

where P_3 is the vapor pressure of acetic acid or 15.6 mm.⁸ at 25°, and m is the number of moles of hydrochloric acid in the absorption tube. The other symbols are as given in Table I.

Results.—The vapor pressure curve over the range studied is a straight line function of the mole fraction. It may be seen that since the partial vapor pressure of the hydrogen chloride from a glacial acetic acid solution for which the mole fraction of hydrogen chloride is 0.011 is 50.9 mm. and since the corresponding partial vapor pressure from an aqueous solution of the same mole fraction is only about 0.0001 mm.,⁹ the relative activity is more than a hundred thousand times greater in the former case. Earlier results on much stronger solutions indicate a sharp increase in the slope of the curve. The following approximate results are given: 5% hydrochloric acid, 470 mm.; 3% hydrochloric acid, 300 mm.

Summary

A discussion is given of the effect of solvent upon the activity of acids in solution together with measurements of the vapor pressure of hydrogen chloride in glacial acetic solution.

⁸ "International Critical Tables."

⁹ *Ibid.*, Vol. 3.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

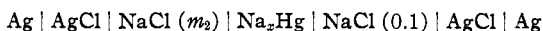
THE THERMODYNAMIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 0 TO 40°

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Although flowing amalgam cell measurements have been used with considerable success to determine the activity coefficients of alkali and alkaline earth halides at 25°, few reliable measurements are available at other temperatures. The present communication contains electromotive force measurements of the cells



from which the activity coefficient and partial molal heat content of sodium chloride have been computed through a concentration range from 0 to 4 *M* and a temperature range of from 0 to 40° at 5° intervals.

Experimental Procedure and Results

All precautions pertaining to accurate flowing amalgam cell measurements were taken.² A vacuum technique was employed which excluded

¹ This paper contains the material and calculations originally presented by Leslie F. Nims to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1931.

² Harned, *THIS JOURNAL*, **51**, 416 (1929).

dissolved air from the solutions which came in contact with either the amalgam or the silver-silver chloride electrodes. Carefully repurified salt was used. The silver chloride electrodes were of the kind designated by Harned as Type 2, and were prepared from very carefully purified silver oxide paste by electrolysis. A new silver-silver chloride electrode was made for each measurement. The sodium amalgam of 0.02% sodium was made according to the customary method.³ A small correction was added to the electromotive forces to compensate for the slight changes in concentrations of the solutions caused by the boiling in vacuo which was employed to remove the dissolved air. Consequently, all the results are reported at round concentrations. Since measurements were at eight temperatures, the thermostat was equipped with eight thermoregulators set for the desired temperatures. This facilitated operations considerably.

Table I contains the observed electromotive forces which represent the mean of the number of separate cell measurements given in the column immediately preceding. It is important to note that every measurement was made with a freshly constructed cell, since with cells of this type it is not practicable to measure the same cell at a series of temperatures.

TABLE I
ELECTROMOTIVE FORCES OF THE CELLS
Ag | AgCl | NaCl (*m*) | Na₂Hg | NaCl (0.1) | AgCl | Ag

<i>m</i>	No. of cells	<i>E</i> 0.3°C.	No. of cells	<i>E</i> 12.5°C.	No. of cells	<i>E</i> 15°C.	No. of cells	<i>E</i> 20°C.
0.05	4	-0.02970			4	-0.03151	5	-0.03209
0.2	4	.02964	2	0.03102	6	.03137	6	.03214
0.5	4	.06876	2	.07254	4	.07304	8	.07425
1.0	6	.09876	2	.10437	4	.10562	5	.10741
1.5	2	.11726			2	.12533	6	.12784
2.0	2	.13099	2	.13898	2	.14044	2	.14339
2.5	6	.14267			4	.15286	2	.15625
3.0	2	.15261	2	.16196	4	.16390	2	.16751
3.5	2	.16162			4	.17351	2	.17738
4.0	2	.16996	2	.18074	3	.18282	2	.18655

<i>m</i>	No. of cells	<i>E</i> 25°C.	No. of cells	<i>E</i> 30°C.	No. of cells	<i>E</i> 37.5°C.	No. of cells	<i>E</i> 40°C.
0.05	4	-0.03245	2	-0.03290	2	-0.03377	2	-0.03401
0.2	4	.03252	2	.03314	2	.03357	2	.03414
0.5	2	.07584	2	.07686	2	.07875	2	.07954
1.0	6	.10955	4	.11128	4	.11417	6	.11529
1.5	2	.13041	4	.13249	4	.13618	5	.13740
2.0	2	.14627	4	.14892	4	.15279	2	.15427
2.5	8	.15925	4	.16213	2	.16648	4	.16804
3.0	4	.17070	2	.17396	2	.17855	3	.18031
3.5	4	.18094	4	.18422	2	.18916	2	.19091
4.0	5	.19036	2	.19380	2	.19920	2	.20100

³ Harned, THIS JOURNAL, 47, 677 (1925).

A Graphical Method of Determination of the Temperature Coefficient.—

The equation for the cells of the type under consideration may be written

$$E - \frac{2RT}{F} \ln \frac{m}{0.1} = \frac{2RT}{F} \ln \frac{\gamma}{\gamma_{0.1}} \tag{1}$$

If the left side of this equation be plotted against the temperature, a very sensitive series of graphs is obtained from which the electromotive forces at 5° temperature intervals may be read with a very high degree of accuracy.

If the first order differences of the electromotive forces at equal temperature intervals of cells of constant composition of this type and of other types containing uni-univalent electrolytes be plotted against the temperature, the plots are straight lines. That this relation is valid from 0 to 40° to within ±0.01 to 0.02 millivolt is shown by Fig. 1, in which the values of

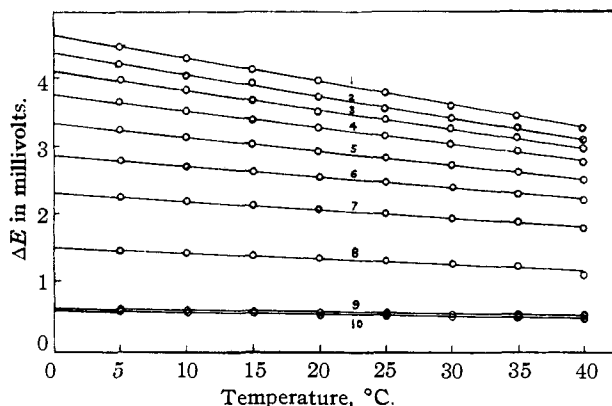


Fig. 1.—Variation of the first order difference of electromotive force with temperature: (1) 4 M (2) 3.5 M (3) 3 M (4) 2.5 M (5) 2 M (6) 1.5 M (7) 1 M (8) 0.5 M (9) 0.2 M (10) 0.05 M.

ΔE , the first order differences of the electromotive forces, are plotted against the temperature. This fact shows that for the case under consideration, the usual equation for computing temperature coefficients

$$E_T = E_{T_0} + a_{T_0} (T - T_0) + b (T - T_0)^2 \tag{2}$$

is sufficient to express exactly the experimental results without the introduction of a third term of the power series.

To obtain the constants of this equation, the following method was adopted. Let T_0 be a reference temperature. For a series of electromotive forces at intervals of temperature of 5°, the equations

$$\left. \begin{aligned} E_{T_0+15} &= \dots\dots\dots \\ E_{T_0+10} &= E_{T_0} + a_{T_0} \cdot 10 + b \cdot 10^2 \\ E_{T_0+5} &= E_{T_0} + a_{T_0} \cdot 5 + b \cdot 5^2 \\ E_{T_0} &= E_{T_0} \\ E_{T_0-5} &= E_{T_0} - a_{T_0} \cdot 5 + b \cdot 5^2 \\ E_{T_0-10} &= E_{T_0} - a_{T_0} \cdot 10 + b \cdot 10^2 \\ E_{T_0-15} &= \dots\dots\dots \end{aligned} \right\} \tag{3}$$

are easily obtained from equation (2). The first order differences are then seen to be given by

$$\left. \begin{aligned} E_{T_0+15} &= \dots\dots \\ E_{T_0+10} &= 5 a_{T_0} + 75 b \\ E_{T_0+5} &= 5 a_{T_0} + 25 b \\ E_{T_0} &= 5 a_{T_0} - 25 b \\ E_{T_0-5} &= 5 a_{T_0} - 75 b \\ E_{T_0-10} &= \dots\dots \end{aligned} \right\} \quad (4)$$

and the general equation for the first order differences is

$$\Delta E_T = 5 a_{T_0} - b [25 + (T_0 - T)10] \quad (5)$$

This is the equation for the family of straight lines in Fig. 1. Upon differentiation

$$\frac{\partial \Delta E_T}{\partial T} = 10 b \quad (6)$$

so that b is 0.1 of the slope of the plots in Fig. 1, a condition which makes the numerical evaluation of b very accurate. b is independent of the reference temperature.

When T equals T_0

$$\Delta E_T = \Delta E_{T_0} = 5 a_{T_0} - 25 b \quad (7)$$

and equals the ordinate readings at this temperature. From this

$$a_{T_0} = \frac{\Delta E_{T_0}}{5} + 5 b \quad (7a)$$

an equation by which a_{T_0} may readily be computed, and which shows that a_{T_0} depends on the temperature chosen as reference. Further, upon differentiation of equation (2), we obtain

$$\frac{\partial E}{\partial T} = a_{T_0} + 2 b (T - T_0) \quad (8)$$

which becomes

$$\left. \frac{\partial E}{\partial T} \right]_{T=T_0} = a_{T_0} = \frac{\Delta E_{T_0}}{5} + 5 b \quad (9)$$

when $T = T_0$. Since b is small, the temperature coefficient at $T = T_0$ approaches $\Delta E_{T_0}/5$.

From equation (9) it is seen that the accuracy with which $\partial E/\partial T$ may be obtained depends upon the accuracy of evaluation of ΔE . Little difficulty was encountered except with the results at salt concentrations above 2.5 M . This is caused by an uncertainty introduced by the appreciable solubility of the silver chloride in the concentrated salt solutions, which causes an indeterminate error of the order of a few tenths of a millivolt. This difficulty was overcome to a certain extent by plotting ΔE against the log m at constant temperature. By combining these plots with those at constant composition given in Fig. 1, the above uncertainty was partially removed. In any case, the accuracy in the determination of $\partial E/\partial T$ is thought to be 1% in all cases, and better than 1% in the more favorable cases at the lower concentrations.

Table II contains the electromotive forces at 5° intervals determined by this graphical method, as well as the values of a and b of equation (2).

TABLE II

(1) ELECTROMOTIVE FORCES OF THE CELLS: Ag AgCl NaCl (m) Na ₂ Hg NaCl (0.1)					
AgCl Ag, FROM 0 TO 40° AT 5° INTERVALS					
$T, ^\circ\text{C.}$	$m = 0.05$	$m = 0.2$	$m = 0.5$	$m = 1.0$	$m = 1.5$
0	0.02966	0.02957	0.06867	0.09882	0.11708
5	.03126	.03019	.07015	.10109	.11990
10	.03084	.03079	.07160	.10330	.12263
15	.03141	.03138	.07301	.10545	.12528
20	.03196	.03195	.07438	.10753	.12784
25	.03250	.03251	.07571	.10955	.13032
30	.03302	.03305	.07700	.11151	.13272
35	.03353	.03358	.07825	.11341	.13503
40	.03402	.03409	.07946	.11524	.13725
25 ⁴		.03247	.07566	.10957	.13033
	$m = 2.0$	$m = 2.5$	$m = 3.0$	$m = 3.5$	$m = 4.0$
0	0.13096	0.14214	0.15215	0.16136	0.16969
5	.13422	.14581	.15615	.16559	.17418
10	.13738	.14936	.16000	.16965	.17850
15	.14043	.15278	.16370	.17356	.18265
20	.14338	.15607	.16727	.17731	.18663
25	.14622	.15923	.17070	.18090	.19044
30	.14896	.16227	.17398	.19433	.19407
35	.15159	.16518	.17711	.18760	.19755
40	.15412	.16796	.18010	.19071	.20085
25 ⁴	.14621	.15923	.17037	.18088	.19079
(2) CONSTANTS OF EQUATION (2) $E_T = E_{T_0} + a\tau_0(T - T_0) + b(T - T_0)^2$; $T_0 = 298.1$					
m	0.05	0.2	0.5	1.0	1.5
$a \times 10^{-6}$	106	110	262	398	487
$b \times 10^{-6}$	-0.30	-0.30	-0.78	-1.24	-1.68
m	2.0	2.5	3.0	3.5	4.0
$a \times 10^{-6}$	558	620	670	702	745
$b \times 10^{-6}$	-2.10	-2.54	-2.88	-3.18	-3.40

The Partial Molal Heat Content of Sodium Chloride.—The partial molal heat content referred to the 0.1 M reference solution may readily be computed from the above electromotive forces. By substituting the value for the temperature coefficient of electromotive force given by equation (9) in the Gibbs-Helmholtz equation

$$(-\Delta\bar{H}) = NF \left[E - T \left(\frac{\Delta E_{T_0}}{5} + 5b \right) \right] \quad (10)$$

⁴ In this row are the results obtained by Harned [THIS JOURNAL, 51, 416 (1929)] at 25°. Up to 2.5 M the agreement between the two series of observations is excellent since the differences are considerably less than 0.05 millivolt in five out of the six observations. At 3 M and 4 M , the agreement is not nearly so good, a fact which we attribute to the solubility of the silver chloride.

is readily obtained. By means of this equation, the partial heat content changes corresponding to the transfer NaCl (m) to NaCl (0.1) were obtained. These are given in Table III, and their graphs are in Fig. 2.

TABLE III

THE PARTIAL MOLAL HEAT OF DILUTION OF SODIUM CHLORIDE SOLUTIONS REFERRED TO THE 0.1 M SOLUTION

m	\sqrt{m}	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.05	0.224	81	62	44	23	2	-16	-37	-60	-81
.1	.316	0	0	0	0	0	0	0	0	0
.2	.447	-108	-90	-69	-51	-30	-9	12	32	53
.5	.707	-309	-258	-209	-157	-103	-76	-2	58	115
1.0	1.000	-630	-549	-468	-383	-302	-214	-129	-39	55
1.5	1.224	-907	-800	-688	-572	-459	-341	-221	-101	-23
2.0	1.414	-1150	-1020	-884	-748	-607	-466	-321	-173	-28
2.5	1.581	-1425	-1265	-1097	-932	-761	-588	-411	-232	-51
3.0	1.732	-1615	-1435	-1250	-1065	-872	-678	-466	-265	-60
3.5	1.871	-1710	-1505	-1300	-1085	-872	-656	-434	-208	23
4.0	2.000	-1850	-1633	-1415	-1190	-962	-732	-480	-267	-12

The dashed line in the figure represents the results obtained by Lewis and Randall at 25°. ⁵ The form of the curve is the same, but the numerical

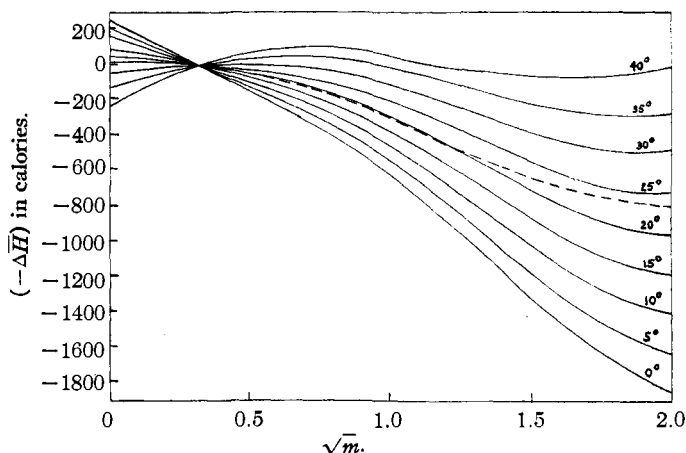


Fig. 2.—Partial molal heat of dilution of sodium chloride in aqueous solution referred to the 0.1 M solution.

agreement is approximate. A part of this discrepancy is due to the fact that the values obtained by Lewis and Randall were computed from calorimetric data by a method which involved extrapolation to infinite dilution and the use of estimated partial specific heats.

Further, it should be mentioned that plots of these partial heats of dilu-

⁵ Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, Chapter VIII, Table 5.

tion against the temperature give a family of straight lines. Since the partial specific heats are known to be practically independent of the temperature, the straight line relation is to be expected because the slopes equal the differences in partial molal specific heats of the solutions at concentrations m and the partial molal specific heat of the 0.1 M solution. The partial molal specific heat of sodium chloride in aqueous solution at 25° has recently been redetermined from calorimetric data by Randall and Rossini.⁶ In Table IV we have compared their results with the values computed from $\bar{C}_p - \bar{C}_{p0.1}$ which were determined from the slopes of the plots of $(-\Delta H)$ against T . The values of $\bar{C}_p - \bar{C}_{p0.1}$ thus obtained were plotted against $m^{1/2}$ and were found to lie on a straight line with a slope of 24.8. By taking \bar{C}_{p0} at zero salt molality equal to -23.3 cal., as found by Randall and Rossini, the results in the third column of the table were compiled from this plot.

TABLE IV

COMPARISON OF THE PARTIAL MOLAL HEAT CAPACITIES WITH RESULTS OBTAINED FROM CALORIMETRIC MEASUREMENTS

m	\bar{C}_p (R. and R.), cal.	\bar{C}_p (H. and N.), cal.
0.00	-23.3	(-23.3)
.05	-18.9	-17.7
.1	-17.0	-15.5
.2	-14.2	-12.2
.5	- 8.6	- 5.7
1	- 2.3	+ 1.5
1.5	+ 2.6	+ 7.1
2	+ 6.9	+11.8
2.5	+10.65	+15.9

The values determined from electromotive force measurements may be represented by $\bar{C}_p = 24.8 m^{1/2} - 23.3$, those determined by Randall and Rossini by $\bar{C}_p = 21 m^{1/2} - 23.3$. Thus, the slopes determined by the two methods differ somewhat from each other, but, considering the difficulties pertaining to both methods and the smallness of the heat magnitudes involved, we consider the agreement fairly satisfactory. The advantage of the present method of determining the slope lies in its simplicity and in the fact that straight line functions were used in deriving the values.

The Activity Coefficients of Sodium Chloride Solutions from 0 to 40°.—The activity coefficients of sodium chloride may be calculated from the electromotive force data by Hückel's equation⁷

$$\log \gamma = - \frac{u \sqrt{c}}{1 + A \sqrt{2c}} + B \cdot 2c - \log(1 + 0.036m) \quad (11)$$

The constants A and B have been evaluated at 0, 25 and 40° and are given in Table V, section (1). Harned⁴ obtained 0.84 and 0.032 for A

⁶ Randall and Rossini, *THIS JOURNAL*, 51, 323 (1929).

⁷ Hückel, *Physik. Z.*, 26, 83 (1925).

and B at 25° . Section (2) of the table gives the comparison between the observed results computed directly by equation (1) and those calculated by equation (11) at these temperatures. Section (3) gives the experimentally determined values at the 5° temperature intervals from 0 to 40° , and a concentration range of from 0.05 to $4 M$.

TABLE V
ACTIVITY COEFFICIENTS

(1) Values of Constants of Equation 11

	0°	25°	40°
D	88.06	78.51	73.36
u	0.4864	0.5067	0.5212
A740	.837	.887
B0264	.0316	.0323

(2) Comparison of Observed Activity Coefficients with Those Computed by Equation 11 at 0 , 25 and 40°

m	0°		25°		40°	
	$\gamma_{\text{calcd.}}$	$\gamma_{\text{ex.}}$	$\gamma_{\text{calcd.}}$	$\gamma_{\text{ex.}}$	$\gamma_{\text{calcd.}}$	$\gamma_{\text{ex.}}$
0.05	0.820	0.823	0.818	0.820	0.816	0.819
.1	(.773)	(.773)	(.773)	(.773)	(.771)	(.771)
.2	.724	.724	.727	.727	.726	.725
.5	.662	.664	.675	.675	.675	.673
1.0	(.631)	(.631)	(.654)	(.652)	(.657)	(.653)
1.5	.623	.620	.657	.651	.662	.654
2.0	.626	.624	.669	.665	.676	.671
2.5	(.634)	(.634)	(.686)	(.686)	(.693)	(.693)
3.0	.645	.653	.694	.714	.717	.723
3.5	.651	.680	.723	.747	.734	.758
4.0	.660	.710	.754	.786	.767	.797

(3) Experimental Activity Coefficients

m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.05	0.823	0.822	0.822	0.821	0.821	0.820	0.822	0.822	0.819
.1	.773	.773	.773	.773	.773	.773	.773	.773	.771
.2	.724	.726	.727	.727	.727	.727	.727	.727	.725
.5	.664	.669	.670	.672	.674	.675	.675	.675	.673
1.0	.631	.637	.642	.646	.649	.652	.653	.654	.654
1.5	.620	.629	.636	.642	.647	.651	.654	.655	.654
2.0	.624	.636	.645	.653	.660	.665	.670	.671	.671
2.5	.634	.652	.660	.671	.679	.686	.691	.694	.693
3.0	.653	.670	.684	.696	.706	.714	.720	.723	.723
3.5	.680	.699	.714	.728	.738	.747	.752	.755	.758
4.0	.710	.732	.749	.765	.777	.786	.793	.797	.797

Figure 3 contains a plot of the activity coefficients against \sqrt{m} at all the temperatures at which it was studied. It is interesting to note that, as the temperature increases, there is a diminishing difference between the values at 5° intervals. Thus, if at a given concentration, γ be plotted against the temperature, it is found that γ approaches a maximum value. Indeed,

there is evidence from other sources that this is a true maximum and that above a certain temperature γ will decrease.

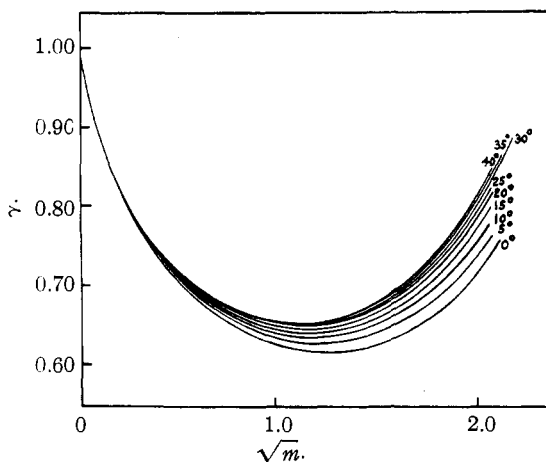


Fig. 3.—Experimental activity coefficients.

In Fig. 4 both the A and B constants of Hückel's equation are plotted against the temperature. Both increase with T . A varies approximately linearly, whereas B approaches a maximum value.

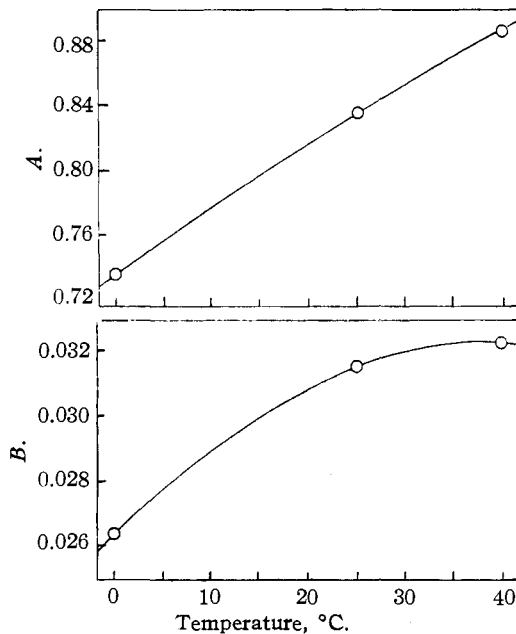


Fig. 4.—The A and B constants of the Hückel equation as a function of the temperature.

Summary

1. Accurate electromotive force measurements of the cells



have been made at 0, 12.5, 15, 20, 25, 30, 37.5 and 40°.

2. The first order difference of the electromotive force varies linearly with the temperature. This fact helps considerably in obtaining the electromotive forces at 5° temperature intervals and affords a very accurate method of obtaining the constants of the equation which expresses the variation of the electromotive force with the temperature.

3. By a graphical method based upon first order differences, the temperature coefficients of electromotive force have been computed, as well as the partial molal heat content decrease of transfer from the concentrated to dilute solutions. This quantity is negative at the lower temperatures and becomes less negative as the temperature rises, reaching zero and assuming positive values in the vicinity of 40°. Since this change takes place uniformly, positive values are to be expected at the higher temperatures. If this is the case, then the activity coefficient will pass through a maximum and decrease with increasing temperature.

4. The activity coefficients at 0, 25 and 40° have been computed by Hückel's equation.

5. Accurate values of the activity coefficients at 0, 5, 10, 15, 20, 25, 30, 35 and 40° have been computed. At constant composition, they increase somewhat with the temperature and reach a maximum at about 40°.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

ERRORS INVOLVED IN THE DETERMINATION OF MINUTE AMOUNTS OF SODIUM BY THE MAGNESIUM URANYL ACETATE METHOD

BY EARLE R. CALEY

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In former papers in this series¹ attention was directed almost entirely to the errors involved in the direct determination of amounts of sodium ranging from one milligram upward. As far as the writer is aware, no systematic experiments have been made on the determination of smaller amounts than this by the particular procedure considered here. Due to the fact that the method has been applied to the determination of amounts of sodium below one milligram in various materials, it seemed advisable to make a systematic series of analyses in order to determine the errors in-

¹ (a) Caley and Foulk, *THIS JOURNAL*, **51**, 1664-74 (1929); (b) Caley, *ibid.*, **52**, 1349-53 (1930); (c) Caley and Sickman, *ibid.*, **52**, 4247-51 (1930).