perature, finally, the double salt is not stable at all; it formed only as a temporary metastable phase a few times, but was too labile in respect to the decahydrate to allow any part of its solubility curve to be determined.

Summary

1. Solubility measurements are given for the system $KClO_3$–K_2SO_4–H_2O at 15, 25 and 45°; no double salt formation is found in this system.

2. The system $NaClO_3$–Na_2SO_4–H_2O has been studied at 15, 25, 45 and 75°. A double salt with the formula $NaClO_3 \cdot 3Na_2SO_4$ is formed at 25° and above, having always a very short range of stable existence, but persisting in metastable equilibrium over a very considerable range of concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Potassium Hydroxide Solutions from Electromotive Force Measurements

BY HERBERT S. HARNED AND MELVIN A. COOK[1]

The electromotive forces of the cell

$$H_2 \mid KOH(m_2) \mid K_xHg \mid KOH(m_1) \mid H_2 \qquad (1)$$

have been measured at 25° by Knobel.[2] Following the procedure which Harned and Hecker[3] employed with sodium hydroxide solutions, a thorough investigation of these cells has been made. Measurements have been obtained from 0 to 35° at 5° intervals and at concentrations from 0.1 to 4 *M*. For purposes of theoretical computations, these measurements have been supplemented with density determinations over the above ranges of temperature and concentration. From these data, the activity coefficient, the relative partial molal heat content and the relative partial molal heat capacity of this hydroxide have been computed.

Experimental Results

The method of measurement and cell technique was with slight modification the same as described by Harned,[4] and Harned and Hecker.[3] The hydrogen electrodes were of the usual platinized platinum foil type. The potassium amalgam was prepared as described by Harned and was approximately 0.02% potassium. The temperature control was ±0.02°. A stock solution of 5 *M* potassium hydroxide was made from the highest grade analyzed chemical. The carbonate present was removed by addition of a slight excess of a barium hydroxide solution. The solution was then boiled under vacuum, and kept under an atmosphere of hydrogen. From this solution a reference solution of 0.05 *M* hydroxide was made. The solutions of varying concentrations were made from the 5 *M* stock solution by weight dilution with water. Potassium hydroxide solutions were analyzed by titration with a gravimetrically standardized hydrochloric acid solution. The concentrations were all known to within ±0.05%.

The densities of the solutions were obtained by means of dilatometers in the manner described by Harned, Keston and Donelson.[5]

The measurements of the electromotive forces were made with a Leeds and Northrup Type K potentiometer. Results were obtained at 25 different potassium hydroxide concentrations and at 5° intervals from 0 to 35°. Duplicate or triplicate results were obtained at each concentration and temperature. The results, all of which were reproducible to within ± 0.08 mv., were smoothed to round concentrations by plotting the function $(E - 2k \log m/0.05)$, where k is $2.303\ RT/F$, against the molality. 8.315, $t + 273.1$ and 96,500 were employed for R, T and F, respectively. Since a table of all these results is voluminous, we have resorted to the expediency of expressing the electromotive forces at a given concentration by means of the equation

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

The constants of this equation were determined by the graphical method used by Harned and Nims.[6] The values of E_{25}, a and b are given in

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[1] This communication contains part of the material of a dissertation to be presented by Melvin A. Cook to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

[2] Knobel, THIS JOURNAL, **45**, 70 (1923).

[3] Harned and Hecker, *ibid.*, **55**, 4838 (1933).

[4] Harned, *ibid.*, **47**, 677 (1925).

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

[6] Harned and Nims, *ibid.*, **54**, 423 (1932).

Table I. The next to last column of the table gives the average magnitude of the deviation of the observed results and those computed by equation (2) at each of the concentrations. b' are smoothed values of b to be used for the computation of the relative partial molal heat capacity.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS:
$H_2 \mid KOH(m) \mid K_xHg \mid KOH(0.05) \mid H_2$
at 25° and Constants of Equation (2). Valid from 0 to 35°

m	E_{25}	$a \times 10^6$	$-b \times 10^6$	Δ, mv.	$-b' \times 10^6$
0.1	0.03426	108.5	0.46	0.01	0.56
.15	.05330	167.0	.60	.05	.58
.25	.07834	252.8	.63	.03	.64
.35	.09451	308.8	.69	.04	.70
.5	.11237	345.9	.83	.05	.81
.75	.13423	429.6	1.06	.05	.97
1.0	.15044	494.2	1.17	.05	1.13
1.5	.17538	579.9	1.23	.02	1.43
2.0	.19511	632.9	1.43	.05	1.74
2.5	.21219	680.7	1.86	.06	2.02
3.0	.22759	699.3	2.54	.07	2.30
3.5	.24240	725.0	2.73	.10	2.65
4.0	.25556	746.0	2.80	.07	2.78

The density data have been expressed by an equation of the form

$$d = d_0 + a'm + b'm^{3/2} \qquad (3)$$ [7]

where d_0 is the density of water at the temperature in question and a' and b' are constants. The latter were evaluated from the observed densities by the method of least squares. Values of the constants of equation (3) are listed in Table II.

TABLE II

DENSITY DATA: CONSTANTS OF EQUATION (3)

t	d_0	a'	b'
0	0.9999	0.05875	0.00667
5	1.0000	.0572	.0065
10	0.9997	.05555	.0058
15	.9991	.0548	.0055
20	.9982	.0535	.0051
25	.9970	.0526	.0047
30	.9957	.0514	.0043
35	.9940	.0516	.0045

Activity Coefficients

Upon rearranging the usual expression for the electromotive force for cells of the type used here, we obtain

$$\log \frac{\gamma}{\gamma_{0.05}} = \frac{E}{2k} - \log \frac{m}{0.05} - {}^1\!/_2 \log \frac{p_{0.05}}{p} \qquad (4)$$

Here γ is the activity coefficient of the hydroxide, $\sqrt{\gamma_K \gamma_{OH}}$, at a concentration m, $\gamma_{0.05}$ the value of this quantity at the reference concentration, 0.05 M, $p_{0.05}$ the vapor pressure of the reference solution and p the vapor pressure of the solution of hydroxide at the concentration m.

The Gibbs–Duhem equation may be converted to the form

$$-\mathrm{d} \log p = \frac{2}{55.51 \times 2.303}\, \mathrm{d}m + \frac{2}{55.51}\, m\, \mathrm{d} \log \gamma \qquad (5)$$

since $\log \gamma_{0.05}$ is a constant, $\mathrm{d} \log \gamma$ in the last term may be written $\mathrm{d} \log \gamma/\gamma_{0.05}$. Making this substitution in equation (5) and integrating, we obtain

$${}^1\!/_2 \log \frac{p_{0.05}}{p} = \frac{1}{55.51} \int_{0.05}^{m} m\, \mathrm{d} \log \frac{\gamma}{\gamma_{0.05}} + \frac{m - 0.05}{55.51 \times 2.303} \qquad (6)$$ [8]

To evaluate the first term on the right of equation (6), values of $\log \gamma/\gamma_{0.05}$, obtained from equation (4) (omitting the last term), are plotted against m, and the area under the curve evaluated. Upon substituting this result in equation (6), 1/2 $\log p_{0.05}/p$ is obtained. This result is substituted in equation (4) and a more exact value of $\log \gamma/\gamma_{0.05}$ is obtained. This result is employed to reëvaluate the first term on the right of equation (6). This method of arithmetical approximation is repeated until both equations (4) and (6) are satisfied. In Table III, values of 1/2 $\log p_{0.05}/p$ are given. This quantity changes at the most only about 3 units in the fourth decimal place between the limits 0 and 35°. Since 1 in this decimal place corresponds to a difference of 0.01 mv. in the electromotive force, an assumption of constancy is within the error of the experiment.

TABLE III

VALUES OF THE VAPOR PRESSURE TERM

m	0.1	0.15	0.25	0.35	0.5	0.75	1.0	1.5	2.0	2.5	3.0	3.5	4.0
$^1/_2 \log p_{0.05}/p$	.0004	.0008	.0015	.0022	.0033	.0053	0.0072	0.0106	0.0154	0.0210	0.0278	0.0344	0.0412

By substitution of these values for the vapor pressure correction in equation (4), values of $\log \gamma/\gamma_{0.05}$ were obtained. For purposes of extrapolation, we have employed the equation of Debye and Hückel which for a 1–1 electrolyte is

$$\log \gamma = -uc^{1/2}/(1 + A(2c)^{1/2}) + Bc - \log(1 + 0.036m) \qquad (7)$$

For the activity coefficient ratio, this equation becomes

$$\log \gamma/\gamma_{0.05} = -u[c^{1/2}/(1 + A(2c)^{1/2}) - (0.05)^{1/2}/(1 + A(0.1)^{1/2})] + B(c - 0.05) - \log(1 + 0.036m)/(1 + 0.0018) \qquad (8)$$

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[7] Root, THIS JOURNAL, **55**, 850 (1933).

[8] Harned and Hecker's[3] equation (5) due to typographical error differs from this equation.

TABLE IV

ACTIVITY COEFFICIENTS OF POTASSIUM HYDROXIDE

m	0°	10°	20°	25°	35°
0.05	(0.829)	(0.828)	(0.825)	(0.824)	(0.822)
.1	.795 (0)	.798 (−2)	.798 (0)	.798 (0)	.793 (2)
.15	.778 (0)	.778 (0)	.776 (0)	.774 (1)	.771 (0)
.25	.758 (−2)	.759 (−2)	.757 (−1)	.757 (−1)	.751 (3)
.35	.738 (0)	.740 (0)	.739 (−2)	.739 (−2)	.733 (0)
.5	.737 (−2)	.735 (1)	.732 (2)	.728 (4)	.724 (3)
.75	.742 (−2)	.743 (−1)	.741 (0)	.740 (1)	.733 (4)
1.0	.755 (0)	.758 (0)	.756 (3)	.756 (2)	.752 (2)
1.5	.809	.815	.814	.814	.809
2.0	.889	.890	.889	.888	.879
2.5	.974	.981	.980	.974	.965
3.0	1.088	1.094	1.087	1.081	1.065
3.5	1.219	1.231	1.219	1.215	1.195
4.0	1.391	1.389	1.361	1.352	1.314
u	0.487	0.494	0.502	0.506	0.516
K'	.2295	.2305	.2317	.2324	.2340
B	.118	.125	.128	.130	.132

(1). $a = 3.7$ Ångström units.

(2). The number in ( ) is the difference in the third decimal place between the observed γ and the value calculated by equation (7), it being positive when the calculated value is greater than the observed.

which is suitable for evaluating A and B. By using values of c computed from the equation

$$c = [1000m/(1000 + 56.1m)](d_0 + a'm + b'm^{3/2}) \quad (9)$$

the constants A and B may be determined by means of equation (8) from two values of the activity coefficient ratio. Firstly, the 0.1 and 1 M results were employed, and secondly, the 0.25 and 0.5 M were used at each temperature. Both computations gave consistent results.

The apparent ionic diameter, a, in Ångström units was obtained from D by means of the equation derived from theory

$$A = K'a \quad (10)$$

by using values of K' computed by Harned and Ehlers.[9] No indication of a variation of this quantity with temperature was found. The results of the calculation indicated a constant value of 3.7 Å.

The values of the constant B may be expressed within narrow limits by the equation

$$B = 0.118 + 0.00072t - 1.06 \times 10^{-5}t^2 \quad (11)$$

The observed activity coefficients at some of the temperatures are given in Table IV. The differences between these values and those computed by equation (7) are designated in the table. Values of the parameters of equation (7) necessary for this computation are given in the bottom rows of the table. The range of validity of equation (7) is from 0 to 1 M.

The Relative Partial Molal Heat Content

$\bar{L}_2$ was evaluated at concentrations from 0.05 to 1 M by the differentiated form of equation (7). If the value of $\ln \gamma$ given by equation (7) be substituted in the equation for $\bar{L}_2$, namely

$$\bar{L}_2 = -\nu RT^2 \partial \ln \gamma/\partial T \quad (12)$$

and the differentiation performed, we obtain

$$\bar{L}_2 = U'c^{1/2}/(1 + A(2c)^{1/2}) - V'/(1 + A(2c)^{1/2})^2 (c\mathrm{d}A/\mathrm{d}T + A\ \mathrm{d}c/2\mathrm{d}T) + W'(B\mathrm{d}c/\mathrm{d}T + c\mathrm{d}B/\mathrm{d}T) \quad (13)$$

where U', V' and W' are isothermal constants[5] (eq. 11, Table VI) derived from theory. $\mathrm{d}B/\mathrm{d}T$ was obtained by differentiating equation (11). $\mathrm{d}A/\mathrm{d}T = a\ \mathrm{d}K'/\mathrm{d}T$ was obtained graphically from the values of K' in Table IV. Since equation (9) may be written $c = A'm + B'm^2 + C'm^{5/2}$, we have that

$$\mathrm{d}c/\mathrm{d}T = m\mathrm{d}A'/\mathrm{d}T + m^2\mathrm{d}B'/\mathrm{d}T + m^{5/2}\mathrm{d}C'/\mathrm{d}T \quad (14)$$

The values of these differential coefficients were determined graphically at each temperature and then used to determine $\mathrm{d}c/\mathrm{d}T$. All the required quantities were then substituted in equation (13) and values of $\bar{L}_2$ at concentrations up to 1 M were obtained.

In addition to this calculation, the partial molal heat content relative to the 0.05 M solution was computed by the Gibbs–Helmholtz equation

$$\bar{H}_m - \bar{H}_{0.05} = NE'F - NF\mathrm{d}E'/\mathrm{d}T \quad (15)$$

in which E' is the electromotive force corrected for the vapor pressure term. Since we have

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(9) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933). The values of u used were also taken from this paper.

shown that this term does not vary sufficiently with the temperature to affect our results, the equation for E' is according to equation (2) simply

$$E' = E'_{25} + a(t - 25) + b(t - 25)^2 \qquad (16)$$

whence

$$\overline{H}_m - \overline{H}_{0.05} = NE'F - NFT[a + 2b(t - 25)] \qquad (17)$$

The values of this quantity obtained by this method were within 20 calories of those computed by equation (13) except in the range of concentration of 0.1 to 0.25 M at temperatures below 15° where a discrepancy of the order of 50 calories sometimes occurred. We consider that in these cases the computation by equation (13) is the more reliable. At concentrations from 1.5 to 4 M, inclusive, equation (17) was employed. These results are given within 10 cal., which is less than the error in their determination, by the equation

$$\overline{L}_2 = \overline{L}_2^0 + \alpha t + \beta t^2 \qquad (18)$$

where $\overline{L}_2^0$ is the value of $\overline{L}_2$ at 0°, and α and β are constants. Table V contains the values of these constants at the designated hydroxide concentrations. A plot of these results is shown in Fig. 1.

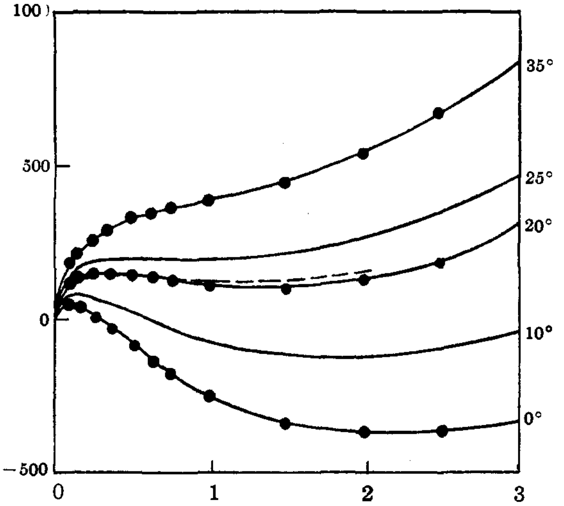

Fig. 1.—The relative partial molal heat content (Rossini's values at 18° are represented by the dotted line).

Rossini[10] has computed $\overline{L}_2$ for potassium hydroxide in aqueous solution at 18° from heat of dilution data. These values are also plotted in the figure whence it is apparent that excellent agreement is obtained in the concentration range from 0.05 to 1 M. At concentrations from 1 to 2 M, the agreement is not so good.

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENT AND SPECIFIC HEAT-CONSTANTS OF EQUATION (18) AND (19)

m	α	β	$\overline{L}_2^0$	$(\overline{C}_{p_2} - \overline{C}^0_{p_2})_{25}$
0.05	2.4	0.017	37	3.2
.1	3.6	.029	41	5.0
.15	4.7	.030	30	6.2
.25	6.4	.032	− 1	8.0
.35	8.2	.034	− 35	9.9
.5	10.4	.036	− 95	12.2
.75	13.6	.040	−180	15.6
1.0	16.2	.043	−270	18.4
1.5	20.6	.050	−335	23.1
2.0	24.6	.057	−381	27.4
2.5	28.2	.063	−390	31.3
3.0	31.5	.070	−356	35.0
3.5	34.5	.078	−335	38.4
4.0	37.4	.081	−226	41.5

The Relative Partial Molal Heat Capacity

By differentiation of $\overline{L}_2$ with respect to the temperature, $(\overline{C}_{p_2} - \overline{C}^0_{p_2})$ is found to be expressed by

$$(\overline{C}_{p_2} - \overline{C}^0_{p_2}) = \alpha + 2\beta t \qquad (19)$$

Values of this quantity at 25° are given in the last column of Table V. In Fig. 2, these results have been plotted against $m^{1/2}$ and are designated by circles. The two solid straight lines represent the equations which Gucker and Schminke[11] and Rossini[12] proposed to express the results obtained from calorimetric data. The limiting slope of the Debye and Hückel theory is also represented. The maximum difference between our results and those of Gucker and Sch-

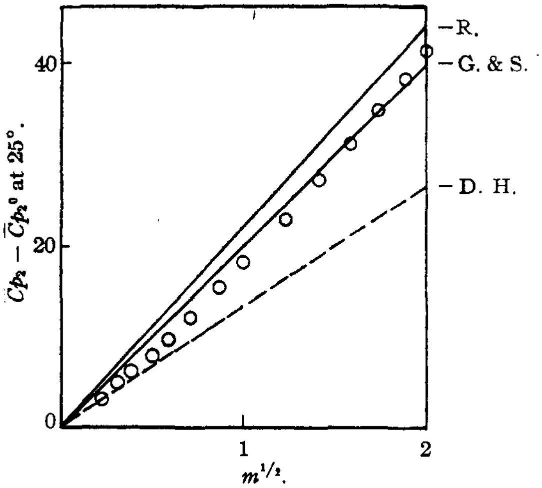

Fig. 2.—The relative partial molal heat capacity; R. Rossini; G. & S., Gucker and Schminke; D. H., Debye–Hückel limiting law.

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[10] Rossini, *Bur. Standards J. Research*, **6**, 791 (1931).

[11] Gucker and Schminke, THIS JOURNAL, **54**, 1358 (1932).

[12] Rossini, *Bur. Standards J. Research*, **7**, 47 (1931).

minke is two calories. This is good agreement considering all the difficulties encountered in this determination. Our results indicate a slight curvature.

Summary

Measurements of the electromotive forces of the cell $H_2 \mid KOH(m) \mid K_xHg \mid KOH(0.05) \mid H_2$ have been made from 0 to 35° inclusive at 5° intervals and m was varied 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 have been computed. Satisfactory agreement with similar results derived from calorimetric data has been obtained.

NEW HAVEN, CONN. RECEIVED DECEMBER 24, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity of Carbon Disulfide from 15 to 300°K. The Entropy and Heat of Fusion of Carbon Disulfide

BY OLIVER L. I. BROWN[1] AND GEORGE G. MANOV

The heat capacity of solid and liquid carbon disulfide, and the heat of fusion have been determined in order to complete the data necessary for the calculation of the entropy of carbon disulfide.

Material.—The carbon disulfide was fractionally distilled several times after drying with calcium chloride. About two liters of material obtained in this way was fractionally distilled using a special column about 60 cm. high, packed with brass shoe eyelets. The distilling flask contained phosphorus pentoxide to remove the last traces of water, and the distillation was carried out in an atmosphere of helium gas to avoid possible oxidation of the carbon disulfide. About half the distillate was collected as a middle fraction, which served as the starting material for a new fractionation. This procedure was repeated a third time before the product was placed in the calorimeter. The calorimeter, which was copper, was filled in such a manner that the carbon disulfide came in contact with only helium, copper, glass and the solder used for sealing the top. A small amount of helium was admitted to ensure heat conduction in the sample before the calorimeter was sealed. From the change in melting point with percentage

TABLE I

HEAT CAPACITY OF CARBON DISULFIDE; 0°C. = 273.1°K.

Run	T, °K.	C_p cal./mole/deg.	ΔT
37	15.05	1.65	2.771
38	17.50	2.22	2.239
39	20.15	2.87	3.113
40	23.06	3.48	2.754
41	26.19	4.18	3.237
42	29.76	4.96	3.953
43	33.68	5.64	3.970
44	37.67	6.32	4.054
45	42.22	6.97	4.676
46	47.39	7.53	5.670
47	52.25	7.91	4.646
48	57.52	8.50	5.884
49	63.47	8.92	6.289
50	69.96	9.36	6.856
51	75.54	9.57	4.579
52	81.19	9.86	6.543
53	87.21	10.31	6.496
5	89.37	10.31	4.584
6	94.17	10.61	4.733
54	94.21	10.76	6.441
7	99.00	10.98	4.950
8	104.00	11.31	4.708
1	108.17	11.48	3.937
9	108.93	11.59	5.114
10	114.03	11.82	5.854
2	119.36	12.04	4.013
11	119.91	12.07	5.913
12	126.03	12.39	5.397
13	131.54	12.58	5.578
14	137.38	12.81	6.112
15	144.31	13.05	6.521
16	150.47	13.26	5.747
3	152.23	13.34	4.720
17	155.63	13.50	4.548
4	156.83	13.53	4.488
18	158.74	14.46	1.621
	161.11	Melting point	
19	163.93	18.10	4.895
20	169.51	17.97	6.314
21	176.17	17.91	6.968
22	183.04	17.94	6.672
23	189.64	17.99	6.418
24	192.30	17.91	5.926
25	198.44	17.90	6.446
26	205.28	18.00	7.007
27	211.83	18.02	5.884
28	219.31	17.95	7.620
29	227.34	17.93	8.347
30	235.80	18.00	7.764
31	244.25	18.00	8.712
32	253.06	17.88	8.430
33	261.66	18.10	8.034
34	269.69	18.08	7.478
35	278.22	18.06	8.932
36	297.43	18.17	9.440

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