

THE  
PHYSICAL REVIEW

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THE FREEZING-POINTS OF DILUTE AQUEOUS  
SOLUTIONS. III.

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THE following measurements were made during the winter months of 1895-96 in the Physical Laboratory of Princeton University.

The conditions under which the work was done were the same as during the preceding period of observation (winter, 1894-95), except that the lower and more nearly uniform temperature throughout the past winter made the maintenance of the room-temperature at about 3° C. much easier. In fact, the room-temperature rarely varied more than 0°.5 C. during an entire day.

This constancy of temperature has reduced the experimental error to one-half its former value, as appears from the fact that the average variation in a series of five entirely distinct and independent observations of the freezing-point of a given solution is now 0°.0005 C., while its former value was about 0°.001 C.

That the experimental errors are considerably lowered by this increased constancy of the room-temperature appears also in the fact that the successive observations of the freezing-point of water present less irregularity than in the previous work. (See Plate opposite p. 295, Fig. 3.)

This reduction of experimental error accounts for the greater regularity in the curves of molecular depressions in the region of

extreme dilution, as compared with the similar curves for the previous results. There seems to be no doubt that this reduction of the experimental error is due wholly to the greater constancy of the temperature of the mercury thread in the projecting stem of the thermometer. I think it now more probable than ever before, that a final degree of accuracy is to be looked for only under the condition of absolute constancy of the room-temperature at  $0^{\circ}$  C. On such days as permitted a close approach to this condition, I found the various manipulations were much more easily made and the different measurements more nearly approached exact concordance. It has not been found necessary to make the slightest change in the apparatus or method, and the measurements here to be submitted may thus be regarded as a mere continuation of those of the preceding winter (1894-95).

The present series of observations comprises the compounds named in columns 1 and 2 in the following table. In column (3) *m* denotes the concentration of the solution in gram-molecules per liter.

To avoid confusion the number of grams of the "water-free" compound per liter of the solution is given in column (4). In column (7) is given, under  $S \frac{18^{\circ}}{4^{\circ}}$ , the specific gravity of the solution whose concentration is found in the column which stands immediately before it. In addition, the table gives the name of the maker of the chemicals used and the particular process by which the original solutions were prepared.

#### *The Chlorides, — Preparation of Solutions.*

*Lithium Chloride* was prepared by treating lithium carbonate, which was obtained in a high state of purity from Merck & Co., with dilute HCl. The solution was then carefully neutralized, care being taken to expel all  $\text{CO}_2$ . The specific gravity of the solution was taken with a Mohr balance, and the solution diluted to approximate normal strength by use of Kohlrausch's tables of specific gravity.<sup>1</sup>

<sup>1</sup> Kohlrausch, Wiede. Ann. 6, p. 38, 1879.

TABLE I.

1	2	3	4	5	6	7		8	9
Compound.	Chemical formula.	<i>m</i>	Grams per liter of solution at 18° C.	Specific gravity, <sup>1</sup> Water at 4° C. = 1.	Electrical conductivity, <sup>2</sup> $\chi \cdot 10^9$ , 18° C.	<i>m</i>	$\frac{18^\circ}{4^\circ}$		Standard solution prepared.
Lithium chloride	LiCl	0.9917	42.13	1.0226	589	0.1983	1.0034	Prepared in laboratory	Kohlrausch tables
Calcium chloride	CaCl <sub>2</sub>	0.5021	55.68	1.0438	635	0.2008	1.0170	" " "	" "
Strontium chloride	SrCl <sub>2</sub>	0.4986	78.98	1.0672	633	0.1994	1.0264	Trommsdorff	" "
Stannic chloride	SnCl <sub>4</sub>	0.250	64.98	1.0486 <sub>(18°)</sub>	195 <sub>0</sub>	0.200	1.0384	Eimer & Amend	Gerlach's tables
Nitric acid	HNO <sub>3</sub>	1.0000	63.04	1.0324	278 <sub>6</sub>	0.2000	1.0054	Prepared in laboratory	Hulett's titration
Potassium hydroxide	KOH	1.0000	56.14	1.0481	170 <sub>0</sub>	0.2000	1.0091	" " "	" "
Sodium hydroxide	NaOH	1.0000	40.06	1.0418	145 <sub>2</sub>	0.2000	1.0079	" " "	" "
Potassium di-hydrogen phosphate	KH <sub>2</sub> PO <sub>4</sub>	0.333	45.38	1.0299	198	0.2000	1.0175	Eimer & Amend	Direct weighing
Di-sodium acid phosphate	Na <sub>2</sub> HPO <sub>4</sub>	0.2000	28.42	1.0260	—	0.2000	1.0260	Merck & Co.	" "
NaNH <sub>4</sub> HPO <sub>4</sub>	NaNH <sub>4</sub> HPO <sub>4</sub>	0.333	45.70	1.0345	282	0.200	1.0207	" "	" "
Tri-sodium phosphate(?)	Na <sub>3</sub> PO <sub>4</sub> (?)	0.33(?)	54.73	1.06	—	—	—	Prepared in laboratory	" "
Sodium silicate	Na <sub>2</sub> SiO <sub>3</sub>	0.523	64.08	1.0636	663	0.21	1.026	Trommsdorff	Kohlrausch tables <sup>3</sup>
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	1.0000	60.01	1.0073	12	0.2000	1.0004	Merck & Co.	Hulett's titration
Oxalic acid	(COOH) <sub>2</sub>	0.5000	45.00	1.0199	551	0.2000	1.0073	" "	Direct weighing
Succinic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	0.4975	58.71	1.0167	17	0.1990	1.0060	Eimer & Amend	" "
Tartaric acid	C <sub>4</sub> H <sub>6</sub> O <sub>6</sub>	0.9970	149.57	1.0653	87	0.1994	1.0122	Marquart	" "
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	0.9983	209.67	1.0777 <sub>(18°)</sub>	64	0.1997	1.0145	Merck & Co.	" "

<sup>1</sup> Temperature of solutions is 18° except when otherwise indicated.<sup>3</sup> Kohlrausch, Zeit. Phys. Chem. XII., p. 773.<sup>2</sup> Conductivity with reference to mercury at 0° C.

The specific gravity of this approximate solution was then exactly determined as described in former papers. This value is given in Table I., 5. The gram-molecular strength of the solution was easily computed by comparing this value with that given by Kohlrausch for a normal LiCl solution,<sup>1</sup> by means of his specific gravity tables. This gram-molecular strength of the original solution is given under (*m*) in Table I., 3. The diluter solutions whose freezing-points were to be measured were uniformly made by the use of most carefully marked flasks and pipettes. It needs perhaps to be said that these flasks and pipettes were marked for absolute volume when "dry." Careful rinsing insures the complete discharge of their contents into the measuring flasks.

*Calcium Chloride.*—An excess of CaCO<sub>3</sub> in the form of natural crystals of Iceland-spar was treated with dilute HCl, until the effervescence ceased. The whole was then boiled to expel CO<sub>2</sub> and the filtered solution carefully neutralized by addition of a slight quantity of HCl. It was then diluted to approximate normal strength, and finally its exact gram-molecular concentration was calculated as in the case of LiCl.

*Strontium Chloride.*—There happened to be a quantity of finely crystallized strontium chloride already in the laboratory (Trommsdorff, c.p.), which was used without recrystallizing. The gram-molecular strength of the final solution was determined as in the foregoing cases. It will be observed in Table I., 6, that the conductivity of this solution differs not inconsiderably from that given by Kohlrausch.<sup>2</sup> This is undoubtedly due to the fact that I did not recrystallize the salt. This error is, however, too slight to affect the measurements of the freezing-points.

*Tin Chloride (stannic).*—The salt was obtained from Eimer & Amend, and was not recrystallized. The normal solution was prepared by use of Gerlach's tables of specific gravity.<sup>3</sup> The temperatures of these particular tables of Gerlach are  $\frac{15^{\circ}}{15^{\circ}}$ .

The chlorides already studied in my former work are NaCl, KCl, NH<sub>4</sub>Cl, BaCl<sub>2</sub>, MgCl<sub>2</sub>, and HCl.

<sup>1</sup> Kohlrausch, Leitfaden d. Physik, Leipzig, 1892, p. 404.

<sup>2</sup> Kohlrausch, Leitfaden, p. 404.

<sup>3</sup> Hoffmann's Tabellen, Berlin, 1877, p. 130.

Observations on the first four have been extended so as to include solutions of greater concentration as follows:—

NaCl, $m = 0.70$ ,	NH <sub>4</sub> Cl, $m = 0.70$ ,
KCl, $m = 0.70$ ,	BaCl <sub>2</sub> , $m = 0.50$ .

The following tables present the experimental results for the chlorides (Table II.). Column (1) contains the value of  $m$  for the various dilutions. The observed depression of the freezing-point is found in (2), while the molecular depression is found in (3).

In order to compute from the present data the molecular depression on the basis of gram-molecular concentration per 1000 grams of water, as Raoult and others are accustomed to do, one needs to know the specific gravity of the solution. Accordingly, this value is given for the solution near the concentration  $m = 0.20$  in column 7, Table I. The difference between the value of the molecular depression so calculated and that given in the tables, which is based on gram-molecular concentration per liter of the solution, is altogether inappreciable in the more dilute solutions, and reaches its maximum value of 1.5 per cent in the case of tin chloride. I have accordingly omitted these second values of  $\frac{\Delta}{m}$ .

#### *Graphic Representation of Results.*

The values of  $\frac{\Delta}{m}$  as functions of  $m$  are represented in Fig. 2. (See Plate opposite p. 295.)

Ordinates represent values of  $\frac{\Delta}{m}$ , abscissæ, values of  $m$ . The scale here is the same as that adopted in the former papers.

#### *Discussion of the Chlorides.*

1. It will be remembered that a very striking fact is presented in the molecular depressions of the freezing-point by HCl and MgCl<sub>2</sub>, as was indicated in the author's account of observations on these compounds;<sup>1</sup> namely, the fact that the molecular depression for each of these compounds reaches a pronounced minimum at about  $m = 0.10$ . It now appears that *all* the chlorides thus

<sup>1</sup> PHYSICAL REVIEW, III., p. 281.

TABLE II.

## LITHIUM CHLORIDE.

[Values in parentheses obtained by interpolation.]

1 Gram- molecules per liter of solution ( <i>m</i> ).	2 Depression of freezing- point ( $\Delta$ ).	3 Molecular depression of freezing- point $\frac{\Delta}{m}$ .	4 Theoretical value of $\Delta$ .	5 Theoretical value of $\frac{\Delta}{m}$ .	6 Difference $\Delta_{th}-\Delta_{ex}$ .	7 Differ- ence $\Delta_{th}-\Delta_{ex}$ in per cent of $\Delta_{ex}$ .
	deg.		deg.		deg.	
0.0099	0.0363	3.67	0.0358	3.61	-0.0005	-1.4
0.0198	0.0710	3.59	(0.0706)	(3.56 <sub>5</sub> )	0.0004	0.6
0.0496	0.1770	3.57	0.1730	3.48 <sub>7</sub>	0.004	2.3
0.0992	0.3520	3.55	0.3388	3.41 <sub>5</sub>	0.013	3.8
0.1983	0.7018	3.54	(0.6626)	(3.34)	0.039	5.6
0.4959	1.809	3.65	1.581	3.19	0.228	12.5

## CALCIUM CHLORIDE.

0.0100	0.0513	5.13	(0.0510)	(5.10)	-0.0003	-0.5
0.0201	0.1013	5.04	(0.1000)	(5.00)	0.0013	1.3
0.0502	0.2437	4.85	0.238	4.74	0.006	2.5
0.1004	0.4823	4.80	(0.460)	(4.58)	0.022	4.5
0.2008	0.9718	4.84	(0.882)	(4.39)	0.090	9.3
0.5021	2.605	5.19	2.048	4.08	0.557	21.3

## STRONTIUM CHLORIDE.

0.0100	0.0508	5.08(?)	(0.0495)	(4.95)	-0.0013	-2.6
0.0199	0.1015	5.10	(0.0966)	(4.83)	0.0049	4.8
0.0499	0.2445	4.90	0.234	4.68	0.011	4.5
0.0997	0.4834	4.85	(0.452)	(4.53)	0.031	6.4
0.1994	0.9608	4.82	(0.862)	(4.31)	0.099	10.3
0.4986	2.532	5.08	1.989	3.99	0.543	21.5

TIN CHLORIDE (SnCl<sub>4</sub>).

0.01	0.1261	12.61	No data	from which be calculated.	these values may	
0.02	0.2487	12.44				
0.05	0.5973	11.95				
0.10	1.1457	11.46				
0.20	1.968	9.84				

TABLE II. (*continued*).

Compound.	$m$	$\Delta$	$\frac{\Delta}{m}$	Compound.	$m$	$\Delta$	$\frac{\Delta}{m}$
NaCl . . . . .	0.70	deg. 2.399	3.43	NH <sub>4</sub> Cl . . .	0.70	deg. 2.384	3.41
KCl . . . . .	0.70	2.346	3.35	BaCl <sub>2</sub> . . . .	0.50	2.412	4.83

far examined, tin chloride excepted, manifest this same minimum, though in the case of NH<sub>4</sub>Cl, NaCl, and KCl it is much less pronounced. To obtain a general survey of this fact, the curves of molecular depression for the various chlorides have been collected in Fig. 1, where the scale of values for  $m$  (abscissæ) has been decreased to one-half its value elsewhere in the plate in order to include the solutions of greater concentration. It is to be remarked that Arrhenius' observations on these chlorides quite generally exhibit this minimum value. Since these early observations lay no claim to a degree of exactness attained in the later methods, it is the more surprising that they so plainly reveal the existence of these minimum values which characterize the chlorides. Although Arrhenius called no attention to them, and evidently believed they were due to experimental errors, it is still difficult to understand why subsequent observers with more precise methods should have failed to find them. The existence of this minimum value in the case of the binary chlorides may be easily demonstrated with no other apparatus than an ordinary  $\frac{1}{10}^{\circ}$  thermometer and beaker glass.

2. The former division of the compounds into two groups, one containing univalent radicals, as LiCl, the other containing bivalent radicals, as CaCl<sub>2</sub>, is confirmed by the new results here presented.

The characteristics of these two groups, as found in the former work, remain unaffected by the addition of this new material.

3. There is no evidence in any of the chlorides, or any other of the compounds examined, of any "kinks" in the curves of molecular depressions, save in the region of extreme dilution,

where they are so small as to be best explained by experimental errors.

It may be safely said, now that I have examined some thirty-five characteristic compounds, that the existence of definite "Hydrates" at particular concentrations is not indicated by the changes in the freezing-point which attend changes in the dilution of the solution.

*Bearing of these Results on the Dissociation Theory.*

In the table of results for the chlorides, and in the subsequent tables for other compounds, are found the theoretical values of the depressions of the freezing-point, and the theoretical values of the molecular depressions, respectively. These values are based on Kohlrausch's value for  $\frac{\mu_x}{\mu_\infty}$ . In column (6) is found the difference between the theoretical and observed value of the depressions, while in (7) this difference is expressed in per cents of the total observed value. It thus appears that the observed values are higher than the theoretical. The differences, however, in the region of extreme dilution in the cases of LiCl and CaCl<sub>2</sub> are surprisingly small. In case of SrCl<sub>2</sub> the difference is very great, the observed depression being 0°.0013 C. higher than the theoretical value, and the observed value is certainly too low, judging from the curve of the molecular depressions as exhibited in Figs. 1 and 2.

It needs to be remarked that the molecular depressions calculated on the basis of the dissociation theory show no minimum value. This accounts for the enormous departure of the observed from the theoretical value in the region of greater concentration.

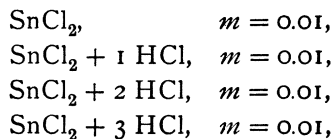
The case of tin chloride needs separate discussion.

First, it is to be observed that the depressions are much more than twice as large as those produced by any other chloride in the same concentration. While it is impossible to compute the theoretical value of the depression on the basis of the dissociation theory, since measurements on the conductivity of these solutions are wanting, it is, however, a striking fact that if it be *assumed* that the salt at the concentration  $m = 0.01$  be *completely* dissociated, and that each molecule splits up into the maximum number of



five parts, Sn-Cl-Cl-Cl-Cl, we would then have for the molecular depression only  $5 \times 1.89$  or 9.45, while the observed value is 12.61. Obviously the depression is not to be explained in this way. It however suggests itself that the  $\text{SnCl}_4$  does not exist at all in aqueous solutions, but that it assumes at once the properties of a mixture of  $\text{SnCl}_2$  and 2 HCl, in solution. No value for the depression of the freezing-point by  $\text{SnCl}_2$  has been found; but assuming that it is about that of  $\text{CdCl}_2$  and  $\text{ZnCl}_2$ , as observed by Jones, *i.e.* 5.20, and taking the observed value for HCl, *i.e.* 3.61, we have for the depression due to  $\text{SnCl}_4$ ,  $5.20 + 2(3.61)$ , or 12.42. This is very nearly the observed value. It should be said that many vain attempts were made to prepare solutions of  $\text{SnCl}_4$ , sufficiently free from  $\text{SnCl}_2$ , to enable the freezing-points to be measured.

The purpose was to measure the depressions in a solution of  $\text{SnCl}_2$  at  $m = 0.01$ , and then add in succession a  $\frac{1}{100}$  gram-molecule of HCl. Thus measurements would be made on



as was done in the cases of the phosphates, p. 288. This would have decided experimentally whether the suggestion just made in regard to the nature of  $\text{SnCl}_4$  in solution is tenable. I hope to return to this difficulty in the near future. It may be well to call attention here to the great importance of exact measurements of the electrical conductivity of this salt, together with that of the various phosphates and the dilute solutions of  $\text{MgCl}_2$  and  $\text{NH}_4\text{NO}_3$  for the purpose of obtaining experimental values for the "degree of dissociation,"  $\frac{\mu_z}{\mu_\infty}$ .

*The Sodium and Potassium Hydroxides, Nitric Acid, and Sodium Silicate.*

The materials used in the first three cases were those prepared in a high degree of purity for the purpose of determining their specific gravity and electrical conductivity.<sup>1</sup> The great care taken

<sup>1</sup> Loomis, PHYSICAL REVIEW, IV., 1896, p. 252.

TABLE III.  
POTASSIUM HYDROXIDE.

[Values in parentheses obtained by interpolation.]

1 <i>m</i>	2 $\Delta$	3 $\frac{\Delta}{m}$	4 $\frac{\Delta}{m}$ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 $\Delta_{th}-\Delta_{exp}$	7 $\frac{\Delta_{th}-\Delta_{exp}}{\Delta_{exp}}$ in per cents
	deg.		deg.		deg.	
0.0100	0.0343	3.43	0.0371	3.71	+0.0028	+ 8.1
0.0200	0.0689	3.45	(0.0738)	(3.69)	0.0049	7.1
0.0500	0.1719	3.44	0.1825	3.65	0.0106	6.1
0.1000	0.3426	3.43	0.360	3.60	0.017	5.0
0.2000	0.6860	3.43	(0.714)	(3.57)	0.028	4.1

SODIUM HYDROXIDE.

0.0100	0.0328	3.28(?)	0.0366	3.66	+0.0038	+11.6
0.0200	0.0691	3.46	(0.0724)	(3.62)	0.0033	4.7
0.0500	0.1727	3.45	0.1765	3.53	0.0038	2.2
0.1000	0.3414	3.41	0.350	3.50	0.0039	1.1
0.2000	0.6814	3.41	(0.696)	(3.48)	0.0015	0.2

NITRIC ACID.

0.0100	0.0350	3.50	0.0373	3.73	+0.0023	+ 6.6
0.0200	0.0712	3.56	—	—	—	—
0.0300	0.1059	3.53	0.1107	3.69	0.0048	4.5
0.0500	0.1754	3.51	0.1835	3.67	0.0081	4.6
0.1000	0.3496	3.50	0.363	3.63	0.013	3.7
0.2000	0.6959	3.48	(0.720)	(3.60)	0.020	2.8

SODIUM SILICATE.

0.0105	0.0676	6.46				
0.0209	0.1339	6.41				
0.0523	0.3068	5.87				
0.1046	0.5533	5.29				
0.2092	0.9785	4.68				
0.5230	2.087	3.99				

No experimental data.

to purify these materials was wholly unnecessary so far as the determination of their freezing-points was concerned, but as the material was at hand it was made use of for the present purpose.

The sodium silicate,  $\text{Na}_2\text{SiO}_3$ , was Trommsdorff's c.p. salt and was not recrystallized. It yielded a perfectly clear solution without filtering. It was reduced to normal solution by using Kohlrausch's values of specific gravity.<sup>1</sup>

The graphic representation of these results is found in Fig. 1. It is to be observed that the molecular depression for KOH, NaOH, and  $\text{HNO}_3$ , as exhibited in column (3), varies very little with the concentration, as has been found also to be the case with HCl. It is to be noted that the values for  $m = 0.01$  in each instance are evidently too low and indicate experimental errors which reach, at least in the case of nitric acid,  $0^\circ.0006$ .

The value for NaOH,  $m = 0.01$ , I am unable to explain. The measurements were twice repeated, making in all thirteen entirely distinct observations on this solution. The average of all was  $0^\circ.0325$ . The value here given,  $0^\circ.0328$ , belongs to the same series to which the other measurements belong, and for this reason was taken. The error, I think, cannot be referred to possible errors of observation. It seems to be connected in some way with the solution. It is also difficult to believe that the conversion of the NaOH and KOH into the carbonates by the  $\text{CO}_2$  of the air would be sufficient to account for the marked irregularity and for the seemingly low values throughout this region of greater dilution. The present method permits no experimental answer to this question.

*Sodium Silicate.*—The molecular depressions are very great, and the rate of decrease with increase in concentration, as in the case of  $\text{SnCl}_4$ , is enormous. Thus, while it is 6.46 at  $m = 0.0105$ , it has fallen to 3.99 at  $m = 0.523$ . It is not without interest to note that the *complete* dissociation of this salt in the solution  $m = 0.0105$ , provided each molecule splits into three parts after the analogy of  $\text{Na}_2\text{SO}_4$ , would still require the theoretical value to be only  $3 \times 1.89$ , or 5.67, which is much less than the observed value.

It seems probable that, as in the case of  $\text{SnCl}_4$ , the aqueous

<sup>1</sup> Kohlrausch, Zeit. Phys. Chem. XII., 1893, p. 774.

solution of  $\text{Na}_2\text{SiO}_3$  has the properties of a mixture of  $\text{NaOH}$  and  $\text{SiO}_2$  where the presence of the  $\text{SiO}_2$  seems to lessen the degree of dissociation of the  $\text{NaOH}$ . The results of Kohlrausch's observations on the electrical conductivity seem to point to the same conclusion.

This point should receive a more careful study than I have thus far been able to give to it.

*The Phosphates.*

TABLE IV.

$\text{KH}_2\text{PO}_4$ .			$\text{Na}_2\text{HPO}_4$ .		
1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$	1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$
	deg.			deg.	
0.01	0.0358	3.58	0.01	0.0499	4.99
0.02	0.0720	3.60	0.02	0.0969	4.85
0.05	0.1740	3.48	0.05	0.2304	4.61
0.10	0.3365	3.37	0.10	0.4345	4.35
0.20	0.6434	3.22	0.20	Beyond limit of solubility at 0° C.	

$\text{Na}(\text{NH}_4)\text{HPO}_4$ .			$\text{Na}_3\text{PO}_4(?)$ .		
1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$	1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$
0.01	0.0495	4.95	0.01	0.0715	7.15
0.02	0.0956	4.78	0.02	0.1369	6.85
0.05	0.2260	4.52	0.05	0.3048	6.10
0.10	0.4242	4.24	0.10	0.5661	5.66
0.20	0.7817	3.91	0.20	Not observed.	

*Preparation of Solutions.*

The  $\text{KH}_2\text{PO}_4$  (Eimer & Amend, c.p.) was carefully recrystallized, and after continued drying at 100° C. the necessary amount was weighed and made into a normal solution ( $m = \frac{1}{2}$ ). Mr. Sill of the Princeton Chemical Laboratory found by the determination of the salt as  $\text{Mg}_2\text{P}_2\text{O}_7$  that there were 45.06 g. of  $\text{KH}_2\text{PO}_4$  per liter of the solution instead of 45.38 g.; thus the solution was apparently 0.7 per cent too weak. As this difference could be due to impurity of the salt as well as to the failure to completely

dry the salt, I have not ventured to make any correction, and the results must be looked upon as affected with an error of 0.7 per cent.

The  $\text{Na}_2\text{HPO}_4$  (Merck & Co., c.p.) was carefully recrystallized, and after heating at  $120^\circ \text{C.}$ , until the weight became constant, the necessary amount was reduced to a normal solution by direct weighing. Mr. Sill's analysis showed that a liter of the solution,  $m = 0.20$ , contained 28.45 g. instead of 28.42 g. The solution was thus apparently 0.1 per cent too strong. This error is less than the probable error of the analysis, and the  $\text{Na}_2\text{HPO}_4$  solutions may be looked upon as exact.

The  $\text{NaNH}_4\text{HPO}_4$  (Merck & Co., c.p.) was recrystallized. It was dried with filter paper and finally in the air at a temperature a little above room-temperature.

Mr. Sill's analysis of the final solution,  $m = \frac{1}{3}$ , showed that it contained per liter 45.45 g. instead of 45.70 g., which is required for the solution,  $m = \frac{1}{3}$ . It was thus 0.55 per cent too weak. For the same reason as that given in the case of  $\text{KH}_2\text{PO}_4$ , no correction was applied to the results, though it is likely that the error here is wholly due to lack of complete drying of the salt.

The  $\text{Na}_3\text{PO}_4$  was prepared in the laboratory by making a solution of molecular equivalents of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$ , taking care that an excess of  $\text{NaOH}$  was present. The solution was then evaporated to the point of crystallization. The abundant crop of crystals was then dissolved in one-half its weight of boiling water and left to recrystallize. The crystals thus prepared are small hexagonal prisms with jagged ends. These crystals were then dried at  $120^\circ \text{C.}$  to constant weight. The resultant compound should be  $\text{Na}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ . The analysis of many solutions prepared on the basis of this formula for the dried salt and  $\text{Na}_3\text{PO}_4 + 12\text{H}_2\text{O}$  for the crystals themselves gave me no confidence that the solutions could be looked upon as having more than a rough approximation to their supposed strength. Mr. Hulett made a very careful series of analyses of the crystals and found a very wide departure from the formula,  $\text{Na}_3\text{PO}_4 + 12\text{H}_2\text{O}$ . Time did not permit a final solution of the difficulty. The matter deserves a thorough study from the chemical side.

*Discussion of Results for the Phosphates.*

The depressions of the freezing-point, caused by phosphoric acid,  $\text{H}_3\text{PO}_4$ , are much less than those caused by the groups of compounds containing univalent and bivalent radicals, and this is the more surprising since phosphoric acid contains a trivalent radical.

For the purpose of examining into this matter more closely, I undertook to measure the freezing-points of the present series of phosphates.

1. The first fact which appears from the results is that the phosphates are entirely unlike the phosphoric acid and differ still more among themselves.

2. In proportion as the hydrogen of phosphoric acid is replaced by a univalent metallic radical, the depression of the freezing-point is increased. See curves for  $\text{H}_3\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_3\text{PO}_4$ . (Fig. 2.)

3. If we assume that in the case of  $\text{H}_3\text{PO}_4$  the molecule splits up into H and  $\text{HPO}_4$ , we may calculate the freezing-points on the basis of the dissociation theory.

The theoretical values so obtained are given in column (4), while in (2) are found the observed values taken from former measurements. The agreement here exhibited makes our assumption fairly probable that in the process of dissociation only a single atom of hydrogen is "split off."

TABLE V.

 $\text{H}_3\text{PO}_4$ .

1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$	4 $\Delta_{th}$	5 $\Delta_{th} - \Delta_{exp}$
	deg.		deg.	
0.01	0.0282	2.82	0.0296	+0.0014
0.02	0.0536	2.68	0.0552	0.0016
0.05	0.1245	2.49	0.1275	0.0030
0.10	0.2358	2.36	0.2400	0.0040
0.20	0.4498	2.25	0.4580	0.0082

It is to be remarked further that the degree of dissociation is much smaller than in the case of any inorganic compound so far examined, being only 56 per cent in the solution  $m = 0.01$ . Kohlrausch value for  $\mu_{\infty}$  is assumed (110).

4. Passing now to the  $\text{KH}_2\text{PO}_4$ , where we have one H atom replaced by K, we find that the depressions produced belong to the group, KCl, NaCl, etc., and it at once suggests itself that with this salt as with all members of this group the molecule splits into two parts, in this case K and  $\text{H}_2\text{PO}_4$ , and that the degree of dissociation is about the same as for other potassium salts of the group.

Unfortunately, no measurements on the conductivity of  $\text{KH}_2\text{PO}_4$  in extreme dilution have been made, so far as is known to the writer.

5. The replacement of a second atom of hydrogen by a metallic atom, as for example in the case of the two phosphates,  $\text{Na}_2\text{HPO}_4$  and  $\text{NaNH}_4\text{HPO}_4$ , at once brings us into the second group, *i.e.* into the group of electrolytes which contain bivalent radicals, as  $\text{K}_2\text{SO}_4$ ,  $\text{BaCl}_2$ , etc.

In this group the dissociation of the molecule is said to be into three parts, and the degree of this dissociation is on the average about 80 per cent in the solutions  $m = 0.01$ . Assuming the dissociation to be into three parts, namely,  $\text{Na-Na-HPO}_4$ , we are able to compute from the present data the degree of dissociation by the formula  $\frac{\Delta}{m} = 1.89 (1 + 2\delta)$ , in which  $\delta$  is the degree of dissociation. In this particular case,  $\text{Na}_2\text{HPO}_4$ , the value of  $\delta$  is accordingly

$$\frac{0.0499}{0.01} = 1.89 (1 + 2\delta), \text{ or } \delta = 0.82.$$

For  $\text{Na}_2\text{HPO}_4$  the degree of dissociation in the solution  $m = 0.01$  is thus 82 per cent. Values for the electrical conductivity of this salt in solution are not yet known, and hence it is not possible to verify this result at present.

Replacing now the *third* H atom with Na, we have  $\text{Na}_3\text{PO}_4$ , and the observed depression for the solution  $m = 0.01$  becomes  $0.0715$ . To account for this very great depression, the disso-

ciation theory requires that the salt be dissociated 93 per cent, each dissociated molecule yielding four parts. Here, however, as in the other cases, no electrical conductivity measurements have as yet been made.

For the sake of inquiring as closely as possible into the interesting matter presented by these phosphates, observations were made on the freezing-points of various mixtures of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$  solutions. The results are given at the end of the following table. The results for  $\text{H}_3\text{PO}_4$  and the other phosphates under discussion are also found in the same table. The coefficients indicate the number of  $\frac{1}{100}$  gram-molecules of the respective constituents in the solutions.

1	2 Depressions.	3 Successive differences.	1	2 Depressions.	3 Successive differences.
	deg.			deg.	
1 $\text{H}_3\text{PO}_4$	0.0282		1 $\text{Na}_2\text{HPO}_4 +$	0.0995	0.0289
1 $\text{KH}_2\text{PO}_4$	0.0358	0.0076	2 $\text{NaOH}$		
1 $\text{Na}_2\text{HPO}_4$	0.0499	0.0141	1 $\text{Na}_2\text{HPO}_4 +$	0.1279	0.0284
1 $\text{Na}_3\text{PO}_4$	0.0715	0.0216	3 $\text{NaOH}$		
1 $\text{Na}_2\text{HPO}_4 +$	0.0706	—			
1 $\text{NaOH}$					

The successive differences which the series presents is not without interest. Assuming that in place of the salt  $\text{KH}_2\text{PO}_4$  we had  $\text{NaH}_2\text{PO}_4$ , and that the depression due to the sodium salt is sensibly the same as that of the potassium salt,<sup>1</sup> then we observe (see table) that the addition of the first atom of Na increases the depression by  $0^\circ.0076$ , the second by  $0^\circ.0141$ , the third by  $0^\circ.0216$ . We have now reached the compound  $\text{Na}_3\text{PO}_4$ , to which the 1  $\text{NaH}_2\text{PO}_4 + 1 \text{NaOH}$  is seen to be equivalent, at least, so far as the limits of accuracy of the latter solution require.

The further addition of 1  $\text{NaOH}$ , as in the solution, 1  $\text{Na}_2\text{HPO}_4 + 2 \text{NaOH}$ , which may be looked upon as equivalent to 1  $\text{Na}_3\text{PO}_4 + 1 \text{NaOH}$ , increases the depression by  $0^\circ.0289$ . Thus far the

<sup>1</sup> My attempts to prepare solutions of  $\text{NaH}_2\text{PO}_4$ , which could be found by analysis to be sufficiently accurate, have thus far failed. All analogy, however, seems to allow the assumption which is made above.



successive differences appear, on the average, to be successive multiples of  $0^{\circ}.0073$ . The further addition of 1 NaOH, as appears in  $1 \text{ Na}_2\text{HPO}_4 + 3 \text{ NaOH}$ , which is equivalent to  $\text{Na}_3\text{PO}_4 + 2 \text{ NaOH}$ , is attended by about the same increase as that caused by the addition of the preceding molecule of NaOH, *i.e.*  $0^{\circ}.0284$ . Thus it would seem probable that the relation of the sodium atom to the rest of the molecule in the series of compounds examined is less and less close as the number of sodium atoms increases, and this fact may be sufficient ground on which to account for the progressive alkaline properties of this series of salts. I regret that these relations did not present themselves until the work was in preparation for publication (May-June), and thus no farther observations could be made. I wish again to emphasize that the results for  $\text{Na}_3\text{PO}_4$  are certainly affected by a very large error, perhaps amounting to 7 per cent. I have no means, at present, of knowing in which direction this error lies. My only apology for presenting the results is the fact that even so large an error as this, either + or -, would not affect the essential nature of the interesting relations which the present study of the phosphates has brought to light. The examination of this question from the standpoint of electrical conductivity is desirable, since it appears that the dissociation theory would here encounter some very decisive tests.

*The Organic Acids. (Acetic, Oxalic, Succinic, Tartaric, and Citric.)*

*The Preparation of the Solutions.* — The acetic acid was reduced to normal strength by titration with the standards used in the preparation of the solutions previously described.<sup>1</sup> The preparation of the oxalic acid is described in the same connection. The succinic, tartaric, and citric acids were obtained from the makers in as high a degree of purity as they furnish them, and after drying as thoroughly in each case as their nature would permit, they were reduced to solutions of desired strength by direct weighing. They were then each titrated and corrected in accordance with the result of the titration, on the assumption that their having less than the supposed strength was due to the difficulty of

<sup>1</sup> Loomis, PHYSICAL REVIEW, IV., 1896, p. 252.

completely drying them. The corrections are relatively very small, even in the case of succinic acid, where they amount to 0.5 per cent.

The results are given below in tabular form, and graphically, near the bottom of Fig. 2.

TABLE VI.  
ACETIC ACID,  $C_2H_4O_2$ .  
 $\mu_x = 364$ .

1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$	4 $\frac{\Delta}{m}$ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 $\Delta_{th}-\Delta_{exp}$	7 $\frac{\Delta_{th}-\Delta_{exp}}{\Delta_{exp}}$ in per cents of $\Delta_{exp}$ .
	deg.		deg.		deg.	
0.0100	0.0196	1.96	0.0196	1.96	+0.0000	+0.0
0.0200	0.0375	1.88	(0.0388)	(1.94)	0.0013	3.5
0.0300	0.0559	1.86	0.0579	1.93	0.0020	3.6
0.0500	0.0928	1.86	0.0960	1.92	0.0032	3.4
0.1000	0.1855	1.86	0.191	1.91	0.0055	3.0
0.2000	0.373?	1.87	0.382	1.91	0.0090	2.4
0.3000	0.5629	1.88	—	—	—	—
0.5000	0.9378	1.88	—	—	—	—
1.0000	1.886	1.89	1.90	1.90	0.01	0.5

OXALIC ACID,  $(COOH)_2$ .  
 $\mu_x = 363(?)$ .

0.0100	0.0328	3.28	(0.0351)	(3.51)	+0.0023	+7.0
0.0200	0.0640	3.20	(0.0676)	(3.38)	0.0036	5.6
0.0500	0.1519	3.04	—	—	—	—
0.1000	0.2848	2.85	—	—	—	—
0.2000	0.5329	2.66	—	—	—	—

SUCCINIC ACID,  $C_4H_6O_4$ .  
 $\mu_x = 356$ .

0.0100	0.0202	2.02	0.0204	2.04	+0.0002	+1.0
0.0199	0.0391	1.96	0.0398	2.00	0.0007	1.8
0.0498	0.0965	1.94	0.0976	1.96	0.0011	1.1
0.0995	0.1876	1.89	—	—	—	—
0.1990	0.3751	1.89	—	—	—	—

TABLE VI. (*continued*).TARTARIC ACID,  $C_4H_6O_6$ . $\mu_\infty = 356$ 

1 $m$	2 $\Delta$	3 $\frac{\Delta}{m}$	4 $\Delta$ theoretical.	5 $\frac{\Delta}{m}$ theoretical.	6 $\Delta_{th}-\Delta_{exp}$	7 $\frac{\Delta_{th}-\Delta_{exp}}{\Delta_{exp}}$ in per cents
	deg.		deg.		deg.	
0.0100	0.0234	2.34	(0.0239)	(2.39)	+0.0005	+2.1
0.0200	0.0435	2.18	(0.0454)	(2.27)	0.0019	4.4
0.0499	0.1042	2.09	(0.1070)	(2.14)	0.0028	2.7
0.0997	0.2018	2.02	—	—	—	—
0.1994	0.3993	2.00	—	—	—	—
CITRIC ACID, $C_6H_8O_7$ .						
0.0100	0.0226	2.26				
0.0200	0.0424	2.12				
0.0499	0.1029	2.06			No data.	
0.0998	0.1999	2.00				
0.1997	0.3978	1.99				

In computing the theoretical values for the depressions, the Kohlrausch values for electrical conductivity are used in the case of acetic acid. In other cases the Ostwald<sup>1</sup> measurements are used. In all cases Ostwald's value for  $\mu_\infty$  was assumed as the most probable. This value is given at the top of the separate tables. No electrical measurements, so far as is known to me, have been made on citric acid. It should be said, perhaps, that the particular acids examined were chosen for the sole reason that they may be had in a high state of purity and are easily made into solutions of exact molecular strength.

This series of organic acids is chiefly interesting on account of the relation which is presented by them between the observed depressions and those required by the dissociation theory.

It appears that in the case of acetic, succinic, and tartaric acids, the agreement between the observed and the theoretical values for extreme dilution is so nearly exact that, barring experimental errors, it may be regarded as complete. Further, these theoretical values of the depressions indicate that the Ostwald values for  $\mu_\infty$  are

<sup>1</sup> Ostwald, *Zeit. Phys. Chem.*, III., 1889, pp. 174, 281, 371.

very probable, although in the case of acetic acid the experimental values for the electrical conductivity as found by Kohlrausch would not perhaps warrant the assumption of so high a value.

The exception presented by oxalic acid is not to be overlooked. This acid presents difficulties in other directions, as well as in the present instance, and it may happen that fuller knowledge of its nature may be able to reconcile the "theoretical" with the observed depressions of the freezing-point.

*The Constancy of the Thermometer.*

In conclusion I wish to submit the entire series of observations on the zero point of the  $\frac{1}{100}^{\circ}$  thermometer, which were made during the period of the present measurements.

This thermometer has been in use four years. It has been kept at room-temperature except during the period of the measurements, when it is kept constantly within the limits,  $-3^{\circ}$  and  $+1^{\circ}$  C.

In the following table the observed zero points are given in (4), and the values when corrected to 760 mm., and a room-temperature  $0^{\circ}$  C. are given in (5).

1 1896.	2 Barometer.	3 Room- temperature.	4 Observed zero point.	5 Zero point corrected.
		deg.	deg.	deg.
Jan. 6	769.9 mm.	0 C.	0.0438	0.0422
7	766.6	0	0.0439	0.0428
20	763.3	5	0.0468	0.0439
22	762.0	6	0.0469	0.0438
29	765.6	6	0.0475	0.0438
Feb. 3	754.6	5	0.0457	0.0442
10	753.1	5	0.0458	0.0447
13	754.4	5	0.0460	0.0446
17	770.1	0	0.0451	0.0433
19	749.3	5	0.0454	0.0449
22	766.1	2	0.0456	0.0437
26	750.3	2	0.0440	0.0447
Mar. 3	751.6	3	0.0447	0.0447
4	753.1	3	0.0447	0.0445
5	753.9	5	0.0465	0.0452
11	749.1	4	0.0450	0.0449
12	747.8	4	0.0449	0.0452
16	756.2	4	0.0458	0.0445
17	756.4	5	0.0466	0.0449

The results are graphically represented in Fig. 3. Ordinates represent thermometer readings, abscissæ time of observations.

The scale is so chosen that the observed changes in the thermometer readings are magnified 125-fold. In order to facilitate comparison between the observed course of the zero point and what it would have been in case it had made a strictly uniform rise of  $0^{\circ}.0022$  during the period, a straight line has been drawn from  $0^{\circ}.0428$  to  $0^{\circ}.0450$ . We observe, first, that the initial reading is  $0^{\circ}.0422$ . The last reading of the preceding winter was  $0^{\circ}.0417$ .

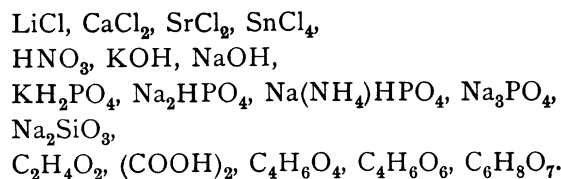
It thus appears that during the nine months of rest the zero of the thermometer remained constant. The total rise during the present period is about  $0^{\circ}.002$  C. ; during the preceding winter it was a little more than  $0^{\circ}.002$  C. Further, it is noticeable that the course of the observed zero point is much less of a "zig-zag" than in former periods of use. This, I think, is due to a reduction of the experimental error of the method and to a greater constancy of the thermometer itself, due to its age and continued use.

The sharp changes between Feb. 13 and Feb. 22 must, I think, be referred to the thermometer itself and not to experimental errors, since the series of depressions which were measured on these particular days indicate no corresponding errors. The  $\text{HNO}_3$  series was measured on Feb. 19, when the zero point seems to be too high. While this particular series of observations show unusually large experimental errors, these errors seem to suggest that the zero point was too low rather than too high. The other zero points in this period of marked variation of the thermometer were made in connection with solutions which are not yet ready for publication, which, however, show no cause for assuming that the zero points were erroneously determined. This matter will be noticed fully at the proper time.

#### *Summary of Results.*

1. The method developed in 1893 has been used, with no change whatever (except an enlargement of the "freezing-tube"), to de-

termine the depression of the freezing-point for the following solutions:—



2. It has been found that the average variation in a series of five entirely independent determinations of the freezing-point of a solution is now  $0^\circ.0005$ , or about half its former value. This indicates a reduction of the experimental errors, and this indication is confirmed by the greater regularity of the results in the region of extreme dilution. It is thought that this decrease in the experimental error is due wholly to a greater constancy of the room-temperature.

3. The observations on the four chlorides of the present series, together with additional observations on the five chlorides previously studied, establish the fact that the *molecular depression of the freezing-point for all chlorides reaches a minimum value*. This depression is very pronounced for the binary chlorides. See Fig. 1.

$\text{SnCl}_4$  yields such enormous depressions that the measurements could not be carried far enough to establish any conclusion in this regard. There is no reason, however, for believing that this chloride would not also reveal a minimum in the molecular depression if the measurements had been extended into the region of greater concentration.

4. Tin chloride in extreme dilution produces a molecular depression of 12.61. This is more than five times the van't Hoff constant (1.89). The hypothesis of Arrhenius fails thus to explain the depression, since the greatest possible number of "active molecules" which a molecule of  $\text{SnCl}_4$  could yield would be *five*, and so the maximum molecular depression which this salt could produce would be  $5 \times 1.89$ , or 9.45. The observed molecular depression, however, is 12.61, at  $m = 0.01$ . It may be suggested that  $\text{SnCl}_4$  in solution possesses the properties of a mixture

of  $\text{SnCl}_2$  and  $2\text{HCl}$ . If this be so, the molecular depression would be about 12.42. This is not far from the observed result. The strong acid reaction of solutions of  $\text{SnCl}_4$  favors the suggestion.

5. The study of the phosphates makes it probable that  $\text{H}_3\text{PO}_4$  in aqueous solution is dissociated simply into two parts, —  $\text{H}$  and  $\text{H}_2\text{PO}_4$ .

This appears from the fact that its salt,  $\text{KH}_2\text{PO}_4$ , gives a depression which belongs to the first group, namely, to the class of electrolytes which yield two parts in the process of dissociation ( $\text{NaCl}$ ,  $\text{KCl}$ , etc.). Thus the *salt* probably splits into  $\text{K}$  and  $\text{H}_2\text{PO}_4$ , and this points to the conclusion that the acid behaves similarly.

Further, it appears that the successive introduction of a univalent metallic radical into a salt of phosphoric acid increases the depression by a constant amount for each radical so added. This would be explained on the basis of the dissociation theory by saying that the introduction of each metallic radical increases by one the number of parts into which the molecule is dissociated, and causes no essential change in the *degree* of dissociation.

Thus in  $\text{KH}_2\text{PO}_4$  there are two parts,  $\text{K}$  and  $\text{H}_2\text{PO}_4$ ,

in  $\text{Na}_2\text{HPO}_4$  there are three parts,  $\text{Na-Na-HPO}_4$ ,

in  $\text{Na}_3\text{PO}_4$  there are four parts,  $\text{Na-Na-Na-PO}_4$ .

6. Sodium silicate,  $\text{Na}_2\text{SiO}_3$ , presents the same difficulty as  $\text{SnCl}_4$ , *i.e.* the depression is much greater than the simple hypothesis of Arrhenius can account for.

7. The organic acids — acetic, oxalic, succinic, tartaric, and citric — exhibit the characteristics of the electrolytes, and not those of the non-electrolytes. The only exception is acetic acid, which in the more concentrated solutions behaves exactly like the non-electrolytes; namely, beyond  $m = 0.10$ , the molecular depression *increases uniformly* with the concentration.

8. A comparison of the experimental results with those required by the hypothesis of van't Hoff and Arrhenius shows that in the case of  $\text{LiCl}$  and  $\text{CaCl}_2$  the agreement is practically complete. A most striking agreement is also presented by acetic, tartaric, and succinic acids.

The agreement is fairly good in the case of  $\text{SrCl}_2$ .

On the contrary  $\text{HNO}_3$ ,  $\text{KOH}$ , and  $\text{NaOH}$  deviate very widely from the "theory." The differences between the observed values and those required by the hypothesis of Arrhenius are 8-11 per cent for the most dilute solutions. The fact that these differences become very small in the region of greatest concentration suggests the existence of some unknown source of error peculiar to the solutions.

In the remaining cases,  $\text{SnCl}_4$ , citric acid, and the salts of phosphoric acid, no measurement of the electrical resistances have been made, and thus no data are at hand for computing the theoretical values of the depressions.

These measurements are much needed, together with those for the extremely dilute solutions of  $\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$ .

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