U.PORTO
FACULDADE DE CIÊNCIAS
UNIVERSIDADE DO PORTO

MAT 2020

MÉTODOS DE ANÁLISE TÉRMICA

DSC … Metodologia e Aplicações

DQB... 2019-2020

PHASE EQUILIBRIA: Mixtures

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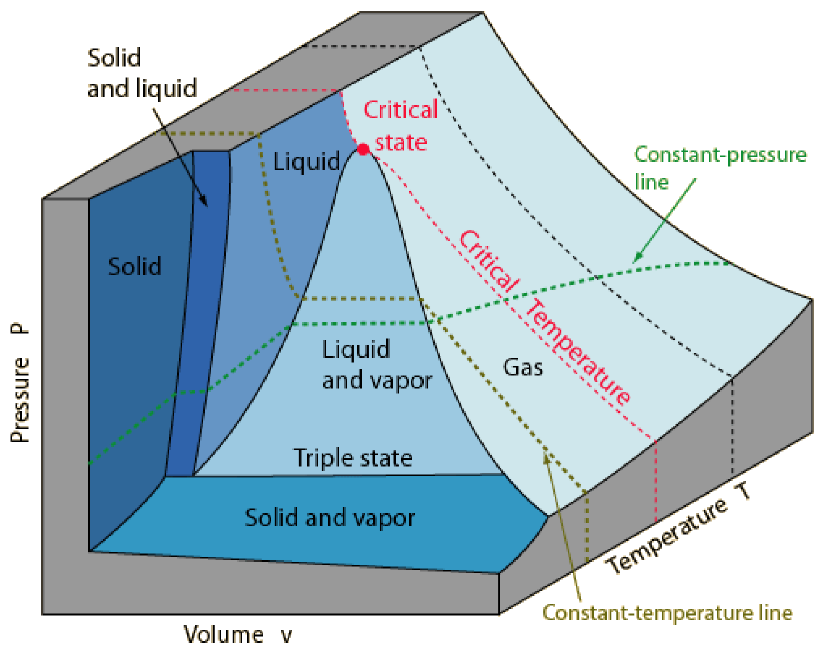
Pure substances & Mixtures

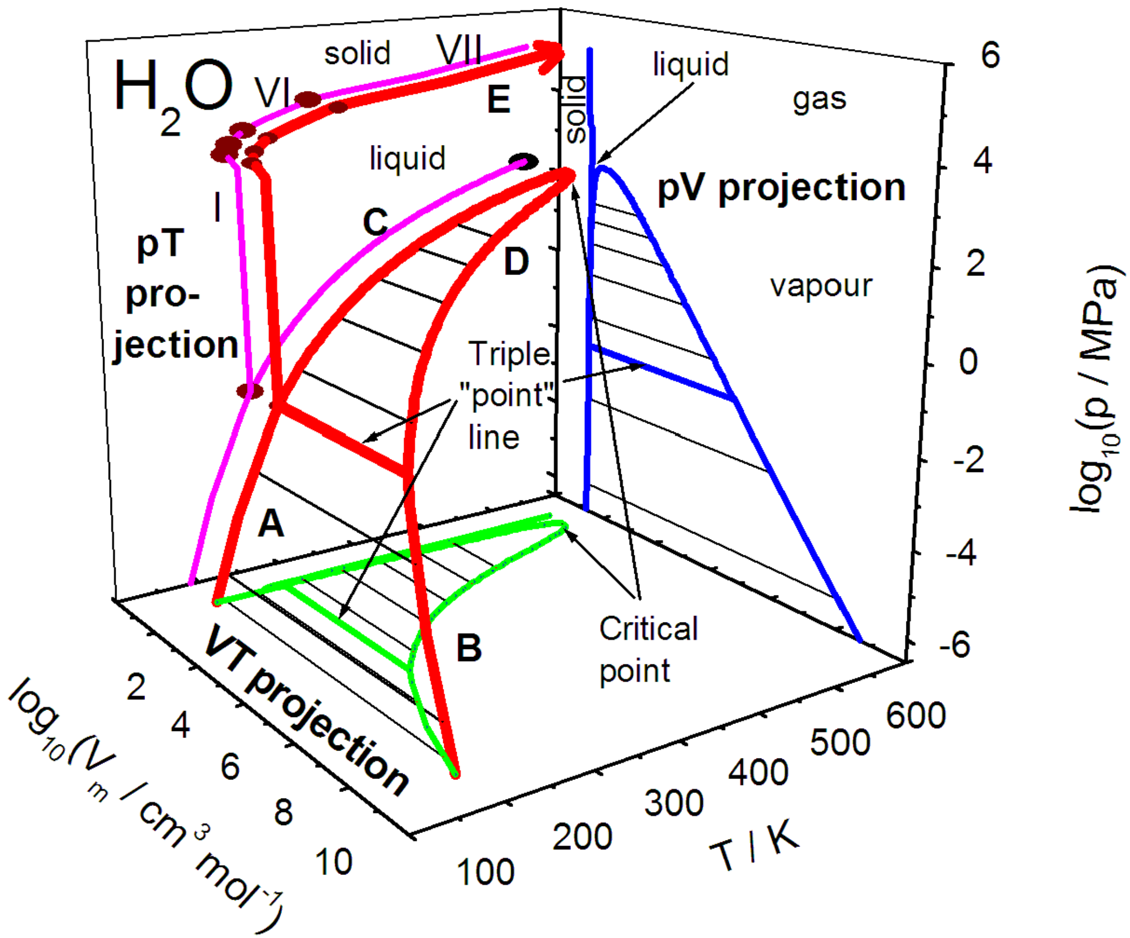
PVT diagram



-**Why each compound have a different PVT surface profile?**

- C-H-π and π-π .. interactions
- H-bond
- Electrostatic .. interactions
- Molecular shape
- ...???

Properties of pure substances



PVT diagram

- PT projection :

Complex and interesting profile!

- VT projection :

Little dependence of the liquid / solid phases

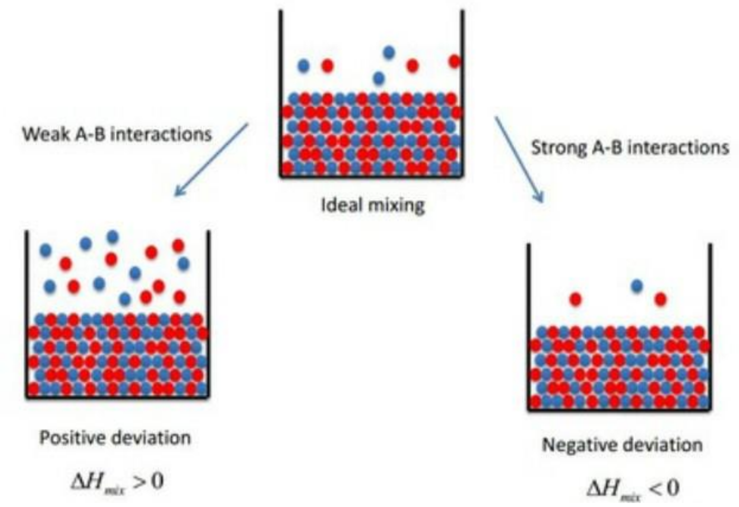
- PV projection :

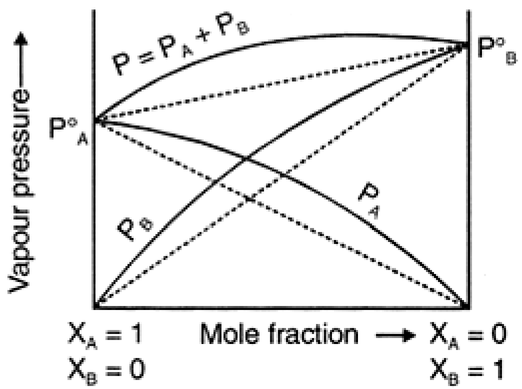
Little dependence of the liquid / solid phases

Liquid Solutions

On the basis of **Raoult's Law**, liquid-liquid solutions can be of two types.

- *Ideal Solutions*
- *Non-ideal Solutions*





P-X graph for non-ideal solution showing +ve deviation

Liquid Solutions

On the basis of **Raoult's Law**, liquid-liquid solutions can be of two types.

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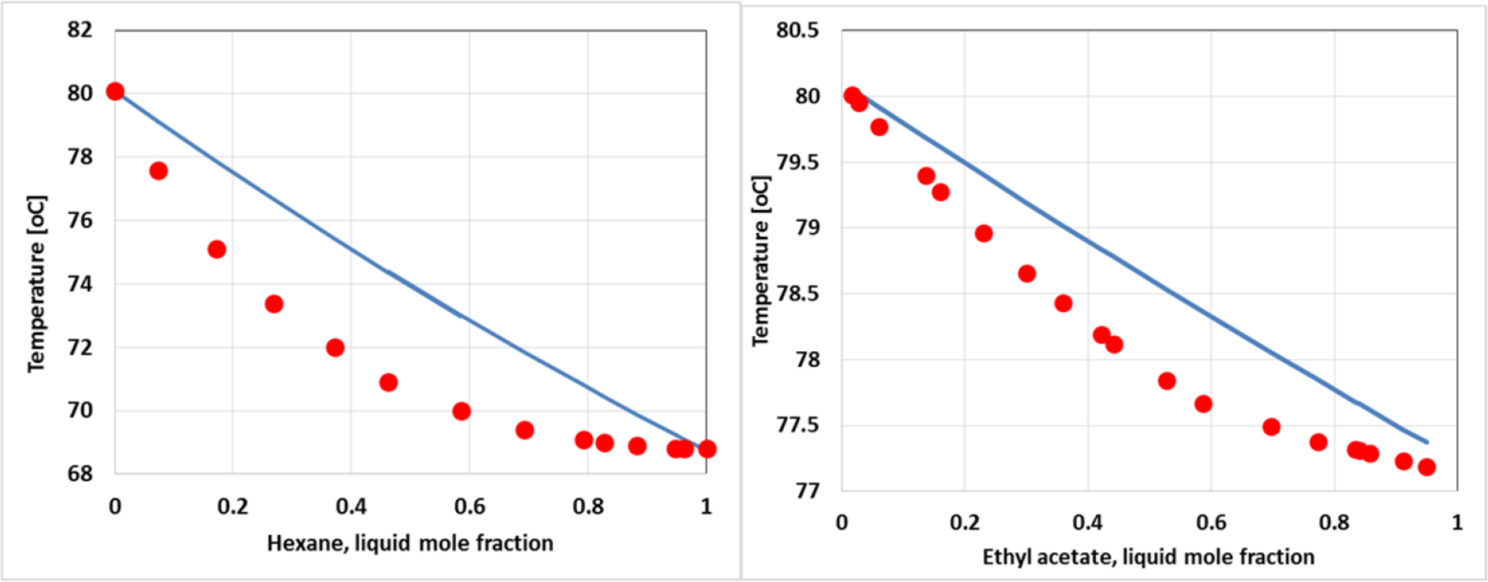

T-x-y diagram for the binary systems of hexane-benzene (left) and ethyl acetate-benzene (right) at a pressure of 101.33 kPa.

Liquid Solutions

On the basis of **Raoult's Law**, liquid-liquid solutions can be of two types.

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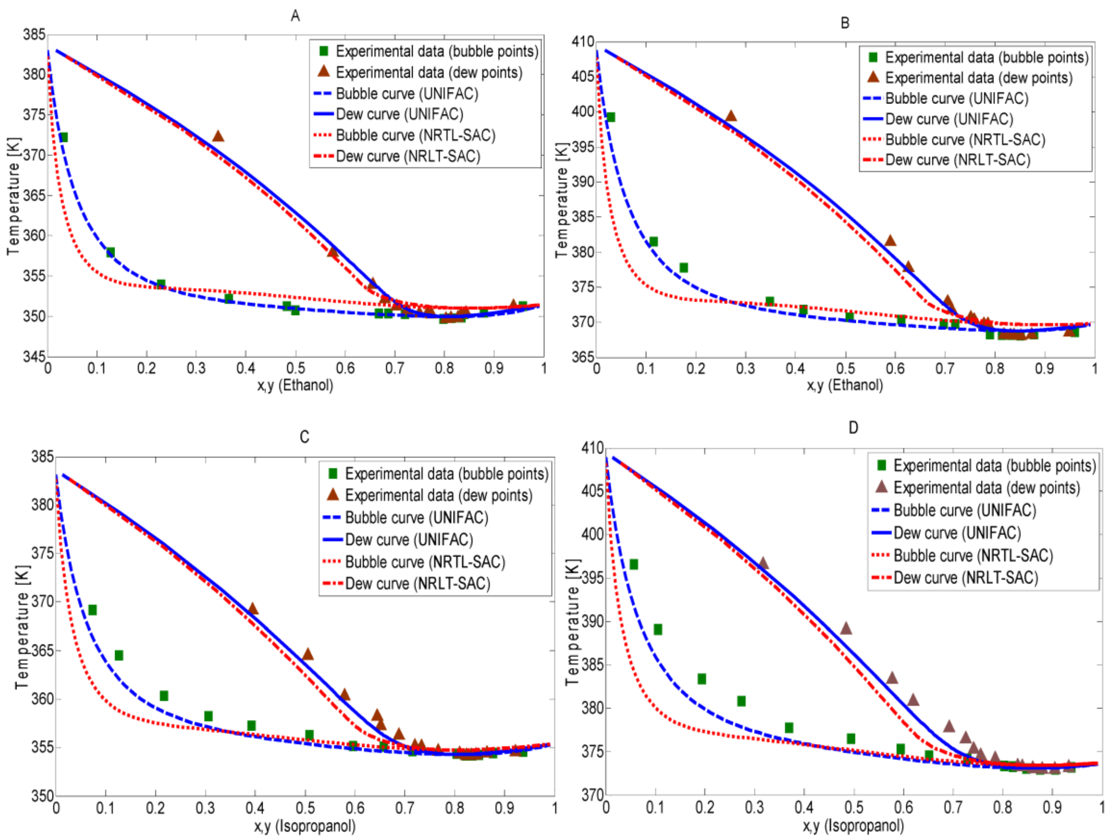
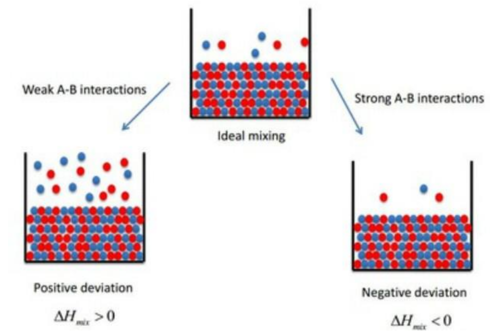


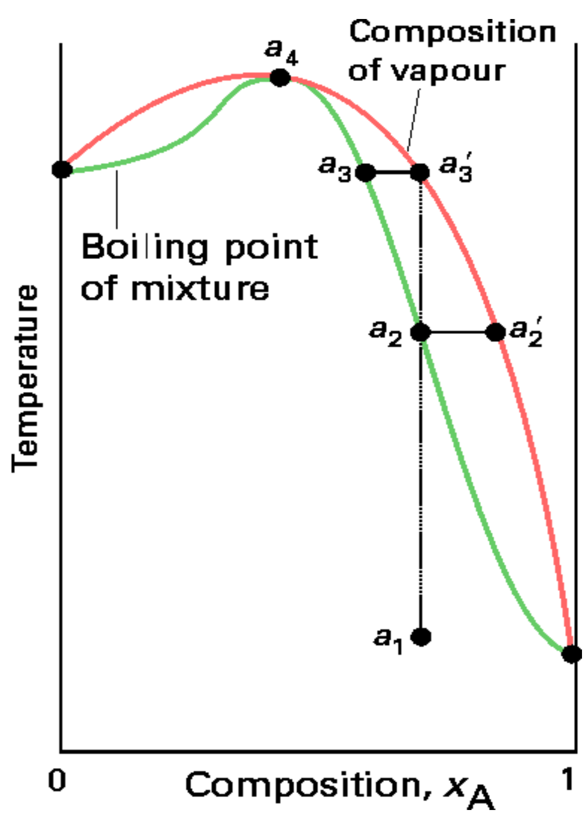
The results for the systems
(A) ethanol-toluene at 101.3 kPa,
(B) **ethanol-toluene** at 201.3 kPa,
(c) **isopropyl alcohol-toluene** at 101.3 kPa,
(D) isopropyl alcohol-toluene at 201.3 kPa

Liquid Solutions

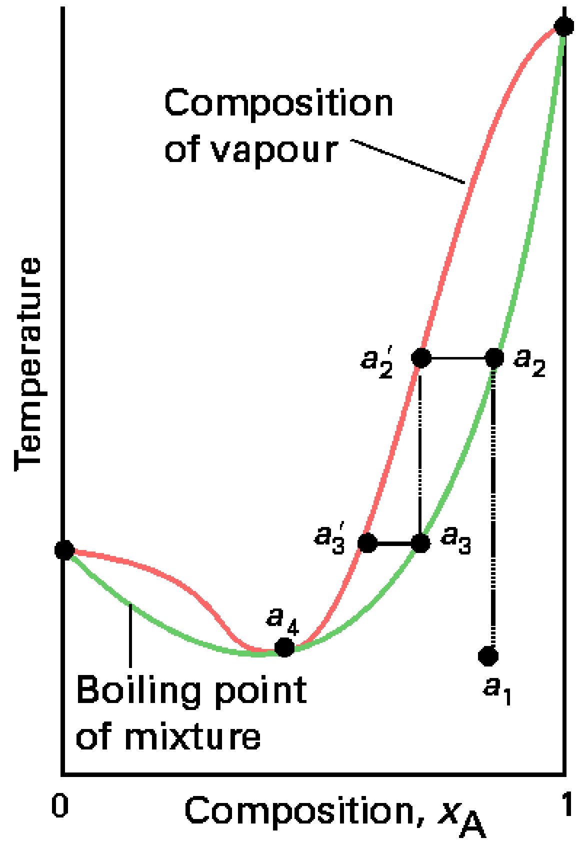


***p* ...fixed**

High-boiling azeotrope, e.g., nitric acid/water



Low-boiling azeotrope, e.g., ethanol/water

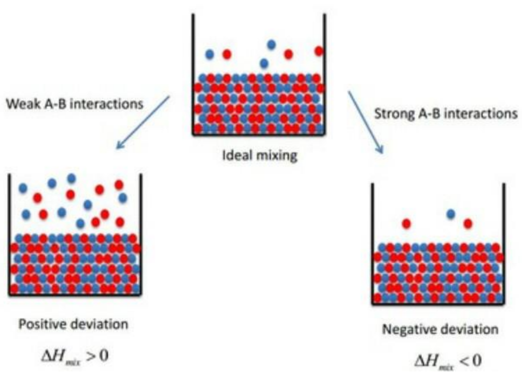


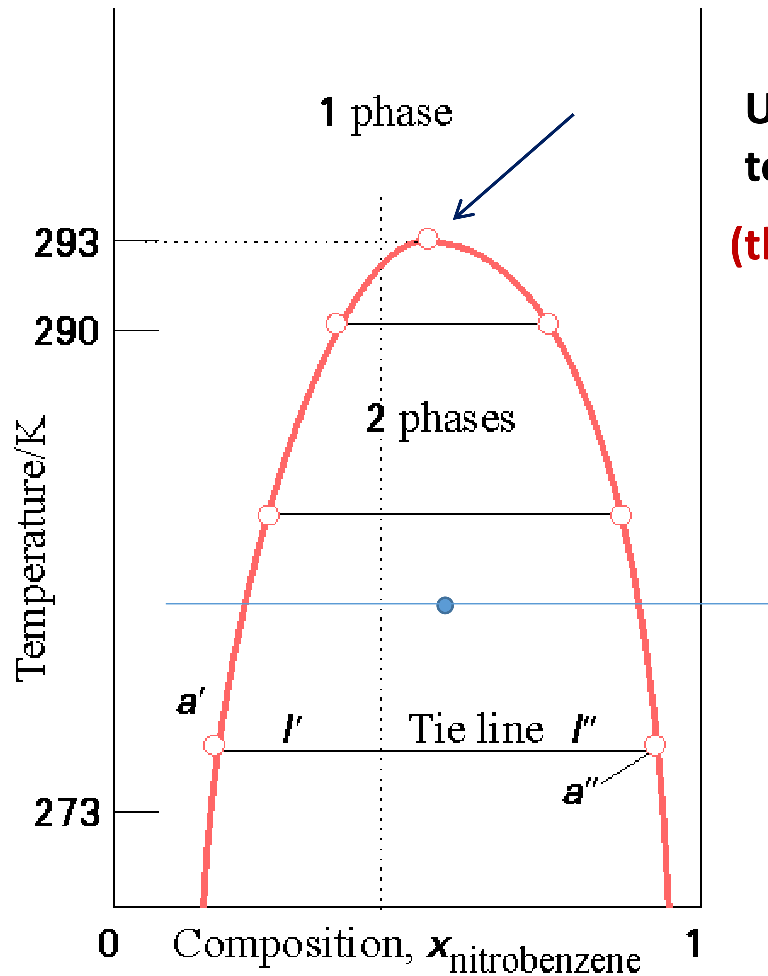
Liquid Solutions

Phase diagrams

Phase separation

E.g., hexane/nitrobenzene:





Upper critical temperature

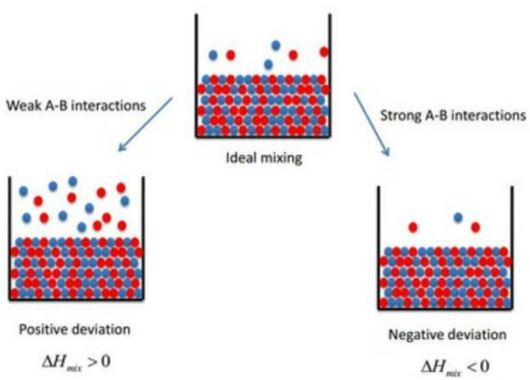
(thermal motion)

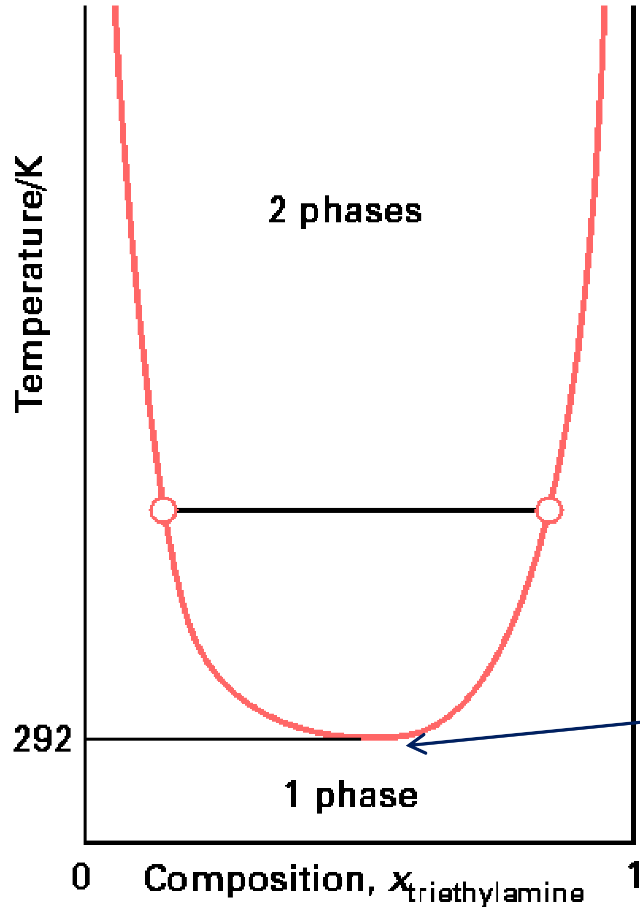
Liquid Solutions

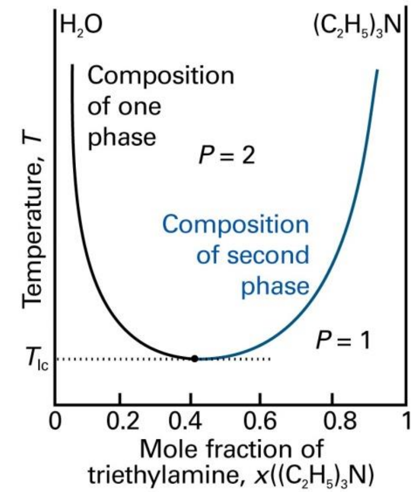
Phase diagrams

Phase separation

E.g., triethylamine /water:





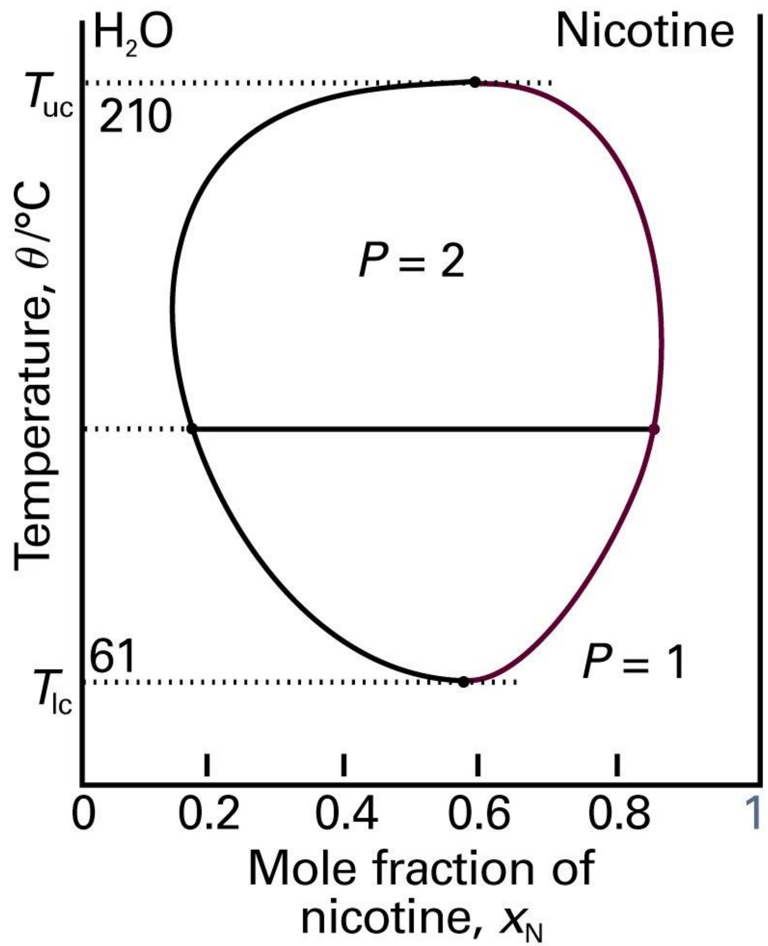


Lower $T_{critical}$
(complex formed)

Liquid Solutions

Phase diagrams

Phase separation



Upper critical temperature
(thermal motion)

Lower $T_{critical}$
(complex formed)

Liquid Solutions

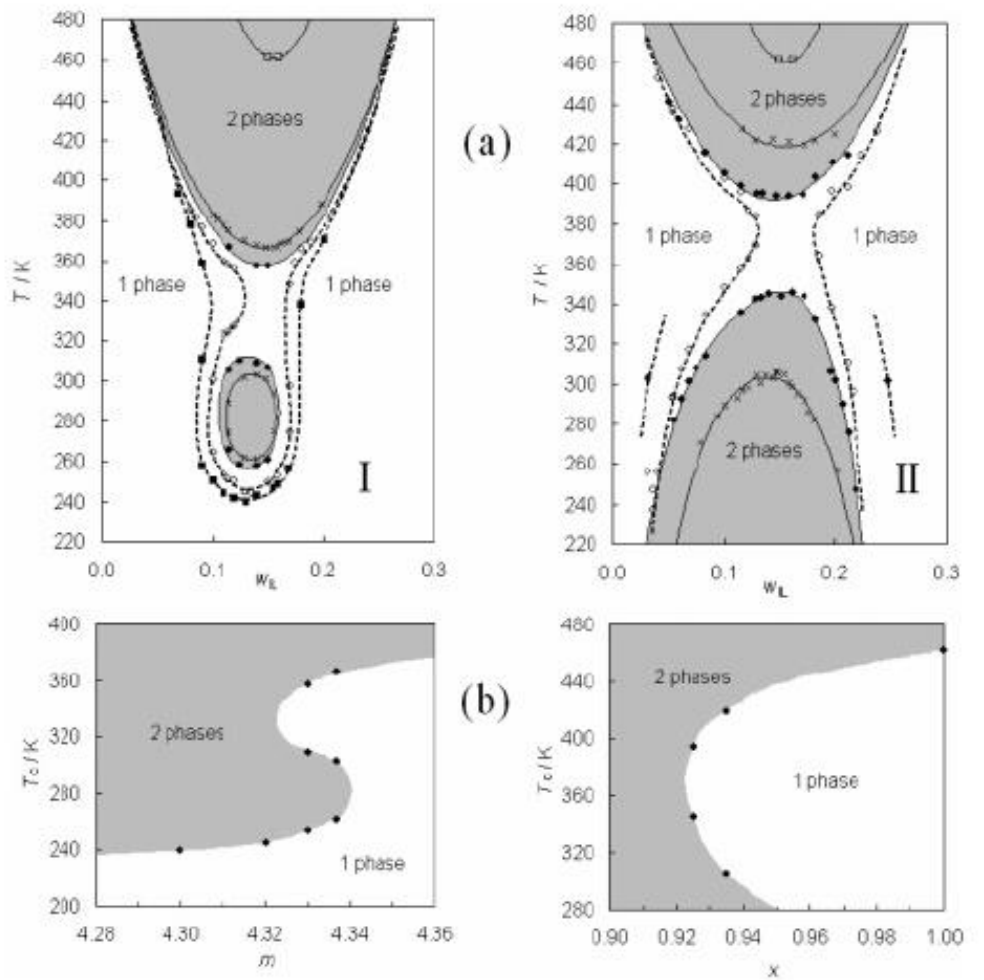
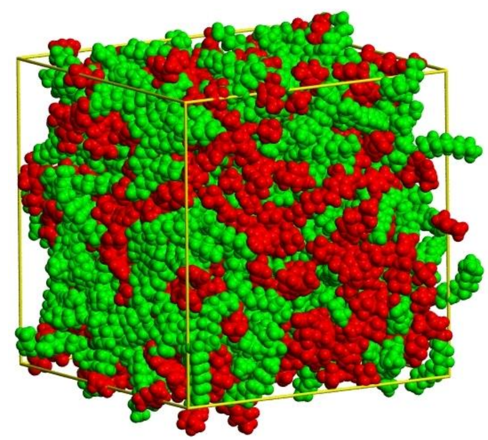


Figure 1. Phase equilibria of $[C_m mim][NTf_2]$ + CH_xCl_{4-x}; w_{IL} = weight



Two domains

Evidence for Lower Critical Solution Behavior in Ionic Liquid Solutions

Joanna Lachwa, Jerzy Szydlowski, Vesna Najdanovic-Visak, Luís P. N. Rebelo,* Kenneth R. Seddon,* Manuel Nunes da Ponte, José M. S. S. Esperança, and Henrique J. R. Guedes

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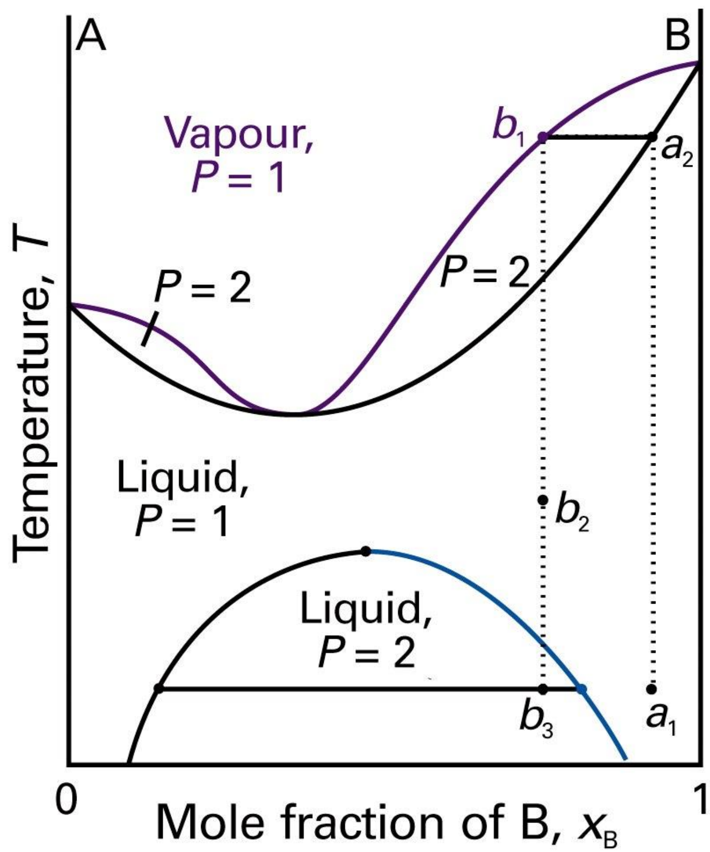
Liquid Solutions

Low-boiling azeotrope

Upper critical temperature

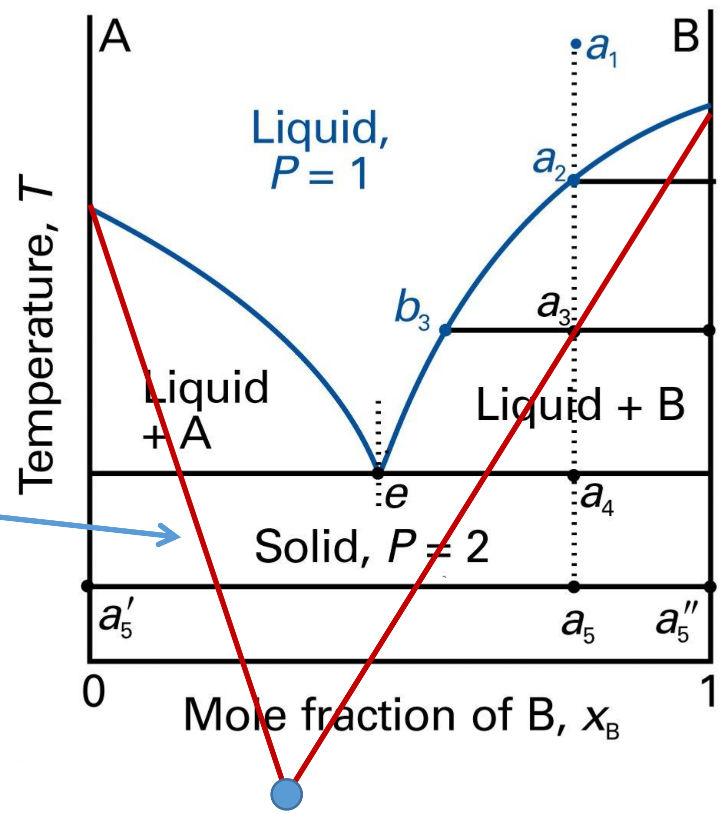
(thermal motion)



Liquid ..eutetic

Deep eutetic

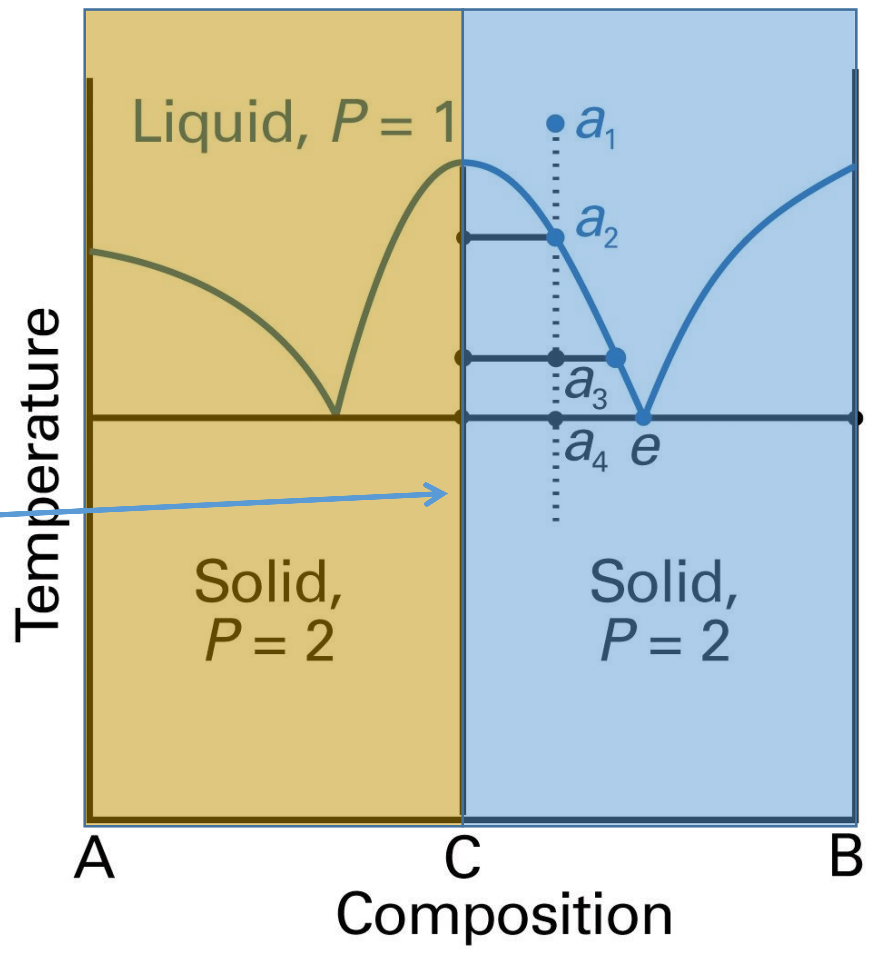
Strong Liquid
solution stabilization



Liquid Solutions

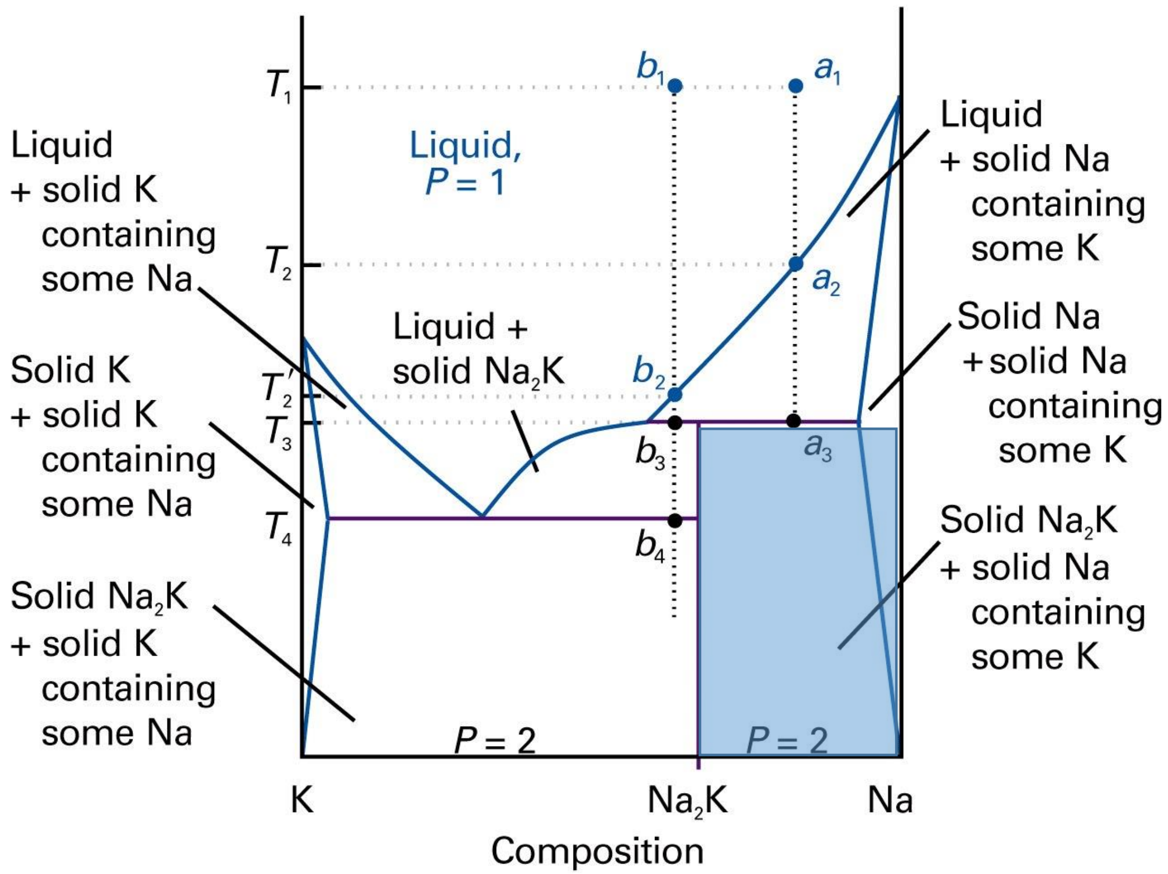
Congruente melting

Solid C stabilization



Liquid Solutions

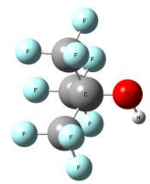
Phase diagrams



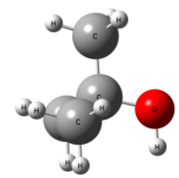
Liquid Solutions

Phase diagrams

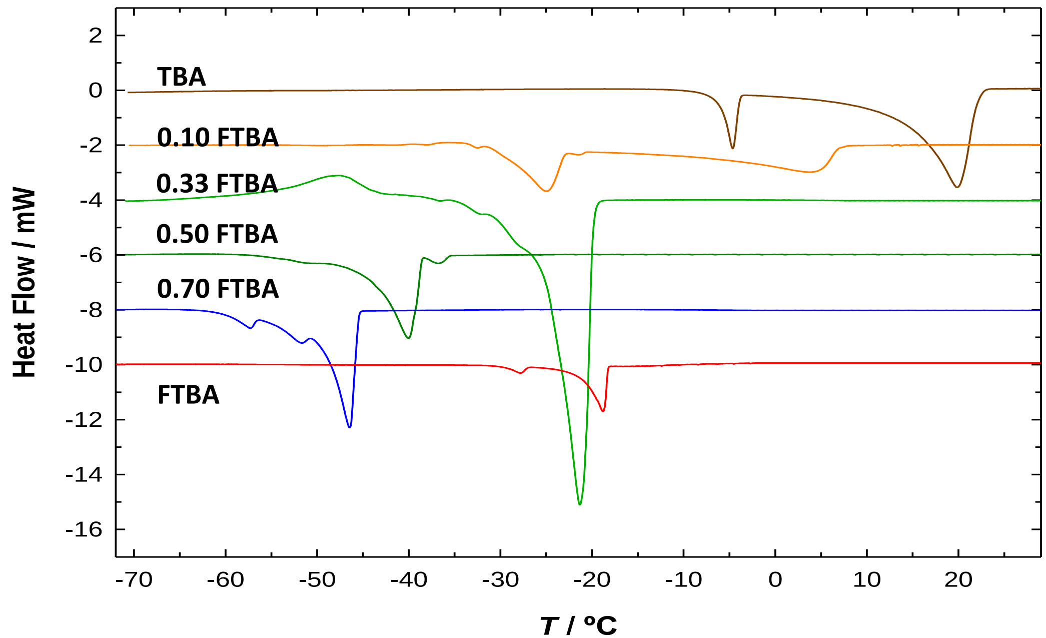
DSC....



FTBA



TBA



R-OH ..acidity

H-bond interaction

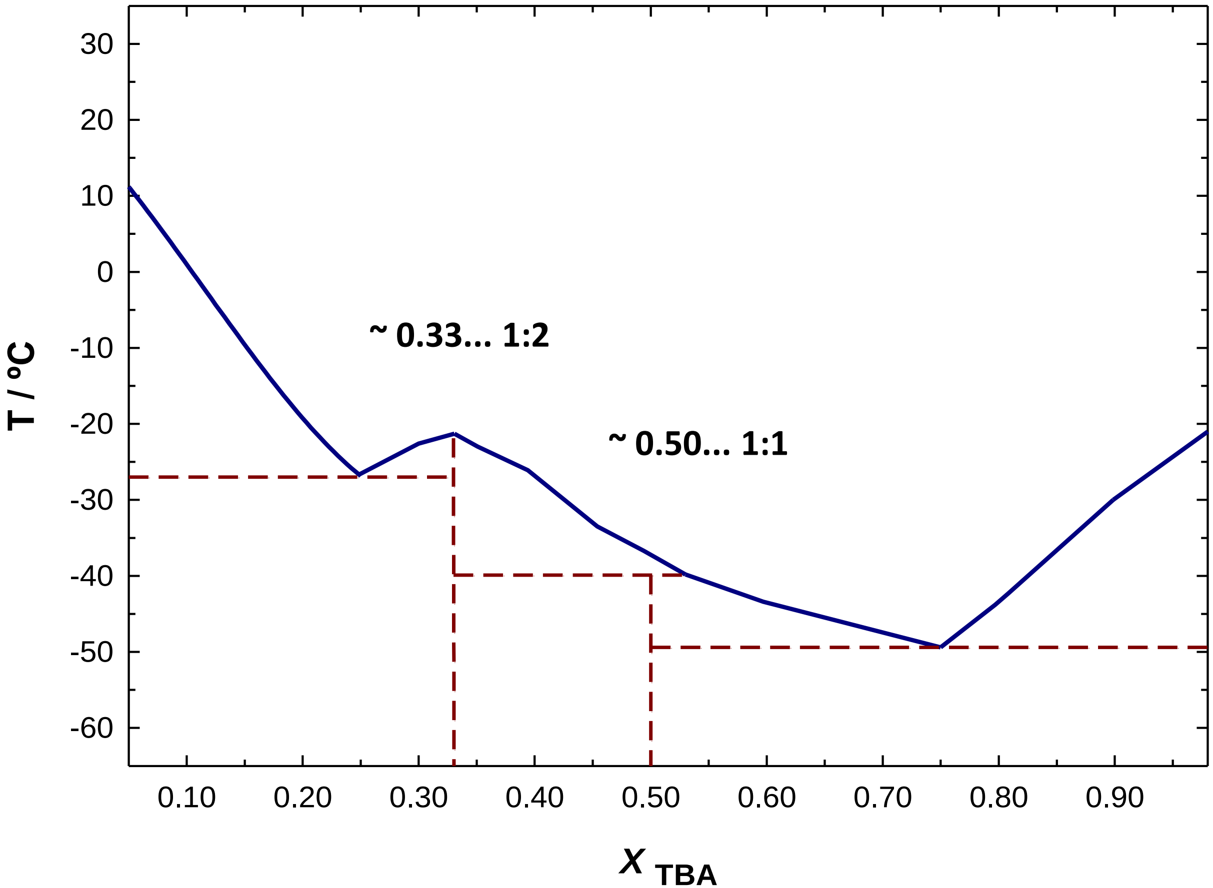
Steric hindrance

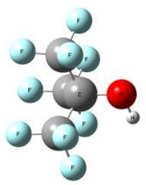
……

Liquid Solutions

Phase diagrams

DSC.... **Solid – Liquid Equilibrium**





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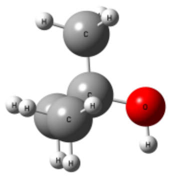


TBA

R-OH ..acidity

H-bond interaction

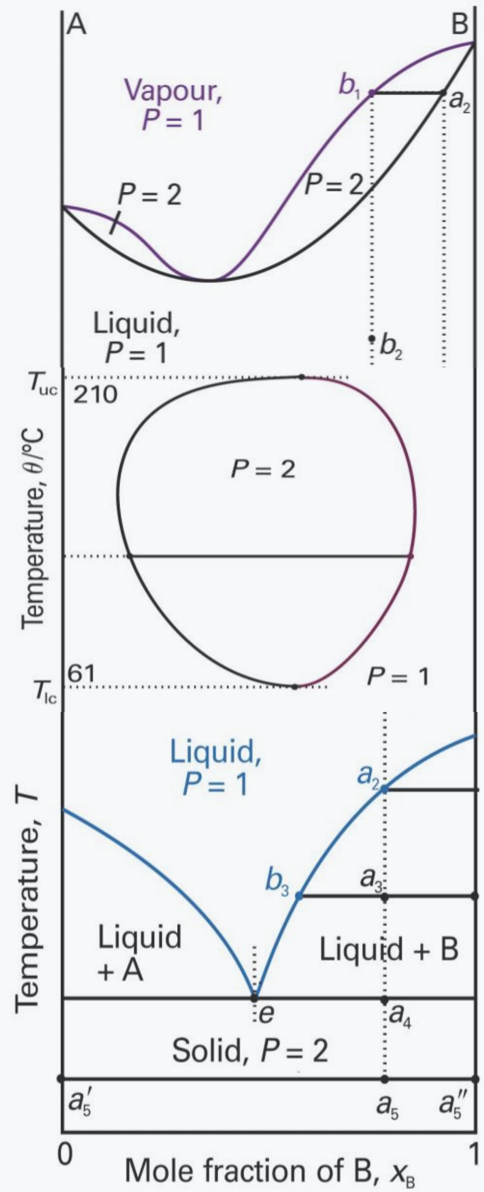
Steric hindrance

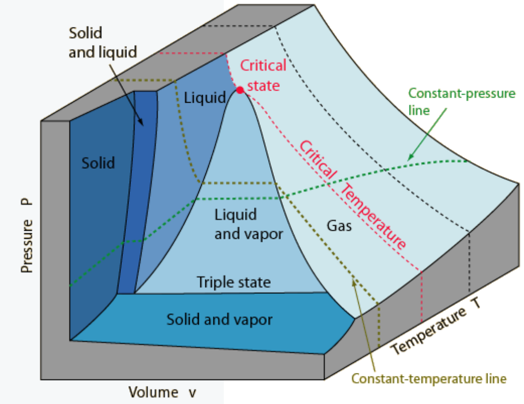
……

Liquid ..vapor

Liquid ..Liquid

Solid ..Liquid





All together