The authors consider this a very satisfactory method for the determination of small amounts of iodine in natural waters.

Manhattan, Kansas

[Contribution from the Chemical Laboratory of Washington State College]

THE ACTIVITY COEFFICIENTS AND TRANSFERENCE NUMBERS OF BARIUM BROMIDE

By Ralph W. Gelbach and Walter F. Huppke

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Experimental

Electromotive forces of concentration cells of the following types have been measured.

(A) $Hg_xBa \mid BaBr_2, m_1, AgBr \mid Ag - Ag \mid AgBr, BaBr_2, m_2 \mid BaHg_x$

(B) $Hg_xBa \mid BaBr_2, m_1 \mid BaBr_2, m_2 \mid BaHg_x$

(C) $Ag \mid AgBr, BaBr_2, m_1 \mid BaBr_2, m_2, AgBr \mid Ag$

(D) $Ag \mid AgBr, BaBr_2, 0.03m \mid BaHg_x, 0.0424\%$

All measurements were made at 25 ± 0.01°.

Materials, Apparatus and Method.—Chemically pure barium bromide was twice recrystallized from distilled water and finally from conductivity water. A stock solution was made from this and the barium bromide content determined gravimetrically by the silver bromide method. Weighed portions of this solution were diluted to the approximate concentrations, boiled to remove oxygen and finally diluted with oxygen-free water to the desired molality. The dilutions were made with an accuracy of about 0.1%.

The mercury and amalgams were prepared in the manner previously described.[1]

The apparatus was essentially the same as used before. The amalgam electrodes were similar to those used by T. W. Richards[2] with the exception that the platinum contact was sealed in beyond the bend in the electrode so that the solution could not so easily come in contact with the platinum. This difficulty was further overcome by filling the tip with paraffin oil which formed a film on the inner wall and prevented the water from entering the capillary. The amalgam was permitted to flow from the tip at the rate of about one drop per second.

The silver bromide electrodes were prepared by heavily coating the platinum foil electrodes with silver and then electrolytically forming the silver bromide from a solution of potassium bromide. A rotating electrode was used which aided materially in the plating processes. Electrodes prepared in this way usually deviated among themselves by not more than 0.03 millivolt.

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[1] Pearce and Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

[2] Richards and Conant, This Journal, **44**, 601 (1922).

In Table I are given the electromotive forces of the concentration cells with and without liquid junction. The value given in each case is the mean of at least two separate sets of readings. The maximum deviation seldom exceeded 0.1 millivolt.

TABLE I

ELECTROMOTIVE FORCES OF CELLS WITH AND WITHOUT TRANSFERENCE

m_1	m_2	E	E_B	E_C
0.003	0.030	0.07741	....	0.03390
.005	.050	.07641	0.04323	.03320
.010	.050	.05270	.03001	.02266
.010	.100	.07444	....	.03224
.030	.100	.03904	.02259	.01639
.030	.300	.07588	.04450	.03133
.050	.500	.07822	.04681	.03136
.100	1.000	.08223	.05028	.03189

The voltage of the cell, Ag | AgBr, $BaBr_2$, 0.03*m* | BaHg 0.0424%, was measured and found to be 1.84807 volts. The values for each of the remaining concentrations have been calculated and are shown in Col. 2 of Table II.

The activity coefficients were calculated from the equation, $E = (3RT/2F)\ ln\ (\gamma_2 m_2/\gamma_1 m_1)$. Assuming the activity in 0.01 *M* barium bromide solution to be equal to that in an equivalent concentration of barium chloride and substituting the value, 0.716, as determined by Lewis and Linhart,[3] we have,

$$\log \gamma m = 0.4343 \times (2FE/3RT) + \log 0.01 \times 0.716$$

The values thus calculated are shown in Col. 5 of Table II.

TABLE II

ACTIVITY COEFFICIENTS AND TRANSFERENCE NUMBERS OF BARIUM BROMIDE SOLUTIONS

m	E_m	E_t	γ_{BaCl_2} L. & L. f. pt. data	γ_{BaBr_2}	N_{Ba}
0.003	1.92548	0.00000	0.807	0.802	0.462
.005	1.90718	.00931	.771	.774	.454
.010	1.88347	.01985	.716	.716	.444
.030	1.84807	.03390	.617	.598	.429
.050	1.83077	.04251	.568	.575	.422
.100	1.80903	.05209	.501	.494	.413
.300	1.77219	.06523	..	.428	.397
.500	1.75255	.07397	..	.428	.389
1.000	1.72680	.08398	..	.417	.378

The transference numbers were calculated by a modification of the method of MacInnes and Beattie.[4] Calling *E* the electromotive force at each concentration determined from cells *A* with the value in the most dilute solution arbitrarily taken as zero, and E_t the corresponding values

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[3] Lewis and Linhart, THIS JOURNAL, **41,** 1952 (1919).

[4] MacInnes and Beattie, *ibid.*, **42,** 1117 (1920).

for cells C, the equation $E_t = 0.00037 + 0.462\,E - 0.211\,E^2$ was obtained by the method of averages.[5] From this were obtained the values of $N_{\text{Ba}} = \text{d}E_t/dE = 0.462 - 0.422\,E$ given in Col. 6 of Table II. The transference numbers determined from Cell B agree with those determined from cell C within 0.2%.

Summary

1. The electromotive forces of concentration cells of barium bromide, both with and without transference, have been measured. From these data the transference numbers have been calculated.
2. The geometric mean activity coefficients have been calculated and are found to agree closely with those calculated for barium chloride from freezing-point data.

PULLMAN, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THERMAL DATA ON ORGANIC COMPOUNDS. III. THE HEAT CAPACITIES, ENTROPIES AND FREE ENERGIES OF TERTIARY BUTYL ALCOHOL, MANNITOL, ERYTHRITOL AND NORMAL BUTYRIC ACID

BY GEORGE S. PARKS AND C. TRAVIS ANDERSON

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In the preceding paper[1] of this series the hypothesis was suggested that the entropy of an organic compound is related in a simple definite manner to its constitution. At that time considerable data were adduced in support of this hypothesis which, moreover, seems inherently plausible in view of the well-known regularities in other thermal properties, such as the heats of formation, of organic substances. However, we have believed that the proposition should be further tested. With this end in mind, we have now determined the heat capacities of four compounds, namely, *tert.*-butyl alcohol, mannitol, erythritol and *n*-butyric acid, in order that the entropies obtainable thereby might be compared with the values predicted from the constitution.

Materials

tert.-Butyl Alcohol.—A good grade of *tert.*-butyl alcohol (m. p., 20°) was first dehydrated by distillation over lime in the ordinary manner. The resulting distillate was then subjected to eight successive fractional crystallizations. The final product melted at 25.4° as measured in the heat of fusion determinations. De Forcrand[2] has

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[5] Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, **1918**, p. 163.

[1] Parks and Kelley, THIS JOURNAL, **47**, 2094 (1925).

[2] de Forcrand, *Compt. rend.*, **136**, 1034 (1903).