[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA, AND THE COLLEGE OF ST. THOMAS]

The Temperature Coefficient of the Standard Silver Electrode. The Entropy of Silver Ion

BY J. J. LINGANE AND W. D. LARSON

The only direct measurement of the temperature coefficient of the standard electrode e. m. f. of silver reported in the literature is that of Skotnický,[1] who measured the temperature coefficient of various half-cells against reference electrodes maintained at constant temperature. This method has the disadvantage of involving a small thermal e. m. f. in the bridge solution, as well as correction for the change in activity of the electrolyte with temperature.

In the present study the temperature coefficient of the standard silver electrode, that is, the temperature coefficient of the hypothetical cell H_2 (1 atm.) | H^+ (a = 1) || Ag^+ (a = 1) | Ag, has been determined by measuring the temperature coefficient of cells of the type

$$\mathrm{Pt} \mid \mathrm{Quinhydrone(s)},\ \mathrm{HClO_4}(C_1) \mid \mathrm{HClO_4}(C_1),\ \mathrm{AgNO_3}(C_2) \mid \mathrm{Ag} \quad \text{(I)}$$

The concentration of perchloric (or nitric) acid was the same in both half-cells and was much larger than the concentration of silver nitrate in the silver half-cell. Under these conditions the liquid junction e. m. f. was negligibly small, and the temperature coefficient between 19 and 32° was practically linear.

Experimental

The cell consisted of two half-cell vessels of the ordinary type with goose-neck side tubes, which dipped into an intermediate vessel containing acid of the same concentration as in the cell. The measurements were made in the presence of air, with the entire cell in a water thermostat. The temperature control was ±0.02°. Temperatures were read with a carefully calibrated 0.1° thermometer. The potentiometer system allowed readings to ±0.01 mv.

The cell solutions were prepared from reagent quality materials, and were standardized carefully by the usual methods. Concentrations were known to ±0.1%.

Two types of silver electrodes were used. The first type were silver–silver chloride electrodes prepared according to the directions of Carmody.[2] The second type was prepared by plating platinum electrodes from a slightly acid 0.1 N silver nitrate solution with very low current density. There was no significant difference in the temperature coefficients of these two types of electrodes.

Bright platinum wire electrodes were used in the quinhydrone half-cells, which contained an excess of solid quinhydrone.

Readings were taken every ten or fifteen minutes at each temperature until the e. m. f. remained constant to within 0.05 mv. for at least thirty minutes. The cells attained constant e. m. f. within a few minutes after a change in temperature, and remained constant for several hours. The data and results are given in Table I.

TABLE I
THE TEMPERATURE COEFFICIENT OF CELL I WITH VARIOUS CONCENTRATIONS OF ELECTROLYTE

	Acid, molar	$AgNO_3$, molar	t, °C.	$E_{\text{obsd.}}$, mv.	$\left(\frac{dE_{\text{obsd.}}}{dT}\right)_{298}$, mv. deg.$^{-1}$	$\left(\frac{dE^0_{\text{Ag}}}{dT}\right)_{298}$, mv. deg.$^{-1}$
1	0.1227[a]	0.00100	19.23	−19.46[c]		
			25.00	−23.17	−0.642	+0.964
			25.42	−23.44		
			31.38	−27.28		
2	.1092[b]	.00100	22.10	−19.06[d]		
			25.00	−20.83	− .633	.965
			31.25	−24.85		
3	.1005[b]	.00100	20.80	−16.12[d]		
			25.00	−18.80	− .634	.973
			30.38	−22.20		
4	.0503[b]	.000500	21.85	−16.22[d]		
			25.00	−18.20	− .629	.969
			31.15	−22.07		
5	.0503[b]	.000500	21.85	−16.20[c]		
			25.00	−18.22	− .630	.970
			31.15	−22.06		
6	.0402[b]	.000500	21.00	−10.41[c]		
			25.00	−12.85	− .602	.960
			29.30	−15.40		
					Av.	+0.967 ±0.004

[a] Nitric acid. [b] Perchloric acid. [c] Silver electrodes from silver nitrate. [d] Silver–silver chloride electrodes.

In addition to the data given in this table, we measured several cells with higher acid concentrations. These measurements are not given in the table because when the acid concentration was greater than 0.2 M the measurements were only reproducible to two or three-tenths of a millivolt. This poor reproducibility may have been due to a slight attack of the silver electrodes in the stronger acid.

Calculations

In the following computations we distinguish between *electromotive force* and *electrode potential* as recommended by MacDougall.[3] We use the sign conventions of the same author, which are in accord with common American usage.

Neglecting the very small liquid junction e. m. f., the e. m. f. of Cell I is given by

$$E = E^0_{\text{QH.}} - E^0_{\text{Ag}} - \frac{RT}{F} \ln \frac{C_{\text{H}^+}\gamma_{\text{H}^+}}{C_{\text{Ag}^+}\gamma_{\text{Ag}^+}} \qquad (1)$$

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(1) J. Skotnický, *Coll. Czech. Chem. Comm.*, **8**, 498 (1936).

(2) W. R. Carmody, THIS JOURNAL, **54**, 188 (1932).

(3) F. H. MacDougall, "Physical Chemistry," The Macmillan Co., New York, 1936, Chap. XVIII.

In this equation E^0_{QH} is the standard e. m. f. of the quinhydrone electrode, that is, the e. m. f. of the cell Pt/Quinhydrone(s), H^+ (a = 1) | H_2 (1 atm.), and E^0_{Ag} is the standard e. m. f. of the silver electrode, that is, the e. m. f. of the cell Ag | Ag^+ (a = 1) || H^+ (a = 1) | H_2 (1 atm.).

Differentiating eq. (1) with respect to temperature, and rearranging, we find

$$\frac{dE^0_{Ag}}{dT} = \frac{dE^0_{QH.}}{dT} - \frac{dE}{dT} - \frac{R}{F}\ln\frac{C_{H^+}\gamma_{H^+}}{C_{Ag^+}\gamma_{Ag^+}} - \frac{RT}{F}\left(d\ln\frac{C_{H^+}\gamma_{H^+}}{C_{Ag^+}\gamma_{Ag^+}}\Big/dT\right) \qquad (2)$$

We may assume without appreciable error, since the coefficients of expansion of the solutions in the two halves of Cell I must be very nearly equal, that $d\ln\frac{C_{H^+}}{C_{Ag^+}}\Big/dT$ is zero. Since the ionic strengths of the solutions in the two half-cells are practically the same, and since hydrogen and silver ions are both univalent, it is reasonable to assume that $\gamma_{H^+} = \gamma_{Ag^+}$ and hence that $d\ln\frac{\gamma_{H^+}}{\gamma_{Ag^+}}\Big/dT$ is zero. Using these assumptions eq. (2) becomes simply

$$\left(\frac{dE^0_{Ag}}{dT}\right)_{298} = \left(\frac{dE^0_{QH.}}{dT}\right)_{298} - \left(\frac{dE}{dT}\right)_{298} - 0.1985\log\frac{C_{H^+}}{C_{Ag^+}} \qquad (3)$$

On the basis of the convention that the temperature coefficient of the hydrogen electrode is zero, dE^0_{Ag}/dT is the temperature coefficient in mv. deg.$^{-1}$ of the cell Ag | Ag^+(a = 1) || H^+(a = 1) | H_2(1 atm.), $dE^0_{QH.}/dT$ is the temperature coefficient of the cell Pt | Quinhydrone(s), H^+ (a = 1) | H_2 (1 atm.), and dE/dT is the observed temperature coefficient of Cell I.

According to the precise measurements of Harned and Wright[4] $dE^0_{QH.}d/T$ is equal to +0.736 mv. deg.$^{-1}$ at 25°. This value and the observed values of dE/dT have been used in eq. (3) to compute the values of dE^0_{Ag}/dT given in the last column of Table I.

Discussion

From Skotnický's measurements[1] we find that dE^0_{Ag}/dT is equal to +0.978 mv. deg.$^{-1}$ at 25°, which is in reasonably good agreement with the value +0.967 mv. deg.$^{-1}$ found in this study. Skotnický's value is based upon direct measurements of the individual temperature coefficients of the hydrogen and silver electrodes, and it involves corrections for the change in activity of the electrolytes with temperature, as well as small errors due to the thermal e. m. f. in the bridge solutions.

We may compute dE^0_{Ag}/dT indirectly from the measurements of the temperature coefficient of solubility of silver chloride given by Kohlrausch,[5] the temperature coefficient of the standard e. m. f. of the silver–silver chloride electrode given by Harned and Wright,[4] and the activity product of silver chloride given by Brown and MacInnes.[6]

The relation between the standard e. m. f. of the silver–silver chloride electrode E^0_{AgCl}, the standard e. m. f. of the silver electrode E^0_{Ag}, and the activity product, K, of silver chloride is given by

$$E^0_{Ag} = E^0_{AgCl} + \frac{RT}{F}\ln K \qquad (4)$$

Differentiating this equation, and introducing the numerical values of R, F, and T, we find at 25°

$$\left(\frac{dE^0_{Ag}}{dT}\right)_{298} = \left(\frac{dE^0_{AgCl}}{dT}\right)_{298} + 0.1985\log K + 59.15\left(\frac{d\log K}{dT}\right)_{298} \qquad (5)$$

From the conductance data of Kohlrausch[5] $d\log K/dT$ at 25° is +0.0385 deg.$^{-1}$. By direct calorimetric measurements Lange and Fuoss[7] found that the heat of solution of silver chloride was 15.98 kcal. mol.$^{-1}$ at 22.5°, which gives a value for $d\log K/dT$ of 0.0400 deg.$^{-1}$ at 22.5°. Kohlrausch's value at 22.5° is 0.0398 deg.$^{-1}$ which is in good agreement with the value of Lange and Fuoss.

According to Brown and MacInnes[6] K is 1.721 × 10^{-10} at 25°, and from the measurements of Harned and Wright[4] dE^0_{AgCl}/dT is +0.645 mv. deg.$^{-1}$ at 25°. Substituting these data, and Kohlrausch's value for $d\log K/dT$ at 25° into eq. 5, we obtain a value for $(dE^0_{Ag}/dT)_{298}$ of +0.98 ± 0.01 mv. deg.$^{-1}$, which is in good agreement with Skotnický's and our values.

The Entropy of Silver Ion

From the value of dE^0_{Ag}/dT found in this study we find for the standard change in entropy of the reaction $Ag(s) + H^+ (a=1) = Ag^+ (a=1) + {}^1/_2 H_2$ (1 atm.)

$$\Delta S^0_{298} = F\left(\frac{dE^0_{Ag}}{dT}\right)_{298} = 23{,}070 \times 0.000967 = 22.3 \text{ cal. deg.}^{-1}\text{ mol.}^{-1} \qquad (6)$$

ΔS^0_{298} is also given by

$$\Delta S^0_{298} = S^0_{Ag^+} + {}^1/_2 S^0_{H_2} - S^0_{Ag} - S^0_{H^+} \qquad (7)$$

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[4] H. S. Harned and D. D. Wright, This Journal, **55**, 4849 (1933).

[5] F. Kohlrausch, *Z. physik. Chem.*, **64**, 168 (1908).

[6] A. S. Brown and D. A. MacInnes, This Journal, **57**, 459 (1935).

[7] E. Lange and R. M. Fuoss, *Z. physik. Chem.*, **125**, 431 (1927).

Using the convention that $S^0_{H^+}$ is zero, and the values for S^0_{Ag} (10.0 e. u.) and $S^0_{H_2}$ (31.2 e. u.) given by Latimer, Schutz, and Hicks,[8] we find from equations (6) and (7) that $S^0_{Ag^+}$ is equal to 16.7 cal. deg.$^{-1}$ mol.$^{-1}$ at 25°.

From Skotnický's value for dE^0_{Ag}/dT, as well as from the value we have computed from the data of Kohlrausch, Brown, and MacInnes, and Harned and Wright, we find that ΔS^0_{298} is 22.6 e. u. and that $S^0_{Ag^+}$ is 17.0 e. u. at 25°. These values are in agreement with the values found in this study.

On the other hand, Latimer, Schutz, and Hicks[8] give the four values 18.5, 18.4, 18.4, and 18.3 e. u. for $S^0_{Ag^+}$ at 25°. However, in computing the first two of these values they used the heat of solution of silver chloride at 22.5° given by Lange and Fuoss,[7] and they apparently assumed that this quantity had the same value at 25 as at 22.5°. It may be shown readily from the data given by Kohlrausch[5] (variation of the heat of solution of silver chloride with temperature) that this assumption leads to a calculated value of $S^0_{Ag^+}$ that is too high by about 1.2 e. u. If this correction is applied, the first two values given by Latimer, Schutz, and Hicks become 17.3 and 17.2 e. u., which are in fair agreement with the values we have computed.

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Summary

1. The temperature coefficient of the silver electrode was determined by measuring the temperature coefficients of cells of the type Pt/Quinhydrone(s), $HClO_4(C_1)/HClO_4(C_1)$, $AgNO_3(C_2)$/Ag, in which C_1 was much larger than C_2. The temperature coefficient of the standard electrode e. m. f. of silver, *i. e.*, the temperature coefficient of the cell Ag/Ag^+ (a = 1) || H^+ (a = 1)/H_2 (1 atm.), is +0.967 ± 0.004 mv. deg.$^{-1}$ at 25°.

2. The standard entropy of silver ion computed from this temperature coefficient is 16.7 cal. deg.$^{-1}$ mol.$^{-1}$ at 25°.

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(8) W. M. Latimer, P. W. Schutz, and J. F. Hicks, Jr., *J. Chem. Phys.*, **2**, 82 (1934).

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Potassium Chloride–Lithium Chloride Mixtures at Constant Total Molalities[1]

BY BENTON BROOKS OWEN AND THEODORE F. COOKE, JR.

If the total ionic strength of a solution of mixed electrolytes is maintained constant and the relative concentration varied, the activity relationships of the various components are governed by specific ionic parameters and their interaction. The determination of these relationships is a very important feature of the study of specific ionic interaction. It has been established[2] by electromotive force measurements that the activity coefficient of hydrochloric acid in salt solutions at constant total ionic strength closely follows the equation

$$d \log \gamma_1 = \alpha_1 dm_1 \qquad (1)$$

in which m_1 is the molality of the acid, and the parameter α_1 is independent of m_1, but dependent upon the nature of the components, the total ionic strength and the temperature. If the activity coefficient of each electrolyte is known as a function of m in the pure solvent, and the plausible assumption made that

$$d \log \gamma_2 = \alpha_2 dm_2 \qquad (2)$$

describes the behavior of the co-solute (salt), it is possible to evaluate α_2 from experimentally determined values of α_1. The reciprocal relationships expressed by equations (1) and (2) are not generally valid in mixtures of salts with strong bases,[3] but the hydroxides are probably exceptional in this connection, as their activities are anomalous in other respects. Solubility measurements[4] show that the activity coefficient of silver sulfate in mixtures of magnesium and cadmium sulfates obey equation (1), but this may only be taken as presumptive evidence of its generality.

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(1) This communication embodies part of the thesis presented by Theodore F. Cooke, Jr., to the Graduate School of Yale University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Harned, THIS JOURNAL, **57**, 1865 (1935). Bibliography of this subject is given in his Ref. 1.

(3) Harned and Cook, *ibid.*, **59**, 1890 (1937).

(4) Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934).