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°.

NEW HAVEN, CONN. RECEIVED JUNE 11, 1938

[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).

on both sides of the junction, but a small fraction, x, of the total salt in the right-hand solution is silver acetate. The electromotive force of this cell is given by

$$E = -E^0_{\mathrm{Ag}} - k \log a_{\mathrm{H}}/a'_{\mathrm{Ag}} \pm E_{\mathrm{j}} \qquad (1)$$

where $k = 0.00019844T$, and a_{H} and a'_{Ag} denote the activities of the hydrogen and silver ion in the left and right-hand solutions, respectively. The ionization of acetic acid requires that

$$a_{\mathrm{H}} = K a_{\mathrm{HAc}}/a_{\mathrm{Ac}} \qquad (2)$$

and by substitution, equation (1) becomes

$$E = -E^0_{\mathrm{Ag}} + k \log a'_{\mathrm{Ag}} a_{\mathrm{Ac}}/a_{\mathrm{HAc}} - k \log K \pm E_{\mathrm{j}} \qquad (3)$$

With a buffer ratio unity, it is permissible to write $m_{\mathrm{H}} = K$ throughout the concentration range investigated. Accordingly equation (3) becomes

$$E - k \log mx(m + K)/(m - K) + k \log K = -E^0_{\mathrm{Ag}} + k \log \gamma'_{\mathrm{Ag}} \gamma_{\mathrm{Ac}}/\gamma_{\mathrm{HAc}} \pm E_j \qquad (4)$$

by rearrangement, and introduction of concentrations and the corresponding ionic activity coefficients.

It is evident that when $x = 0$ the solutions are identical, and E_{j} vanishes. At constant m, a plot of the left-hand member against some convenient function of x yields the intercept

$$[E - k \log mx(m + K)/(m - K) + k \log K]_{x \to 0} = -E^0_{\mathrm{Ag}} + k \log \gamma_{\mathrm{Ag}} \gamma_{\mathrm{Ac}}/\gamma_{\mathrm{HAc}} \qquad (5)$$

Since the two solutions are identical, it is no longer necessary to retain the prime on the activity coefficient term. At high dilutions, this term becomes equal to $-2k\alpha\sqrt{m}$, where α is the Debye–Hückel limiting slope. Therefore we may add $2k\alpha\sqrt{m}$ to the values of the bracketed term of equation (5), and extrapolate[3] the resulting quantities to zero ionic strength. The intercept is $-E^0_{\mathrm{Ag}}$.

Materials and Technique

Baker C. P. glacial acetic acid was purified further by one partial freezing, and two distillations from chromic oxide in an all-glass still. The acid was diluted with conductivity water to form a stock solution approximately 0.2 molal. It was standardized by comparison with Bureau of Standards potassium acid phthalate and an independently standardized hydrochloric acid solution. The titer was known to ±0.04%. The solution was stored under hydrogen. Eimer and Amend C. P. silver acetate was analyzed gravimetrically, as silver bromide, and found to be 99.45 ± 0.03% silver acetate. It was used on this basis without further purification. Baker and Adamson sodium bicarbonate was recrystallized once from distilled water saturated with carbon dioxide, and dried in an atmosphere of carbon dioxide. Commercial nitrogen and hydrogen were freed from oxygen by passing them over copper turnings at 700°. Sodium carbonate was prepared fresh for each cell solution by heating the bicarbonate, in a platinum dish, in an electric furnace at 290 ± 10° for at least ten hours.

The calculated amounts of sodium carbonate, silver acetate, acetic acid stock solution and water were weighed into the solution flasks to obtain solutions with the desired values of x, m and a buffer ratio of unity. Conductivity water was used, and vacuum corrections applied. The solutions for the hydrogen half-cell were swept with hydrogen which had passed through a saturator of large volume, and they were then kept under hydrogen. The silver half-cell solutions were swept with nitrogen, and stored under this gas. The silver solutions were protected from light.

The essential features of the cell have been described by Owen.[2] No intermediate solution was required, and our cell differs from his only in the elimination of one of the junction stopcocks, and the necessary modifications for the electrodes employed. The silver electrodes were prepared by the thermal decomposition of silver oxide at 450°. The sample of silver oxide which was used was the same as for the previous investigation.[2] The hydrogen electrodes were of the usual type employed in work from this Laboratory. The measuring equipment was the same as that of the previous investigation, and the technique was practically identical. The cells were filled twelve hours before the first measurement, the usual vacuum technique being employed. Measurements were made from 5 to 45° at 10° intervals, and the cells were refilled frequently during the course of the measurements.

Discussion of the Results

The observed electromotive forces of the cells were corrected to a partial pressure of hydrogen of one atmosphere, and to round temperatures. They are recorded in Table I. The reported values are the mean of two cells (of four cells, in a few cases) differing by no more than 0.03 mv. In one case ($m = 0.05$, $x = 0.089$), the value represents two independent runs. The first group of cells were taken from 5 to 45° in one day. The second were taken from 5 to 25°, maintained at 25° for three days, returned to 5° and then taken to 45°. All values for the two runs agree within the deviation noted above. The cells therefore appear to be very stable once equilibrium is attained. Reproducible results were not obtained for silver concentrations below 0.002 molal, and these results have been discarded.

The values for the dissociation constant of acetic acid were taken from a paper by Harned and Ehlers.[4] The left-hand member of equation (4) is plotted against x in Fig. 1 at the five temperatures investigated. The results at 25° are similarly plotted on a larger scale in Fig. 2 to illustrate

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(3) Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

(4) Harned and Ehlers, *ibid.*, **55**, 652 (1933). Equation 7.

TABLE I

OBSERVED ELECTROMOTIVE FORCES AND INTERCEPTS FROM THE FIRST EXTRAPOLATION (FIG. 1)

x	t°......5°	15°	25°	35°	45°
m = 0.05					
0.2299	0.96085	0.95477	0.94944	0.94452	0.93977
.1660	.95428	.94793	.94258	.93748	.93252
.1299	.94917	.94265	.93717	.93166	.92659
.0892	.94101	.93413	.92837	.92283	.91737
.0652	.93389	.92626	.92083	.91493	.90938
.0475	.92612	.91944	.91296	.90696	.90109
Intercept	.80910	.79830	.78805	.77740	.76630
m = 0.03					
0.40	0.96512	0.95960	0.95461	0.95021	0.94598
.30	.95893	.95323	.94807	.94347	.93892
.2299	.95312	.94718	.94177	.93675	.93202
.1299	.93990	.93350	.92789	.92234	.91716
.10	.93385	.92725	.92141	.91572	.91029
Intercept	.81070	.80015	.79015	.77950	.76870
m = 0.02					
0.50	0.96302	0.95748	0.95248	0.94801	0.94367
.40	.95807	.95235	.94708	.94245	.93796
.30	.95143	.94549	.94006	.93513	.93042
.20	.94222	.93583	.93018	.92491	.91983
.15	.93544	.92887	.92295	.91750	.91222
Intercept	.81195	.80155	.79145	.78105	.77040
m = 0.01					
0.60	0.95285	0.94691	0.94165	0.93657	0.93202
.40	.94370	.93739	.93175	.92642	.92146
.30	.93701	.93055	.92468	.91918	.91402
.20	.92748	.92073	.91458	.90878	.90334
Intercept	.81370	.80335	.79330	.78315	.77255

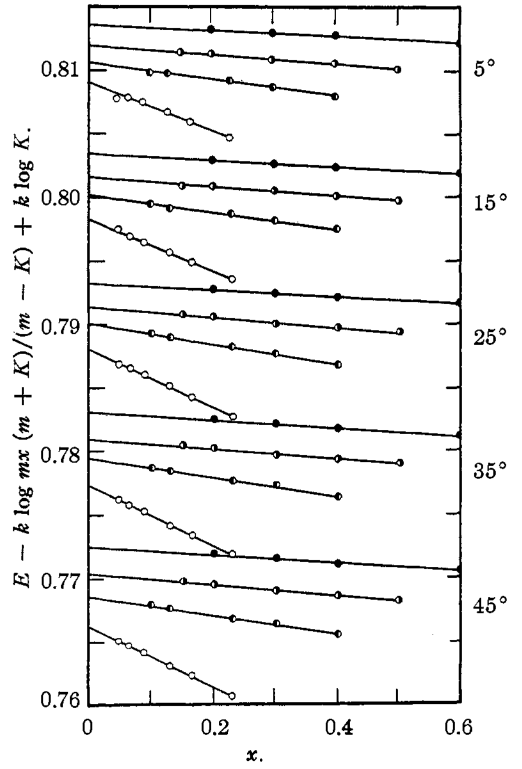

Fig. 1.—Extrapolation to eliminate liquid junction potentials: ○, m = 0.05; ◐, m = 0.03; ◑, m = 0.02; ●, m = 0.01.

the accuracy of the extrapolation. In Fig. 2, the radius of the experimental points represents an uncertainty of 0.1 mv. With the exception of a single point at 5° (m = 0.05, x = 0.047), the deviations from linearity are in no cases greater than 0.10 mv. This result for cells with buffer solutions corroborates the linearity previously observed[2] without buffer solutions. In that investigation, the slope of the extrapolation function increases with increase in ionic strength; in this investigation, the slope has the opposite sign, and shows an algebraic decrease with increasing ionic strength that is more rapid than in the former case. By reason of its steeper slope, the extrapolation at m = 0.05 is probably of no greater accuracy than that at m = 0.02, although in the former case it was possible to extend the measurements to a lower value of x. It should be noted that a plot of the electromotive forces of these cells against x does not form a basis for the estimation of the magnitude of the liquid junction potential, or of its variation with total ionic strength or temperature, since these plots also contain the variation of the unknown activity coefficient term, log $\gamma'_{Ag^+}\gamma_{Ac^-}/\gamma_{HAc}$. The linearity of the extrapolation *function* seems established within the experimental error for the concentration range which has been investigated with both types of cells.

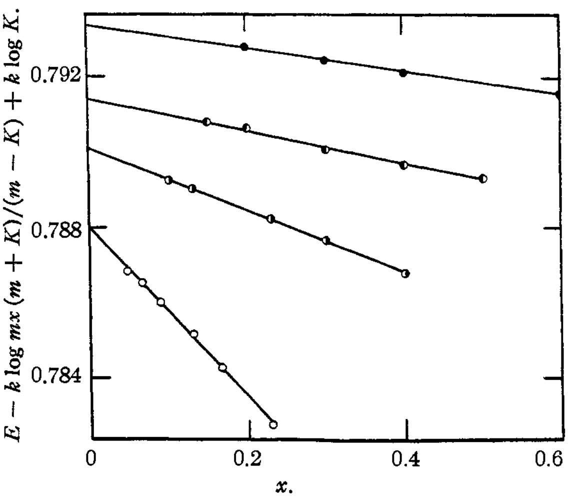

Fig. 2.—Extrapolation to eliminate liquid junction potentials at 25°. Radius of circles is 0.1 mv.: ○, m = 0.05; ◐, m = 0.03; ◑, m = 0.02; ●, m = 0.01.

The intercepts from the extrapolation in Fig. 1 are recorded in Table I to the nearest 0.05 mv. The term $2k\alpha\sqrt{m}$ is added to these intercepts as explained above, and the resulting quantities ex-

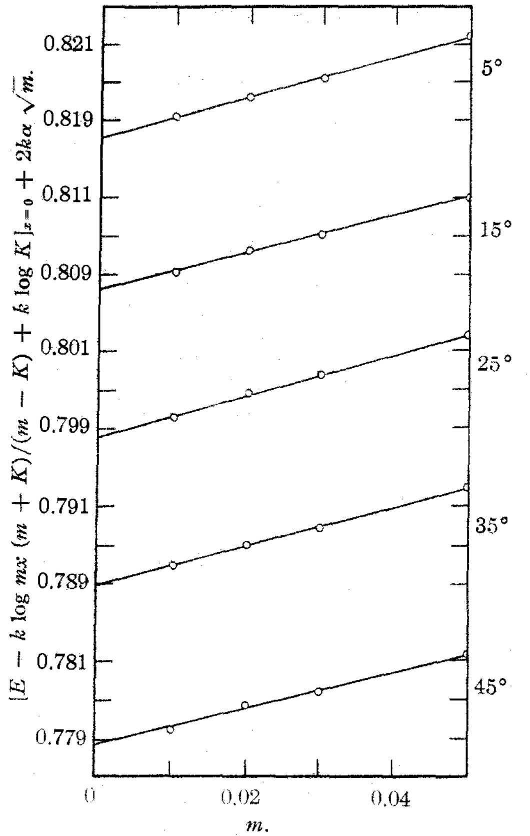

Fig. 3.—Extrapolation to eliminate activity coefficients.

trapolated to infinite dilution in Fig. 3. The values of E^0_{Ag} thus obtained are recorded in Table II. Uncertainties in concentrations, temperature and the measurement of the electromotive force are not likely to cause an error as great as 0.1 mv. and hence the uncertainties in E^0_{Ag} may be assigned to that of the two extrapolations, which we estimate to be less than ±0.2 mv.

TABLE II

STANDARD ELECTRODE POTENTIAL OF SILVER, AND DERIVED THERMODYNAMIC QUANTITIES FOR THE ELECTRODE REACTION

t, °C.	$-E^0_{\mathrm{Ag}}$ Obsd.	$-E^0_{\mathrm{Ag}}$ Ref. 2	$-E^0_{\mathrm{Ag}}$ Eq. (7)	ΔS^0	ΔH^0	ΔC_p^0
5	0.8185_5	0.8187	0.8185_8	...	....	..
15	.8087	.8090	$.8089_1$	22.46	25.127	9.30
25	.7990	.7992	$.7991_0$	22.79	25.221	9.62
35	.7891	.7892	$.7891_5$	23.10	25.319	9.95
45	.7788	$.7791_5$	$.7790_6$	...	....	..

In the previous paper,[2] values of the logarithm of the solubility product of silver chloride have been tabulated. E^0_{Ag} can be calculated from the relation

$$E^0_{\mathrm{Ag}} = k \log K + E^0_{\mathrm{AgCl}} \qquad (6)$$

We have employed Harned and Ehlers' values[5] of E^0_{AgCl} because their investigation led to the values of the dissociation constant of acetic acid[4] which we have used above. The result of this calculation is given in column three of Table II. The two sets of data constitute a satisfactory check on the precision of the measurements. The difference between the two sets of values is well within the combined experimental uncertainties of the two determinations. Accordingly, we consider the best values of E^0_{Ag} to be the mean of the two determinations. This can be expressed satisfactorily by the equation

$$E^0_{\mathrm{Ag}} = -0.7991 + 0.000988(t - 25) + 7 \times 10^{-7}(t - 25)^2 \qquad (7)$$

Values calculated from this equation are given in Table II, column 4. The maximum deviation of observed from calculated values is 0.26 mv., and the average deviation is 0.11 mv. for both series of results. Since the temperature coefficient of E^0_{Ag} is of particular interest, it should be remarked that by a change in the constant term this equation will reproduce either set of values with a maximum deviation of 0.1 mv., and an average deviation of 0.05 mv. The values from the equation are used in all subsequent calculations.

Lewis[6] and Noyes and Brann[7] have compared the silver electrode in a 0.1 normal silver nitrate solution with the 0.1 normal calomel electrode. On the basis of various values for the reference electrode potential, and of various assumptions regarding the liquid junction potential and ionic activities, different authors have obtained the values −0.7995[6-8] and −0.7978[9] for E^0_{Ag} at 25° from these data. Chloupek and Daneš[10] have compared the silver electrode in a silver sulfate solution with the decinormal calomel electrode, using various bridge solutions. They obtain −0.7996 for E^0_{Ag} at 25°. Considering the diversity of the methods used to eliminate liquid junction potentials, the agreement of these values with ours seems satisfactory.

Differentiation of equation (7) yields

$$\mathrm{d}E^0_{\mathrm{Ag}}/\mathrm{d}T = 0.000988 + 1.4 \times 10^{-6}(t - 25) \qquad (8)$$

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[5] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). Equation 7.

[6] Lewis, *ibid.*, **28**, 158 (1906).

[7] Noyes and Brann, *ibid.*, **34**, 1016 (1912).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923, p. 414; Gerke, *Chem. Rev.*, **1**, 377 (1925).

[9] "International Critical Tables," Vol. VI, p. 333.

[10] Chloupek and Daneš, *Coll. Czech. Chem. Comm.*, **4**, 124 (1932).

Skotnický[11] has measured the temperature coefficient of various half-cells against reference electrodes maintained at constant temperature. His method involves a thermal e. m. f. in the bridge solution, and a correction for the change in activity of the electrolyte with temperature, which is estimated from conductance measurements. He obtained the value 0.978 mv./deg. for dE^0_{Ag}/dT at 25°. Lingane and Larson[12] have measured the temperature coefficient of the cell

$$\text{Quinhydrone} \mid \text{HClO}_4 c_1 \mid \text{HClO}_4 c_1,\ \text{AgNO}_3 c_2 \mid \text{Ag}$$

They obtain the value 0.967 mv./deg. for dE^0_{Ag}/dT at 25°. Their lowest concentration is 0.04 molar, and they made no extrapolation to infinite dilution. Their silver ion concentrations are lower than those with which we could obtain reproducible results, and no account was taken of liquid junction potentials. In view of the nature of the calculations employed by Skotnický, and by Lingane and Larson, we regard our value, 0.000988, as the most reliable figure.

Derived Thermodynamic Quantities

By application of familiar thermodynamic relations to equations (7) and (8), ΔS^0, ΔH^0 and ΔC^0_p are computed readily for the electrode reaction

$$\text{Ag} + \text{H}^+ \longrightarrow {}^1/_2\text{H}_2 + \text{Ag}^+$$

The values of these quantities are given in Table II for 15, 25 and 35°, the three temperatures at which equation (7) best reproduces the experimental results.

The solubility products of the silver halides may be computed from the relation

$$k \log K_{AgX} = E^0_{Ag} - E^0_{AgX} \qquad (6a)$$

By substitution of equation (7) from this paper, and the equations for the temperature variation of the standard silver halide electrode potentials[5,13,14] into equation (6a), the following expressions for the logarithm of the solubility product are obtained

$$\begin{aligned} k \log K_{AgCl} &= -0.57671 + 0.00034248(t - 25) - 2.584 \times 10^{-6}(t - 25)^2 + 9.948 \times 10^{-9}(t - 25)^3 \\ k \log K_{AgBr} &= -0.72776 + 0.000490(t - 25) - 2.9 \times 10^{-6}(t - 25)^2 \qquad (9) \\ k \log K_{AgI} &= -0.95129 + 0.000660(t - 25) - 2.9 \times 10^{-6}(t - 25)^2 \end{aligned}$$

or

$$\begin{aligned} -\log K_{AgCl} &= 5905.8/T - 22.8538 + 0.057854T - 5.0131 \times 10^{-5}T^2 \\ -\log K_{AgBr} &= 5702.2/T - 11.1822 + 0.014610T \qquad (10) \\ -\log K_{AgI} &= 7084.0/T - 12.0389 + 0.014610T \end{aligned}$$

Values of the logarithms of the solubility products and the corresponding solubilities are given in Table III. The solubilities have been converted into moles per liter of solution in order to facilitate comparison with the literature. Activity coefficients were calculated by the Debye–Hückel limiting law.

TABLE III

SOLUBILITY PRODUCTS AND SOLUBILITIES OF THE SILVER HALIDES

t, °C.	AgCl		AgBr		AgI	
	$-\log K$	$c \times 10^5$	$-\log K$	$c \times 10^6$	$-\log K$	$c \times 10^8$
5	10.5945	0.506	13.3860	0.203	17.4980	0.178
15	10.1520	0.842	12.8201	.380	16.7598	.417
25	9.7492	1.337	12.3026	.704	16.0813	.908
35	9.3809	2.038	11.8280	1.213	15.4562	1.859
45	9.0425	3.002	11.3920	1.997	14.8792	3.599

The discordance between the values in the literature for the solubility of silver chloride has been discussed in the previous paper.[2] The same considerations apply to the bromide and iodide. Comparison with previously recorded results does not, therefore, constitute a criterion of the absolute accuracy of the results in Table III. Our values do constitute a self-consistent set of solubilities which have been derived from e. m. f. methods alone. It is important to note in this connection that identical values of the standard potential of the silver–silver chloride electrode[5] were used in all of the supplementary data[13,14] involved in the construction of Table III. The solubilities in Table III are 0.25% higher than those recorded by the first paper[2] due to the combination of those data with ours in equation (7). The values in the literature for the solubility of silver bromide and silver iodide consist of determinations at a single temperature. The mention of a few of these will be sufficient. The determination of the solubility of silver bromide at 21.1° by Kohlrausch and Dolezalek[15] is 5% lower than our interpolated value. That of Bodländer and Fittig[16] at 25° is 2% higher than ours. The discordance with other values is considerably greater. The disagreement with the few recorded values of the solubility of silver iodide is even greater. The value of Goodwin[17] at 25° is 5% higher than ours, and that of Thiel[18] at the same temperature is 15% higher than ours.

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[11] Skotnický. *Coll. Cseck. Chem. Comm.*. **8**, 498 (1936).

[12] Lingane and Larson. THIS JOURNAL. **59**, 2271 (1937).

[13] Owen and Foering. *ibid.*. **58**, 1575 (1936). Equation 2.

[14] Owen. *ibid.*. **57**, 1526 (1935). Equation 5.

[15] Kohlrausch and Dolezalek. *Berl. Sitzber.*. 1021 (1901).

[16] Bodländer and Fittig. *Z. physik. Chem.*. **39**. 605 (1902).

[17] Goodwin. *ibid.*. **13**. 646 (1894).

[18] Thiel. *Z. anorg. Chem.*. **24**. 57 (1900).

TABLE IV

DERIVED THERMODYNAMIC QUANTITIES FOR THE REACTION

$AgX \longrightarrow Ag^+ + X^-$

	AgCl			AgBr			AgI		
t, °C.	ΔS^0	ΔH^0	ΔC_p^0	ΔS^0	ΔH^0	ΔC_p^0	ΔS^0	ΔH^0	ΔC_p^0
15	9.19	16,022	−34.7	12.64	20,542	−38.5	16.56	26,865	−38.5
25	7.90	15,653	−35.5	11.30	20,150	−39.9	15.22	26,473	−39.9
35	6.77	15,313	−36.3	9.96	19,749	−41.2	13.88	26,068	−41.2

TABLE V

SUPPLEMENTARY THERMODYNAMIC DATA[23]

	C_p^0					S^0				
t, °C.	½ H_2	Ag	AgCl	AgBr	AgI	½ H_2	Ag	AgCl	AgBr	AgI
15	3.43	6.09	12.05	12.38	12.87	15.50	10.00	22.59	25.16	26.66
25	3.43	6.10	12.14	12.52	13.01	15.61	10.20	23.00	25.60	27.10
35	3.44	6.12	12.23	12.66	13.15	15.73	10.40	23.40	26.03	27.53
	6.62	5.65	9.37	8.81	8.81	$= a$				
	0.81	1.50	9.29	14.1	14.1	$= b \times 10^3$				

TABLE VI

RELATIVE IONIC ENTROPIES AND HEAT CAPACITIES

t, °C.	$S^0_{Ag^+}$	$S^0_{Cl^-}$	$S^0_{Br^-}$	$S^0_{I^-}$	$C^0_{pAg^+}$	$C^0_{pCl^-}$	$C^0_{pBr^-}$	$C^0_{pI^-}$
15	16.96	14.82	20.84	26.26	12.0	−34.6	−38.1	−37.6
25	17.38	13.52	19.52	24.94	12.3	−35.7	−39.6	−39.2
35	17.87	12.30	18.12	23.54	12.6	−36.7	−41.2	−40.7

By application of the usual thermodynamic relations to equations (9) or (10), it is possible to compute ΔS°, ΔH° and ΔC_p^0 for the reaction, $AgX \longrightarrow Ag^+ + X^-$. The values of these quantities for the silver halides are given in Table IV for 15, 25 and 35°. Pitzer and Smith[19] have calculated the heat of solution at 25° of silver chloride from the heat of precipitation data of Lange and Fuoss.[20] They obtain the value $\Delta H^0 =$ 15,740 cal. Latimer, Schutz and Hicks[21] report 26,710 cal. for the heat of solution of silver iodide. at 25° using the data of Lange and Shibata.[22]

The supplementary thermodynamic data necessary for the computation of relative ionic entropies and heat capacities are summarized in Table V.[23] Using the convention that the entropy of the hydrogen ion is zero at all temperatures, the relative ionic entropies and heat capacities of the silver and halide ions have been calculated from the values in Tables II, IV and V. These quantities are summarized in Table VI at 15, 25 and 35°.

Skotnický's[11] value of dE^0_{Ag}/dT leads to 17.0 cal./deg. mole for $S^0_{Ag^+}$ at 25°. Lingane and Larson[12] obtain 16.7 cal./deg. mole for the same quantity. A more reliable value from calorimetric methods is from the recent heat capacity data for silver oxide of Pitzer and Smith.[19] They obtained 17.46 ± 0.2 cal./deg. mole for $S^0_{Ag^+}$ at 25°. They have also recalculated the value given by Latimer, Schutz and Hicks,[21] based upon the heat of precipitation data of Lange and Fuoss,[20] and obtained 17.62 ± 0.2. They proposed the mean of these two figures as the best value, but in view of the approximate heats of dilution used to correct the data of Lange and Fuoss, and the close agreement with our value, we suggest the adoption of 17.4 ± 0.2 cal./deg. mole as the most probable value of $S^0_{Ag^+}$ at 25°.

From a number of sources, Latimer, Schutz and Hicks[21] have selected 13.5 ± 0.1, 19.4 ± 0.4 and 25.7 ± 0.7 cal./deg. mole for the best values[24] of $S^0_{Cl^-}$, $S^0_{Br^-}$ and $S^0_{I^-}$, respectively, at 25°. The agreement with the values in Table VI is well within the estimated uncertainties for the chloride and bromide ions, and is probably also satisfactory in the case of the iodide ion.

Summary

A method for the elimination of heterionic liq-

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(19) Pitzer and Smith, THIS JOURNAL, **59**, 2633 (1937).

(20) Lange and Fuoss, *Z. physik. Chem.*, **125**, 431 (1927).

(21) Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

(22) Lange and Shibata, *Z. physik. Chem.*, **A149**, 456 (1930).

(23) The entropy and heat capacity data at 25°, except for hydrogen, are from the review of Kelley, *Bur. Mines*, Bull., 394, 35 (1935). The heat capacity of hydrogen [*cf.* Murphey, *J. Chem. Phys.*, **5**, 637 (1937)] and the temperature coefficients of all heat capacities are from the review of Kelley, *ibid.*, Bull. 371 (1934), being described by the equation, $C_p^0 = a + bT$. "a" was recalculated from "b" and C_p^0 at 298.1°K. (given in Bull. 394). The entropy at temperatures other than 298.1°K. is then given by $S^0 = S^0_{298.1} + a(2.303 \log T/298.1) + b(T - 298.1)$.

(24) While this paper was in press, Latimer, Pitzer and Smith [THIS JOURNAL, **60**, 1829 (1938)] have published another review of the subject. Their revised "best" values are 13.5 ± 0.1, 19.7 ± 0.2 and 25.3 ± 0.5 for the entropies of the halide ions, and 17.54 ± 0.15 for the silver ion.

uid junction potentials by extrapolation has been tested in cells with buffer solutions. 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 standard potential of the silver electrode at 5, 15, 25, 35 and 45°. Values of ΔS^0, ΔH^0 and ΔC_p^0 have been calculated for the electrode reaction at 15, 25 and 35°.

By combination of the normal potentials of the silver and silver–silver halide electrodes, the solubility products and solubilities of (electrolytic) silver chloride, bromide and iodide have been computed from 5 to 45°. Values of ΔS^0, ΔH^0 and ΔC_p^0 for the reaction $AgX = Ag^+ + X^-$ have been recorded at 15, 25 and 35°.

A self-consistent table of relative ionic entropies and heat capacities from electromotive force data has been made for the silver ion, chloride ion, bromide ion and iodide ion at 15, 25 and 35°.

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Infrared Absorption Studies. V. Association in the Carboxylic Acids

BY A. M. BUSWELL, W. H. RODEBUSH AND M. F. ROY

The electron conception of valence proposed some twenty years ago led to the prediction in 1920 of two types of associated liquids.[1] In one of these the molecules should be combined with the formation of definite polymers (dimers in the case of acetic acid) while in the other type polymers of indefinite molecular weight and structure were anticipated. Radically different behavior, especially in the case of solvent properties, was predicted in the two cases. The liquids composed of polymers of indefinite molecular weight comprised the typically polar solvents such as water or alcohol, while in those having definite polymer molecules non-polar properties were to be expected.

Since then a great deal of additional evidence has been accumulated to emphasize this difference. For example, acetic acid shows no dipole moment in benzene solution whereas alcohols show an increasing polarization with increasing concentration. Alcohols also form glasses at low temperatures, which have been shown by Zachariasen[2] to involve polymerization with hydrogen bond formation. It is not possible, of course, to anticipate or predict in every case the type of polymer to be expected and that problem is one which still holds the greatest interest. The data from which conclusions could be drawn have been available for a long time; witness the excellent review by Lassettre[3] based entirely upon the ordinary data of physical chemistry. More recently a study of simple solubility by Zellhoefer, Copley and Marvel[4] has yielded a surprising amount of additional confirmatory data along these lines.

The existence of these two types of association has perhaps contributed to the confusion which for many years characterized the attempts of physical chemists to discuss the behavior of the so-called "normal" and "associated" liquids. This confusion was all the more inevitable because it is now obvious that the normal or unassociated liquid lies intermediate in its properties between the two types of associated liquids.

It should be mentioned at this point that a third type of association through hydrogen, namely, intramolecular association or chelation, may occur, which has the result of producing a "normal" behavior in a molecule which would otherwise show abnormal behavior as a liquid and solvent. This type of association has been much studied by Sidgwick[5] and his collaborators. The conditions under which it occurs are well defined, and one of the important ones is apparently the possibility of two configurations of the molecule with respect to the hydrogen, thus giving an opportunity for resonance.

All of the types of association of interest in the liquid state appear to involve hydrogen bonding. The formation of polymers depends upon potential cross linkages or additional valences between

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[1] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1432 (1920).

[2] W. H. Zachariasen, *J. Chem. Phys.*, **3**, 158 (1935).

[3] E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

[4] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337 (1938); G. F. Zellhoefer and M. J. Copley, *ibid.*, **60**, 1343 (1938).

[5] N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1929.