the characteristic liquid structure, if any, by the released glycerol molecules, (*3*) breaking down the characteristic liquid structure of the other solvents, if any, so that the solvent molecules may be free to solvate the ion transferred, and (4) building up the ordered structure by the solvent molecules released by process 3 around the ion. The observed $\Delta S°_{\mathrm{tr(HX)}}$ may thus be represented as

$$\Delta S°_{\mathrm{tr(HX)}} = \sum_{1}^{4} \Delta S°_{i(\mathrm{H^+ + X^-})} = \Delta S°_{1(\mathrm{H^+ + X^-})} - \Delta S°_{2(\mathrm{H^+ + X^-})} + \Delta S°_{3(\mathrm{H^+ + X^-})} - \Delta S°_{4(\mathrm{H^+ + X^-})} \quad (13)$$

where $\Delta S°_i$ refers to the magnitudes of the entropy changes accompanying the respective steps indicated above. The sign and magnitude of the overall change depend on the relative magnitudes of the individual steps. In the glycerol-rich region (up to about 10 wt % DMF), the $\Delta S°_{\mathrm{tr}}$ increases may be due to a less negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ combined with an increasingly positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$. From 10 to 20 wt % DMF, the $\Delta S°_{\mathrm{tr}}$ decreases (the value being more negative), which indicates a decrease in the value of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ and a less positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$. This suggests that in this region there occurs a breakdown of the individual solvent structures. In the intermediate region (20–50 wt % DMF), the $\Delta S°_{\mathrm{tr}}$ values are positive, indicating an increasingly positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$ over the less negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$. Finally, in the DMF-rich region, the $\Delta S°_{\mathrm{tr}}$ value is negative, which indicates the dominance of the negative magnitude of $-\Delta S°_{4(\mathrm{H^+ + X^-})}$ over the positive magnitude of $\Delta S°_{3(\mathrm{H^+ + X^-})}$ (This is true in the case of HCl around 60 wt % DMF). The same type of variation of $\Delta S°_{\mathrm{tr}}$ is observed for both HCl and HBr with the magnitudes in the case of HBr being somewhat smaller than those of HCl. The same trend is also observed in the case of variation of $\Delta H°_{\mathrm{tr}}$. In the case of HCl, around 40 wt % DMF an endothermic maximum is observed whereas in the case of HBr such an endothermic maximum is not noticed although the magnitude of the $\Delta H°_{\mathrm{tr}}$ decreases. It is worthwhile to mention that the variation of $\Delta S°_{\mathrm{tr}}$ with solvent composition observed in the present case is similar to that reported earlier by Kundu et al. (*14b*) in the isodielectric mixtures of methanol and propylene glycol.

Nomenclature

${}_{\mathrm{s}}E°_m$, ${}_{\mathrm{s}}E°_c$, ${}_{\mathrm{s}}E°_N$, standard potentials in the solvent on molality, molarity, and mole fraction scales
$E°_m{}'$, extrapolation function
M_{xy}, mean molar mass of solvent mixture
$\mathrm{s}\gamma_{\pm}$, mean molal activity coefficient of solute in the solvent "s"
$\mathrm{m}\gamma_{\pm}$, mean ionic medium effect
$\Delta G°_{\mathrm{tr}}$, $\Delta H°_{\mathrm{tr}}$, $\Delta S°_{\mathrm{tr}}$, standard free energies, enthalpies, and entropies of transfer
$\Delta G°_{\mathrm{tr(nonel)}}$, $\Delta G°_{\mathrm{tr(el)}}$, nonelectrostatic and electrostatic parts of the free energy of transfer

Registry No. DMF, 68-12-2; HCl, 7647-01-0; HBr, 10035-10-6; Ag, 7440-22-4; AgCl, 7783-90-6; AgBr, 7785-23-1; glycerol, 56-81-5.

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Excess Molar Enthalpies of Nine Binary Steam Mixtures: New and Corrected Values

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Heats of mixing of binary mixtures of steam + H_2, + N_2, + CO, + CO_2, + CH_4, + C_2H_4, + C_2H_6, + C_3H_8, and + C_4H_{10} at temperatures up to 698.2 K and pressures up to 12 MPa have been reported in the literature. In some experiments, the gas flow rate was measured by condensing out the water, reducing the pressure of the gaseous component to atmospheric, and measuring the volumetric flow rate. Two corrections were overlooked in calculating the flow rate. Some gas remains dissolved in the water, and some gas is displaced from the flow system as water accumulates in the high-pressure receiver. While the dissolved gas correction is around 1%, the displacement correction is around 10% at high pressures. Previously reported heats of mixing have been recalculated, and for $0.5H_2O + 0.5H_2$ and $0.5H_2O + 0.5N_2$ some new measurements are reported.

Excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ of nine binary mixtures containing steam have been measured with a high-pressure flow mixing calorimeter (*1*). The mixtures investigated are steam + nitrogen (*1*), + methane (*2*), + hydrogen (*3*), + carbon monoxide (*4*), + carbon dioxide (*4*), + ethene (*5*), + ethane (*5*), + propane (*6*), and + butane (*6*). Most of the measurements extend up to 698.2 K at pressures up to about 12 MPa and at $x = 0.5$. For some mixtures, measurements of $H^{\mathrm{E}}_{\mathrm{m}}(x)$ were also made over a range of composition at temperatures and pressures where it was expected that the composition dependence would be most informative. As the work progressed, improvements in both technique and data analysis were made. For measurements reported at say 698.2 K and $x = 0.50$, the actual experimental conditions under which any one measurement was made may have differed from these conditions by 1 or 2 K and by 1% or 2% in composition. Small corrections were applied to the measurements to obtain the value of H^E_m under the desired conditions. A recent reexamination of sources of possible systematic error has revealed that some small corrections that are negligible at low pressures become significant at high pressures and that in ref 1-5 one source of significant systematic error was overlooked completely. The aim of this paper is to make clear what the sources of error are and to present recalculated H^E_m values for the nine mixtures.

Temperature and Composition Corrections

Measurements on most of the mixtures were made at nine temperatures in the range 448.2-698.2 K. In adjusting the apparatus, it was not always possible to obtain the desired temperature and composition exactly, though actual temperatures achieved were usually distributed fairly evenly on either side of the desired temperature. The $H^E_m(x=0.5)$ measurements on all nine mixtures were fitted to empirical equations of the form

$$H^E_m(x=0.5) = \alpha p + \beta p^2 + \gamma p^3 \quad (1)$$

where

$$\alpha = \exp(a + b/T + c/T^2) \quad (2)$$

and β and γ were given by similar equations, each with different values of a, b, and c.

This equation fitted most of the measurements well, though it was evident (*6*) that the fit to $0.5H_2O + 0.5C_4H_{10}$ was not as good as that for other mixtures. Equation 1 was used to calculate $(\delta H^E_m/\delta T)_{p,x}$ and hence to correct the individual measurements to the chosen temperature.

It was not always possible to adjust the apparatus to obtain a mixture at $x = 0.50$, and deviations of 1% or 2% were not unusual. Where the $H^E_m(x)$ curves were nearly parabolic, correction to $x = 0.50$ was made with graphs of $H^E_m(x)/4x(1-x)$ against x. As it was impossible to measure the composition dependence of $H^E_m(x)$ at all temperatures and pressures, extrapolation of the measurements made under selected conditions was necessary.

For mixtures containing steam, we have now developed a cubic equation of state and appropriate combining rules. The equation is a good overall fit to the H^E_m values of all the mixtures so far investigated. Details are given elsewhere (*7*). We have now used this equation rather than eq 1 and 2 to make a better correction of the measurements to the chosen temperature and have also used it in place of the graphs of $H^E_m(x)/4x(1-x)$ to adjust the measurements to $x = 0.50$. The maximum uncertainty in any value of T is 0.2 K, and the maximum uncertainty in any value of x is 0.01. The uncertainty on the corrected values of $H^E_m(x)$ is the same as that on the uncorrected value.

Corrections to the Flow Rate

For the mixtures $0.5H_2O + 0.5C_3H_8$ (*6*), $0.5H_2O + 0.5C_4H_{10}$ (*6*), and $0.5H_2O + 0.5CO_2$ (*4*) at pressures greater than 6 MPa and for $0.5H_2O + 0.5C_2H_6$ (*5*) at pressures greater than 4 MPa, the nonaqueous component was pumped into the flow system as liquid and its flow rate was determined from the known volumetric pumping rate and the density of the liquid. Details of the method are given in ref 4. For some of the measurements on mixtures containing C_2, C_3, and C_4 *n*-alkanes, it was found that the densities of the liquified hydrocarbons had been wrongly calculated and were too large by 2% or 3%. The effect of this error was to make values of $H^E_m(x=0.5)$ too small by 1-1.5%. The error has now been corrected.

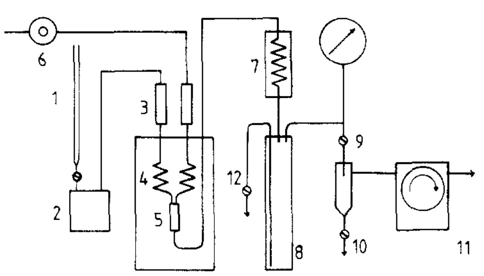

Figure 1. Simplified diagram of the flow calorimetric apparatus.

For all other measurements, the flow rate of the nonaqueous component was obtained by reducing the pressure of the mixture that had passed through the calorimeter to atmospheric and measuring the gas flow rate with a calibrated dry gas meter. While this technique may appear straightforward, it entails making some corrections that we initially overlooked. To explain the method and the associated corrections, we refer to the simplified diagram of the apparatus shown in Figure 1.

Water from buret 1 was pumped by metering pump 2 into flash vaporizer 3. The steam passed through heat-exchange coil 4 into calorimeter 5. The gaseous component of the mixture entered at 6, passed through a heat-exchange coil, and mixed with the steam in calorimeter 5. The mixture was condensed at 7 and entered a receiver 8 of approximately 2-dm^3 capacity. Water collected in the receiver, but the gas escaped through needle valve 9, which controlled the gas flow rate. The pressure on the downstream side of the needle valve was atmospheric. Trap 10 collected water carried over by the gas, and flowmeter 11 indicated the volumetric flow rate of the gas at ambient temperature and pressure. Tap 12 allowed the receiver to be drained when necessary.

The molar flow rate of the gas leaving the apparatus was calculated from the measured volumetric flow rate at ambient temperature and pressure with known second virial coefficients and corrections were made for the presence of water vapor at its saturation pressure. While this is straightforward, there are two reasons why the flow rate of the gas leaving the apparatus is not necessarily the same as the flow rate of gas entering and passing through the calorimeter. Some gas is displaced by the accumulating condensate, and some gas remains dissolved in the condensate.

Gas Displacement by Condensate

As the run progresses, receiver 8 slowly fills with water thus diminishing the volume of the system. As the water accumulates, it displaces an equal volume gas from the system so that the flow rate of gas leaving the apparatus is slightly bigger than the flow rate entering. At low pressures, the effect is negligible, but the effect increases in proportion to the density of the gas in the receiver. A correction for this effect is easily calculated from the known water flow rate and the molar volume of the gas at the temperature and pressure of the receiver. This correction was unfortunately overlooked in ref 1-5. For runs on $0.5H_2O + 0.5CH_4$ at 1 MPa, the correction is 1%, but for runs at 12 MPa, the displacement effect gives a methane flow rate that is too high by 10%, so that the value of H^E_m is too low by this amount.

Solubility of Gas in Aqueous Condensate

Water collected in receiver 8 is saturated with dissolved gas at the system pressure. This gas remains in the apparatus, causing the flow meter readings to be too low. Correction for this effect is small for all mixtures except $0.5H_2O + 0.5CO_2$ and $0.5H_2O + 0.5C_2H_4$ at high pressures and was originally made only for these mixtures. We now apply this correction to all our measurements, using the following method.

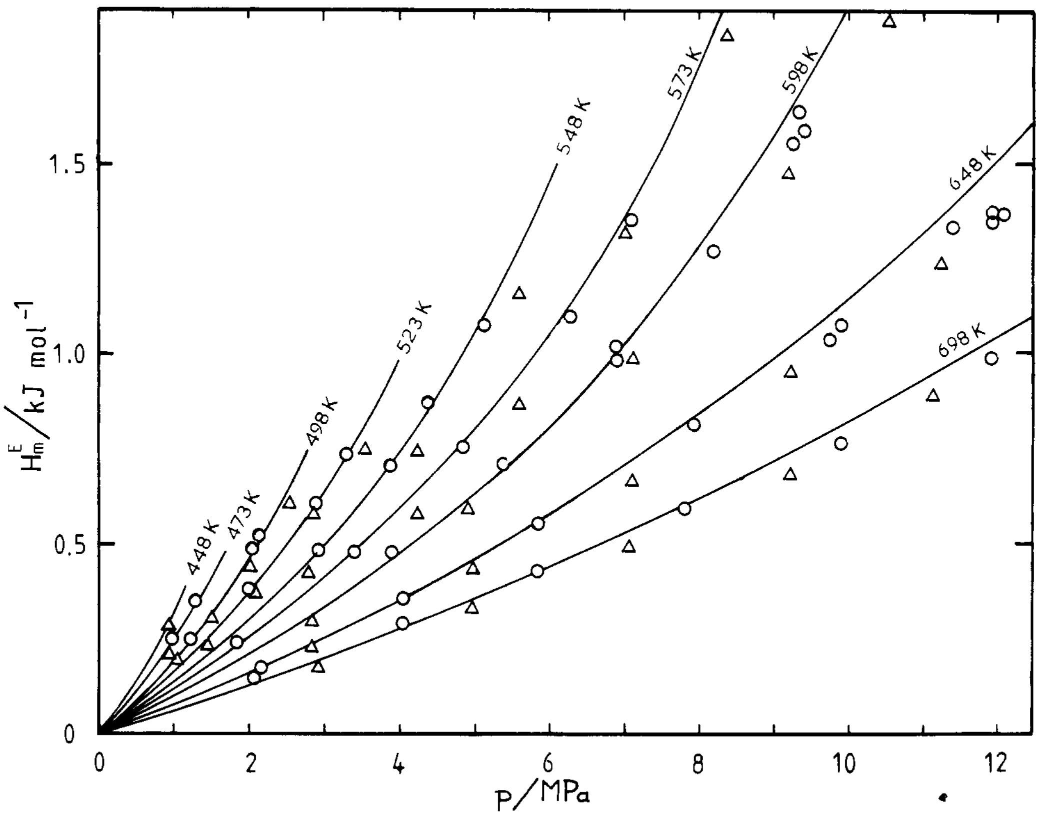

Figure 2. Excess molar enthalpies H^E_m of $0.5H_2 + 0.5H_2O$ plotted against pressure: ○, new measurements, Table I; △, old measurements (*3*). The solid curves were calculated from the cubic equation of state (*7*).

The solubility of a sparingly soluble gas in water can be calculated from the equation of Krichevsky and Kasarnovsky (*8*)

$$\ln (f^l_2/x_2) = \ln (H_{2,1}) + \bar{v}^\infty_2 (p - p^s_1)/RT \qquad (3)$$

where subscript 2 refers to the nonaqueous component and $H_{2,1}$ is the Henry's law constant. In the Poynting correction term, $\bar{v}^\infty_2$ is the partial molar volume of component 2 at infinite dilution, assumed to be independent of the pressure, and f^l_2 is the fugacity of component 2 in water. At equilibrium, $f^l_2 = f^l_2$, and as $y_2 \simeq 1$, a good approximation is to set $f^v_2 = f^v_{(\text{pure } 2)}$. This was calculated with good accuracy with use of the virial equation of state truncated after the third term. Where solubility data were available $H_{2,1}$ and $\bar{v}^\infty_2$ were obtained from plots of ln (f^l_2/x_2) against $p - p^s_1$. The temperature dependence of $H_{2,1}$ was determined from values of x_2 at standard atmospheric pressure compiled by Wilhelm et al. (*9*). $\bar{v}^\infty_2$ is only weakly temperature dependent.

Equation 3 does not apply when the solubility of the gas is appreciable. Gibbs and Van Ness (*10*) demonstrated that a plot of ln (f^l_2/x_2) against $p - p^s_1$ for carbon dioxide + water yielded a straight line but that its slope was not $\bar{v}^\infty_2/RT$. They showed that $H_{2,1}$ was a function of x_2 unless $x_2 \ll 1$. Krichevsky and Il'inskaya (*11*) showed that this concentration dependence could be accounted for by writing

$$\ln (f^l_2/x_2) = \ln (H_{2,1}) + (x_1^2 - 1)A/RT + \bar{v}^\infty_2 (p - p^s_1)/RT \qquad (4)$$

The slope of ln (f^l_2/x_2) against pressure is

$$\mathrm{d}[\ln (f^l_2/x_2)]/\mathrm{d}p = -2Ax_1/(H_{2,1}RT) + \bar{v}^\infty_2/RT \qquad (5)$$

To a good approximation, the slope is independent of pressure but changes with temperature due to the strong temperature dependence of A. We plotted $[\ln (f^l_2/x_2) - \ln (H_{2,1}) - v_2(p - p^s_1)/RT]$ against $(x_1^2 - 1)$ for carbon dioxide and ethene in water to obtain A/RT at 283, 293, and 303 K. Plotting $[\ln (f^l_2/x_1) - (x_2^2 - 1)A/RT]$ against p then gave straight lines of slope $\bar{v}^\infty_2/RT$.

In practice a rough value of v_2 was adequate as the Poynting correction term $\exp(p\bar{v}^\infty_2/RT)$ near 298 K does not differ greatly from unity in the range 0–15 MPa. At 6 MPa the calculated solubility of carbon dioxide in water changes by only 2% if $\bar{v}^\infty_2$ is changed from 30 to 40 cm^3 mol^{-1}.

Corrected Measurements

To recalculate the H^E_m values, we went back to the measurements for each run recorded in laboratory notebooks. Recalculated values of $H^E_m(x=0.5)$ are listed in Table I, and recalculated values of $H^E_m(x)$ are listed in Table II. The correction for gas dissolved in the condensate is biggest for $0.5H_2O + 0.5CO_2$ at 6.5 MPa where $H^E_m(x=0.5)$ is reduced by 2.8%. However, the gas displacement correction increases $H^E_m(x=0.5)$ by 10.3%. For $0.5H_2O + 0.5CH_4$ at 12.62 MPa, the dissolved gas correction is −0.24% and the gas displacement correction is +12.1%. At lower pressures, the corrections are smaller and to a first approximation are proportional to the pressure.

The gas displacement correction is bigger when $x > 0.5$. At high mole fractions of water, the receiver fills up faster than at $x = 0.5$ and a larger volume of gas is displaced. The biggest correction is for $0.759H_2O + 0.241CH_4$ at 598.2 K and 10.51 MPa, where the solubility correction is −0.63% and the displacement correction is +29%. However, the effect of these corrections taken over all the measurements is to increase the average value of H^E_m by only 4%.

New Measurements

In addition to the recalculated values of H^E_m, some new measurements are reported. These include a complete set of measurements on $0.5H_2O + 0.5H_2$ and measurements on $0.5H_2O + 0.5N_2$ at 573.2, 598.2, and 648.2 K. These mea-

Table I. Recalculated and New Excess Molar Enthalpies H^{E}_{m} at $x = 0.5$[a]

T/K	p/MPa	H^{E}_{m}/(J mol^{-1})	p/MPa	H^{E}_{m}/(J mol^{-1})	p/mPa	H^{E}_{m}/(J mol^{-1})	p/MPa	H^{E}_{m}/(J mol^{-1})	p/MPa	H^{E}_{m}/(J mol^{-1})
$0.5H_2O + 0.5H_2$*										
448.2	0.55	163	0.62	194	0.69	226	0.76	247	0.93	283
473.2	0.68	160	0.93	210	0.98	254	1.28	349	1.34	337
498.2	0.48	75	0.70	111	1.22	254	2.04	490	2.14	524
523.2	1.06	182	2.00	386	2.90	609	3.31	736	3.55	750
548.2	1.47	225	2.93	489	3.91	706	4.42	873	5.13	1072
573.2	1.84	247	3.42	488	4.84	758	6.28	1103	7.08	1356
598.2	2.13	241	5.38	710	6.93	1020	9.27	1555	9.38	1586
	3.88	480	6.88	983	8.20	1269	9.32	1646	10.69	1971
648.2	2.14	179	7.96	813	9.89	1077	11.86	1456	11.90	1438
	4.01	365	9.75	1039	11.38	1345	11.89	1436	12.04	1472
	5.88	557								
698.2	2.09	149	4.05	292	5.85	433	9.20	687	11.13	891
	2.93	173	4.96	321	7.80	594	9.84	785	11.90	992
$0.5H_2O + 0.5N_2$										
448.2	0.45	157	0.58	164	0.71	223				
498.2	1.14	213	1.65	318	1.83	360	2.17	478		
548.2	0.72	121	2.86	405	3.84	642	4.24	694	4.97	950
	1.83	244								
573.2	0.72	67	3.51	452	5.62	817	6.31	1065	7.72	1470
	2.10	225	4.89	696						
598.2	0.72	77	4.24	435	7.69	1090	9.74	1670	11.13	2072
	1.47	135	5.62	663	8.37	1260	10.51	1990	11.17	2010
	2.86	273	6.96	940	9.10	1450				
648.2	1.47	104	5.48	476	8.31	812	10.03	1020	12.58	1460
	2.89	222	7.06	611	9.06	900	11.13	1240	12.58	1471
	4.20	327								
698.2	1.48	67	4.24	253	7.07	465	9.82	716	11.13	843
	2.86	159	5.62	352	8.48	595	10.44	777	12.59	1006
$0.5H_2O + 0.5N_2$*										
573.2	4.87	741	5.45	856	7.16	1240	7.19	1301	7.19	1273
598.2	2.39	229	7.41	1046	7.89	1164	8.72	1336	8.90	1390
	5.57	665	7.76	1097	8.58	1250	8.79	1378		
	6.17	758	7.79	1118	8.70	1361	8.88	1422		
648.2	4.40	343	5.51	477	7.08	663	7.87	736	8.44	849
$0.5H_2O + 0.5CO$										
473.2	0.76	170	1.40	351	1.91	525				
523.2	2.17	360	2.86	519	3.56	707				
573.2	3.58	470	4.79	688	5.75	861	6.99	1201		
623.2	3.55	305	5.27	496	6.99	695				
648.2	3.55	266	5.27	413	6.99	596				
673.2	4.24	286	5.62	395	6.99	517				
698.2	10.10	687	11.32	807	12.18	901				
$0.5H_2O + 0.5CO_2$										
448.2	0.37	75	0.58	130	0.71	174				
473.2	0.45	72	0.69	114	0.90	155	1.12	221	1.16	224
	0.68	114								
498.2	0.47	60	0.64	89	1.54	245	1.91	329	1.97	341
	0.64	86	1.08	158						
523.2	0.73	84	1.55	196	2.62	381	3.27	549	3.31	554
	1.51	188	2.40	337	3.16	524				
548.2	0.64	64	2.20	244	3.13	389	4.36	644	4.97	785
	1.53	155	2.92	355	4.08	576				
573.2	0.74	61	3.09	312	5.32	665	6.42	912	6.81	1028
	1.48	124	4.49	512	5.69	742	6.53	943	6.96	1082
	2.33	214	5.18	623	6.10	830	6.60	977	7.21	1161
598.2	1.40	99	5.01	474	6.81	763	8.79	1183	10.3	1622
	2.68	203	5.37	528	7.34	825	8.92	1195	10.4	1672
	3.91	331	5.69	559	7.76	947	9.24	1289	11.2	1889
	4.19	381	5.90	606	8.22	1033	9.62	1413	11.4	1982
648.2	0.44	24	4.08	253	6.00	417	9.41	776	12.4	1189
	1.38	74	4.41	285	6.52	455	10.4	948	12.6	1263
	2.40	136	5.25	349	7.51	588	11.5	1073	13.4	1435
	3.19	187	5.56	370	8.44	661	11.8	1106	13.5	1329
698.2	0.73	27	3.48	158	5.76	296	7.38	434	10.8	682
	1.57	64	4.46	209	6.51	369	8.26	487	11.9	809
	2.53	107	5.68	302	6.93	396	9.34	568	13.4	928
$0.5H_2O + 0.5CH_4$										
448.2	0.35	77	0.65	169	0.93	278				
473.2	0.52	91	0.93	203	1.34	326				
498.2	0.60	92	1.05	185	1.55	294	2.02	411	2.51	569
523.2	0.79	110	1.48	218	2.17	358	2.86	533	3.58	726
548.2	0.80	98	2.86	439	4.21	726	4.98	979	5.55	1112

Table I (Continued)

T/K	p/MPa	H_m^E/(J mol^{-1})	p/MPa	H_m^E/(J mol^{-1})	p/mPa	H_m^E/(J mol^{-1})	p/MPa	H_m^E/(J mol^{-1})	p/MPa	H_m^E/(J mol^{-1})
548.2	1.55	204	2.93	452						
573.2	0.86	87	3.55	432	5.00	730	6.33	972	7.77	1483
	2.15	236								
598.2	0.80	54	3.53	371	6.27	755	7.69	1076	10.44	1727
	2.16	190	5.00	553	6.31	785	9.20	1410	10.51	1754
648.2	1.41	78	4.27	318	7.06	595	10.03	1010	11.31	1202
	2.82	187	5.65	455	8.44	796	10.51	1043	12.62	1458
	2.86	229	6.86	605	9.79	1008				
698.2	1.55	76	4.20	266	7.03	458	9.82	707	12.58	973
	2.82	163	5.69	361	8.38	587	11.13	822		
$0.5H_2O + 0.5C_2H_4$										
448.2	0.46	105	0.71	172	0.73	170				
473.2	0.61	114	0.75	146	1.04	217				
498.2	0.85	128	1.24	213	1.86	349	2.02	386		
523.2	0.71	85	1.61	221	2.46	382	3.23	573		
548.2	1.04	114	2.44	313	3.71	563	4.72	813		
573.2	1.22	115	3.49	412	4.51	570	5.47	775	6.65	1090
	2.55	280								
598.2	1.04	88	2.37	207	3.73	367	4.97	550		
648.2	1.17	67	2.39	154	3.77	265	4.51	337		
$0.5H_2O + 0.5C_2H_6$										
448.2	0.57	159	0.72	208	0.74	215				
473.2	0.66	154	0.67	157	1.01	247				
498.2	0.55	104	1.09	218	1.87	406				
523.2	0.95	158	1.65	279	2.34	450	3.15	659		
548.2	1.25	171	3.04	493	4.09	764	4.94	1014	5.35	1176
	2.26	339	3.76	650	4.53	875				
573.2	1.01	115	2.95	392	4.53	699	5.80	1007	6.67	1275
	1.98	238	3.82	559	5.19	828	6.04	1085	7.07	1389
598.2	0.93	94	2.95	335	4.94	650	8.24	1360	9.77	1821
	1.94	205	3.74	452	6.21	898	8.97	1586	10.7	2172
648.2	0.80	63	4.05	384	6.79	710	9.00	1039	12.1	1478
	1.86	151	5.25	517	7.03	753	9.13	1074	12.9	1558
	2.48	209	5.80	592	7.96	884	9.96	1188	13.2	1692
	3.53	320	6.10	636	8.62	961	11.4	1368	13.4	1765
698.2	0.77	48	3.69	250	7.55	591	9.48	810	11.8	1045
	1.74	108	5.14	368	8.10	660	10.9	961	12.4	1126
	2.52	164	6.17	464	9.31	787	11.4	1024		
$0.5H_2O + 0.5C_3H_8$										
448.2	0.56	183	0.72	243	0.78	264				
473.2	0.53	137	0.72	194	0.79	206	0.96	288	1.18	369
498.2	0.70	151	1.08	262	1.44	371	1.89	526		
523.2	0.68	125	1.31	269	1.79	388	2.39	542	3.26	801
	0.74	136								
548.2	0.77	162	1.79	330	3.20	646	4.18	902	4.97	1184
	1.27	184	2.40	463	3.96	859	4.80	1127	5.40	1343
573.2	0.77	110	2.28	376	2.71	436	4.12	733	5.42	1063
	1.03	151	2.47	395	2.80	448	4.90	927	5.97	1194
	1.92	303	2.50	405	4.05	736	5.09	990	6.88	1479
598.2	0.79	101	2.48	355	3.81	589	5.86	990	9.00	1737
	2.09	286	2.95	424	4.22	645	6.85	1190	9.62	2000
	2.23	318	3.64	545	5.01	794	8.10	1498	10.2	2225
648.2	1.17	118	3.02	325	5.08	577	8.20	1005	11.5	141
	1.51	160	3.26	358	6.43	781	8.72	1107	13.1	1988
	1.62	172	3.79	406	8.10	1007	9.79	1344	13.7	2092
698.2	1.43	120	5.38	483	9.37	913	13.2	1404		
	3.31	297	7.49	711	11.4	1168				
$0.5H_2O + 0.5C_4H_{10}$										
448.2	0.63	260	0.76	341						
473.2	0.68	242	0.97	355	1.31	522				
498.2	0.62	181	1.12	336	1.62	558	2.06	786	2.27	838
	0.87	273								
523.2	1.10	283	1.56	421	1.99	555	2.41	745	3.29	1092
548.2	1.65	375	3.16	824	3.60	1019	4.59	1360	5.36	1751
	3.05	789								
573.2	1.80	355	3.22	684	4.60	1098	6.10	1588	7.45	2199
598.2	1.31	232	2.33	430	5.14	1084	7.89	1934	9.34	2391
	2.27	425	3.67	717	6.59	1500	8.13	2011	10.6	2853
648.2	1.47	208	4.46	686	7.76	1300	10.8	1910	12.3	2209
	3.02	448	6.04	968	9.27	1595				
698.2	1.62	187	4.60	571	7.63	1012	8.03	999	11.3	1431
	2.85	342	6.14	755	7.69	959	9.55	1233	13.0	1706

[a] New measurements are indicated by an asterisk.

Table II. Recalculated Excess Molar Enthalpies H^E_m over a Range of Mole Fraction x.

x	$H^E_m/(J\ mol^{-1})$	x	$H^E_m/(J\ mol^{-1})$	x	$H^E_m/(J\ mol^{-1})$	x	$H^E_m/(J\ mol^{-1})$	x	$H^E_m/(J\ mol^{-1})$
$[xH_2O + (1 - x)H_2]$, T = 598.2 K, p = 10.51 MPa									
0.310	1482	0.412	1783	0.519	1990	0.629	2025	0.737	1789
$[xH_2O + (1 - x)H_2]$, T = 698.2 K, p = 11.13 MPa									
0.307	743	0.409	852	0.518	941	0.630	878	0.743	804
$[xH_2O + (1 - x)N_2]$, T = 548.2 K, p = 4.24 MPa									
0.305	581	0.405	690	0.509	724	0.610	686	0.713	592
$[xH_2O + (1 - x)N_2]$, T = 648.2 K, p = 10.03 MPa									
0.307	850	0.407	992	0.518	1058	0.628	1038	0.743	921
$[xH_2O + (1 - x)N_2]$, T = 648.2 K, p = 12.58 MPa									
0.308	1178	0.415	1401	0.523	1461	0.637	1460	0.752	1314
$[xH_2O + (1 - x)N_2]$, T = 698.2 K, p = 10.44 MPa									
0.205	485	0.307	644	0.411	753	0.517	792	0.628	772
$[xH_2O + (1 - x)CH_4]$, T = 548.2 K, p = 4.98 MPa									
0.304	699	0.408	836	0.508	893	0.612	895	0.717	809
$[xH_2O + (1 - x)CH_4]$, T = 598.2 K, p = 10.44 MPa									
0.310	1392	0.413	1652	0.525	1847	0.631	1888	0.743	1697
$[xH_2O + (1 - x)CH_4]$, T = 648.2 K, p = 10.51 MPa									
0.304	822	0.412	958	0.524	1020	0.637	1036	0.759	894
$[xH_2O + (1 - x)CO_2]$, T = 548.2 K, p = 4.96 MPa									
0.301	559	0.405	665	0.502	718	0.608	723	0.716	640
$[xH_2O + (1 - x)CO_2]$, T = 598.2 K, p = 4.96 MPa									
0.301	352	0.409	408	0.508	433	0.618	420	0.718	351
$[xH_2O + (1 - x)CO_2]$, T = 648.2 K, p = 5.00 MPa									
0.305	253	0.408	296	0.511	313	0.611	301	0.713	266

surements are believed to be uncertain to no more than ±1.5% and are marked with an asterisk in Table I.

Comparison of our early H^E_m measurements for $0.5H_2O + 0.5H_2$ with the new cubic equation of state showed that they lay below the calculated curves by an amount greater than that observed for water + C_1 to C_6 *n*-alkanes. To see if this was due to an error in the measurements or was a real effect, new measurements were made with upgraded apparatus. The source of the biggest experimental error is the signal-to-thermal-noise ratio seen on the chart recorded that monitors the temperature of the calorimeter. Over a period of years this has been reduced by smoother pumping of the fluids, better temperature control, and thermal insulation of the calorimeter. The two sets of measurements are shown in Figure 2. All corrections described above were applied to both sets. The figure shows that at pressures up to 8 MPa the new measurements are closer to the curve calculated from the cubic equation.

At pressures below 8 MPa, the mean deviation of the new points from the curves is −1.5%, whereas the old points it is −3.5%. Above 8 MPa, the mean deviation of the new points from the curves is −6%, and for the old points, it is −8%. On average the new H^E_m measurements are 2% bigger than the old, but they still lie below the curve calculated from the cubic equation. As the new measurements were made after we had obtained greater experience with the apparatus, we recommended that they should replace those obtained earlier.

With any new technique, improvements are made as experience is gained, and early measurements may be found to be less accurate than was originally thought. By going back to original laboratory notebooks and recalculating the H^E_ms from the source data, we now have values that are all calculated in a consistent way. We estimate the overall uncertainty on the recalculated H^E_m values to be ±2%.

Glossary

A	coefficient of fitting equation, eq 4
a,b,c	coefficients of fitting equation, eq 3
f^l_2	fugacity of gas (2) in water (1)
f^v_2	fugacity of gas (2) in vapor phase
$H_{2,1}$	Henry's Law constant of gas (2) in water (1)
p^s_1	saturation pressure of water (1)
v_2	molar volume of gas (2)
$\bar{v}^\infty_2$	partial molar volume of 2 at infinite dilution
y_2	mole fraction of 2 in vapor phase

Greek letters

α,β,γ	coefficients of fitting equation, eq 1

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