

H_m^E and V_m^E thermodynamic surfaces for binary mixtures in the near critical region

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Abstract

Even for such simple mixtures as (argon+methane), the excess enthalpy H_m^E and the excess volume V_m^E in the near critical region are about two orders of magnitude higher than for the liquid mixture at low temperatures and pressures near ambient conditions. Mixtures for which the critical temperatures are close together, and for which the critical pressures are far apart, have similar $H_m^E(x,p,T)$ and $V_m^E(x,p,T)$ surfaces, and near critical isotherms show double maxima in the supercritical fluid region. Mixtures for which the critical pressures are close together, and the critical temperatures are far apart, also have similar $H_m^E(x,p,T)$ and $V_m^E(x,p,T)$ surfaces, but isobars on the surfaces are 'S' shaped. The shapes of these near-critical excess-function surfaces can be understood from an inspection of the enthalpy, or residual enthalpy curves of the mixture and of the pure components. Examples of both are given. Attention is drawn to the large value that these excess functions can have close to a pure component critical point. © 1997 Elsevier Science B.V.

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1. Introduction

The invitation to review progress in measuring and understanding the shapes of heats of mixing and volumes of mixing in the near critical region for such a notable journal is welcome. It provides the opportunity to explain how some of the curiously shaped excess function curves arise, and to report some work which has not previously been presented. When I began work in Professor Guggenheim's laboratory, at Reading, in the early 1960's, measurements of the excess volume V_m^E and excess enthalpy H_m^E were made using only batch techniques, and were all made under near ambient conditions. To measure an excess

volume bigger than $3 \text{ cm}^3 \text{ mol}^{-1}$ was regarded as unusual. The batch calorimeter of Larkin and McGlashan [1], which allowed liquids to be mixed without there being a vapour space, was developed at that time, and their design was much copied by others. I myself was not engaged in making these measurements but was involved with the development of a flow calorimeter for the measurement of Joule–Thomson coefficients. Another group in the UK which was doing much of the excellent early work on liquefied gases, at Oxford, was led by Staveley. Staveley and his co-workers developed a low temperature batch calorimeter [2] to measure heats of mixing of liquefied gases, but the problem was that corrections for evaporation of the fluids into the vapour space increased with increasing pressure and introduced ever larger errors. Measure-

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ments to about one quarter of the critical pressure could be made, but that was about the limit. A revolution in measurement of the excess molar enthalpy H_m^E was brought about by the development of flow-mixing calorimetric techniques, and later a parallel revolution in the measurement of densities came with the invention of the vibrating tube densimeter. Flow-mixing calorimeters have the advantage of having no vapour space, and so measurements up to high temperatures and pressures are possible. They are faster than batch calorimeters, though this is at the expense of the much larger amount of material which must be used. Excess enthalpy measurements on compressed gases were begun by Beenakker and Coremans [3] who used a simple apparatus and a mixing calorimeter with a heater wound on the outside. Measurement of H_m^E for simple gas mixtures in the liquid, two phase, critical and supercritical regions were pioneered at Bristol, where a low-temperature high pressure flow-mixing calorimeter was developed by Wormald et al. [4]. At that time it seemed surprising that, for a mixture as simple as (argon+methane) for which H_m^E in the liquid phase [5] at 91.5 K and $x = 0.5$ was 101 J mol^{-1} , increase of temperature and pressure should cause H_m^E to be about 6 times larger and exothermic, and further increase should cause it to be ~ 10 times larger and endothermic as shown in Fig. 1. This figure neatly summarises the state-of-the-art at that time. The squares are the liquid phase measurements of Staveley et al. [5], the circles are

those of Wormald et al. [4], and the triangles are gas phase measurements made by Beenakker et al. [3], all at $x = 0.5$. Once the behaviour had been modelled by an equation of state [4], the Redlich–Kwong (1949) equation was used to generate the curve shown in the figure, it became clear how the three sets of measurements were related.

More recently the excellent calorimeters at Brigham Young University [6] and at the Oak Ridge laboratory [7] have produced a large body of excellent H_m^E measurements. Christensen et al. [6] developed, firstly, a flat spiral Peltier-cooled flow-mixing calorimeter and, subsequently [8], a cylindrical Peltier-cooled calorimeter, and then for higher temperatures [9] a controlled heat-leak calorimeter. At Oak Ridge, Busey et al. [7] developed a flow calorimeter module which could be inserted into a high-temperature Calvet calorimeter, thus making possible measurements up to 700 K and 40 MPa. Wormald and Eyears [10], reported a low temperature flat spiral Peltier-cooled calorimeter coupled with an in-line vibrating tube densimeter so that two measurements could be performed simultaneously. The apparatus was capable of handling liquefied gases and operating at pressures up to 15 MPa at temperatures down to 220 K. To obtain values of V_m^E , measurement of the density of the pure components had to be separately made under the same conditions, and this was only possible because of the high degree of repeatability attained by computer control. Another development from this laboratory

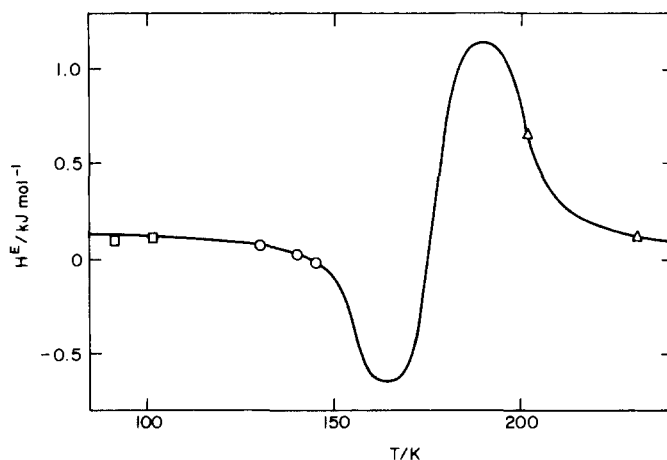


Fig. 1. The excess molar enthalpy H_m^E for (0.5 argon+0.5 methane) at 6.0 MPa: (□) – Lewis et al. [5]; (○) – Wormald et al. [4]; (△) – Beenakker and Coremans [3]; and (—) – calculated from the Redlich–Kwong equation of state [4].

was a high-temperature – high-pressure gas phase flow-mixing calorimeter constructed by Wormald et al. [11,12], which has subsequently been used to make measurements on 18 mixtures containing steam up to the critical point. Some of the current pioneering work is on H_m^E measurements of electrolyte solutions at high temperatures and pressures, much of it being done at the Oak Ridge National Laboratory. Because of corrosion problems this is a difficult area, and those who work in the field have my admiration. Most of the calorimeters described here have been used to make measurements on non-electrolyte mixtures, and the scope of this paper will be restricted to a discussion of a few of these systems.

2. The shapes of H_m^E and V_m^E surfaces

At 10 or 20 K above the critical temperature of the mixture, and at pressures greater than the critical, graphs of H_m^E and V_m^E vs. either pressure or temperature

show maxima in the supercritical region, which fade as the distance from the critical locus increases. Good examples of this include measurements of Wormald et al. [13] on (carbon dioxide+ethane) shown in Fig. 2, where the excess functions at ($x = 0.5$) are plotted as functions of pressure. The continuous curves shown in the figure were drawn through the experimental measurements using a flexicurve, the broken curves were calculated using the Patel–Teja [14] equation of state with the interaction parameter $k_{12} = 0.1325$ in the cross-term critical-temperature combining rule.

$$T_{12}^c = (1 - k_{12})(T_1^c T_2^c)^{1/2} \quad (1)$$

This mixture exhibits two successive maxima in the scans of $H_m^E(x = 0.5, T)$ vs. pressure and corresponding maxima in the $V_m^E(x = 0.5, T)$ curves. These maxima do not, as was initially thought, lie on extensions into supercritical region of the pure component vapour pressure curves, nor are they due to molecular clustering in the supercritical region. Moreover, the maxima in H_m^E are not at exactly the same values of T

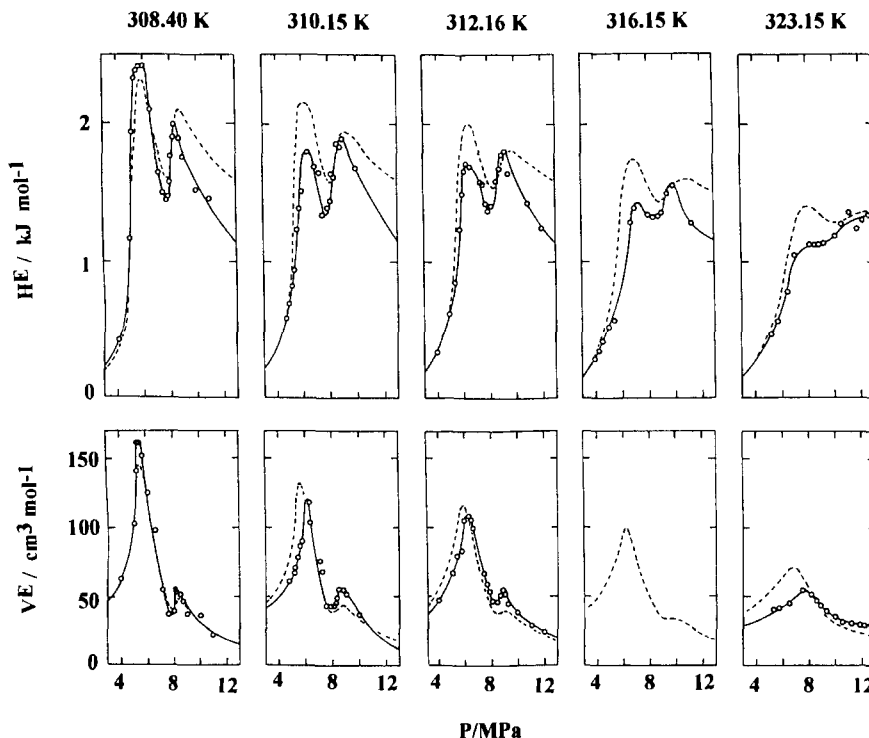


Fig. 2. Excess molar enthalpies H_m^E and excess molar volumes V_m^E for (0.5 carbon dioxide+0.5 ethane) measured in the supercritical region over a range of pressure: (O) – [10]; (—) – drawn with a flexicurve; and (---) – calculated from the Patel–Teja equation of state [14] as described in the text.

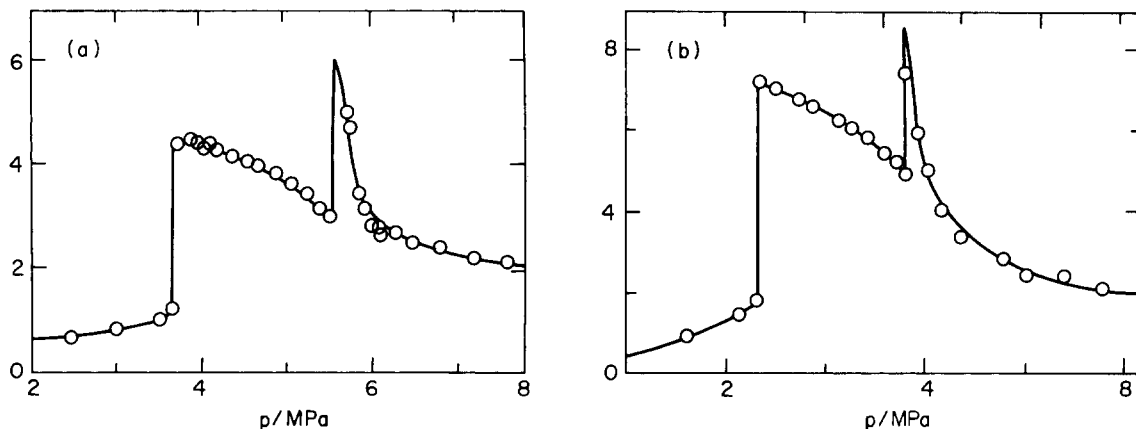


Fig. 3. (a) H_m^E for (0.5 carbon dioxide+ethane) at 291 K measured over a range of pressure: (○) – [10]; (—) – drawn with a flexicurve. (b) H_m^E for (0.5 propanone+*n*-hexane) at 510 K measured over a range of pressure: (○) – [15]; (—) – drawn with a flexicurve.

and p as those in V_m^E , though they are very close. V_m^E and H_m^E are related through the equation,

$$H_m^E = V_m^E - T(dV_m^E/dT) \quad (2)$$

Wormald et al. [15] discovered that the $H_m^E(x = 0.5, T)$ against pressure curves for the (propanone+hexane) mixture in the supercritical region showed two successive maxima as the pressure was increased, and the shape of the curves was very similar to those for the (carbon dioxide+ethane) system. At subcritical temperatures, the behaviour of the (carbon dioxide+ethane) mixture at 291.6 K and of the (propanone+hexane) mixture at 510.2 K are of the same shape as shown in Fig. 3(a, b). It was also found that

the shape of the $H_m^E(x = 0.5, p)$ against temperature curve for (propanone+benzene) [16] at a pressure of 5.68 MPa is almost the same as that for the (argon+methane) mixture curve at 6.0 MPa shown in Fig. 1. The first thing to note about these two pairs of mixtures is that the critical region phase diagrams of (carbon dioxide+ethane) and (propanone+hexane) are similar, as shown in Fig. 4(a, b), and this is also the case for the (propanone+benzene) and (argon+methane) systems as shown in Fig. 4(c, d).

To understand the origins of the maxima, and indeed the shapes of the H_m^E and V_m^E curves for any mixture, it is necessary to examine either the total molar enthalpy (or volume) curves or the residual

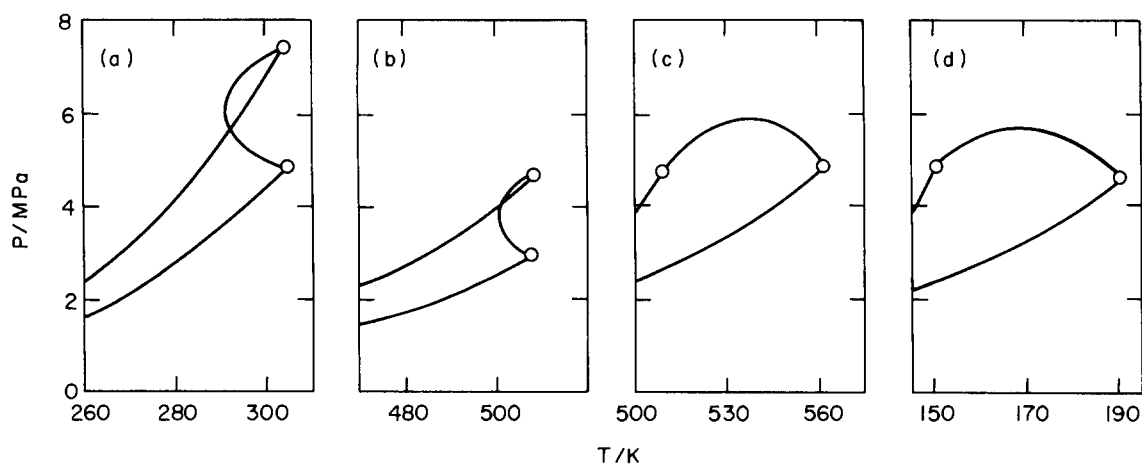


Fig. 4. Critical locii for the systems: (a) carbon dioxide+ethane; (b) propanone+*n*-hexane; (c) propanone+benzene; and (d) argon+methane.

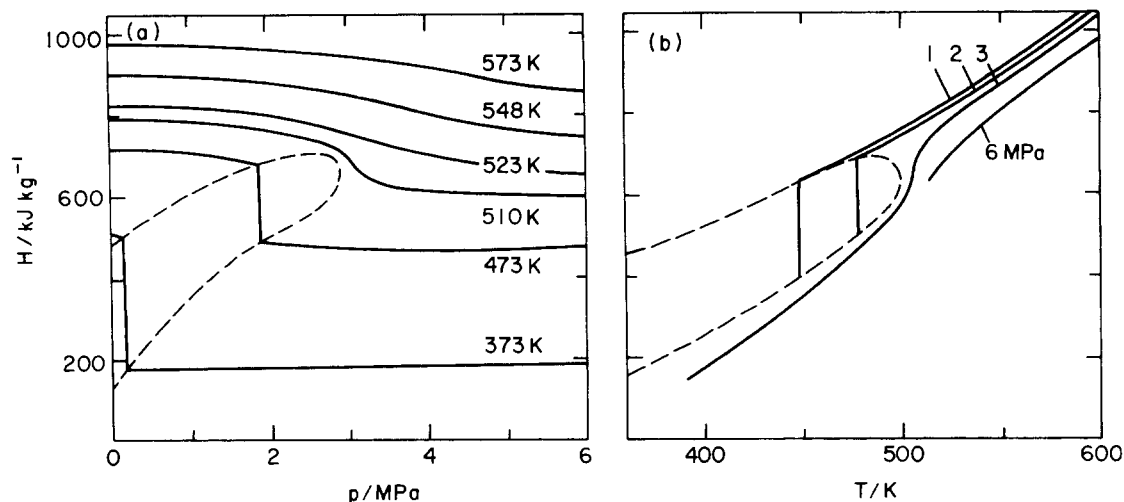


Fig. 5. (a) An enthalpy – pressure diagram for *n*-hexane [17]. (b) An enthalpy – temperature diagram for *n*-hexane. The broken curve indicates the two phase region.

molar enthalpy (or volume) curves of the two pure components and of the mixture, and it is instructive to give examples of both. The residual molar enthalpy is defined by the equation,

$$H^R(p, T) = H(p, T) - H(p = 0, T) \quad (3)$$

and it can be obtained either from enthalpy measurements or calculated from an equation of state, using the formula,

$$H^R(p, T) = \int (V - T\partial V/\partial T) dp \quad (4)$$

The excess molar enthalpy is then calculated from the formula,

$$H^E(x, p, T) = H^R(x, p, T) - xH_1^R(p, T) - (1 - x)H_2^R(p, T) \quad (5)$$

where $H^R(x, p, T)$ for the mixture can be obtained either from enthalpy measurements on the mixture or calculated from an equation of state using suitable combining rules. For the (propanone+*n*-hexane) mixture, Wormald and Yerlett [17–19] used an enthalpy increment calorimeter to measure the enthalpy of both pure components and of the ($x = 0.5$) mixture. In addition, a high-temperature flow-mixing calorimeter [11,12] was used to make measurements of H_m^E in subcritical and supercritical regions so that the values of H_m^E derived from the measurements made using the

enthalpy increment calorimeter could be compared with those measured using the mixing calorimeter. Enthalpy increments for *n*-hexane plotted as a function of pressure at constant temperature are shown in Fig. 5(a), and enthalpy increments plotted as a function of temperature at constant pressure are shown in Fig. 5(b). Similar diagrams for propanone and for an equimolar (propanone+*n*-hexane) mixture can be drawn. Residual enthalpy curves for hexane can be constructed by subtracting the zero pressure values of the enthalpy from those at $p > 0$. The shape of the enthalpy–pressure curves is retained, but all the residual enthalpy curves now pass through zero at zero pressure. However, for the (propanone+hexane) mixture, for which the critical temperatures of the pure components are almost the same, we will show how the shape of H_m^E curves arise using a total enthalpy diagram. This will be done by inspecting enthalpy isotherms in the supercritical region at 510.2 K as shown in Fig. 6. All the isotherms lie above their respective two phase regions and have a shape similar to the supercritical isotherm shown in Fig. 5(a). In Fig. 6, the dotted curves are for the two pure components, the long-dashed curve is the mean of the two pure component curves, and the continuous curve is for the equimolar mixture. The excess enthalpy at $x = 0.5$ is the difference between the enthalpy of mixture (the continuous curve) and the arithmetic mean (the long-dashed curve) of the pure component

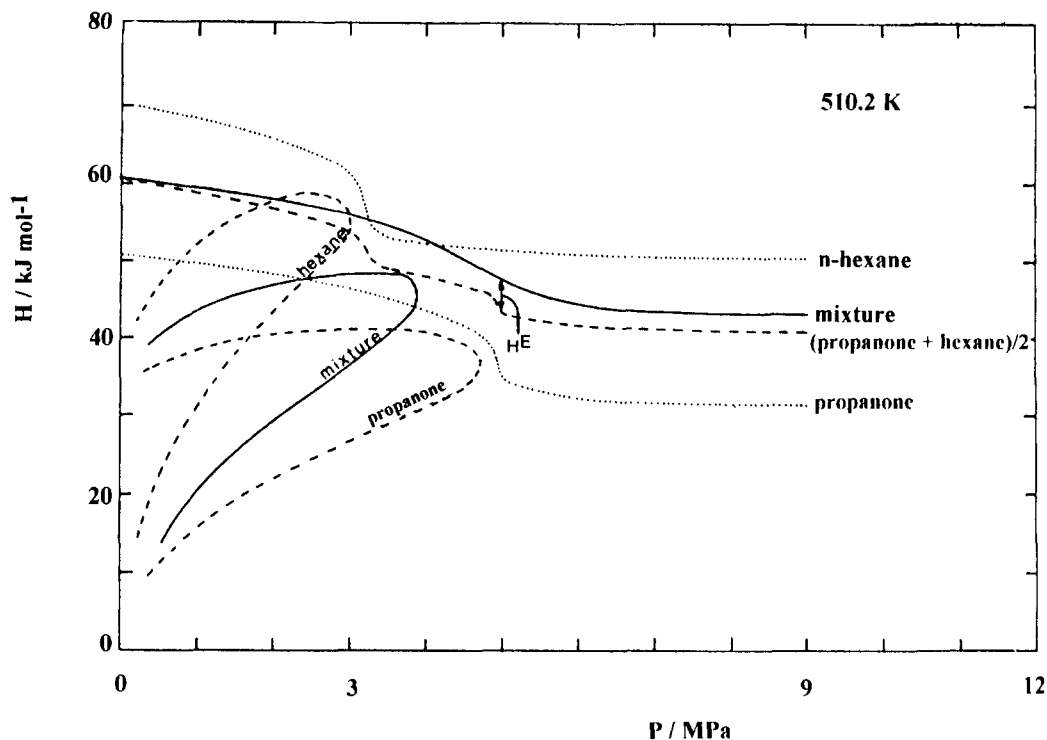


Fig. 6. A composite diagram showing experimentally determined enthalpies of *n*-hexane, propanone, and of a (0.5 hexane+0.5 propanone) mixture at 510 K. The difference between the continuous curve for the mixture and the dashed curve, which is the mean of the two pure component curves, is the excess enthalpy shown in Fig. 7.

enthalpies. If one follows along these two curves from low to high pressures, and plots the difference between them as a function of pressure, the curve passing through the experimental excess enthalpies shown in Fig. 7 is generated. This curve is similar to the curves for (carbon-dioxide+ethane) shown in Fig. 2, and diagrams similar to Fig. 6 could have been constructed for this mixture.

The origin of the $H_m^E(x = 0.5, T)$ against pressure curves at subcritical temperatures shown in Fig. 3 can be understood from a residual enthalpy diagram such as that for (carbon-dioxide+ethane) at 291.6 K shown in Fig. 8. Here, two of the continuous curves are the residual enthalpies of carbon dioxide and ethane. They are of the same shape as the subcritical isotherm shown in Fig. 5(a). The vertical sections correspond to the enthalpy of vapourisation of the pure fluids. The long-dashed curve is the mean of these pure component curves, and the upper continuous curve is the residual enthalpy of the mixture which is in a supercritical state. The difference between the long dashed

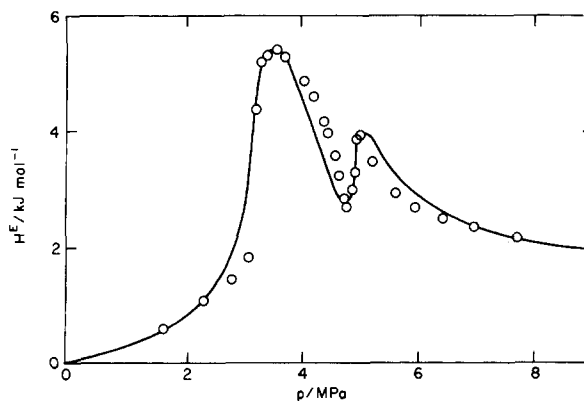


Fig. 7. The excess enthalpy H_m^E of (0.5 *n*-hexane+0.5 propanone) at 510 K. (○) – values of H_m^E measured with a flow-mixing calorimeter [15]. (—) – calculated using the Patel-Teja equation of state [14].

curve and upper continuous curve is H_m^E , and if one follows the difference from low to high pressure, it can be seen that Fig. 3(a) is generated.

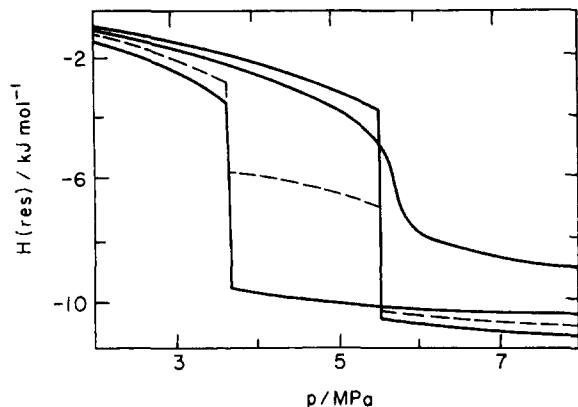


Fig. 8. Residual enthalpies of carbon dioxide, and a (0.5 carbon dioxide+ethane) mixture at 291.6 K. At this temperature the pure gases are subcritical fluids and the residual enthalpy curves have discontinuities at the saturation pressures, but the mixture is a supercritical fluid and gives a continuous curve. The broken line is the mean of the two pure component curves. The difference between the broken line and the continuous curve is the excess enthalpy shown in Fig. 3(a).

One more example is worth discussing. The shape of the $H_m^E(x=0.5, p)$ vs. temperature curves for (argon+methane) shown in Fig. 1, and for (propanone+benzene) shown in Fig. 9(a), can be understood by reference to an enthalpy vs. temperature diagram.

Isobars on this diagram have shapes like those shown in Fig. 5(b). Fig. 9(b) shows enthalpy increments for hexane, propanone, and for an equimolar mixture, all at 5.68 MPa, plotted against temperature. The upper continuous curve is the enthalpy of pure propanone whereas the lower one is the enthalpy of hexane, and the central broken curve is the mean of these two pure component curves. The central continuous curve, on which experimental points measured at 5.68 MPa are marked, is the enthalpy curve for the equimolar mixture. The difference between this curve and the broken curve is H_m^E , and, if this difference is plotted against temperature, the continuous curve which passes through the independently determined H_m^E measurements at 5.68 MPa – shown in Fig. 9(a) – is obtained. A diagram similar to Fig. 9(b) can be constructed for (argon+methane), and the explanation of the shape of the continuous curve shown in Fig. 1 is the same. The general conclusion that can be drawn is that the shape of the $H_m^E(x, p, T)$ and $V_m^E(x, p, T)$ surfaces depends on the relative position of the two critical points T_c and P_c . If the two critical temperatures are nearly the same the excess function curves will be like those (carbon dioxide+ethane), and if the two critical pressures are the same the excess function curves will be like those of (propanone+benzene). All other cases are inter-

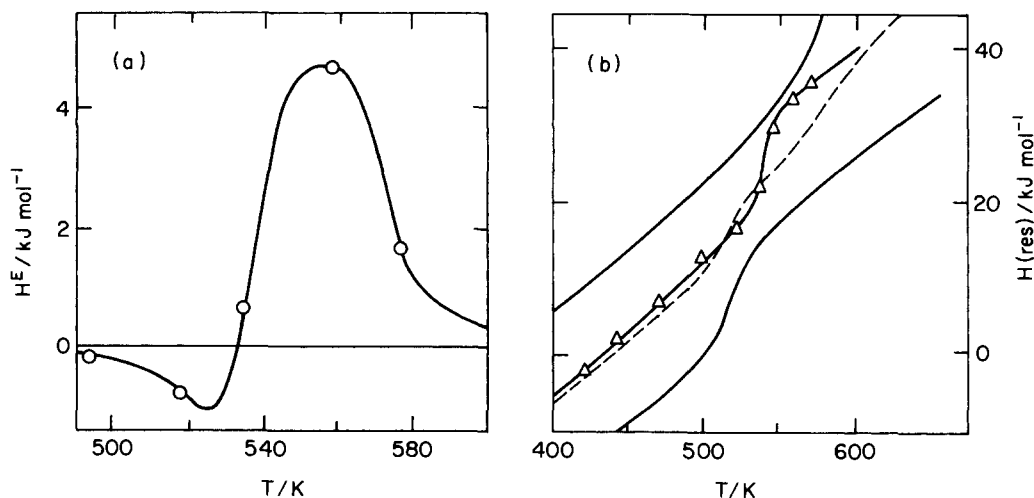


Fig. 9. (a) The excess enthalpy at 5.98 MPa of (0.5 benzene+0.5 propanone) mixture: (○) – experimental values measured by flow-mixing calorimetry [16]; and (—) – draw with a flexicurve. (b) Residual enthalpies of benzene, propanone, and of a (0.5 benzene+0.5 propanone) mixture at 5.98 MPa. The shapes of these supercritical residual enthalpy curves are the same as those shown in Fig. 5(b). The broken curve (Δ) is the mean of the pure component values [16]. The difference between the central continuous curve for the mixture and the broken curve is the excess enthalpy shown in Fig. 9(a).

Table 1

Fluid pairs with almost the same T_c			Fluid pairs with almost the same P_c		
	T_c /(K)	P_c /(MPa)		T_c /(K)	P_c /(MPa)
Carbon dioxide	304.2	7.37	Ethane	305.4	4.88
Ethane	305.4	4.88	Benzene	562.1	4.89
Carbon dioxide	304.3	7.37	Toluene	591.7	4.11
Nitrous dioxide	309.6	7.24	Cyclohexane	553.4	4.07
Propane	369.8	4.24	Ethane	305.4	4.88
Chlorodifluoromethane	369.2	4.98	Chlorodifluoromethane	369.2	4.98
Propanone	509.6	4.78	Butane	425.2	3.80
<i>n</i> -Hexane	507.4	2.96	Sulphurhexafluoride	318.7	3.76
Methanol	512.6	8.09	Propanone	508.1	4.78
Hexane	507.4	2.97	Benzene	562.1	4.89

mediate. The amplitudes of the maxima and minima will depend on the distance between the two critical points. If they are close together, small values of the excess functions can be expected. The third important parameter is the shape of the critical locus itself, and no generalisation can be made about this. From the vast number of possible binary mixtures, two small but very interesting groups can be identified: fluid pairs with almost the same critical temperature, and pairs with almost the same critical pressure. For flow-mixing calorimetry considerable quantities of material are needed, and some pairs of readily available fluids are listed in Table 1.

Wormald [20] used the van der Waals equation of state to investigate the shapes of $H_m^E(x, p, T)$ and $V_m^E(x, p, T)$ surfaces in the near critical region, and all the behaviour discussed here was predicted. How-

ever, the equation is not very realistic, but some of the more recent cubic equations of state give a much closer fit to experiment. After testing several modern cubic equations, it was found that the equation of Patel and Teja [14] was as good as any, and its use can be made easier with the Valderrama [21] modification. Using this equation, we found that a good overall fit to the near critical region measurements on (carbon dioxide+ethane) could be obtained with the choice $k_{12} = 0.1325$ in the critical temperature combining rule, Eq. (1).

In Fig. 10(a) we show the $H_m^E(x, p)$ surface for (carbon dioxide+ethane) in the supercritical region at 308.4 K, which is about 3 K higher than the critical temperature of the pure components, and 18 K higher than the critical temperature of the ($x = 0.5$) mixture. The surface was generated using the Patel–Teja

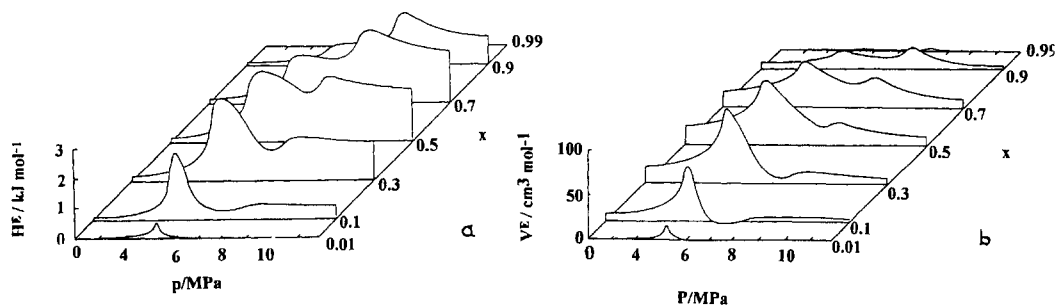


Fig. 10. The $H_m^E(x, P)$ and $V_m^E(x, P)$ surfaces for (carbon dioxide+ethane) mixture at 308.4 K in the supercritical region. These surfaces were calculated using the Patel–Teja equation of state [14] as described in the text.

equation. Fig. 2 shows how closely this equation describes the experimentally determined excess functions. In Fig. 10(b), the (carbon dioxide+ethane) $V_m^E(x,p)$ surface is shown. It can be seen that the shapes of the peaks are different from those on the $H_m^E(x,p)$ surface and the maxima at the higher pressures are smaller than those on the $H_m^E(x,p)$ surface. At $x = 0.3$, the peak in V_m^E is approximately $100 \text{ cm}^3 \text{ mol}^{-1}$, which means that the density of the mixture is about 40% less than the mole fraction weighted mean density of the pure components. This sort of the behaviour has consequences for supercritical extraction processes using mixed solvents, and indicates that there can be conditions in the supercritical region where the solubility of a solute in a mixed solvent could be less than that in the pure solvent.

An interesting feature of Fig. 10 is the behaviour of the H_m^E and V_m^E curves at very low mole fractions. We have explored this further by calculating excess function curves at 306.3 K, which is 1 K above the critical temperature of ethane. At $x = 0.001$ and at a pressure of $\sim 5.3 \text{ MPa}$, there is a peak in the H_m^E curve which is $\sim 400 \text{ J mol}^{-1}$ high, and another peak in the V_m^E curve which is $\sim 15 \text{ cm}^3 \text{ mol}^{-1}$ high. Three such peaks, calculated at the values of $x = 0.01, 0.001$ and 0.0001 , are shown in Fig. 11. These peaks are close

to the critical pressure $P_c = 4.87 \text{ MPa}$ of ethane. The scale shown in the figure is marked as decimal fractions of P_c . While the peaks become narrower as x decreases, the striking feature is that even at these very low values of x the peak amplitudes are still very high. The size of the peak in the V_m^E surface highlights the need to use materials of the highest purity when making critical point measurements on 'pure' fluids.

Wormald and Hodgetts [22] have recently reported H_m^E measurements for (carbon dioxide+ethane) at 291.6 K, which is 0.5 K above the critical temperature of the minimum in the critical locus shown in Fig. 4(a). The measurements were all made at this single temperature but over a range of pressure starting from the gas region at 3.1 MPa and finishing just above the critical locus in the supercritical region at 6.2 MPa. At 5.6 and 5.87 MPa, some unusual results were obtained. Under these conditions, both carbon dioxide and ethane enter the flow-mixing calorimeter in the liquid state, and over most of the composition range a liquid mixture is formed. However, some of the composition scans just intersect the top of the two phase liquid–vapour envelope and, here, the mixture formed is more like a dense gas than a liquid. Where the measurements graze the two-phase region, there is a large peak in the $H_m^E(x)$ curve corresponding to vapourisation into the gas-like state. This behaviour is

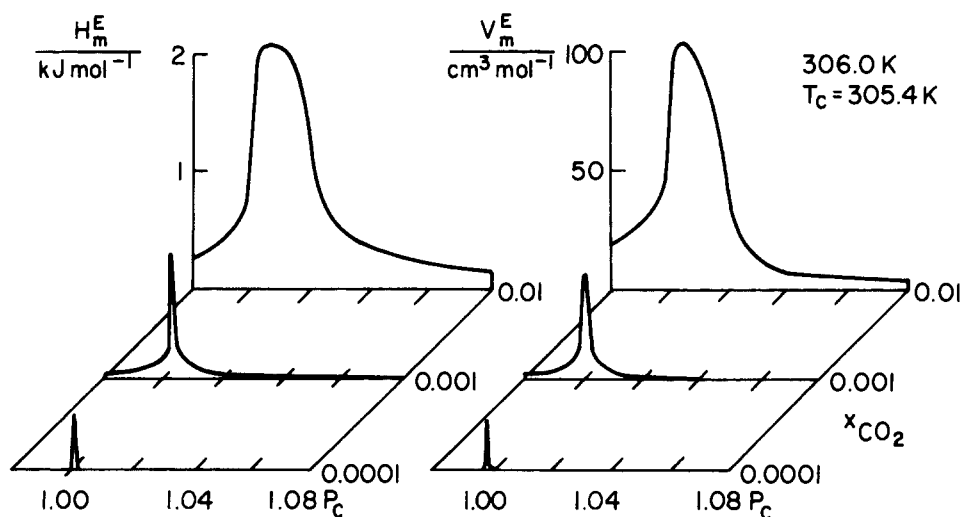


Fig. 11. H_m^E and V_m^E for (carbon dioxide+ethane) mixture in the supercritical region at 306.0 K, and at very low mole fractions of carbon dioxide. The pressure scale is in multiples of the critical pressure (4.88 MPa) of ethane. The chosen temperature is 0.6 K above the critical temperature of ethane. The curves were calculated using the Patel–Teja equation of state [14] as described in the text.

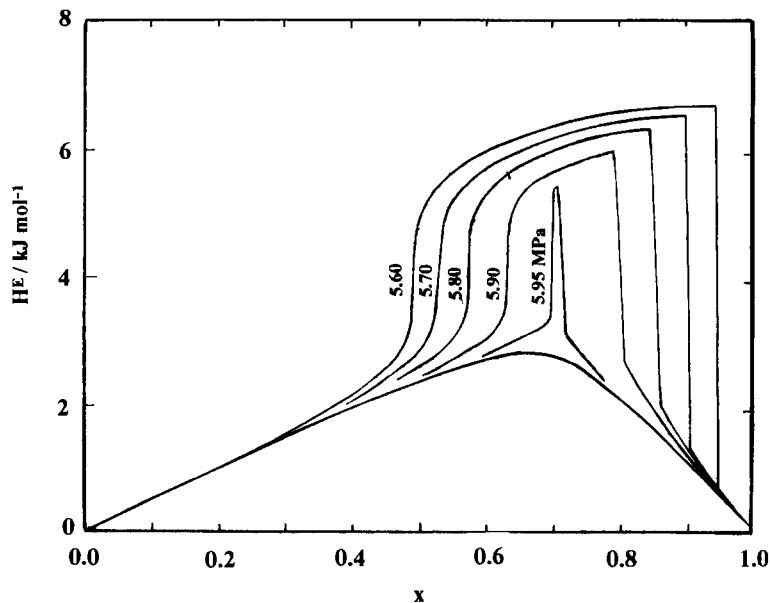


Fig. 12. $H_m^E(x)$ for (carbon dioxide+ethane) mixture at 291.6 K. The measurement [22] on which these curves are based lie very close to the critical locus of the mixture and just graze the top of the two phase loop, at which point the mixture becomes gas-like rather than liquid-like. (—) — Curves calculated using the Patel–Teja equation of state [14] as described in the text.

well reproduced by the Patel–Teja equation using $k_{12} = 0.1325$. This equation has been used to explore the shape of the excess functions curves in this region by calculating the set of curves shown in Fig. 12, which slice into the two-phase region at pressures from 5.6 to 5.95 MPa. At 5.95 MPa, the peak is 0.02 mole fraction wide, and 2 kJ mol^{-1} high. At 6.0 MPa, the peak vanishes completely as the pressure exceeds the saturation pressure of the mixture at this temperature and at all compositions, and the H_m^E curve is the usual skewed parabola.

The (carbon dioxide+ethane system) has been widely used to test theories of near-critical fluid behaviour. The most notable work is that of Sengers et al. [23,24], who have developed a crossover model which describes the free energy of binary fluid mixtures in the critical region. Their model works best in the one phase near critical region, and for the (carbon dioxide+ethane) mixture in this region, they have attempted a fit of all the available thermodynamic data, critical loci, specific heats, coexisting vapour and liquid densities, and heats of mixing in the supercritical region. Because of errors in the different data sets, they found it impossible to fit all the measurements within the claimed experimental uncertainties.

Their fit to H_m^E measurements [10] at 306.4 and 308.4 K at 7.5 MPa in the supercritical region are shown in Fig. 13. The model does not quite fit the measurements but does confirm that the asymmetric shape of the experimental $H_m^E(x)$ curves is correct.

Before closing the discussion on H_m^E curves for (carbon dioxide+ethane) mixture, it is worth making a point that is often lost sight of. The value of an excess enthalpy is that it can be added to the mole fraction weighted mean of the enthalpies of the pure components to give the enthalpy of the mixture. This procedure is adopted because it is more difficult to measure the enthalpy of an equimolar binary mixture in the critical region than to measure excess enthalpy. Using enthalpies for carbon dioxide [25] and for ethane [26], calculated from equations of state, and adding to these the values of $H_m^E(x = 0.5)$ determined experimentally, the enthalpy–pressure curve at the critical temperature (290.86 K) of the equimolar mixture can be constructed. This curve is shown in Fig. 14. Points calculated from the experimental H_m^E measurements are shown as circles. The one triangular point is at the critical pressure of the mixture, and is the one point that can be calculated from the scaled equations of Chang and Doiron [27]. The broken curve

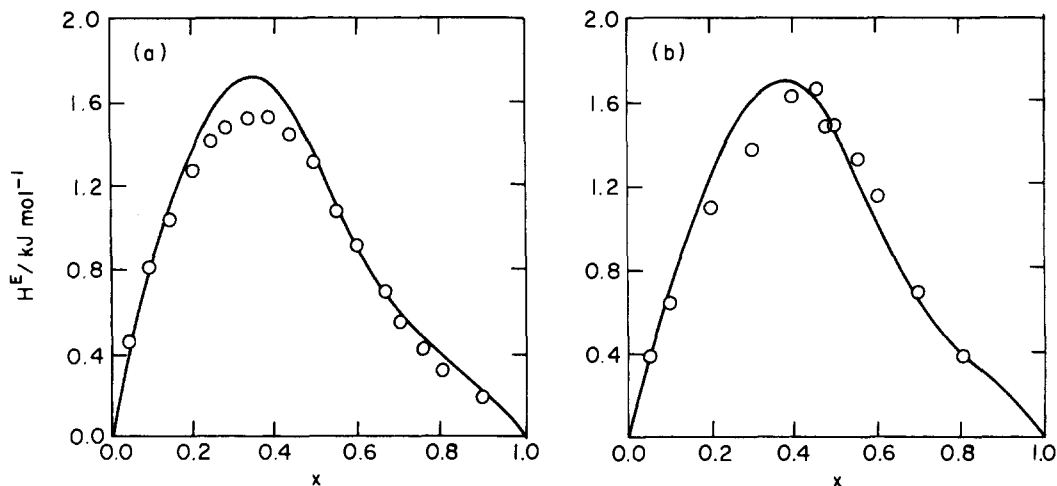


Fig. 13. $H_m^E(x)$ curves for (carbon dioxide+ethane) mixture at (left) 306.4 K and (right) 308.4 K and (○) at 7.50 MPa. [13]. (—) – Curves calculated using the cross-over model of Sengers et al. [23,24].

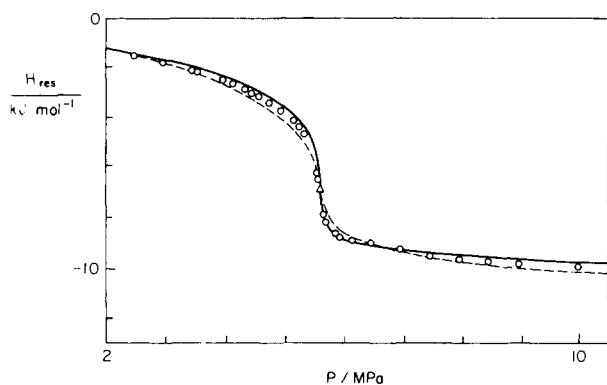


Fig. 14. The molar enthalpy of a (0.5 carbon dioxide+0.5 ethane) mixture at 290.86 K. The points were calculated by adding experimental values of H_m^E to the mean of the pure component enthalpies. (△) – Curves calculated from the scaling equation of Chang and Doiron [27]; (---) – Curves calculated from the Patel–Teja equation of state [14]; (—) – Curves calculated from Patel–Teja equation with correction for non-analytic behaviour [28].

was calculated from the Patel–Teja equation of state, and the continuous curve was calculated using a modification, suggested by Vine and Wormald [28], which attempts to correct for non-analytic behaviour in the critical region. Evidently, better equations are needed if the experimental enthalpies are to be fitted within experimental error.

The foregoing survey shows how the shapes of the excess function surfaces arise. The measurements on

(carbon dioxide+ethane) mixture have been referred to extensively because the system has been the subject of so many studies. There are, of course, many other simple systems of interest and, in concluding, it is worth showing some of the results for one more mixture. We have recently made H_m^E and V_m^E measurements [29] on the two mixtures, namely (carbon dioxide+sulphur hexafluoride) and (ethane+sulphur hexafluoride), and these systems have $H_m^E(x,p)$ and $V_m^E(x,p)$ surfaces which are similar to those for the (carbon dioxide+ethane) mixture, and yet the differences are quite marked. T_c for SF_6 is 318.7 K and P_c is 3.76 MPa, so the shape of the phase diagram is a little different to that for the (carbon dioxide+ethane) mixture. Recall that $T_c\text{CO}_2 = 304.2$ K, and $T_c\text{C}_2\text{H}_6 = 305.4$ K. Some of our measurements on $(x\text{CO}_2 + (1-x)\text{SF}_6)$ at 301.95 are shown in Fig. 15. We estimate that the critical temperature of the mixture at $x = 0.5$ is 290 K, so these measurements are in a region where the two liquid phase components are being mixed together to form a supercritical fluid; similar conditions under which the measurements shown in Fig. 3 were made. The continuous curves in Fig. 15 were calculated using the Patel–Teja equation of state for $k_{12} = 0.1495$, and the agreement with experiment is clearly quite good. Despite the very different intermolecular potentials of the two pure substances, this equation seems to perform as well in the critical region

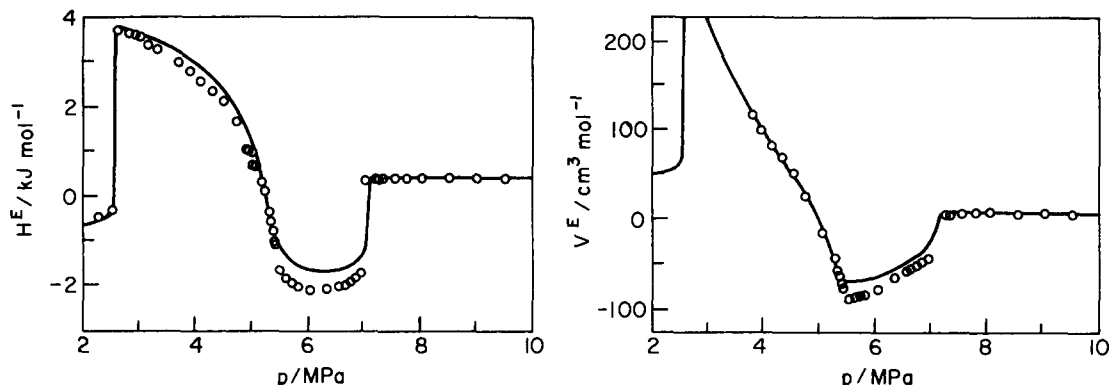


Fig. 15. (○) – $H_m^E(x=0.5)$ and $V_m^E(x=0.5)$ for (carbon dioxide+sulphur hexafluoride) at 305.65 K [29]. The continuous curves were calculated from the Patel–Teja equation of state [14] using $k_{12} = 0.1495$.

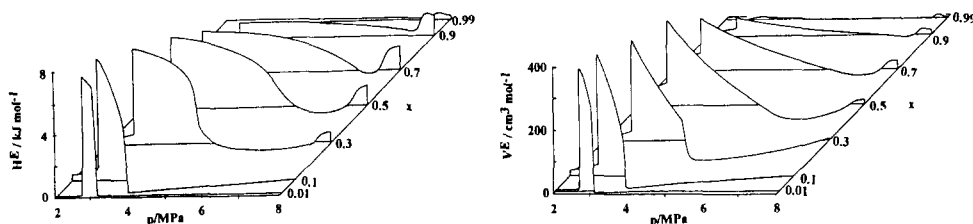


Fig. 16. The $H_m^E(x, p)$ and $V_m^E(x, p)$ surfaces of (carbon dioxide+sulphur hexafluoride) mixture at 305.65 K calculated from the Patel–Teja equation of state [14] using $k_{12} = 0.1495$.

as it does for mixtures of more similar substances. Fig. 16 shows the $H_m^E(x, p)$ and $V_m^E(x, p)$ surfaces calculated for the mixture at 305.65 K, another temperature at which many measurements were made. The surface is interesting because the conditions are such that CO_2 enters the calorimeter as a supercritical fluid, SF_6 enters as a subcritical liquid, and over much of the composition range – though not all of it – the mixture is a supercritical fluid. Vertical lines in Fig. 16 correspond to the evaporation of the SF_6 into the supercritical CO_2 , and the near vertical lines at values of $x < 0.3$ and, at ~ 4 MPa, correspond to a region of composition where the mixture is liquid rather than a supercritical fluid. That the excess volumes here are so very large, $\sim 400 \text{ cm}^3 \text{ mol}^{-1}$, is a consequence of the collapse of the supercritical fluid mixture to the liquid state. That the lines are not vertical like those at the lower pressures arises because the lower pressure lines correspond to the change of phase of a pure component, whereas the higher pressure near-vertical lines correspond to the change of phase of a mixture starting

at a certain composition in the gas-like phase and finishing in the liquid phase at another composition. In theory, the $(x\text{CO}_2 + 1(1-x)\text{C}_2\text{H}_6)$ mixture should also show this behaviour but the critical temperatures of the two pure components are so close that similar measurements are almost impossible.

For the foregoing mixtures considered, there is total miscibility in the liquid phase. For unlike fluids, such as mixtures of water or alcohol with a hydrocarbon, there are often large regions of the phase diagram where the liquids are only partially miscible. These are indicated by linear sections of the heat of mixing curves, and Ott et al. [30] have published some good examples of this behaviour. At Bristol, a large number of measurements of heats of mixing of (water+hydrocarbon) mixtures in the vapour phase at high temperatures and pressures have been made, and an equation of state which describes the behaviour of the gas-like mixture has been constructed [31]. At near critical temperatures, water and alcohols are far less polar than under ambient conditions and the properties

of mixture of these fluids with hydrocarbons can be described fairly well, though less so than for the systems discussed here, using cubic equations of state. For the most part, the $H_m^E(x, p, T)$ surfaces are similar to those for mixtures of non-polar fluids, but where the phase diagrams show limited miscibility at high pressures there are some differences. These, however, are outside the scope of this review.

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