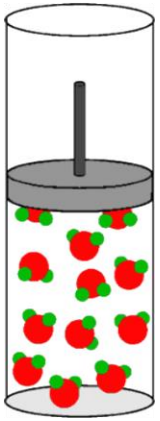
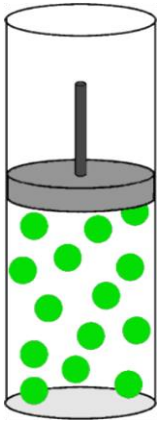
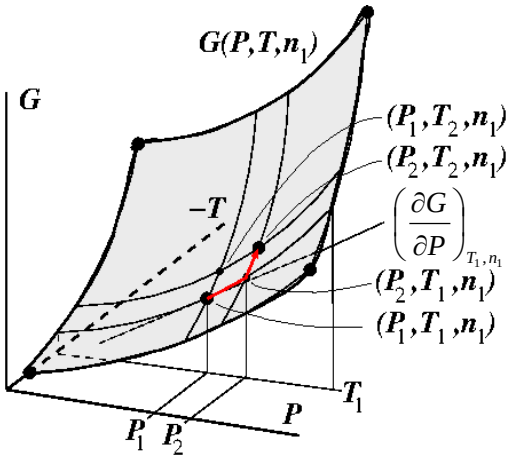
Summary of Lecture 1

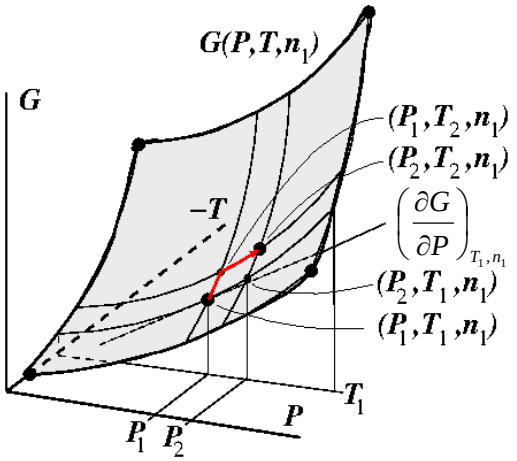
- **Molecular (perfect) gases *vs* atomic gases**



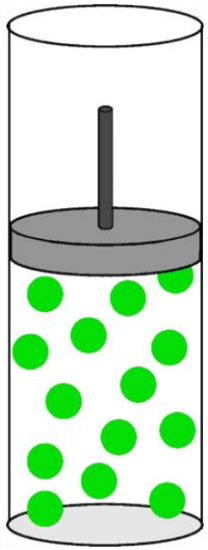


- **Total differential of (thermodynamic) functions**





Molecular (perfect) gases *vs* atomic gases



Perfect gas

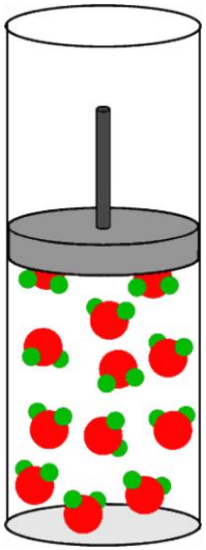
$$PV = nRT$$

obeys equipartition theorem

(high T and low P)

$$U = \frac{1}{2}kT$$

per degree of freedom



Atomic perfect gas (SG p.17-18) **Molecular perfect gas**

$$U = U^{\mathrm{T}} = \frac{3}{2}NkT$$

$$U = \left(3 + N_{\mathrm{R}} + 2N_{\mathrm{V}}\right)\frac{1}{2}MkT$$

$Nk = nR$

$$C_V = \frac{3}{2}nR$$

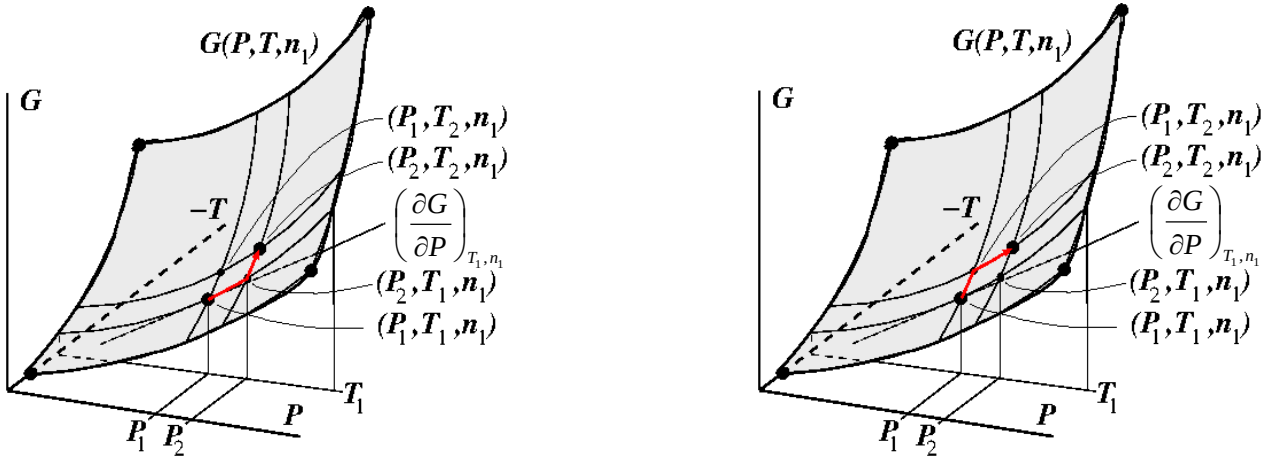
$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

$Mk = nR$

$$C_V = \left(3 + N_{\mathrm{R}} + 2N_{\mathrm{V}}\right)\frac{1}{2}nR$$

Total differential of (thermodynamic) functions

(Gibbs free energy *G* as an example)



$$\Delta G(P_1,T_1 \rightarrow P_2,T_2)\big|_n = \int_{P_1}^{P_2}\left(\frac{\partial G}{\partial P}\right)_{T_1,n} \mathrm{d}P + \int_{T_1}^{T_2}\left(\frac{\partial G}{\partial T}\right)_{P_2,n} \mathrm{d}T = \int_{T_1}^{T_2}\left(\frac{\partial G}{\partial T}\right)_{P_1,n} \mathrm{d}T + \int_{P_1}^{P_2}\left(\frac{\partial G}{\partial P}\right)_{T_2,n} \mathrm{d}P$$

Characteristic equ. *G*

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P$$

***G* is state function**

$$\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial^2 G}{\partial P \partial T}\right)$$

Maxwell relation

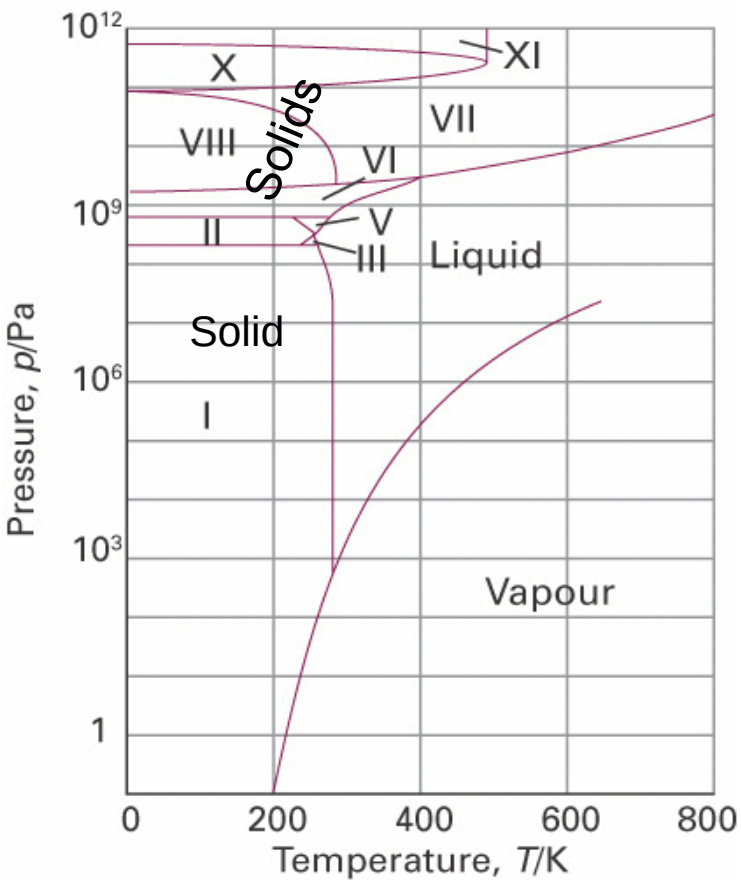
$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Lecture 2

Phase diagrams and phase transitions of unary systems

Lecture 2

Phase diagrams and phase transitions of unary systems

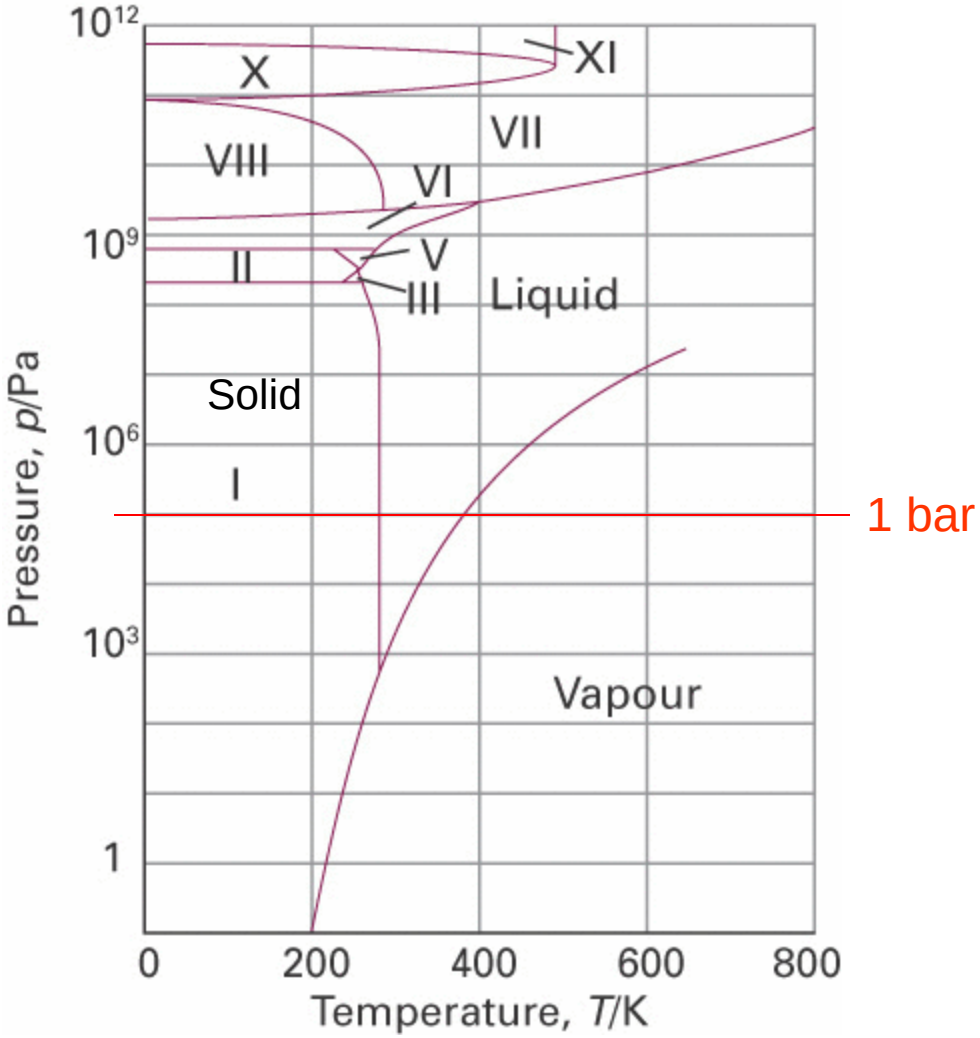


(**Equilibrium**) Phase Diagram H_2O

- Phase transitions
- Phase boundaries
- Phase transition temperature
- Melting point
- Boiling point
- Triple point
- Critical point
- Polymorphic forms

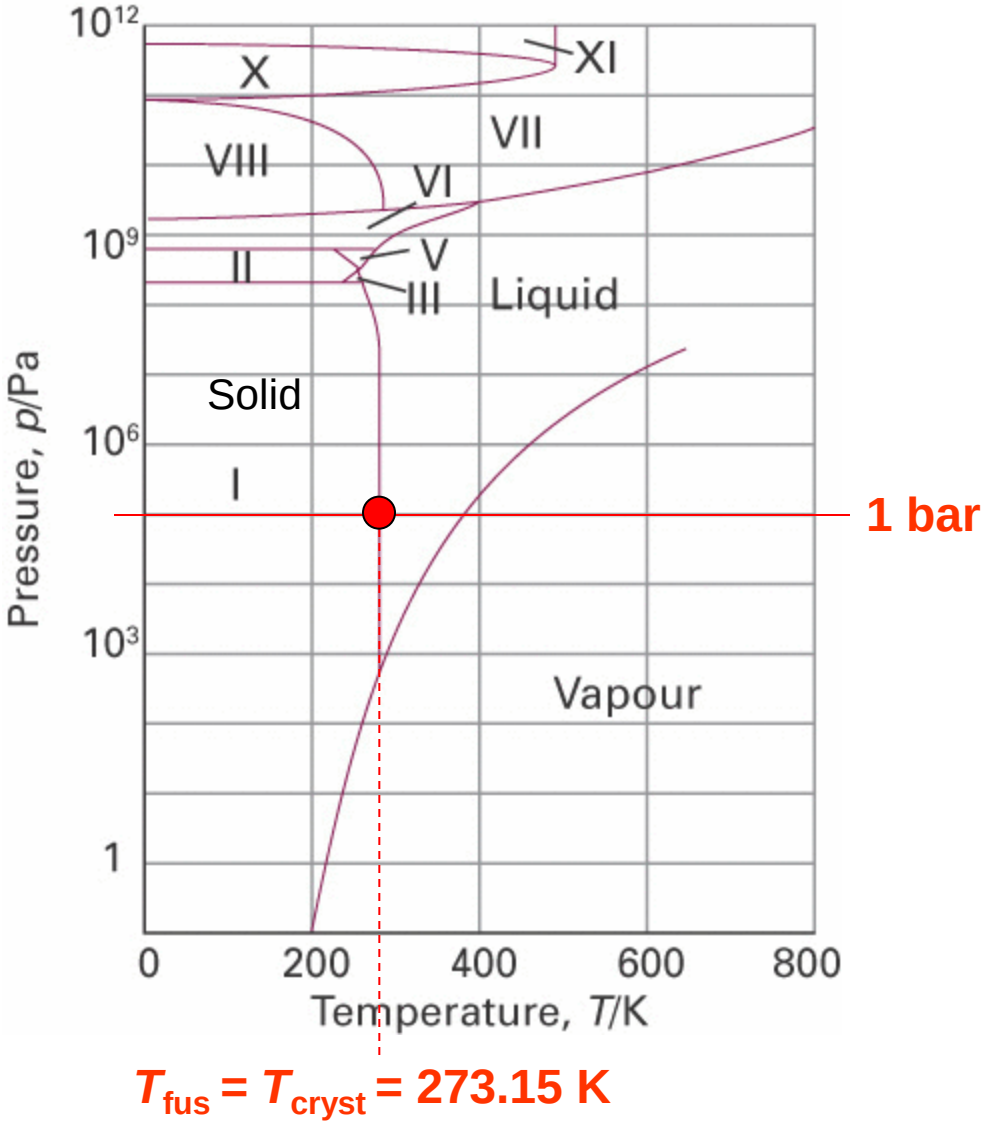
- Thermodynamics *vs* kinetics
- Metastable phases

Phase diagrams and phase transitions of unary systems



(**Equilibrium**) P,T phase diagram H_2O

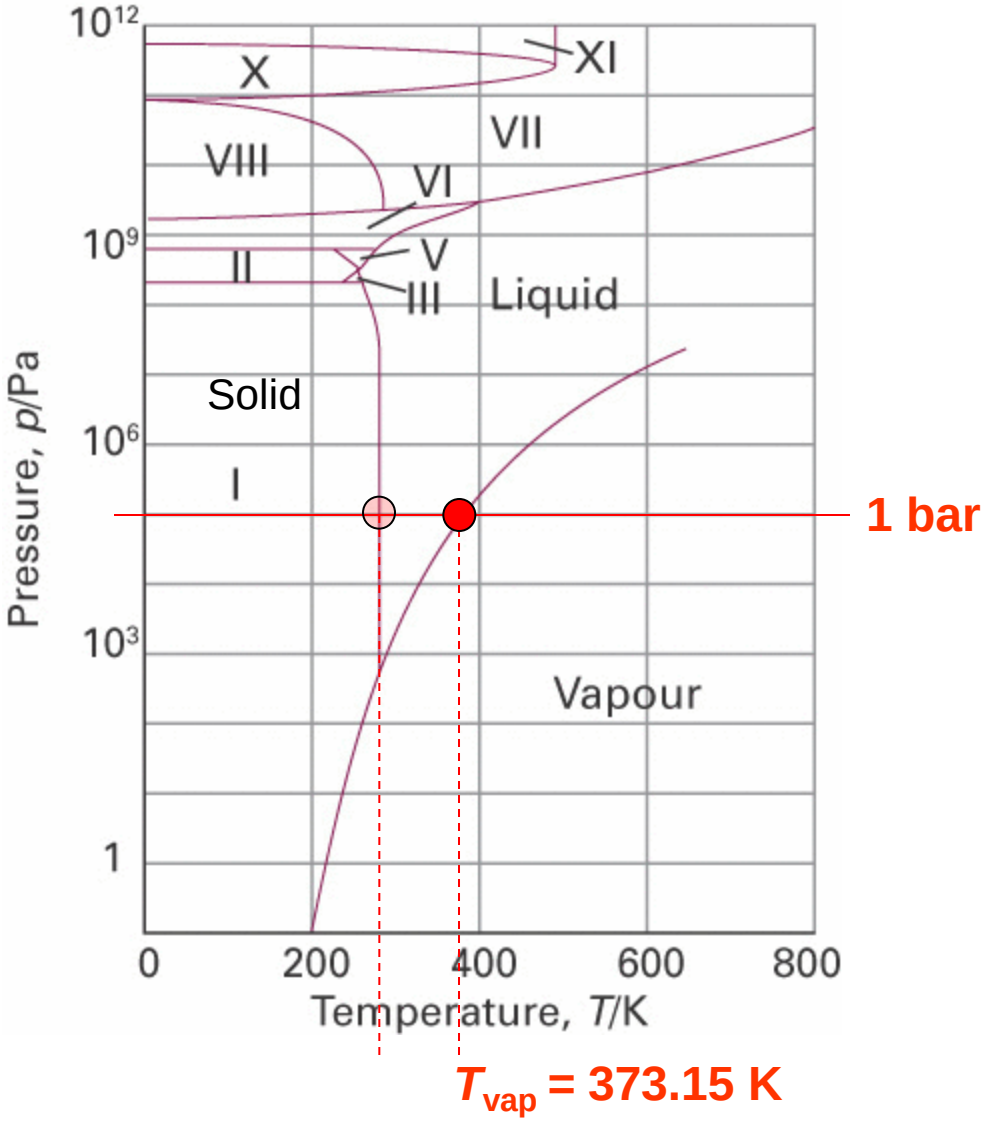
Phase diagrams and phase transitions of unary systems



$T_{fus} = T_{cryst} = 273.15$ K

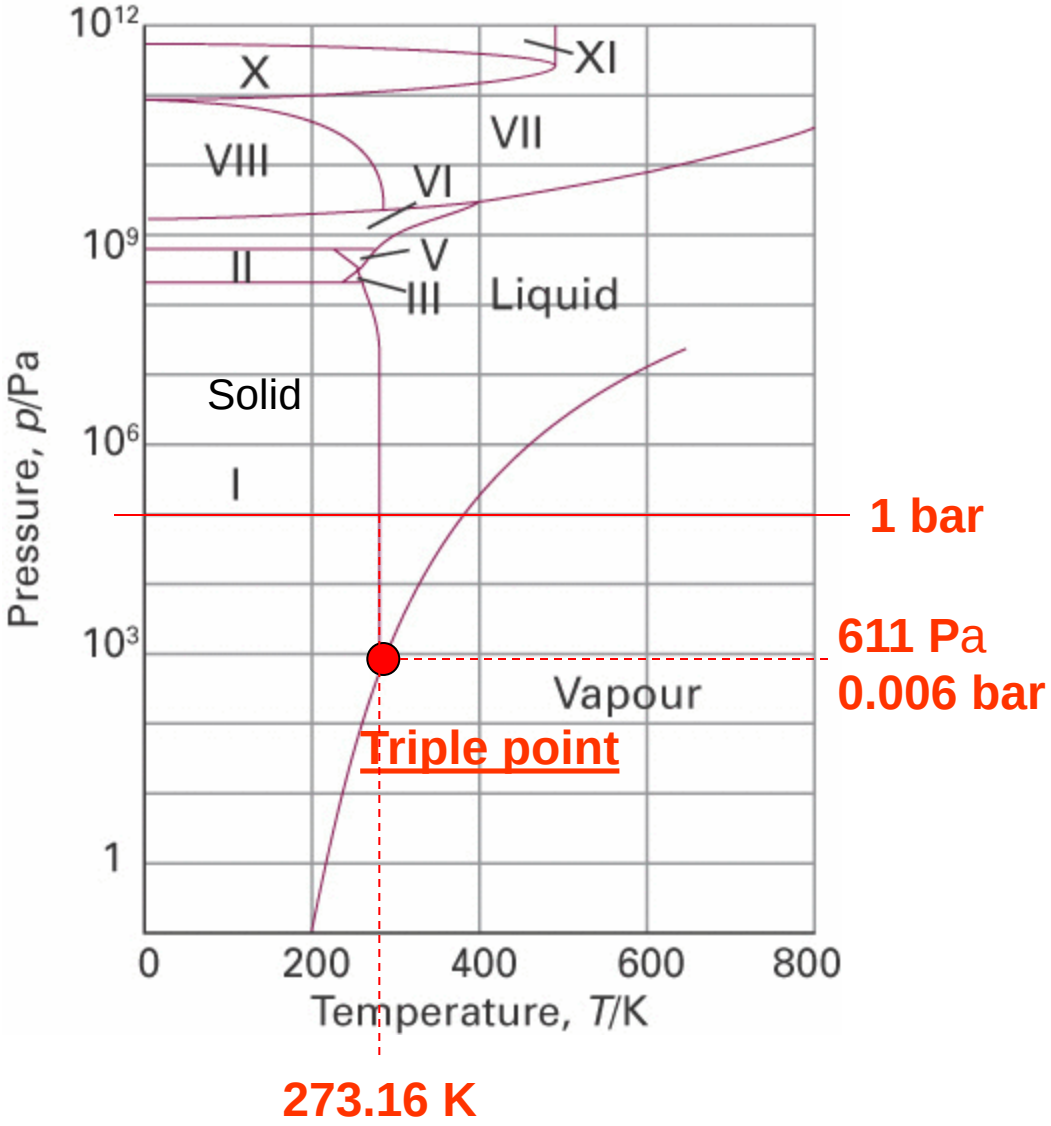
(**Equilibrium**) P,T phase diagram H_2O

Phase diagrams and phase transitions of unary systems



(**Equilibrium**) P,T phase diagram H_2O

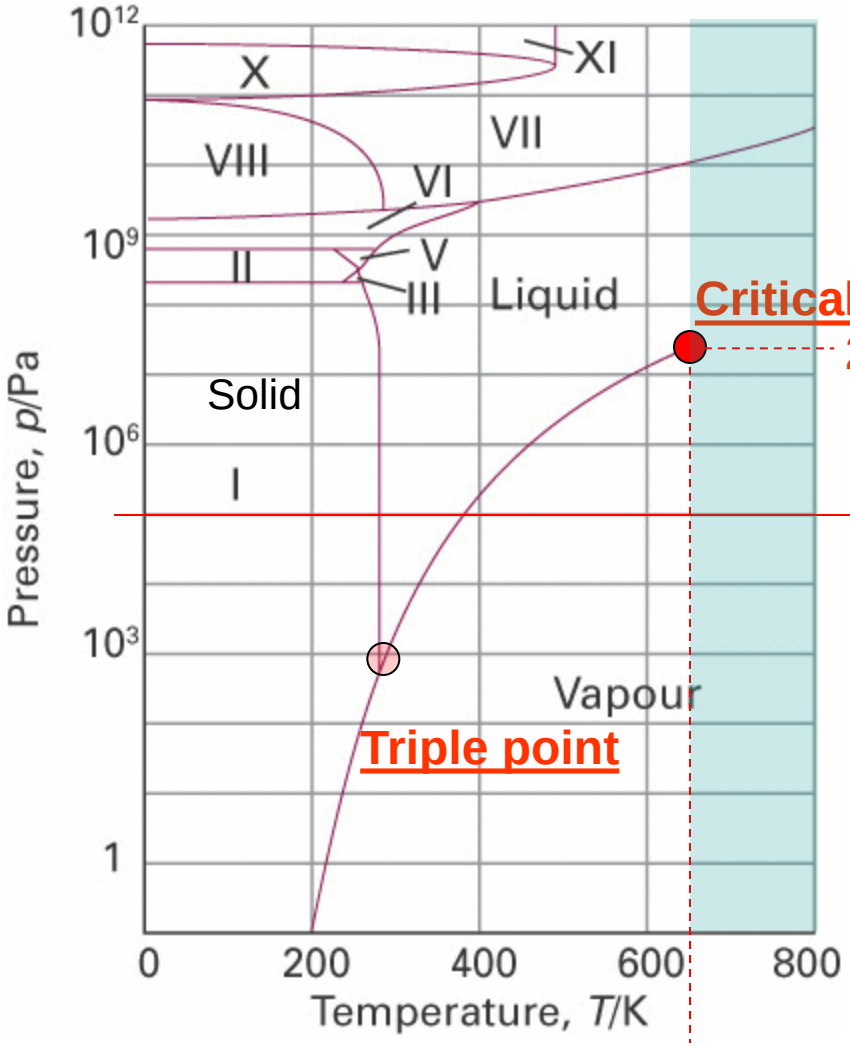
Phase diagrams and phase transitions of unary systems



Youtube_link

(**Equilibrium**) P,T phase diagram H_2O

Phase diagrams and phase transitions of unary systems



Critical point

220.6 bar

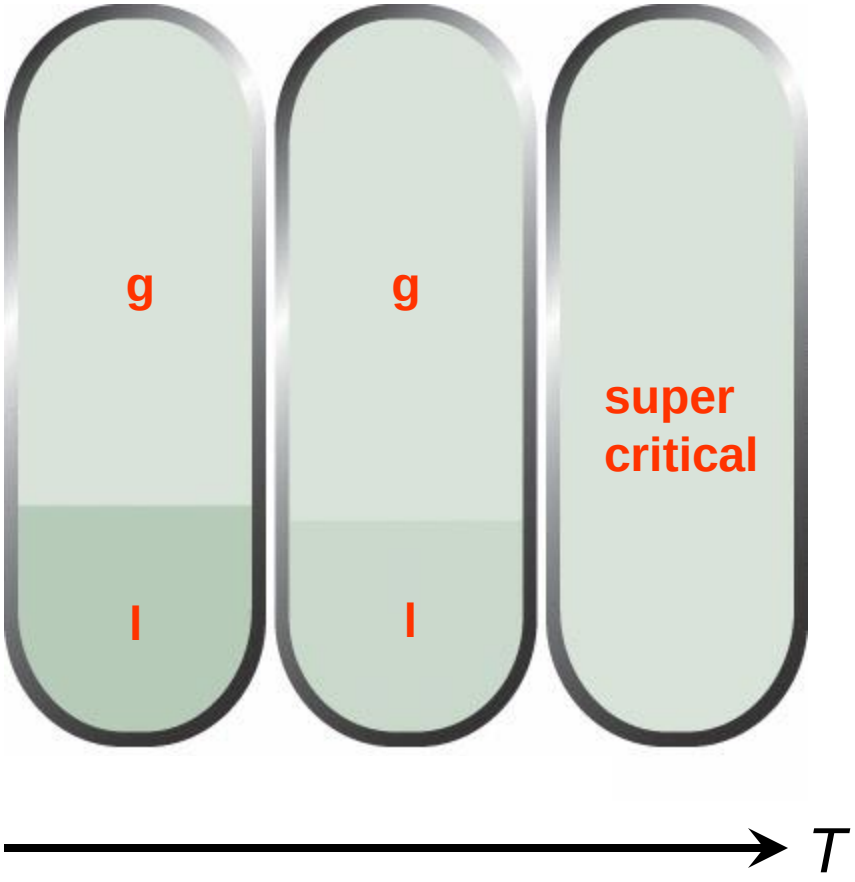
1 bar

647.1 K

Super critical

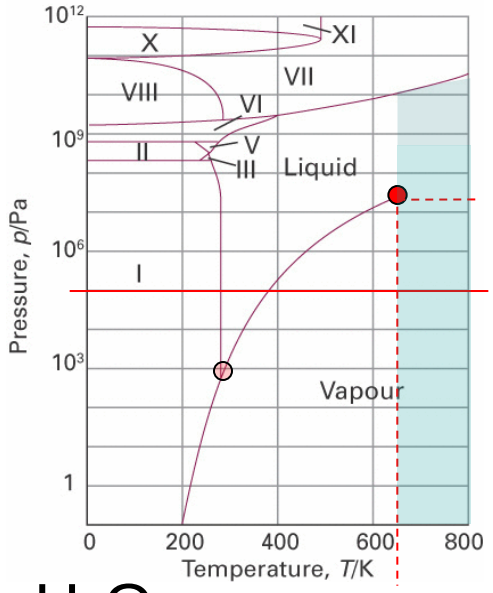
(**Equilibrium**) P,T phase diagram H_2O

Phase diagrams and phase transitions of unary systems



Critical point

Phase diagrams and phase transitions of unary systems

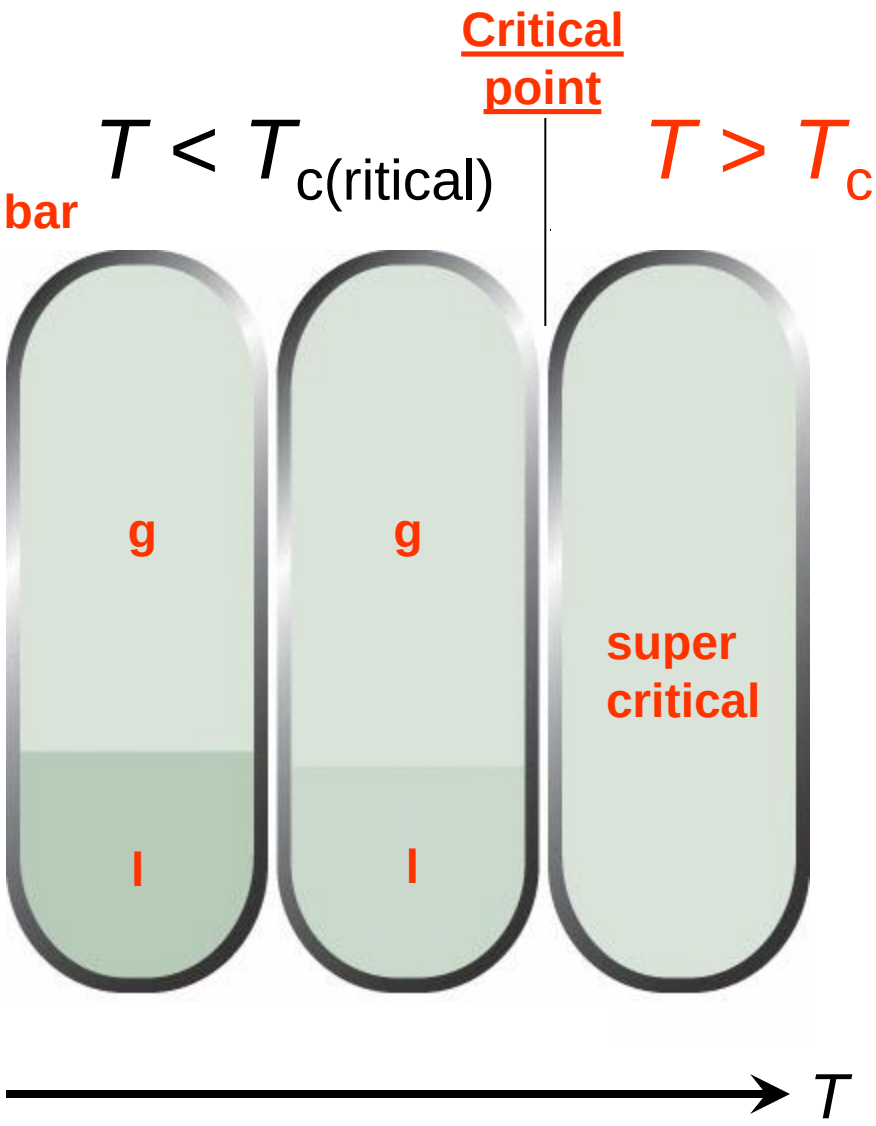


220.6 bar

H_2O

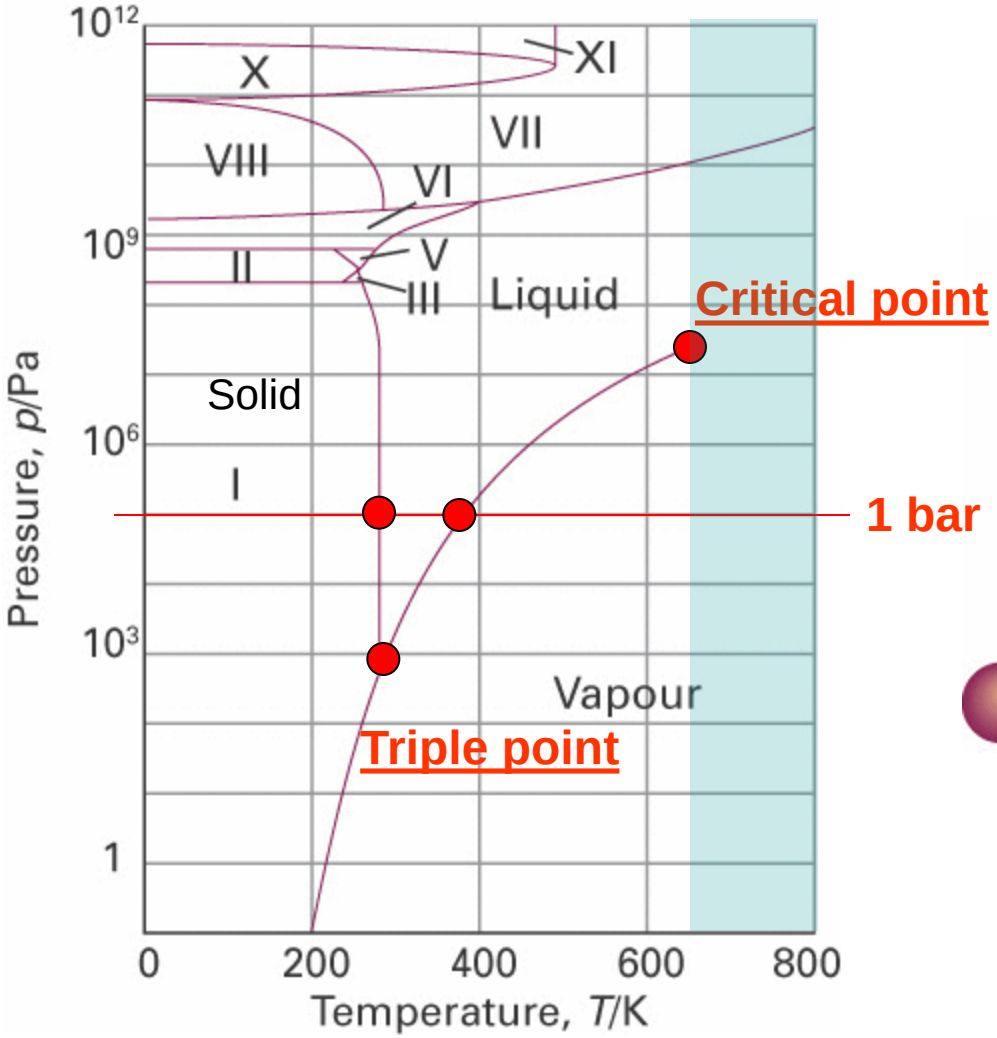
647.1 K

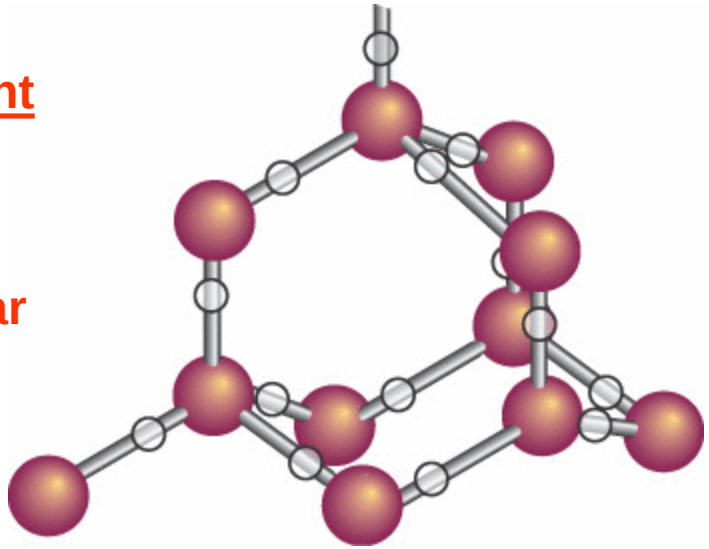
Youtube_link



Critical point

Phase diagrams and phase transitions of unary systems

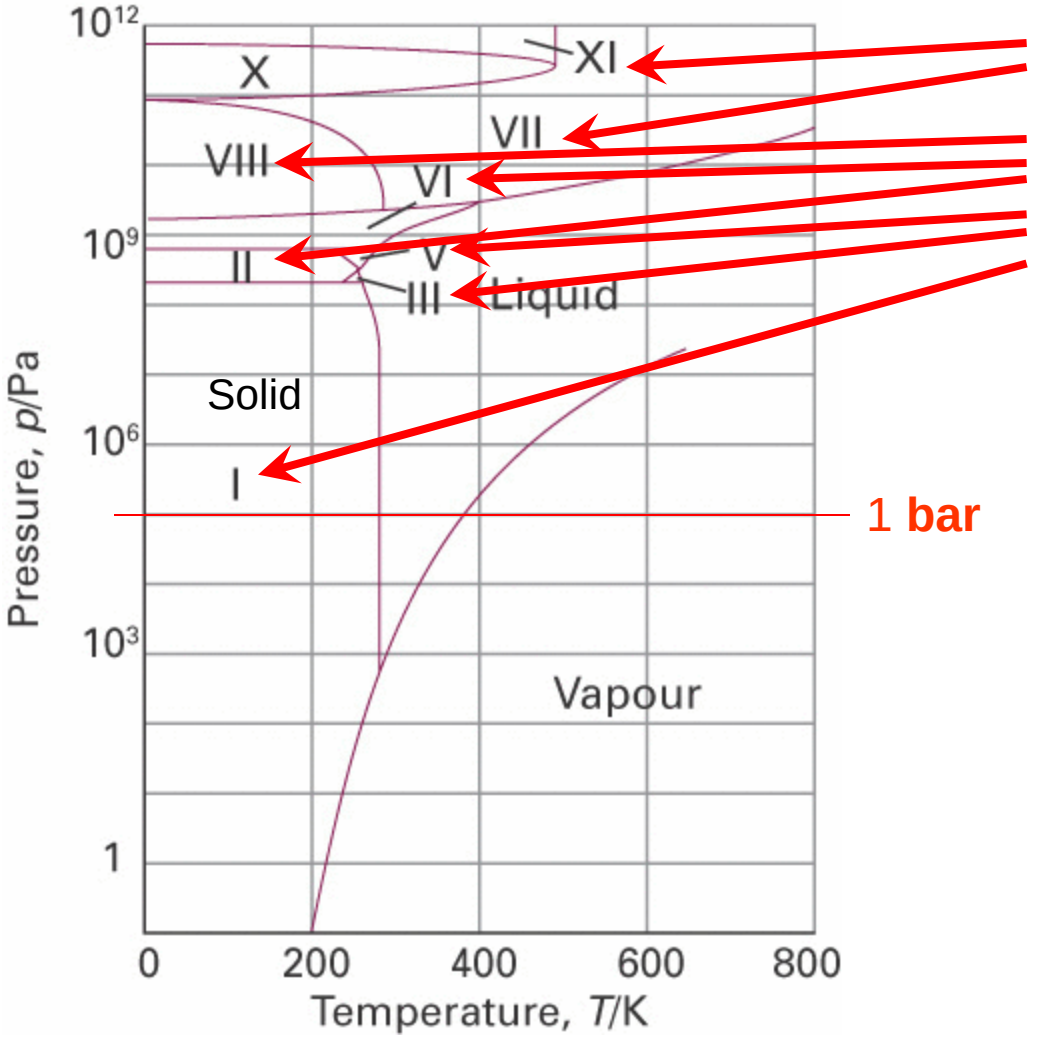




H-bonding

(**Equilibrium**) P,T phase diagram H_2O

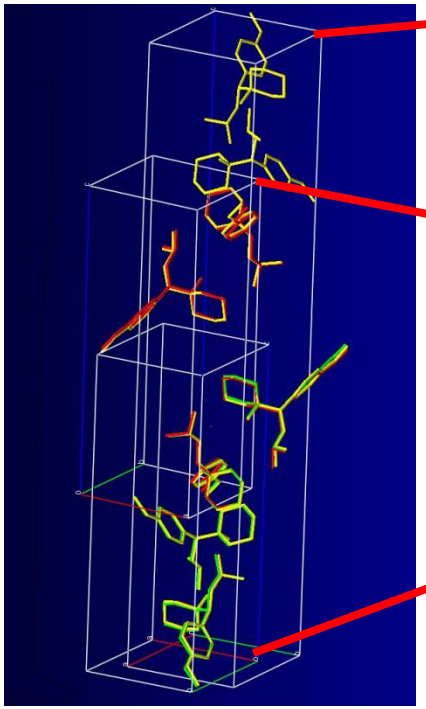
Phase diagrams and phase transitions of unary systems

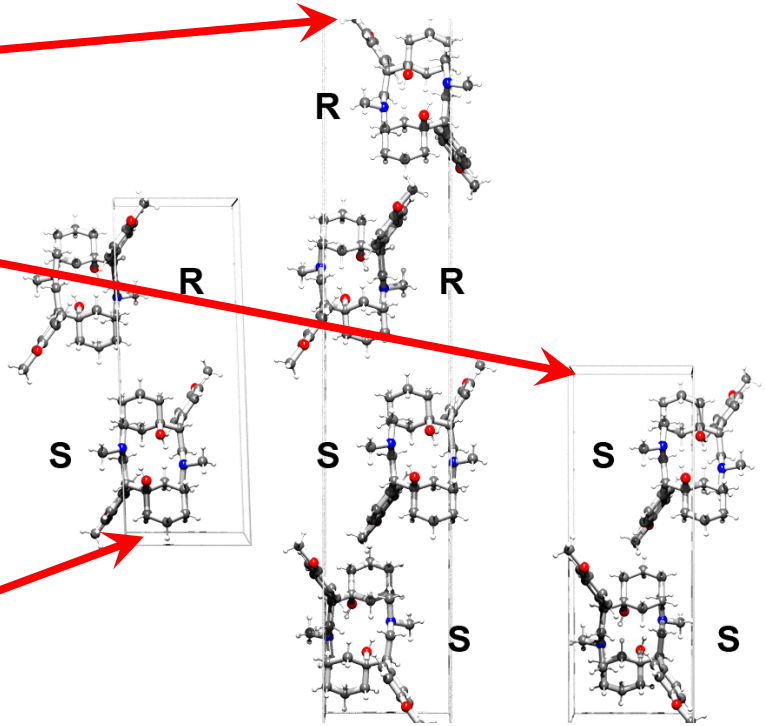


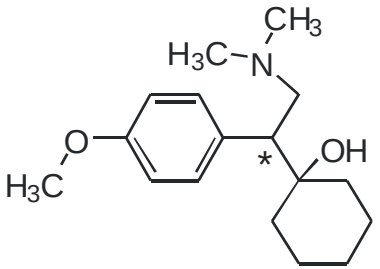
Polymorphic forms for the solids

(**Equilibrium**) P,T phase diagram H_2O

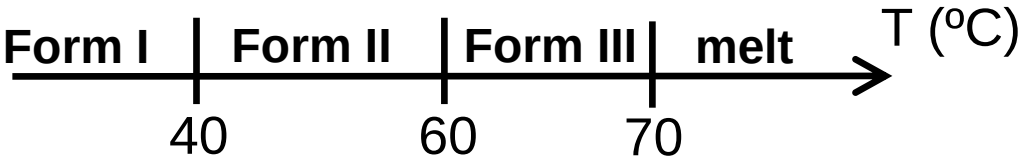
Phase diagrams and phase transitions of unary systems





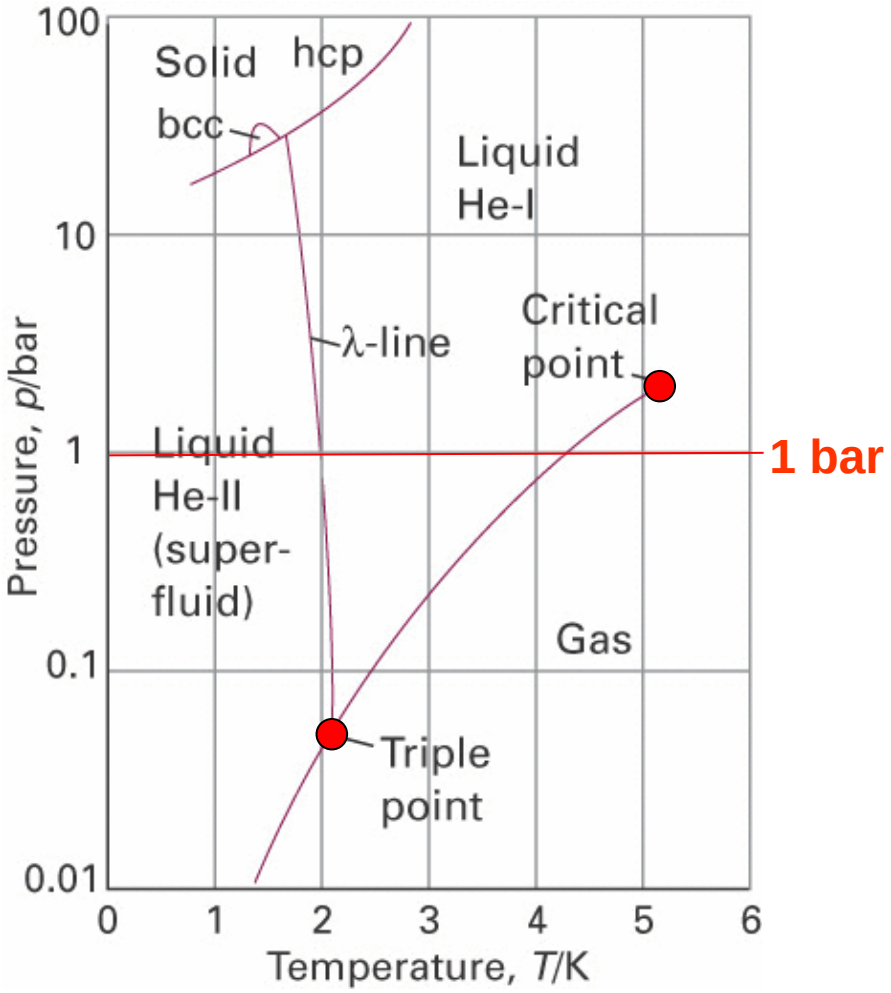


Venlafaxine

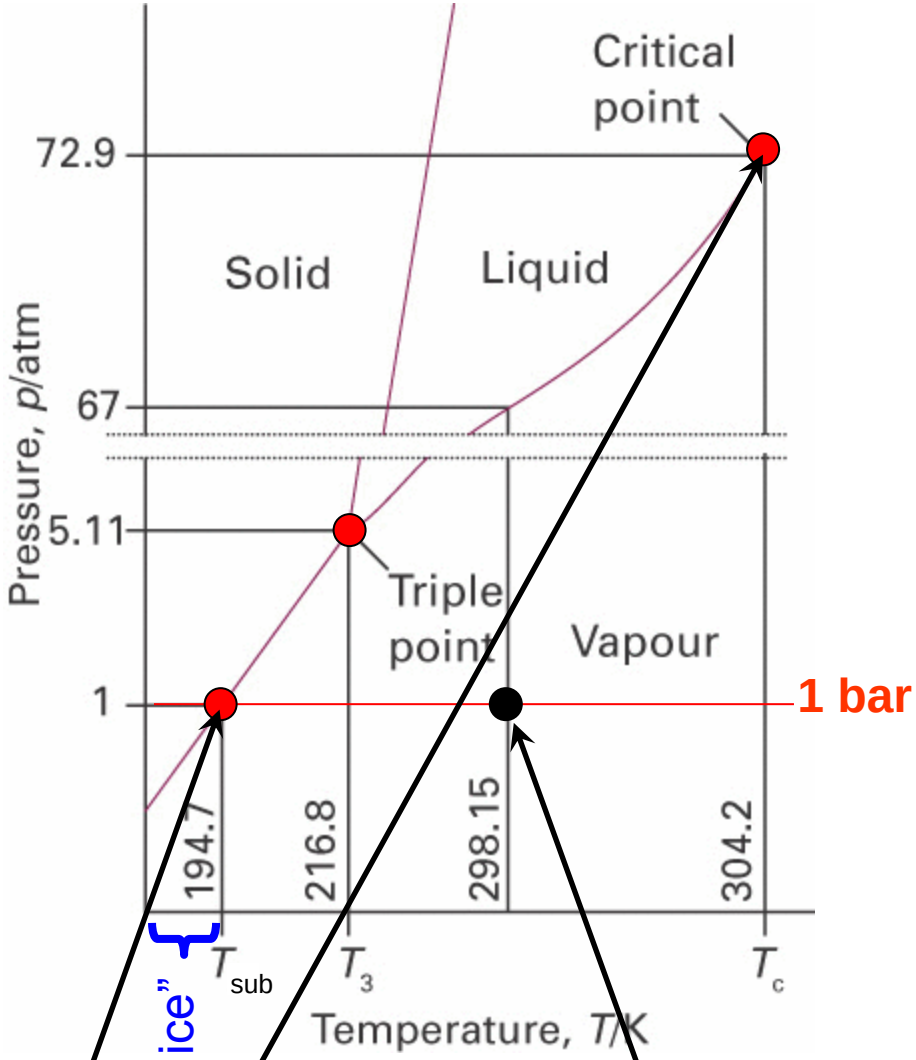


Polymorphic (solid state) phase transitions

Phase diagrams and phase transitions of unary systems



^{4}He



CO_2

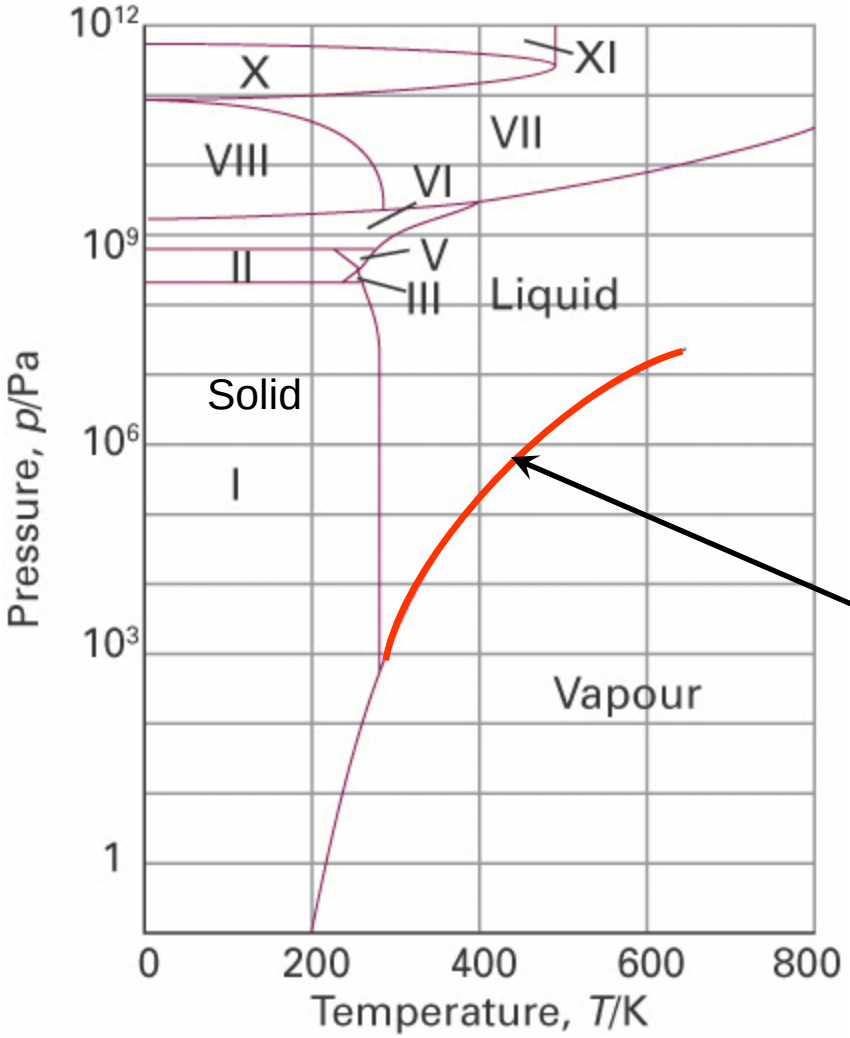
sublimation point at 1 bar

ambient conditions

See link on slide 12

Phase boundary lines in diagrams of unary systems

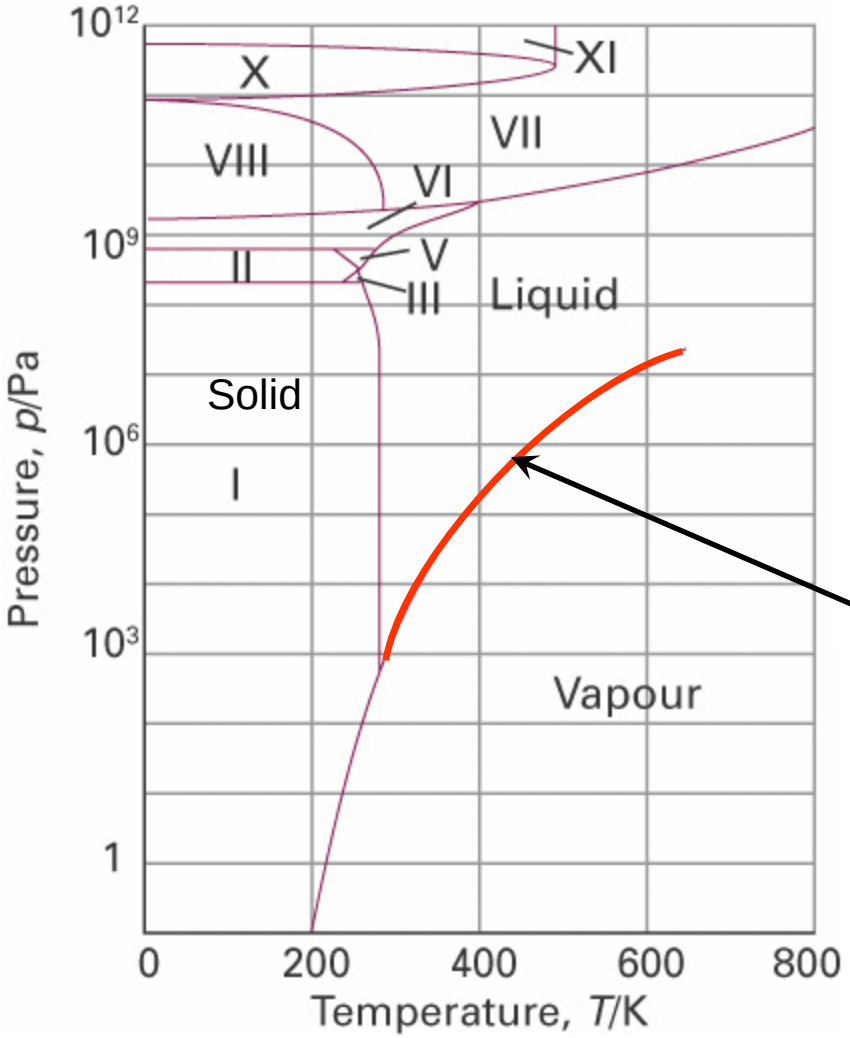
Phase boundary lines in diagrams of unary systems

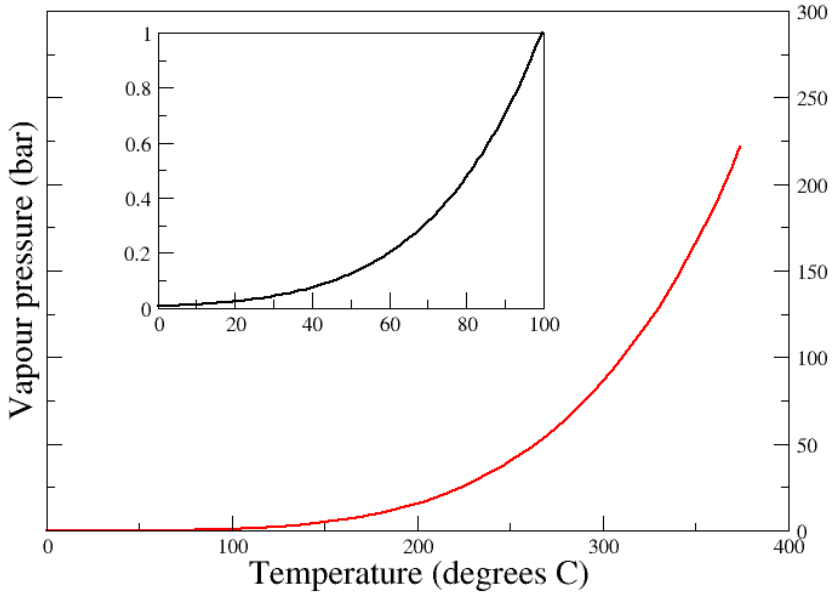


Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(Equilibrium) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems

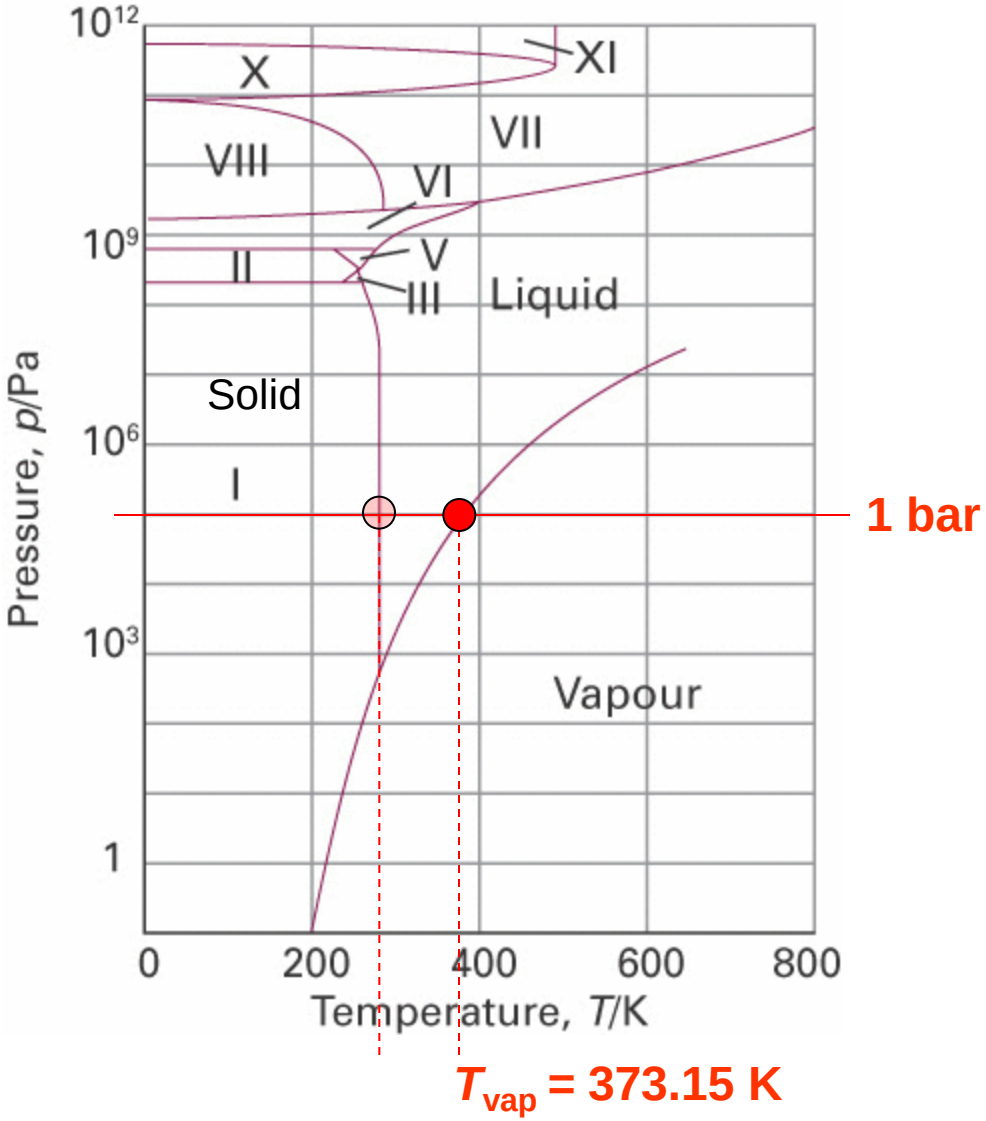




Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(Equilibrium) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems

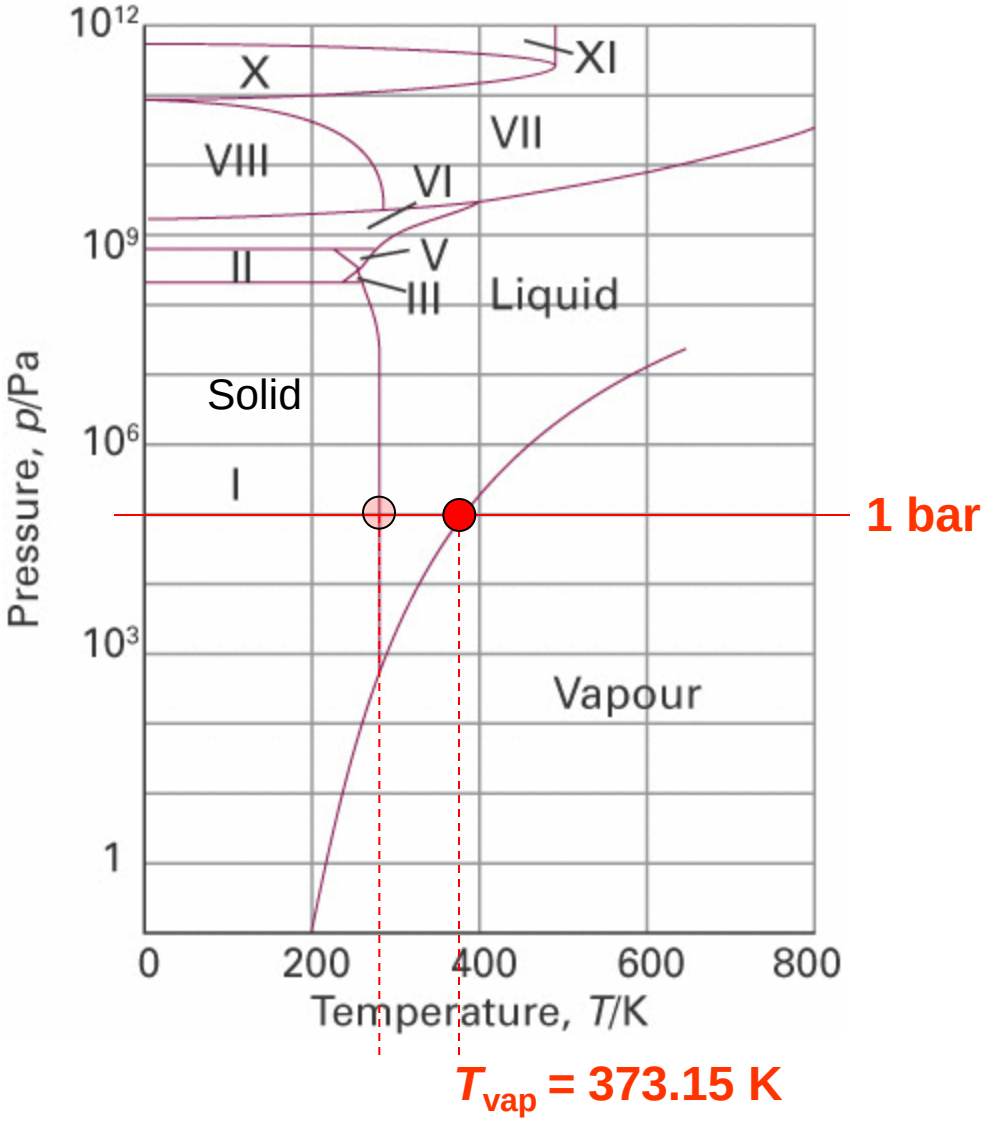


T = 373.15 K and $P = P^{\ominus}$ = 1 bar

Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(Equilibrium) P,T phase diagram H_2O

Phase diagrams and phase transitions of unary systems



(**Equilibrium**) P,T phase diagram H_2O

Intermezzo:

in open system

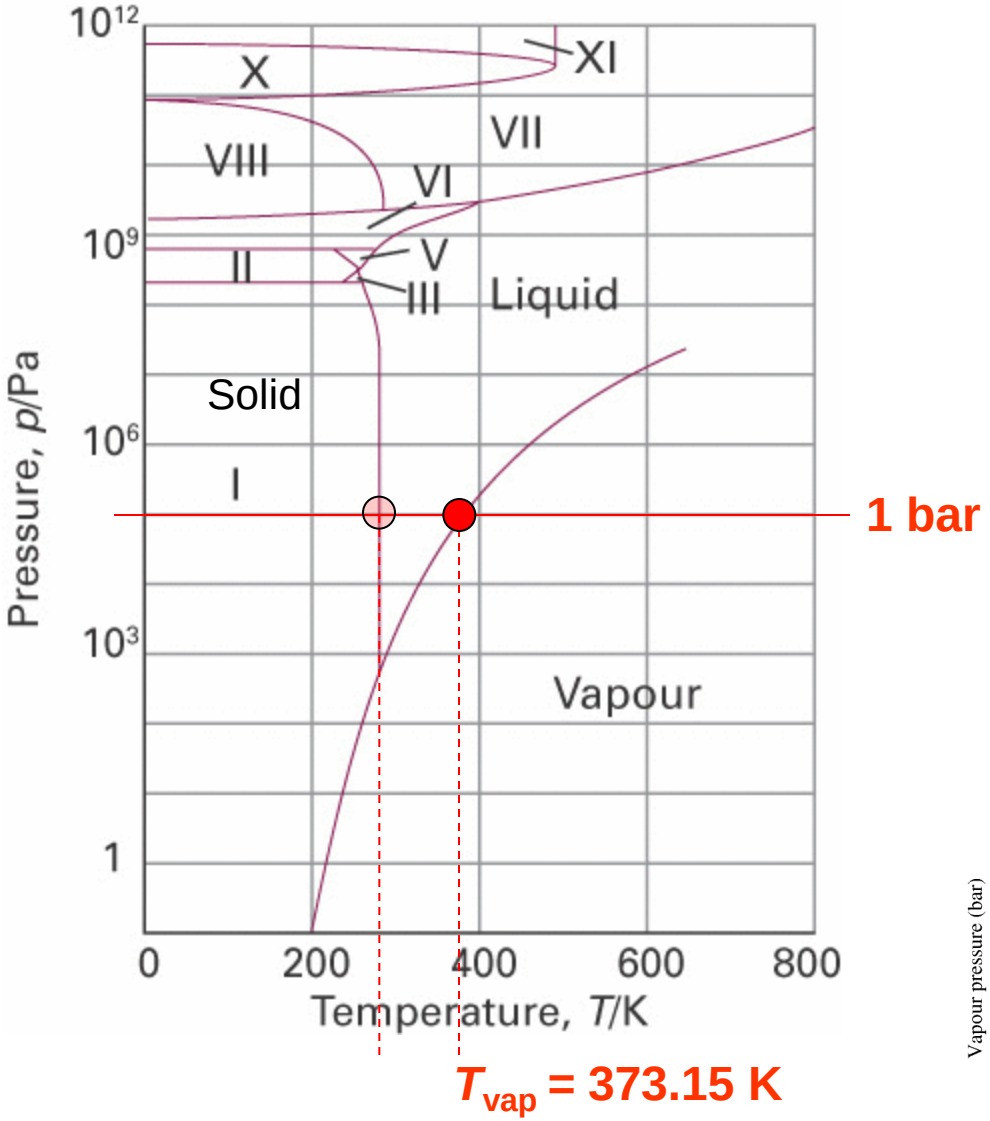
@ T_{vap} = 373.15 K

Water starts to boil as

$$P_{H_2O}(\text{air}) < 1\,\text{bar}$$

Non-equilibrium situation

Phase diagrams and phase transitions of unary systems



(**Equilibrium**) P,T phase diagram H_2O

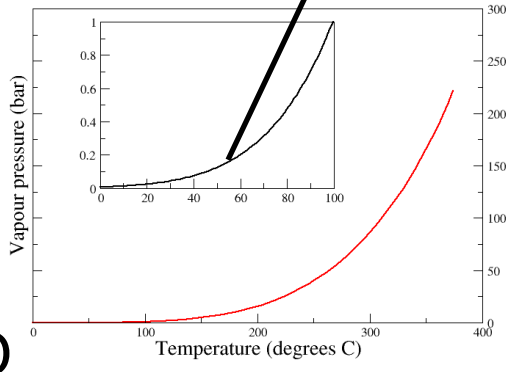
Intermezzo:

Relative Humidity

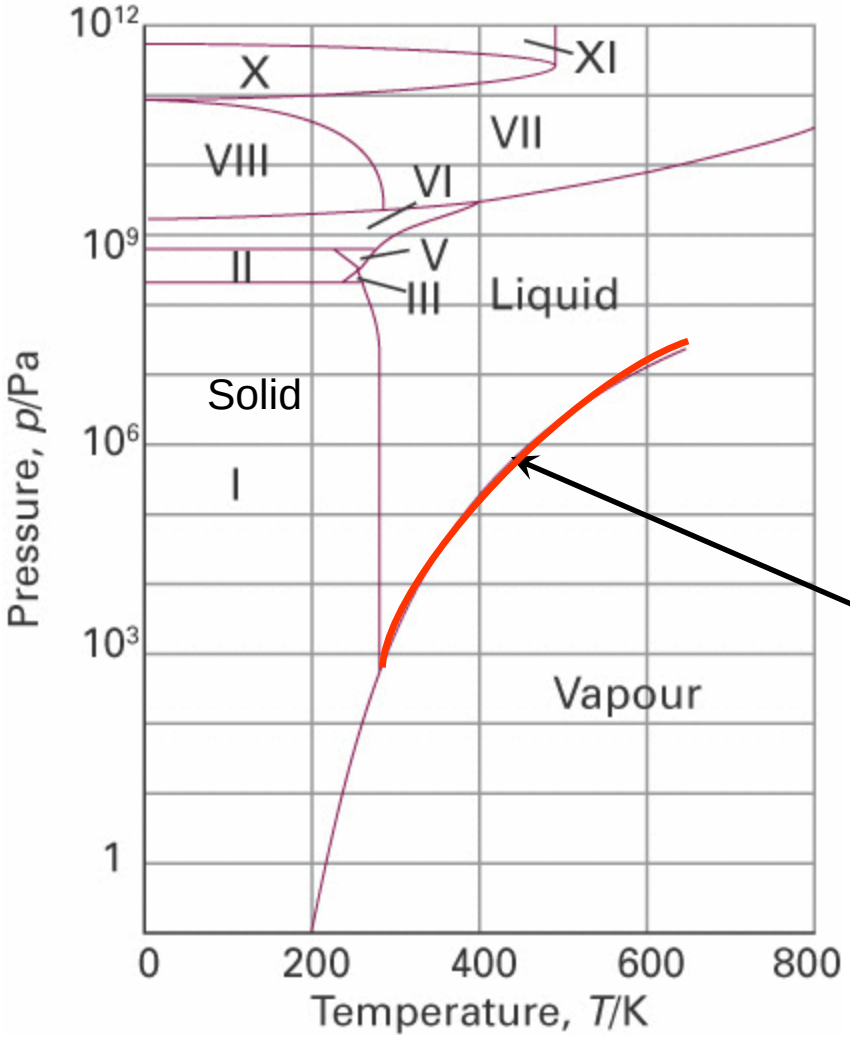
$$RH = \phi \equiv \frac{P_{H_2O}(\text{air})}{P^*_{H_2O}}$$

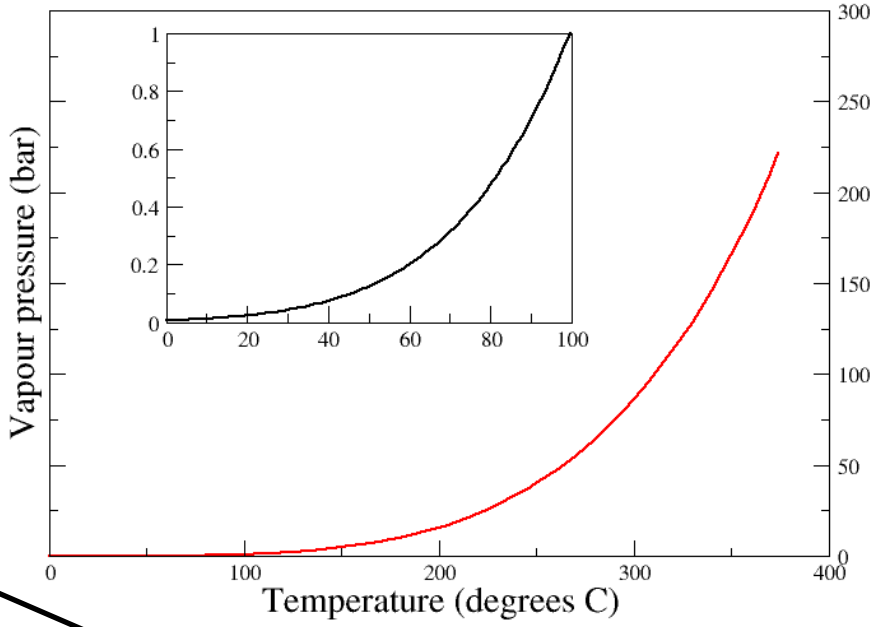
RH < 100%→

Non-equilibrium



Phase boundary lines in diagrams of unary systems





Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(**Equilibrium**) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems

Equilibrium between phases $\mathrm{H_2O}(l) \leftrightarrow \mathrm{H_2O}(g)$

$n_g \leftrightarrow n_l$ $\Rightarrow$ $dn_i \neq 0$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

The chemical potential of phase i $(i = l,g)$ **(Study guide p.11-13)**

Note: we are dealing with a unary system

$\mu_i \equiv G_{i,\mathrm{m}}$ **(pure compound)**

Phase boundary lines in diagrams of unary systems

Importance of the chemical potential:

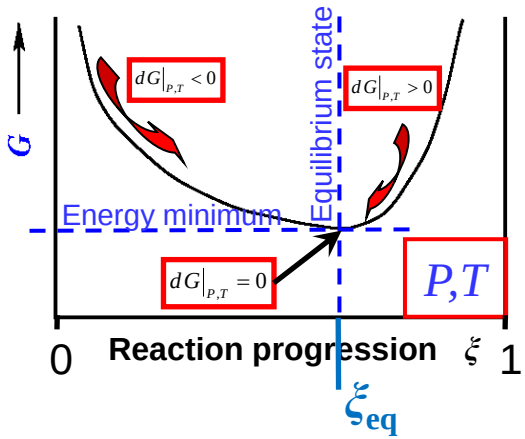
Equilibrium between phases

$$H_2O(l) \leftrightarrow H_2O(g)$$

$$dG = VdP - SdT + \mu_l dn_l + \mu_g dn_g$$

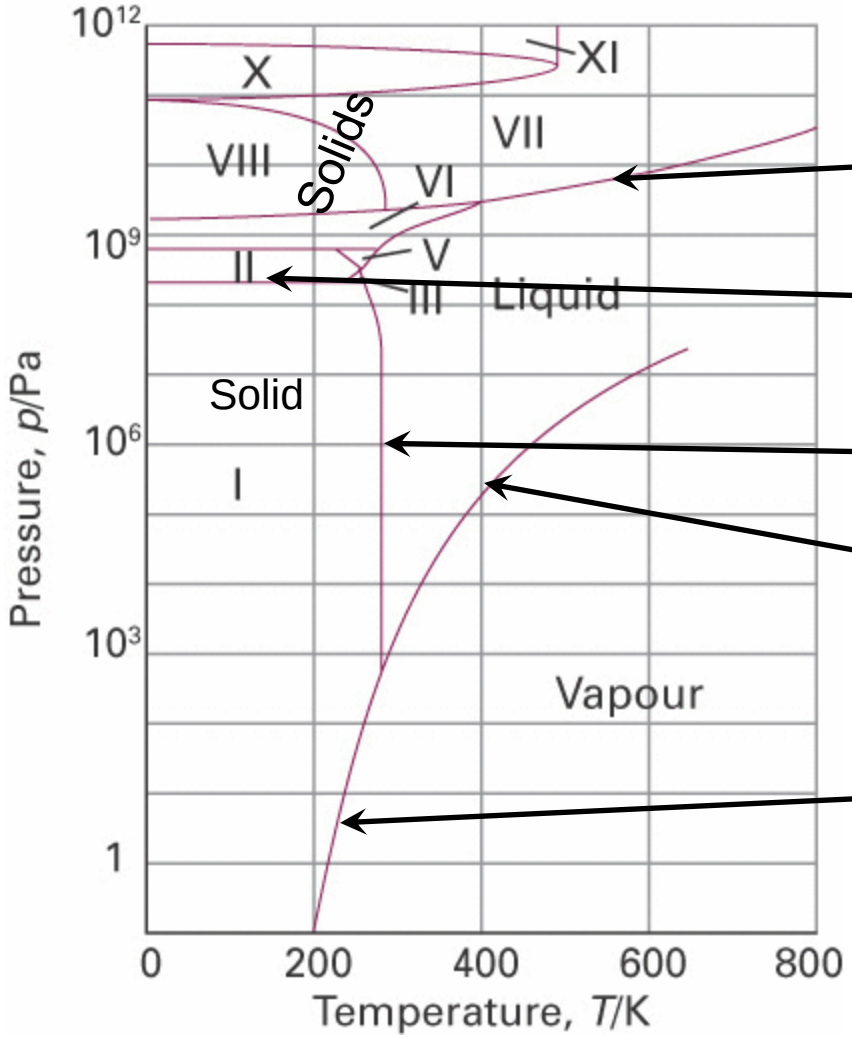
Equilibrium $\Rightarrow$ $dG_{T,P} = 0$

$$dn_l = -dn_g$$



$\Rightarrow$ $\mu_l = \mu_g$

Phase boundary lines in diagrams of unary systems



$\mu_{s_{\mathrm{VII}}} = \mu_l$

$\mu_{s_{\mathrm{I}}} = \mu_{s_{\mathrm{II}}}$

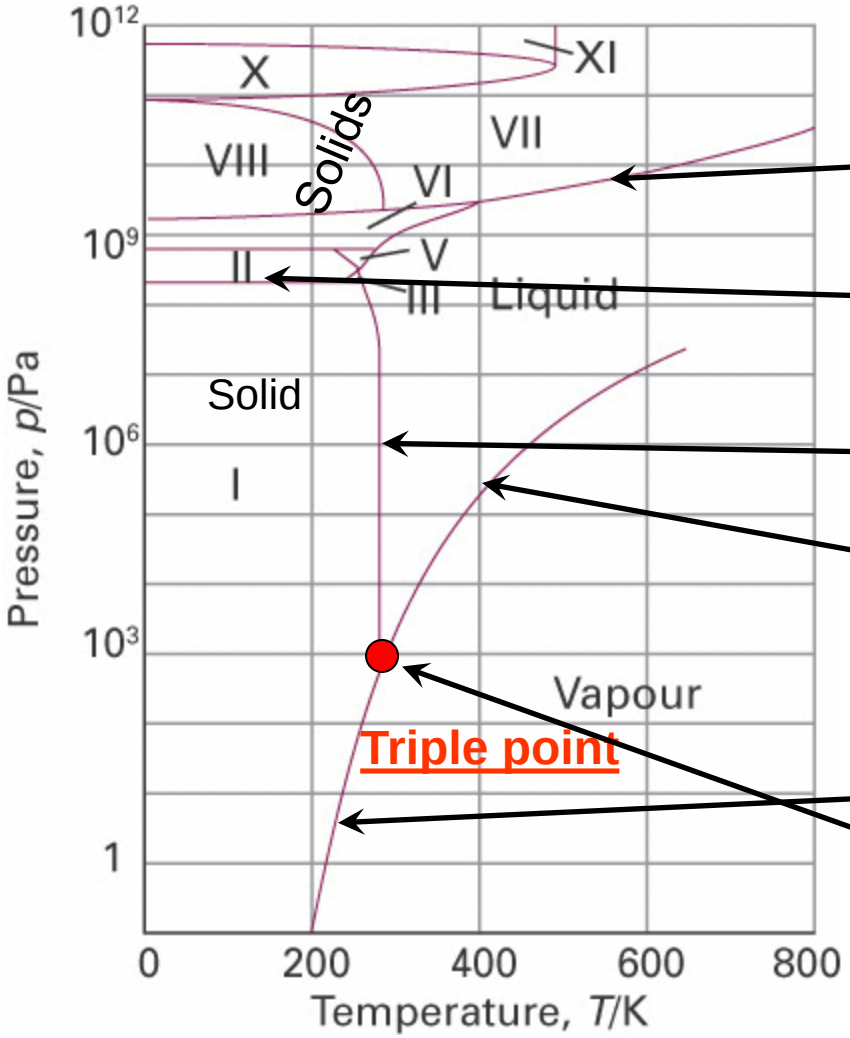
$\mu_{s_{\mathrm{I}}} = \mu_l$

$\mu_l = \mu_g$

$\mu_{s_{\mathrm{I}}} = \mu_g$

(Equilibrium) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems



$\mu_{s_{\mathrm{VII}}} = \mu_l$

$\mu_{s_{\mathrm{I}}} = \mu_{s_{\mathrm{II}}}$

$\mu_{s_{\mathrm{I}}} = \mu_l$

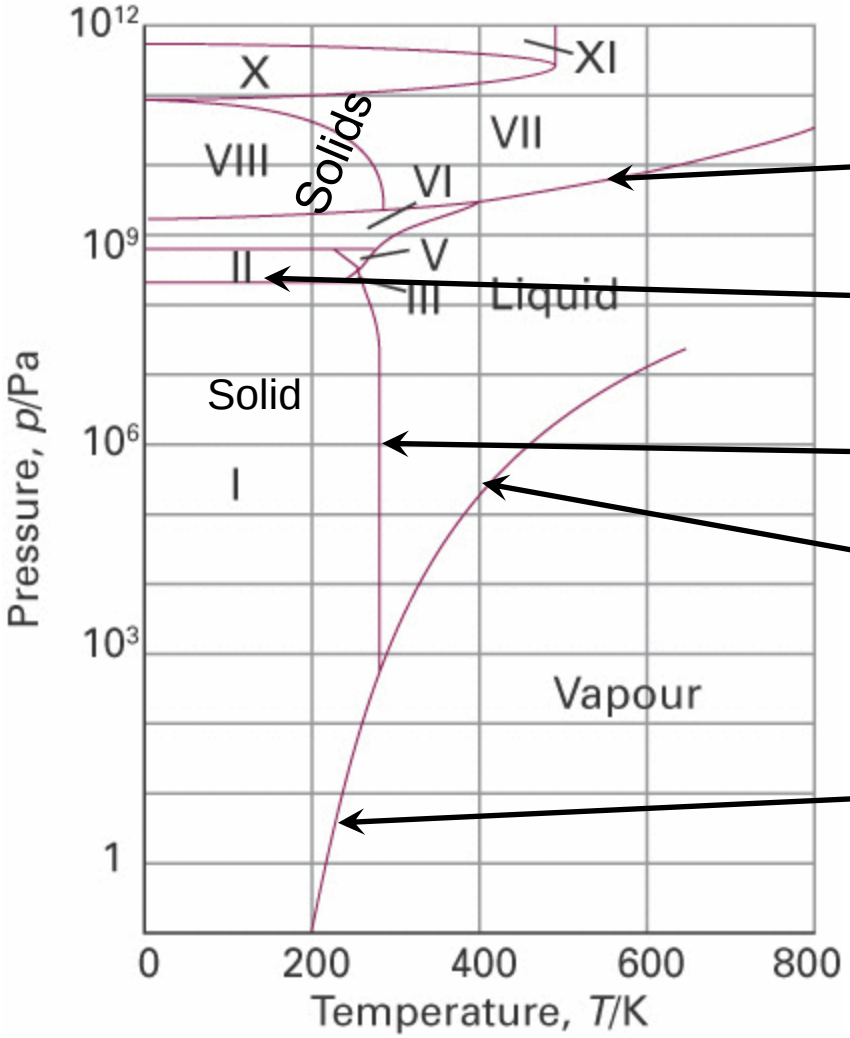
$\mu_l = \mu_g$

$\mu_{s_{\mathrm{I}}} = \mu_g$

$\mu_{s_{\mathrm{I}}} = \mu_l = \mu_g$

(Equilibrium) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems



$$G_{s_{\mathrm{VII}},\mathrm{m}} = G_{l,\mathrm{m}}$$

$$G_{s_{\mathrm{I}},\mathrm{m}} = G_{s_{\mathrm{II}},\mathrm{m}}$$

$$G_{s_{\mathrm{I}},\mathrm{m}} = G_{l,\mathrm{m}}$$

$$G_{l,\mathrm{m}} = G_{g,\mathrm{m}}$$

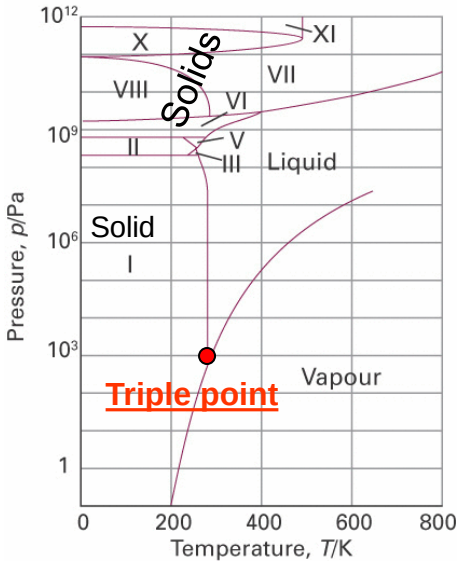
$$G_{s_{\mathrm{I}},\mathrm{m}} = G_{g,\mathrm{m}}$$

pure compound: $\mu_i \equiv G_{i,\mathrm{m}}$

(*i* = *s*, *l*, *g*)

(**Equilibrium**) P,T phase diagram H_2O

Phase boundary lines in diagrams of unary systems



Along any phase boundary line:

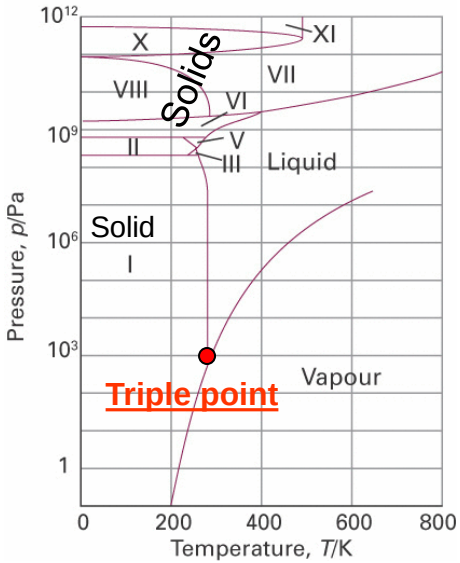
(between two phases α and β)

$$dG_{\alpha,\mathrm{m}} = dG_{\beta,\mathrm{m}}$$

$$dG_{i,\mathrm{m}} = V_{i,\mathrm{m}}\,dP - S_{i,\mathrm{m}}\,dT$$

$$V_{\alpha,\mathrm{m}}\,dP - S_{\alpha,\mathrm{m}}\,dT = V_{\beta,\mathrm{m}}\,dP - S_{\beta,\mathrm{m}}\,dT$$

Phase boundary lines in diagrams of unary systems



Along any phase boundary line:

(between two phases α and β)

$$dG_{\alpha,\mathrm{m}} = dG_{\beta,\mathrm{m}}$$

$$dG_{i,\mathrm{m}} = V_{i,\mathrm{m}}\,dP - S_{i,\mathrm{m}}\,dT$$

$$V_{\alpha,\mathrm{m}}\,dP - S_{\alpha,\mathrm{m}}\,dT = V_{\beta,\mathrm{m}}\,dP - S_{\beta,\mathrm{m}}\,dT$$

Clapeyron equation:

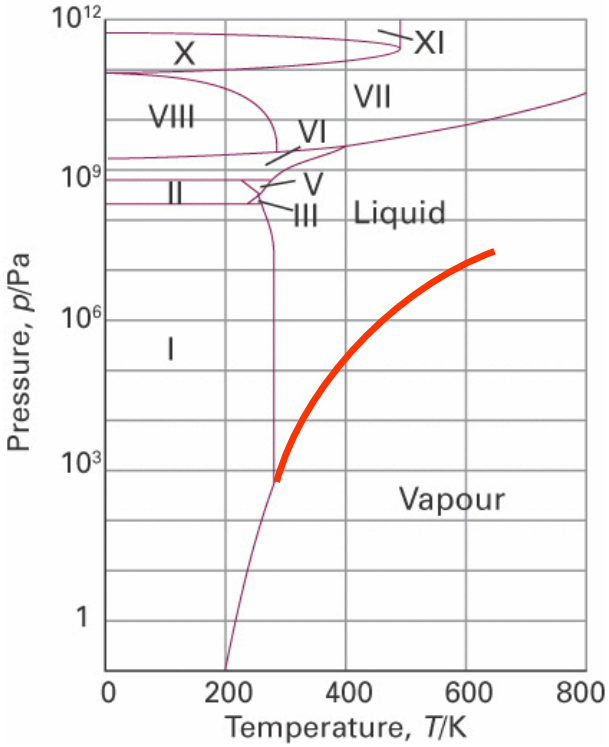
$$\frac{dP}{dT} = \frac{\Delta_{trs} S_{\mathrm{m}}}{\Delta_{trs} V_{\mathrm{m}}}$$

$$\Delta_{trs} G_{\mathrm{m}} = 0$$

$$\frac{dP}{dT} = \frac{\Delta_{trs} H_{\mathrm{m}}}{T_{trs}\,\Delta_{trs} V_{\mathrm{m}}}$$

(is exact)

Phase boundary lines in diagrams of unary systems



Along *l-g* phase boundary line:

Clapeyron equation:

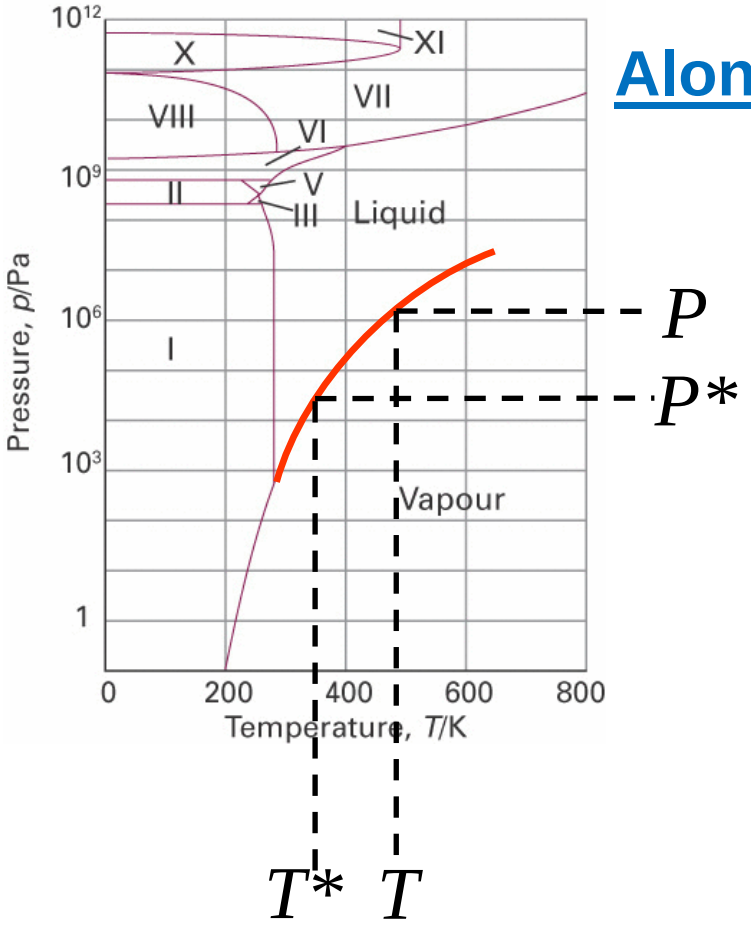
$$dP = \frac{\Delta_{vap} H_m}{T_{vap} \Delta_{vap} V_m} dT$$

Perfect gas: $PV_m = RT$

$$\Delta_{vap} V_m \approx V_{g,m} = \frac{RT}{P}$$

$$\frac{dP}{P} = \frac{\Delta_{vap} H_m}{RT_{vap}^2} dT \quad \Rightarrow \quad \int \frac{dP}{P} = \int \frac{\Delta_{vap} H_m}{RT_{vap}^2} dT$$

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

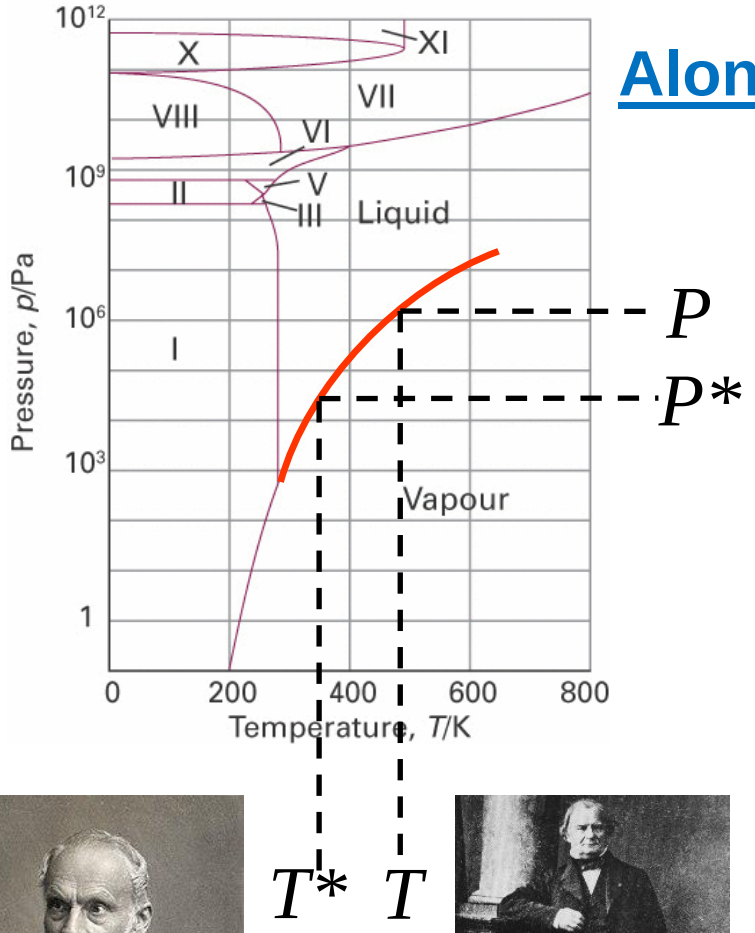
$$\int_{P^*}^{P} \frac{dP}{P} = \int_{T^*}^{T} \frac{\Delta_{vap}H_m}{RT_{vap}^2}\,dT$$

$$\Delta_{vap}H_m(T) \approx \Delta_{vap}H_m$$

$$\int_{P^*}^{P} \frac{dP}{P} = \frac{\Delta_{vap}H_m}{R}\int_{T^*}^{T} \frac{dT}{T_{vap}^2}$$

$$\ln\frac{P}{P^*} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T} - \frac{1}{T^*}\right]$$

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

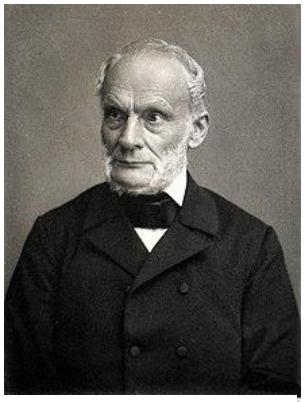
Clausius-Clapeyron equation:

$$\ln\frac{P}{P^*} = -\frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T}-\frac{1}{T^*}\right]$$

$$P = P^*\exp\left[-\chi\right]$$

$$\chi = \frac{\Delta_{vap}H_m}{R}\left[\frac{1}{T}-\frac{1}{T^*}\right]$$

Clausius-Clapeyron equation



Rudolf Clausius
1822-1888

Benoît Clapeyron
1799-1864

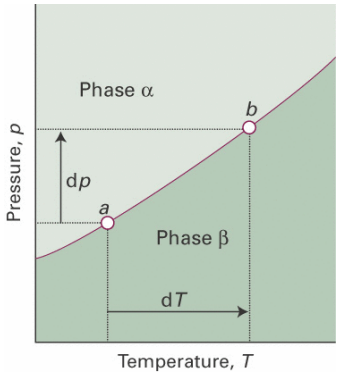
Phase boundary lines in phase diagrams of unary systems

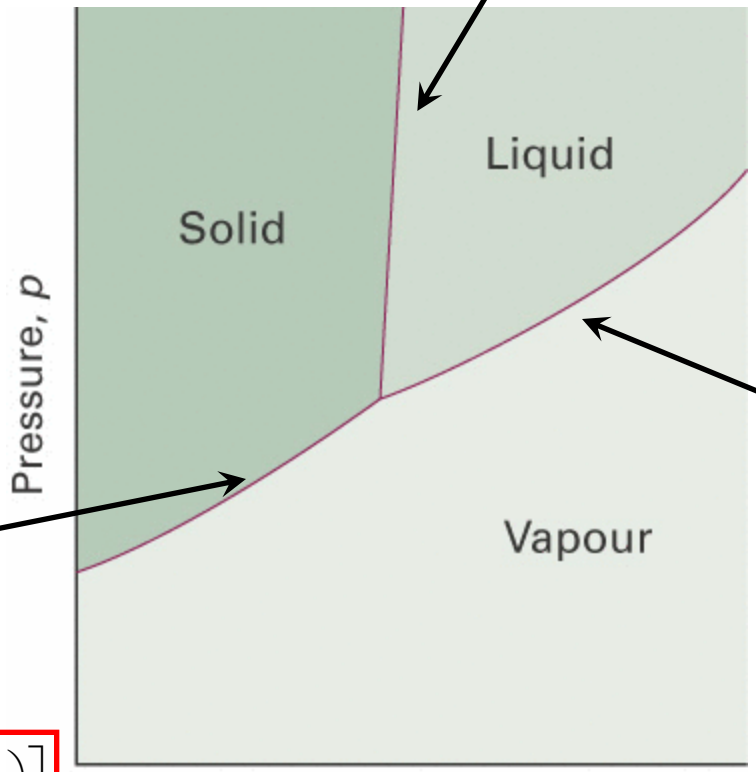
$$\frac{dP}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V} = \frac{\Delta_{trs}H}{T_{trs}\Delta_{trs}V}$$

Clapeyron

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_{fus}\Delta_{fus}V}$$

$$P \approx P^* + \frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\frac{T}{T^*} \approx P^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V}\left(T - T^*\right)$$





$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{T_{vap}\Delta_{vap}V}$$

$$\frac{d\ln P}{dT} \approx \frac{\Delta_{vap}H}{RT^2}$$

$$P \approx P^* \exp\left[-\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right]$$

Clausius-Clapeyron

$$\frac{dP}{dT} = \frac{\Delta_{sub}H}{T_{sub}\Delta_{sub}V}$$

$$\frac{d\ln P}{dT} \approx \frac{\Delta_{sub}H}{RT^2}$$

$$P \approx P^* \exp\left[-\frac{\Delta_{sub}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right]$$

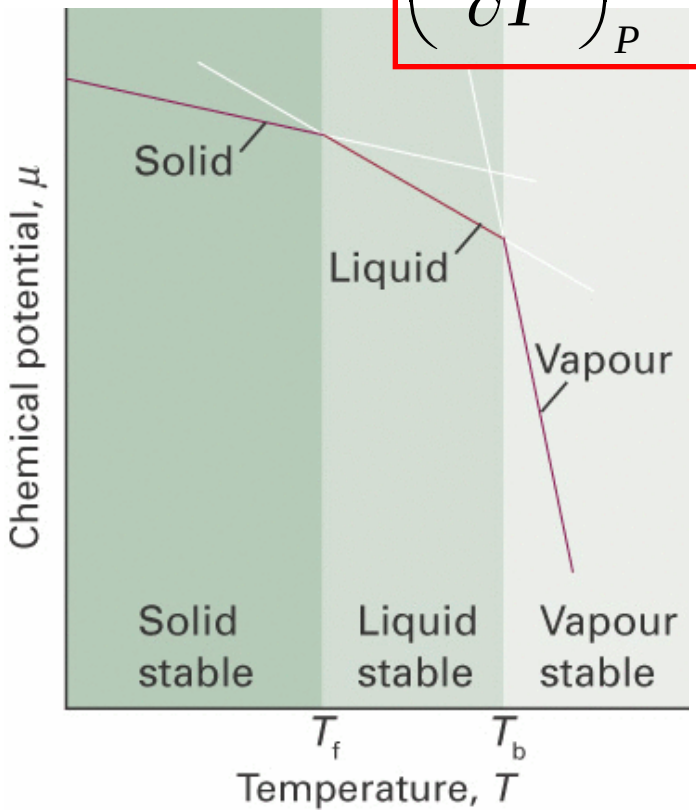
Exercise 5-8

Phase transitions in phase diagrams of unary systems

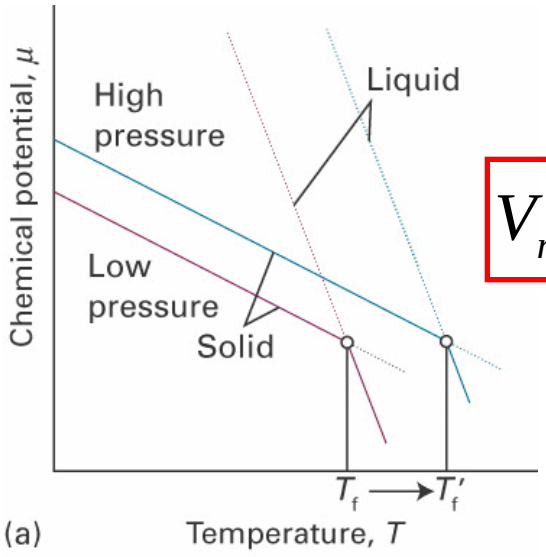
Phase transitions in phase diagrams of unary systems

$$dG_m^{\alpha} = d\mu^{\alpha} = V_m^{\alpha} dP - S_m^{\alpha} dT$$

$$\left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_P = -S_m^{\alpha}$$

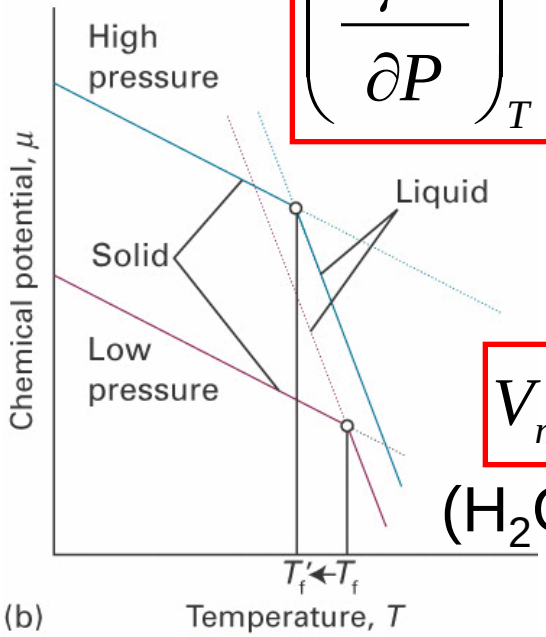


$$S_m^s < S_m^l << S_m^g$$



$$V_m^l > V_m^s$$

$$\left(\frac{\partial \mu^{\alpha}}{\partial P}\right)_T = V_m^{\alpha}$$



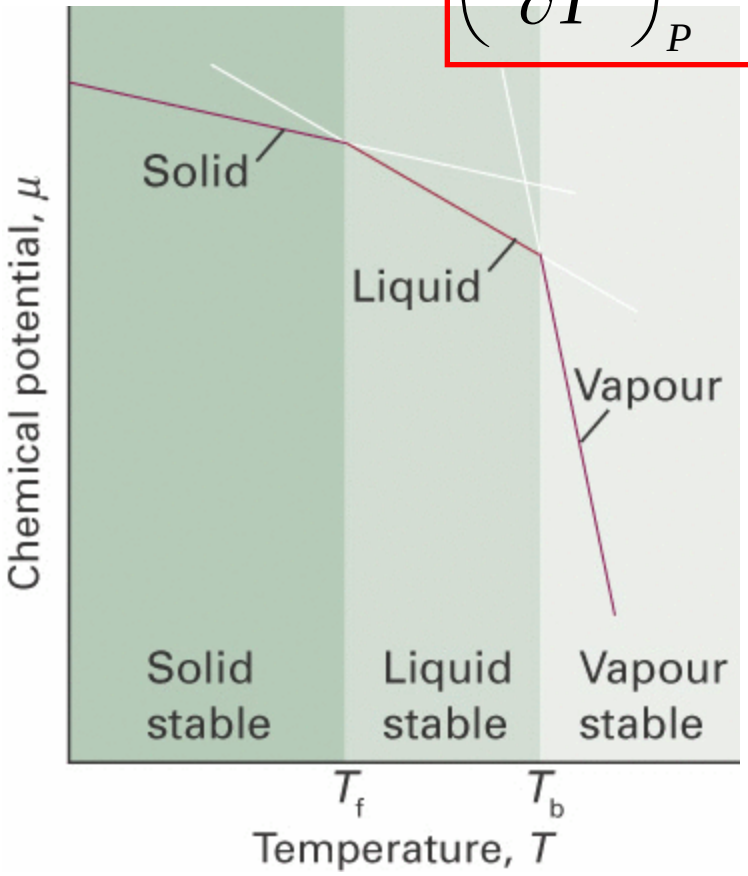
$$V_m^l < V_m^s$$

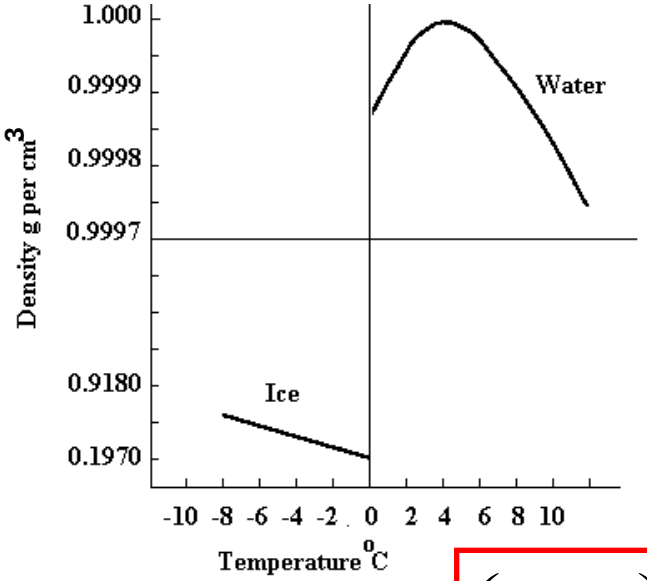
(H_2O)

Phase transitions in phase diagrams of unary systems

$$\mathrm{d}G_m^{\alpha} = \mathrm{d}\mu^{\alpha} = V_m^{\alpha}\mathrm{d}P - S_m^{\alpha}\mathrm{d}T$$

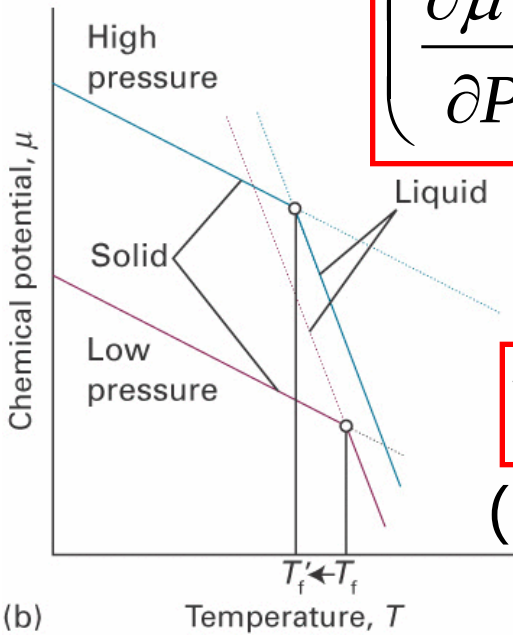
$$\left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_P = -S_m^{\alpha}$$





(H_2O)

$$\left(\frac{\partial \mu^{\alpha}}{\partial P}\right)_T = V_m^{\alpha}$$

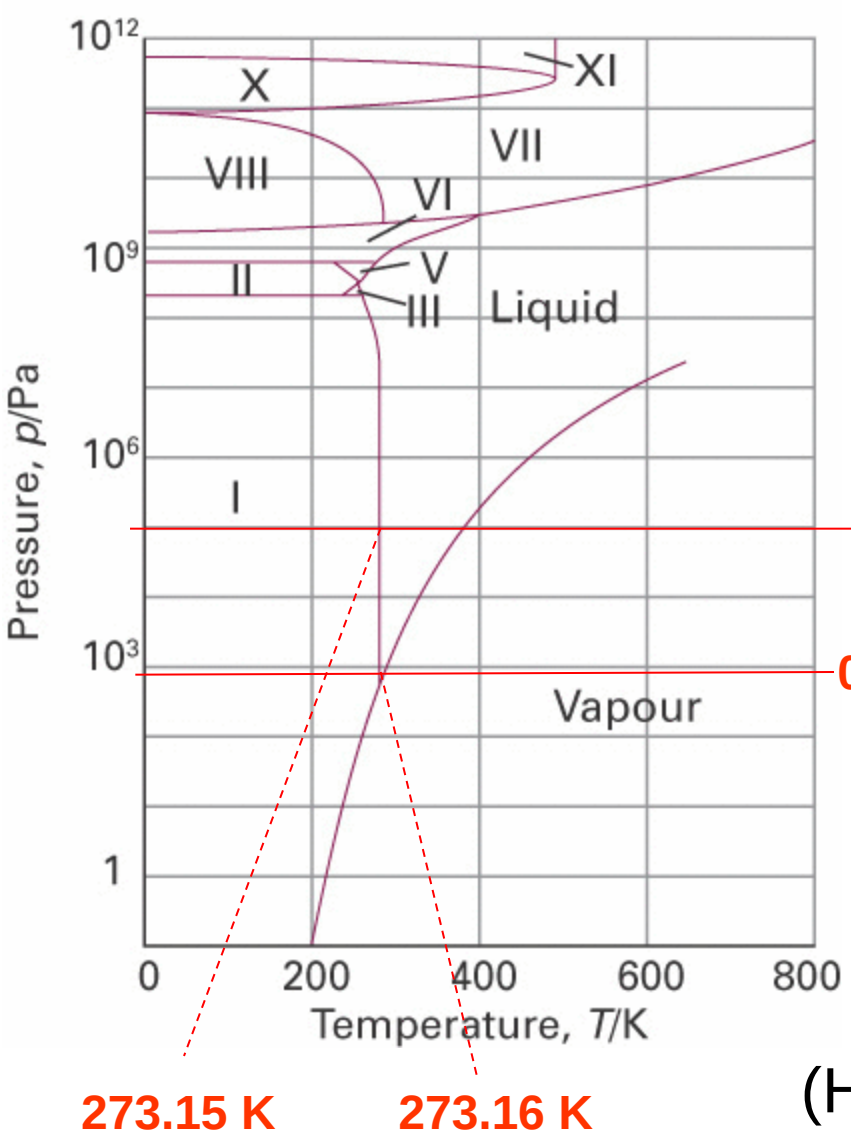


$$V_m^{l} < V_m^{s}$$

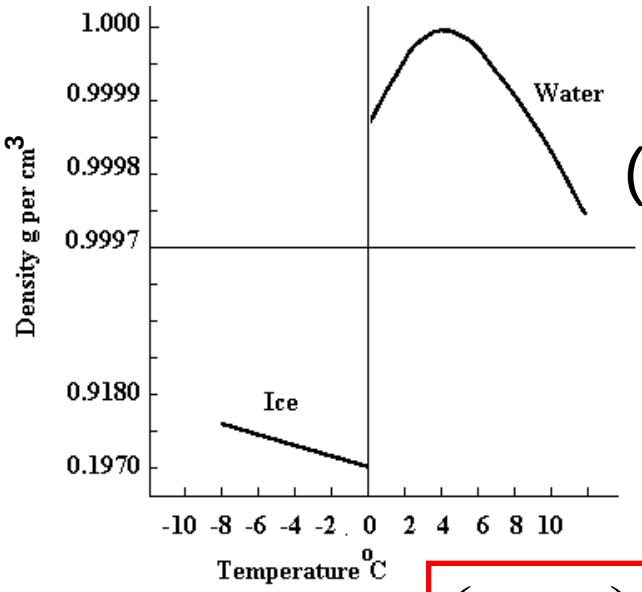
(H_2O)

Phase transitions in phase diagrams of unary systems

$$\mathrm{d}G_m^{\alpha} = \mathrm{d}\mu^{\alpha} = V_m^{\alpha}\mathrm{d}P - S_m^{\alpha}\mathrm{d}T$$

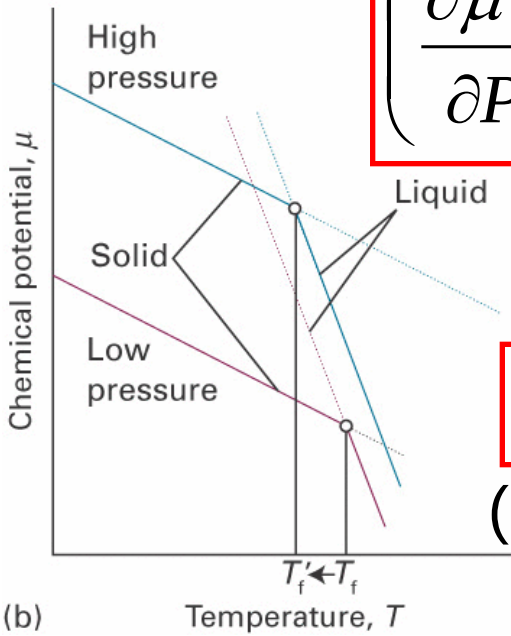


(H$_2$O)



(H$_2$O)

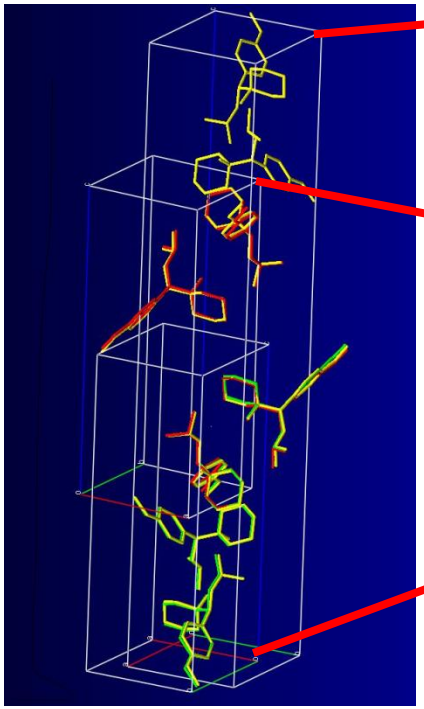
$$\left(\frac{\partial \mu^{\alpha}}{\partial P}\right)_T = V_m^{\alpha}$$

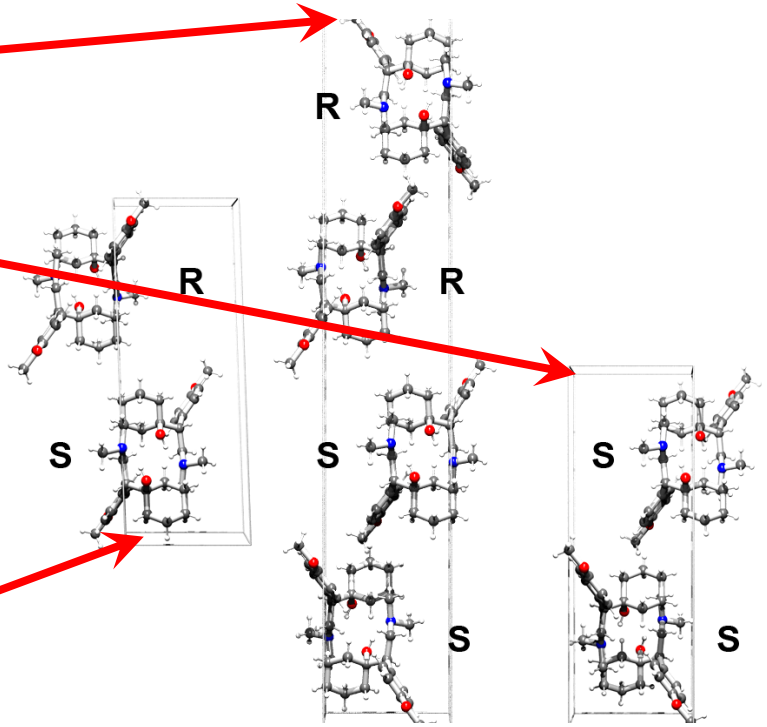


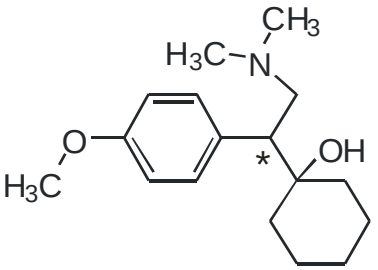
$$V_m^{l} < V_m^{s}$$

(H$_2$O)

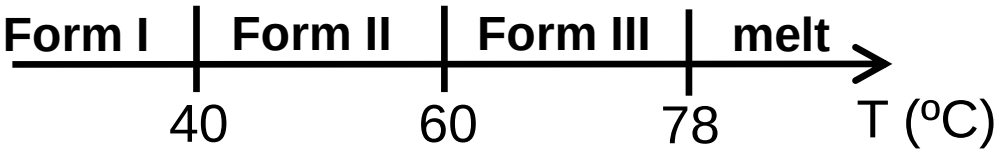
Phase diagrams and phase transitions of unary systems





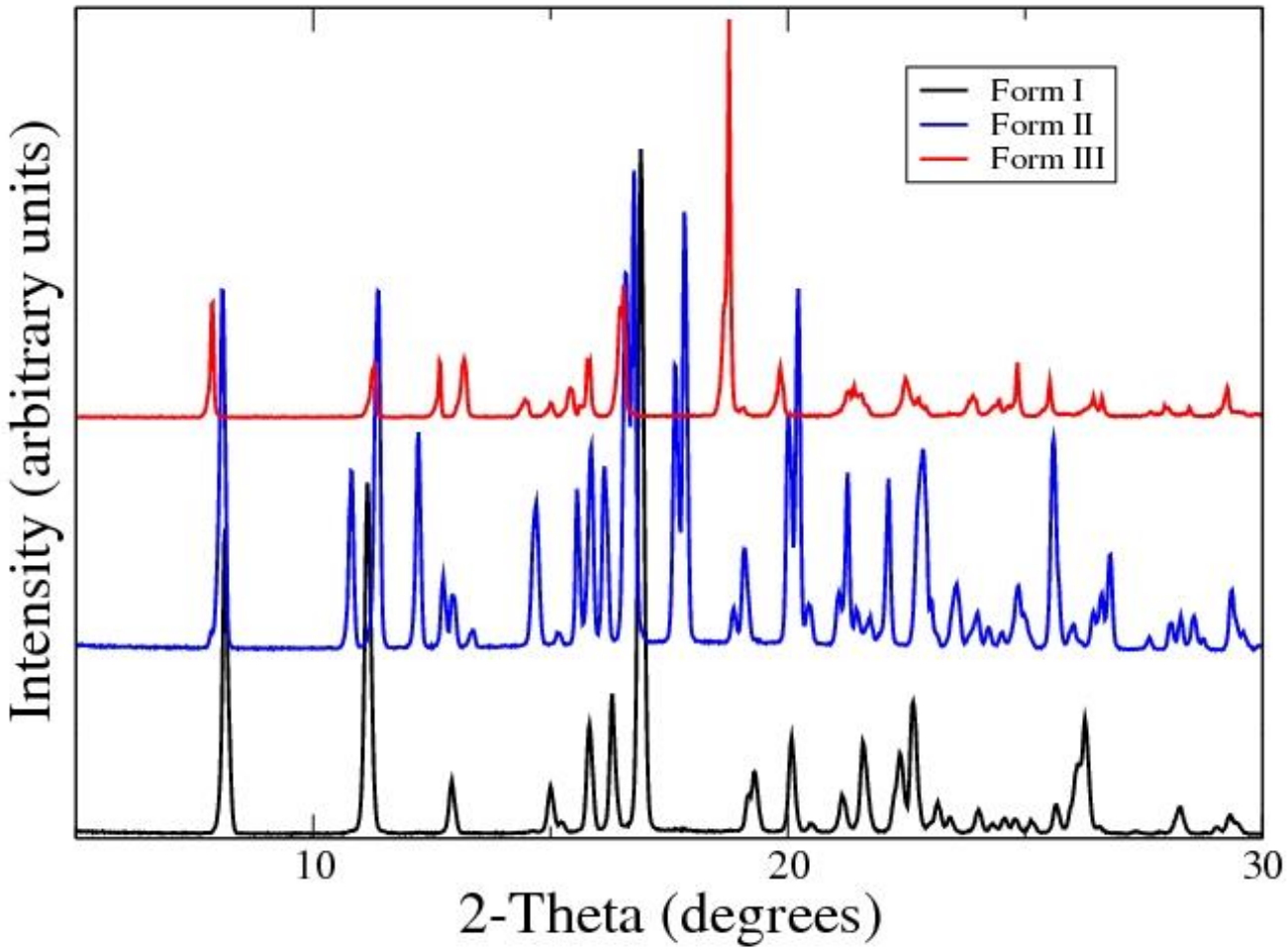


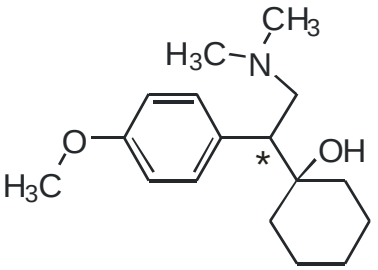
Venlafaxine



Polymorphic (solid state) phase transitions

Characterization (polymorphic) crystal structures

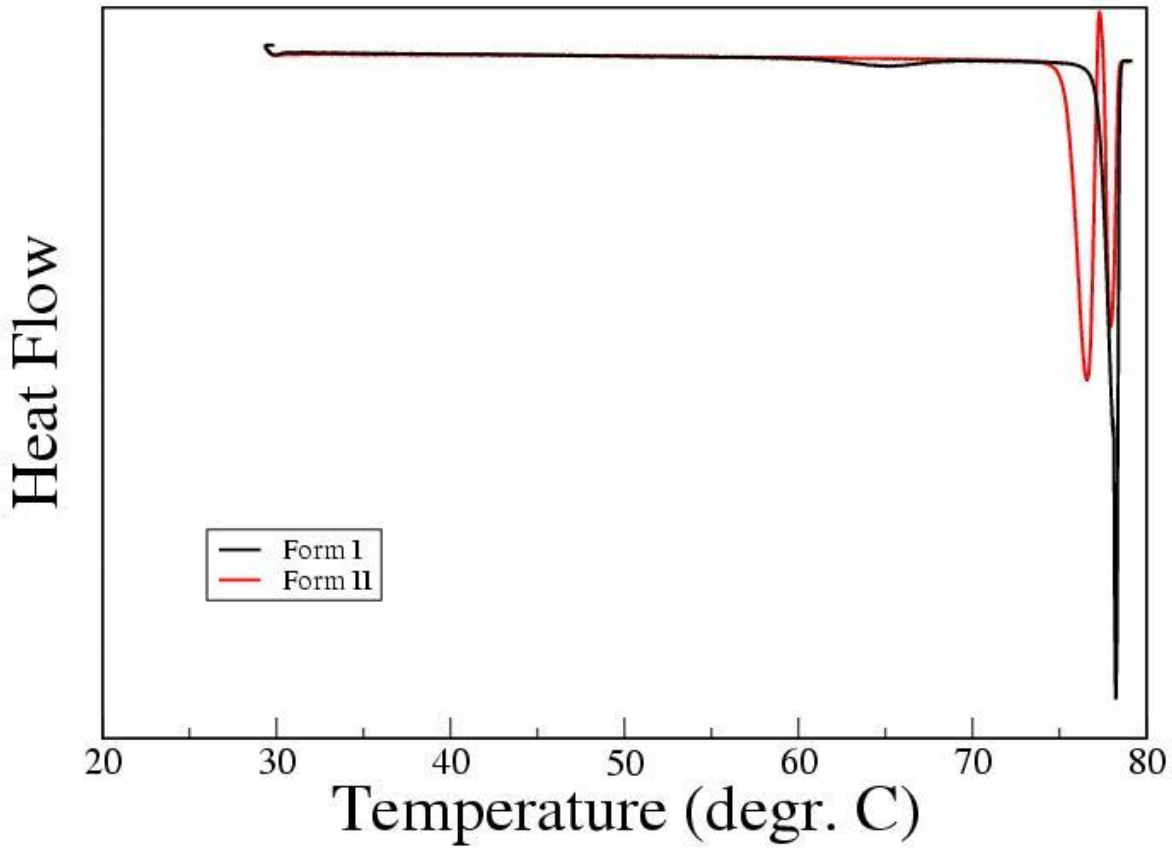


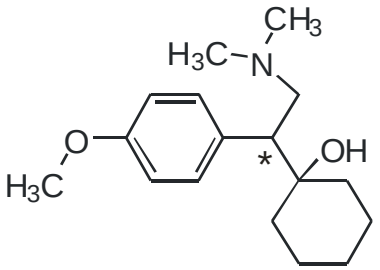


Venlafaxine

Polymorphic forms characterized using X-Ray (Powder) Diffraction

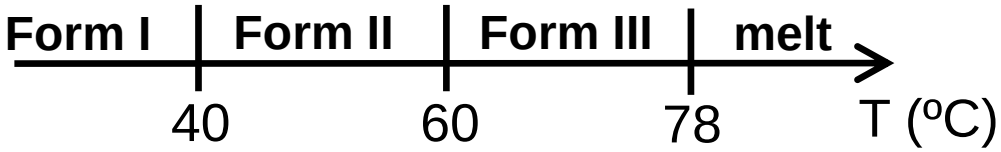
Characterization (polymorphic) phase transitions



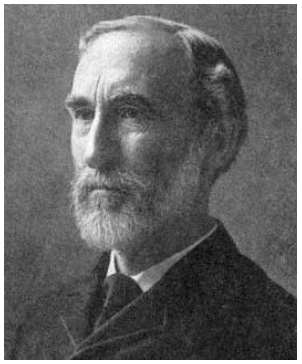


Venlafaxine

Characterized using Differential Scanning Calorimetry

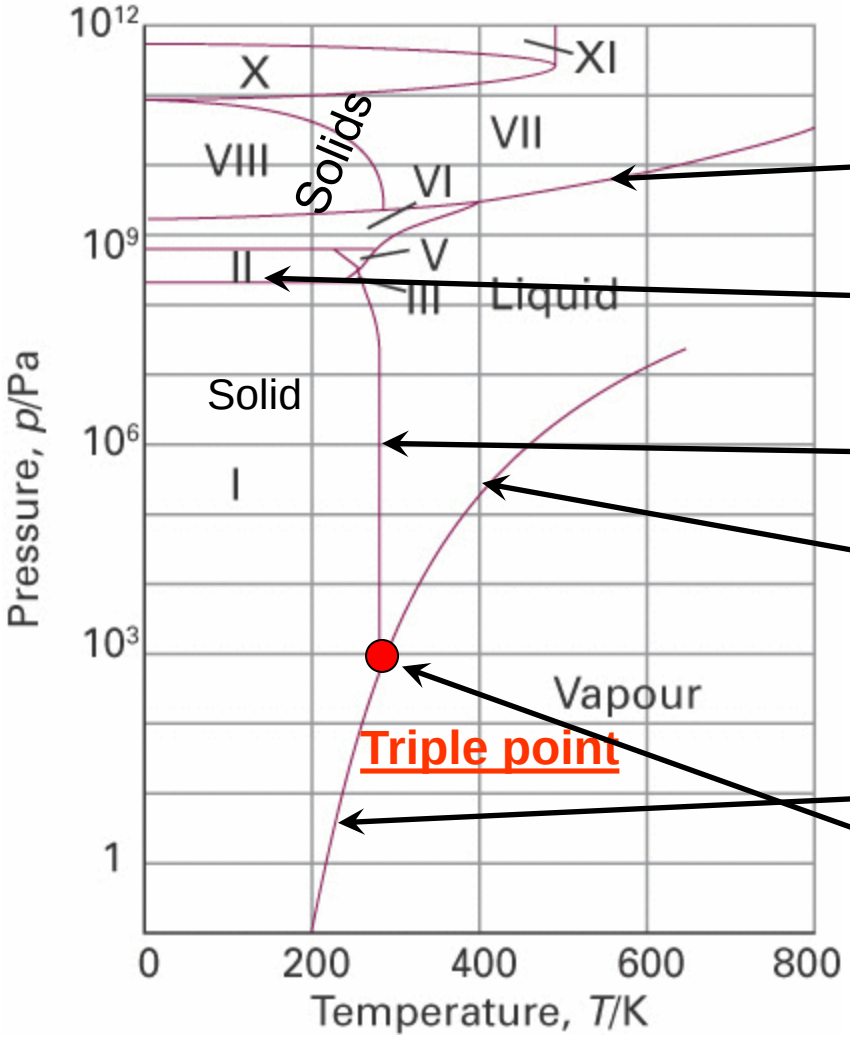


Gibbs phase rule: multicomponent phases



Sneak Preview

Phase boundary lines in diagrams of unary systems



(**Equilibrium**) Phase Diagram H_2O

$\mu_{s_{\mathrm{VII}}} = \mu_l$

$\mu_{s_{\mathrm{I}}} = \mu_{s_{\mathrm{II}}}$

$\mu_{s_{\mathrm{I}}} = \mu_l$

$\mu_l = \mu_g$

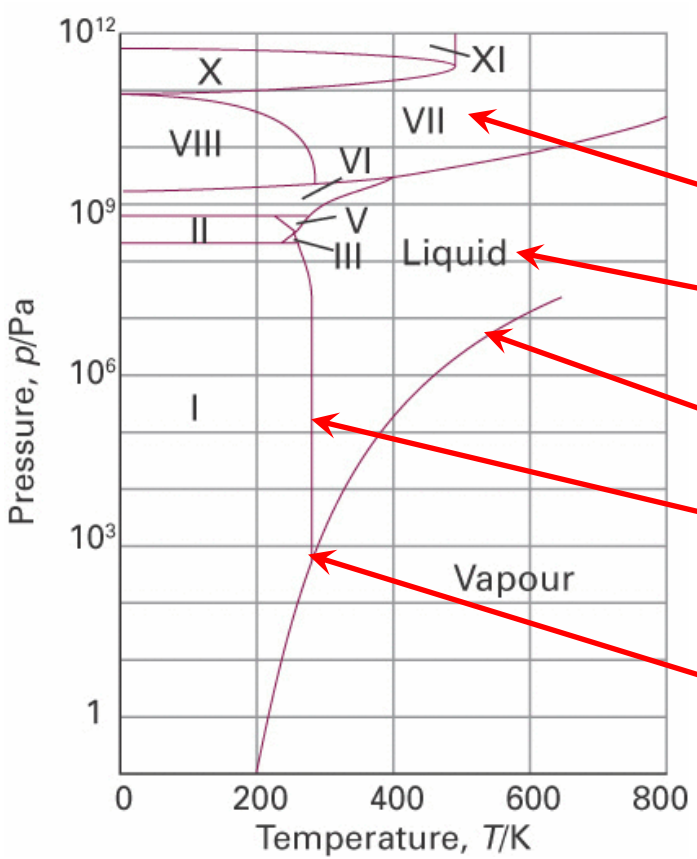
$\mu_{s_{\mathrm{I}}} = \mu_g$

$\mu_{s_{\mathrm{I}}} = \mu_l = \mu_g$

unary phase diagram

Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases α, β, γ, ...**; **components i =1**



P: # phases in mutual equilibrium

$P = 1$

$P = 2$

$P = 3$

$P = 4$?

What about mixtures of compounds in the phases?

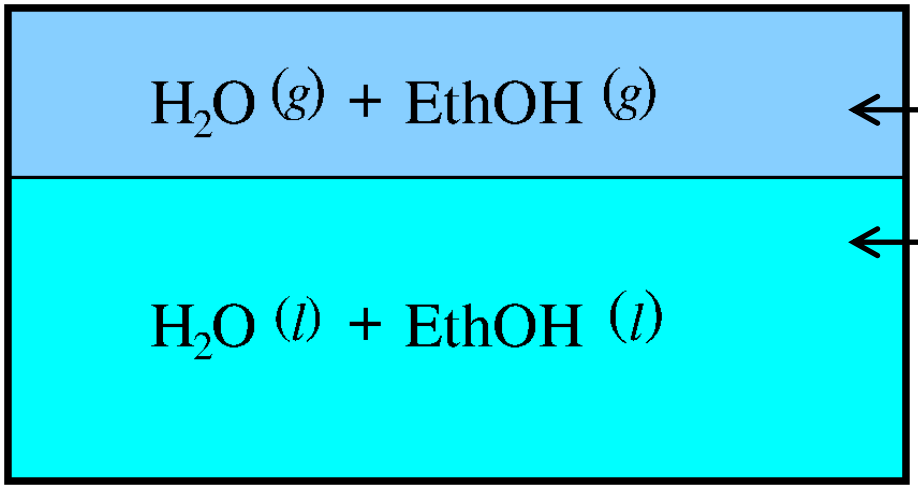
Gibbs phase rule: multicomponent phases

Importance of the chemical potential:

Equilibrium between phases $\mathrm{H_2O}(\alpha) \leftrightarrow \mathrm{H_2O}(\beta)$

in equilibrium: $\mu_\alpha = \mu_\beta$

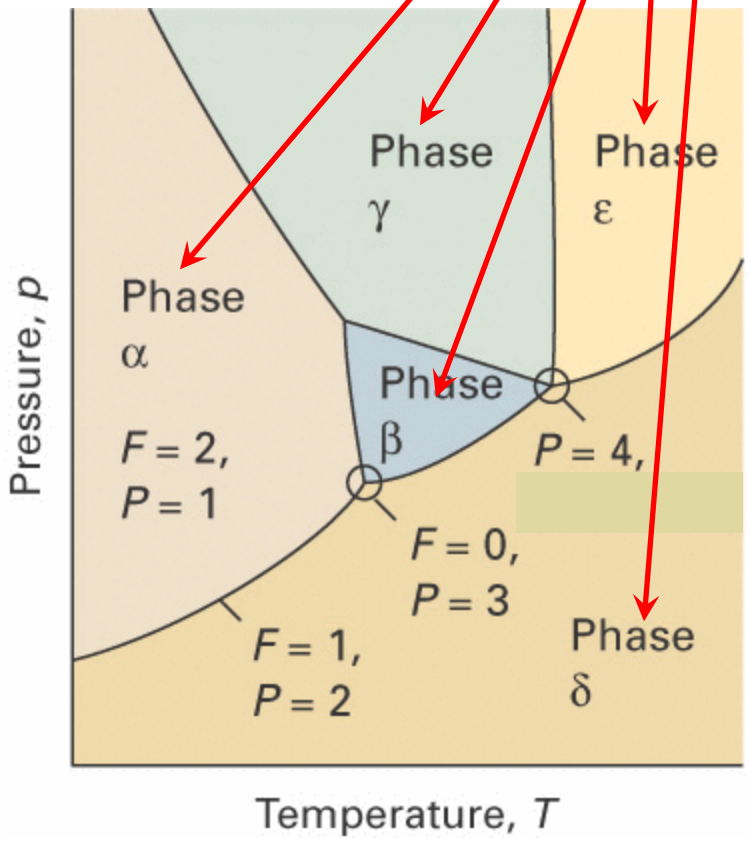
Equilibrium between phases of components *i* in mixtures



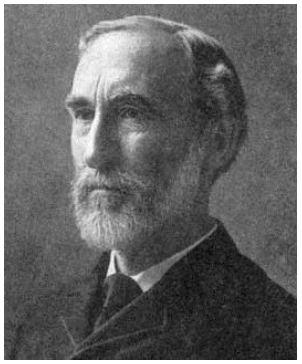
in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases α, β**; **components *i***

Gibbs phase rule: unary phase diagrams

$C = 1$, $P = 1$ $\rightarrow$ $F = 2$ (T and P)



unary phase diagram



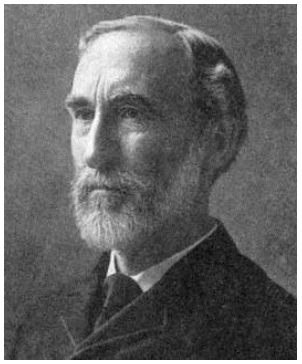
Gibbs phase rule

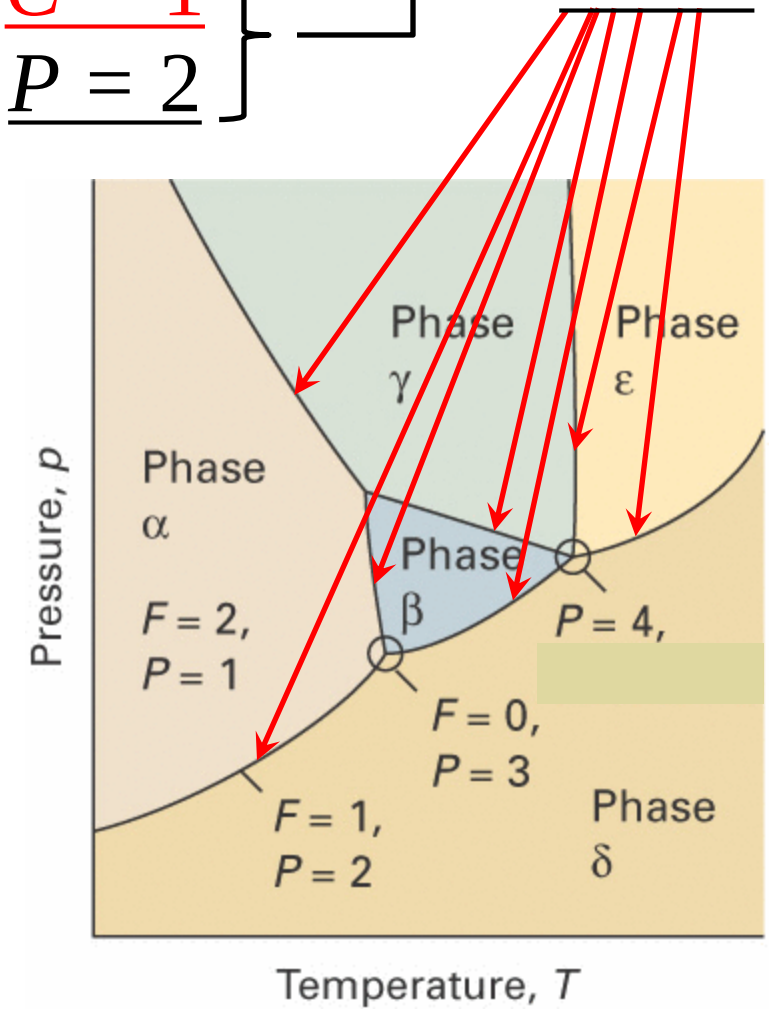
$$F = C - P + 2$$

F: # degrees of freedom
C: # components
P: # phases

Gibbs phase rule: unary phase diagrams

$$\left.\begin{array}{l} C = 1 \\ P = 2 \end{array}\right\} \rightarrow F = 1 \quad (T \rightarrow P \text{ or } P \rightarrow T)$$





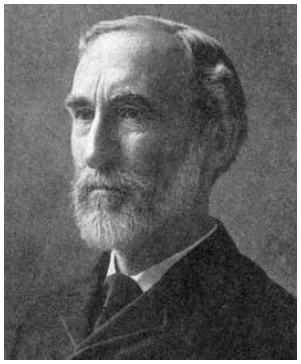
Gibbs phase rule

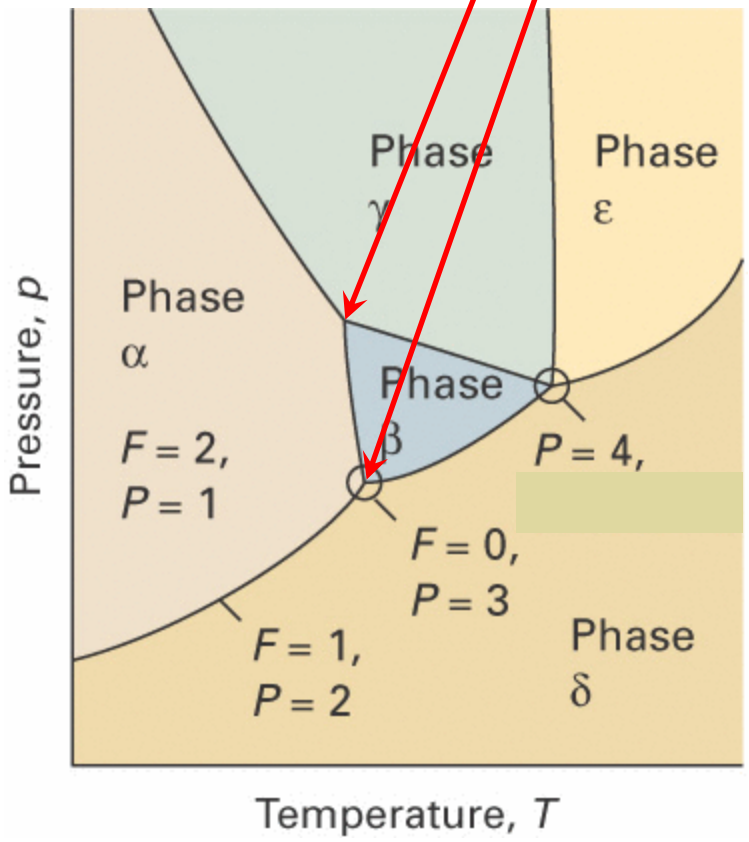
$$F = C - P + 2$$

unary phase diagram

Gibbs phase rule: unary phase diagrams

$C = 1$
$P = 3$
$\rightarrow F = 0$ (fixed T and P)





Gibbs phase rule

$$F = C - P + 2$$

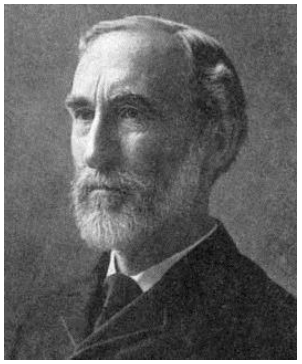
unary phase diagram

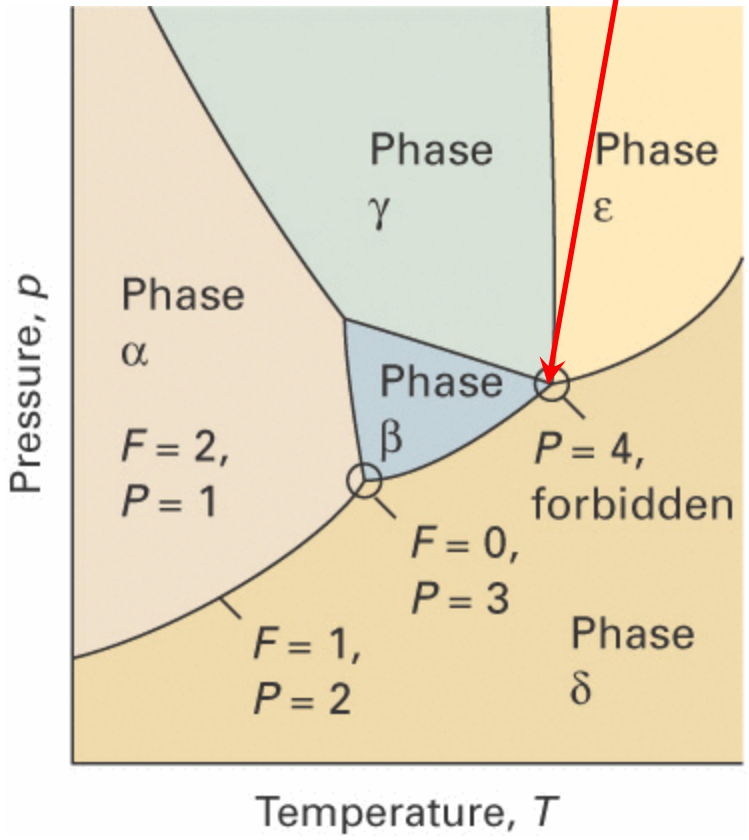
Gibbs phase rule: unary phase diagrams

$C = 1$

$P = 4$

$\rightarrow F = -1$





Gibbs phase rule

$$F = C - P + 2$$

unary phase diagram

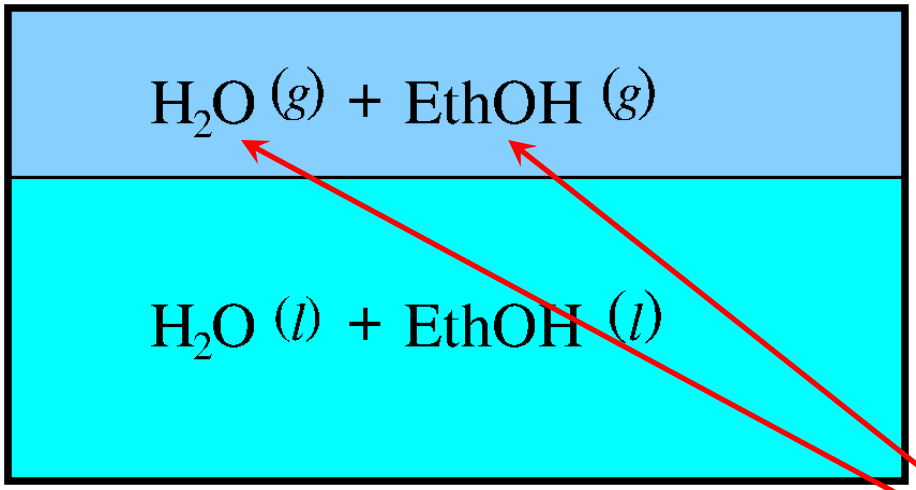
Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases $\alpha, \beta, \gamma, \ldots$**; **components $i = 1, 2$**

C components in each phase

$$x_i \equiv \frac{n_i}{n} = \frac{n_i}{\sum_{j=1}^{C} n_j}$$

mole fraction of component *i*



$C = 2$ **So.....?**

binary system