$$\log \gamma_1 = x_2^2\,(0.4 - 0.1\,x_1) + 0.176\,x_3^2 + x_2x_3[(0.48 - 0.012\,x_3 + 0.028\,(1 - 2\,x_1)]$$

$$\log \gamma_2 = x_3^2\,(0.052 - 0.012\,x_2) + x_1^2\,(0.35 + 0.1\,x_2) + x_1x_3[(0.22 + 0.1\,x_2 + 0.028\,(1 - 2\,x_2)]$$

$$\log \gamma_3 = 0.176\,x_1^2 + x_2^2\,(0.046 + 0.012\,x_3) - x_1x_2[(0.128 - 0.012\,x_3 + 0.1\,x_2 - 0.028\,(1 - 2\,x_3)]$$

Table II compares the experimental and calculated activity coefficient data for each experimental run. Excellent agreement was obtained in most cases. The average error between the estimated and the experimental activity coefficients of all the runs expressed as $(\gamma_{\text{cal.}} - \gamma_{\text{expt.}})\,100/\gamma_{\text{cal.}}$ was $+\,1.72$ in γ_1, $-\,0.48$ in γ_2, and $-\,1.13$ in γ_3, and these are within reasonable limits of experimental accuracy.

From the equilibrium curve for the system, acetone–carbon tetrachloride, drawn on a benzene-free basis with per cent benzene as the parameter, the azeotrope for this system disappeared at 50% benzene. This was further confirmed by estimating the relative volatility of acetone to carbon tetrachloride in presence of benzene and on benzene-free basis at this composition.

NOMENCLATURE

(A_{12}, A_{21}) = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 1-2 binary
(A_{23}, A_{32}) = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 2-3 binary
(A_{31}, A_{13}) = end values from the plot of logarithms of the activity coefficients *vs.* % composition for 1-3 binary
C = ternary constant
P° = pure component vapor pressure
P = total pressure
R = gas constant
t = temperature, ° C.
T = absolute temperature, ° K.
V = liquid molal volume
x = mole fraction of component in liquid
y = mole fraction of component in vapor
Z = correction factor for the nonideality in vapor phase
γ = activity coefficient
ρ = density
β = second virial coefficient

Subscripts

$1, 2. \ldots i$ = components $1, 2. \ldots i$

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Thermodynamic Functions of Aqueous Hydrobromic Acid at Various Concentrations and Temperatures

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Mean molal activity coefficients of aqueous hydrobromic acid have been calculated from electromotive force measurements over a HBr concentration range from 0° to 70° C. Moreover, the values of the thermodynamic functions of aqueous hydrobromic acid at 25° C. have been determined over the same concentration range.

THIS investigation has been carried out as a preliminary contribution to research on the electrochemical processes concerning the bromine electrode, within the more general problem of the electrochemical behavior of the halogen-halide systems.

The purpose of this work is to determine the mean molal activity coefficients and the thermodynamic functions of aqueous hydrobromic acid at a wide range of HBr concentrations and temperatures.

Harned, Keston, and Donelson (*7*), Owen and Foering (*14*), Harned and Donelson (*6*), Hetzer, Robinson, and Bates (*8*), and Gupta, Hills, and Ives (*5*) have all studied HBr concentrations lower than 1 molal, at temperatures ranging from 0° to 60° C. Livingston (*10*) has investigated HBr concentrations up to 1.5 molal, at 25° C. Biermann and Yamasaki (*3*) have studied 0.5-, 1-, 2-, and 3-molal HBr at 20°, 25°, and 30° C.

The present investigation covers particularly the HBr concentrations higher than 1 molal, over a 0° to 70° C. range of temperatures. In fact, the thermodynamic functions of HBr in this range of concentrations and temperatures were hitherto largely lacking. These data may actually be of interest for basic thermodynamic considerations on fuel cells involving halogen electrodes, and dealing with aqueous acid electrolytes at low temperatures (0° to 70° C.).

EXPERIMENTAL

The measurements apparatus included a Type K 3 Leeds & Northrup potentiometer having a Type Keithley 610 B electrometer as a null-point detector. The input impedance of this electrometer is greater than 10^{14} ohm. Thus, it enabled us to study the cell (*7*) while keeping closed a stopcock between the two half-cells.

The hydrogen electrode was prepared according to a new technique (*1, 2*), by making use of a porous graphite support whose surface is activated with platinum-black catalyst. A thin network of sinter Teflon drops protects the catalyst layer during operation from mechanical crumblings without screening the catalyst.

The silver–silver bromide electrode was prepared according to the electrolytic type, by anodizing a silver-plated platinum sheet (6 sq. cm. total surface) in a 0.1-molar KBr solution under a 0.25-ma. cm.$^{-2}$ current density for 1 hour. This electrolytic-type electrode gave a reproducibility to ±0.00002 volt (*9*). The temperature of the cell was regulated to ±0.02° C. by means of a specially designed air-thermostat. All e.m.f. values were corrected to 760 mm. of Hg pressure of hydrogen.

The solutions were made up with doubly distilled water and reagent-grade chemicals. Analysis of solutions and of other substances involved in the cell was carried out according to the conventional technique.

RESULTS AND DISCUSSION

Mean Molal Activity Coefficients of Aqueous Hydrobromic Acid. From measurements of the e.m.f., E, of the cell

$$-\ \mathrm{Pt/H_2,\ (1\ atm.)/HBr}\ (m)\mathrm{/AgBr/Ag/Pt}\ + \qquad (1)$$

it is possible to calculate the mean molal activity coefficients, $\gamma_\pm$, of hydrobromic acid at various concentrations and temperatures because $\gamma_\pm$ relates to E according to the equation

$$E = E^\circ_{\mathrm{Ag/AgBr/Br}} - \frac{2RT}{F}\ln(m\,\gamma_\pm)_{\mathrm{HBr}} \qquad (2)$$

where $E^\circ_{\mathrm{Ag/AgBr/Br}}$ is the standard potential of the silver–silver bromide half-cell (afterwards identified as E°) and m is the molality of aqueous hydrobromic acid. The measured e.m.f.'s, E, are given in Table I, with an estimated error not exceeding ±0.00002 volt. The mean activity coefficients calculated through Equation 2 are given in Table II. For these calculations, the following constants were used (*11*): $R = 1.98719 \pm 0.00008$ cal. deg.$^{-1}$ mole^{-1}; $T_{0^\circ\mathrm{C.}} = 273.16 \pm 0.01°$ K.; $F = 23060.5 \pm 2.4$ cal. abs.-volt^{-1} gram-equiv.$^{-1}$

When HBr molalities greater than 2 are used, the effect of increasing AgBr solubility in HBr begins to be significant and may affect the $\gamma_\pm$ values calculated from Equation 2. This uncertainty has been considered as follows. In the compartment of the silver-bromide half-cell some AgBr dissolves in HBr forming silver complexes, so that m_{Br} differs from m_{HBr} to some extent. This difference is negligible for HBr molalities lower than 2 and is very small for HBr molalities ranging from 2 to 6—namely, corresponding to the highest concentrations used in the present work—but it increases rapidly (*4*) for HBr molalities greater than 6. The compartment of the hydrogen half-cell is not affected by diffusion of such silver complexes in solution, since our normal experimental procedure involves a stopcock kept continuously closed between the two half-cells, as mentioned above. Thus, between the hydrogen half-cell and the silver-bromide half-cell a liquid-junction potential exists, which is, however, negligibly small since m_{H} is the same for both half-cells and m_{Br} in the former differs only slightly from m_{Br} in the latter.

If the logarithmic term in Equation 2 is rewritten as a sum of two contributions—one of them referring to the silver-bromide half-cell and the other to the hydrogen half-cell—one obtains

$$E = E^\circ - \frac{RT}{F}\ln[(m + \delta m)\ (\gamma_\pm + \Delta\gamma_\pm)] - \frac{RT}{F}\ln(m\,\gamma_\pm) \qquad (2\text{-A})$$

where $\Delta\gamma_\pm$ is the variation in $\gamma_\pm$ due to the Δm variation in $\mathrm{Br^-}$ molality. Assuming that, from 2 to 6 molal HBr, $\gamma_\pm$ increases linearly with m_{HBr} (at least as a first approximation), then $\Delta m/m = \Delta\gamma_\pm/\gamma_\pm$, from which $\Delta\gamma_\pm = \gamma_\pm\Delta m/m$. Substituting this $\Delta\gamma_\pm$ value in Equation 2-A, one obtains:

$$E = E^\circ - \frac{RT}{F}\ln[(m + \Delta m)\ (1 + \Delta m/m)\gamma_\pm] - \frac{RT}{F}\ln(m\gamma_\pm) \qquad (2\text{-B})$$

$\gamma_\pm$ values calculated from Equation 2 do not differ greatly from $\gamma_\pm$ values calculated from Equation 2-B, since Δm is small within the range of HBr molalities used for the present work. The difference between $\gamma_\pm$'s calculated from Equation 2 and $\gamma_\pm$'s calculated from Equation 2-B (where Δm has been evaluated on the basis of the Erber's data (*4*) of AgBr solubility in HBr, considering only the formation of the $\mathrm{AgBr_2^-}$ complex) has been assumed to represent the uncertainty due to the AgBr solubility in HBr, at each

Table I. E.M.F. of Cell (1), in A.B.S. Volts at Various HBr Molalities and Temperatures Corrected to 760 Mm. of Hg Pressure of Hydrogen[a]

Molalities of HBr	0° C.	10° C.	20° C.	25° C.	30° C.	40° C.	50° C.	60° C.	70° C.
5.551	−0.08621	−0.09381	−0.10161	−0.10561	−0.10971	−0.11800	−0.12664	−0.13565	−0.14547
4.629	−0.04702	−0.05248	−0.05857	−0.06190	−0.06537	−0.07210	−0.07939	−0.08727	−0.09483
3.700	−0.01777	−0.02392	−0.03055	−0.03380	−0.03717	−0.04392	−0.05167	−0.05901	−0.06683
2.775	0.01225	0.00687	0.00104	−0.00191	−0.00488	−0.01142	−0.01862	−0.02593	−0.03363
1.850	0.04633	0.04231	0.03715	0.03445	0.03176	0.02618	0.01916	0.01274	0.00584
1.388	0.06851	0.06465	0.06016	0.05774	0.05512	0.04957	0.04339	0.03664	0.02945
1.119	0.08184	0.07854	0.07461	0.07245	0.07013	0.06520	0.05983	0.05385	0.04761
0.925	0.09200	0.08906	0.08546	0.08345	0.08125	0.07664	0.07176	0.06652	0.06059
0.555	0.11945	0.11760	1.11499	0.11356	0.11184	0.10828	0.10461	0.10086	0.09660
0.277	0.15277	0.15201	0.15058	0.14970	0.14853	0.14591	0.14294	0.13965	0.13547
0.139	0.18297	0.18324	0.18279	0.18235	0.18175	0.18021	0.17839	0.17587	0.17292
0.0555	0.22574	0.22752	0.22854	0.22883	0.22903	0.22904	0.22843	0.22753	0.22610

[a] The negative sign before e.m.f. values means that the cell polarities in such cases are inverse to the ones indicated on the text.

Table II. Mean Molal Activity Coefficients of Aqueous HBr at Various Molalities and Temperatures

Molalities of HBr	0° C.	10° C.	20° C.	25° C.	30° C.	40° C.	50° C.	60° C.	70° C.
5.551	6.32	6.06	5.76	5.61	5.45	5.15	4.86	4.60	4.36
4.629	3.298	3.114	2.945	2.871	2.798	2.642	2.496	2.373	2.221
3.700	2.217	2.170	2.116	2.079	2.041	1.957	1.898	1.815	1.731
2.775	1.562	1.539	1.510	1.491	1.467	1.429	1.398	1.360	1.316
1.850	1.136	1.117	1.108	1.102	1.091	1.068	1.064	1.040	1.013
1.388	0.945	0.942	0.936	0.933	0.931	0.923	0.918	0.914	0.906
1.119	0.883	0.879	0.873	0.870	0.866	0.857	0.848	0.840	0.827
0.925	0.861	0.857	0.852	0.849	0.846	0.839	0.829	0.815	0.803
0.555	0.801	0.796	0.791	0.788	0.786	0.778	0.765	0.747	0.728
0.277	0.791	0.788	0.784	0.781	0.780	0.776	0.770	0.762	0.756
0.139	0.830	0.828	0.826	0.825	0.823	0.819	0.812	0.808	0.800
0.0555	0.838	0.837	0.836	0.836	0.834	0.830	0.828	0.823	0.815

Table III. Thermodynamic Functions of Aqueous HBr at 25° C. and 1 Atm.

Molalities of HBr	[a]Moles HBr per Mole H_2O	dE/dT (Mv. Deg.$^{-1}$)	G (Kcal. Mole^{-1})	H (Kcal. Mole^{-1})	S (Cal. Deg^{-1} Mole^{-1})
5.551	1/10	−0.81	−20.495	−26.91	12.3
4.629	1/12	−0.68	−21.510	−27.03	15.3
3.700	1/15	−0.66	−22.151	−27.54	15.8
2.775	1/20	−0.60	−22.886	−27.86	17.2
1.850	1/30	−0.53	−23.724	−28.22	18.8
1.388	1/40	−0.50	−24.261	−28.55	19.5
1.119	1/49.6	−0.45	−24.601	−28.55	20.6
0.925	1/60	−0.41	−24.854	−28.52	21.6
0.555	1/100	−0.31	−25.549	−28.53	23.8
0.277	1/200	−0.20	−26.382	−28.61	26.4
0.139	1/400	−0.10	−27.135	−28.67	28.7
0.0555	1/1000	+0.05	−28.207	−28.71	32.2

[a] The column "moles HBr per mole H_2O" has been included to facilitate the comparison with the values of thermodynamic functions of HBr that are available in literature.

HBr molality examined. The cumulative error for the values of $\gamma_{\pm}$ quoted in Table II, including the effect of AgBr solubility in HBr, is ± 0.04 for the values on the first line, ± 0.009 on the second, ± 0.005 on the third, ± 0.002 on the fourth, and ± 0.001 on the others.

The numerical values substituted in Equation 2 for E° were determined over a temperature range of experiment from 0° to 60° C. by Harned, Keston, and Donelson (*7*) who also determined a least-squares equation for E° as a function of temperature (*7*). Since experimental values of E° at temperatures higher than 60° C. had not hitherto been determined, E° at 70° C. was obtained through the cited least-squares equation, and a correction from international volts to absolute volts was carried out. Consequently, the $\gamma_{\pm}$ values at 70° C. in Table II may be influenced by some uncertainty by the present assumption for E°. It is impossible to specify the limits of this uncertainty until the experimental E° value at 70° C. is available.

Thermodynamic Functions of Aqueous Hydrobromic Acid. The thermodynamic functions of aqueous hydrobromic acid at 25° C. and 1 atm. can be calculated from the measured e.m.f.'s, E, of cell 1 which is characterized by the over-all reaction

$$AgBr + \tfrac{1}{2} H_2 \text{ (1 atm.)} = Ag + HBr \qquad (3)$$

The free energy change, ΔG, and the corresponding entropy change, ΔS, for Reaction 3 are related to the electromotive force, E, of cell 1 and to the temperature coefficient dE/dT of such e.m.f., according to the following equations (where F is the Faraday constant):

$$\Delta G = G_{\mathrm{HBr},m} - G_{\mathrm{AgBr}} = -EF \qquad (4)$$

$$\Delta S = S_{\mathrm{HBr},m} + S_{\mathrm{Ag}} - \tfrac{1}{2}S_{\mathrm{H_2,1\,atm.}} - S_{\mathrm{AgBr}} = F dE/dT \qquad (5)$$

$$\Delta H = \Delta G + T\Delta S = -EF + FT dE/dT = H_{\mathrm{HBr},m} - H_{\mathrm{AgBr}} \qquad (6)$$

From Equations 4, 5, and 6, respectively, it follows that

$$G_{\mathrm{HBr},m} = G_{\mathrm{AgBr}} - EF \qquad (7)$$

$$S_{\mathrm{HBr},m} = S_{\mathrm{AgBr}} + \tfrac{1}{2}S_{\mathrm{H_2,1\,atm.}} - S_{\mathrm{Ag}} + F dE/dT \qquad (8)$$

$$H_{\mathrm{HB},m} = H_{\mathrm{AgBr}} - EF + FT dE/dT \qquad (9)$$

For the terms G_{AgBr}, H_{AgBr}, S_{AgBr}, S_{Ag}, and $S_{\mathrm{H_2}}$ under the standard conditions, the N.B.S. data (*12*) were used. The E values are given in Table I. The temperature coefficient dE/dT can be computed by plotting E against temperature, this plot shows that dE/dT in the range from 20° to 30° C. varies less than ± 0.01 mV. deg.$^{-1}$. Consequently, one may assume the mean dE/dT values calculated over the range from 20° to 30° C. to be the dE/dT values at 25° C. Table III summarizes such dE/dT at 25° C. as a function of the corresponding HBr molalities. Table III also gives the values of the thermodynamic functions of HBr calculated from Equations 7, 8, and 9. The cumulative errors for G_{HBr}, H_{HBr}, and S_{HBr} do not exceed ± 0.002 kcal. mole^{-1}, ± 0.08 kcal. mole^{-1}, and ± 0.2 cal. deg.$^{-1}$ mole^{-1}, respectively.

The single H_{HB} values given in Table III and the corresponding N.B.S. data (*13*) differ less than $\pm 0.7\%$, excepting the first four terms. A maximum deviation about -3.2% was observed for the term corresponding to 4.629 *m* HBr. An analogous comparison for the G_{HBr} and S_{HBr} values is impossible because the corresponding N.B.S. data are missing.

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Phase Equilibria in the System Hydrazine Perchlorate–Water

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Phase equilibria between hydrazine monoperchlorate and water were determined experimentally. The relation of solubility to temperature was completely defined. Important features include the limiting melting temperature of the salt (142.4° C.), the occurrence of a solid hydrate decomposing at 64° C., and of a eutectic point at −4.1° C. and 80% water. A further determination was made of pressures of water vapor in equilibrium with the condensed phases from 5.0 to 75.6° C. These experiments identified the hydrate as $N_2H_5ClO_4 \cdot \frac{1}{2}\ H_2O$, and fixed the quadruple point at 64° C., and 88 mm. of Hg.

THE PRACTICAL USE of anhydrous hydrazine monoperchlorate requires that it be isolated as free-flowing, void-free crystals of regulated size, and stored without change. Decrepitation, agglomeration, and surface caking, which are produced by traces of moisture, must be scrupulously avoided.

Thus it is necessary to define the conditions under which the salt absorbs or loses water. The equilibria among phases of the binary system, which control these tendencies, must be completely determined.

The principal experimental difficulty is the nature of the salt, which is an extremely sensitive high explosive. Quantities of more than a few milligrams must be handled with tongs and kept removed from the body.

Some of the requisite data have already been published. Christensen and Gilbert (*4*) determined the vapor pressure of water over a mixture of hydrazine perchlorate and hydrazine perchlorate hydrate in the range 24° to 59° C. They stated the hydrate contained one-half molecule of water, and decomposed into anhydrous salt and water at 60.5° C. ± 0.5° C. The same composition of the hydrate was indicated by other workers (*3, 6*). However, the existence of higher hydrates had been suggested in earlier papers, and has never been positively confirmed or disproved. Moreover, reported values of the melting point of the anhydrous salt, (*1, 3, 7, 8*) and of the solubilities in water, (*1, 3, 7*) were rather discrepant.

EXPERIMENTAL

Materials. Because a single large batch of high-purity salt was not available at the beginning of the phase equilibrium studies, it was necessary to use several different specimens. (All preparations were originally small, because of the hazards of handling.) These were prepared by neutralization in either water or isopropanol, followed by isolation of the solid salt and vacuum drying at elevated temperatures. The conditions used were known, on the basis of much previous experience with elemental analyses, titrations, melting determenations, and other tests, to give salts of high purity. An additional, final purification step was applied to all samples used in compositions of low-water content. After charging the tubes used for observation of melting points, the last trace of volatiles was removed by melting under vacuum. In this step, a slight degassing of the water-white melt was first observed, after which the evolution of gas ceased. No decomposition was observable.

The melting point of pure hydrazine perchlorate was determined in a separate experiment. Two additional specimens were used, prepared by neutralization in water, with the final product vacuum-dried as the melt, and by neutralization in isopropanol, with the solid product vacuum-dried at 60° C. The impurity of these products was estimated incidentally in determining the melting point, as described in the following section.

The hydrazine perchlorate used for determining vapor pressures was prepared by titrating pure hydrazine with pure aqueous perchloric acid to the neutral end point. A solid, presumed to be the hydrate, crystallized out, and this was vacuum-dried for 2 days. (After charging to the apparatus, this sample was also melted under vacuum, so that removal of the last vestiges of volatiles was assured.)

Descriptions and analyses of all preparations used in the various measurements are given in Table I.

Phase Equilibria. The various regions of the phase diagram were mapped by different experimental techniques, as follows:

The high-temperature region, directly below the melting point of pure salt, was defined by observing melting temperatures (temperatures of disappearance of solid phase)

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