cedure was followed. Metallic sodium was dissolved in absolute alcohol, the malonic ester nitrile added and the mixture refluxed for a few minutes with the alkyl halides, methyl iodide and ethyl bromide, respectively.

The alcoholic solution was filtered and the alcohol evaporated under reduced pressure. The residue was suspended in water and extracted with ether. The ether extract was dried, the ether evaporated and the remaining oil fractionally distilled.

The authors desire to express their appreciation to the Reed and Carnrick Co., Jersey City, N. J., for a fellowship grant.

Summary

1. p-Methoxyphenylmalonic acid and several of its derivatives were prepared and characterized.

2. Its use in general alkylation reactions has been demonstrated.

NEW YORK, N. Y. RECEIVED MAY 27, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Aqueous Sodium Bromide Solutions from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND CHESTER C. CRAWFORD

The electromotive forces of the cells

$$\text{Ag–AgBr} \mid \text{NaBr } (m) \mid \text{Na}_x\text{Hg} \mid \text{NaBr } (0.1) \mid \text{AgBr–Ag} \qquad (1)$$

have been obtained at 25° by Harned.[2] In this communication, a more extensive series of measurements of these cells, covering the ranges of temperature and concentration from 0 to 40° and 0.1 to 4 M has been obtained. From the results, the activity coefficient, relative partial molal heat content and the relative partial molal heat capacity of sodium bromide in aqueous solutions have been calculated.

Experimental Results

With minor variations, the cell technique was the same as that employed by Harned.[2] Large amalgam droppers were employed so as to facilitate measurement at different temperatures. Four cells were measured at each concentration and at 5° intervals from 0 to 40° inclusive. These were corrected slightly so that all results were obtained at round concentrations. The silver[3]-silver bromide electrodes were made according to the method of Keston[3] by heating a mixture of silver bromate and oxide.

The electromotive forces 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 contained in Table I. In the last column of the table, the average values of the deviations between the observed results and those calculated by equation (2) are given. The third column contains the results at 25° obtained by Harned.[2] The agreement of these with present results is good, particularly since Harned employed silver–silver bromide electrodes prepared by electrolysis. Smoothed values of b which are useful for the computation of the relative partial molal heat capacity are given in the next to last column of the table.

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Ag–AgBr | NaBr (m) | Na$_x$Hg | NaBr (0.1) | AgBr–Ag AT 25° AND CONSTANTS OF EQUATION (2). VALID FROM 0 TO 40°

m	E_{25}	$E_{25}{}^2$	$a \times 10^4$	$-b \times 10^6$	$-b' \times 10^6$	Δ, mv.
0.2	0.03276	0.0327	1.08	0.45	0.35	0.14
.3	.05202	....	1.77	.55	.55	.15
.5	.07657	.0769	2.63	.93	.93	.07
.7	.09327	....	3.29	1.30	1.25	.06
1	.11163	.1118	4.20	1.50	1.50	.05
1.5	.13373	.1333	5.25	1.80	1.76	.05
2	.15069	.1507	6.06	2.03	2.02	.05
2.5	.16511	.1650	6.74	2.33	2.28	.08
3	.17757	.1776	7.31	2.50	2.35	.07
3.5	.18865	.1884	7.72	2.83	2.81	.08
4	.19871	.1988	9.12	3.15	3.07	.15

The computations required concentrations in moles per liter of solution, c. These may be computed accurately from the molalities by the equation

$$c/m = d_0 + A'm + B'm^2 \qquad (3)$$

in which d_0 is the density of water, and A' and B' are isothermal constants. Values of d_0, A' and B' computed from density data by the method of least squares are given in Table II.

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[1] This contribution contains material from a dissertation presented by Chester C. Crawford to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1937.

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

[3] Keston, *ibid.*, **57**, 1671 (1935).

TABLE II

CONSTANTS OF EQUATION (3)

t	d_0	$-A'$	B'
0	0.99987	0.02125	−0.00029
5	.99999	.02223	− .00014
10	.99973	.02306	− .00004
15	.99913	.02375	.00003
20	.99823	.02436	.00010
25	.99707	.02482	.00016
30	.99568	.02518	.00021
35	.99406	.02548	.00025
40	.99225	.02574	.00030

Activity Coefficients

The equation for the electromotive force, E, of the cell is

$$\log \frac{\gamma}{\gamma_{0.1}} = \frac{E}{2k} - \log \frac{m}{0.1} \tag{4}$$

from which the activity coefficient γ, relative to its value at 0.1 M, $\gamma_{0.1}$, may be calculated. k equals $2.303\,RT\,/\,F$. 8.315, $t + 273.1$, and 96,500 were employed for R, T and F, respectively.

TABLE III

ACTIVITY COEFFICIENTS OF SODIUM BROMIDE AND CONSTANTS OF EQUATION (5)[a,b]

$a = 4.1$ Å. $A = K'a$

m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0.1	(0.784)	(0.784)	(0.784)	(0.783)	(0.783)	(0.782)	(0.781)	(0.779)	(0.777)
.2	.738 (2)	.739 (1)	.741 (0)	.740 (1)	.741 (0)	.740 (0)	.739 (0)	.737 (0)	.734 (1)
.3	.713 (2)	.716 (0)	.718 (0)	.720 (−2)	.718 (0)	.718 (0)	.717 (0)	.715 (0)	.712 (1)
.5	.685 (1)	.689 (1)	.693 (0)	.693 (2)	.695 (0)	.695 (1)	.694 (2)	.692 (2)	.689 (2)
.7	.670 (0)	.675 (1)	.681 (0)	.684 (0)	.683 (0)	.687 (−1)	.686 (1)	.685 (0)	.685 (2)
1	.659 (−1)	.667 (−1)	.675 (−1)	.680 (−1)	.684 (−2)	.686 (−2)	.687 (−3)	.686 (−3)	.686 (−2)
1.5	.664	.673	.686	.693	.699	.703	.706	.708	.707
2	.679	.693	.708	.719	.727	.734	.739	.741	.743
2.5	.709	.727	.745	.738	.769	.773	.784	.789	.791
3	.745	.766	.787	.802	.815	.826	.834	.839	.842
3.5	.787	.811	.834	.852	.866	.878	.887	.893	.896
4	.832	.858	.885	.905	.921	.934	.945	.951	.954
u	.487	.490	.494	.498	.502	.506	.511	.516	.522
K'	.2295	.2300	.2305	.2311	.2317	.2324	.2332	.2340	.2348
B	.0420	.0494	.0554	.0602	.0636	.0664	.0684	.0698	.0702

[a] Values of γ at 0.1 M in parentheses were calculated by equation (5).

[b] The numbers in parentheses following the observed values of γ are the differences in the third decimal place between these and the values computed by equation (5). They are positive when the calculated are greater than observed values.

The extrapolation was made by means of the Debye and Hückel equation

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

The parameters A and B were evaluated from two values of the activity coefficient ratios in the region of concentration from 0.1 to 1 M.

Table III contains the activity coefficient data. The values in parentheses at 0.1 M were calculated by equation (5). The results tabulated were computed from electromotive forces by equation (4) and these values of $\gamma_{0.1}$. The numbers in parentheses immediately following the γ-values are the deviations in the third decimal between the observed and calculated results. Equation (5) is valid up to 1 M. The isothermal constants of equation (5) are recorded at the bottom of the table. It was found that a satisfactory computation was possible by using a value of the apparent ionic diameter, α, of 4.1 Å. at all temperatures.

The Relative Partial Molal Heat Content and Heat Capacity

A reference value of $\overline{L}_2$ at 0.1 M was obtained by the differentiated form of equation (5)

$$\overline{L}_2 = \frac{U'c^{1/2}}{1 + A(2c)^{1/2}} - \frac{V'}{(1 + A(2c)^{1/2})^2}\left[c\,\frac{\mathrm{d}A}{\mathrm{d}T} + \frac{A}{2}\,\frac{\mathrm{d}c}{\mathrm{d}T}\right] + W'\left[B\,\frac{\mathrm{d}c}{\mathrm{d}T} + c\,\frac{\mathrm{d}B}{\mathrm{d}T}\right] \tag{6}$$

where U', V', and W' are isothermal constants.[4,5] The temperature coefficients $\mathrm{d}A/\mathrm{d}T$, $\mathrm{d}B/\mathrm{d}T$ and $\mathrm{d}c/\mathrm{d}T$ were determined by suitable graphical methods. In addition to this, the partial molal heat content relative to its value at 0.1 M, $(\overline{H}_\mathrm{m} - \overline{H}_{0.1})$, was computed by the Gibbs–Helmholtz equation. This was added to the extrapolated value $\overline{L}_{2(0.1)}$. The final values of $\overline{L}_2$ were expressed by the equation

$$\overline{L}_2 = \overline{L}_{2(0)} + \alpha t + \beta t^2 \tag{7}$$

where $\overline{L}_{2(0)}$ is the value of the relative partial molal heat content at 0°, and α and β are constants at constant composition. Table IV contains these constants.

Values of $\overline{L}_2$ determined calorimetrically are not available for comparison with the present re-

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(4) Harned, Keston and Donelson, THIS JOURNAL, **58**, 989 (1936).

(5) Harned and Cook, *ibid.*, **59**, 496 (1937); **59**, 1290 (1937).

TABLE IV

RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY. CONSTANTS OF EQUATION (7)

m	$\bar{L}_{2(0)}$	α	β	$(\bar{C}_p-\bar{C}_{p0})_{18}$	$(\bar{C}_p-\bar{C}_p)_{18-25}$
0.1	− 23	4.6	0.015	5.1	6.4
.2	− 140	8.2	.023	9.0	9.1
.3	− 210	11.8	.027	12.8	11.1
.5	− 400	17.3	.036	18.6	14.4
.7	− 580	21.8	.044	23.4	17.1
1	− 830	23.5	.049	25.3	20.4
1.5	−1140	27.4	.055	29.4	(25)
2	−1390	30.6	.061	32.8	(29)
2.5	−1600	33.6	.066	36.0	(33)
3	−1790	37.0	.073	39.6	(35)
3.5	−1940	41.4	.079	44.2	(38)
4	−2020	43.2	.086	46.3	(41)

sults. However, values of $(\bar{C}_p - \bar{C}_{p0})$ up to 1 M have been determined by Randall and Rossini[6] by heat measurement. In the fifth column of the table are given values of this quantity computed from our results by the equation

$$(\bar{C}_p - \bar{C}_{p0}) = \alpha + 2\beta t \qquad (8)$$

In the last column the values computed by Rossini's equation are given.[7] Those in parentheses are extrapolated by this equation to regions of concentration where experimental results were not available. The agreement between the calorimetric and electromotive force determinations although fairly good does not equal that recently obtained with potassium hydroxide and potassium chloride solutions.[5]

Summary

1. The electromotive forces of the cells

Ag–AgBr | NaBr (m) | Na$_x$Hg | NaBr (0.1) | AgBr–Ag

have been obtained at temperatures from 0 to 40° inclusive and at concentrations, m, varying from 0.1 to 4 M.

2. From these, the activity coefficient, relative partial molal heat content and heat capacity of sodium bromide have been calculated.

NEW HAVEN, CONN. RECEIVED AUGUST 7, 1937

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

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

The Atomic Weight of Carbon. The Ratio of Benzoyl Chloride to Silver[1]

BY ARTHUR F. SCOTT AND FRANK H. HURLEY, JR.

In the current report of the Committee on Atomic Weights of the International Union of Chemistry,[2] the atomic weight of carbon has been changed from 12.00 to 12.01. Evidence favoring the higher value has been accumulating for the past few years as a result of gas-density and mass-spectrographic measurements, but it was not until very recently that this evidence was supported by a purely chemical determination. Such a determination was made by Baxter and Hale,[3] who obtained the value 12.010 from measurements of the ratio C:O$_2$ made by the combustion of hydrocarbons. This value is appreciably higher than the value 12.001 obtained by Richards and Hoover[4] from very careful measurements of the ratios Na$_2$CO$_3$:2Ag and Na$_2$CO$_3$:2AgBr, perhaps the best of the older chemical determinations.

Of all the other chemical determinations of the atomic weight of carbon, only one was made by the most accurate method developed for atomic weights, namely, the direct titration of halides with silver, and this one determination, the ratio of tetraethylammonium bromide to silver measured by A. Scott in 1909,[5] was not made with the improvements in technique characteristic of modern atomic weight work. In view of this rather striking fact, it seemed desirable to attempt such a determination as a check on the recent work of Baxter and Hale. Of the innumerable organic halides which might be used for fixing the atomic weight of carbon, benzoyl chloride appeared to be the most desirable. It has a simple formula and its properties are well known. It contains seven atoms of carbon per molecule and the atomic weights needed in the calculation are all well established. It is not difficult to prepare and the parent substance, benzoic acid, is capable of a high degree of purification. Finally, its boiling point (197°) is sufficiently high to suggest that it could be separated from

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[1] Abstract of a thesis by Frank H. Hurley, Jr., presented to the faculty of the Rice Institute in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May 19, 1937.

[2] THIS JOURNAL, **59**, 219 (1937).

[3] Baxter and Hale, *ibid.*, **58**, 510 (1936); **59**, 506 (1937).

[4] Richards and Hoover, *ibid.*, **37**, 95 (1915).

[5] A. Scott, *J. Chem. Soc.*, **95**, 1200 (1909).