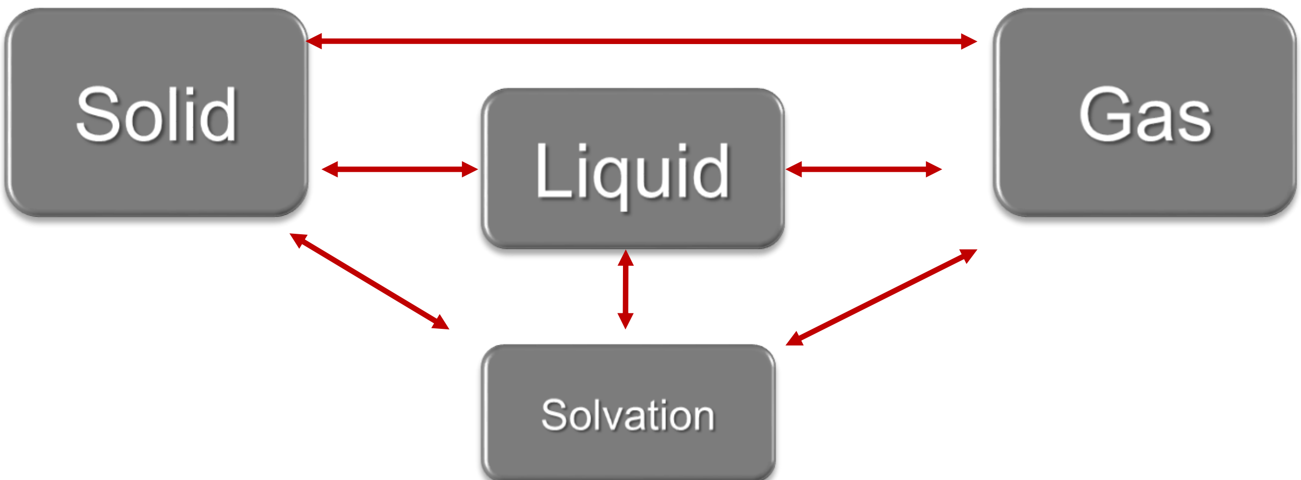
PHASE EQUILIBRIA:
A methodological and thermodynamic approach"

Luís M. N. B. F. Santos
CIQUP, Departamento de Química e Bioquímica
Faculdade de Ciências Universidade do Porto
Porto, Portugal

email: lbsantos@fc.up.pt
email: lbelchiorsantos@gmail.com
URL: http://www.fc.up.pt/pessoas/lbsantos

Overview …working strategy

- **Understanding & Modeling**



- Molecular **Symmetry**
- Molecular and Supramolecular **Structure**

- C-H-π and π-π .. interactions
- H-bond
- Electrostatic .. interactions

Thermodynamics of solid / liquid / gas

Enthalpies of formation (s/l)
(Combustion calorimetry)
(high precision solution-reaction calorimetry)

Entropies and Enthalpies of sub/vap (s/l)
(Knudsen effusion methods; static methods)
(Micro calorimetry)

p (*T*)

Solid → Liquid → gas

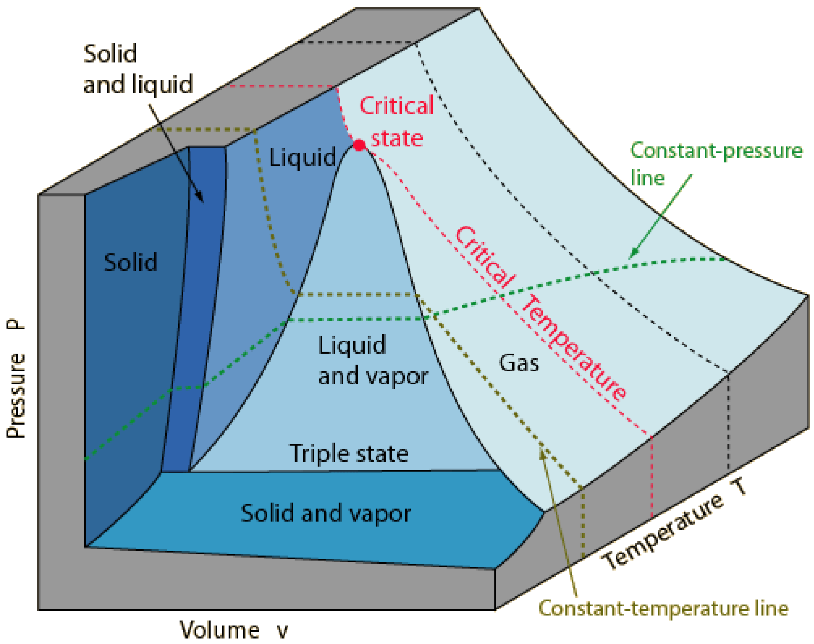
Solid → gas

- Heat capacities; enthalpies and entropies of fusion;
- temperature of fusion
(DSC, adiabatic calorimetry; drop calorimetry)

Gas phase ENERGETICS
(Computational thermochemistry)

Pure substances

PVT diagram

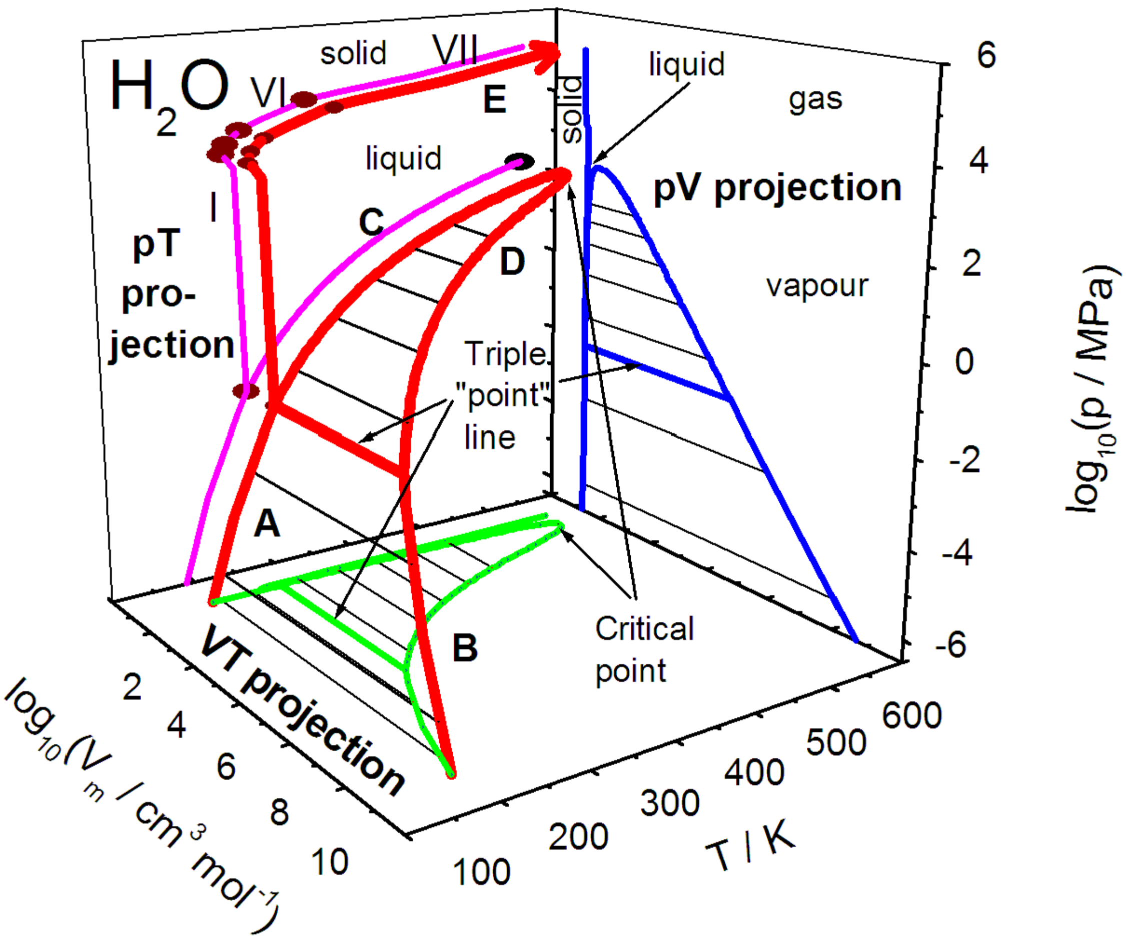


-**Why each compound have a different PVT surface profile?**

- 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 :

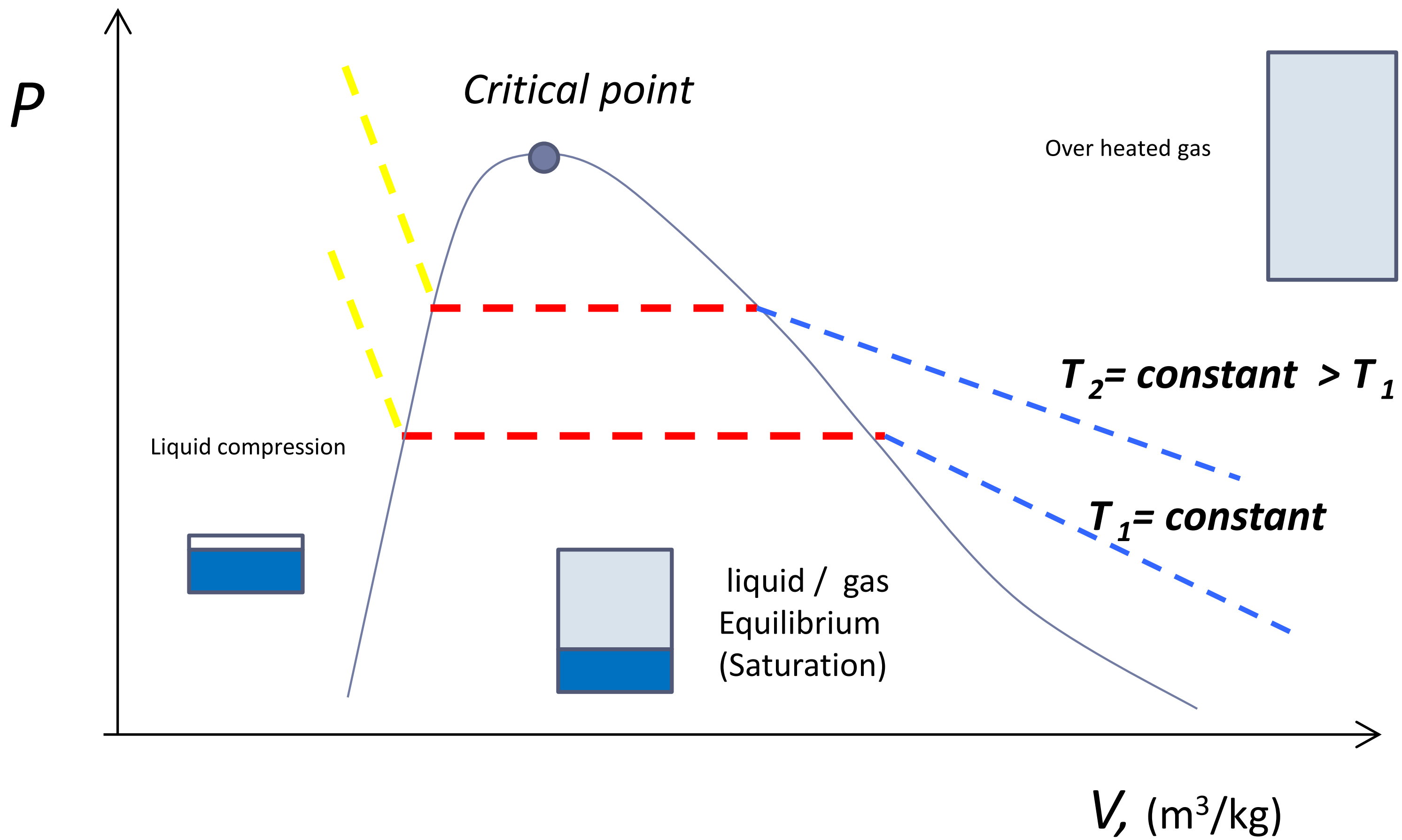
Little dependence of the liquid / solid phases

- PV projection :

Little dependence of the liquid / solid phases

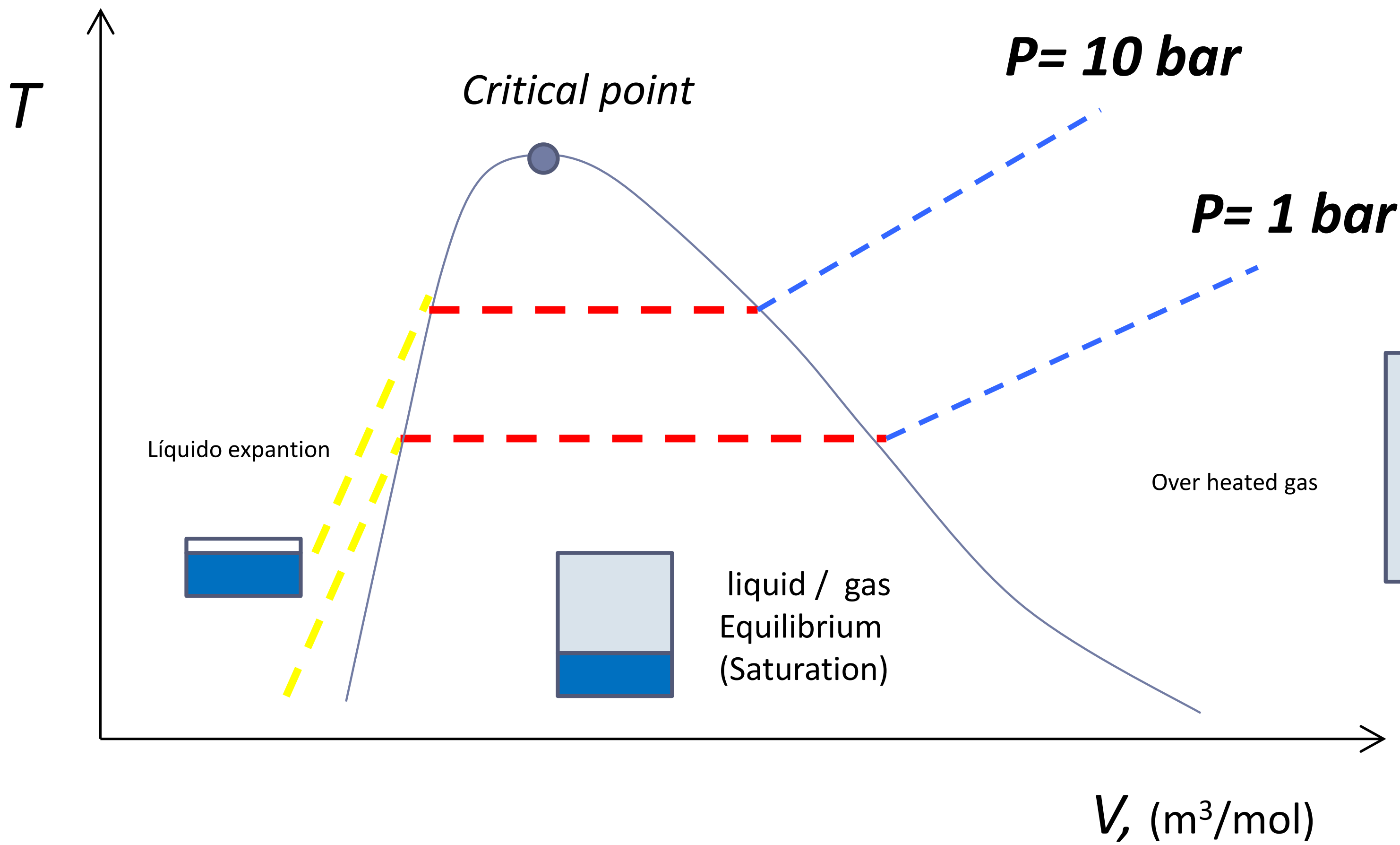
Properties of pure substances

Pressure–volume diagram



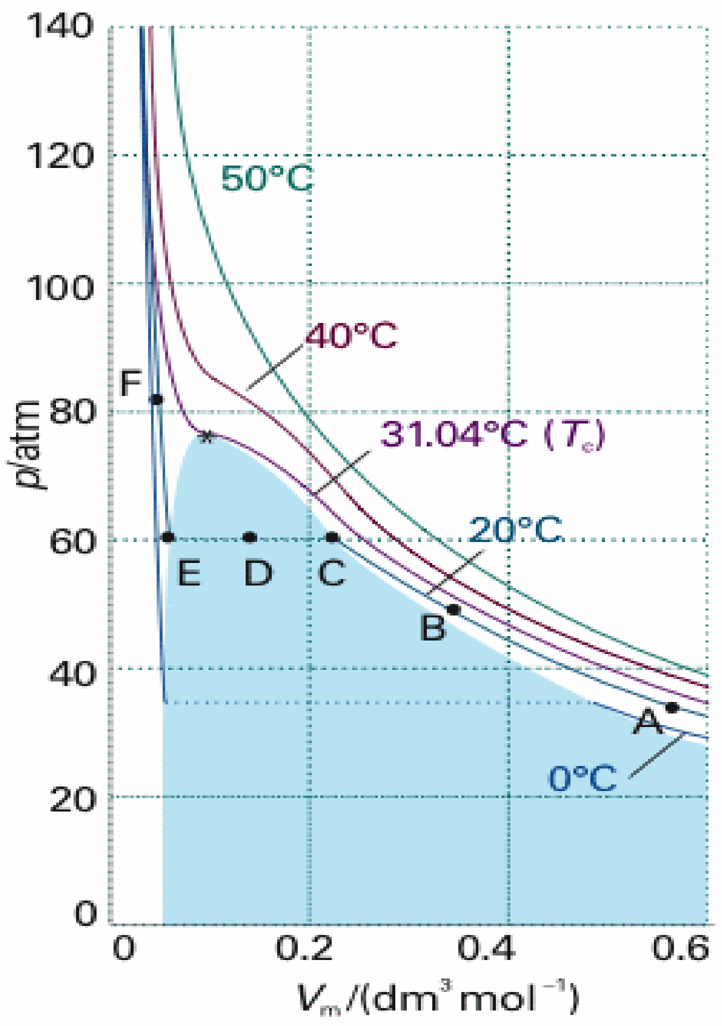
Properties of pure substances

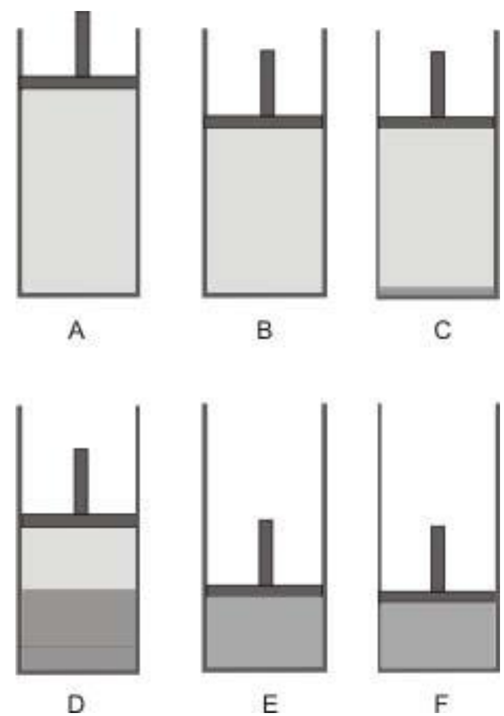
Temperature –volume diagram

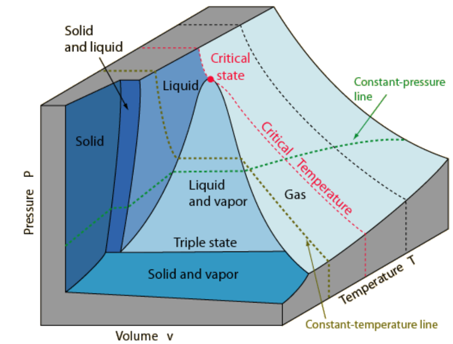


P-V …Isothermic lines

41st Conference on Phase Equilibria
XLIèmes Journées d'Étude des Équilibres entre Phases

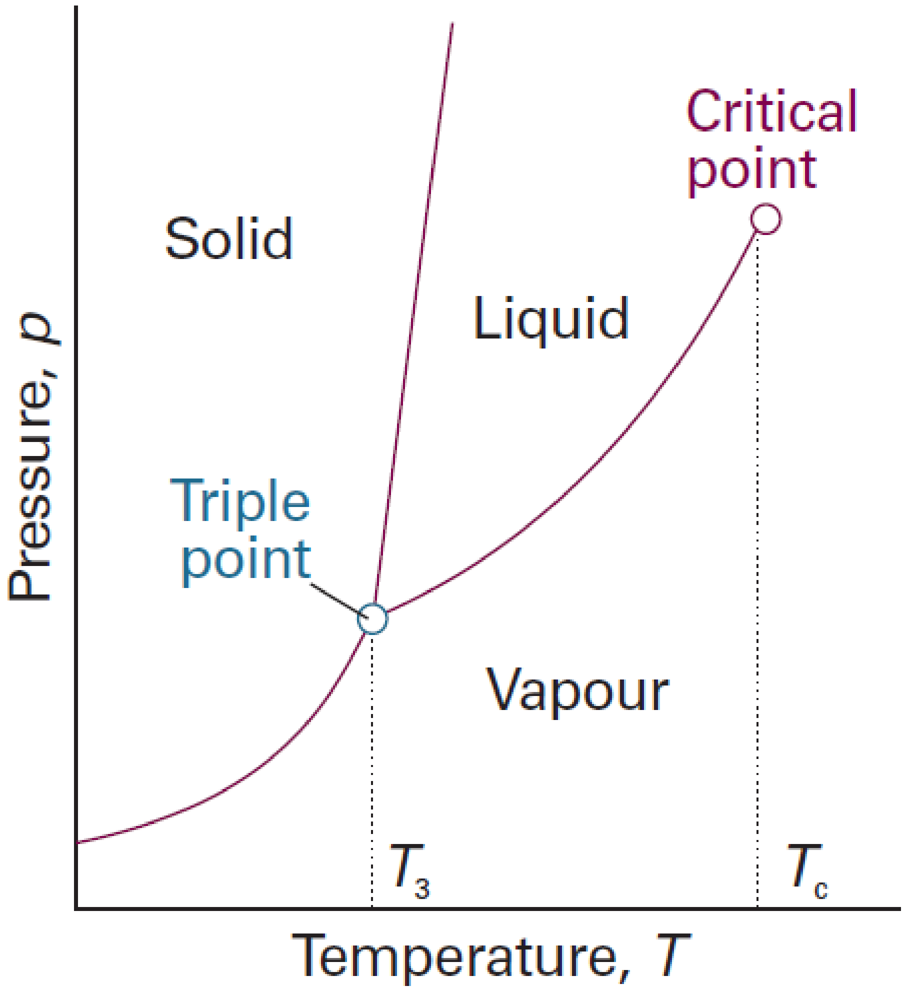






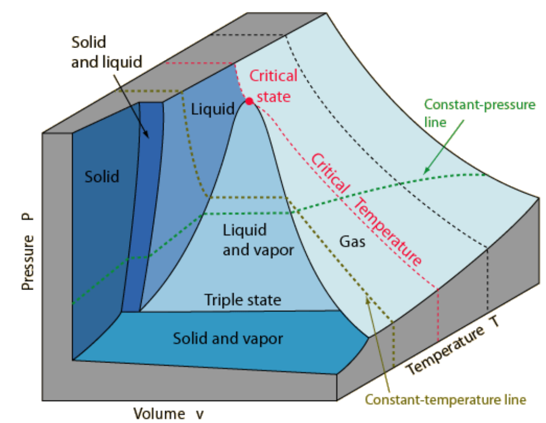
Properties of pure substances

PT diagram



- PT projection :

Complex and interesting profile!

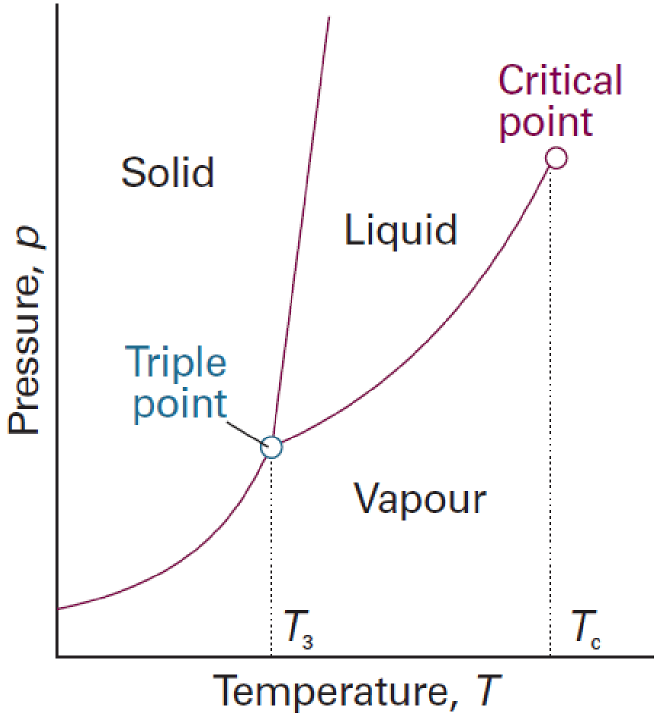


Phase

of a substance is a form of matter that is **uniform** throughout in **chemical composition** and **physical state**.

Phase transition,

the spontaneous **conversion** of one **phase** into another phase, occurs at a characteristic ***T*** for a given ***p***



Gibbs Phase Rule

p,T

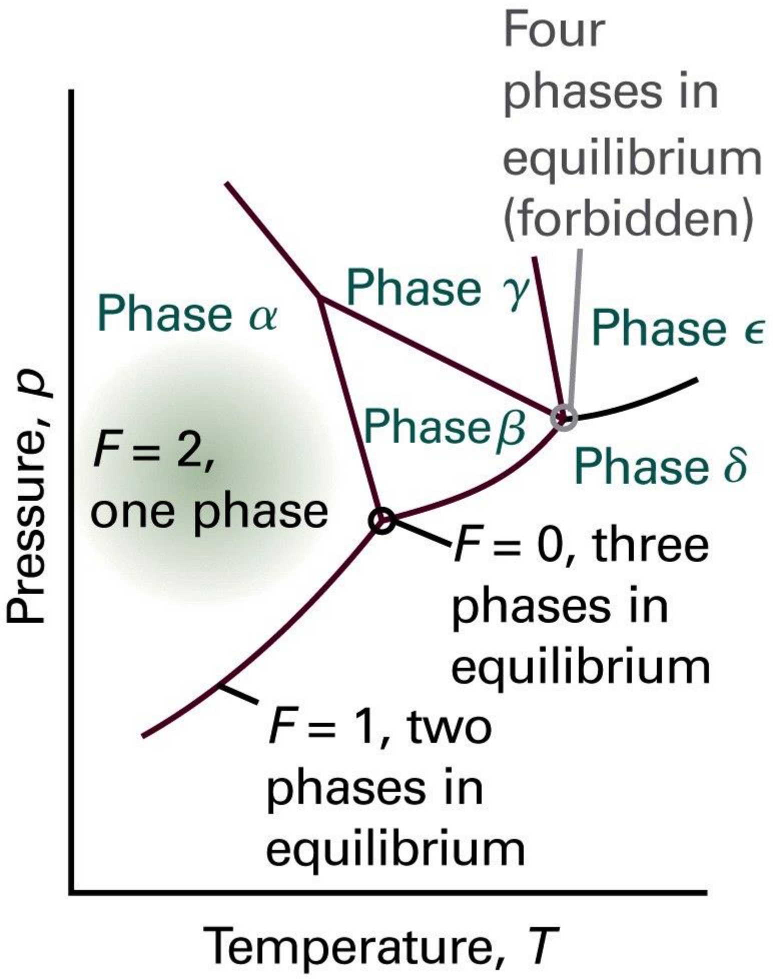
Gibbs Phase rule :

v or F = C - P + 2

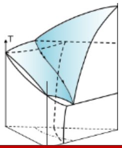
for binary mixtures C= 2

 # Phases P

Variance: Number of degrees of freedon



Properties of pure substances

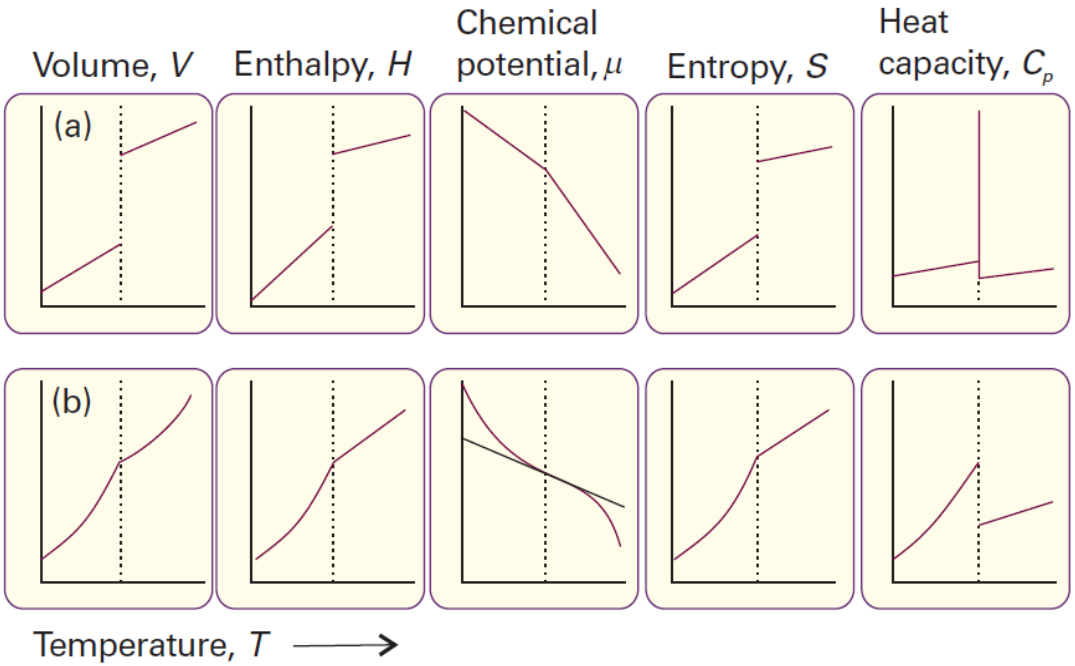


First-order phase

e.g… fusion, vaporization ..etc

Second-order

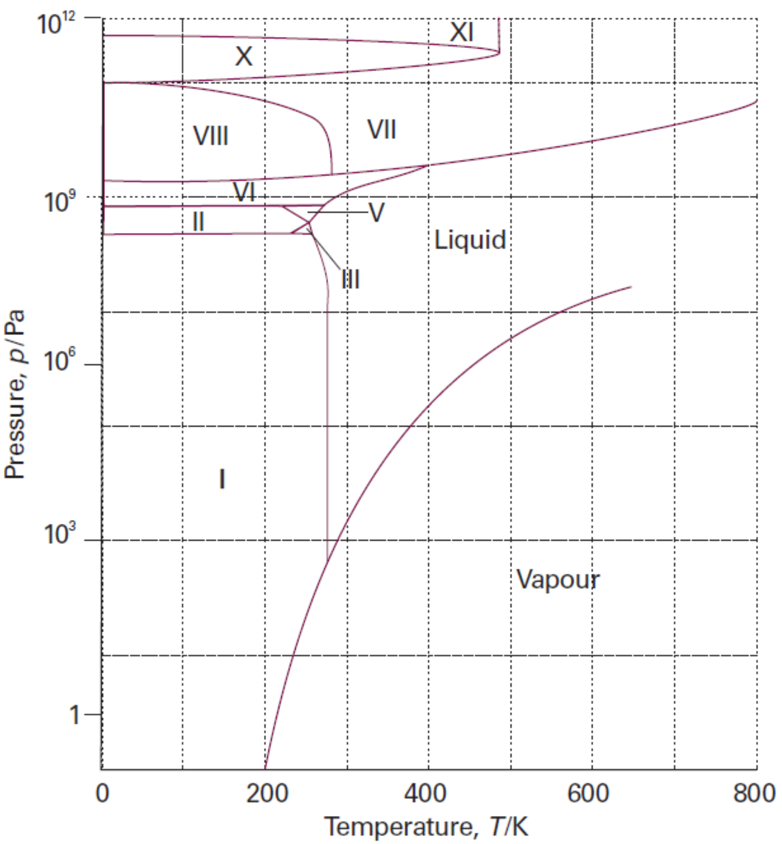
e.g… some ….. solid- solid ..etc



Properties of pure substances

PT diagram

Complex Phase diagram of H_2O



Phase stability

$$((\partial G/\partial T)_p = -S)$$

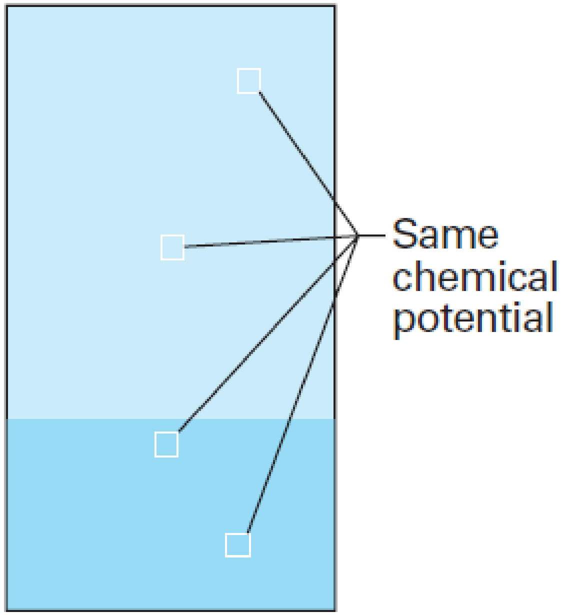
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

Sol $\rightleftarrows$ Liq

$$S_m(g) > S_m(l)$$

$$S_m(l) > S_m(s)$$



Properties of pure substances

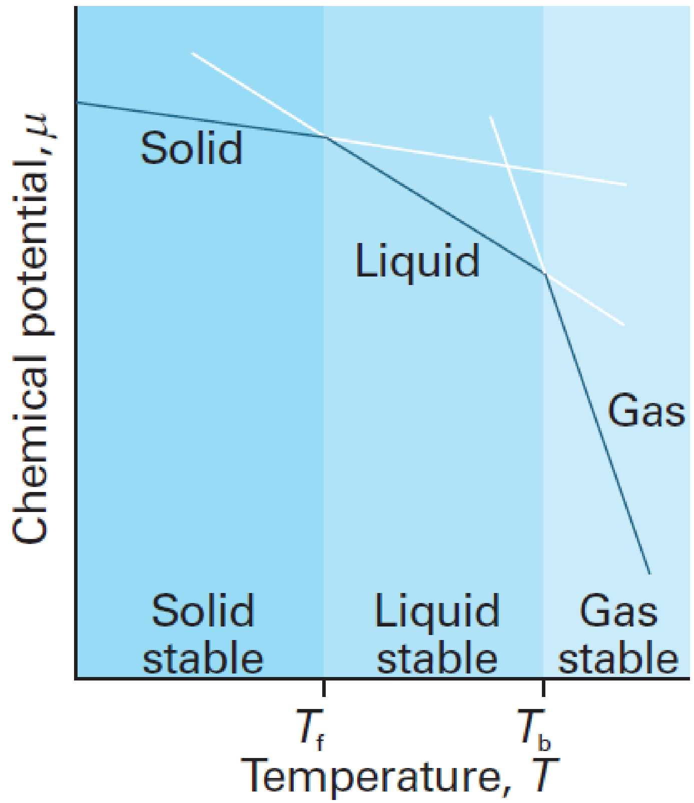
PT diagram

Phase stability

Sol $\rightleftharpoons$ Liq   Liq $\rightleftharpoons$ gas

$$\left(\left(\partial G/\partial T\right)_p = -S\right)$$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$



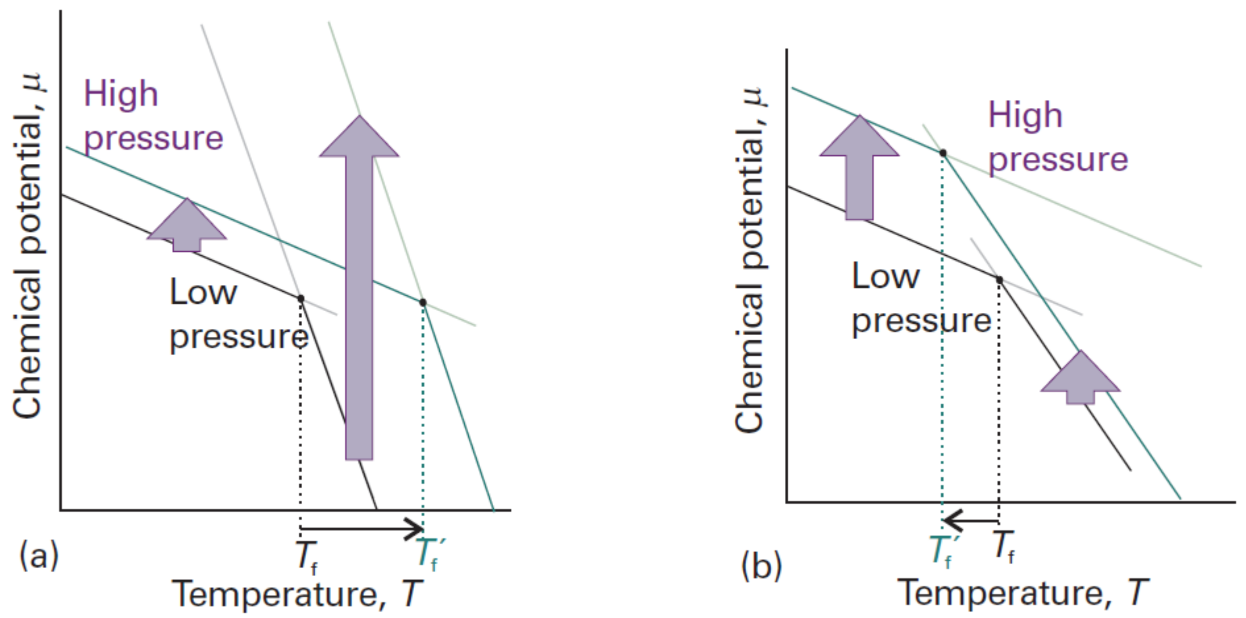
$$S_m(g) > S_m(l)$$

$$S_m(l) > S_m(s)$$

Phase stability

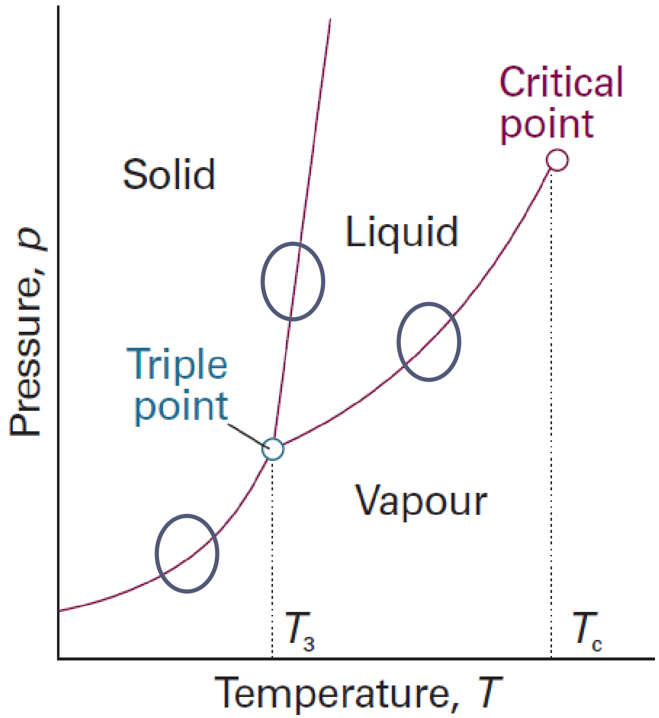
liq ⇄ Gas   Sol ⇄ Liq

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$



Properties of pure substances

PT diagram



shape of the equilibrium lines

$$\frac{dp}{dT}$$

Properties of pure substances

PT diagram

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

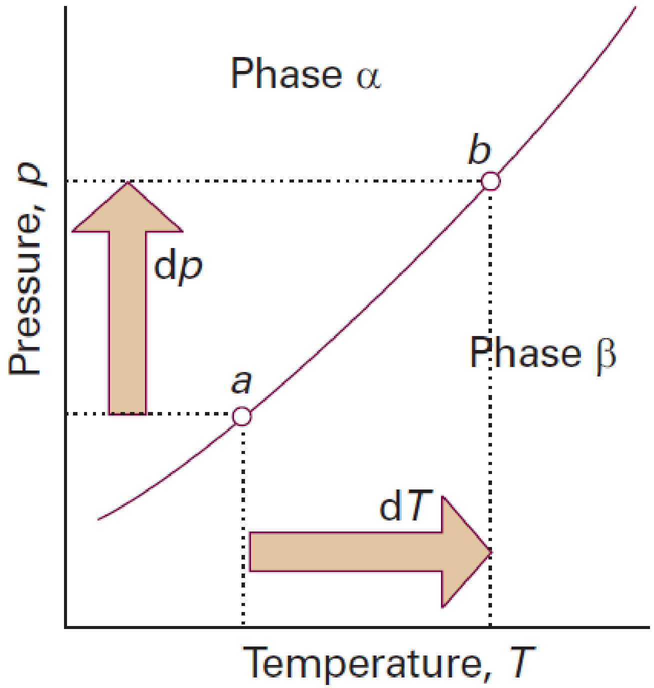
Phase_α $\rightleftarrows$ Phase_β

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

$$\left(\frac{\partial \mu_\beta}{\partial p}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial p}\right)_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{trs}V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_p - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_p = -S_{\beta,m} + S_{\alpha,m} = \Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$



Phase_α ⇌ Phase_β

Shape of the equilibria lines

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

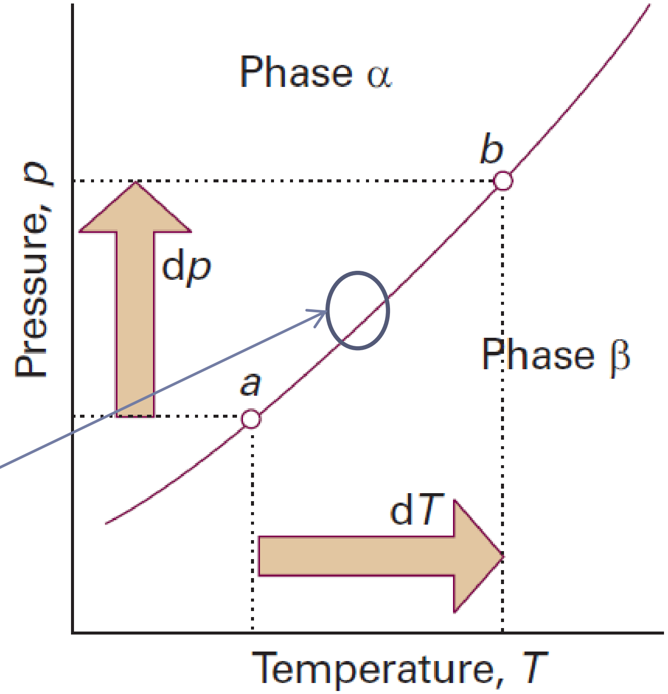
$$-S_{\alpha,\mathrm{m}}\mathrm{d}T + V_{\alpha,\mathrm{m}}\mathrm{d}p = -S_{\beta,\mathrm{m}}\mathrm{d}T + V_{\beta,\mathrm{m}}\mathrm{d}p$$

$$(V_{\beta,\mathrm{m}} - V_{\alpha,\mathrm{m}})\mathrm{d}p = (S_{\beta,\mathrm{m}} - S_{\alpha,\mathrm{m}})\mathrm{d}T$$

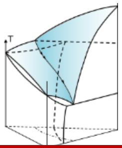
Clapeyron equation

$$\boxed{\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}}S}{\Delta_{\mathrm{trs}}V}}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T}$$



Properties of pure substances



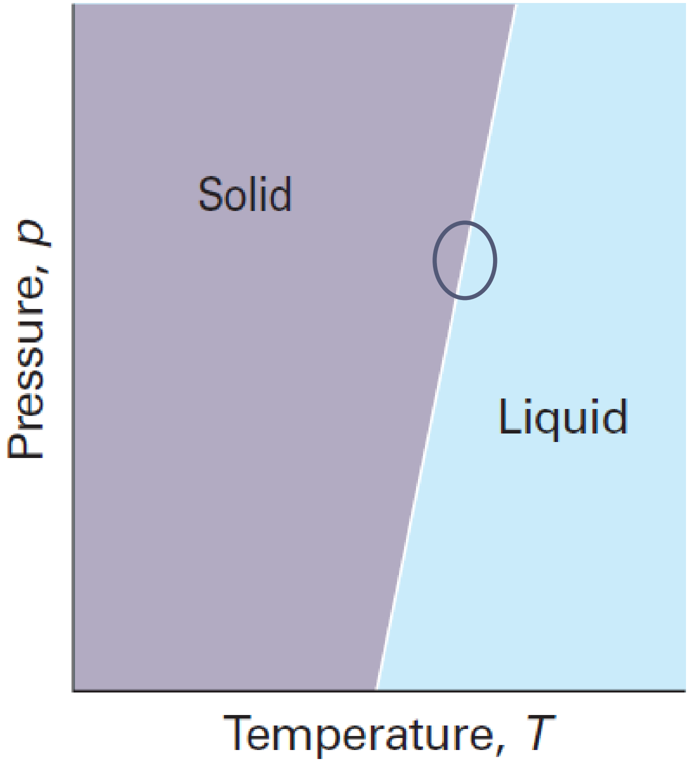
PT diagram

$\Delta_{fus}V = V_m\,(l) - V_m(s)$

$\Delta_{fus}S = S_m(l) - S_m(s)$

$\Delta_{fus}S = \Delta_{fus}H / T_{fus}$

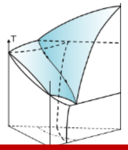
Solid -Liquid ..condensed phases



Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$$

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$$

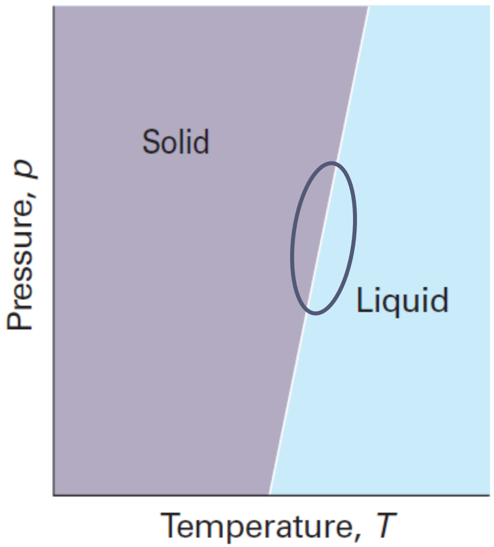


Properties of pure substances

PT diagram

Solid -Liquid ..condensed phases

Clapeyron equation $$\frac{dp}{dT}=\frac{\Delta_{trs}S}{\Delta_{trs}V}$$



$$\frac{dp}{dT}=\frac{\Delta_{fus}H}{T\Delta_{fus}V}$$

$$\int_{p^*}^{p} dp=\frac{\Delta_{fus}H}{\Delta_{fus}V}\int_{T^*}^{T}\frac{dT}{T}$$

$$p\approx p^*+\frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*}$$

$$\ln\frac{T}{T^*}=\ln\left(1+\frac{T-T^*}{T^*}\right)\approx\frac{T-T^*}{T^*}$$

therefore,

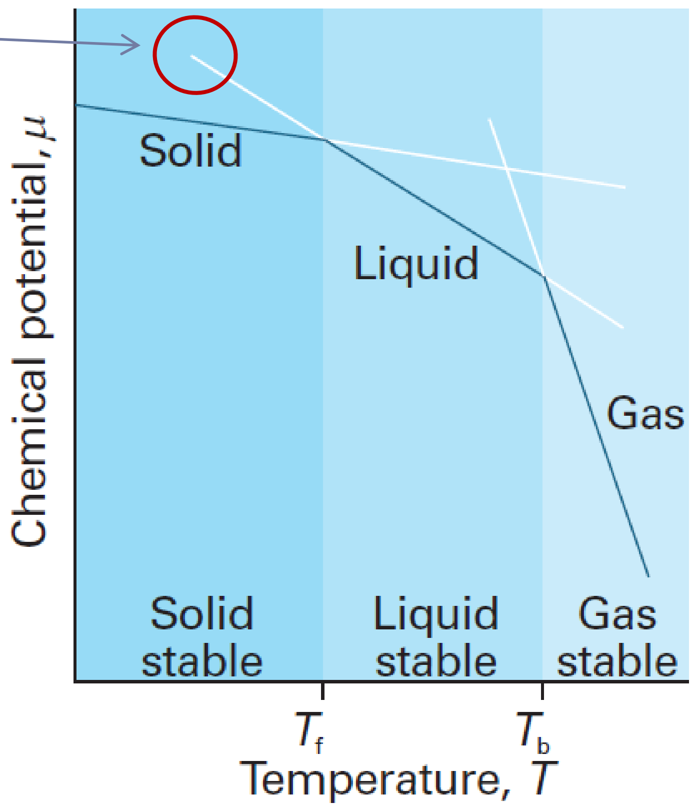
$$p\approx p^*+\frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T-T^*)$$

Linear approximation

DSC: Supercooled Liquid

Supercooled Liquid

e.g. quenching the liquid



Properties of pure substances

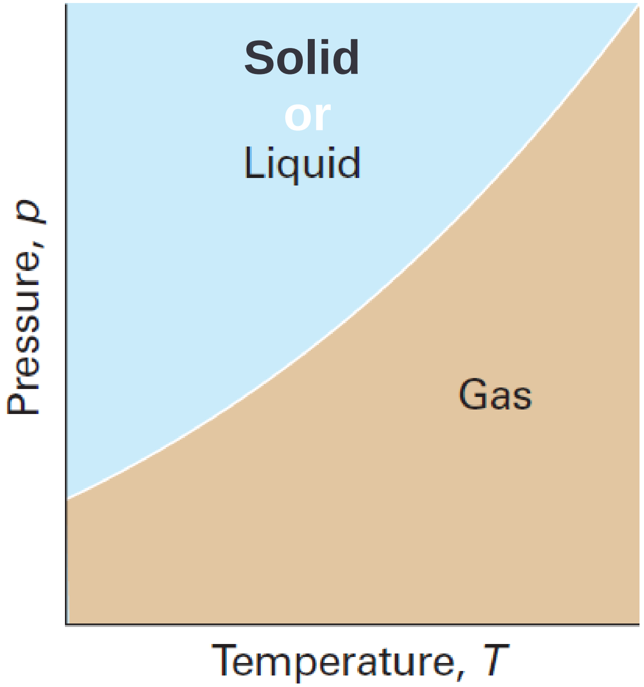
PT diagram

liquid–vapour

solid–vapour

Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$$



$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)}$$

$$V_m(g) = RT/p$$

$$\Delta_{vap}V \approx V_m(g)$$

$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

$$\boxed{\ln\frac{p}{p^o} = -\frac{\Delta^{g}_{cr/l}H^o_m}{R}\cdot\frac{1}{T} + \frac{\Delta^{g}_{cr/l}S_m}{R}}$$

Clausius–Clapeyron equation

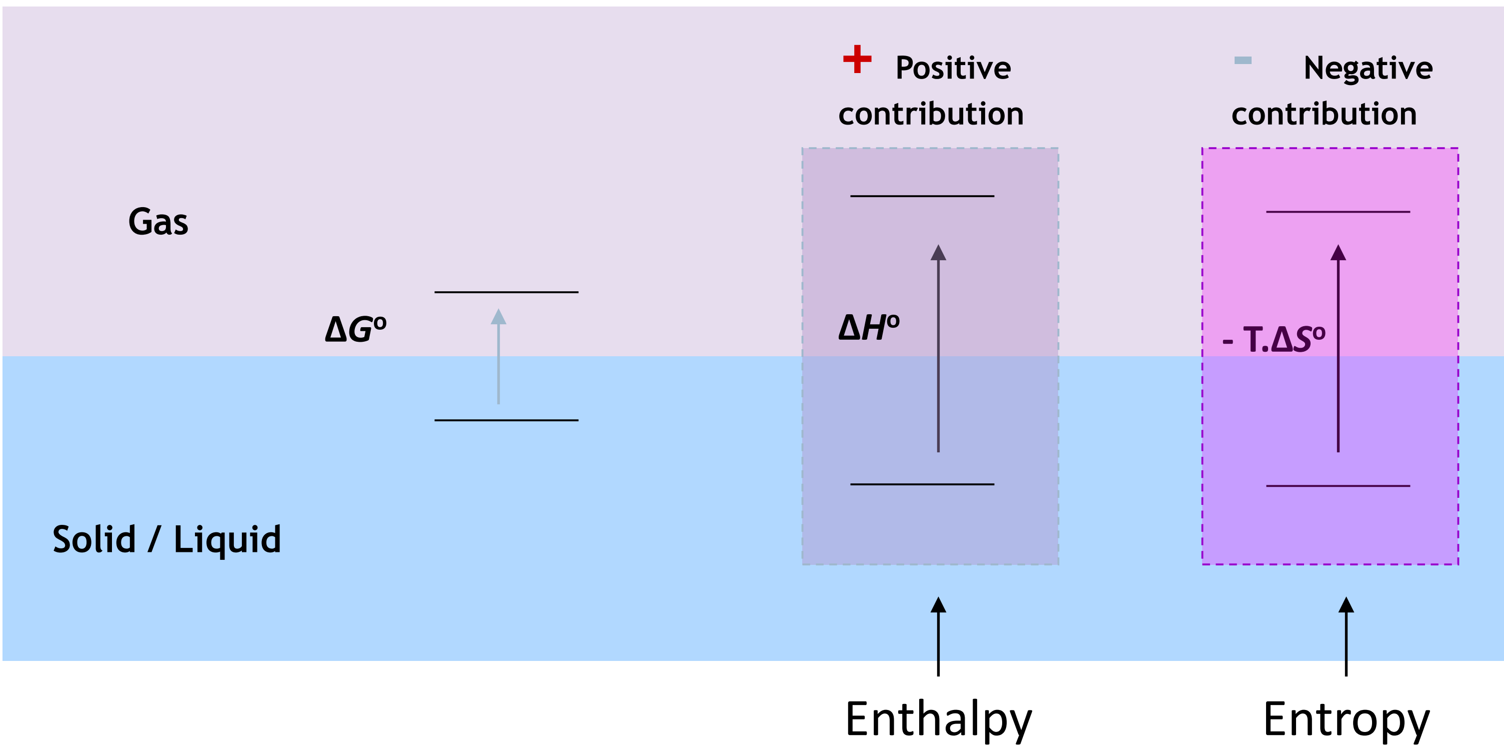
Properties of pure substances

PT diagram

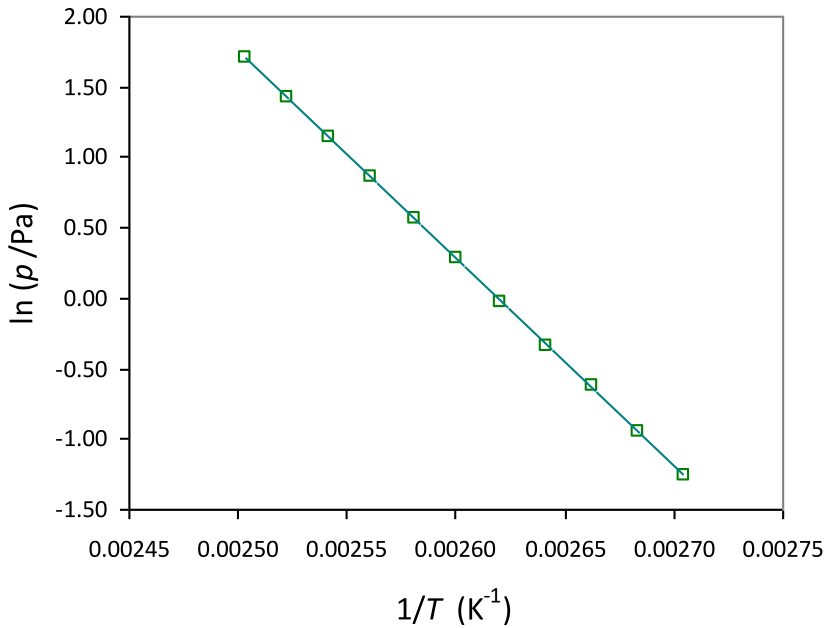
***P= f(T)* … vapor pressure Measurements**

$$\ln\frac{p}{p^{o}} = -\frac{\Delta_{cr/l}^{g}H_{m}^{o}}{R}\cdot\frac{1}{T}+\frac{\Delta_{cr/l}^{g}S_{m}}{R}$$

$$\Delta G^{o} = \Delta H^{o} - T.\,\Delta S^{o} = -\,RT\cdot\ln\,(p/p^{o})$$



p=f(T).........Phase diagrams



Clausius-Clapeyron equation

$$\ln\frac{p}{p^{\circ}} = -\frac{\Delta^{g}_{cr/l}H^{\circ}_{m}}{R}\cdot\frac{1}{T}+\frac{\Delta^{g}_{cr/l}S_{m}}{R}$$

Clarke & Glew equation

$\uparrow$

Cp ..correction

Vapour pressures (T) $\rightarrow$ $\Delta^{g}{}_{cr/l}\, H^{o}{}_{m}$

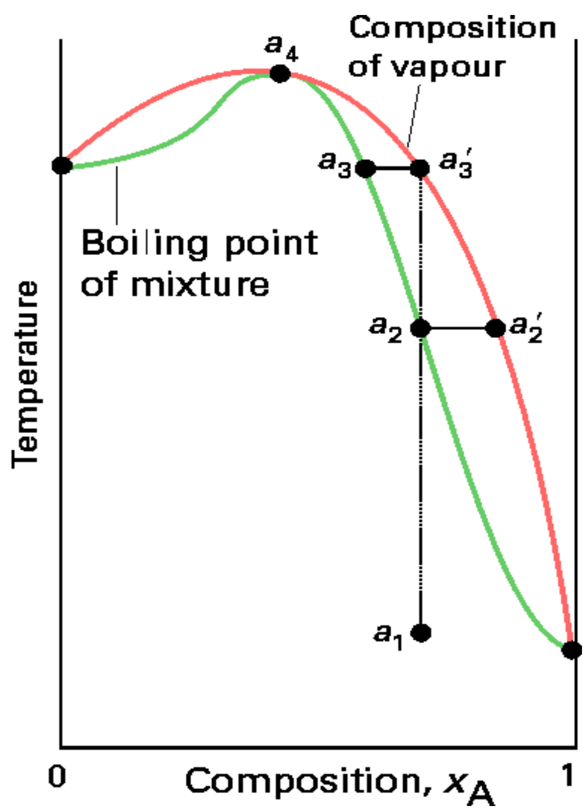
Vapour pressures (T) $\rightarrow$ $\Delta^{g}{}_{cr/l}\, S^{o}{}_{m}$

Vapour pressures (T) $\rightarrow$ $\Delta^{g}{}_{cr/l}\, G^{o}{}_{m}$

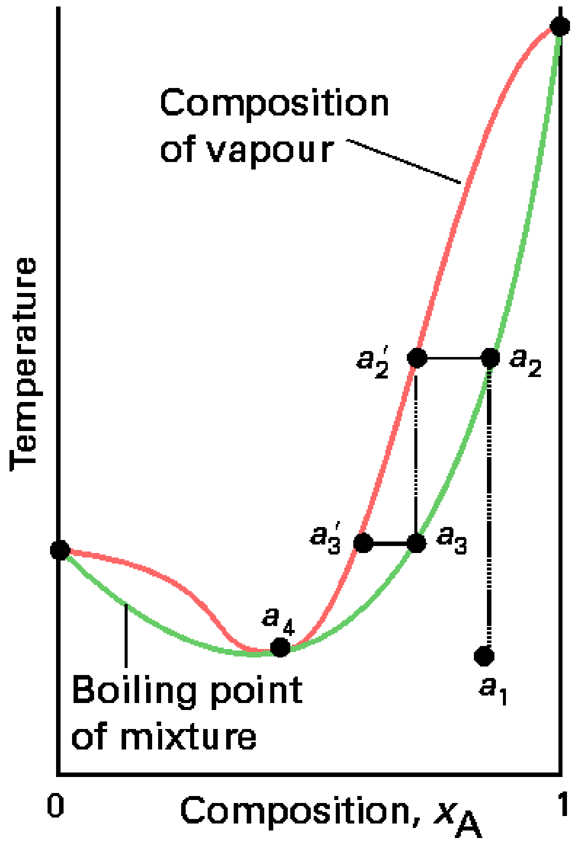
Liquid Solutions

p ...fixed

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



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

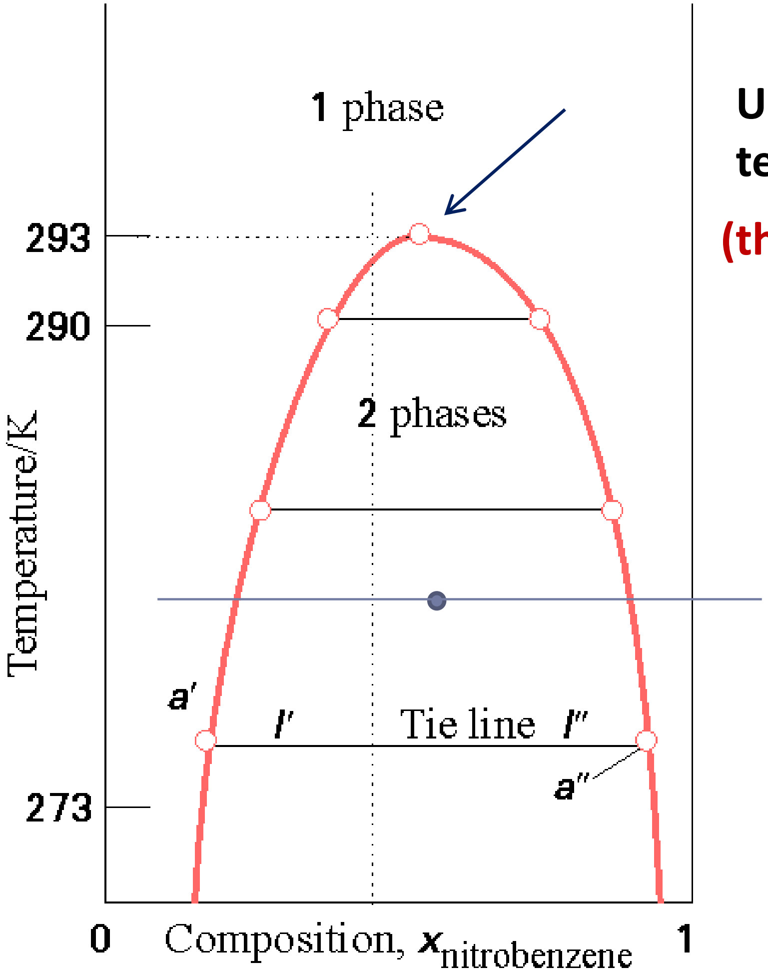


Liquid Solutions

Phase diagrams

Phase separation

E.g., hexane/nitrobenzene:



Upper critical temperature

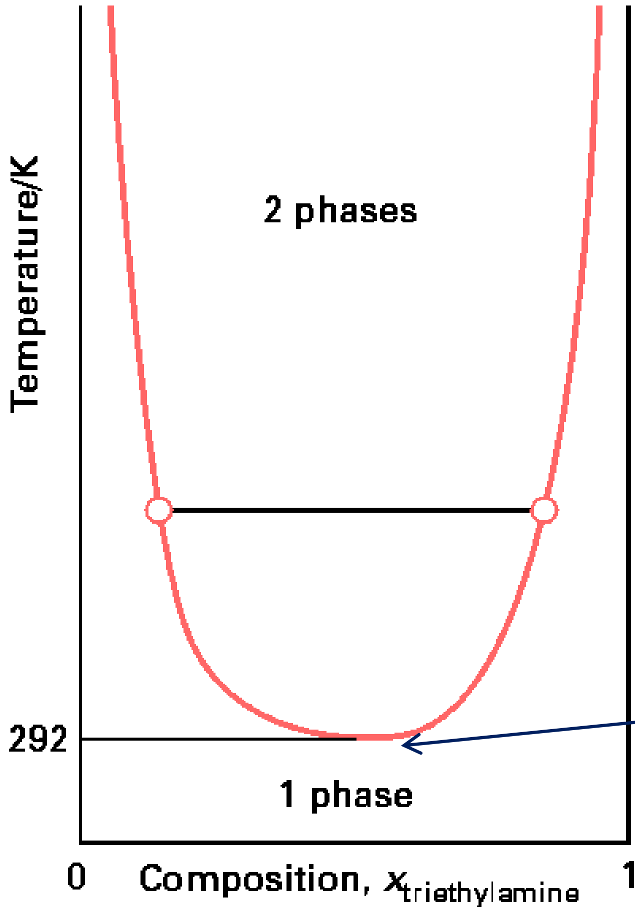
(thermal motion)

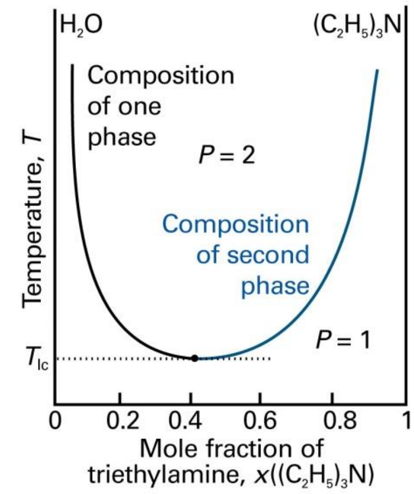
Liquid Solutions

Phase diagrams

Phase separation

E.g., triethylamine /water:

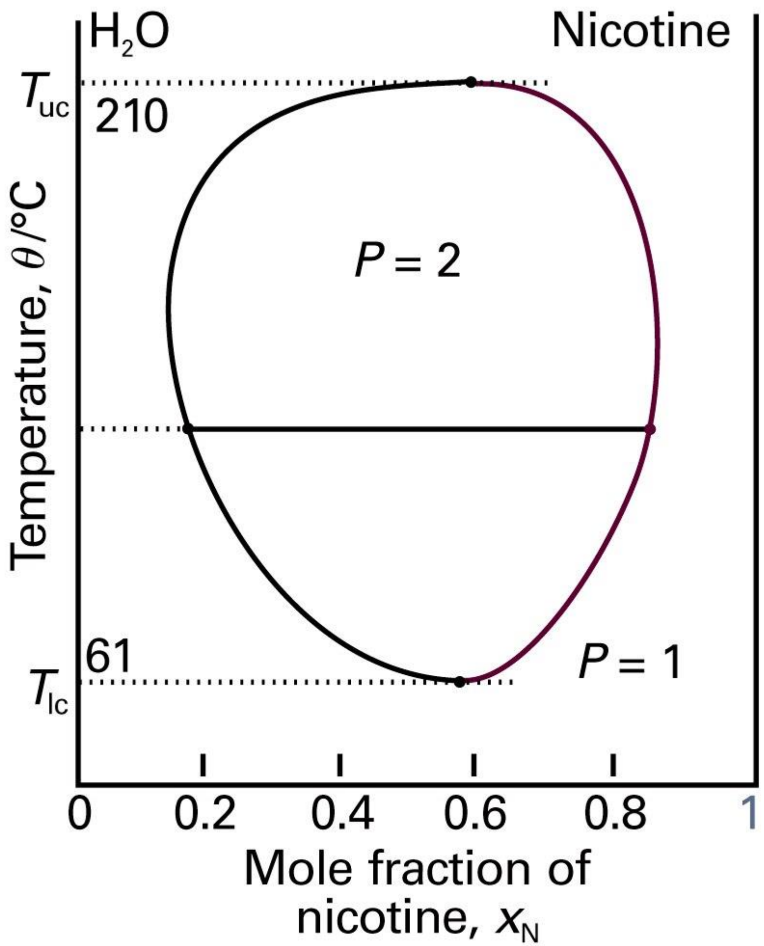




Lower $T_{critical}$
(complex formed)

Liquid Solutions

Phase separation



Upper critical temperature

(thermal motion)

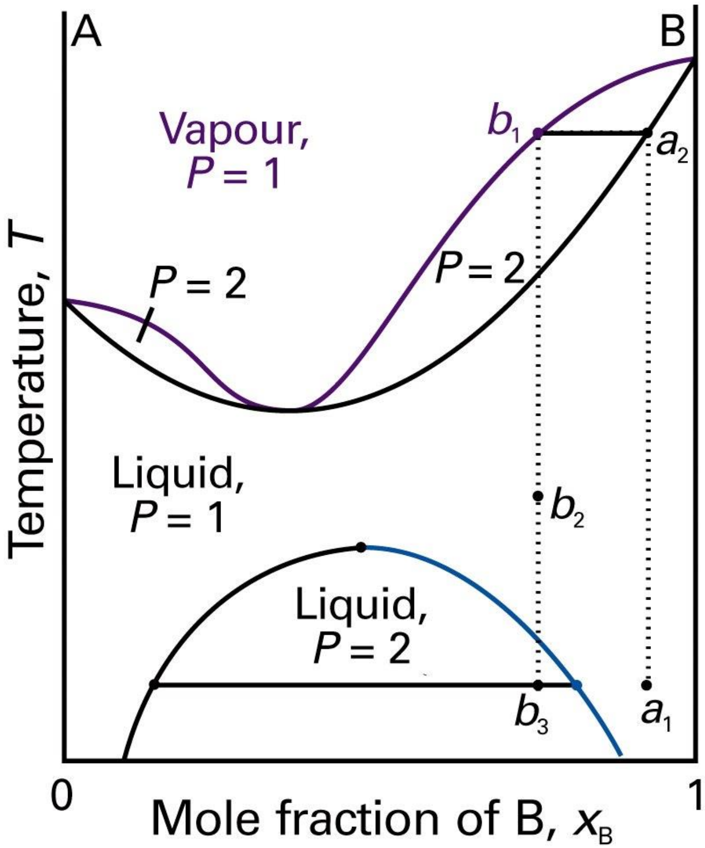
Lower $T_{critical}$
(complex formed)

Liquid Solutions

Low-boiling azeotrope

Upper critical temperature

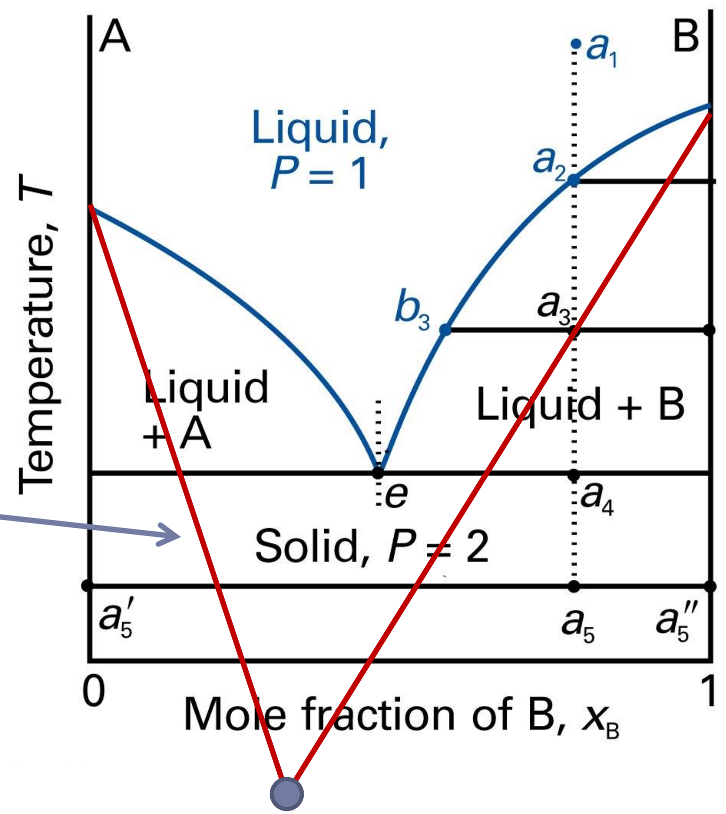
(thermal motion)



Liquid ..eutetic

Deep eutetic

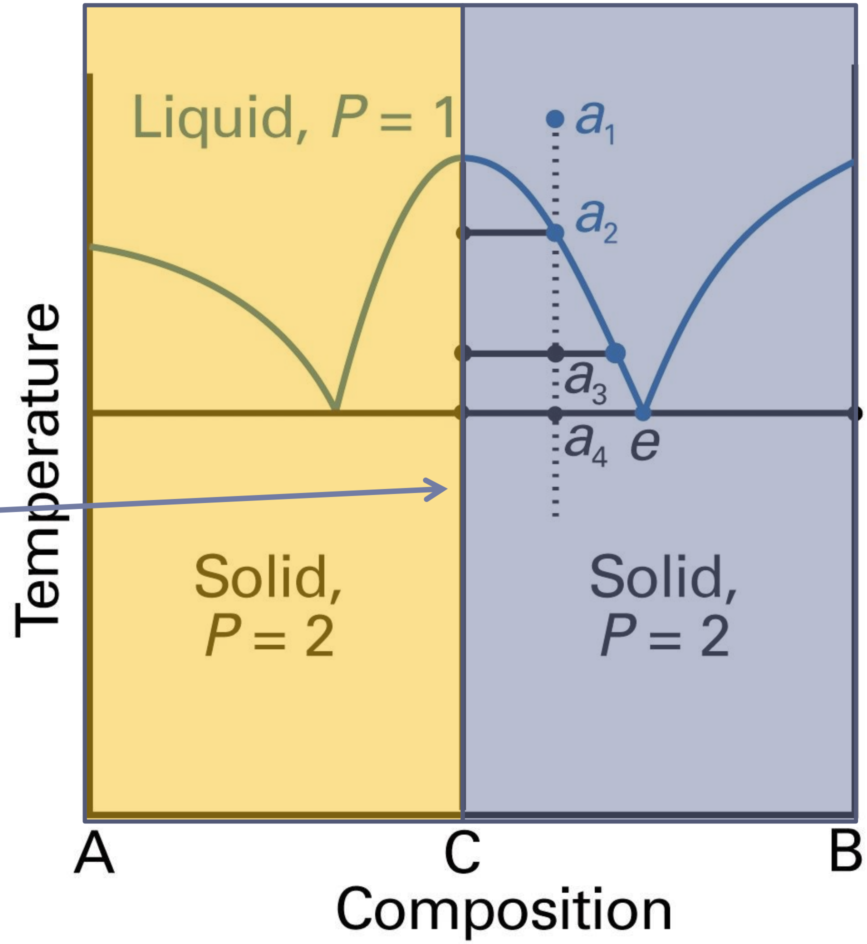
Strong Liquid
solution stabilization



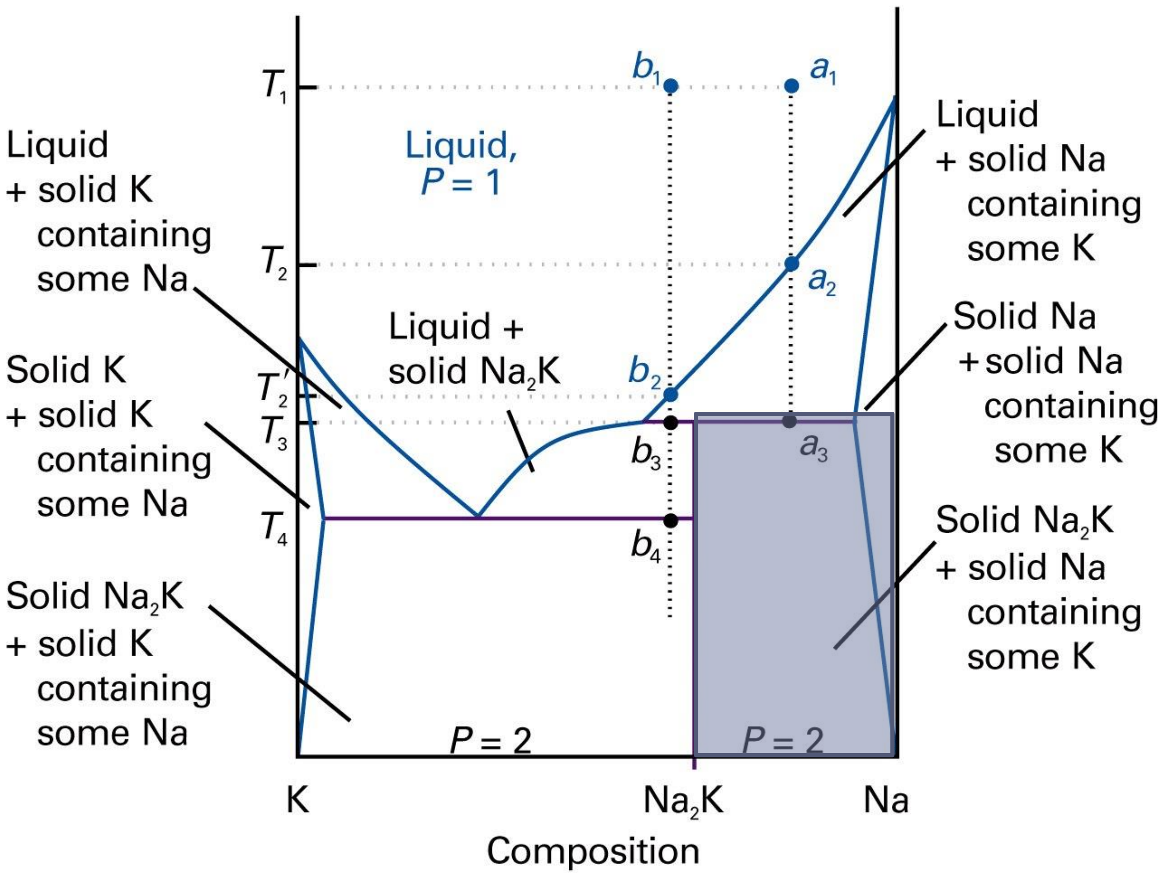
Liquid Solutions

Congruent e melting

Solid C stabilization



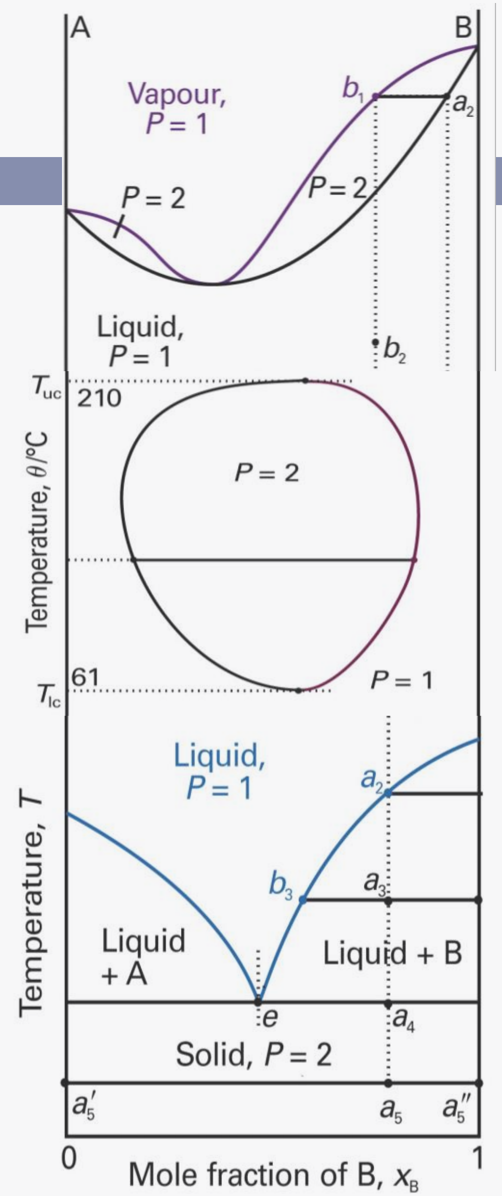
Liquid Solutions



Liquid ..vapor

Liquid ..Liquid

Solid ..Liquid



All together