NOTES

Activity Coefficients of Aqueous Hydrobromic Acid Solutions to Four Molal[1]

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The accuracy and completeness of the thermodynamic characterization of hydrochloric acid solutions by Akerlof and Teare with the silver–silver chloride electrode[2,3] suggested that an analogous investigation of hydrobromic acid by an extension of the work of Harned, Keston and Donelson[4] with the silver–silver bromide electrode would be practical. Electromotive forces of the cell H_2; HBr(m); AgBr; Ag were measured over a range of concentration and temperature.

Experimental

Hydrobromic acid was prepared by distilling reagent grade 48% hydrobromic acid over tin and collecting the constant boiling middle fraction. The distillate was diluted as required and analyzed gravimetrically as silver bromide. The cell was modeled after those of Akerlof and Teare[2] and Hamer and Acree.[5] Silver–silver bromide electrodes were prepared by heating a mixture of silver oxide and silver bromate on a platinum spiral.[6] The hydrogen electrodes were of the usual platinized platinum foil type. Potentials were compared on a Rubicon Type B potentiometer to unsaturated Weston cells calibrated by the Physics Division of the National Research Council of Canada. Temperatures were measured by a platinum resistance thermometer, also calibrated by the National Research Council. Potentiometer, Mueller bridge, weights, etc., were calibrated in conventional manners, and the usual precautions against oxygen contamination and electrical leakages were observed.

Results and Discussion

It was found that the rate of establishment of equilibrium became very slow at high concentrations, and that above three molal equilibrium was not reached after three days. This behavior we ascribe to the solubility of silver bromide in the more concentrated acid solutions, and this view is confirmed by the failure of the silver–silver iodide electrode to function in hydriodic acid above the low concentration region.[7]

The lower limit of the concentration region examined was 0.5 molal, and agreement with the Harned, Keston and Donelson[4] data in this vicinity was satisfactory. The average electromotive forces observed by us at various cell concentrations and temperatures are summarized in Table I. These results were reproducible to within ±0.05 mv.

At least partially as a result of the uncertainty in extrapolation, several sets of values of the standard potentials of the silver–silver bromide electrode over a temperature range are reported.[8] The mean ionic activity coefficients and relative partial molal free energies of hydrobromic acid solutions in Tables II and III were calculated using the standard potentials of Harned and Donelson.[9]

Table I

Average Potentials of the Cell H_2 (1 atm.); HBr (m); AgBr; Ag in Absolute Volts

m (moles/1000 g. H_2O)	Temp., °C. 20	25	30
0.4871	0.12150	0.12016	0.11868
0.9703	.08176	.07983	.07778
2.009	.02939	.02676	.02399
2.017	.02884	.02621	.02343
2.932	− .00658	− .00959	− .01272
2.977	.00828	.01123	.01430

Table II

The Mean Ionic Activity Coefficients of Hydrobromic Acid Solutions

m (moles/1000 g. H_2O)	Temp., °C. 20	25	30
0.5	0.800	0.796	0.791
1.0	0.886	0.881	0.874
2.0	1.196	1.183	1.171
3.0	1.722	1.693	1.664

Table III

Relative Partial Molal Free Energies of Hydrobromic Acid Solutions, in Defined Calories

m (moles/1000 g. H_2O)	Temp., °C. 20	25	30
0.5	−1065	−1089	−1114
1.0	138	148	160
2.0	+1018	+1023	+1027
3.0	1914	1927	1938

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[2] G. Akerlof and J. W. Teare, This Journal, **59**, 1855 (1937).

[3] P. Bender and W. J. Biermann, *ibid.*, **74**, 322 (1952).

[4] H. A. Harned, A. S. Keston and J. G. Donelson, *ibid.*, **58**, 989 (1936).

[5] W. J. Hamer and S. F. Acree, *J. Research Natl. Bur. Standards*, **23**, 647 (1939).

[6] A. S. Keston, This Journal, **57**, 1671 (1935).

[7] J. N. Pearce and N. B. Hart, *ibid.*, **43**, 2483 (1921).

[8] G. W. Janz and H. Taniguchi, *Chem. Revs.*, **53**, 392 (1953).

[9] H. S. Harned and J. G. Donelson, This Journal, **59**, 1280 (1937).

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The Direct Synthesis of Boron Hydrides

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While working with several metal borides in 1945, we observed that reactions with hydrogen or hydrocarbons occurred at about 400° to produce boron hydrides. Recently, we observed the formation of diborane from commercial boron and hydrogen at about 840°. We believe the formation of boron hydrides from borides and hydrogen may be a general reaction similar to the reactions of carbides with hydrogen to produce hydrocarbons. Our observations, which were incidental to other work, are recorded herein.

Borides.—The classical method of preparing boron hydrides is by the action of acids on mag-