Chemistry in Near-critical Fluids

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1 Introduction

The physico-chemical description of the fluid state of matter has been accomplished in two steps separated by a significant time-interval. Gases were among the first systems to be studied in Physical Chemistry; it was possible to obtain an explanation of many of their properties in terms of intermolecular parameters – a well known case is the van der Waals equation of state.[1] On the other hand, the liquid phase proved more elusive and in fact the properties of solids had a firmer theoretical basis much earlier than those of liquids. It was only in the second half of this century that the theory of high density fluids showed significant progress, and this has been strongly accelerated in the past thirty years by the increasing capacity of computer simulation to deal with more complex systems.[2,3]

In spite of this progress the behaviour of fluids in the thermodynamic region which surrounds the critical point are not so well understood. This thermodynamic region is essential in order to bridge completely the gaseous and liquid states of matter, and fluid systems in the neighbourhood of critical conditions are now attracting increasing interest. Critical phenomena had been studied before any successful molecular theory for liquids was available,[4] but widespread study of near-critical behaviour has only occurred quite recently. The reason for its increasing popularity is related to the interest in using supercritical fluids as suitable reaction media for many processes, in particular for extraction and purification of thermally labile substances; they have also found wide acceptance as mobile chromatographic phases. The most appealing feature they exhibit is that their density may be varied in a continuous manner without the occurence of a liquid–vapour phase transition. This feature allows the control of their density providing a means of *fine tuning* intermolecular interactions, thus helping to optimize chemical processes.

It is also true that fluids close to a critical point show a behaviour which is different from that of ordinary fluids, thus increased scientific interest has accompanied the recent interest in the application of these fluids. For the purpose of clarifying the scientific aspects of their behaviour, it is useful to consider the properties of subcritical fluid systems which are close to the critical region, but may undergo phase transition. Their study has shed light on the characteristic features of near-critical behaviour.

The near-critical state of fluid matter is affected by an enhanced susceptibility (long-range effect) typical of the proximity to the critical region, and by the fluids' lower density (short range effect). The main interest for the purpose of their applications resides in understanding dilute solutions which are the most frequently used and which exhibit the most unusual behaviour. While this article was being written Tom and Debenedetti published[5] a study of supercritical mixtures with a very similar approach which inspired and influenced the final version of the present review. We shall attempt to rationalize some of the observations in terms of intermolecular interactions and the resulting thermodynamic properties; this will be illustrated with some examples selected from the great number of practical applications. Some critical phenomena which occur very close to the critical point, *e.g.* critical opalescence, density stagnation by gravitational effects, *etc.* will not be considered in this work – they are relevant when inquiring into the behaviour observed in a thermodynamic region which is much closer to the critical points than the one considered in the present work.

2 Critical State of Matter

It is convenient to start by illustrating the critical phenomenon with the relatively simpler behaviour observed in a pure fluid. A

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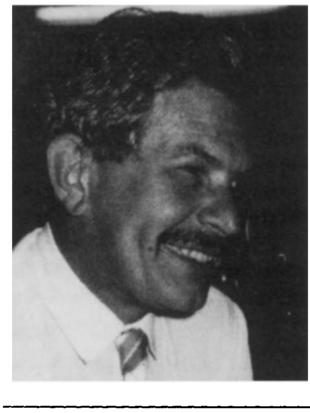

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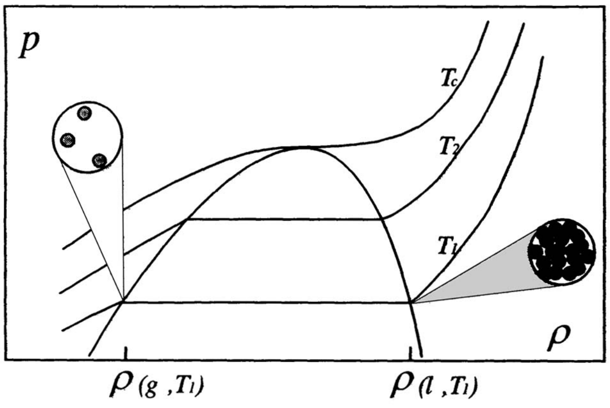

Figure 1 Liquid–vapour equilibrium illustrating the difference in particle densities between equilibrium liquid and vapour phases.

substance in the gaseous state at very low pressure is slowly compressed at temperature T_1 (Figure 1), when its density reaches a certain value, $\rho(g, T_1)$, two equilibrium states having very different densities become possible: (i) a low-density vapour having a large entropy content, but a relatively small (absolute) enthalpy since intermolecular interactions are weak because the average distance between molecules is relatively long;* (ii) a liquid phase of higher density $\rho(l, T_1)$, having a consequently smaller entropy, the decrease in fluid entropy upon condensation is compensated by a larger enthalpic contribution due to stronger interactions among molecules which are now much more closely packed. The substance is in two equilibrium states which are a compromise between the greater number of spatial configurations (vapour phase) and an increase in attractive interactions (liquid phase).

As the temperature increases it will be necessary to compress the vapour more before it can coexist with another fluid phase having higher density. Increasing the temperature reduces the enthalpic contribution because the ratio of intermolecular energy to average thermal energy decreases; hence it becomes more difficult for the dense phase to compensate the loss of entropy due to condensation with an increase in intermolecular interactions, and the difference in densities between the two coexisting phases is reduced. A temperature will be reached, called the critical temperature, T_c, above which the system will not be able to generate another stable phase by a discontinuous change of its density – phase separation will not be possible.

For vapour–liquid equilibrium at constant (T,p_{sat}) the fluid density (or its molar volume $V = \rho^{-1}$) has only two possible values which correspond to the densities of the phases in equilibrium, *i.e.* $\rho(g, T_1)$ and $\rho(l, T_1)$. In Figure 2 the isotherm T_1 illustrates the dependence of the Gibbs energy, G, with the molar volume at a temperature much lower than T_c and at p_{sat}. The two equilibrium states correspond to minima in $G = f(V)$ which are of the same depth; its curvature is a measure of the mechanical stability of the equilibrium states of the fluid, and is equal[6] to $-(\partial p/\partial V)_T = (V\kappa_T^*)^{-1}$, where κ_T^* is the isothermal compressibility (susceptibility). At low temperatures the minima are sharp (small susceptibility) – the probability of existence of states close to, but different from, the minima is very low. The particle density exhibits only small deviations from its mean equilibrium values (fluctuations) which are only appreciable within the molecular range; they are averaged out when larger (macroscopic) scales are considered. As shown in Figure 2, closer to the critical region the minima in $G(V)$ become closer to each other and the height of the barrier separating them and the curvatures at the minima are significantly reduced. As a consequence, density fluctuations become more important and they persist beyond the immediate molecular region. The size of the fluctuating domains, the correlation length ξ, becomes increasingly bigger as the critical point is approached.† In Figure 2 the critical isotherm illustrates the fact that at the critical point the curvature of G is zero, its susceptibility becomes infinite, and the state has only marginal stability.

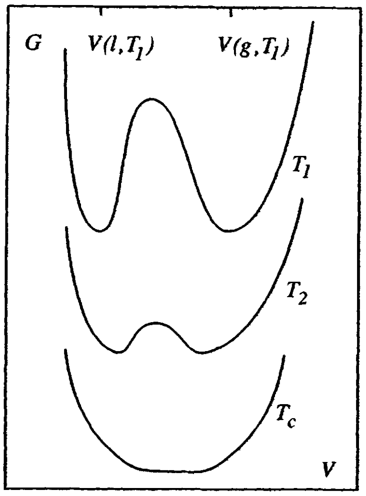

Figure 2 Gibbs energy of a pure fluid as function of its molar volume at constant T,p. The minima correspond to the states of equilibrium. Temperatures as in Figure 1.

The important role of long-range fluctuations in critical phenomena cannot be overemphasized. A spontaneous local density fluctuation in a fluid may be construed as the response of that region of the fluid to a local pressure perturbation. Since at the critical point the fluid's susceptibility is infinite, the system responds strongly to perturbations. Thus a local pressure change will affect all the system, because at the critical point fluctuations have an infinite range, *i.e.* all the molecules in the fluid are correlated and the correlation length becomes infinite. Far from the critical point a perturbation which takes the fluid away from an equilibium state will be strongly resisted according to the laws of Thermodynamics (Le Chatelier principle). Close to the critical region the fluid will be in a state highly indifferent to molecular configuration, this at the expense of thermodynamic stability which is strongly reduced, hence intermolecular interactions will be expected to affect the macroscopic properties differently.

Macroscopic properties in this region reflect the presence of all-scale fluctuations. Analytical mean-field equations are unable to describe the observed critical behaviour.[4] The strategy to formulate the state of the system is a step-by-step renormalization which leads to a rescaling of all spatial vectors averaging out fluctuations over increasing length scales, from molecular microscopic to macroscopic.[7] The dimensionalities of the spatial and order parameters enter into the theoretical calculations determining what is known as the universality class of the critical phenomena. One-component systems at the liquid–vapour critical point and binary mixtures at liquid–vapour or liquid–liquid consolute points, belong to the same universality class, hence these systems exhibit the same behaviour while approaching a critical point.

3 Mixtures

For the description of the critical behaviour of mixtures it is convenient to classify the thermodynamic variables into: **densities**, which are extensive quantities having different values in the two coexisting phases, like entropy, volume, enthalpy, density, or composition; and **fields**, which are intensive quantities having the same value in both phases at equilibrium, like pressure, temperature, and chemical potential. Griffiths and Wheeler[8] established a convenient generalization of the divergent behav-

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* The fluid packing fractions, *i.e.* the fraction of space occupied by the molecules, is typically 0.5 for liquids near their triple points and ≤ 0.05 for vapours.

† The phenomenon known as critical opalescence, which occurs very close to T_c, indicates that the fluctuating domains have the size of the wavelength of visible light.

iour of thermodynamic quantities in terms of fields and densities. Thus, at the critical point the partial derivative of a density with respect to a field will diverge strongly if the path along which the differentiation is made is defined only in terms of constant fields; it will diverge weakly (*i.e.* noticable only very close to the critical point) if one density is kept constant; it will not diverge if more than one density is fixed along the path. Other differential quotients can be reduced to the above in order to ascertain whether they are bound when approaching a critical point.

The thermodynamics of solutions at temperatures close to the solvent's triple point is usually described in terms of partial molar properties X_i, *i.e.* derivatives of a density X with respect to the number of moles of component i at constant fields (temperature and pressure). The solute's partial molar properties at infinite dilution may be expressed by,

$$X_2^\infty = X_1^* + \left(\frac{\partial X_m}{\partial x}\right)_{p,T}^\infty = X_1^* - \left(\frac{\partial X_1^*}{\partial p}\right)_T \left(\frac{\partial p}{\partial x}\right)_{T,X}^\infty \qquad (1)$$

where X_1^* is the molar property of the pure solvent. For dilute solutions, which are the most important systems for applications of near-critical fluids, partial molar quantities are dominated by the properties of the highly susceptible near-critical solvent. According to the criterion of Griffiths and Wheeler, $(\partial X_1^*/\partial p)_T$ in equation 1 will diverge strongly, while the other factor will tend weakly to zero as the critical point of the solvent is approached. Consequently all infinite dilution (standard) partial molar properties of the solute will diverge strongly at the solvent's critical point; this is a universal feature of dilute solutions in the neighbourhood of the critical point. On the other hand, the sign and amplitude of the divergence are determined by the solute–solvent molecular interactions relative to the solvent–solvent interactions as given by $(\partial p/\partial x)_{T,X}^\infty$.

The origin of this divergence can be better understood by remembering that X_2^∞ represents the change in X at constant (p, T) when one solute molecule is added to the solvent. Equation 1 divides this process into two steps, which we shall illustrate for the case $X = V$. First an exchange of solvent by solute molecules occurs at constant V, T which will give rise to a change of pressure [term $(\partial p/\partial x)_{V,T}^\infty$ in equation 1], in the second step the pressure is returned to the initial value. If the system is very close to the critical point, whilst the quantity $(\partial p/\partial x)_{V,T}^\infty$ will not be substantially different from the values it had far from the critical region, the volume change required to bring the system back to the initial pressure will be very large because $(\partial V_1^*/\partial p)_T$ in equation 1 will diverge near the solvent critical point according to the rules of Griffiths and Wheeler. Figure 3 depicts schematically the divergence observed when $X = V$ for a non-volatile solute; it also gives $(\partial p/\partial x)_{V,T}^\infty$ as function of ρ.

One of the most unusual features of near-critical solutions is the path dependence of the partial molar properties. It was shown experimentally[9] that the limiting values of the partial molar volume of SF_6 (solvent) is $-230\ cm^3\ mol^{-1}$ when its critical point is approached along the critical curve of the binary mixture with CO_2 (solute), while the critical volume of pure SF_6 is $198\ cm^3\ mol^{-1}$. Moreover, when the extrapolation to the critical point was made along the isothermal–isochoric path, it was found that $V_1 = -40\ cm^3\ mol^{-1}$. The path dependence of the limiting value of the solvent's partial molar volume may be understood, within the classical description, if the Helmholtz energy of the system, $A(V, T, x)$, is expanded in a Taylor series in δT, δV, and x, the differences of the variables from the values at the solvent's critical point. Thus,[10]

$$\begin{aligned} V_1 &= V_m + x\frac{(\partial p/\partial x)_{VT}}{(\partial p/\partial V)_{Tx}} \\ &= V_m + x\frac{A_{Vx}}{A_{VV}} \\ &\sim V_m + x\frac{A_{Vx}^c + \cdots}{A_{2Vx}^c x + A_{2VT}^c \delta T + (1/2)A_{4V}^c(\delta V)^2 + \cdots} \qquad (2) \end{aligned}$$

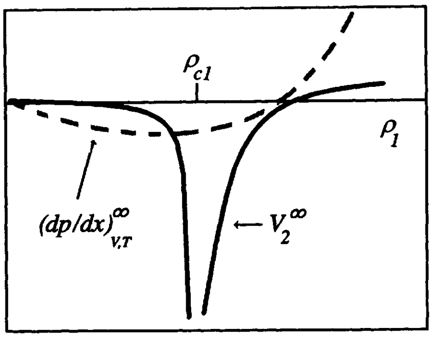

Figure 3 Near-critical behaviour of V_2^∞ (full curve) and $(\partial p/\partial x)_{T,V}^\infty$ (dashed curve) as function of the fluid density.

Here we have adopted an abridged notation for the derivatives of $A(T, V, x)$, the subscripts indicate the variables of differentiation. From equation 2 it is obvious that $V_1 \rightarrow V_{c1}$ whenever the limit $x \rightarrow 0$ is taken first. But, along the isothermal–isochoric path the limiting value $V_1(T_{c1}, \rho_{c1}, x \rightarrow 0) = V_{c1} + A_{Vx}^c/A_{2Vx}^c$ which is different from the critical molar volume of the solvent, V_{c1}. In general, only those paths that approach the critical point of the solvent with an x dependence weaker than x^1 will lead to non-anomalous limiting values of solvent's partial properties. All other paths, including the critical line and the critical isotherm–isochore, will show different limiting values of the solvent's partial molar properties from $X_1^{*,c}$.

To illustrate this characteristic of near-critical behaviour, Figure 4 depicts the dependence of the molar volume on the solute's concentration x at T_{c1} and different pressures. The example corresponds to a solution of a volatile solute in a near-critical solvent. The path $[(\delta T, \delta V) = 0]$ corresponds to the horizontal line $V = V_{c1}$. For each isobar the tangent of the (V, x) curve at the point $\delta V = 0$ is shown in the figure, the intersections of these lines with the two pure component axes give the partial molar volumes at $(x, \delta T = 0, \delta V = 0)$. Figure 4 illustrates the fact that when $x \rightarrow 0$ the partial molar volume of the solute diverges, while $V_1(x)$ reaches a constant value that is different than the critical molar volume of the pure solvent.

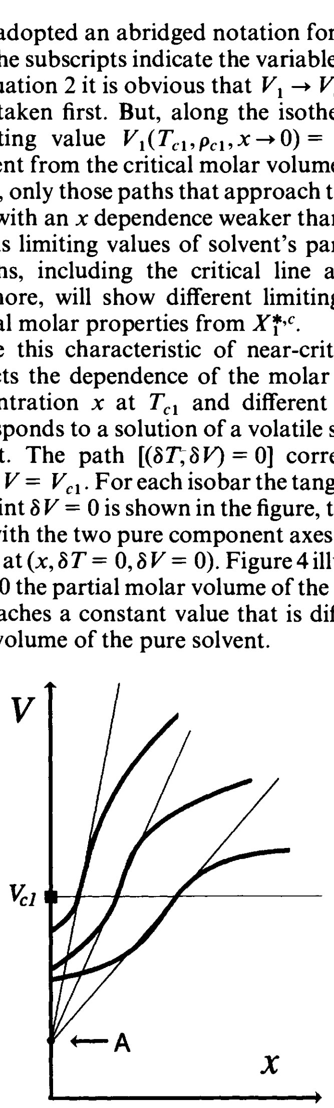

Figure 4 Molar volume of a dilute binary mixture at T_{c1} as function of the composition. The curves represent isobars. A is the value obtained for V_1^* at the critical point following an isothermal–isochoric path.

4 The Dissolution Process

The dissolution process of solids, liquids and gases may be conveniently discussed jointly if solutes in condensed phases are first considered to vaporize at the equilibrium pressure, p_2^*. The first step is accounted for by the enhancement factor, $\mathcal{E}$, which gives the ratio of the actual solubility in the fluid to that in an ideal gas phase (ideal solubility). Thus,

$$\mathcal{E} = \frac{x}{x^{id}} = \frac{xp}{p_2^*} \qquad (3)$$

Perturbation models[2,11] provide a very convenient physical description of the dissolution of *ideal gaseous* substances in fluids because they relate, in a simple way, molecular parameters to thermodynamic properties; however they do not always give the most accurate quantitative description. According to perturbation theory[12] (*cf.* scheme in Figure 5) the dissolution of gaseous substances in fluids may be divided in two steps: (i) A cavity is opened in the fluid to host the solute molecule, considered at this stage to be a hard body having no attractive interactions with the solvent. (ii) The attractive solute–solvent interactions are switched on. Adding both contributions, the change in chemical potential when the solutes go from ideal gas to infinitely dilute solution may be calculated. Step (i) makes a positive contribution to the change of solute chemical potential upon dissolution, while step (ii) contributes a negative term.

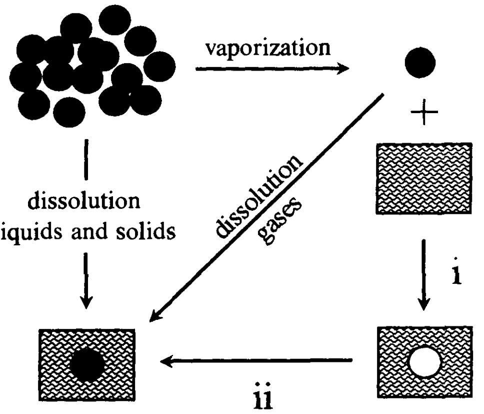

Figure 5 Schematic representation of the dissolution process. Steps (i) and (ii) illustrate the perturbational model. The circles represent solute particles; they are shaded when attractive interactions are switched on.

Thus the perturbation model separates the repulsive contribution due to the solvent structure [expressed in terms of its packing fraction, η, in step (i)], from that due to solute–solvent attractive interactions described in step (ii). Both contributions to $\Delta_{\mathrm{sol}}H$ are the product of the solvent's expansivity and a function of η; while $\Delta_{\mathrm{I}}H > 0$ is a strong function of η, $\Delta_{\mathrm{II}}H < 0$ depends directly on the solvent–solute interactions and less strongly on η. It is interesting to compare the features exhibited by the dissolution process when the fluid density (*i.e.* η) changes from that of a liquid to that of a gas through the near-critical state. For liquid and solid solutes $\Delta_{\mathrm{sol}}H$ contains the contribution of the enthalpy of vaporization which is the dominant contribution when the solvent density is very low.

4.1 Solvents at their Triple Point

Liquids typically have $\eta \simeq 0.5$ close to their triple point, water being a notable exception. The perturbation model tells us that:

Step (i) Local density fluctuations are very small and opening a cavity in the liquids demands the expenditure of much work. This step leads to a large positive contribution to the solute's chemical potential (resistance to dissolution). Thus $\Delta_{\mathrm{I}}\mu > 0$ and $\Delta_{\mathrm{I}}H > 0$. Fluids like water, having a very weak dependence of density on temperature close to the triple point, are exceptional because then the enthalpic contribution of step (i) is very small.

Step (ii) For all solutes the attractive interactions involved in this step contribute terms which facilitate the dissolution (*i.e.* $\Delta_{\mathrm{II}}\mu < 0$ and $\Delta_{\mathrm{II}}H < 0$); however their magnitude depends critically upon the intermolecular solute–solvent interactions.

The triple point dissolution picture is the one that we are most familiar with. It seems natural to expect the solubility of a solid solute not having very strong interactions with the solvent, *e.g.* naphthalene or Cl_4 in CCl_4, to increase with temperature because in these fluids $\Delta_{\mathrm{sol}}H$ is dominated by the positive term $\Delta_{\mathrm{I}}H$, to which for solids and liquids $\Delta_{\mathrm{vap}}H$, another positive term, should be added.

4.2 Solvents with Gas-like Density

These systems typically have $\eta < 0.05$. The perturbation model gives:

(i) Since the fluid has very low density the probability of opening a cavity to locate the solute will be large, consequently this repulsive term will be very small.

(ii) Although this contribution is smaller than for triple-point liquids, it is of the same nature; the number of solvent molecules surrounding the solute has decreased significantly and the average solute–solvent distance has increased. Both effects will reduce the magnitude of this term compared with that in triple-point fluids.

Thus at gas-like density the dissolution of gaseous solutes and the enhancement factor for liquids and solids will be dominated by step (ii), *i.e.* $\Delta_{\mathrm{I}}\mu + \Delta_{\mathrm{II}}\mu$ will decrease with increasing temperature. For solid solutes, the term, $\Delta_{\mathrm{vap}}H$ will cause a change in the sign of the enthalpy of dissolution at low densities, generally around $\eta \simeq 0.1$.[13]

4.3 Near-critical Solvents

If the solvent were not in a region of high susceptibility, the expected behaviour would be intermediate between the two cases discussed previously (η is close to 0.15, the critical packing fraction). The perturbation model indicates:

(i) Its contribution to the chemical potential of the solute will be similar to that in a fluid far from the critical region having the same packing fraction. $\Delta_{\mathrm{I}}H$, although positive as in the two other cases, will be dominated by the divergence of the solvent's expansivity and will tend strongly to infinity.

(ii) $\Delta_{\mathrm{II}}\mu$ will be also intermediate between that for the high and that for the low density fluids, but $\Delta_{\mathrm{II}}H$ will diverge to $-\infty$ due to the dependence of the solvent density on the temperature.

For near-critical fluids $\Delta_{\mathrm{sol}}H = \Delta_{\mathrm{vap}}H + \Delta_{\mathrm{I}}H + \Delta_{\mathrm{II}}H \simeq \Delta_{\mathrm{I}}H + \Delta_{\mathrm{II}}H$ will depend on the relative weight of the attractive and repulsive interactions: typically solids and liquids will show negative values $\Delta_{\mathrm{sol}}H$ in near critical solvents, while for gases they will be positive. In either case the absolute values of ΔH are anomalously large.

Figure 6 depicts the change with temperature of the isobaric solubility for a solid in the three density regions. When ρ_1^* is close to ρ_{c1} the temperature dependence of the isobaric solubility is

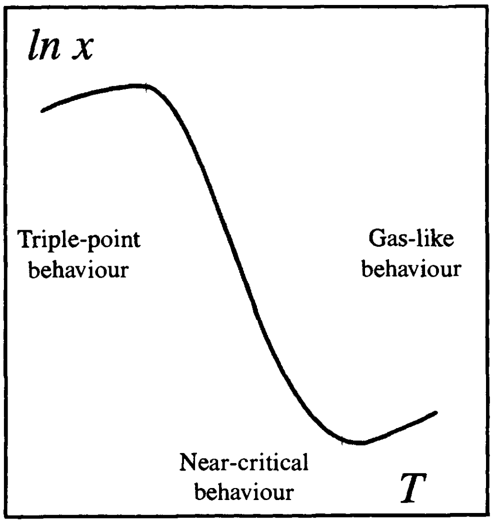

Figure 6 Scheme of the temperature dependence of the isobaric solubility of a solid solute throughout the three fluid regions.

complicated because a change in temperature at constant pressure will strongly affect ρ_1^* and the solute properties are dominated by the solvent density, thus the solubility will *decrease* with increasing temperatures for near-critical conditions implying that $\Delta_{\mathrm{sol}}H < 0$. The change of sign of $\Delta_{\mathrm{sol}}H$ with ρ_1^* does not imply a change in the nature of the solvent–solute interactions with density, it is due to the strong density dependence of the enthalpy of cavity formation. On the other hand, for a solid solute an increase of temperature at very low density must lead to an increase of solubility because the solute's vapour pressure increases.

According to equation 1, the thermodynamic description of near-critical behaviour in dilute solutions may be conveniently formulated in terms of a contribution related to the solvent's susceptibility which tends to diverge, and contributions arising in the specific solute–solvent interactions. The latter are governed by $(\partial p/\partial x)_{V,T}^{\infty}$, a quantity whose sign reflects the volatility of the solute compared to that of the solvent and does not diverge; moreover this important quantity is directly related to V_2^{∞} and S_2^{∞}; thus equation 1 gives for $X = A$,

$$\mu_2(T,p,x) = \mu_1(T,p,x) + A_x \qquad (4)$$

which by proper differentiation yields,

$$V_2^{\infty} = V_1^*\left[1 + \kappa_{T1}^*\left(\frac{\partial p}{\partial x}\right)_{T,V}^{\infty}\right] \qquad (5)$$

$$S_2^{\infty} = S_1^* - A_{xT} + V_1^*\alpha_{p1}^*\left(\frac{\partial p}{\partial x}\right)_{T,V}^{\infty} \qquad (6)$$

where α_{p1}^* is the isobaric expansivity of the solvent. Equation 5 shows that it is important to measure V_2^{∞} since it is only related to the two factors which model the behaviour of dilute near-critical solutions. According to equations 4—6 thermodynamics leads naturally to a separation of the diverging factor from the well-behaved factors which contribute to the properties. Figure 7 illustrates the effect of intermolecular parameters upon V_2^{∞}/V_1^* at different densities calculated with the Percus–Yevick approximation.[14] It may be observed that the *sign* of the partial molar volume of the solute changes with solvent density, moreover at low density V_2^{∞} becomes more negative for bigger solutes, as discussed below (*cf.* equation 10) this is a typical gas-like feature.

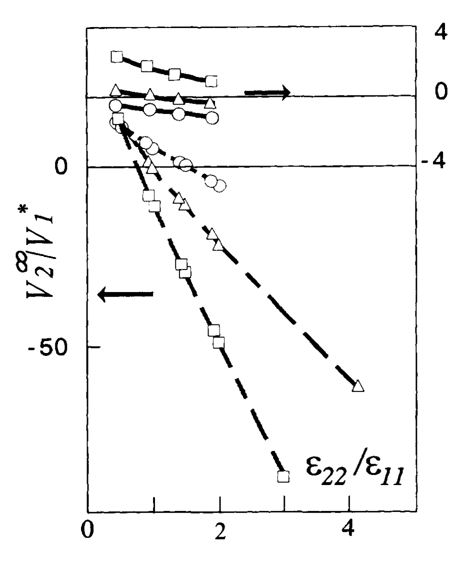

Figure 7 (V_2^{∞}/V_1^*) against the ratio of solute to solvent intermolecular energies $(\epsilon_{22}/\epsilon_{11})$.
(ρ_1^*/ρ_{c1}): 2.4, full curves; 1.05, dashed curves.
$(\sigma_{22}/\sigma_{11})$: 1.5, □; 1.0, △; 0.5, ○.

4.4 Microscopic Interpretation

An imaginative, albeit somewhat misleading terminology has been coined to describe the *not-to-be-expected* behaviour of solutions, including near-critical behaviour, *e.g.* hydrophobic hydration, frustration effect, charisma, critical clustering, and critical local-density enhancement. This terminology frequently reflects our lack of a thorough understanding of the phenomena. In particular, the unusual behaviour of near-critical systems have stimulated speculation about the meaning of partial molar properties diverging to plus or minus infinity; a dramatic change of solvent density around the solute molecules has been proposed to explain it.

In order to inquire into the structure of the solutions it is important to use the pair distribution function $g_{ij}(r; T,\rho)$, a quantity which is central to modern theories of liquids.[15] $g_{ij}(r; T,\rho)$ is proportional to the probability of finding a particle i at a distance r from particle j. As indicated in Figure 8 it contains the short-range structural information typical of a liquid. This figure also shows $g_{ij}(r; T,\rho)$ for a gas and for a crystalline solid.

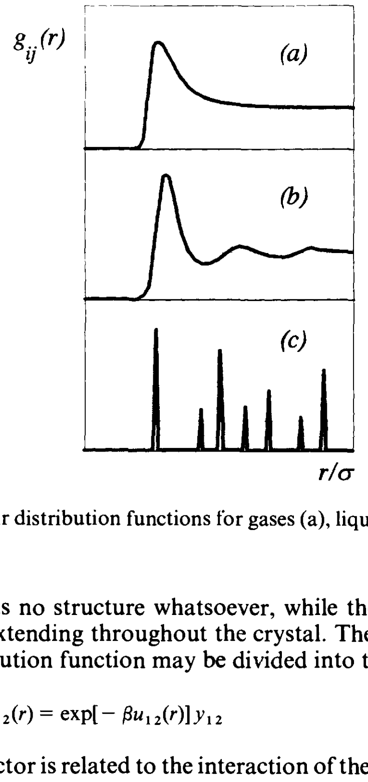

Figure 8 Pair distribution functions for gases (a), liquids (b), and solids (c).

The gas has no structure whatsoever, while the solid shows a structure extending throughout the crystal. The solute–solvent pair distribution function may be divided into two terms.

$$g_{12}(r) = \exp[-\beta u_{12}(r)]\,y_{12} \qquad (7)$$

The first factor is related to the interaction of the two particles *in vacuo* while y_{12}, known as the cavity distribution function,[11] reflects all indirect interactions between particles 1 and 2, and will be strongly dependent on fluid density. When the fluid density goes to zero,

$$\lim_{p\to 0} g_{12}(r) = \exp[-\beta u_{12}(r)] \qquad (8)$$

(*cf.* Figure 8a) and the cavity distribution function becomes unity, the whole process of dissolution from the gas phase will then be dominated by the attractive solute–solvent interaction energy. For dilute gaseous mixtures this is conveniently reflected by the cross second virial coefficient, B_{12}, which is related to the intermolecular solvent–solute interaction energy by,

$$B_{12} = -\tfrac{1}{2}\int[\exp(-\beta u_{12}(r)) - 1]\mathrm{d}V \qquad (9)$$

Hence B_{12} is related to the pair correlation function in the limit of vanishing total density where indirect correlations between molecules 1 and 2 are negligible.

Second virial coefficients may be expressed in terms of the reduced temperature $T_{\mathrm{R}} = kT/\epsilon_{12}$ by,[16]

$$B_{12}(T_R;\sigma_{12}) = A\sigma_{12}^3 B_{12}^*(T_R) \tag{10}$$

For slightly volatile solids B_{12}^* will be negative because of the strong solute intermolecular energy, *i.e.* low T_R. Since according to equation 10, B_{12} is proportional to the cube of the solute–solvent contact length, σ_{12}, it will be more negative for larger solutes. This gas-like feature is already observed at near-critical densities, as illustrated by Figure 7.

Pair distribution functions facilitate distinguishing between long-range effects, which cause the enhanced susceptibility in the near-critical fluid, and short-range effects shaped by the intermolecular interactions plus the decreasing fluid density. Many thermodynamic properties are related to integrals which contain the pair correlation function,[17] so they will tend to diverge when $g_{ij}(r)$ has a long-range tail. This situation has frequently been interpreted as a very large excess or defect of solvent molecules around the solute particle, but really there is no evidence of *critical clustering* around the solute. Figure 9 shows the total correlation function $h_{ij}(r) = (g_{ij}(r) - 1)$ for a model Lennard–Jones mixture according to the Percus–Yevick approximation.

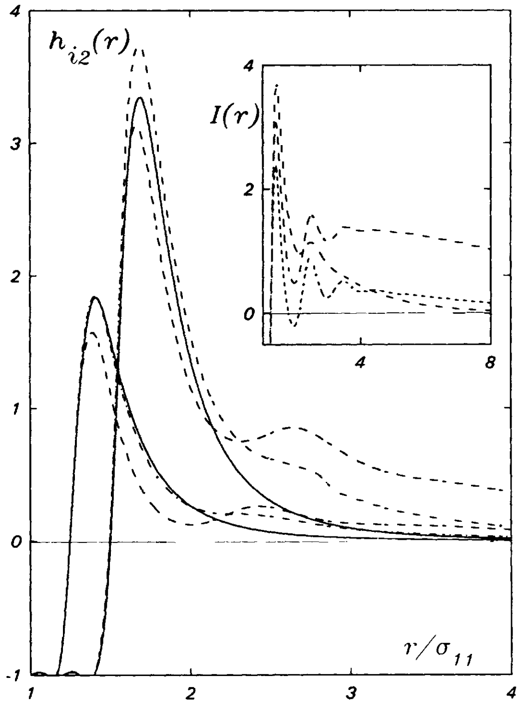

Figure 9 Total correlation functions against the distance from a solute molecule. Lower curves, $i = 1$; higher curves, $i = 2$. The inset gives the quantity $I(r) = r^2h_{12}(r)$.
(ρ_1^*/ρ_{c1}) is 0: ——, 0.33: —·—·—, 1.02: – – – –, 1.33: - - - - -.
$\epsilon_{22}/\epsilon_{11} = 2.0$; $\sigma_{22}/\sigma_{11} = 1.5$; $kT/\epsilon_{11} = 1.36$; $T/T_{c1} = 1.031$

It is evident that the number of first neighbours of the solute is not too much affected by the vicinity of the critical point, its long range tailing-off being its most notable feature and the reason for the divergence of the integral of $h_{ij}(r)$ taken over all the system.

For the case of gases, *i.e.* ($\rho_1^* \rightarrow 0$), $h_{ij}(r)$ has a single peak and is short-ranged, according to equation 9 its integral is equal to $-2B_{ij}$. As the density increases, indirect interactions become more important, giving rise to an incipient increase of $h_{ij}(r)$ beyond the first peak, as shown in Figure 9. The fact that the first peak of $h_{22}(r)$ is higher than that of $h_{12}(r)$ is due to the stronger solute–solute interactions.

The relative excess fraction of particles *i* surrounding a central *j* molecule, f_{ij}^{ex},[5] is a relevant quantity to establish the existence of *critical clustering*, it is defined by,

$$f_{ij}^{ex} = \frac{\int_{\sigma_{ij}}^{R^{\max}} (g_{ij}(r) - 1)\,\mathrm{d}V}{\int_{\sigma_{ij}}^{R^{\max}} \mathrm{d}V} \tag{11}$$

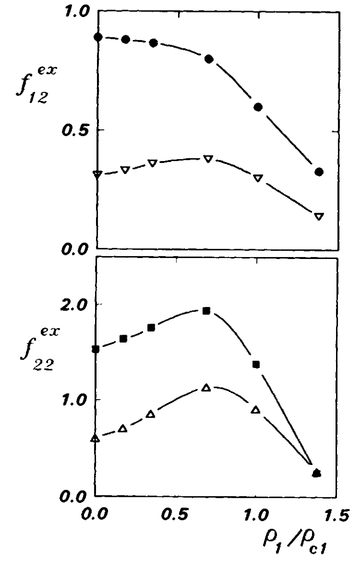

Figure 10 f_{12}^{ex} as function of the reduced density. Full symbols, first neighbours; open symbols, second neighbours.

Figure 10 shows the effect of solvent density upon f_{ij}^{ex} for two different choices of $R_{\max}$: (a) corresponding to first neighbours ($R_{\max} = \sigma_j/2 + \sigma_{ij}$), and (b) also including neighbours separated by a solvent molecule. As illustrated in Figure 10, f_{ij}^{ex} passes through a sharper maximum for the (2–2) case than for (1–2); the (1–2) interaction does not even show a maximum for the smallest value of $R_{\max}$. For the (2–2) case, the maximum occurs at a density *lower* than the critical density, reinforcing the conclusion that the *short-range* microstructure is not coupled with the long-range critical fluctuations.[18]

The maxima in the curves are due to indirect interactions, hence an incipient manifestation of a characteristic feature of dense fluids. Since the solute or co-solvent[+] molecules have $\epsilon_{i2} > \epsilon_{12}$, at low density $f_{i2}^{ex} > f_{12}^{ex}$; as the solvent density increases, its molecules will occupy positions close to the central solute. The solvent moiety surrounding the central solute particle provides a region where more solute or cosolvent may be preferentially attached. This incipient microheterogeneity can explain the role of co-solvents in enhancing the solubility of solutes.

5 Near-critical Behaviour of Dilute Solutions

From the discussion in the preceding sections, a general picture of the critical state of dilute solutions emerges. Anomalies in the susceptibility of the pure solvent, (*e.g.* κ_1^* or C_{p1}^*) driven by long-ranged, long-lived fluctuations which reflect the solvent's critical state, produce diverging partial molar properties of dilute solutes. A short-ranged microstructure, which depends upon the solute–solvent interactions is superimposed on the long-range fluctuations.

Statistical thermodynamic models, which were very successful in describing the properties of liquids and gases with the proper physical insight, have difficulties in including the effect of long-range fluctuations for the correct description of the thermodynamic properties of near-critical systems. However, for the basic understanding of the processes which occur and for the design and control of several technological applications, a correct description of supercritical fluids is of fundamental importance.

5.1 Asymptotic Behaviour

Most of the processes involving supercritical fluids occur in dilute solutions subjected to phase and/or chemical equilibria:

[+] The co-solvent is a substance added to increase the solubility of the solutes at concentrations which usually are close to 1%

extraction, chromatography and chemical reactions in supercritical fluids. Equation 4 shows that the solute and the solvent chemical potentials are related through the derivative of the Helmholtz energy with respect to composition, A_x. The solute's chemical potential may be expressed by,

$$\mu_2(T,p,x) = \mu_2^{\infty}(T,p) + RT\ln x\gamma_2 = \mu_2^{\ominus}(T) + RT\ln\frac{xp\Phi_2}{p^{\ominus}} \qquad (12)$$

where Φ_2 and γ_2 are the solute's fugacity and activity coefficients respectively. The solute's standard state may be chosen either as the ideal gas, $\mu_2^{\ominus}(T)$, or as the infinitely dilute (Henry) solution, $\mu_2^{\infty}(T,p)$.

Since near-critical systems show unusual behaviour it is extremely helpful to have exact asymptotic relationships as guides for the description of the properties in the neighbourhood of the critical point. For this purpose A_x in equation 4 is expanded in a Taylor series around the solvent critical point (classical description).[10] Thus $\mu_2^{\infty}(T,p)$ is given by,

$$\mu_2^{\infty}(T,p) = \mu_1^{\star} + A_x^c + A_{xV}^c\delta V + A_{xT}^c\delta T + \cdots \qquad (13)$$

Even in the critical region $\mu_1^{\star}$ is a well-behaved function, hence when the path is isothermal or corresponds to the coexistence of two phases, the leading term in the expansion is the δV term and an asymptotic linear dependence of μ_2^{∞} on solvent volume or density results,

$$\mu_2^{\infty}(T,p) \approx \mu_2^{\infty,c} - \frac{A_{xV}^c}{\rho_{c1}^2}\delta\rho \qquad (14)$$

The validity of this expression for the description of the liquid–vapour phase equilibrium in dilute solution has been tested with the solute partition constant, K_D^{∞}, defined by,

$$K_D^{\infty} = \lim_{x\to 0}\frac{y}{x}$$

where y is the solute mole fraction in the vapour phase. The condition for liquid–vapour equilibrium $\mu_2(\mathrm{l}) = \mu_2(\mathrm{v})$, determines that

$$RT\ln K_D^{\infty} = \mu_2^{\infty}(\mathrm{l}) - \mu_2^{\infty}(\mathrm{v})$$

which, combined with equation 14, yields

$$RT\ln K_D^{\infty} = -\frac{A_{xV}^c}{\rho_{c1}^2}[\rho_1^*(\mathrm{l}) - \rho_1^*(\mathrm{v})] \qquad (15)$$

or the asymptotically equivalent expression,

$$RT\ln K_D^{\infty} = -\frac{2A_{xV}^c}{\rho_{c1}^2}[\rho_1^*(\mathrm{l}) - \rho_{c1}] \qquad (16)$$

For several binary systems, equation 16 was shown to apply over an unexpectedly wide temperature range. Figure 11 shows that the linear relationship between $T\ln K_D^{\infty}$ and $[\rho_1^*(\mathrm{l}) - \rho_{c1}]$ holds over 150 K for some aqueous systems. The range of validity of the linear equation 16 will depend on the magnitude of the solvent–solute interactions, *i.e.* on $A_{xV}^c = -(\partial p/\partial x)_{T,V}^{\infty}$; the approximation of using only the first term in expansion 13 will be more valid when the pressure change with composition is bigger.

It should be noted that equation 14 correctly predicts that the standard partial molar volume and entropy of the solute (equations 5 and 6) will diverge at the critical point of the solvent similar to the derivatives of ρ_1^* with pressure and temperature. The sign of the divergence will be that of $-A_{xV}^c$. Equation 14 can also be used to describe the asymptotic solubility of solids in a near-critical solvent. In that case, phase equilibrium implies that,

$$\mu_2^*(\mathrm{s}) = \mu_2(\mathrm{sln})$$

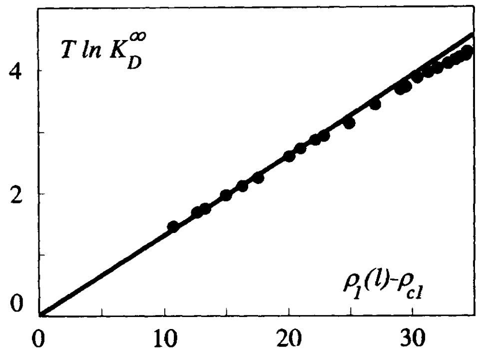

Figure 11 $T\ln K_D^{\infty}$ against the $(\rho_1(l) - \rho_{c1})$ for the partition of N_2 between liquid and vapour H_2O. Experimental points from ref. 19.

and

$$\mu_2^{\ominus} + RT\ln\left(\frac{f_2^*}{p^{\ominus}}\right) + \int_{p_2^*}^{p} V_2^*(\mathrm{s})\mathrm{d}p = \mu_2^{\infty,c} - \frac{A_{xV}^c}{\rho_{c1}}[\rho(l) - \rho_{c1}] + RT\ln(x\gamma_2)$$

where f_2^* is the fugacity and $V_2^*(\mathrm{s})$ the molar volume of the pure solid. For dilute solutions (sparingly soluble solids) $\gamma_2(x \to 0) = 1$ and the last term in the left-hand side member may be neglected, and the solubility can therefore be expressed as

$$RT\ln x = (\mu_2^{\ominus} - \mu_2^{\infty,c}) + RT\ln\left(\frac{f_2^*}{p^{\ominus}}\right) + \frac{A_{xV}^c}{\rho_{c1}^2}[\rho(\mathrm{l}) - \rho_{c1}]$$
$$= f(T) + \frac{A_{xV}^c}{\rho_{c1}^2}\rho(\mathrm{l}) \qquad (17)$$

where by $f(T)$ we denote a well-behaved and slowly varying function of the temperature. On the other hand, from equation 3 we have,

$$RT\ln\mathcal{E} = (\mu_2^{\ominus} - \mu_2^{\infty,c}) + \frac{A_{xV}^c}{\rho_c^2}[\rho(l) - \rho_{c1}] + RT\ln\left(\frac{p}{p^{\ominus}}\right)$$
$$= g(T) + \frac{A_{xV}^c}{\rho_{c1}^2}\rho(\mathrm{l}) + RT\ln\left(\frac{p}{p^{\ominus}}\right) \qquad (18)$$

Once more the second term dominates and for non-volatile solid solutes in common solvents $A_{xV}^c > 0$, hence the solubility and $\mathcal{E}$ *increase* with increasing solvent density. This is illustrated in Figure 12 for the system $Xe-I_2$.[20] Solutes with large A_{xV}^c appear to be more soluble, but the contribution of its vapour pressure, given in equation 17 by f_2^*, may dominate the magnitude of the relative solubility of different solutes. This is not the case for $\mathcal{E}$ which will always increase with A_{xV}^c. Equations 17 and 18 show that in a near-critical solvent the solubility and the enhancement factor are well-behaved functions of the solvent's density albeit strongly affected by changes in pressure and temperature. In other words, because supercritical fluids are very compressible, small changes in pressure result in large variations of their solvent power. A relatively high dissolution capacity and strong response to external perturbations are two important features of solutes in supercritical fluids.

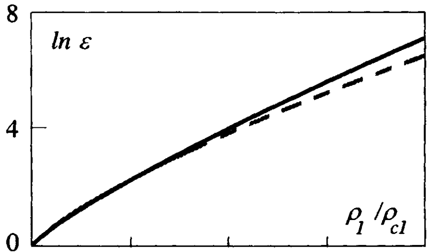

Figure 12 $\ln\mathcal{E}$ for I_2 against the reduced density of xenon. Full curve, isothermal run $(T/T_{c1}) = 1.031$; dashed curve, isobaric run $(p/p_{c1}) = 1.23$.

6 Chemical Reactions in Near-critical Fluids

Critical phenomena, characterized by a high susceptibility due to long-lived, long-ranged fluctuations, can strongly influence chemical kinetics and equilibrium. The effect on the kinetics of reaction could be expected to be twofold. Critical phenomena are characterized by a slowing down of most transport properties,[21,22] hence reaction rates may drop to zero at a critical point. On the other hand, near-critical dilute solutions exhibit anomalies in the temperature and pressure dependence of the reaction rate constant k which are related to the enthalpy and volume of activation respectively.

The first effect[21] would be related to the fact that near a critical point the rate of equalization of the density (concentration) gradients by diffusion is markedly reduced. Since the driving force for diffusion, $(\partial\mu/\partial x))_{pT}$, is very small (it actually equals zero at the critical point) the system becomes *indifferent* to changes in density (concentration) near a critical point.[22] When the reaction occurs at constant fields this would reduce the rate of reaction, which is proportional to the restoring force $(\partial\mathscr{A}/\partial\xi)$ defined in terms of the affinity $\mathscr{A} = -\sum\nu_i\mu_i$.

The second effect has been observed in many dilute near-critical systems. Examples are the decomposition of α-chlorobenzyl methyl ether in 1–1 difluoroethane[23] where, even 16 K away from the solvent critical point, the rate constant increased 20 times when the pressure changed from 4.5 to 6.9 MPa, implying an activation volume of − 6.0 dm^{3}mol^{-1}; or the spin–exchange reaction between very dilute nitroxide free radicals in C_2H_6 close to the diffusion limit, where the rate constant decreases by a factor of 4 to 5 when pressure increases from 4 to 5 MPa (activation volumes of 7.5 dm^{3}mol^{-1}).[24]

The effect of criticality on chemical equilibrium is better understood. For example, the chemical equilibrium condition when p changes along an isothermal path is,

$$\mathrm{d}\mathscr{A} = (\partial\mathscr{A}/\partial p)_{T\xi Y}\mathrm{d}p + (\partial\mathscr{A}/\partial\xi)_{TpY}\mathrm{d}\xi = 0$$

where, together with T, other variables denoted by Y may be kept constant. The pressure derivative of the equilibrium extent of reaction is then,

$$\left(\frac{\partial\xi}{\partial p}\right)_{TY}^{\mathrm{eq}} = \frac{1}{RT(\partial\mathscr{A}/\partial\xi)_{TpY}}\sum\nu_i V_i$$

Equivalently, for the isobaric path

$$\left(\frac{\partial\xi}{\partial T}\right)_{pY}^{\mathrm{eq}} = -\frac{1}{RT(\partial\mathscr{A}/\partial\xi)_{TpY}}\sum\nu_i S_i$$

There are two possible reasons for $(\partial\xi/\partial p)^{\mathrm{eq}}_{TY}$ (or $(\partial\xi/\partial T)^{\mathrm{eq}}_{pY}$) to diverge:

$\sum\nu_i V_i = \Delta_r V$ ($\sum\nu_i S_i = \Delta_r S$) may diverge. If the reactants and the products are at infinite dilution in a near-critical, almost pure, solvent, V_i and S_i will diverge to plus or minus infinity (depending on the interaction with the solvent), making $\Delta_r V$ and $\Delta_r S$ diverge. This effect has been reported extensively. As an example, the equilibrium constant for the tautomerization of 2-hydroxypyridine into 2-pyridone in 1,1-difluoroethane at $\delta T = 16$ K increased by a factor 2 due to a pressure change from 4.5 to 5.9 MPa (volume change of reaction − 1.4 dm^{3}mol^{-1}).[25]

If the change in pressure occurs while none of the other Y variables that are kept constant are densities, then $(\partial\mathscr{A}/\partial\xi)_{TpY}$ tends to zero while the critical conditions are approached. In the case of binary mixtures in a single phase having 3 degrees of freedom with frozen chemical equilibrium or 2 degrees of freedom if equilibrium is allowed, only one variable needs to be fixed, the temperature. In that case, divergence of the isothermal pressure dependence of the extent of reaction should be observed only under conditions where criticality can be encountered for this system, *i.e.* at the critical point. For systems having three or more components, additional variables need to be fixed; only those paths corresponding to constant activities (or chemical potentials) are expected to exhibit strong anomalies. To date there is no reliable evidence of strong anomalies in multicomponent systems. Weak anomalies have been reported, *e.g.* for the degree of dimerization of NO_2 near the liquid–liquid critical point of the solvent system perfluoromethylhexane–carbon tetrachloride, the observed effect being very small (about 4%).

7 Some Applications of Near-critical Fluids

The peculiar combination of equilibrium and transport properties which has been described, constitutes the reason for the successful applicaton of supercritical fluids in many processes.

7.1 Supercritical Fluid Chromatography (SFC)[27]

Gas chromatography is not well-suited for the separation of thermally unstable compounds or of non-volatile solids which have a very low concentration in the gas phase. On the other hand, high-performance liquid chromatography has the disadvantage of a poorer resolution because the higher liquid viscosity restricts the length of the columns and the low diffusivity implies wider chromatographic peaks. In SFC, the solute partitions between a mobile supercritical fluid phase and a stationary phase. The distribution coefficient, and therefore the retention time, will depend smoothly on the density of the supercritical fluid and the separation of solutes can be performed by controlling this variable easily. Other chemical parameters, like the presence of co-solvents, may be manipulated to improve the separation performance in SFC.

7.2 Supercritical Fluid Extraction (SFE)[28]

This is another technological application that takes advantage of the strong T and p dependence of the solubility in near-critical solvents. In this process the solvent fluid changes its density and consequently its capacity for dissolution. The adjustment of the thermodynamic variables (temperature, pressure, or co-solvent concentration) can result in changes of orders of magnitude in the solubility as the density changes between the stages of dissolution and that of separation, thus improving extraction yields. Reprecipitation of extracted products can be achieved easily and with fine control of the variables to facilitate the separation steps.

The two best known examples of technological application of SFE, are the extraction of caffeine from green coffee beans and of hops in the beer industry. Also becoming increasingly important are the extraction of essential oils (terpenes among the more soluble), natural flavours, and fragancies. These are mostly employed by the food and pharmaceutical industries. It is also used to eliminate impurities and regenerate activated charcoal filters.

In most of these processes of SFE the solvent employed is CO_2 since it is neither toxic for industrial manipulation nor contains hazardous impurities which might be incorporated into the purified products. Moreover CO_2 is environmentally safe. Its critical temperature is close to room temperature (304.2 K), an important advantage for processes applied to thermolabile substances, it is inexpensive and non-flammable. The use of co-solvents, can greatly improve the selectivity and efficiency of the SFE process.

7.3 The Synthesis of Fine and Ultrafine Powders

This process takes advantage of the very large difference in solvent power of near-critical fluids produced by moderate changes in its temperature and pressure. It is similar to SFE, but the interest is now centered in the reprecipitation stage: a supercritical solution is suddenly expanded as it flows through a nozzle and during its expansion the fluid may attain supersonic velocities. The abrupt reduction of the medium's solvent capacity leads to the formation of very small monodisperse particles of solid solute A good control of the pre- and post-expansion variables (pressure and temperature) and of the solute concentration determine the size and morphology of the crystalline or amphous solids that precipitate The technological applications[29] of this new process are oriented towards very specific areas, like biotechnology (production of bioerodible polymeric microspheres and microparticles for controlled drug release) or materials science (production of ultrafine ceramic precursor powders, pure or intimately mixed)

7.4 Use of Near-critical Fluids as Media for Chemical Reactions

Diffusion-controlled reactions exhibit reaction rates several orders of magnitude higher than in normal liquids because in supercritical fluids typical viscosities are around 0 01 mPa s, *i e* one hundred times smaller than that of typical liquids The advantage of supercritical fluids arises from the combination of liquid-like solvent capacity (higher concentration of reactants) and gas-like transport properties (higher rate constants) Moreover rate constants may be strongly modified by moderate changes of the state variables

Not only the kinetics of the reactions can be precisely controlled in supercritical fluids, equilibrium properties also are strongly affected by the solvent conditions For reactions having more than one possible reaction path involving different products, the change in the solvent properties will affect the type of intermediate species which are formed by reaction, thus modifying the yield of the various possible products This feature is dramatically enhanced when the supercritical fluid solvent is water [30] as solvent density is increased, the increasing dielectric constant preferentially stabilizes ionic intermediate species over radicals, with the concomitant change in the reaction mechanism Examples can be found in the pyrolysis of coal model compounds and in the processes of catalytic and non-catalytic oxidation and dehydration in supercritical water

Other technologically interesting processes of chemical reactions in supercritical fluids include enzymatic reactions (like the oxidation of steroids, virtually insoluble in liquid water, in supercritical CO_2), oxidation of hazardous materials in supercritical water, and catalysed heterogenous reactions, where the catalyst deactivation can be avoided by the interplay of solvation power and mass-transfer properties

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