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Determination of the composition and molar volume of H₂O-CO₂ fluid inclusions by microthermometry

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Abstract—H₂O-CO₂ fluid inclusions are common in nature but their accurate analysis by microthermometry has been hindered by insufficient characterisation of the fluid properties along the solvus (high temperature miscibility boundary) of the system. Thus some of the previous methods of calculating fluid inclusion composition (x) and molar volume (V) have relied on notoriously unreliable optical estimates of phase volume fractions. Although the T - V - x properties of the solvus can be modelled thermodynamically from equations of state, a review shows that none of the published equations are accurate enough to be useful in fluid inclusion microthermometry. Therefore, the available experimental data have been used to construct a new V - x diagram, contoured for phase transition temperatures and phase volume fractions. This diagram allows the bulk composition and molar volume of individual fluid inclusions to be determined accurately from two microthermometric measurements: the temperature of partial homogenisation of the carbonic phases (in the presence of excess aqueous liquid), and the temperature of total homogenisation. Copyright © 2000 Elsevier Science Ltd

1. INTRODUCTION

H₂O-CO₂ fluids are known to play an important role in many hydrothermal, metamorphic and igneous environments (e.g., Fyfe et al., 1978), and they are often included in thermodynamic calculations of fluid-mineral equilibria (e.g., Kerrick, 1974; Holland and Powell, 1998). Furthermore, H₂O-CO₂ fluids are one of the most common binary systems in fluid inclusions (e.g., Roedder, 1984; Bodnar et al., 1986; Diamond, 1994a) and they frequently constitute the major subsystem of compositionally more complex inclusions. Besides its broad significance for the earth sciences, the H₂O-CO₂ system is also important in energy technology, and determination of the volumetric properties of H₂O-CO₂ mixtures is a fundamental scientific problem. Yet although the system is extensively treated in the literature (see review by Mäder, 1991), a complete, accurate description of its phase behaviour and the relationship between pressure, temperature, molar volume, and composition (p - T - V - x properties) is still lacking.

In the study of fluid inclusions, the most accurate method of characterising the p - T - V - x properties of the entrapped fluids is microthermometry. For simple one-component fluids, such as pure H₂O or CO₂, melting temperatures are diagnostic of the chemical system, whereas homogenisation temperatures directly reflect bulk molar volumes (or densities). Several purely empirical thermodynamic models are available to calculate the molar volumes, e.g., Wagner and Pruss (1993) for H₂O and Duschek et al. (1990) for CO₂. For binary fluids, however, the only successful thermodynamic model that includes volumetric properties of liquid-vapour conditions is that presented by Thiéry et al. (1994), although it applies only to H₂O-free systems. Thiéry et al. (1994) adjusted the equation of state of Soave (1972) to reproduce p - T - x values for liquid-vapour equilibria in CO₂-CH₄ and CO₂-N₂ mixtures, but volumetric prop-

erties were obtained separately from another equation of state (Lee and Kesler, 1975). A disadvantage of this approach is that, by using two equations, the coherency of the various fluid parameters is lost.

In binary isochoric systems, such as those approximated by H₂O-CO₂ fluid inclusions, only two independent parameters need to be measured at known temperature to solve for bulk V and x . Inasmuch as three relevant parameters can be measured by microthermometry, viz. (1) The temperature at which CO₂ liquid and CO₂ vapour homogenise in the presence of liquid H₂O, i.e. $Th(car)$. (2) The temperature at which the immiscible aqueous and carbonic phases homogenise at high temperature, i.e. $Th(total)$. (3) The volume fractions of phases in the inclusions, i.e., F , the system is analytically overdetermined. However, errors associated with phase volume estimates can be as high as $\pm 20\%$ (Roedder, 1984; Anderson and Bodnar, 1993), and these propagate through the calculations of bulk composition and molar volume. By comparison, measurements of bubble-point transitions (i.e., homogenisation to the liquid phase) are highly accurate, typically $\pm 0.2^\circ\text{C}$ for $Th(car)$ and $\pm 2.0^\circ\text{C}$ for $Th(total)$. The only obstacle to using these two phase transitions to determine bulk V - x properties, hitherto, has been the lack of well-defined T - V - x properties along the solvus of the system (Fig. 1), where the total homogenisation transition occurs.

Unfortunately, the available experimental data that describe the H₂O-CO₂ solvus are incomplete and to some extent inconsistent, as will be reviewed below. Moreover, it will be demonstrated in the following that thermodynamic (equation of state) modelling of the solvus is effective only over small temperature ranges at relatively low pressures, whereas it is highly inaccurate in the important pressure range exceeding 30 MPa. An alternative to the microthermometric approach of analysing H₂O-CO₂ fluid inclusions is Raman spectroscopy. Although liquid-like H₂O has a broad Raman peak, Dubessy et al. (1992) and Frantz et al. (1993) developed a method to analyse the water content of fluid inclusions at temperatures

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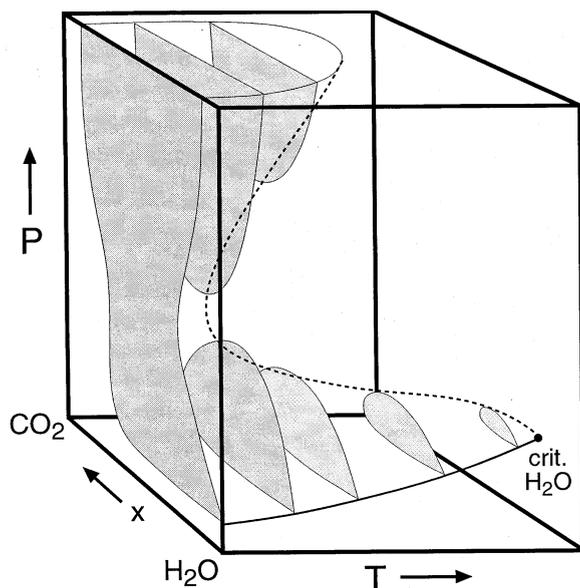


Fig. 1. Schematic p - T - x diagram of the H_2O - CO_2 fluid system (after Tödheide and Franck, 1963), showing the high-temperature portion of the immiscibility region (shaded) and the upper critical curve.

above their total homogenisation. The Raman bands of H_2O reflect hydrogen bonds, the vibrational energies of which are very sensitive to temperature and density. For example, Frantz et al. (1993) reported a relation between the Raman spectrum of pure H_2O and its density. Dubessy et al. (1999) found that the presence of CO_2 modifies this spectrum, indicating weaker hydrogen bonding. Bodnar et al. (1996) demonstrated systematic variations in the peak ratios of various compositions of synthetic H_2O - CO_2 inclusions. However, this method is no more accurate than the calculations that are based on optical estimates of phase volume fractions in fluid inclusions, and the thorough calibration of the Raman spectra needed for quantitative analysis of H_2O - CO_2 inclusions is not yet available.

In view of the deficiencies outlined above, this study presents a refinement of earlier microthermometric approaches of analysing H_2O - CO_2 inclusions. A new V - x diagram of the H_2O - CO_2 solvus is constructed, based on the high quality experiments of Sterner and Bodnar (1991), the only pertinent data set published so far. The diagram allows the bulk composition and molar volume of individual H_2O - CO_2 fluid inclusions to be determined from pairs of $Th(car)$ and $Th(total)$ measurements, without recourse to optical estimates of phase volume fractions. The performance of the new diagram is tested using synthetic fluid inclusions of known V - T - x properties, demonstrating its superior accuracy compared to previous plots in the literature.

The results of this study are most applicable to H_2O - CO_2 inclusions found in rocks formed under elevated pressures, where aqueous CO_2 solubility is enhanced. Some fluid inclusions contain too little CO_2 (typically less than 3 mol%) to condense liquid above the ice- or clathrate nucleation temperatures, precluding measurement of $Th(car)$. Other inclusions that permit ready determination of $Th(car)$ undergo total homogenisation via a dew-point transition, in which the phase boundary slowly expands upon heating, disappearing gradually into the shadow that surrounds the inclusion, and rendering

accurate measurements of $Th(total)$ impossible. Still other inclusions decrepitate prior to homogenising, when microthermometry is conducted in a conventional heating-stage under atmospheric confining pressure. The analysis of all these inclusions must be tackled by methods other than those presented here (e.g., Roedder, 1984; Schmidt et al., 1998).

In addition to enabling accurate analysis of the main class of H_2O - CO_2 fluid inclusions, the V - T - x relation presented in this study serves as an indispensable stepping stone towards interpreting and modelling the phase relations and p - V - T - x properties of more complex natural fluids and their fluid inclusions.

2. AVAILABLE EXPERIMENTAL DATA

Fluid properties in the one-phase region of the H_2O - CO_2 system have been studied at relatively low densities by Greenwood (1969); Crovetto et al. (1991); and Fenghour et al. (1996), among others. Experimental data for higher densities have been collected by Franck and Tödheide (1959); Shmulovich et al. (1980); Gehrig (1980); Zakirov (1984); and Sterner and Bodnar (1991). Brodholt and Wood (1993) reported data from molecular dynamics simulations of H_2O - CO_2 mixtures under extremely high pressures, up to 2 GPa. These studies include thorough evaluations of the accuracy of equations of state for H_2O - CO_2 fluids in the one-phase region. In particular, the equations of Holloway (1981); Kerrick and Jacobs (1981); Duan et al. (1992a,b) are able to reproduce accurately most of the supercritical experimental data, and they are therefore very useful for the construction of high-temperature isochores in this fluid system.

Tödheide and Franck (1963); Takenouchi and Kennedy (1964); and Mather and Franck (1992) all presented p - T - x descriptions of the solvus, such as shown schematically in Figure 1, but their methods were not designed to measure molar volumes at the phase boundary. Tödheide and Franck (1963) measured the composition of coexisting phases at temperatures between 50 and 350°C and at pressures between 20 and 350 MPa. They found a temperature minimum in the critical curve at 41.5 mol% CO_2 , 266°C and 245 MPa. Takenouchi and Kennedy (1964) made similar measurements at 10–150 MPa and 110–350°C. Measurements of the compositions of the H_2O -rich phase are similar to those of Tödheide and Franck (1963), but the amount of H_2O in the CO_2 -rich phase at certain pressures is much higher. They estimated the temperature minimum in the critical curve to lie at 31 mol% CO_2 , 265°C and 215 MPa. The inconsistencies between these data sets along the 270°C and 300°C isotherms are illustrated in p - x projection in Figure 2. The contradictions and the lack of volumetric data make these studies insufficient for any conclusive understanding of microthermometric results from fluid inclusions.

The only set of internally consistent, experimentally derived volumetric properties that can be applied to the H_2O - CO_2 solvus are those determined indirectly by Sterner and Bodnar (1991). They introduced a new approach for this fluid system, synthesising fluid inclusions with controlled compositions at selected temperatures and pressures in the one-phase region. The bulk molar volumes of the mixtures were obtained from measurements of $Th(car)$ combined with the calculated molar volumes and compositions of the coexisting phases at $Th(car)$. Pressures on the solvus were obtained indirectly from the

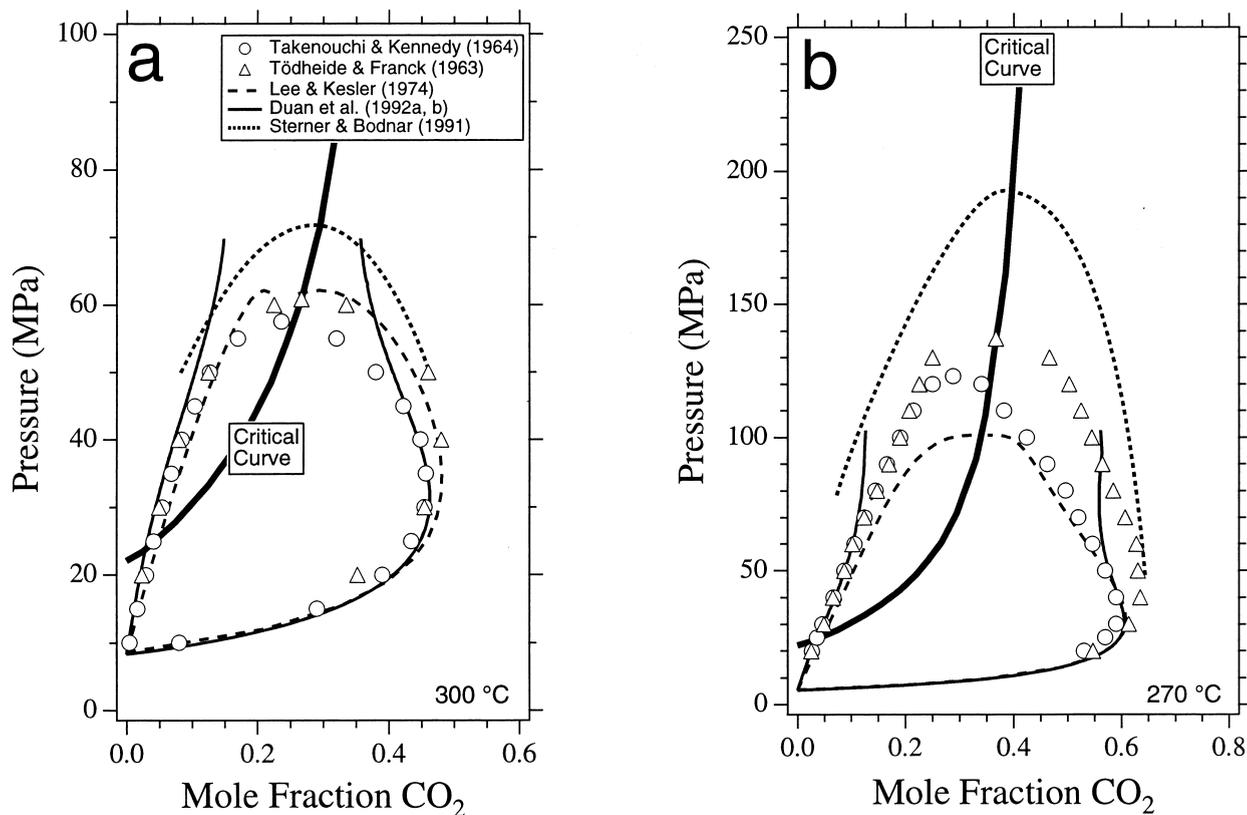


Fig. 2. Comparison of experimental data and thermodynamic modelling in p - x diagrams for the H₂O-CO₂ fluid system at selected temperatures (a) 300 °C and (b) 270 °C.

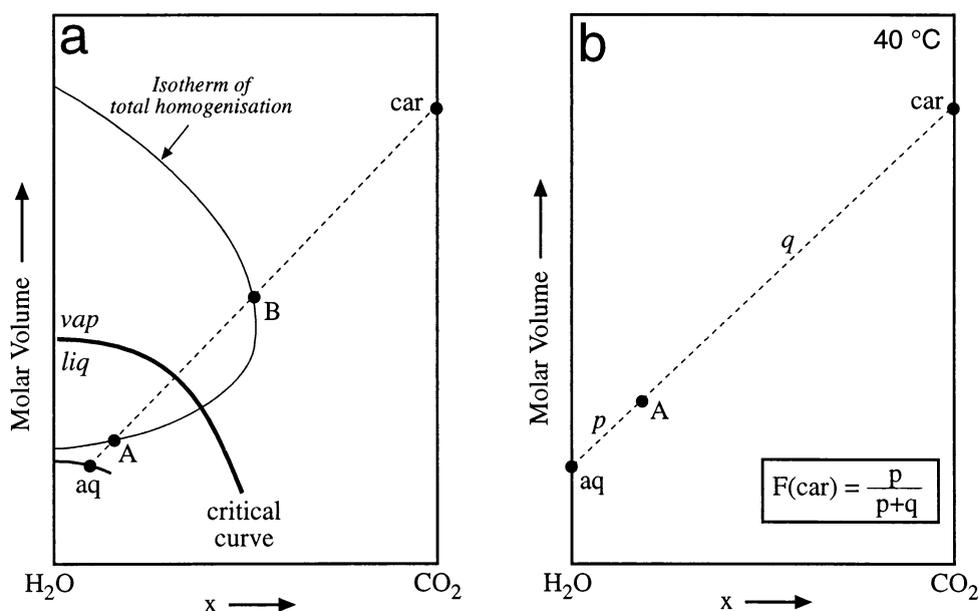


Fig. 3. Schematic V - x diagrams illustrating different methods of calculating bulk fluid properties of H₂O-CO₂ fluid inclusions. (a) In the method of Walther (1981) and Lüttge et al. (1996), a tie-line is constructed between the two phases coexisting at the CO₂ homogenisation temperature: *car* represents the pure CO₂ phase (liquid or vapour) and *aq* represents the CO₂-saturated aqueous solution. Intersection points A and B on the solvus represent total homogenisation to the liquid and vapour phases, respectively, for a specific inclusion. (b) In the method of Burruss (1981) and Brown and Lamb (1986), a tie-line is constructed between the aqueous and carbonic phases, which are assumed to be pure CO₂ and pure H₂O end-members. The line-segments p and q are defined by the volume fraction of the two immiscible phases, i.e., $F(car) = \frac{p}{p+q}$ and $F(aq)$, estimated at 40 °C.

intersection of the measured homogenisation temperatures with isochores calculated using an unpublished modified Redlich-Kwong equation of state (see abstract by Connolly and Bodnar, 1983). Sterner and Bodnar (1991) plotted the locus of the solvus in T - p and p - x diagrams, but they did not explicitly provide the relation between measured total homogenisation temperatures and bulk molar volumes. Nevertheless, these data collectively constitute a unique p - V - T - x description of the solvus over essentially the entire compositional range. The extrapolated solvus pressures are assumed to be the main source of uncertainties in their results, because most modified Redlich-Kwong equations of state are unable to reproduce liquid-like fluid properties near solvus conditions. This could be the reason that the smoothed pressure estimates of Sterner and Bodnar (1991) significantly exceed the values of Tödheide and Franck (1963) and of Takenouchi and Kennedy (1964), as is evident in p - x diagrams such as Figure 2. Stretching of the inclusions during microthermometric heating at atmospheric confining pressure, as described by Schmidt et al. (1998), would tend to lower the derived solvus pressures, and therefore such an effect could not be responsible for the observed discrepancies.

3. BULK PROPERTIES AND SOLVUS MODELLING

Molar volume–composition diagrams, i.e., V - x diagrams, are extremely useful in fluid inclusion studies, because they allow the parameters needed to construct isochores to be estimated directly from microthermometric data, as shown by Lentz (1979); Walther (1981); Burruss (1981); and Kerkhof (1988). Walther (1981) developed a conode method (see also Lüttge et al., 1996), from which bulk V - x properties of H_2O - CO_2 fluids can be determined graphically, as illustrated in Figure 3a. Walther projected isotherms of total homogenisation, by combining the p - T - x data of Franck and Tödheide (1959) with the extrapolated high-temperature volumetric data of Gehrig (1980). This study gives p - T - V - x data of only supercritical one-phase H_2O - CO_2 mixtures at temperatures above $400^\circ C$, at some distance from the solvus. Walther's method also employs the homogenisation temperature of the CO_2 phases and the calculated V - x properties of the coexisting aqueous phase at $Th(car)$.

Touret (1977) combined phase volume fraction estimates with microthermometric data to calculate bulk fluid compositions in the three-component system H_2O - CO_2 - $NaCl$, using equations similar to Eqn.1.

$$n_i = \sum_M \left[\frac{F}{V} \right]^M x_i^M \quad (1a)$$

$$x_i^{bulk} = \frac{n_i}{\sum_j n_j} \quad (1b)$$

where n_i is the number of moles of component i , M is the specific phase; F and V are the volume fraction and molar volume of phase M , respectively; and x_i^M is the mole fraction of component i in phase M . Burruss (1981) also resorted to the use of phase volume-fractions measured at a fixed temperature (at $40^\circ C$), because of the lack of experimental data for the H_2O - CO_2 solvus. Burruss reduced the calculation procedure to a pure end-member approach, in which the

mutual solubility between H_2O and CO_2 in the coexisting carbonic and aqueous phases is ignored (Fig. 3b). Thus the bulk molar volume (V^{bulk}) is geometrically calculated using Eqn.2:

$$\frac{1}{V^{bulk}} = \left[\frac{F}{V} \right]^{pure H_2O} + \left[\frac{F}{V} \right]^{pure CO_2} \quad (2)$$

The bulk composition is obtained from Eqn. 1 where x_i^M is unity for each phase. Brown and Lamb (1986, 1989) used a similar model of ideal geometrical mixing and neglected mutual solubility. Sterner and Bodnar (1991) improved this calculation method by including the CO_2 solubility in aqueous solutions (Dodds et al., 1956) and by using other data sources compared to Walther (1981) for the density of a pure CO_2 phase along the liquid-vapour curve (Ely et al., 1989). The density of CO_2 -saturated aqueous solutions was calculated according to Parkinson and Nevers (1969). The bulk composition of the synthetic fluid inclusions was known from the experimental work of Sterner & Bodnar (1991), therefore bulk molar volumes could be calculated.

In principle, equations of state can be used to calculate liquid-vapour equilibria, i.e., solvus p - V - T - x properties, for any type of fluid mixture, because the chemical potential of each component can be calculated (Fig. 4). In practice, however, only pure fluids can be described accurately by this approach, using recently published unified Helmholtz energy func-

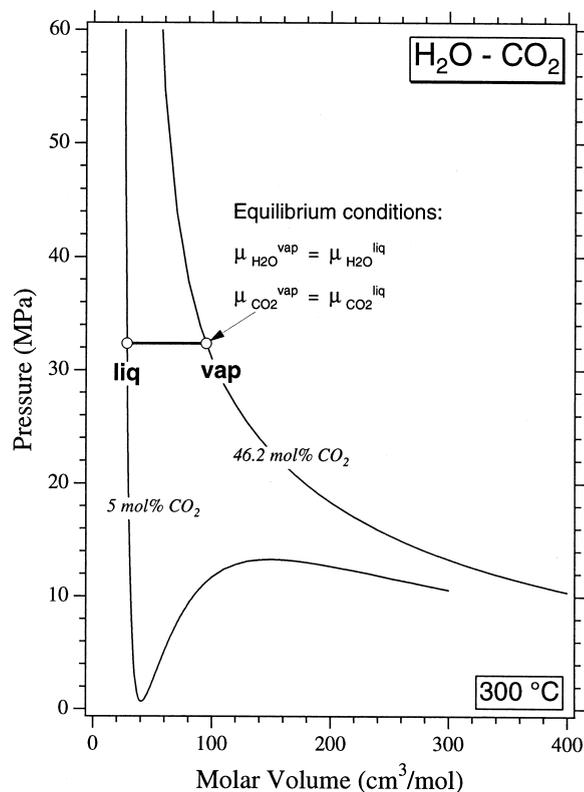


Fig. 4. p - V diagram showing $300^\circ C$ isotherms for 5 mol% CO_2 and 46.2 mol% CO_2 fluid mixtures, according the equation of state of Duan et al. (1992a,b). These compositions are in equilibrium at 32.4 MPa, where the chemical potential of each component in the liquid is equal to that of its counterpart in the vapour.

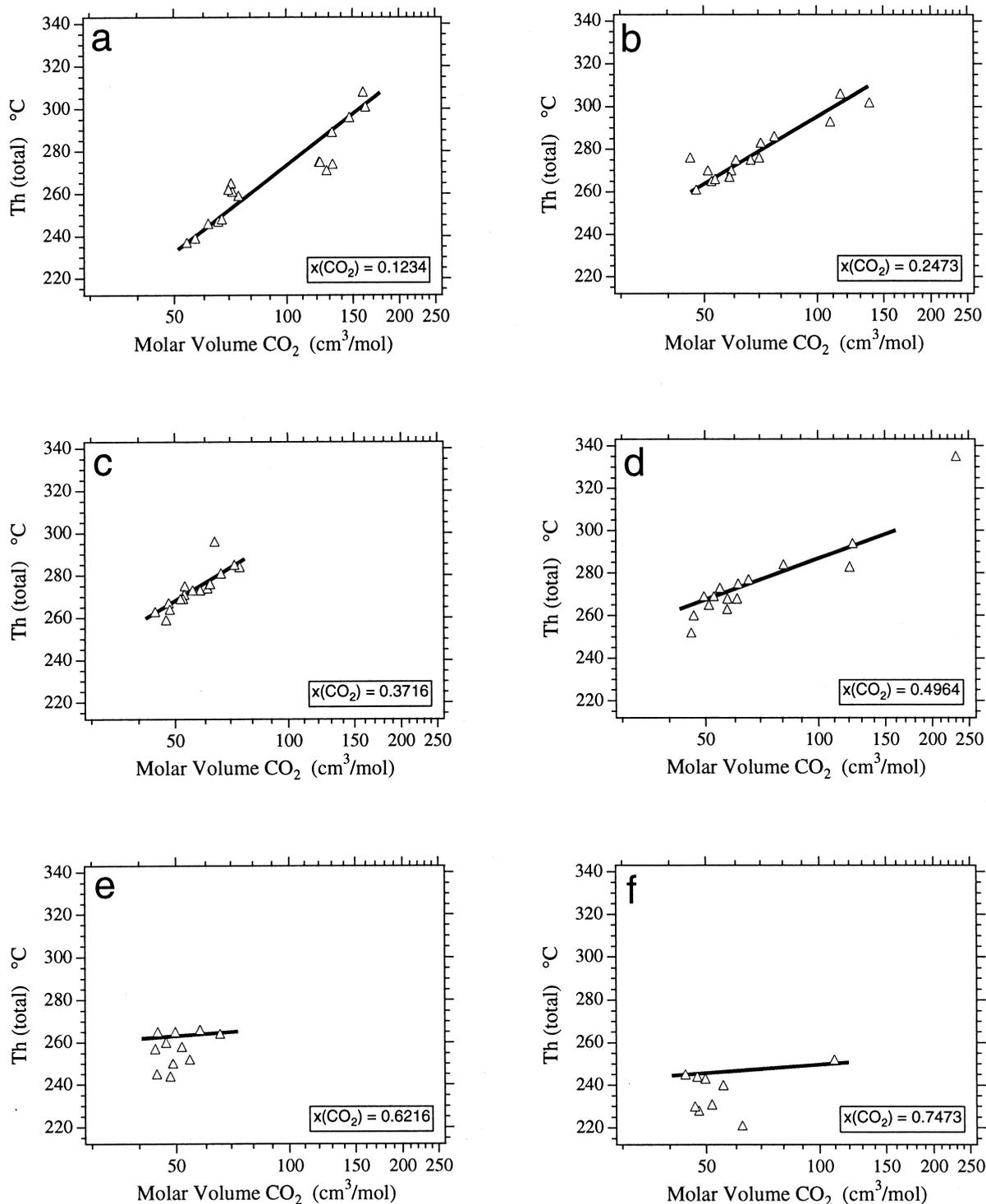


Fig. 5. CO₂ molar volume - total homogenisation diagrams based on the experimental data of Sterner and Bodnar (1991) at 12.34 mol% CO₂ (a), 24.73 mol% CO₂ (b), 37.16 mol% CO₂ (c), 49.64 mol% CO₂ (d), 62.16 mol% CO₂ (e), 74.73 mol% CO₂ (f).

tions (Haar et al., 1984; Hill, 1990; Span and Wagner, 1996). The complexity of molecular interactions between unlike molecules in fluid mixtures has so far hindered the development of accurate equations of state for fluids consisting of more than one component. Moreover, equations of state have been devel-

oped only for subsets of the desired fluid properties, e.g., for *p-T-x* properties, excluding volumetric parameters.

Lee and Kesler (1975) modified the equation of state of Benedict et al. (1940) for petroleum-related fluids, including many hydrocarbons. Their equation, which is based on the

Table 1. Molar volume V , in cm^3/mol , and CO_2 homogenisation temperature $Th(car)$, in $^\circ\text{C}$, as a functional of total homogenisation temperature and bulk fluid composition. (*liq*), (*vap*) and (*crit*) stand for CO_2 homogenisation in the liquid phase, vapour phase, and critical homogenisation, respectively. Values in bold face illustrate total homogenisation in the liquid phase; the rest in the vapour phase. The smoothed numbers are based on experimental data from Sterner and Bodnar (1991).

$Th(total)$ $^\circ\text{C}$	$x(\text{CO}_2)$											
	0.1234		0.2473		0.3716		0.4964		0.6216		0.7473	
	V	$Th(car)$	V	$Th(car)$	V	$Th(car)$	V	$Th(car)$	V	$Th(car)$	V	$Th(car)$
240	56	18.8 (liq)	—	—	—	—	—	—	—	—	—	—
245	62	25 (liq)	—	—	—	—	—	—	—	—	47	-1.5 (liq)
250	67	27.9 (liq)	—	—	—	—	—	—	—	—	114	30.7 (vap)
255	73	29.8 (liq)	—	—	—	—	—	—	—	—	—	—
260	80	30.7 (liq)	45	-9.1 (liq)	42	-23.6 (liq)	38	-51 (liq)	—	—	—	—
265	87	30.9 (liq)	51	9.8 (liq)	47	-1.5 (liq)	45	-9.1 (liq)	58	21.3 (liq)	—	—
270	94	31 (crit)	57	20.1 (liq)	52	11.9 (liq)	56	18.8 (liq)	—	—	—	—
275	103	30.9 (vap)	63	25.8 (liq)	58	21.3 (liq)	66	27.5 (liq)	—	—	—	—
280	112	30.7 (vap)	72	29.5 (liq)	64	26.4 (liq)	78	30.5 (liq)	—	—	—	—
285	122	30.3 (vap)	80	30.7 (liq)	72	29.5 (liq)	93	31 (crit)	—	—	—	—
290	132	29.7 (vap)	90	31 (crit)	87	30.8 (liq)	113	30.7 (vap)	—	—	—	—
295	145	28.7 (vap)	98	30.9 (vap)	—	—	137	29.3 (vap)	—	—	—	—
300	157	27.6 (vap)	110	30.6 (vap)	—	—	161	27.1 (vap)	—	—	—	—
305	172	26 (vap)	125	30.2 (vap)	—	—	—	—	—	—	—	—
310	185	24.6 (vap)	140	29.1 (vap)	—	—	—	—	—	—	—	—

corresponding-states principle (Pitzer, 1939), and which describes fluids in terms of two end-members, i.e., simple fluid versus reference fluid, has proven to be an excellent predictor of fluid properties. Unfortunately, this equation has not been tested on H_2O and CO_2 , and therefore it has not been used to interpret natural fluid inclusions. In this study, the equation of state of Lee and Kesler (1975) has been used to calculate liquid-vapour equilibria for H_2O - CO_2 mixtures along the 270°C and 300°C isotherms (Fig. 2). The 300°C isotherm agrees well with some of the experimental p - T - x data, although the liquid phase has slightly overestimated CO_2 contents and molar volumes. The 270°C isotherm underestimates the experimental pressures markedly and, again, the CO_2 content of the coexisting liquid is overestimated.

Christoforakos and Franck (1986) attempted to model thermodynamically the solvi of binary H_2O -gas systems. Their approach was mainly directed at accurate modelling of the critical curves of fluid mixtures, and resulted in rough estimates of the p - T - x properties of the solvi. The molar volumes computed from their equation of state are too inaccurate for the purposes of this study.

Gallagher et al. (1993) combined the unified Helmholtz energy function for pure H_2O , according to Haar et al. (1984), with the corresponding-states principle for H_2O - CO_2 mixtures. The critical properties of these fluid mixtures are described by arbitrary mixing rules. This approach applies only to low-density fluid mixtures and compositions up to 30 mol% CO_2 , thereby precluding calculation of the properties of the coexisting CO_2 -rich vapour phase.

Duan et al. (1992a,b) modified the equation of state of Lee and Kesler (1975) for H_2O - CO_2 - CH_4 mixtures. This equation can describe the p - V - T properties of the unary subsystems in both the vapour and liquid regions to nearly within experimental error up to 8 kbar and between 0 and 1000°C . For mixtures, mixing rules as defined for Virial-like equations of state were adopted (Duan et al., 1992b). The 270°C and 300°C isotherms

for H_2O - CO_2 mixtures have been calculated for the present study using the Duan et al. (1992b) equation of state, and plotted in Figures 2 and 4. Surprisingly, the results are markedly different from the supposedly equivalent figure published in Duan et al. (1992b; their Fig. 3 on p. 2623). Contrary to the conclusions in Duan et al. (1992b), the published equation in fact does not close the solvus at high pressure, and the switching fitting functions for the binary interaction parameters of H_2O - CO_2 , which are crucial for the calculation of the solvus, are discontinuous. Thus for loci of the solvus above 40 MPa, their equation of state is no more accurate than the equation of state of Holloway (1977); Holloway (1981) and Flowers (1981). Below 30 MPa, however, the Duan et al. (1992a,b) equation accurately predicts the experimental data of Tödheide and Franck (1963) and Takenouchi and Kennedy (1964).

4. CONSTRUCTION OF V - X DIAGRAMS

In the following the experimental data of Sterner and Bodnar (1991) are reinterpreted to extract the explicit relationship between $Th(car)$ values and $Th(total)$ values for fixed bulk compositions. The molar volume of the carbonic phase at $Th(car)$ is obtained from the equation of Duschek et al. (1990), neglecting the small amount of dissolved H_2O , and plotted against total homogenisation temperature (Fig. 5). Straight lines are fitted to these data, based on a logarithmic scale for the molar volume of the carbonic phase. The measurements of total homogenisation to the vapour phase set only minimum constraints on the locus of the solvus, because the final film of liquid wetting the inclusion walls is difficult to observe during microthermometry. Thus the lines were fitted through the highest temperature values of the data shown in Figure 5d,e,f. Smoothed values of CO_2 molar volumes are estimated for selected temperatures and summarised in Table 1.

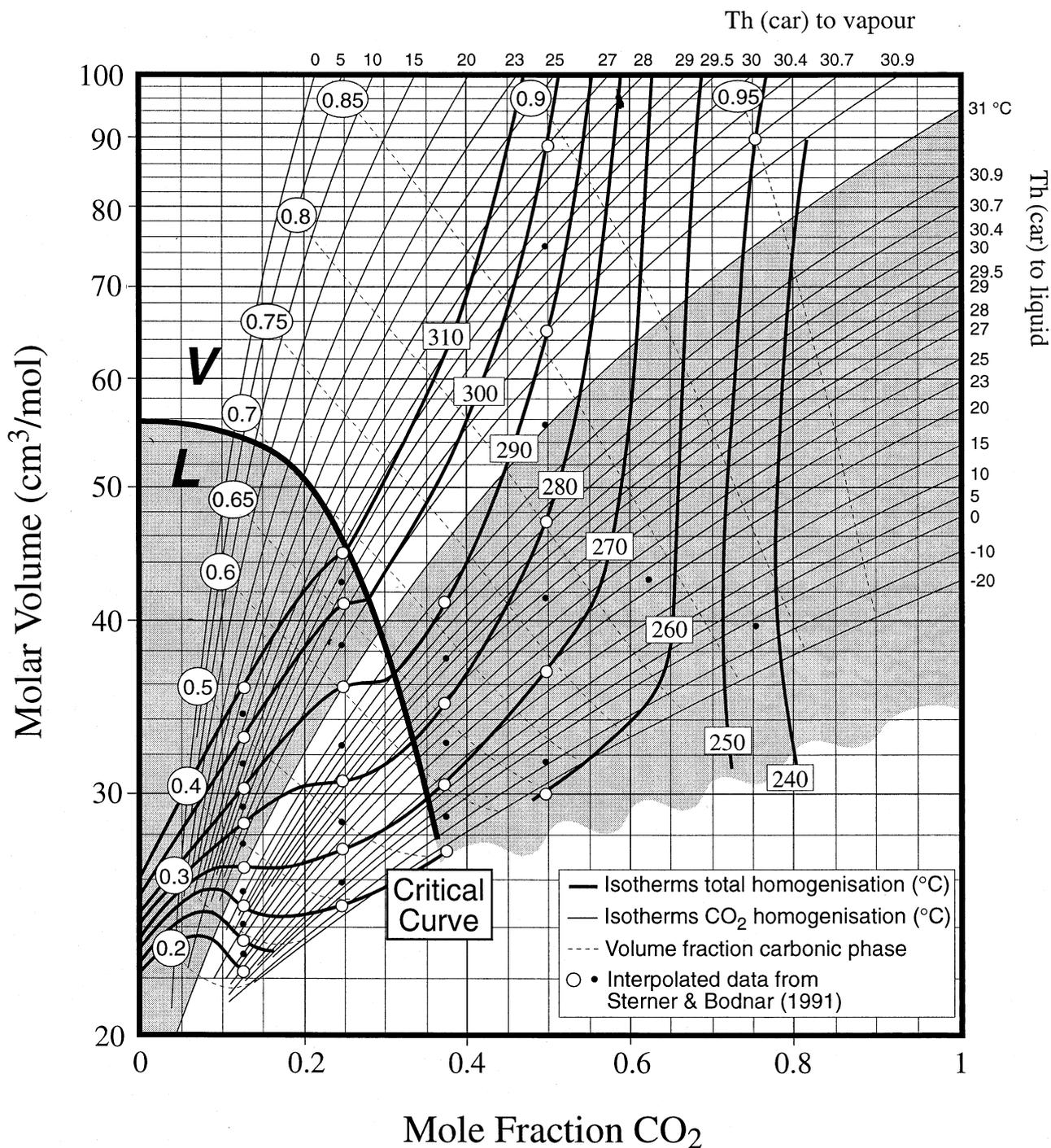


Fig. 6. V-x diagram of the H₂O-CO₂ fluid system. Numbers within squares represent total homogenisation temperatures in °C, and L and V denote the mode of total homogenisation to the liquid and vapour phases, respectively. Thin curves represents loci of equal CO₂ homogenisation temperature. Shaded areas illustrate the four principal modes of fluid inclusion behaviour during microthermometry, divided by the lower critical temperature (equal to that of pure CO₂) and the upper critical curve of the bulk fluid mixture. Thin dashed curves are loci of equal volume fraction of the carbonic phase at Th(car), with fractions indicated by the numbers in circles.

The aqueous solubility of CO₂ has recently been reviewed by Carroll et al. (1991). Their highly accurate model using Henry's law (Eqn. 3), which takes into account H₂O-saturation of the coexisting carbonic phase, has been used to calculate the

CO₂ content of the aqueous phase at the p-T conditions of CO₂ homogenisation, i.e. ph(car), Th(car):

$$x_{CO_2}^{liq} \cdot H_{CO_2,water} = f_{CO_2}^{vap}(T, p, n_{H_2O}, n_{CO_2}) \quad (3a)$$

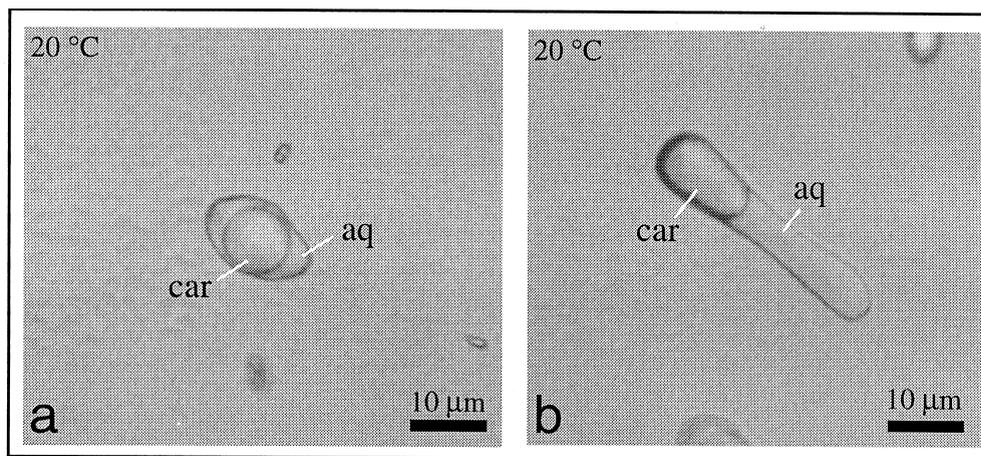


Fig. 7. Synthetic H₂O-CO₂ fluid inclusions with 30 mol% CO₂, synthesised at 600 ± 5°C and 500 ± 0.5 MPa. The aqueous and the carbonic phases are labelled *aq* and *car*, respectively.

$$x_{\text{H}_2\text{O}}^{\text{liq}} \cdot P_s = f_{\text{CO}_2}^{\text{vap}}(T, p, n_{\text{H}_2\text{O}}, n_{\text{CO}_2}) \quad (3b)$$

$$\ln(H_{\text{CO}_2, \text{water}}) = -6.8346 + \frac{1.2817 \cdot 10^4}{T} - \frac{3.7668 \cdot 10^6}{T^2} + \frac{2.997 \cdot 10^4}{T^3} \quad (3c)$$

where $x_{\text{CO}_2}^{\text{liq}}$ and $x_{\text{H}_2\text{O}}^{\text{liq}}$ are the mole fractions of CO₂ and H₂O in the aqueous solution; $H_{\text{CO}_2, \text{water}}$ is Henry's constant of CO₂ in water; $f_{\text{CO}_2}^{\text{vap}}$ and $f_{\text{H}_2\text{O}}^{\text{vap}}$ are the fugacity of CO₂ and H₂O in the vapour phase; P_s is the saturation pressure of pure H₂O; T and p are temperature in Kelvin and pressure in MPa. The effect of pressure on Henry's constant is obtained from the equation of Krichevsky and Kasarnowsky (1935). Carroll and Mather (1992) demonstrated that this model can be applied reliably to the H₂O-CO₂ fluid system below 373 K and 100 MPa. The density of the CO₂-saturated aqueous solution is calculated by the equation of state of Duan et al. (1992a,b).

These calculations allow lines of equal $Th(\text{car})$ to be projected in a V - x diagram (Fig. 6). Based on these temperatures, a relation between bulk composition and bulk molar volume can be traced according to Eqns. 1 and 3. These isotherms almost converge at the saturation conditions of the aqueous solution. Their positive slope illustrates that addition of small amounts of H₂O to CO₂-richer fluids always results in a decrease in molar volume. The derived relation between bulk composition, CO₂ homogenisation and total homogenisation in Table 1 permits construction of smoothed isotherms of equal total homogenisation temperatures in the V - x diagram (Fig. 6). Thus the bulk composition and bulk molar

volume of individual fluid inclusions can be obtained from Figure 6 by plotting pairs of $Th(\text{car})$ and $Th(\text{total})$ measurements.

5. DISCUSSION

A large amount of independent data is necessary to derive a p - V - T - x model that is generally applicable over a wide temperature and pressure range. Modelled fluid properties based on only one experimental data set may be erroneous, especially when the original measurements have a certain amount of scatter. Unfortunately, the data of Sterner and Bodnar (1991) are the sole experimental set of volumetric properties of the H₂O-CO₂ solvus, and hence the accuracy of the V - x plot in Figure 6 cannot be evaluated independently.

A potential source of error in the total homogenisation temperatures measured by Sterner and Bodnar (1991) is the effect of plastic deformation of the quartz host around the inclusions as they are heated during microthermometry under atmospheric confining pressure. Sterner and Bodnar (1991) carefully corrected the p - T paths followed by the inclusions using the equations of Hosieni et al. (1985), which quantitatively describe the expansivity and compressibility of bulk quartz. Later, however, Schmidt et al. (1998) demonstrated by homogenising synthetic fluid inclusions in quartz under high confining pressure, that the degree to which the inclusions expand upon heating may significantly exceed that expected from the equation of state of quartz. Zhang (1998) attributed most of this expansion to stress gradients around the inclusions. It follows that even the corrected $Th(\text{total})$ values reported by Sterner and

Table 2. Microthermometric data and optically estimated area and volume fractions of the synthetic fluid inclusions in Fig. 7. The error of the volume fraction estimated could not be evaluated.

	Inclusion a	Inclusion b
Th(car)	16.6 ± 0.1°C (liq)	16.4 ± 0.1°C (liq)
Th(total)	269 ± 2°C (liq, nearly crit.)	268 ± 2°C (liq, nearly crit.)
Area fraction of carbonic bubble	0.54 ± 0.01	0.42 ± 0.01
Estimated volume fraction	0.52	0.39

Table 3. Comparison of bulk V-x properties of the synthetic fluid inclusions in Fig. 7 according to the methods described in the text. No errors are given for calculations made with the method of Burruss (1981) and Brown and Lamb (1986), because these rely on $F(car)$ values (see Table 2).

Method	Inclusion	Molar volume (cm ³ /mol)	Mole fraction CO ₂
Experimental values Fig. 6 (this study)	a and b	29.0 ± 0.1	0.2999 ± 0.0002
	a	27.8 ± 1.5	0.27 ± 0.03
	b	27.3 ± 1.5	0.26 ± 0.03
Walther (1981) Lüttge et al. (1996)	a and b	32 ± 3	0.37 ± 0.06
Burruss (1981), Brown and Lamb (1986)	a	27.6	0.263
	b	24.4	0.175

Bodnar (1991) may be artificially elevated due to stretching. This means that the bulk molar volumes of the fluid inclusions, which were calculated exclusively from low p - T data, at $Th(car)$ and $ph(car)$, may have been assigned $Th(total)$ temperatures that are too high. Whether the $Th(total)$ values are actually too high or not cannot be judged at present, owing to the lack of an independent T - V - x description of the H₂O-CO₂ solvus. However, the consequences for the application of the new V - x diagram to natural fluid inclusions are unlikely to be significant. Firstly, certain segments of the solvus are very steep in P - T projection, and hence stretching would lower the pressures at which isochores are interpreted to emanate from the solvus, but it would not alter $Th(total)$ values perceptibly at low bulk molar volumes. Secondly, natural quartz-hosted H₂O-CO₂ inclusions heated at atmospheric confining pressure are likely to undergo the same amount of stretching as their synthetic counterparts. Thus the V - x diagram derived from Sterner and Bodnar's (1991) synthetic fluid inclusion data is more likely to reflect the behaviour of natural fluid inclusions, than data collected by other experimental methods. As such, the diagram is most probably internally consistent, even though the absolute errors cannot be assessed.

To compare the accuracy of the presented method with previously published models, an example is provided using synthetic fluid inclusions with known composition, molar volume and microthermometric properties. The inclusions were synthesised in quartz from silver oxalate and water according to the method of Bodnar and Sterner (1987), using the procedure and laboratory apparatus described in Diamond (1994b). Bulk composition was set at 30 mol% CO₂ and the run conditions were 600 ± 5°C and 500 ± 0.5 MPa. According to the data in Sterner and Bodnar (1991), the molar volume of the homogeneous fluid at these conditions is 29.4 cm³/mol. Correcting for the compressibility and expansion of the host quartz, the inclusions have a molar volume of approximately 29 cm³/mol at $Th(car)$. The microthermometric and volumetric properties of two sample inclusions shown in Figure 7 are given in Table 2. Volume fractions of the carbonic phases were estimated optically, by first measuring the area fractions of the phases by digital integration of two-dimensional, high-magnification images (using LinkSys 2.02 from Linkam Scientific Instruments Ltd.), and then correcting these fractions for the thickness of the inclusions by assuming they have cylindrical geometries. Although both inclusions in Figure 7 yield similar phase transition temperatures, the apparent volume fraction of the carbonic bubble in inclusion a is much larger than in b, because, as is usual for this optical method, the true shape of the inclusions in the third dimension could not be measured accurately.

The results of applying the methods of Walther (1981), Burruss (1981) and the new diagram in Figure 6 are shown in Table 3. Comparison of the V - x diagram of Walther (1981) and Lüttge et al. (1996) with Figure 6 reveals significant differences in the positions of solvus isotherms, presumably owing to their inaccurate down-temperature extrapolation of experimental data measured at temperatures above 400°C. The example calculation shows that their method overestimates the bulk V - x values. It should be mentioned, however, that the diagram of Walther (1981) is not strictly applicable to the test inclusions, as its isotherms do not cover the example conditions, hence some extrapolation was necessary to perform the test calculation. The method of Burruss (1981) and Brown and Lamb (1986) results in a large range of possible compositions and molar volumes (Table 3) because the volume fraction estimates of the two inclusions differ by 33%. The errors inherent in all these methods far exceed those associated with the new V - x diagram. Nevertheless, the new diagram yields slightly underestimated V - x values, presumably owing to inaccuracies arising from the small number of experimental data upon which the model is based.

Isotherms of total homogenisation for H₂O-CO₂ mixtures can also be calculated from the previously mentioned equations of state. To illustrate this, the equations of Duan et al. (1992a,b) and Lee and Kesler (1975) have been chosen to calculate the molar volumes and compositions of coexisting liquid and vapour at selected solvus temperatures, i.e., $Th(total)$ values. The discrepancy between these thermodynamic models and the experimental data obvious in the p - x diagram (Fig. 2) is also apparent in the V - x diagrams (Fig. 8). The difference between the equations of state is most pronounced at liquid-like H₂O-rich compositions. The equation of Duan et al. (1992a,b) accurately reproduces the properties of only those mixtures that have less than 5 mol% CO₂. Their equation is not consistent with experimental data of CO₂-richer compositions. The thermodynamic model of Lee and Kesler (1975) extensively overestimates molar volumes at compositions between 0 and 40 mol% CO₂ at higher temperatures. For vapour-like fluids both thermodynamic models are very similar, but they still deviate significantly from the smoothed curves in Figure 6. These examples illustrate the incapacity of published equations of state to predict the p - T - V - x properties of liquid-vapour equilibria in H₂O-CO₂ mixtures.

6. CONCLUSIONS

As reviewed above, the available experimental data on the properties of the H₂O-CO₂ solvus are incomplete and to some

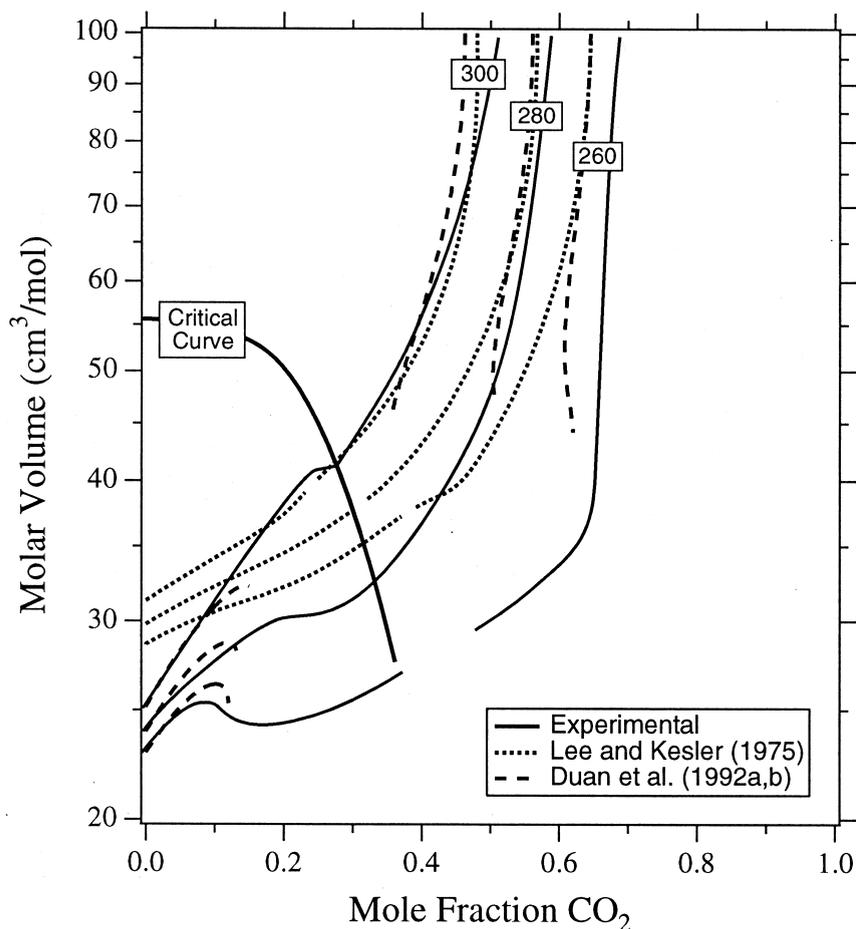


Fig. 8. V - x comparison of thermodynamic models with the smoothed experimental curves illustrated in Fig. 6. The equations of state of Lee and Kesler (1975), Duan et al. (1992a,b) were used to calculate the solvus (liquid-vapour) equilibria. Numbers represent temperatures in °C.

extent inconsistent. Moreover, thermodynamic modelling of the solvus is currently effective only over small temperature ranges at relatively low pressures, whereas it is highly inaccurate at pressures exceeding 30 MPa. Sterner and Bodnar (1991) provide the sole experimental set of volumetric properties of the solvus at geologically relevant conditions. These data have been used to construct a V - x diagram, which allows the bulk composition and molar volume of individual fluid inclusions to be determined from two microthermometric measurements: the temperature of partial homogenisation of the carbonic phases, and the temperature of total homogenisation. This approach, essentially a refinement of earlier less accurate attempts, avoids the need to incorporate in the calculations the notoriously unreliable optical estimates of phase volume fractions.

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