

Fig. 1.—Temperature-composition diagram: O, this report; ●, Neuman and Bergve.

The very low freezing point of Neumann and Bergve¹ and their failure to even record the transition temperature indicate that their measurements on the sodium hydroxide-sodium carbonate system may be considerably in error. The fact that additional carbonate does not lower the transition temperature indicates that solid solution formation must be slight. If the logarithm of the mole fraction of sodium hydroxide is plotted against the reciprocal of the freezing tempera-

tures where the solid phase is sodium hydroxide, the first four points lie on a straight line from the slope of which the heat of fusion of sodium hydroxide is calculated to be 1670 cal. per mole in agreement with 1600 cal. obtained by von Hevesy³ by an independent method. From the heat of fusion of sodium carbonate as given by Kelley,⁵ 7000 cal., and its melting point, the calculated solubility of sodium carbonate at 320° is 7 mole % compared to the observed solubility of 11 mole %. Since 320° is more than five hundred degrees below the m. p. of sodium carbonate, this calculation is of no quantitative significance but indicates that the solution under consideration is not far from ideal. This calculation is based on the assumption that the solid phase at 320° is sodium carbonate, which seems likely but has not been proved since the maximum content of carbonate employed was only 35%.

Summary

Freezing point measurements have been made on sodium hydroxide-sodium carbonate mixtures up to 35% carbonate. The freezing point of sodium hydroxide was found to be 320° and the transformation point 294°. The addition of sodium carbonate reduces the freezing point until a eutectic at 286° with a sodium carbonate content of 22% is reached. The heat of fusion of sodium hydroxide was calculated to be 1670 cal. per mole.

(5) Kelley, "U. S. Bureau of Mines," Bulletin 393 (1936).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON STATE COLLEGE]

The Secondary Ionization and Activity Coefficients of Selenic Acid*

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Experimental

Electromotive forces of cells of the type QH: H_2SeO_4 , Ag_2SeO_4 : Ag have been measured at $25 \pm 0.02^\circ$.

Preparation and Purification of Materials.—The preparation of selenic acid has been described previously.¹ The acid was twice recrystallized and gave a melting point of 58° . Stock solutions of the acid, approximately 0.2 molar, made from the crystalline acid and conductivity water, were standardized by titration with standard alkali.

* Original manuscript received August 12, 1940.

(1) Gilbertson and King, *THIS JOURNAL*, **58**, 180 (1936).

Solutions of various concentrations were made by dilution of the stock solution with conductivity water.

Molal concentrations were calculated from the densities at the concentrations studied. Density determinations were made at 25° , using a 25-ml. Weld specific gravity bottle. All weights were corrected to vacuum. The values are shown in Table I.

Quinhydrone Electrodes.—The quinhydrone was a laboratory preparation which was recrystallized and compared with good commercial samples. Results of such comparison were identical.

Electrodes were of heavy platinum foil, 0.005 inch in thickness, sealed into Pyrex glass tubing. Several methods of cleaning the electrodes were tried before reproducible

results were obtained. The following procedure was found to be most satisfactory. The electrodes were cleaned in concentrated sulfuric acid-chromic acid mixture, then washed thoroughly with distilled water and finally heated to redness in a Bunsen flame, the gas supply being "Flamo," practically pure propane. Electrodes prepared in this manner gave results reproducible within 0.1 mv. and remained constant for a period of one to two hours.

Silver-Silver Selenate Electrodes.—Silver electrodes were prepared in the usual manner by plating silver on platinum foil from a cyanide solution. These electrodes were allowed to stand in distilled water from twelve to twenty-four hours, the water being changed frequently during that period. Silver selenate was formed electrolytically on the silver electrodes from a selenic acid solution (approximately 0.1 molar) using a platinum cathode. A current of 1.2 to 1.3 ma. per sq. cm. was allowed to flow for ten minutes. It was necessary to employ a cell minimizing diffusion, as selenium was formed rapidly at the cathode. The silver selenate appeared as a light gray coating on the surface of the silver. The electrodes were washed with selenic acid solution of the same concentration as was to be used in the subsequent measurements. These electrodes were easily reproducible to 0.05 mv., and remained stable for a period of at least twenty-four hours. Electrodes which showed greater deviation were replaced.

Apparatus.—The potentiometer was a Leeds & Northrup, Type K, with a Type R galvanometer. The standard cell was a Weston, saturated type, which was checked frequently against a primary standard. The deviation did not exceed 0.01%.

The cell was constructed so as to prevent diffusion of the quinhydrone into the chamber containing the saturated silver selenate solution. Quinhydrone did not appear to undergo oxidation in the selenic acid solutions.

Two silver selenate electrodes and three platinum electrodes were used in each set-up, thus allowing six measurements of e. m. f. in the solution, as well as a measurement of potential difference between like electrodes. The silver selenate electrodes were immersed in the selenic acid solution which had previously been saturated with silver selenate; the platinum electrodes were immersed in the acid solution saturated with quinhydrone. Equilibrium conditions were reached rapidly, usually in a few minutes.

Readings were taken at intervals of ten minutes for a period of one to two hours, depending on the constancy of the cell potential. Duplicate set-ups were reproducible in every case within 0.1 mv.

The Solubility of Silver Selenate at 25°

Since the solubility of silver selenate was needed in the calculation of the activity coefficients of selenic acid by the method proposed in this paper, its determination has been made in water and selenic acid solutions at 25°. A search of the literature reveals no previous study of the solubility of silver selenate at this temperature. Lenher and Kao² state that a liter of water dissolves 1.182 g. of silver selenate at 20°. No de-

tails of the method of determination of this solubility are given in their paper. E. Mulder³ states that a saturated solution of the salt contains 0.835 g. per liter (the temperature is not recorded).

Silver selenate was prepared from recrystallized magnesium selenate hexahydrate and analytical reagent silver nitrate. The salt was precipitated slowly by the addition of 10% silver nitrate solution to a 10% solution of magnesium selenate hexahydrate. The solution was stirred continuously during the reaction. The precipitated salt was washed ten times with distilled water and dried in an oven at 110°. The dried salt was analyzed for silver by precipitation as bromide: silver, theoretical, 60.15%; found, 60.03%. The salt was stored in the dark, since it decomposes slowly when exposed to light.

Saturated solutions of the salts were prepared by approaching equilibrium from both undersaturation and supersaturation. Equilibrium was reached from undersaturation by stirring for forty-eight hours but in the case of the supersaturated solutions twenty-four hours or less were required. Portions of the saturated solution were pipetted and analyzed for silver by precipitation as silver bromide. Maximum deviations of all analyses were less than 1%. Solubility data are shown in Table I. The density of the saturated solution at 25° was determined and found to be 0.99793. The solubility product of silver selenate was calculated as 5.65×10^{-8} .

TABLE I

Molarity of H ₂ SeO ₄	Moles of Ag ₂ SeO ₄ per liter
0.0000	0.00242
.00564	.00177
.01113	.00162
.0222	.00147
.0566	.00135
.1218	.00134

Calculation of Activity Coefficients

Activity coefficients were calculated from the values given in Tables I and III, employing the equation

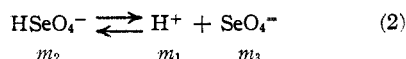
$$E_0' = E + \frac{RT}{2F} \ln 4m^2(m + m_4) = E_0 - \frac{3RT}{2F} \ln \gamma \quad (1)$$

where the term, $m + m_4$, expresses the total concentration of SeO₄²⁻. The value of E_0 was obtained using a method suggested by O. Redlich (private communication). Assuming the primary ionization of selenic acid complete, partial dis-

(2) Lenher and Kao, THIS JOURNAL, 47, 1521 (1925).

(3) Mulder, *Rec. trav. chim.*, 23, 387 (1904).

sociation of HSeO_4^- , and complete dissociation of the dissolved silver selenate, relationships have been derived, which have been used to determine the value of E_0 . If



represents the secondary ionization, the molarities of the ions as indicated are given by

$$m_1 = (1 + \alpha)m; \quad m_2 = (1 - \alpha)m; \quad m_3 = m_4 + \alpha m \quad (3)$$

where m is the molarity of the selenic acid, α the fraction of HSeO_4^- ionized, and m_4 the moles SeO_4^- per liter from dissolved silver selenate.

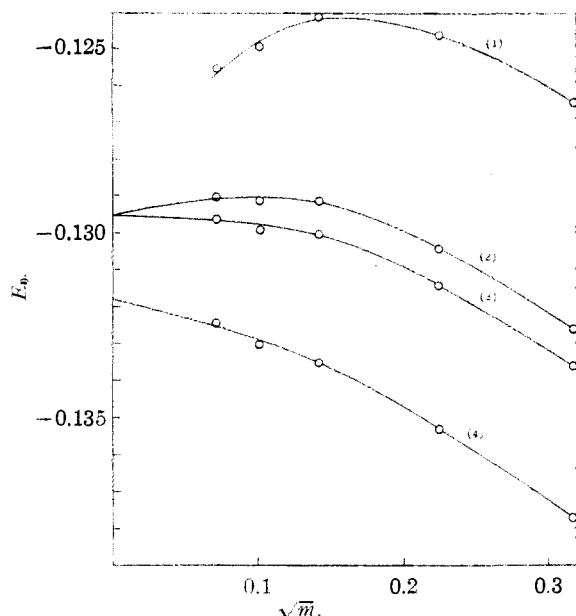


Fig. 1.—Relationship between E_0 and the secondary ionization constant: (1) $K = 2 \times 10^{-2}$; (2) $K = 1.1 \times 10^{-2}$; (3) $K = 1 \times 10^{-2}$; (4) $K = 7 \times 10^{-3}$.

The secondary ionization constant, K , may be written as

$$K = \frac{m_1 \gamma_1 m_3 \gamma_3}{m_2 \gamma_2} = \frac{m_1 m_3}{m_2} \beta^3 = \frac{1 + \alpha}{1 - \alpha} (\alpha m + m_4) \beta^4 \quad (4)$$

The activity coefficient, β , appearing in this equation is equal to $(\gamma_1 \gamma_3 / \gamma_2)^{1/4}$, where γ_1 , γ_2 , and γ_3 represent the activity coefficients of the individual ions, H^+ , HSeO_4^- , and SeO_4^- , respectively. Using the modified form of the Debye-Hückel equation,⁴ values of β have been calculated

$$\log \beta = -0.5056 \mu^{1/2} / (1 + \mu^{1/2}) \quad (5)$$

where the ionic strength is given by

$$\mu = \frac{1}{2} \sum c z^2 = m(1 + 2\alpha) + 3m_4 \quad (6)$$

Employing the preceding relationships, the following may be derived

(4) Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1934).

$$\alpha = \frac{(K/\beta^4) - m_4}{m + m_4 + \alpha m + (K/\beta^4)} \quad (7)$$

Using values of m_4 interpolated from the data in Table I and assumed values for the ionization constant, corresponding values of α and β were calculated by approximation.

Since the electromotive force may be given by

$$E = E_0 - \frac{RT}{2F} \ln a_1^2 a_3 \quad (8)$$

where a_1 and a_2 are the activities of H^+ and SeO_4^- , respectively, by substitution the following is obtained

$$E = E_0 - \frac{RT}{2F} \left[2 \ln(1 + \alpha) + \ln \left(\frac{m_4}{m} + \alpha \right) + 6 \ln \beta + 3 \ln m \right] \quad (9)$$

Values of E_0 calculated from e. m. f. data and values of α and β in Table II should approach constancy as dilution increases. The value of K most nearly fulfilling this condition has been selected as 1×10^{-2} . By extrapolation, Fig. 1, $E_0 = -0.1295$ v. Using this value in Eq. (1) the activity coefficients were calculated and are shown in column 7, Table III.

The activity coefficients of Harned and Hamer⁵ have been calculated from e. m. f. data of cells of $\text{H}_2 : \text{H}_2\text{SO}_4 : \text{Hg}_2\text{SO}_4 : \text{Hg}$, while the activity coefficients of selenic acid have been calculated from e. m. f. measurements of the cell $\text{QH} : \text{H}_2\text{SeO}_4 : \text{Ag}_2\text{SeO}_4 : \text{Ag}$. Since the molar solubilities in water of mercurous sulfate and of silver selenate are of the same order of magnitude, 0.8×10^{-3} and 2.4×10^{-3} , respectively, the activity coefficients calculated from these data should be comparable. Accordingly, the values presented in Table III indicate that sulfuric acid is somewhat stronger.

The secondary ionization constant of sulfuric acid recorded by Latimer⁶ at 25° is 1.2×10^{-2} . The corresponding value for selenic acid has been determined as 1.0×10^{-2} . Sherrill and Lyons⁷ in comparing the activities of selenic and sulfuric acids concluded from their studies that in dilute solutions the acids were ionized to the same extent. In view of their results and the small differences indicated by our calculations, it appears that a reasonably accurate estimate of the secondary ionization constant of selenic acid has been accomplished.

(5) Harned and Hamer, *THIS JOURNAL*, **57**, 27 (1935).

(6) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., p. 316.

(7) Sherrill and Lyons, *THIS JOURNAL*, **54**, 979 (1932).

TABLE II

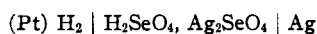
Molal	$K = 2 \times 10^{-2}$			$K = 1 \times 10^{-2}$			$K = 7 \times 10^{-3}$		
	α	β	$-E_0$	α	β	$-E_0$	α	β	$-E_0$
0.005016	0.728	0.872	0.1255	0.569	0.877	0.1296	0.473	0.880	0.1324
.01003	.653	.846	.1249	.486	.854	.1299	.395	.858	.1330
.02007	.564	.812	.1241	.396	.819	.1300	.313	.828	.1335
.05023	.442	.757	.1246	.286	.771	.1314	.217	.778	.1353
.1006	.359	.708	.1264	.219	.723	.1336	.163	.730	.1377

TABLE III

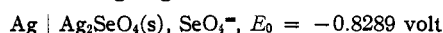
Molarity	Density 25/4	Molality	$E_{obs.}$	$-E_0'$	$\gamma_{H_2SO_4}^a$	$\gamma_{H_2SeO_4}$
0.00500	0.99761	0.005016	+0.07413	0.10814	0.637	0.574
.01000	.99823	.01003	.05540	.10218	.543	.492
.02000	.99933	.02007	.03690	.09496	.452	.408
.05000	1.0027	.05023	.01250	.08459	.338	.312
.1000	1.0083	.1006	-.00643	.07694	.263	.255

^a Interpolated from data of Harned and Hamer, THIS JOURNAL, 57, 27 (1935).

Molal Electrode Potential.—The molal electrode potential has been calculated from the extrapolated value -0.1295 volt, the potential referred to the quinhydrone electrode. The standard potential for the cell



is -0.8289 volt, assuming E_0 for quinhydrone -0.6994 volt. This yields for the standard potential of the $Ag-Ag_2SeO_4$ electrode at 25°



Summary

1. Electromotive forces of cells, $QH | H_2SeO_4,$

$Ag_2SeO_4 | Ag$, have been measured at 25° in concentrations of selenic acid ranging from 0.005 to 0.1 molar.

2. A new method for determining E_0 has been presented.

3. The secondary ionization constant for selenic acid has been approximated: 1×10^{-2} .

4. The standard electrode potential, $Ag | Ag_2SeO_4, SeO_4^{2-}$, has been determined: $E_0 = -0.8289$ volt.

5. The solubility of silver selenate in water and in selenic acid solutions has been determined.

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

Freezing Points of Binary Mixtures of Diphenylamine and Other Organic Compounds

BY O. A. NELSON AND L. E. SMITH

In the search for a material that would prevent wounds of livestock from becoming infested with larvae of the screwworm (*Cochlyomyia americana* C. and P.), Bushland¹ tested a number of organic compounds. Among the compounds that appeared promising when applied in the form of a dry powder or dust in small-scale field tests were diphenylamine, phenoxathiin (phenothioxin), *p*-nitrophenetole, 1-nitronaphthalene, dibenzofuran, and phenothiazine. With the exception of phenothiazine all of these compounds have a low melting point, and mixtures of them were found to liquefy or become pasty at room temperature.

While some of the compounds are more effective at lower concentrations, diphenylamine possesses

a number of desirable properties from a practical point of view, such as availability and cost. It was deemed desirable, therefore, to determine the freezing points of binary mixtures of diphenylamine with the other compounds.

Experimental

The compounds were purified as follows.

Diphenylamine.—Distilled under vacuum and then recrystallized three times from ligroin, b. p. $70-90^\circ$; m. p. $52.8-53.0^\circ$.

Phenoxathiin (commercial).—Distilled under reduced pressure and then recrystallized from ethyl alcohol; m. p. $55.3-55.5^\circ$.

***p*-Nitrophenetole (purified).**—Recrystallized twice from petroleum ether; b. p. $40-60^\circ$; m. p. $57.8-58^\circ$.

1-Nitronaphthalene (purified).—Recrystallized twice from ligroin; b. p. $70-90^\circ$; m. p. $55.8-56.0^\circ$.

(1) R. C. Bushland, *J. Econ. Ent.*, 33, 866, 869 (1940).