INTERNATIONAL UNION OF PURE AND
APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON THERMODYNAMICS

NOMENCLATURE FOR PHASE DIAGRAMS WITH PARTICULAR REFERENCE TO VAPOUR–LIQUID AND LIQUID–LIQUID EQUILIBRIA

(Technical Report)

Prepared for publication by

ANDREAS BOLZ,[1] ULRICH K. DEITERS,[1]
COR J. PETERS[2] AND THEO W. DE LOOS[2]

[1] Institute for Physical Chemistry, University at Cologne, F.R. Germany
[2] Laboratory of Applied Thermodynamics and Phase Equilibria, Delft University of Technology, the Netherlands

Nomenclature for phase diagrams with particular reference to vapour–liquid and liquid–liquid equilibria (Technical Report)

Abstract: The phase diagrams of binary fluid mixtures are classified with regard to the topology of their critical curves and three-phase curves. A new nomenclature for the phase diagram classes is proposed, which can be applied to the previously known as well as to recently discovered phase diagram classes. The class names of the new nomenclature are systematic and descriptive; the *(P,T)* projection of a binary fluid phase diagram can always be constructed qualitatively from the class name.

INTRODUCTION

Phase equilibria in binary systems are usually depicted graphically in pressure, temperature, composition *(P,T,x)* space, in *(P,T)* and *(T,x)* projections or in isothermal *(P,x)* sections, isobaric *(T,x)* sections and in constant composition *(P,T)* sections, so called isopleths. In these diagrams the different types of phase equilibria are represented by areas, curves or points. Some of these equilibrium states are characterized by special values of thermodynamic variables and will be referred to as special states. In the scope of this work a special state or point is defined as a state or point where

1. Either a phase is added or disappears.

2. Where the composition of two phases become identical.

The composition of two phases can become identical in three different ways (Rowlinson & Swinton, 1982). The curves representing the composition of two coexisting phases can intersect at $x = 0$ or $x = 1$. This is shown in Fig. 1a, which shows a vapour-liquid equilibrium gl where the curve that represents the composition of the liquid phase l intersects the curve for the vapour phase g in the boiling points of both pure components. Also these curves can merge in a horizontal tangent point $(\partial T/\partial x)_p = 0$ or $(\partial P/\partial x)_T = 0$. This type of special point is a critical point, where not only the composition but all thermodynamic properties of the two phases become identical. A diagram with a critical point is shown in Fig. 1b. The third possibility is that the two curves have a common horizontal tangent. In this case only the compositions of the two phases are equal, but not the other thermodynamic properties. An example is an azeotropic point (Fig. 1c).

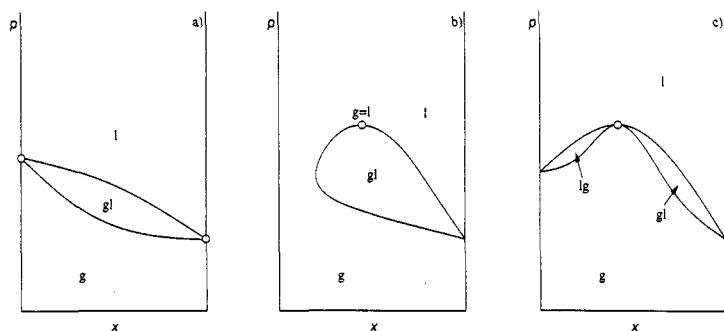**Fig. 1.** Three cases where the compositions of the two phases of a two-phase equilibrium are equal. (a) Pure component boiling points. (b) Critical point g = l. (c) Azeotropic point $(gl)_{az}$.

In literature and text books many confusing terms are used to describe special states of binary fluid mixtures. People working in the field of fluid phase equilibria feel a need for one specific term for these

special states. The only existing systematic nomenclature is that of Griffiths (1975), which is not detailed enough and which is hardly ever used.

Closely related to this problem is the nomenclature for fluid phase diagram classes. In the last decades many new types have been discovered from mathematical analysis of computational models (Furman *et al.*, 1977; Mazur *et al.*, 1984; Mazur *et al.*, 1985; Boshkov & Mazur, 1986; Boshkov, 1987; van Pelt *et al.*, 1991), which can not be classified in a logical way by extension of the classification scheme of van Konynenburg & Scott (1980), which is discussed extensively in Rowlinson & Swinton (1982). In this case there is the need for a general classification scheme, which can be used to classify the known types of fluid phase behaviour and which is flexible enough to include today unknown types of fluid phase behaviour.

In this paper a new nomenclature for phase diagram classes of binary fluid mixtures is presented and recommendations for nomenclature for special states of these mixtures are given. Also recommendations for the graphical representation of these special states are included.

NOMENCLATURE FOR SPECIAL STATES OF FLUID MIXTURES

According to the phase rule, which reads for a non reacting system with N components

$$F = N - \Pi + 2 - \phi$$

the phase behaviour of a binary system can be represented in a three-dimensional pressure, temperature, composition (P,T,x) space. Π is the number of phases in equilibrium, F is the number of degrees of freedom and ϕ is the number of extra relations that hold in a special state. Usually for the composition variable the mole fraction x is used. Different types of phase equilibria in binary systems and their representations in (P,T,x) space are given in Table 1. In the example of the critical point in Fig. 1b $\Pi = 1$ and $\phi = 2$ and in the example of the azeotropic point in Fig. 1c $\Pi = 2$ and $\phi = 1$. For a binary system the maximum number of phases in equilibrium is four, the minimum number of degrees of freedom is zero.

Since it is tedious to draw three-dimensional diagrams in perspective, it is common practice to use two- dimensional sections and projections of the (P,T,x) space to represent the phase behaviour of a binary system. Sections at constant temperature are called (P,x) sections, at constant pressure (T,x) sections and at constant composition (P,T) sections or isopleths. Among the projections, the projection on the (P,T) plane, the (P,T) projection, is the most common. Of course, the sections and projections do not contain the complete information of the (P,T,x) space, e.g., in projections only information on nonvariant $(F = 0)$ and monovariant $(F = 1)$ equilibria can be found.

Table 1. Phase equilibria in binary systems and their representation in (P,T,x) space, with $x = x_2$, Π is the number of coexisting phases and F the number of degrees of freedom according to the phase rule.

		Representation in (P,T,x)	Examples
$\Pi = 1$	$F = 3$	region	$s_1, s_2, l, g, l_1, l_2, s$
$\Pi = 2$	$F = 2$	two surfaces: $x^\alpha(P,T)$; $x^\beta(P,T)$	gl, s_1l, l_1l_2
$\Pi = 3$	$F = 1$	three curves: $x^\alpha[P(T)]$; $x^\beta[P(T)]$; $x^\gamma[P(T)]$	s_1gl, s_1ls_2, l_1gl_2
critical curve $\Pi = 1$	$F = 1$	$x^c[P(T)]$	$g = l, l_1 = l_2$
azeotropic curve $\Pi = 2$	$F = 1$	$x^{az}[P(T)]$	
$\Pi = 4$	$F = 0$	four points at one P and T	s_1gls_2, gl_1l_2s
critical endpoint $\Pi = 2$	$F = 0$	two points at one P and T	$g(l_1 = l_2), (g = l_1)l_2,$ $s(g = l)$
critical azeotrope $\Pi = 1$	$F = 0$	one point	

The variables P and T and the variable x are of a different nature (Griffiths & Wheeler, 1970). P and T are "field" variables, variables that have the same value for all coexisting phases and the mole fraction x is a "density" variable, a variable which has in general a different value from phase to phase. Phase diagrams can also be represented in graphs using only fields as variables. This is not common practice,

but it has the advantage that the phase diagram only shows the intrinsic features of the phase behaviour and not the "accidental" consequences of the choice of the coordinates (Furman *et al.*, 1977). For instance, for a three-phase equilibrium in a binary system we have $F = 1$. Such an equilibrium is represented by three curves in (P,T,x) space, because the composition of the three phases is different at one P and T, but this equilibrium is represented by one curve in a three-dimensional diagram using P, T and the chemical potential of one of the components as variables, which are all "fields".

The term *global phase diagram* has been introduced by Furman *et al.* (1977). This type of phase diagram is generated by a theory or a model, using the molecular parameters of the model as additional field variables. From this multi-dimensional global phase diagram also two-dimensional projections or sections can be constructed. An example of such a two-dimensional global phase diagram is the ζ, λ masterchart of van Konynenburg & Scott (1980) for constant ξ. These authors used the van der Waals equation of state with

$$\zeta = (a_{22}/b_{22}^2 - a_{11}/b_{11}^2)/(a_{22}/b_{22}^2 + a_{11}/b_{11}^2)$$

$$\lambda = (a_{11}/b_{11}^2 - 2a_{12}/b_{11}b_{22} + a_{22}/b_{22}^2)/(a_{22}/b_{22}^2 + a_{11}/b_{11}^2)$$

$$\xi = (b_{22} - b_{11})/(b_{22} + b_{11})$$

as additional field variables. a_{11} and b_{11} are the pure component van der Waals constants. A region in this master chart represents one of the classes of fluid phase diagrams, which are discussed in the section *A new nomenclature for phase diagram classes of binary fluid mixtures.*

In the following we propose a nomenclature for special states in phase diagrams for binary fluid systems, which is more informative than the notation suggested by Griffiths (1975). These states will be arranged in levels. Level n means that the number of degrees of freedom according to the phase rule for states in this level is $F = (3 - n)$. A binary system with components A and B can be denoted with [A + B], [x_AA + x_BB] or [$(1 - x)$A + xB], where x is the mole fraction of component B. In this paper we will use the last notation. The states of aggregation will be denoted with g (gas or vapour), l (liquid) or s (solid), according to the IUPAC recommendations (Mills *et al.*, 1993). The distinction between gas and liquid is to some extent arbitrary. A fluid phase (i.e. gas or liquid) can be denoted with f. In binary systems more than one solid phase and more than one liquid phase can coexist. In general these phases have a different composition. A right subscript 1, 2 can be used to distinguish between these phases. In the notation for multiphase equilibria it is advised to list the phases in the order of increasing x.

Example s_1gl_1 is the recommended notation for a three-phase equilibrium with phases s_1, g, and l_1
            $(x(s_1) < x(g) < x(l_1))$.

For all states discussed in level 4 and higher the number of degrees of freedom F is negative and hence it is very unlikely that these states can be realized experimentally in a binary system. These special states are mainly of interest to theory and especially help us to understand the transitions between the various types of phase diagrams.

Level 0: volume in (P,T,x) space

For $F = 3$, $\Pi = 1$ and we are dealing with a homogeneous phase. Griffiths denoted this state with A. We advise to use s, l or g.

Level 1: area in (P,T), (P,x) or (T,x) section

For $F = 2$, $\Pi = 2$ and we are dealing with two-phase equilibria. All these states were denoted AA or A_2 by Griffiths. Again we recommend to use a more informative notation, like gs, gl, l_1l_2, or gl_1 equilibria.

Level 2: curve in (P,T) projection

In this case $F = 1$ and we are dealing either with a critical curve, with the coexistence of three phases, or with the coexistence of two phases with the same composition.

Coalescence of two phases

In our nomenclature a critical curve is denoted with C, or more specific, depending on the nature of the critical curve, with $g = 1$, $l_1 = l_2$, $l_1 = g$, etc. An upper or lower critical point is indicated with UC or LC, respectively. For instance, a lower critical (solution) temperature can be denoted with LC_P , where the subscript P means "at constant pressure", and an upper critical (solution) pressure with UC_T. The notation UC and LC defaults to UC_P and LC_p, respectively. In (P,x), (T,x) and (P,T) sections the critical state is represented by a point, for which the same nomenclature can be used. The critical state was denoted by Griffiths with B.

Coexistence of three phases

The recommended notation for a three-phase curve is gl_1l_2, l_1gl_2, s_1gl, s_1ls_2, etc., depending on the nature of the three-phase curve. The notation of Griffiths for a three-phase equilibrium is AAA or A_3.

Coexistence of two phases with the same composition

If, in case of a two-phase equilibrium, the compositions of the two phases are equal as in the case of an azeotrope, then according to the phase rule $F = 1$. We propose to use the notation $(gl)_{az}$ for the azeotropic curve in (P,T,x) space, and in (P,T) or (T,x) projection and also for the azeotropic point in (T,x), (P,x), or (P,T) sections. Further distinction can be made between a maximum pressure and a minimum pressure azeotrope. The notation used by Griffiths (A_{2az}) is too general, because similar points can be found for other phase equilibria, e.g. of sl two-phase equilibria.

Temperature or pressure maximum of an isopleth

Often the temperature maximum of the gl equilibrium in a (P,T) section is called maxcondentherm or cricondentherm and the pressure maximum maxcondenbar or cricondenbar (Rowlinson & Swinton, 1982). These points do not represent special states according to the definition.

Level 3: point in (P,T) projection, area in two-dimensional global phase diagram

Extrema of the critical curve in (P,T) projection

A pressure maximum of the critical curve in the (P,T) projection is not a special point of the critical curve. However, it brings about a special point in the (T,x) section at the pressure of the pressure maximum (see Fig. 2). In Fig. 2a on pressure increase the two-phase region $\alpha\beta$ disappears, since we are dealing with upper critical pressures. In Fig. 2b two separate two-phase regions $\alpha\beta$ join on pressure increase. Schneider (1966) used the term hypercritical point of the first kind for the pressure maximum of the critical curve for the case of Fig. 2a and hypercritical point of the second kind for the pressure maximum of the critical curve for the case of Fig. 2b. This latter point was called homogeneous double plait point by van der Waals & Kohnstamm (1927). Since the term hypercritical should be reserved for another phenomenon and we are not dealing with a double point of the critical curve, we propose simply to call a pressure maximum of the critical curve a *maximum pressure critical point*. To differentiate between the case of Fig. 2a and that of Fig. 2b, the pressure maximum of the critical curve in Fig. 2a can be called an *elliptic maximum pressure critical point* and that in Fig. 2b a *hyperbolic maximum pressure critical point.*

The critical curve can also show pressure minima and temperature maxima and minima in a (P,T) projection. Following the proposed terminology for a pressure maximum, these points can be denoted with *minimum pressure critical point, maximum temperature critical point* and *minimum temperature critical point*, if necessary with the addition *elliptic* or *hyperbolic.*

Critical phase coexisting with another (noncritical) phase: critical endpoint

A three-phase curve in a binary system involving two or three fluid phases can be terminated in a (P,T) projection by a so-called critical endpoint in case of coalescence of two fluid phases $(F = 1)$ in the presence of the third phase. The notation of Griffiths for this kind of special point is BA. The critical

endpoint can be the lower or the upper temperature limit of a three-phase curve. These endpoints are conventionally called *lower critical endpoints* or, respectively, *upper critical endpoints**. It is also possible that a critical endpoint is the low pressure or the high pressure limit of a three-phase curve.

(a)

(b)
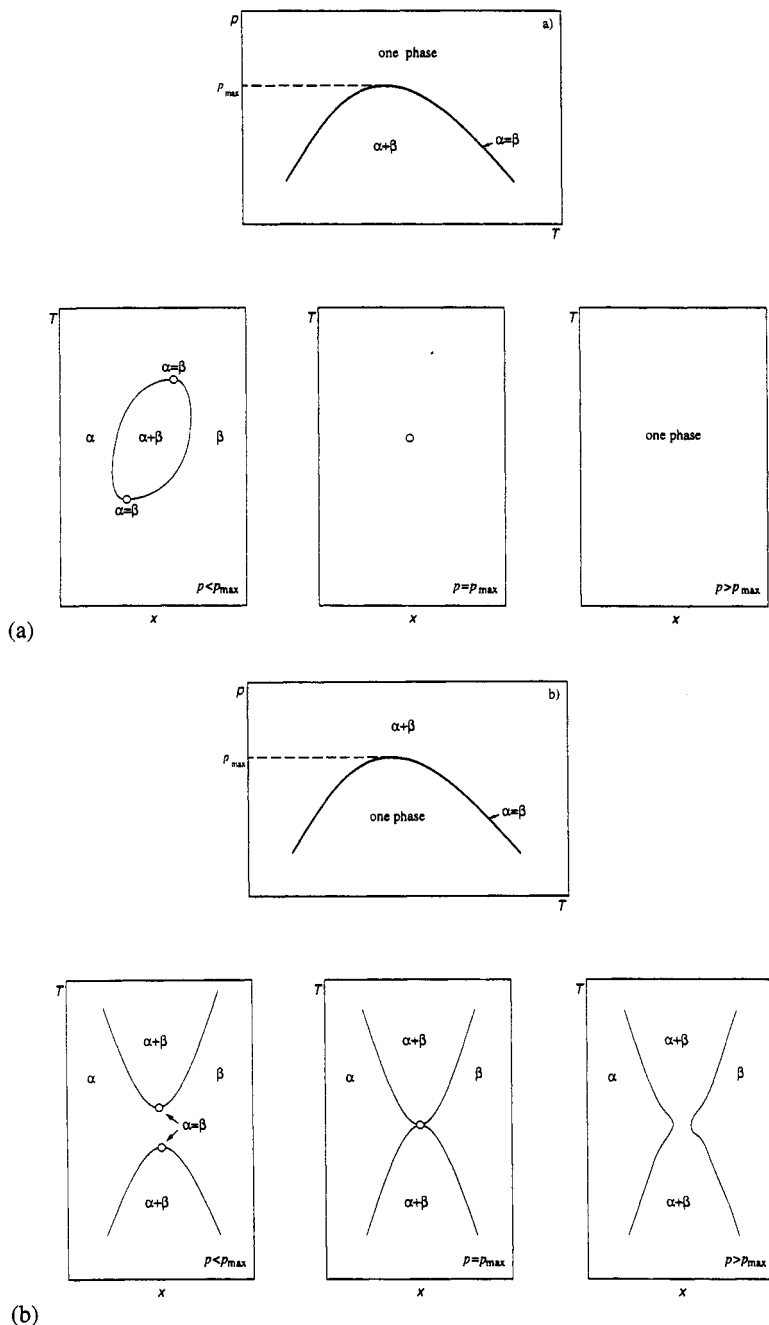
Fig. 2. A critical curve $\alpha = \beta$ with a pressure maximum. (a) Two critical points coincide such that the two-phase region disappears: an elliptic maximum pressure critical point. (b) Two two-phase regions join at the pressure maximum of the critical curve: an hyperbolic maximum pressure critical point. O: critical point.

---

*Sometimes the distinction between upper and lower critical endpoint is not clear. In these cases it is better not to make a distinction at all.

To be in line with the proposed notation for critical points we propose to denote a critical endpoint with CE. A critical endpoint which is the low-temperature limit of a three phase curve can be denoted with LCE(T) and a critical endpoint which is the high-temperature limit of a three-phase curve can be denoted with UCE(T). These critical endpoints are conventionally denoted with LCEP and UCEP, which has the disadvantage that no distinction can be made with critical endpoints that limit a three-phase curve towards low or high pressure. For these critical endpoints we propose to use LCE(P), respectively UCE(P). The notation LCE and UCE is by default the notation for a critical endpoint which limit a three-phase curve towards low or high temperature, respectively. For some types of phase diagrams the UCE(T) is denoted with K-point and the LCE(T) with L-point. This notation, which is mainly used by American authors, is non-systematic and we advise not to use it.

Examples of critical endpoints are $g(l_1 = l_2)$ and $(g = l)s_2$ equilibria.

Azeotrope coexisting with another (noncritical) phase

In the P-T projection an azeotropic curve can end on a three-phase curve. In this point, which is called *azeotropic endpoint*, the three-phase curve and the azeotropic curve are tangent. This type of point was indicated with $A_{2az}A$ by Griffiths. We propose a more informative notation, which includes the nature of the phases involved and which is in line with the proposed notation for two- and three-phase equilibria, e.g., $(gl_1)_{az}l_2$ (Fig. 3a) or $s(gl)_{az}$ (Fig. 3b).
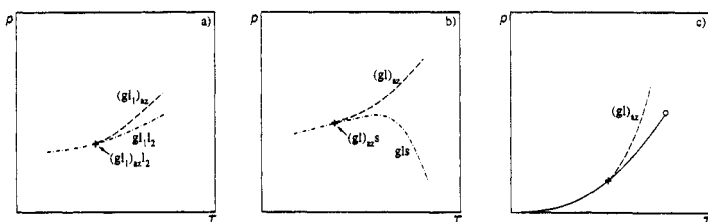

Fig. 3. Azeotropic endpoints. (a) $(gl_1)_{az}l_2$. (b) $s(gl)_{az}$. (c) Limiting azeotrope — · — — · — · —: three-phase curves; — — — — : azeotropic curves; —————: vapour pressure curve.

Coalescence of two azeotropic phases

Another possible limit of an azeotropic curve is a *critical azeotropic point* or critical azeotrope. This point is a point where the azeotropic curve is tangent to a $g = l$ curve. For this reason we propose to denote this point with $(g = l)_{az}$. Griffiths' notation for a critical azeotrope is B_{az}.

Azeotrope at x = 0 or x = 1

Furthermore an azeotropic curve can end in a tangent point on a pure-component vapour-pressure curve (Fig. 3c). This case is called a limiting azeotrope or an azeotropic boundary. If necessary this point can be denoted with $(gl)_{az}(x = 0)$ or $(gl)_{az}(x = 1)$.

Intersection (only in (P,T) projection) of pure-component vapour pressure curves

This point of intersection, which is sometimes called Bancroft-point (van Konynenburg, 1968), is only a point of intersection in the (P,T) projection and we do not recommend the use of a special notation.

Critical point on the boundary of local stability

This point is a point on the critical curve where $\partial^4 G/\partial x^4 = 0$ and it separates the stable or metastable part of the critical curve $(\partial^4 G/\partial x^4 > 0)$ from the unstable part of the critical curve $(\partial^4 G/\partial x^4 < 0)$. This point, which was named heterogeneous double plait point by van der Waals & Kohnstamm (1927), is a cusp-like double point of the critical curve in the (P,T) projection; hence, we propose to name this type

of point a *critical cusp* and denote it with CC. (See Fig. 4). Critical cusps are usually not stable, and hence cannot be observed experimentally.

Coexistence of four phases

The (P,T) projection of the four points which represent the composition of a four-phase equilibrium in (P,T,x) space is one point. This point is called *quadruple point* and in line with the conventional notation we propose to denote this point with Q. Griffiths' notation for this equilibrium is A_4. Examples are $gl_1l_2l_3$, s_1gls_2, $gl_1l_2s_2$, and $s_1l_1l_2s_2$ equilibria.
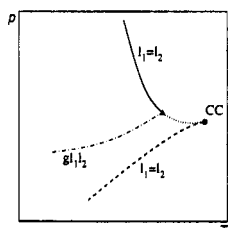
Fig. 4. A critical cusp (CC). —————: stable part of the critical curve; ·············: metastable part of the critical curve; ------------: unstable part of the critical curve; — · — — · — · —: three-phase curve; ▲: upper critical endpoint.

Level 4: line in a two-dimensional global phase diagram

Osculation point of a critical curve and a three-phase curve

The osculation point of a critical curve and a three-phase curve in a (P,T) projection is called a double critical endpoint (van Konynenburg, 1968). In this point two critical endpoints of the same nature and on different three-phase curves coincide, such that the three-phase curves are joined (see Fig. 5a). In a binary phase diagram such a situation is very unlikely to be observed experimentally $(F = -1)$. We propose to denote this equilibrium with DCE. Examples are the coincidence of two $g(l_1 = l_2)$ or two $(g = l_1)l_2$ critical endpoints.

Coincidence point of two critical endpoints of a different nature on the same three-phase curve , such that the three-phase curve collapses

This special point is a point of coalescence of three phases. It can also not be realized in a binary system and is called (unsymmetrical) *tricritical point*. The notation of Griffiths for such a point is C. Because we propose to denote an ordinary critical point with C, we propose to use the notation C^n for a higher order critical point. n is the number of phases that become identical. So our proposed notation for a tricritical point is C^3. An example is the coincidence of an LCE $g(l_1 = l_2)$ with an UCE $(g = l_1)l_2$ on the same three-phase curve gl_1l_2 in such a way that the length of the three-phase curve in the (P,T) projection becomes zero (see Fig. 5b).

Coincidence point of two critical endpoints of the same nature on the same three-phase curve, such that the three-phase curve collapses

For this special point we propose the name *isolated critical endpoint* and the notation ICE. Again this special point can not be realized in a binary system. An example is the coincidence of a LCE $g(l_1 = l_2)$ with an UCE $g(l_1 = l_2)$ on the same three-phase curve gl_1l_2 in such a way that the length of the three-phase curve in the (P,T) projection becomes zero (see Fig. 5c).

Critical azeotrope coexisting with another (noncritical) phase

Griffiths' notation for this critical azeotropic endpoint is $B_{az}A$. We propose the notation CE_{az}.

Critical phase in the presence of two noncritical phases

We propose to name this point *bicritical three phase point* and to denote it with BT. Griffiths' notation for this point is BA_2. An example is a $(g = l_1)l_2s_2$ equilibrium.
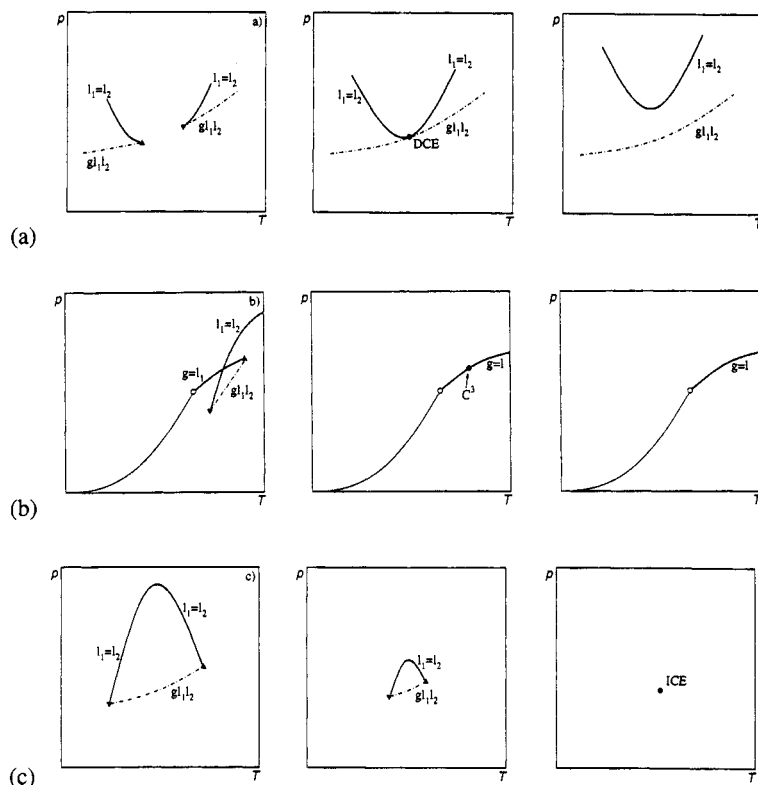

(a)

(b)

(c)

Fig. 5. Two critical endpoints coincide. (a) A double critical endpoint (DCE). (b) A tricritical point (C). (c) An isolated critical endpoint (ICE). ————: stable part of the critical curve; — · — — · — · —: three-phase curve; ————: pure component vapour pressure curve; O: pure component critical point; ▲, ▼: upper and lower critical endpoints.

Collision of two critical curves

When two separated parts of the critical curve meet and exchange branches we are dealing with a double point of the critical curve. Two cases can be distinguished. In the first case two critical cusps coincide. See Fig 6a. Often this point is referred to as an unstable mathematical double point. In line with the above we propose to name this type of point *double critical cusp* and to denote it with DCC.

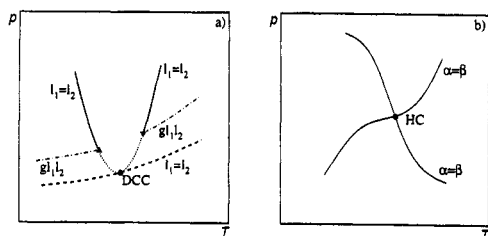**Fig. 6.** Collision of two critical curves. (a) Coincidence of two critical cusps in a double critical cusp (DCC). (b) Coincidence of two stable branches of a critical curve in a hypercritical point (HC). ————: stable part of the critical curve; ·············: metastable part of the critical curve; ----------: unstable part of the critical curve; — · — · — · —: three-phase curve; ▲, ▼: upper and lower critical endpoints.

In the second case two stable branches of the critical curve meet (see Fig. 6b). This type of double point has been referred to as stable mathematical double point. For this point we propose the name *hypercritical point* and the notation HC.

Level 5: point in two-dimensional global phase diagram

Tricritical point coexisting with another (noncritical) phase

We propose to name this point *tricritical endpoint* or *tricritical quadruple point* with the notation C^3E or C^3Q. Griffiths' notation for this type of point is CA. An example is a $(g = l_1 = l_2)l_3$ equilibrium.

Coincidence of a tricritical point and double critical endpoint

After Meijer *et al.* (1988) we propose to name this type of point *van Laar point* with the notation VL. Jackson (1991) named this type of point tricritical endpoint, but this name is not in line with the nomenclature of ordinary critical points and critical endpoints. Also this type of point has been referred to as symmetrical tricritical point.

Level 6: point in three-dimensional global phase diagram

Coalescence of four phases

In line with the name and notation for a tricritical point we propose the name *tetracritical point* and notation C^4 for a fourth order critical point where four fluid phases become identical. Griffiths' notation for a fourth order critical point is D.

RECOMMENDATIONS FOR THE GRAPHICAL REPRESENTATION OF BINARY PHASE DIAGRAMS

Although less important than an unique nomenclature for special states in phase diagrams it can also be useful to use a unique graphical representation for the different types of equilibria. In Table 2 a proposal is given for the representation of nonvariant and monovariant states in (P,T) projections.

Table 2. Graphical representation of nonvariant and monovariant states

Equilibrium state	Representation
pure component vapour pressure curve	————————
critical curve stable part	————————
critical curve metastable part	····················
critical curve unstable part	- - - - - - - - - - -
three-phase curve	—·—·—·—·—·—·—·—
azeotropic curve	— — — — — — — —
critical point pure component	○
critical point in P-T, T-x, and P-x section	○
pure component triple point	△
azeotropic endpoint	✚
lower critical endpoint	▼
upper critical endpoint	▲
quadruple point	□

A new nomenclature for phase diagram classes of binary fluid mixtures

In his 1968 dissertation on global phase behaviour of binary fluid mixtures, P. van Konynenburg found five different classes of phase diagrams, to which he gave the names I to V. Today, more than 16 basic classes are known. The additional phase diagram classes are usually referred to by a roman number in connection with a modifier (*, **, and/or subscript 4, subscript b or superscript h). However, the meaning of the modifier symbol is not always the same. This nomenclature, the product of a number of different research groups , is very confusing. Therefore, we want to present a new system of names which is able to describe all known and yet unknown phase diagrams in a rational way.

Rational nomenclature

The nomenclature described here regards primarily the topology and connectivity of critical curves. The vapour-pressure curves of the pure components are always present and need not to be designated explicitly. The number and extent of three-phase curves, if present, can be deduced from the location of the critical curves and their endpoints, hence only the latter curves and points need to be designated. The construction of a rational phase diagram is done in four steps:.

1. The critical point of a pure component is always the starting point of a critical curve or a sequence of critical curves connected by three-phase lines. We begin by describing the behaviour of the critical curve starting at the critical point of the component with the higher critical temperature. All critical curve segments in the sequence originating from this point are counted; next the "target" of this sequence is indicated with a superscript. Possible targets are:

   C for sequences going upwards to a *compact* fluid state at very high pressure. Many theories of fluid mixtures use the concept of limiting critical states at infinite pressure,

   P for sequences ending at the critical point of the other *pure* component,

   Z for sequences terminating at a critical endpoint, from which a three-phase curve emerges which terminates at absolute *zero* of temperature,

   Q for curves going to an endpoint from which a three-phase curve runs to a *quadruple* point (4 fluid states in equilibrium). Usually another three-phase curve runs from here to absolute zero temperature. If no different topology of the quadruple point is specified by other critical curve symbols, this three-phase curve and its target are implied by the Q symbol and must not be mentioned in the class name.

   If this part of the diagram is not known, this can be indicated by X^{target}, or, if also the target is unknown, X^X.

2. The behaviour of the critical curve sequence starting at the critical point of the lower boiling component is described. However, if the target of the critical curve sequence described in step 1 is P (the critical point of the other pure component), this description is not necessary.

3. Critical curves which were not counted in steps 1 and 2 are classified as follows:

   l curves coming from high pressure (C state) and going to a critical endpoint; in practice, of course, l-type critical curves end on crystallization surfaces,

   n curves with two critical endpoints,

   u curves coming from high pressure and going through a pressure minimum back to high pressure, which have no endpoints (if solidification is disregarded),

   o closed loops.

   These symbols have been chosen to mimic the shape of the critical curves.

   With these symbols, the remaining critical curves are now listed in the order of their appearance from high to low temperature. Except in clear cases, the target or targets (names of the connected curves) must be written as superscripts. Parentheses can be used to group critical curves forming a sequence, i.e., joined by three-phase curves. If this is still ambiguous, it is necessary to label each critical curve with a Greek character subscript and use this symbol as target indication.

4. It may be desirable to follow these symbols with detailed information. The following abbreviations should be used:

    H for heteroazeotropic behaviour,

    A for azeoptropy,

    Q for quadruple point,

    M for pressure maxima; the number of maxima may be indicated by a superscript,

    W for pressure minima: the number of minima may be indicated by a superscript.

    This information usually refers to a specific sequence, so it must be written directly behind this sequence symbol. To connect it to a particular line of a sequence starting at a pure component, it is possible to write the whole sequence in parentheses.

5. Sometimes it may be important to give more information. This could be given after a decimal point. Also, it may be desirable to include information about solid phases. This could follow after a slash (/); a nomenclature system has yet to be designed.

EXAMPLES

Several examples for the construction of the rational phase diagram names are given in this section. Furthermore, a translation table of the van Konynenburg class names as well as some of the new names is given in Table 3, and schematic (P,T) phase diagrams of some of the most important phase diagram classes are shown in Fig. 7.
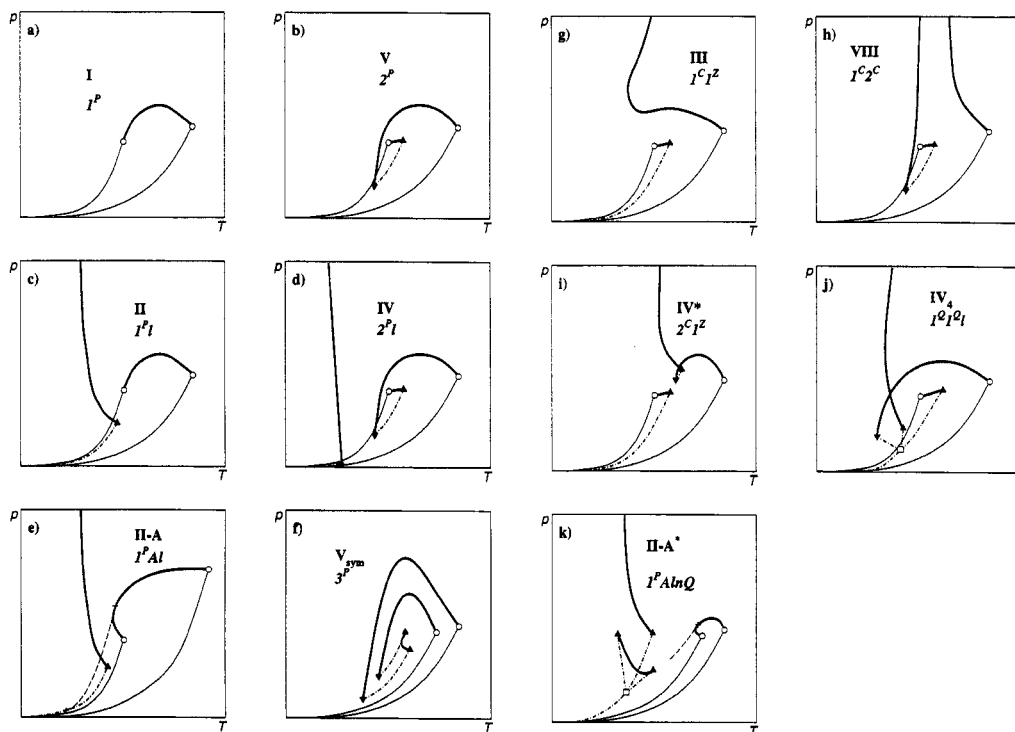

Fig. 7. Phase diagram classes of binary fluid mixtures. ————: vapour-pressure curves; ————: critical curves; — · — · — · —: three-phase curves; — — — —: azeotropic curves; O: pure component critical points; □: quadruple point; ▲, ▼: upper and lower critical endpoints, ✚: azeotropic endpoints.
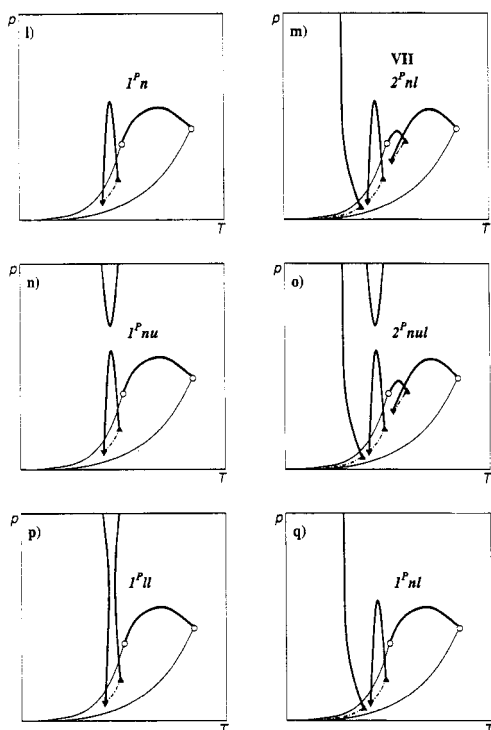
Fig. 7. *Continued.*

In the phase diagram class I (van Konynenburg-Scott nomenclature) only one critical line exists, which connects the critical points of the pure components. The new class name is therefore 1^P (see Fig. 7a). For class II a liquid-liquid critical line is added: $1^P l$ (Fig. 7c).

In class IV, a critical curve runs from the critical point of the less volatile component to a lower critical endpoint. From here a three-phase curve runs to an upper critical endpoint, and from here a critical curve to the other pure component critical point. Hence the critical curve sequence has two critical segments. In addition, there is a liquid-liquid critical curve. The new class name is therefore $2^P l$. A lengthier, but admissible alternative name is $(nn)^P l$ (here the pure component critical points are treated as endpoints). This latter expression is useful, if additional characteristics of a critical curve need to be specified. For instance, if the critical curve originating at the critical point of the less volatile component passes through a maximum, this could be specified by $(nMn)^P l$. The "transition" phase diagram between all 1^P and 2^P phase diagrams contains a tricritical point (see Fig. 5b).

The shield region class II-A* (Fig. 7k) can be translated into $1^P AnlQ$ or $1^P An^{QQ} l^Q$. The latter name is longer, but does not contain more information: A quadruple point is the intersection point of four three-phase lines, one of which is usually connected to absolute zero. The three remaining three-phase curves originate at the endpoints of the n and l critical lines. Since no other combination is possible, it is not necessary to give the target three times, and the shorter name $1^P AnlQ$ is sufficient.

For some mixtures containing strongly polar compounds closed immiscibility domains have been observed (van Konynenburg-Scott class VI). This is caused by a n critical curve segment; the new class name is therefore $1^P n$ (see Fig. 7l). It has been suggested that in this class an additional low-temperature liquid-liquid critical curve might appear (Boshkov, 1987); this would change the name to $1^P nl$ (see Fig. 7q). If a high-pressure immiscibility is found, the class name becomes $1^P nu$ (see Fig. 7n). If high- and low-pressure immiscibility domains overlap (compare Figs. 7n & 7p), a new diagram type is created which has no name in the old nomenclature system. The new name is $1^P ll$ or, more precisely, $1^P (ll)$. The parentheses indicate that the two l critical curves form a sequence, i.e., that they are joined by a three-phase curve. But since there are no other ways of placing the two l critical curves without leaving

one three-phase curve open-ended, the parentheses are not strictly necessary. The "transition" phase diagram between *nu* and (*ll*) contains a hypercritical point.

Table 3. Comparison of phase diagram class names according to the van Konynenburg-Scott system and the rational nomenclature.

Old nomenclature	New nomenclature	Figure
I	1^P	7a
II	$1^P l$	7c
II-A*	$1^P AlnQ$	7k
III	$1^P AlnQ$	7g
III-A*	$1^C 1^Q nA$	
III-A**	$1^C 1^Q An$	
IV	$2^P l$	7d
IV*	$2^C 1^Z$	7i
IV$_4$	$1^Q 1^Q l$	7j
IV$_4^*$	$2^P lnQ$	
V	2^P	7b
V$_{sym}$	3^P	7f
VI	$1^P nl$	7l
VI$_b$	$1^P nul$	
VII	$22^P nl$	7m
VII^h	$2^P nul$	
VIII	$1^C 2^C$	7h

DISCUSSION

For all realistic phase diagram classes which are known until now, the new nomenclature leads to reasonably short, but nevertheless descriptive names.

The nomenclature is based on observable curves only. This is an advantage for its application to experimentally determined phase diagrams. In some lattice gas theories, the high pressure target (C) is shown to bear some analogy to a pure component critical point (Furman *et al.*, 1977; Furman & Griffiths, 1978). This fact might be used to devise a more "symmetric" nomenclature of phase diagrams for such theories. More realistic models, however, may have more than one high-pressure target (Deiters & Kraska, 1992). Hence it would be impossible to classify a real mixture correctly by comparison with lattice models.

The old nomenclature has the disadvantage that the addition of a new feature to a phase diagram leads to a completely new class name. E.g., if a mixture has been classified as type I because of VLE measurements, and if later on a low-temperature liquid-liquid phase splitting is discovered, the class name must be changed to "II", and the assignment "I" must be considered wrong. With the new nomenclature system, the class name merely changes from 1^P to $1^P l$. Thus the correct knowledge of the gas-liquid critical behavior is preserved by the nomenclature.

Since the number of symbols in a class name is not limited, in principle an arbitrary number of phase diagram classes can be encoded. In reality, we must expect this to be a yet unknown finite number. It is possible, however, to give at least an estimate of the maximum number of phase diagram classes in a binary mixture:

We denote this number by n_t and assume

$$n_t \leq n_1 n_2 n_a$$

where n_1 is the number of ways to construct a critical curve or critical curve sequence originating from the critical point of species 1, n_2 is the analogous number for species 2, and n_a is the number of additional critical curve segments (not attached to the pure species critical points). However, experience with several equations of state, for which global phase diagrams have been investigated, shows that the number of critical segments is limited:

- A sequence of critical curves (joined by three-phase lines) cannot have more than 3 elements.

- There are no more than 3 additional critical segments.

- There is no more than 1 u-type critical curve.

- There is no more than one Q-point (four-phase state lllg)

Under these conditions only three sets of phase diagram classes have to be considered:

1. The P set:

    It contains phase diagram classes which have a continuous critical curve between the critical points of the pure species. Their class names are constructed as follows:

1st symbol: $1^P, 2^P, 3^P$	$n_2 = 3$
2nd symbol: not required	$n_1 = 1$
symbol group: may be void, $l, u, lu, n, nu, ll, nul, nlQ, nlQu$	$n_a = 10$

Hence there are $n_t(P) = 30$ classes in this set.

2. The C set:

1st symbol: $1^C, 2^C, 3^C$	$n_2 = 3$
2nd symbol: $1^Z, 2^Z, 1^C, 2^C, 3^C$	$n_1 = 5$
symbol group: as above	$n_a = 10$

    This would give $n_t(C) = 150$ classes. However, there are some forbidden combinations, l, lu, or nul with 1^Z or 2^Z (there can only be 1 three-phase line running towards zero), or $2^C, 3^C$. Hence the estimate for this set is $n_t(C) = 144$.

3. The Q set:

1st symbol: $1^Q, 2^Q, 3^Q$	$n_2 = 3$
2nd symbol: $1^Q, 2^Q, 3^Q$	$n_1 = 3$
Symbol group: u, n, nu, ll	$n_a = 4$

    Hence the number of phase diagram classes in this set is $n_t(Q) = 36$.

The total number of phase diagram classes in all three sets is then 210. This number is probably too large; other, yet to be discovered restrictions on phase diagram topology might decrease it to some extent. But even the number of classes known today from experiment or equations of state is so large that a rational nomenclature is required.

ACKNOWLEDGEMENTS

REFERENCES

1   Boshkov, L.Z., *Dokl. Akad. Nauk SSSR*, 1987, **294**, 901.

2   Boshkov, L.Z. & Mazur, V.A., *Russ. J. Phys. Chem.*, 1986, **60**, 16.

3   Davenport, A.J. and Rowlinson, J.S., *Trans. Farad. Soc.*, 1963, **59**, 78.

4   Deiters, U.K. & Pegg, I. L, *J. Chem. Phys.*, 1989, **90**, 6632.

5   Deiters, U.K. & Kraska, T., *J. Chem. Phys.*, 1992, **96**, 539.

6   Ellis, C.M., *J. Chem. Ed*, 1967, **44**, 405.

7   Enick, R., Holder, G.D. & Morsi, B.I., *Fluid Phase Equilibria*, 1985, **22**, 209.

8   Fall, D.J. & Luks, K.D., *J. Chem. Eng. Data* 1985, **30**, 276.

9   Furman, D. & Griffiths, R.B., *Phys. Rev. A*, 1978, **17**, 1139.

10 Furman, D. & Dattagupta, S. & Griffiths, R.B., *Phys. Rev. B*, 1977, **15**, 441.

11 Griffiths, R.B., *Phys. Rev. B*, 1975, **12**, 345.

12 Griffiths, R.B. & Wheeler, J.C., *Phys. Rev. A*, 1970, **2**, 1047.

13 Hottovy, J.D., Luks, K.D. & Kohn, J.P., *J. Chem. Eng. Data*, 1981, **26**, 256.

14 Jackson, G., *Mol. Phys.*, 1991, **72**, 1365.

15 Kohn, J.P., Kim, Y.J. & Pan, Y.C., *J. Chem. Eng. Data* 1966, **11**, 33.

16 van Konynenburg, P.H., *Critical lines and phase equilibria in binary mixtures*, PhD-thesis, UCLA, 1968.

17 van Konynenburg, P.H. & Scott, R.L., *Philos. Trans. Royal Soc. London Ser. A*, 1980, **298**, 495.

18 de Loos, Th.W., Wijen, A.J.M. & Diepen, G.A.M., *J. Chem. Thermodynamics*, 1980, **12**, 193.

19 Mazur, V.A., Boshkov, L.Z. & Murakhovsky, V.G., *Physics Letters*, 1984, **104**, 415.

20 Mazur, V.A., Boshkov, L.Z. & Fedorov, V.B., *Dokl. Akad. Nauk SSSR*, 1985, **282,** 137.

21 Meijer, P.H. E., Keskin, M. & Pegg, I.L., *J. Chem. Phys.*, 1988, **88**, 1976.

22 Mills, I., Cvitaš, T., Homann, K., Kallay, N. & Kuchitsu, K., *Quantities, Units and Symbols in Physical Chemistry*, 2nd. ed., Blackwell Scietific Publications, Oxford, U.K., 1993.

23 de Roo, J.L., Peters, C.J. & de Swaan Arons, J.; *Fluid Phase Equilibria*, 1995, **109**, 99.

24 Rowlinson, J.S. & Swinton, F.L., *Liquids and Liquid Mixtures*, 3rd. ed., Butterworth Scientific, London, 1982.

25 Schneider, G.M., *Ber. Bunsenges. Phys. Chem.*, 1966, **5**, 497.

26 Schneider, G.M. In *Chemical Thermodynamics* Vol. 2; McGlashan, M.L. Ed.; The Chemical Society, London, 1978, Chapter 4.

27 de Swaan Arons, J. & Diepen, G.A.M., *J. Chem. Phys.*, 1966, **44**, 2322.

28 van Pelt, A., Peters, C.J. & de Swaan Arons, J., *J. Chem. Phys.*, 1991, **95**, 7569.

29 van der Waals, J.D. & Kohnstamm, Ph., *Lehrbuch der Thermostatik, zweiter Teil*, 2nd edn, Barth Verlag, Leipzig, 1927.

APPENDIX I. LIST OF SYMBOLS

1. Properties

a,b	parameters in the van der Waals equation
F	number of degrees of freedom
G	Gibbs energy
N	number of components
P	pressure
T	temperature
x	mole fraction

Greek letters

ϕ	number of extra relations in the phase rule
Π	number of phases

Superscripts

az	azeotropic
c	critical
α, β, γ	phases

Subscripts

A, B, 1, 2   components

2. Thermodynamic states

f	fluid phase
g	gas phase
l	liquid phase
s	solid phase
BT	bicritical three-phase point
C	critical point
C^3	tricritical point
C^4	tetracritical point
C^n	nth-order critical point
CC	critical cusp
CE	critical endpoint
C^3E, C^3Q	tricritical endpoint or tricritical quadruple point
DCC	double critical cusp
HC	hypercritical point
ICE	isolated critical endpoint
LC	lower critical point
LCE	lower critical endpoint
Q	quadruple point
UC	upper critical point
UCE	upper critical endpoint
VL	van Laar point

Subscripts

1,2	subscripts to distinguish between two phases of the same state of aggregation
az	azeotropic

3. Phase diagram classes

i	critical curve sequence with i segments
l	critical curve coming from high pressure
n	critical curve with two critical endpoints
o	closed loop critical curve
u	critical curve coming from high pressure and going through a pressure minumum back to high pressure, which have no endpoints
A	azeotrope
H	heteroazeotrope
M	pressure maximum
Q	quadruple point
W	pressure minimum

Superscripts

C	compact fluid state (critical curve target)
P	critical point of pure component (critical curve target)

Q critical end point of three-phase curve that runs to a quadruple point (critical point target)

Z critical end point of three-phase curve that extends to $T = 0$ K (critical curve target)

APPENDIX II

Class 1^P phase behaviour

In Figure 8 the combined (P,T) and (T,x) projections of class 1^P phase behaviour (type I according to the classification of van Konynenburg & Scott) are shown. In a class 1^P system only one critical curve is found. This is the vapour-liquid critical curve $g = 1$ which runs continuously from the critical point of component 1 to the critical point of component 2. Class 1^P phase behaviour is found, for instance, in binary mixtures of methane with n-alkanes up to n-pentane (Rowlinson & Swinton, 1982).
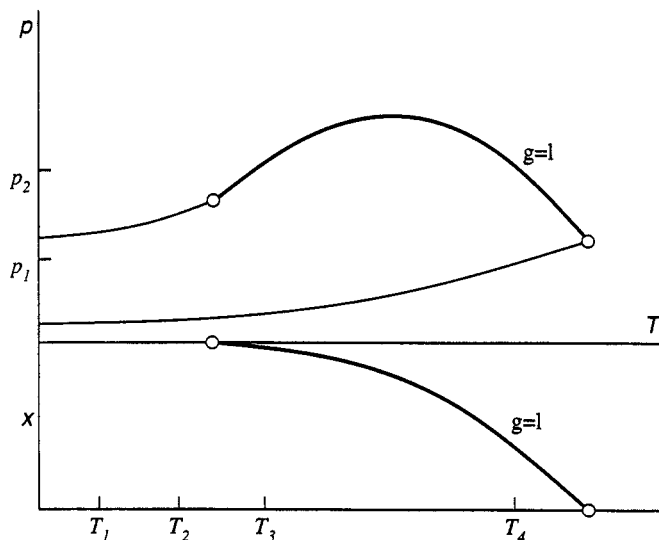
Fig. 8. Combined (P,T) and (T,x) projections of class 1^P fluid phase behaviour. ————: vapour–pressure curves; ————: critical curve; O: pure component critical point.

In Figure 9 some (P,x) and (T,x) sections are shown. The (P,x) sections at T_1 and T_2 have the shape of Figure 1a. At T_3 and T_4 component 1 is supercritical and the (P,x) sections show a binary critical point as in Figure 1b. In the T,x-sections the two-phase gl region has a reversed position compared with the P,x-section. Note that the (T,x) section at P_2 shows two critical points, which is a consequence of the pressure maximum of the critical curve in the (P,T) projection. These pressure maxima are often found in class 1^P systems.
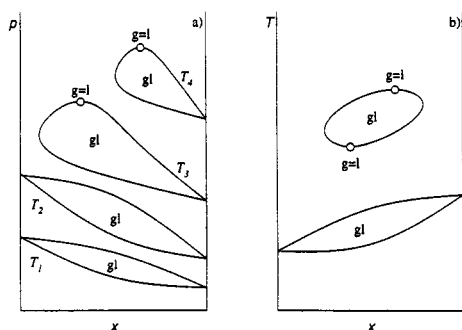

Fig. 9. Class 1^P fluid phase behaviour. (a) (P,x) sections at constant T. See Figure 8. (b) (T,x) sections at constant P. See Fig. 8.

Class $1^P l$ phase behaviour

Class $1^P l$ phase behaviour (type II according to the classification of van Konynenburg & Scott) has a continuous vapour-liquid critical curve just as in the case of class 1^P phase behaviour. In addition, systems of this type show a liquid-liquid critical curve $l_1 = l_2$ and a three-phase equilibrium gl_1l_2 . See Fig. 10, which shows the P,T- and T,x-projection of a class $1^P l$ system. In the (P,T) projection the curves $l_1 = l_2$ and gl_1l_2 intersect in a UCE $g(l_1 = l_2.)$ In the diagram shown the liquid-liquid critical curve has a positive slope in the (P,T) projection, but this curve can also have a negative slope or a temperature minimum. If not interrupted by the formation of a solid phase, the $l_1 = l_2$ curve runs to infinite pressure. Both the $l_1 = l_2$ curve and the gl_1l_2 curve can be completely hidden by a solid-liquid equilibrium surface, so in practice it may be impossible to distinguish between class 1^P phase behaviour and class $1^P l$ phase behaviour. For instance, in the binary systems of carbon dioxide + n-alkanes for carbon number n $6<n<13$ type II phase behaviour is found (Schneider, 1978). For lower values of n no stable liquid-liquid equilibria are found, but it is very likely that the system carbon dioxide + n-pentane, for instance, is also of class $1^P l$.
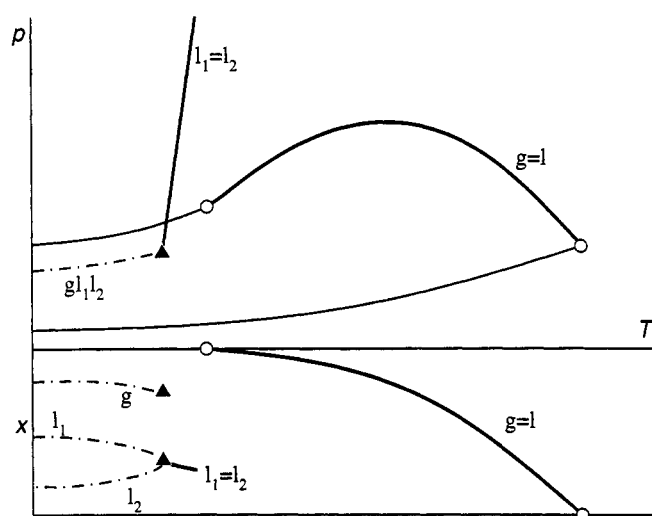

Fig. 10. Combined (P,T) and (T,x) projections of class $1^P l$ fluid phase behaviour. —————: vapour-pressure curves; ————: critical curves; — · — — · — — · —: three-phase curve; O: pure component critical point; ▲: upper critical endpoint.

In Fig. 11 four characteristic (P,x) sections are shown. At low temperature the P,x-sections show a gl_1l_2 equilibrium. At higher pressure than the three-phase pressure the gl_1 and l_1l_2 two-phase regions are found, and at lower pressure the two-phase region gl_2. With increasing temperature the compositions of the two liquid phases of the gl_1l_2 equilibrium approach each other, as can be seen from the (T,x) projection in Fig. 10. At the temperature of the UCE a critical phase $l_1 = l_2$ is in equilibrium with a vapour phase and, as a consequence, the gl_1 and gl_2 regions join in one two-phase region gl, which shows a horizontal point of inflection at the $l_1 = l_2$ critical point. At higher temperatures the gl region and the l_1l_2 region are separated by a region of a homogeneous liquid phase. At even higher temperatures the l_1l_2 region shifts to higher pressures and the gl region may detach on the left hand side, as shown in Fig. 9a.
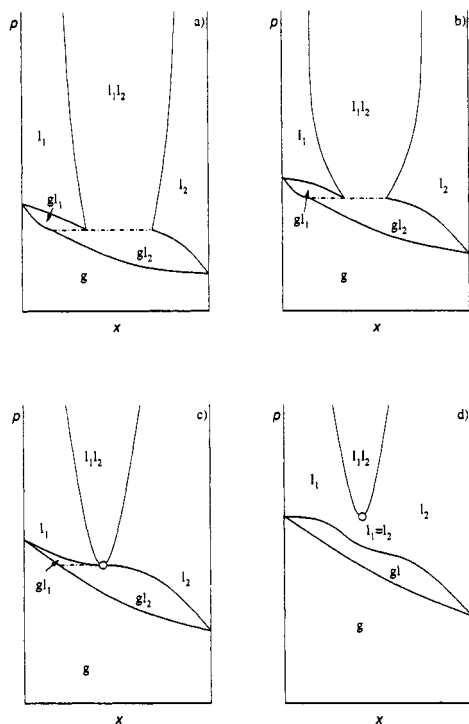
Fig. 11. Class $1^{P}l$ fluid phase behaviour. (P,x) sections at constant T. (a, b) $T<T(g(l_1 = l_2))$. (c) $T = T(g(l_1 = l_2))$. (d) $T(g(l_1 = l_2))<T<T(g = l)_{x = 0})$ See Fig. 10.

Class 2^{P} phase behaviour

The phase behaviour class 2^{P} systems (type V according to the classification of van Konynenburg & Scott)is is represented by (P,T) and (T,x) projections given in Fig. 12. Characteristic for this type of phase behaviour is a three-phase equilibrium gl_1l_2 with a LCE $g(l_1 = l_2)$ and a UCE $(g = l_1)l_2$, and a discontinuous critical curve.
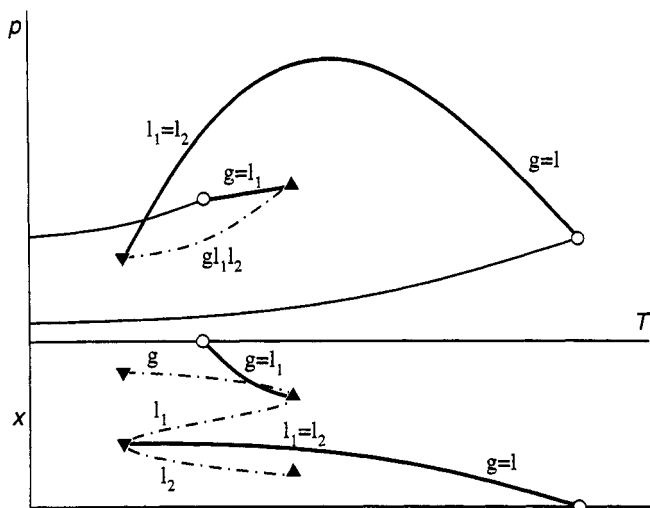
Fig. 12. Combined (P,T) and (T,x) projections of class 2^{P} fluid phase behaviour. : vapour-pressure curves; : critical curve; : three-phase curve; O: pure component critical point; ▲, ▼: upper and lower critical endpoints.

The first branch of the critical curve connects the critical point of the more volatile component with the UCE. The second branch runs from the LCE to the critical point of the less volatile component. Examples of class 2^P systems are the systems methane + n-hexane (Davenport & Rowlinson, 1963) and ethane + n-eicosane (Kohn *et al.*, 1966), although there are reasons to believe that these systems are in reality class $2^P l$ systems (see section on class $2^P l$ systems).

In Fig. 13 four (P,x) sections are shown at temperatures $T(g(l_1 = l_2)) \leq T \leq T((g = l_1)l_2)$. At lower and at higher temperatures the (P,x) sections are comparable with those of class 1^P systems. In Figure 13b a (P,x) section is shown at a temperature between the LCE and the critical point of the more volatile component. This (P,x) section is comparable with Fig. 11a. On lowering the temperature, the composition of the l_1 phase and of the l_2 phase of the gl_1l_2 equilibrium approach each other and the pressure of the $l_1 = l_2$ critical point approaches the three-phase pressure. At the temperature of the LCE (see Fig. 13a) the l_1 and l_2 points of the three-phase equilibrium and the critical point $l_1 = l_2$ coincide. The l_1l_2 two-phase region disappears and the gl_1 and gl_2 two-phase regions join in one gl two-phase region. The gl region shows a horizontal point of inflection at the $l_1 = l_2$ critical point. At higher temperatures than the temperature of Fig. 13b the gl_1 region will detach from the axis x = 0 (Fig. 13c) and at even higher temperatures the composition of the l_1 phase and of the vapour phase of the gl_1l_2 equilibrium approach each other. At the temperature of the UCE the l_1 and g points of the three-phase equilibrium and the $g = l_1$ critical point coincide. See Figure 13d. At this temperature the gl_1 two-phase region disappears and the gl_2 and l_1l_2 two-phase regions again join in one gl two-phase region. Now the gl region shows a horizontal point of inflection at the $g = l_1$ critical point.
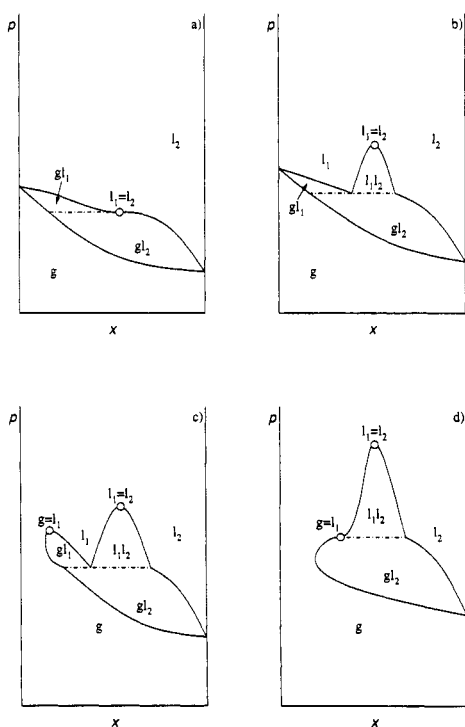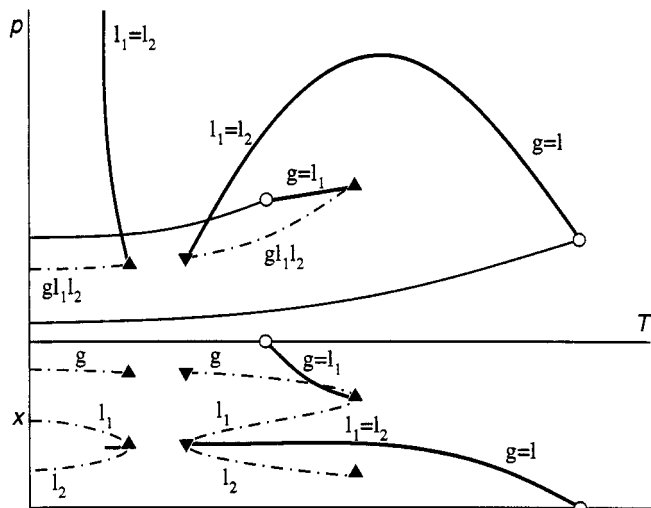

Fig. 13. Class 2^P fluid phase behaviour fluid. (P,x) sections at constant T. (a) $T = T(L = L\ V)$. (b) $T(g(l_1 = l_2)) < T < T(g = l)_{x=0}$. (c) $T < T(g = l)_{x=0} < T < T((g = l_1)l_2)$. (d) $T = T((g = l_1)l_2)$. See Fig. 12.

Class $2^P l$ phase behaviour

The combined (P,T) and (T,x) projections of a class $2^P l$ system (type IV according to the classification of van Konynenburg & Scott) is given in Fig. 14. In this type of phase behaviour the three-phase equilibrium gl_1l_2 consist of two branches. The low-temperature branch shows a UCE $g(l_1 = l_2)$ and is comparable with the gl_1l_2 equilibrium that is found in class $1^P l$ systems. The high-temperature branch

shows a LCE $g(l_1 = l_2)$ and a UCE $(g = l_1)l_2$ and is comparable with the gl_1l_2 equilibrium that is found in class 2^P systems. Not many binary class 2^Pl systems are known, but for similar reasons as mentioned for class 1^Pl phase behaviour it is likely that many systems that are supposed to show class 2^P phase behaviour in fact are of class 2^Pl and the low-temperature branch of the gl_1l_2 equilibrium is masked by the solidification surface. The system carbon dioxide + tridecane (Enick *et al.*, 1985; Fall & Luks, 1985) is an example of a system showing class 2^Pl fluid phase behaviour.

Fig. 14. Combined (P,T) and (T,x) projections of class 2^Pl fluid phase behaviour. ————: vapour-pressure curves; ————: critical curves; — · — · — · —: three-phase curves; O: pure component critical point; ▲, ▼: upper and lower critical endpoints.

Since class 1^Pl and class 2^P phase behaviour is combined in class 2^Pl phase behaviour, the (P,x) sections at low temperatures are those of class 1^Pl (Fig. 11) and at high temperature those of class 2^P (Fig. 13). However phase diagrams at constant temperature can show two separated regions of liquid-liquid immiscibility. An example of a (T,x) section is given in Fig. 15. At this pressure the high-temperature branch of the gl_1l_2 curve is intersected in the P,T-projection. The (T,x) section shows three critical points. At low temperature a critical point $l_1 = l_2$ is the maximum temperature of a l_1l_2 two-phase region. This kind of critical point is called upper critical solution temperature (UC$_P$). The other l_1l_2 critical point is the minimum temperature of a second l_1l_2 two-phase region, which ends at higher temperature at the gl_1l_2 equilibrium. This critical point is called a lower critical solution temperature (LC$_P$). The third critical point is a vapour-liquid critical point $g = l_2$.
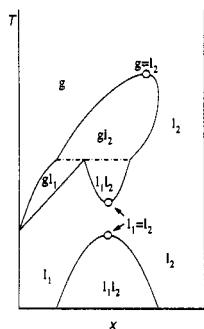

Fig. 15. Class 2^Pl fluid phase behaviour. (T,x) section at constant P for: $P(\text{LCE}) < P < P(g = 1)_{x=0}$. See Fig. 14.
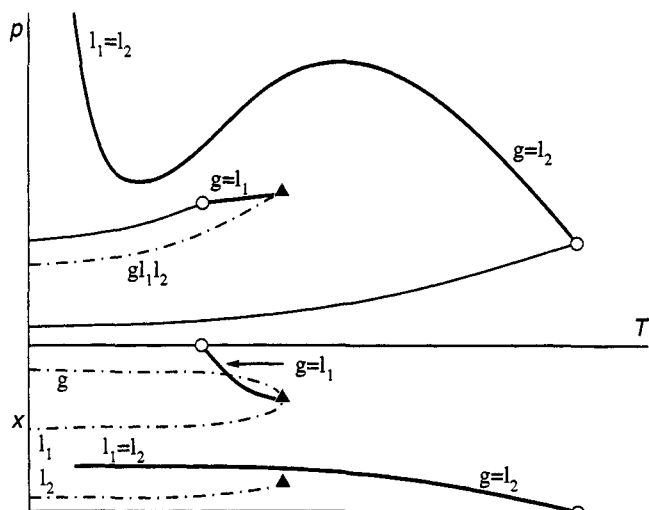
Fig. 16. Combined (P,T) and (T,x) projections of class 1^C1^Z fluid phase behaviour. ————:vapour-pressure curves; ————: critical curves; — - — - — - —: three-phase curves; O: pure component critical point; ▲: upper critical endpoints.

Class 1^C1^Z phase behaviour

In class 1^C1^Z phase behaviour (type III according to the classification of van Konynenburg & Scott) the two branches of the gl_1l_2 equilibrium of class 2^Pl phase behaviour are combined, and also two of the three branches of the critical curve that are found for class 2^Pl. Only the UCE $(g = l_1)l_2$ remains. The (P,T) and (T,x) projection of class 1^C1^Z phase behaviour are given in Fig. 16. In the example shown the branch of the critical curve that runs from high pressure to the critical point of the less volatile component shows a pressure minimum and a pressure maximum. An example of this behaviour is found in the system propane + triphenylmethane (de Roo *et al.*, 1995). This branch of the critical curve can also show a temperature minimum combined with a pressure minimum and a pressure maximum(i.e. carbon dioxide + tetradecane (Hottovy *et al.*, 1981), or only a temperature minimum (i.e. propane + water (de Loos *et al.*, 1980) or can have a positive value of (dP/dT) in the critical point of the less volatile component (i.e., He + Xe (de Swaan Arons & Diepen, 1966)). See Fig. 17. Since in the latter two types of systems two-phase equilibria can exist at higher temperatures than the critical temperature of the less volatile component these equilibria are often referred to as gas-gas equilibria. The system He + Xe is said to show gas-gas equilibria of the first kind (no minimum critical temperature), the system propane + water gas-gas equilibria of the second kind (the critical line passes through a minimum in temperature).
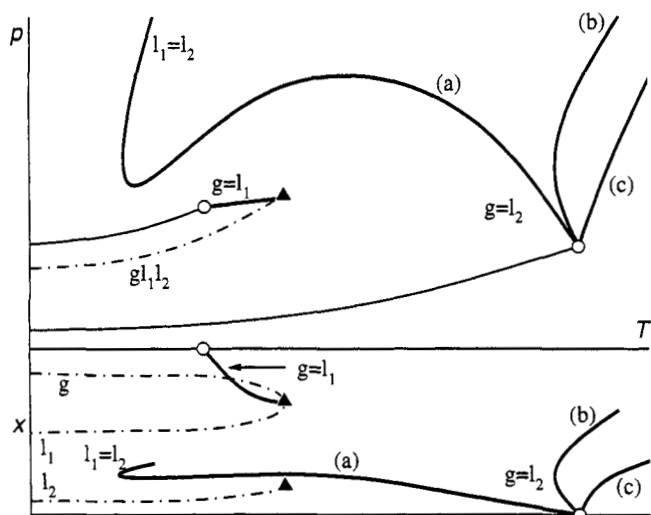
Fig. 17. Combined (P,T) and (T,x) projections of class $1^{C}1^{Z}$ fluid phase behaviour type III fluid phase behaviour: (a) Critical curve with a pressure maximum, a pressure minimum and a temperature minimum; (b) Critical curve with a temperature minimum (gas-gas equilibria of the second kind); (c) Critical curve without a pressure maximum and a temperature minimum (gas-gas equilibria of the first kind). ————: vapour-pressure curves; ————: critical curves; — · — · — · —: three-phase curves; O: pure component critical point; ▲: upper critical endpoints.

At temperatures lower than the UCE ($g = l_1$)l_2, the (P,x) sections corresponding to Fig. 16 resemble those in Fig. 13b. At the temperature of the UCE, a (P,x) section such as that in Fig. 13c is found. In Fig. 18 some (P,x) sections of a system showing gas-gas equilibria of the second kind are shown, in Fig. 19 (P,x) sections of a system showing gas-gas equilibria of the first kind.
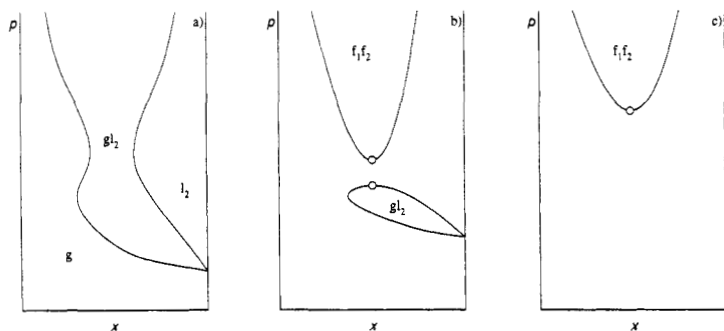

Fig. 18. Gas-gas equilibria of the second kind. (P,x) sections at constant T. (a) $T(\text{UCE})<T<T_{min}(g = l_2)$. (b) $T_{min}(g = l_2)<T<T(g = l)_{x = 1}$. (c) $T>T(g = l)_{x = 1}$.
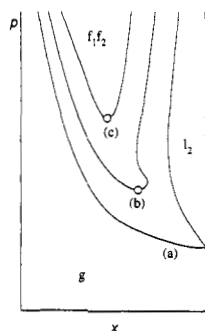

Fig. 19. Gas-gas equilibria of the first kind. (P,x) sections at constant T: a, $T = T(g = l)_{x = 1}$; $T(a)<T(b)<T(c)$.

Class 1^{P}n phase behaviour

Class 1^{P}n phase behaviour (type VI according to the classification of van Konynenburg & Scott) is found in systems with specific chemical interactions, i.e., water + 2-butoxyethanol (Ellis, 1967) In the (P,T) projection a three phase equilibrium gl_1l_2 is found with a LCE $g(l_1 = l_2)$ and a UCE $g(l_1 = l_2)$. In Figure 20 the LCE and UCE are connected by a $l_1 = l_2$ critical curve which shows a pressure maximum. Another possibility is the existence of a second $l_1 = l_2$ critical curve at high pressure with a pressure minimum. This phenomenon is called high pressure immiscibility (class 1^{P}nu). Also the low-pressure immiscibility region and the high-pressure immiscibility region can be combined in one uninterrupted l_1l_2 region (Schneider, 1978). These systems are of class 1^{P}ll.

At temperatures between the temperature of the LCE and of the UCE the (P,x) sections which correspond to Fig. 20 resemble those of Fig. 13b. At the temperature of the LCE and the UCE, the P,x-section is like that in Figure 13a. A typical (T,x) section is shown in Fig. 21. At the pressure of this (T,x) section two separate two-phase regions gl and l_1l_2 are found. The l_1l_2 two-phase region is a closed loop with a LC$_P$ and a UC$_P$.
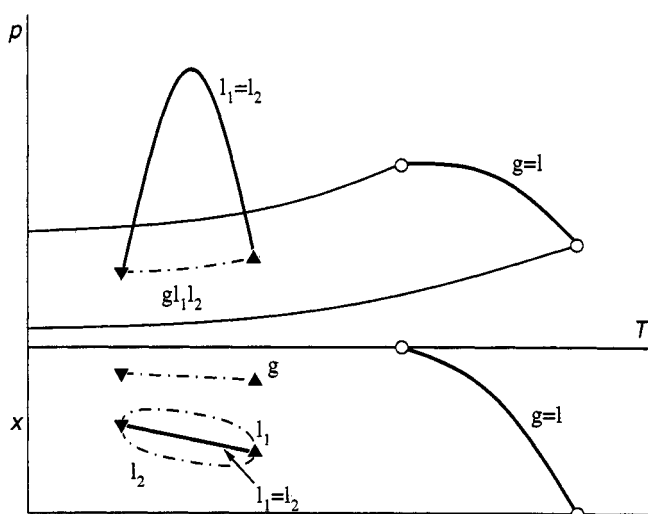

Fig. 20. Combined (P,T) and (T,x) projections of class 1^{P}n fluid phase behaviour. ————: vapour-pressure curves; —————: critical curves; — · — · — · —: three-phase curve; O: pure component critical point; ▲, ▼: upper and lower critical endpoints.
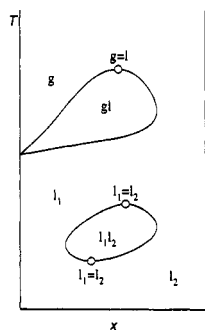

Fig. 21. Class 1^{P}n fluid phase behaviour. (T,x) section at P(UCE)$<P<P$(g = l)$_{x = 0}$.