

NOTES

Activity Coefficients of Aqueous Hydrobromic Acid Solutions to Four Molal¹

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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 Donelson⁴ 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 Teare² 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 Donelson⁴ 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

(1) This work was aided by a grant from the National Research Council of Canada.

(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).

TABLE I

AVERAGE POTENTIALS OF THE CELL H_2 (1 atm.); $HBr(m)$; $AgBr$; Ag IN ABSOLUTE VOLTS

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

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

(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-

nesium boride. Stock¹ observed, however, that magnesium boride forms only traces of boron hydrides when treated with liquid water, or with water vapor at 450°, and only hydrogen with water vapor at 900°. Magnesium boride is prepared by heating magnesium with boron trioxide, and generally has been considered to be Mg₃B₂. Recent work by Russell, Hirst, Kanda and King² and by Jones and Marsh,³ has indicated the existence of several magnesium borides, but not an Mg₃B₂.

In our first work, magnesium boride was prepared from boron trioxide and magnesium according to the directions of Brandauer,⁴ then ground in an iron ball mill with steel balls. The powdered boride was placed in a length of "Pyrex" tubing 1 cm. in diameter, where it was contained between glass wool plugs. The portion of the tubing containing the sample was enclosed in an electrical heating unit. Commercial cylinder hydrogen was passed through the tube and burned at a small jet at the exit. As the magnesium boride was heated, the flame remained colorless until the temperature reached about 400°, when the flame became a brilliant green. A cool glass plate held above the flame first received a deposit of liquid droplets (water) which evaporated as the plate warmed, leaving a solid, white deposit (boric oxide or boric acid). With the flame extinguished, a piece of moist red litmus paper held above the jet turned blue, and a piece of filter paper wet with 1% silver nitrate solution became a silvery black. A hanging drop of dilute potassium permanganate solution was decolorized. These reactions and the color of the flame indicated the presence of boron hydrides.

Volatile boron compounds also were obtained, although in lesser amounts, when the hydrogen was replaced by ethane, ethylene or methyl chloride. In no case was the exit gas spontaneously inflammable.

Magnesium boride prepared similarly, but ground in a porcelain ball mill with agate balls, gave only traces of boron hydrides when tested by the sensitive method of Etherington and McCarty.⁵

Table I summarizes our results with other metal borides. In each case, stoichiometric proportions of anhydrous reagents were pulverized and thoroughly mixed before firing in hydrogen to form the boride.

TABLE I

Boride mix.	Temperature of, °C.		Tests for boron hydrides		
	Formation	Reaction	Green flame	1% AgNO ₃	Dil. KMnO ₄
B + Ni	1500-1800	350-400	pos.	pos.	pos.
Ca + B ₂ O ₃	400	400	pos.	pos.	
Al + B ₂ O ₃	500	500	neg.	v. weak	v. weak
Zn + B ₂ O ₃	250	250	pos.	pos.	pos.

In several of the above experiments, including the tests with magnesium boride, the hydrogen was alternately dried and saturated with water vapor

(1) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 42.

(2) V. Russell, R. Hirst, F. A. Kanda and A. S. King, *Acta Cryst.*, **6**, 870 (1953).

(3) M. E. Jones and R. E. Marsh, *THIS JOURNAL*, **76**, 1434 (1954).

(4) R. Brandauer, M.S. Thesis, Cornell University, 1938.

(5) T. L. Etherington and L. V. McCarty, *Arch. Ind. Hyg. and Occup. Med.*, **5**, 447 (1952).

without any significant effect on the production of boron hydrides.

Boron.—Negative results were obtained when a boron, prepared by the reaction of borax and aluminum, was fired to over 460° in hydrogen; mixing the boron with copper had no effect. However, a recent experiment with a sample of commercial boron gave strongly positive results at 840°, using hydrogen that had been passed through a "Deoxo" unit, then dried in a liquid nitrogen cooled trap packed with glass wool. The sample of boron was contained within the furnace tube in a quartz boat. The exit gas was passed through an uncooled trap and thence to a jet, where it burned with a green flame. When the exit trap was cooled with liquid nitrogen, the flame became colorless. After one hour, the contents of the trap were examined with a mass spectrometer; a spectrum characteristic of diborane was obtained.⁶ The sample of commercial boron was analyzed by sodium peroxide fusion as described by Winslow and Liebhafsky⁷ and found to contain 96.9% boron. A limited spectrographic analysis showed Fe, present; Ti, sl. trace; Mg, present; Ta, sl. trace; Ni, trace; Si, trace; Cu, present.

We wish to thank Dr. P. D. Zeman of this Laboratory for examining the reaction product with the mass spectrometer.

(6) F. J. Norton, *THIS JOURNAL*, **71**, 3438 (1949).

(7) E. H. Winslow and H. A. Liebhafsky, *ibid.*, **64**, 2725 (1942).

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Osmotic and Activity Coefficients of *p*-Toluenesulfonic Acid and *p*-Ethylbenzenesulfonic Acid and their Relationship to Ion-exchange Equilibria

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The determination of activity coefficients of cation-exchange resins, except for the most weakly cross-linked resins, is impossible because of the inability of the resins to swell sufficiently, when immersed in water, to form very dilute solutions. The monomeric structure representing these resins is very similar, however, to certain sulfonic acids which are not subject to this restriction. *p*-Toluenesulfonic acid (equiv. wt. 172.19), 2,5-dimethylbenzenesulfonic acid (equiv. wt. 186.22) and *p*-ethylbenzenesulfonic acid (equiv. wt. 186.22) are examples of acids which may be compared with this monomeric structure (equiv. wt. in the dry hydrogen form, 195-200).

Activity and osmotic coefficients of the lithium, sodium and potassium salts of *p*-toluenesulfonic acid have been previously determined.¹ The relative values of the activity coefficients for these salts and also for the acid should be of special significance in the interpretation of ion-exchange equilibria because of the rather unusual position of hydrogen ion in the ion-exchange selectivity scale. If the same standard state (*e.g.*, the hypo-

(1) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).