[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

The Thermodynamics of Aqueous Solutions of Potassium Bromide at 25° from e. m. f. Measurements on Cells with Transference

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Previous papers from this Laboratory[1,2] have reported thermodynamic data for aqueous solutions of potassium and sodium chloride at temperatures from 15 to 45°; isopiestic comparison[3] at concentrations up to tenth molar has shown that the results for the two salts were mutually consistent, and this fact, combined with the agreement between the activity and the thermal data, is good evidence for the reliability of the e. m. f. measurements from which the activity and osmotic coefficients were obtained. Both e. m. f. investigations, however, involved the use of silver–silver chloride electrodes; we have therefore carried out at 25° measurements on the cell with transference

$$\text{Ag, AgBr/KBr}(m_1)//\text{KBr}(m_2)\text{/AgBr, Ag}$$

From these, it is possible to obtain isopiestically a further check, independent of the Ag, AgCl electrode.

Experimental

The cell and the experimental technique have been adequately described.[1] After silver plating, the electrodes were bromidized anodically for twenty-five minutes in a tenth normal solution of potassium bromide at a current of 0.65 milamp.; later, it was discovered that a lower current (0.4 milamp.) for a longer time (forty minutes) gave somewhat steadier electrodes. As in the earlier work, the bias potential between the electrodes was determined both before and after a run with both electrodes in the same solution; if these two values were not the same within 2 or 3 microvolts, and if they did not agree within the same limits with the bias obtained from the difference in the e. m. f. for the original and the reversed filling of the cell, the run was rejected. In general, the silver–silver bromide electrodes were much more erratic in their behavior than were the corresponding chloride electrodes, and independent measurements on the same pair of solutions, each with a different pair of electrodes, did not agree as closely among themselves as did those for potassium and sodium chlorides. For example, the fourth observation posted in Table I, −7.792, is the mean of three results, corrected for bias potential, −7.776, −7.800, −7.801 mv., showing a mean absolute deviation from the mean of 11 microvolts; cells with silver–silver chloride electrodes and potassium or sodium chloride as electrolyte, will as a rule show mean deviations of half this amount or less.

The potassium bromide was British Drug Houses Analar, twice crystallized from conductivity water, filtered through sintered glass, and crystallized again. The solutions were made gravimetrically from the salt, which had been fused in platinum in an atmosphere of dry carbon dioxide-free nitrogen, and conductivity water (specific conductance 1.0 to 1.5 × 10^{-6}). Before being forced into the cells, the solutions were swept out with carbon dioxide-free, water-saturated air. In computing molalities, all weights were reduced to vacuum.

In Table I, m_1 and m_2 are the molalities and $E_{\text{obs.}}$ is the average in millivolts of the e. m. f. of the individual cells, each corrected for bias potential. The e. m. f. can be expressed as usual by

$$E = kt^0_+ \ \Delta \log \gamma m + k \int_{m_2}^{m_1} t_\delta \, d \log \gamma m \qquad (1)$$

where $k = 2.3026 \times 2RT/F = 118.29$, t^0_+ is the transference number[4] of potassium ion at infinite dilution, *viz.*, 0.4847, $t_\delta = t_+ - t^0_+$, and the other symbols have their usual significance. In evaluating the last term of Eq. 1, the transference numbers of Keenan and Gordon's Table II were employed,[4] the final values of the integral

$$- k \int_0^m t_\delta \, d \log \gamma m \qquad (2)$$

in mv. being 0.050, 0.095, 0.140, 0.150 and 0.145 for $m^{1/2}$ = 0.08, 0.16, 0.24, 0.28 and 0.32, respectively. In effecting the extrapolation of the activity coefficients, Stonehill and Berry's recent values[5] of the Debye–Hückel coefficients were used so that the a of the equation

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[1] W. J. Hornibrook, G. J. Janz and A. R. Gordon, THIS JOURNAL, **64**, 513 (1942).

[2] G. J. Janz and A. R. Gordon, *ibid.*, **65**, 218 (1943).

[3] A. R. Gordon, *ibid.*, **65**, 221 (1943).

[4] A. G. Keenan and A. R. Gordon, *J. Chem. Phys.*, **11**, 172 (1943).

[5] H. I. Stonehill and M. A. Berry, THIS JOURNAL, **64**, 2724 (1942). See also "Footnote added in proof," reference 2.

$$\log \gamma = -a\sqrt{m}/(1 + b\sqrt{m}) + Dm \quad (3)$$

is 0.5095; the final value selected for b was 1.420, corresponding to a distance of closest approach of 4.3 Å., and the resulting D is -0.014. Tables II and III give activity and osmotic coefficients corresponding to these values of the constants. The last column of Table I, headed $E_{\text{calcd.}}$, gives the e. m. f. computed from Table II and a large scale plot of the integral (2) above; the agreement on the whole is satisfactory, the discrepancy in only one instance corresponding to as much as 0.0003 in $\Delta \log \gamma$.

TABLE I

m_1	m_2	$E_{\text{obs.}}$	$E_{\text{calcd.}}$
0.049983	0.009986	+37.552	+37.555
.050043	.019877	+21.379	+21.385
.049902	.029957	+11.762	+11.765
.049942	.070214	− 7.792	− 7.780
.049993	.079835	−10.692	−10.680
.049972	.089866	−13.388	−13.375
.049925	.097568	−15.250	−15.265

TABLE II

$m^{1/2}$	0.04	0.8	0.12	0.16
$1 + \log \gamma$	0.9807	0.9633	0.9476	0.9332
$m^{1/2}$	0.20	0.24	0.28	0.32
$1 + \log \gamma$	0.9201	0.9080	0.8968	0.8865

TABLE III

$$\varphi = 1 + (1/m) \int_0^m m \, d \ln \gamma$$

$m^{1/2}$	0.08	0.16	0.24	0.32
φ	0.9733	0.9537	0.9390	0.9277

In 1929, Harned[6] investigated potassium bromide solutions at this temperature by means of e. m. f. measurements on cells without transference. The difficulty of extrapolating activity coefficient data obtained from measurements on such cells is well known, since their use is restricted to fairly concentrated solutions. It is therefore not surprising that the value he gives for γ at 0.1 m, 0.765, is less than that obtained by interpolation in Table II, *viz.*, 0.771_6. If, however, his value for 0.1 m be adjusted to agree with ours, his coefficients for 0.2, 0.3 and 0.5 m become 0.721, 0.692 and 0.658, respectively; these may be compared with the extrapolated values given by Eq. 3 with our values of the constants, 0.720, 0.690 and 0.651. Thus with potassium bromide, just as with potassium chloride and sodium chloride, the data from cells with transference below 0.1 m pass smoothly into those for cells without transference above this concentration.

Since potassium bromide and potassium chloride solutions differ only slightly in their thermodynamic properties, an isopiestic comparison at low concentrations such as was made for potassium and sodium chloride solutions[3] is unnecessary, for the reason that an unambiguous extrapolation of the isopiestic data from higher concentrations is possible. Robinson's measurements[7] up to one molal can be represented within experimental error by

$$m_{\text{KCl}}/m_{\text{KBr}} = 1 + 0.011_6 m_{\text{KBr}} \quad (4)$$

Thus the potassium chloride solutions in isopiestic equilibrium with 0.05 and 0.10 m potassium bromide solutions are 0.05003 and 0.10012 m. The osmotic coefficients for the potassium bromide solutions from Table III are 0.9417 and 0.9282, respectively, while the coefficients for the corresponding potassium chloride solutions, from Table V of ref. 1, are 0.9409 and 0.9269. Thus the quantity $(m\varphi)_{\text{KBr}}/(m\varphi)_{\text{KCl}}$ is 1.0003 for the twentieth molal solutions and 1.0002 for the tenth. These differ from unity by less than the experimental error of the isopiestic measurements and thus provide satisfactory confirmation of the previously reported data for the two chlorides.

In conclusion, we wish to express our thanks to Mr. H. G. McLeod of this department for his assistance in making some of the measurements.

Summary

1. The e. m. f. of the cell with transference Ag, AgBr/KBr(m_1)//KBr(m_2)/AgBr, Ag has been measured at 25°, for concentrations up to 0.1 m. Activity and osmotic coefficients have been tabulated for round values of the square root of the molality.

2. The measurements are consistent with Harned's results for cells without transference at concentrations greater than 0.1 m.

3. Comparison of the potassium bromide data with those previously reported for potassium chloride by means of Robinson's isopiestic ratios shows that the osmotic coefficients for the two salts are in very satisfactory agreement.

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(6) H. S. Harned, THIS JOURNAL, **51**, 416 (1929).

(7) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).