Transference Numbers of Aqueous Hydrobromic Acid from E.M.F. Measurements

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Transference numbers of aqueous hydrobromic acid have been determined from measurements of e.m.f.'s of concentration cells with and without transference, over a HBr concentration range up to 5.5 molal, at temperatures from 20° to 40° C.

THE DATA available in the literature for transference numbers of aqueous hydrobromic acid are very scanty and discrepant (*1, 2, 6, 10, 17*). Such a lack is surprising if one considers that, in the parallel case of hydrochloric acid, accurate and consistent data on transference numbers are available over a wide range of concentrations and temperatures (*7, 11*).

The purpose of this work is to determine the transference numbers for aqueous hydrobromic acid over the concentration range from 0.140 to 5.450 molal, at temperatures from 20° to 40° C. The method based on e.m.f.'s of corresponding concentration cells with and without transference has been used here, as it gives reliable results and is particularly suitable for an extensive study.

The transference numbers determined in this investigation correspond to the thermodynamic definition (*7, 8, 11, 12, 14, 16, 18*)

$$t^- = dE_{TR}/dE \qquad (1)$$

where E_{TR} is the e.m.f. of the cell with transference

$$\text{Pt/H}_2\text{, 1 atm./HBr } (m_1)//\text{HBr } (m_2)/\text{H}_2\text{, 1 atm./Pt} \qquad (2)$$

and E is the e.m.f. of the corresponding cell without transference

$$\text{Pt/H}_2\text{, 1 atm./HBr } (m_1)/\text{AgBr/Ag/AgBr/HBr } (m_2)/\text{H}_2\text{, 1 atm./Pt} \qquad (3)$$

The expression for E as a function of HBr concentration is

$$E = \frac{2RT}{F} \ln \frac{m_2\gamma_2}{m_1\gamma_1} \qquad (4)$$

the m's being molalities and the γ's being mean molal activity coefficients of HBr.

As indicated by Equation 1, t^- is given by the slope of the plot of E_{TR} against E at any particular molality m_2, the molality m_1 being fixed as implied by the method (*11, 12*). The fixed molality was m_1 = 0.058, while the molality m_2 was varied from 0.140 to 5.450.

E_{TR}'s were measured following the procedure described below. E's were calculated according to Equation 4 from the data of γ's available in the literature (*5, 9*). Corresponding values of E_{TR} and E are given in Table I for various values of m_2. The details for the calculation of t^- are explained later. The values of the cation transference numbers of HBr are given in Table II as a function of HBr molalities.

EXPERIMENTAL

The measurement apparatus included a Type-K 3 Leeds & Northrup potentiometer with a Type-610 B Keithley electrometer as a null-point detector.

The hydrogen electrodes used for transference cell 2 were of the capillary-imbibition type, whose assemblage and performance were recently described by Bianchi and collaborators (*3, 4*). The cell design was substantially equivalent to the one previously described by Stokes and Levien (*22*), but the junction between the two solutions was made through a capillary having a 0.1-mm. inner diameter, and two additional stopcocks were kept closed between the two half cells as a further precaution in order to prevent diffusion of solutions. These closed stopcocks, of course, increased the cell resistance considerably but the precision of measurements was not affected because the null-point detector used in this investigation had an input resistance greater than 10^{14} ohms.

The measured e.m.f.'s became steady after half an hour and remained steady generally within ±0.05mv. for 2 days. The E_{TR} values collected in Table I are averages of measurements in triplicate, and the deviations from the mean do not exceed ±0.1 mv.

Solutions were made up with doubly distilled water and certified reagent-grade Carlo Erba hydrobromic acid. Before each experiment the solution to be measured was degassed by a 99.99% purity hydrogen stream. Concentrations of HBr solutions were determined by the potentiometric titration method (*13, 15*). The uncertainty in the values of HBr molalities quoted in this paper does not exceed ±0.1%.

Cell temperatures were regulated to ±0.02° C. by means of a specially designed air thermostat.

Table I. E.M.F.'s of Cell 2 (E_{TR}) and Cell 3 (E), in Millivolts, as Functions of $(m_2)_{\text{HBr}}$, at Various Temperatures

	20° C.		25° C.		30° C.		40° C.	
m_2	E_{TR}	E	E_{TR}	E	E_{TR}	E	E_{TR}	E
0.140	7.4	42.7	7.8	43.3	8.2	44.1	9.0	45.6
0.279	13.0	76.1	13.8	77.2	14.4	78.6	15.8	81.1
0.573	20.8	113.1	21.9	114.8	22.8	116.8	24.8	120.3
1.180	29.2	155.2	30.6	157.7	31.9	160.2	34.4	165.2
1.930	36.8	192.9	38.4	195.8	39.9	198.7	42.9	204.3
2.891	43.9	230.1	45.8	233.3	47.6	236.2	51.1	242.7
3.920	50.5	264.3	52.6	267.7	54.5	271.3	58.3	278.0
5.020	58.2	306.2	60.4	310.0	62.6	313.9	66.8	321.7
5.450	61.4	324.2	63.8	328.4	66.0	332.6	70.4	340.8

Table II. Cation Transference Numbers of HBr at Various Molalities and Temperatures

m_{HBr}	20° C.	25° C.	30° C.	40° C.
0.140	0.80	0.79	0.79	0.78
0.279	0.800	0.794	0.789	0.780
0.573	0.802	0.796	0.792	0.783
1.180	0.804	0.799	0.795	0.787
1.930	0.806	0.802	0.798	0.790
2.891	0.808	0.805	0.801	0.794
3.920	0.810	0.807	0.803	0.797
5.020	0.812	0.810	0.807	0.800
5.450	0.813	0.811	0.808	0.802

RESULTS AND DISCUSSION

For comparison purposes, the e.m.f.'s of concentration cell 2 with transference (E_{TR}) and those of the corresponding cell 3 without transference (E) are given side by side in Table I as functions of the molality m_2 of hydrobromic acid, at various temperatures.

With the aid of a Type 1620-20K IBM computer, a least-squares process was carried out to fit E_{TR} and E values to a polynomial of the type

$$E_{TR} = A + BE + CE^2 \qquad (5)$$

for each temperature of the experiment. Constants A, B, and C were: at 20° C., $A = -1.8203$, $B = 0.20445$, $C = -2.7535 \times 10^{-5}$; at 25° C., $A = -1.7798$, $B = 0.21154$, $C = -3.4783 \times 10^{-5}$; at 30° C., $A = -1.7829$, $B = 0.21672$, $C = -3.7146 \times 10^{-5}$; at 40° C., $A = -1.7809$, $B = 0.22713$, $C = -4.2902 \times 10^{-5}$. The E_{TR} values calculated from Equation 5 reproduce the measured E_{TR} values with a mean deviation of 0.2 mv., the maximum deviation being 0.5 mv., which corresponds to the most dilute HBr solution.

From Equation 5 one obtains

$$dE_{TR}/dE = B + 2CE \qquad (6)$$

Substitution of Equation 6 into Equation 1, combined with $t^{+} + t^{-} = 1$, yields

$$t^{+} = 1 - t^{-} = 1 - dE_{TR}/dE = 1 - B - 2CE \qquad (7)$$

for the cation transference number corresponding to each molality, m_2, of HBr used. Values of t^{+}_{HBr} calculated according to Equation 7 are given in Table II, as a function of HBr molalities at various temperatures.

The estimated errors for t^{+}_{HBr} are ±0.01 at 0.140 molal HBr, ±0.007 at 0.279 molal, ±0.005 at 0.573 molal, ±0.002 at 1.180 and 1.930 molal, and ±0.001 at the other four molalities of hydrobromic acid.

The following least-squares expression for t^{+} as a function of the molality, m, of HBr is useful for interpolations of t^{+} at any required molality:

$$t^{-} = a + bm + cm^2 \qquad (8)$$

The constants for Equation 8 are: at 20° C., $a = 0.79879$, $b = 4.4471 \times 10^{-3}$, $c = -3.6564 \times 10^{-4}$; at 25° C., $a = 0.79236$, $b = 5.7807 \times 10^{-3}$, $c = -4.6009 \times 10^{-4}$; at 30° C., $a = 0.78766$, $b = 6.1294 \times 10^{-3}$, $c = -4.7645 \times 10^{-4}$; at 40° C., $a = 0.77815$, $b = 7.2262 \times 10^{-3}$, $c = -5.6836 \times 10^{-4}$. These constants are valid over the range 0.279 to 5.450 molal HBr. Equation 8 reproduces the data in Table II within ±0.001.

For the calculations involved throughout this paper, the following constants were used (*19, 20, 21*): $F = 23062.4 \pm 0.2$ cal. abs.-volt^{-1} gram-equiv.$^{-1}$; $T_{0° C.} = 273.16 \pm 0.01$° K.; and $R = 1.98719 \pm 0.00008$ cal. degree^{-1} mole^{-1}.

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