

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Silver-Silver Oxalate Electrode¹

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The silver-silver oxalate electrode has been used by Schafer,² Thomas and Fraser,³ and Haas and Jellinek⁴ for the determination of the solubility product of silver oxalate. Since the electromotive force measurements in these investigations were made only to the nearest millivolt and liquid junctions of uncertain effect were involved, a more precise determination of the electrode potential has been undertaken. It has been found that under suitable conditions silver oxalate electrodes can be reproduced to within a few hundredths of a millivolt. The electromotive forces of some cells of the type $H_2(Pt), H_2C_2O_4(m), Ag_2C_2O_4, Ag$ have been measured and the standard electrode potential and the solubility product of silver oxalate calculated. In addition the cell $Hg, Hg_2C_2O_4, H_2C_2O_4, Ag_2C_2O_4, Ag$ has been measured in order to compare the results of this investigation with those of Larson and Tomsicek⁵ for the mercurous oxalate electrode.

Materials and Apparatus.—Silver oxalate was prepared by slow addition of 0.2 *M* silver nitrate solution to an equal volume of 0.11 *M* oxalic acid solution, both of reagent grade. The precipitate was dissolved by ammonia in the presence of a little ammonium oxalate and reprecipitated by addition of oxalic acid. This was repeated at least once, except as otherwise noted.

Oxalic acid for use in the hydrogen-silver oxalate cells was recrystallized as described by Koltzoff and Sandell.⁶ Solutions were prepared and standardized by titration with a sodium hydroxide solution that had been standardized against Bureau of Standards potassium acid phthalate. The oxalic acid for the mercury-silver oxalate cells was twice recrystallized. The solutions for these cells were not standardized since the electromotive force should be independent of acid concentration.

Potassium tetroxalate was prepared from oxalic acid and potassium acid oxalate and recrystallized. A solution of known concentration was prepared by weight and also standardized by titration with standard sodium hydroxide solution. The two values agreed very well.

Hydrogen was prepared by electrolysis of 20% sodium hydroxide solution and passed over hot copper to remove traces of oxygen. Mercury was purified by prolonged treatment with mercurous nitrate solution. Mercury oxalate ($Hg_2C_2O_4$) was prepared by the slow addition of 0.1 *M* mer-

cury nitrate solution to 0.06 *M* potassium oxalate solution. It was preserved under 0.1 *M* oxalic acid solution.

The electromotive force measurements were made by means of a calibrated Type K potentiometer. The working standard cell was checked carefully against fifteen reference standards which have been used for a number of years in This Laboratory.⁷ Excellent agreement with some newly purchased cells together with excellent agreement among the fifteen standards indicated that there had been no drift in electromotive force large enough to be of significance in the present work.

Silver Oxalate Electrodes.—Difficulty in the reproduction of silver oxalate electrodes was encountered in this Laboratory by Bishop.⁸ He found that the electrodes could be reproduced fairly well when the electrolyte was oxalic acid, but not satisfactorily with an oxalate electrolyte. In the early part of this investigation the same trouble was experienced. At that time the silver electrodes were made by the thermal method from silver oxide.⁹ These silver electrodes were immersed in an oxalic acid solution saturated with silver oxalate and surrounded by excess solid. Two or more electrodes in the same solution usually disagreed by 0.1 to 0.3 mv. and agreement within 0.1 mv. was rare. Assuming that impurities were responsible, some electrodes were made by thermal decomposition of silver nitrate, with no improvement. When the silver electrodes were made by thermal decomposition of silver oxalate definite improvement was noticed.¹⁰ Recrystallized silver oxalate gave better electrodes than unrecrystallized, twice recrystallized still better, and thrice recrystallized silver oxalate gave electrodes agreeing in most cases within 0.01 mv. when in the same solution.

It seems probable that the impurity responsible for the trouble was a nitrogen compound. This impurity seems to be effective when present in very small quantity since three recrystallizations were necessary to eliminate its effect. The possibility of so little having a measurable effect is not unreasonable in view of the extreme precautions Carinody¹¹ found necessary for removal of traces of cyanide from electrolytic silver electrodes.

Cell: $H_2, H_2C_2O_4(m), Ag_2C_2O_4, Ag$.—With the improved technique, hydrogen-silver oxalate

(1) Part of the work reported here was carried out under Contract N6ori-107 with the Office of Naval Research.

(2) Schafer, *Z. anorg. Chem.*, **45**, 293 (1905).

(3) Thomas and Fraser, *J. Chem. Soc.*, **123**, 2973 (1923).

(4) Haas and Jellinek, *Z. physik. Chem.*, **162A**, 153 (1932).

(5) Larson and Tomsicek, *THIS JOURNAL*, **63**, 3329 (1941).

(6) Koltzoff and Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, p. 554.

(7) Ten of these cells were used by Clayton and Vosburgh, *THIS JOURNAL*, **59**, 2414 (1937).

(8) Bishop, Master's Thesis, Duke University.

(9) Harned, *THIS JOURNAL*, **51**, 416 (1929).

(10) When silver oxalate is heated to the point of decomposition it spatters more than silver oxide. It was found necessary to wipe spattered silver from the glass tube before results of the highest precision could be obtained.

(11) Carinody, *THIS JOURNAL*, **51**, 2902 (1929).

cells were prepared. The vessels were of Pyrex glass and of the form shown in Fig. 1. Two silver electrodes were placed in the compartment on the right and covered with a mixture of silver oxalate and oxalic acid solution. Agreement of the two was usually excellent. Some of the acid solution free from silver oxalate was placed in the left-hand compartment and the cell allowed to stand overnight before the hydrogen electrode was completed. The stopcock was kept closed except during measurements. A nitrogen-vacuum technique was used in the preparation of most of the silver oxalate electrodes. The agreement of the results with and without this technique indicated that it was not essential, but it did seem to hasten the attainment of equilibrium.

In Table I are given the electromotive forces at 25° of some cells made without exclusion of oxygen and with silver electrodes made from once recrystallized silver oxalate. Under these conditions the silver oxalate electrodes agreed within 0.1 mv.

TABLE I

CELL: $H_2(p = 1)(Pt)$, $H_2C_2O_4(m)$, $Ag_2C_2O_4(SATD.)$, Ag AT 25°

Molality, m	0.1002	0.0563	0.0282
No. of cells	2	2	2
E. m. f., international volts	0.67693	0.68731	0.70069
Deviation from mean	0.00003	0.00001	0.00006

In Table II are shown the electromotive forces of another group of cells at three to five temperatures between 22 and 40°. These cells were made by a different one of the authors, and the silver electrodes were made from thrice recrystallized silver oxalate. Electromotive force measurements were made over a period of an hour after attainment of equilibrium before the temperature was changed. After temperature changes the attainment of equilibrium was rapid, an hour being sufficient time. The first and last measurements were at 30° and gave values differing by not more than 0.08 mv. The results are given in Table II. Corrections to one atmosphere of hydrogen pressure have been made as well as corrections amounting to a few hundredths of a millivolt needed because the actual temperatures differed a little from the even temperatures of the Table. Average values for groups of cells are given; all the cells of each group were measured at 30°, but in most cases only part of them at any one other temperature. The maximum difference between

TABLE II

CELL: $H_2(p = 1)(Pt)$, $H_2C_2O_4(m)$, $Ag_2C_2O_4(SATD.)$, Ag

No. of cells	Molality, m	Electromotive force, volts				
		22°	25°	30°	35°	40°
1	0.07961	0.68092	0.68010	0.67923
4	.07918	0.68144	.68106	.68018	.67935	0.67847
4	.04028	.69384	.69345	.69286	.69216	.69141
3	.02000 ^a	.701687008669966

^a Potassium tetroxalate electrolyte.

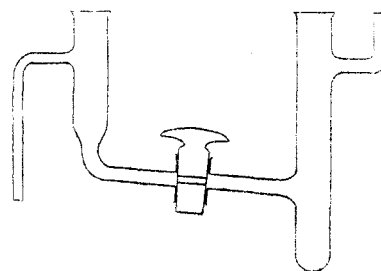


Fig. 1.—Cell vessel.

duplicate cells was 0.11 mv. and the average deviation from the average values given in Table II was 0.03 mv.

The approximate standard electromotive force, E^0 , was calculated by the equation

$$E^0 = E + \frac{RT}{2F} \ln f_{H^+}^2 f_{C_2O_4} m_{H^+}^2 m_{C_2O_4}$$

The ion molalities were calculated from the oxalic acid molalities by an approximation method using the first and second ionization constants of Darken¹² and Pinching and Bates,¹³ respectively, and activity coefficients calculated by the Debye-Hückel equation. Darken's ionization constant was determined only at 25°. When converted to a molality basis it is 0.0538. To obtain provisional values for 30 and 35°, it was assumed that the constant would vary with temperature in proportion to the corresponding values of Parton and Nicholson¹⁴ even though the value of the latter at 25° is not in agreement with that of Darken. In this way the provisional first constants 0.0647 at 30° and 0.0625 at 35° were calculated. In the application of the Debye-Hückel equation for the calculation of activity coefficients the values of the constants A' and B' given by Manov, Bates, Hamer and Acree¹⁵ and the effective ionic diameters calculated by Kielland¹⁶ were used.

The values for E^0 for each temperature were plotted against the ionic strength and straight lines drawn through the points were extrapolated to zero ionic strength as shown in Fig. 2 to give E^0 . It is to be noticed that the two sets of data at 25° gave excellent agreement. The values for E^0 so obtained are 0.4723 v. at 25°, 0.4679 v. at 30°, and 0.4624 v. at 35°, the first being more reliable than the other two. Multiplication of these values by 1.00033 converts them to absolute volts.¹⁷ The values in absolute volts are 0.4725, 0.4681, and 0.4626, respectively.

Comparison with the Mercury-Mercurous Oxalate Electrode.—Since Larson and Tom-sicek⁶ have determined the standard electrode potential of the mercurous oxalate electrode, meas-

(12) Darken, *THIS JOURNAL*, **68**, 1007 (1941).

(13) Pinching and Bates, *J. Research Natl. Bur. Standards*, **40**, 405 (1943).

(14) Parton and Nicholson, *Trans. Faraday Soc.*, **35**, 546 (1939).

(15) Manov, Bates, Hamer and Acree, *THIS JOURNAL*, **65**, 1766 (1943).

(16) Kielland, *ibid.*, **59**, 1675 (1937).

(17) Vinal, *J. Electrochem. Soc.*, **93**, 95 (1948).

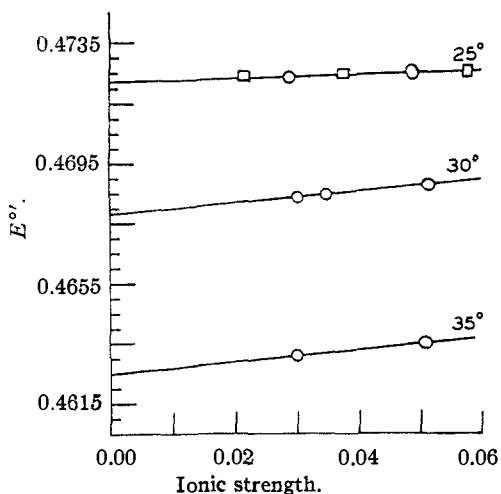


Fig. 2.—Extrapolation to zero ionic strength: squares represent data from Table I and circles data from Table II.

urement of the cell $\text{Hg}, \text{Hg}_2\text{C}_2\text{O}_4(\text{satd.}), \text{H}_2\text{C}_2\text{O}_4, \text{Ag}_2\text{C}_2\text{O}_4(\text{satd.}), \text{Ag}$ would allow comparison of the above results with theirs. This cell was made most successfully with the use of separate vessels for the two electrodes, since each electrode system must be kept free from contamination by material from the other. The mercurous oxalate electrodes were made by essentially the procedure of Larson and Tomsicek and with exclusion of air by use of nitrogen. The silver oxalate electrodes were made as described above. The cells were allowed to stand for twelve hours before measurements were begun, with diffusion between electrodes prevented by closed stopcocks. The electromotive forces were then measured at 25, 30 and 35°. The mercurous oxalate electrodes did not agree as well as silver oxalate electrodes. They usually agreed within 0.3 mv. at the beginning of the measurements and sometimes came to closer agreement during the measurements. The results are given in Table III. Larson and Tomsicek gave -0.4173 v. at 25° for the standard potential of the mercurous oxalate electrode. Combination with -0.4723 v. for the silver oxalate electrode gives 0.0550 v. as compared with 0.0579 v. from Table III.

TABLE III

Temperature, °C.	25	30	35
No. of cells	6	3	4
E. m. f., v., average	0.0579	0.0565	0.0551
Av. deviation	0.00005	0.00004	0.00006

The method used by Larson and Tomsicek for calculation of E^0 does not seem to take sufficient account of the secondary ionization of oxalic acid. Therefore, calculations from their data were made by the method used for the silver oxalate electrodes. From the data for the four lowest con-

centrations the value 0.4158 v. was thus obtained for E^0 at 25°. This leads to a calculated value of 0.0565 v. for the mercury-silver oxalate cell, which still differs by 1.4 mv. from the experimental value. It is probable that this difference is the result of lack of reproducibility of the mercurous oxalate electrode.

The Solubility Product of Silver Oxalate.—

From the standard electrode potentials of the silver oxalate electrode and the silver electrode the solubility product of silver oxalate can be calculated. From the data of Owen and Brinkley¹⁸ the values 0.7991, 0.7941 and 0.7892 international volts can be obtained for the silver electrode at 25, 30 and 35°, respectively. Using the values obtained in this investigation for the silver oxalate electrode, the solubility products ($K_{s.p.} = a_{\text{Ag}}^2 a_{\text{C}_2\text{O}_4}$) $8.8_8 \times 10^{-12}$, $1.4_1 \times 10^{-11}$ and $2.0_2 \times 10^{-11}$ at 25, 30 and 35°, respectively, are obtained. The last two are less certain than the value at 25° because of the uncertainty of the ionization constant of oxalic acid at 30 and 35°.

Scholder¹⁹ has determined solubility of silver oxalate by analysis of the saturated solution, finding 34.2 mg. per liter at 18°. From the above solubility products and activity coefficients calculated by the Debye-Hückel equation it can be calculated that the apparent solubility (neglecting any un-ionized or associated portion and also hydrolysis, which was estimated to be small) is 40.5 mg. per liter at 25°, 47.3 at 30° and 53.3 at 35°. The variation with temperature is nearly linear, and extrapolation to 18° gives 31.7 mg. per liter of ionized silver oxalate. On the basis of Scholder's value for the total solubility, silver oxalate appears to be about 93% dissociated into silver and oxalate ions. Scholder estimated 97% on the basis of conductivity measurements. In his calculation he took no account of the possibility of the association of silver and oxalate ions to give complex ions of a type that would contribute to the conductivity. Some association, perhaps of such a type, might be expected in view of the conclusions of MacDougal and Peterson²⁰ and Leden²¹ on the association of silver and acetate ions.

Summary

The silver-silver oxalate electrode has been measured against the hydrogen electrode and the standard electrode potential calculated at 25, 30 and 35°, the last two being somewhat provisional. The solubility product of silver oxalate has been calculated at these temperatures. The solubility calculated from the solubility product on the assumption of complete dissociation has been compared with data for the actual solubility.

Silver electrodes prepared by the thermal

(18) Owen and Brinkley, *THIS JOURNAL*, **60**, 2233 (1938).

(19) Scholder, *Ber.*, **60B**, 1510 (1927).

(20) MacDougal and Peterson, *J. Phys. Colloid Chem.*, **51**, 1346 (1947).

(21) Leden, *Svensk. Kem. Tid.*, **58**, 129 (1946).

method from purified silver oxalate were superior to electrodes prepared from silver oxide for making silver-silver oxalate electrodes.

The silver-silver oxalate and mercury-mercurous oxalate electrodes have been compared.

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The Solubility Relations of White Phosphorus

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White phosphorus, P_4 , has an extraordinarily high internal pressure, as measured in the liquid state, higher than iodine and sulfur, and so far exceeding the internal pressures of the usual non-polar solvents that its solutions show enormous deviations from Raoult's law, so great that even with carbon disulfide, one of its best solvents, unmixing to two liquid phases, one of them supercooled, occur below -6° . Its solutions, therefore, put maximum strain upon the theory of deviations from Raoult's law. The three solutions for which data existed were discussed by the senior author¹ in 1935 in the light of the theory of regular solutions. It was shown that the solubility of the liquid and solid phases can be correlated by aid of the equation for regular solutions

$$RT \ln (a_2/x_2) = v_2\phi_1^2(\delta_2 - \delta_1)^2 \quad (1)$$

where a_2 is the activity of the phosphorus referred to its own pure liquid; x_2 its mole fraction in saturated solution, v_2 its liquid molal volume, ϕ_1 the volume fraction of the solvent, and δ_2 and δ_1 the square roots of the internal pressures of the phosphorus and solvent, respectively, defined by $\delta_2 = \Delta E^V/v \approx a/v^2$, ΔE^V being the molal energy of vaporization of the pure liquid. We shall designate δ as the "solubility parameter." In a solution saturated with solid P_4 , $a_2 = a_2^s$, the activity of the solid form, which can be calculated from its melting point, $T_m = 317.4^\circ\text{K}$., its heat of fusion, ΔH^F , and the difference in heat capacity of the liquid and solid. Since the publication of the earlier paper we have secured more accurate values than we then had for the heat terms. Young and Hildebrand² obtained $\Delta H^F = 601$ cal./mole (earlier value, 625 cal./mole) and $c_p^s = 21.46 + 2.872 \times 10^{-2}t$ and $c_p = 24.47 - 9.521 \times 10^{-3}t - 3.927 \times 10^{-5}t^2$. These values give, for example, $a_2^s = 0.865$ at 0° and 0.941 at 25° . The remarkably small heat of fusion of P_4 is responsible for a correspondingly small temperature coefficient of solubility, and gives room for the appearance of a liquid-liquid curve with carbon sulfide beginning at -6° , far below the melting point of P_4 , 44.2° .

The present investigation was undertaken in

order to extend the study to additional common typical solvents; carbon tetrachloride, a symmetrical molecule, and normal heptane, a linear molecule.

We first experimented with a procedure designed to measure solubilities at different temperatures with a single filling of an apparatus consisting of two connecting bulbs with a cylindrical tube, or "tail" attached to one. The apparatus was charged with a solvent and an excess of phosphorus. After saturation, the solution was decanted into the other bulb and the phosphorus was melted and transferred to the tail tube when its volume could be measured. The difference between this and the total phosphorus present gave the amount dissolved. Unfortunately, the molten phosphorus had a tendency to stick to the glass, making it often impossible to collect for a volume measurement, therefore the method was abandoned in favor of an analytical method. We report only the values for acetone solutions although it should be remarked that the points we obtained for benzene solutions agreed with those of Christomanos within the errors evident for both sets. The method adopted consisted in saturating a solution with solid P_4 in an apparatus similar to that described by Negishi, Donally and Hildebrand,³ sealing off little bulbs of saturated solution and analyzing the contents. For liquid P_4 , the little bulbs were filled with both liquid phases and sealed off, the cloud points were determined and the contents analyzed. The method of analysis⁴ consisted in treating with a solution of copper nitrate, which gives copper phosphide and phosphorous acid, oxidizing to phosphoric acid with concentrated nitric acid saturated with bromine and determining as ammonium phosphomolybdate.⁵ Due attention was paid to careful manipulation and to the precautions necessary to prevent oxidation, to retard the formation of red phosphorus, to ensure saturation, and to secure reasonable accuracy of analysis. These details can be learned by private correspondence with either author by anyone interested.

The solvents were of high purity from commercial sources and boiled within narrow limits.

(1) (a) J. H. Hildebrand, *THIS JOURNAL*, **57**, 866 (1935); (b) "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1936, Chap. X, see also, (c) J. H. Hildebrand and T. F. Buehrer, *THIS JOURNAL*, **42**, 2213 (1920), for consolute temperatures with liquid phosphorus.

(2) F. E. Young and J. H. Hildebrand, *ibid.*, **64**, 839 (1942).

(3) G. R. Negishi, L. H. Donally and J. H. Hildebrand, *THIS JOURNAL*, **55**, 4793 (1933).

(4) E. H. Brown, H. H. Morgan and E. R. Rushton, *Ind. Eng. Chem., Anal. Ed.*, **9**, 524 (1937).

(5) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929.