U.PORTO
FACULDADE DE CIÊNCIAS
UNIVERSIDADE DO PORTO

MAT 2020

MÉTODOS DE ANÁLISE TÉRMICA

DSC … Metodologia e Aplicações

DQB... 2019-2020

PHASE EQUILIBRIA:

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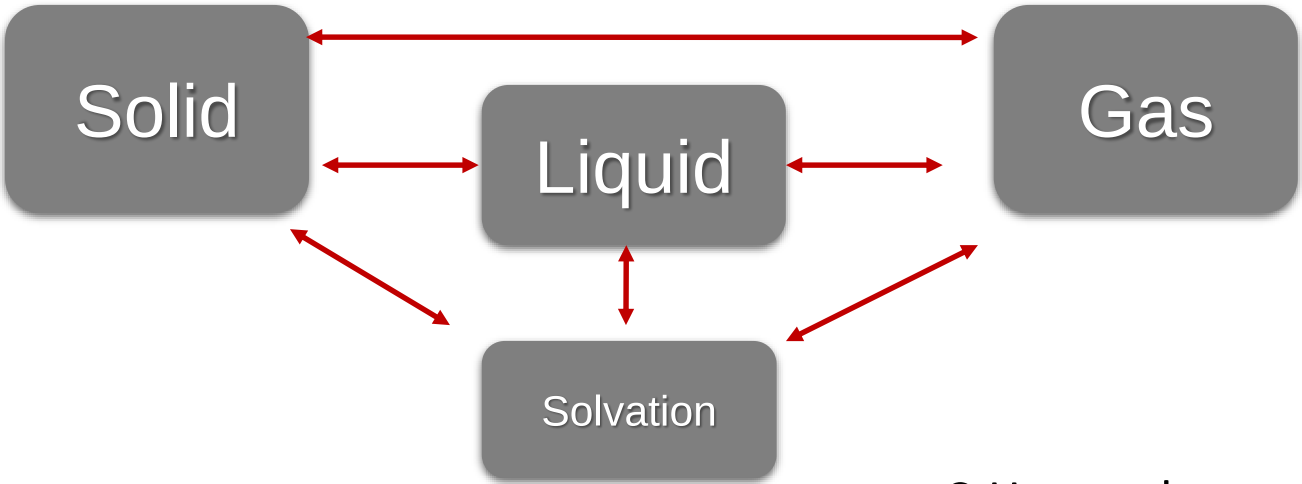
Overview

- **Understanding & Modeling**



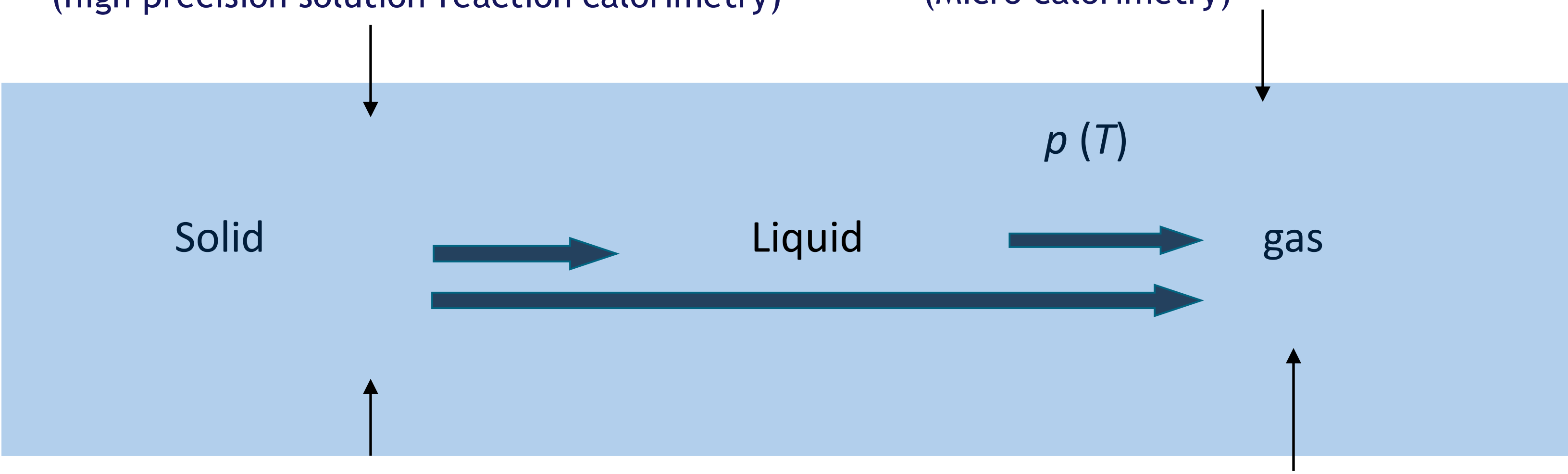
- C-H-π and π-π .. interactions
- H-bond
- Electrostatic .. interactions

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

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)

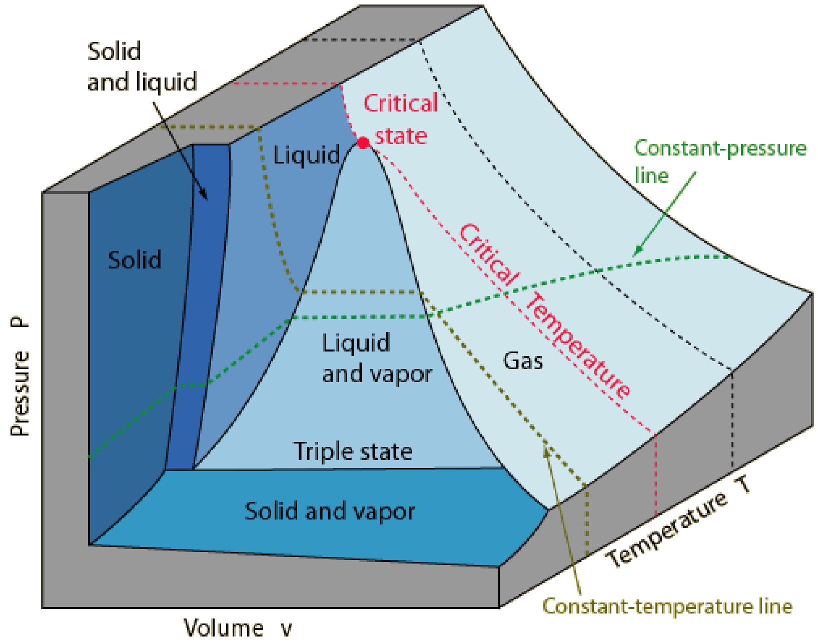


- Heat capacities; enthalpies and entropies of fusion;
- temperature of fusion
(DSC, adiabatic calorimetry; drop calorimetry)

Gas phase ENERGETICS
(Computational thermochemistry)

Pure substances

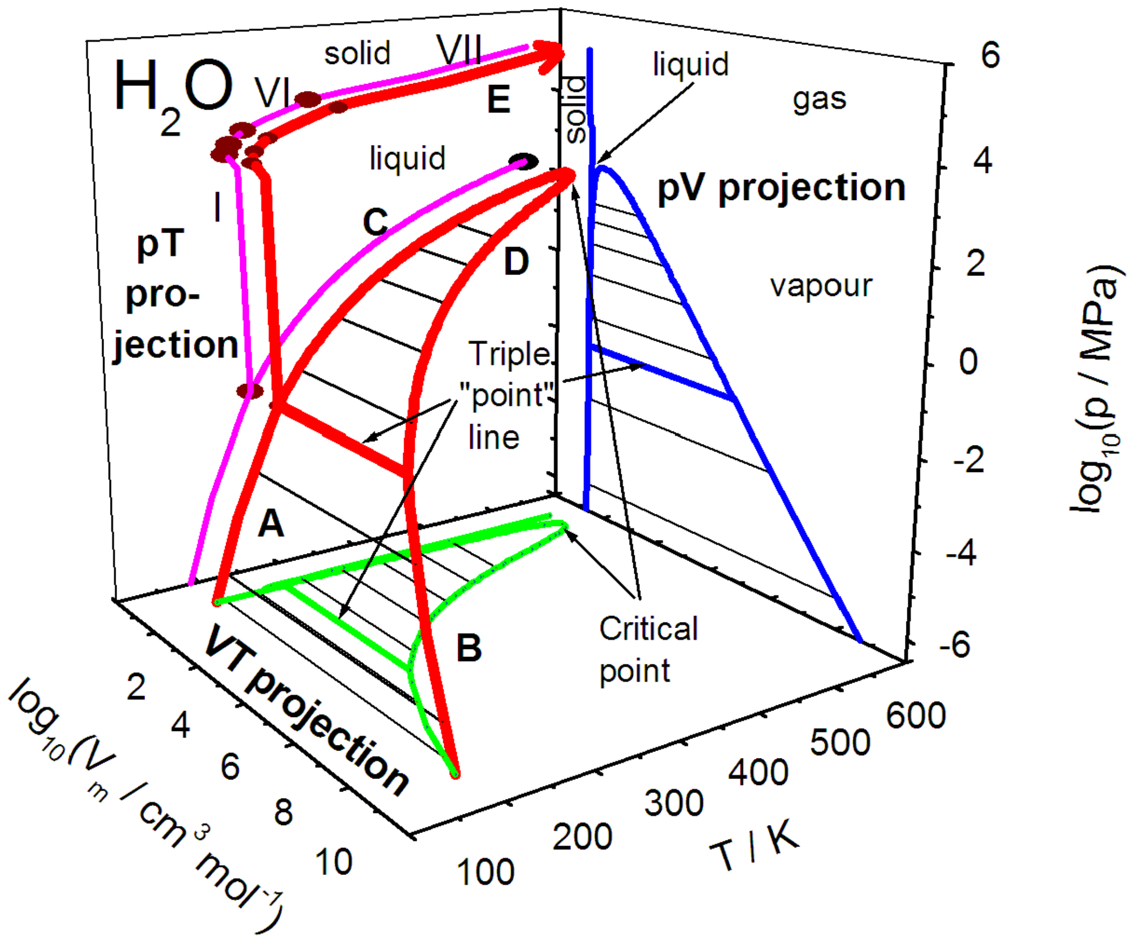
PVT diagram



-**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!

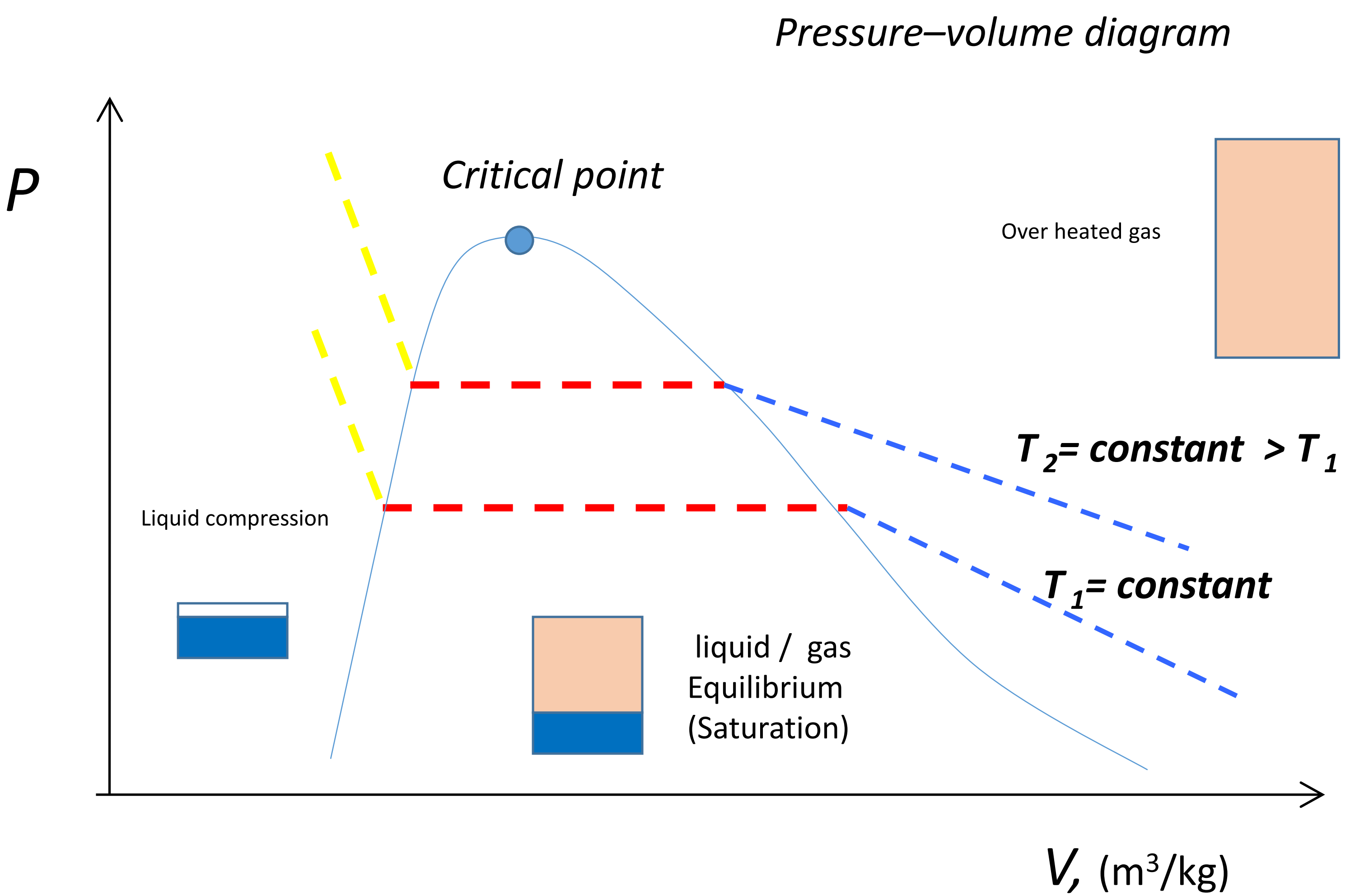
- VT projection :

Little dependence of the liquid / solid phases

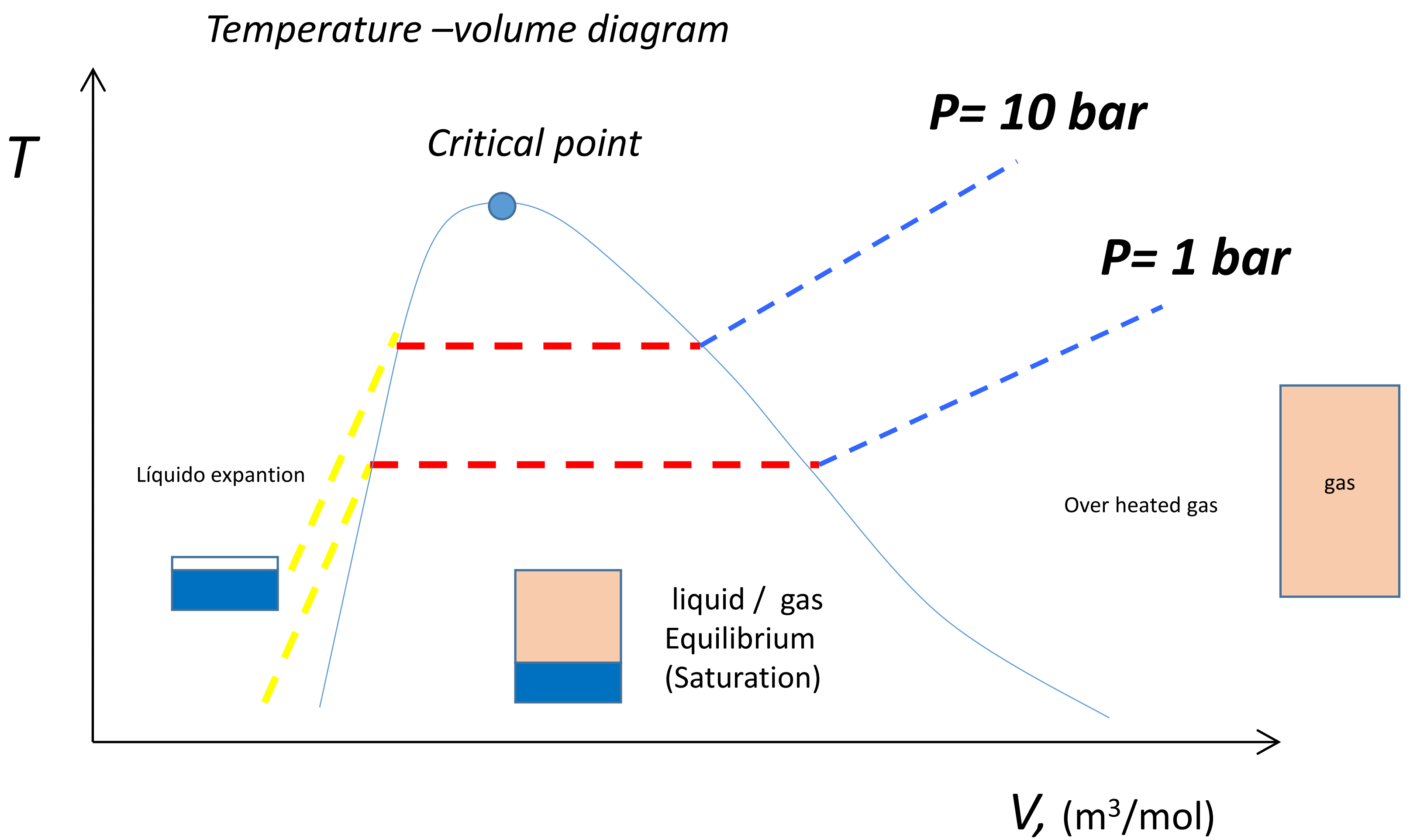
- PV projection :

Little dependence of the liquid / solid phases

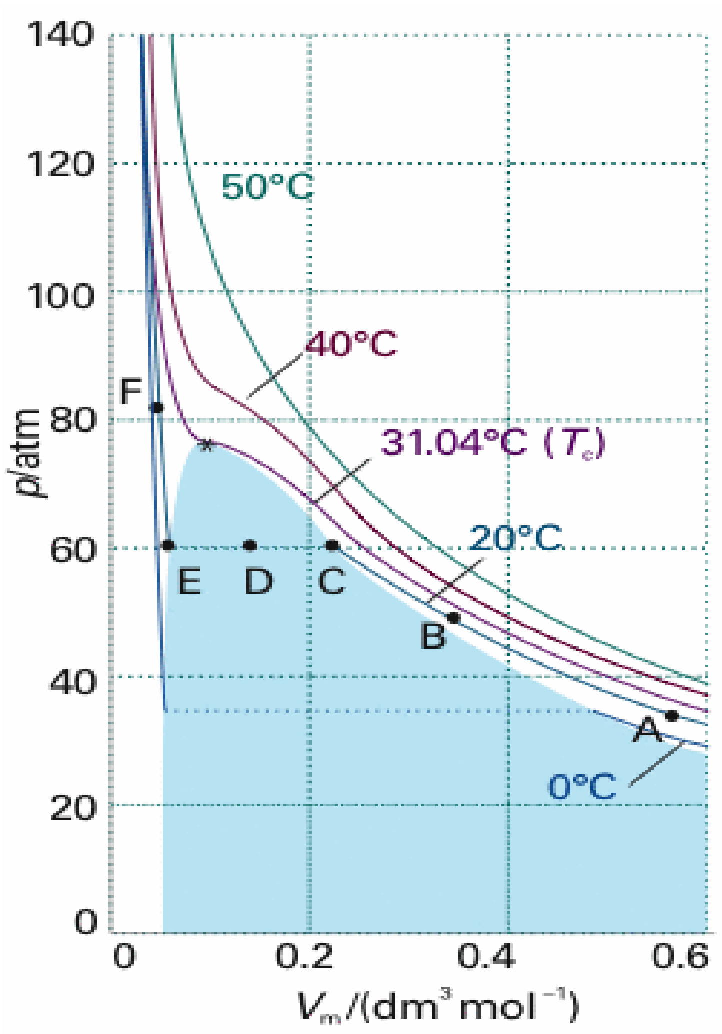
Properties of pure substances

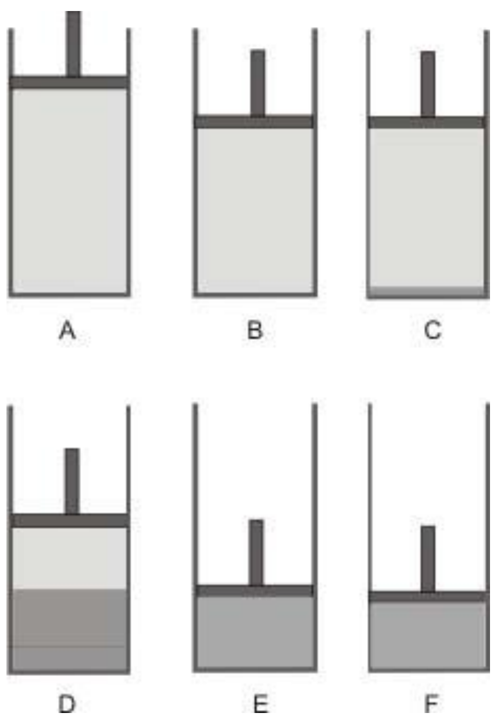


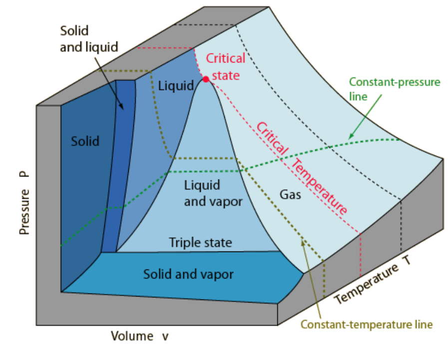
Properties of pure substances



P-V …Isothermic lines

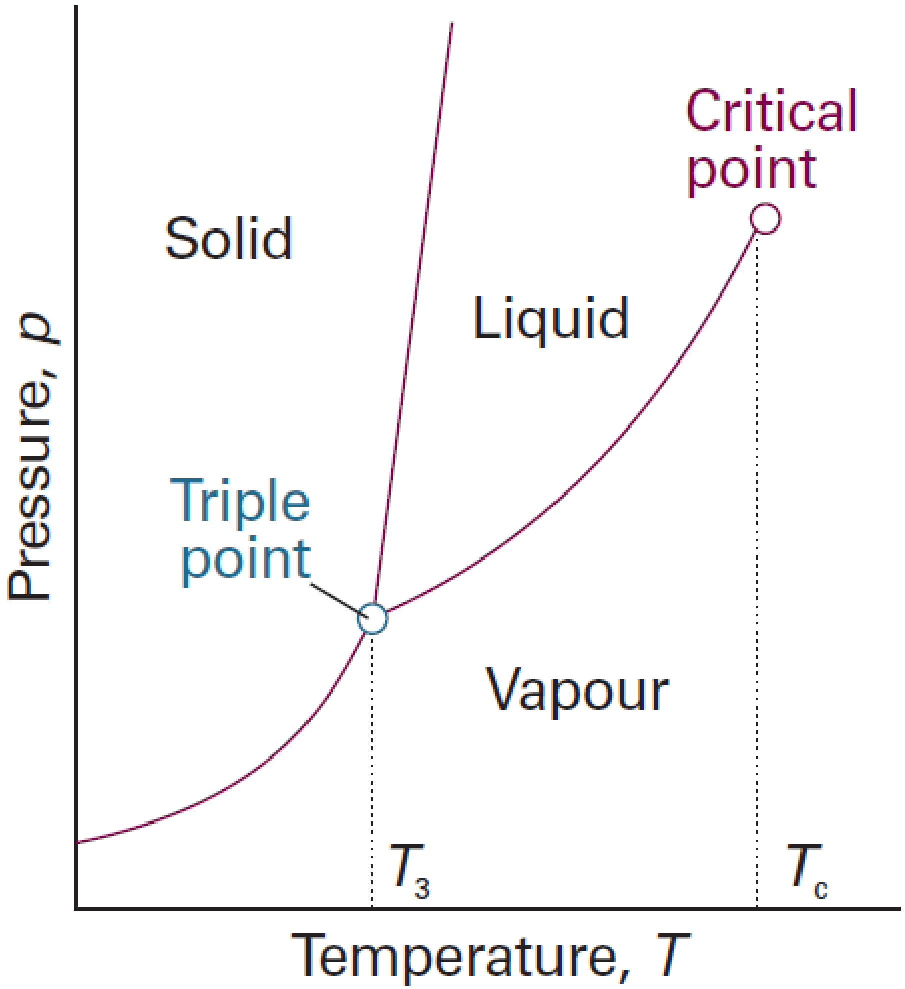






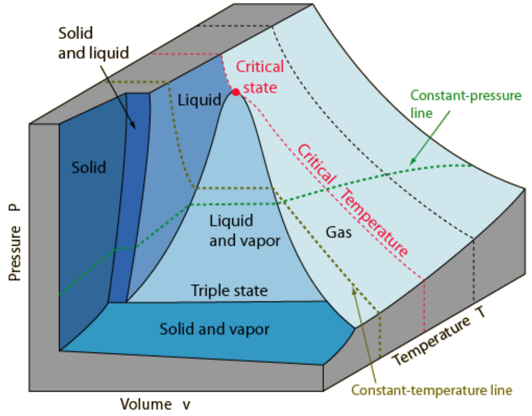
Properties of pure substances

PT diagram



- PT projection :

Complex and interesting profile!

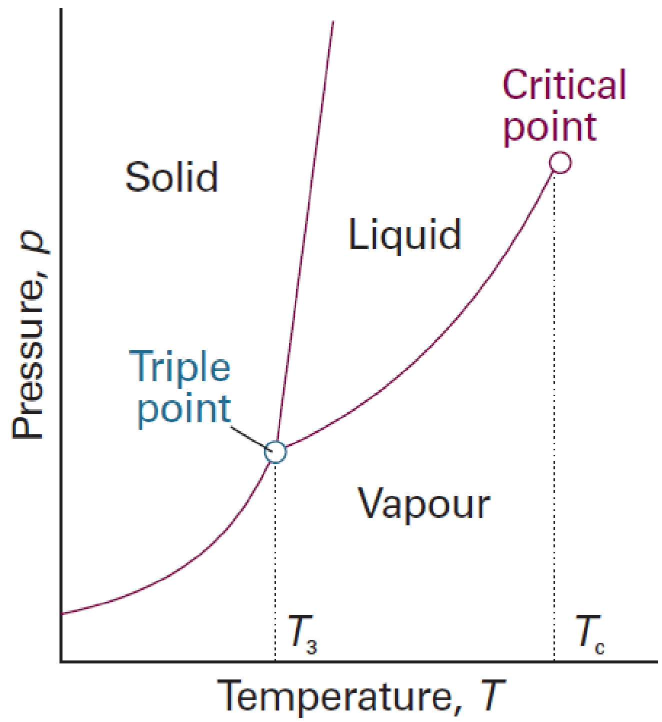


Properties of pure substances

PT diagram

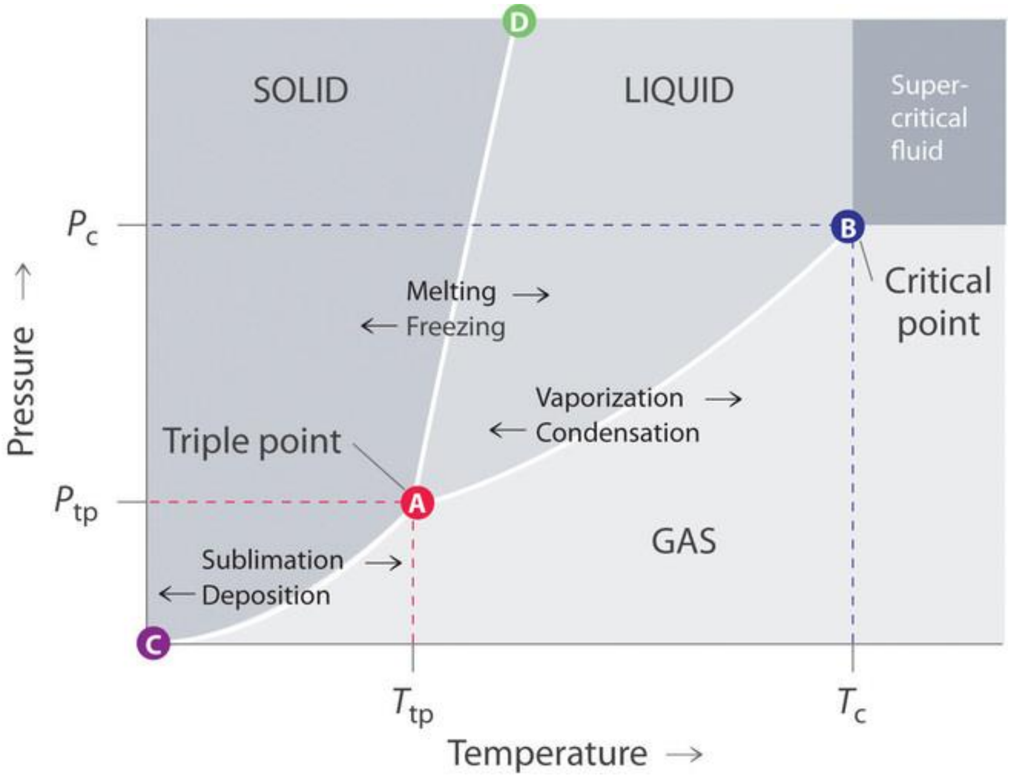
Phase
of a substance is a form of matter that is **uniform** throughout in **chemical composition** and **physical state**.

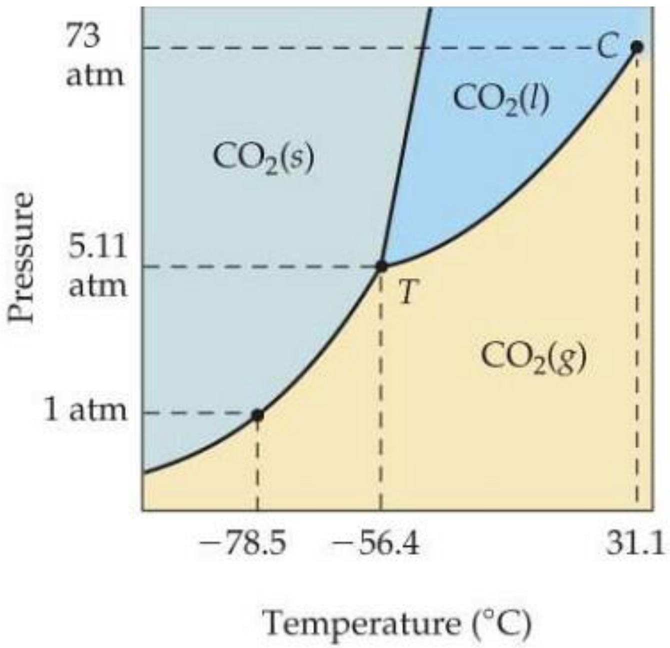
Phase transition,
the spontaneous **conversion** of one **phase** into another phase, occurs at a characteristic ***T*** for a given ***p***



Properties of pure substances

PT diagram





Gibbs Phase Rule

Gibbs Phase rule :

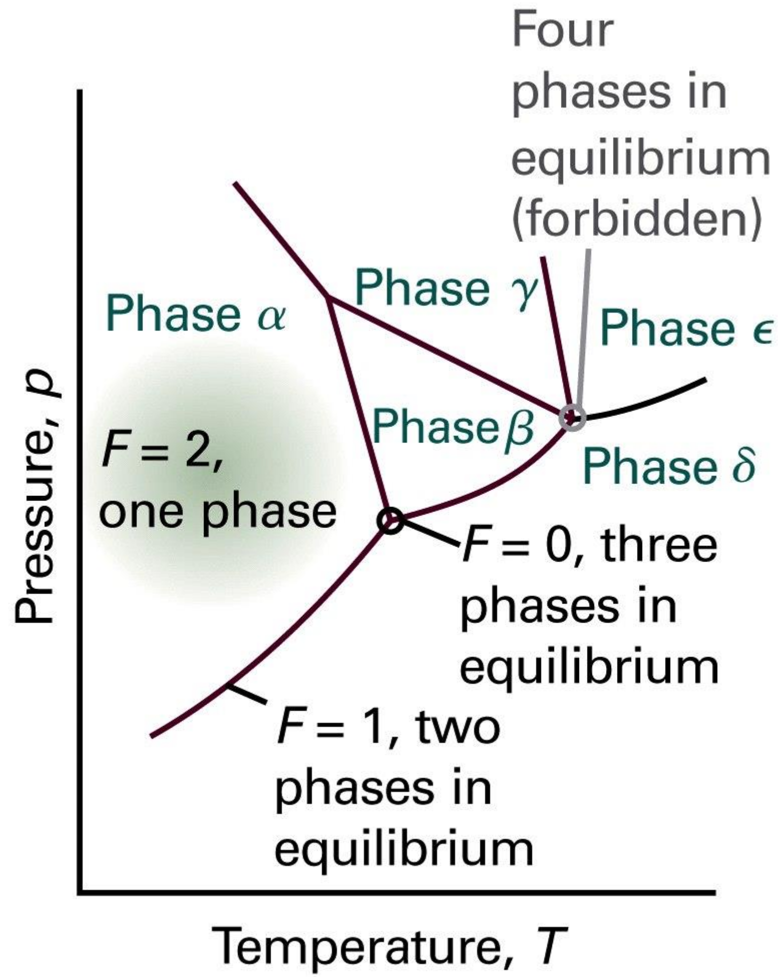
v or F = C - P + 2

p,T

for binary mixtures C= 2

 # Phases P

Variance: Number of degrees of freedon



Properties of pure substances

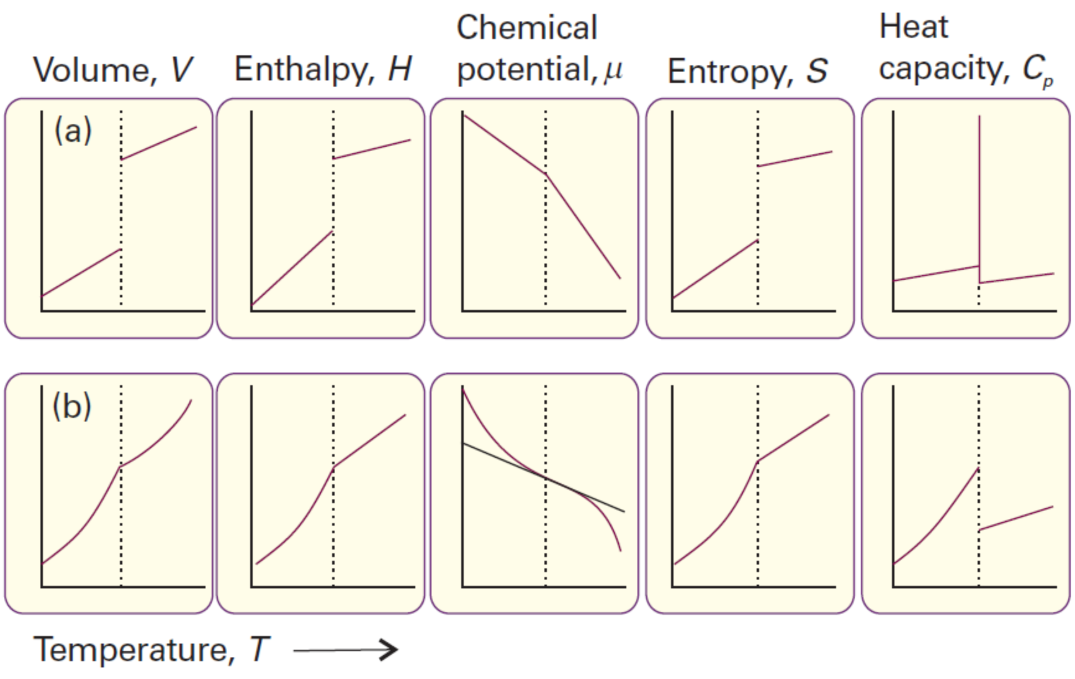
PT diagram

First-order phase

e.g… fusion, vaporization ..etc

Second-order

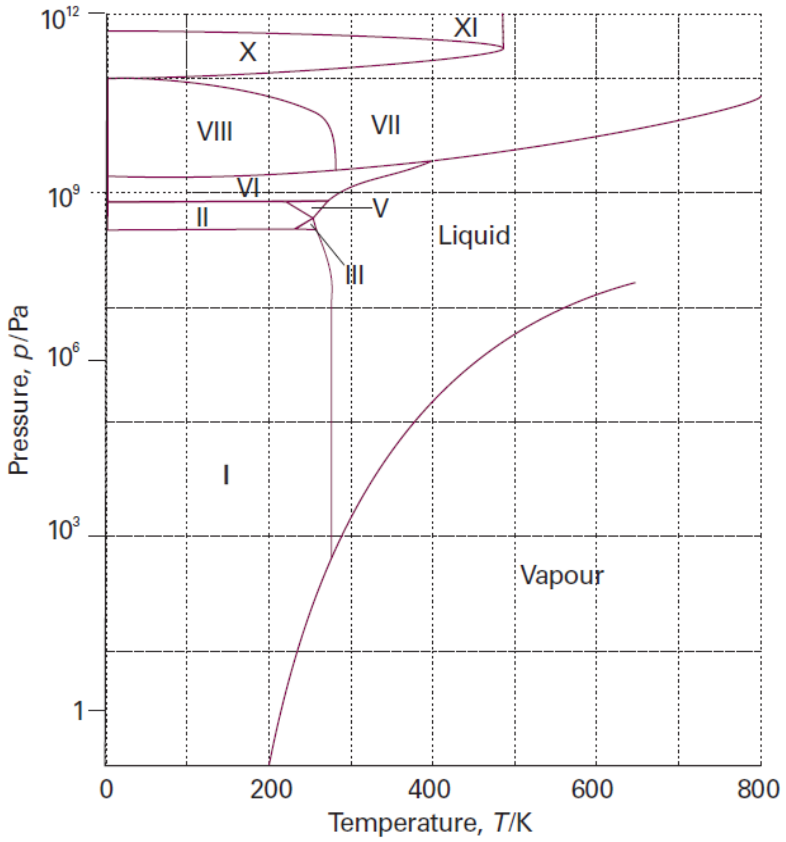
e.g… some ….. solid- solid ..etc



Properties of pure substances

PT diagram

Complex Phase diagram of H_2O



Properties of pure substances

PT diagram

Phase stability

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

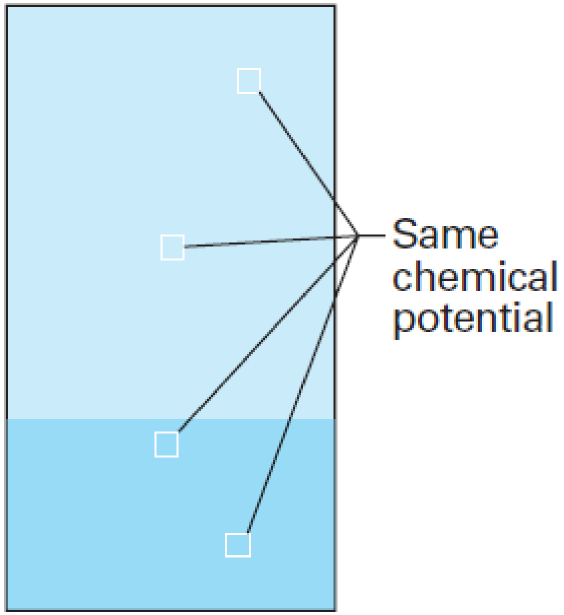
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

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

Sol $\rightleftarrows$ Liq

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

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



Properties of pure substances

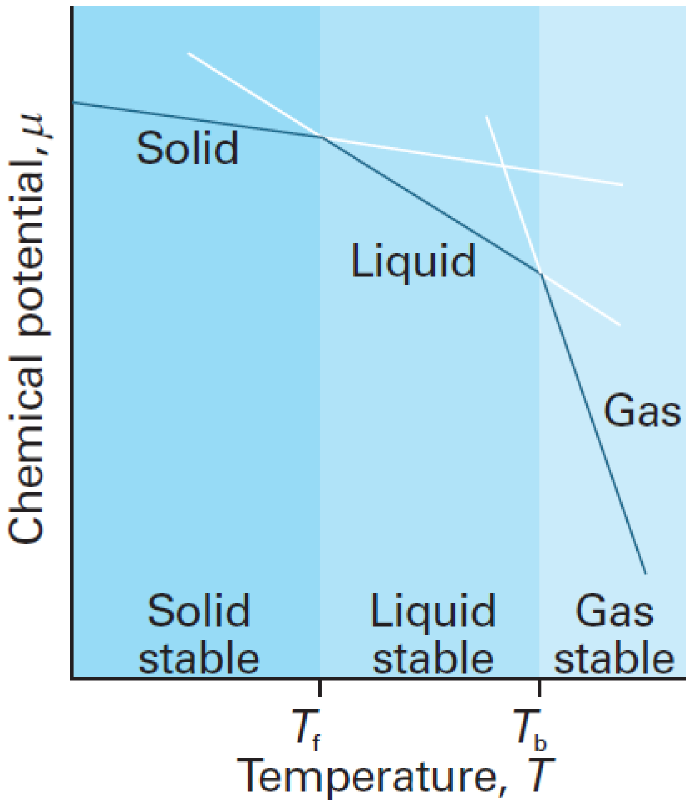
PT diagram

Phase stability

Sol ⇄ Liq   Liq ⇄ gas

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

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



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

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

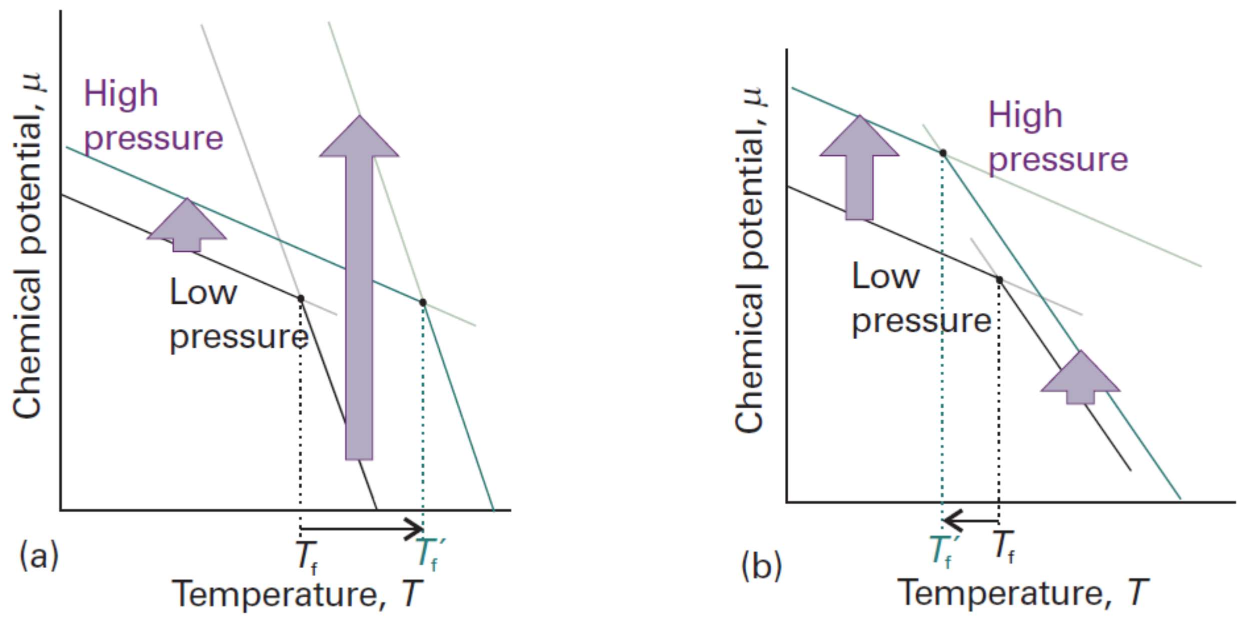
Properties of pure substances

PT diagram

Phase stability

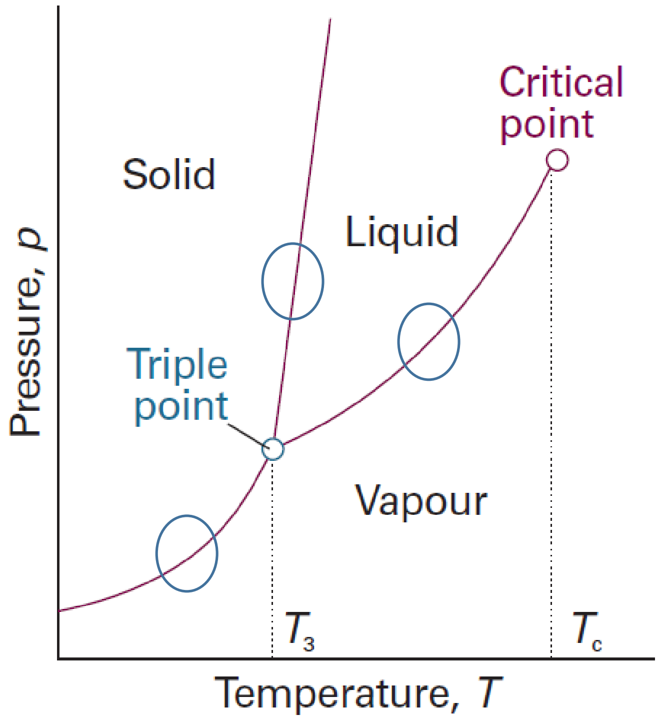
liq ⇌ Gas   Sol ⇌ Liq

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



Properties of pure substances

PT diagram



shape of the equilibrium lines

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

Properties of pure substances

PT diagram

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

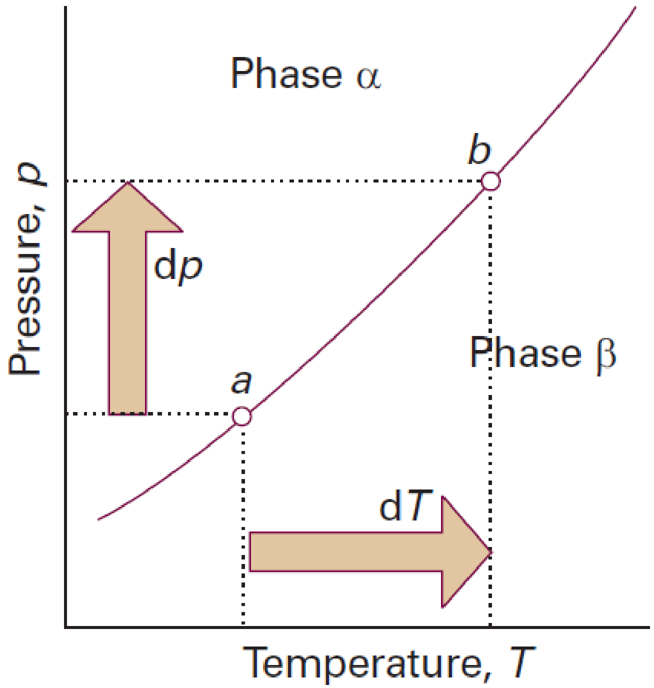
Phase_α ⇄ Phase_β

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

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

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

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



Properties of pure substances

PT diagram

Phase_α ⇄ Phase_β

Shape of the equilibria lines

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

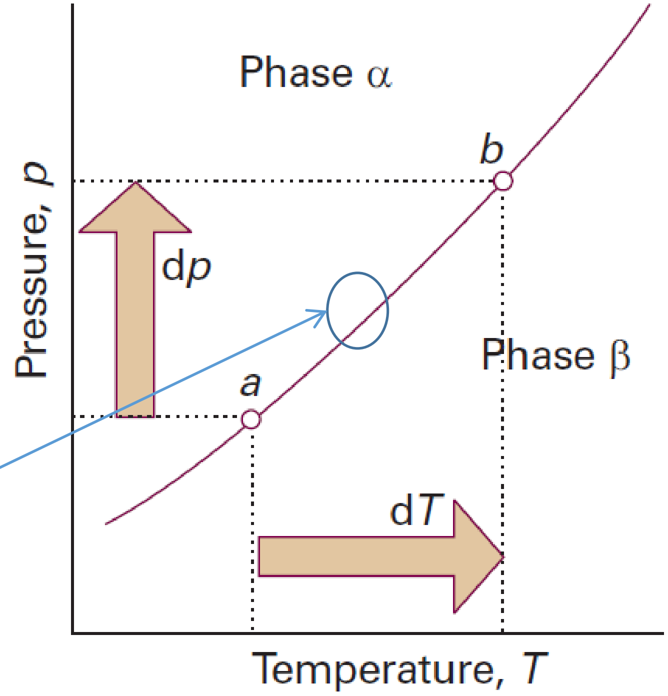
$$-S_{\alpha,m}\mathrm{d}T + V_{\alpha,m}\mathrm{d}p = -S_{\beta,m}\mathrm{d}T + V_{\beta,m}\mathrm{d}p$$

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

Clapeyron equation

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

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



Properties of pure substances

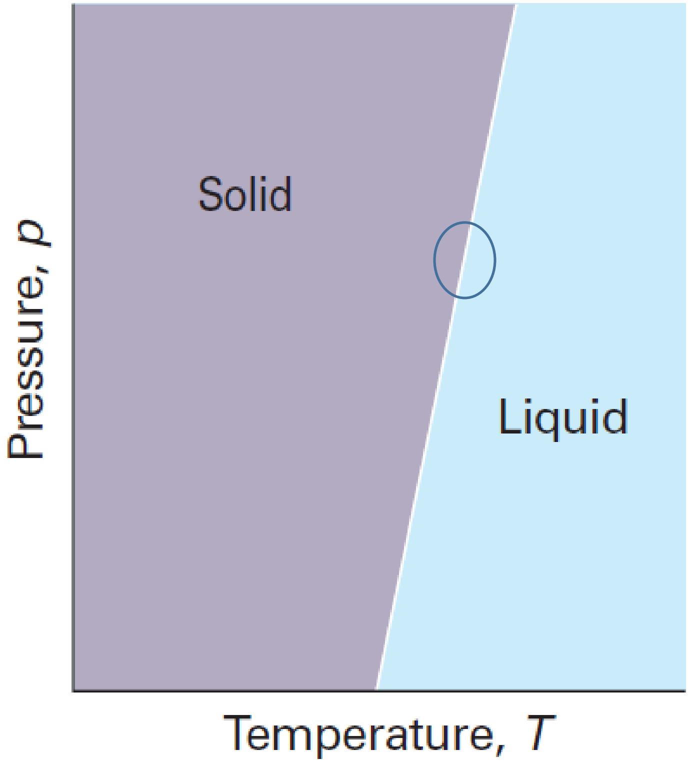
PT diagram

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

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

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

Solid -Liquid ..condensed phases



Clapeyron equation

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

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

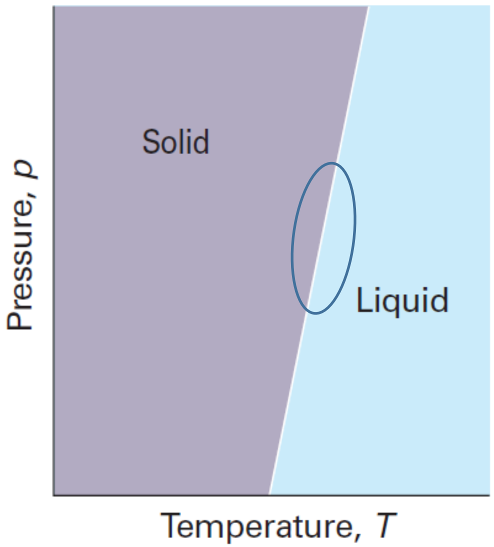
Properties of pure substances

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,

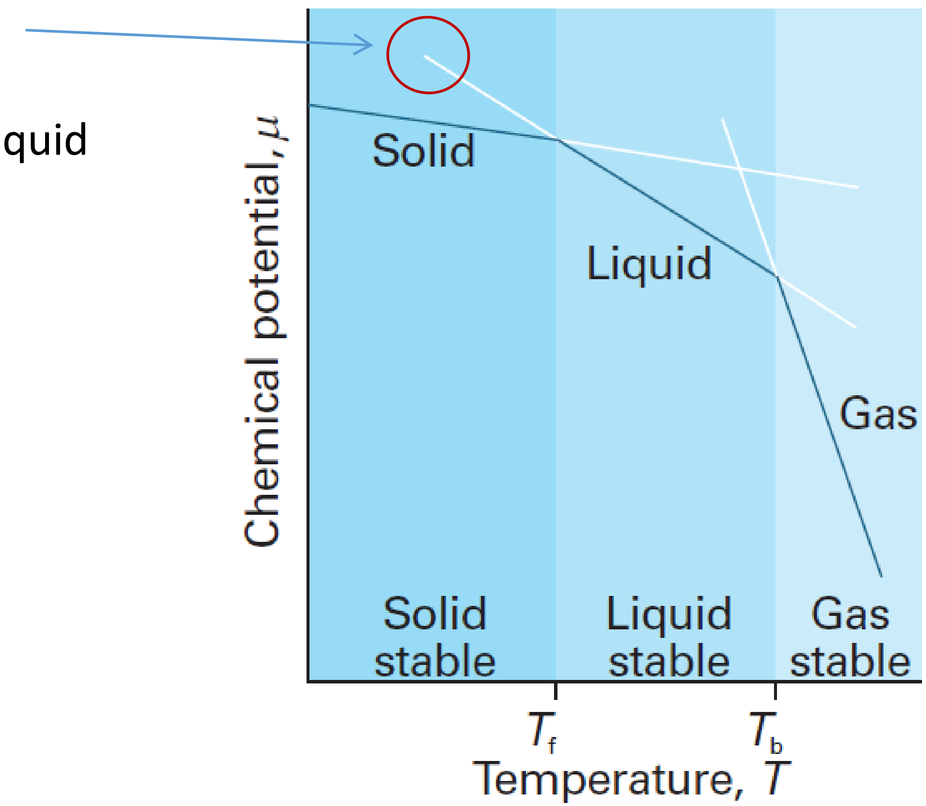
$$p \approx p^* + \frac{\Delta_{fus} H}{T^* \Delta_{fus} V}(T - T^*)$$

Linear approximation

DSC: Supercooled Liquid

Supercooled Liquid

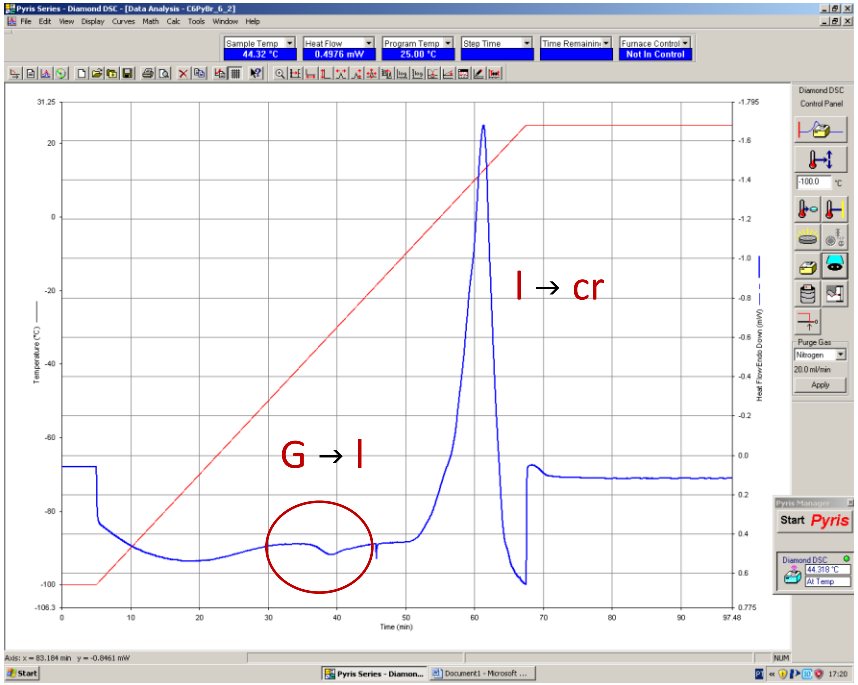
e.g. quenching the liquid



DSC: Supercooled Liquid

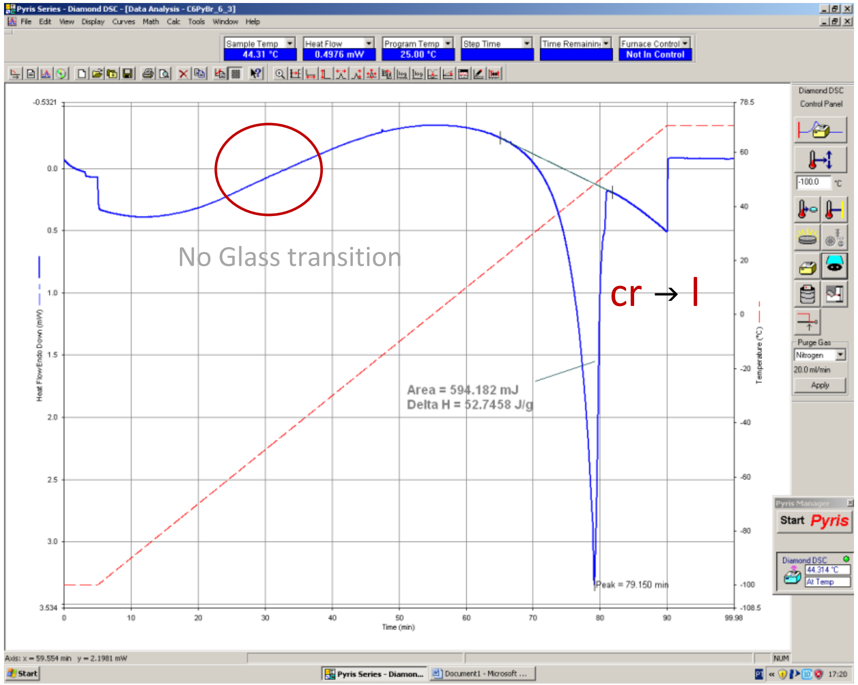
Cold Crystallization

Glass to Liquid .. T_g

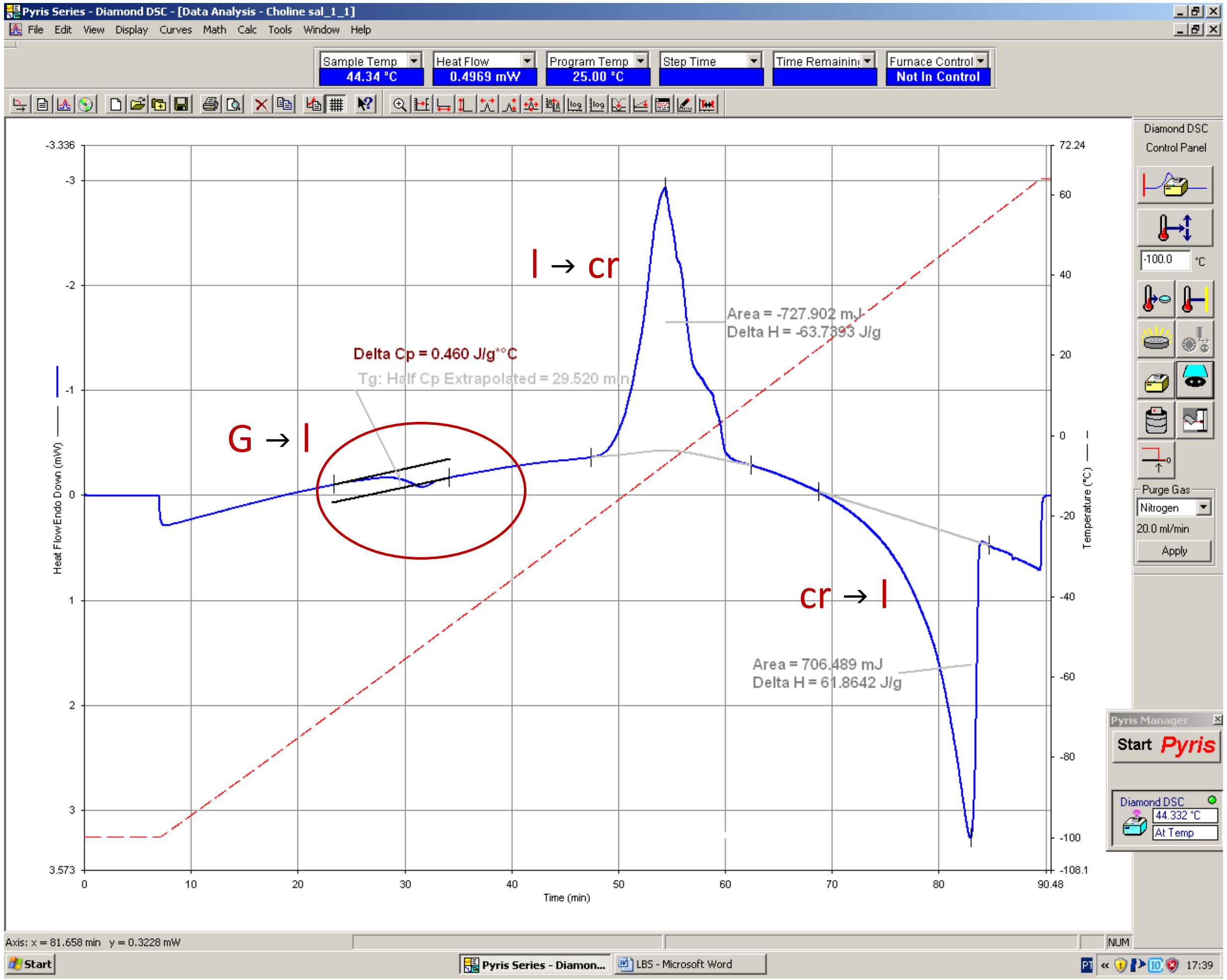


Melting

No Glass transition found .. T_g



DSC: Supercooled Liquid



Properties of pure substances

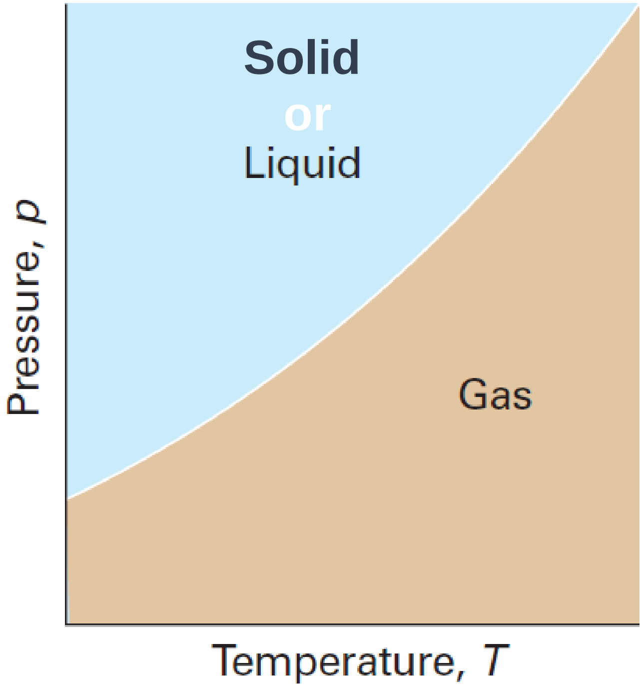
PT diagram

liquid–vapour

solid–vapour

Clapeyron equation

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



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

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

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

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

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

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

Clausius–Clapeyron equation

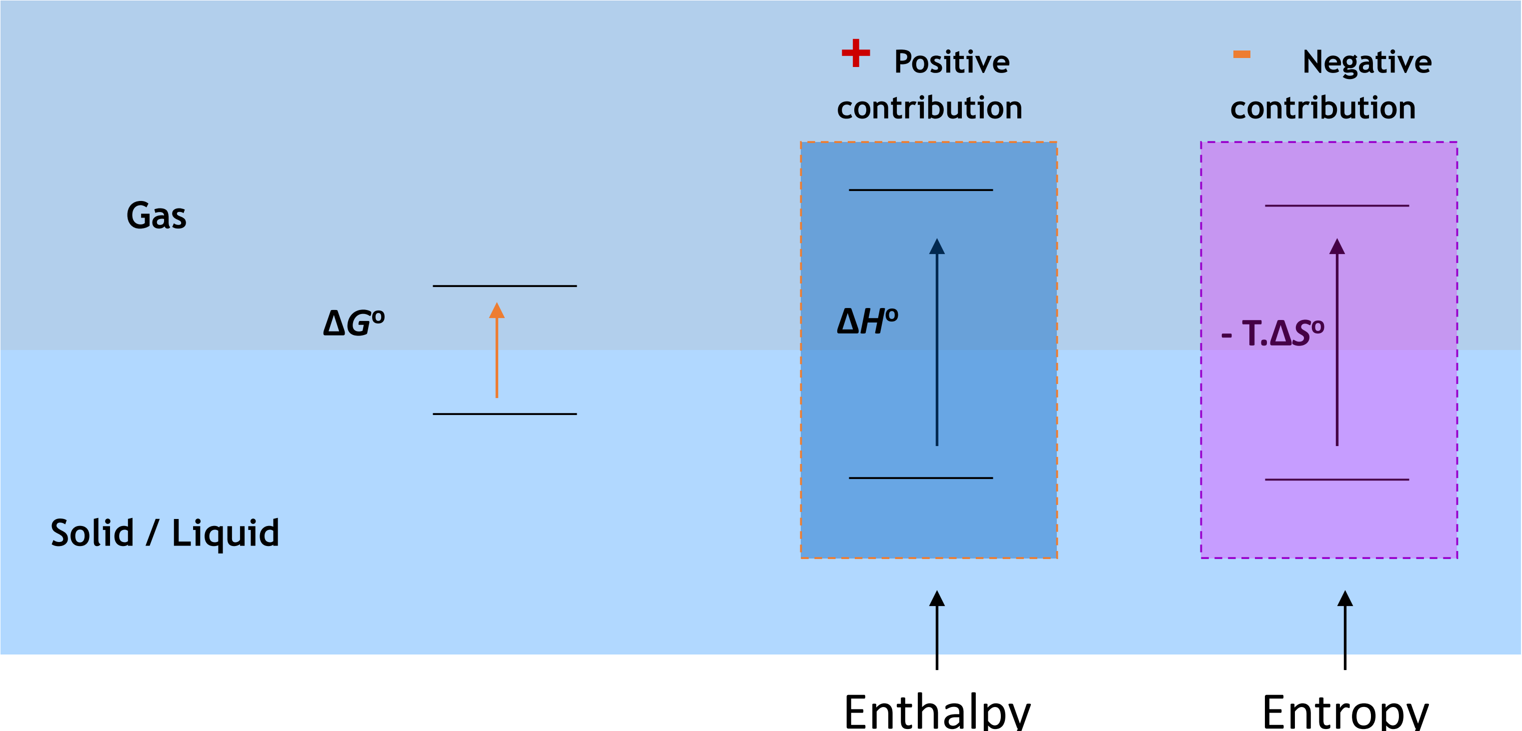
Properties of pure substances

PT diagram

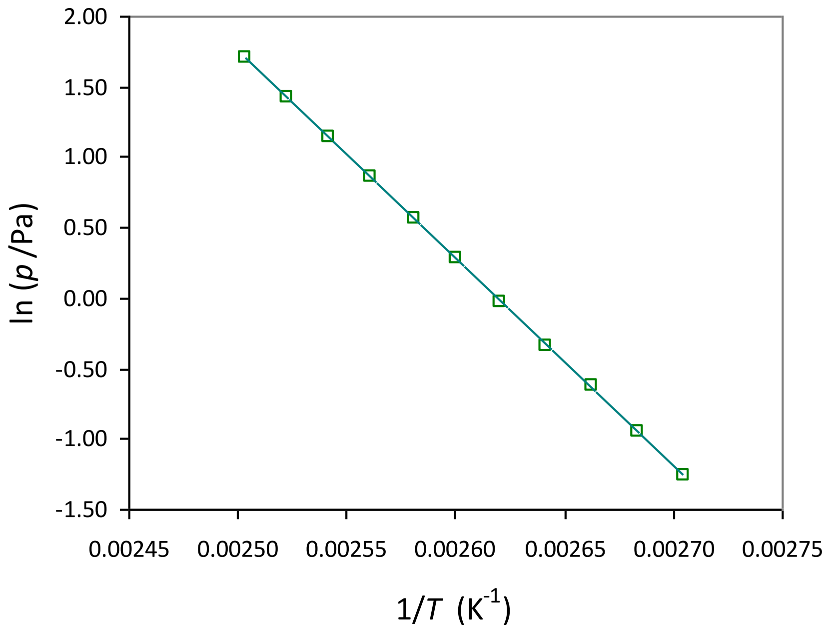
P= f(T) **… vapor pressure Measurements**

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

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



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



Clausius-Clapeyron equation

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

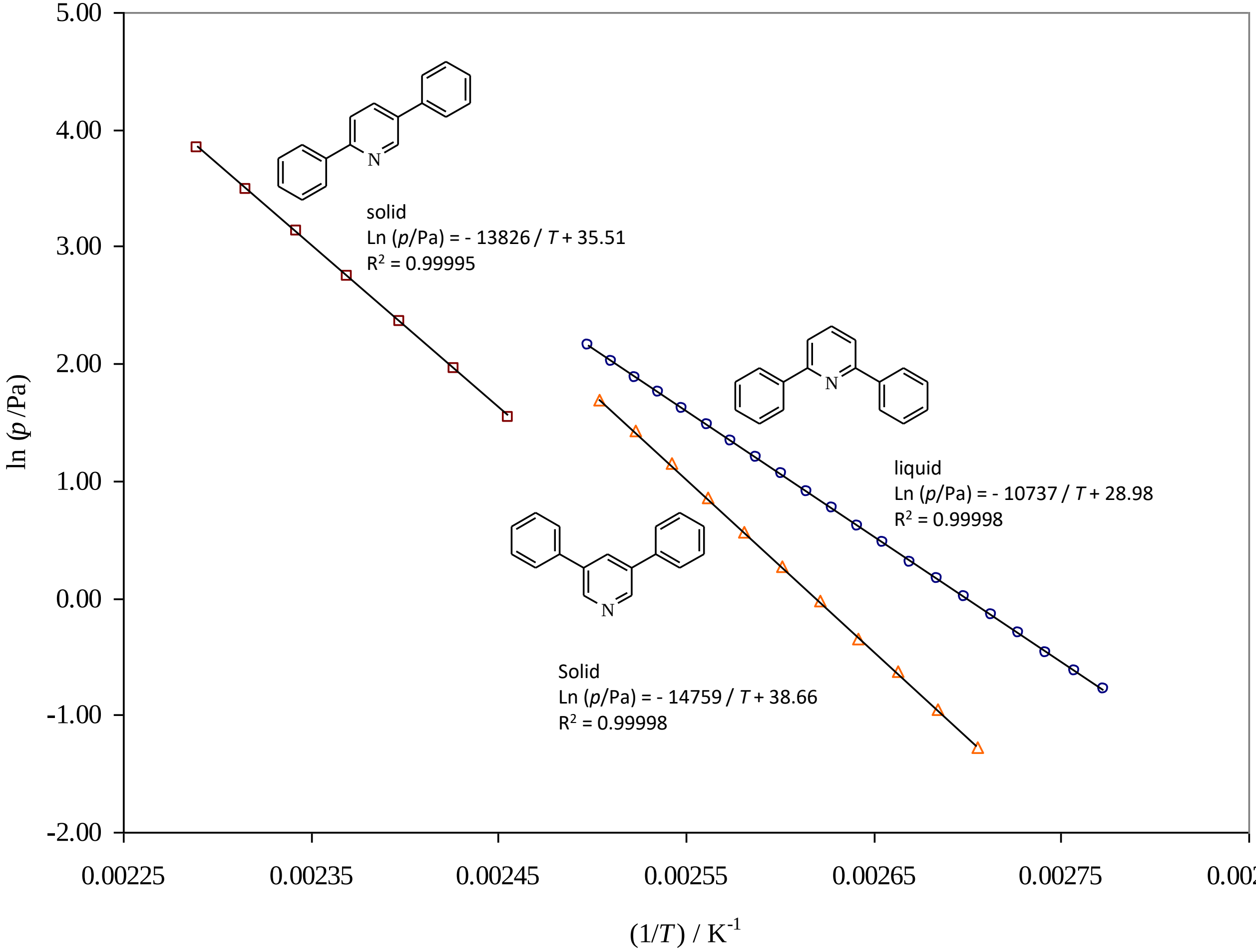
Clarke & Glew equation

↑

Cp ..correction

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

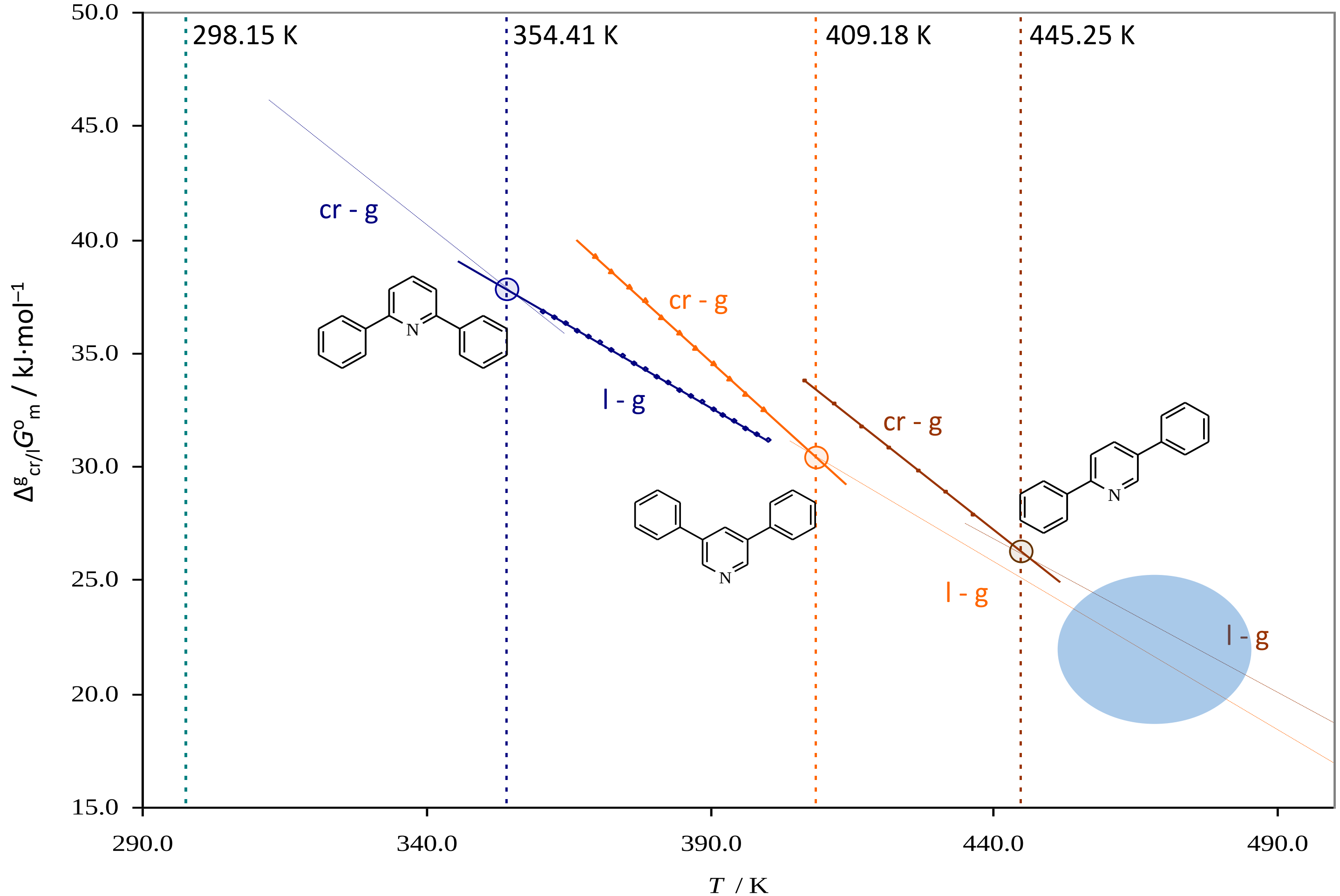
p=f(*T*).........Phase diagrams



MKS (0-1333 Pa)

MKS (0-133 Pa)

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



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- H-bond
- Electrostatic .. interactions
- Molecular shape
- ...???

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