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The Excess Enthalpy of (Steam + Ethane) in the Supercritical Region up to $T = 699.4$ K and $p = 25.3$ MPa

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Flow calorimetric measurements of the excess molar enthalpy H_m^E of $(0.5H_2O + 0.5C_2H_6)$ in the supercritical region carried out at temperatures from 573.7 to 699.4 K and at pressures in the range 5.05 to 25.3 MPa are reported. The measurements are fitted by a two-reference-fluid corresponding-states model which gives a good representation of the excess enthalpies up to the highest pressure.

KEY WORDS: excess enthalpy; fluid mixture; steam + ethane; supercritical region.

1. INTRODUCTION

This paper reports flow calorimetric measurements of the excess molar enthalpy H_m^E of (water + ethane)(g) made at pressures up to 25.3 MPa, temperatures up to 699.4 K, and the composition $x = 0.5$. These measurements parallel similar work [1] on (water + carbon dioxide)(g). Some measurements of H_m^E for (water + ethane) have already been reported. Lancaster and Wormald [2] used a low-pressure differential-flow mixing calorimeter to make excess enthalpy measurements at standard atmospheric pressure over the temperature range 363.2 to 393.4 K, and second virial cross coefficients B_{12} were derived from the results. At lower temperatures, Coan and King [3] measured the solubility of water in compressed ethane gas and obtained values of B_{12} down to 298 K. To fit these, it was necessary to use a temperature-

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dependent interaction parameter $(1-k_{12})=0.974+0.09\times10^{18}T^{-8}$ (with T in K) in the pair potential combining rule $\varepsilon_{12}=(1-k_{12})(\varepsilon_{11}\varepsilon_{22})^{1/2}$.

Lancaster and Wormald [4] then reported H_m^E measurements at temperatures from 448.2 to 698.2 K at pressures from 0.55 to 12.2 MPa. The values of H_m^E extrapolated back to standard atmospheric pressure were shown to be consistent with the measurements obtained using the low-pressure differential mixing calorimeter. Excess enthalpy isotherms were fitted to an empirical equation, and compression factors for the $(0.5H_2O+0.5C_2H_6)$(g) mixture were calculated. The measurements at all pressures were well fitted using a cubic equation of state which was originally developed to fit properties of (water + alkane)(g) mixtures [5]. The phase diagram for (water + ethane) was determined by Danneil et al. [6] and is of Type IIIm in the classification of van Konynenburg and Scott [7]. The critical line originating at pure water ($T_c=647.096$ K, $p_c=22.064$ MPa) initially moves to lower temperatures and slowly rising pressures. The critical locus of the mixture passes through a minimum temperature at about 624 K; then the pressure increases rapidly with temperature.

2. EXPERIMENTAL

The high-pressure-flow mixing calorimetric apparatus was the same as that described previously [8] for measurements on (water + carbon dioxide). Liquid ethane at 253 K was confined over mercury and was pumped by displacing the mercury with water from a metering pump. The apparatus was back-pressured with nitrogen, and the pressure was controlled to ±20 kPa. To obtain isothermal conditions in the mixing calorimeter, the heater was adjusted manually rather than by computer. Ethane of mole fraction purity $(0.993C_2H_6)$ was used, and the water was ordinary degassed distilled water.

Our previous high-pressure measurements [4] were made at $x=0.5$ over the pressure range 0.57 to 12.2 MPa and over the temperature range 448.5 to 698.2 K. The new measurements overlap this previous work and extend over the pressure range 5.15 to 24.95 MPa and the temperature range 573.7 to 699.4 K. All temperatures are on the IPTS-68 scale. The new measurements include a pressure scan at 650.7 K, just 3.6 K above the critical temperature of water. The measurements at this temperature, particularly at pressures in the range 21 to 24 MPa bracketing the critical pressure (22.064 MPa) of water, were very difficult to make, and under these experimental conditions great care had to be taken. There was no difficulty in adjusting the flow rates so as to obtain a composition of $x=(0.50\pm0.01)$, but in this region where H_m^E increases rapidly with pressure, very small fluctuations in temperature or pressure produced large perturbations of the steady state we were trying to obtain, and we often had to monitor the apparatus for several hours until conditions stablilized sufficiently to allow reliable measurements. The measurements at the higher temperatures 674.2 and 699.4 K were easier to make. In all, we achieved a total of 46 measurements at pressures greater than 10 MPa, and these included 15 measurements at pressures greater than 20 MPa.

We estimate that the average uncertainty of all measurements up to 20 MPa is ±4%. Beyond this pressure and for the measurements at 674.2 K, it is about the same; for those at 699.4 K, it is about ±5%; and for those at 650.7 K and at the pressures 21.6 and 22.7 MPa, where the isotherm is steepest, it is about ±6%. The random error in the measurements depends upon the amplitude of the temperature fluctuations monitored by the platinum resistance thermometers attached to the calorimeter. Where the isotherms shown in Fig. 1 are steep, low-pressure fluctuations, arising either in the flash boilers or in the pressure control system, produced larger than usual temperature fluctuations, and good measurements proved difficult to achieve. Our further concern was that there might be a systematic error in the measurements, particularly in the region where H_m^E was greater than 8 kJ · mol^{-1}. As the mixing process is endothermic, we would expect heat to leak into the calorimeter rather than out of it, and if heat leaks are significant, they will result in low values

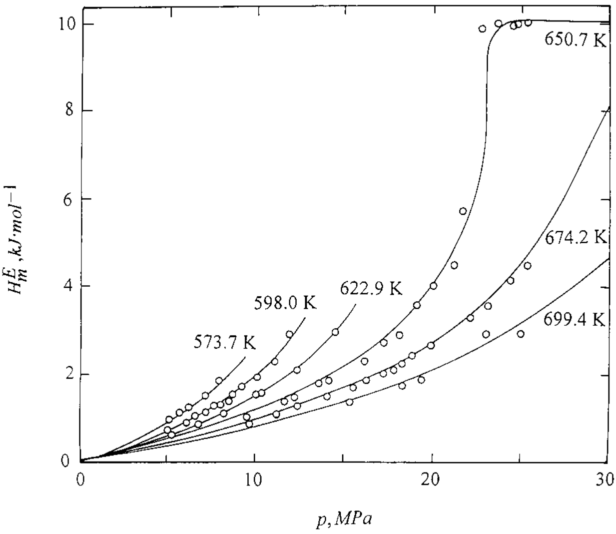

Fig. 1. The excess molar enthalpy H_m^E of $(0.5H_2O + 0.5C_2H_6)(g)$ plotted as a function of the pressure *p*. (○) This work (Table I); (——) calculated from the two-fluid corresponding-states model.

of H_m^E. The only indication that systematic errors are in fact small comes from the analysis presented in the next section. The results are listed in Table I and are plotted in Fig. 1.

3. COMPARISON WITH THEORY

Our previous H_m^E measurements at pressures up to 12.2 MPa were all well fitted by a cubic equation of state [5] which we had developed to fit measurements on (water + alkane)(g) mixtures. This equation fits the new measurements at 699.4 K and up to 24.95 MPa well but fails to fit the measurements at 650.7 K at pressures higher than 21 MPa. As can be seen from Fig. 1, H_m^E in this region increases to almost $10\ \mathrm{kJ \cdot mol^{-1}}$, but the equation from Ref. 5 (not shown in the figure) gave values of about $8\ \mathrm{kJ \cdot mol^{-1}}$. Other cubic equations were tried, but with similar lack of success in this region. The inadequacy of analytic equations in the critical region is well known, and to obtain a description of a binary fluid mixture in this region, elaborate equations capable of describing the crossover from singular thermodynamic behavior at the critical point to regular behavior far away from the critical point have been proposed [9, 10]. However, to obtain the necessary parameters for these equations an extensive database of accurate measurements is needed, and even for a well-studied system such as (carbon dioxide + ethane) the inconsistencies between the different sets of measurements severely limit what can be achieved [10].

The lack of an adequate equation of state which is capable of fitting the thermodynamic surfaces of water and ethane and which has adequate combining rules for fitting the properties of the mixture left us with the concern that our measurements might be in error. Fenghour et al. [11] faced the same problem when they analysed their isochoric density measurements on (water + carbon dioxide). They tested the Peng–Robinson [12] equation of state and found it to be inadequate at high densities and for water-rich compositions. They then investigated the one-fluid and two-fluid corresponding-states models suggested by Rowlinson and Watson [13, 14] and found the latter to be superior. A software package using the two-fluid corresponding-states model for the prediction of mixture properties has been developed, and as full details are given elsewhere [15, 16], only an outline is needed here.

In this model, the real fluid mixture consisting of components i and j is considered to be an ideal mixture of two hypothetical components. The residual Helmholtz energy $A_{\mathrm{mix}}^{\mathrm{res}}$ of the mixture is given by

$$A_{\mathrm{mix}}^{\mathrm{res}}(V, T, x) = \sum_i x_i A_i^{\mathrm{res}}(V, T) \tag{1}$$

where x_i is the mole fraction of component i, $A_i^{\mathrm{res}}(V, T)$ is the residual Helmholtz energy of the ith hypothetical component, and V and T are the volume and temperature of the mixture, respectively. To utilize the principle of corresponding states, the residual Helmholtz energy of each hypothetical component is expressed in terms of the properties of a real reference fluid r_i so that

$$A_i^{\mathrm{res}}(V, T) = f_i A_{r_i}^{\mathrm{res}}(V/h_i, T/f_i) \tag{2}$$

where f_i and h_i are scaling parameters. For the van der Waals two fluid model the scaling parameters are given by

$$h_i = \sum_j x_j h_{ij} \tag{3}$$

$$f_i h_i = \sum_j x_j h_{ij} f_{ij} \tag{4}$$

The cross-term scaling parameters h_{ij} and f_{ij} are obtained using Lorentz–Berthelot combining rules.

$$h_{ij} = \eta_{ij}[0.5(h_{ii}^{1/3} + h_{jj}^{1/3})]^3 \tag{5}$$

$$f_{ij} = \xi_{ij}(f_{ii} f_{jj})^{1/2} \tag{6}$$

The binary interaction parameters η_{ij} and ξ_{ij} are adjustable. All that is needed are equations of state which describe the Helmholtz energy of the two real fluids. For water, the equation of state of Saul and Wagner [17] was used, and for ethane the equation used was that of Friend et al. [18].

The density or enthalpy of the fluid mixture is obtained by taking the appropriate derivatives of the Helmholtz energy, and the adjustable parameters η and ξ can be optimized to fit the desired property of the mixture. When this optimization was done for the measurements listed in Table I the parameters $\xi = 0.710$ and $\eta = 0.999$ were obtained. The curves shown in Fig. 1 were calculated using these parameters. The above method provides a way of testing the internal consistency of the set of $H_{\mathrm{m}}^{\mathrm{E}}$ measurements. [If measurements at one of the experimental temperatures are wrong, it follows that none of the calculated curves will be a good fit to experiment.] However, Fig. 1 shows that a good fit to all the measurements is obtained, and the fit to the measurements at 650.7 K is particularly pleasing. As all the measurements are fitted to within experimental error, we are reassured that our measurements at near-critical pressures are consistent with the rest of the data set.

Table I. The Excess Molar Enthalpy H_m^E of $(0.5H_2O + 0.5C_2H_6(g)$

T (K)	p (MPa)	H_m^E $(J \cdot mol^{-1})$	p (MPa)	H_m^E $(J \cdot mol^{-1})$	p (MPa)	H_m^E $(J \cdot mol^{-1})$	p (MPa)	H_m^E $(J \cdot mol^{-1})$	p (MPa)	H_m^E $(J \cdot mol^{-1})$
573.7	5.15	1009	5.70	1133	6.30	1287	7.20	1511	7.95	1847
598.0	5.05	681	6.65	1073	7.70	1311	9.20	1728	11.05	2349
	5.85	1028	7.15	1199	8.15	1336	9.25	1737	11.90	2909
	6.15	897	7.25	1152	8.60	1575	10.10	1844		
622.9	5.25	610	8.25	1119	10.35	1591	14.50	2946		
	6.80	847	10.30	1567	12.35	2085				
650.7	9.55	1015	14.15	1839	19.15	3550	22.70	8468	24.80	10047
	11.60	1385	16.20	2329	20.00	4003	23.35	10687	25.30	10164
	12.25	1465	17.35	2775	21.26	4479	23.65	10375		
	12.65	1813	18.10	2881	21.60	5690	24.55	9953		
674.2	9.50	836	15.45	1730	17.25	2017	19.80	2651	24.40	4174
	11.25	1102	15.65	1696	17.85	2095	19.90	2659	25.30	4581
	12.40	1245	16.36	1893	18.30	2251	22.10	3330		
	14.15	1455	17.20	2089	18.80	2478	23.10	3592		
699.4	15.35	1374	18.30	1752	19.35	1893	23.00	2950	24.95	2957

A revealing way to examine the measurements is to plot (H_m^E/p) against the pressure p, and the previous H_m^E measurements [4] were plotted in this way. On this type of plot, the intercepts at zero pressure are simply related to the excess isothermal Joule–Thomson coefficient of the gas mixture by the equation [19]

$$\lim(p \to 0)(H_m^E/p) = x(1-x)(2\phi_{12} - \phi_{11} - \phi_{22}) \tag{7}$$

where the isothermal Joule–Thomson coefficients ϕ are related to the second virial coefficients by the equation

$$\phi = (B - T dB/dT) \tag{8}$$

Figure 2 shows some of the measurements made previously [4] at pressures below 12 MPa and the measurements listed in Table I. The curves were calculated from the two-fluid corresponding-states model. The figure shows overlap between the earlier measurements and those listed in Table I. The two sets of measurements were obtained using calorimeters of different design, and the generally good consistency between the two sets of measurements is reassuring. The figure shows that the model is a poor fit

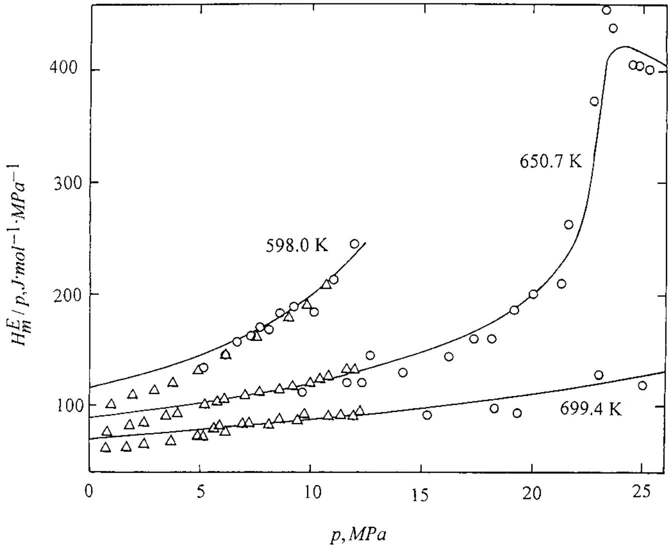

Fig. 2. The quantity (H_m^E/p) calculated from values of H_m^E $(0.5H_2O + 0.5C_2H_6)(g)$, plotted against the pressure p. (○) This work (Table I); (△) Ref. 4; (——) calculated from the two-fluid corresponding-states model.

to the measurements at pressures below 6 MPa. Both the virial equation of state [20] and the cubic equation of state [5] reported previously fit these low-pressure measurements to almost within the experimental error and are better equations for low pressure calculations. At pressures above 6 MPa, the two-fluid corresponding-states model is a good fit to the measurements. The figure reveals that at 650.7 and 699.4 K some of the points in the range 14 to 19 MPa are low, but the measurements in the range 6 to 12 MPa reported earlier are well fitted by the corresponding-states model.

4. COMPOSITION DEPENDENCE OF H_m^E

The composition dependence of H_m^E is of interest, but we made no measurements other than those at $x = 0.5$. Experience with other near-critical mixtures [21] leads us to expect that in the gas phase at low densities,

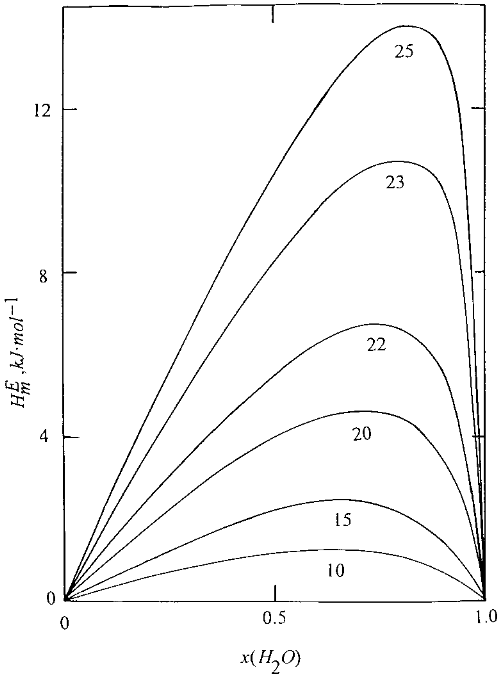

Fig. 3. Values of the excess enthalpy H_m^E for $(xH_2O + (1-x)C_2H_6)(g)$, calculated over a range of pressure and composition from the two-fluid corresponding-states model.

the $H_m^E(x)$ curves will not be far from parabolic, but as the pressure increases the parabola will become progressively more skewed. To investigate this, we used the two-fluid corresponding states model to calculate the composition dependence of H_m^E at selected pressures, concentrating particularly on the region between 20 and 25 MPa, where the H_m^E curve at 650.7 K rises rapidly. A selection of $H_m^E(x)$ curves at this temperature is shown in Fig. 3. We see that at 10 MPa the $H_m^E(x)$ curve is a slightly skewed parabola, with a maximum at $x = 0.65$, and at 25 MPa the curve is extremely skewed, with a maximum at $x = 0.82$. At this pressure, the calculated value of H_m^E at $x = 0.82$ is approximately 30% larger than that at $x = 0.5$. Although the curves shown in Fig. 3 are correct at $x = 0.5$, they may be inaccurate at high values of x, as the fitting parameters are slightly composition dependent. The curves are a good guide as to what shape the $H_m^E(x, p, T)$ surface might have, though they may well be in error by ±5% or more at the water-rich end.

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