free energy of solution at molal-ion concentration, that is, the change in free energy in passing from solid salt to ions of hypothetical molal concentration,

$$NaCl(s) = Na^+ + Cl^-; \quad \Delta F^\circ_{298} = -1917.$$

Substituting this value in Equation 9 and solving for n we get as the actual concentration at molal-ion concentration

$$n = 1.64.$$

For potassium chloride we have the values

n.	t.
4.80	15.57
1.0	3.23
0.1	0.345[1]

This gives us for the free energies of solution:

$$\Delta F_{298} \text{ sat. to } 1.0 M = -1550$$
$$\Delta F_{298}\ 1.0\ M \text{ to } 0.1\ M = -2410$$
$$\Delta F_{298} \text{ sat. to } 0.1\ M = -3960$$

Hence for the free energy of solution at molal-ion concentration

$$KCl(s) = K^+ + Cl^-; \ \Delta F^\circ_{298} = -936$$
$$n \text{ (molal-ion concentration)} = 1.85.$$

This work was done under the direction of Major G. N. Lewis, to whom the writer wishes to acknowledge his indebtedness. It is because of Major Lewis' absence with the American Expeditionary Force in France that this paper has not been written in collaboration with him.

Summary.

1. Recent improvements in the method of determining freezing-point depression have been utilized in measuring the freezing points of concentrated solutions and the data for a number of salts have been obtained.

2. The thermodynamic equations necessary for the calculation of free energy of solution are given and their application illustrated by a calculation of the free energies of solution of sodium and potassium chlorides.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA.]

THE TITRATION OF OXALIC ACID BY THE CONDUCTANCE METHOD.

BY HERBERT S. HARNED AND CLINTON N. LAIRD.

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Introduction.

Kuster, Gruters and Geibel[2] have shown that acids can be accurately titrated with sodium or barium hydroxides by means of the conductance

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[1] L. H. Adams, *Loc. cit.*

[2] *Z. anorg. Chem.*, **35**, 455 (1903); **42**, 225 (1904).

method.[1] It is very interesting to note that a strong acid can be titrated by this method in the presence of a much weaker acid by using a standardized sodium hydroxide solution. A solution containing equimolecular quantities of hydrochloric and acetic acids may be taken as an example. The titration of this solution by a sodium hydroxide solution can be most readily seen by plotting the conductance against cc. of sodium hydroxide solution added (Fig. 1). The conductance of the solution before adding the base will be high owing to the high degree of dissociation of hydrochloric acid and the high mobility of the hydrogen ion. Since the relative strength of hydrochloric acid is so much greater than that of acetic acid, the addition of a sodium hydroxide solution will neutralize the hydrochloric acid almost completely before the acetic acid will be affected.[2] Along *ab* (Fig. 1) the conductance will fall, due to the replacing of the very fast hydrogen ion by the very much slower sodium ion. The number of hydrogen ions removed will nearly equal the number of sodium ions produced, because the degrees of dissociation of sodium chloride and hydrochloric acid are approximately the same. When all the hydrochloric acid has been neutralized, the further addition of sodium hydroxide will result in the formation of highly dissociated sodium acetate. Along *bc* the conductance rises because a very large number of sodium and acetate ions are substituted for the relatively few hydrogen and acetate ions produced from the acetic acid present. After the acetic acid has been completely neutralized, the further addition of sodium hydroxide will cause a more rapid increase in conductance than before, because of the addition of a large excess of the highly mobile hydroxyl ions. The larger change, however, in the direction of the conductance plots comes at the point where the hydrochloric acid is neutralized. Determinations of hydrochloric acid in the presence of acetic acid give excellent results.

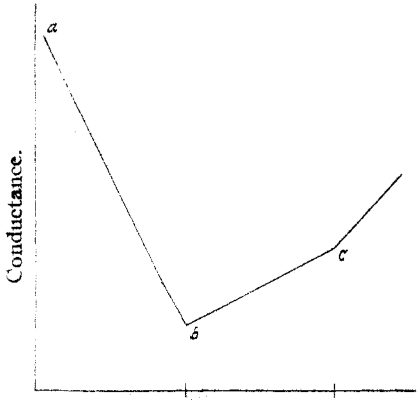

Fig. 1.

A case quite similar to this is that of oxalic acid, the titration of which is the subject of this paper. The acid readily gives off one hydrogen ion,

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[1] The general non-mathematical theory of these titrations has been discussed by Harned, This Journal, 39, 252 (1917).

[2] This can be shown to be true from a study of the ionic equilibria relationships in such solutions.

but only in much more dilute solution does it give off the second ion. Such a behavior was observed by Ostwald in the cases of other organic dibasic acids. The dissociation of oxalic acid can be represented as follows:

$$H_2C_2O_4 = H^+ + HC_2O_4^- \qquad (1)$$

$$HC_2O_4^- = H^+ + C_2O_4^{--} \qquad (2)$$

Step 1 represents the strong acid, step 2 the weak acid. The conductance of an oxalic acid solution should behave in the same way as a mixture of hydrochloric and acetic acids in equimolecular quantities on the addition of a standardized sodium hydroxide solution. In other words, the conductance methods should make possible an accurate titration of one-half of the oxalic acid. The second conductance end-point (where the neutral oxalate is formed), using sodium hydroxide as a titrating agent, will not be sharp enough to warrant its recommendation as a method for the determination of oxalic acid. On the other hand, a barium hydroxide solution used as a titrating agent will give the maximum change in conductance at this end-point, or at a point identical with the color change of phenolphthalein. This behavior is due to the insolubility of neutral barium oxalate.

Measurements.

The apparatus used when titrating with either barium hydroxide or carbon dioxide-free sodium hydroxide was that previously used by Harned.[1] The carbon dioxide-free sodium hydroxide solution was made from metallic sodium, and was standardized against hydrochloric acid (using phenolphthalein as an indicator), which had in turn been standardized by adding silver nitrate and weighing the precipitated silver chloride. The conductance was measured by the simplest kind of a conductance apparatus. The measurements were carried out at room temperature; no further precautions were taken to maintain a constant temperature.

The procedure in making a determination was as follows: The weighed sample of pure oxalic acid was introduced into the flask, 50 cc. of carbon dioxide-free water and a drop of phenolphthalein added and the stoppers pressed in tightly. It was found unnecessary to sweep out any carbon dioxide in the flask at the beginning of the experiment if carbon dioxide-free water was used in dissolving the oxalic acid and if the titrating solution was kept at all times free from contamination with carbon dioxide. Readings were taken near the end-point at successive additions of from 0.3 to 0.5 cc. of the titrating solution. Sodium hydroxide was added until the solution was just pink, which amount of sodium hydroxide is double the amount required to give the first end-point by conductance.

That this is true can be most readily seen from Table I, A. Col. 1 gives the number of grams of oxalic acid taken, Col. 2 the number of cc.

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[1] *Loc. cit.*

of sodium hydroxide required to completely neutralize the acid using phenolphthalein as an indicator. Col. 3 gives one-half the number of cc. of sodium hydroxide used in Col. 2, Col. 4 gives the number of cc. of sodium hydroxide calculated from grams of oxalic acid taken necessary to neutralize one-half of the acid or form the acid oxalate, Col. 5 gives the number of cc. of sodium hydroxide found by conductance, and Col. 6 gives the ratio of the value in Col. 5 to Col. 4.

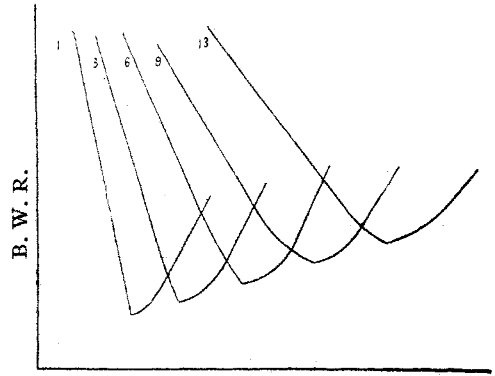
Table I.

A. Titration of Oxalic Acid with 0.17523 *N* Sodium Hydroxide.

Expt. number.	1.	2.	3.	4.	5.	6.
1	0.0604 g.	5.52	2.76	2.735	2.73	0.9982
2	0.0707	6.34	3.17	3.20	3.20	1.0000
3	0.0799	7.22	3.61	3.62	3.61	0.9955
4	0.0907	8.20	4.10	4.11	4.15	1.0098
5	0.0999	9.06	4.53	4.52	4.54	1.0046
6	0.1107	9.96	4.98	5.01	5.05	1.0081
7	0.1210	10.70	5.35	5.48	5.45	0.9955
8	0.1311	11.90	5.95	5.94	6.00	1.0100
9	0.1402	12.66	6.33	6.335	6.33	0.9991
10	0.1503	13.80	6.90	6.81	6.85	1.0060
11	0.1607	14.50	7.25	7.28	7.27	0.9986
12	0.1799	16.20	8.10	8.14	8.10	0.9952
13	0.2000	18.00	9.00	9.05	8.96	0.9902
14	0.2506	22.74	11.37	11.35	11.26	0.9921
					Mean,	1.0002

B. Titration of Oxalic Acid with 0.14324 *N* Barium Hydroxide.

Expt. number.	Oxalic acid (gram).	Cc. BaO_2H_2 (phenolphthalein).	Cc. BaO_2H_2 (calculated).	Cc. BaO_2H_2 (found by conductance).
15	0.0407	4.60	4.57	4.58
16	0.0802	8.95	9.01	8.98
17	0.1007	11.18	11.31	11.24
18	0.1507	16.88	16.93	16.85



Cc. of sodium hydroxide.
Fig. 2.

The effect of dilution is important, as is clearly shown in Fig. 2, where typical curves obtained from a number of these titrations are drawn. Bridge wire readings (denoted B.W.R.) are plotted against cc. of sodium hydroxide. (The numbers refer to the number of the experiment in Table I, A, above.) As the concentration of the original solution increases the relative change in conductance due to increased amounts of sodium hydroxide decreases, because of the presence of larger amounts of highly dissociated sodium acid oxalate, and the more concentrated this solution, the flatter the curve near the end-point. This flattening of the curve at the point where the change from acid oxalate begins makes it difficult to get a definite end-point when titrating more than 0.3 g. oxalic acid with 0.1 *N* sodium hydroxide. Quantities up to 0.8 g. oxalic acid can be titrated with 0.5 *N* sodium hydroxide with fair results.

Barium hydroxide gave a sharp end-point which checked the color change with phenolphthalein closely. A few results are given in Table I, B, on the preceding page.

Another series of experiments was made using 0.10029 *N* sodium hydroxide, standardized against known hydrochloric acid, but no effort was made to keep it from carbon dioxide. As was expected, the results were high. Table II gives the results obtained. The column headings are the same as in Table I.

TABLE II.

Titration of Oxalic Acid with 0.10029 *N* Sodium Hydroxide.

Expt. number.	1.	2.	3.	4.	5.	6.
1	0.0106	1.68	0.84	0.84	0.85	1.0119
2	0.0210	3.36	1.68	1.66	1.68	1.0121
3	0.0404	6.40	3.20	3.20	3.24	1.0125
4	0.0599	9.44	4.72	4.74	4.80	1.0125
5	0.0809	12.74	6.37	6.40	6.45	1.0079
6	0.1002	15.80	7.90	7.93	8.00	1.0088
7	0.1610	25.40	12.70	12.74	12.92	1.0142
8	0.2020	31.88	15.94	15.98	16.10	1.0075
9	0.2515	39.70	19.85	19.90	20.05	1.0075
10	0.3000	47.32	23.66	23.73	24.05	1.0135
					Mean,	1.0108

As can be seen from Col. 6, the mean ratio of the cc. of sodium hydroxide obtained by conductance to the required number of cc. of sodium hydroxide computed from the weight of oxalic acid used is 1.011, which shows a constant error of 1%. The separate determinations, however, vary little from each other (±0.34% from the mean). This error can be corrected by standardizing the sodium hydroxide used against a weighed amount of pure oxalic acid by the conductance method under the same experimental conditions. By such a procedure concordant results can be obtained.

Conclusion.

Mixtures of acid and neutral carbonates of sodium or potassium can be titrated using both methyl orange and phenolphthalein as indicators, but this cannot be done with mixtures of the sodium acid and neutral salts of dibasic organic acids such as oxalic acid, or malonic acid, or *o*-phthalic acid, etc., because in these cases methyl orange fails to give a color change when one-half the acid or one-half the salt has been titrated by sodium hydroxide or hydrochloric acid, respectively. For this reason a method for obtaining the half-way end-point for these acids, or salts of these acids, by titrations with sodium hydroxide or hydrochloric acid is highly desirable. In this paper results have been presented which show that the conductance method can be used in obtaining the acid oxalate end-point of oxalic acid by titration with a standardized sodium hydroxide solution. Doubtless the reverse is also possible, that is, the titration of neutral sodium oxalate with hydrochloric acid by the conductance method.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

MAGNETIC SUSCEPTIBILITY OF MIXTURES OF LIQUIDS.

BY ALPHEUS W. SMITH AND ALVA W. SMITH.

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A study of the physical properties of mixtures of liquids affords an interesting field of investigation, for by it those properties which follow the additive law can be discovered. Such properties must be uninfluenced by intramolecular actions and are, therefore, determined solely by conditions which exist within the atom or molecule. With the increasing care and accuracy of investigation the number of such truly additive properties has been found to be small. Recently Morgan and Griggs[1] and Morgan and Scarlett[2] studied the surface tension of several series of liquid mixtures and found marked departures from the additive law in most cases. The viscosities of certain mixtures of liquids have been examined by Kendall and Monroe,[3] who show that in this case the cube root of the viscosity seems to be an additive function. Many other properties of mixtures of liquids have been studied as a means of testing the validity of the additive law but a fairly careful examination of the literature on the subject seems to indicate that the magnetic susceptibility of mixtures of liquids has not been studied, although the additive law has often been used in calculating the magnetic susceptibility of a salt from the susceptibility of the solution and of the solvent. It seemed worth while, therefore, to study the magnetic susceptibilities of a few series of mixtures of liquids in order to see how nearly the observed susceptibility agrees with that calculated from the concentration of its components by an application of the additive law.

The method of taking the observations was that devised by Quincke as modified by Oliver and recently used by Piccard[4] in his study of the magnetic susceptibility of water. The arrangement of the apparatus

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[1] Morgan and Griggs, THIS JOURNAL, 39, 2261 (1917).

[2] Morgan and Scarlett, *Ibid.*, 39, 2275 (1917).

[3] Kendall and Monroe, *Ibid.*, 39, 1787 and 1802 (1917).

[4] Piccard, *Arch. Phys. Nat. Sci.*, 35, 340 (1913).