Enthalpies of Dilution and Related Thermodynamic Properties of Aqueous Hydrobromic Acid

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Enthalpies of dilution were measured at 25°C for hydrobromic acid solutions in the molality range 0.003–22.35*m*, and values of the relative apparent molar enthalpy, ϕ_L, and of the relative partial molar enthalpy L_2, were calculated. A form of the Debye-Hückel equation was used for smoothing and reliable extrapolation to $m = 0$.

In connection with measurements already reported on the enthalpy of solution of HBr(g) (*16*), we needed values for the enthalpy of dilution of HBr(aq) which were more reliable than those then available in the literature (*13*). The tabulated values were based on direct dilution measurements by Thomsen (*14*) and Berthelot (*1*) at 19° and 15.5°C and on indirect measures of partial molar enthalpies from emf sources (*8*).

The measurements reported in this paper were begun immediately after completion of our measurements on the enthalpy of solution of HBr(g) (*16*), and most were completed at the time Parker's revision (*12*) of previously tabulated (*13*) relative apparent molar enthalpies, ϕ_L, appeared in print. Subsequent measurements involved a closer examination of the region between 8 and 12*m* to determine whether any anomalous trend in ϕ_L existed at the azeotrope composition. The results reported here reveal no anomaly. Measurements were extended to 22.35*m*, and the relative partial molar enthalpy L_2 was evaluated over the whole range of molalities studied.

Experimental

Materials and analyses. All solutions were prepared from freshly distilled water which was collected at about 85°C. The specific resistance of samples was above 1×10^6 ohm cm. The CO_2 content of portions handled as in calorimetric procedures was established as in the previous work (*16*).

Reagent grade HBr (46–48%) solutions were treated with a small amount of granulated tin or red phosphorus to remove traces of bromine and were then distilled. Several stock solutions were prepared during the course of the work. In some cases, the stock solutions were first analyzed, and other less concentrated solutions were prepared by dilution on a mass basis. In other cases, the final calorimetric solution, after dilution, was analyzed, and the composition of initial and final solutions calculated from the known masses of materials used. In several runs, both the initial stock solutions and the final calorimetric solutions were analyzed as a check on the analytical procedures for dealing with CO_2 content in the water used as diluent.

Solutions of HBr with molalities above the azeotropic composition were prepared by dissolving gaseous HBr in cold azeotrope solution. Such solutions were usually handled by a glass ampul technique rather than the sample holders used in other work with the calorimeter (*17, 18*), and analyses were made on the final calorimetric solution. No significant decomposition was observed in the short intervals between preparation and dilution in the calorimeter. Some of the solutions have rather high vapor pressure at 25°C, and appropriate safety precautions were taken in handling the ampuls.

The solutions were analyzed against standard NaOH solution by weight buret techniques and potentiometric determination of the equivalence points, as in the previous work (*16*). Three different NaOH solutions were used during the work. Each of the NaOH solutions was standardized on at least two occasions against primary standard potassium hydrogen phthalate and also against one other primary standard. Constant-boiling HCl (*5*), constant-boiling HCl checked against borax, and $HClO_4$ referred to tris(hydroxymethyl)aminomethane were used. Almost half of the runs are based on the same NaOH solution that was used in measurements of the enthalpies of solution of HCl and HBr (*16*), and the same constant-boiling HCl solution was used to check the second NaOH solution. The second and third NaOH solutions were intercompared by analysis of one of the azeotrope stock solutions.

By these procedures we hoped to minimize systematic differences attributable to different standard NaOH solutions in the analyses. Intercomparisons against different primary standards and of replicate analyses agreed within 0.03%. Such an uncertainty in the analysis of HBr solutions on a mass percent basis leads to 0.06% uncertainty in the molality at 12*m* and to about 0.1% at 20*m*. The results of all weighings were reduced to mass by use of appropriate densities from handbook sources. Molar masses were based on the 1961 Table of Atomic Weights (*3*).

Calorimetric equipment and procedures. For the first 42 runs, the configuration and performance levels of the instrument were those already described (*16*), with a temperature sensitivity of 1×10^{-5} K/mm of recorder chart and a mean noise level somewhat less. For the remainder of the runs, the temperature control of the calorimeter jacket (bath) was improved to $\pm 5 \times 10^{-4}$ K with a Leeds and Northrup DC null detector, CAT controller and magnetic amplifier, and with a thermistor bridge as the set-point unit.

Corrected temperature changes were evaluated by Dickinson's method (*4*), and the calorimetric results refer to the isothermal dilution process at 25°C. Dilutions were initiated at (25.00 ± 0.02)°C, and energy equivalents were run on the final state of the system. The accuracy of the electrical energy equivalents, based on certificate, calibration, and performance factors, is estimated at ±0.03%.

The calorimeter vessel was charged with about 1040 cm^3 of water (or dilute solution of known molality) weighed to ±0.02 gram, and samples were released from sample holders, 39 and 10 cm^3 volume, described previously (*17, 18*), or by breaking ampuls, prepared as described in a preceding paragraph for solutions of high vapor pressure.

The pattern of dilution measurements followed that of other studies in this laboratory (*15, 17, 19*). In summary,

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a series of interconnected dilutions were made to delineate the low molality range, and individual dilutions from higher molalities were referred to the low molality region after it had been fitted to the Debye-Hückel smoothing and extrapolation function used for previous studies (*15, 17*). The solutions used to delineate the range of molalities below 1*m* were all referred to the same NaOH solution to eliminate possible distortion from analytical errors.

Treatment of experimental data. Values of the apparent molar enthalpy ϕ_i relative to an arbitrary reference point were fitted to the Debye-Hückel function (*15, 17*) by a combination of graphical and numerical procedures. Calculations were made by digital computation at the University of Nebraska Computing Center. The fitting procedures involved finding the two adjustable parameters for the Debye-Hückel function, plus determination of the limiting value ϕ_i° at $m = 0$, from which the usual relative apparent molar enthalpies ϕ_L were obtained from the relation: $\phi_L = \phi_i - \phi_i^\circ$.

For an ion-size parameter $a = 0.44$ nm, the parameters $(\partial \ln a/\partial T)_p = -0.00073\ \mathrm{K}^{-1}$ and $b = 80$ cal kg mol^{-2}, where b is the coefficient of the term linear in molality, and where the equation was fitted as a function of molality rather than concentration, gave best fit of ϕ_L values up to 0.7*m*. With these parameters, a smooth curve was constructed for ϕ_L vs. $m^{1/2}$, and values of ϕ_L for higher molalities were then calculated by reference to the smoothed portion. Other combinations of the parameters gave almost as good fit of the data, but a negative non-zero value of the temperature coefficient $(\partial \ln a/\partial T)_p$ was required for acceptable representations of the data for the ion-size parameter $a = 0.44$ nm given for HBr by Harned and Owen (*8*).

A later modification (*15*) of the Debye-Hückel function includes a term cm^2, where m is molality and c is an additional adjustable parameter. This equation represents the data up to 2.5*m* with a standard deviation of 1.5 cal mol^{-1}, with the parameters: $a = 0.44$ nm; $(\partial \ln a/\partial T)_p = -9.2 \times 10^{-4}\ \mathrm{K}^{-1}$; $b = 59$ cal kg mol^{-2}; $c = 19$ cal kg^2 mol^{-3}. An equally good fit was found with the values: $a = 0.50$ nm; $(\partial \ln a/\partial T)_p = -1.1 \times 10^{-4}\ \mathrm{K}^{-1}$; $b = 63$ cal kg mol^{-2}; $c = 18.4$ cal kg^2 mol^{-3}. Variation of the range of fit from 0.75 to 2.5*m* caused practically no change in the adjustable parameters for a fixed value of *a*.

Values of ϕ_L at selected molalities were calculated from the fitting equations up to 2*m*, and above that molality were taken from a large-scale plot of ϕ_L against *m*. Above 3*m*, the trend of ϕ_L with *m* becomes almost linear and is especially so above 6*m*. This regularity was very helpful in smoothing the experimental results for interpolations to obtain selected values, but care was taken not to force linearity into the plots. The selected values of ϕ_L are considered to be reliable to ±2 cal mol^{-1} from 0.02 to 1*m*, with uncertainty then increasing in rough proportion to molality up to ±30 cal mol^{-1} at 22.35*m*. As pointed out in a foregoing paragraph, errors in analysis are magnified in computing the molality, so contribute to displacements from the curves in both $\Delta\phi_L$ and Δm, and are believed to be the dominant source of errors above 4*m*, where sample size was large enough to reduce errors in temperature measurement to little significance.

Table I (deposited with the ACS Microfilm Depository Service) contains the primary experimental data from the calorimetric measurements. Table II contains the values of ϕ_L at the experimental molalities. In Table III are presented values of ϕ_L and also of L_2, the relative partial molar enthalpy, at selected molalities and mole ratios. At the lower molalities, below 1*m*, values of L_1 and L_2 were calculated from the parameters of the Owen and Brinkley equations used for fitting and extrapolation of the results (*11, 15, 17*). Above that region, sections of the ϕ_L curve were fitted to a polynomial, and values of L_1 and L_2 were calculated by standard procedures from these equations.

Table II. Relative Apparent Molar Enthalpies of HBr Solutions at Experimental Molalities at 25 °C[a]

m, mol kg^{-1}	ϕ_L, exp, cal mol^{-1}	ϕ_L, calc, cal mol^{-1}	*m*, mol kg^{-1}	ϕ_L, exp, cal mol^{-1}	ϕ_L, calc, cal mol^{-1}
0.0	0.0	0.0	0.30675		198.9
0.00010	4.8	4.7	0.30769		199.2
0.00011	5.0	4.9	0.30825		199.3
0.00330	25.9	25.9	0.30964		199.7
0.00637	37.0	35.5	0.31293		200.6
0.00699	30.4	37.0	0.31343		200.7
0.00931	41.0	42.4	0.31562		201.4
0.01105	45.8	46.0	0.31766		201.9
0.01115	44.3	46.2	0.31937		202.4
0.01379	52.4	51.1	0.32298		203.4
0.01578		54.5	0.7241	288	289
0.02019	62.7	61.1	0.9940	337	337
0.02168	61.6	63.0	1.3808	400	402
0.02282		64.6	1.8045	480	474
0.02622	68.7	68.6	1.8475	480	481
0.03204	75.3	75.2	2.1693	533	536
0.03586	79.0	79.1	2.4183	579	578
0.03661		79.8	2.490	589	590
0.03721		80.4	3.192	710	710
0.03748		80.7	3.998	855	856
0.04121		84.2	4.005	855	857
0.04195	85.2	84.9	4.766	1002	1001
0.04620		88.4	5.371	1118	1118
0.04907	92.7	90.7	5.433	1129	1131
0.05147	92.6	92.6	5.994	1247	1245
0.06375		101.6	6.408	1339	1332
0.06404		101.7	8.045	1697	1695
0.07527		109.4	8.532	1810	1810
0.07600	109.5	109.8	8.578	1821	1821
0.08409		114.5	8.694	1842	1848
0.06822	116.1	115.7	9.308	1994	2000
0.09719	122.4	122.6	9.592	2074	2071
0.10458		126.3	9.626	2073	2079
0.10865		128.3	9.719	2097	2103
0.10874		128.4	9.986	2178	2173
0.13582		140.9	10.383	2275	2275
0.14267	142.1	143.9	10.401	2273	2280
0.14427		144.7	10.408	2277	2282
0.15107		148.0	10.547	2319	2319
0.17361		157.0	10.614	2330	2336
0.17806		159.0	10.616	2337	2337
0.18960	163.0	162.4	10.647	2343	2344
0.19548		164.5	10.726	2376	2365
0.19670		164.9	10.923	2404	2415
0.24792		181.7	11.276	2519	2508
0.24884		181.9	11.283	2506	2510
0.25451		183.7	11.283	2520	2510
0.26117		185.7	11.304	2517	2515
0.27635		190.2	12.47_0	2815	2815
0.27675		190.4	13.60_4	3125	3110
0.27934		191.1	13.61_2	3126	3112
0.28730		193.4	14.23	3240	3270
0.28917		194.0	16.48	3847	3850
0.30046		197.2	19.40	4554	4610
0.30123		197.4	21.48_8	5161	5160
0.30346	199.0	198.0	22.35	5423	5390
0.30490		198.4			

[a] Up to 0.323*m*, an extra significant figure is retained to avoid "round-off" and interpolation errors. The experimental points listed below 1*m* are those used to fit the Debye-Hückel function.

Table III. Selected Values of ϕ_L and of L_2 for HBr Solutions at Selected Molalities and Mole Ratios

$n(\mathrm{H_2O})/n(\mathrm{HBr})$	m, mol kg^{-1}	ϕ_L, cal mol^{-1}	L_2, cal mol^{-1}	$n(\mathrm{H_2O})/n(\mathrm{HBr})$	m, mol kg^{-1}	ϕ_L, cal mol^{-1}	L_2, cal mol^{-1}
∞	0	0	0	25	2.2202	543	922
500,000	0.000111	5	7	22.20	2.5000	591	1024
100,000	0.000555	10	16	20	2.7753	639	1132
50,000	0.00111	14	22	18.50	3.0000	677	1210
20,000	0.00278	23	35	15.86	3.5000	764	1400
10,000	0.00555	33	50	15	3.7004	801	1480
7,000	0.00793	39	59	13.88	4.0000	857	1595
5,000	0.01110	46	67	12.33	4.5000	950	1800
4,000	0.01388	51	75	12	4.6255	974	1855
3,000	0.01850	58	86	11.10	5.0000	1045	2015
2,000	0.02775	70	103	10	5.5506	1154	2270
1,500	0.03700	80	116	9.5	5.8427	1211	2400
1,110	0.05000	92	132	9.251	6.0000	1246	2475
1,000	0.05551	96	138	9.0	6.1674	1281	2565
900	0.0617	100	144	8.5	6.5301	1360	2755
800	0.0694	106	152	8.0	6.9383	1450	2960
700	0.0793	112	161	7.929	7.0000	1474	3005
600	0.0925	120	172	7.5	7.4008	1553	3200
555.1	0.1000	124	178	7.0	7.9295	1669	3485
500	0.1110	130	185	6.938	8.0000	1685	3515
400	0.1388	143	204	6.5	8.5394	1812	3860
300	0.1850	161	230	6.167	9.0000	1924	4145
277.5	0.2000	166	237	6.0	9.2510	1986	4295
200	0.2775	191	272	5.551	10.0000	2177	4740
150	0.3700	216	308	5.5	10.0920	2200	4790
110.0	0.5000	246	352	5.0	11.1020	2462	5330
100	0.5551	257	370	4.5	12.3346	2780	5960
75	0.7401	292	428	4.0	13.8765	3180	6760
55.51	1.0000	337	507	3.70	15.0000	3469	7350
50	1.1101	356	540	3.5	15.8589	3690	7795
40	1.3877	402	631	3.25	17.0788	4005	8435
37.00	1.5000	421	669	3.0	18.5000	4375	9195
30	1.8502	480	789	2.775	20.0000	4770	10110
27.75	2.0000	506	844	2.5	22.2024	5350	11320

Consistency checks involved graphical examination of the slope, $(d\phi/dm)$, for the whole range of molality to guard against computational artifacts. Above 12*m*, the values of L_2 are based primarily on smooth curves of $(d\phi/dm)$ and of ϕ against m, since experimental errors in this region are larger and distort the polynomial results. The uncertainties in the values of L_2 are two to three times as large as those in ϕ_L, especially above 12*m*.

Results and Discussion

The values of ϕ_L for HBr(aq) given by Parker were guided by results from emf studies (*8*) at molalities below 0.4*m*, and used the results from Thomsen (*14*) and Berthelot (*1*) up to 26*m*, together with indirect values from 3 to 16*m* based on neutralization studies by Biermann and Weber (*2*). Our results are slightly higher than Parker's at low molalities (2 cal mol^{-1} at 0.0111*m* and 5 cal mol^{-1} at 0.1*m*), and are increasingly larger up to 130 cal mol^{-1} at 11 to 12*m*, above which the differences decrease essentially to zero from 17 to 22*m*. The differences put considerable strain on the results from the neutralization measurements (NaOH + HBr) of Biermann and Weber (*2*) in the range 3-15*m*, or upon ϕ_L of NaOH in that molality range. In the region from 17 to 22*m*, the close agreement lends considerable support to Parker's selections at molalities above that range, based on results from Thomsen (*14*) and Berthelot (*1*).

In a foregoing paragraph we mentioned that the trend of ϕ_L with m for HBr(aq) is almost linear above 6*m*. Comparison with the behavior of ϕ_L (*12, 15*) for other strong acids (HCl, HI, $HClO_4$) reveals similar behavior for these substances also, with approximately the same slopes, $(d\phi_L/dm)$. Similar behavior is also observed for lithium salts and appears to be typical of highly soluble substances with small, strongly hydrated cations in the region where much of the water is affected by primary hydration of the ions, characterized by large negative values of L_1. In the region where $0 < (d\phi_L/dm) =$ constant, L_1 is proportional to $-m^2$, and L_2 increases linearly with m, with a slope equal to $2(d\phi_L/dm)$.

Our calorimetrically based values of L_2 are a few percent larger than those based on emf measurements (*6, 7, 9, 10*). Best agreement is with those based on work by Harned et al. (*7, 9*), and poorest agreement is with the results from Gupta et al. (*6*) based on the mercury-mercurous bromide electrode, which is less well characterized than the silver-silver bromide electrodes used in the other work (*7, 9, 10*). The only emf results between 0.1 and 1*m* are those of Harned et al. (*7*), and in the region 0.5-1.0*m*, their values of L_2 are only a few calories less than ours. The values of L_2 based on work of Hetzer et al. (*10*) are in nearly as good agreement as the others (*7*) based on the silver-silver bromide electrode.

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Supplementary Material Available. Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-74-320.

Enthalpies of Dilution and Relative Apparent Molar Enthalpies of Aqueous Calcium and Manganous Perchlorates

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Enthalpies of dilution for $Ca(ClO_4)_2$ and $Mn(ClO_4)_2$ solutions were measured by solution calorimetry at 298.15K. Values of ϕ_L, the relative apparent molar enthalpy, were obtained over the range 0.003–7.7m for $Ca(ClO_4)_2$ and 0.008–4.2m for $Mn(ClO_4)_2$. A form of the Debye-Hückel equation guided reliable extrapolation to $m = 0$.

This paper is part of a series of investigations on the relative apparent molar enthalpy ϕ_L for 2-1 perchlorates. Values of ϕ_L for $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ were reported by Wood and Jongenburger (*17*) and for $Ba(ClO_4)_2$ by Vanderzee and Swanson (*14*). This work on $Ca(ClO_4)_2$ was undertaken to fill the gap in information for the above group of cations, for exploration of the effects of ion size and hydration on ϕ_L. The work on $Mn(ClO_4)_2$ is part of a related study on the first-row transition elements. Latysheva and Karavan (*2*) have measured enthalpies of dilution of saturated $Mn(ClO_4)_2$ solution and also the enthalpy of solution of $Mn(ClO_4)_2 \cdot 6H_2O(s)$ at 25°, 35°, and 45°C, but the results are not reduced to the reference state of infinite dilution. Values of ϕ_L derivable from their data, referred to the same reference state, agree well with ours, and from their data the standard enthalpy of solution of the hydrated salt can be calculated.

Experimental

Materials and analyses. A $Ca(ClO_4)_2$ stock solution was prepared by dissolving Mallinckrodt AR calcium carbonate (Lot XVX) in AR perchloric acid (60%). The resultant solution was slightly yellow; therefore, a small amount of charcoal was added, the solution was warmed and stirred, then cooled, and filtered to remove the charcoal and excess $CaCO_3$. The filtrate was warmed, concentrated by evaporation, and then enough distilled water added to give a solution near saturation at room temperature. A portion of this solution, diluted 1:100 with twice distilled water, had a pH of 4. The degree of acidity was ample to avoid possible thermal effects from hydrolysis (*6*) without making a significant contribution to ϕ_L for $Ca(ClO_4)_2$. The solution was analyzed with EDTA by recommended procedures (*15*), and other working solutions were prepared by mass dilution. Confirmatory analysis of a final solution from a calorimetric run supported the original assay. The initial stock solution was (7.686 ± 0.008)m, from three determinations.

$Mn(ClO_4)_2 \cdot 6H_2O$, G. F. Smith Co., was dissolved directly in twice distilled water to form an almost saturated solution at room temperature. A portion diluted 1:100 with twice distilled water had a pH of 4.4. At this level of acidity, hydrolytic effects should be negligible, and no significant thermal effects from excess acid should occur. The solution was analyzed with EDTA according to procedures by Welcher (*16*) and was (4.206 ± 0.005)m from three determinations. The assay was confirmed by potentiometric titration of a product solution from a calorimetric run with a standard permanganate solution (*18*). Other working solutions were prepared by mass dilution of the stock solution. The results of all weighings were reduced to mass, with densities from published tables for $Ca(ClO_4)_2$ (*5*) and $Mn(ClO_4)_2$ (*3*).

To suppress possible thermal effects from hydrolysis, dilutions were made into $10^{-4}m$ $HClO_4$ solutions prepared from twice distilled water. Thermal effects from this amount of background $HClO_4$ affect ϕ_L for the 2-1 electrolytes by less than 0.3 cal mol^{-1} and were not corrected for.

Calorimetric equipment and procedure. The calorimeter used in this investigation has been described elsewhere (*1, 10–14*). Temperatures were measured with a Hewlett-Packard HP-M40-2801A quartz thermometer, op-

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