[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Cryoscopic Studies in Anhydrous Acetic Acid

BY WILLIAM C. EICHELBERGER[1]

Because of its high acidity and low dielectric constant, acetic acid is a particularly important solvent for studying the thermodynamic behavior of dissolved acids. Recently, several interesting contributions to this problem[2,3,4] have been made by the use of electromotive force methods which are of sufficient importance to warrant a study by an independent method. The purpose of the present paper was to investigate cryoscopically the behavior of a binary salt, ammonium nitrate, and a strong acid, sulfuric acid, in this typical acid solvent of low dielectric constant.

No data are listed in the "International Critical Tables" for the freezing point lowerings of acid solutes in anhydrous acetic acid solutions. The only cryoscopic data for salts in dilute solutions of this solvent worthy of consideration are those of T. J. Webb[5] for sodium bromide, sodium acetate and lithium bromide. Unfortunately, Webb does not give either the observed freezing point depressions or the molal freezing point constant employed in calculating his "j"-values. His numerical value of the limiting law would correspond to a value of about 9.6 for the dielectric constant D, assuming a molal freezing point constant k_F of 3.90, whereas the more recent measurements of Smyth and Rogers[6] indicate a value of D equal to 6.11 and Wyman (quoted by Seward and Hamblet[7]) gives 6.12 at 16.60°, the freezing point of acetic acid. The value of k_F for glacial acetic acid is given in the "International Critical Tables" (Volume 4) as 3.90. We calculate values of 3.575 from the latent heat of fusion data of Parks and Kelley,[8] 3.595 from the latent heat of fusion data of De Visser[9] and 3.625 from the data of De Visser[9] for the freezing point lowering produced by 0.1% water. Webb's interpretation may therefore be considerably in error, and a reinvestigation is desirable.

Theory.—To assist in interpreting the experimental data, we have plotted in Fig. 1 the theoretical curves for the Lewis and Randall "j"-function. These represent the osmotic deviation of uni-univalent electrolytes as a function of the square root of the concentration, calculated on the basis of the Debye–Hückel theory in its various forms using values of "a" equal to 6, 8, 10 and 12 Å. The broken curves are computed on the basis of the first approximation of the Debye–Hückel theory, while the solid curves are calculated from the Gronwall, La Mer and Sandved extension[10] of the theory through the fifth approximation. The irregularities are due to the failure of the series to converge at even the fifth approximation for values of "a" less than 12 Å. when D = 6.11. Calculations[5] based on the first approximation consequently are quite misleading.

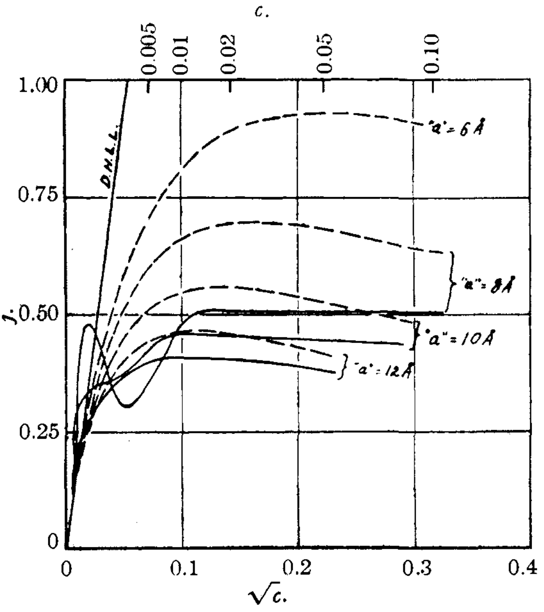

Fig. 1.—Theoretical curves of the "j"-function in anhydrous acetic acid solution: $j = 1$, complete association; $j = 0.5$, no association nor dissociation, assuming two ions and no interionic forces; $j = 0$, complete dissociation, assuming an ideal solute and no interionic forces. Broken curves, Debye–Hückel first approximation for (1, −1) electrolyte. Solid curves, Gronwall, La Mer and Sandved fifth approximation for (1, −1) electrolyte.

---

(1) National Research Fellow, 1930–1931; Research Assistant, 1931–1932.

(2) Hall and Conant, THIS JOURNAL, **49**, 3047, 3062 (1927); Hall and Werner, *ibid.*, **50**, 2367 (1928); Conant and Werner, *ibid.*, **52**, 4436 (1930); Hall, *ibid.*, **52**, 5115 (1930).

(3) Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).

(4) La Mer and Eichelberger, *ibid.*, **54**, 2763 (1932).

(5) T. J. Webb, *ibid.*, **48**, 2263 (1926).

(6) Smyth and Rogers, *ibid.*, **52**, 1825 (1930).

(7) Seward and Hamblet, *ibid.*, **54**, 554 (1932).

(8) Parks and Kelley, *ibid.*, **47**, 2089 (1925).

(9) De Visser, *Rec. Trav. Chim.*, **12**, 101 (1893).

(10) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

The experimental value of j is given by the formula $j = 1 - \Delta T/\nu m k_F$ where ΔT is the freezing point lowering, ν is the number of ions, m is the concentration in moles per thousand grams of solvent and k_F is the molal freezing point constant. A value of $j = 0$ would mean complete dissociation of an ideal solute without interionic attraction. For $j = 1$ the salt would have to be so highly associated into complex molecules that no perceptible freezing point depression would be exhibited. A value of $j = 0.5$ would correspond to a case where no association or dissociation of the molecular solute occurred for a perfect non-electrolyte on the assumption that it is dissociated into two ions, *i. e.*, $\nu = 2$.

In order to compute j from experimental data, it is necessary to make some assumption regarding the normal dissociation mechanism. Thus, in the case of sulfuric acid[4] we are at liberty to compute our results on the assumption that the secondary dissociation into sulfate ion may be neglected in such a highly acid solvent as anhydrous acetic acid, *i. e.*, $\nu = 2$; or, if we assume dissociation into two hydrogen and one sulfate ion, then $\nu = 3$. For ammonium nitrate, $\nu = 2$.

Experimental

Apparatus.—The apparatus was designed after that used by Robertson and La Mer[11] but with certain changes necessary with non-aqueous solvents. Two 500-cc. Dewar flasks were mounted each in a brass cylinder, thermally insulated from them. The cylinders were fastened to a brass plate on top of which was a brass manifold which encased the U-tube of the thermocouple (described below) and was filled with paraffin. Since cork is attacked by acetic acid, it was necessary to use silver-plated brass caps as covers for the Dewar flasks, insulated from them with rubber. Into each vessel extended one leg of the thermocouple, a hand-operated glass stirrer mounted in a glass tube, and glass tubes for removing the liquid from the bottom of the vessel and for determining the height of the liquid in the vessel. These glass tubes were mounted in copper tubes soldered to the brass plate. The exposed end of the stirring rod was covered with a flexible rubber cap to exclude moisture. A 2-cm. glass tube provided an opening into each vessel for introducing the solid phase of the solvent and the solutions. All joints were made water-tight with "piceïn" cement. The assembly was suspended in a 16.60° thermostat.

The solutions were stored in the thermostat in eight 500-cc. Pyrex bottles. Compressed air, dried over calcium chloride, admitted to the bottles through side tubes, forced the solutions out of them through glass tubing into the apparatus.

The Thermocouple.—In our endeavor to build a satisfactory thermocouple we found that both rubber and shellac used by previous investigators[11,12] to insulate the junctions of multiple thermocouples deteriorated with age. Mr. C. E. White, Department of Chemical Engineering, Columbia University, in his work with thermocouples, developed a special cellulose acetate varnish[13] which we found satisfactory for the purpose. Since nickel wire develops inhomogeneities on bending,[14] we discarded it as a thermoelement.

Taking into consideration these facts and meeting the resistance requirements for maximum sensitivity,[15] we constructed a 24-junction thermocouple from No. 24 double silk covered constantan wire,[16] which had been carefully checked for homogeneity, and No. 30 double silk-covered copper wire,[17] their cross-section ratios[15] being 2:1. The junctions of the thermocouple were staggered, coated four times with cellulose acetate varnish and dried in an oven at 80°. The legs of the thermocouple were inserted in gold-plated silver shields, after thrusting the wires through a glass U-tube which supported the shields. The assembly was filled with paraffin, which had been heated to 200° to expel moisture.

The electrical apparatus, described in detail elsewhere,[11] is accurate to better than 0.01 microvolt, or 0.00001° with this thermocouple.

The following temperatures were used in the calibration of the thermocouple: (1) $Na_2SO_4 \cdot 10H_2O$ transition point, 32.384°; (2) the transition point[18] of $NaNO_3 + Na_2SO_4 \cdot 10H_2O$, 13.154°; (3) a 25.000° thermostat checked against a Bureau of Standards Beckmann thermometer and a platinum resistance thermometer (Dr. MacInnes' laboratory, Rockefeller Institute, New York, N. Y.), yielding the equation

$$E = 924.28t - 0.6128t^2 + 0.03124t^3$$
$$dE/dt(16.60°) = 929.8 \text{ microvolts per degree}$$
$$d^2E/dt^2(16.60°) = 1.887 \text{ microvolts per degree}$$

where E is e. m. f. in microvolts and t is degrees centigrade. This equation was checked against the platinum resistance thermometer at 29.825 and 13.899°. No perceptible change was observed on recalibration at the end of a year.

Preparation of Materials.—Purification of the anhydrous acetic acid is described elsewhere.[19] The ammonium nitrate (Merck reagent) was recrystallized from distilled water, dried at 120° and kept in a desiccator over sulfuric acid. Baker and Adamson 30% c. p. fuming sulfuric acid was added to redistilled concentrated sulfuric acid to bring the melting point of the acid to that of 100% sulfuric acid; namely, 10.5°.

Analyses of Solutions.—The *ammonium nitrate solutions* were analyzed by the Kjeldahl method, using a quartz distilling column. The weighed sample of the

---

(11) Campbell Robertson and Victor K. La Mer, *J. Phys. Chem.*, **35**, 1953 (1931).

(12) W. P. White, This Journal, **36**, 2292 (1914); L. H. Adams, *ibid.*, **37**, 481 (1915).

(13) Composition: 4.5 g. cellulose acetate (acetone soluble), 60 cc. acetone, 10 cc. methyl ethyl ketone, 14 cc. ethyl alcohol, 14 cc. benzene, 2 cc. benzyl alcohol.

(14) T. Tsutsui, *Tokio Scientific Papers*, Institute of Physical Chemical Research, **11**, 93 (1929).

(15) Robertson and La Mer, *loc. cit.*, pp. 1962–1964.

(16) Driver-Harris Co., Newark, N. J.

(17) Leeds and Northrup Co., Philadelphia, Pa.

(18) Redlich and Löffler, *Z. Elektrochem.*, **36**, 716 (1930).

(19) Eichelberger and La Mer, This Journal, **55**, 3633 (1933).

acetic acid solution containing ammonia sufficient to neutralize half of the standard acid was introduced through a side-tube into the distilling flask containing sufficient 20% potassium hydroxide to free the ammonia from the salt. (Potassium hydroxide was used instead of sodium hydroxide because of the much greater solubility of potassium acetate over that of sodium acetate.) Distilled water was then added to the distilling flask through the side-tube to bring the total volume to about 400 cc. so that 300 to 350 cc. could be distilled.[20] The excess acid was titrated with standard sodium hydroxide, using methyl red indicator. Duplicate analyses were accepted when checks to within 0.3% were obtained.

The sulfuric acid solutions were analyzed by conductimetric titrations[21] and were accurate to 0.2%.

One liter each of four concentrations of solutions was prepared and divided between two of the solution bottles so that duplicate samples could be measured. The entire freezing point apparatus and solutions were placed in the 16.60° thermostat twelve hours preceding measurements.

Anhydrous acetic acid, in wide-mouthed bottles, was frozen to a mush of desirable particle size and dumped quickly through the large tube into the freezing point vessel. The unfrozen acid was sucked out immediately. Moisture absorbed during this transfer was removed by repeated rinsings with pre-cooled dry acid (transferred through glass tubing from bottles to the apparatus) until the thermocouple readings were constant to within 0.0001° for at least fifteen minutes. At the end of this process there were about 100 cc. of solid particles to 300 cc. of liquid in each vessel.

Attempts were made to improve upon this lengthy rinsing process by freezing the acid *in situ* and also by transferring the frozen mush through glass tubes, but without significant success.

When no further changes in temperature occurred on rinsing, the solid in one vessel was sucked dry and rinsed twice with the solution to be measured. The vessel was filled with the solution and thermocouple readings were made every three minutes until at least six consecutive readings agreed to 0.0001°, when the solution was removed promptly for analysis. About an hour was required for a satisfactory equilibrium state. The duplicate solution was then introduced and the procedure repeated in the same manner.

Although equilibrium to 0.0001° for a given solution was maintained for at least fifteen minutes, duplicate samples differed from 0.0002 to 0.005°, the latter value being attributable mainly to moisture.

Experimental Results

Since 0.01% water, corresponding to 0.00555 mole of an ideal solute, produces a lowering of 0.02° in the freezing point, precautions were taken to maintain conditions as anhydrous as possible. Although measurements were attempted at higher dilutions, we shall not report values below 0.02 molal (except for one experiment with ammonium nitrate).

TABLE I

MOLAL LOWERINGS OF AMMONIUM NITRATE IN ANHYDROUS ACETIC ACID

m	ΔT	j	$j/\sqrt{m}$	$\sqrt{c}$
Series No. 3 (Circles, lower half shaded)				
0.04126	0.112	0.623	3.07	0.208
.02215	.0593	.627	4.21	.153
Series No. 4 (Solid circles)				
0.0427	0.1130	0.631	3.05	0.212
.04337	.1197	.616	2.96	.213
.02594	.0716	.616	3.82	.165
.02441	.0659	.624	4.00	.160
Series No. 5 (Open circles)				
0.00441	0.01658	0.476	7.21	0.068
.00470	.01255	.628	9.10	.070
.00891	.02911	.545	5.80	.098
.01972	.06578	.535	3.82	.144
.02007	.06576	.544	3.83	.145
.04387	.1211	.616	2.95	.215
.04408	.1404	.556	2.65	.215

Series No. 5 was performed with the solvent more carefully purified than was used for the first four series. At the close of this experiment it was observed that the anhydrous acetic acid was decomposing the ammonium nitrate; hence, the smaller "*j*'s" in some cases because of more particles present in the solution.

The highest concentration used was a saturated solution of ammonium nitrate in anhydrous acetic acid: 0.044 molal. The solubility of ammonium chloride in the anhydrous acid is 0.013 molal. These values are considerably lower than the qualitative results recorded in the literature. They attribute the discrepancy to the presence of water.

TABLE II

MOLAL LOWERINGS OF SULFURIC ACID IN ANHYDROUS ACETIC ACID

m	ΔT	$j_{1,-1}$	$j_{1,-2}$	$j_{11}/\sqrt{m}$	$j_{12}/\sqrt{m}$	$\sqrt{c}$
Series No. 6 (Solid circles)						
0.0497	0.225	0.369	0.579	1.65	2.60	0.228
.0513	.222	.397	.598	1.76	2.65	.232
.0988	.378	.467	.644	1.49	2.05	.322
Series No. 7 (Circles, right half shaded)						
0.0481	0.218	0.369	0.579	1.68	2.64	0.225
.1001	.395	.450	.633	1.42	2.00	.324
.1004	.399	.446	.630	1.41	1.99	.324
Series No. 8 (Open circles)						
0.01948	0.117	0.163	0.442	1.16	3.16	0.143
.01947	.118	.156	.437	1.11	3.12	.143
.0369	.180	.320	.546	1.67	2.84	.197
.0400	.186	.352	.568	1.76	2.84	.205
.0795	.303	.469	.646	1.66	2.29	.289
.0805	.303	.476	.650	1.68	2.29	.291
Series No. 9 (Circle, left half shaded)						
0.0305	0.156	0.288	0.525	1.64	3.00	0.179

---

[20] See C. F. Mason, Dissertation, Columbia University, 1926, for precautions to be taken; also V. K. La Mer and C. F. Mason, THIS JOURNAL, **49**, 410 (1927).

[21] Eichelberger and La Mer, *ibid.*, **55**, 3635 (1933).

In the columns of Tables I and II are listed: the molal concentrations, m, *i. e.*, moles per 1000 g. of solvent; the freezing point lowerings, ΔT, corrected for any difference in temperature between the vessels after completing the initial rinsing process; the values of $j = 1 - \Delta T/\nu m k_F$, where $k_F = 3.59$ (see page 799 of this paper); and $\sqrt{c}$ computed by using for the densities the formula[3] $d = d_{16.6°} + 0.062\ m$, where[6] $d_{16.6°} = 1.053$.

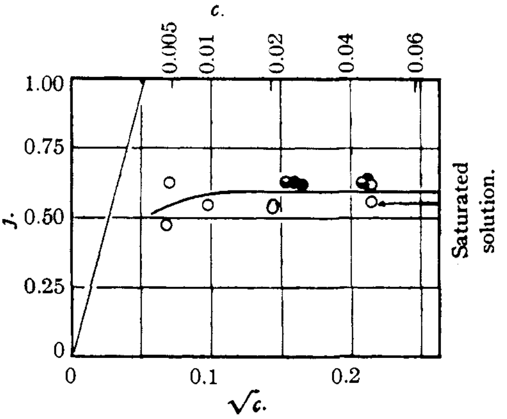

Fig. 2.—Ammonium nitrate in anhydrous acetic acid.

The results are plotted in Figs. 2, 3 and 4. The Debye–Hückel limiting slope is $j = 18.7\sqrt{c}$, or $19.2\sqrt{m}$ for a (1, -1) electrolyte, and $j = 64.8\sqrt{c}$, or $66.5\sqrt{m}$ for a (1, −2) electrolyte, when[6,7] $D = 6.11$.

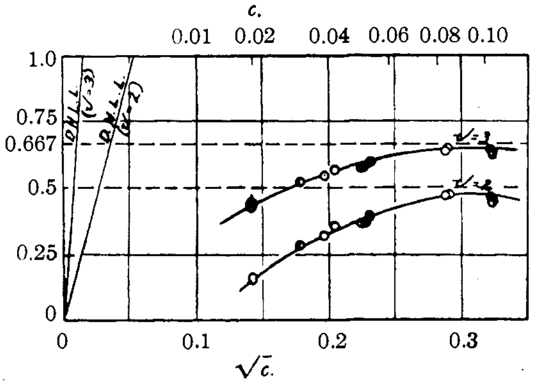

Fig. 3.—Sulfuric acid in anhydrous acetic acid

The plot of j, $\sqrt{c}$ for ammonium nitrate, Fig. 2, resembles in form those obtained by Webb[5] for lithium bromide, sodium bromide and sodium acetate in that j is approximately 0.6 between 0.005 and 0.5 molal. However, as mentioned above, our data are computed using different values of k_F and D from those which he used.

Comparing the experimental curves in Figs. 2 and 3 with the theoretical curves in Fig. 1, our data give no definite information as to the ion size of the particles in solution. This is due partially, as mentioned in the theoretical discussion, to the fact that the series does not converge sufficiently at even the fifth approximation for values of "a" less than 12 Å. when $D = 6.11$. We may say that the value of "a" for ammonium nitrate apparently is less than 8 Å. Our data shed no further light upon the question whether $\nu = 2$ or $\nu = 3$ for sulfuric acid[4] nor upon its probable ion size. All our data lie far below the limiting law. Experimental difficulties are too great to study these solutions cryoscopically at sufficient dilution to determine the answer to these questions.

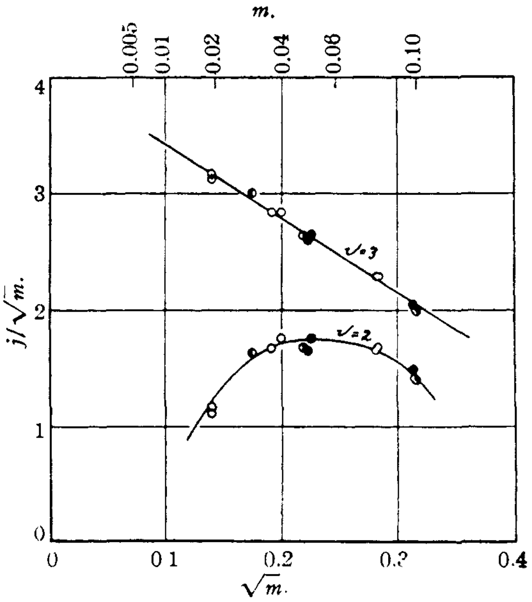

Fig. 4.—The function $j/\sqrt{m}$ plotted against $\sqrt{m}$ for solutions of sulfuric acid in anhydrous acetic acid: limiting law, $j/\sqrt{m} = 19.2$ for $\nu = 2$; $j/\sqrt{m} = 66.5$ for $\nu = 3$.

The author wishes to thank Professor Victor K. La Mer, Columbia University, for his interest in the problem and for placing at his disposal the apparatus necessary for prosecuting it.

Conclusions

1. A freezing point apparatus for anhydrous, non-aqueous solutions and its manipulation are described. Its potential precision is 0.00001°, but with the solvent employed experimental conditions reduce the precision to 0.0001°.

2. Computations using the Gronwall, La Mer and Sandved development of the Debye–Hückel theory for osmotic deviations show that for solvents of such low dielectric constant calculations based on the first approximation will yield erroneous values for the parameter "a," and those based on the fifth approximation are valid only when "a" is greater than 10 Å. due to the slow convergence of the series.

3. From our data we may conclude that: (a) in the region of 0.005 to 0.05 molal, ammonium nitrate when dissolved in anhydrous acetic acid behaves as though associated into at least binary ion pairs. (b) When the concentration of the solute is small, 100% sulfuric acid is appreciably dissociated in anhydrous acetic acid. At concentrations of about 0.1 molal it behaves as though highly associated in the Bjerrum sense.

4. As might be expected, these electrolytes, ammonium nitrate and sulfuric acid, when dissolved in anhydrous acetic acid deviate widely from the predictions of the Debye–Hückel limiting law.

NEW YORK, N. Y. RECEIVED NOVEMBER 2, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Oxidation by Oxygen of the Tellurides, Selenides, and Sulfides of Sodium in Liquid Ammonia

BY R. L. MCCLEARY AND W. CONARD FERNELIUS

The present investigation had as its object the determination of the products of the action of gaseous oxygen on the mono- and polytellurides, -selenides, and -sulfides of sodium. Although the principal products of these reactions have been determined, such information has been gathered largely as a by-product of studies not bearing directly on this topic. The studies reported here were carried out in liquid ammonia (1) because the preparation of the pure compounds in this solvent is a relatively easy matter, (2) because liquid ammonia is a good solvent for all of the salts having polyatomic anions, and (3) because liquid ammonia possesses a relatively low solvolyzing power and would thus tend to diminish complicating side reactions. This technique is not all that may be desired, however, because the monosulfides, -selenides, etc., and oxygen gas are only slightly soluble in liquid ammonia.

Experimental

The reaction cell was that of Kraus and Chiu,[1] with minor modifications. In the preparation and purification of materials, the methods of Kraus and Chiu and of Bergstrom[2] were used. It should be remembered that the colors of solutions of the polytellurides, etc., are: Na_2Te_2, purple; Na_2Te_4, dark red; Na_2S_2, red; Na_2Se_3, green; Na_2Se_4, red; Na_2Se_5, red-green; Na_2S_2, orange; Na_2S_{3-5}, red.[1,2,3]

Standard analytical methods were used throughout although certain ones are not so familiar.[4]

Oxidation of the Sodium Tellurides.—Upon treating the suspension of the monotelluride with gaseous oxygen, the solution acquired first a deep lavender color, then changed to red, and soon became water clear above the white precipitate. The products of this reaction, except for a trace of free tellurium, were water soluble and consisted of tellurite and tellurate in varying amounts. On oxidation the lavender color of the ditelluride changed to the red of the saturated compound (apparently Na_2Te_4 but possibly a mixture of Na_2Te_2 and Na_2Te_6).[1,5] At the end of the oxidation of both Na_2Te_2 and Na_2Te_4 a clear liquid and a gray precipitate remained. From substances of the following compositions: $Na_2Te_{1.10}$, $Na_2Te_{2.18}$ and $Na_2Te_{3.86}$; there were obtained 0.14, 1.02 and 2.06 atoms of free Te; 0.52, 0.71 and 1.00 atoms of Te as $TeO_3^=$; and 0.46, 0.44 and 0.34, respectively, atoms of Te as $TeO_4^=$. The substance Na_2Te_2 gave 0.93 atom of free Te and 1.06 atoms of Te as a mixture of $TeO_3^=$ and $TeO_4^=$.

Oxidation of the Sodium Selenides.—Upon treating the suspension of sodium selenide with oxygen (two to three hours) a transitory light orange coloration appeared. The reaction product (in three cases) contained no unchanged selenide and consisted approximately of 0.1 atom of free Se and 0.9 atom of Se as a mixture of $SeO_3^=$ and $SeO_4^=$. Moderately soluble diselenide (red) exhibited the following behavior when treated with oxygen. The red color soon changed to a very brilliant green which rapidly became darker and then suddenly changed to a wine red. This latter red color slowly altered to a much

---

(1) C. A. Kraus and C. Y. Chiu, THIS JOURNAL, **44**, 2003 (1922).

(2) F. W. Bergstrom, *ibid.*, **48**, 147 (1926).

(3) *Cf.* W. C. Johnson and W. C. Fernelius, *J. Chem. Ed.*, **7**, 986 (1930); E. Zintl, J. Goubeau and W. Dullenkopf, *Z. physik. Chem.*, **154A**, 1–46 (1931).

(4) Separation of tellurites and tellurates: P. E. Browning and W. R. Flint, *Z. anorg. Chem.*, **64**, 104–111 (1909). Determination of selenite in the presence of selenate: E. Müller, *Z. physik. Chem.*, **100**, 347 (1922).

(5) C. A. Kraus and S. W. Glass, *J. Phys. Chem.*, **35**, 999 (1929); *cf.* E. Zintl, J. Goubeau and W. Dullenkopf, *loc. cit.*, p. 30.