimental error, we notice a marked parallelism between λ and $\Delta\Lambda$. We consider this very simple observation as particularly significant and illuminating in view of the fact that several of the mixtures certainly contain large amounts of complex ions (CdI$_3^-$, CdI$_4^{=}$, etc.). A survey of the other data in the literature has convinced us that this parallelism is quite general, provided one excludes mixtures containing an acid and mixtures for which the sign of $\Delta\Lambda$ changes as concentration increases. Cases of this type of behavior have been reported by Smith and Gortner.[3] It seems worth mentioning that,

TABLE III

Mixtures		λ	$-\Delta\Lambda$
0.5 *N*	$CdI_2 + KI$	100.26	14.7
1 *N*	$CdI_2 + KI$	99.65	16.0
2 *N*	$CdI_2 + KI$	99.52	16.8
2 *N*	$CdBr_2 + KBr$	96.21	12.07
1 *N*	$CdBr_2 + KBr$	95.92	9.75
2 *N*	$CdCl_2 + KCl$	91.43	8.17
1 *N*	$CdCl_2 + KCl$	89.26	5.66
4 *N*	$ZnI_2 + KI$	70.92	6.84
6 *N*	$ZnI_2 + KI$	67.80	8.33
1 *N*	$CdSO_4 + K_2SO_4$	53.26	3.30
2 *N*	$ZnI_2 + KI$	50.87	2.86
1 *N*	$ZnI_2 + KI$	39.23	1.47
4 *N*	$MgCl_2 + NaCl$	17.85	0.73
5 *N*	$MgCl_2 + NaCl$	17.44	.65
2 *N*	$MgCl_2 + NaCl$	16.36	.27
1 *N*	$MgCl_2 + NaCl$	14.51	.51
9 *N*	$MgCl_2 + LiCl$	5.39	.30
5 *N*	$MgCl_2 + LiCl$	5.28	.11
2 *N*	$CdSO_4 + MgSO_4$	3.34	.03
4 *N*	$CdSO_4 + MgSO_4$	0.57	.14

for several mixtures of cadmium and zinc halides with the corresponding potassium salt, the equivalent conductivity is smaller than the contribution deduced from the mixture rule for the potassium salt alone.

Summary

1. Specific and equivalent conductivities of eight groups of binary mixtures of 2-1, 2-2 and 1-1 electrolytes with a common anion have been measured at total equivalent concentrations ranging from 0.5 to 9 *N*.

2. It is pointed out that there is a marked parallelism between the difference of the conductivities of the pure salts and the maximum departure from the mixture rule observed with the mixtures of the same total concentration.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 3, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Solubility. XV. The Solubility of Liquid and Solid Stannic Iodide in Silicon Tetrachloride

BY J. H. HILDEBRAND AND G. R. NEGISHI

Stannic iodide and silicon tetrachloride differ considerably in molecular size and very greatly in internal pressure or molecular field strength, so much so, indeed, that not only is the solubility of solid stannic iodide at 25° only 3% of the ideal solubility, but also in the liquid state they form two liquid phases below 140°. This system is particularly adapted to an investigation of the critical mixing phenomenon in its simplest aspects, because it is free from the complications introduced by the presence of electric dipoles or hydrogen bonds such as are present in most known cases of incomplete liquid miscibility. We have turned to it, therefore, in an effort to throw light upon the question of the extent to which the randomness of thermal mixing is affected by the tendency toward molecular clustering due to differences in the strength of intermolecular forces.[1]

The substances were prepared and purified by methods previously described.[2] The solubility of solid stannic iodide from 0 to 40° was determined by analysis of a solution saturated by shaking in a thermostat, as in earlier investigations in this Laboratory. The bulb containing a sample of saturated solution was placed, for analysis, in a thick-walled glass-stoppered 750-cc. flask containing 100 to 150 cc. of water. The air was displaced by carbon dioxide to prevent oxidation of iodide ion. The bulb was then broken and the flask shaken till the reaction was complete. The contents were transferred to a 500-cc. separatory funnel, about 25 cc. of carbon tetrachloride and a little concentrated tartaric acid solution added and the iodide ion oxidized to iodine by permanganate.[3] The iodine was extracted, separated and titrated with thiosulfate. The method proved rapid, simple and accurate. Three determinations of solubility were made at each temperature, 0.2, 25 and 40°, and the largest deviation from the mean was 0.5%.

The determinations at higher temperatures were made by the "synthetic method." The stannic iodide was introduced into each tube in a dry box, the air in the tube displaced by strongly dried and purified nitrogen and the stannic iodide melted into a single mass. The tube was then evacuated and a capillary seal broken, permitting the distillation of silicon chloride into it, after which it was sealed. The tube was weighed, both empty and after each substance had been added.

The solution temperature for each tube was determined in an oil-bath contained in a one-gallon (4-liter) unsilvered Dewar flask and heated electrically. Near the solution temperature the rate of heating was slow, 0.01° or less per

---

[1] *Cf.* (a) E. A. Guggenheim, *Proc. Roy. Soc.* (London), **148A**, 304 (1935); (b) J. H. Hildebrand, *Chem. Rev.*, **18**, 315 (1936); *Trans. Faraday Soc.*, in press, "Symposium on the Liquid State" September, 1936.

[2] G. R. Negishi, THIS JOURNAL, **58**, 2293 (1936).

[3] W. C. Bray and C. M. J. Mackay, *ibid.*, **32**, 1193 (1910).