1. On the search for a Van Laar point, one has to study quasi-binary systems composed from at least 4 components, as the Gibbs phase rule requires. (This dissertation, Chapter 10).

2. It is suggested by experimental observations that the double critical endpoint is the starting point of the geometrical locus of barotropic inversion points at a temperature, carbon number or a pressure, carbon number diagram in a family of systems exhibiting the II=IV=III transition pattern. (This dissertation, Chapter 6).

3. In a binary system the liquid phase which is richer -with respect to composition- in the more-volatile component is not also necessarily the heavier -with respect to density-liquid phase. (This dissertation, Chapters 1, 6).

4. If a binary or a quasi-binary system of type III exhibits L₂L₁ liquid immiscibility at low temperatures and the heavier -with respect to density- liquid phase is richer -with respect to composition- in the more-volatile component, then before the appearance of the L₂L₁=V upper critical endpoint a barotropic inversion point L₂*L₁*V has to occur. (This dissertation, Chapter 6).

5. It is suggested by calculations that in a type III system which approaches the double critical endpoint, the Pₓ projection of its L₂=V/L₂=L₁ critical curve forms a closed loop. As a consequence, there is a region, where for the same critical pressure three different critical compositions and critical temperatures correspond. Also at the point, where the looping curve crosses itself, for the same critical pressure and critical composition two different critical temperatures correspond. (This dissertation, Chapter 9).

6. Brunner (1990) suggested a direct transition from subtype IIIa to subtype IIIb via a tricritical point (indeed a Van Laar point) for the family H₄O + n-alkanes. Instead of an abrupt transition, an intermediate zone with a fluid phase behaviour showing three critical endpoints (like types IV and IV*) must exist. This zone is bounded by the zones of behaviour IIIa and IIIb. (This dissertation, Chapter 4; ; Brunner, E., 1990. Fluid mixtures at high pressures. IX. Phase separation and critical phenomena in 23 (n-alkane+H₂O) mixtures. J. Chem. Thermodynamics, 22 : 335-353).

7. For the asymptotic behaviour close to the double critical endpoint it can be assumed that the "width" of the gap between the two branches of the three-phase L₂L₁V equilibrium curve in a type IV system, as measured by the difference in temperature or by the difference in pressure between the lower and upper L₂=L₁*V critical endpoints, scales as the square root of the difference in carbon numbers between the system at the double critical endpoint and the type IV system. (This dissertation, Chapter 6).

8. The special closed-loop curves in the µ₁,µ₂ plots of binary systems provide a method for the calculation of three-phase equilibria and also a thorough insight in the background of phase diagrams in binary systems. (This dissertation, Chapter 3).
9. When the chain of a n-alkane or a n-alkanol (after n-hexanol) becomes longer, when the chain of a n-alkanol (before n-hexanol) becomes shorter and when the shape of a branched alkane or a branched alkanol becomes more spherical, then the fluid phase behaviour in mixtures of these components with a more-volatile component moves towards the direction of type III or if it is already type III behaviour, the characteristic features of this behaviour become more pronounced. *(This dissertation, Chapters 4, 7).*

10. Correlating fluid phase behaviour by means of molecular geometry may be a successful approach when the physical insight of the phenomena is absent. *(This dissertation, Chapter 10).*

11. "The ordinary gaseous and liquid state are, in short, only widely separated forms of the same condition of matter and can be made to pass into one another by a series of graduations so gentle that the passage shall nowhere present any interruption of breach or continuity ... but if any one ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply." *(Thomas Andrews, 1869, Philos. Trans. Roy. Soc. 159 : p.575).*
   The names we attribute to ordinary physical states of matter or phenomena are not proper under all ranges of conditions.

12. "Engineering involves the practical application of scientific knowledge, and hence I have made a conscious effort to emphasize the practical phases of engineering work. In so doing it has often been necessary to resort to empirical relationships. No apology is necessary for such a treatment because engineers must build and operate plants regardless of inadequate information. In fact the history of industrial development shows that commercial plants are usually built before the theory of the process is fully understood." *(Wilbur L. Nelson, 1958, Petroleum Refining Engineering, 4th ed., Mc Graw Hill, New York).*
   The practical application of an experimental observation cannot wait for its full theoretical explanation. Engineers must try out good ideas before they forget them.

13. Pure substances exist only in the imagination of chemists, like dimensionless points exist only in the imagination of mathematicians. Engineers work with mixtures and ranges of conditions. When the prediction resulting from a simulation is questionable, experiment has to be performed. The cost of experiment is sometimes less than the loss from a wrong design and construction and this must be taken into account in our internal rate of return calculations.

14. If we forget to mention the original ideas of van der Waals and his school in our modern lessons of thermodynamics then we contribute to the entropy of our knowledge about physical phenomena.

15. The power of rich people is that they have a lot to spend trying. The power of poor people is that they have nothing to lose trying. Therefore people must keep trying.

16. If you understand the question, then you know half of the answer.
STELLINGEN

1. Volgens de fasenregel moet men voor de praktische realisatie van een Van Laar punt quasi-binaire systemen onderzoeken die minimaal uit vier componenten bestaan. *(Dit proefschrift, Hoofdstuk 10).*

2. Experimentele resultaten suggeren dat voor een familie van systemen die het overhangspatroon II=IV=III vertoont, het dubbel kritische eindpunt het beginpunt is van de verzameling van barotropische inversiepunten in het temperatuur, koolstofgetal- of druk, koolstofgetal- diagram. *(Dit proefschrift, Hoofdstuk 6)*

3. In een binair systeem waarin ontmenging in de vloeistof fase optreedt is de vloeistof fase die rijker is aan de meest vluchtige component niet noodzakelijk ook de vloeistof fase met de hoogste dichtheid. *(Dit proefschrift, Hoofdstuk 1, 6).*

4. In een binair of quasi-binair systeem van type III, waarin bij lagere temperatuur de vloeistof fase met de hoogste dichtheid het rijst is aan de meest vluchtige component moet op de drijfassenlijn L2L1V bij hogere temperatuur voóŕ het bovenkritische eindpunt L2=L1=V een barotropisch inversiepunt L2=L1-V optreden. *(Dit proefschrift, Hoofdstuk 6).*

5. Berekeningen suggeren dat als in een type III systeem het dubbelkritische eindpunt nadert de P,x projectie van de L2=V/L2=L1 kritische curve een lus vormt. Dit heeft tot gevolg dat er een gebied is waar voor dezelfde kritische druk drie verschillende kritische samenstellingen met bijbehorende kritische temperaturen gevonden worden. In het punt van de P,x projectie waarin de kritische lijn zichzelf snijdt worden voor één waarde van de kritische druk en de kritische samenstelling twee verschillende kritische temperaturen gevonden. *(Dit proefschrift, Hoofdstuk 9).*


7. Voor het asymptotische gedrag dichtbij het dubbelkritische eindpunt kan worden aangenomen dat de afstand van de twee takken van het drijfasceneevenwicht L2L1V van een type IV systeem gemeten met het verschil in temperatuur of het verschil in druk van het onderkritisch eindpunt L2=L1-V en het bovenkritisch eindpunt L2=L1-V evenredig is met de wortel van het verschil van het koolstofgetal van het betrokken systeem en het koolstofgetal in het dubbelkritische eindpunt. *(Dit proefschrift, Hoofdstuk 6).*

8. Het gebruik van μ,μ2 diagrammen verschaft een methode voor het berekenen van drijfasceneevenwichten in binaire systemen en geeft bovendien een diepgaand inzicht in de achtergrond van fasendiagrammen voor binaire systemen. *(Dit proefschrift, Hoofdstuk 3).*
9. Het fasengedrag van families van een meer vluchtige component en een n-alkaan of een n-alkanol verschuift in de richting van type III of wordt meer uitgesproken type III als de ketenlengte van het n-alkaan groter wordt, als de ketenlengte van het n-alkanol groter wordt, indien het koolstofgetal groter is dan zes, en als de ketenlengte van het n-alkanol kleiner wordt, indien de ketenlengte van het n-alkanol kleiner is dan zes. *(Dit proefschrift, Hoofdstuk 4, 7).*

10. Het correleren van fluide fasengedrag met moleculaire geometrie kan een succesvolle benadering zijn als het fysisch inzicht in de verschijnselen ontbreekt. *(Dit proefschrift, Hoofdstuk 10).*

11. "The ordinary gaseous and liquid state are, in short, only widely separated forms of the same condition of matter and can be made to pass into one another by a series of graduations so gentle that the passage shall nowhere present any interruption of breach or continuity ... but if any one ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply." *(Thomas Andrews, 1869, Philos. Trans. Roy. Soc. 159 : p.575).*

De gebruikelijke benaming van de verschillende aggregatietoestanden is niet voor alle toestanden geschikt.

12. "Engineering involves the practical application of scientific knowledge, and hence I have made a conscious effort to emphasize the practical phases of engineering work. In so doing it has often been necessary to resort to empirical relationships. No apology is necessary for such a treatment because engineers must build and operate plants regardless of inadequate information. In fact the history of industrial development shows that commercial plants are usually built before the theory of the process is fully understood." *(Wilbur L. Nelson, 1958, Petroleum Refining Engineering, 4th ed., Mc Graw Hill, New York).*

De praktische implementatie van een experimenteel waargenomen verschijnsel kan niet wachten op de volledige theoretische verklaring voor dit verschijnsel. Ingenieurs moeten goede ideeën uitproberen voor deze vergeten zijn.

13. Zuivere stoffen bestaan alleen in de verbeelding van chemici, net zoals dimensieloze punten alleen in de verbeelding van mathematici bestaan. Ingenieurs werken met mengsels in een groot gebied van de toestandsvariabelen. Als de voorspellingen gebaseerd op simulaties onbetrouwbaar zijn dan moeten experimenten verricht worden. De kosten van experimenten zijn soms minder dan de verliezen die geleden worden ten gevolge van een verkeerd ontwerp of een verkeerde konstruktie en hiermee moeten we rekening houden bij onze "internal rate or return" berekeningen.

14. Als de originele ideeën van Van der Waals en zijn school onvermeld blijven in ons moderne onderwijs in de thermodynamica dan dragen we bij tot de entropie van onze kennis van fysische verschijnselen.

15. De kracht van rijke mensen is dat zij zich kunnen veroorloven veel te onderzoeken. De kracht van arme mensen is dat zij niets te verliezen hebben als ze veel onderzoeken. Daarom moeten mensen blijven onderzoeken.

16. Het begrijpen van een vraag vormt het halve antwoord.
PATTERNS OF FLUID PHASE BEHAVIOUR
IN BINARY AND QUASI-BINARY MIXTURES

PATRONEN VAN FLUÏDE FASENGEDRAG
IN BINAIRE EN QUASI-BINAIRE MENGSELS
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This book is the result of the author’s research work in the field of fluid phase equilibrium during the years 1990-1993 at Delft University of Technology. The author is greatly indebted to all those who have contributed to its accomplishment:
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The best is the enemy of the good. I hope that the material included here will be of some use in the future.

Athens, December 1994

Diomidis Stamoulis

COVER: Isothermal V,P,x plot for a binary system exhibiting fluid two-phase equilibria at conditions where mechanical instability interferes with material instability. The material binodals are located along the solid curve, while the mechanical binodals are located along the short-dashed curve. The material spinodals are located along the long-dashed curve, while the mechanical spinodals are located along the dotted curve. The dashed-dotted curve as well as the dashed-triple-dotted curve represent isobars. For details see Chapter 3, Fig.3.9.a.
PATTERNS OF FLUID PHASE BEHAVIOUR IN BINARY AND QUASI-BINARY MIXTURES

PATRONEN VAN FLUÏDE FASENGEDRAG IN BINAIRE EN QUASI-BINAIRE MENGSELS

Proefschrift

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DIOMIDIS STAMOULIS

scheikundig ingenieur geboren te Chios, GRIEKENLAND afgestudeerd aan de Faculteit der Scheikundige Technologie, Nationaal Metsovion Technishe Universiteit, Athene, Grieekenland
Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. ir. Jakob de Swaan Arons

Toegevoegd promotor: Dr. ir. Theodoor W. de Loos

Samenstelling promotiecommissie:

Prof. ir. K. Wakker,  
Prof. dr. ir. J. de Swaan Arons,  
Dr. ir. Th. W. de Loos,  
Prof. dr. J. Schouten,  
Prof. dr. G. M. Schneider,  
Prof. dr. U. K. Deiters,  
Prof. dr. H. A. J. Oonk,  

Rector Magnificus  
Promotor  
Toegevoegd Promotor  
Van der Waals Lab., University of Amsterdam  
Ruhr Universität, Bochum, Germany  
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# TABLE OF CONTENTS

## 1 INTRODUCTION

1.1 Historical background, objectives of this work, perspectives of use of the results 5  
1.2 The Gibbs phase rule 7  
1.3 Volatility and density 12  
1.4 Practical significance of this investigation 13

## 2 TYPES OF FLUID PHASE EQUILIBRIA IN BINARY MIXTURES

2.1 P-T-x space nomenclature 19  
2.2 Classification schemes 30  
2.3 Transitions between different types of fluid phase behaviour 33

## 3 CALCULATIONAL METHODS FOR FLUID PHASE EQUILIBRIA IN BINARY MIXTURES

3.1 Introduction to the problem 45  
3.2 Criteria for equilibrium and equation of state 49  
3.3 Basic formulae 50  
3.4 Two-phase equilibrium for an unary system 52  
3.5 Two-phase equilibrium for a binary system (mechanically stable case) 55  
3.6 Generalization of the method 58  
3.7 Three-phase equilibrium for a binary system (mechanically stable case) 59  
3.8 Fluid phase equilibrium for a binary system under combined mechanical and material instability 64  
3.9 Some illustrative examples 69  
3.10 Discussion 83
Table of contents

4 EXPERIMENTAL INFORMATION FROM LITERATURE

4.1 Carbon dioxide with n-alkanes or n-alkanols 88
4.2 Nitrous oxide with n-alkanes or n-alkanols 93
4.3 Methane with hydrocarbons and ethane with n-alkanes or n-alkanols 97
4.4 Ammonia with n-alkanes 102
4.5 Water with n-alkanes 104
4.6 Perfluoroalkanes with n-alkanes 109

5 EXPERIMENTAL SETUP

5.1 Apparatus 120
5.2 Procedure of filling 122
5.3 Procedure of measurements 123
5.4 Experiments performed 125
5.5 Chemicals used 125

6 EXPERIMENTAL RESULTS FOR THE SYSTEMS C₃F₈ + ALKANES

6.1 Introduction 131
6.2 Experimental results 135
6.3 Discussion 148

7 EXPERIMENTAL RESULTS FOR THE SYSTEMS C₄F₁₀ + n-ALKANES

7.1 Introduction 157
7.2 Experimental results 158
7.3 Discussion 166
# Table of contents

## 8 EXPERIMENTAL RESULTS FOR THE SYSTEMS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>172</td>
</tr>
<tr>
<td>8.2</td>
<td>Experimental results and discussion</td>
<td>174</td>
</tr>
</tbody>
</table>

## 9 MODELLING

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>Introduction</td>
<td>193</td>
</tr>
<tr>
<td>9.2</td>
<td>Transitions in the family of carbon dioxide with n-alkanes</td>
<td>194</td>
</tr>
<tr>
<td>9.3</td>
<td>Transitions in the family of perfluorobutane with n-alkanes</td>
<td>196</td>
</tr>
<tr>
<td>9.4</td>
<td>Calculated versus experimental results for the transitions</td>
<td>209</td>
</tr>
<tr>
<td>9.5</td>
<td>Typical fluid phase diagrams</td>
<td>211</td>
</tr>
<tr>
<td>9.6</td>
<td>The influence of the interaction parameter ( l )</td>
<td>220</td>
</tr>
<tr>
<td>9.7</td>
<td>Barotropic inversion point</td>
<td>221</td>
</tr>
<tr>
<td>9.8</td>
<td>Some interesting cross-sections</td>
<td>225</td>
</tr>
<tr>
<td>9.9</td>
<td>Conclusions</td>
<td>230</td>
</tr>
</tbody>
</table>

## 10 EMPIRICAL CORRELATIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>Review of existing work. Theoretical: equation of state parameters, semi-empirical: solubility parameter</td>
<td>232</td>
</tr>
<tr>
<td>10.2</td>
<td>The effect of the shape of alkanes on their binary mixture behaviour with perfluoropropane (Randić topological index)</td>
<td>240</td>
</tr>
<tr>
<td>10.3</td>
<td>The combined effect of the size, the shape and the polarity of alkanols on the phase behaviour of systems of alkanols with perfluoropropane or perfluorobutane</td>
<td>242</td>
</tr>
<tr>
<td>10.4</td>
<td>The effect of the nature of the more-volatile component on the phase behaviour of binary systems of that component with n-alkanes</td>
<td>247</td>
</tr>
</tbody>
</table>
# Table of contents

APPENDIX A

The Peng-Robinson equation of state 257

APPENDIX B

Derivatives of thermodynamic functions with respect to composition 267

APPENDIX C

Slope of a critical curve 273
Slope of a three-phase curve (generally) 274
Slope of a three-phase curve at a critical endpoint 275

SUMMARY 277

SAMENVATTING (Dutch Summary) 279

ΠΕΡΙΛΗΨΗ (Greek summary) 281
1. INTRODUCTION

In this thesis a systematic experimental investigation of some of the different types of fluid phase behaviour as well as of the transition mechanisms amongst them is described.

In the first chapter the basic ideas which motivated this work are outlined. The main objectives are presented and the possible application of the results is suggested. Also, a short recapitulation of the thermodynamics of phase equilibria is given. The Gibbs phase rule is discussed using the language of "fields" and "densities" and a nomenclature for the volatility and density of pure components or fluid phases of binary mixtures is presented. The chapter closes with some comments on the practical significance of this work.

1.1 Historical background, objectives of this work, perspectives of use of the results

The classification scheme of van Konynenburg and Scott (1968, 1970, 1980) was the first systematic categorization of the different types of fluid phase behaviour in binary systems. These authors predicted all the experimentally known types of phase diagrams using the van der Waals equation of state and revealed the mechanisms of transitions amongst these diagrams, when the characteristic parameters of the two components were changing. Chapter 2 contains a more detailed description of their work.

Afterwards, other investigators (Furman et al., 1977; Furman and Griffiths, 1978; Clancy et al., 1978; Mazur et al., 1985; Jackson et al., 1986; Deiters and Pegg, 1989; van Pelt, 1992) used different equations of state revealing new types of phase diagrams, some of them never supported by experimental evidence. It must be stressed here that the inspiring ideas and the fundamental framework for these calculations were already developed to an astonishing level by the work of van der Waals and Kohnstamm (1927) many decades ago. Unfortunately or fortunately the modern computer facilities were not available at that time.

Although the resulting classification charts are very handsome and educative tools, they lack in the quantitative agreement with the experiment. Pegg et al. (1990) mention such discrepancies for simple systems of hydrocarbons. In addition, if systems of complex molecules are considered, then the pure component data, like saturation curves and critical point coordinates, are not adequate any more to evaluate the different geometrical (size and shape) properties of the constituents of the system as well as the various intermolecular forces between them, which in principle determine the fluid phase behaviour of the mixture.
Chapter 1

The literature provides us with some experimental information on the -in many cases-complex fluid phase behaviour of binary systems, like critical curves and three-phase equilibrium curves. In Chapter 4 a brief survey of three-phase equilibrium behaviour in binary systems as found in literature is presented. However this information is not considered to be enough to support general conclusions on specific topics like the transition mechanism from type II, via type IV, towards type III (and vice versa) fluid phase behaviour (see Chapter 2). Therefore it was decided to start an additional experimental project in this field and the main objective of the work presented in this thesis was to perform a series of suitable experiments revealing more details of the above transition mechanism. An important aspect of this project was the interpretation of the results on the fluid phase behaviour of binary systems in terms of the molecular structure and the interactions of the mixture constituents.

The experimental work which is presented in Chapters 6, 7 and 8 had to be organised systematically since experiments are expensive and time consuming, although indispensable. Therefore a suitable and in the past well tested experimental technique was used and a collection of interesting binary systems was selected, as is explained in Chapter 5. The results revealed some general patterns which have been organized in the form of phenomenological rules. The advantages and limitations of these rules are carefully outlined. Some empirical correlations based on the above phenomenological rules are developed in Chapter 10 in terms of the molecular structure of the pure components.

Another objective of this work was to model the systems investigated experimentally. The Peng-Robinson equation of state was selected for that purpose because of its simplicity and engineering popularity. It was necessary to develop special calculational methods, discussed in Chapter 3, in order to deal with complex phase equilibria of binary mixtures, like three-phase equilibria. The results of the calculations, presented in Chapter 9, were in qualitative agreement with the experiment. Quantitative agreement was achieved by fitting suitable adjustable parameters appearing in the mixing rules of the model. Unfortunately, the adjustable parameters have a weak physical background and cannot be predicted in advance.

During the experiments several interesting phenomena like barotropy or the coincidence of the tricritical point and the double critical endpoint behaviour (van Laar point) were encountered. Special attention was given to these phenomena.

The experimental results of this work can be used as a guide for future experiments. The calculation procedures that were developed can serve for the calculation of complex fluid phase behaviour in binary mixtures and give additional insight in the structure of phase
diagrams and the stability limits (see Chapter 3). Finally the modelling results offer a
guideline for similar calculations with other equations of state which perhaps lead to better
quantitative agreement with the experiment without adjustable parameters.

1.2 The Gibbs phase rule

We consider an equilibrium in a system of N components distributed over π separate
phases. In general each phase contains every component in a different proportion than any
other phase containing the same component. Also the overall composition of the system (all
the phases) is in general different from the specific composition of any phase. There are
several variables which describe the equilibrated system. Following the definition of Griffiths
and Wheeler (1970) we recognize as "fields" the variables having the same value for all the
coexisting phases and as "densities" the variables which have a different value from phase to
phase. Fields are the temperature, T, the pressure, P, and the chemical potentials of the
various components, μᵢ (i=1,2,…,N), which are identical in every phase as follows from the
equilibrium conditions. Densities are the compositions, xᵢ (i=1,2,…,N and j=α,β,…,π), the mass
densities, ρᵢ, the molar volumes, Vᵢ, the molar entropies, Sᵢ, etc., which differ from phase to
phase.

Let F be the number of independent field variables that are free to change while the system
still contains the same number of components distributed over the same amount of phases.
The number F is often called number of degrees of freedom of the system. Notice that F =
2 implies that T and P, or T and μᵢ, or μᵢ and μᵢ, etc. can be chosen as independent variables.
In other words the number of independent fields has nothing to do with the kind of fields. The
Gibbs phase rule determines F as

\[ F = N - π + 2 \quad (1.1) \]

If k is the number of critical -with each other- phases then the Gibbs phase rule can be
formulated as (Zernike, 1955; Widom, 1973)

\[ F = N - π - (k - 1) + 2 \quad (1.2) \]

In Eq.(1.2) π and k are counted as distinct phases, no matter if some of them (for π) or all
of them (for k) are critical and therefore are observed as a single phase. (k-1) is the number
of the additional restrictions of the equilibrium, resulting from the conditions of criticality;
in fact they are the (k-1) interfaces that have to be specified as disappearing. According to Eq.(1.2) a L=V equilibrium in a binary system (N=2, π=2 and k-1=2-1=1) has F=2-2-1+2=1 degrees of freedom and a L₂=V-L₁ equilibrium in a binary system (N=2, π=3 and k=2-1=1) has F=2-3-1+2=0 degrees of freedom. Also an arbitrary L₃=L₂-L₁=V equilibrium in a quaternary system (N=4, π=4 and k-1=(2-1)+(2-1)=1+1=2) has F=4-4-2+2=0 degrees of freedom. An equivalent formulation is

\[ F = N - \pi - 2k + 2 \quad (1.3) \]

In Eq.(1.3) π and k are counted as observable phases i.e. a critical phase -no matter how many phases become critical together in this phase- is counted as 1; k=1 always for one critical phase. According to Eq.(1.3) a L=V equilibrium in a binary system (N=2, π=1 and k=1) has F=2-1-2+2=1 degrees of freedom and a L₂=V-L₁ equilibrium in a binary system (N=2, π=2 and k=1) has F=2-2-2+2=0 degrees of freedom. Also an arbitrary L₃=L₂-L₁=V equilibrium in a quaternary system (N=4, π=2 and k=2) has F=4-2-2*2+2=0 degrees of freedom. In this thesis Eq.(1.2) will be applied.

For F = 0 the system is characterized as nonvariant, for F = 1 the system is monovariant, for F = 2 bivariant, etc. Before giving examples of the application of the Gibbs phase rule we incorporate the azeotropic case for the sake of completeness. According to Zernike (1949) for a system with N ≥ 2 not more than 2 phases of the same composition can be in equilibrium and if so we have to reduce the F value by (N-1). (N-1) is the additional number of restrictions resulting from the azeotropic condition for these 2 phases (x₁=y₁, x₂=y₂, x₃=y₃,...,xₙ₋₁=yₙ₋₁). In this case the formulation of the Gibbs phase rule is

\[ F = \pi + 3 \quad (1.4) \]

For a unary system N = 1 and therefore if π = 1 then F = 2. The single-phase equilibrium situations are represented by surfaces (dimensionality = 2) on a P,T plane as it is depicted in Fig.1.1. This is also true for any other equivalent plane for example T,μ or P,μ. If π = 2 then F = 1 and the two-phase equilibrium states are curves (dimensionality = 1) on the P,T plane.

If we have only 3 single phases, the solid (S), the liquid (L) and the vapour (V), then there are 3 possible two-phase equilibria, the L.V, the S.L and the S.V equilibrium which are forming the vaporization, the melting, and the sublimation curve, respectively. We may have more than one solid phase and then we have more than 3 two-phase equilibrium curves. If π = 3 then F = 0, which means that the system is nonvariant and that there is a unique value for all
the fields in order to achieve such an equilibrium case (SLV). This state is represented by a point (dimensionality = 0) on the P,T plane, the triple point. Finally if \( \pi = 2 \) but also \( k = 2 \) (the state for a critical point) then \( F = 0 \) again. The common experimentally known case for such a state is the liquid-vapour critical point (L=V) of a single component system which terminates the vaporization curve. The points S=L and S=V have never been observed experimentally. The element Cerium shows a solid-solid critical point.

![Phase Diagram](image)

**Fig. I.1 The phase equilibria of an unary system on a P,T plane. Solid lines: two-phase equilibrium lines and single-phase boundaries, dotted lines: metastable branches of the two-phase equilibria, open triangle: triple point (SLV), open circle: critical point (L=V).**

We see that the dimensionality of the geometrical locus representing a certain type of equilibrium is equal to F if a proper field space is used. We see also that the geometrical locus of order F is bordered by loci of order F-1. The border loci of order F-1 terminate either by crossing a similar border locus or by reaching a point where the degeneration of one field occurs (like a critical point). This termination produces loci of order F-2 (like the triple point or the L=V critical point of a unary system). After the terminal degeneration point the locus
of order $F$ merges with another locus with the same order, (like the $L$ area and the $V$ area merge into the fluid area on the $P,T$ plane of a unary system, see Fig. 1.1).

For a binary system $N = 2$ and consequently if $\pi = 1$ then $F = 3$. In order to depict this case we need at least a three-dimensional space of fields. Obviously the dimensionality of that space must be greater than or equal to $F$. A proper selection could be the $P,T,\mu_z$ space (for simplicity we use $\mu$ instead of $\mu_z$ so we speak about the $P,T,\mu$ space). In this space the one-phase equilibria will form closed volumes bordered by surfaces and curves which terminate these surfaces. Instead of the $P,T,\mu$ space, another popular and convenient but not equivalent space is the $P,T,x$ space ($x$ is the mole fraction of the less-volatile component, $x = x_2$). Although $x$ is a density variable and the dimensionality of the equilibrium loci do not follow the magnitude of $F$, the $P,T,x$ space has become our common system of coordinates for binary systems. The one-phase equilibria in a $P,T,x$ space are again volumes because $x$ refers only to one phase which has the same composition as the whole system and thus counts as one single variable. The situation is different when $\pi = 2$ and so $F = 2$. In the $P,T,\mu$ space the two-phase equilibria are represented by surfaces bordered by curves and points terminating the curves. However in the $P,T,x$ space a locus of two-phase equilibria is a pair of single-phase surfaces which enclose a volume where one-phase equilibria are unstable (phase envelope). This is due to the dual character of $x$ which has a different value in the two phases.

Generally if one density variable is used instead of one field variable in the space where the phase diagram is plotted, then the geometrical locus of a $\pi$-phase equilibrium with $F$ degrees of freedom is a set of $\pi$ loci with dimensionality $F$, which enclose another locus of dimensionality $F+1$ which is unstable. In the case of the binary mixture if the pressure, the temperature and the overall composition of the mixture are such that they determine a point inside the phase envelope (unstable point), then a phase split occurs creating two phases that are in stable equilibrium with each other. The compositions of these phases are such that the condition of equality of the chemical potentials of both components in the two phases is satisfied. These equilibrium points are situated on the two outer single-phase surfaces of the envelope and are connected by a straight segment which is called tie-line. The tie-line contains the unstable point inside the envelope. A mole (mass) balance determines the relative number of moles of the two phases, which is equivalent with the application of the lever rule along the tie-line.

For a binary system with $\pi = 2$ and $k = 2$, $F = 1$. This is the case of the critical curve ($L=V$) of a binary mixture. It is the curve where the two-phase surface of the $P,T,\mu$ space
terminates because of degeneration of one field. It is also the curve where the two outer surfaces of the \(P,T,x\) envelope merge because the \(x\) variable loses its dual character as a consequence of the criticality of the two phases and the equality of their compositions.

If we consider the liquid-vapour envelope of a binary system in the \(P,T,x\) space we already described how this is bordered by the critical curve \((L=V)\) towards high \(P\) and \(T\). At extreme \(x\) values, \(x=0\) or \(x=1\), the same envelope terminates along the two pure component vaporization (saturation) curves where again \(x\) loses its dual character and the two outer surfaces, representing the liquid and the vapour, coincide. Towards the direction of low \(T\) the appearance of solid-liquid-vapour or liquid-liquid-vapour three-phase equilibria terminates the liquid-vapour envelope in most cases.

For a binary mixture with \(\pi = 3\), \(F = 1\). The three-phase equilibria in a \(P,T,\mu\) space are represented by a curve and in a \(P,T,x\) space by a set of 3 curves which enclose a surface (dimensionality \(F+1=2\)) of instability. On the \(P,T\) plane on which the \(P,T,x\) space can be projected, the three-phase equilibria are still on one curve because \(P\) and \(T\) are field variables. This means that the instability surface, formed by the set of the 3 curves \(x_m[P(T)]\) \((m=L_2, L_1, V)\) of the three-phase equilibria in the \(P,T,x\) space, is a ruled surface. In other words a cylinder with an axis vertical to the \(P,T\) plane can be rolled along the three phase surface being continuously in contact with this surface along one of its generating lines. If \(\pi = 3\) and \(k = 2\) then \(F = 0\). As a result the equilibrium among three phases, from which two become critical with each other, is represented by one single point in the \(P,T,\mu\) space and by 2 points in the \(P,T,x\) space. According to the general rule we established previously for the \(P,T,x\) space we expected three \((\pi = 3)\) points \((F = 0)\) instead of two but due to the criticality of the two phases two of the three points degenerate to one, resulting in a total of two \([\pi - (k-1) = 2]\) points \((F = 0)\). This is the case of the so-called critical endpoint which is one of the terminating possibilities of a three-phase equilibrium curve.

When \(\pi = 4\) then \(F = 0\). This means that an equilibrium among four phases for a binary system is a nonvariant one and is represented by a point in the \(P,T,\mu\) space or with a set of four points in the \(P,T,x\) space. This is the quadruple point. The set of four points in the \(P,T,x\) space forms a straight line of instability which is perpendicular to the \(P,T\) field plane. This is because the projection of that line has to be a point in the \(P,T\) plane due to the nonvariant character of that equilibrium.
Examples of the P,T,x space for different types of binary mixtures will be presented in Chapter 2, where also the detailed nomenclature of the various equilibrium loci will be discussed.

1.3 Volatility and density

Our common sense says that ethanol is more volatile than water and that water is denser than ethanol. However the argument that the less-volatile component is also the denser component is not always true and this will be discussed here.

First it is needed to define volatility and density. For a single component system exhibiting a vapour-liquid equilibrium at a certain temperature volatility is the trend of the molecules to escape from the liquid phase and jump to the vapour one. An experimentally measured quantity which is proportional to that trend is the vapour (or saturated) pressure of this component at that temperature. So if we have two components at a specified temperature the more volatile will be the one having the greater vapour pressure. Sometimes the vapour pressure curves of two different components intersect in a so called Bancroft point (Rowlinson and Swinton, 1982, p.19,109) and this means that the order of volatility changes as we pass through the Bancroft temperature. In order to avoid the confusion raised for these pairs of components we will establish a different definition which is better suited for our region of interest. First we select component 1 as the component which has the lower critical temperature of the two components. The other component will be component 2 (Tc₁ < Tc₂). In the systems we study it is always the case that the vapour pressure of component 1 at its critical temperature, in other words its critical pressure Pc₁, is greater than the vapour pressure of component 2 at the same temperature Tc₁ (i.e Pc₁ > Ps₂(Tc₁)). In these cases the more volatile component is component 1.

The density is defined as the mass per unit volume. The consequence of the fact that a phase α is denser than a phase β is the positioning due to the gravitational field of α below β inside the vessel where equilibrium is established. Looking in a glass tube containing a binary system under conditions of three-phase liquid-liquid-vapour equilibrium we distinguish the three phases as vapour (V), light liquid (L₂) and heavy liquid (L₁) from the top to the bottom of the tube:
\[ \rho^V < \rho^L_1 < \rho^L_2 \] (1.5)

The question that arises here is: Is the sequence of the three phases with respect to the density the same as the sequence with respect to the mole fraction \( x_2 \) (i.e. the sequence with respect to the less-volatile component composition)? Or more specifically, does the order vapour (V), light liquid (L\(_1\)), heavy liquid (L\(_2\)) corresponds to the order vapour (V), liquid with the smaller mole fraction with respect to the less-volatile component 2 (L\(_1\)), liquid with the greater mole fraction with respect to the less-volatile component 2 (L\(_2\))? Or with symbols, does the sequence V \( \rightarrow \) L\(_1\) \( \rightarrow \) L\(_2\) of increasing densities corresponds always to the sequence V \( \rightarrow \) L\(_1\) \( \rightarrow \) L\(_2\) of increasing mole fractions \( x_2 \)?

The answer to this question is no. In the case of heteroazeotropy the sequence V \( \rightarrow \) L\(_1\) \( \rightarrow \) L\(_2\) of increasing densities corresponds to the sequence L\(_1\) \( \rightarrow \) V \( \rightarrow \) L\(_2\). Also in some cases of dense more-volatile components the sequence V \( \rightarrow \) L\(_1\) \( \rightarrow \) L\(_2\) of increasing densities may correspond under certain conditions of pressure and temperature to the sequence V \( \rightarrow \) L\(_2\) \( \rightarrow \) L\(_1\). The reasons for this latter behaviour as well as the consequences (barotropic inversion phenomena) will be discussed when the experimental data of the corresponding binary mixtures will be presented (Chapter 6).

1.4 Practical significance of this investigation

Although the objective of this work is to investigate some fundamental questions concerning the fluid phase behaviour of binary mixtures, the results can be very useful for practical applications.

In Fig.1.2 a schematic isobaric T-x plot for fluid phase equilibria in a binary system is given. The overall phase diagram does not correspond to a specific real system but its regions may be encountered in real world as separate cases. The upper part corresponds to the behaviour of the system carbon dioxide with n-tridecane while the lower part corresponds to the behaviour of the system water with n-butanol. We observe various regions of liquid-liquid immiscibility. Without entering into details we can give an explanation for this variety of immiscibility phenomena in terms of the molecular characteristics of the components of the mixture and of the intermolecular forces exerted on their molecules. We denote as component A the more-volatile component and as component B the less-volatile component.
For temperatures close to $T_{eA}$ the molar volume of liquid A increases drastically. There is a large difference in free volume for pure liquid A and liquid B. This large difference in free volume causes the $L_1 + L_2$ phase split above $T_1$ (Patterson and Delmas, 1968).

At lower temperatures the competition between the internal energy (U) and the entropy (S) is more significant than the free volume effects and determines the miscibility situation according to the minimum free energy (A=U-TS) criterion. Above $T_2$ mixing between unlike molecules A-B is favoured because it increases the compositional entropy (entropy due to the random mixing of dissimilar species) and therefore reduces the free energy of the system. The temperature is high so the entropic term is significant. Below $T_2$ the van der Waals attraction
forces between like molecules A-A and B-B are more important because they reduce the internal energy and consequently the free energy. Somewhere in between one of the two effects dominates and reverses the situation from liquid mixing to liquid demixing or vice versa.

The immiscibility region $L_1 + L_2$ below $T_2$ continues until $T_3$. Below $T_3$ hydrogen bonding between unlike molecules A-B is favoured because it reduces the internal energy and so the free energy. The reduction of the internal energy is enough to anticipate for the loss of the orientational entropy (entropy due to random orientation of mixed species) caused by the hydrogen bonding. In addition the temperature is low and the entropic term is less significant. Therefore below $T_3$ miscibility occurs again.

As the temperature diminishes further the temperature $T_4$ is reached. Below this point hydrogen bonding between like molecules A-A and B-B is favoured because it reduces the internal energy and another immiscibility loop is created. For a detailed discussion on these matters see Walker and Vause (1983 and 1987).

The example given in Fig.1.2 stresses the importance of fluid phase behaviour knowledge. In industrial separation processes like distillation or extraction the above phenomena are possibly encountered depending on the conditions and the nature of the constituents of the mixture. If one knows in advance what is expected then the process can be operated in a more profitable way and problems due to these phenomena can be avoided by proper design. As we will discuss in subsequent chapters barotropic phenomena where a density inversion of two fluid phases occurs can be also involved either as an extra difficulty or a lucky coincidence. The process engineer who is aware of these cases can save time and money.

Symbols

A or 1  more-volatile component
A  Helmholtz free energy
B or 2  less-volatile component
F  number of degrees of freedom
L  liquid phase
$L_\text{L}$  light (less-dense) liquid phase
$L_\text{H}$  heavy (denser) liquid phase
Chapter 1

$L_1$ liquid phase richer in the more-volatile component
$L_2$ liquid phase richer in the less-volatile component
$N$ number of components
$P$ pressure
$P_c$ critical pressure
$P_s$ vapour (or saturation) pressure
$S$ molar entropy
$S_s$ solid phase
$T$ temperature
$T_c$ critical temperature
$U$ internal energy
$V$ molar volume
$V_v$ vapour phase
$x$ composition (mole fraction) - without component index refers always to the less-volatile component of a binary mixture

Greek

$\mu$ chemical potential
$\pi$ number of distinct phases in an equilibrated system
$\rho$ mass density

Superscripts

$j$ phase index ($j=\alpha, \beta, ..., \pi$)

Subscripts

$i$ component index ($i=1, 2, ..., N$)
References


2. TYPES OF FLUID PHASE EQUILIBRIA IN BINARY MIXTURES

In this chapter the basic features of fluid phase equilibria in binary mixtures are briefly discussed. The nomenclature of the various kinds of equilibria as well as their geometrical representation is outlined. The different types of fluid phase behaviour are recognized and the transitions among them are identified. The scope of this introduction is to explain the basic types of diagrams which are used throughout this work and to organize them in a logical scheme.

2.1 P,T,x space nomenclature

In Chapter 1 the Gibbs phase rule was discussed and a geometrical consideration of the domains of fluid phase equilibria was based on this rule. Below a more detailed description of fluid phase equilibria in binary mixtures will be given. Instead of the three-dimensional space its two-dimensional projections and cross-sections will be preferred.

The simpler case for a binary mixture is the one where the critical points of the two pure components are connected by a continuous critical curve. In Fig.2.1.a the three-projections of the P,T,x space for this case are depicted. We must stress here that the schematic diagrams we will use are often exaggerated in order to make their specific details of construction visible. Therefore we should not expect that in reality the same phenomena are extended over similar ranges of conditions and it is advisable not to use these schematic graphs as arguments to prove anything. In Chapter 9 many calculated diagrams of the same kind will be presented. Although the calculations also often do not match the experimental data, they preserve at least the qualitative features of phase diagrams and lead to safer conclusions about the possible fluid phase equilibria. The binary phase behaviour of Fig.2.1.a is named type I in the classification scheme of van Konynenburg and Scott (1981). This classification scheme will be examined in detail in a subsequent section.

The P,T projection in Fig.2.1.a contains the monovariant (F = 1) equilibria of the system which are represented by curves (one dimensional loci). The two solid curves are the saturation curves or the vapour pressure curves of the two pure components. They originate in the triple points of the pure components (not shown in this picture, see Fig.1.1) and they terminate at the critical points of the pure components. Their course is approximately described by the Clapeyron equation written as \[ \ln(P) = \frac{A + B}{T}. \] The dashed curve is the
vapour-liquid critical curve of the mixture. Every point along that curve represents the critical point of a specific mole fraction from 0 to 1. In the example given here the critical curve is monotonous with respect to the temperature and shows a pressure maximum. In addition, as can be seen from the P,x projection, there is an inflection point with respect to the pressure.

![Diagram](image)

**Fig. 2.1.** A Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type I. Solid curves: vapour pressure curves of pure components, dashed curves: critical curves, empty circles: critical points.

This is one of the various possibilities for the vapour-liquid critical curve of type I systems. Rowlinson and Swinton (1982, p.204) discuss several other cases but in principle even more cases are possible in real systems. The various-cross sections of the P,T,x space of type I systems are presented in many textbooks. Here we remind briefly the P,T cross-section (or isopleth - from the Greek "ισοπληθής" which means equal amount) because in this work the experimental method is based on the measurement of isopleths (see Chapter 5).

In Fig.2.1.b several isopleths are projected together with the saturation curves of the pure components and the vapour-liquid critical curve of the mixture. The isopleths are tangent to the critical curve at the critical point of the specific composition they represent. Inside an
isopleth, for example $x = x_2$, at the point of conditions $T_e$ and $P_e$ which is symbolized as an empty square, the mixture with that specific overall composition ($x_2$) exhibits vapour-liquid equilibrium. The high-pressure branch of the isopleth ending in the critical point is the bubble-point curve and the low-pressure branch starting at the critical point is the dew-point curve of the isopleth. For the isopleth $x = x_2$ at the equilibrium point ($T_e, P_e$) the vapour phase composition is $x_1$ because the dew-point curve of the isopleth $x_1$ is passing through the point ($T_e, P_e$) and the liquid phase composition is $x_3$ because the bubble-point curve of the isopleth $x_3$ is passing through the point ($T_e, P_e$). From the same point ($T_e, P_e$) it is not possible that any other bubble or dew-point curve passes because for a binary system the bubble or dew points of a specific composition are monovariant equilibria. If the temperature is fixed at $T_e$ the pressure for a dew point with composition $x_1$ can only be $P_e$ and the pressure for a bubble point with composition $x_3$ can only have the value $P_e$.

Fig.2.1.b (left) Schematic $P,T$ projection of the monovariant fluid phase equilibria for a type I binary system together with some selected isopleths (see text).

Fig.2.1.c (right) Schematic representation of an isopleth in a type I binary system. Empty circle (point C): vapour-liquid critical point, up solid circles (point B): cricondenbar, (point A): cricondentherm, shaded regions: retrograde phenomena during isothermal or isobaric processes.
In Fig. 2.1.c one specific isopleth is considered. The position of the critical point C is generally different from that of the maximum pressure point B (cricondenbar) or of the maximum temperature point A (cricondentherm). Depending on the relative positions of these three points retrograde phenomena appear in the shaded regions of the graph (Katz and Kurata, 1940).

Fig. 2.2 Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type II. Solid curves: vapour pressure curves of pure components, dashed curves: critical curves, dashed-dotted curves: three-phase equilibria curves, empty circles: critical points, up solid triangle: UCEP \([L_2=L_1-V]\).

In Fig. 2.2 the three projections of the monovariant equilibria for a type II system are plotted. The difference between this type and type I behaviour is the existence of a liquid-liquid immiscibility region at low temperatures. The liquid-liquid immiscibility region terminates along a liquid-liquid critical curve. The temperatures where the two liquid phases become indistinguishable are called upper critical solution temperatures (UCST's). For any temperature where liquid-liquid immiscibility exists, there is a unique pressure where the vapour phase coexists. The locus of temperatures and pressures where the above three phases
are present is a curve, the three-phase \( L_2 L_1 V \) equilibrium curve which is plotted as a dashed-dotted curve. The three-phase \( L_2 L_1 V \) equilibrium curve terminates at a point where the two liquid phases are critical with each other. This point is an UCST and it is also the endpoint of the liquid-liquid critical curve. Therefore it is named upper critical endpoint (UCEP). This point is symbolized by an up solid triangle. The liquid-liquid critical curve may have a positive or negative steep slope at the UCEP. Schneider (1970) gives a systematic classification scheme for the various types of these critical curves.

The three-phase equilibria are projected on an area in the \( T_x \) and the \( P_x \) planes. As we have mentioned in Chapter 1 they form a ruled surface in the \( P,T,x \) space which is vertical to the \( P,T \) plane. In the \( T_x \) or \( P_x \) projection the three-phase equilibria area is enclosed between the branches representing the \( V \) and the \( L_2 \) phases. \( V \) is the vapour phase and \( L_2 \) is the richer in the less-volatile component liquid phase. The third branch, \( L_1 \), is located between the two others. This is not always true for three-phase equilibria; for example in systems with heteroazeotropy the \( V \) branch is between the \( L_1 \) and \( L_2 \) branches as we will see in Chapter 9. Any mixture with a composition between the two outer branches of the three-phase equilibria splits in three phases for any pair of \( P \) and \( T(P) \) along the three-phase \( L_2 L_1 V \) equilibrium curve. The compositions of these phases are determined by the intersection of the tie-line (a line in the \( P,T,x \) space vertical to the \( P,T \) plane at the three-phase conditions \( P \) and \( T \)) with the three branches \( V \), \( L_1 \) and \( L_2 \).

In Fig.2.3 the projections of a system with type III fluid phase behaviour are depicted. In this binary system there is no continuous critical curve connecting the critical points of the two pure components. The critical curve starting from the critical point of the more-volatile component finishes at a critical endpoint where a three-phase \( L_2 L_1 V \) equilibrium curve terminates. This critical endpoint is also an UCEP as in the type II behaviour, but the two critical phases are not the two liquids \( L_2 \) and \( L_1 \) but the vapour, \( V \), and the liquid richer in the more-volatile component, \( L_1 \). In order to distinguish between these two UCEP's we characterize the type II UCEP as UCEP \( [L_2=L_1=V] \) and the type III UCEP as UCEP \( [L_2-L_1=V] \). The UCEP \( [L_2-L_1=V] \) is symbolized by an up empty triangle. The critical curve starting from the critical point of the less-volatile component goes to lower temperatures passing successively through a pressure maximum and a pressure minimum. Afterwards it turns back to higher temperatures and pressures. The above features of that critical curve as well as its looping in the \( P_x \) projection are not common to all type III systems but only to them which are located close to the transition towards type IV behaviour as it will be shown
In Chapter 9. Other possibilities for the course of the above critical curve are mentioned by Rowlinson and Swinton (1982, p.214).

![Diagram](image)

**Fig. 2.3 Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type III. For curves and points see Fig. 2.2. Also: up empty triangle: UCEP \([L_2-L_1-V]\).**

In Fig. 2.4 the projections for a type IV system are given. A type IV system shows like a type II system a \(L_2L_1V\) equilibrium curve with an UCEP \([L_2=L_1-V]\), but in addition, at higher temperatures, a second branch of the \(L_2L_1V\) equilibrium curve is found. Also in this type there is no continuous vapour-liquid critical curve. The branch of the critical curve starting from the critical point of the more-volatile component finishes at an UCEP \([L_2-L_1=V]\) of the high temperature branch of the \(L_2L_1V\) equilibrium curve as in type III. The branch of the critical curve originating from the critical point of the less-volatile component goes to lower temperatures via a pressure maximum and ends in a lower critical endpoint of the high temperature branch of the \(L_2L_1V\) equilibrium curve where two liquid phases are critical with each other and in equilibrium with the vapour phase. This critical endpoint is not the same as the UCEP \([L_2=L_1-V]\) of the type II behaviour. In this case the two liquids become critical
with each other upon a temperature reduction, instead of a temperature increase as is happening in a type II system. Therefore this critical endpoint is characterized as a lower critical endpoint (LCEP) in contradiction to the upper critical endpoint of the type II behaviour. The LCEP \([L_2=L_1-V]\) is symbolized by a down solid triangle. These UCEP and LCEP limit the high temperature branch of the \(L_2L_1V\) equilibrium curve in a type IV system.

![Diagram of phase equilibria](image)

*Fig.2.4 Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type IV. For curves and points see Figs. 2.2 and 2.3. Also: down solid triangle: LCEP \([L_2=L_1-V]\).*

The type V system of Fig.2.5 may be considered as a special case of a type IV system where the lower branch of the three-phase equilibria as well as the related liquid-liquid immiscibility region has been shifted to negative temperature. In practice, the occurrence of a solid phase (consisting possibly of the less-volatile component) can mask the liquid-liquid equilibria. So, it is difficult to distinguish between type IV and type V phase behaviour. For the same reason, it is difficult to distinguish between type I and type II phase behaviour.
Fig. 2.5 Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type V. For curves and points see Fig. 2.4.

Fig. 2.6 As Fig. 2.4, with indicated values of P, T and x for the construction of Figs. 2.7, 2.8 and 2.9.
In Fig. 2.6 some values of $T$, $P$ and $x$ are indicated. At these values $P, x, T, x$ and $P, T$ cross-sections are constructed. Fig. 2.7 contains the isothermal cross sections. At $T_1$ the two liquid-liquid immiscibility regions are the result of the double crossing of the isotherm with the liquid-liquid critical curve. At a temperature below $T_1$, where the isotherm crosses the critical curve at its minimum temperature point, a double critical point (DCP) occurs and the two immiscibility regions $L_1 + L_2$ merge. At $T_2$ we have a typical example of three-phase equilibrium above the critical temperature of the more-volatile component. Both $L_1 + V$ and $L_2 + L_1$ two-phase regions end in a critical point. At $T_3$ the liquid-liquid immiscibility region is vanished and a typical isotherm for all the types we have discussed appears.

![Diagram](image)

**Fig. 2.7 Isothermal $P,x$ plots for the temperatures $T_1$, $T_2$ and $T_3$ of Fig. 2.6. Solid curves: binodals, dashed-dotted curve: three-phase (these phases are symbolized with up empty triangles) equilibrium, empty circles: critical points, empty squares: saturation pressures of pure components.**

In Fig. 2.8 the isobaric plots for $P$-values given in Fig. 2.6 are depicted. Notice that at $P_3$ we have a closed-loop two-phase region $L_2 + V$. At a pressure above $P_3$, where the isobar
crosses the critical curve at its maximum pressure point, the above closed loop of $L_2+V$ vanishes in a DCP.

Fig. 2.8 Isobaric T-x plots for the pressures $P_1$, $P_2$ and $P_3$ of Fig. 2.6. For curves and points see Fig. 2.7. Here: empty squares: saturation temperatures of pure components.

In Fig. 2.9 the third kind of cross-sections, the isopleths, are plotted. They are more complicated than those of Fig. 2.1.b because of the occurrence of the three-phase equilibria. At the isopleth for $x = x_1$ the three-phase curve can be observed up to the point where the vapour phase has the same composition as the overall mixture (solid square). At higher temperatures the three-phase equilibrium is not found since the overall composition of the mixture is smaller than the compositions of all three phases. For the isopleth $x = x_2$ the whole course of the three-phase curve can be observed. At a point between the UCEP [$L_2$+$L_1$=$V$] and the LCEP [$L_2$=$L_1$-$V$] along the three-phase $L_2$+$L_1$+$V$ equilibrium curve, symbolized as a solid square, the $V$ and the $L_2$ phases vanish at the same time upon a volume decrease and the whole mixture is in the homogeneous phase $L_1$ which has composition $x_3$ in that point. Before and after that point all three phases coexist. At the isopleth for $x = x_3$ neither the UCEP [$L_2$=$L_1$-$V$] nor the LCEP [$L_2$=$L_1$-$V$] can be observed.
Fig 2.9 Isopleth P,T plots for the compositions $x_1$, $x_2$ and $x_3$ of Fig 2.6. Solid curves: binodals, dashed-dotted curve: three-phase equilibria, empty circles: critical points, up solid triangle: UCEP [$L_2=L_1-V$], down solid triangle: LCEP [$L_2=L_1-V$], up empty triangle: UCEP [$L_2=L_1-V$]. solid squares: crossing points of the binodal curves with the three-phase curve (at these points one phase is present with a composition equal to the overall composition of the mixture).

For this composition at low temperatures liquid-liquid immiscibility occurs above the three-phase $L_2L_1V$ equilibrium curve. This means that at low temperatures (before the temperature of the UCEP [$L_2=L_1-V$]) as we compress the system above the three-phase equilibrium pressure the V phase disappears. In contrast, for the same low temperature range, at the isopleths for $x=x_1$ and $x=x_2$ compressing the system above the three-phase equilibrium pressure results in the disappearance of the $L_2$ phase.

The scope of this section was not to cover the variety of diagrams that can represent the realm of fluid phase equilibria in binary mixtures. There are books and review articles devoted to the subject from which we mention here the works of Bakhuis Roozeboom (1901-1913), Zernike (1955) and Vogel (1959). In subsequent sections when a special case arises we will provide further explanations.
2.2 Classification schemes

The idea of systematic calculations of phase diagrams by means of an equation of state was first realized by van Konynenburg (1968) and Scott and van Konynenburg (1970). They applied the van der Waals equation for binary systems and they predicted qualitatively almost all the types of fluid phase equilibria known from experiment. More specifically they predicted the types I up to V discussed above and they speculated about the existence of some other types that were never found experimentally.

The van der Waals equation has the form

\[ P(V,T,x) = \frac{R}{V-b(x)} \left( \frac{T}{V-b(x)} - \frac{a(x)}{V^2} \right) \]

where the parameters a, b for the pure components are given by

\[ a = \frac{27}{64} \frac{R^2 \tau^2}{P_c} \quad \text{and} \quad b = \frac{1}{8} \frac{RT_c}{P_c} \]

The mixture parameters a(x) and b(x) depend on the pure components parameters a_{11}, a_{22}, b_{11} and b_{22} according to quadratic mixing rules with respect to composition

\[ a(x) = (1-x)^2 a_{11} + 2(1-x)x a_{12} + x^2 a_{22} \]
\[ b(x) = (1-x)^2 b_{11} + 2(1-x)x b_{12} + x^2 b_{22} \]

with cross interaction parameters a_{12} and b_{12} given by:

\[ a_{12} = (1-k) \sqrt{a_{11} a_{22}} \quad \text{and} \quad b_{12} = (1-l) \frac{b_{11} + b_{22}}{2} \]

The parameters k and l are used to correct for deviations from the geometric mean and arithmetic mean assumptions respectively. In the work of van Konynenburg and Scott it was supposed that l=0. Some dimensionless parameters which characterize the properties of the two components of the mixture are defined as

\[ \zeta = \frac{a_{22} - a_{11}}{a_{22} + a_{11}} , \quad \lambda = \frac{a_{22} - 2a_{12} + a_{11}}{a_{22} + a_{11}} \quad \text{and} \quad \xi = \frac{b_{22} - b_{11}}{b_{22} + b_{11}} \]
Fig. 2.10 The domains of various types of fluid phase equilibria in binary systems (components 1, 2), according to calculations by means of the van der Waals equation of state. The solid curve is the locus of binary mixtures exhibiting a TCP behaviour and the dashed-dotted curve is the locus of binary mixtures exhibiting a DCEP behaviour. The dashed curve is the locus of the geometric mean condition, i.e. the locus where the parameter \( k \) in Eq. (2.4) is zero. The geometric mean condition is expressed as \( (1-\lambda)^2=(1-\xi^2) \). The relative size \( \xi \) of the components 1, 2 is assumed to be constant. Along the diagonals (dotted curves) the conditions \( a_{12}=a_{11} \) and \( a_{22}=a_{12} \) hold. The diagonals are the limits of azeotropy.

The parameter \( \zeta \) denotes the difference between the 1-1 and the 2-2 attractive forces. The parameter \( \lambda \) denotes the difference between the like (1-1, 2-2) and the unlike (1-2) attractive forces. Finally the parameter \( \xi \) accounts for the size difference between the molecules of type 1 and the molecules of type 2. Solving for several numerical combinations of the above parameters different kind of phase diagrams are created. The results are organized in a map of the form of Fig. 2.10. In this specific diagram the parameter \( \xi \) has been kept constant at the value 0, i.e. any system consists of equal sized molecules 1 and 2. In Fig. 2.11 another map for \( k=0 \) is presented. In this case the systems obey the geometric mean condition.
Fig. 2.11 The domains of various types of fluid phase equilibria in binary mixtures (components 1, 2), according to calculations by means of the van der Waals equation of state. The solid curves are the loci of binary mixtures exhibiting a TCP behaviour and the dashed-dotted curve is the locus of binary mixtures exhibiting a DCEP behaviour. The dotted curves are the limits of azeotropy. The geometric mean condition holds for this diagram.

In Figs. 2.10 and 2.11 the solid curves represent tricritical point (TCP) loci and the dashed-dotted curves represent double critical endpoint (DCEP) loci. They are calculated using the conditions imposed by Eqs. (C.16) and (C.17), (see Appendix C). In Chapter 10 some applications of charts of this kind for real systems will be discussed. Various other investigators used different equations of state and repeated the classification chart calculations with more quantitative success (Furman et al., 1977; Furman and Griffiths, 1978; Clancy et al., 1978; Mazur et al., 1985; Jackson et al., 1986; Deiters and Pegg, 1989; van Pelt, 1992).
2.3 Transitions between different types of fluid phase behaviour

In our work only the types II, IV and III of fluid phase behaviour are encountered. As can be seen from Fig.2.12, which is a schematic enlargement of the corresponding section of Fig.2.10 including the type IV* region that was found later, there are several possible transitions between these types of fluid phase behaviour. Type IV* (see Fig.2.13) resembles type IV but the critical endpoints and the connectivity of the critical branches are different. This type is thermodynamically possible but was never observed in the laboratory. Later in this thesis the feasibility of such a type of fluid phase behaviour on the basis of experimental evidence is discussed.

Fig.2.12 Schematic enlargement of Fig.2.10 around the transitions among types II, III and IV area; IV* type is also included. The solid curve is the locus of binary mixtures exhibiting a TCP behaviour and the dashed curve is the locus of binary mixtures exhibiting a DCEP behaviour. The crossing point (solid square) represents a binary mixture exhibiting a VLP behaviour.
Fig. 2.13 Schematic representation of the projections of the monovariant fluid phase equilibria in binary mixtures of type IV*. Solid curves: vapour pressure curves of pure components, dashed curves: critical curves, dashed-dotted curves: three-phase equilibria curves, empty circles: critical points, up solid triangle: UCEP \([L_2=L_1-V]\), down empty triangle: LCEP \([L_2=L_1-V]\), up empty triangle: UCEP \([L_2=L_1-V]\).

A transition can be practically realized in a family of binary systems when the more-volatile component is kept fixed while the less-volatile component is changing as a member of a certain homologous series. A typical example is the family of carbon dioxide with n-alkanes (see also Chapters 3, 4 and 9). The mixture of carbon dioxide with n-dodecane exhibits type II fluid phase behaviour, the mixture of carbon dioxide with n-tridecane belongs to type IV and the mixture of carbon dioxide with n-tetradecane exhibits type III behaviour.

Studying ternary mixtures of the type carbon dioxide - dodecane - tridecane or carbon dioxide - tridecane - tetradecane we achieve a kind of experimental interpolation between the binary systems. The ternary systems are considered as quasi-binary systems and this assumption, the quasi-binary approximation, can be validated as we will see in Chapter 5.
Fig. 2.14.a Transition from type II to type IV via a TCP behaviour. P, T and T, x projections of the monovariant fluid phase equilibria. For curves and symbols see Figs. 2.2 and 2.4. Also: solid diamond: TCP.

Fig. 2.14.b Transition from type IV to type III via a DCEP behaviour. P, T and T, x projections of the monovariant fluid phase equilibria. For curves and symbols see Figs. 2.3 and 2.4. Also: empty square: DCEP.
In this way we can approach the behaviour around the TCP and the DCEP much closer. In Figs. 2.14.a and 2.14.b it is explained how the behaviour in the neighbourhood of the TCP (transition from type II to type IV and vice versa) and of the DCEP (transition from type IV to type III and vice versa) would look like. In Figs. 2.15.a and 2.15.b similar diagrams are shown for the transition from type IV* to type III and for the transition from type II to type IV*. If the transition from type II to type III is direct without the intermediate types IV or IV* then the transition behaviour is called a van Laar point (VLP) behaviour. This name was given by Meijer (1989) as van Laar was the first who calculated the position of a mathematical double point (MDP) according to the van der Waals equation and the geometric mean conditions. The MDP in this case coincides with the VLP.

Fig 2.15.a Transition from type IV* to type III via a TCP behaviour. P,T and T,x projections of the monovariant fluid phase equilibria. For curves and symbols see Figs. 2.3 and 2.13. Also: solid diamond: TCP. This TCP is symbolized as TCP* because it is related with the type IV* behaviour.
Fig. 2.15.b Transition from type II to type IV* via a DCEP behaviour. $P, T$ and $T, x$ projections of the monovariant fluid phase equilibria. For curves and symbols see Figs. 2.2 and 2.13. Also: empty square: DCEP. This DCEP is symbolized as DCEP* because it is related with the type IV* behaviour.

The Gibbs phase rule for a system in equilibrium where $k$ phases are critical with each other has the form, see also Eq.(1.1)

$$F = N - \pi + 2 - (k - 1)$$

(2.6)

For a binary mixture at a tricritical point the above formula results in $F = 2 - 3 + 2 - (3-1) = -1$, therefore the Gibbs phase rule does not allow a tricritical point in a binary mixture. For a ternary mixture at a tricritical point we have $F = 3 - 3 + 2 - (3-1) = 0$ and for a quaternary mixture at a tricritical point $F = 1$. Consequently the minimum number of components to be able to observe a tricritical point is 3 according to the Gibbs phase rule and for a N component system the locus of the tricritical points is a space of dimensionality N-3.
Fig. 2.16 Direct transition from type II to type III via a VLP behaviour. P,T and T,x projections of the monovariant fluid phase equilibria. For curves and symbols see Figs. 2.2 and 2.3. Also: solid square: VLP.

In Fig. 2.16 the transition from type II to type III through a VLP is schematically drawn. The VLP may be considered as the coincidence of a TCP and a DCEP. In principle it is also the L₂=L₁ endpoint of a three-phase curve on a continuous liquid-vapour critical curve which proceeds to both sides of the endpoint, therefore it can alternatively be named as tricritical endpoint (TCEP).

In Fig. 2.17.a the three-phase equilibrium curves of some binary and/or quasi-binary systems belonging to the same family are plotted together with the vapour pressure curve of the more-volatile component. The systems are exhibiting the transition from type II, via type IV, towards type III fluid phase behaviour. The graph is schematic but is very similar for all the experimental results collected in this thesis. In Fig. 2.17.b the critical endpoints of this hypothetical family are projected on a T,n plane, where n is the carbon number of the less-volatile component.
Fig. 2.17. a Schematic representation - in a P,T projection- of various types of three-phase equilibrium curves for binary mixtures. Solid curve: saturation curve of pure more-volatile component, long dashed curve and medium dashed curve: three-phase L₂L₁V equilibrium curves for binary mixtures of type II fluid phase behaviour, short dashed curve and dotted curve: three-phase L₂L₁V equilibrium curves for binary mixtures of type IV fluid phase behaviour, dashed-dotted curve and dashed-triple-dotted curve: three-phase L₂L₁V equilibrium curves for binary mixtures of type III fluid phase behaviour, empty circle: critical point of pure more-volatile component, up solid triangles: UCEP's [L₂-L₁-V], down solid triangles: LCEP's [L₂-L₁-V], up empty triangles: UCEP's [L₂-L₁=V].

If the less-volatile component is a member of the homologous series of n-alkanes the carbon number is a parameter which systematically describes the passing from member to member, but if the less-volatile component is a branched alkane then n cannot distinguish any more between various members (for instance between n-pentane, iso-pentane and neo-pentane). In such a case another parameter has to be used, as will be discussed in Chapter 10. As we can see from Fig. 2.17.b the locus of the UCEP's [L₂=L₁-V] meets the locus of the LCEP's [L₂=L₁-V] at the DCEP and the locus of the LCEP's [L₂=L₁-V] meets the locus of the UCEP's [L₂=L₁=V] at the TCP.
Fig. 2.17(b) Schematic representation of the transition from type II, via type IV, towards type III of fluid phase behaviour in binary mixtures. \( n \) is the carbon number of the less-volatile component. Dashed-dotted curve: UCEP's \([L_2-L_1-V]\), solid curve: LCEP's \([L_2-L_1-V]\), long dashed curve: UCEP's \([L_2-L_1-V]\), horizontal short dashed curves: transition borders, vertical dashed-triple-dotted curve: critical temperature of pure more-volatile component, empty square: DCEP, solid diamond: TCP.

According to the classical theory for tricritical points of Creek et al. (1981) the "width" of the upper part of the three phase region in a type IV system, as measured by the difference \( \Delta T_{UL} \) or by the difference \( \Delta P_{UL} \) scales as \( \Delta z^{1/2} \), where

\[
\Delta T_{UL} = T_{UCEP} - T_{LCEP}, \quad \Delta P_{UL} = P_{UCEP} - P_{LCEP}
\]

and \( \Delta z = z - z_{TCP} \). Here the UCEP is of the type \( L_2-L_1-V \) and \( z \) is the carbon number \( n \) (see Fig.2.18.a).

The classical theory suggests also that the difference \( \Delta T_m \) between the "average" temperature of the upper branch of the three-phase equilibrium curve \( T_m \) and the \( T_{TCP} \) scales as \( \Delta z \). The same holds for the corresponding pressures, \( \Delta T_m = T_m - T_{TCP} \) and \( T_m = (T_{UCEP} + T_{LCEP}) / 2 \).
Fig. 2.18.a (left) and 2.18.b (right) Schematic representations of the transition borders around the TCP and the DCEP. Up solid triangle: UCEP [L₂=L₁-V], down solid triangle: LCEP [L₂=L₁-V], up empty triangle: UCEP [L₂=L₁-V], solid diamond: TCP, empty square: DCEP.

If $\Delta T_{UL}$ scales as $\Delta z^{3/2}$ and $\Delta T_m$ scales as $\Delta z$, then it is concluded that $\Delta T_{UL}^{2/3}$ scales as $\Delta T_m$. But $T_{TCP}$ is constant so $\Delta T_{UL}^{2/3}$ scales as $T_m$.

For the asymptotic behaviour close to the DCEP there is no theoretical treatment analogous to the classical theory which applies close to the TCP. However the shape of the region from Fig.2.18.b suggests a quadratic relationship. In other words, it can be assumed that the "width" of the gap between the two branches of the three-phase $L_2L_1V$ equilibrium curve in a type IV system, as measured by the difference $\Delta T_{LU}$ or by the difference $\Delta P_{LU}$ scales as $\Delta z^{1/2}$. Here $\Delta T_{LU} = T_{LCEP} - T_{UCEP}$, $\Delta P_{LU} = P_{LCEP} - P_{UCEP}$ and $\Delta z = z_{DCEP} - z$. In this case the UCEP is of the type $[L_2=L_1-V]$. From the above is concluded that $\Delta T_{LU}^2$ scales as $z$ (here as n).
Symbols

DCEP  double critical endpoint
DCP   double critical point
LCEP  lower critical endpoint
LCSP  lower critical solution pressure
LCST  lower critical solution temperature
MDP   mathematical double point
P     pressure
P_e   equilibrium pressure
T     temperature
TCEP  tricritical endpoint
TCP   tricritical point
T_e   equilibrium temperature
UCEP  upper critical endpoint
UCSP  upper critical solution pressure
UCST  upper critical solution temperature
VLP   van Laar point

References


3. CALCULATIONAL METHODS FOR FLUID PHASE EQUILIBRIA IN BINARY MIXTURES

In this Chapter a general procedure for the calculation of fluid phase equilibria is discussed. The method is based on the construction of closed-loop curves formed when the independent field variables determining the equilibrium are plotted against each other. Both material and mechanical stability criteria are considered and illustrated by appropriate Gibbs energy analysis. In principle the method can be used for multicomponent systems, but becomes too ineffective for systems of more than two components. However it provides a thorough insight in the background of phase diagrams and it is very useful for the calculation of complicated binary phase diagrams. As an illustration the fluid phase equilibria of the binary system of carbon dioxide and n-tridecane and of the binary systems of methane with n-pentane or n-decane are calculated using the Peng-Robinson equation of state. For these systems experimental data are available. The material developed in this chapter will be used for the modelling of the experimentally measured systems in Chapter 9.

3.1 Introduction to the problem

The calculation of liquid-liquid-vapour equilibria in binary systems by means of equations of state often gives rise to convergence problems. The direct calculation of the three-phase equilibrium, solving numerically the system of non-linear equations provided by the equilibrium conditions (Mc Hugh and Krukonis, 1986), is very sensitive to starting values. The Michelsen (1982) flash method is not so easy to apply, because at a given temperature the three-phase equilibrium is found at one discrete pressure. The calculation of the three-phase equilibrium from the intersection of two two-phase regions is computer time consuming and it is complicated by the occurrence of metastable two-phase regions.

Van Konynenburg and Scott (1980) used a different approach for the calculation of three-phase curves in binary systems based on the analysis of $\mu_1, \mu_2$ plots. This method is very robust and gives a lot of insight in the background of phase diagrams.

In Fig.3.1 a survey of different possible techniques to solve the flash problem for a two-phase equilibrium is given. An "energy" quantity $f$ depending on a "density" variable $z$ through the relation $f(z)$ is adequate to describe the problem.
Fig. 3.1 Representation of possible ways to calculate fluid phase equilibria (see text).

The meaning of the term "density" variable is the same as discussed in Chapter 1 and will become more clear in the following section. For a pure component, $f(z)$ is equivalent to $A(V)$ at constant $T$, and for a binary, $f(z)$ corresponds to $G(x)$ at constant $P$ and $T$. The left part of Fig. 3.1 includes from top to bottom the zero ($f$), the first ($f_z$) and the second ($f_{zz}$) derivatives of $f$ with respect to $z$ plotted against the "density" $z$.

For the $f,z$ curve the solution of the flash problem is achieved by the construction of a double tangent B1-B2 to the curve. The two tangent points B1, B2 are called binodals or connodals according to van der Waals theory. The values of the "density" variable $z$ at these
points represent for a pure component the molar volumes of the two equilibrated phases and for a binary mixture the compositions of them. In this work the one-fluid approach is used. In order to have a feasible solution to the problem the existence of the two points S1, S2 is necessary. These points are called spinodals. The spinodals are defined by $f_z = 0$, so they are inflection points of the $f_z$ curve and extremes of the $f_z,z$ curve.

Binodals are the limits of absolute stability and spinodals the limits of essential instability (Gibbs, 1873, pp.44-45). The region of values of $z$ before B1 and after B2 is the region of stability, the region between B1 and S1 and between S2 and B2 is the region of metastability and the region between S1 and S2 is the region of instability. For the function $A(V)$ the terms mechanical stability, metastability and instability are used because $V$ is a mechanical variable. When $A_2V$ is negative it means that $P_V$ is positive and an increase in pressure induces an increase of the volume. This is an unstable state and leads spontaneously to the formation of two stable states, the binodals with volumes at B1 and B2. For the function $G(x)$ the terms material stability, metastability and instability are used because $x$ is a material variable. When $G_2x$ is negative it means that for a system with such a composition $x$ the Gibbs free energy level is unfavourable with respect to a two-phase equilibrium. This is an unstable state and leads spontaneously through material diffusion to the formation of two stable states, the binodals with compositions at B1 and B2.

Above, the simplest case of an $f_z,z$ curve was discussed. In more complex situations the $f_z,z$ curve has more than one double tangent lines. Then we select the double tangent which does not cross the curve $f_z,z$ in any other point except the two tangent points B1, B2 for the whole domain of definition of the variable $z$ (Michelsen, 1982).

An alternative technique to answer the flash problem is by using the $f_z,z$ curve. The construction of a straight line parallel to the $z$ axis in a way that it creates two equal area regions by crossing the $f_z,z$ curve in three points B1, B2 and B3 gives the stable binodals B1 and B2. The third point of intersection B3 is unstable. This procedure was suggested by Maxwell (Rowlinson and Swinton, 1982, p.60).

The third possibility to solve the flash problem, which is the one discussed in detail in this Chapter, is depicted in the right part of Fig.3.1. An $f_z,\mu$ curve is constructed, where $\mu$ represents a generalized chemical potential given by the relation

$$\mu = f(z) - z \frac{\partial f(z)}{\partial z} \tag{3.1}$$

which for a pure component gives
\[ \mu = A(V) - V \frac{\partial A(V)}{\partial V} = A - V (-P) = A + PV = G \] (3.2)

and for a binary mixture gives

\[ \mu = G(x) - x \frac{\partial G(x)}{\partial x} = \mu_1 \] (3.3)

The special closed-loop shape of the \( f_x \mu \) curve and the positioning of the binodals at the point of self-crossing of that curve is the key for the numerical solution of the problem as it will be explained in subsequent sections. These type of curves were used by van Konynenburg and Scott (1980) for three-phase equilibrium calculations and by Walas (1985, p.369) for liquid-liquid equilibrium calculations. These authors used other but equivalent coordinates (as it will be explained below) than \( f_x \) and \( \mu \).

The difference between this approach and the alternative techniques will be discussed in the rest of this introductory section and suggestions for where it is beneficial to follow this procedure will be mentioned. In subsequent sections we will illuminate the basic features of this approach giving special attention to the stability criteria. The analysis will be restricted to unary and binary systems with emphasis to equilibria of three fluid phases, but some generalizations will be outlined. Finally we will give examples for selected binary systems where the applicability of the method will be tested.

In this approach different attributes of the binary \( P,T,x \) space can be treated as special cases of a general aspect. Therefore we handle pure component saturation curves, regions of two-phase equilibria, three-phase equilibrium curves, critical curves and critical endpoints as one common problem. That makes this method more general and more flexible in special cases, so it can be applied for the calculation of complex phase diagrams like type II, III and IV phase behaviour according to the classification scheme of van Konynenburg and Scott (1980).

Additionally a graphical representation of the equilibrium problem is feasible. This is very helpful if an insight in a particular case is necessary or a "strange" case of equilibrium is encountered. Throughout this chapter the graphical interpretation is used to illustrate the details of the procedure discussed.
3.2 Criteria for equilibrium and equation of state

According to the Gibbs phase rule the number of degrees of freedom for an equilibrated system of N components distributed over π phases is given by:

\[ F = N - \pi + 2 \]  

(3.4)

Following Griffiths and Wheeler (1970) we distinguish between "field" and "density" variables in an equilibrated system (see also Chapter 1). Fields are the variables identical in all the π phases \((P, T, \mu_1, \mu_2, ..., \mu_N)\) and densities the variables different from phase to phase \((x_1^a, x_1^b, ..., x_1^\pi, x_2^a, ..., x_N^a, ..., x_N^\pi)\). Using this terminology \(F\) represents the number of independent "field" variables of the system because by choosing values for these \(F\) fields the other fields and the densities of the system are fixed.

The criteria for equilibrium are the equalities of all the "field" variables among the various phases.

\[ P^a = P^b = ... = P^\pi \]  

(3.5)

\[ T^a = T^b = ... = T^\pi \]  

(3.6)

\[ \mu_1^a = \mu_1^b = ... = \mu_1^\pi \]
\[ \mu_2^a = \mu_2^b = ... = \mu_2^\pi \]

...  

\[ \mu_N^a = \mu_N^b = ... = \mu_N^\pi \]  

(3.7)

For the evaluation of chemical potentials a thermodynamic model is necessary. We have selected the Peng-Robinson (1976) cubic equation of state because of its simplicity and engineering popularity (see Appendix A).

\[ P(V, T, x) = \frac{RT}{V - b(x)} - \frac{a(x)}{V[V + b(x)] + b(x)[V - b(x)]} \]  

(3.8)

The parameters \(a, b\) for the pure components are given by
\[ a = 0.45724 \frac{R^2 T_c^2}{P_c} \left[ 1 + m \left( 1 - \sqrt{\frac{T}{T_c}} \right)^2 \right] \]  
\[ b = 0.07780 \frac{R T_c}{P_c} \]  
(3.9)

where the coefficient \( m \) is correlated as a polynomial function of the acentric factor \( \omega \) (Robinson and Peng, 1978).

\[ m = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \text{ for } \omega \leq 0.5 \quad \text{and} \quad m = 0.3796 + 1.485 \omega - 0.1644 \omega^2 + 0.01667 \omega^3 \text{ for } \omega > 0.5 \]  
(3.10)

For a binary mixture we use quadratic mixing rules for both \( a \) and \( b \),

\[ a(T,x) = (1-x)^2 a_{11}(T) + 2(1-x)x a_{12}(T) + x^2 a_{22}(T) \]
\[ b(x) = (1-x)^2 b_{11} + 2(1-x)x b_{12} + x^2 b_{22} \]  
(3.11)

with cross interaction parameters \( a_{12} \) and \( b_{12} \) given by:

\[ a_{12} = (1-k) \sqrt{a_{11} a_{22}} \quad \text{and} \quad b_{12} = (1-l) \frac{b_{11} + b_{22}}{2} \]  
(3.12)

The parameters \( k \) and \( l \) are used to correct for deviations from the geometric mean and arithmetic mean assumptions for \( a_{12} \) and \( b_{12} \) respectively.

### 3.3 Basic formulae

For a binary mixture the chemical potentials of components 1 and 2 in a certain phase can be calculated from:

\[ \mu_1 = G - x G_x \quad \text{and} \quad \mu_2 = G + (1-x) G_x \]  
(3.13)

where \( G \) is the molar Gibbs energy of the phase under consideration and \( G_x \) is the partial derivative of \( G \) with respect to \( x \) under constant \( P \) and \( T \). The mole fraction \( x \) we use, refers always to the less-volatile component 2 of the binary system.

What is required now is to develop expressions for \( G \) and \( G_x \) using our equation of state. The latter has as independent variables \( V \) and \( T \). However the characteristic variables of \( G \) are \( P \) and \( T \). Thus we employ the Helmholtz energy function \( A \) as a bridge because it also
has $V$ and $T$ as characteristic variables. For the molar Helmholtz energy of the mixture $A(V,T,x)$ we have the following expressions (Sandler, 1989, p.313):

\[
A(V,T,x) = (1-x)A_1 + xA_2 + \Delta A_{mix}^{id}(T,x) + A^E(V,T,x) \tag{3.14}
\]

\[
\Delta A_{mix}^{id}(T,x) = RT \left[ (1-x) \ln(1-x) + x \ln(x) \right] \tag{3.15}
\]

\[
A^E(V,T,x) = -\int_{V_0}^V P(V,T,x) \, dV = -\int P \, dV + A_0^E \tag{3.16}
\]

We are not interested in absolute values of $A$ so we assume $A_1$, $A_2$ and $A_0^E$ to be zero. Using the equation of state we calculate the integral in Eq.(3.16) and we get

\[
A(V,T,x) = \Delta A_{mix}^{id}(T,x) + A^{repuls}(V,T,x) + A^{atrac}(V,T,x) \tag{3.17}
\]

where

\[
A^{repuls}(V,T,x) = -RT \ln[V-b(x)] \tag{3.18}
\]

\[
A^{atrac}(V,T,x) = -\frac{a(T,x)}{2\sqrt{2} \, b(x)} \ln \left[ \frac{V+(1+\sqrt{2})b(x)}{V+(1-\sqrt{2})b(x)} \right] \tag{3.19}
\]

Now we can move to the Gibbs energy and its derivatives with respect to composition at constant $P$ and $T$ (see Appendix B).

\[
G = A + PV \quad , \quad G_x = A_x \quad and \quad G_{2x} = A_{2x} - \frac{A_{Vx}^2}{A_{2V}} \tag{3.20}
\]

We will use $G_{2x}$, as we shall see later, for the calculation of spinodals. The general calculation pattern one has to follow for vapour-liquid equilibria calculations in a unary system is:

1. We fix $P$ (or $T$) of the system.
2. We select a $T$ (or $P$) and calculate the volume $V$ from Eq.(3.8). One or three real roots in $V$ are obtained. For a phase split three real roots are necessary.
3. We evaluate the three corresponding energies $G$ using Eq.(3.20). $G$ is identical to $\mu$. 
We repeat steps 2 to 3 until we locate the proper T (or P) in order to satisfy the equilibrium criteria of Eq.(3.7).

The calculations for a binary system are performed as follows:

1. We fix P and T of the mixture.
2. We select a composition x.
3. We calculate the volume V from Eq.(3.8). The stable root is the one corresponding to the lowest value of G.
4. We evaluate $G_x$ using Eq.(3.20).
5. We determine $\mu_1$ and $\mu_2$ from Eq.(3.13).
6. We repeat steps 2 to 5 until we locate sets of proper compositions which satisfy the equilibrium criteria of Eq.(3.7).

How the above steps are performed in an efficient and organized way it is described in the next sections. We will restrict our extended analysis to unary and binary systems but we will provide also the general directions for multi-component systems, although the method is not recommended for such use.

3.4 Two-phase equilibrium for an unary system

To illustrate the two-phase equilibrium calculation for a single component system a P,V isotherm (see Fig.3.2) is plotted. The problem involves the determination of the vapour pressure P(B) and the orthobaric densities V(B1), V(B2) for that specific T.

We see that the equation of state has three roots for volume V if the pressure P takes values between P(S1) and P(S2). So there is a range of pressures where a phase split can occur. But the plot P,µ reveals, that only at pressure P(B), two of the three candidate phases have equal chemical potentials, so they satisfy Eq.(3.7). The P,µ plot suggests a procedure for the determination of P(B). Before we describe it, we mention that V is increasing along the P,µ curve from B1 to B2 so V is considered to be the "running" variable along that curve. First V is calculated for the mechanical spinodals S1 and S2. In these points $A_{2V}= 0$. For that, the sign of the derivative $A_{2V}$ is examined, as V is increased from the limiting value of b (covolume parameter of the equation of state) towards higher values. A change in sign points to the existence of a root of $A_{2V}= 0$. A bisectional technique applied in the interval where the sign was changed can provide the root in any desired accuracy.
Fig. 3.2 Calculation of a fluid two-phase equilibrium for a pure component using isothermal \( P,V \) and \( P,\mu \) diagrams.

At the \( P,\mu \) plot, the mechanically unstable part S1-S2 is the base of the "triangular structure" with sides the two metastable sections B1-S1 and B2-S2 and a vertex which corresponds to the binodal solution B1=B2. The procedure to determine the volume values for the binodal points B1 and B2 is the following:

We start with the spinodals S1 and S2 as two "base points" for V. These points define a straight "base segment", with its edges laying at the metastable parts B1-S1 and B2-S2. Then a new pair of "base points" closer to the vertex B1=B2 is selected. For that we decrease by a step value dV the "base point" of the metastable branch B1-S1 and we increase by the same step value dV the "base point" of the metastable branch B2-S2. In this way the "triangular" structure consisting of the moving "base segment" and the vertex, which is the solution, shrinks by one step.

The \( P,\mu \) curve is not "isomorph" with respect to the "running" variable V. In other words, the same step change dV corresponds to different lengths on the \( P,\mu \) curve, depending on the central value of V around which we perform the change dV. Consequently if we continue moving both "base points" of the "base segment" by one step dV each, this will result in the
situation where one of the "base points" will pass out of the vertex B1=B2 in the stable part, while the other will still remain along its metastable track. To avoid that, the slope of the "base segment" is examined after each movement by one dV for both "base points". If this slope is different from the initial slope where the "base points" were the spinodals, then only one of the "base points" changes position by the appropriate amount of dV steps, until the slope of the "base segment" is corrected.

As far as the "base segment" is approaching the vertex its length is reduced and this indicates that the vertex is not surpassed. If the length of the "base segment" starts to increase while the "base points" are still moving away from the spinodals that indicates that the vertex is surpassed. When this happens both "base points" are returned backwards for a few steps (4 or 5), adequate to guarantee that the "base segment" is again before the vertex. Afterwards the movement of the "base segment" towards the vertex ("shrinking triangle" technique) is repeated with a smaller step dV (typically 1/10 of the previous step). The binodal solution is acceptable when the step has become fairly small in accordance with our desired accuracy. Sometimes one of the "base points" passes the vertex while the other is still before the vertex, however the length of the "base segment" still reduces. This causes a delayed detection of the passing from the vertex, but as far as the number of steps by which the "base segment" returns backwards is enough, no problem occurs.

When the "base segment" coincides with the vertex with the desired accuracy, the two "base point" values of V are the orthobaric volumes we are looking for. Both of them substituted in Eq.(3.8) result in the same P value, which is the vapour pressure P(B) for that T. There is also a third value of V (the one at the point B3) that leads to the same pressure P(B) but B3 is unstable.

For the step dV it is better to use a logarithmic formula for the vapour phase (low density) and a linear formula for the liquid phase. Although it is safer to use small enough steps this can cost a lot of calculation time and if the step is very small also round-off errors may occur. The movement of the "base points" is performed according to the formulae (V in cm³/mol):

\[ V^v(n+1) = 10 ^ \{ \log[V^v(n)] + dV \}, \quad dV = 0.1 \text{ for vapour}, \]
\[ V^l(n+1) = V^l(n) - dV, \quad dV = 1 \text{ for liquid}, \]

where \( V^v(n) \) and \( V^l(n) \) are the values of volume for the "base points" at their \( n^{th} \) position. For \( n=1 \) the spinodal solutions are used.

For pressures \( P \) above \( P(S2) \) or below \( P(S1) \) Eq.(3.8) has only one real root for the volume \( V \), therefore no phase split occurs and we have either a single liquid phase for \( P > P(S2) \) or
a single vapour phase for $P < P(S_1)$. Mathematically the polynomial has always three roots, but in this case the other two are a pair of complex numbers without physical meaning. For every other $T$ less than $T_c$ there is always a phase split for a unique value of $P$ (the vapour pressure at that $T$). Just above or below that pressure there are also three real roots for $V$ from Eq.(3.8) but only one is stable. Of the other two, one is metastable (along the branch $B_1-S_1$ or $B_2-S_2$) and the other is unstable (along the branch $S_1-S_2$). At $P(S_1)$ or $P(S_2)$ we have one double real root (the metastable and unstable coincide) and one single real root (the stable one). When the temperature $T$ reaches its critical value $T_c$ then the spinodal points coincide, the metastable and unstable regions shrink to zero length and the "triangular structure" contracts to a point. The critical point is the upper border in $T$ of the two-phase region and the corresponding $P,V$ isotherm has a horizontal inflection point there. The equation of state, Eq.(3.8), has three equal real roots for $V$ (triple root).

3.5 Two-phase equilibrium for a binary system (mechanically stable case)

The equation of state, Eq.(3.8), is used also for the binary system with parameters $a$ and $b$ given as a composition dependent combination of the pure component parameters (one-fluid approach with mixing rules given by Eqs.(3.11) and (3.12)). We start from the $G_x^c$ curve at constant $T$ and $P$ (see Fig.3.3). At the present stage, it is supposed for simplicity that for every $x$ the equation of state has only one real root for $V$ resulting in a unique value of $G$, or that we have for every $x$ mechanical stability. This is the case for example of liquid-liquid equilibria at high pressures. Therefore the $G_x^c$ curve is a smooth curve with the familiar binodal and spinodal points which define the limits of material stability, metastability and instability, all of them under mechanical stability. Cases with mechanical metastability and instability will be examined in a subsequent section. At the binodal points $B_1$ and $B_2$ the slope $G_x$ of the $G_x^c$ curve is the same and the straight line through these points separates the $G_x^c$ plane in two parts leaving the whole $G_x^c$ curve in one of them (Michelsen, 1982). The $x$ values at these points are the compositions of the two equilibrated phases for these specific conditions of $P$ and $T$.

The determination of the binodal compositions is achieved by the use of the $\mu_1,\mu_2$ curve of Fig.3.3 which is equivalent to the $f_p,\mu$ plot of Fig.3.1. As it will be shown later in a generalization of the method it is equivalent to use the $\mu_1,\mu_2$ closed-loop curve instead of the $G_x,\mu_1$ curve which is suggested from Fig.3.1.
Fig. 3.3 Calculation of a fluid two-phase equilibrium for a binary mixture using isothermal and isobaric $G, x$ and $\mu_1, \mu_2$ diagrams.

The analogy with the $P, \mu$ curve of Fig. 3.2 is relevant. Here the "running" variable is $x$, there it was $V$. Here the instability borders are "material" and coincide with the roots of $G_{2x}=0$, there the instability borders were "mechanical" and coincided with the roots of $A_{2V}=0$. Therefore the "shrinking triangle" procedure can also be used in the $\mu_1, \mu_2$ plot. The roots of $G_{2x}=0$ are determined in a similar way as the roots of $A_{2V}=0$ discussed in the previous section. Here the interval $x=0$ to $x=1$ is examined for a change in sign.

For the step $dx$ is better to use a logarithmic formula for the vapour phase (very small composition - $x$ refers to the less-volatile component) and a linear step for the liquid phase. The movement of the "base points" is performed according to the formulae:

$$x^V(n+1) = 10^\{ \log[x^V(n)] dx \}, \ dx = 0.1 \text{ for vapour},$$

$$x^L(n+1) = x^L(n) + dx, \ dx = 0.0001 \text{ for liquid},$$

where $x^V(n)$ and $x^L(n)$ are the values of composition for the "base points" at their $n^{th}$ position. For $n=1$ the spinodal solutions are used.

It is not difficult to explain the peculiar closed-loop structure of the $\mu_1, \mu_2$ plot. The point of self crossing of the $\mu_1, \mu_2$ curve (vertex of the triangle) is a consequence of the condition
given by Eq.(3.7). The angular shape of the region around the spinodals is due to the change of the sign of $G_{2x}$ around these points. The last argument will be further analyzed. From Eq.(3.13) we have

$$\frac{\partial \mu_1}{\partial x} = -x G_{2x}, \quad \frac{\partial \mu_2}{\partial x} = (1-x) G_{2x} \quad \text{and} \quad (3.21)$$

$$\frac{\partial \mu_2}{\partial \mu_1} = \frac{1-x}{x} \quad (3.22)$$

From Eq.(3.22), which is the Gibbs-Duhem equation for constant P and T, it is concluded that the slope of the $\mu_1, \mu_2$ curve (derivative of $\mu_2$ with respect to $\mu_1$ for constant P and T) is always negative as $x$ and $(1-x)$ are always positive. Also it is concluded that this slope is a universal function only of $x$ independent of the kind of the components in the binary system and of the conditions P, T. When $x$ approaches 0 the slope goes to $-\infty$ and when $x$ approaches 1 it goes to 0.

From Eq.(3.21) it is inferred that when $G_{2x}$ is positive (stable and metastable parts), the slope of $\mu_1$ with respect to $x$ is negative and the slope of $\mu_2$ with respect to $x$ is positive. Consequently as $x$ is increased, $\mu_1$ is decreased and $\mu_2$ is increased. However when $G_{2x}$ is negative (unstable parts), the slope of $\mu_1$ with respect to $x$ is positive and the slope of $\mu_2$ with respect to $x$ is negative. So as $x$ is increased, $\mu_1$ is increased and $\mu_2$ is decreased. This means that as we reach the first spinodal and $G_{2x}$ changes sign from positive to negative, $\mu_1$ stops decreasing and starts increasing with increasing $x$, while $\mu_2$ stops increasing and starts decreasing with increasing $x$. This creates the angle point on the curve. Similar but reverse changes are performed when the second spinodal is reached.

Before continuing with three-phase equilibria we will discuss some generalities which can be speculated from the above.
3.6 Generalization of the method

For the unary system (N=1) at two-phase equilibrium (π=2) there is one degree of freedom (F=1) as follows from Eq. (3.4). By taking T=constant, F becomes zero. Then, a plot with as coordinates the remaining dependent field variables P and μ is constructed. The equilibrium solution is the point produced by the self crossing of the P,μ curve, which is generated by the "running" of the density variable V.

For the binary system (N=2) at two-phase equilibrium (π=2) there are two degrees of freedom (F=2). Now P,T=constant are chosen. Then, a plot with as coordinates the remaining dependent fields μ₁ and μ₂ (or Gₓ and μ₂ because μ₂-μ₁=Gₓ) is constructed. The equilibrium solution is the point produced by the self crossing of the μ₁,μ₂ curve, which is generated by the "running" of the density variable x.

Generalizing we can say that for a system of N components, distributed over π phases at equilibrium, F (F=N-π+2) field variables can be fixed at a constant value. Then the thermodynamic space having as coordinates the remaining dependent field variables is considered. "Running" of the independent densities in their domain of values produces a generalized hyper-surface in the above space. The crossing point of the curves (curves which are produced by the crossing of surfaces which are produced in turn by the crossing of volumes, etc. until the loci produced by the self crossing of the hyper-surface) is the equilibrium solution.

For a multi-component system (N≥2) the independent densities are the N-1 mole fractions. Their domain of values is generally a simplex of dimension N-1 having N vertices (Palatnik and Landau, 1964, pp.1-7). The vertices represent the pure components. For a binary the simplex is a straight segment, so as x varies from 0 to 1, (1-x) varies from 1 to 0. For a ternary the simplex is an equilateral triangle (Gibbs triangle) and for a quaternary is an equilateral tetrahedron (Roozeboom-Fedorov tetrahedron).

So, although the method is in principle applicable for systems of more than two components it becomes rather complex and therefore is not advised to be used in process calculations.
3.7 Three-phase equilibrium for a binary system (mechanically stable case)

Now the case of a three-phase equilibrium in a binary system will be examined. In particular the case discussed here corresponds to L2-L1-V equilibria of the type found in the carbon dioxide and n-tridecane system. Eq.(3.4) gives $F = 1$ and suppose $T = \text{constant}$ is selected. There are three remaining fields $(P, \mu_1$ and $\mu_2)$ and thus we have to analyze a three dimensional plot where the equilibrium solution is a point of self crossing of a surface instead of a curve. The location of that point can be performed by a generalised "shrinking pyramid" technique but an alternative simpler way is preferred. This is to analyze the cross sections $\mu_1, \mu_2$ at different $P$ until the three-phase equilibrium pressure $P(3\text{ph})$ which gives the situation depicted in Fig.3.4 is found.

In the $G_x$ as well as in the $\mu_1, \mu_2$ plots of Fig.3.4 the stable parts are represented by solid curves, the metastable parts are represented by dashed curves and the unstable parts are represented by dotted curves. In the $G_x$ curve six double tangent lines (dashed-dotted lines) are defining six pairs of binodal points: $A1-A2, B1-B2, C1-C2, D1-D2, E1-E2, F1-F2$. Three of these double tangent lines coincide, creating thus a triplet of points $A1=B1, B2=F1, F2=A2$ laying along a triple tangent line to the $G_x$ curve. These points are in some sense the three "trinodals" of the three-phase equilibrium. The triple tangent line divides the $G_x$ plane into two parts leaving again, like in the two-phase equilibrium, the $G_x$ curve totally in one of them. The three pairs of binodals $A1-A2, B1-B2, F1-F2$ which degenerate to the triplet $A1=B1, B2=F1, F2=A2$ of "trinodals" are all stable. The binodal $D1-D2$ is unstable and the binodals $C1-C2$ and $E1-E2$ are mixed metastable and unstable. Points $D1, E1, C2, D2$ are not local maxima of the $G_x$ curve and points $A1, B1, C1, B2, F1, E2, F2, A2$ are not local minima, in the sense that the $G_x(x)=0$ has no roots at these compositions. At the spinodals $S1$, $S3$ the $G_{2x}(x)$ changes sign from positive to negative so the $G_x$ curve becomes concave instead of convex as it was before and at the spinodals $S2, S4$ the $G_{2x}(x)$ changes sign from negative to positive so the $G_x$ curve becomes convex instead of concave as it was before.

The parts $A1-S1, S2-S3$ and $S4-A2$ are the metastable parts of the $G_x$ curve and the parts $a-A1$ and $A2-b$ are the stable parts of the $G_x$ curve.

The character of all these points and segments becomes more clear and comprehensive in the $\mu_1, \mu_2$ plot of Fig.3.4. Here there are two triangular structures because two pairs of spinodals are present and the looping of Fig.3.3 is happening twice.
Fig. 3.4 $G$, $x$, and $\mu_1, \mu_2$ plots for a binary mixture at a temperature and pressure where a three-phase equilibrium exists.

At this unique pressure $P(3\text{ph})$ of the three-phase equilibrium the two triangles have a common vertex where the three stable binodals A, B and F coincide. The unstable binodal D is the crossing point of the two unstable "bases" of the triangles S1-S2 and S3-S4. The semi-metastable, semi-unstable binodals C and E are crossing points of one unstable branch (dotted curve) with one metastable branch (dashed curve).
Fig. 3.5 $G,x$ and $\mu_1,\mu_2$ plots for a binary mixture at a temperature where three-phase equilibrium exists. The pressure is selected slightly below the pressure of the three-phase equilibrium.

In Fig. 3.5 the $G,x$ and $\mu_1,\mu_2$ curves are plotted for a pressure slightly below the pressure $P(3\text{ph})$ of the three-phase equilibrium. The nomenclature of the points is the same as in Fig. 3.4. Only the binodal A is stable at this pressure. The binodals B and F are metastable and the binodals C, E and D have the same character as in Fig. 3.4. The two triangular structures B-S1-S2 and F-S3-S4 are giving the two metastable binodals. In order to obtain the solution for the stable binodal A the shrinking triangle technique is applied to the triangle A-S1-S4.
Fig. 3.6 $G, x$ and $\mu_1, \mu_2$ plots for a binary mixture at a temperature where three-phase equilibrium exists. The pressure is selected slightly above the pressure of the three-phase equilibrium.

In Fig. 3.6 the $G, x$ and $\mu_1, \mu_2$ curves are plotted for a pressure slightly above the pressure $P(3\text{ph})$ of the three-phase equilibrium. The nomenclature of the points is the same as in Figs. 4 and 5. Here the binodals B and F are stable, the binodal A is metastable and the binodals C, E and D have the same character as in Figs. 4 and 5. The triangles B-S1-S2 and F-S3-S4 result in the stable binodals while the triangle A-S1-S4 results in the metastable one.
It is interesting to notice the relative positions of points A, B, F in the sequence of Figs. 3.5 to 3.4 to 3.6. When multiple binodal solutions are possible then the stable or the two stable solutions (case of three-phase equilibrium) are located at the low-left part of the \( \mu_1, \mu_2 \) plane along the stable branches of the \( \mu_1, \mu_2 \) curve (see point A in Fig.3.5 and points B, F in Fig.3.6).

Fig.3.7 \( P,x \) isothermal plot at pressures close to the three-phase equilibrium pressure for a binary system. This plot summarizes Figs. 3.4, 3.5 and 3.6.
Fig. 3.7 summarizes Figs. 3.4, 3.5 and 3.6 in the form of an isothermal $P_x$ plot at pressures close to the three-phase pressure $P(3ph)$. The diagram shows the binodals and spinodals using the same nomenclature as in Figs. 3.4, 3.5 and 3.6. In terms of real binary system behaviour such a case occurs at the upper branch of the three-phase line $L_2-L_1-V$ of a type IV system where mechanical instability is not involved. For pressures above the $P(3ph)$ a phase split of the type $L_1+V$ or $L_2+L_1$ is found depending on the overall composition and for pressures below the $P(3ph)$ a phase split of the type $L_2+V$ occurs. An example is given later for the binary CO$_2$ and n-tridecane.

3.8 Fluid phase equilibrium for a binary system under combined mechanical and material instability.

We will proceed with applications of the above but first we will mention the cases where mechanical instability interferes with material instability and produces $G_x$ curves of the types depicted in Fig. 3.8. At the top of Fig. 3.8, an isothermal $P_x$ diagram of a binary system showing a vapour-liquid equilibrium with a critical point, is given. This is for example the case for a binary system at a temperature between the critical temperatures of its two pure components 1, 2 and at pressures from the vapour pressure of the less volatile component 2 for that temperature up to the critical pressure of the mixture for the same temperature.

As the pressure decreases we successively obtain the $G_x$ curves plotted at the lower part of Fig. 3.8. Down to the pressure $P3$ the situations are the familiar ones already examined in detail in preceding sections. A pair of material spinodals $S1, S2$ creates a materially unstable region of compositions which leads to phase split (binodal pair $B1-B2$). Exactly at the critical pressure $P1$ the two spinodals and the two binodals coincide all together in the critical point.

However the situation changes for pressures below $P3$. Mechanical instability starts to interfere, creating closed-loop $G_x$ curves instead of the smooth $G_x$ curves we have dealt with up to this section. The reason for the formation of this closed-loop is that the equation of state, Eq. (3.8), has for a certain range of compositions (between points $M2$ and $M1$ at pressure $P4$) three real roots for the volume $V$ (see in analogy Fig. 3.2 for pressures between points $S1$ and $S2$), producing thus three corresponding values for the Gibbs energy $G$. Consequently, in addition to the material spinodals and binodals we have also mechanical spinodals and binodals. Mechanical spinodals and binodals can be considered to be the
spinodals and binodals of a pseudo-pure component having the same a and b, as the mixture has at a fixed composition x through application of Eq.(3.11). This is the one-fluid approach.

Fig.3.8 Fluid two-phase equilibria for a binary system at conditions where mechanical instability interferes with material instability. A P,x isothermal plot is provided at the top and G,x plots for selected pressures P1 to P9 are plotted at the bottom.

The mechanical spinodals M2 and M1 are located at the compositions between which the equation of state has three real roots for volume V. At these specific points the equation of state has one double real root and one single real root for V (see mechanical spinodal points
of Fig.3.2) leading to one double and one single value for G. Between M2 and M1 the equation of state has three real distinct roots for V, but at point C the two of them lead to the same value for G. This situation is comparable with the one plotted in Fig.3.2 where the points B1 and B2 in the P,V plot lead to one point B1=B2 in the P,G plot. Point C is thus the mechanical binodal composition and is depicted as a dashed-dotted curve in the P,x plot at the top of Fig.3.8. The branches C-M2 and C-M1 of the G,x curves in Fig.3.8 are mechanically metastable (dashed curves) and the branch M2-M1 is mechanically unstable (dotted curve).

As the pressure is decreased further (see P5) the material spinodals S1, S2 enter into the mechanically metastable parts of the G,x curve. In this case we can say that we have two material spinodals which are both mechanically metastable. At pressures between P4 and P5 we have situations where we have again two material spinodals from which one is mechanically stable and the other is mechanically metastable. For the pressure P6 the mechanical spinodal M1 reaches the composition x=1. This pressure corresponds to the pressure maximum (point S2 in Fig.3.2) of the P,V isotherm of pure component 2 at this specified temperature. At the same pressure the material spinodal S1 has also the composition value x=1, so it coincides with M1. At the even lower pressure P7 points M1 and S1 have disappeared at the right of the composition axis x=1. Finally we reach the vapour pressure of the pure component 2 (pressure P8) where the mechanical binodal C has composition x=1. In this case the two material binodals B1, B2 have degenerated and coincide with the mechanical binodal C. Pressure P9 is a pressure between the vapour pressure of pure component 2 at this temperature and the pressure minimum of the P,V isotherm of the same component.

In Figs. 3.9.a and 3.9.b three-dimensional V,P,x plots (under constant T) for the discussed transitions from pure material instability until combined material and mechanical instability are provided. In Fig.3.9.a the material binodals are solid lines and the mechanical binodals are short-dashed lines while the material spinodals are long-dashed lines and the mechanical spinodals are dotted lines. Two isobars are plotted as dashed-dotted and dashed-triple-dotted lines. For clarity logarithmic scales are chosen for the P and V axes. We notice at the composition axis x=1 the merging of the two kinds of binodal curves as well as the merging of the two kinds of spinodal curves. In Fig.3.9.b the mechanical binodals and spinodals are omitted. Several P,V isopleths are added showing that the critical composition and pressure for this temperature, obtained from the binary critical conditions, are not identical with the
composition and pressure obtained from the conditions $P_y=0$ and $P_{2y}=0$ (isopleth with an inflection point).

Figs. 3.9.a and 3.9.b Isothermal V.P.x plots for a binary exhibiting fluid two-phase equilibria at conditions where mechanical instability interferes with material instability (see text for details).
In general the pseudo-component critical constants resulting from the mixing rules of the one fluid approximation (Eqs.(3.11), (3.12)) are different from those obtained from the binary critical conditions (see Appendix A). A detailed analysis of the V,x projection of Fig.3.9.a has been given elsewhere (Van der Waals and Kohnstamm, 1927, pp.75-82 and 112-116; Rowlinson and Swinton, 1982).

![Diagram](image)

Fig.3.10  Isothermal and isobaric G,x and $\mu_1,\mu_2$ plots for $P=P_5$ in Fig.3.8.

For the calculation of fluid phase equilibria however the determination of the material spinodals when mechanical instability interferes is not necessary. The material binodals B1, B2 are always on mechanically stable branches. Therefore we can start the "shrinking triangle" procedure not from the material spinodals S1, S2 but from the mechanical binodal C. The position of the mechanical binodal C is easy to be located by means of the G,x curve. For x values between the points M2 and M1 the difference between the metastable value of G and the stable one is calculated. When this difference vanishes to zero then point C is reached.

Finally it is worthwhile to mention that in a case of combined mechanical and material instability the $\mu_1,\mu_2$ curve is not continuous. Some triplets of its points correspond to the same
x, so x does not change along the curve in a monotonous way. In spite of that the $\mu_1, \mu_2$ curve preserves its triangular shape. An example of such a $\mu_1, \mu_2$ plot is given in Fig.3.10. It corresponds to the pressure level P5 of Fig.3.8.

The discussion in this section was limited to the case of a two-phase equilibrium. It is easy to extend it to three-phase equilibrium where in one region of compositions material instability is involved as discussed above.

3.9 Some illustrative examples

A first example concerns the binary mixture of carbon dioxide and n-tridecane. This binary was selected because it exhibits the complicated type IV behaviour according to the classification scheme of van Konynenburg and Scott (1980). Also the literature provides adequate experimental information for this system (Schneider, 1967; Hottovy et al., 1981; Fall and Luks, 1985; Enick et al., 1985), so an evaluation of the modelling is possible.

A set of different routines to calculate the main quantities, like the various derivatives of the Gibbs function, was developed (see Appendix B) and organized in dedicated programs dealing with separate cases like the calculation of spinodals, of binodals and of three-phase equilibria. Below some examples of what can be calculated are given.

The values of the $k$ and $l$ parameters are selected in order to locate reasonably well the pressure and temperature coordinates of the critical endpoints of the $L_2L_1V$ equilibria. Regression optimization was not attempted. A sensitivity analysis test for the influence of these parameters on various features of the P,T,x space was performed. It revealed that an unique set of $k$ and $l$ is not capable to describe a broad range of fluid phase equilibria, so either a modification of mixing rules or a temperature dependence of $k$ and $l$ has to be introduced. In this work a $k$ parameter equal to 0.08 is used for the whole P,T,x space. In addition an $l$ parameter is used only for temperatures greater than the critical temperature of CO$_2$ and has the value 0.06. This creates a discontinuity at the critical temperature of CO$_2$ but for simplicity any functional dependence of the parameter $l$ on temperature was avoided.

In Fig.3.11a the P,T projection of the mono-variant equilibria of the binary system is plotted and magnifications around the lower and the upper branch of the three-phase equilibrium curve are provided in Figs. 3.11b and 3.11c respectively. Comparison of the predictions with the available experimental data reveals that the agreement is reasonable in the P,T projection in spite of the very rough evaluation of the parameters $k$ and $l$. 
Fig. 3.11a P,T projection of the monovariant equilibria for the binary mixture of carbon dioxide and n-tridecane; overall view. Solid lines: saturation curves of pure components, dashed lines: critical curves, dashed-dotted lines: three-phase curves, empty circles: pure component critical points, up empty triangle: UCEP \([L_2-L_1=V]\), down solid triangle: LCEP \([L_2=L_1-V]\), up solid triangle: UCEP \([L_2=L_1-V]\), solid circles: experimental \(L_2-L_1\) and \(L_2=V\) points (Schneider, 1968).

Fig. 3.11b Enlargement of Fig. 3.11a near the region of the lower branch of the three-phase equilibria. Solid line: saturation curve of pure carbon dioxide, dashed line: critical curve \(L_2=L_1\), dashed-dotted line: lower branch of the three-phase equilibria, solid circles: experimental \(L_2=L_1\) points (Schneider, 1968), solid diamonds: experimental \(L_2L_1V\) points (Hottovy et al., 1981), solid square: experimental UCEP \([L_2=L_1-V]\) (Hottovy et al., 1981).
Fig 3.11.c: Enlargement of Fig 3.11.a near the region of the upper branch of the three-phase equilibria. Dashed lines: critical curves, dashed-dotted line: upper branch of the three-phase equilibria, up empty triangle: UCEP \([L_2-L_1-V]\), down solid triangle: LCEP \([L_2=L_1-V]\), solid circles: experimental \(L_2-L_1\) points (Enick et al., 1985), open circles: experimental \(L_1-V\) points (Enick et al., 1985), empty diamonds: experimental \(L_2L_1V\) points (Enick et al., 1985), solid diamonds: experimental \(L_2L_1V\) points (Fall and Luks, 1985), solid squares: experimental critical endpoints (Fall and Luks, 1985).

Fig 3.12: \(T,x\) projection of the monovariant equilibria for the binary mixture of CO\(_2\) and \(n-C_{13}\). Enlargement around the region of the three-phase equilibria. Dashed lines: critical curves, dashed-dotted lines: three-phase equilibria, up empty triangle: UCEP \([L_2-L_1-V]\), down solid triangle: LCEP \([L_2=L_1-V]\), up solid triangle: UCEP \([L_2=L_1-V]\), solid circles: experimental \(L_2-L_1\) points (Enick et al., 1985), empty diamonds: experimental \(L_2L_1V\) points (Enick et al., 1985) and (Fall and Luks, 1985), solid diamonds: experimental \(L_2L_1V\) points (Fall and Luks, 1985), solid squares: experimental critical endpoints (Fall and Luks, 1985).
Fig. 3.13 $P_x$ projection of the monovariant equilibria for the binary mixture of $CO_2$ and $n-C_{13}$. Enlargement around the region of the three-phase equilibria. For lines and symbols see Fig. 3.12.

Fig. 3.14 $P_x$ isothermal diagram for the binary mixture of $CO_2$ and $n-C_{13}$ at $T/K = 278$. Solid lines: binodal curves, dashed-dotted line: three-phase equilibrium, solid circle: saturation point of pure $n-C_{13}$. 
In Figs. 3.12 and 3.13 the T,x and P,x projections of the monovariant equilibria are depicted. The prediction of the composition of the phases is rather poor, especially for the composition of the L_2 phase. The vapour branch of the lower three-phase equilibrium curve has x_{C_{13}} mole fractions very close to zero.

Fig.3.14 is a calculated P,x isothermal diagram at T/K = 278. The selected temperature corresponds to the lower branch of the three-phase equilibrium curve where mechanical instability interferes with material instability close to the three-phase equilibrium pressure. Another isothermal plot, this time at a temperature corresponding to the upper branch of the three-phase curve (T/K = 312.5) is given in Fig.3.15.a. Here around the three-phase equilibrium pressure we have mechanical stability. Fig.3.15.b provides a magnification around the three-phase equilibrium.

![Diagram](image)

Fig.3.15.a P,x isothermal diagram for the binary mixture of CO_2 and n-C_{13} at T/K = 312.5; overall view. Solid lines: binodal curves, dashed-dotted line: three-phase equilibrium, solid circle: saturation point of pure n-C_{13}, open circles: critical points L_1=V and L_2=L_1.
Fig. 3.15.b $P, x$ isothermal diagram for the binary mixture of CO$_2$ and n-C$_{13}$ at $T/K = 312.5$; enlargement around the region of the three-phase equilibrium.

Fig. 3.16.a $T, x$ isobaric diagram for the binary mixture of CO$_2$ and n-C$_{13}$ at $P/\text{MPa} = 8.5$; overall view. Solid lines: binodal curves, dashed-dotted line: three-phase equilibrium, open circles: critical points $L_1=V$, $L_2=L_1$ and $L_2=V$. 
Fig. 3.16.b $T_x$ isobaric diagram for the binary mixture of CO$_2$ and n-C$_{13}$ at P/MPa = 8.5; enlargement around the region of the three-phase equilibrium.

Fig. 3.17.a $P_T$ isopleth (diagram for constant $x$) for the binary mixture of CO$_2$ and n-C$_{13}$ at $x = 0.01$; overall view.
Fig. 3.17.b $P,T$ isopleth for the binary mixture of CO$_2$ and $n$-C$_{13}$ at $x = 0.01$; enlargement around the region of the lower branch of the three-phase equilibria.

Fig. 3.17.c $P,T$ isopleth for the binary mixture of CO$_2$ and $n$-C$_{13}$ at $x = 0.01$; enlargement around the region of the upper branch of the three-phase equilibria.
In Fig.3.16.a an isobaric T,x diagram for P/MPa = 8.5 is constructed. Two different liquid-liquid immiscibility loops, one for the low temperature range and one for the high temperature range, are appearing. Fig.3.16.b provides a magnification around the three-phase equilibrium. It is interesting to note that the L₁+V domain covers a range of temperatures, from the three-phase temperature up to the critical point L₁=V of less than 0.5 K. One can imagine the experimental difficulties to locate and measure such equilibrium regions.

In Fig.3.17.a an isopleth, a P,T diagram for constant x, is plotted for x = 0.01. The composition is such that the whole course of the three-phase equilibrium curve is included. This can be verified from Figs. 3.12 and 3.13. In Fig.3.17.b an enlargement around the lower three-phase equilibrium branch is made. A steep L₂+L₁↔L₁ binodal curve comes down with a negative slope to the three-phase equilibrium curve. The two curves are crossing each other in a point from where another binodal curve, L₁+V↔L₁, begins and proceeds to higher temperatures and pressures above and very close to the three-phase equilibrium curve until it crosses the upper branch of the three-phase equilibria curve (see enlargement of Fig.3.17.c). From the crossing point a L₂+L₁↔L₁ binodal curve evolves. For temperatures above the UCEP [L₂-L₁=V] temperature there is no distinction between L₁ and V phases, therefore the binodal curve is a L₂+V↔V one (like a usual dew point curve L+V↔V). As we can see from Figs. 3.12 and 3.13 there is no critical point L=V on this isopleth.

In Figs. 3.18.a and 3.18.b isothermal V,x plots at 312.5 K is depicted. The three-phase equilibrium is represented by a triangle which cuts the binodal lines in such a way that three two-phase equilibria regions, L₂+L₁, L₁+V and L₂+V are formed. In Fig.3.19 some of the three-phase triangles for the upper branch of the three-phase equilibria are projected together on a V,x diagram. The triangles degenerate to straight segments at the two critical endpoints (two vertices coincide because of the criticality of the two phases). This diagram is characterized as "the crescent moon" by Pegg et al. (1990).

In Fig.3.20 the P,T projection of the monovariant equilibria (except for the three-phase equilibria) for the binary systems of methane with n-pentane and methane with n-decane are plotted and compared with existing experimental data from Sage et al., (1942); Reamer et al., (1942); Bett et al., (1968) and Wiese et al., (1970). Both mixtures exhibit type V fluid phase behaviour with both the k and l parameter equal to zero. Experimentally only the binary mixture of methane and n-decane shows type V behaviour, while the system of methane and n-pentane is of type I.
Fig. 3.18a Isothermal $V_x$ diagram for the binary mixture of CO$_2$ and n-C$_{13}$ at $T/K = 312.5$; overall view. Solid lines: binodal lines, triangle formed by the three dotted lines: three-phase triangle, open circles: critical points $L_1=V$ and $L_2=L_3$. The triangle crosses the binodals at the three points marked with empty triangles defining three two-phase regions: $L_2+L_1$, $L_1+V$, $L_2+V$. The dashed and the dashed-dotted lines are tie-lines in the region of the $L_2+V$ equilibria.

Fig. 3.18b Isothermal $V_x$ diagram for the binary mixture of CO$_2$ and n-C$_{13}$ at $T/K = 312.5$; enlargement around the region of the three-phase triangle (see Fig. 3.18a). The dashed and the dashed-dotted lines are tie-lines in the three regions of two-phase equilibria.
Fig. 3.19 $V, x$ diagram including all the three-phase triangles (formed by dashed, dashed-dotted or dotted lines) of the upper branch of the three-phase equilibria in the binary mixture of $CO_2$ and $n-C_{15}$. The two straight solid segments represent the upper and the lower critical endpoints. Solid circles: the two critical phases of the critical endpoints, empty circles: the two "third" phases of the critical endpoints.

Fig. 3.20 $P,T$ projection of the monovariant equilibria for the binary mixtures of methane with $n$-decane and of methane with $n$-pentane. Solid lines: saturation curves of pure components, long-dashed line: calculated critical curve of the mixture of methane with $n$-decane (type V system), short-dashed line: calculated critical curve of the mixture of methane with $n$-pentane (type V system). The three-phase equilibria lines are omitted. Empty diamonds: pure component critical points, empty squares: calculated critical points of the mixture of methane with $n$-decane at compositions $x = 0.05$, $x = 0.10$, $x = 0.20$, $x = 0.40$, $x = 0.70$, solid squares: experimental critical points of the mixture of methane with $n$-decane (Reamer et al., 1942; Bett et al., 1968; Wiese et al., 1970), empty circles: calculated critical points of the mixture methane with $n$-pentane at compositions $x = 0.05$, $x = 0.10$, $x = 0.20$, $x = 0.40$, $x = 0.70$, solid circles: experimental critical points of the mixture methane with $n$-pentane (Sage et al., 1942).
In Figs. 3.21 and 3.22 the T,x and P,x projections for these systems are depicted. We can observe the interrupted critical lines due to the presence of an intermediate three-phase equilibria region.

**Fig. 3.21** $T,x$ projection of the monovariant equilibria for the binary mixtures of methane with $n$-decane and of methane with $n$-pentane. For lines and symbols see Fig. 3.20. The critical curves are interrupted because both systems exhibit type V fluid phase behaviour.

**Fig. 3.22** $P,x$ projection of the monovariant equilibria for the binary mixtures of methane with $n$-decane and of methane with $n$-pentane. For lines and symbols see Fig. 3.20. The critical curves are interrupted because both systems exhibit type V fluid phase behaviour.
Fig. 3.23 $P,T$ projection of some of the fluid phase equilibria for the binary mixture of methane with n-pentane. The monovariant equilibria, the isopleth for $x = 0.20$ and some constant $L/F$ ($F = L+V$) lines for $x = 0.20$ are included. Solid lines: saturation curves of pure components, short-dashed line: calculated critical curve, empty circles: calculated critical points at compositions $x = 0.05$, $x = 0.10$, $x = 0.20$, $x = 0.40$, $x = 0.70$, tiny-dashed line: bubble point (or $L/F = 1$) curve for $x = 0.20$, long-dashed line: $L/F = 0.25$ curve for $x = 0.20$, dashed-triple-dotted line: $L/F = 0.50$ curve for $x = 0.20$, dotted line: $L/F = 0.75$ curve for $x = 0.20$, dashed-dotted line: dew point (or $L/F = 0$) curve for $x = 0.20$. All the constant $L/F$ curves end up to the critical point of the mixture for $x = 0.20$.

In Figs. 3.23 and 3.24 liquid-vapour isopleths for $x = 0.20$ and various values for the ratio $L/F$ are added to the $P,T$ projections of the two binary systems ($L$: amount of liquid, $F$: amount of feed). In the case of the binary mixture of methane and $n$-decane (Fig. 3.24) the retrograde region for this isopleth is relevant.
Fig. 3.24 $P, T$ projection of some of the fluid phase equilibria for the binary mixture of methane with $n$-decane. The monovariant equilibria, the isopleth for $x = 0.20$ and some constant $L/F (F = L+V)$ lines for $x = 0.20$ are included. Solid lines: saturation curves of pure components, long-dashed line: calculated critical curve, empty squares: calculated critical points at compositions $x = 0.05$, $x = 0.10$, $x = 0.20$, $x = 0.40$, $x = 0.70$, tiny-dashed line: bubble point (or $L/F = 1$) curve for $x = 0.20$, short-dashed line: $L/F = 0.25$ curve for $x = 0.20$, dashed-triple-dotted line: $L/F = 0.50$ curve for $x = 0.20$, dotted line: $L/F = 0.75$ curve for $x = 0.20$, dashed-dotted line: dew point (or $L/F = 0$) curve for $x = 0.20$. All the constant $L/F$ curves end up to the critical point of the mixture for $x = 0.20$.

The critical point is positioned between the cricondenbar and the cricondentherm points and therefore the same iso-$L/F$ line may be cut twice by some isobars or isotherms (see Chapter 2).
3.10 Discussion

The presented method for the calculation of fluid phase equilibria performed well during our test calculations. The same main routines allowed the calculation of different kinds of binary fluid phase equilibria. The solution (binodals) was always found after several iterations and until the desirable accuracy in the step of the "running variable" (tolerance of convergence) was reached, as far as the starting points (material spinodals or mechanical binodals) were available. Initial estimates for the phase compositions were not necessary. The fact that for a binary system x varies from 0 to 1 was adequate. When problems arose a graphical illustration of the case provided hints to remove them. The $\mu_1, \mu_2$ graphs discussed in detail before suggested also the correct direction for tuning the parameters $k$ and $l$. A clear idea about instabilities was established and various cases were classified.

A disadvantage we encountered was that the procedure is relatively slow, especially when one of the equilibrated phases has an extreme composition (for a binary system when the vapour phase has a composition very close to 0). This is due to the stepwise character of the "running" variable (x) and the non-isomorphous character (see above) of the hyper-surface that it creates ($\mu_1, \mu_2$ curve for a binary). A solution to this problem was the use of a logarithmic step (dx) for the vapour phase.

Another drawback of the method is that for multi-component systems it becomes too complex to be implemented in case of process calculations. If the number of the dependent fields, after fixing F fields at constant values, is more than two then the procedure that has to be followed is ineffective. In this Chapter only the case of three dependent fields was examined (see section: three-phase equilibrium for a binary system). In this case, one of the three fields (the pressure P) was kept constant, the solution in terms of the other 2 fields $\mu_1, \mu_2$ was determined, then the pressure was changed until the three-phase equilibrium was found. Also if the number of independent densities is higher than 1 (ternary systems, quaternary systems, etc.) then the domains of their values are triangles, tetrahedra, etc., therefore the paths of changing these densities in order to locate the solution are not so straightforward as the straight segment of mole fractions between 0 and 1 that we have for a binary system.

The main advantage of the method is that it is very robust and that it is very successful for the calculation of complicated binary phase diagrams, therefore it can be recommended for use in special cases of phase equilibria in binary systems where other algorithms may fail.
Chapter 3

Symbols

A \quad \text{molar Helmholtz energy}
a \quad \text{intermolecular interaction parameter}
b \quad \text{molecular volume parameter}
F \quad \text{number of degrees of freedom}
f \quad \text{generalized energy function}
G \quad \text{molar Gibbs energy}
k \quad \text{correction term for } a_{12} \text{ in Eq.}(12)
L_{2}, L_{1} \quad \text{liquid phases}
l \quad \text{correction term for } b_{12} \text{ in Eq.}(12)
m \quad \text{coefficient in Eq.}(9) \text{ evaluated by Eq.}(10)
P \quad \text{pressure}
R \quad \text{gas constant}
T \quad \text{temperature}
V \quad \text{molar volume}
V \quad \text{vapour phase}
x \quad \text{mole fraction of the less-volatile component}

Greek

\mu \quad \text{chemical potential}
\omega \quad \text{acentric factor}

Superscripts

\alpha, \beta, ..., \pi \quad \text{phase index}
attrac \quad \text{attractive term}
E \quad \text{excess term}
id \quad \text{ideal mixing}
repuls \quad \text{repulsive term}
Subscripts

1, 2, ..., N  component index

C  critical point

Mix  mixing process

References


4. EXPERIMENTAL INFORMATION FROM LITERATURE

In this chapter a literature survey of experimental data concerning three-phase $L_2L,V$ equilibria in binary systems is presented. The systems considered are so-called families with a common more-volatile component and less-volatile components which are successive members of the same homologous series. The selection is made to cover as many cases as possible revealing the complexity of the phenomena and the difficulty of developing a common interpretation.

The literature information is summarized in plots of the critical endpoint temperatures and/or pressures of the various binary or quasi-binary systems against the carbon numbers of the $n$-alkanes or the $n$-alkanols, which are the less-volatile components of those systems. The similarities and the differences among the various families are demonstrated and some explanations for them, based on the comparison of the thermodynamic properties of the constituents of the mixture, are attempted. Although the best approach would be one based on intermolecular interaction considerations, this is very difficult to achieve.

The selection of the systems to be investigated experimentally in this thesis is guided by some remarks mentioned in this Chapter.

4.1 Carbon dioxide with $n$-alkanes or $n$-alkanols

The family of carbon dioxide ($CO_2$) with $n$-alkanes is a classical example of a binary family which shows the transition pattern from type II, via type IV, towards type III fluid phase behaviour. This transition takes place as the size of the less-volatile component in the system is progressively increased. Systems of $CO_2 + n$-alkanes up to $n$-dodecane exhibit type II phase behaviour, while systems with $n$-alkanes having a carbon number $n$ greater or equal than 14 exhibit type III phase behaviour. $CO_2 + n$-tridecane is a type IV system. The modelling of this system was discussed in Chapter 3.

In Figs. 4.1.a and 4.1.b $T_{CEP}$ and $P_{CEP}$ as a function of carbon number for $CO_2 + n$-alkanes from Im and Kurata (1971), Hottovy et al. (1981, 1982), Fall et al. (1985), and Fall and Luks (1985) are combined together in $T,n$ and $P,n$ plots (see Fig. 2.17.b). The shape of the curves connecting the critical endpoints (CEP's) is preserved in both plots. The transition from type II to type III occurs in a range of $n$ less than 2 (from dodecane until tetradecane). Using a
quasi-binary approximation for the same family, de Loos et al. (1993a), added more data in the neighbourhood of the transition zone.

Figs. 4.1.a (up) and 4.1.b (down). Three-phase \( L_2L_1V \) equilibria in the family of binary systems of \( \text{CO}_2 \) with \( n \)-alkanes. Short dashed line with up empty triangles: UCEP's \( [L_2-L_1=V] \), down solid triangle: LCEP \( [L_2=L_1=V] \) (for \( n \)-tridecane), dashed-dotted line with up solid triangles: UCEP's \( [L_2=L_1=V] \), solid circles: quadruple points \( [S_2-L_2-L_1=V] \), solid squares: quadruple points \( [S_2-L_2-L_1=V] \), dotted lines: three-phase \( L_2L_1V \) equilibria curves, long dashed line: critical point of pure \( \text{CO}_2 \).
These data suggest a tricritical point (TCP) for \( n=12.33 \) and \( T=317.5 \) K and a double critical endpoint (DCEP) for \( n=13.55 \) and \( T=296.0 \) K, defining an intermediate type IV zone for \( n=12.33 \) to \( n=13.55 \) in a temperature range of 21.5 K. The procedure for the estimation of the positions of the TCP and the DCEP will be discussed in chapter 6. They are based on theoretical models dealing with the asymptotic approach to the TCP or the DCEP (see Chapter 2).

In diagrams shown we can see the extend of the three-phase \( L_2L_1V \) equilibria of the binary systems with increasing size of the less-volatile component. For the smaller \( n \)-alkane molecules the three-phase \( L_2L_1V \) equilibrium curve starts in the quadruple point (QP) of the system. For \( n=7, 8 \) at the QP the solid phase is solid CO\(_2\). The melting point of CO\(_2\) is 216.6 K, while n-heptane melts at 182.6 K and n-octane at 216.4 K. For \( n \geq 9 \) the solid phase in the QP is the solid \( n \)-alkane. The upper critical endpoint (UCEP) is the upper critical solution temperature (or consolute temperature) when also vapour is present. The temperatures of QP and UCEP rise, as the carbon number of the \( n \)-alkane increases, but that of QP less than that of UCEP. The net effect is a three-phase \( L_2L_1V \) equilibrium curve expanding in size and shifting to higher temperatures.

The above is typical for the type II zone of fluid phase behaviour. As the TCP is reached, another branch of three phase equilibria evolves at higher temperatures close to the critical region of the more-volatile component. The upper branch of the three-phase \( L_2L_1V \) equilibria which characterizes the type IV behaviour, as in the system CO\(_2\) + \( n \)-tridecane, is bounded by two critical endpoints, the UCEP \([L_2=L_1=V]\) and the LCEP \([L_2=L_1,V]\). It is believed that the onset of immiscibility after the LCEP is caused by free volume effects (Patterson and Delmas, 1968). The LCEP is near the critical region of the more-volatile component where the density of component 1 changes drastically and component 2 is "expelled" from the \( L_1 \) phase and "conforms" to its own rich liquid phase \( L_2 \) (see Chapter 1). The extension of the high-T branch of three-phase \( L_2L_1V \) equilibria increases and the whole branch shifts to lower temperatures and pressures as the less-volatile component chain-length increases. As the UCEP \([L_2=L_1,V]\) and the LCEP \([L_2=L_1,V]\) approach, they finally meet in the DCEP and the three-phase \( L_2L_1V \) equilibrium curve becomes again continuous, a characteristic feature of type III behaviour.

The three-phase \( L_2L_1V \) curves for systems of type III shrink in size as the chain-length of the less-volatile component increases. The UCEP moves to lower temperatures and pressures and asymptotically approaches the critical point of the more-volatile component. The
QP moves to higher temperatures and pressures until it eventually passes the UCEP. Then the three-phase $L_2L_1V$ equilibrium region is completely covered by the presence of the solid phase. This occurs in the $CO_2 + n$-alkane family for $n\geq 22$ (Fall et al., 1985).

In Figs. 4.2.a and 4.2.b the CEP's for systems of $CO_2 + n$-alkanols are plotted using data taken from Lam et al. (1990c). In this family there is no binary system which exhibits type IV fluid phase behaviour. For the systems up to $n$-pentanol the behaviour is of type II and from $n$-hexanol type III evolves. The nature of the QP which terminates the three-phase $L_2L_1V$ curve at low temperature is different for the first $n$-alkanols as in the family with the $n$-alkanes. For systems with $n$-alkanol molecules with $n\geq 7$ the solid formed at the low temperature end of the three-phase $L_2L_1V$ equilibrium curve is the alkanol. For $n\leq 6$ the solid formed at the QP is $CO_2$. $CO_2$ has a melting point of 216.6 K, while $n$-heptanol melts at 239.2 K and $n$-pentanol at 195.0 K. $n$-Hexanol melts at a higher temperature than $CO_2$ (229.2 K), however the QP of the system $CO_2 + n-C_6$ is solid $CO_2$ phase.

We see that the transition zone of type IV behaviour is narrower than the corresponding zone in the family of $CO_2 + n$-alkanes. Actually it is smaller than 1 carbon number. The temperature difference between the TCP and the DCEP seems to be about the same as with $n$-alkanes, around 20 K. We see also that the carbon number of the $n$-alkanol where the transition between types II and III occurs is almost half the carbon number of the $n$-alkane in $CO_2 + n$-alkanes family. A $n$-alkanol with carbon number $n$ is more or less comparable in size as a $n$-alkane with carbon number $n+1$, assuming that the hydroxyl-group (-OH) is similar in size with one methyl-group (-CH$_3$). Therefore only the relative size of the constituents of a binary system does not seem adequate to explain its fluid phase behaviour. In the case of the $n$-alkanols the polarity is of course very important.

As the linear alkanol molecule becomes shorter the effect of the (-OH's) in the solution becomes more dominant. In terms of relative concentration of (-OH's) and (-CH$_3$'s) we may consider the following example. In two systems with the same mole fraction of the less-volatile component, one with $CO_2 + n$-octanol and a second with $CO_2 + n$-butanol, the ratio of the concentrations of (-CH$_3$'s) over (-OH's) is 8:1 for the first system and 4:1 for the second. If the mole fraction of the $CO_2$ in both systems is 0.80 and if we consider normalized mole fractions of $CO_2$ molecules, (-CH$_3$) segments and (-OH) segments then the mole fraction of the (-OH) segments in the first system is 1:13 and in the second 1:9. So the concentration of the (-OH's) in the second system is increased by 45%, while the size of the alkanol chain is decreased by 45%. As the concentration of (-OH's) increases and the alkanol molecule
becomes smaller, the tendency of alkanol molecules to associate in clusters via hydrogen bonds increases.

Figs. 4.2a (up) and 4.2b (down). Three-phase $L_2L_1V$ equilibria in the family of binary systems of CO$_2$ with n-alkanols. Short dashed line with up empty triangles: UCEP's [$L_2$-$L_1$-$V$], dashed-dotted line with up solid triangles: UCEP's [$L_2$-$L_1$-$V$], dashed-triple-dotted line with solid circles: quadruple points [$S_2$-$L_2$-$L_1$-$V$], dashed-triple-dotted line with solid squares: quadruple points [$S_2$-$L_2$-$L_1$-$V$], dotted lines: three-phase $L_2L_1V$ equilibria curves, long dashed line: critical point of pure CO$_2$. 
In the $\text{CO}_2 + n$-alkanols family the transition from type II to type IV phase behaviour occurs at an average carbon number $n \approx 5.5$, while in the $\text{CO}_2 + n$-alkanes family this transition occurred at an average carbon number $n \approx 13$. According to the hydrogen bonding effect discussed above we may conclude that $n$-hexanol corresponds approximately to $n$-tridecane in systems with $\text{CO}_2$. Therefore it seems that $n$-hexanol forms to a great percentage dimers. The smaller $n$-alkanols form also clusters of molecules but their effective size corresponds to $n$-alkanes smaller than $n$-tridecane thus their binary systems with $\text{CO}_2$ exhibit type II fluid phase behaviour.

4.2 Nitrous oxide with $n$-alkanes or $n$-alkanols

In Figs. 4.3.a and 4.3.b the CEP conditions (temperature and pressure) for the family of nitrous oxide ($\text{N}_2\text{O}$) with $n$-alkanes, measured by Jangkamolkulchai et al. (1989), are plotted against the carbon number of the $n$-alkane. The TCP is estimated at $n=17.73$ and $T=317.4$ K, while the DCEP is found by rough extrapolation at $n \approx 25$ and $T \approx 275$ K. $\text{N}_2\text{O}$ has the same molecular weight as $\text{CO}_2$ and very similar critical properties. The critical temperature of $\text{CO}_2$ is 304.1 K while that of $\text{N}_2\text{O}$ is 309.6 K. The critical pressure of $\text{CO}_2$ is 7.38 MPa and that of $\text{N}_2\text{O}$ is 7.24 MPa. However the carbon number of the $n$-alkane which gives a TCP with one of these gases is $n=12.33$ for $\text{CO}_2$ and $n=17.73$ for $\text{N}_2\text{O}$ as was mentioned above. In addition the type IV intermediate zone for the systems of $\text{CO}_2 + n$-alkanes extends over a carbon number interval of $\Delta n = 1.2$ and a temperature range of $\Delta T = 21.5$ K as we have seen already, while for the $\text{N}_2\text{O}$ family the type IV zone occurs at a carbon number interval of $\Delta n = 6.9$ (almost six times larger) and a temperature range of $\Delta T = 42.4$ K (almost twice as large). Of course $\text{CO}_2$ and $\text{N}_2\text{O}$ are rather different molecules with respect to their polarity and geometrical structure, but it is hard to explain the differences in phase behaviour of these gases with $n$-alkanes in terms of molecular parameters. A two-parameter equation of state like the van der Waals equation which was used in the classification scheme of van Konynenburg and Scott with parameters evaluated from the critical points of the pure components cannot distinguish between these two families without using rather different $k$ and $l$ parameters.

In Figs. 4.3.a and 4.3.b the region of the DCEP is hidden below the crystallization surface. Therefore the estimation of its position was based on extrapolations according to the scaling laws described in Chapter 2. In both families of $\text{CO}_2$ and $\text{N}_2\text{O}$ with $n$-alkanes the DCEP is
positioned at lower temperature and pressure than the critical point of the pure more-volatile component.

Figs. 4.3.a (up) and 4.3.b (down). Three-phase $L_2L_1V$ equilibria in the family of binary systems of $N_2O$ with $n$-alkanes. Short dashed line with up empty triangles: UCEP's [$L_2=L_1=V$], solid line with down solid triangles: LCEP's [$L_2=L_1-V$], dashed-triple-dotted line with solid squares: quadruple points [$S_2-L_2-L_1-V$], dotted lines: three-phase $L_2L_1V$ equilibria curves, long dashed line: critical point of pure $N_2O$. 
The same happens for the families of these two gases with n-alkanols. The CEP's of the three-phase $L_2L_1V$ equilibria for the systems of $\text{N}_2\text{O} + \text{n-alkanols}$ (Lam et al., 1990b) are plotted in Figs. 4.4.a and 4.4.b.

Figs. 4.4.a (up) and 4.4.b (down). Three-phase $L_2L_1V$ equilibria in the family of binary systems of $\text{N}_2\text{O}$ with n-alkanols. Short dashed line with up empty triangles: UCEP's [$L_2-L_1=V$], solid line with down solid triangles: LCEP's [$L_2=L_1-V$], up solid triangle: UCEP [$L_2=L_1-V$] (for n-decanol), dashed-triple-dotted line with solid squares: quadruple points [$S_2-L_2-L_1-V$], dotted lines: three-phase $L_2L_1V$ equilibria curves, long dashed line: critical point of pure $\text{N}_2\text{O}$. 
In this family the DCEP is expected to be found before solidification occurs, at a carbon number between 10 and 11. The type IV zone extends over almost 4 carbon numbers. So it is narrower than in the family of N₂O + n-alkanes. However the temperature interval between the TCP and the DCEP is about 40 K as in the previous family. The same trends were noticed for the families of CO₂ with n-alkanes or n-alkanols.

![Graph showing critical endpoint temperatures in binary systems of CH₄ with hydrocarbons as a function of the solubility parameter of the hydrocarbon at 25 °C.](image)

In addition we see again that the carbon number of the alkanol where the transition between types II and III occurs is almost half the carbon number of the corresponding alkane and this reinforces the suggestion of agglomeration of the n-alkanol molecules via hydrogen bonding (formation of dimers to a greater extend).

4.3 Methane with hydrocarbons and ethane with n-alkanes or n-alkanols

Davenport and Rowlinson (1963) as well as van Konynenburg (1968) determined experimentally the immiscibility patterns in the family of methane (CH₄) with linear, branched and unsaturated hydrocarbons. In Fig. 4.5 the UCEP's [L₂=L₁-V] and the LCEP's [L₂=L₁-V] of these systems are plotted. Here the carbon number of the less-volatile component cannot serve any more as a proper parameter to describe the continuous variation of the three-phase L₂L₁V equilibrium extension. Hydrocarbons with the same carbon number but with a different shape or polarity (caused by double bonds) show a different three-phase L₂L₁V equilibrium behaviour in binary systems with CH₄.

Here the solubility parameter (Hildebrand and Scott, 1950) of the less-volatile component is used instead of its carbon number. Details about this parameter, like its physical meaning and the way to estimate it, will be discussed in Chapter 10 together with other possibilities to characterize branched alkanes. From Fig. 4.5 it seems that CEP's of systems with a less-volatile component with six carbon atoms fall onto a parabolic curve similar to the one suggested for the CO₂ and the N₂O families. The DCEP, where the LCEP and UCEP loci merge, is found at the maximum δ value along this curve, in analogy to the maximum n value for the CO₂ and N₂O families. For CH₄ + C₇ systems a similar behaviour is found, in this case at lower δ values.

In Figs. 4.6.a and 4.6.b the temperature and the pressure of the CEP's for binary systems of ethane (C₂H₆) with n-alkanes are plotted against the carbon number of the n-alkane using data from Estrera and Luks (1987). These systems follow the transition sequence from type I, via type V, towards type III (or the transition sequence from type II, via type IV, towards type III with the low-temperature L₂L₁V branch probably always hidden by solidification) as the carbon number of the less-volatile component increases. In this family the quadruple point curve intersects the LCEP curve at a carbon number between 23 and 24, which suggests that in a quasi-binary system of C₂H₆ + a mixture of C₂₃ and C₂₄ a quadruple point [S₂-L₂=L₁-V]
can be realized (empty diamond in Figs. 4.6.a and 4.6.b). The same occurs for the family of 
\( \text{N}_2\text{O} + n\text{-alkanes} \) at a carbon number between 22 and 23 (see Figs. 4.3.a and 4.3.b).
Figs. 4.6.a (previous page up), 4.6.b (previous page down), 4.6.c (this page). Three-phase \( L_2L_1V \) equilibria in the family of binary systems of \( C_2H_6 \) with n-alkanes. Short dashed line with up empty triangles: UCEP's \( [L_2-L_1=V] \), solid line with down solid triangles: LCEP's \( [L_2=L_1-V] \), solid square: quadruple point \( [S_2-L_2-L_1-V] \) (for n-tetracosane), dashed-dotted lines: hypothetical extrapolations of LCEP's \( [L_2=L_1-V] \) and quadruple points \( [S_2-L_2-L_1-V] \), empty diamond: hypothetical quadruple point of the type \( [S_2-L_2-L_1-V] \), dotted lines: three-phase \( L_2L_1V \) equilibria curves, long dashed line: critical point of pure \( C_2H_6 \).

The TCP is located at \( n=17.58 \) and \( T=312.9 \) K. The scale of Fig.4.6.a is very coarse to support graphically such a conclusion. The measurements of Goh et al. (1987) provide much more details for the region close to the TCP (see Fig.4.6.c) and determine with a greater accuracy the TCP at \( n=17.61 \) and \( T=313.21 \). The DCEP occurs at \( n=42\pm5 \) and \( T=186\pm50 \) K as a rather doubtful extrapolation into the solid region suggests. This creates a rather wide intermediate type IV zone extending over 24 carbon numbers and about 130 K. Systems of \( C_2H_6 + n \)-alkanes show a TCP very close to the TCP of systems of \( N_2O + n \)-alkanes, although the transition zone of type IV for \( C_2H_6 \) systems is more than 3 times wider in carbon number and temperature than the one for \( N_2O \) systems. The critical temperature of \( C_2H_6 \) is 305.3 K, very similar to the corresponding temperatures of \( CO_2 \) and \( N_2O \). The critical pressure of \( C_2H_6 \)...
is 4.87 MPa, about 2/3 of the critical pressure of either CO₂ or N₂O. From the difference in the critical pressures is hard to explain the large differences in the phase behaviour of these binary families. Therefore a two-parameter equation of state like the van der Waals equation will heavily underpredict these differences.

Of course C₂H₆ is apolar and also a member of the n-alkane homologous series, so only size differences between the constituents of the systems C₂H₆ + n-Cₙ affect the three-phase L₂L₁V equilibrium patterns. In contrast with C₂H₆, the N₂O molecule has a non-zero dipole moment and the CO₂ molecule has a large quadrupole moment. These electric moments introduce additional intermolecular interactions. Just examining the properties of the pure gases we may notice the strong influence of the molecular structure on the fluid phase behaviour. The acentric factor for C₂H₆ is 0.099, for N₂O 0.165 and for CO₂ 0.239 (an approximated ratio 3 : 5 : 7). The acentric factor can be viewed as a measure of the complexity of a molecule with respect to both its geometry and polarity. Another property strongly related to molecular structure is the normal freezing point which approximates the triple point temperature. For the above gases holds that the higher the acentric factor is, the higher is also the temperature of the freezing point. For C₂H₆ it is 89.9 K, for N₂O 182.3 K and for CO₂ 216.6 K (an approximated ratio 3 : 6 : 7). If the behaviour of the pure components is so different we can expect that this even more will be the case for the binary systems. A three-parameter equation of state like the Peng-Robinson equation, which takes also into account the molecular complexity by means of the acentric factor, seems more appropriate than the van der Waals equation for the modelling of these systems, but as we will see later it is not also adequate for a quantitative description.

The behaviour of the binary systems of C₂H₆ + n-alkanols (Lam et al., 1990a) is depicted in Figs. 4.7.a and 4.7.b. It can be noticed that a transition of the type II↔IV↔III never occurs in this family. As it was discussed before, the effect of reducing the size of an associating component is to increase its trend for agglomeration and therefore to produce a higher effective carbon number than the actual one. In the systems of CO₂ or N₂O + n-alkanols we have seen that in the region of type IV (or V) phase behaviour, the n-alkanol has effectively half of the carbon number the n-alkane has, in the same transition region, for the corresponding families with n-alkanes as the less-volatile component. Consequently since the type V region in the systems of C₂H₆ + n-alkanes starts at a carbon number around 18 we should expect a TCP for the C₂H₆ + n-alkanols family at a carbon number around 9. Indeed
type V phase behaviour is found at n≈9, but even at lower carbon numbers of the n-alkanols a TCP (type V to type I transition) does not occur.

Figs. 4.7.a (up) and 4.7.b (down). Three-phase L₂L₁V equilibria in the family of binary systems of C₂H₆ with n-alkanols. Short dashed line with up empty triangles: UCEP's [L₂-L₁=V], solid line with down solid triangles: LCEP's [L₂-L₁-V], dashed-triple-dotted line with solid squares: quadruple points [S₂-L₂-L₁-V], dotted lines: three-phase L₂L₁V equilibria curves, long dashed line: critical point of pure C₂H₆.
As the n-alkanol molecule becomes smaller (till n-butanol) the loci of the UCEP's [$L_2^*-L_1=V$] and of the LCEP's [$L_2=L_1-V$] approach each other suggesting a possible TCP. But when n-propanol is used as the less-volatile component the polar and association effects are so strong that the decrease in actual size is surpassed by the increase in effective size due to agglomeration. Therefore the phase behaviour still is of type V and as the carbon number of the n-alkanol is reduced further (ethanol) it becomes more pronounced type V (longer three-phase $L_2L_1V$ curve). In the case of methanol the three-phase $L_2L_1V$ equilibria extends to very low temperatures and an LCEP is not detected until 240 K. Possibly the three-phase $L_2L_1V$ equilibria terminates at a quadruple point where methanol is solid (around 175 K).

4.4 Ammonia with n-alkanes

Ammonia (NH$_3$) is a molecule with a large dipole moment (1.5 Debye where N$_2$O has a dipole moment of only 0.2 Debye). Its critical temperature is about 100 K higher that the critical temperature of CO$_2$, N$_2$O or C$_2$H$_6$. Its critical pressure is 1.5 times larger than the critical pressure of CO$_2$ or N$_2$O and 2.3 times larger than that of C$_2$H$_6$. In Figs. 4.8.a and 4.8.b the experimental CEP's for systems of NH$_3$ with n-alkanes (Brummer, 1988) are plotted against the carbon number of the n-alkane. The familiar transition scheme from II, via IV, towards III type behaviour is observed for n-alkanes between C$_{18}$ and C$_{19}$. Brummer found type IV behaviour in a quasi-binary system of NH$_3$ with a pseudo-n-alkane consisting of C$_{18}$ and C$_{19}$ in a molar ratio of 75:25. Therefore, in this case, the carbon number of the less-volatile pseudo-component is 18.25. The quasi-binary approximation is valid since the size of the two constituents of the pseudo-component is almost the same (they differ less than 6% in molecular weight).

The carbon number of the II$\leftrightarrow$IV$\leftrightarrow$III transition is found in the same region where this transition in the families of N$_2$O + n-alkanes or C$_2$H$_6$ + n-alkanes occurred. However, the size of the type IV zone is much smaller. It has a width less than 0.5 in carbon number and an extent in temperature of about 10 K, so it is even smaller than the corresponding type IV zone in the family of CO$_2$ + n-alkanes. We cannot give an explanation for this phenomenon based on molecular properties as will be discussing in greater detail in Chapter 10.

In the NH$_3$ + n-alkanes family we have the opportunity to observe the UCEP [$L_2=L_1-V$] locus down to very small carbon numbers for the n-alkane. As n decreases, the curve in Fig.
4.8.a (temperature plot) goes through an inflection point, where it becomes concave instead of convex and at further decrease of n it passes a second inflection point, after which becomes convex again. In Fig. 4.8.b (pressure plot) such inflection points do not exist and the curve of the UCEP locus remains always convex.

Figs. 4.8.a (up) and 4.8.b (down). Three-phase \(L_2L_1V\) equilibria in the family of binary systems of \(NH_3\) with \(n\)-alkanes. Short dashed line with up empty triangles: UCEP's \([L_2L_1=V]\), down solid triangle: LCEP \([L_2=L_1V]\) (for the quasi-binary system: \(NH_3 + \{0.75\ n-C_{18} + 0.25\ n-C_{19}\}\) ), dashed-dotted line with up solid triangles: UCEP's \([L_2=L_1V]\), long dashed line: critical point of pure \(NH_3\).
Both plots show a minimum at a carbon number around 3. The critical temperature of propane is 369.9 K and that of n-butane is 425.3 K. The critical temperature of NH₃ (405.5 K) is between them. The critical pressure of NH₃ is almost 3 times larger than the critical pressures of both n-C₃ and n-C₄. However with decreasing temperature the vapour pressure of NH₃ decreases, while the critical pressure of the n-alkane increases with decreasing carbon number. This changes the relative roles of NH₃ and n-alkanes with respect to volatility and for the system of NH₃ and C₂H₆ the more-volatile component is not any more NH₃ but the alkane (C₂H₆). In the systems of NH₃ with n-alkanes up to n-C₅ the three-phase L₂L₁V equilibrium curves are located above the vapour-pressure curve of the more-volatile component, which suggests heteroazeotropy.

4.5 Water with n-alkanes

In the family of binary systems of water (H₂O) + n-alkanes (Brunner, 1990) the situation is totally different from what we have discussed up to now. This is something that can be expected from the peculiar properties of H₂O. H₂O has a liquid region (from triple point temperature to critical point temperature) extended over 374 K. This is almost 2 times larger than the liquid region of C₂H₆ and NH₃, 3 times larger than the liquid region of N₂O and more than 4 times larger than the liquid region of CO₂. H₂O has a higher dipole moment than NH₃ and is known to form hydrogen bonds to a great extend. Its critical temperature is 2 times larger than the critical temperature of CO₂, N₂O and C₂H₆ and 1.6 times larger than the critical temperature of NH₃. Its critical pressure is 2 times larger than that of NH₃, 3 times larger than that of CO₂ and N₂O and 4.5 times larger than that of C₂H₆.

Systems of H₂O + n-alkanes exhibit type III fluid phase behaviour with heteroazeotropy (III-HA according to the van Konynenburg and Scott classification). The systems with alkanes higher than C₂₈ exhibit the familiar type III behaviour described in Chapter 2 as it is depicted in the right part of Fig. 4.9. The critical curve starting at the critical point of the less-volatile component (n-alkane) moves first to lower temperatures passing successively through a pressure maximum and a pressure minimum and then turns back to higher temperatures and pressures. The critical curve starting at the critical point of the more-volatile component (H₂O) terminates at the UCEP [L₂-V=L₁] of the three-phase L₂VL₁ equilibrium curve. The L₂ phase is the alkane-rich liquid phase and the L₁ phase is the H₂O-rich liquid phase. This subtype is called type IIIb by Brunner (1990) in order to be distinguished from another type III
behaviour observed in the systems of \( \text{H}_2\text{O} + n\text{-alkanes} \) with a carbon number \( n \leq 26 \). The latter type is designated by Brunner as type IIIa.

![TYPE IIIa and TYPE IIIb diagrams]

*Fig. 4.9 Schematic \( P,T \) and \( T,x \) projections of the monovariant equilibria of types IIIa and IIIb fluid phase behaviour in binary systems. Solid lines: vapour pressure curves of pure components, dashed lines: critical lines, dashed-dotted lines: three-phase \( L_2L_1V \) equilibria curves, open circles: critical points of pure components, up solid triangle: UCEP \([L_1-L_2=V]\), up empty triangle: UCEP \([L_2L_1=V]\), empty diamond: barotropic inversion point.*

In type IIIa (see left part of Fig. 4.9) the critical curve starting from the critical point of the less-volatile component (\( n\)-alkane) covers the whole temperature range between the critical points of the two components passing through a pressure maximum and a pressure minimum and terminates at an UCEP \([L_2=V-L_1]\) at the end of a three-phase \( L_2VL_1 \) equilibrium curve. This UCEP is different in nature from the UCEP of type IIIb, although in both cases they represent a critical endpoint where a liquid phase is in equilibrium with a critical phase \( L=V \). The difference is that in type IIIa the critical phase is a \( L_2=V \) phase, while in type IIIb is a \( V=L_1 \) phase. Therefore in type IIIa the UCEP is of the \([L_2=V-L_1]\) kind and in type IIIb it is
of the \([L_2-V=L_1]\) kind. For the systems of type IIIa the critical curve which starts at the critical point of the more-volatile component \((H_2O)\) goes through a temperature minimum (and in some cases also through a pressure minimum) before it turns to higher temperatures and pressures.

In type IIIb a barotropic inversion of the two liquid phases occurs along the three-phase \(L_2 VL_1\) equilibrium curve before the UCEP. In the low temperature range before the UCEP the heavier liquid phase is the \(H_2O\)-rich phase \((L_1\) phase). \(H_2O\) at low temperature has a density about 1 g/ml, while \(C_{28}\) has a density about 0.8 g/ml. As the critical temperature of \(H_2O\) is approached the density of \(H_2O\) and consequently the density of the \(H_2O\)-rich phase drops drastically (the critical density of \(H_2O\) is 0.316 g/ml). Therefore the \(L_1\) phase becomes lighter and moves to above the alkane-rich phase \((L_2\)-phase\) in the vessel where the experiment takes place (see Chapter 6 for a more detailed description of these phenomena). The two phases have exactly the same density at the so-called barotropic inversion temperature.

It should be stressed that the lighter phase of all, the vapour phase, has continuously a composition between the compositions of the two liquid phases (see \(T_x\) projections in Fig. 4.9). This phenomenon is related to the heteroazeotropic behaviour. The heteroazeotropy is a consequence of the very poor miscibility between the \(H_2O\) and the alkanes and results in a three-phase \(L_2 VL_1\) equilibrium pressure higher than the saturation pressures of both pure components at the same temperature. In some systems, like the \(H_2O + n-C_6\) system, the three-phase \(L_2 VL_1\) pressure at a certain temperature is even higher than the sum of the two saturation pressures of the pure components at the same temperature (Scheffer, 1960).

In Figs. 4.10.a and 4.10.b the temperatures and the pressures of the two types of upper critical endpoints for binary systems of \(H_2O + n\)-alkanes are plotted against the carbon number \(n\) of the \(n\)-alkane. In Fig. 4.10.a the barotropic inversion points are also included. The locus of the UCEP’s \([L_2-V-L_1]\) of type IIIa is concave in the temperature plot (Fig. 4.10.a) up to a carbon number close to the transition IIIa\(\leftrightarrow\)IIIb. Then after an inflection point it becomes convex. The same locus in the pressure plot (Fig. 4.10.b) has one more inflexion point at low carbon numbers. All the CEP’s have a temperature and pressure lower than the critical temperature and critical pressure of pure \(H_2O\), respectively.

The critical point of the \(n\)-alkanes passes the critical temperature of \(H_2O\) \((T_c=647.3\) K) between \(n-C_{11}\) \((T_c=638.9\) K) and \(n-C_{12}\) \((T_c=658.7\) K). Therefore, for carbon numbers \(n\leq 12\), the \(n\)-alkanes may be considered as the more-volatile components of the binary systems \(H_2O + n\)-alkanes. However, according to the definition of the volatility of pure components given in
Chapter 1, only for \( n \leq 6 \) the \( n \)-alkanes may be considered as the more-volatile components of the binary systems \( \text{H}_2\text{O} + \text{n-alkanes} \), since \( \text{n-C}_6 \) is the first \( n \)-alkane with a vapour pressure curve found at higher pressure than that of the vapour pressure curve of \( \text{H}_2\text{O} \).

Figs. 4.10.a (up) and 4.10.b (down). Three-phase \( L_2L_1V \) equilibria in the family of binary systems of \( \text{H}_2\text{O} \) with \( n \)-alkanes. Short dashed line with up empty triangles: UCEP's \([L_1-L_2=V]\), solid line with empty diamonds: liquid-liquid-vapour barotropic inversion points, dashed-dotted line with up solid triangles: UCEP's \([L_2-L_1=V]\), long dashed line: critical point of pure \( \text{H}_2\text{O} \).
Brunner (1990) claims that the transition from subtype IIIa to subtype IIIb occurs via a tricritical endpoint (a TCP which is also the end of a three-phase $L_2L_1V$ equilibrium curve or in other words a van Laar point as defined in Chapter 2). This is not likely because this can happen only by accident as will be explained in detail in Chapter 10. What seems more reasonable is an intermediate zone with a fluid phase behaviour showing three critical endpoints, like in the type IV or IV* zones, which will be bounded by zones of types IIIa and IIIb and transition states like TCP and DCEP behaviour. Of course these transition states can only be realized in quasi-binary systems.

![Graph showing upper critical endpoints for various binary systems](image)

Fig. 4.11 Upper critical endpoints [$L_2=L_1-V$] in several families of binary systems of $n$-perfluoroalkanes with $n$-alkanes. All the systems are of type II fluid phase behaviour. Solid line with empty circles: the family of $C_3F_8$ with $n$-alkanes, dashed line with crosses: the family of $C_4F_{10}$ with $n$-alkanes, dashed-dotted line with empty squares: the family of $C_6F_{14}$ with $n$-alkanes, dotted line with X's: the family of $C_7F_{16}$ with $n$-alkanes, solid horizontal line: the critical point of pure $C_3F_8$, dashed horizontal line: the critical point of pure $C_4F_{10}$, dashed-dotted horizontal line: the critical point of pure $C_6F_{14}$, dotted horizontal line: the critical point of pure $C_7F_{16}$. 
4.6 Perfluoroalkanes with n-alkanes

The families of perfluoroalkanes with n-alkanes are very interesting because the TCP and the DCEP of the transition zone of type IV are located close to each other. One aim of this thesis was to investigate the possibility of a direct transition from type II to type III fluid phase behaviour via a system exhibiting a van Laar point. For this purpose the above families seemed to be promising for a more detailed study.

In Fig. 4.11 the UCEP's \( L_2 = L_1 - V \) for various families of perfluoroalkanes with n-alkanes are plotted against the carbon number of the n-alkane according to experimental data from Hicks et al. (1978). A common feature of all the curves is that they are convex for high carbon numbers (approaching a DCEP) and concave for low carbon numbers with an inflexion point at intermediate carbon number.

The CEP's for the family of perfluoropropane \((C_3F_8) + n\)-alkanes (Loos et al., 1993b) are depicted in Fig. 4.12.a. The transition zone of type IV is entirely located between the binary systems of \( C_3F_8 \) with \( n \)-octane and \( C_3F_8 \) with \( n \)-nonane. The quasi-binary approximation was used to study in more detail the transition and the special border regions close to the TCP and the DCEP. The topology of the various loci resembles the one already seen in the family of \( CO_2 + n \)-alkanes (see Fig. 4.12.b).

The TCP is found at \( n=8.428 \) and \( T=378.7 \) K while the DCEP is located at \( n=8.473 \) and \( T=370.6 \). This defines a type IV intermediate zone over a carbon number interval \( \Delta n=0.045 \) and a temperature interval \( \Delta T=8.1 \) K. This zone is 27 times narrower in carbon number and 2.7 times smaller in temperature than the corresponding one in the family of \( CO_2 + n \)-alkanes. Also the average transition carbon number is 8.45, much lower than the corresponding carbon number in all the other families examined up to now. It is difficult to give an explanation based on molecular structure for these differences. \( C_3F_8 \) is a large molecule (its critical volume is 3 times larger than that of \( C_2H_6 \) and more than 3 times larger than that of \( CO_2 \)). It has no dipole moment, but has strong octapole moment. Its critical temperature is about 40 K above the critical temperatures of \( CO_2, N_2O \) or \( C_2H_6 \) and 60 K below the critical temperature of \( NH_3 \). In contrast its critical pressure is the lowest of all the other more-volatile components examined up to now (2.7 times smaller than the critical pressure of \( CO_2 \) and \( N_2O \) and more than 8 times smaller than the critical pressure of \( H_2O \)).
Figs. 4.12.a (up) and 4.12.b (down). Three-phase $L_2L_1V$ equilibria in the family of binary systems of $C_3F_8$ with n-alkanes. Short dashed line with up empty triangles: UCEP's $[L_2L_1V]$. Solid line with down solid triangles: LCEP's $[L_2L_1V]$. Dashed-dotted line with up solid triangles: UCEP's $[L_2L_1V]$. Long dashed line: critical point of pure $C_3F_8$. 
The last family examined in this literature survey on three-phase L2L1V equilibria in binary systems, is the family of 1,1,1 trifluoro-ethane (C₂H₃F₃) + n-alkanes. C₂H₃F₃ has the strongest dipole moment of all the more-volatile components mentioned above (2.3 Debye against 1.8 Debye for H₂O and 1.5 Debye for NH₃). Its critical temperature (346.3 K) is close to the critical temperature of C₃F₈ (345.1 K), but its liquid range is 1.4 times smaller than the corresponding one for C₃F₈. This is because the strong electrostatic forces between the dipole molecules of C₂H₃F₃ lead to the formation of a solid phase earlier than the weak van der Waals forces between the apolar molecules of C₃F₈. The critical pressure of C₂H₃F₃ is 1.4 times larger than the critical pressure of C₃F₈, which is in line with its more polar character.

![Graph of three-phase L2L1V equilibria](image)

*Fig. 4.13 Three-phase L₂L₁₁V equilibria in the family of binary systems of 1,1,1 C₂H₃F₃ with n-alkanes. Short dashed line with up empty triangles: UCEP's [L₂-L₁-V], solid line with down solid triangles: LCEP's [L₂-L₁-V], dashed-dotted line with up solid triangles: UCEP's [L₂-L₁-V], long dashed line: critical point of pure 1,1,1 C₂H₃F₃.*

The CEP's of this family are depicted in Fig. 4.13 according to measurements performed in our laboratory (de Loos et al., 1993c). The TCP is located at n=11.65 and T=369 K and the DCEP is estimated at n=12.13 and T=347 K. Therefore the type IV zone is 0.48 wide in
carbon number and 22 K wide in temperature. Compared to the type IV region of the family of CO₂ + n-alkanes, it has the same height in temperature but it is 2.5 times narrower with respect to the carbon number. In general the proportions in temperature extension and carbon number width, among the type IV zones of the families discussed, are not preserved. Perhaps a dimensionless temperature extension and a properly reduced carbon number difference will be more suitable for keeping the proportions.

**TABLE 4.1**

*Physical properties of pure more-volatile components from the book of Reid et al. (1988).*

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>CO₂</td>
<td>216.6</td>
<td>184.7(^\dagger)</td>
<td>304.1</td>
<td>7.38</td>
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<td>N₂O</td>
<td>182.3</td>
<td>184.7</td>
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<td>C₂H₆</td>
<td>89.9</td>
<td>184.6</td>
<td>305.4</td>
<td>4.88</td>
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<td>NH₃</td>
<td>195.4</td>
<td>239.8</td>
<td>405.5</td>
<td>11.35</td>
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<td>H₂O</td>
<td>273.2</td>
<td>373.2</td>
<td>647.3</td>
<td>22.12</td>
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<td>C₃F₈</td>
<td>90.0</td>
<td>236.5</td>
<td>345.1</td>
<td>2.68</td>
</tr>
<tr>
<td>1,1,1 C₂H₃F₃</td>
<td>161.9</td>
<td>225.6</td>
<td>346.3</td>
<td>3.76</td>
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<table>
<thead>
<tr>
<th>Gas component</th>
<th>MW [g/mol]</th>
<th>(\omega)</th>
<th>Vc [ml/mol]</th>
<th>(\mu) [Debye]</th>
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<tr>
<td>CO₂</td>
<td>44.01</td>
<td>0.239</td>
<td>93.9</td>
<td>0.0</td>
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<td>N₂O</td>
<td>44.01</td>
<td>0.165</td>
<td>97.4</td>
<td>0.2</td>
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<td>0.099</td>
<td>148.3</td>
<td>0.0</td>
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<tr>
<td>NH₃</td>
<td>17.03</td>
<td>0.250</td>
<td>72.5</td>
<td>1.5</td>
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<tr>
<td>H₂O</td>
<td>18.02</td>
<td>0.344</td>
<td>57.1</td>
<td>1.8</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>188.02</td>
<td>0.325</td>
<td>299.8</td>
<td>0.0</td>
</tr>
<tr>
<td>1,1,1 C₂H₃F₃</td>
<td>84.04</td>
<td>0.251</td>
<td>194.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^\dagger\) The normal boiling point of CO₂ is estimated by extrapolation using the Peng-Robinson equation of state.
In Table 4.1 the properties of the pure more-volatile components discussed in the previous sections are summarized.

![Fig. 4.14 Saturation curves of pure more-volatile components from their boiling to their critical temperature. It is assumed that \( \ln(P) = A + B/T \) where \( A \) and \( B \) are constants. Open circles: critical points, solid circles: normal boiling points, solid line: \( \text{CO}_2 \), short-dashed line: \( \text{N}_2\text{O} \), medium-dashed line: \( \text{H}_2\text{O} \), long-dashed line: \( \text{NH}_3 \), dotted line: 1,1,1 \( \text{C}_2\text{H}_3\text{F}_3 \), dashed-dotted line: \( \text{C}_2\text{H}_6 \), dashed-triple-dotted line: \( \text{C}_2\text{F}_8 \).](image1)

![Fig. 4.15 Saturation curves of pure more-volatile components from their freezing point to their critical point, placed according to the acentric factor \( \omega \) of the component. Open circles: critical points, solid circles: normal boiling points, solid squares: normal freezing points (the freezing temperature is approximately equal to the triple point temperature). For the meaning of the various lines see Fig. 4.14.](image2)
### TABLE 4.2

The carbon number and the temperature where a TCP or a DCEP occurs in several families of a more-volatile component (here characterized as gas) with n-alkanes. Δn is the carbon number interval and ΔT is the temperature range in K of the intermediate type IV zone.

<table>
<thead>
<tr>
<th>Gas component</th>
<th>TCP</th>
<th>DCEP</th>
<th>type IV zone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>T/K</td>
<td>n</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.33</td>
<td>317.5</td>
<td>13.55</td>
</tr>
<tr>
<td>N₂O</td>
<td>17.73</td>
<td>317.4</td>
<td>24.6</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>17.58</td>
<td>312.9</td>
<td>42</td>
</tr>
<tr>
<td>NH₃</td>
<td>18.00</td>
<td>417.5</td>
<td>18.35</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>8.428</td>
<td>378.7</td>
<td>8.473</td>
</tr>
<tr>
<td>1,1,1 C₂H₃F₃</td>
<td>11.65</td>
<td>369.0</td>
<td>12.13</td>
</tr>
</tbody>
</table>

**Fig. 4.16** Relationship between the ratio $\lambda = \Delta T(K) / \Delta n$ of the type IV transition zone and the acentric factor
In Fig. 4.14 the vapour pressure curves of these gases are depicted and in Fig. 4.15 their liquid regions from their melting until their critical point are plotted against their acentric factor, \( \omega \) (the selection of \( \omega \) as abscissa is related to the use of \( \omega \) as characteristic variable for these gases; see Fig.4.16, Fig.10.11).

In Table 4.2 the positions of the TCP and the DCEP in several of the families discussed as well as the dimensions of their type IV zone are summarized. If \( \lambda \) is defined as the ratio of the temperature height in K (\( \Delta T \)) over the carbon number width (\( \Delta n \)) of the type IV transition zone, then the relationship of \( \lambda \) with respect to the acentric factor \( \omega \) of the more-volatile component is given in Fig.4.16.

Symbols

- **CEP** critical endpoint
- **DCEP** double critical endpoint
- \( \mu \) dipole moment
- **LCEP** lower critical endpoint \([L_2=L_1\cdot V]\)
- **MW** molecular weight
- \( n \) carbon number (number of carbon atoms in a molecule)
- **QP** quadruple point \([S_1\cdot L_2\cdot L_1\cdot V]\) or \([S_2\cdot L_2\cdot L_1\cdot V]\)
- **P** pressure
- \( P_c \) critical pressure
- **T** temperature
- \( T_b \) normal boiling temperature
- \( T_c \) critical temperature
- \( T_f \) normal freezing temperature
- **TCP** tricritical point
- **UCEP** upper critical endpoint \([L_2=L_1\cdot V]\) or \([L_2\cdot L_1=V]\)
- \( V_c \) critical volume

Greek

- \( \omega \) acentric factor
References


Loos, Th.W. de, Poot W. and Swaan Arons, J. de, 1993c. 1,1,1 C₃H₃F₃ and n-alkanes. To be submitted to Fluid Phase Equilibria.


5. EXPERIMENTAL SETUP

In this chapter the apparatus used in the experiments is described and the procedure followed for the preparation of the mixtures is outlined. The way the measurements are performed is discussed and the mixtures that were studied are summarized. The chapter closes with information on the chemicals that were used.

![Diagram of the Cailletet apparatus](image)

Fig. 5.1 The Cailletet apparatus.
5.1 Apparatus

The measurements were carried out in an apparatus designed for the synthetic method. With this so-called Cailletet apparatus (Fig. 5.1) described earlier by de Loos et al. (1983, 1986), phase equilibria for mixtures of known overall composition can be determined visually in a temperature range from 250 up to 500 K and at pressures up to 15 MPa.

A sample of the mixture is confined over mercury in the sealed end of a thick walled, capillary Pyrex glass tube. The tube is 50 cm long and has an inner diameter of 4 mm and an outer diameter of 12 mm. At about 2/3 of its length the tube has a conical thickening which fits in the closing plug of the stainless-steel autoclave. Glass to metal and metal to metal sealing is achieved by means of Viton O-rings. An enlargement of the section around the closing plug is drawn in Fig. 5.2.

![Diagram](image)

Fig. 5.2 Enlargement of the Cailletet apparatus around the closing plug of the autoclave.
The autoclave is filled with mercury up to the line where the pressure generating system (Fig. 5.3) begins. The open end of the Cailletet tube is immersed in mercury. The mercury serves as a pressure intermediate between the sample and the hydraulic oil of the pressure generating system. The sample can be agitated by a stirrer activated by two external button magnets. The stirrer is a rod made from soft-iron and has a diameter slightly less than the bore of the glass capillary tube. The button magnets move up and down via a connection to the rotating disk of an electric motor.

![Diagram of the pressure generating system]

\textit{Fig. 5.3 The pressure generating system.}

The Cailletet tube is kept at the desired temperature by a thermostat with circulating ethanol, water or silicon oil depending on the temperature range of interest. The temperature is measured to an accuracy within 0.01 K by using a platinum resistance thermometer. The thermostat maintains the temperature constant to better than 0.05 K at temperatures up to 370 K and to better than 0.1 K at higher temperatures. The pressure is generated hydraulically with a screw type hand pump and is measured by means of a dead-weight pressure gauge to an accuracy within 0.005 MPa; see Fig. 5.3.
5.2 Procedure of filling

The samples of the binary systems investigated consisted of a more-volatile component (gas at room temperature) and a less volatile component (liquid at room temperature). First the liquid component is dosed in the sealed end of the Cailletet tube by means of a micrometer syringe. The exact mass of the liquid is determined by weighing. The liquid is thoroughly degassed by successive freezing and melting using liquid nitrogen under high vacuum supplied via a high vacuum oil diffusion pump or a high vacuum turbo pump. The vacuum quality is measured with an ionization vacuum meter.

![Diagram of the gas rack construction](image)

Fig. 5.4 The gas rack construction.

The gaseous component is added to the evacuated tube afterwards by displacement with mercury in a gas rack construction (Fig. 5.4). Nitrogen gas is used for the mercury displacement. The exact amount of the gaseous component is determined from the knowledge of the pressure it exerts, at the known room temperature, when it is restricted to a glass bulb of known volume.
After the filling procedure the sample is frozen in the sealed end of the Cailletet tube. The rest of the tube is filled with the mercury used for displacing the gaseous component. Under these conditions the tube is transferred from the gas rack to the Cailletet apparatus where the system is pressurized before it is warmed up to room temperature.

5.3 Procedure of measurements

The way of measuring a specific type of phase equilibrium for a binary system depends on the number of coexisting phases. The Gibbs phase rule applied on a binary system results in $F = N - \pi + 2 = 4 - \pi$.

For a two-phase equilibrium $F = 2$, therefore two field variables can be adjusted (bivariant equilibrium). Setting the temperature of the thermostat to a certain value only the pressure remains free. Experimentally speaking the temperature is never fixed to a value according to its mathematical sense but always fluctuates between an upper and a lower limit. Therefore the final accuracy of the observation is always beyond the accuracy of the measuring instrument. Bubble or dew points can be observed if the pressure is adjusted in such a way that the vapour or the liquid phase just disappears, respectively. For a bubble point the meniscus between the two phases rises upon compression. For a dew point between the critical point and the cricondentherm (part CA in Fig.2.1.c) the meniscus descents upon compression, while for a dew point after the cricondentherm the meniscus descends upon expansion. When the meniscus disappears in the middle of the system a critical point is encountered and the behaviour changes from bubble-point behaviour to dew-point behaviour or vice versa.

For a three-phase equilibrium $F = 1$. If the temperature is fixed then the volume can be adjusted in order to observe three phases. Then the pressure recorded is the required equilibrium pressure (monovariant equilibrium). The dead-weight pressure gauge cannot be used in this case because it imposes a pressure on the system, while the pressure in this case is a free variable. Instead a pressure transducer calibrated against the dead-weight pressure gauge is used for the pressure measurement. In a critical endpoint $F = 0$. This point can only be found by interpolation.
Fig. 5.5 Some cases of fluid phase equilibria in binary mixtures as they appear at the sealed top of the capillary tube.

In Fig. 5.5 several one-, two- and three-phase situations for binary mixtures, as they appear in the top of the measuring capillary tube, are drawn schematically. More details about specific cases like the barotropic inversion phenomena will be discussed later.

In this work mainly three-phase equilibria are measured. When the quasi-binary approximation is used, the three-phase equilibrium curve is not a curve any more but rather an area in the P,T projection because the system is a ternary system. A rough test for the validity of the quasi-binary approximation is the measurement of the extent of this region in terms of pressure of the three-phase equilibrium at a certain temperature. If this is less than
0.02 MPa then it is assumed that our ternary system behaves approximately as a binary one. A better test should be to take and analyze samples of the three phases of a three-phase equilibrium. If the quasi-binary approximation holds then the distribution of the two constituents of the pseudo-component is almost the same in all the coexisting phases. However, such a facility is not available in our experimental setup.

For a binary or a quasi-binary mixture a three-phase equilibrium is monovariant as it was explained above. That means that independent of the overall composition of the mixture the measured three-phase equilibrium curve is always the same. However, the overall composition of the mixture must be suitable in order to observe the three-phase $L_1L_2V$ equilibria. For instance an overall composition $x$ larger than the composition of the liquid phase $L_2$, which is the richer in the less-volatile component liquid phase, is not suitable for the observation of the three-phase $L_1L_2V$ equilibria. The reason for this is that this overall composition cannot split up into three phases, each with a composition lower than the overall composition.

5.4 Experiments performed

The binary systems examined in this work consisted of a more-volatile component (solvent) from the homologous series of n-perfluoroalkanes and a less-volatile component (solute) from the family of alkanes, or alkanols, or ethers. Linear and branched molecules of solutes were used in order to study both the effect of the size and of the shape of the solute on the behaviour of the binary system. The alkanols and the ethers offered the possibility to investigate also the influence of the polarity of the solute molecule on the mixture behaviour. The n-perfluoroalkanes were selected because of the fact that in their binary mixtures with n-alkanes the tricritical point behaviour and the double critical endpoint behaviour are located close to each other (de Loos et al., 1989, 1993). Therefore it was worthwhile to test for the possibility of observing a van Laar point behaviour (see Chapter 2).

5.5 Chemicals used

Table 5.1 contains information about the chemical compounds used in this work. The names of the components and an abbreviated formula of them are followed by their origin and stated purity. Table 5.2 gives some of the thermodynamic properties of these components
based on information from Reid et al. (1988). Further purification of any component except of perfluorobutane and of methanol was not attempted.

**TABLE 5.1**

Chemicals used (*n*-perfluoroalkanes, linear and branched alkanes, linear and branched alkanols, and ethers). Their origin and purity.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Abbreviated formula</th>
<th>Origin</th>
<th>Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>perfluoroethane</td>
<td>C₂F₆</td>
<td>UCAR</td>
<td>99.9</td>
</tr>
<tr>
<td>perfluoropropane</td>
<td>C₃F₈</td>
<td>Intermar</td>
<td>99.8</td>
</tr>
<tr>
<td>perfluorobutane</td>
<td>C₄F₁₀</td>
<td>Intermar</td>
<td>99</td>
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<td>n-octane</td>
<td>n-C₈</td>
<td>Merck-806910</td>
<td>99</td>
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<td>n-nonane</td>
<td>n-C₉</td>
<td>Merck-806838</td>
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<td>n-decane</td>
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<td>Baker-8066</td>
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<td>1-butanol</td>
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### TABLE 5.1 (continued)

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<td>1-octanol</td>
<td>n-C₈OH</td>
<td>Fluka-74850</td>
<td>99.5</td>
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<td>2-propanol</td>
<td>i-C₃OH</td>
<td>Fluka-59309</td>
<td>99.5</td>
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<td>2-butanol</td>
<td>s-C₄OH</td>
<td>Fluka-19440</td>
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<td>Merck-9630</td>
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<td>Baker-8254</td>
<td>99.5</td>
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<td>methyl - n-butyl - ether</td>
<td>C₄-O-nC₄</td>
<td>Fluka-20250</td>
<td>99</td>
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### TABLE 5.2

*Chemicals used and some of their thermodynamic properties.*

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<th>Compound Name</th>
<th>Tb / K</th>
<th>Tc /K</th>
<th>Pc / MPa</th>
<th>ω</th>
</tr>
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<td>293.0</td>
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<tr>
<td>perfluoropropane</td>
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<td>0.325</td>
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<tr>
<td>perfluorobutane</td>
<td>271.2</td>
<td>386.4</td>
<td>2.32</td>
<td>0.374</td>
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<tr>
<td>n-octane</td>
<td>398.8</td>
<td>568.8</td>
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<td>0.398</td>
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<tr>
<td>n-nonane</td>
<td>424.0</td>
<td>594.9</td>
<td>2.29</td>
<td>0.445</td>
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</table>
### TABLE 5.2 (continued)

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Tb / K</th>
<th>Tc /K</th>
<th>Pc / MPa</th>
<th>ω</th>
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All the liquids were thoroughly degassed during the filling procedure of the capillary tube. Methanol was stored overnight prior to the filling over dried molecular sieves in order to remove traces of captured water. A further purification procedure was proved to be necessary for perfluorobutane. From preliminary measurements of its vapour-pressure curve it appeared that it contained more-volatile impurities, presumably air and possibly semi-fluorinated compounds. Additional analysis with Gas Chromatography - Mass Spectrometry suggested the same. Therefore perfluorobutane prior to its filling into the capillary tube was successively
cooled down with liquid nitrogen and degassed under high vacuum. The procedure was continued until no sign of volatile components was detected by a sensitive vacuum-meter. In this way a vapour-pressure curve close to the experimental data of Brown and Mears (1958) was obtained. Only the critical temperature was underestimated by about 0.7 K, which is rather large.

Symbols

1 more-volatile component
2 less-volatile component
$L_2L_1V$ liquid-liquid-vapour
$L_1$ liquid phase richer in the more-volatile component
$L_2$ liquid phase richer in the less-volatile component
$P_c$ critical pressure
$T_b$ temperature of normal boiling point
$T_c$ critical temperature
$V$ vapour phase
$\omega$ acentric factor

References


6. EXPERIMENTAL RESULTS FOR THE SYSTEMS \( \text{C}_3\text{F}_8 + \text{ALKANES} \)

In the family of binary and quasi-binary systems of perfluoropropane with alkanes a transition from type II, via type IV, towards type III fluid phase behaviour may occur for various combinations of alkanes. A tricritical point and a double critical endpoint bound the intermediate type IV zone. The effect of branching of the alkane is studied when the above transition is experimentally verified for quasi-binary systems of perfluoropropane with 2,2,4-trimethyl-hexane and n-nonane.

The binary and quasi-binary systems of perfluoropropane with n-alkanes having a carbon number from 8.7 to 14 exhibit type III phase behaviour. These systems show also barotropic inversion phenomena which are systematically measured and phenomenologically explained.

An attempt for an empirical characterization of the effect of the shape of a molecule on the phase behaviour of its systems with other components will be described in Chapter 10.

6.1 Introduction

In the pioneering classification scheme of van Konynenburg and Scott (1980) described in Chapter 2, the transition mechanism between types II and III of fluid phase behaviour was examined by means of the van der Waals equation of state. As was also pointed out later by Deiters and Pegg (1989), who used for their calculations the Redlich-Kwong equation of state, this transition is performed either directly or via one of the intermediate types IV or IV* of fluid phase behaviour. The transition via type IV has been experimentally verified in various families like that of carbon dioxide with n-alkanes (Hottovy et al., 1981), or that of carbon dioxide with n-alkanols (Lam et al., 1990). De Loos et al. (1993a) used the quasi-binary approximation suggested by Creek et al. (1981) for the family of carbon dioxide with n-alkanes. This permitted to approach very close the tricritical point (TCP) and the double critical endpoint (DCEP) behaviour. The crossing of the locus of TCP's with the one of DCEP's in Fig.2.12 as well as the existence of the zone of type IV* behaviour after the crossing point, are pure predictions from the equations of state. There is no experimental evidence up to date of a system showing type IV* phase behaviour. The type IV* fluid phase diagram is similar to the one of type IV, but it is characterized by a different connectivity of the various branches of the critical curves (Fig.2.13). At the point of intersection of the loci of TCP's and DCEP's a very interesting type of fluid phase behaviour is produced where a
binary or a quasi-binary system possesses a three-phase $L_2L_1V$ equilibrium curve extending up to the $L=V$ critical curve where it ends in a tricritical point (Fig. 2.16). Meijer (1989) suggested the name van Laar point for this type of tricritical point since van Laar had discovered that the van der Waals equation of state for a binary system can be solved analytically at the DCEP using the geometric mean rule for $a_{12}$. The van Laar point behaviour is up to date never found experimentally. A part of our investigation concerning the feasibility of this behaviour in real systems will be presented in a subsequent chapter.

Creek et al. (1981) used the quasi-binary approximation to investigate the TCP behaviour in systems of methane with alkanes. From this work two points become evident:

The first is the significant influence of the shape of the alkane on the behaviour of the system. n-Hexane gives type IV phase behaviour with methane, as 2,3-dimethyl-butane also does, however the binary system of methane and n-hexane is closer to a DCEP behaviour while the system methane and 2,3-dimethyl-butane is closer to a TCP behaviour. In addition the binary system of methane and 2,2-dimethyl-butane exhibits type II fluid phase behaviour. If we consider the direction of increased immiscibility to be from type II towards type III fluid phase behaviour, then we can conclude that the more spherical the alkane molecule is, the better is its mutual miscibility with methane.

The second point of interest is that by appropriate mixing of two alkanes a kind of experimental interpolation can be achieved where the quasi-binary (in reality ternary) system simulates a hypothetical binary system of methane with a pseudo-alkane having the same properties as the combination of the two real alkanes mixed together. The limits of this approximation are mainly determined by the dissimilarity of the two original alkanes which are mixed together to produce the desired pseudo-component. As it will be explained in the experimental part a test whether the quasi-binary approximation holds or not is necessary if reliable data are required. It is worthwhile to mention that the experimental interpolation can be achieved with different combinations of two pure alkanes. For example an equimolar mixture of n-pentane and n-nonane corresponds to a pseudo-n-heptane and the same holds for an equimolar mixture of n-hexane and n-octane. However the resulting quasi-binary systems with methane are not equivalent and according to experimental investigation they also differ from the binary system of methane and n-heptane.

Barotropic inversion phenomena in type III systems are encountered by de Loos et al. (1989). Along the three-phase $L_2L_1V$ equilibrium curve of the binary system of tetrafluoromethane and n-butane and just before the upper critical endpoint (UCEP) an
inversion of the density of the two liquid phases was found. The same inversion takes place for higher temperatures and pressures in the domain of liquid-liquid equilibria (vapour has disappeared). These inversion points form a curve (almost a straight line) which ends on the binodal border which separates the two-phase region from the region of one fluid phase. In Fig 6.2 similar phenomena are depicted for the binary system of perfluoropropane (C₃F₈) with n-nonane (see below).

Fig 6.1. Fluid phase equilibria for the binary system: [(1-x) C₃F₈ + x 2,2,4-trimethyl-hexane]. Solid curve: saturation curve of C₃F₈, long-dashed curve : L=V critical line (regression), dotted-dashed curve: three-phase L₂L₁V equilibrium line, short-dashed curve: liquid-vapour binodal for x=0.2459, dotted curve: liquid-vapour binodal for x=0.1375, empty circle: L=V critical points, up solid triangle: UCEP [L₂=L₁V].
Fig. 6.2. Fluid phase equilibria for the binary system: [(1-x) $C_3F_8 + x n-C_6$]. Solid curve: saturation curve of $C_3F_8$, dotted-dashed curve: three-phase $L_2L_1V$ equilibrium line, dotted curve: liquid-liquid binodal for $x=0.1999$, dashed curve: liquid-liquid barotropic inversion line for $x=0.1999$, empty circle: critical point of pure $C_3F_8$, up empty triangle: UCEP [$L_2-L_1-V$], empty diamond: $L_2L_1V$ BIP, empty square: crossing point of the liquid-liquid barotropic inversion line and the liquid-liquid binodal.

The measurements were carried out in capillary glass tubes sealed at one end, according to the synthetic method (de Loos et al., 1986). With this so-called Cailletet apparatus isopleths (constant composition P,T cross sections) can be constructed (see Chapter 5). Achieved accuracies are: $\Delta x=0.001$, $\Delta T=0.01$ K and $\Delta P=0.003$ MPa.
Experimental results for the systems $C_3F_8 +$ alkanes

The method of measurement is the visual observation of the disappearance or appearance of a phase when the pressure is varied at constant temperature. In this way binodals, three-phase equilibrium curves $L_2L_1V$, critical points and CEP's are determined. For a critical point or a CEP the meniscus between the two phases which become critical has to disappear in the middle of them. The barotropic phenomena are affected by the interfacial tensions between the two liquids and between each liquid and the vapour which is rather dense at the conditions where the density inversion occurs. This makes it difficult to determine the exact location of the barotropic inversion point (BIP) along the three-phase $L_2L_1V$ equilibrium curve (see below).

From previous work in our laboratory (de Loos et al., 1993b), it was concluded that the quasi-binary family of $C_3F_8$ with n-alkanes exhibits a transition scheme similar to that of Fig.2.17.b. Quasi-binary systems of $C_3F_8$ with mixtures of n-octane and n-nonane were studied in order to locate precisely the position of the TCP and the DCEP. Extrapolating the experimental data according to the classical theory (see below) the TCP was estimated to be at a carbon number of 8.425. Assuming also a quadratic asymptotic approach to the DCEP (see below) the carbon number for the DCEP was approximated to be 8.47.

In an attempt to approach a TCP or a DCEP in a real binary system, it seems logical to select a single alkane with similar properties as a pseudo-n-alkane with carbon number 8.425 or 8.47 respectively. To find exactly the TCP or DCEP behaviour in a binary system is a matter of pure chance. The same holds for a binary system with a van Laar point behaviour. The criteria for the selection of the proper single alkane to replace the pseudo-n-alkane are not straightforward because similar pure component properties do not guarantee as well a similar phase behaviour of the binary systems. 2,2,4-trimethyl-hexane was used. This alkane has a critical temperature and pressure which can be compared with the corresponding critical properties of a pseudo-n-alkane composed of 55 mol % n-octane and 45 mol % n-nonane. The carbon number 8.45 was chosen between the carbon numbers for the TCP and the DCEP.

6.2 Experimental results

In Table 6.1 the experimental data of the three-phase equilibrium curves $L_2L_1V$ for the binary systems of $C_3F_8$ with 2,2,4-trimethyl-hexane, with n-nonane and with 2-methyl-octane are given. The binary system of $C_3F_8$ and 2,2,4-trimethyl-hexane exhibits fluid phase behaviour of type II (see Fig.6.1).
### TABLE 6.1

Three-phase \( L_2 L_1 V \) equilibria in binary systems of perfluoropropane \( (C_3F_8) \) with 2,2,4-trimethyl-hexane \( (A) \), with n-nonane \( (B) \) and with 2-methyl-octane \( (C) \)

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\( ^a \) UCEP \( [L_2 = L_1 - V] \), \( ^b \) \( L_2 L_1 V \) BIP, \( ^c \) UCEP \( [L_2 - L_1 = V] \).

The experimentally measured three-phase \( L_2 L_1 V \) equilibrium curve ends in an UCEP where the two coexisting liquid phases become critical and are in equilibrium with the vapour phase \( [L_2 = L_1 - V] \). From the UCEP a \( L_2 = L_1 \) critical curve originates and moves towards higher pressures (not measured in this work and not shown in Fig.6.1). Two, also experimentally determined, vapour-liquid binodals which show a \( L = V \) critical point are included in Fig.6.1. The data points of these binodals are given in Table 6.2.
Experimental results for the systems C₅F₈ + alkanes

**TABLE 6.2**

Two-phase L+V binodal borders for binary mixtures of perfluoropropane + 2,2,4-trimethylhexane (a: x = 0.2459, b: x = 0.1375); L₂+L₁ binodal border (c) and L₂+L₁, barotropic inversion line (d) for the binary mixture perfluoropropane + n-nonane (x = 0.1999)

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$^a$ L=V critical point

The binary system of C$_3$F$_8$ and n-nonane exhibits fluid phase behaviour of type III. As can be seen from the P,T projection in Fig.6.2 the three-phase L$_2$L$_1$V equilibrium curve ends at an UCEP where the vapour and the liquid L$_1$ phases become critical and are in equilibrium with the other liquid phase L$_2$ [L$_2$-L$_1$=V]. The UCEP is connected with a L$_1$=V critical curve with the critical point of pure C$_3$F$_8$ (not measured in this work and not shown in Fig.6.2). On
the three-phase \( L_2 L_1 V \) equilibrium curve a density inversion of the two liquid phases occurs at the so-called liquid-liquid-vapour barotropic inversion point (\( L_2 L_1 V \) BIP).

![Diagram showing the T-x and T-p projection of the three-phase L-L-V equilibrium for a type III system. At the right side the relative positions of the three phases V, L₁, L₂ inside the measuring glass tube are depicted. Up empty triangle: UCEP [L₂-L₁=V], empty diamond: L₂L₁V BIP.]

In Fig.6.3 the T-x projection of the L₂L₁V equilibrium curve of a system with type III fluid phase behaviour and barotropic inversion phenomena is drawn schematically. This is the type of behaviour that was found for the system \( C_3 F_8 + n \)-nonane. As it will be discussed below, the denser liquid phase is not always the liquid phase richer in the less-volatile pure component (L₂).

\( C_3 F_8 \) has a critical volume of 300 cm³/mol and a molecular weight of 188 g/mol resulting in a critical density of 0.63 g/cm³. At lower temperatures saturated liquid \( C_3 F_8 \) has even higher densities. For instance at 293 K its density is 1.35 g/cm³, while for \( n \)-nonane at the same temperature the density is 0.72 g/cm³. Therefore it can happen that the liquid phase L₁ which is richer in the more-volatile component, \( C_3 F_8 \), is also the denser liquid phase. If instead of
Chapter 6

C₃F₈, propane is considered, then the situation changes. Propane has a critical volume of 203 cm³/mol (2/3 of that of C₂F₆) but a molecular weight of 44 g/mol (less than 1/4 of that of C₃F₈). This results in a critical density of 0.22 g/cm³ (1/3 of that of C₃F₈). Even at lower temperatures the density of saturated liquid propane is not larger than the critical density of C₃F₈. For instance at 231 K liquid propane has a density of 0.58 g/cm³. It seems that the chances for barotropic phenomena in the family of systems of propane and n-alkanes is small and indeed no experimental evidence was found. The reasoning given above is of course a rough approximation because pure component properties do not necessarily reflect the behaviour of the binary system. The densities of the binary liquid phase are of course composition dependent. In spite of that, the above logic can serve as a first indication of barotropic behaviour.

Returning to Fig.6.3, we see in the T,ρ (temperature, density) plot that as the temperature rises, the density of L₁ decreases and moves towards the density of the vapour phase. Finally at the UCEP the two phases, L₁ and V, become critical and all their properties including the density are identical. At the same time the density of L₂, which was smaller than that of L₁ and higher than that of V at low temperatures, changes in such a way that it remains always higher than the density of the L₁=V critical phase at the UCEP. This leads to the geometrical necessity of the existence of a crossing point for the two liquid branches, L₁ and L₂, in terms of density. At the temperature where this crossing point occurs the two liquid phases have the same density. Their relative position in the measuring tube changes passing this point along the L₂-L₁ curve as a consequence of gravitational forces.

In addition to gravitational forces also surface tension forces are exerted on the two liquids and these are not necessarily equal. This makes the observation of the BIP difficult, in that sense that close to the BIP when the two liquids are fully dispersed after stopping the stirring mechanism, it is hard to decide if L₁ or L₂ is the more dense phase. The two liquid phases are stabilized in rather peculiar shapes and forms. The L₁ phase, which before the BIP is at the bottom of the mixture, gradually joins the meniscus between the L₂ and V phases and via a bottleneck through the L₂ phase slowly goes up as the temperature raises. At the same time the L₂ phase is expelled to the walls of the glass tube from where it glissades down. In this way the inversion seems to start before the real BIP temperature and the full inversion seems to be established after the real BIP temperature. The criterion for the exact location of the BIP temperature is the movement of the droplets of the L₂ phase created inside the L₁ phase when the mixture is vigorously agitated and before the two liquid phases are fully separated. If the
Experimental results for the systems C₃F₈ + alkanes 141

droplets move towards the V phase before they rest and collapse then the temperature is before the BIP temperature, but if the droplets precipitate towards the mercury surface then the temperature is after the BIP temperature.

Returning to the P,T projection of Fig.6.2 we see that from the BIP a L₂-L₁ barotropic inversion curve originates which is the locus of the L₂-L₁ barotropic inversion points for higher temperatures. Since the density is a function of both temperature and pressure, the two liquid phases in the L₁+L₂ region may also have equal densities at a temperature above the BIP temperature, but at higher values of pressure. At these conditions the vapour phase is not present. The L₂-L₁ barotropic inversion curve, which is almost a straight line, is positioned above the three-phase L₁L₂V equilibrium curve and has a larger slope than that. At the left side of this curve the L₁ phase is denser than the L₂ phase while at its right side the opposite is true. The L₂-L₁ barotropic inversion curve ends on the L₂-L₁ binodal curve for this specific mixture composition. Data for the L₂-L₁ barotropic inversion curve and the L₂-L₁ binodal curve of Fig.6.2 are included in Table 6.2. The binodal curve separates the homogeneous one-fluid region (at higher pressures) from the L₁+L₂ two-phase region (at lower pressures). For other mixture compositions the L₂-L₁ barotropic inversion curve has a different slope in the P,T projection but always starts in the L₂L₁V BIP.

The binary system of C₃F₈ and 2-methyl-octane exhibits fluid phase behaviour of type II but the three-phase L₁L₂V equilibrium curve ends at an UCEP much higher in temperature than that of the binary system of C₃F₈ and 2,2,4-trimethyl-hexane. Combining the three binary systems: C₃F₈ with n-nonane, C₃F₈ with 2-methyl-octane and C₃F₈ with 2,2,4-trimethyl-hexane into a common P,T projection (Fig.6.4) we end up again with the conclusion mentioned in the introduction, that the more spherical the molecule of the less-volatile component is, the better its mutual miscibility is with the more-volatile component.

The binary system of C₃F₈ and n-heptane is also of type II with an UCEP temperature at 303.2 K (Hicks et al., 1978). The UCEP temperature of the binary system of C₃F₈ and 2,2,4-trimethyl-hexane is 302.0 K. So, the selection of 2,2,4-trimethyl-hexane as a pseudo-n-alkane of carbon number 8.45 resulted in a pseudo-n-alkane of carbon number around 7. If we assume that 2,2,4-trimethyl-hexane behaves like n-heptane we need a mixture of 2,2,4-trimethyl-hexane and n-nonane with 72.5% n-nonane in order to get the intermediate fluid phase behaviour of type IV at a carbon number around 8.45 (if of course a linear mixing of properties with respect to carbon number is assumed). In practice the percentage of n-nonane
must extend from 67.5% till 70.2% as will be discussed below, so the assumption that 2,2,4-trimethyl-hexane behaves like n-heptane in its mixtures with C₃F₈ is rather good.

Fig 6.4. L₂L₁V equilibria for binary systems of C₃F₈ with isomeric alkanes of carbon number 9. Solid curve: saturation curve of C₃F₈, long-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system of C₃F₈ and n-nonane, short-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system of C₃F₈ and 2-methyl-octane, dotted-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system of C₃F₈ and 2,2,4-trimethyl-hexane, empty circle: critical point of C₃F₈, up solid triangles: UCEP's [L₂−L₁−V], up empty triangle: UCEP [L₂−L₁−V], empty diamond: L₂L₁V BIP.

A series of measurements in quasi-binary systems of C₃F₈ and [ (1−z) 2,2,4-trimethyl-hexane + (z) n-nonane ] was performed in order to get a more detailed picture of the transition from type II, via type IV, towards type III fluid phase behaviour with increasing z; z is the mole fraction of n-nonane in the mixture of 2,2,4-trimethyl-hexane and n-nonane. The data points of the three-phase L₂L₁V equilibrium curves are given in Table 6.3. In the P,T projection of Fig 6.5 some selected systems are plotted. One can notice the approach of the
three-phase L\(_2\)-L\(_1\)-V equilibrium curves towards the pure C\(_3\)F\(_8\) saturation curve with increasing z.

![Graph](image)

Fig. 6.5. L\(_2\)-L\(_1\)-V curves of binary and quasi-binary systems of \{(1-x) C\(_3\)F\(_8\) + x \{(1-z) 2,2,4-trimethyl-hexane + z n-C\(_n\)\}}. Solid curve: saturation curve of C\(_3\)F\(_8\), long-dashed curve: three-phase L\(_2\)-L\(_1\)-V equilibrium curve of the binary mixture with z=1 (type III), short-dashed curve: three-phase L\(_2\)-L\(_1\)-V equilibrium curve of the quasi-binary mixture with z=0.700 (type IV), dotted-curve: three-phase L\(_2\)-L\(_1\)-V equilibrium curve of the quasi-binary mixture with z=0.502 (type II), dotted-dashed curve: three-phase L\(_2\)-L\(_1\)-V equilibrium curve of the binary mixture with z=0 (type II), empty circle: critical point of C\(_3\)F\(_8\), up solid triangles: UCEP's \([L_2=L_1-V]\), down solid triangle: LCEP \([L_2=L_1-V]\), up empty triangles: UCEP's \([L_2-L_1]=V\), empty diamond: L\(_2\)-L\(_1\)-V BIP.

In an attempt to investigate the shape of the locus of the L\(_2\)-L\(_1\)-V BIP's in a T,z plot several binary and quasi-binary systems of C\(_3\)F\(_8\) and n-alkanes or pseudo-n-alkanes were measured. The data points of the three-phase L\(_2\)-L\(_1\)-V equilibrium curve for various values of carbon number n, are presented in Table 6.4. In the P,T projection of Fig.6.6 the three-phase L\(_2\)-L\(_1\)-V equilibrium curves for these systems are depicted.
### TABLE 6.3

Three-phase $L_2L_1V$ equilibria in quasibinary systems of perfluoropropane with the pseudo-alkanes of the type $(1-z)$ 2,2,4-trimethyl-hexane + $(z)$ n-nonane

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<td>T/K</td>
<td>P/MPa</td>
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$^a$ Indicates supersaturation; $^b$ Indicates supersaturation; $^c$ Indicates supersaturation.
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| T/K       | P/MPa  |
| 372.64    | 3.479  |

<sup>a</sup> UCEP [L<sub>2</sub>=L<sub>1</sub>-V],  <sup>b</sup> LCEP [L<sub>2</sub>=L<sub>1</sub>-V],  <sup>c</sup> UCEP [L<sub>2</sub>-L<sub>1</sub>-V],  <sup>d</sup> L<sub>2</sub>L<sub>1</sub>V BIP.
### TABLE 6.4

Three-phase $L_LV$ equilibria in binary and quasi-binary systems of perfluoropropane with $n$-alkanes or pseudo-$n$-alkanes of carbon number $n$

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$^a$ UCEP [$L_2=L_1-V$], $^b$ $L_2L_1V$ BIP.
Fig. 6.6. $L_2 L_1 V$ curves of binary and quasi-binary systems of $[C_3 F_8 + n$-alkane or pseudo-$n$-alkane of carbon number $n]$ Solid curve: saturation curve of $C_3 F_8$, long-dashed curve: three-phase $L_2 L_1 V$ equilibrium curve for $n=14$, medium-dashed curve: $L_2 L_1 V$ for $n=12$, short-dashed curve: $L_2 L_1 V$ for $n=11$, tiny-dashed curve: $L_2 L_1 V$ for $n=10$, dotted curve: $L_2 L_1 V$ for $n=9.5$, dotted-dashed curve: $L_2 L_1 V$ for $n=9$, triple-dotted - dashed curve: $L_2 L_1 V$ for $n=8.7$, empty circle: critical point of $C_3 F_8$, up empty triangles: UCEP's $[L_2 L_1 = V]$, empty diamonds: $L_2 L_1 V$ BIP's.

It can be seen that with increasing carbon number both the UCEP $[L_2 - L_1 = V]$ and the $L_2 L_1 V$ BIP move towards the critical point of pure $C_3 F_8$. The same conclusion can be drawn from Fig. 6.7 where the temperatures of UCEP's and $L_2 L_1 V$ BIP's are plotted against the carbon number, $n$. From this plot we can notice that the distance between UCEP and BIP is diminishing as the carbon number is increasing.
Fig. 6.7. CEP's of $L_2L_1V$ curves of binary and quasi-binary systems of $[C_3F_8 + n$-alkane or pseudo-$n$-alkane of carbon number $n]$. Solid curve: critical point of $C_3F_8$, up empty triangles: UCEP's [$L_2L_1=V$], empty diamonds: $L_2L_1V$ BIP's.

6.3 Discussion

In Fig. 6.8.a the CEP's and two $L_2L_1V$ BIP's of the system $C_3F_8 + [(1-z) 2,2,4$-trimethylhexane + (z) n-nonane] are plotted as a function of $z$. Fig. 6.8.b is an enlargement of Fig. 6.8.a around the region of the transition from type II, via type IV, towards type III fluid phase behaviour. The crosses represent the three CEP's of a quasi-binary system with $z=0.6906$. In this experiment it was attempted to check the influence of the purity of the components on the mixture behaviour. We used a different bottle of n-nonane of the same stated purity (>98%), but from another production batch. The three CEP's moved to the left of the main graph to a distance of $\Delta z$(impurities)$\approx 0.005$. The same occurred with another quasi-binary system which is not plotted here. This can be understood if one bottle of n-nonane had a purity of 98% and the other of 98.7% or if both contained the same overall impurities but with a different distribution with respect to their chemical nature.
Fig. 6.8.a. CEP's of $L_2L_1V$ curves of binary and quasi-binary systems of \{C$_3$F$_8$ + [(1-z) 2,2,4-trimethyl-hexane + z n-nonane]\}. Up solid triangles: UCEP's [$L_2$-$L_1$-$V$], down solid triangles: LCEP's [$L_2$-$L_1$-$V$], up empty triangles: UCEP's [$L_2$-$L_1$-$V$], empty diamonds: $L_2L_1V$ BIP's.

Fig. 6.8.b. Enlargement of Fig. 6.8.a near the transition zone of type IV. For explanation of symbols see Fig. 6.8.a. Also: cross: quasi-binary system for z=0.6906.
It must be noticed here, that the preparation of the pseudo-component \([(1-z) \ 2,2,4\text{-trimethyl-hexane} + (z) \ n\text{-nonane}]\) involves a weighing technique which can result in an error of \(\Delta z (\text{weighing}) \approx 0.001\). This number includes also the possibility of gradual evaporation during the weighing and filling stages of the two constituents of the pseudo-component. However the error \(\Delta z (\text{impurities})\) seems to be systematic when one should expect \(\Delta z (\text{weighing})\) to be random (at least the pure weighing error), so \(\Delta z (\text{impurities})\) can mainly be attributed to impurities.

According to the classical theory for tricritical points of Creek et al. (1981) the "width" of the upper part of the three phase region in a type IV system, as measured by the difference \(\Delta T_{ul}\) or by the difference \(\Delta P_{ul}\) scales as \(\Delta z^{3/2}\). \(\Delta T_{ul} = T_{UCEP} - T_{LCEP}\), \(\Delta P_{ul} = P_{UCEP} - P_{LCEP}\) and \(\Delta z = z - z_{TCP}\). Here the UCEP is of the type \([L_2 - L_1 = V]\) and \(z\) is the mole fraction of \(n\text{-nonane}\) in the pseudo-component \([(1-z) \ 2,2,4\text{-trimethyl-hexane} + (z) \ n\text{-nonane}]\).

The classical theory suggests also that the difference \(\Delta T_m\) between the "average" temperature of the upper branch of the three-phase equilibrium curve \(T_m\) and the temperature of the tricritical point \(T_{TCP}\) scales as \(\Delta z\). The same holds for the corresponding pressures. \(\Delta T_m = T_m - T_{TCP}\) and \(T_m = (T_{UCEP} + T_{LCEP})/2\).

If \(\Delta T_{ul}\) scales as \(\Delta z^{3/2}\) and \(\Delta T_m\) scales as \(\Delta z\), then it is concluded that \(\Delta T_{ul}^{2/3}\) scales as \(\Delta T_m\). But \(T_{TCP}\) is constant, so \(\Delta T_{ul}^{2/3}\) scales as \(T_m\). This relationship is depicted in Fig.6.9.a. One can see that avoiding the use of the variable \(z\) and using instead its proportional variable \(T_m\), also the deviating system with \(z = 0.6906\) in Fig.6.8.b is at a correct position in Fig.6.9.a. From Fig.6.9.a it can be easily estimated that the TCP, which by definition corresponds to \(\Delta T_{ul}^{2/3} = 0\), is located at a temperature of 378.2 K.

In Fig.6.9.b the pairs \((T_m, z)\) for all the quasi-binary systems are plotted. The symbols have the same meaning as in Fig.6.9.a. Although a linear relationship was expected according to the classical theory, a rather curved shape is suggested by the points. However the number of experimental points is too small to draw any conclusion and in addition the points cover the whole range from the TCP to the DCEP, while the classical theory applies only to the asymptotic behaviour in the vicinity of the TCP. Finally it can be noticed that the use of the parameter \(z\) brings the deviating system of Fig.6.8.b in a wrong position with respect to the other points in the plot in Fig.6.9.b. From Fig.6.9.b and for the tricritical temperature of 378.2 K we can estimate a value of \(z\) for the TCP around 0.675.
Figs. 6.9.a (up) and 6.9.b (down). Asymptotic behaviour near the TCP according to the classical theory. Cross: quasi-binary system for $z=0.6906$, solid line: regression straight line for the experimental points, dashed line: regression parabolic curve for the experimental points.
Figs. 6.10.a (up) and 6.10.b (down). Asymptotic approach to the DCEP (for details see text).
Experimental results for the systems $C_8F_8 +$ alkanes

For the asymptotic behaviour close to the DCEP there is no theoretical treatment analogous to the classical theory which applies close to the TCP. However the shape of the curve in Fig.6.8.b suggests a quadratic relationship. In other words, it can be assumed that the "width" of the gap between the two branches of the three-phase $L_2L_1V$ equilibrium curve in a type IV system, as measured by the difference $\Delta T_{LU}$ or by the difference $\Delta P_{LU}$ scales as $\Delta z^{1/2}$. $\Delta T_{LU} = T_{LCEP} - T_{UCEP}$, $\Delta P_{LU} = P_{LCEP} - P_{UCEP}$ and $\Delta z = z_{DCEP} - z$. Here the UCEP is of the type $[L_2 = L_1 - V]$.

From the above it is concluded that $\Delta T_{LU}^2$ scales as $z$. This assumption is tested in Fig.6.10.a. The deviating system of Fig.6.8.b is again because of the use of $z$ in a wrong position with respect to the other data points. In Fig.6.10.b a parabola of the type: $z = c_1T^2 + c_2T + c_3$ where $c_1$, $c_2$, $c_3$ are fitted parameters, is passed through the experimental points (solid curve). A parabola is the simplest analytic function with a quadratic approach to its maximum. As can be seen from Fig.6.10.b the real shape of the experimental points is more skewed than that of the symmetric parabola. This results in a maximum of the parabola (symbolized by the empty square) at the left of the experimental DCEP. If instead of the parabola a cubic regression polynomial is used (dashed curve) the skewness is represented in a better way (here the empty circle, the maximum of the regression curve, corresponds to the DCEP).

From Figs.6.8.a and 6.8.b it is concluded that the DCEP is found at a temperature around 370 K and a $z$ value around 0.702. This results in a difference in temperature between the TCP and the DCEP of around 8 K. If this difference was zero then we would have a van Laar point behaviour. It is also important to notice that the type IV intermediate fluid phase behaviour extends in a range of $z$ values with $\Delta z$ (IV type) = 0.025, just five times the estimated error due to impurities ( $\Delta z$ (impurities) = 0.005 ). This gives a good idea about the experimental difficulties in order to obtain more reliable data.

An interesting question is where the locus of $L_2L_1V$ BIP's in Fig.6.8.a finishes towards the direction of the DCEP. In all type III systems measured there was always a $L_2L_1V$ BIP. In contrast, in none of the type IV systems such a phenomenon was observed, neither at the lower nor at the upper branch of the three-phase $L_2L_1V$ equilibrium curve. In addition, in the type IV systems the two liquid phases of the upper branch of the $L_2L_1V$ equilibrium curve are positioned inside the glass tube from top to bottom as $L_1$, $L_2$ so $L_2$ is the denser liquid phase, and the two liquid phases of the lower branch of the $L_2L_1V$ equilibrium curve are positioned inside the glass tube from top to bottom as $L_2$, $L_1$ so $L_1$ is the denser liquid phase (see Fig.6.3). Therefore if a $L_2L_1V$ BIP exists for these systems of type IV, then it should be
located somewhere in the gap between the two branches of the three-phase $L_2L_1V$ equilibrium curve. But when the lower branch of the three-phase $L_2L_1V$ equilibrium curve ends in the UCEP [$L_2=L_1-V$] the two liquids are critical so their densities are also the same. In addition when the upper branch of the three-phase $L_2L_1V$ equilibrium curve starts at the LCEP [$L_2=L_1-V$] the two liquids are again critical and their densities are also the same. Therefore the $L_2L_1V$ BIP could have trivially been considered as identical with either the UCEP [$L_2=L_1-V$] or the LCEP [$L_2=L_1-V$]. All the above lead to the suggestion that the $L_2L_1V$ BIP locus may finish at the DCEP but this cannot be proven experimentally because the criticality of the two liquid phases hinders the observation of the possible barotropic phenomena.

It was shown experimentally that the binary system of $C_3F_8$ and 2,2,4-trimethyl-hexane had a similar immiscibility region as the binary system of $C_3F_8$ and n-heptane. This suggested the idea of characterizing 2,2,4-trimethyl-hexane as an alkane with an "effective" carbon number $n_{\text{eff}}$ equal to 7. However, based on the pure component critical properties, 2,2,4-trimethyl-hexane was selected to have an $n_{\text{eff}}$ around 8.45. Unambiguously the pure component critical properties that were used as a criterion do not reflect properly the shape effect. Looking at the normal boiling point as an alternative criterion we also get large deviations. The normal boiling point of 2,2,4-trimethyl-hexane (399.7 K) suggests an $n_{\text{eff}}$ around 8 (n-octane has a normal boiling point of 398.8 K). From the above it seems that the vapour-liquid properties of the pure less-volatile component are not adequate to be used as independent variables in a correlation providing an $n_{\text{eff}}$ for that component, in a way that the $n_{\text{eff}}$ will characterize the binary $L_2L_1V$ behaviour of the same component. An alternative approach for solving this problem will be discussed in Chapter 10. It is based on a topological index which characterizes the molecular shape.

Symbols

1 more-volatile component
2 less-volatile component
BIP liquid-liquid-vapour barotropic inversion point
CEP critical endpoint
$\rho$ mass density
DCEP double critical endpoint
$L_1$ liquid phase richer in component 1
Experimental results for the systems $C_3F_8 +$ alkanes

$L_2$ liquid phase richer in component 2
$L_2L,V$ liquid-liquid-vapour equilibrium
LCEP lower critical endpoint
$n$ actual carbon number
$n_{eff}$ effective carbon number
$P$ pressure
$T$ temperature
TCP tricritical point
UCEP upper critical endpoint
$x$ mole fraction of component 2 in the mixture
$V$ vapour phase
$z$ mole fraction of the less-volatile constituent of the pseudo-component

References


Loos, Th.W. de, Poot, W. and Swaan Arons, J. de, 1993a. Transition from type II to type IV fluid phase behaviour in the family of CO₂ + (n-C₁₂ + n-C₁₃). To be submitted to Fluid Phase Equilibria.

Loos, Th.W. de, Poot, W. and Swaan Arons, J. de, 1993b. Transition from type II to type III (via type IV) fluid phase behaviour in the family of C₃F₈ + (n-C₈ + n-C₉). To be submitted to Fluid Phase Equilibria.


7. EXPERIMENTAL RESULTS FOR THE SYSTEMS $C_4F_{10} + n$-ALKANES

In the family of binary and quasi-binary systems of perfluorobutane with $n$-alkanes or pseudo-$n$-alkanes a transition from type II, via type IV, towards type III fluid phase behaviour occurs for carbon numbers between 10.647 and 10.673. A tricritical point and a double critical endpoint bound the intermediate type IV zone.

7.1 Introduction

In the context of this thesis three types of binary fluid-phase equilibria are of special interest. Using the terminology of van Konynenburg and Scott (1980) they are named type II, type III and type IV (see Chapter 2). These types are experimentally well known and a typical example of a sequence of binary systems which systematically change from type II to type III via a type IV phase behaviour is the family of carbon dioxide and $n$-alkanes (Hottovy et al., 1981). The system of carbon dioxide + n-dodecane exhibits type II fluid phase behaviour, while the system of carbon dioxide + n-tridecane belongs to type IV and the system of carbon dioxide + n-tetradecane exhibits type III fluid phase behaviour. It is relevant to notice that the transition from type II, via type IV, towards type III phase behaviour occurs as the size of the less-volatile component is increased. Between types II and IV the transition occurs via a so called tricritical point (TCP) and between types IV and III the transition occurs via a double critical endpoint (DCEP). More details on these two special points can be found in Chapters 2 and 6.

The types of fluid phase behaviour mentioned above were predicted by means of the van der Waals equation of state (van Konynenburg and Scott, 1980) and later with more quantitative success on the basis of the Redlich-Kwong equation of state (Deiters and Pegg, 1989). Different other equations of state have been tried since then, but they do not really give a different qualitative pattern for the transition II$\leftrightarrow$IV$\leftrightarrow$III. A common feature of all these theoretical predictions is the existence of type IV* fluid-phase behaviour (see Fig.2.13). This type offers the possibility of the transition II$\leftrightarrow$IV*$\leftrightarrow$III. Type IV* is similar to type IV but the connectivity of the various branches of the critical curve and the nature of the critical endpoints (CEP's) differs.

In Fig.2.12, in a $\lambda$, $\zeta$ plot of binary systems (van Konynenburg and Scott, 1980), with constant relative size $\xi$ of the molecules, the locus of the TCP systems and the locus of the
DCEP systems are drawn. According to the theoretical predictions these two curves cross, creating the additional intermediate zone of type IV* fluid phase behaviour and offering the possibility of a direct transition from type II to type III via the phase behaviour represented by a so-called van Laar point (the crossing point of the TCP and DCEP curves). The name van Laar point was suggested by Meijer (1989) for this type of system, because van Laar had discovered that the van der Waals equation of state for a binary system can be solved analytically at the DCEP if the geometric mean rule for $a_{12}$ is used. For the hypothetical van Laar point system the three-phase $L_2L_1V$ equilibrium curve continues up to the vapour-liquid critical curve where it terminates in a point which is simultaneously a TCP and a DCEP. From this van Laar point a liquid-liquid critical curve evolves tangentially and is directed towards higher pressures. Neither type IV* behaviour nor a van Laar point is ever experimentally verified.

Creek et al. (1981) used the quasi-binary approximation to investigate the TCP in systems of methane with alkanes (see Chapter 6). In Fig.2.17.b the transition pattern II↔IV↔III in terms of temperatures of the CEP's is depicted as a function of the carbon number $n$ of the less-volatile component. The distance between the TCP and the DCEP either in terms of carbon number or temperature defines the extent of the intermediate type IV zone behaviour. This distance should be zero for the hypothetical transition via a van Laar point. In Chapter 10 the extent of the intermediate type IV zone behaviour is examined with respect to the nature of the more-volatile component in families of binary systems.

### 7.2 Experimental results

The measurements were carried out in capillary glass tubes sealed at one end, according to the synthetic method (de Loos et al., 1986). With this so-called Cailletet apparatus isopleths (constant composition $P,T$ cross sections) can be constructed (see Chapter 5). Achieved accuracies are: $\Delta x=0.001$, $\Delta T=0.01$ K and $\Delta P=0.003$ MPa.

The data for the experimental three-phase $L_2L_1V$ equilibrium curves of the binary systems $\text{C}_4\text{F}_{10} + \text{n-nonane}$, $\text{C}_4\text{F}_{10} + \text{n-decane}$, $\text{C}_4\text{F}_{10} + \text{n-undecane}$ and $\text{C}_4\text{F}_{10} + \text{n-dodecane}$ are given in Table 7.1. The corresponding plots are collected in Fig.7.1.

The binary systems of $\text{C}_4\text{F}_{10} + \text{n-nonane}$ and $\text{C}_4\text{F}_{10} + \text{n-decane}$ exhibit fluid phase behaviour of type II. Their three-phase $L_2L_1V$ equilibrium curves end in UCEP's where the two coexisting liquid phases become critical and are in equilibrium with a vapour phase.
Therefore these UCEPs are of the type \([L_2=L_1-V]\). Compared with data of Hicks et al. (1978) the UCEP of the binary system \(C_4F_{10} + n\)-nonane is found at 0.2 K higher temperature (348.2 K instead of 348.0 K) and the UCEP of the binary system of \(C_4F_{10} + n\)-decane is found at 3 K lower temperature (374.7 K instead of 377.7 K). In particular the last difference is quite large. The \(L_2=L_1\) critical curves originating in the UCEP's and moving towards higher pressures with an almost vertical slope were not measured in this work. The critical points of the two pure components of both binary systems are connected with a continuous vapour-liquid critical curve, which also is not measured in this work.

Fig. 7.1. Binary systems of \([C_4F_{10} + n\text{-alkanes}]\). Solid curve: saturation curve of \(C_4F_{10}\), long-dashed curve: three-phase \(L_2L_1V\) equilibrium curve for the binary system \(C_4F_{10} + n\)-nonane, short-dashed curve: three-phase \(L_2L_1V\) equilibrium curve for the binary system \(C_4F_{10}\) and \(n\)-decane, dotted-dashed curve: three-phase \(L_2L_1V\) equilibrium curve for the binary system \(C_4F_{10} + n\)-undecane, dotted curve: three-phase \(L_2L_1V\) equilibrium curve for the binary system \(C_4F_{10} + n\)-dodecane, empty circle: critical point of \(C_4F_{10}\), up solid triangles: UCEP's \([L_2=L_1-V]\), up empty triangles: UCEP's \([L_2-L_1-V]\), empty diamonds: \(L_2L_1V\) BIP's.
TABLE 7.1
Three-phase L₂L₁V equilibrium curves in the binary systems of perfluorobutane and n-alkanes of carbon number n

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* UCEP [L₂=L₁-V],  b LLV BIP,  c UCEP [L₂-L₁=V]

The binary systems of C₄F₁₀ + n-undecane and C₄F₁₀ + n-dodecane exhibit fluid phase behaviour of type III. Their three-phase L₂L₁V equilibrium curves end in UCEP's with a different nature than the UCEP's of type II. Here the vapour phase becomes critical with the less-dense liquid phase and both of them are in equilibrium with the denser liquid phase, [L₂-L₁-V]. In both systems the UCEP [L₂-L₁=V] is connected by a vapour-liquid critical curve with the critical point of C₄F₁₀ (these critical curves are not measured in this work). From the critical point of the less-volatile component, in this case the n-alkane, a vapour-liquid critical
Experimental results for the systems $C_4F_{10} + n$-alkanes

curve originates and moves to lower temperatures passing successively through a pressure maximum and a pressure minimum. This critical curve changes its character from vapour-liquid to liquid-liquid criticality and goes towards higher pressures with an almost vertical slope. This curve was not also measured in this work for both systems.

The two binary systems of type III fluid phase behaviour exhibit also barotropic inversion phenomena. Thus along the three-phase $L_2L_1V$ equilibrium curve and at a temperature lower than that of the UCEP [$L_2L_1=V$] the two liquid phases have equal density at the so called $L_2L_1V$ barotropic inversion point (BIP). At temperatures lower than the temperature of BIP the liquid phase with the lower mole fraction of the less-volatile component, $L_1$, has a higher density than the liquid phase with the higher mole fraction of the less-volatile component, $L_2$.

For temperatures above the BIP this situation is reversed. As a consequence of gravitational forces, the above phenomenon causes a change in the position of the two liquid phases in the measuring tube when the temperature changes around the BIP. A more detailed discussion about the barotropic inversion phenomena is given in Chapter 6. Here we mention only that a possible explanation for these phenomena is found in the relatively high density of $C_4F_{10}$. This results in the possibility, that the liquid phase richer in $C_4F_{10}$, $L_1$, is also the denser liquid phase in the low temperature range of the three-phase $L_2L_1V$ equilibrium curve. The critical density of $C_4F_{10}$ is 0.63 g/cm$^3$, while at 293 K it has a saturated liquid density of 1.52 g/cm$^3$ (Reid et al., 1988). The n-undecane on the other hand has a saturated liquid density of 0.74 g/cm$^3$ at 293 K.

The transition from type II to type III fluid phase behaviour was studied using the quasi-binary approximation with mixtures of n-decane and n-undecane as a pseudo-less-volatile component. This yields continuous carbon numbers between 10 and 11 for the pseudo-less-volatile component. Using these pseudo-n-alkanes characterized as $[(1-z)\text{ n-decane} + z \text{ n-undecane}]$ with a carbon number $n=10+z$, the intermediate type IV fluid phase behaviour can be located. In Table 7.2 the three-phase $L_2L_1V$ equilibrium curve data points for the quasi-binary systems measured in this work are presented. In Fig 7.2 the three-phase $L_2L_1V$ equilibrium curves of some selected quasi-binary systems are plotted together with the vapour-pressure curve of $C_4F_{10}$. The system with $z=0.5003$ shows type II phase behaviour, the system with $z=0.6699$ shows type IV phase behaviour and the system with $z=0.7519$ shows type III phase behaviour. When the carbon number of the less-volatile component increases the three-phase $L_2L_1V$ equilibrium curve approaches more and more the vapour-pressure curve of the more-volatile component.
TABLE 7.2

Three-phase $L_2L,V$ equilibrium curves in the quasi-binary systems of perfluorobutane + pseudo-n-alkanes of type \([(1-z) \text{ n-decane } + z \text{ n-undecane}]$. The pseudo-n-alkanes have a carbon number $n$ ($n=10+z$).

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<sup>a</sup> UCEP [L<sub>2</sub>=L<sub>1</sub>-V]<br><sup>b</sup> LCEP [L<sub>2</sub>=L<sub>1</sub>-V]<br><sup>c</sup> UCEP [L<sub>2</sub>-L<sub>1</sub>=V]<br><sup>d</sup> L<sub>2</sub>L<sub>1</sub>V BIP
Fig. 7.2. Quasi-binary systems of \{C₄F₁₀ + [(1-z) n-decane + z n-undecane]\}. Solid curve: saturation curve of C₄F₁₀, long-dashed curve: three-phase L₃L₁V equilibrium curve for the quasi-binary system of z=0.5003 (type II), short-dashed curve: three-phase L₂L₁V equilibrium curve for the quasi-binary system of z=0.6699 (type IV), dotted curve: three-phase L₂L₁V equilibrium curve for the quasi-binary system of z=0.7519 (type III), empty circle: critical point of C₄F₁₀, up solid triangles: UCEP's [L₂=L₁-V], down solid triangle: LCEP [L₂=L₁-V], up empty triangles: UCEP's [L₂-L₁-V], empty diamond: L₂L₁V BIP.

In Fig.7.3.a the CEP's and BIP's of the binary and quasi-binary systems investigated are plotted as a function of the carbon number of the less-volatile component. Fig.7.3.b is an enlargement of Fig.7.3.a around the intermediate zone of type IV phase behaviour. The position of the TCP is established at the meeting point of the UCEP [L₂-L₁-V] curve and the LCEP [L₂=L₁-V] curve. The position of the DCEP is located at the point where the UCEP [L₂=L₁-V] curve and the LCEP [L₂=L₁-V] curve merge. As it was mentioned in Chapter 6 the locus of the L₂L₁V BIP's (dotted curve in Fig.7.3.b) seems to terminate in the CEP [L₂=L₁-V] loci close to the DCEP. We speculated in that Chapter that the above curve ends exactly at the DCEP, although our speculation was not based on real experimental evidence.
Fig. 7.3.a. Binary and quasi-binary systems of \( \{C_4F_{10} + [(1-z) n-decane + z n-undecane]\} \). Up solid triangles: UCEP's \([L_2=L_1=V] \), down solid triangles: LCEP's \([L_2=L_1=V] \), up empty triangles: UCEP's \([L_2-L_1=V]\), empty diamonds: \(L_2L_1V\) BIP's.

Fig. 7.3.b. Enlargement of Fig. 7.3.a near the transition zone of type IV phase behaviour. For explanation of symbols see Fig. 7.3.a.
7.3. Discussion

As is shown in Chapters 2 and 6 according to the classical theory for tricritical points of Creek et al. (1981) the "width" of the upper part of the three phase region in a type IV system, as measured by the difference $\Delta T_{UL}$ or by the difference $\Delta P_{UL}$ scales as $\Delta n^{3/2}$. $\Delta T_{UL} = T_{UCEP} - T_{LCEP}$, $\Delta P_{UL} = P_{UCEP} - P_{LCEP}$ and $\Delta n = n - n_{TCP}$. The classical theory suggests also that the difference $\Delta T_m$ between the "average" temperature of the upper branch of the three-phase equilibrium curve $T_m$ and the temperature of the tricritical point $T_{TCP}$ scales as $\Delta n$. The same holds for the corresponding pressures. $\Delta T_m = T_m - T_{TCP}$ and $T_m = (T_{UCEP} + T_{LCEP})/2$. If $\Delta T_{UL}$ scales as $\Delta n^{3/2}$ and $\Delta T_m$ scales as $\Delta n$, then it is concluded that $\Delta T_{UL}^{2/3}$ scales as $\Delta T_m$. But $T_{TCP}$ is constant, so $\Delta T_{UL}^{2/3}$ scales as $T_m$.

This relationship is depicted in Fig. 7.4.a. Indeed the data can be represented within the experimental uncertainty by a straight line (solid line), although a better representation of the data is achieved by a second order polynomial curve (dotted curve). The data points in the whole transition region, from the TCP until the DCEP, were used. However the classical exponent of $2/3$ is obtained from a series expansion around the TCP and it is in principle only valid in the vicinity of the TCP. Using the linear relationship in Fig. 7.4.a it can easily be estimated that the TCP, which by definition corresponds to $(T_{U} - T_{L})^{2/3} = 0$, is located at a temperature $T_{TCP}/k = 420.80 \pm 0.52$ (95% confidence interval).

In Fig. 7.4.b the relationship of $T_m$ versus $n$ is plotted. The carbon number $n$ is linearly dependent on the $z$ parameter, $n = 10 + z$. The error bars for $n$ correspond with $\Delta n = \pm 0.003$. This error can be attributed to the weighing procedure of the constituents of the pseudo-less-volatile component and to the higher extend of evaporation of the more-volatile constituent of the pseudo-component in the period between the preparation of the pseudo-component and the filling of the Cailletet tube. The linear relationship holds within the experimental uncertainty. Extrapolating the straight line to the temperature of the TCP we find for the TCP a carbon number $n_{TCP} = 10.647 \pm 0.007$ (95% confidence interval).

For the asymptotic behaviour close to the DCEP there is no theoretical treatment analogous to the classical theory which applies close to the TCP. However the shape of the $[L_2 - L_1 - V]$ CEP curve in Fig. 7.3.b suggests a quadratic relationship. In other words, it can be assumed that the "width" of the gap between the two branches of the three-phase $L_2 - L_1 - V$ equilibrium curve in a type IV system, as measured by the difference $\Delta T_{UL}$ scales as $\Delta n^{1/2}$. $\Delta T_{UL} = T_{LCEP} - T_{UCEP}$, $\Delta P_{LU} = P_{LCEP} - P_{UCEP}$ and $\Delta n = n_{DCEP} - n$. Here the UCEP' is of the type $[L_2 - L_1 - V]$. 
Figs. 7.4.a (up) and 7.4.b (down). Asymptotic behaviour near the TCP according to the classical theory (for details see text).
Fig. 7.5.a. Asymptotic approach to the DCEP (for details see text).

Fig. 7.5.b. Asymptotic approach to the DCEP. The solid line is a fitted parabola. Up solid triangles: UCEP's \(L_2=L_1-V\), down solid triangles: LCEP's \(L_2=L_1-V\), empty square: DCEP (maximum of the parabola).
From the above it follows that $\Delta T_{LU}$ may scale as $n$ (see also Chapter 6). In Fig. 7.5.a this relationship is depicted. The fitted straight line has a regression coefficient $R^2 = 0.986$. For $\Delta T_{LU} = 0$ we get $n_{DCEP} = 10.673 \pm 0.004$ (95% confidence interval). In Fig. 7.5.b a parabola of the type $n = c_1 T^2 + c_2 T + c_3$ is fitted to the experimental $[L_2-L_1-V]$ CEP's (solid triangles). The maximum in $n$ (empty square) corresponds to the DCEP and it is located at $T_{DCEP}/K = 413.6$ and $n_{DCEP} = 10.673$.

Comparing the coordinates of the estimated TCP and DCEP we conclude that they differ in temperature by $\Delta T_{TCP-DCEP}/K = 7.2$ and in carbon number by $\Delta n_{DCEP-TCP} = 0.026$. These differences characterize the extend of the type IV phase behaviour region. If they were zero then we should have a van Laar point phase behaviour. It is worthwhile to notice that the uncertainty for $n_{TCP}$ is $\Delta n_{TCP} = \pm 0.007$, which is about 1/4 of the width of the type IV phase behaviour region and the uncertainty for $n_{DCEP}$ is $\Delta n_{DCEP} = \pm 0.004$, which is about 1/6 of the width of the type IV phase behaviour region. This stresses how difficult it is to obtain reliable experimental information in such narrow zones of carbon number.

Symbols

1  more-volatile component
2  less-volatile component
$a_{12}$  binary interaction parameter in the equation of state
BIP  barotropic inversion point
CEP  critical endpoint
DCEP  double critical endpoint
$L_2L_1V$  liquid-liquid-vapour equilibrium
LCEP  lower critical endpoint
$n$  carbon number
$P$  pressure
$T$  temperature
TCP  tricritical point
UCEP  upper critical endpoint
$x$  mole fraction of component 2
$z$  mole fraction of the less-volatile constituent of the pseudo-component
References


Loos, Th.W. de, Poot, W. and Swaan Arons, J. de, 1993b. The family of perfluoroethane + \( \text{n-alkanes} \). To be submitted to Fluid Phase Equilibria.

Loos, Th.W. de, Poot, W. and Swaan Arons, J. de, 1993c. The family of perfluoropropane + \( \text{n-alkanes} \). To be submitted to Fluid Phase Equilibria.

Loos, Th.W. de, Poot, W. and Swaan Arons, J. de, 1993d. The family of 1,1,1-trifluoro-ethane + \( \text{n-alkanes} \). To be submitted to Fluid Phase Equilibria.


8. EXPERIMENTAL RESULTS FOR THE SYSTEMS
\( C_2F_6 \) or \( C_3F_8 \) or \( C_4F_{10} \) + ETHERS or ALKANOLS

In the families of binary systems of perfluoropropane or perfluorobutane + n-alkanes a transition from type II, via type IV, towards type III fluid phase behaviour occurs. No such transition is observed for the families of binary systems of perfluoroethane or perfluoropropane or perfluorobutane + n-alkanols. The above transition however is identified in the family of binary systems of perfluoroethane + ethers.

The influence on the binary system fluid phase behaviour of the size of the more-volatile component (perfluoroalkane), the relative polarity of the less-volatile component (alkanols, ethers), the competition between the relative size and the polarity of the less-volatile component (n-alkanol) and the combined effect of polarity and shape of the less-volatile component (isomer propanols, isomer butanols) is systematically investigated.

8.1 Introduction

In Chapters 6 and 7 the results of an investigation on the fluid phase behaviour of the families of perfluoropropane + alkanes and perfluorobutane + n-alkanes were reported. In both cases a transition from type II, via type IV, towards type III fluid phase behaviour (II\( \leftrightarrow \)IV\( \leftrightarrow \)III) was observed.

The transition pattern II\( \leftrightarrow \)IV\( \leftrightarrow \)III is described in Fig. 2.17.b, where the temperatures of the critical endpoints (CEP’s) of the three-phase \( L_2L_1V \) equilibrium curves for the various systems of a family exhibiting the transition scheme II\( \leftrightarrow \)IV\( \leftrightarrow \)III are plotted as a function of the carbon number of the less-volatile component. In this family a sequence of binary systems is considered with a fixed more-volatile component and a systematically varied less-volatile component. The carbon number of the less-volatile component is a meaningful variable when the less-volatile components belong to a homologous series with a variable linear-chain length like the series of n-alkanes or n-alkanols. In other cases like the series of branched alkanes (see Chapters 6 and 10) an effective carbon number is defined.

In the region of systems with type II fluid phase behaviour the three-phase \( L_2L_1V \) equilibrium curve extends to progressively higher temperatures as the size of the less-volatile component is increased. At the border between types II and IV a system with a tricritical point (TCP) behaviour occurs. At this point the three-phase \( L_2L_1V \) equilibrium curve consists
of two branches. The upper branch has degenerated into a point, the TCP. As the size of the less-volatile component increases further we enter the region of type IV systems where the two branches of the three-phase L2L1V equilibrium curve are continuously modified. The lower branch extends to higher temperatures, while the upper one shifts to lower temperatures. In the upper branch the two critical endpoints move with a different speed towards lower temperatures. The LCEP \([L_2=L_1-V]\) moves faster than the UCEP \([L_2-L_1=V]\). Therefore the upper branch of the three-phase \(L_2L_1V\) equilibrium curve expands in size. At the border between types IV and III a system with a double critical endpoint (DCEP) occurs. The LCEP \([L_2=L_1-V]\) of the upper branch coincides with the UCEP \([L_2=L_1-V]\) of the lower branch and the three-phase \(L_2L_1V\) equilibrium curve becomes one single curve. In the region of systems exhibiting type III phase behaviour, the three-phase \(L_2L_1V\) equilibrium curve shrinks progressively and the UCEP \([L_2-L_1=V]\) approaches asymptotically the critical temperature of the more-volatile component as the size of the less-volatile component is increased. Although the three-phase \(L_2L_1V\) equilibrium curve shrinks with increasing size of the less-volatile component the \(L_2+L_1\) immiscibility zone expands to a larger temperature range. Therefore the mutual miscibility of the two components becomes worse. This remark, which will become useful below, is explained by means of the Figs. 2.2, 2.3 and 2.4. For a type II binary system the \(L_2+L_1\) immiscibility zone terminates along the \(L_2=L_1\) critical curve. The same holds for the lower temperature \(L_2+L_1\) immiscibility zone of a type IV system. The type IV system possesses an additional \(L_2+L_1\) immiscibility region above the upper branch of the three-phase \(L_2L_1V\) equilibrium curve. This region terminates along the \(L_2=L_1\) part of the critical curve originating from the critical point of the less-volatile component and finishing in the LCEP \([L_2=L_1-V]\). For a type III system the \(L_2+L_1\) immiscibility zone finishes along the \(L_2=L_1\) part of the critical curve originating from the critical point of the less-volatile component. As the carbon number of the less-volatile component of a type III binary system increases this \(L_2=L_1\) critical curve shifts towards higher temperatures and the same does the \(L_2+L_1\) immiscibility zone.

The subject of the present work is to investigate if the transition II\(\leftrightarrow\)IV\(\leftrightarrow\)III occurs also in the families of binary systems of perfluoroalkanes + polar compounds. According to the work of Goh et al. (1987) and Estrera and Luks (1987) a TCP behaviour is observed for systems of ethane + \(n\)-alkanes at a carbon number of the \(n\)-alkane around 17.6 (quasi-binary approximation). However for systems of the same more-volatile component (ethane) + \(n\)-alkanols a TCP fails to occur whatever the carbon number of the \(n\)-alkanol. This is because
the reduction in size of the less-volatile component is anticipated by an increase of its polarity (Lam et al., 1990).

It is also interesting to see what the effect is of the relative polarity of the less-volatile component on the binary system fluid phase behaviour and for that purpose ethers and alkanols are compared in mixtures with perfluoroethane. In addition the combined influence of the polarity and the shape of the alkanol molecule is examined in mixtures of isomer propanols or butanols with perfluoropropane. Finally the effect of the size of the more-volatile component on the behaviour of the binary system is investigated in systems of different perfluoroalkanes with the same alkanol.

8.2 Experimental results and discussion

The measurements were carried out according to the synthetic method in capillary glass tubes sealed at one end (de Loos et al., 1986), as described in Chapter 5. Achieved accuracies are: \( \Delta x=0.001 \), \( \Delta T=0.01 \) K and \( \Delta P=0.003 \) MPa.

First the results for the binary systems of \( \text{C}_2\text{F}_6 + \) polar compounds are presented. The experimentally measured three-phase \( \text{L}_2\text{L}_1\text{V} \) equilibrium curves for the binary systems of \( \text{C}_2\text{F}_6 + \) ethers and \( \text{C}_2\text{F}_6 + \) n-alkanols are given in Table 8.1.

In Fig.8.1 the measurements for the binary systems of \( \text{C}_2\text{F}_6 + \text{C}_2\text{-O-C}_2 \) and \( \text{C}_2\text{F}_6 + \text{C}_1\text{-O-C}_4 \) are depicted in a \( P,T \) projection. The binary system \( \text{C}_2\text{F}_6 + \text{C}_2\text{-O-C}_2 \) shows type II fluid phase behaviour and its three-phase \( \text{L}_2\text{L}_1\text{V} \) equilibrium curve terminates at an UCEP [\( L_2=L_1=V \)], while the system \( \text{C}_2\text{F}_6 + \text{C}_1\text{-O-C}_4 \) behaves as a type III system and its three-phase \( \text{L}_2\text{L}_1\text{V} \) equilibrium curve terminates at an UCEP [\( L_2=L_1=V \)] after a liquid-liquid-vapour barotropic inversion point (\( L_2L_1V \) BIP). The appearance of barotropic inversion phenomena was discussed in previous Chapters where it was attributed to the high density of perfluoroalkanes. It should be possible to observe the transition pattern \( \text{II} \leftrightarrow \text{IV} \leftrightarrow \text{III} \) between the binary system \( \text{C}_2\text{F}_6 + \text{C}_2\text{-O-C}_2 \) and the binary system \( \text{C}_2\text{F}_6 + \text{C}_1\text{-O-C}_4 \) with proper mixing of the two ethers (quasi-binary approximation). It was not attempted to prove this experimentally, because of the difficulties encountered when a pseudo-component is made from two very volatile components. It must be noticed here that the two ethers \( \text{C}_2\text{-O-C}_2 \) and \( \text{C}_1\text{-O-C}_4 \) which have carbon numbers 4 and 5, respectively, are not the only ethers with these carbon numbers as is the case in the homologous series of n-alkanes. There are more isomeric ethers with the same carbon numbers.
### TABLE 8.1

Three-phase $L_2L_1V$ equilibrium curves in binary systems of perfluorooctane + alkanols and perfluorooctane + ethers.

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$^a$ L$_2$L$_1$V BIP, $^b$ UCEP [L$_2$-L$_1$=V], $^c$ UCEP [L$_2$-L$_1$-V].
Fig. 8.1. Binary systems of \( \text{C}_2\text{F}_6 + \) ethers. Solid curve: saturation curve of \( \text{C}_2\text{F}_6 \), dashed curve: liquid-vapour critical curve of the binary system \( \text{C}_2\text{F}_6 + \text{C}_2\text{O-C}_2 \) (regression), dotted-dashed curve: three-phase \( L_2L_1V \) equilibrium curve of the binary system \( \text{C}_2\text{F}_6 + \text{C}_2\text{O-C}_2 \), dotted curve: liquid-vapour binodal line of the binary mixture \( \text{C}_2\text{F}_6 + \text{C}_2\text{O-C}_2 \) \( (x=0.2235) \), triple dotted-dashed curve: three-phase \( L_2L_1V \) equilibrium curve of the binary system \( \text{C}_2\text{F}_6 + \text{C}_1\text{-O-C}_2 \), empty circle: critical point of \( \text{C}_2\text{F}_6 \) and liquid-vapour critical point of the binary system \( \text{C}_2\text{F}_6 + \text{C}_2\text{O-C}_2 \) \( (x=0.2235) \), up solid triangle: UCEP \( [L_2=L_1=V] \), up empty triangle: UCEP \( [L_2=L_1=V] \), empty diamond: \( L_2L_1V \) BIP.

In the family of binary systems of \( \text{C}_2\text{F}_6 + n \)-alkanols no transition between different types of fluid phase behaviour occurs. The phase behaviour is always that of type III with an UCEP \( [L_2=L_1=V] \) and a \( L_2L_1V \) BIP (see Figs. 8.2.a and 8.2.b).

While \( \text{C}_2\text{F}_6 \) and an ether with carbon number 4 (\( \text{C}_2\text{-O-C}_2 \)) shows type II fluid phase behaviour, \( \text{C}_2\text{F}_6 \) and an alkanol with carbon number 4 (\( \text{C}_4\text{OH} \)) shows type III fluid phase behaviour. From de Loos et al. (1993) we see that \( \text{C}_2\text{F}_6 \) and a \( n \)-alkane with carbon number 5 (\( n \)-pentane) shows type II fluid phase behaviour, while Fig. 8.2.a shows that \( \text{C}_2\text{F}_6 \) and an ether with carbon number 5 (\( \text{C}_5\text{-O-C}_4 \)) has a type III fluid phase behaviour.
Figs. 8.2.a (up) and 8.2.b (down). UCEP's \( [L_2-L_1=V] \) and \( L_2L_1V \) BIP's for several binary systems of \( C_2F_6 + \text{alkanols} \) against the carbon number \( n \) of the alkanol. Dashed line: critical point of pure \( C_2F_6 \), up empty triangles: UCEP's \( [L_2-L_1=V] \) for binary systems with \( n \)-alkanols, up solid triangle: UCEP \( [L_2-L_1=V] \) for the binary system with 2-propanol, empty diamonds: \( L_2L_1V \) BIP's for binary systems with \( n \)-alkanols, solid diamond: \( L_2L_1V \) BIP for the binary system with 2-propanol.
### TABLE 8.2

Three-phase $L_2L_1V$ equilibrium curves in binary systems of perfluoropropane + alkanols.

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$^a$ $L_2L_1V$ BIP, $^b$ UCEP [$L_2$-$L_1$=$V$].
 Experimental results for the systems $C_2F_6$ or $C_3F_8$ or $C_4F_{10}$ + ethers or alkanols

As the sequence of increased polarity is alkanes $\rightarrow$ ethers $\rightarrow$ alkanols we can draw the following conclusion for a less-volatile component with a fixed carbon number (size): The more polar the less-volatile component is, the worse is its mutual miscibility with the same more-volatile component. In other words as the less-volatile component becomes more polar, in its binary system behaviour with the same more-volatile component type III fluid phase behaviour is more and more favoured above type II fluid phase behaviour.

In Figs. 8.2.a and 8.2.b, where the UCEP's $[L_2-L_1=V]$ and $L_2L_1V$ BIP's for the binary systems of $C_2F_6 +$ alkanols are depicted against the carbon number of the alkanol, we may notice the influence of the shape of the alkanol molecule on the immiscibility behaviour of the binary system. The more spherical the molecule of the polar less-volatile component is (2-propanol instead of 1-propanol), the better its mutual miscibility with the more-volatile component of the binary system becomes. The three-phase $L_2L_1V$ equilibrium curve of the binary system of $C_2F_6 + 2$-propanol extends to higher temperatures than the three-phase $L_2L_1V$ equilibrium curve of the binary system of $C_2F_6 + 1$-propanol. Although the three-phase $L_2L_1V$ equilibrium curve of the binary system of $C_2F_6 + 2$-propanol is longer, the region of the $L_2+L_1$ immiscibility for the same system is shorter according to the remark made in the introductory section of this Chapter. Therefore the more spherical the alkanol is, the closer to type II phase behaviour is the behaviour of its binary system with $C_2F_6$.

This is exactly the same as what was found in families with alkanes as less-volatile components. In Chapter 6 the systems perfluoropropane + isomeric nonanes were discussed and Creek et al. (1981) investigated the systems methane + isomeric hexanes. In these systems it was also found that the more spherical the alkan is, the better is the mutual miscibility of the two components in the binary mixture. In other words if an alkan molecule is more spherical then its "effective" size is reduced and consequently the behaviour of the binary system is shifted in the direction III$\rightarrow$II. If an alkanol molecule is more spherical, then in addition to the reduction of its "effective" size, probably also its hydroxyl-group becomes less active. As the molecule becomes more spherical, the carbon atom of the hydroxyl-group (C-atom in the -C-OH group), is progressively connected with other carbon atoms (groups -CH$_3$, -CH$_2$, -CH) instead of hydrogen atoms (-H). Therefore the acidity/polarity of the hydroxyl-group decreases. It has to be clarified here that the acidity/polarity property mentioned as a characteristic property for the alkanol molecules is not a property correlated quantitatively with the dipole moment of those alkanols.
Fig. 8.3. Binary systems of $C_3F_8$ + isomer butanols. Solid curve: saturation curve of $C_3F_8$, short-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + C_4OH$, dashed-curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + i-C_4OH$, dotted curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + s-C_4OH$, dotted-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + t-C_4OH$, empty circle: critical point of $C_3F_8$, up empty triangles: UCEP's $[L_2-L_1-V]$, empty diamonds: $L_2L_1V$ BIP's.

For the isomer butanols (see below) the dipole moments are practically the same independently of the branching geometry of the molecule (1.7-1.8 Debye). Therefore saying that the polarity/acidity probably decreases or that the hydroxyl-group probably becomes less active due to the branching of the molecule, we mean the change in the polarity/acidity property which characterizes the miscibility of the polar molecule in a mixture with another component and nothing else. As we noticed above the more polar the less-volatile component is, the worse becomes its mutual miscibility in binary systems with the same more-volatile component, so also we may say that the less spherical the polar less-volatile component is, the worse becomes its mutual miscibility in binary systems with the same more-volatile component.
Experimental results for the systems $C_3F_8$ or $C_3F_8$ or $C_4F_{10}$ + ethers or alkanols

The last argument is also supported by the experimental results for the binary systems of $C_3F_8$ and isomeric propanols or isomeric butanols. The data of the three-phase $L_2L_1V$ equilibrium curves for binary systems of $C_3F_8$ + alkanols are given in Table 8.2. From this table we see that in the binary system $C_3F_8 + 2$-propanol the temperatures and pressures of both the UCEP and $L_2L_1V$ BIP are higher than for the binary system of $C_3F_8 + 1$-propanol, as was observed for the corresponding systems with $C_2F_6$.

Also from Table 8.2 it can be seen that the sequence of increasing temperatures and pressures of both UCEP's and $L_2L_1V$ BIP's for the binary systems of $C_3F_8$ + isomer butanols correspond with the sequence of isomeric butanols: $C_4OH \rightarrow i-C_4OH \rightarrow s-C_4OH \rightarrow t-C_4OH$. The above reinforces the previous conclusion that the more spherical the polar less-volatile component is, the better becomes its mutual miscibility in binary systems with the same more-volatile component (always in the sense that better miscibility means closer to type II behaviour and further away from type III behaviour). In Fig.8.3 the measurements for the three-phase $L_2L_1V$ equilibrium curves for the binary systems of $C_3F_8$ + isomer butanols are plotted. Geometrically the branches of $i-C_4OH$ and $s-C_4OH$ are similar but in $s-C_4OH$ the hydroxyl-group is less acid/polar, because its carbon atom (the C-atom of the group -C-OH) is connected with 2 C-atoms (groups -CH₃ and -CH₂) while in $i-C_4OH$ the C-atom of the group -C-OH is connected with 1 C-atom (group -CH). We may notice that the sequence of normal boiling points for the above alkanols is reversed compared with the sequence of increasing temperatures and pressures of both UCEP's and $L_2L_1V$ BIP's of the corresponding binary systems with $C_3F_8$: $C_4OH$ ($T_b=390.9$ K), $i-C_4OH$ ($T_b=381.0$ K), $s-C_4OH$ ($T_b=372.7$ K), $t-C_4OH$ ($T_b=355.5$ K) (Reid et al., 1988). The normal boiling point is a property strongly dependent on the position of the hydroxyl-group and the geometry of the molecule. More specifically for equal size molecules the more polar compound has the higher normal boiling point. In Table 8.3 the sequence of acidity/polarity for isomeric propanols and isomeric butanols according to the connectivity of the C-atom of the C-OH group is summarized.

Fig.8.4 depicts the measurements for the three-phase $L_2L_1V$ equilibrium curves for some of the binary systems of $C_3F_8 + n$-alkanols. From the position of the three-phase $L_2L_1V$ equilibrium curves we can see that for relatively large carbon numbers (4 to 8) with increasing carbon number the three-phase $L_2L_1V$ equilibrium curves approach closer to the saturation curve of the more-volatile component ($C_3F_8$). Also the UCEP $[L_2-L_1=V]$ moves asymptotically with increasing carbon number towards the critical point of the more-volatile component.
Fig. 8.4. Binary systems of $C_3F_8 + n$-alkanols. Solid curve: saturation curve of $C_3F_8$, short-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + C_1OH$, triple dotted-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + C_2OH$, dotted curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + C_3OH$, long-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system $C_3F_8 + C_4OH$, dotted-dashed curve: three-phase $L_2L_1V$ equilibrium curve of the binary system of $C_3F_8 + C_5OH$, empty circle: critical point of $C_3F_8$, up empty triangles: UCEP's $[L_2-L_1=V]$, empty diamonds: $L_2L_1V$ BIP's.

This behaviour was already noticed in the families of binary systems of perfluoroalkanes + $n$-alkanes where with decreasing carbon number the transition pattern III $\rightarrow$ IV $\rightarrow$ II occurred. Here with decreasing carbon number no transition is observed. More specifically for the range of relatively small carbon numbers (smaller than 4) with decreasing carbon number the three-phase $L_2L_1V$ equilibrium curves again approach the saturation curve of the more-volatile component and eventually pass to the other side above of this curve (for $C_3F_8 + C_2OH$ and $C_3F_8 + C_1OH$ systems).
Experimental results for the systems $\text{C}_2\text{F}_6$ or $\text{C}_3\text{F}_8$ or $\text{C}_4\text{F}_{16} + \text{ethers or alkanols}$ 183

**TABLE 8.3**

*Acidity/Polarity sequence for isomeric propanols and isomeric butanols*

**PROPANOLS**

1-propanol

$T_b=370.3$ K

C*-atom connected with 1 C-atom

(group -CH$_2$

2-propanol

$T_b=355.4$ K

C*-atom connected with 2 C-atoms

(2 groups -CH$_3$

**BUTANOLS**

1-butanol / n-butanol

$T_b=390.9$ K

C*-atom connected with 1 C-atom

(group -CH$_3$

2-methyl-1-propanol / isobutanol

$T_b=381.0$ K

C*-atom connected with 1 C-atom

(group -CH which is branched
<table>
<thead>
<tr>
<th>Compound</th>
<th>Tb (K)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanol / sec-butanol</td>
<td>372.7</td>
<td><img src="image" alt="Structure of 2-butanol" /></td>
</tr>
<tr>
<td>2-methyl-2-propanol / tert-butanol</td>
<td>355.5</td>
<td><img src="image" alt="Structure of 2-methyl-2-propanol" /></td>
</tr>
</tbody>
</table>

C$_3$F$_8$ + C$_2$OH and C$_3$F$_8$ + C$_4$OH systems are likely to belong to the class of type III systems with heteroazeotropy, i.e. type III-HA according to van Konynenburg and Scott (1980). In case of heteroazeotropy the three-phase L$_2$L$_1$V equilibrium pressure is above the saturation pressures of both pure components and this is an indication of the dissimilarity and incompatibility of the two species. Also the vapour phase composition is in between the compositions of the two liquid phases L$_2$ and L$_1$, another example of the fact that the phase containing the more of the less-volatile component is not necessarily the denser one (see also barotropy).

Another case where the three-phase L$_2$L$_1$V equilibrium pressure can be above the saturation pressures of both pure components is the case of a type III system with azeotropy (III-A). In Fig.8.5 schematic isothermal P,x plots for the case of a three-phase L$_2$L$_1$V equilibrium with heteroazeotropy and for the case of a three-phase L$_2$L$_1$V equilibrium with azeotropy are given.

The decrease in mutual miscibility of the two components of the binary system when the size of the polar less-volatile component decreases is quite natural. When the alkanol molecule becomes shorter, it becomes also more polar in a rather fast way. The amount of hydrogen bonds due to the presence of the -OH groups is fairly increased as the relative
concentration of them in the solution rises and as the alkanol molecule becomes smaller and the -OH group becomes more exposed (see Chapter 4).

**Fig. 8.5.** Schematic isothermal P,x plots showing a three-phase \( L_2L_1V \) equilibrium combined with heteroazeotropy (a), or azeotropy (b). Dotted-dashed curve: three-phase \( L_2L_1V \) equilibrium, solid curves: binodal curves.

Consequently in the homologous series of n-alkanols there is a competition between size and polarity when the carbon number is increased or decreased. When the size is reduced the polarity is increased and vice versa. This explains why the transition II\( \rightarrow \)IV\( \rightarrow \)III in perfluoroalkane + n-alkanol families does not appear at all. If this transition requires a rather small size of a n-alkanol then the polarity of that n-alkanol is already large enough to prevent the transition. Further decrease of the size has apparently no effect, on the contrary it increases additionally the polarity and brings the binary system behaviour further away from the transition border.

The above is clearly illustrated in Figs. 8.6.a and 8.6.b where the temperatures (or pressures) of the UCEP's and \( L_2L_1V \) BIP's of the binary systems of \( C_4F_8 + n \)-alkanols are plotted against the carbon number \( n \) of the n-alkanol.
### TABLE 8.4

*Three-phase L₂L₃V equilibrium curves in binary systems of perfluorobutane + alkanols.*

<table>
<thead>
<tr>
<th></th>
<th>C₁OH</th>
<th></th>
<th>C₂OH</th>
<th></th>
<th>C₃OH</th>
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<tr>
<td><strong>T/K</strong></td>
<td><strong>P/MPa</strong></td>
<td><strong>T/K</strong></td>
<td><strong>P/MPa</strong></td>
<td><strong>T/K</strong></td>
<td><strong>P/MPa</strong></td>
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<td>313.04</td>
<td>0.466</td>
<td>361.67</td>
<td>1.437</td>
<td>313.00</td>
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<td>322.79</td>
<td>0.617</td>
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<td>1.764</td>
<td>332.43</td>
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<td>332.62</td>
<td>0.807</td>
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<td>2.216</td>
<td>351.81</td>
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<tr>
<td>342.47</td>
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<td>1.682</td>
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<td>1.321</td>
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<td>361.87</td>
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<tr>
<td>371.63</td>
<td>2.080</td>
<td><strong>T/K</strong></td>
<td><strong>P/MPa</strong></td>
<td><strong>C₅OH</strong></td>
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<tr>
<td>381.45</td>
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<td>312.97</td>
<td>0.423</td>
<td>312.98</td>
<td>0.427</td>
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<td>322.69</td>
<td>0.554</td>
<td>332.14</td>
<td>0.711</td>
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<td>0.712</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td><strong>P/MPa</strong></td>
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<td>1.127</td>
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<td>1.714</td>
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<tr>
<td>313.00</td>
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<td>1.390</td>
<td>387.61</td>
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<td>2.371</td>
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<tr>
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<td>0.922</td>
<td>389.16</td>
<td>2.364</td>
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<tr>
<td>351.70</td>
<td>1.156</td>
<td>390.59</td>
<td>2.427</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* L₂L₃V BIP,  b UCEP [L₂-L₁=V].
Figs. 8.6.a (up) and 8.6.b (down). Temperatures and pressures of the UCEP's $[L_2-L_1=V]$ and the $L_2L_1V$ BIP's for binary systems of $C_3F_8 + n$-alkanols against the carbon number $n$ of the $n$-alkanol. Dashed line: critical point of pure $C_3F_8$, up empty triangles: UCEP's $[L_2-L_1=V]$ (solid curve: regression curve through the experimental points), empty diamonds: $L_2L_1V$ BIP's (dotted-dashed curve: regression curve through the experimental points).
The temperature curves show a maximum at a carbon number n≈3 where the raise in polarity becomes more important than the decrease of size. Somewhere in the same region of carbon numbers (n≤2) heteroazeotropy or azeotropy emerges. A quasi-binary approximation technique could enlighten more the details of this region, but it seems inadequate because the molecules of ethanol, 1-propanol and 1-butanol are relatively different and so volatile that a reproducible preparation of a pseudo less-volatile component is very difficult (see Chapters 6 and 7). The curves of the pressures of the UCEP's and BIP's (Fig.8.6.b) are monotonous and increase with decreasing carbon number.

![Graph](image)

Fig.8.7. Binary systems of C₄F₁₀ + n-alkanols. Solid curve: saturation curve of C₄F₁₀, short-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system C₄F₁₀ + C₁OH, triple dotted - dashed curve: three-phase L₂L₁V equilibrium curve of the binary system C₄F₁₀ + C₂OH, dotted-curve: three-phase L₂L₁V equilibrium curve of the binary system C₄F₁₀ + C₃OH, long-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system C₄F₁₀ + C₄OH, dotted-dashed curve: three-phase L₂L₁V equilibrium curve of the binary system C₄F₁₀ + C₅OH, empty circle: critical point of C₄F₁₀ up empty triangles: UCEP's [L₂-L₁=V], empty diamonds: L₂L₁V BIP's.
Figs. 8.8.a (up) and 8.8.b (down). Temperatures and pressures of the UCEP's $[L_2-L_1-V]$ and the $L_2L_1V$ BIP's for several binary systems of $C_4F_{10}$ + $n$-alkanols against the carbon number $n$ of the $n$-alkanol. Dashed line: critical point of pure $C_4F_{10}$, up empty triangles: UCEP's $[L_2-L_1-V]$ (solid curve: regression curve through the experimental points), empty diamonds: $L_2L_1V$ BIP's (dotted-dashed curve: regression curve through the experimental points).
The observations and the conclusions concerning the family of binary systems of $\text{C}_3\text{F}_8 + n$-alkanols are also confirmed by measurements on the family of binary systems of $\text{C}_4\text{F}_{10} + n$-alkanols. The experimental data for the three-phase $L_2L_1V$ equilibrium curves of the binary systems of $\text{C}_4\text{F}_{10} + n$-alkanols are given in Table 8.4. In Fig.8.7 P,T projections of the three-phase $L_2L_1V$ equilibrium curves for some of the binary systems of $\text{C}_4\text{F}_{10} + n$-alkanols are plotted. Again it can be noticed that for the range of relatively large carbon numbers (5 to 8), as the carbon number increases, the three-phase $L_2L_1V$ equilibrium curves shift closer to the saturation curve of the more-volatile component ($\text{C}_4\text{F}_{10}$), while for the range of relatively small carbon numbers (1 to 4), with decreasing carbon number (so with increasing polarity) the three-phase $L_2L_1V$ equilibrium curves pass gradually above the saturation curve of the more-volatile component, giving rise to type III-HA or type III-A fluid phase behaviour.

In Figs. 8.8.a and 8.8.b the temperatures and pressures respectively of the UCEP's and $L_2L_1V$ BIP's of the binary systems of $\text{C}_4\text{F}_{10} + n$-alkanols are plotted against the carbon number $n$ of the $n$-alkanol. The temperature curves have a maximum defining, as we noticed in Fig.8.6.a, the carbon number area where the polarity increase of the $n$-alkanol becomes more significant than the size decrease. In the binary systems of $\text{C}_3\text{F}_8$ and $n$-alkanols the maximum was located around the carbon number 3, but here in the binary systems of $\text{C}_4\text{F}_{10} + n$-alkanols the maximum is located around the carbon number 4. This indicates that as far as we consider families of binary systems containing a more-volatile component which is a member of a homologous series from family to family (here perfluoroalkanes) and a less-volatile component which is a member of the same homologous series in all the families (here $n$-alkanols), then the position of the maximum temperature of the UCEP's [$L_2$-$L_1$=$V$] of the family of binary systems occurs at a carbon number which depends on the size of the more-volatile component. More specifically the larger the molecule of the more-volatile component is, the higher is the carbon number of this maximum.

This last conclusion is also supported by the experimental results for perfluoroalkanes + $n$-alkanes presented in previous Chapters. In these families a transition pattern of the type II$\leftrightarrow$IV$\leftrightarrow$III is observed, which does not appear here, but the curve of the UCEP's [$L_2$-$L_1$=$V$] of the binary systems has also a maximum in temperature which is the TCP. As was mentioned in Chapter 4 $n_{TCP}\approx8.4$ for the family $\text{C}_3\text{F}_8 + n$-alkanes and as was mentioned in Chapter 7 $n_{TCP}\approx10.6$ for the family $\text{C}_4\text{F}_{10} + n$-alkanes. Also from de Loos et al. (1993) $n_{TCP}\approx6.1$ for the family $\text{C}_2\text{F}_6 + n$-alkanes. Therefore for larger perfluoroalkanes, higher carbon numbers of the $n$-alkane for the TCP are required.
Experimental results for the systems C₂F₆ or C₃F₆ or C₄F₁₀ + ethers or alkanols

From the above arguments it may be expected that the maximum temperature of the UCEP's \( L_2 - L_1 = V \) in the family of binary systems of C₂F₆ with n-alkanols is located somewhere around C₂OH, so at \( n \approx 2 \).

Symbols

1  more-volatile component
2  less-volatile component
CEP  critical endpoint
DCEP  double critical endpoint
\( L_1 \)  liquid phase having smaller \( x \)
\( L_2 \)  liquid phase having greater \( x \)
\( L_2L_1V \)  liquid-liquid-vapour equilibrium
\( L_2L_1V \) BIP  liquid-liquid-vapour barotropic inversion point
LCEP  lower critical endpoint
\( n \)  carbon number
P  pressure
T  temperature
TCP  tricritical point
UCEP  upper critical endpoint
V  vapour phase
\( x \)  mole fraction of the less-volatile component 2

\( C_2OH \)  1-butanol (n-butanol)
\( s-C_4OH \)  2-butanol (sec-butanol)
\( i-C_4OH \)  2-methyl-1-propanol (iso-butanol)
\( t-C_4OH \)  2-methyl-2-propanol (tert-butanol)
\( C_2-O-C_2 \)  diethyl - ether
\( C_1-O-C_4 \)  methyl - n-butyl - ether
References


9. MODELLING

In this Chapter the modelling of several systems for which the experimental results are presented in Chapters 6, 7 and 8 is attempted. Quantitative agreement is limited by the drawbacks of the thermodynamic models used. The calculational procedures developed in Chapter 3 are applied and special areas of interest are analyzed. The transition pattern from type II, via type IV, towards type III fluid phase behaviour is examined and the predictions are compared with the experiments. The barotropic inversion phenomena as well as the heteroazeotropy encountered in the family of perfluorobutane with n-alkanols are calculated in detail.

9.1 Introduction

Until this point of the thesis, the fluid phase equilibrium phenomena found for binary systems were presented on the basis of experimental data, either provided by the literature or measured in the context of this work. Although experimental information is more reliable to draw conclusions, in some cases it does not provide all the necessary details or it is very difficult to be obtained.

If several isotherms and isobars, like those of Fig.2.7 and Fig.2.8, are to be constructed experimentally by means of the facilities discussed in Chapter 5, then an effort comparable to the experimental work presented in Chapters 6, 7 and 8 has to be performed again. Even with a specialized experimental setup, suitable to measure the compositions of the various phases at equilibrium at fixed T and P, the work is not significantly less while the accuracy can be much lower according to experience obtained in our laboratory.

Even if these expensive and time consuming experiments are available, areas of Fig.2.7 and Fig.2.8 like those close to the three-phase equilibria or those close to the critical points are very difficult to be measured in detail. The exact shape of binodal curves in these areas is hard to obtain even with very expensive controllers of temperature, very fine measuring devices of T and P and very sophisticated sample preparation procedures.

Another approach to the above difficult situations is to calculate the corresponding diagrams using appropriate thermodynamic models and suitable calculational algorithms. In this way the details can be magnified at any desirable level and the cost to study any specific
area of interest is limited to computer-time expenditure. However there are other drawbacks as we shall see in the rest of this chapter.

9.2 Transitions in the family of carbon dioxide with n-alkanes

In Chapter 3 fluid phase equilibria in the binary system of CO$_2$ + n-tridecane were calculated. In the family of CO$_2$ + n-alkanes a transition from type II, via type IV, towards type III fluid phase behaviour takes place for binary systems with n-dodecane, n-tridecane and n-tetradecane, respectively, as mentioned in Chapter 4. It was shown that in the case of CO$_2$ + n-tridecane the agreement of the Peng-Robinson equation of state with experimental data can be obtained when the parameters $k$ and $l$ are adjusted (Chapter 3). The predicted phase behaviour for the other two binary systems (CO$_2$ + n-dodecane or n-tetradecane), using the same values of the parameters $k$ and $l$ is presented below.

In order to observe a type IV phase behaviour in the system of CO$_2$ + n-tridecane it was necessary to use different values for the parameter $l$ above and below the critical temperature of pure CO$_2$ (see Table 9.1). The discrete step of $l$ at the critical temperature of CO$_2$ causes problems of discontinuity in the equilibrium loci which pass that temperature. For the systems of CO$_2$ + dodecane or CO$_2$ + tridecane there are no such loci for the monovariant fluid phase equilibria. However for the system of CO$_2$ + tetradecane both the L$_2$=V/L$_2$=L$_1$ critical curve and the three-phase L$_2$L$_1$V equilibrium curve pass the critical temperature of CO$_2$. In order to keep them continuous we use the $l$ value of the region above the critical temperature of CO$_2$ for the whole L$_2$=V/L$_2$=L$_1$ critical curve and the $l$ value of the region below the critical temperature of CO$_2$ for the whole three-phase L$_2$L$_1$V equilibrium curve.

In Table 9.2 the P,T coordinates of the critical endpoints resulting from our calculations and from the experimental data provided by literature (Hottovy et al., 1981) are compared. The average absolute error in temperature is 0.4 % and in pressure 1.8 %. The compositions are predicted with larger error. For example at the UCEP [L$_2$=L$_1$-V] of both binary systems of CO$_2$ + n-dodecane and CO$_2$ + tridecane, the critical phase L$_2$=L$_1$ has a mole fraction around 0.135, while the experimental value is around 0.086. The binary system of CO$_2$ + n-dodecane is predicted to be a type IV system while experimentally it is found to be a type II system. The predicted upper branch of the three-phase L$_2$L$_1$V equilibrium curve extends over a temperature range of only 0.43 K and a pressure range of only 0.091 MPa.
**TABLE 9.1**

*Binary systems calculated by means of the Peng-Robinson equation of state, binary interaction parameters used for the specified range of conditions and the type of fluid phase behaviour encountered.*

<table>
<thead>
<tr>
<th>System</th>
<th>$k$</th>
<th>$l$</th>
<th>Range</th>
<th>Type</th>
</tr>
</thead>
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<tr>
<td>CO$<em>2$-C$</em>{12}$</td>
<td>0.0800</td>
<td>0.0600</td>
<td>$T&gt;T_{c1}$</td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td>0.0800</td>
<td>0.0000</td>
<td>$T&lt;T_{c1}$</td>
<td></td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{13}$</td>
<td>0.0800</td>
<td>0.0600</td>
<td>$T&gt;T_{c1}$</td>
<td>IV</td>
</tr>
<tr>
<td></td>
<td>0.0800</td>
<td>0.0000</td>
<td>$T&lt;T_{c1}$</td>
<td></td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{14}$</td>
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<td>0.0000</td>
<td>$L_2=V$</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>0.0800</td>
<td>0.0600</td>
<td>$L_2=L_1$</td>
<td></td>
</tr>
<tr>
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<td>III</td>
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<td>0.1220</td>
<td>0.0000</td>
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<td>III</td>
</tr>
<tr>
<td></td>
<td>0.1220</td>
<td>0.0140</td>
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<td>0.0340</td>
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<td>0.0000</td>
<td>all</td>
<td>III</td>
</tr>
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</table>
TABLE 9.2

Temperatures and pressures of the critical endpoints encountered in the binary systems of carbon dioxide with n-dodecane, n-tridecane and n-tetradecane. Comparison of the calculated values versus the experimental ones provided by the literature.

<table>
<thead>
<tr>
<th>System</th>
<th>UCEP ([L_2=L_1-V])</th>
<th>LCEP ([L_2=L_1-V])</th>
<th>UCEP ([L_2-L_1=V])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T/K</td>
<td>T/K</td>
<td>T/K</td>
</tr>
<tr>
<td></td>
<td>exp calc</td>
<td>exp calc</td>
<td>exp calc</td>
</tr>
<tr>
<td>CO(<em>2) - C(</em>{12})</td>
<td>267.31 268.22</td>
<td>- 316.84</td>
<td>- 317.27</td>
</tr>
<tr>
<td>CO(<em>2) - C(</em>{13})</td>
<td>278.95 280.51</td>
<td>310.75 310.16</td>
<td>314.01 314.07</td>
</tr>
<tr>
<td>CO(<em>2) - C(</em>{14})</td>
<td>- -</td>
<td>- -</td>
<td>311.15 313.80</td>
</tr>
</tbody>
</table>

|          | P/MPa                | P/MPa                | P/MPa                |
|          | exp calc             | exp calc             | exp calc             |
| CO\(_2\) - C\(_{12}\) | 2.882 2.915        | - 9.147             | - 9.238             |
| CO\(_2\) - C\(_{13}\) | 3.933 4.033       | 8.114 8.006         | 8.716 8.763         |
| CO\(_2\) - C\(_{14}\) | - -                | - -                | 8.260 8.540         |

In Fig.9.1 the monovariant fluid phase equilibria for the three binary systems CO\(_2\) + n-dodecane, CO\(_2\) + n-tridecane and CO\(_2\) + n-tetradecane are projected on a P,T plane. In Figs. 9.2 and 9.3 the corresponding T,x and P,x projections are plotted.

9.3 Transitions in the family of perfluorobutane with n-alkanes

The results of our experiments for the family of C\(_4\)F\(_{10}\) + n-alkanes were presented in Chapter 7. In this section the fluid phase equilibria for several binary and quasi-binary systems belonging to this family are calculated by means of the Peng-Robinson equation of state. We are interested to see if the transition zone of type IV is predicted at the same carbon
numbers of the n-alkane and if it is extended over the same temperature range. The quasi-binary approach is realized here by considering the less-volatile component of the system as a pseudo-pure component with critical properties and acentric factor resulting from a linear interpolation between the corresponding properties of the two constituents of the pseudo-pure component.

![Graph](image)

**Fig.9.1.** P,T projection of monovariant fluid phase equilibria for the binary systems of CO₂ + n-dodecane or n-tridecane or n-tetradecane calculated by the Peng-Robinson equation of state. Solid curves: vapour pressure curves of pure components, medium-dashed curves: critical loci for the binary system of CO₂ + n-dodecane; long-dashed curves: critical loci for the binary system of CO₂ + n-tridecane; short-dashed curves: critical loci for the binary system of CO₂ + n-tetradecane; dashed-dotted curves: three-phase equilibrium curves; empty circles: pure component critical points; up solid triangles: UCEP's [L₂=L₁+V]; down solid triangles: LCEP's [L₂=L₁-V]; up empty triangles: UCEP's [L₁-L₂=V].

In Table 9.1 the values of the binary interaction parameters for the various systems are given and in Table 9.3 the critical properties and the acentric factor for the pure components
are listed. For the binary system \( \text{C}_4\text{F}_{10} + \text{n-decane} \) the parameters \( k \) and \( l \) were fitted using the experimental temperatures and pressures of the UCEP \( [L_2=L_1-V] \).

Fig. 9.2 \( T,x \) projection of the monovariant fluid phase equilibria for the binary systems of \( \text{CO}_2 + \text{n-dodecane or n-tridecane or n-tetradecane} \) calculated by the Peng-Robinson equation of state. For curves and symbols see Fig. 9.1.

Fig. 9.3 \( P,x \) projection of the monovariant fluid phase equilibria for the binary systems of \( \text{CO}_2 + \text{n-dodecane or n-tridecane or n-tetradecane} \) calculated by the Peng-Robinson equation of state. For curves and symbols see Fig. 9.1.
TABLE 9.3

**Pure component critical constants and acentric factors used in the calculations.**

<table>
<thead>
<tr>
<th>Name</th>
<th>T_c/K</th>
<th>P_c/MPa</th>
<th>(\omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2</td>
<td>304.1</td>
<td>7.38</td>
<td>0.239</td>
</tr>
<tr>
<td>C_{4F_{10}}</td>
<td>386.4</td>
<td>2.32</td>
<td>0.375</td>
</tr>
<tr>
<td>C_9</td>
<td>594.9</td>
<td>2.29</td>
<td>0.443</td>
</tr>
<tr>
<td>C_{10}</td>
<td>617.7</td>
<td>2.11</td>
<td>0.490</td>
</tr>
<tr>
<td>C_{11}</td>
<td>638.9</td>
<td>1.96</td>
<td>0.533</td>
</tr>
<tr>
<td>C_{12}</td>
<td>658.7</td>
<td>1.83</td>
<td>0.573</td>
</tr>
<tr>
<td>C_{13}</td>
<td>676.0</td>
<td>1.71</td>
<td>0.618</td>
</tr>
<tr>
<td>C_{14}</td>
<td>693.0</td>
<td>1.61</td>
<td>0.654</td>
</tr>
<tr>
<td>C_{1OH}</td>
<td>512.6</td>
<td>8.09</td>
<td>0.556</td>
</tr>
<tr>
<td>C_{5OH}</td>
<td>588.0</td>
<td>3.91</td>
<td>0.579</td>
</tr>
</tbody>
</table>

For the binary system C_{4F_{10}} + n-undecane \(k\) and \(l\) were fitted to match the experimental UCEP [L_2=V]. For the other binary and quasi-binary systems of C_{4F_{10}} + n-alkanes these parameters are estimated from a linear interpolation or extrapolation of the fitted \(k\) and \(l\) values using the carbon number of the n-alkane as weighing variable. Table 9.4 summarizes the calculated UCEP's [L_2=V], LCEP's [L_2=V] and UCEP's [L_2=V] for all the systems considered in this chapter.

In Fig. 9.4 the P,T projections of the calculated critical curves for the binary systems of C_{4F_{10}} + n-alkanes from n-nonane until n-dodecane are plotted. The first two binary systems exhibit type II fluid phase behaviour and the last two exhibit type III fluid phase behaviour. Quasi-binary systems with n-alkanes between n-decane and n-undecane offer the possibility of type IV behaviour. Figs. 9.5 and 9.6 contain the T,x and P,x projections, respectively, of the critical curves. In Fig. 9.6 we notice the looping of the L_2=V/L_2=V critical curves for the type III binary systems.
Temperature, pressure and composition coordinates of the UCEP's $[L_2=L_1-V]$, the LCEP's $[L_2=L_1-V]$ and the UCEP's $[L_2=L_1]=V$ for the various binary systems calculated using the Peng-Robinson equation of state.

<table>
<thead>
<tr>
<th>System</th>
<th>Type</th>
<th>T/K</th>
<th>P/MPa</th>
<th>x(V)</th>
<th>x($L_2=L_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$<em>2$-C$</em>{12}$</td>
<td>IV</td>
<td>268.22</td>
<td>2.915</td>
<td>0.000003</td>
<td>0.087665</td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{13}$</td>
<td>IV</td>
<td>280.51</td>
<td>4.033</td>
<td>0.000007</td>
<td>0.085000</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_9$</td>
<td>II</td>
<td>368.52</td>
<td>1.212</td>
<td>0.027272</td>
<td>0.519600</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10}$</td>
<td>II</td>
<td>375.25</td>
<td>1.465</td>
<td>0.016274</td>
<td>0.409741</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.25}$</td>
<td>II</td>
<td>382.67</td>
<td>1.707</td>
<td>0.017813</td>
<td>0.374779</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.36}$</td>
<td>II</td>
<td>387.41</td>
<td>1.868</td>
<td>0.019877</td>
<td>0.360159</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.5003}$</td>
<td>IV</td>
<td>399.19</td>
<td>2.289</td>
<td>0.029290</td>
<td>0.330290</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>Type</th>
<th>T/K</th>
<th>P/MPa</th>
<th>x(V)</th>
<th>x($L_2=L_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$<em>2$-C$</em>{12}$</td>
<td>IV</td>
<td>316.84</td>
<td>9.147</td>
<td>0.009612</td>
<td>0.040247</td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{13}$</td>
<td>IV</td>
<td>310.16</td>
<td>8.006</td>
<td>0.001140</td>
<td>0.052580</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.503}$</td>
<td>IV</td>
<td>412.61</td>
<td>2.796</td>
<td>0.053878</td>
<td>0.297132</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System</th>
<th>Type</th>
<th>T/K</th>
<th>P/MPa</th>
<th>x($L_1=V$)</th>
<th>x($L_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$<em>2$-C$</em>{12}$</td>
<td>IV</td>
<td>317.27</td>
<td>9.238</td>
<td>0.017269</td>
<td>0.055324</td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{13}$</td>
<td>IV</td>
<td>314.07</td>
<td>8.763</td>
<td>0.008858</td>
<td>0.088584</td>
</tr>
<tr>
<td>CO$<em>2$-C$</em>{14}$</td>
<td>III</td>
<td>313.80</td>
<td>8.540</td>
<td>0.005375</td>
<td>0.160112</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.5003}$</td>
<td>IV</td>
<td>423.00</td>
<td>3.241</td>
<td>0.136410</td>
<td>0.350332</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.53}$</td>
<td>III</td>
<td>422.58</td>
<td>3.236</td>
<td>0.131528</td>
<td>0.357683</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.54}$</td>
<td>III</td>
<td>422.15</td>
<td>3.222</td>
<td>0.129796</td>
<td>0.361548</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.56}$</td>
<td>III</td>
<td>421.54</td>
<td>3.220</td>
<td>0.126382</td>
<td>0.371690</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10.6151}$</td>
<td>III</td>
<td>420.46</td>
<td>3.178</td>
<td>0.116769</td>
<td>0.383738</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{11}$ a</td>
<td>III</td>
<td>412.10</td>
<td>2.948</td>
<td>0.075318</td>
<td>0.454076</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{11}$ b</td>
<td>III</td>
<td>412.64</td>
<td>2.984</td>
<td>0.075481</td>
<td>0.411105</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{11}$ c</td>
<td>III</td>
<td>412.73</td>
<td>3.003</td>
<td>0.074817</td>
<td>0.371290</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{12}$</td>
<td>III</td>
<td>401.37</td>
<td>2.697</td>
<td>0.031865</td>
<td>0.501402</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{10}$</td>
<td>III</td>
<td>383.22</td>
<td>2.325</td>
<td>0.255100</td>
<td>0.995930</td>
</tr>
<tr>
<td>C$<em>4$F$</em>{10}$-C$_{4}$OH</td>
<td>III</td>
<td>294.39</td>
<td>2.454</td>
<td>0.064439</td>
<td>0.955663</td>
</tr>
</tbody>
</table>
Fig. 9.4 $P,T$ projection of the critical curves for the binary systems of $C_4F_{10} + n$-nonane, $n$-decane, $n$-undecane and $n$-dodecane calculated by the Peng-Robinson equation of state. Solid curves: vapour pressure curves of pure components; dashed-dotted curve: $L=V$ critical curve for the binary system of $C_4F_{10} + n$-nonane; short-dashed curve: $L=V$ critical curve for the binary system of $C_4F_{10} + n$-decane; dashed-triple-dotted curve: $L_2=L_1/L_2=V$ critical curve for the binary system of $C_4F_{10} + n$-undecane; long-dashed curve: $L_2=L_1/L_2=V$ critical curve for the binary system of $C_4F_{10} + n$-dodecane; empty circles: pure component critical points.

Fig. 9.5 $T,x$ projection of the critical curves for the binary systems of $C_4F_{10} + n$-nonane, $n$-decane, $n$-undecane and $n$-dodecane calculated by the Peng-Robinson equation of state. For curves and symbols see Fig. 9.4.
Fig. 9.6 P,x projection of the critical curves for the binary systems of C₄F₁₀ + n-nonane, n-decane, n-undecane and n-dodecane calculated by the Peng-Robinson equation of state. For curves and symbols see Fig. 9.4.

Fig. 9.7 P,x projection of the three-phase equilibrium curves for the binary systems of C₄F₁₀ + n-nonane, n-decane, n-undecane and n-dodecane and the quasi-binary system of C₄F₁₀ + pseudo-n-alkane with n=10.5 (50% mole fraction n-decane + 50% mole fraction n-undecane). Solid curves: three-phase equilibrium curves for the quasi-binary system of C₄F₁₀ + C₁₀₅; up solid triangles: UCEP's [L₂=L₁-V]; down solid triangle: LCEP [L₂-L₁-V]; up empty triangles: UCEP's [L₂-L₁-V]. For other curves see Fig. 9.4.
For a range of pressures there are three different critical points occurring at different temperatures and overall compositions. At the self-crossing point of the loop we have two critical points at the same pressure and overall composition but at a different temperature. The loop reduces in size from undecane to dodecane and for longer n-alkanes (more pronounced type III behaviour) it vanishes. Therefore it can be considered to be a feature of type III systems close to the transition towards type IV phase behaviour.

In Fig. 9.7 the P,x projections of the three-phase L₂L₁V equilibrium curves for the four binary systems discussed above and a quasi-binary system with a carbon number n = 10.5 are plotted. The T,x projections are similar. Every three-phase L₂L₁V equilibrium curve consists of three branches, one for every phase. The branch at the left is the vapour branch, V, the middle branch is the L₁ branch and the right branch is the L₂ branch. Here L₁ is the liquid phase with the smaller mole fraction with respect to the less-volatile component 2. As we shall see below L₁ is not necessarily also the lighter phase with respect to the density (see also Chapter 6). For the type II systems the L₂ and L₁ branches join at the UCEP [L₂=L₁-V]. The same happens for the L₁ and V branches of the type III systems at the UCEP [L₂-L₁=V]. For the type IV systems we have in addition the LCEP [L₂=L₁-V] where the L₂ and L₁ branches join, if the temperature and pressure are decreased.

In Figs. 9.8, 9.9 and 9.10 we have plotted the P,T, T,x and P,x projections of the calculated L₂=L₁ critical curves for the binary and quasi-binary systems of C₄F₁₀ + n-alkanes of carbon number n from 9 to 10.5. The first four systems exhibit fluid phase behaviour of type II and the last one is of type IV. We see that the critical curve of the system C₄F₁₀ + n-nonane crosses all the other critical curves in the P,T projection and looks quite different from them. This occurs probably as a consequence of the linear extrapolation of k and l values used to calculate the above binary system.

In Fig.9.11 the L=V or L₂=L₁ / L₂=V critical curves for the binary and quasi-binary systems discussed in the above paragraph are projected on a P,T plane. We notice that as the less-volatile component (n-alkane) becomes larger in size the pressure maximum of the critical curve moves to higher pressure. As the behaviour approaches the one of type IV the critical curves bend somewhere close to the critical point of the more-volatile component. For n>n_TCP the critical curve is interrupted. In Figs. 9.12 and 9.13 the T,x and the P,x projections of the critical lines are drawn. The TCP occurs at a horizontal inflection point where the derivatives {\partial T/\partial x, \partial P/\partial x, \partial^2 T/\partial x^2, and \partial^2 P/\partial x^2} are zero. Notice that the L₁=L₂/L₂=V branch of the type IV system starting from the LCEP [L₂=L₁-V] moves first towards lower critical compositions and
afterwards turns back. Therefore one isopleth can show two different critical points. This behaviour is comparable with the behaviour found for the critical curves of the type III systems discussed in Fig.9.6.

Fig.9.8 P,T projection of the \( L_2-L_1 \) critical curves for the binary and quasi-binary systems of \( C_4F_{10} + n \)-alkanes of carbon numbers \( n \) from 9 to 10.5, calculated by the Peng-Robinson equation of state. Solid curve: vapour pressure curve of \( C_4F_{10} \); long-dashed curve: \( n=9 \) (type II system); short-dashed curve: \( n=10 \) (type II system); dashed-dotted curve: \( n=10.25 \) (type II system); dashed-triple-dotted curve: \( n=10.36 \) (type II system); dotted curve: \( n=10.50 \) (type IV system); empty circle: critical point of \( C_4F_{10} \); up solid triangles: UCEP's \( [L_2=L_1-V] \).

Fig.9.9 T,x projection of the \( L_2=L_1 \) critical curves for the binary and quasi-binary systems of \( C_4F_{10} + n \)-alkanes of carbon numbers \( n \) from 9 to 10.5. For curves and symbols see Fig.9.8.
Fig. 9.10 P-x projection of the $L_2=L_1$ critical curves for the binary and quasi-binary systems of $C_4F_{10} + n$-alkanes of carbon numbers $n$ from 9 to 10.5. For curves and symbols see Fig. 9.8.

Fig. 9.11 P,T projection of the $L=V$, $L_1=V$ and $L_2=L_1/L_2=V$ critical curves for the binary and quasi-binary systems of $C_4F_{10} + n$-alkanes of carbon numbers $n$ from 9 to 10.5, calculated by the Peng-Robinson equation of state. Solid curves: vapour pressure curves of pure components; long-dashed curve: $L=V$ critical curve for $n=9$ (type II system); short-dashed curve: $L=V$ critical curve for $n=10$ (type II system); dashed-dotted curve: $L=V$ critical curve for $n=10.25$ (type II system); dashed-triple-dotted curve: $L=V$ critical curve for $n=10.36$ (type II system); dotted curve: $L_1=V$ critical curve for $n=10.50$ (type IV system); alternatively-dashed curve: $L_2=L_1/L_2=V$ critical curve for $n=10.50$ (type IV system); empty circles: critical points of pure components; down solid triangle: LCEP [$L_2=L_1-V$]; up empty triangle: UCEP [$L_2-L_1-V$].
Fig. 9.12 $T_x$ projections of the critical curves plotted in Fig. 9.11. For curves and symbols see Fig. 9.11.

Fig. 9.13 $P_x$ projections of the critical curves plotted in Fig. 9.11. For curves and symbols see Fig. 9.11.
Fig. 9.14 $P,T$ projection of the $L_2=L_1/L_2=V$ critical curves for the binary and quasi-binary systems of $C_4F_{10} + n$-alkanes of carbon numbers $n$ from 10.53 to 12, calculated by the Peng-Robinson equation of state. All these systems exhibit type III phase behaviour. Solid curves: vapour pressure curves of pure components; long-dashed curve: critical curve for $n=10.53$; short-dashed curve: critical curve for $n=10.54$; dashed-dotted curve: critical curve for $n=10.56$; dashed-triple-dotted curve: critical curve for $n=10.615$; dotted curve: critical curve for $n=11$; alternatively-dashed curve: critical curve for $n=12$; empty circles: critical points of pure components.

Fig. 9.15 $T,x$ projections of the critical curves plotted in Fig. 9.14. For curves and symbols see Fig. 9.14.
Fig. 9.16 $P,x$ projections of the critical curves plotted in Fig. 9.14. For curves and symbols see Fig. 9.14.

Fig. 9.17 $P,T$ projection of the $L_1=V$ critical curves and of the $L_2 L_1 V$ three-phase equilibrium curves for the binary and quasi-binary systems of $C_4F_{16} + n$-alkanes of carbon numbers $n$ from 10.53 to 12, calculated by the Peng-Robinson equation of state. All the above systems are of type III. Solid curve: vapour pressure curve of $C_4F_{16}$; long-dashed curve: $L_1=V$ critical curve and $L_2=L_1/L_3=V$ critical curve for $n=10.53$; medium-dashed curve: $L_1=V$ critical curve for $n=11$; short-dashed curve: $L_1=V$ critical curve for $n=12$; dashed-dotted curves: $L_2 L_1 V$ three-phase equilibrium curves; empty circle: critical point of $C_4F_{16}$; up empty triangles: UCEP's $[L_2 L_1 = V]$. 
The binary and quasi-binary systems of C₄F₁₀ with n-alkanes of carbon number from 10.5 to 12 exhibit type III fluid phase behaviour. Their L₂=L₁/L₂=V critical curves are plotted in the P,T graph of Fig.9.14. Originating from the critical point of the less-volatile component (or pseudo-component) they pass through two successive extremes of pressure (maximum and minimum). As the double critical endpoint (DCEP) is approached the minimum in pressure approaches the three-phase equilibrium line (not shown in this graph, see Fig.9.17). Fig. 9.15 contains the T,x projections of the critical lines for these systems. Notice the existence of a composition minimum at T=430-440 K. Fig. 9.16 contains the P,x projections of the same critical curves which form a closed loop. The composition minimum is found between the pressure maximum and the pressure minimum. After the pressure minimum ∂P/∂x is very large. In Fig.9.17 the three-phase L₂L₁V equilibrium curves together with the L₁=V critical curves for some of the discussed type III systems are plotted. The region of temperature and pressure is around the critical point of pure C₄F₁₀. For n=10.53 also the L₂=L₁/L₂=V critical curve is shown. We observe the approach of this critical curve to the three-phase curve as the DCEP behaviour is reached.

9.4 Calculated versus experimental results for the transitions

The temperatures of the calculated critical endpoints in the family of binary and quasi-binary systems of C₄F₁₀ + n-alkanes are plotted against the carbon number n of the n-alkane in Fig.9.18. The locus of UCEP's [L₂-L₁=V] is fitted by a second order polynomial curve, i.e. n(T)=aT²+bT+c. The locus of [L₂=L₁-V] CEP's (both UCEP's and LCEP) is fitted by a third order polynomial curve, i.e. n(T)=aT³+bT²+cT+d. The UCEP [L₂=L₁-V] for the binary system C₄F₁₀ + n-nonane is not taken into account for this regression. If this UCEP is included, then the third order regression becomes bad. This means either that the third order polynomial is not adequate for the whole range of n, or that the k and l parameters are not a linear function of n, as it was supposed.

In Table 9.5, the sensitivity of the L₂=L₁ temperature to the value of the interaction parameter l is examined for the system C₄F₁₀ + n-nonane. A change of ∆l=0.02 causes a change of ∆T_L₂T₁=10 K. This shows that if the linear dependency of l on n is not valid, then large errors can be produced by this approximation.

In Fig.9.19 the calculated critical endpoint loci (solid curves) are compared with the experimental critical endpoint loci (dashed curves). Of course for the systems C₄F₁₀ + n-
decane and C₄F₀₁₀ + n-undecane there is a perfect agreement, because we fitted the values of the interaction parameters for these systems in order to represent the experimental measurements. Also the UCEP's \([L_2-L_1=V]\) are predicted very well, however for \(n<10\) the UCEP's \([L_2=L_1-V]\) are predicted at much too high temperature. This shows that indeed the \(k\) and \(l\) parameters are not a linear function of \(n\), as it was supposed, and explains why the system C₄F₀₁₀ + n-nonane deviates from the regression curve of Fig.9.18. Therefore the choice of a third order polynomial seems not to be the reason for the deviation of system C₄F₀₁₀ + n-nonane from the regression curve of Fig.9.18.

\[\text{TABLE 9.5}\]

*Calculated } L_2=L_1 \text{ critical points for the system } C_4F_{10} + C_9 \text{ at different values of the binary interaction parameter } l.\]

<table>
<thead>
<tr>
<th>(k)</th>
<th>(l)</th>
<th>(P/\text{MPa}=3)</th>
<th>(P/\text{MPa}=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.082</td>
<td>-0.094</td>
<td>366.66</td>
<td>367.42</td>
</tr>
<tr>
<td>0.082</td>
<td>-0.084</td>
<td>356.54</td>
<td>356.96</td>
</tr>
<tr>
<td>0.082</td>
<td>-0.074</td>
<td>346.24</td>
<td>346.46</td>
</tr>
</tbody>
</table>

\[\text{TABLE 9.6}\]

*Carbon number and temperature coordinates for the TCP and the DCEP in the family of binary systems of } C_4F_{10} \text{ with } n\text{-alkanes.}\]

<table>
<thead>
<tr>
<th></th>
<th>TCP</th>
<th>DCEP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\exp)</td>
<td>(\text{calc})</td>
</tr>
<tr>
<td>(n)</td>
<td>10.653</td>
<td>10.437</td>
</tr>
<tr>
<td>(T / K)</td>
<td>420.00</td>
<td>424.83</td>
</tr>
</tbody>
</table>

In Table 9.6 the calculated and the experimental temperatures and carbon numbers of the TCP and the DCEP for the family of binary system C₄F₀₁₀ + n-alkanes are listed. We notice
that the intermediate zone of type IV is predicted more than 4 times wider in carbon number and more than 3 times longer in temperature than is found experimentally (see also Fig.9.19).

![Graph showing temperatures of critical endpoints vs. carbon number](image)

Fig.9.18 Temperatures of the critical endpoints in the family of binary systems of C₄F₁₀ + n-alkanes plotted versus the carbon number n of the n-alkane. Up solid triangles: UCEP's [L₂=L₁=V], down solid triangle: LCEP [L₂=L₁=V], up empty triangles: UCEP's [L₂-L₁=V]. The DCEP (solid square) is located at the maximum n of the third order polynomial curve which correlates the [L₂=L₁=V] CEP's. The TCP (empty diamond) is located at the crossing point of this polynomial curve and the second order polynomial curve which correlates the [L₂-L₁=V] UCEP's.

9.5 Typical fluid phase diagrams

The monovariant fluid phase equilibria and the critical curves for the binary system of C₄F₁₀ + n-nonane, calculated using the Peng-Robinson equation of state, are depicted in the P,T,x plot of Fig.9.20.a. The system exhibits type II fluid phase behaviour. In Figs. 9.20.b, 9.20.c and 9.20.d the P,T ,the T,x and the P,x projections for this system are drawn.
Fig. 9.19 Temperatures of the critical endpoints in the family of binary systems of $C_4F_{10} + n$-alkanes plotted versus the carbon number $n$ of the $n$-alkane. Solid curve: regression of the calculated results according to Fig 9.18; dashed curve: regression of the experimental results (presented in Chapter 7).

Fig. 9.20. (a) $P, T, x$ plot of the monovariant equilibria for the binary system of $C_4F_{10} + n$-nonane (type II), calculated by the Peng-Robinson equation of state. Solid curves: pure component vapour pressure curves; dashed curves: critical curves; dashed-dotted curves: three-phase equilibrium curves; empty circles: critical points of the pure components; up solid triangle: UCEP [$L_2 = L_1 - V$].
Fig. 9.20 (b) $P,T$ projection.

Fig. 9.20 (c) $T,x$ projection.
Fig. 9.20 (d) P,x projection.

Fig. 9.21 (a) P,T,x plot of the monovariant equilibria for the quasi-binary system of $C_4F_{10} +$ pseudo-n-alkane of carbon number $n=10.5$ (type IV), calculated by the Peng-Robinson equation of state. Solid curves: pure component vapour pressure curves; dashed curves: critical curves; dashed-dotted curves: three-phase equilibrium curves; empty circles: critical points of the pure components; up solid triangle: UCEP [$L_2=L_1-V$]; down solid triangle: LCEP [$L_2=L_1-V$]; up empty triangle: UCEP [$L_2-L_1=V$].
Fig. 9.21 (b) P,T projection.

Fig. 9.21 (c) T,x projection.
Fig. 9.21 (d) P,x projection.

Fig. 9.22 (a) P,T,x plot of the monovariant equilibria for the binary system of C₄F₁₀ + n-decane (type III), calculated by the Peng-Robinson equation of state. Solid curves: pure component vapour pressure curves; dashed curves: critical curves; dashed-dotted curves: three-phase equilibrium curves; empty circles: critical points of the pure components; up empty triangle: UCEP [L₂-L₁=V].
Fig. 9.22 (b) $P,T$ projection.

Fig. 9.22 (c) $T,x$ projection.
Fig. 9.22 (d) P,x projection.

Fig. 9.23 (a) P,T projection of the $L_2=L_1/L_2=V$ critical curves for the binary system of $C_4F_{10} + n$-undecane for different values of the binary interaction parameter $l$. All the above systems exhibit phase behaviour of type III. Solid curves: vapour pressure curves of pure components; long-dashed curve: critical curve for $l=0.014$; medium-dashed curve: critical curve for $l=0.000$; short-dashed curve: critical curve for $l=-0.014$; empty circles: critical points of pure components. For all cases $k=0.122$. 
Fig. 9.23 (b) T,x projection.

Fig. 9.23 (c) P,x projection.
The bending of the L=V critical curve indicates the appearance of a TCP for a system with a slightly longer n-alkane. In Figs. 9.21.a, b, c, d the corresponding graphs for the quasi-binary system of C₄F₁₀ with the pseudo-n-alkane of carbon number 10.5 are given. This system exhibits type IV fluid phase behaviour. Finally the P,T,x plot and its three corresponding projections for the system of C₄F₁₀ + n-undecane are contained in Figs. 9.22.a, b, c, d. Here the behaviour is type III and the L₂=L₁/L₂=V critical line originating from the critical point of the less-volatile component forms a closed loop in the P,x projection.

9.6 The influence of the interaction parameter /

The influence of the k interaction parameter on the phase behaviour of a binary system is rather broadly examined in literature. Although the physical meaning of both interaction parameters k and l is very vague it is worthwhile to study their influence on the various features of fluid phase behaviour because this can reveal their connection with the actual intermolecular interactions. Here as an example the k parameter of a binary system is kept constant and the value of the l parameter is varied. The system C₄F₁₀ + n-undecane is chosen and we concentrate on the critical curve originating from the less-volatile component. Notice in Fig.9.23.a that as l is decreased, the L₂=L₁ part of the critical curve moves upwards and to the right in the P,T plot. The L₂=V part is hardly affected.

In Figs. 9.23.b and 9.23.c the same critical curves are depicted in a T,x and in a P,x projection respectively. As l is decreased the loop in the P,x projection shrinks. It can be said that if l decreases the system obtains progressively a more pronounced type III character. Finally in the T,x plot of Fig.9.24 the T,x projections of the three-phase L₂L₁V equilibrium curves for the different l values are depicted. When l decreases the L₁-V parabolic dome becomes narrower as the L₁ branch approaches the almost unchanged V branch. At the same time the L₂ branch moves to higher compositions creating a larger gap between the two liquid branches.

The influence of the value of the interaction parameter l on the L₂=L₁ temperature of the system C₄F₁₀ + n-nonane has been already examined in Table 9.5.

More sensitivity analyses have to be performed for other types of fluid phase behaviour and other kinds of pure components. The influence of the k and l parameters on the shape of critical curves, three-phase L₂L₁V equilibrium curves as well as binodal curves could then systematically be organized. The importance of such a work is relevant. It will provide a
guide for tuning $k$ and $l$ parameters in order to correlate experimental data instead of performing a blind mathematical optimization which may lead to multiple solutions inconsistent from system to system.

![Graph of T,x projection of the three-phase equilibrium curves for the binary system of C$_4$F$_{10}$ + n-undecane for different values of the binary interaction parameter l. All the above systems exhibit phase behaviour of type III. Alternatively-dashed curves: three-phase equilibria for l=0.014; dashed-triple-dotted curves: three-phase equilibria for l=0.000; dashed-dotted curves: three-phase equilibria for l=-0.014; up empty triangles: UCEP's [L$_2$-L$_1$=V]. For all cases k=0.122.]

9.7 Barotropic inversion point

The three branches V, L$_1$ and L$_2$ of the three-phase L$_2$L$_1$V equilibrium curve for the system C$_4$F$_{10}$ + n-undecane calculated with $k=0.122$ and $l=-0.014$ are projected on a T,x plane in Fig.9.25.a. At a certain temperature the molar volumes of the two liquid phases are equal, as it can be seen from the T,V projection in Fig.9.25.b (empty circle). At a higher temperature
the mass densities of the two liquid phases become equal, at the so-called barotropic inversion point (see Chapters 6 and 7), as it can be seen from the T,p projection in Fig.9.25.c (empty diamond). The calculated coordinates of the molar volume inversion point as well as of the mass density (barotropic) inversion point are collected in Table 9.7. The \( L_2 L_1 V \) BIP is predicted with an error around -2% for \( T \) and -12% for \( P \) compared with experimental data from Chapter 7.

### TABLE 9.7

Temperature, pressure and composition coordinates of the mass density inversion point (barotropic inversion point; BIP) and of the molar volume inversion point (MVIP) in the binary mixture of \( C_4F_{10} + C_{11} \).

<table>
<thead>
<tr>
<th></th>
<th>BIP</th>
<th>MVIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T/K )</td>
<td>401.17</td>
<td>377.50</td>
</tr>
<tr>
<td>( P/MPa )</td>
<td>2.491</td>
<td>1.673</td>
</tr>
<tr>
<td>( x(V) )</td>
<td>0.028035</td>
<td>0.010086</td>
</tr>
<tr>
<td>( x(L_1) )</td>
<td>0.137245</td>
<td>0.151154</td>
</tr>
<tr>
<td>( x(L_2) )</td>
<td>0.466486</td>
<td>0.518591</td>
</tr>
<tr>
<td>( V(V) / cm^3/mol )</td>
<td>606.06</td>
<td>1169.12</td>
</tr>
<tr>
<td>( V(L_1) / cm^3/mol )</td>
<td>249.58</td>
<td>212.91</td>
</tr>
<tr>
<td>( V(L_2) / cm^3/mol )</td>
<td>220.00</td>
<td>212.91</td>
</tr>
<tr>
<td>( \rho(V) / g/cm^3 )</td>
<td>0.389109</td>
<td>0.214553</td>
</tr>
<tr>
<td>( \rho(L_1) / g/cm^3 )</td>
<td>0.908670</td>
<td>1.062676</td>
</tr>
<tr>
<td>( \rho(L_2) / g/cm^3 )</td>
<td>0.908670</td>
<td>0.918933</td>
</tr>
</tbody>
</table>
Fig. 9.25 (a) T,x projection of the three-phase equilibrium curves for the binary system of $C_4F_{10} + n$-undecane for k = 0.122 and l = 0.014. Solid curve: V branch; dashed-dotted curve: $L_1$ branch; dashed curve: $L_2$ branch; up empty triangle: UCEP ($L_2$-$L_1$=$V$); empty diamond: mass density inversion point (barotropic inversion point); empty circle: molar volume inversion point.

Fig. 9.25 (b) T,V projection.
Fig. 9.25 (c) $T, \rho$ projection.

Fig. 9.26 $P,T$ projection of the monovariant equilibria for the binary system of $CO_2 + n$-tridecane. Dashed curves: critical loci; dashed-dotted curve: upper branch of the three-phase equilibria; horizontal dashed-triple-dotted curves: isobars; up empty triangle: UCEP [$L_2-L_1-V$]; down solid triangle: LCEP [$L_2-L_1-V$].
9.8 Some interesting cross-sections

In Fig. 9.26 the P,T projection of the critical curves and of the upper branch of the three-phase equilibrium curve for the system CO$_2$ + n-tridecane are plotted. The critical branch at lower temperature is the L$_2$=L$_1$ locus originating from the UCEP [L$_2$=L$_1$-V], which moves steeply to high pressures. The high T branch of the L$_2$L$_1$V curve is found between 310 and 315 K. The L$_1$=V curve connects the CO$_2$ critical point and the UCEP [L$_2$-L$_1$=V]. The L$_2$=L$_1$/L$_2$=V curve starts at the LCEP [L$_2$=L$_1$-V] and goes to the critical point of n-tridecane.

In Figs. 9.27.a and 9.27.b four isobars for this system are shown in a T,x plot. Fig. 9.27.a zooms in on the three-phase L$_2$L$_1$V equilibria and Fig. 9.27.b zooms in on the L$_2$=V area. Notice the shrinking of the L$_2$+V area with increasing pressure.

In Fig. 9.28.a an isopleth (x=0.05) for the system CO$_2$ + n-tridecane is shown. Notice in the enlargements of Figs. 9.28.b and 9.28.c the very narrow two-phase strips between the three-phase L$_2$L$_1$V equilibrium curve and the binodal borders above that. Especially the L$_1$+V area in Fig. 9.28.b is so narrow that it is very difficult to observe in an experiment. This illustrates that sometimes calculations can provide qualitative information, which is very hard to be obtained from experiment.

In Fig. 9.29 an isothermal P,x plot for the binary system CO$_2$ + n-dodecane is given. The temperature is lower than the temperature of the UCEP [L$_2$=L$_1$-V]. The L$_2$+L$_1$ two-phase region widens with increasing pressure, reflecting the positive slope of the L$_2$=L$_1$ critical curve. Fig. 9.30 shows an isothermal P,x plot for the binary system CO$_2$ + n-tetradecane at a temperature between the temperature of the LCEP [L$_2$=L$_1$-V] and the critical temperature of CO$_2$. This diagram shows the rather peculiar shape of the L$_1$+V region at temperatures close to the critical temperature of CO$_2$.

The last isothermal plot refers to the system C$_4$F$_{10}$ + methanol and it is of special interest because it corresponds with the case of heteroazeotropy (see Chapter 8). As we can see from Fig. 9.31 the three-phase equilibrium pressure is above the vapour pressure of both pure components. Another characteristic feature of this type of phase behaviour is that the composition of the vapour phase at the three-phase L$_2$L$_1$V equilibrium is between the compositions of the phases L$_2$ and L$_1$. 
Fig. 9.27 (a) *T,x* isobaric sections at pressures indicated in Fig. 9.26, around the region of the three-phase equilibria. Long-dashed curves: binodal curves for $P/MPa=8.0$; medium-dashed curves: binodal curves for $P/MPa=8.2$; solid curves: binodal curves for $P/MPa=8.5$; short-dashed curves: binodal curves for $P/MPa=9.0$; dashed-dotted curves: three-phase equilibria; empty circles: critical points.

Fig. 9.27 (b) *T,x* isobaric sections at pressures indicated in Fig. 9.26, around the region of the $L_2=V$ critical points.
Fig. 9.28.a P,T isopleth (constant overall composition plot) for the binary system of CO$_2$ + n-tridecane at $x=0.05$. Solid curves: binodals; dashed-dotted curves: three-phase equilibrium curves; up solid triangle: UCEP [L$_2$=L$_1$+V]; down solid triangle: LCEP [L$_2$=L$_1$-V]; up empty triangle: UCEP [L$_2$-L$_1$=V].

Fig. 9.28.b Enlargement of Fig. 9.28.a around the region of the lower three-phase equilibrium branch.
Fig. 9.28c Enlargement of Fig. 9.28a around the region of the upper three-phase equilibrium branch.

Fig. 9.29 Isothermal P,x plot for the binary system of CO₂ + n-dodecane at T/K = 265. Solid curves: binodals; dashed-dotted curve: three-phase equilibrium pressure; solid circle: n-dodecane saturation pressure.
Fig. 9.30  \( P_x \) isothermal plot for the binary system of \( \text{CO}_2 + \text{n-tetradecane} \) at \( T/K = 303 \). Solid curves: binodals; dashed-dotted curve: three-phase equilibrium pressure; solid circle: \( \text{n-tetradecane} \) saturation pressure; open circle: \( L_2 = L_1 \) critical point.

Fig. 9.31  \( P_x \) isothermal plot for the binary system of \( \text{C}_7\text{H}_{16} + \text{methanol} \) at \( T/K = 380 \) showing heterogeneous. Solid curves: binodals; dashed-dotted curve: three-phase equilibrium pressure.
9.9 Conclusions

The large variety of the calculated diagrams in this Chapter offer a good guide for the complex fluid phase behaviour that may be encountered in binary and quasi-binary systems. These calculated diagrams also show that the algorithm we developed to calculate fluid phase equilibria (Chapter 3) is also able to deal with rather subtle effects, which can easily lead to convergence problems using conventional methods for the calculation of fluid phase equilibria. Some qualitative features revealed by the calculations cannot be observed easily by experiment, because they are located in very narrow ranges of conditions or they occur at extreme values of composition, temperature or pressure. Therefore it can be useful to perform calculations before starting an experiment. Not only someone can save time and money but also he can be guided to look for new phenomena predicted by the calculations.

On the other hand the models we used cannot represent quantitatively the experimental results. Probably more realistic models have to be used (other equations of state, other mixing rules for the interaction parameters etc.), but this was not the goal of this work.

Symbols

1 more-volatile component
2 less-volatile component
DCEP double critical endpoint
$L_1$ liquid phase having smaller $x$
$L_2$ liquid phase having greater $x$
$L_{2L_1V}$ liquid-liquid-vapour equilibrium
$L_{2L_1V}$ BIP liquid-liquid-vapour barotropic inversion point
LCEP lower critical endpoint
n carbon number
P pressure
T temperature
TCP tricritical point
UCEP upper critical endpoint
V vapour phase
V \quad \text{molar volume}

x \quad \text{mole fraction of the less-volatile component 2}

\rho \quad \text{mass density}

\omega \quad \text{acentric factor}

\textbf{References}

10. EMPIRICAL CORRELATIONS

As was discussed in Chapters 2 and 9 the classification schemes based on an equation of state approach are only in qualitative agreement with the experimental results presented in Chapters 4, 6, 7 and 8. It was shown that a variety of phenomena was reproduced by Peng-Robinson equation if state but the results depended heavily on artificially adjusted parameters. Unfortunately these parameters are hardly correlated with the nature of the individual components and the characteristic interactions between the constituents of a mixture.

A more empirical approach based on the concept of the solubility parameter was used by Davenport and Rowlinson (1963) for the characterization of systems of methane + hydrocarbons. In this chapter the concept of the effective carbon number is introduced. In this way, next to the size, also the shape and the polarity of the molecule of the less-volatile component in a binary system is taken into account.

The carbon number of the less-volatile component where the transition from type II to type IV occurs (tricritical point) depends on the nature of the more-volatile component. In this chapter the discussion is restricted only to the influence of the size of the more-volatile component.

The extent of the intermediate type IV zone depends also on the nature of the more-volatile component but not in a straightforward manner. The acentric factor of that component is tried as a correlation parameter. The possibilities for the occurrence of a so-called van Laar point, i.e a direct transition from type II to type III without an intermediate type IV phase behaviour, are discussed on the basis of experimental data.

10.1 Review of existing work. Theoretical: equation of state parameters, semi-empirical: solubility parameter

In Chapter 2 the classification schemes according to equation of state predictions were discussed. The first work of this kind was performed by van Konynenburg (1968) and it was based on the van der Waals equation of state. His results were organized in classification charts like those of Figs. 2.10 and 2.11. In these charts the domains of different types of fluid phase equilibrium are separated by transition loci. For example the locus of tricritical points (TCP's) separates the type II region from the type IV region and the locus of double critical endpoints (DCEP's) separates the type IV region from type III region.
Fig. 10.1 The domains of various types of fluid phase equilibria in binary systems (components 1, 2), according to calculations by means of the van der Waals equation of state and the TCP's (empty squares) and DCEP's (solid circles) of several families of binary systems according to Table 10.1. Solid curve: locus of binary mixtures exhibiting a TCP behaviour; dashed-dotted curve: locus of binary mixtures exhibiting a DCEP behaviour; dashed curve: locus of the geometric mean condition, i.e. the locus where the parameter \( k \) in Eq.(2.4) is zero. The geometric mean condition is expressed as \( (1-\lambda)^2 = (1-\zeta)^2 \). The relative size \( \zeta \) of the components 1, 2 is assumed to be constant. Along the diagonals (dotted curves) the conditions \( a_{12} = a_{11} \) and \( a_{12} = a_{22} \) hold. The diagonals are the limits of azeotropy.

Fig. 10.2 The domains of various types of fluid phase equilibria in binary mixtures (components 1, 2), according to calculations by means of the van der Waals equation of state and the TCP's (empty squares) and DCEP's (solid circles) of several families of binary systems according to Table 10.1. Solid curve: locus of binary mixtures exhibiting a TCP behaviour; dashed-dotted curve: locus of binary mixtures exhibiting a DCEP behaviour. The geometric mean condition holds for this diagram.
**TABLE 10.1**

*Fluid phase behaviour of binary families of solvents + n-alkanes: carbon number and \( \zeta \), \( \lambda \), \( \xi \) parameters for the TCP and the DCEP using \( a_{12} = \sqrt{a_{11} a_{22}} (k_{12} = 0) \)*

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TCP</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3F_8 )</td>
<td>8.428</td>
<td>0.5161</td>
<td>0.1434</td>
<td>0.3019</td>
</tr>
<tr>
<td>( C_2H_3F_3 )</td>
<td>11.65</td>
<td>0.7578</td>
<td>0.3475</td>
<td>0.5881</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>12.33</td>
<td>0.9060</td>
<td>0.5766</td>
<td>0.8053</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>17.58</td>
<td>0.9214</td>
<td>0.6113</td>
<td>0.8193</td>
</tr>
<tr>
<td>( N_2O )</td>
<td>17.73</td>
<td>0.9457</td>
<td>0.6749</td>
<td>0.8744</td>
</tr>
<tr>
<td>( NH_3 )</td>
<td>18.00</td>
<td>0.9423</td>
<td>0.6651</td>
<td>0.8963</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DCEP</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3F_8 )</td>
<td>8.473</td>
<td>0.5190</td>
<td>0.1452</td>
<td>0.3047</td>
</tr>
<tr>
<td>( C_2H_3F_3 )</td>
<td>12.13</td>
<td>0.7715</td>
<td>0.3637</td>
<td>0.6049</td>
</tr>
<tr>
<td>( CO_2 )</td>
<td>13.55</td>
<td>0.9191</td>
<td>0.6059</td>
<td>0.8264</td>
</tr>
<tr>
<td>( C_2H_6 )</td>
<td>42</td>
<td>0.9818</td>
<td>0.8102</td>
<td>0.9480</td>
</tr>
<tr>
<td>( N_2O )</td>
<td>24.61</td>
<td>0.9653</td>
<td>0.7389</td>
<td>0.9120</td>
</tr>
<tr>
<td>( NH_3 )</td>
<td>18.35</td>
<td>0.9442</td>
<td>0.6706</td>
<td>0.8991</td>
</tr>
</tbody>
</table>
In Fig.10.1 a part of Fig.2.10, and in Fig.10.2 a part of Fig.2.11 are reproduced. The parameters $\zeta$, $\lambda$, and $\xi$ are defined by

$$\zeta = \frac{a_{22} - a_{11}}{a_{22} + a_{11}}, \quad \lambda = \frac{a_{22} - 2a_{12} + a_{11}}{a_{22} + a_{11}} \quad \text{and} \quad \xi = \frac{b_{22} - b_{11}}{b_{22} + b_{11}}$$

(10.1)

The empty squares represent experimental TCP's and the solid circles represent experimental DCEP's for several families of binary systems of solvents $+ n$-alkanes, discussed in Chapter 4. In Table 10.1 the corresponding data are given. Notice that the deviations from the predictions are rather large. The cross parameter $a_{12}$ was calculated using the geometric mean rule of Eq.(2.4), where the a and b parameters for the pure components were calculated from Eq.(2.2). The solvent $T_c$ and $P_c$ values were taken from Reid et al. (1988), while for the critical properties of the $n$-alkanes the following relationships were used

$$\ln(959.98 - T_c) = 6.81536 - 0.211145 \frac{n^2}{3}$$

(10.2)

$$\ln(P_c) = 2.01718 - 0.274281 \frac{n^2}{3} \quad \text{for } n \leq 20$$

(10.3)

$$\ln(10 \times P_c) = 4.3398 - 0.3155 n^{0.6032} \quad \text{for } n > 20$$

(10.4)

In Eqs. (10.2), (10.3) and (10.4) $T_c$ is in K and $P_c$ is in MPa. Eqs. (10.2) and (10.3) are proposed by Tsonopoulos (1987) and Eq.(10.4) is a modification of Eq.(10.3) proposed by Magoulas and Tassiou (1990).

Figs. 10.1 and 10.2 show large deviations between predictions and experiments. The calculated curves in Fig.10.1 are based on two assumptions. The first assumption is that the parameter $\xi$ is equal to 0, which means that the molecules in the binary mixture have equal size. For our experimental TCP's and DCEP's this is far from true, which explains partly the poor agreement between experimental and predicted points. The second assumption is that the geometric mean rule for the evaluation of the parameter $a_{12}$ was adopted, or in other words a $k=0$ in Eq.(2.4) was used. The parameter $\lambda$ in Eq.(10.1) is linearly dependent on $k$ parameter. Therefore if a value of $k$ different from 0 is used, then the TCP's and DCEP's in Fig.10.1 are vertically shifted. The selection of $k=0$ is not a strong reason for the poor agreement between experimental and predicted points because the experimental points can be
vertically shifted for a different value of $k$ without coinciding with the theoretical loci of TCP’s or DCEP’s. The $C_3F_8 + n$-alkanes family is an exception to the above.

In Fig. 10.2 the same experimental points are plotted in $\zeta$, $\xi$ coordinates. The theoretical loci are calculated with $\lambda$ values obtained using the geometric mean rule for $a_{12}$. The deviations between prediction and experiment are again large. It can be concluded that the two-parameter van der Waals equation of state is not adequate for a quantitative representation of the complex binary mixture behaviour found in real systems.

In Fig. 10.3 the experimental TCP’s and DCEP’s are plotted in the three dimensional $\zeta, \lambda, \xi$ space. The locus of TCP’s and the locus of DCEP’s are generally located along the diagonal from small $\zeta, \lambda, \xi$ towards large $\zeta, \lambda, \xi$.

Another way of classification can be based on the idea of a characteristic parameter for the less-volatile component, if the more-volatile component of the binary system is fixed. For example in the family $CO_2 + n$-alkanes the carbon number of the $n$-alkane is such a parameter. Using this parameter as independent variable we can correlate several characteristic quantities of the binary mixture behaviour from member to member in the family. For instance if we consider the temperatures or the pressures of the critical endpoints then we can construct the familiar type of diagrams depicted in Figs. 4.1.a and 4.1.b. But what we can do for the systems of $CH_4 +$ hydrocarbons, discussed in Chapter 4? This set of systems is not a family in the same sense as the set of systems $CH_4 + n$-alkanes. The phase behaviour of binary systems of $CH_4$ with different $C_6$ hydrocarbons, as discussed in Chapter 4, cannot be classified using the carbon number of the hydrocarbon. The system of $CH_4$ with the 9 different $C_6$ hydrocarbons show very different fluid phase behaviour (see Table 10.2). Davenport and Rowlinson (1963) and van Konynenburg in his thesis (1968) suggested to use the solubility parameter as the characteristic parameter for the less-volatile component. According to the regular solution theory (Hildebrand and Scott, 1950), the solubility parameter $\delta$ for a pure component is defined as

$$
\delta = (c)^{\frac{1}{2}} = \left( \frac{\Delta U}{\nu^2} \right)^{\frac{1}{2}}
$$  \hspace{1cm} (10.5)

where $\nu$ is the cohesive energy density of the pure liquid state, $\Delta U$ is the required energy for the isothermal evaporation of the saturated liquid to the ideal gas state and $\nu^t$ is the molar volume of the liquid. At temperatures far below the critical
$\Delta U = \Delta H^V - RT$ \hfill (10.6)

where $\Delta H^V$ is the molar enthalpy of vaporization of the pure liquid at temperature $T$.

Van Konynenburg (1968) calculated $\delta$ parameter values according to Eq.(10.5) with data from API (ed. 1953). These data are not mentioned explicitly in his thesis. The $\delta$ parameters in this chapter (see Table 10.2) are estimated according to the generalized correlation of Lyckman et al., (1965)

$$\frac{\delta}{P_c^2} = \delta_r^{(0)} + \omega \delta_r^{(1)} + \omega^2 \delta_r^{(2)}$$ \hfill (10.7)

with

$$\ln \delta_r^{(0)} = -0.104423 + 1.02489 T_r - 1.4406 T_r^2 \quad T_r \geq 0.5$$

$$\ln \delta_r^{(0)} = 0.25752 - 0.4157 T_r \quad T_r < 0.5$$

$$\ln \delta_r^{(1)} = 1.34055 - 2.13473 T_r$$

$$\ln \delta_r^{(2)} = 1.51291 + 4.38252 T_r^2 \quad T_r < 0.5$$

$$\ln \delta_r^{(2)} = -4.503624 + 11.96286 T_r - 7.580341 T_r^2 \quad 0.5 \leq T_r \leq 0.7891$$

$$\delta_r^{(2)} = 0.216095 \quad T_r > 0.7891$$ \hfill (10.8)

In Eq.(10.7) $\delta$ is in (cal/cm$^3$)$^{1/2}$ and $P_c$ is in atm. $\delta$ parameters for the solutes of the CH$_4$ + hydrocarbons systems, calculated from Eq.(10.7), are given in Table 10.2 together with the graphical reproduction of some calculated values by Van Konynenburg (1968). $T_c$ and $P_c$ of the hydrocarbons were taken from Reid et al. (1988).

In Fig.10.4 the CEP temperatures of these systems are plotted against the solubility parameters $\delta$ of the solutes calculated from Eq.(10.7). We see that the familiar shape of Fig.4.1.a is found for C$_5$+C$_6$ systems and for C$_1$+C$_7$ systems. The DCEP is located at the highest value of $\delta$ where a [L$_2$=L$_1$-V] equilibrium can be observed.

From the good fit of the regression curve in Fig.10.4 it is concluded that $\delta$ is a good parameter for the characterization of CH$_4$ + hydrocarbons systems instead of the carbon number parameter $n$, which is inadequate in this case.
**Table 10.2**

Fluid phase behaviour of methane + hydrocarbon systems: critical endpoint temperatures for different C₆ and C₇ hydrocarbons with given solubility parameter at 298 K

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>n</th>
<th>UCEP [L₂=L₁-V] in K</th>
<th>LCEP [L₂=L₁-V] in K</th>
<th>δ (J/cm³)⁰.⁵ or (MPa)⁰.⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-dimethyl-butane</td>
<td>6</td>
<td>195.5</td>
<td></td>
<td>14.27</td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td>6</td>
<td>120.4</td>
<td>190.5</td>
<td>14.22</td>
</tr>
<tr>
<td>trans-4-methyl-2-pentene</td>
<td>6</td>
<td></td>
<td>188.7</td>
<td>14.46</td>
</tr>
<tr>
<td>2-methyl-1-pentene</td>
<td>6</td>
<td>141.7</td>
<td>176.3</td>
<td>15.03¹</td>
</tr>
<tr>
<td>2-methyl-pentane</td>
<td>6</td>
<td></td>
<td>194.7</td>
<td>14.31</td>
</tr>
<tr>
<td>4-methyl-1-pentene</td>
<td>6</td>
<td>196.2</td>
<td></td>
<td>14.34¹</td>
</tr>
<tr>
<td>3-methyl-pentane</td>
<td>6</td>
<td>188.5</td>
<td></td>
<td>14.61</td>
</tr>
<tr>
<td>n-hexane</td>
<td>6</td>
<td>182.6</td>
<td></td>
<td>14.70</td>
</tr>
<tr>
<td>1-hexene</td>
<td>6</td>
<td>134.6</td>
<td>179.6</td>
<td>14.87</td>
</tr>
<tr>
<td>2,2-dimethyl-pentane</td>
<td>7</td>
<td></td>
<td>184.4</td>
<td>14.14</td>
</tr>
<tr>
<td>3,3-dimethyl-pentane</td>
<td>7</td>
<td>124.3</td>
<td>169.0</td>
<td>14.55</td>
</tr>
<tr>
<td>2,4-dimethyl-pentane</td>
<td>7</td>
<td></td>
<td>182.5</td>
<td>14.22</td>
</tr>
<tr>
<td>2,2,4-trimethyl-pentane</td>
<td>8</td>
<td>171.8</td>
<td></td>
<td>14.05</td>
</tr>
</tbody>
</table>

¹ estimated by graphical methods from Fig.V-11 of Van Konynenburg thesis (1968).
Fig. 10.3 The TCP's (empty squares) and DCEP's (solid circles) of several families of binary systems plotted in a $\zeta, \lambda, \xi$ system of coordinates according to Table 10.1.

Fig. 10.4 Critical endpoint temperatures in binary systems of methane (CH$_4$) with hydrocarbons as a function of the solubility parameter of the hydrocarbon at 298 K (see Table 10.2). Down solid triangles: LCEP's [L-L-V]; up solid triangles: UCEP's [L-L-V]; (1): 2,3-dimethyl-butane; (2): 4-methyl-1-pentene; (3): 2-methyl-pentane; (4) and (13): 2,3-dimethyl-1-butene; (5): 3-methyl-pentane; (6): trans-4-methyl-2-pentene; (7): n-hexane; (8) and (12): 1-hexene; (9) and (11): 2-methyl-1-pentene; (10): estimated DCEP for hydrocarbons with 6 carbon atoms; (14): 2,2-dimethyl-pentane; (15): 2,4-dimethyl-pentane; (16) and (18): 3,3-dimethyl-pentane; (17): estimated DCEP for hydrocarbons with 7 carbon atoms; (19): 2,2,4-trimethyl-pentane. Solid line: a third order regression polynomial of $\delta$ as a function of $T$ for the systems with hydrocarbons with 6 carbon atoms; dashed line: a second order regression polynomial of $\delta$ as a function of $T$ for the systems with hydrocarbons with 7 carbon atoms.
10.2 The effect of the shape of alkanes on their binary mixture behaviour with perfluoropropane (Randić topological index)

As discussed above, the carbon number is not a useful parameter for characterizing the less-volatile component of a binary system except for families of the type solvent + n-alkanes. For the characterization of CH₄ + hydrocarbons systems δ was a good parameter, but still C₆'s and C₇'s were located along different curves. Searching for a more general parameter, we investigated the use of a parameter which reflects closer the geometry of the molecule of the less-volatile component. The Randić molecular-connectivity index (RI) discussed by Rouvray (1986) in a paper dealing with predictions of chemistry from topology was tried and found rather successful. In this approach a molecule is treated as an assembly of vertexes (segments) linked by edges (bonds). Each vertex has a "degree": the number of other vertexes it is linked to. Similarly each edge has a "value": the product of the reciprocals of the square roots of the "degrees" of the vertexes it joins. The RI of a molecule is equal to the sum of the "values" of all the molecule's edges. In Fig.10.5 the structure of several molecules and the procedure of calculating their RI is explained. Notice that in the present context we deal only with hydrocarbon molecules.

![Diagram of molecular connectivity index](image)

Fig. 10.5. The procedure to calculate the Randić molecular-connectivity index of a molecule and the values of RI for some hydrocarbon molecules of interest in this work.

\[
\begin{align*}
\text{RI} &= a + b + c + d = 2.269 \\
\text{RI} &= 2,2,4\text{-trimethyl-hexane, RI} = 3.955 \\
\text{RI} &= 2\text{-methyl-octane, RI} = 4.270 \\
\text{RI} &= \text{n-nonane, RI} = 4.414
\end{align*}
\]
For a n-alkane with carbon number \( n \), its Randić index \( RI \), according to the above definition, is

\[
RI = (n-3) \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} + 2 \frac{1}{\sqrt{2}} \frac{1}{\sqrt{1}} = \frac{1}{2} (n+2 \sqrt{2} - 3) \quad \text{for} \ n \geq 3
\]  

(10.9)

Inversely, if for a n-alkane its RI is known, then its carbon number \( n \) is given by

\[
n = 2RI + 3 - 2\sqrt{2} \quad \text{for} \ RI \geq \sqrt{2}
\]  

(10.10)

Using Eq.(10.10) for branched alkanes we can determine an effective carbon number, \( n_{\text{eff}} \), for these alkanes and assume that the properties of the branched alkane are the same as the properties of an n-alkane with carbon number \( n_{\text{eff}} \). For 2,2,4-trimethyl-hexane we estimate a \( n_{\text{eff}} \) of 8.08 (RI=3.955) and for 2-methyl-octane we estimate an \( n_{\text{eff}} \) of 8.71 (RI=4.270). According to experimental data from de Loos et al. (1993b) 2,2,4-trimethyl-hexane should have a \( n_{\text{eff}} \) of 6.96 and 2-methyl-octane should have a \( n_{\text{eff}} \) of 8.29 in order to give the same temperatures of UCEP's \( [L_2=L_1-V] \) as the corresponding pseudo-n-alkanes. Therefore it can be concluded that Eq.(10.10) overpredicts \( n_{\text{eff}} \) in these two cases with errors of 16% and 5%, respectively.

To account for this overprediction, for branched molecules a perturbation around the n-alkanes formula of Eq.(10.10) can be built on the basis of experimental data. Let \( n \) and \( RI \) be the real carbon number and the Randić index of any molecule, e.g. for 2,2,4-trimethyl-hexane, \( n=9 \) and \( RI=3.955 \). The carbon number \( n^* \) of a n-alkane which corresponds to RI is given by Eq.(10.10) and the Randić index \( RI^* \) of a n-alkane which has carbon number \( n \) is given by Eq.(10.9). The effective carbon number of the molecule, \( n_{\text{eff}} \), will be given by a perturbation of the form

\[
n_{\text{eff}} = n^* + C_1 [RI-RI^*] + C_2 [RI-RI^*]^2 + ...
\]  

(10.11)

where the parameters \( C_1, C_2, ... \) can be fitted to represent experimental data.

Using data from Hicks et al. (1978) for binary systems of perfluoroalkanes with various linear and branched alkanes (all these systems exhibit type II fluid phase behaviour), we evaluate the perturbation of Eq.(10.11) truncated after the first linear term. The optimum value for the parameter \( C_1 \) is 1.8 (± 0.7). Substituting \( RI^* \) and \( n^* \) from Eqs.(10.9) and (10.10) respectively as well as the optimum value of \( C_1 \) in the truncated form of Eq.(10.11) we obtain finally the following approximate empirical correlation.
\[ n_{\text{eff}} = 3.8 \text{RI} - 0.9 \, n + 0.327 \]  
(10.12)

Using Eq.(10.12) we estimate the \( n_{\text{eff}} \) of 2,2,4-trimethyl-hexane to be 7.25 and the \( n_{\text{eff}} \) of 2-methyl-octane to be 8.45. Eq.(10.12) overpredicts, as Eq.(10.10) also does, the \( n_{\text{eff}} \) of 2,2,4-trimethyl-hexane and 2-methyl-octane (see experimental data from de Loos et al., 1993b), with errors of 4.2% and 1.9%, respectively. This can be ascribed to two factors:

First the correlation was constructed on the basis of data for perfluoroalkanes from perfluoropropane until perfluoroheptane and for branched alkanes with real carbon number \( n \) from 4 to 8. Consequently the application in our case is affected by the dangers of extrapolation.

Secondly the experimental points correlated by Eq.(10.11) were rather dispersed, for instance 2,2,4-trimethyl-pentane should have an \( n_{\text{eff}} \) of 5.7 in its mixture with perfluoropropane and an \( n_{\text{eff}} \) of 7.0 in its mixture with perfluoroheptane, so the correlation was poor from a statistical point of view. The regression coefficient \( R^2 \) was only 0.30 and as we mentioned before \( C_1 \) has a big uncertainty, \( C_1 = 1.8 \pm 0.7 \). Also \( (n_{\text{eff}}-n^*) = C_1 (\text{RI-RI}^*) \pm 0.66 \) which is also a large uncertainty.

10.3 The combined effect of the size, the shape and the polarity of alkanols on the phase behaviour of systems of alkanols with perfluoropropane or perfluorobutane

In Fig.10.6 the temperature of the UCEP [\( L_2-L_1=V \)] of the binary systems \( C_3F_8 + n \)-alkanes and \( C_3F_8 + n \)-alkanols is plotted against the carbon number \( n \) of the less-volatile component. The temperature of the UCEP for systems with \( n \)-alkanols are always lower than the temperature of the UCEP for systems with \( n \)-alkanes with the same value of \( n \). If the curve for \( n \)-alkanes is extrapolated to higher carbon numbers and lower temperatures, then we can define an effective carbon number \( n_{\text{eff}} \) of an \( n \)-alkanol as the carbon number of an \( n \)-alkane that has the same UCEP temperature as the alkanol. The \( n_{\text{eff}} \) of \( n \)-alkanes is of course the carbon number \( n \), while the \( n_{\text{eff}} \) for the \( n \)-alkanols has to be assigned values from 14.5 till 16; see Fig.10.7.

The relationship of the two carbon numbers \( n_{\text{eff}} \) and \( n \) for \( n \)-alkanols in systems with \( C_3F_8 \) is depicted in Fig.10.8, where also the corresponding relationship for \( n \)-alkanols in systems with \( C_4F_{10} \) is included. The points, which are based on experimental data, are correlated with a formula of the type
\[ n_{\text{eff}} = c_1 + c_2 \frac{n}{n} + c_3 \quad (10.13) \]

where the parameters \(c_1\), \(c_2\), \(c_3\) can be fitted with a least squares technique. The structure of Eq.(10.13) suggests that for large values of \(n\) the second term of Eq.(10.13) is more eminent (increase of the size of the molecule increases its \(n_{\text{eff}}\)), while for small values of \(n\) the principal term is the third one (decrease of the size of the molecule increases its polarity and hence increases its \(n_{\text{eff}}\)). For the binary systems of \(n\)-alkanols with \(C_3F_8\) Eq.(10.13) becomes

\[ n_{\text{eff}} = 13.187 + 0.217 \frac{n}{n} + 2.596 \quad (10.14) \]

and for the binary systems of \(n\)-alkanols with \(C_4F_{10}\) Eq.(10.13) becomes

\[ n_{\text{eff}} = 12.479 + 0.188 \frac{n}{n} + 3.018 \quad (10.15) \]

It should be noted that the empirical formulae of Eqs. (10.14) and (10.15) were developed with as a criterion a smooth sequence for the temperatures of the UCEP's of the binary systems of \(C_3F_8\) or \(C_4F_{10}\) + \(n\)-alkanes or \(n\)-alkanols. If instead of the temperature of the UCEP the pressure of the UCEP is used, then other values of \(c_1\), \(c_2\), \(c_3\) in Eq.(10.13) are obtained. Eq.(10.14) has a minimum \(n_{\text{eff}}\) equal to 14.7 for \(n=3.46\), while Eq.(10.15) has a minimum \(n_{\text{eff}}=14.0\) for \(n=4.00\).

Using Eq.(10.14) we account for the combined effect of the size and the polarity of a \(n\)-alkanol molecule on the phase behaviour of binary systems with \(C_3F_8\) (in this case we deal with the effect of size and polarity on the UCEP \([L_2-L_1=V]\) temperature). Using the data for the system \(C_3F_8 + i-C_3OH\) and for the systems \(C_3F_8 + i-C_4OH\), \(C_3F_8 + s-C_4OH\), \(C_3F_8 + t-C_4OH\), also the effect of shape can be incorporated. This influence can be large. Note that for the system \(C_3F_8 + t-C_4OH\) the UCEP \([L_2-L_1=V]\) is 14 K higher in \(T\) than the UCEP \([L_2-L_1=V]\) of the system \(C_3F_8 + n-C_4OH\). For these molecules a shape effective carbon number \((n'_{\text{eff}})\) can be established, in which the branching effect is also taken into account. In order to characterize the shape of the alkanol molecule we follow the topological index approach discussed in a previous section of this chapter.
Figs. 10.6 (up) and 10.7 (down). UCEP's \([L_2-L_1=V]\) for the binary systems of \(C_3F_8 + n\)-alkanes (symbolized by up empty triangles) and \(C_3F_8 + n\)-alkanols (symbolized by empty circles) against the actual carbon number \(n\) (Fig. 10.6) or the effective carbon number \(n_{eff}\) (Fig. 10.7) of the less-volatile component (see text).
Fig. 10.8. Relationship of the effective carbon number \( (n_{\text{eff}}) \) of \( n \)-alkanols against the actual carbon number \( (n) \). Empty circles: \( n \)-alkanols in binary systems with \( C_3F_8 \), empty squares: \( n \)-alkanols in binary systems with \( C_4F_{10} \).

Fig. 10.9. UCEP’s [\( L_2-L_1=V \)] for binary systems of \( C_3F_8 + n \)-alkanes (up empty triangles), \( C_3F_8 + n \)-alkanols (empty circles), and \( C_3F_8 + \) branched alkanols (down solid triangles) against the carbon number of the less-volatile component. \( (n) \) for \( n \)-alkanes, \( n_{\text{eff}} \) for \( n \)-alkanols and \( n'_{\text{eff}} \) for branched alkanols. The solid curve is constructed from empirical correlations (see text).
The definition of RI applies only to alkane molecules, but it can be easily extended to alkanol molecules. For an alkanol the hydroxyl-group is considered also as a vertex (like the CH₃, CH₂, CH, and C groups in the alkanes). The "degree" of the hydroxyl-vertex is taken to be k and not one (as it is suggested from the fact that the hydroxyl-vertex it is linked with one carbon vertex). The parameter k is fitted to the experimental data.

For a n-alkanol with carbon number n, its Randić index, RI, is

\[ RI = \frac{1}{\sqrt{1} \sqrt{2}} + (n-2) \frac{1}{\sqrt{2} \sqrt{2}} + \frac{1}{\sqrt{2} \sqrt{k}} = \frac{(n-2)}{2} + \frac{1}{\sqrt{2}} \left( 1 + \frac{1}{\sqrt{k}} \right) \quad \text{for} \ n \geq 2 \quad (10.16) \]

For the branched alkanols the \( n'_{\text{eff}} \) can be expressed as a perturbation around the \( n_{\text{eff}} \) of the corresponding (the same carbon number n) n-alkanols. As a perturbation variable the difference between the RI* of the branched alkanol and the RI of the corresponding n-alkanol is considered.

\[ n'_{\text{eff}} = n_{\text{eff}} + c_0 + c_1 \left[ RI^s - RI \right] + c_2 \left[ RI^s - RI \right]^2 + \ldots \quad (10.17) \]

where the parameters \( c_0, c_1, c_2, \ldots \) can be fitted to the experimental data.

Using the experimental data of Table 8.2 (temperatures of the UCEP's [L₂-L₁=V]) we evaluate the perturbation of Eq.(10.17) truncated after the first linear term. The optimum value for the parameter \( c_0 \) is 0.707 and for the parameter \( c_1 \) is 11.094. Also the optimum value for the "degree" k of the hydroxyl-vertex is 0.3. Substituting Eqs.(10.15) and (10.16) as well as the optimum values of \( c_0, c_1 \) and k in the truncated form of Eq.(10.17) we obtain finally the following approximate empirical correlation

\[ n'_{\text{eff}} = 2.821 + 11.094 \ RI - 5.330 \ n + \frac{2.596}{n} \quad (10.18) \]

The above correlation is applicable only for binary systems of C₃F₈ + branched alkanols. The application of Eq.(10.14) for the n-alkanols and of Eq.(10.18) for the branched alkanols results in the solid line of Fig.10.9. We see that the line is in a good agreement with the experimental data so at least it can serve as a good descriptive tool for our experimental results. It must be stressed however that the above empirical correlations are not recommended for extrapolation. They were evaluated mainly to show how a quantitative
treatment of the combined effect of size, polarity and shape of the alkanols on their binary system UCEP \([L_2-L_1=V]\) temperature could be performed.

10.4 The effect of the nature of the more-volatile component on the phase behaviour of binary systems of that component with n-alkanes

In Chapters 6 and 7 a transition scheme from type II, via type IV, towards type III fluid phase behaviour was reported for the families of the binary and quasi-binary systems of \(C_3F_8 + n\)-alkanes and \(C_4F_{10} + n\)-alkanes, respectively. The same transition scheme has been observed in several other families of binary systems of a more-volatile or gaseous component (solvent) and \(n\)-alkanes. Although the quasi-binary approximation was not applied to all of them, reasonable approximations of the positions of the TCP and DCEP can be made.

In our laboratory several families have been investigated by means of the quasi-binary approximation. For carbon dioxide and \(n\)-alkanes (de Loos et al., 1993a) the TCP was estimated at a carbon number \(n_{TCP}=12.330\) and a temperature \(T_{TCP}/K=317.5\), while the DCEP was located at \(n_{DCEP}=13.55\) and \(T_{DCEP}/K=296.0\). For perfluoropropane and \(n\)-alkanes (de Loos et al., 1993c) the TCP appeared at \(n_{TCP}=8.425\) and \(T_{TCP}/K=378.8\), while the DCEP was located at \(n_{DCEP}=8.47\) and \(T_{DCEP}/K=371.0\). Finally for 1,1,1-trifluoro-ethane and \(n\)-alkanes (de Loos et al., 1993d) the TCP was found at \(n_{TCP}=11.645\) and \(T_{TCP}/K=369.0\), while the DCEP was estimated at \(n_{DCEP}=12.126\) and \(T_{DCEP}/K=347.1\). For the TCP calculation the classical theory was used (see Chapters 6, 7). For the DCEP calculation a quadratic asymptotic approach to the DCEP was assumed and a parabola was fitted through the \([L_2=L_1=V]\) CEP's, as a function of carbon number.

Using these approximations (which by definition are only asymptotically valid) to determine the TCP and the DCEP, it was also possible to make reasonable estimations for the TCP and the DCEP in several other families where only binary system data were available. However more assumptions were necessary where the lack of data was severe. According to the work of Goh et al. (1987) the TCP in the family of ethane + \(n\)-alkanes (quasi-binary systems) is located at \(n_{TCP}=17.61\) and \(T_{TCP}/K=313.2\). From the paper of Estrera and Luks (1987) it was estimated that in the same family (only data for binary systems) the TCP is located at \(n_{TCP}=17.58\) and \(T_{TCP}/K=312.9\), while the DCEP is found by a rough extrapolation to be at \(n_{DCEP}\) around 42 and a temperature \(T_{DCEP}\) around 186 K. It can be seen that the classical theory approximation for TCP is rather good, when is applied to binary systems,
although it loses its asymptotic validity. From Jangkamolkulchai et al. (1989) information on the family of nitrous oxide and n-alkanes was obtained. The TCP appears at $n_{TCP}=17.73$ and $T_{TCP}/K=317.4$, while the DCEP is calculated by means of a rough extrapolation at $n_{DCEP}=24.6$ and $T_{DCEP}/K=275$. Finally from the work of Brunner (1988) it was found graphically that in the family of ammonia and n-alkanes the TCP is around a $n_{TCP}$ of 17.9 with a $T_{TCP}$ of 418 K, while the DCEP occurs around a $n_{DCEP}$ of 18.3 with a $T_{DCEP}$ of 409 K.

**TABLE 10.3**

*Fluid phase behaviour of binary families of solvents + n-alkanes: carbon number and temperature for TCP and DCEP*

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TCP</th>
<th>DCEP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>T/K</td>
</tr>
<tr>
<td>C₄F₁₀</td>
<td>10.647</td>
<td>420.8</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>8.425</td>
<td>378.8</td>
</tr>
<tr>
<td>NH₃</td>
<td>17.9</td>
<td>418</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.33</td>
<td>317.5</td>
</tr>
<tr>
<td>C₂H₃F₃</td>
<td>11.645</td>
<td>369.0</td>
</tr>
<tr>
<td>N₂O</td>
<td>17.73</td>
<td>317.4</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>17.61</td>
<td>313.2</td>
</tr>
</tbody>
</table>

The above estimates for TCP's and DCEP's are collected in Table 10.3. Some additional information on the carbon number of several other TCP’s was also collected from literature. From the paper of de Loos et al. (1989) a reasonable estimate for the TCP of the family of tetrafluoromethane and n-alkanes is $n_{TCP}=3.7$. Again from de Loos et al. (1993b) for the family of perfluoroethane and n-alkanes it is found that the TCP occurs at $n_{TCP}=6.1$. In the family of methane and n-alkanes according to the work of Creek et al. (1981) the TCP carbon number is $n_{TCP}=5.28$ and finally in the family of propane and n-alkanes (Peters et al., 1989) an estimate for the TCP carbon number is $n_{TCP}=29.5$. 
TABLE 10.4

 Fluid phase behaviour of binary families of solvents + n-alkanes: molecular weight of solvent and the carbon number of TCP

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \text{MW}_{\text{solvent}} )</th>
<th>( n_{\text{TCP}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₄</td>
<td>88.01</td>
<td>3.7</td>
</tr>
<tr>
<td>C₂F₆</td>
<td>138.01</td>
<td>6.1</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>188.02</td>
<td>8.425</td>
</tr>
<tr>
<td>C₄F₁₀</td>
<td>238.02</td>
<td>10.647</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.01</td>
<td>12.33</td>
</tr>
<tr>
<td>N₂O</td>
<td>44.01</td>
<td>17.73</td>
</tr>
<tr>
<td>C₂H₃F₃</td>
<td>84.04</td>
<td>11.645</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.04</td>
<td>5.28</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>30.07</td>
<td>17.61</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>44.09</td>
<td>29.5</td>
</tr>
</tbody>
</table>

In Table 10.4 the TCP carbon number \( n_{\text{TCP}} \) for several families of gaseous components (solvents) and n-alkanes is provided together with the molecular weight of the solvent (Reid et al., 1988). These data points are plotted in Fig.10.10. Several systematic patterns may be observed. All the families with a n-alkane as solvent lay on an almost straight line (dashed line), also found by Peters et al. (1989). The same is true for all the families with a perfluoroalkane as solvent (solid line). However the two lines have totally different slopes. A jump from member to member in the families n-alkanes + n-alkanes (the solvents are n-alkanes) causes a change of about \( \Delta n=12 \) in the TCP carbon number. The same jump in the families of perfluoroalkanes + n-alkanes (the solvents are perfluoroalkanes) causes a change of \( \Delta n=2.3 \) in the TCP carbon number, less than one fifth of the previous change. We can give no reasonable explanation for this effect.
Fig. 10.10. The carbon number $n$ of a pseudo-$n$-alkane which is suitable to give a TCP phase behaviour in a mixture with a certain solvent, versus the molecular weight of that solvent. solid curve: solvents of the type $C_mF_{2m+2}$ for $m=1,2,3,4$, dashed curve: solvents of the type $C_mH_{2m+2}$ for $m=1,2,3$, dotted curve: solvents of the type $C_2H_{6+3m}F_{3m}$ for $m=0,1,2$, up solid triangle: the solvent is $N_2O$, up empty triangle: the solvent is $CO_2$.

Another interesting point is that the 1,1,1-trifluoro-ethane + $n$-alkanes family, has a TCP carbon number which is almost the arithmetic mean of the TCP carbon numbers for the families of perfluoroethane + $n$-alkanes and ethane + $n$-alkanes (dotted line in Fig.10.10).

Finally we may observe the positions of the TCP's in the families of carbon dioxide + $n$-alkanes (up empty triangle) and nitrous oxide + $n$-alkanes (up solid triangle). Carbon dioxide and nitrous oxide have the same molecular weight and very similar critical properties. The critical temperature for carbon dioxide is 304.1 K while for nitrous oxide it is 309.6 K. The critical pressure for carbon dioxide is 7.38 MPa while for nitrous oxide it is 7.24 MPa (Reid et al., 1988). However the TCP carbon number in their families with $n$-alkanes differs by almost 5.5 units. In addition the type IV intermediate zone for the family of carbon dioxide + $n$-alkanes extends over a carbon number interval of $\Delta n=1.2$ and a temperature interval of $\Delta T/K=21.5$, while the type IV zone for the family of nitrous oxide + $n$-alkanes extends over a carbon number interval of $\Delta n=6.9$ (almost six times larger) and a temperature interval of
$\Delta T/K = 42.4$ K (almost two times larger). Of course carbon dioxide and nitrous oxide are rather different molecules with respect to their polarity and structure but it is hard to give an explanation in terms of molecular parameters for the differences found for these binary families.

The conclusion from the above is that as far as data for the TCP carbon number in some families of a solvent + n-alkanes -with solvents being members of the same homologous series- are available, we may extrapolate or interpolate these data to estimate the TCP carbon number for the family of another solvent (member of the same homologous series) + n-alkanes. However to make a prediction for a family of a different type solvent + n-alkanes, for which no data are available, is very difficult with our present knowledge.

### Table 10.5

**Fluid phase behaviour of binary and quasi-binary families of solvents + n-alkanes: the acentric factor $\omega$ of solvent and the temperature difference $\Delta T$ in K between TCP and DCEP**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\omega_{\text{solvent}}$</th>
<th>$\Delta T/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>4\text{F}</em>{10}$</td>
<td>0.374</td>
<td>7.2</td>
</tr>
<tr>
<td>$\text{C}_3\text{F}_8$</td>
<td>0.325</td>
<td>7.8</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>0.250</td>
<td>9</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>0.239</td>
<td>21.5</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_3\text{F}_3$</td>
<td>0.251</td>
<td>21.9</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$</td>
<td>0.165</td>
<td>42</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>0.099</td>
<td>127</td>
</tr>
</tbody>
</table>

In Table 10.5 the extent of the intermediate type IV zone, in terms of the temperature difference between the TCP and the DCEP, is given for several families of solvents + n-alkanes. In the same table the acentric factor $\omega$ of the solvent is listed. These data are plotted
in Fig. 10.11. The points represent the experimental data for these families, while the solid line is a regression curve through these points. The regression function has the form

$$\Delta T = -\frac{1.27947}{\omega} + \frac{1.37119}{\omega^2}$$

(10.19)

Any extrapolation outside the interval of the data points should be avoided.

![Graph showing the relationship between temperature difference (ΔT) and acentric factor (ω). The graph includes data points for different solvents and a regression line.]

Fig. 10.11. The temperature difference $\Delta T$ in K between the TCP temperature and the DCEP temperature for quasi-binary systems of solvents with n-alkanes, versus the acentric factor $\omega$ of the solvent. Empty square: ethane; up solid triangle: nitrous oxide; solid square: carbon dioxide; down empty triangle: 1,1,1-trifluoro-ethane; empty circle: ammonia; down solid triangle: perfluoropropane; up empty triangle: perfluorobutane; solid curve: regression curve through the experimental points.

Although the selection of the acentric factor as a characteristic property for the more-volatile component is very subjective and some of the data points used contain a lot of uncertainty, because they were estimated with rough extrapolations, some preliminary conclusions may be drawn. The acentric factor can be viewed as a measure of the complexity...
of a molecule with respect to both its geometry and polarity. It seems that with increasing complexity of the solvent molecule the extent of the region of type IV behaviour becomes smaller. But whereas for small values of the acentric factor the sensitivity is large, for large values of $\omega$, $\Delta T$ seems to approach asymptotically zero. Actually the family of perfluorobutane was selected to investigate this assumption for large values of $\omega$. Unfortunately solvents with even higher $\omega$ have also a relatively high critical temperature. This makes it difficult to investigate experimentally the phase behaviour of their binary systems with n-alkanes and to check if $\Delta T$ indeed goes to zero or even may become negative. Our present experimental setup can be used only up to 500 K.

If the above observation is correct then it seems that a van Laar point behaviour cannot be achieved, presumably because some physical reason forbids it. According to the Gibbs phase rule in a TCP of a binary system $F = N - \pi + 2 - (c - 1) = 2 - 3 + 2 - 2 = -1$, (c is the number of phases which are critical with each other). This is impossible and therefore at least a ternary system (or a quasi-binary one) is required to achieve a TCP behaviour. In a van Laar point the DCEP and the TCP coincide. This requires the fulfilment of extra conditions, therefore the satisfaction of the Gibbs phase rule requires even more components than three to have a van Laar point for $F \geq 0$. This means that a binary system or a ternary system is not adequate for the observation of a van Laar point and one has to study quaternary systems or quasi-binary systems composed of 4 components (e.g. solvent + \([n\text{-alkane}_1 + n\text{-alkane}_2 + n\text{-alkane}_3]\). If in a quasi-binary system a value of $\Delta T$ smaller than zero could be found, then this system shows type IV* fluid phase behaviour and a van Laar point should be found at $\Delta T = 0$.

**Symbols**

- CEP: critical endpoint
- DCEP: double critical endpoint
- $n$: carbon number
- $n_{\text{eff}}$: effective carbon number
- $n'_{\text{eff}}$: shape effective carbon number
- $P_c$: critical pressure
- RI: Randić molecular-connectivity index
$T_c$  critical temperature
TCP  tricritical point

$\delta$  solubility parameter
$\zeta, \lambda, \xi$  parameters in Eq.(10.1)
$\omega$  acentric factor

References


APPENDIX A

The Peng-Robinson equation of state

The Peng-Robinson cubic equation of state has the form

\[
P(V) = \frac{R T}{V-b} - \frac{a}{V(V+b) + b(V-b)} = \frac{(RT)V^2 + (2RTb-a)V + (ab-RTb^2)}{V^3 + bV^2 - (3b^2)V + b^3} \tag{A.1}
\]

In Eq.(A.1) \( a=a(T) \), \( b \), \( T \) are considered to be constants for a specific component at a fixed temperature. The roots in \( V \) of the denominator of Eq.(A.1) define the asymptotes of the function:

\[
egin{align*}
P & \to +\infty \quad \text{for} \quad V\to[b]^+ \quad \text{or} \quad V\to[-(\sqrt{2}-1)b]^+ \quad \text{or} \quad V\to[-(\sqrt{2}+1)b]^+ \\
P & \to -\infty \quad \text{for} \quad V\to[b]^– \quad \text{or} \quad V\to[-(\sqrt{2}-1)b]^– \quad \text{or} \quad V\to[-(\sqrt{2}+1)b]^–
\end{align*} \tag{A.2}
\]

The roots in \( V \) of the numerator of Eq.(A.1) are the roots of \( P(V) = 0 \)

\[
V_{1,2} = \frac{a}{2RT} - b \pm \frac{\sqrt{a^2 + 8R^2T^2b^2 - 8RTba}}{2RT} \tag{A.3}
\]

From Eq.(A.1) we also conclude that

\[
\begin{align*}
P & \to 0^+ \quad \text{for} \quad V\to +\infty \quad \text{and} \quad P \to 0^- \quad \text{for} \quad V\to -\infty
\end{align*} \tag{A.4}
\]

The extremes of Eq.(A.1) are the roots of

\[
\frac{\partial P}{\partial V} = 0 \Rightarrow \frac{RT}{(V-b)^2} = \frac{2a(V+b)}{(V^2 + 2bV - b^2)^2} \Rightarrow (RT)V^4 + (4bRT - 2a)V^3 + (2ab + 2b^2RT)V^2 + (2ab^2 - 4b^3RT)V + (b^4RT - 2ab^3) = 0 \tag{A.5}
\]

The various features discussed above are summarized in Fig.A.1. Values of \( V \) smaller than \( b \) have no physical meaning, therefore any routine that calculates the roots in \( V \) of Eq.(A.1) must check their validity. As we can see from the schematic graph we may have three real roots for pressures between the extremes E3 and E4, for higher pressures above the pressure of the extreme E1, and for negative pressures below the pressure of the extreme E2. In the second case, which may be encountered in practical applications as we will see below, only
the root at the right side of the asymptote A1 has physical meaning. The diagram of Fig.A.1 is similar to the one discussed by Van Ness and Abbott (1982) and later by Mohamed and Holder (1987). In the Pr,Vr plot of Fig.A.2.a three isotherms are depicted which are calculated from the Peng-Robinson equation of state. The extremes E1 are the up triangles while the extremes E2 are the down triangles. Extremes E3 (empty circle) and E4 (empty square) exist only for the subcritical isotherm Tr = 0.75. Fig.A.2.b is an enlargement of Fig.A.2.a around the physically meaningful area. Fig.A.2.c is an enlargement of Fig.A.2.a around the branch which starts from the extreme E2.

Fig.A.1. Schematic isothermal P,V plot for the Peng-Robinson equation of state. A1, A2, A3: asymptotes; E1, E2, E3, E4: extremes, R1, R2: roots of P(V) = 0.

Fig.A.3.a is a Pr,Tr plot of the extreme E1 for different values of the acentric factor \( \omega \). For Tr = 1 (see also Fig.A.3.b) the parameter a of the equation of state is independent from \( \omega \) (see Chapter 3), therefore all the curves have the same extreme at Pr = 31.2. In Figs.A.4 and A.5 the loci of the four extremes are plotted for a fixed \( \omega \) in a Pr,Vr and a Pr,Tr plot respectively. We see that the extreme E1 approaches the low pressure area for Tr around 2 and as \( \omega \)
increases this happens at lower $T_r$. In a binary mixture $E_1$ may approach the low pressure area for a temperature between the critical temperatures of the two components and the roots in $V$ of Eq. (A.1) must checked to fulfil the condition $V > b$. 
Figs. A.2.a (previous page up), A.2.b (previous page down), A.2.c (this page). Pr,Vr isotherms predicted from the Peng-Robinson equation of state for a pure component with \( \omega = 0.375 \). The values of Vr lower than b/Vc have no physical meaning. The negative values of Pr for Vr greater than b/Vc can only refer to metastable or unstable states. Solid lines: Tr = 0.75, short-dashed lines: Tr = 1.00, dashed-dotted lines: Tr = 1.50. The vertical long-dashed lines are the asymptotes. The points represent extremes (see text).

Fig. A.3.a. Loci of the extreme E1 (up empty triangles in Fig. A.2.a) on a Pr,Tr plane for different values of \( \omega \). Vr is variable. Solid line: \( \omega = 0.177 \), short-dashed line: \( \omega = 0.251 \), dotted-dashed line: \( \omega = 0.375 \), double-dotted-dashed line: \( \omega = 0.618 \).
Fig.A.3.b. Enlargement of Fig. Fig.A.3.a around the critical temperature (Tr = 1). Independently of the value of ω, all the lines pass through the point (Tr=1, Pr=31.2); (see text).

Fig.A.4. Loci of the extremes E1, E2, E3, E4 on a Pr,Vr plane for ω = 0.375. Tr is variable. Solid line: locus of the extreme E1 (up empty triangles in Fig.A.2.a), dashed line: locus of the extreme E2 (down empty triangles in Fig.A.2.a), dashed-dotted line: locus of the extreme E3 (empty circles in Fig.A.2.a), dashed-triple-dotted line: locus of the extreme E4 (empty squares in Fig.A.2.a).
Fig. A.5. Loci of the extremes E1, E2, E3, E4 on a Pr,Tr plane for $\omega = 0.375$. $Vr$ is variable. For the various lines see Fig. A.4

The parameters a and b of the equation of state are calculated from the critical conditions

$$\left( \frac{\partial P}{\partial V} \right)_{T_c} = \left( \frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \quad (A.6)$$

The Eqs. (A.6) together with Eq. (A.1) define a system which is solved for a, b, Vc. The solution is

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} , \quad b = \Omega_b \frac{R T_c}{P_c} , \quad V_c = \Omega_V \ b \quad (A.7)$$

with \( \Omega_a = 0.475235528921 \), \( \Omega_b = 0.077796073904 \)

and \( \Omega_V = 3.951373035591 \)
Figs. A.6.a (previous page up), A.6.b (previous page down) and A.6.c (this page). Vapour-liquid critical curve of the system methane and n-pentane in a P,T , a T,x and a P,x projection respectively. Solid lines: vapour pressure curves of pure components, dashed lines: critical lines calculated from the equilibrium conditions, dashed-dotted-lines: critical lines calculated from pseudo-critical constants, empty circles: critical points of pure components.

Using the equations for a and b we find Tc and Pc

\[ T_c = \frac{\Omega_b}{\Omega_a} \frac{a}{R_b} , \quad P_c = \frac{\Omega_b^2}{\Omega_a} \frac{a}{b^2} \]  \hspace{1cm} (A.8)

Therefore if we use some mixing rules for a and b we can find the pseudo-critical constants for the mixture from Eq.(A.8). For instance one can use the quadratic mixing rules discussed in Chapter 3.
The Peng-Robinson equation of state

\[ a(T,x) = (1-x)^2 a_{11}(T) + 2(1-x)x a_{12}(T) + x^2 a_{22}(T) \]
\[ b(x) = (1-x)^2 b_{11} + 2(1-x)x b_{12} + x^2 b_{22} \] (A.9)

with cross interaction parameters \( a_{12} \) and \( b_{12} \) given by:

\[ a_{12} = (1-k) \sqrt{a_{11} a_{22}} \quad \text{and} \quad b_{12} = (1-l) \frac{b_{11} + b_{22}}{2} \] (A.10)

The parameters \( k \) and \( l \) are used to correct for deviations from the geometric mean and arithmetic mean assumption, respectively. The pseudo-critical constants calculated from this method are generally very different from the mixture critical constants calculated from the critical conditions for multicomponent fluids. For example in Figs. A.6.a, A.6.b and A.6.c the vapour-liquid critical line for the binary mixture of methane with n-pentane is calculated in both ways and it is compared in a \( P,T \) a \( T,x \) and a \( P,x \) projection respectively. The parameters \( k \) and \( l \) were selected to be zero. According to this calculation this binary system exhibits type \( V \) fluid phase behaviour, thus its critical line is broken (see Chapter 3 for further calculations for that system).

Symbols

- \( a, b \) parameters of the Peng-Robinson equation of state
- \( k, l \) correction parameters; see Eq.(A.10)
- \( P \) absolute pressure
- \( Pc \) critical pressure
- \( T \) absolute temperature
- \( Tc \) critical temperature
- \( V \) molar volume
- \( Vc \) critical molar volume

Greek

- \( \Omega_a, \Omega_b, \Omega_V \) constants; see Eq.(A.7)
References


APPENDIX B

Derivatives of thermodynamic functions with respect to composition

The functional dependence of the variable $Y$ upon the independent variables $x_1, x_2, x_3, ..., x_N$ is denoted as $Y(x_1, x_2, x_3, ..., x_N)$. Constant parameters of the relationship are not mentioned. For some partial derivatives, when no confusion arises, we use a simplified notation. In such a case we mention it explicitly.

$$\frac{\partial^{k_1+k_2+...+k_N}(Y)}{\partial x_1^{k_1} \partial x_1^{k_1} ... \partial x_1^{k_1}}_{c_1,c_2,...,c_M}$$

we use $Y_{k_1,k_2,k_3,...,k_N,c_1,c_2,...,c_M}$

For any function $z(y,x)$ and for any variables $w,r$ we have

$$\left(\frac{\partial z}{\partial w}\right)_{r} = \left(\frac{\partial z}{\partial y}\right)_{x} \cdot \left(\frac{\partial y}{\partial w}\right)_{r} + \left(\frac{\partial z}{\partial x}\right)_{y} \cdot \left(\frac{\partial x}{\partial w}\right)_{r} \quad (B.1)$$

For the special case of $w = x$, Eq.(B.1) becomes

$$\left(\frac{\partial z}{\partial x}\right)_{r} = \left(\frac{\partial z}{\partial y}\right)_{x} \cdot \left(\frac{\partial y}{\partial x}\right)_{r} + \left(\frac{\partial z}{\partial x}\right)_{y} \quad (B.2)$$

For the thermodynamic variable $G$, its partial derivative with respect to composition under constant $P$ and $T$ ($P$ and $T$ are the characteristic variables for $G$, $dG = -SdT + VdP$) can be obtained by applying Eq.(B.2). The algebraic variables $z, y, x, r$ are replaced by the thermodynamic variables $G, V, x, P$. The variables $V, x, P$ are correlated by the equation of state $P = P(V,x)$. The variable $T$ is always constant and will not be mentioned in the notation that follows. Eq.(B.2) gives

$$\left(\frac{\partial G}{\partial x}\right)_{P} = \left(\frac{\partial G}{\partial V}\right)_{x} \cdot \left(\frac{\partial V}{\partial x}\right)_{P} + \left(\frac{\partial G}{\partial x}\right)_{y} \quad (B.3)$$

Another property for the general function $z(y,x)$ is
\[
\left( \frac{\partial z}{\partial y} \right)_x \cdot \left( \frac{\partial y}{\partial x} \right)_z \cdot \left( \frac{\partial x}{\partial z} \right)_y = -1
\]  
(B.4)

For the equation of state \( P(V,x) \), Eq.(B.4) becomes

\[
\left( \frac{\partial P}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_P \cdot \left( \frac{\partial x}{\partial P} \right)_V = -1 \Rightarrow \left( \frac{\partial V}{\partial x} \right)_P = - \frac{\left( \frac{\partial P}{\partial x} \right)_V}{\left( \frac{\partial P}{\partial V} \right)_x}
\]  
(B.5)

From \( dA = -S \, dT - P \, dV \) we get

\[
\left( \frac{\partial A}{\partial V} \right)_T = -P \quad \text{and} \quad \left( \frac{\partial A}{\partial T} \right)_V = -S
\]  
(B.6)

Using Eq.(B.6) and the notations

\[
\left( \frac{\partial V}{\partial x} \right)_P = V_x \quad \left( \frac{\partial P}{\partial x} \right)_V = P_{x|V} \quad \left( \frac{\partial P}{\partial V} \right)_x = P_{V|x} \quad \text{and}
\]

\[
\left( \frac{\partial A}{\partial V} \right)_x = A_{Vx} \quad \left( \frac{\partial^2 A}{\partial V \partial x} \right) = A_{2V}
\]  
(B.7)

we get from Eq.(B.5)

\[
V_x = - \frac{P_{x|V}}{P_{V|x}} = - \frac{A_{Vx}}{A_{2V}}
\]  
(B.8)

Using \( G = A + P \, V \), Eq.(B.3) becomes

\[
\left( \frac{\partial G}{\partial x} \right)_P \left( A_{V|x} + P_{V|x} \cdot V + P \right) \left( - \frac{P_{x|V}}{P_{V|x}} \right) + \left( A_{x|V} + P_{x|V} \cdot V \right)
\]  
(B.9)

Using Eq.(B.6) and Eq.(B.8) in Eq.(B.9) we get

\[
\left( \frac{\partial G}{\partial x} \right)_P = A_{x|V} \quad \text{or} \quad G_x = A_x
\]  
(B.10)

Applying Eq.(B.2) for \( z = G_x \) we get
\[
\left( \frac{\partial G_x}{\partial x} \right)_p = \left( \frac{\partial G_x}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_p + \left( \frac{\partial G_x}{\partial x} \right)_V = A_{Vx} \cdot \left( - \frac{A_{Vx}}{A_{2V}} \right) + A_{2x}
\]  \hspace{1cm} (B.11)

or shortly
\[
G_{2x} = A_{2x} - \frac{A_{Vx}^2}{A_{2V}}
\]  \hspace{1cm} (B.12)

Applying Eq.(B.2) for \(z = G_{2x}\) we get
\[
\left( \frac{\partial G_{2x}}{\partial x} \right)_p = \left( \frac{\partial G_{2x}}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_p + \left( \frac{\partial G_{2x}}{\partial x} \right)_V
\]
\[
= \left( A_{Vx} \cdot \frac{-2 A_{Vx} A_{2Vx} A_{2V} + A_{3V} A_{Vx}^2}{A_{2V}^2} \right) \cdot V_x
\]
\[
+ \left( A_{3x} \cdot \frac{-2 A_{Vx} A_{Vx} A_{2V} + A_{2Vx} A_{Vx}^2}{A_{2V}^2} \right)
\]  \hspace{1cm} (B.13)

or shortly
\[
G_{3x} = A_{3x} + 3 A_{Vx} V_x + 3 A_{2Vx} V_x^2 + A_{3x} V_x^3
\]  \hspace{1cm} (B.14)

Applying Eq.(B.2) for \(z = V_x\) we get
\[
\left( \frac{\partial V_x}{\partial x} \right)_p = \left( \frac{\partial V_x}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_p + \left( \frac{\partial V_x}{\partial x} \right)_V
\]
\[
= \left( - \frac{A_{Vx} A_{2V} - A_{3V} A_{Vx}}{A_{2V}^2} \right) \cdot V_x + \left( - \frac{A_{2V} A_{2V} - A_{2Vx} A_{Vx}}{A_{2V}^2} \right)
\]  \hspace{1cm} (B.15)

or shortly
\[
V_{2x} = - \frac{A_{Vx} + 2 A_{2Vx} V_x + A_{3V} V_x^2}{A_{2V}}
\]  \hspace{1cm} (B.16)

Another useful function in our analysis is the molar entropy \(S\) of the mixture. Starting from Eq.(B.6) we get
\[ S(V,T,x) = (1-x)S_1 + xS_2 + \Delta S_{\text{mix}}^{\text{id}}(x) + S^E(V,T,x) \]  

(B.17)

\[ \Delta S_{\text{mix}}^{\text{id}}(x) = -R \left[ (1-x) \ln(1-x) + x \ln(x) \right] \]  

(B.18)

\[ S^E(V,T,x) = S^{\text{repuls}}(V,x) + S^{\text{attract}}(V,T,x) + S_0^E \]  

(B.19)

We are not interested in absolute values of \( S \) so we assume \( S_1, S_2 \) and \( S_0^E \) to be zero. From Eqs. (B.18) and (B.19) it follows

\[ S(V,T,x) = \Delta S_{\text{mix}}^{\text{id}}(x) + S^{\text{repuls}}(V,x) + S^{\text{attract}}(V,T,x) \]  

(B.20)

where

\[ S^{\text{repuls}}(V,x) = -R \ln[V-b(x)] \]  

(B.21)

\[ S^{\text{attract}}(V,T,x) = -\frac{\partial a(T,x)}{\partial T} \ln \left[ \frac{V+(1+\sqrt{2})b(x)}{V+(1-\sqrt{2})b(x)} \right] \]  

(B.22)

\[ \frac{\partial a(T,x)}{\partial T} = (1-x)^2 \frac{\partial a_{11}(T)}{\partial T} + 2(1-x)x \frac{\partial a_{12}(T)}{\partial T} + x^2 \frac{\partial a_{22}(T)}{\partial T} \]  

(B.23)

and

\[ \frac{\partial a_{11}(T)}{\partial T} = 0.45724 \frac{R^2}{P_{c_{11}}} \frac{T_{c_{11}}^2}{T_{c_{11}}} \left( \frac{m_{11}^2}{T_{c_{11}}} - \frac{m_{11}(1+m_{11})}{\sqrt{T_{c_{11}}}} \right) \]  

(B.24)

\[ \frac{\partial a_{22}(T)}{\partial T} = 0.45724 \frac{R^2}{P_{c_{22}}} \frac{T_{c_{22}}^2}{T_{c_{22}}} \left( \frac{m_{22}^2}{T_{c_{22}}} - \frac{m_{22}(1+m_{22})}{\sqrt{T_{c_{22}}}} \right) \]  

(B.25)

\[ \frac{\partial a_{12}(T)}{\partial T} = \frac{1-k}{2\sqrt{a_{11}a_{22}}} \left( a_{11} \frac{\partial a_{22}(T)}{\partial T} + a_{22} \frac{\partial a_{11}(T)}{\partial T} \right) \]  

(B.26)
Applying Eq.(B.2) for \( z = S \) we get

\[
\left( \frac{\partial S}{\partial x} \right)_p = \left( \frac{\partial S}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_p + \left( \frac{\partial S}{\partial x} \right)_V = S_x = - A_{Tx} - V_x A_{TV} \quad \text{(B.27)}
\]

Applying Eq.(B.2) for \( z = S_x \) we get

\[
\left( \frac{\partial S_x}{\partial x} \right)_p = \left( \frac{\partial S_x}{\partial V} \right)_x \cdot \left( \frac{\partial V}{\partial x} \right)_p + \left( \frac{\partial S_x}{\partial x} \right)_V = (- A_{TVx} - V_x A_{TV}) \cdot V_x + (- A_{T2x} - V_x A_{TV} - V_x A_{TVx}) - S_{2x} = (- A_{T2x} + 2 A_{TVx} V_x + A_{TV} V_x^2 + A_{TV} V_x) \quad \text{(B.28)}
\]

Symbols

A molar Helmholtz energy
a intermolecular interaction parameter
b molecular volume parameter
G molar Gibbs energy
k correction term for \( a_{i2} \) in Eq.(3.12)
m coefficient in Eq.(3.9) evaluated by Eq.(3.10)
P pressure
R gas constant
S molar entropy
T temperature
V molar volume
x mole fraction of the less-volatile component
Superscripts

attrac  attractive term
E       excess term
id      ideal mixing
repuls  repulsive term

Subscripts

mix     mixing process
APPENDIX C

Slope of a critical curve

Along a critical curve in a binary system both $G_{2x}(P,T,x)$ and $G_{3x}(P,T,x)$ are zero. Also the total differential of $G_{2x}(P,T,x)$ will be zero. Therefore

$$d(G_{2x}) = \frac{\partial G_{2x}}{\partial P} dP + \frac{\partial G_{2x}}{\partial T} dT + \frac{\partial G_{2x}}{\partial x} dx = 0 \quad \text{or}$$

$$\frac{\partial G_{2x}}{\partial P} dP + \frac{\partial G_{2x}}{\partial T} dT + G_{3x} dx = \frac{\partial G_{2x}}{\partial P} dP + \frac{\partial G_{2x}}{\partial T} dT + 0 = 0 \quad (C.1)$$

From $dG = V\ dP - S\ dT$ we have

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad (C.2)$$

Manipulating the partial derivatives of Eq.(C.1) using Eq.(C.2) we get

$$\frac{\partial G_{2x}}{\partial P} = \frac{\partial^2 G}{\partial x^2} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial^2 V}{\partial x^2} = V_{2x} \quad \text{and}$$

$$\frac{\partial G_{2x}}{\partial T} = \frac{\partial^2 G}{\partial x^2} \left(\frac{\partial G}{\partial T}\right) = -\frac{\partial^2 S}{\partial x^2} = S_{2x}$$

and substituting in Eq.(C.1)

$$V_{2x} \ dP - S_{2x} \ dT = 0 \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_{\text{crit line}} = \frac{S_{2x}}{V_{2x}} \quad (C.3)$$
Slope of a three-phase curve (generally)

The Gibbs-Duhem equation for a binary system is

\[-S\,dT + V\,dP - (1-x)\,d\mu_1 - x\,d\mu_2 = 0\]  \hspace{1cm} (C.4)

where the differentials dT, dP, d\mu_1, d\mu_2 refer to field variables which have the same value in every phase and their multiplication factors -S, V, (1-x), x refer to their conjugate density variables which have different values in every phase. Application of Eq.(C.4) for the three coexisting phases (say \(\alpha, \beta, \gamma\)) gives

\[-S^\alpha\,dT + V^\alpha\,dP - (1-x^\alpha)\,d\mu_1 - x^\alpha\,d\mu_2 = 0\]
\[-S^\beta\,dT + V^\beta\,dP - (1-x^\beta)\,d\mu_1 - x^\beta\,d\mu_2 = 0\]  \hspace{1cm} (C.5)
\[-S^\gamma\,dT + V^\gamma\,dP - (1-x^\gamma)\,d\mu_1 - x^\gamma\,d\mu_2 = 0\]

Dividing the above equations by dT and using a matrix form for the resulting system we have

\[
\begin{bmatrix}
V^\alpha - (1-x^\alpha) & -x^\alpha \\
V^\beta - (1-x^\beta) & -x^\beta \\
V^\gamma - (1-x^\gamma) & -x^\gamma \\
\end{bmatrix}
\begin{bmatrix}
\frac{dP}{dT} \\
\frac{d\mu_1}{dT} \\
\frac{d\mu_2}{dT} \\
\end{bmatrix}
= 
\begin{bmatrix}
S^\alpha \\
S^\beta \\
S^\gamma \\
\end{bmatrix}
\]  \hspace{1cm} (C.6)

The above linear system is solved for dP/dT applying Cramer's rule

\[
\left(\frac{dP}{dT}\right)_3 = 
\begin{vmatrix}
S^\alpha - (1-x^\alpha) & -x^\alpha & 1 \\
S^\beta - (1-x^\beta) & -x^\beta & 1 \\
S^\gamma - (1-x^\gamma) & -x^\gamma & 1 \\
\end{vmatrix}
= 
\begin{vmatrix}
V^\alpha - (1-x^\alpha) & x^\alpha & 1 \\
V^\beta - (1-x^\beta) & x^\beta & 1 \\
V^\gamma - (1-x^\gamma) & x^\gamma & 1 \\
\end{vmatrix}
\]  \hspace{1cm} (C.7)
Slopes of critical and three-phase lines

Slope of a three-phase curve at a critical endpoint

The total differentials of the functions $G(P,T,x)$ and $G_x(P,T,x)$ are written according to Eq. (C.2) as

$$dG = -SdT + VdP + G_xdx \quad \text{and} \quad dG_x = -S_xdT + V_xdP + G_{2x}dx$$  \hspace{1cm} (C.8)

We define the following partial molar properties

$$\mu_1 = G - xG_x \quad \mu_2 = G + (1-x)G_x
\quad S_1 = S - xS_x \quad S_2 = S + (1-x)S_x
\quad V_1 = V - xV_x \quad V_2 = V + (1-x)V_x$$  \hspace{1cm} (C.9)

From (C.9) we take according to (C.8)

$$d\mu_1 = dG - dx G_x - x dG_x$$
$$= -(S-xS_x) dT + (V-xV_x) dP - x G_{2x} dx$$
$$= -S_1 dT + V_1 dP - x G_{2x} dx \quad \text{and}$$

$$d\mu_2 = dG - dx G_x + (1-x) dG_x$$
$$= [S+(1-x)S_x] dT + [V+(1-x)V_x] dP + (1-x) G_{2x} dx$$
$$= -S_2 dT + V_2 dP + (1-x) G_{2x} dx$$  \hspace{1cm} (C.10)

At a critical endpoint we have a critical phase (say c) in equilibrium with one additional phase (say a), therefore

$$d\mu_1^c = d\mu_1^a, \quad d\mu_2^c = d\mu_2^a, \quad dP^c = dP^a = dP \quad \text{and} \quad dT^c = dT^a = dT$$  \hspace{1cm} (C.11)

Combining Eqs. (C.10) and (C.11) and using the condition for criticality $G_{2x}^c = 0$ we get

$$-S_1^c dT + V_1^c dP - x^c G_{2x}^c dx = -S_1^a dT + V_1^a dP - x^a G_{2x}^a dx \quad \rightarrow$$
$$-(S_1^c - S_1^a) + (V_1^c - V_1^a) \frac{dP}{dT} = -x^a G_{2x}^a \frac{dx}{dT}$$  \hspace{1cm} (C.12)

$$-S_2^c dT + V_2^c dP + (1-x^c) G_{2x}^c dx = -S_2^a dT + V_2^a dP + (1-x^a) G_{2x}^a dx \quad \rightarrow$$
$$-(S_2^c - S_2^a) + (V_2^c - V_2^a) \frac{dP}{dT} = (1-x^a) G_{2x}^a \frac{dx}{dT}$$

Eliminating the term $G_{2x}^a dx/dT$ from the pair of the above equations and solving for $dP/dT$ we obtain
\[
\left( \frac{dP}{dT} \right)_{3\phi \text{ CEP}} = \frac{(1-x^a) \left( S_1^c - S_1^a \right) + x^a \left( S_2^c - S_2^a \right)}{(1-x^a) \left( V_1^c - V_1^a \right) + x^a \left( V_2^c - V_2^a \right)}
\]  
(C.13)

Replacing in the numerator and the denominator of Eq.(C.13) the partial molar properties by their equivalent from Eq.(C.9) we have finally
\[
\left( \frac{dP}{dT} \right)_{3\phi \text{ CEP}} = \frac{(S^c - S^a) + (x^c - x^a) S_x^c}{(V^c - V^a) + (x^c - x^a) V_x^c}
\]  
(C.14)

For a critical point the thermodynamic conditions are
\[
G_{2x} = G_{3x} = 0 \quad \text{and} \quad G_{4x} > 0 \quad \text{when } P, T \text{ constant}
\]  
(C.15)

For a tricritical point the thermodynamic conditions are
\[
G_{2x} = G_{3x} = G_{4x} = G_{5x} = 0 \quad \text{and} \quad G_{6x} > 0 \quad \text{when } P, T \text{ constant}
\]  
(C.16)

Finally for a double critical endpoint where a critical line is tangent to a three-phase line at its two coinciding critical endpoints UCEP \([L2=L1-V]\) and LCEP \([L2=L1-V]\), the thermodynamic condition results from the Eqs.(C.3) and (C.14)
\[
\frac{S_{2x}}{V_{2x}} = \frac{(S^c - S^a) + (x^c - x^a) S_x^c}{(V^c - V^a) + (x^c - x^a) V_x^c}
\]  
(C.17)

Symbols

- \(G\) molar Gibbs energy
- \(P\) pressure
- \(S\) molar entropy
- \(T\) temperature
- \(V\) molar volume
- \(x\) mole fraction of the less-volatile component

\[\mu\] chemical potential

Greek
SUMMARY

The objective of this thesis is the systematic investigation of some of the different types of fluid phase behaviour and the transitions between them in binary and quasi-binary systems. This objective is achieved by selected experiments, guided by a literature survey, and dedicated calculations, using specially developed algorithms. The results are interpreted either on the basis of molecular considerations, or just phenomenologically. At the end a quantitative correlation of the results is attempted.

An introduction to the subject and a short recapitulation of the thermodynamics of fluid phase equilibria is given in Chapters 1 and 2. The nomenclature, the diagrams, the classification and the transitions between types are discussed. In Chapter 3, a method for the calculation of fluid phase equilibria in terms of Gibbs energy analysis is introduced. The algorithm is graphically illustrated and the mechanical and material stability criteria are discussed. This method provides a thorough insight in the background of phase diagrams and is very useful for the calculation of complicated phase diagrams of binary systems. In Chapter 4, a literature survey of experimental data concerning three-phase L_2L_1V equilibria in families of binary systems is presented. In Chapter 5, the apparatus and the procedure followed during the experiments are described.

In Chapter 6, the experimental results for the family of binary and quasi-binary systems of perfluoropropane + alkanes are given. A transition from type II, via type IV, towards type III fluid phase behaviour may occur for increasing carbon number of the alkane. A tricritical point and a double critical endpoint bound the intermediate type IV zone. The effect of branching of the alkane is studied when the above transition is experimentally verified for quasi-binary systems of perfluoropropane + (2,2,4-trimethyl-hexane + n-nonane). The binary and quasi-binary systems of perfluoropropane + n-alkanes with carbon numbers above 8.7 exhibit type III phase behaviour. These systems show also barotropic inversion phenomena which are systematically measured (up to carbon number 14) and phenomenologically explained.

In Chapter 7 the experimental results in the family of binary and quasi-binary systems of perfluorobutane + n-alkanes or pseudo-n-alkanes are given. A transition from type II, via type IV, towards type III fluid phase behaviour occurs for carbon numbers of the n-alkane between 10.647 and 10.673.
In Chapter 8 the experimental results in the families of binary systems of perfluoroethane or perfluoropropane or perfluorobutane + n-alkanols and perfluoroethane + ethers are given. The influence on the fluid phase behaviour of the size of the more-volatile component (perfluoroalkane), the relative polarity of the less-volatile component (alkanols, ethers), the competition between the relative size and the polarity of the less-volatile component (n-alkanol) and the combined effect of polarity and shape of the less-volatile component (isomers of propanol, isomers of butanol) is systematically investigated.

In Chapter 9 the modelling of several systems, for which experimental results exist, is presented. A quantitative agreement is limited by the drawbacks of the thermodynamic models used. The calculational procedures developed in Chapter 3 are applied and special areas of interest are analyzed in such a detail that is experimentally impossible to achieve. The transition pattern from type II, via type IV, towards type III fluid phase behaviour is examined and the predictions are compared with the experiments. The barotropic inversion phenomena as well as the heteroazeotropy encountered in the family of perfluorobutane with n-alkanols are calculated in detail.

In Chapter 10 the concept of an effective carbon number is introduced. This concept allows to take into account not only the size, but also the shape and the polarity of the molecule of the less-volatile component in a binary system. The carbon number of the less-volatile component, where the transition from type II to type IV occurs, depends on the size of the more-volatile component. Also the extent of the intermediate type IV zone depends on the nature of the more-volatile component but not in a straightforward manner. The acentric factor of the more-volatile component is tried as a correlation parameter. Finally the possibilities for the occurrence of a so-called van Laar point are discussed on the basis of experimental data.
Het doel van het in dit proefschrift beschreven onderzoek is het systematisch onderzoek van de verschillende typen van fluïde fasengedrag en de overgangen tussen deze typen fasengedrag in binaire en quasi-binaire systemen. Dit doel wordt nagestreefd door het uitvoeren van geselecteerde experimenten, aangevuld met uit de literatuur verkregen experimentele resultaten en door het uitvoeren van fasenevenwichtsberekeningen, waarbij gebruik gemaakt is van speciaal hiervoorontwikkeld algoritmen. De resultaten worden zowel fenomenologisch geïnterpreteerd als ook op basis van moleculaire overwegingen. In het laatste hoofdstuk van dit proefschrift wordt een poging ondernomen om de resultaten quantitatief te corruleren.

In Hoofdstuk 1 wordt een korte introductie tot het onderwerp van dit proefschrift gegeven. Hoofdstuk 2 bevat een korte recapitulatie van de thermodynamica van fluïde fasenevenwichten. Hierbij komen nomenclatuur, typen diagrammen en de classificatie van en de overgangen tussen typen van fluïde fasengedrag aan de orde. In Hoofdstuk 3 wordt een methode voor de berekening van fluïde fasenevenwichten met behulp van Gibbs-energie analyse geïntroduceerd. Het ontwikkelde algoritmeme wordt grafisch geïllustreerd en de criteria voor mechanische en materiële stabiliteit worden besproken. De ontwikkelde methode geeft een diepgaand inzicht in de thermodynamische achtergronden van fasendiagrammen en is erg nuttig voor de berekening van gecomplieerde fasendiagrammen in binaire systemen. In Hoofdstuk 4 wordt een literatuuroverzicht gepresenteerd van experimenteel bepaalde $L_2L_1V$ drie-fasenevenwichten in binaire families. In Hoofdstuk 5 wordt de gebruikte apparatuur en de meetmethode beschreven.

In Hoofdstuk 6 worden de experimentele resultaten gepresenteerd voor de familie van binaire en quasi-binaire systemen van perfluoropropaan + alkanen. In deze familie wordt met toenemend koolstofgetal van het alkaan een overgang waargenomen van type II naar type IV en van daar naar type III fasengedrag. Het gebied van het koolstofgetal waarin het intermediaire type IV gevonden wordt, wordt begrensd door het optreden van een trikritisch punt en een dubbelkritisch eindpunt. De invloed van vertakkingen van het alkaan op deze overgang is onderzocht aan de hand van quasi-binaire systemen van perfluoropropaan en pseudo-componenten bestaande uit mengsels van 2,2,4-trimethyl-hexaan en n-nonanaan. Binaire en quasi-binaire systemen van perfluoropropaan + n-alkaan met koolstofgetal van 8,7 tot 14 vertonen type III fasengedrag. In deze systemen wordt ook barotropie gevonden. Dit verschijnsel is systematisch onderzocht en wordt fenomenologisch verklaard.
De experimentele resultaten voor de familie van binaire en quasi-binaire systemen van perfluorobutaan en n-alkanen en pseudo-componenten bestaande uit mengsels van n-alkanen worden in Hoofdstuk 7 besproken. In deze familie wordt eveneens een overgang van type II fasengedrag naar type III fasengedrag via type IV fasengedrag gevonden. Type IV fasengedrag wordt waargenomen bij een koolstofgetal van het n-alkaan tussen 10,647 en 10,673.

In Hoofdstuk 8 worden de experimentele resultaten gepresenteerd voor de binaire families van perfluoroethaan, perfluoropropaan en perfluorobutaan met n-alkanol en van perfluoroalkaan met ethers. De invloed van de grootte van de meest-vluchtige component, de perfluoroalkaan, de relatie polariteit van de minst-vluchtige component, de alkanolen en de ethers, de competitie tussen relatie grootte en de polariteit van de minst-vluchtige component, voor systemen met n-alkanol en het gecombineerde effect van polariteit en vorm van de minst-vluchtige component, voor systemen met isomeren van propanol en butanol, is systematisch onderzocht.

De resultaten van het modelleren van verschillende systemen waarvoor experimentele data voorhanden zijn worden gegeven in Hoofdstuk 9. Een quantitative overeenkomst van de resultaten van de berekeningen met experimentele data wordt beperkt door de tekortkomingen van de gebruikte thermodynamische modellen. De berekeningsmethoden die in Hoofdstuk 3 zijn besproken zijn gebruikt bij het modelleren. Bizondere gebieden in fasendiagrammen kunnen met deze methoden met een nauwkeurigheid worden geanalyseerd die niet haalbaar is met de huidige experimentele methoden. Het overgangsmechanisme van type II naar type III fasengedrag via type IV is onderzocht en de voorspellingen worden vergeleken met experimentele gegevens. Zowel barotropische inversie verschijnselen, als de heteroazeotropie die optreedt in de familie van perfluorobutaan + n-alkanol zijn in detail berekend.

In Hoofdstuk 10 wordt het concept van het effectieve koolstofgetal geïntroduceerd. Hiermee kunnen zowel de invloed van de grootte, als ook van de vorm en de polariteit van de moleculen van de minst-vluchtige component beschreven worden. Het koolstofgetal van de minst-vluchtige component waarvoor de overgang van type II naar type IV fasengedrag optreedt hangt af van de grootte van de meest-vluchtige component. Ook de grootte van de zone waarin het indermediaire type IV optreedt hangt af van de eigenschappen van de meest-vluchtige component, echter niet op een eenvoudige manier. Een correlatie op basis van de acentriciteitsfactor van de meest-vluchtige component lijkt redelijke resultaten op te leveren. Tot slot wordt, op basis van de experimentele data, de mogelijkheid voor het optreden van een zogenaamd Van Laar punt besproken.
ΠΕΡΙΛΗΨΗ (greek summary)

Ο αντικειμενικός στόχος της παρούσας διατριβής είναι η συστηματική διερεύνηση μερικών από τους διαφορετικούς τύπους συμπεριφοράς ρευστών φάσεων -καθώς και των μεταβάσεων από τον ένα τύπο στον άλλο- σε δυαδικά και ψευδο-δυαδικά συστήματα. Ο στόχος αυτός υλοποιείται μέσω διενέργειας επιλεγμένων πειραματικών μετρήσεων, υποδεικνυόμενων από βιβλιογραφική επισκόπηση, καθώς και μέσω εξειδικευμένων υπολογιστικών προβλέψεων, με τη βοήθεια αναπτυγμένων και προσαρμοσμένων για το σκοπό αυτό αλγορίθμων. Τα αποτελέσματα επεξηγούνται είτε στη βάση μοριακών θεωρησεών, είτε απλώς φαινομενολογικά. Στο τέλος της μελέτης πραγματοποιείται κάποια απόπειρα ποσοτικής συσχετίσεως των αποτελεσμάτων.

Στα κεφάλαια 1 και 2 το θέμα προλογίζεται και μία λακωνική ανακεφαλαίωση της θερμοδυναμικής της ισορροπίας ρευστών φάσεων επιχειρείται. Η ονοματολογία, τα είδη των διαγραμμάτων, η ταξινόμηση των διαφόρων τύπων καθώς και τις μεταβάσεις από τον ένα στον άλλο τύπο συμπεριφοράς φάσεων συζητούνται. Στο κεφάλαιο 3 εισάγεται μία μέθοδος για τον υπολογισμό της ισορροπίας ρευστών φάσεων σύμφωνα με όρους της ενεργειακής ανάλυσης κατά Gibbs. Ο αλγόριθμος επεξηγείται γραφικώς και τα κριτήρια μηχανικής και χημικής ευστάθειας σχολιάζονται. Η εν λόγω μέθοδος παρέχει την δυνατότητα μιας λεπτομερούς διασφάλισης των θεμελιωδών αρχών που διέπουν την κατασκευή διαγραμμάτων φάσεων και αποδεικνύεται πολύ χρήσιμη για τον υπολογισμό πολυπλοκών διαγραμμάτων φάσεων σε δυαδικά συστήματα. Στο κεφάλαιο 4 παρουσιάζεται μία βιβλιογραφική επισκόπηση πειραματικών δεδομένων που αφορούν στην ισορροπία τριών φάσεων υγρού-υγρού-ατμού σε οικογένειες δυαδικών συστημάτων. Στο κεφάλαιο 5 περιγράφονται η πειραματική συσκευή και οι διαδικασίες που ακολουθούνται κατά την διεξαγωγή των μετρήσεων.

Στο κεφάλαιο 6 παρουσιάζονται τα αποτελέσματα των πειραματικών μετρήσεων για την οικογένεια των δυαδικών και ψευδο-δυαδικών συστημάτων του οκτα-φθόρο-προπανίου + αλκανίων. Για διάφορους συνδυασμούς αλκανίων παρατηρείται μία μετάβαση στον τύπο της συμπεριφοράς ρευστών φάσεων, από τον τύπο II, μέσω του τύπου IV, στον τύπο III. Ενα τρικρίσμιο σημείο και ένα διπλό κρίσμα τελικό σημείο οριοθετούν την ενδιάμεση ζώνη τύπου IV. Στην περίπτωση που η
προαναφερθείσα μετάβαση επιβεβαιώνεται πειραματικώς σε δυαδικά συστήματα του όκτα-φθόρο-προπανίου + (2,2,4-τριμεθυλο-εξάνιου + κανονικού εννεανίου), μελετάται η επίπτωση του βαθμού διακλάδωσης του μορίου του αλκανίου στον τύπο της συμπεριφοράς ρευστών φάσεων. Τα δυαδικά και ψευδο-δυαδικά συστήματα του όκτα-φθόρο-προπανίου + αλκανίων με αριθμό ατόμων άνθρακα από 8,7 έως 14 συμπεριφέρονται κατά τον τύπο III. Τα συστήματα αυτά εμφανίζουν επίσης βαροτροπικά φαινόμενα αντιστροφής φάσεων τα οποία μετρήθηκαν συστηματικώς και επεξηγήθηκαν φαινομενολογικώς.

Στο κεφάλαιο 7 παρουσιάζονται τα αποτελέσματα των πειραματικών μετρήσεων για την οικογένεια των δυαδικών και ψευδο-δυαδικών συστημάτων του δέκα-φθόρο-βουτανίου + κανονικών αλκανίων. Για αριθμούς ατόμων άνθρακα του κανονικού ψευδο-αλκανίου μεταξύ 10,647 και 10,673 παρατηρείται μια μετάβαση στον τύπο της συμπεριφοράς ρευστών φάσεων, από τον τύπο II, μέσω του τύπου IV, στον τύπο III.

Στο κεφάλαιο 8 παρουσιάζονται τα αποτελέσματα των πειραματικών μετρήσεων για την οικογένεια των δυαδικών συστημάτων του εξα-φθόρο-αιθανίου ή οκταφθόρο-προπανίου ή δέκα-φθόρο-βουτανίου + κανονικών αλκανωλών καθώς και του εξα-φθόρο-αιθανίου + αιθερών. Εδώ διερευνάται συστηματικώς, η επίδραση των εξής παραγόντων στην συμπεριφορά ρευστών φάσεων των παραπάνω συστημάτων:

Μέγεθος του πλέον πτητικού συστατικού του μίγματος (φθοροαλκανίου).
Σχετική πολικότητα του λιγότερο πτητικού συστατικού (αλκανόλες, αιθέρες).
Συναγωγισμός μεταξύ του σχετικού μεγέθους και πολικότητας του λιγότερο πτητικού συστατικού (κανονικές αλκανόλες).
Συνδυασμός πολικότητας και γεωμετρικού σχήματος του λιγότερο πτητικού συστατικού (ισομερή της προπανόλης, ισομερή της βουτανόλης).
Στο κεφάλαιο 9 επιχειρείται η μοντελοποίηση ορισμένων συστημάτων για τα οποία υφίστανται διαθέσιμα πειραματικά δεδομένα. Η συμμετοχή σε ποσοτική βάση μεταξύ των υπολογισμών και των πειραματικών μετρήσεων περιορίζεται από τις απελευθερώσεις των θερμοδιαφανών μοντέλων που χρησιμοποιούνται. Εφαρμόζονται οι υπολογιστικές μέθοδοι που αναπτύχθηκαν στο κεφάλαιο 3 και ειδικού ενδιαφέροντος περιοχές φαινομένων αναλύονται σε πολύ λεπτομερή βαθμό. Τέτοια λεπτομέρεια είναι πρακτικώς αδύνατο να επιτευχθεί στη διεξαγωγή
πειραμάτων. Η μετάβαση από τον τύπο II, μέσω του τύπου IV, στόν τύπο III συμπεριφοράς ρευστών φάσεων εξετάζεται και οι θεωρητικές προβλέψεις συγκρίνονται με τις πειραματικές μετρήσεις. Τα φαινόμενα βαροτροπικής αντιστροφής φάσεων καθώς και τα φαινόμενα ετεροαξιοποιίας που παρατηρούνται στην οικογενεια συστημάτων του δέκα-φθόρο-βοϋτανίου + κανονικών αλκανολών υπολογίζονται λεπτομερώς.

Στο κεφάλαιο 10 εισάγεται η ιδέα χρησιμοποίησης ενός πλασματικού αριθμού ατόμων άνθρακα για μη γραμμικά μόρια και πολυκά μόρια. Με τη βοήθεια αυτού του αριθμού μαζί με το μέγεθος του μορίου του λιγότερο πτητικού συστατικού συνυπολογίζεται και η επιρροή του σχήματος του και της πολυκότητας του. Ο αριθμός ατόμων άνθρακα του λιγότερο πτητικού συστατικού για τον οποίο συμβαίνει η μετάβαση από τον τύπο II, μέσω του τύπου IV, στόν τύπο III συμπεριφοράς ρευστών φάσεων εξαρτάται από το μέγεθος του πλέον πτητικού συστατικού. Επίσης το εύρος της ενδιάμεσης ζώνης τύπου IV εξαρτάται από τη φύση του πλέον πτητικού συστατικού αλλά όχι κατά έναν άμεσο και σαφή τρόπο. Ο συντελεστής εκκεντρότητας του μορίου του πλέον πτητικού συστατικού δοκιμάζεται ως παράμετρος συσχέτισης. Τέλος οι πιθανότητες ύπαρξης ενός σημείου του θερμοδυναμικού χώρου συμπεριφοράς ρευστών φάσεων που ονομάζεται von Laar συζητούνται στη βάση πειραματικών δεδομένων.