in the table gives the maximum variation in per cent. of this deviation at each temperature. This is a maximum at 0° and reaches a minimum of only 3% at about 30°. Further, k_h at each temperature from 10 to 40° is a maximum at some salt concentration.

Summary

1. From measurements of the cells without liquid junction,

$$H_2 \mid NaOH\ (m_0),\ NaCl\ (m) \mid AgCl - Ag$$
$$H_2 \mid HAc\ (M),\ NaCl\ (m) \mid AgCl - Ag$$

the thermodynamics of the hydrolytic reaction

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

has been studied from 0 to 40° and from 0 to 3 M sodium chloride concentration.

2. Of the quantities in the equation of equilibrium

$$K_h = \frac{\gamma_{OH}\gamma_{HAc}}{\gamma_{Ac}a_{H_2O}} \frac{m_{OH}m_{HAc}}{m_{Ac}} = \gamma^2_h k_h$$

K_h, γ_h and k_h have been evaluated. By this method the concentration term, k_h, has been separated from the activity coefficient term, γ_h.

3. Our results show that from 25 to 40°, inclusive, and from 0 to 3 M salt concentration, the total deviation from the mass action law is not greater than 4%.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Potassium Chloride Solutions from Electromotive Force Measurements

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The electromotive forces of the cells

$$Ag–AgCl \mid KCl\ (m) \mid K_xHg \mid KCl\ (m_0) \mid AgCl–Ag \qquad (1)$$

have been measured at 25° by MacInnes and Parker[1] and Harned[2] and at 0° by Smith.[3] These measurements have been extended by us to cover the ranges of temperature and concentration from 0 to 40° and 0.05 to 4 M, respectively. From these data, the activity coefficient, relative partial molal heat content and the relative partial molal heat capacity of potassium chloride in aqueous solutions have been computed.

Experimental Results

The cell technique was essentially the same as that employed by Harned[2] and Smith.[3] The electromotive force at each concentration was measured at 5° intervals from 0 to 40°, inclusive. The results have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

Values of E_{25}, a and b are given in Table I. b' in the fifth column are smoothed values of b which may be used for the calculation of the relative partial molal heat capacity. In the last column of the table, the average value in millivolts of the deviation, Δ, of the observed electromotive forces from those calculated by equation (2) are given.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS $Ag–AgCl \mid KCl(m) \mid K_xHg \mid KCl(0.05) \mid AgCl–Ag$ AT 25° AND CONSTANTS OF EQUATION (2). VALID FROM 0 TO 40°

m	E_{25}	$a \times 10^6$	$-b \times 10^6$	$-b' \times 10^6$	Δ, mv.
0.1	0.03263	114	0.29	0.30	0.07
.2	.06478	224	.49	.50	.06
.3	.08332	284	.70	.66	.07
.5	.10677	372	.90	.87	.05
.7	.12220	440	1.02	1.00	.12
1.0	.13866	498	1.20	1.20	.06
1.5	.15768	574	1.48	1.50	.05
2.0	.17165	634	1.75	1.70	.06
2.5	.18274	682	1.85	1.86	.07
3.0	.19203	710	2.00	2.02	.07
3.5	.20030	745	2.20	2.18	.09
4.0	.20759	784	2.31	2.30	.05

For purposes of theoretical calculation, it is necessary to know the concentrations in formula weights per liter of solution, c. These may be obtained with an accuracy of ±0.04% by the equation

$$c/m = d_0 + Am \qquad (3)$$

TABLE II

CONSTANTS OF EQUATION (3)

t	d_0	$-A$
0	0.9999	0.0263
5	1.0000	.0265
10	0.9997	.0266
15	.9991	.0267
20	.9982	.0270
25	.9970	.0272
30	.9957	.0273
35	.9940	.0274
40	.9922	.0276

[1] MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

[2] Harned, *ibid.*, **51**, 416 (1929).

[3] Smith, *ibid.*, **55**, 3279 (1933).

in which d_0 is the density of water and A an isothermal constant. Values of d_0 and A obtained from the density data for potassium chloride solutions[4] are given in Table II.

Activity Coefficients

From the cell electromotive force, E, the activity coefficient, γ, relative to its value at 0.05 M, $\gamma_{0.05}$, may be computed by the equation

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{E}{2k} - \log \frac{m}{0.05} \qquad (4)$$

where k equals $2.303\,RT/F$; 8.315, $t + 273.1$, and 96,500 were employed for R, T, and F, respectively. In order to extrapolate the results, the Debye and Hückel equation

$$\log \gamma = -u(c)^{1/2}/[1 + A(2c)^{1/2}] + Bc - \log(1 + 0.036m) \qquad (5)$$

has been employed.

By using the values of c computed by equation (3), the parameters, A and B, were computed by a suitable method from two values of the activity coefficient ratios. Values of A and B at some temperatures are given at the bottom of Table III. The apparent ionic diameter a was calculated from A by the equation derived from theory

$$A = K'a \qquad (6)$$

employing the values of K' computed by Harned and Ehlers.[5] The values of a found were all equal to 3.6 ± 0.15 Å. and since no indication of a variation of a with temperature was noted a value of 3.6 Å. was employed in all subsequent calculations. B was found to vary with the temperature according to the equation

$$B = 0.008 + 0.00110t - 1.12 \times 10^{-5}t^2 \qquad (7)$$

Equation (5) is not valid for the computation of γ throughout the entire concentration range so that only those results between 0.05 and 1 M were employed to evaluate A and B. Previous extrapolations[2] are not so accurate as this one since the equations were applied over too extended a concentration range, a procedure which leads to a low value of A and an activity coefficient at the reference concentration which is low to the extent of about 0.003 to 0.004.

The activity coefficients are given in Table III. The extrapolation by equation (5) led to the reference values of 0.05 M which are indicated by brackets. Values at the lower concentrations in parentheses were calculated by equation (5). Comparison with results of other investigations indicates that our values are quite accurate. In the third column, values of γ at 0° obtained from the same type cells by Smith[3] are seen to be in very close agreement with ours at all concentrations between 0.1 and 3.5 M. The fourth column contains values of γ at 0° calculated by Spencer[6] from the freezing point data. Again the agreement is excellent. The results at 0° also closely check the values of the activity coefficient, γ', at the temperature of the freezing point of the solution determined by Scatchard and Prentiss.[7] The results of Harned[2] at 25° in the next to the last column of the table are also in good agreement with the present results. His values were changed to agree with the new reference value of 0.769 at 0.1 M. A very important confirmation of the accuracy of the present results is found when comparison is made with values determined by MacInnes and Shedlovsky[8] from cells with liquid junction and from transference number data. Their results to three decimal places are contained in the eighth column of the table. The agreement throughout the entire range of concentration is excellent. Their extrapolation yields a result at 0.1 M slightly higher than ours. Most likely this is due to the fact that they obtained results at lower concentrations, −0.005 to 0.1 M, while we were required to employ results from 0.05 to 1 M.

The Relative Partial Molal Heat Content

$\overline{L}_2$ was computed from 0.05 to 1 M salt concentration by the differentiated form of equation (5),[5,9,10] namely

$$\overline{L}_2 = \frac{U'c^{1/2}}{1 + A(2c)^{1/2}} - \frac{V'}{(1 + A(2c)^{1/2})^2}\left[c\frac{\mathrm{d}A}{\mathrm{d}T} + \frac{A}{2}\frac{\mathrm{d}c}{\mathrm{d}T}\right] + W'\left[B\frac{\mathrm{d}c}{\mathrm{d}T} + c\frac{\mathrm{d}B}{\mathrm{d}T}\right] \qquad (8)$$

where U', V' and W' are the isothermal constants given by Harned, Keston and Donelson[9] (Table VI). $\mathrm{d}A/\mathrm{d}T$, $\mathrm{d}c/\mathrm{d}T$ and $\mathrm{d}B/\mathrm{d}T$ may be obtained readily from equation (6), the density data and equation (7), respectively. In addition to this, calculation values of the partial molal heat content relative to the 0.05 M solution, $\overline{H}_{\mathrm{m}} - \overline{H}_{0.05}$, were calculated by the Gibbs–Helmholtz equation. Results by the two methods agree closely in the region of concentration where equa-

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[4] "International Critical Constant Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., p. 87.

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

[6] Spencer, *ibid.*, **54**, 4490 (1932).

[7] Scatchard and Prentiss, *ibid.*, **55**, 4355 (1933).

[8] Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937).

[9] Harned, Keston and Donelson, *ibid.*, **58**, 989 (1936).

[10] Harned and Cook, *ibid.*, **59**, 496 (1937).

TABLE III

ACTIVITY COEFFICIENTS OF POTASSIUM CHLORIDE[e,f,g]

m	0°	0°[a]	0°[b]	10° [e]	20°	25°	25°[c]	25°[d]	40°
0.005	(0.929)		0.929			(0.927)	(0.9275)	(0.927)	
.01	(.904)		.903			(.901)	.902	(.901)	
.05	(.819)		.818	(0.818)	(0.816)	(.815)	.817	.818	(0.811)
.1	.768(1)	(0.770)	.771	.769(1)	.770(−2)	.769(−1)	.770	(.769)	.765(0)
.2	.717(0)	.717	.719	.718(0)	.718(0)	.719(−2)	.719	.717	.715(−2)
.3	.683(−1)			.687(−2)	.688(−1)	.688(−1)			.682(1)
.5	.642(−1)	.642	.645	.648(−1)	.651(−1)	.651(−1)	.652	.648	.646(1)
.7	.613(−1)	.615		.623(−1)	.627(−1)	.628(−1)			.626(3)
1.0	.588(0)	.589	.590	.598(0)	.604(−1)	.606(−2)	.607	.601	.603(3)
1.5	.563	.562	.561	.576	.582	.585		.581	.585
2.0	.547	.548		.562	.573	.576	.578	.574	.578
2.5	.540	.541		.556	.568	.572		.572	.575
3.0	.539	.540		.556	.567	.571	.574	.575	.573
3.5	.540	.542		.558	.571	.574	.576	.575	.578
4.0				.563	.574	.579	.581	.585	.585
u	.487			.494	.502	.506			.522
K'	.2295			.2306	.2317	.2324			.2348
A	.826			.830	.834	.837			.845
B	.008			.017	.024	.027			.033

[a] Smith, e. m. f., ref. 3. [b] Spencer, freezing point, ref. 5. [c] Shedlovsky and MacInnes, cells with transference, ref. 8. [d] Harned, e. m. f., ref. 2. [e] $a = 3.6$ Å. [f] Values of γ in parentheses were computed by equation (5). [g] The numbers in parentheses following values of γ are the differences in the third decimal place between the observed γ and that computed by equation (5), it being positive when the calculated value is greater than that observed.

tion (5) was applied—0.05 to 1 M. The values at concentrations from 1.5 to 4 M were obtained by the second method. From $\overline{H}_m - \overline{H}_{0.05}$ and the extrapolated values of $\overline{L}_2$ at 0.05 M, $\overline{L}_2$ was computed. All these results may be expressed to within the error of their determination by the equation

$$\overline{L}_2 = \overline{L}_2^0 + \alpha t + \beta t^2 \qquad (9)$$

where $\overline{L}_2^0$ is the value of $\overline{L}_2$ at 0° and α and β are constants at constant composition. Values of these quantities are contained in Table IV.

TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY. CONSTANTS OF EQUATION (10)

m	$\overline{L}_2^0$	α	β	$\overline{L}_2$ (18°)	$\overline{L}_2$ (18°)[11]	$(\overline{C}_{p_2} - \overline{C}^0_{p_2})_{25°}$	$(\overline{C}_{p_2} - \overline{C}^0_{p_2})_{10-25°}$[12]
0.05	(34)[a]	2.0	0.014	75	66	2.7	3.7
.1	− 15	3.5	.025	56	67	4.7	5.3
.2	− 80	5.1	.030	22	35	6.6	7.5
.3	− 190	7.5	.034	− 44	− 15	9.2	9.2
.5	− 280	9.4	.037	− 99	−110	11.2	11.9
.7	− 430	12.0	.040	−201	−190	14.0	14.1
1.0	− 570	14.4	.045	−296	−306	16.6	16.8
1.5	− 760	18.4	.049	−413	−465	20.8	20.6
2.0	− 920	22.2	.055	−502	−615	24.7	24.8
2.5	−1000	23.0	.060			26.0	26.6
3.0	−1025	25.4	.066			28.7	29.2
3.5	−1200	27.7	.072			31.5	31.5
4.0	−1270	29.6	.079			33.2	33.6

[a] Extrapolated by equation (9).

Rossini has computed $\overline{L}_2$ at 18°, and the relative partial molal heat capacity, $\overline{C}_p - \overline{C}^0_p$, at 18 to 25° from calorimetric measurements. His values of $\overline{L}_2$, listed in the sixth column of the table, agree well with the results from electromotive force measurements, given in the fifth column of the table, up to 1.5 M. Values of $\overline{C}_{p_2} - \overline{C}^0_{p_2}$ may be computed from our results by the equation

$$\overline{C}_{p_2} - \overline{C}^0_{p_2} = \alpha + 2\beta t \qquad (10)$$

The seventh column of the table contains our values of this quantity at 25°, and the last column Rossini's results. The agreement leaves very little to be desired.

Summary

1. Measurements of the electromotive forces of the cells

Ag–AgCl | KCl (m) | K_xHg | KCl (0.05) | AgCl–Ag

have been made from 0 to 40° inclusive at 5° intervals, varying the concentration, m, from 0.1 to 4 M.

2. From these data, the activity coefficient, relative partial molal heat content and the relative partial molal heat capacity of potassium chloride have been calculated. Activity coefficients have been found to agree well with those obtained by other investigators and the heat data derived from the electromotive forces were found to agree satisfactorily with the results obtained from calorimetric measurements.

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(11) Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

(12) Rossini, *ibid.*, **7**, 47 (1931).