NOMENCLATURE

c = concentration of fuel component by volume in liquid fuel mixture, % v/v
C = concentration of fuel component by volume in vapor–air mixture, % v/v
x = mole fraction of fuel component in liquid fuel mixture
y = mole fraction of fuel component in fuel vapor mixture on an "air-free" basis
p = vapor pressure, atm
p' = xp = partial pressure, atm
t = temperature, °C
θ = $t + 230$
ΔH_m = net molar heat of combustion, kcal/mol
C_s = stoichiometric concentration of fuel component by volume in vapor–air mixture (assuming complete combustion to carbon dioxide and water), % v/v
L = concentration of fuel component by volume in vapor–air mixture at lower flammability limit, % v/v
U = concentration of fuel component by volume in vapor–air mixture at upper flammability limit, % v/v
t_L = flash point, °C
E = C/L = flammability index
E' = xE = partial flammability index
Q = L_t/L = lower flammability limit temperature correction factor

SUBSCRIPTS

t = temperature (if t is specified, use its value as subscript—e.g., L_{25})
L = at flash point
i = general component, i
A, B, etc. = specific component A, B, etc.
M = multicomponent mixture

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Enthalpies of Dilution and Relative Apparent Molal Enthalpies of Aqueous Barium Perchlorate

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Relative apparent molal enthalpies (ϕ_L) were measured at 25°C for barium perchlorate solutions over the concentration range 0.006–5.8*m*. The data were fitted to a form of the Debye-Hückel equation which leads to reliable extrapolation to $m = 0$.

This study originated in part from specific need for relative apparent molal enthalpies (ϕ_L) for $Ba(ClO_4)_2$ solutions, and also as part of a broader interest in the behavior of ϕ_L with concentration for 2–1 perchlorates free from hydrolysis effects. Jongenburger and Wood (*4*) have reported ϕ_L values for $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ solutions up to 4.4*m*. The barium cation is the largest of the series, so should be the least solvated and exhibit the least tendency to hydrolyze. The studies reported here cover the concentration range from 0.006–5.755*m*, close to saturation.

EXPERIMENTAL

Materials. Five barium perchlorate stock solutions were prepared by slowly adding J. T. Baker Analyzed

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reagent barium hydroxide, $Ba(OH)_2 \cdot 8H_2O$, in slight excess to Baker and Adamson reagent grade 60% perchloric acid. The slightly basic final solutions were cooled and then filtered to remove a small precipitate of barium carbonate and metal hydroxides. Sufficient perchloric acid was added to the filtrate to bring its pH to between 6.0 and 6.5. For more concentrated solutions, one of the stock solutions was brought to $5.8m$ by evaporation at temperatures near 100°C.

Each of the stock solutions was analyzed gravimetrically (*5*) by precipitation of barium sulfate from weighed samples. Dilute solutions of barium perchlorate were prepared by mass dilution of portions of the stock solutions with freshly distilled water. Occasional analyses were also made on some of the final solutions after a series of dilution runs in the calorimeter. All weights were reduced to mass by use of reported densities for barium sulfate (*3*) and barium perchlorate solutions (*1*). Concentrations are based on molar masses of 233.40 g mol^{-1} for barium sulfate and 336.24 g mol^{-1} for barium perchlorate. Based on analytical precision and on analyses made on final solutions after a dilution series, the concentrations are believed accurate to 0.1%.

Calorimetric Equipment and Procedures. The solution calorimeter used in this work has been described previously (*8*). After each dilution experiment the instrument was calibrated electrically. The electrical energy increments were judged to be accurate to 0.02%. Expected accuracy for the corrected temperature increments was ±0.00005°C, except for a few runs with small increments in which the expected accuracy was ±0.00002°C. Corrected temperature increments were evaluated by Dickinson's method (*2*), with sufficiently long rating periods to ensure equilibrium drift rates, and with "mid-times" based on actual integration of representative time-temperature curves.

The Dewar calorimeter vessel was normally charged with about 1040 ml of distilled water, or with dilute barium perchlorate solution. The mass of water or dilute solution was based on direct weighing with a 5-kg capacity balance to ±0.02 gram. The concentrated solution was weighed into a sample holder with a nominal capacity of 39 ml. Weights were appropriately reduced to mass, traceable to an NBS-calibrated set of standard masses.

All results are for the reaction process at 25.00°C, based on 1 cal = 4.184 J.

The first dilution step in a series involves adding a sample portion of a stock solution to water:

$$Ba(ClO_4)_2(m_0) + H_2O(l) = Ba(ClO_4)_2(m_1) \qquad (1)$$

Successive steps in the series involve adding samples of the stock solution to portions of the solution produced in the preceding step—e.g., for step 2:

$$Ba(ClO_4)_2(m_0) + n_2 Ba(ClO_4)_2(m_1) = (1 + n_2) Ba(ClO_4)_2(m_2) \qquad (2)$$

Several such series of stepwise dilutions were made for different initial molalities m_0. In three cases, the final solution from a series was used as a "stock" solution for a dilution measurement, such as Equation 1, to provide final solutions at rather low concentrations. Additional single runs in the pattern of Equation 1 were made to fill in gaps in the concentration pattern. The several sets of ϕ_L values were then adjusted to a single curve on a large-scale plot with one arbitrary point assigned as a reference value, ($\phi_L' = 0$).

Treatment of Experimental Data. The arbitrary ϕ_L curve was then fitted to the equation from the Debye-Hückel theory following procedures described (*8*). The equation is a modification of that of Owen and Brinkley (*6*), and uses three adjustable parameters: a, the ion-size parameter; $(\partial \ln a/\partial T)_p$, its temperature coefficient; and b, the coefficient of a term linear in concentration. Since the ion-size parameter is already available ($a = 4.80$ Å) from activity coefficient data for barium perchlorate (*7*), the fitting procedures involve finding only two adjustable parameters for the Debye-Hückel equation, plus determination of the arbitrary reference value of ϕ_L' relative to the zero point of the Debye-Hückel curve.

Calculations of the Debye-Hückel functions were made by digital computation at the University of Nebraska Computing Center. Fitting of the experimental data involved both graphical and numerical examination of the deviations from calculated or smoothed curves.

The parameters which gave best fit were: $a = 4.80$ Å, $(\partial \ln a/\partial T)_p = 0.00125K^{-1}$, and $b = -820$ cal kg mol^{-2}. The values of ϕ_L calculated from these parameters represented the data within experimental error up to $0.468m$ after the several series of dilutions were separately scaled to minimize the deviations from the computed curve. The quality of fit for ϕ_L was ±1.5 cal mol^{-1} (standard deviation), and the overall uncertainty in ϕ_L associated with extrapolation to the infinite dilution reference state is judged to be ±5 cal mol^{-1}. Above $2m$, analytical inaccuracy may contribute an additional 2–3 cal

Table I. Relative Apparent Molal Enthalpies of Barium Perchlorate Solutions Studied

m, mol kg^{-1}	ϕ_L, obsd, cal mol^{-1}	ϕ_L, calcd, cal mol^{-1}	m, mol kg^{-1}	ϕ_L, obsd, cal mol^{-1}	ϕ_L, calcd, cal mol^{-1}
0.005779	138	135	0.1265	197	197
0.006908	144	143	0.1323	194	194
0.009928	157	161	0.1364	191	191
0.01500	185	181	0.1395	189	190
0.01587	181	183	0.1605	176	176
0.01613	190	184	0.1920	154	154
0.02430	198	201	0.1927	153	153
0.02946	209	209	0.1962	152	151
0.02961	211	209	0.2509	108	109
0.03349	213	213	0.2851	83	81
0.04481	221	219	0.3775	5	5
0.04763	220	220	0.4244	−34	−35
0.04847	221	221	0.4680	−71	−72
0.05830	221	222	0.7052	−264	−275
0.06490	221	222	0.8810	−399	−427
0.06623	220	221	0.9992	−485	−528
0.07826	218	219	1.360	− 721	−835
0.07851	219	219	1.541	−831	−991
0 08785	215	216	2.220	−1136	−1566
0.09604	213	213	2.679	−1289	−1954
0.09674	213	213	3.557	−1478	
0.09719	211	212	4.585	−1612	
0.09754	214	212	4.816	−1613	
0.09910	210	212	5.755	−1652	
0.1189	201	201			

Table II. Selected Values of Relative Apparent Molal Enthalpies for Barium Perchlorate Solutions, $Ba(ClO_4)_2 \cdot n\text{-}H_2O$

n, mol H_2O	m, mol kg^{-1}	ϕ_L, cal mol^{-1}	n, mol H_2O	m, mol kg^{-1}	ϕ_L, cal mol^{-1}
∞	0.0000	0	200	0.2775	87
500,000	0.0001110	25	100	0.5551	−140
200,000	0.0002775	38	75	0.7401	−289
100,000	0.0005551	52	50	1.110	−565
50,000	0.001110	71	40	1.388	−742
20,000	0.002775	103	30	1.850	−985
10,000	0.005551	133	25	2.220	−1136
7,500	0.007401	147	20	2.775	−1309
5,000	0.01110	166	17	3.265	−1426
3,000	0.01850	190	15	3.700	−1501
2,000	0.02775	206	13	4.270	−1575
1,000	0.05551	222	11	5.046	−1628
800	0.6933	221	10	5.551	−1646
500	0.1110	206	9.5	5.843	−1654
300	0.1850	159			

Table III. Observed Enthalpies of Dilution of Barium Perchlorate for Process: Solution I + Solution II = Solution III

Solution I		Solution II		Solution III,			
m_0, mol kg^{-1}	Mass, g	m_1, mol kg^{-1}	Mass, g	m_2, mol kg^{-1}	ϵ,[a,b] cal K^{-1}	$-Q_x$, obsd,[c,d] cal	$-Q_x$, calcd,[e] cal
3.557	63.522	0.0000	1034.6	0.09674	1178.0	174.16	173.99
3.557	65.115	0.0000	1034.7	0.9910	1176.3	177.99	178.24
3.557	62.849	0.09910	1063.0	0.1927	1169.7	160.27	160.02
3.557	63.952	0.0000	1032.8	0.09754	1176.5	175.34	175.05
3.557	63.994	0.0000	1037.3	0.09719	1176.6	175.08	175.17
3.557	63.978	0.09719	1068.1	0.1920	1172.9	163.45	163.29
3.557	64.043	0.1920	1090.4	0.2851	1163.9	149.17	147.36
0.2851	40.745	0.0000	1030.7	0.009928	1178.6	0.801	0.848
3.557	64.495	0.2851	1107.6	0.3775	1151.7	133.04	133.01
3.557	64.071	0.3775	1122.6	0.4680	1137.9	117.30	117.43
0.4680	42.855	0.0000	1037.6	0.01613	1186.7	4.533	4.419
2.220	56.184	0.0000	1045.9	0.06623	1188.2	96.84	96.92
2.220	56.483	0.06623	1045.1	0.1323	1164.2	93.70	93.68
2.220	56.167	0.1323	1063.2	0.1962	1158.5	86.30	86.10
0.1962	40.097	0.0000	1030.9	0.006908	1179.5	−0.057	−0.059
5.755	74.094	0.0000	1026.2	0.1395	1160.6	267.41	267.61
4.585	69.504	0.0000	1027.4	0.1189	1166.1	227.37	225.81
1.541	51.248	0.0000	1039.3	0.04847	1189.0	54.70	54.71
1.541	51.407	0.04847	1044.9	0.09604	1176.5	54.07	54.06
5.755	73.465	0.0000	1031.0	0.1364	1170.6	265.51	265.47
2.679	59.568	0.0000	1037.9	0.07851	1183.8	126.62	126.67
0.9992	47.918	0.0000	1034.4	0.03349	1182.0	25.11	25.01
0.9992	47.300	0.03349	1039.9	0.06490	1176.2	25.17	25.32
1.360	51.010	0.0000	1027.2	0.04481	1175.2	44.84	44.74
1.360	50.800	0.04481	1045.4	0.08785	1176.3	44.05	44.14
0.4244	43.003	0.0000	1027.1	0.01500	1176.7	3.507	3.450
0.4244	43.067	0.01500	1034.3	0.02946	1180.6	4.262	4.334
0.1605	40.687	0.0000	1033.1	0.005779	1184.7	−0.237	−0.254
0.7052	45.402	0.0000	1028.5	0.02430	1179.8	11.95	12.03
0.7052	45.300	0.02430	1040.3	0.04763	1182.0	13.07	12.97
4.816	70.705	0.0000	1000.5	0.1265	1133.2	235.21	235.54
4.816	70.338	0.1265	1027.8	0.2509	1117.4	211.38	211.97
0.4244	43.357	0.0000	976.9	0.01587	1120.1	3.461	3.510
0.8811	46.679	0.0000	1035.6	0.02961	1187.0	19.35	19.29
0.8811	46.431	0.02961	1037.2	0.05830	1177.8	19.88	19.92
2.679	58.900	0.0000	1029.5	0.07826	1175.0	125.03	125.11

[a] ϵ = energy equivalent of calorimeter. [b] Expected random error in $\epsilon = 0.3$ cal K^{-1}. [c] Q_x, obsd $= \epsilon\Delta\theta_x$, where $\Delta\theta_x$ = corrected temperature increment for reaction. [d] Q_x, calcd is based on smoothed values of ϕ_L for the molalities and amounts of materials in the reaction process. [e] Expected random error in Q_x is 0.06 to 0.12 cal per run, except for $Q < 5$ cal, where it is ± 0.02 cal per run. Values of Q_x carry one extra figure to avoid propagating "round off" errors.

mol^{-1}. There is an uncertainty of $\pm$ 0.0005K^{-1} in the temperature coefficient parameter $(\partial \ln a/\partial T)_p$, and a compensating uncertainty in the parameter b, because there is a range of values for these two parameters which give almost equally good fit and essentially the same absolute values for ϕ_L. A nonzero value for the temperature coefficient parameter was clearly necessary for best fit.

RESULTS AND DISCUSSION

Table I presents the observed values of ϕ_L obtained at the experimental concentrations, together with values calculated from the Debye-Hückel equation for comparison. Table II presents smoothed values of ϕ_L for barium perchlorate solutions at selected molalities and mole ratios: (moles of H_2O)/(mole of salt). Uncertainties in the values of ϕ_L have been discussed in the preceding paragraph.

The primary experimental data from this study are presented in Table III. The last column in this table gives the value of $-Q_x$, calcd, which is based on the assigned ϕ_L values from final smoothing and fitting of the ϕ_L data. The average difference between the values in the last two columns is $\pm$0.10 cal per run, and is a measure of the overall resolution for the instrument and operator when these measurements were made.

The values of ϕ_L for $Ba(ClO_4)_2$ are less than those (*4*) for $Sr(ClO_4)_2$ and $Mg(ClO_4)_2$ at any concentration chosen for comparison, with the differences increasing rapidly with increasing concentrations. The trend of ϕ_L with concentration resembles that for $NaClO_4$, which salt also has large negative values of ϕ_L at high concentrations.

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