[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Elimination of Liquid Junction Potentials. I. The Solubility Product of Silver Chloride from 5 to 45°

BY BENTON BROOKS OWEN

There are two types of liquid junctions commonly encountered in electrochemical studies: homoionic junctions formed by juxtaposition of solutions differing only in ionic concentrations, and heterionic junctions involving differences in ionic species. The potentials of heterionic junctions are not subject to simple thermodynamic definition,[1] which accounts for the necessity of their "elimination" when such junctions occur in cells used for thermodynamic purposes. This elimination has been attempted by both mathematical and physical means, but it always involves some extra-thermodynamic hypothesis which remains to be justified on empirical grounds. In the method described in this communication, the essential hypothesis is so simple in principle, and direct in operation, that the possibility of its adequate experimental verification is unusually high. A variety of data may be used in this connection, and will be presented in this paper, and elsewhere.[2]

Outline of the Method

The method involves the study of series of cells containing solutions of varying concentrations of the dissimilar ions giving rise to the junction potentials, but maintained at constant total ionic strength by the presence of an additional electrolyte which takes no part in the electrode reactions. Extrapolation to zero concentration of the dissimilar ions eliminates the junction potentials. The effect of the inert electrolyte can be eliminated by subsequent extrapolation to zero ionic strength. Somewhat similar schemes have been used, or implied, in the work of previous investigators,[3] but the simplicity of linear extrapolations was not obtained. This practical advantage of the present method is probably a consequence of the simple behavior of electrolytes in mixtures at constant ionic strength,[4] and the attainment of maximum symmetry in the electrode–electrolyte systems.

The determination of the solubility product of silver chloride was selected to illustrate the method because the results may be used as an independent check on the standard potential of the silver electrode.[2] The cells can be represented as follows

$$\mathrm{Ag, AgCl}\left|\begin{array}{l}\mathrm{KCl}(x)m\\ \mathrm{KNO_3}(1-x)m\end{array}\right| \mathrm{KNO_3}(m)\left|\begin{array}{l}\mathrm{AgNO_3}(x)m\\ \mathrm{KNO_3}(1-x)m\end{array}\right| \mathrm{AgCl, Ag^+}$$

The total ionic concentration in each solution is m, but a fraction, x, of this is composed of chloride ion in the left-hand compartment, and silver ion in the right. The e. m. f. of such a cell is given by

$$E = k \log a'_{\mathrm{Ag}}/a_{\mathrm{Ag}} \pm E_{\mathrm{j}} \qquad (1)$$

E_{j} is the sum of the unknown liquid junction potentials, $k = 0.00019844T$, and a'_{Ag} and a_{Ag} represent the activities of the silver ion in the right-hand and left-hand solutions, respectively. The solubility product

$$K = a_{\mathrm{Ag}}a_{\mathrm{Cl}} \qquad (2)$$

can be used to eliminate a_{Ag} in the left-hand solution, and equation (1) becomes

$$E - k \log a'_{\mathrm{Ag}}a_{\mathrm{Cl}} = - k \log K \pm E_{\mathrm{j}} \qquad (3)$$

The introduction of the concentrations, xm, and the individual ionic activity coefficients leads to

$$E - 2k \log xm = -k \log K + k \log \gamma_{\mathrm{Cl}}\gamma'_{\mathrm{Ag}} \pm E_{\mathrm{j}} \qquad (4)$$

The last two terms of this equation are not *independently* defined by thermodynamics alone, and this fact constitutes the essential limitation on the use of cells with heterionic liquid junctions.

Inspection of equation (4), and consideration of the symmetry of the electrochemical system it represents, shows that if m is held constant while x is varied, extrapolation to $x = 0$ must yield

$$[E - 2k \log (xm)]_{x=0} = -k \log K + [k \log \gamma_{\mathrm{Cl}}\gamma'_{\mathrm{Ag}}]_{x=0} \qquad (5)$$

because E_{j} becomes zero under this condition. Since it is no longer necessary to retain the prime on γ'_{Ag} when $x = 0$, the last term is amenable to thermodynamic treatment, and can be expressed as a function of m similar to that for any uni-univalent strong electrolyte.

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[1] Harned, *J. Phys. Chem.*, **29**, 433 (1926); Taylor, *ibid.*, **31**, 1478 (1927); Guggenheim, *ibid.*, **34**, 1758 (1930); **33**, 842 (1929).

[2] Owen and Brinkley, THIS JOURNAL, **60**, 2233 (1938).

[3] Linhart, THIS JOURNAL, **38**, 2356 (1916); Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 418; Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928); Popoff and Kunz, *ibid.*, **51**, 382 (1929).

[4] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); Harned, THIS JOURNAL, **48**, 326 (1926).

To allow compact graphical representation of the experimental results, the term $2k\alpha\sqrt{m}$ will be added to both sides of equation (5) (α = Debye–Hückel limiting slope). Since this term is not a function of x, the extrapolation function may be rewritten as follows

$$[E - 2k \log (xm) + 2k\alpha\sqrt{m}]_{x=0} = -k \log K + [k \log \gamma_{\mathrm{Cl}}\, \gamma_{\mathrm{Ag}} + 2k\alpha\sqrt{m}]_{x=0} \quad (6)$$

The determination of $[E - 2k \log (xm) + 2k\alpha\sqrt{m}]_{x=0}$ by extrapolation at various values of m is shown in Fig. 2. The determination of $-k \log K$ by subsequent extrapolation of these intercepts to $m = 0$ is given in Fig. 3. This final step is equivalent to the familiar Hitchcock[5] extrapolation.

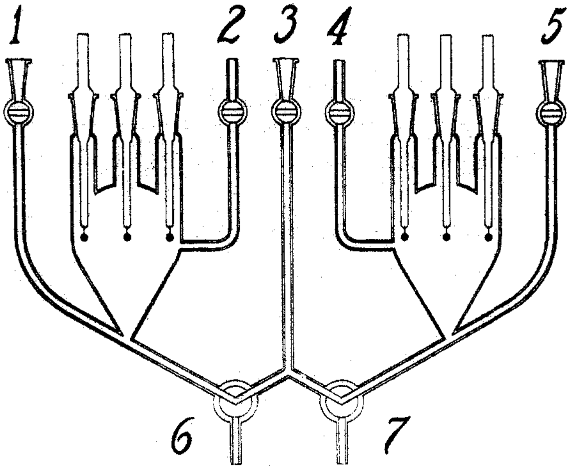

Fig. 1.—Cell assembly.

Materials and Technique

Water from an electrically heated Barnstead still was used in the purification of chemicals, and the preparation of stock solutions. "Jena" sintered glass mats were used in all filtrations. Concentrations of stock solutions were based upon weights of water and dry salts. Vacuum corrections were applied throughout.

The silver nitrate was Merck "Reagent" grade, recrystallized once, and air dried at 85 to 95° for twenty-four hours. Just before use, it was heated for five hours to 100° under reduced pressure (<1 mm.). The 0.05 molal stock solution was shielded carefully from light, and protected from contact with reducing substances and laboratory fumes.

The potassium chloride was Baker "Analyzed" grade, recrystallized twice. It was dried for two days at 95° followed by three days at 115°. The potassium nitrate was from the same source as the chloride, and received the same treatment.

The electrodes were prepared by decomposition of well-washed silver oxide at 450°, followed by electrolysis (series) in 0.5 m hydrochloric acid solutions at 3 m. a. for two or three hours. They were shielded from strong light at all times. An effort was made to have them very similar to those used by Harned and Ehlers,[6] because the standard potentials reported by them are to be combined with the present results to obtain the standard potential of the silver electrode.

The cell construction is illustrated in Fig. 1. The inlets numbered 1 and 5 are connected to flasks containing the air-free chloride and silver solutions, and number 3 is connected to the pure potassium nitrate junction solution. All connections which come in contact with cell solutions are ground glass joints, lightly greased with vaseline which had been boiled with silver nitrate solution, and subjected to numerous rinsings with hot water. The cells are evacuated through the lower outlets to stopcocks 6 and 7. Then nitrogen, freed of oxygen by copper turnings at 700°, is introduced through 2 and 4. By successive evacuation and admission of nitrogen, the air is completely displaced from the cells and connections to solution flasks. After a final evacuation, cell solutions are admitted, under slight pressure, through 1 and 5 until the pressure inside exceeds the atmospheric. The electrodes are lifted slightly, one at a time, to allow the ground glass joints to be rinsed by overflowing cell solutions. After half an hour the cells are emptied through 6 and 7, and fresh solutions admitted. About twelve hours later, this rinsing process is twice repeated before e. m. f. readings are begun at 5°. Since equilibrium is slowly attained at this temperature, the readings usually extended over two or three hours. At higher temperatures one hour is quite sufficient. The temperature of the water-bath varied by ± 0.02° at 5 and 15°, but was controlled within 0.01° at the higher temperatures.

After each reading, the junctions (3-mm. bore of stopcocks) were flushed through the outlets of 6 and 7, but as an additional precaution against contamination by diffusion, or otherwise, the cells and ground glass joints were rinsed several times with fresh solutions during the course of the measurements, usually at 25 and 45°.

Experimental Results and Discussion

The experimental data are collected in Table I. The results of all measurements are included except two early ones in which the product xm was 0.002, or less. Erratic results were obtained with silver ion concentrations of this order unless the electrodes were rinsed thoroughly with the solution, and extra time allowed for equilibrium at the lower temperatures. The recorded values of E are the means of pair-wise combinations of the six electrodes. These were ordinarily concordant well within 0.1 mv. The over-all reproducibility of a cell was also of this order at the higher concentrations, but irregularities as high as 0.1 and 0.15 mv. were sometimes observed at m = 0.02 and m = 0.01, respectively. The effects of these irregularities can be seen in Fig. 2, where the radii of the plotted circles are 0.1 mv.

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[5] Hitchcock, This Journal, **50**, 2076 (1928).

[6] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

The plots for all values of m and T show that a linear extrapolation is indicated on purely empirical grounds. Because of experimental difficulties when $xm < 0.002$, a rather long extrapolation is required at low values of m, but when $m = 0.05$ the linearity of the extrapolation function seems definitely established down to $x = 0.05$. These observations are corroborated by analogous plots from a study of buffer solutions.[2] This is an important point because *the possibility of this extrapolation, and its linearity* (or form ultimately arrived at by further study) *constitute the extrathermodynamic hypothesis upon which this method of eliminating liquid junction potentials is based.*

The intercepts obtained from the extrapolations in Fig. 2 are recorded in Table I to the nearest 0.05 mv.

TABLE I

OBSERVED ELECTROMOTIVE FORCES AND INTERCEPTS FROM THE FIRST EXTRAPOLATION (FIG. 2)

x	t° 5°	15°	25°	35°	45°
			$m = 0.05$		
0.4	0.38790	0.37623	0.36503	0.35455	0.34445
.2	.35432	.34166	.32935	.31771	.30635
.1	.32105	.30720	.29370	.28086	.26836
.05	.28774	.27272	.25807	.24408	.23036
Int.	.58700	.58295	.57930	.57635	.57375
			$m = 0.03$		
0.5	0.37641	0.36436	0.35285	0.34185	0.33129
.3	.35153	.33868	.32632	.31455	.30318
.2	.33205	.31841	.30543	.29289	.28082
.1	.29854	.28386	.26962	.25592	.24273
Int.	.58620	.58200	.57835	.57525	.57270
			$m = 0.02$		
0.6	0.36739	0.35492	0.34302	0.33170	0.32091
.4	.34742	.33440	.32185	.30989	.29825
.3	.33345	.32000	.30695	.29436	.28238
.2	.31371	.29946	.28593	.27286	.26017
Int.	.58560	.58140	.57780	.57465	.57200
			$m = 0.01$		
0.6	0.33592	0.32239	0.30930	0.29683	0.28482
.4	.31610	.30203	.28829	.27520	.26256
.3	.30206	.28725	.27318	.25965	.24655
.2	.28249	.26708	.25226	.23806	.22431
Int.	.58535	.58100	.57730	.57420	.57150

Figure 3 shows the plots of these intercepts against m, which according to equation (6) permits the evaluation of $-k \log K$ by extrapolation to $m = 0$. These extrapolations are also linear within the estimated uncertainty of ± 0.1 mv. for the plotted points, which are drawn with 0.1-mv. radii. It will be noted that the straight lines intersect all the points except two at 5° where experimental difficulties were high, and the accuracy correspondingly low. It appears from the plots that the purely extrapolative uncertainty in $-k \log K$ might exceed 0.2 mv. at 5°, but not at the other temperatures.

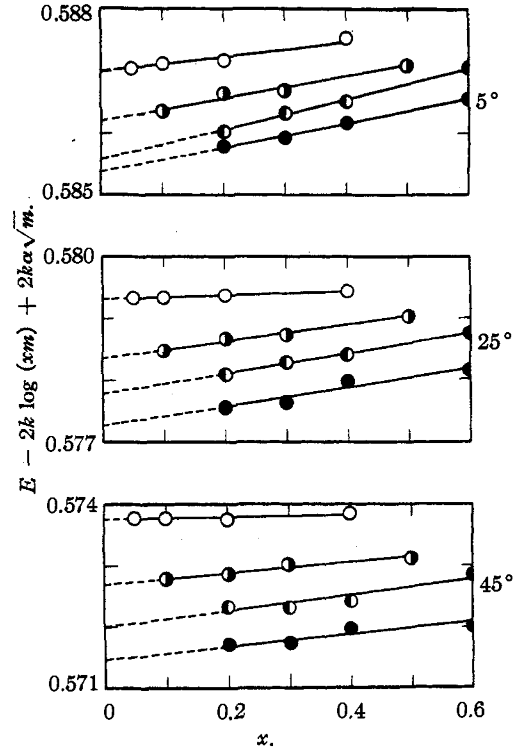

Fig. 2.—Elimination of E_j by extrapolation; ○, $m = 0.05$; ◑, $m = 0.03$; ◐, $m = 0.02$; ●, $m = 0.01$.

The intercepts, $-k \log K$, from the extrapolations in Fig. 3 are recorded in the second column of Table II to the nearest 0.1 mv. Their variation with temperature is satisfactorily expressed by

$$k \log K = -0.5768 + 345\,(t - 25)\,10^{-6} - 25\,(t - 25)^2 10^{-7} \qquad (7)$$

or

$$\log K = 9.2496 - 4544.4/T - 0.012598T \qquad (8)$$

Values calculated by these equations are given in the third and fourth columns, respectively. The solubility of silver chloride in pure water was calculated by the equation

$$\log m_0 = {}^1/_2 \log K + \alpha\sqrt{c_0} \qquad (9)$$

which assumes the applicability of the Debye–Hückel limiting law at such high dilutions. The solubility, m_0, is in moles per kilogram of water, and c_0 is the corresponding value in moles per liter of solution.

The absolute accuracy of the results depends mainly upon three factors. These are the accuracy with which the concentrations are known,

TABLE II

INTERCEPTS FROM SECOND EXTRAPOLATION (FIG. 3) AND SOLUBILITY OF SILVER CHLORIDE

$t°$	$-k \log K$ Int.	$-k \log K$ Eq. (7)	$-\log K$ Eq. (8)	Solubility $m_0 \times 10^5$	Solubility $c_0 \times 10^5$
5	0.5848	0.5847	10.5950	0.505	0.505
15	.5805	.5805	10.1536	0.841	0.840
25	.5768	.5768	9.7508	1.338	1.334
35	.5736	.5736	9.3818	2.048	2.036
45	.5709	.5709	9.0440	3.026	2.997

the physical state (and purity) of the silver chloride, and the validity of the extension of the plots in Fig. 2. The uncertainties in the concentrations could hardly cause an error greater than 0.1 mv.

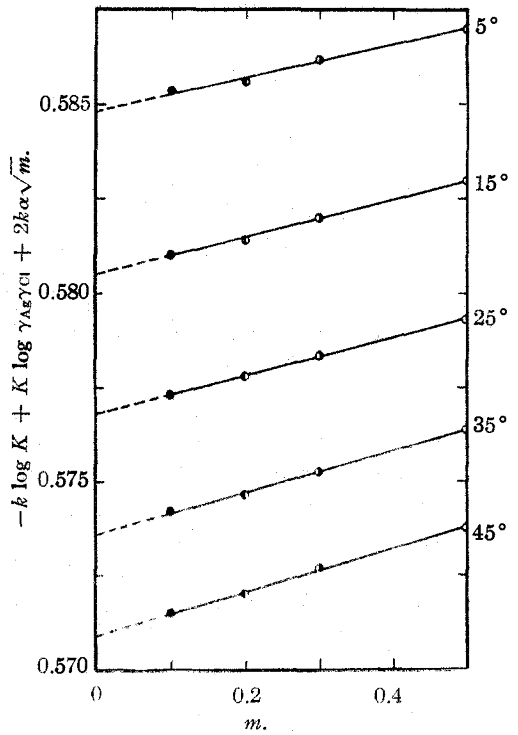

Fig. 3.—Evaluation of $-k \log K$ by extrapolation to infinite dilution.

The preparation of the electrolytic silver chloride has been described in the foregoing section. A review[7] of the determinations of the standard potential of the electrolytic silver–silver chloride electrodes shows that the results of the several independent investigators agree within 0.1 to 0.4 mv. This may be taken as indicative of high thermodynamic reproducibility of electrolytic silver chloride, because this agreement must also include uncertainties in analysis and extrapolation, and possible differences in the physical state and purity of the metallic silver. In the present solubility product determination the thermodynamic properties of the metallic silver cancel in the operation of the cell, so long as they are the same in all of the electrodes. It was to ensure this identity that all six of the electrodes used in any cell were electrolyzed in series, without distinction as to which were to be used in the silver and which in the chloride solutions. It is therefore probable that the absolute accuracy of the final results is of the same order as that of the two extrapolations. This seems to be better than ±0.2 mv. on the basis of the plots as drawn, but if linearity is not strictly maintained, then, in the absence of further data at high dilutions, the uncertainty might easily be twice as great.

Although comparison with values previously recorded in the literature constitutes a satisfactory check upon the essential correctness of the results, it does not furnish a dependable criterion of their absolute accuracy, because the discordance among such values appears to be much greater than the combined experimental errors of the various measurements. Variability in the physical condition of precipitated silver chloride is responsible for most of the difficulty. There are several papers which review[8,9] the literature, and discuss possible explanations of the discrepancies, so this matter need not be elaborated. Three previous investigations cover a considerable temperature range. Kohlrausch[10] determined the solubility of well-aged, precipitated silver chloride conductometrically from 1.55 to 34.12°. His values are about 3% lower than the present results. The results of the electrometric titrations of Hahn and Klockmann[11] (15 to 40°) are in good agreement, while the nephelometric values (0 to 50°) of Dave and Krishnaswami[9] are 3 to 4% higher. This is representative of the agreement to be expected when precipitated silver chloride is involved. Accordingly the score of determinations at single temperatures will not be discussed further than to consider one particular experiment in which electrolytic silver chloride was employed.

Brown and MacInnes[12] found that the solubility of silver chloride is 1.570×10^{-5} mole per liter in a 0.0286 normal solution of potassium nitrate at 25°. Although precipitated silver chlo-

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[7] Prentiss and Scatchard, *Chem. Rev.*, **13**, 139 (1933).

[8] Glowczynski, *Kolloidchem. Beihefte*, **6**, 147 (1914).

[9] Dave and Krishnaswami, *J. Indian Inst. Sci.*, **16**, 153 (1933); *cf.* also Johnson and Hulett, THIS JOURNAL, **55**, 2258 (1933).

[10] Kohlrausch, *Z. physik. Chem.*, **64**, 129 (1908).

[11] Hahn and Klockmann, *ibid.*, **A146**, 394 (1930).

[12] Brown and MacInnes, THIS JOURNAL, **57**, 459 (1935).

ride was formed during the course of their electrometric titrations, the electrodes were coated with the electrolytic variety. If the concentration of silver chloride in the immediate neighborhood of the electrodes was successfully controlled by the electrolytic variety, the results should be comparable with those of the present research. Interpolation based on Fig. 3 leads to 1.577×10^{-5}, in excellent agreement with the above, but the value for the solubility in pure water reported by Brown and MacInnes is 1.314×10^{-5}, which is 1.5% lower than that given in Table III. The discrepancy is caused by the difference between the activity coefficients used by Brown and MacInnes[13] and those which may be obtained from consideration of equation (6) and Fig. 3. The slope of the 25° plot in Fig. 3 is 0.051, which leads to the expression

$$\log \gamma = -0.506\sqrt{\mu} + 0.43\mu \qquad (10)$$

for the activity coefficient of silver chloride. On the basis of this equation, the result of Brown and MacInnes would be increased to 1.332×10^{-5}.

Although this concordance leaves little to be desired, it should be borne in mind that two electrometric determinations of the solubility of identical samples would not be strictly comparable unless the extra-thermodynamic hypotheses used to eliminate liquid junction potentials could be verified experimentally, or shown to be equivalent. It therefore seems necessary to reserve final judgment upon the absolute accuracy of the results reported in this paper until the reliability of the hypothesis represented by Fig. 2 has been established, or discredited, by further experimental work. Some familiar indirect checks upon the accuracy of solubilities and their temperature coefficients will be considered in a later communication.[2]

Summary

A method is proposed by which heterionic liquid junction potentials may be eliminated by extrapolation. Experimental data are presented which indicate that the junction extrapolation is linear as a first approximation.

The method is applied to the determination of the solubility product of electrolytic silver chloride in water at 5, 15, 25, 35, and 45°.

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[13] Values obtained by Neuman [THIS JOURNAL, 54, 2195 (1932)] from solubility measurements in which presence of precipitated silver chloride was determined by Tyndall beam.

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Elimination of Liquid Junction Potentials. II. The Standard Electrode Potential of Silver from 5 to 45°, and Related Thermodynamic Quantities

BY BENTON BROOKS OWEN AND STUART R. BRINKLEY, JR.[1]

In the first paper of this series,[2] an extrapolation method for eliminating heterionic liquid junction potentials was described, and employed in a determination of the solubility product of silver chloride. It was considered desirable to test the validity and generality of the method by applying it to a comparison of the silver and hydrogen electrodes in buffer solutions. The results of these two investigations are interrelated through the potential of the silver–silver chloride electrode, and can be used to check one another. By the use of identical measuring equipment and technique, and consistent supplementary data, the concordance of these results becomes a necessary, but not a sufficient, condition to the validity of the extra-thermodynamic extrapolation upon which the method is based. Complete demonstration of its validity is contingent upon further direct investigation of the extrapolation, and comparison of its consequences with thermodynamic data obtained without recourse to liquid junctions. Several such comparisons can be made with the data at hand, and others will be available in the future.

Buffer solutions were used to depress and stabilize the hydrogen ion concentration, so that transfer of electricity across the liquid junction would be accomplished, for the most part, by ions other than hydrogen. The cell may be represented as follows

$$H_2 \mid HAc_{(m)}, NaAc_{(m)} \mid HAc_{(m)}, NaAc_{(m-mx)}, AgAc_{(mx)} \mid Ag^+$$

The ionic strength, $\mu \simeq m$, is practically identical

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[1] This communication embodies part of the experimental material to be presented by Stuart R. Brinkley, Jr., to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Owen, THIS JOURNAL, 60, 2229 (1938).