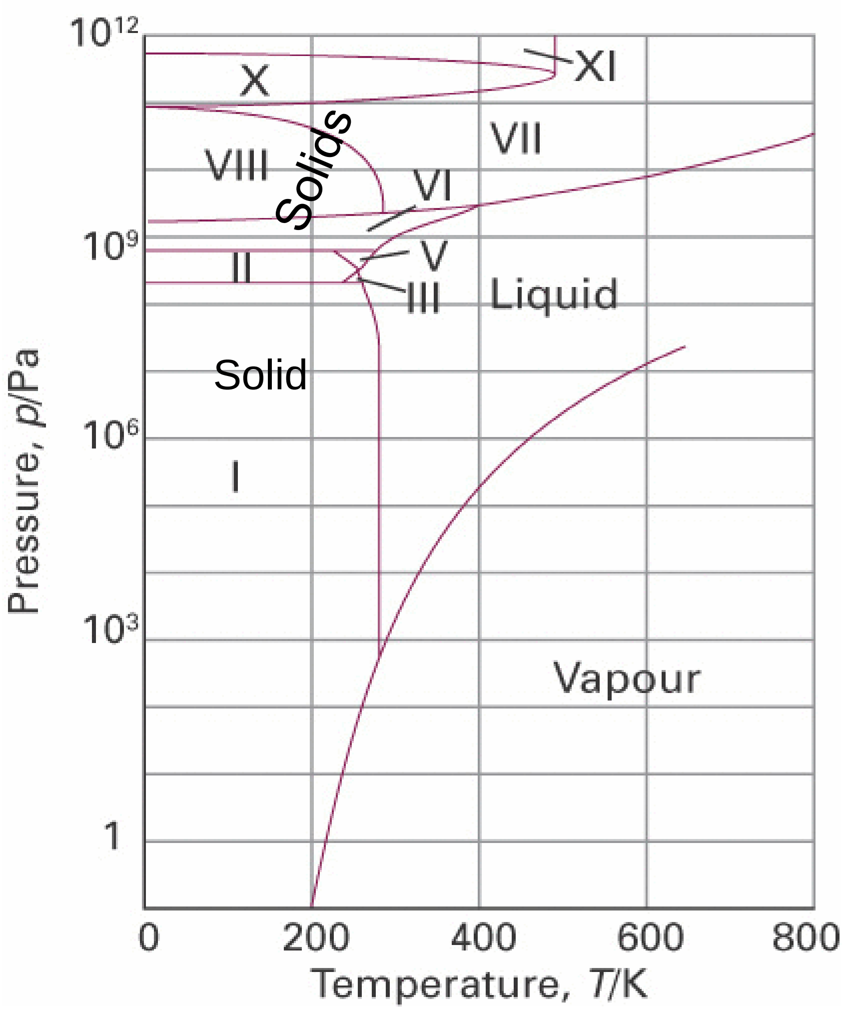
Phase diagrams and phase transitions of unary systems

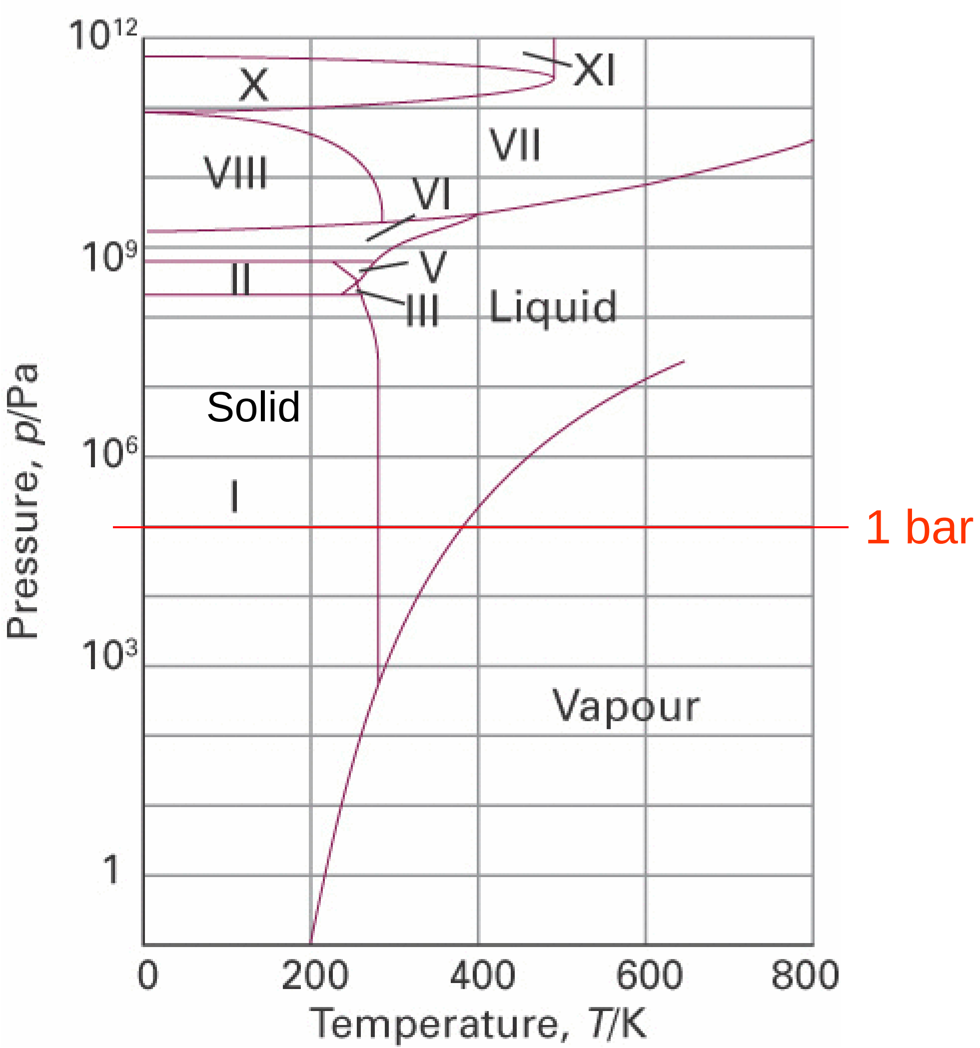


- Phase transitions
- Phase boundaries
- Phase transition temperature
- Melting point
- Boiling point
- Triple point
- Critical point
- Polymorphic forms

- Thermodynamics *vs* kinetics
- Metastable phases

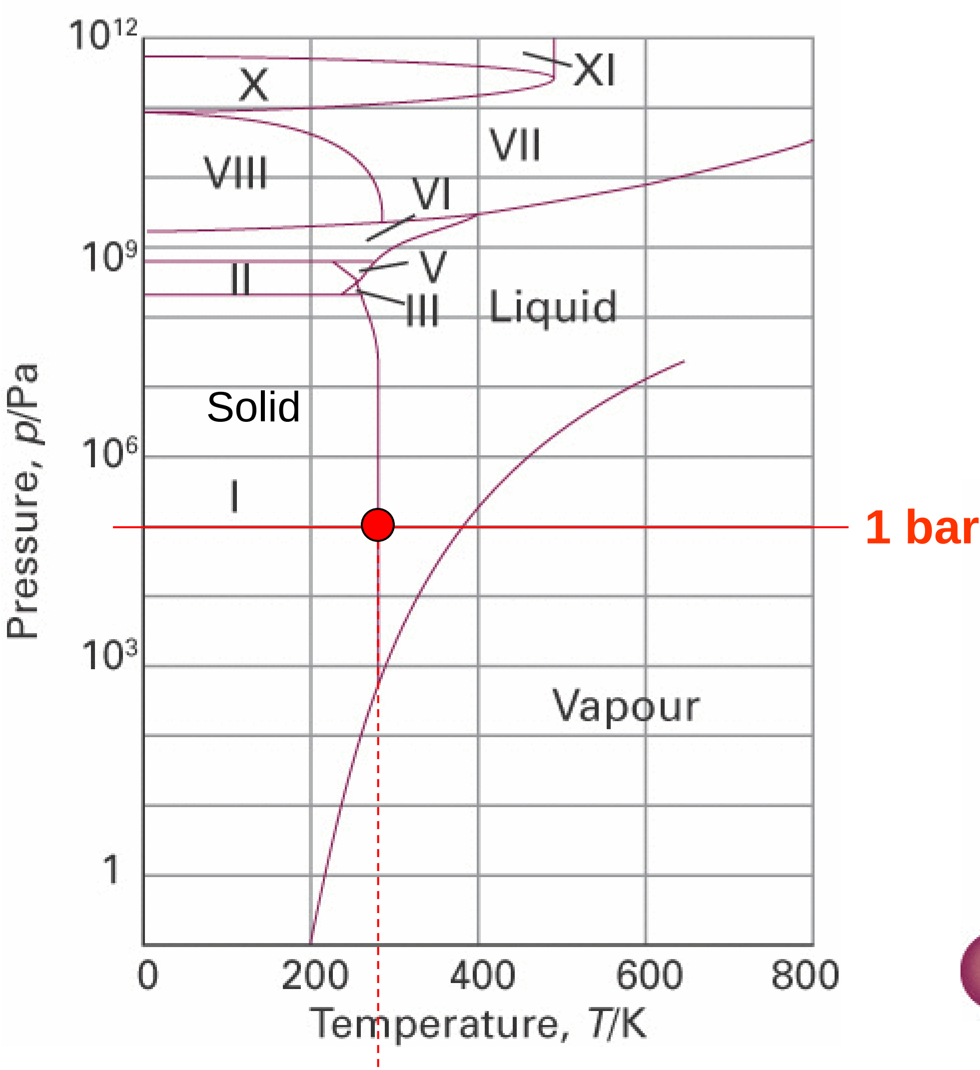
(**Equilibrium**) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems

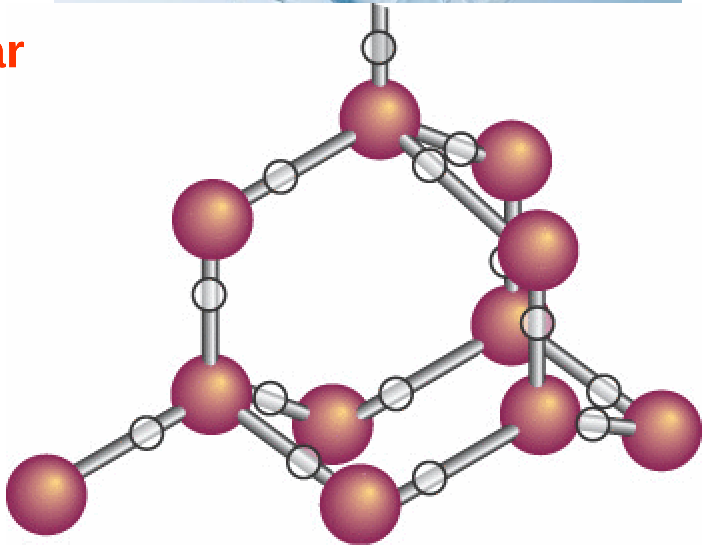


(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems



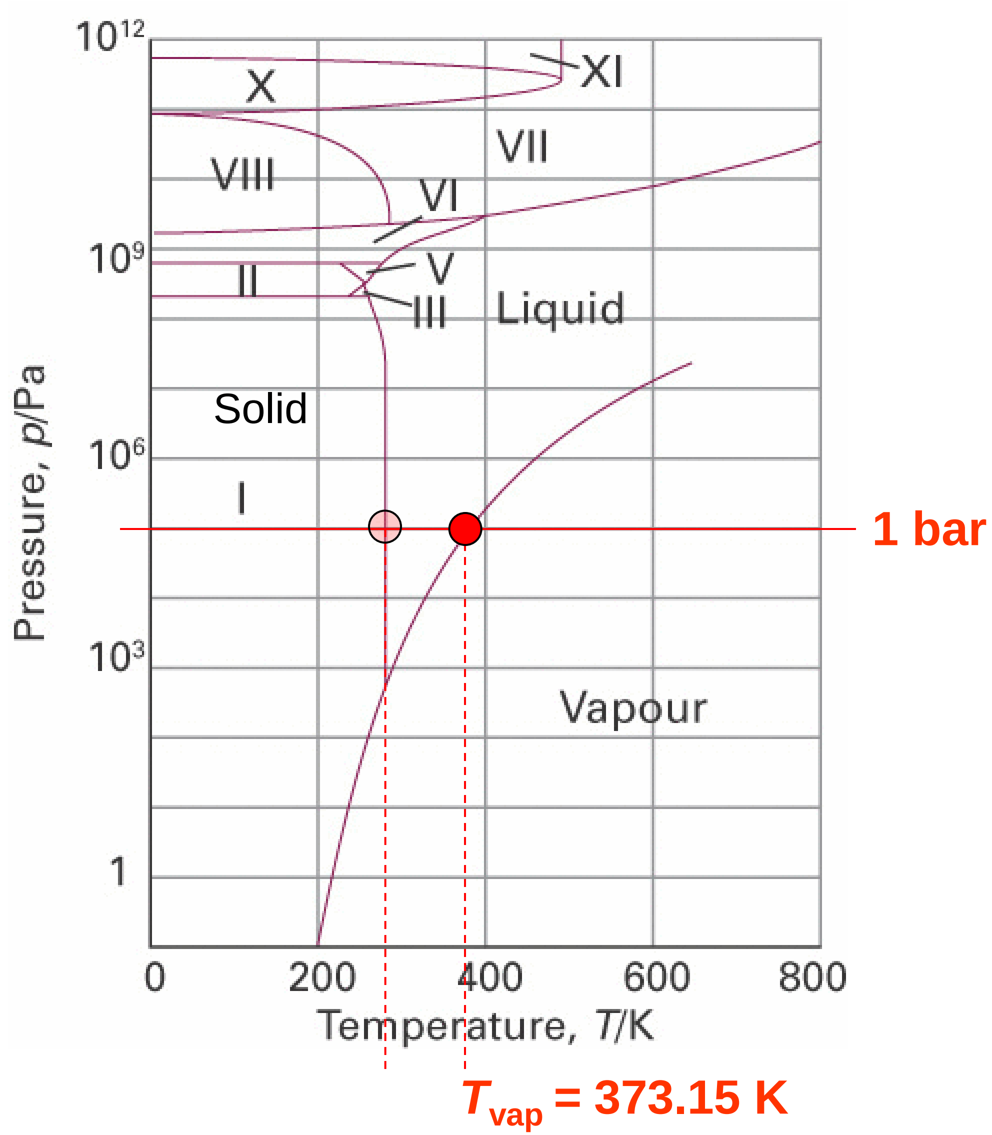
$T_{fus} = T_{cryst} = 273.15$ K



H-bonding

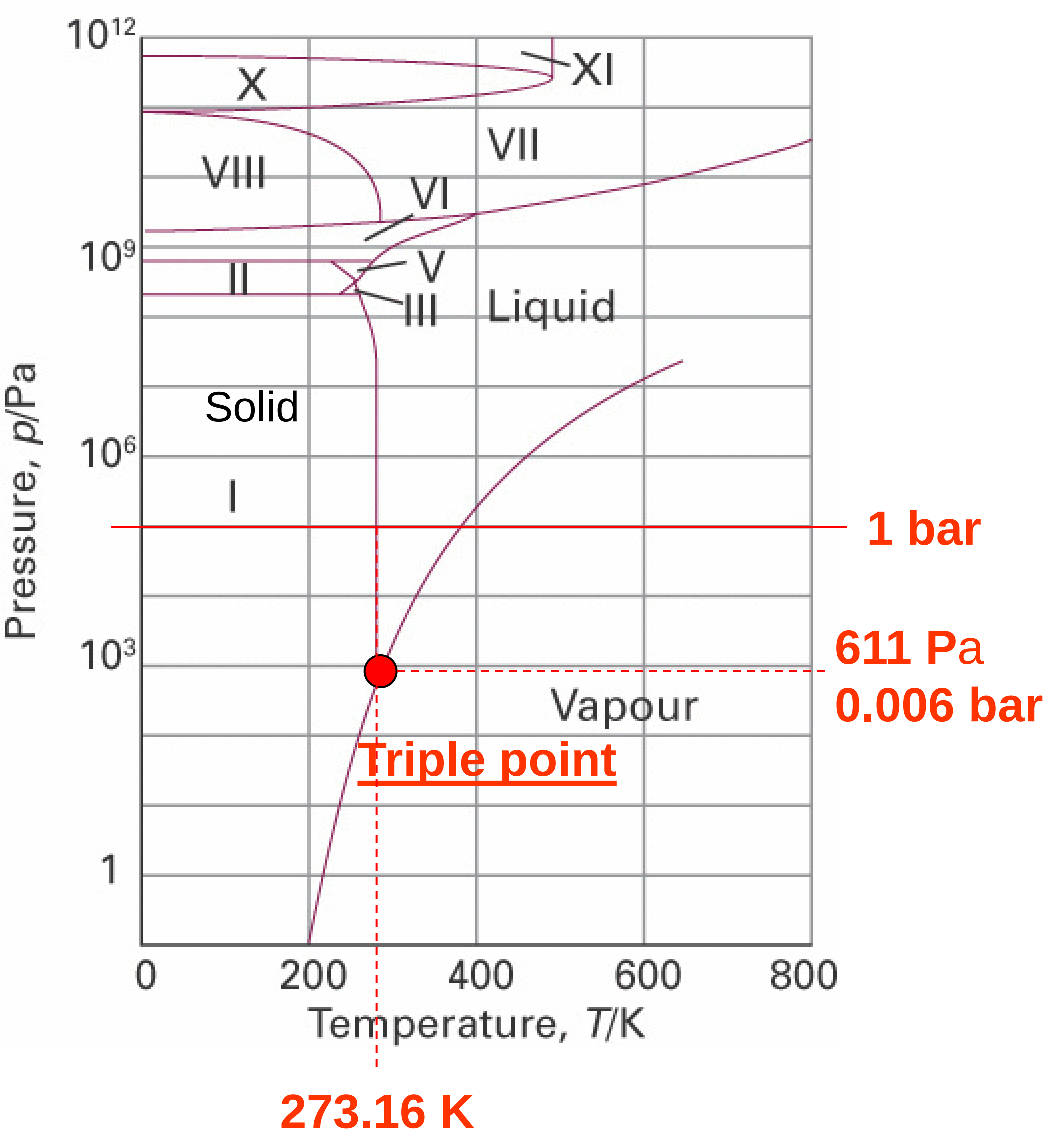
(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems



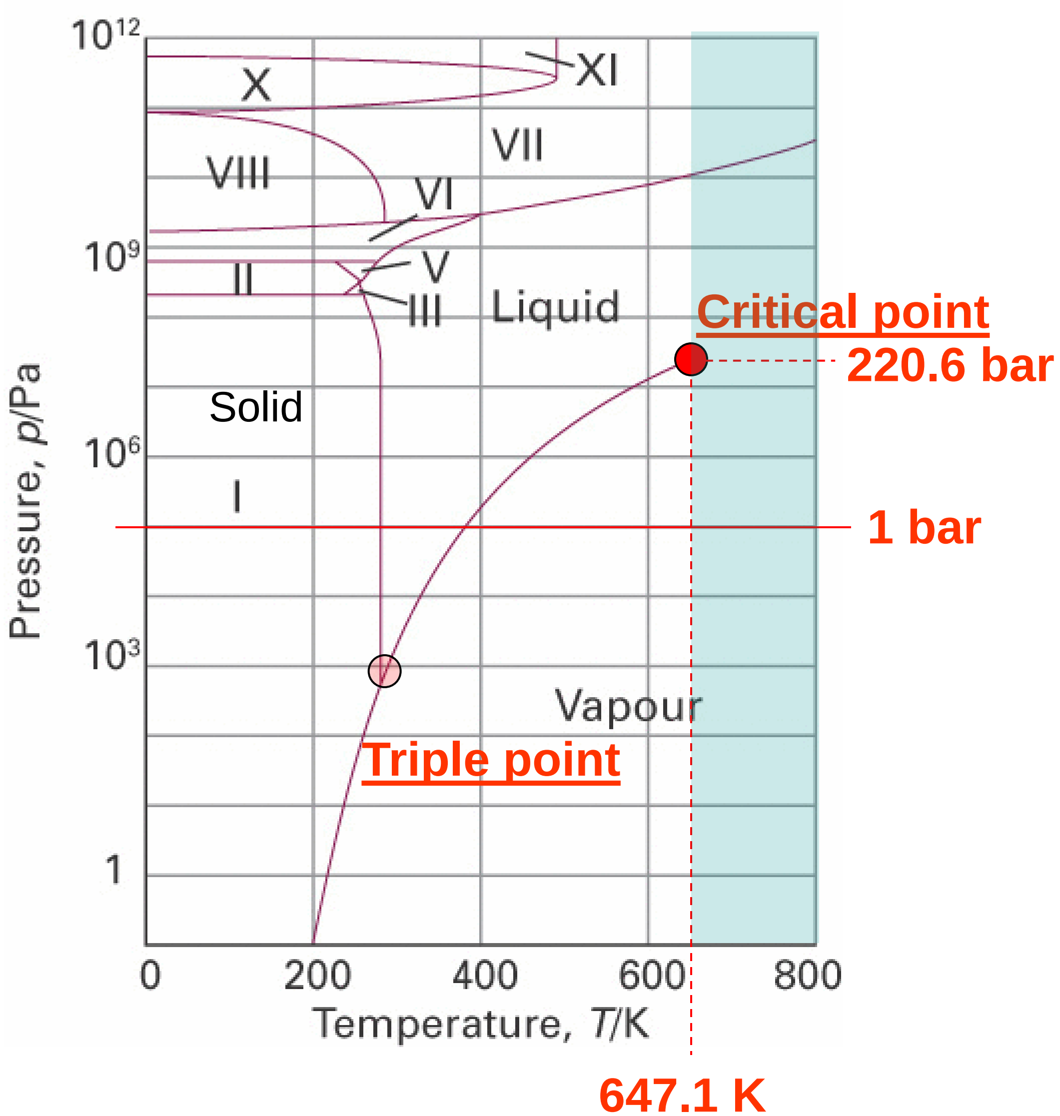
(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems



(Equilibrium) Phase Diagram H_2O

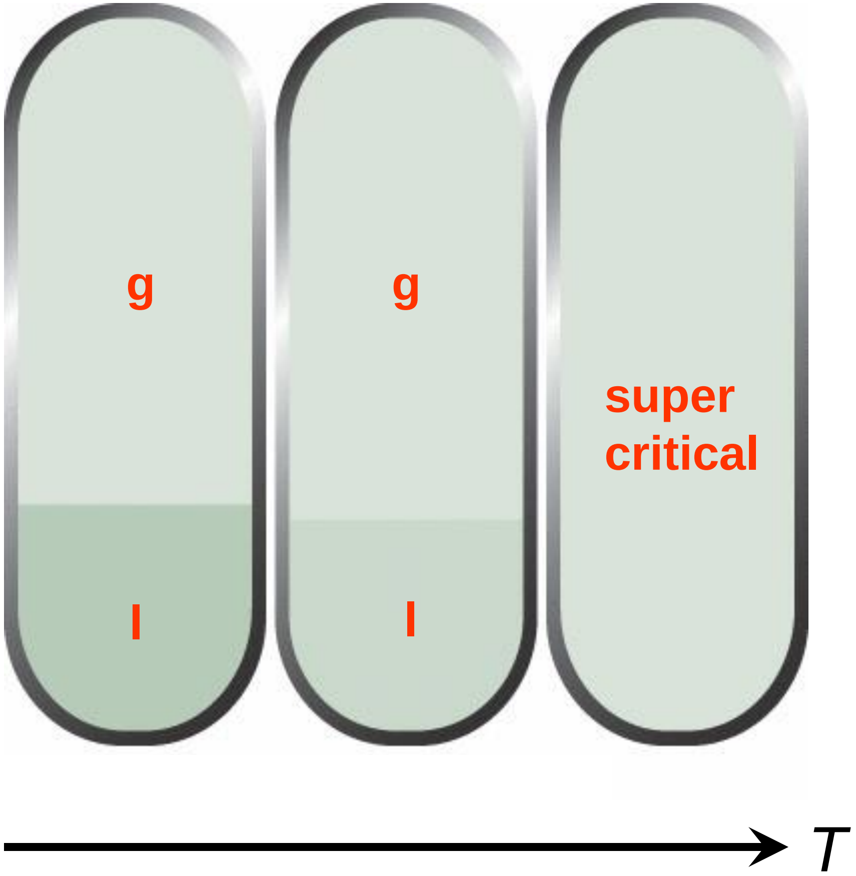
Phase diagrams and phase transitions of unary systems



Super critical

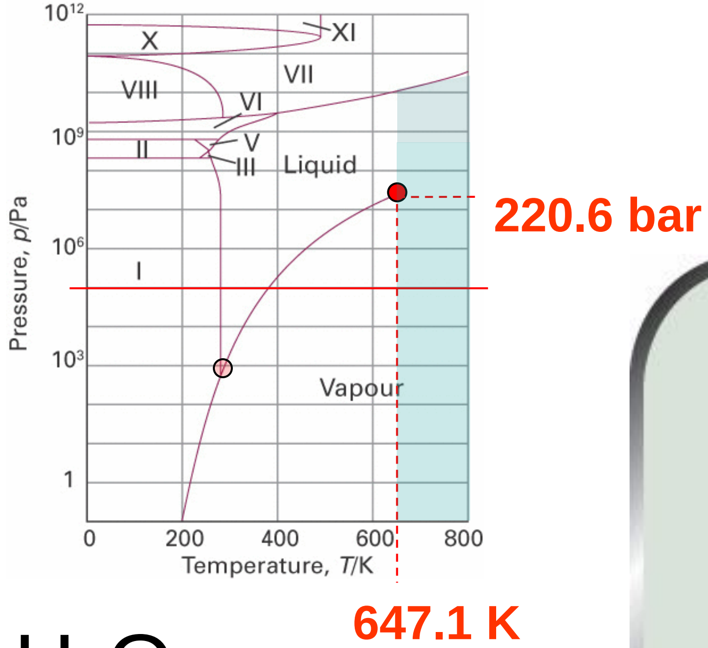
(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems

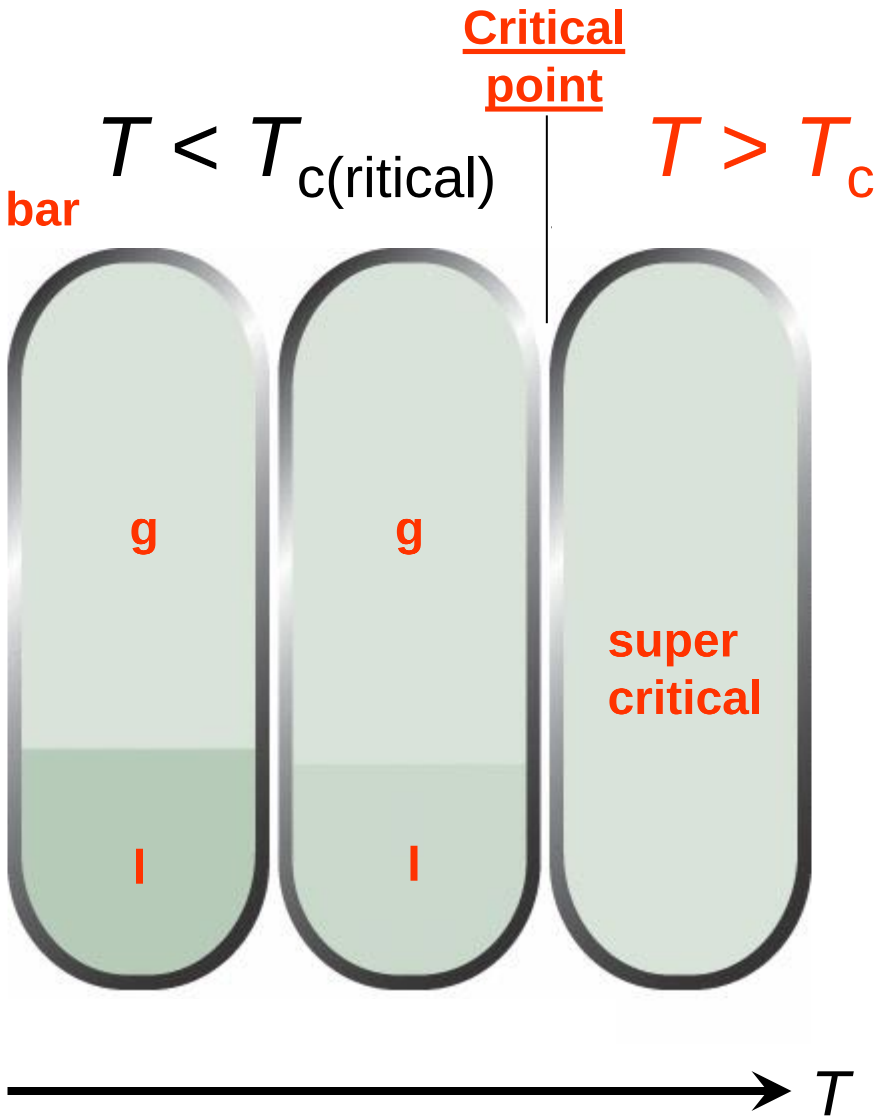


Critical point

Phase diagrams and phase transitions of unary systems

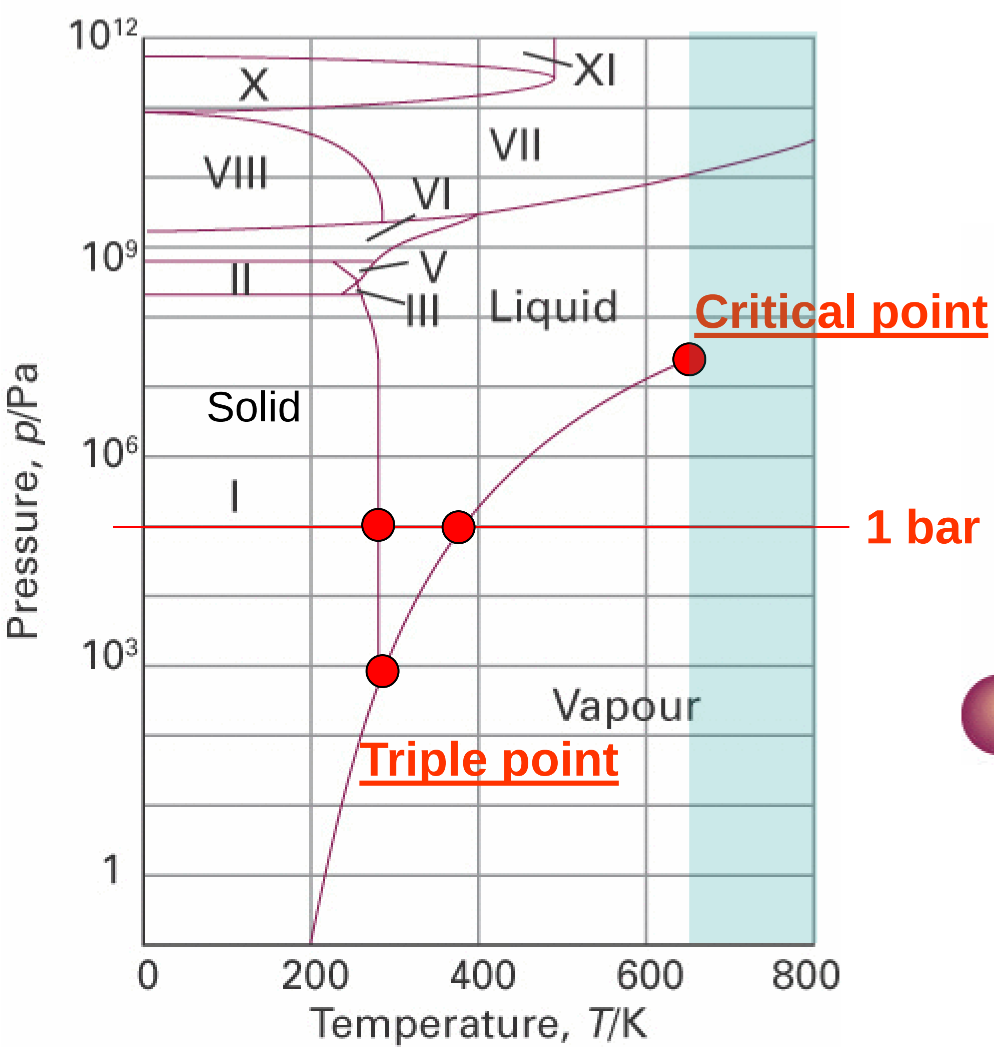


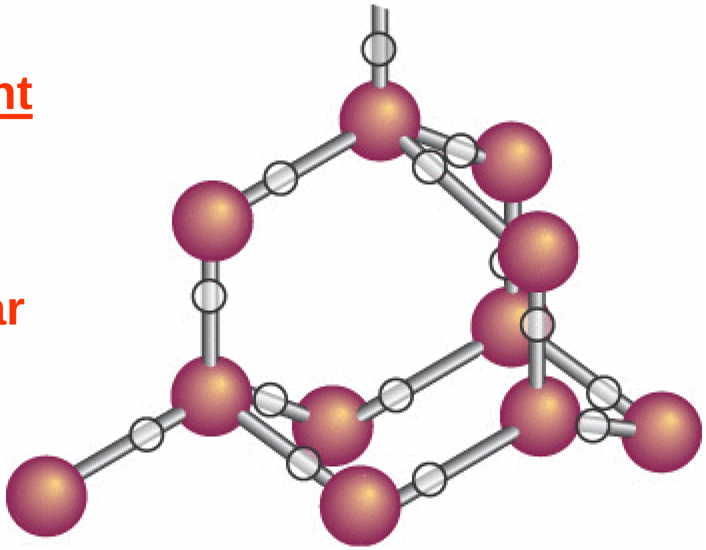
H_2O



Critical point

Phase diagrams and phase transitions of unary systems

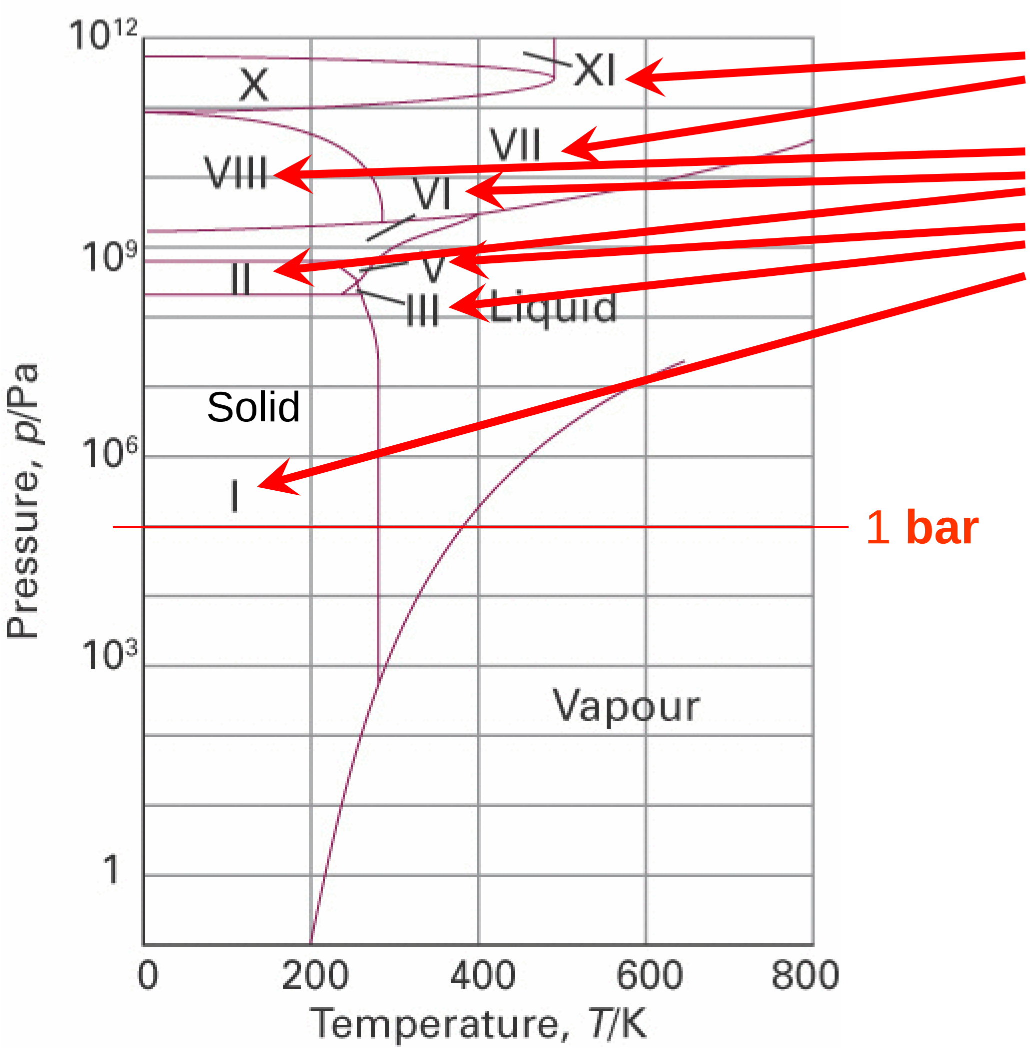




H-bonding

(Equilibrium) Phase Diagram H_2O

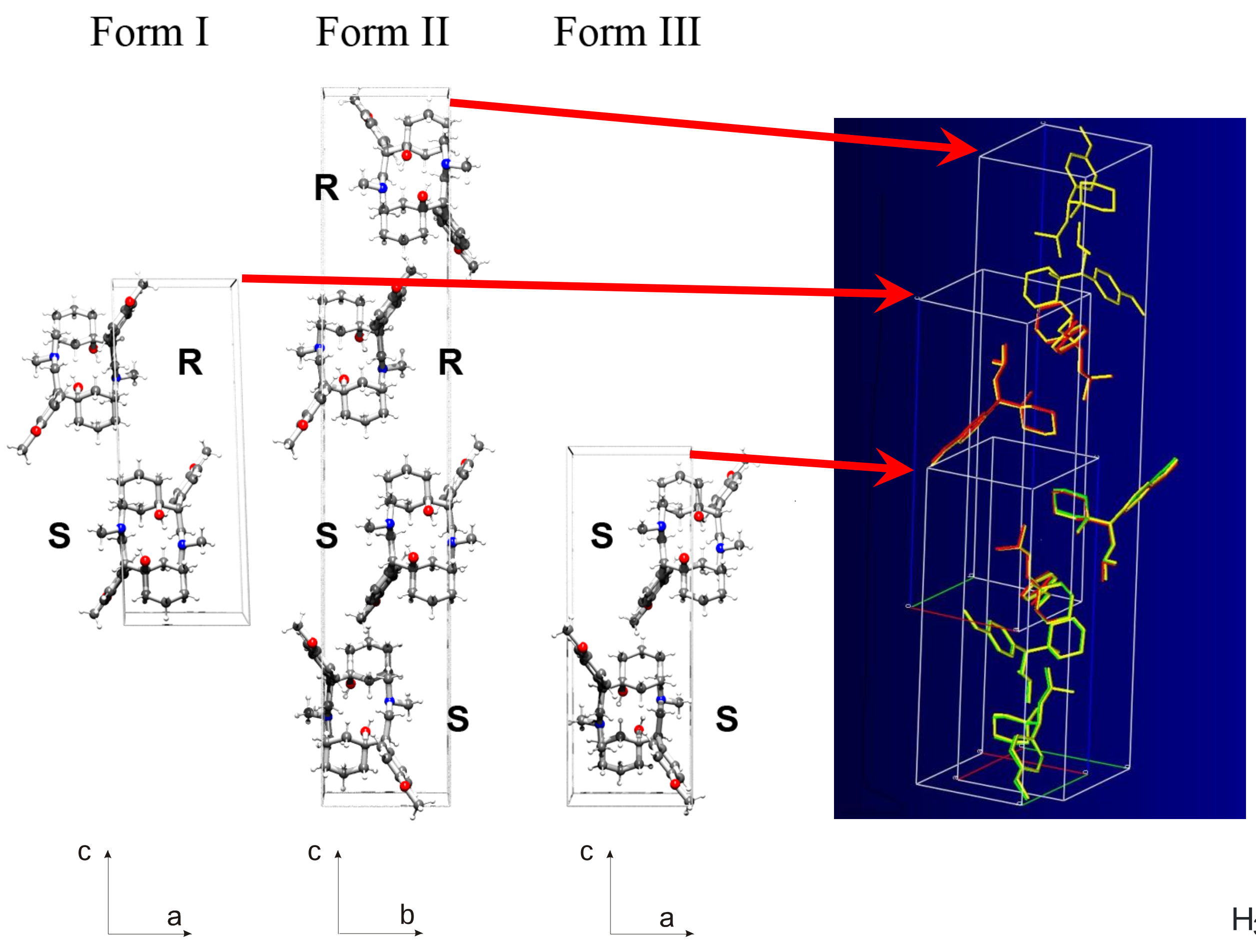
Phase diagrams and phase transitions of unary systems



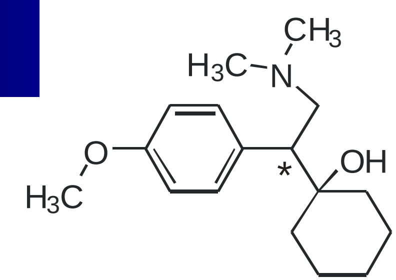
Polymorphic forms for the solids

(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems



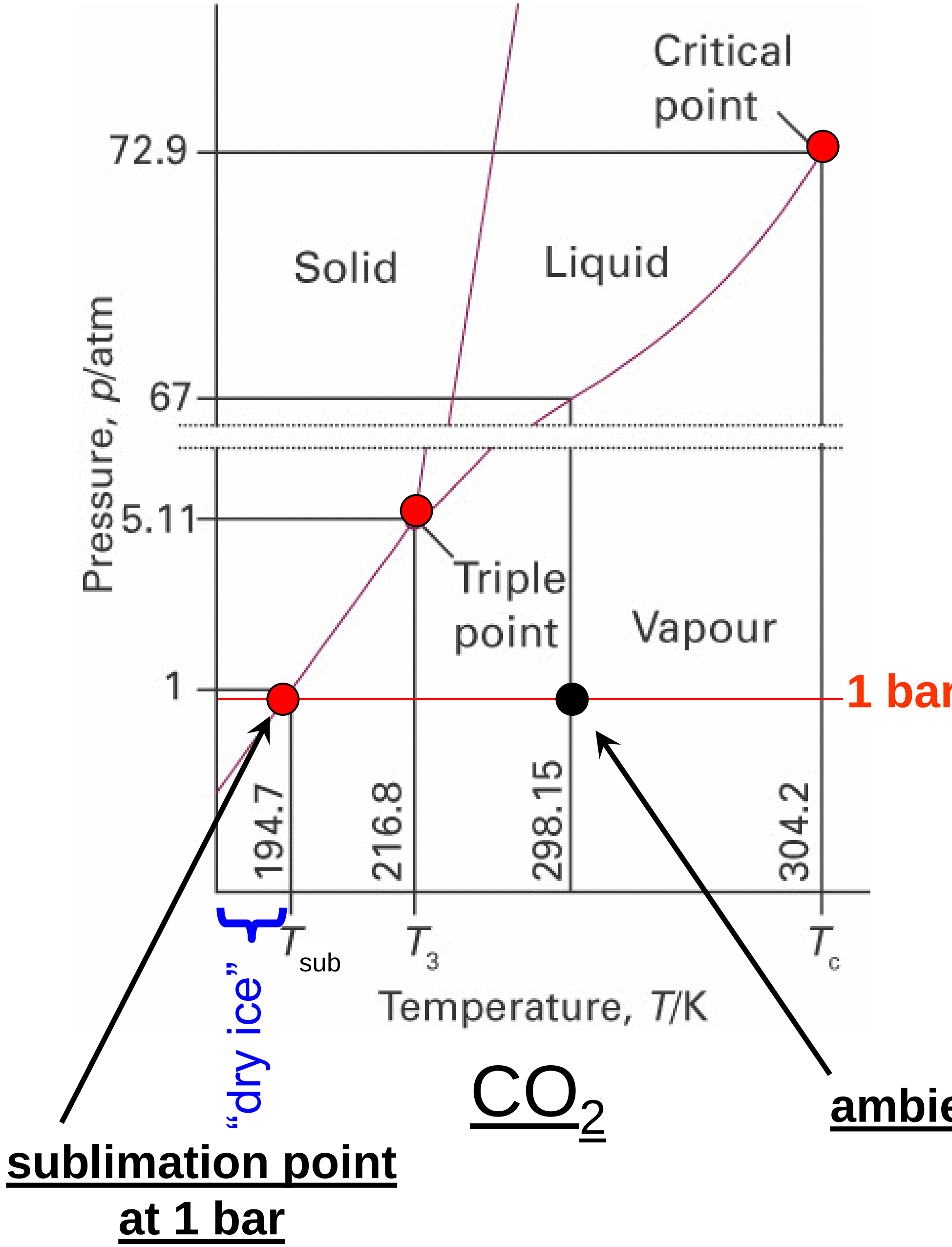
T < 40 ºC   T > 40 ºC   T > 60 ºC   (T_{fus} = 70 ºC)

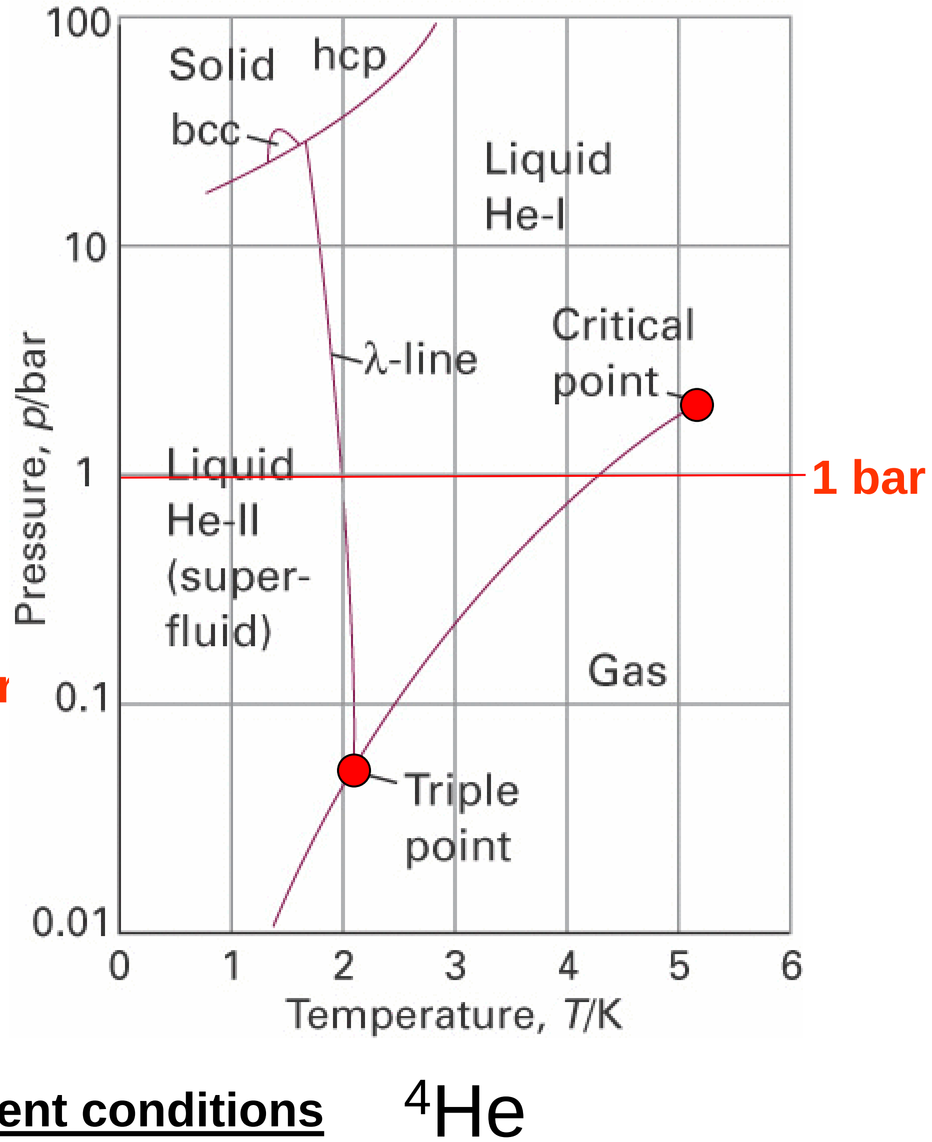


Venlafaxine

Polymorphic (solid state) phase transitions

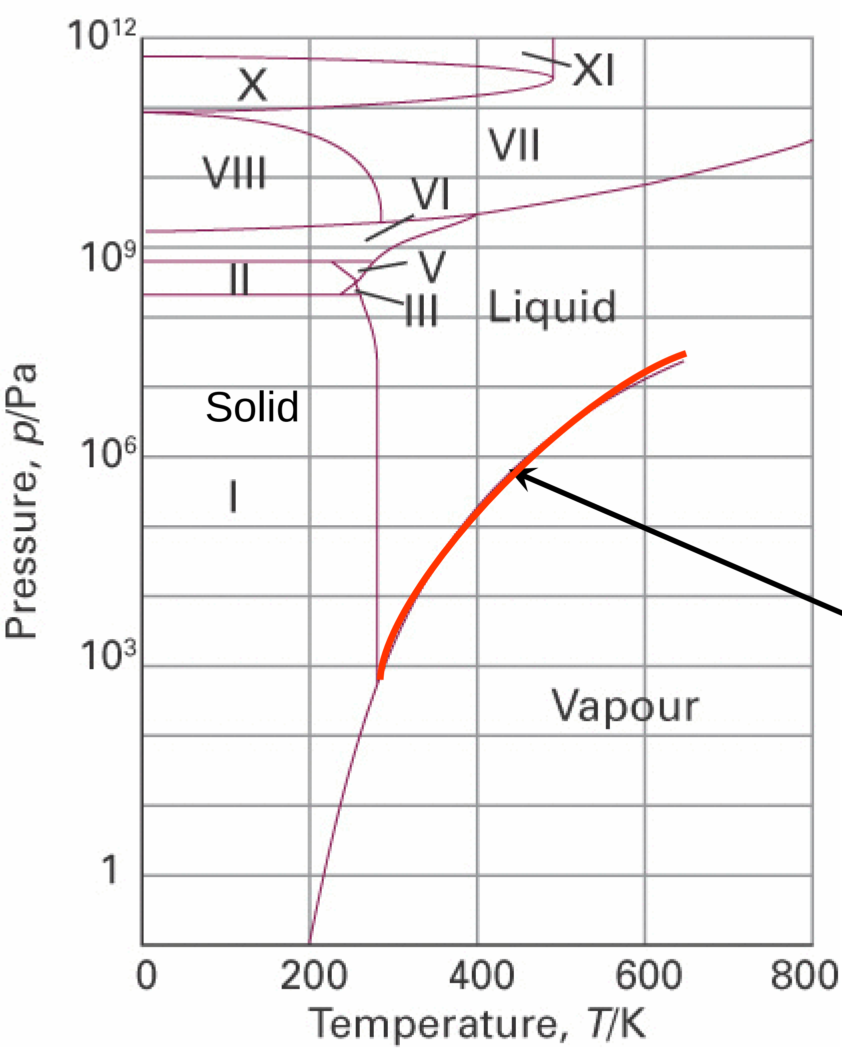
Phase diagrams and phase transitions of unary systems





Phase boundary lines in diagrams of unary systems

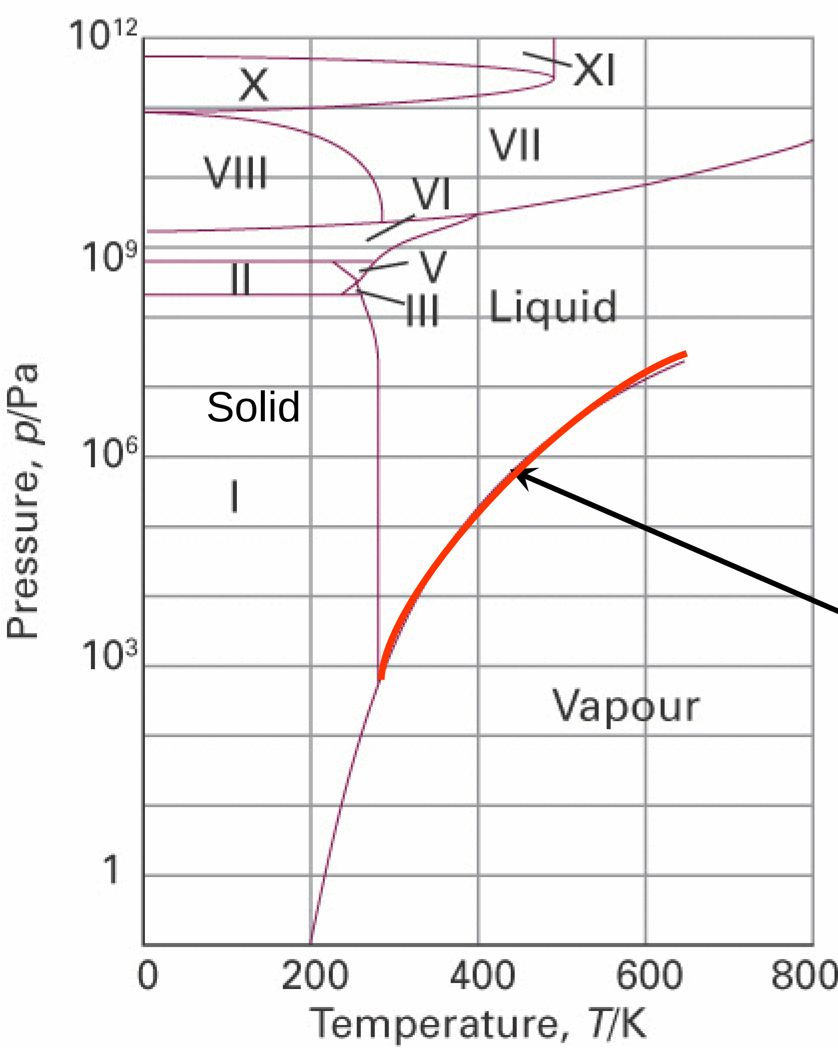
Phase boundary lines in diagrams of unary systems

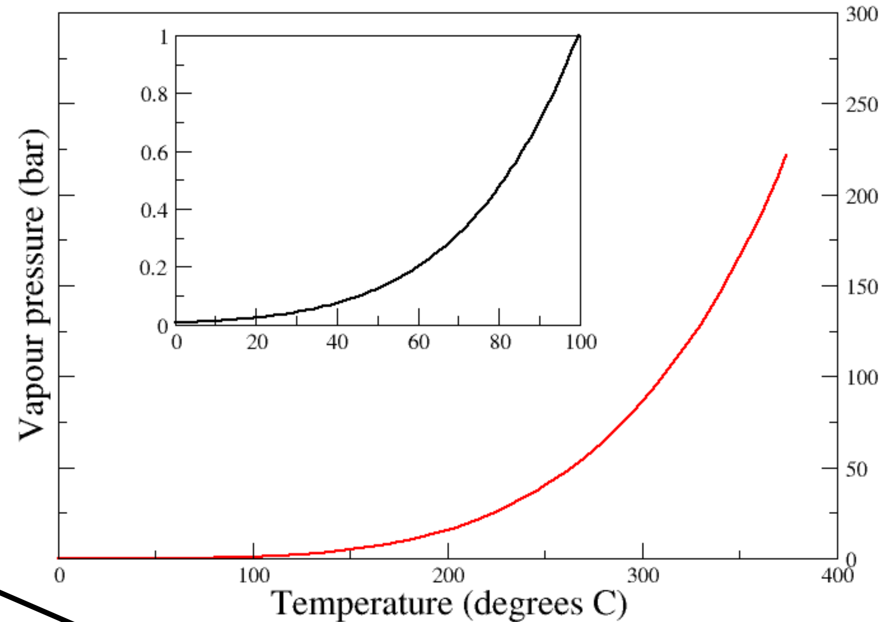


Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems

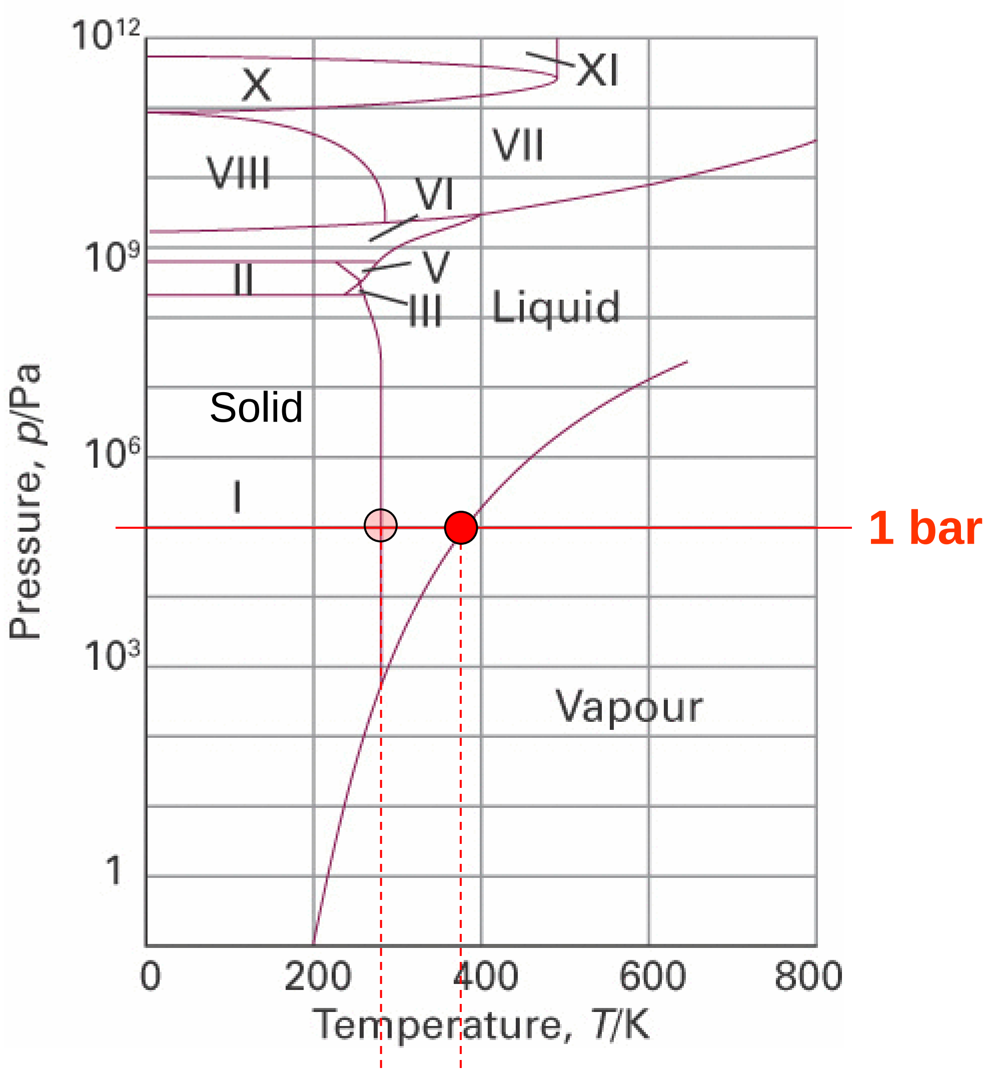




Vapour and liquid are in mutual equilibrium only for (P,T) values on the line

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



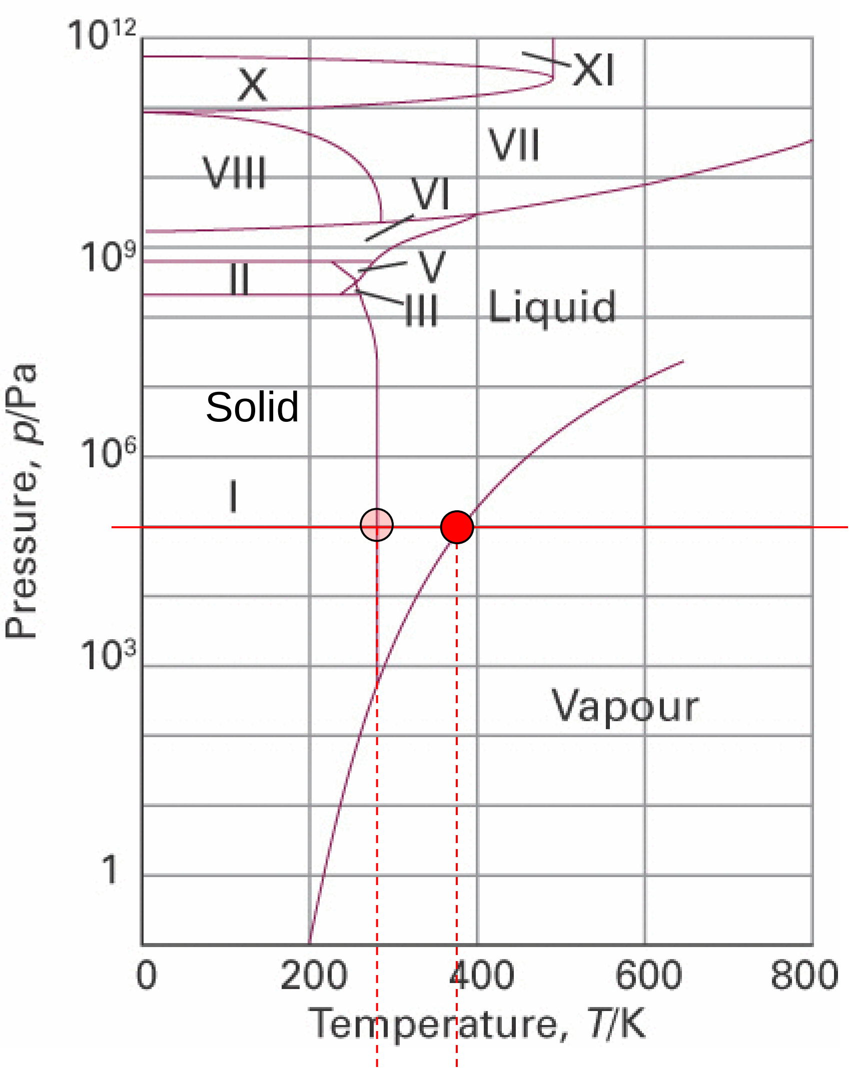
T_{vap} = 373.15 K

***T* = 373.15 K and *P* = 1 bar**

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

(Equilibrium) Phase Diagram H_2O

Phase diagrams and phase transitions of unary systems



T_{vap} = 373.15 K

Intermezzo:

in open system

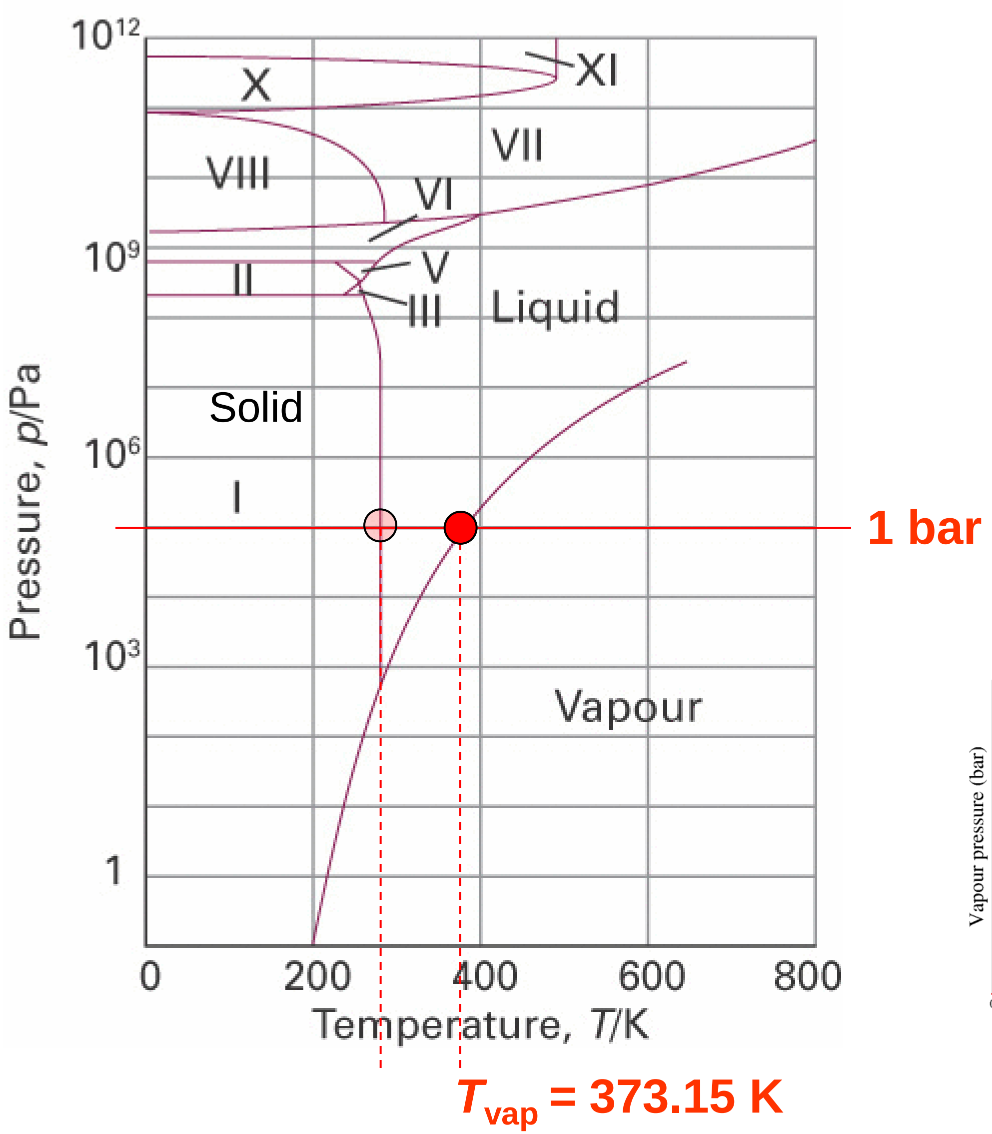
@ T_{vap} = 373.15 K

Water starts to boil as

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

(**Equilibrium**) Phase Diagram H_2O

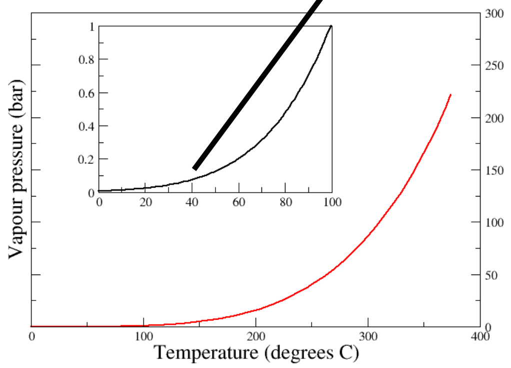
Phase diagrams and phase transitions of unary systems



Intermezzo:

Relative Humidity

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



(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems

Equilibrium between phases

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

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

$\Rightarrow$

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

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

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

Note: we are dealing with a unary system

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

Phase boundary lines in diagrams of unary systems

Importance of the chemical potential:

Equilibrium between phases

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

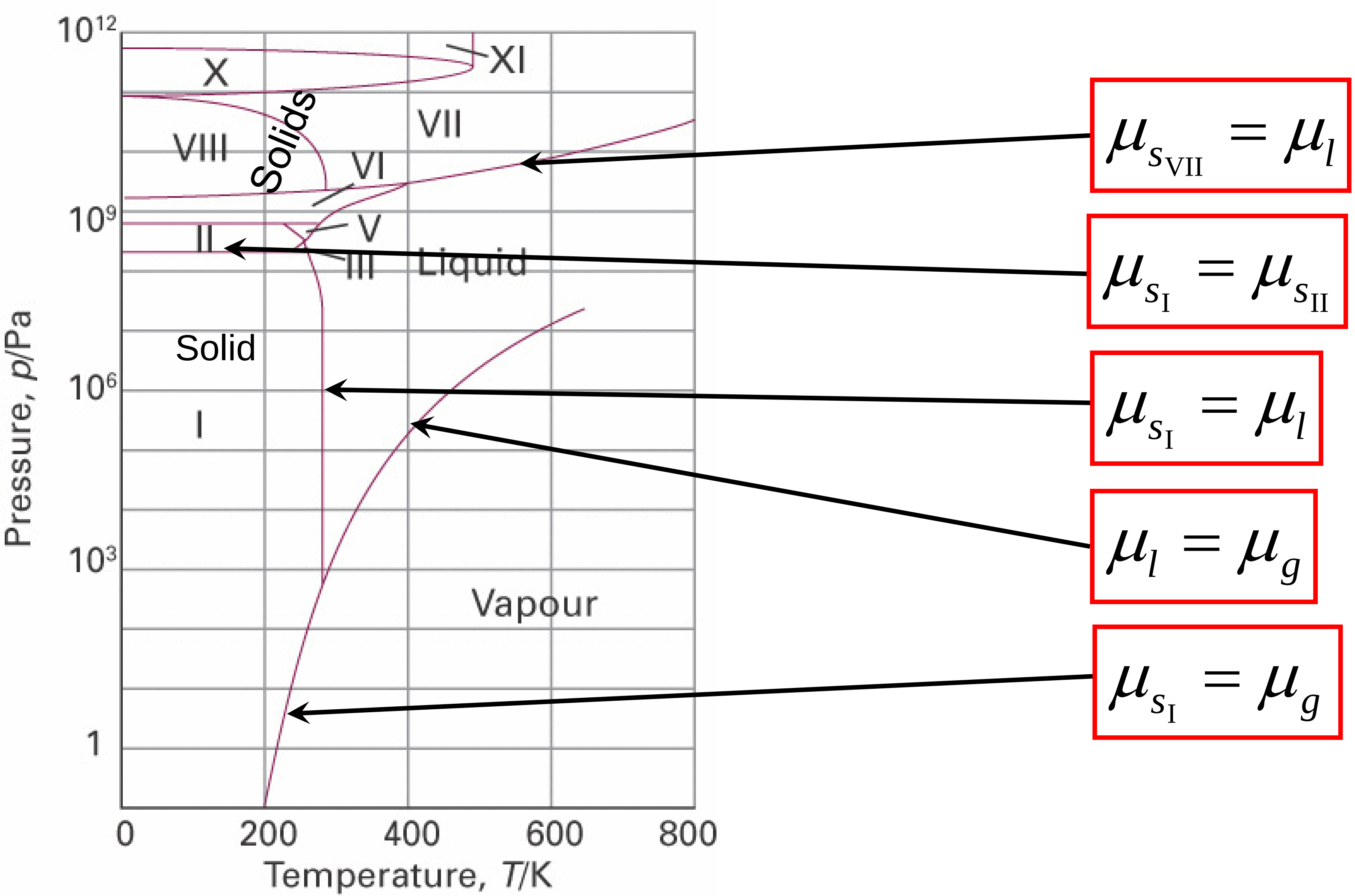
$$dG = VdP - SdT + \mu_l dn_l + \mu_g dn_g$$

Equilibrium → $$dG_{T,P} = 0$$

$$dn_l = -dn_g$$

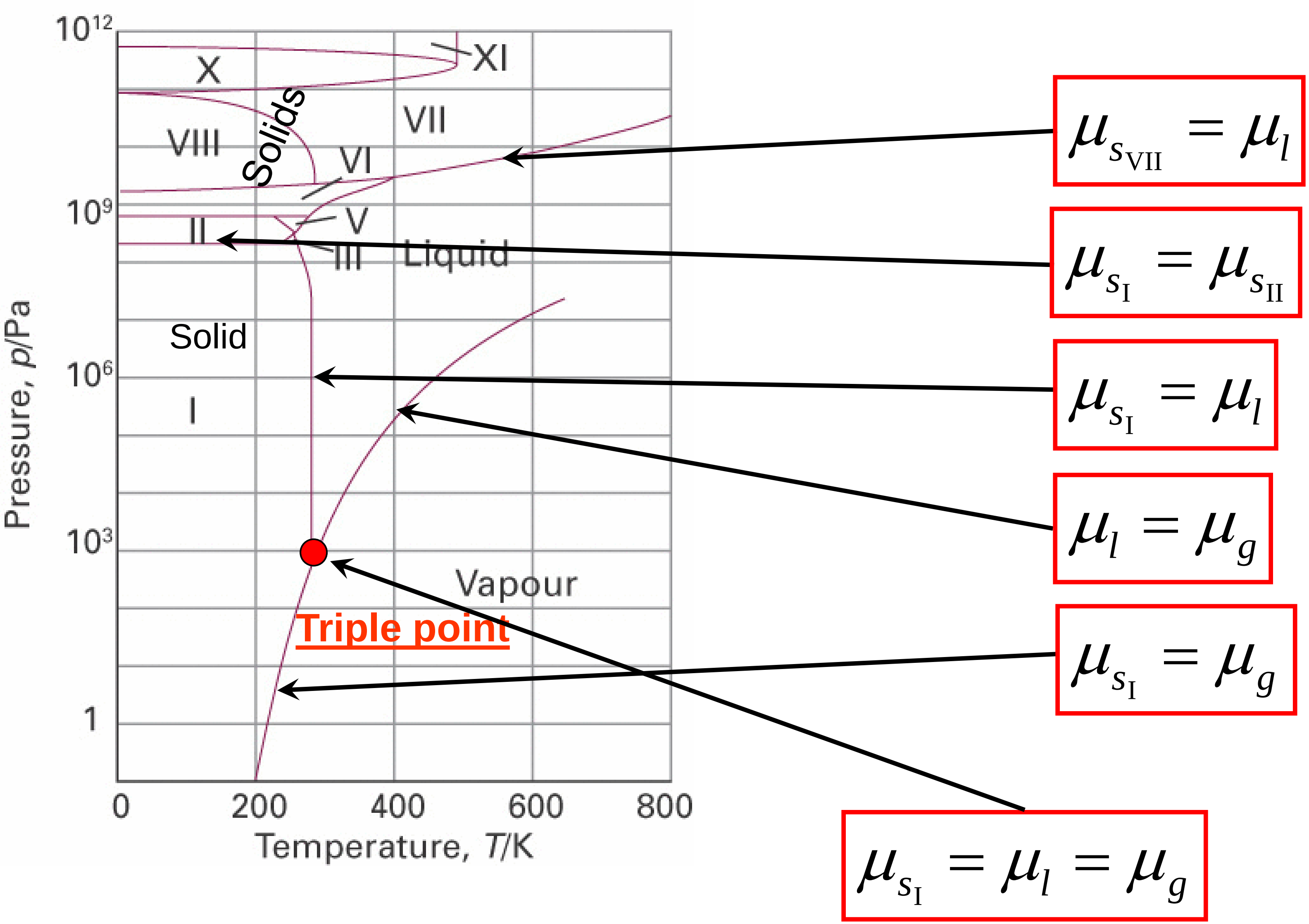
$$\mu_l = \mu_g$$

Phase boundary lines in diagrams of unary systems



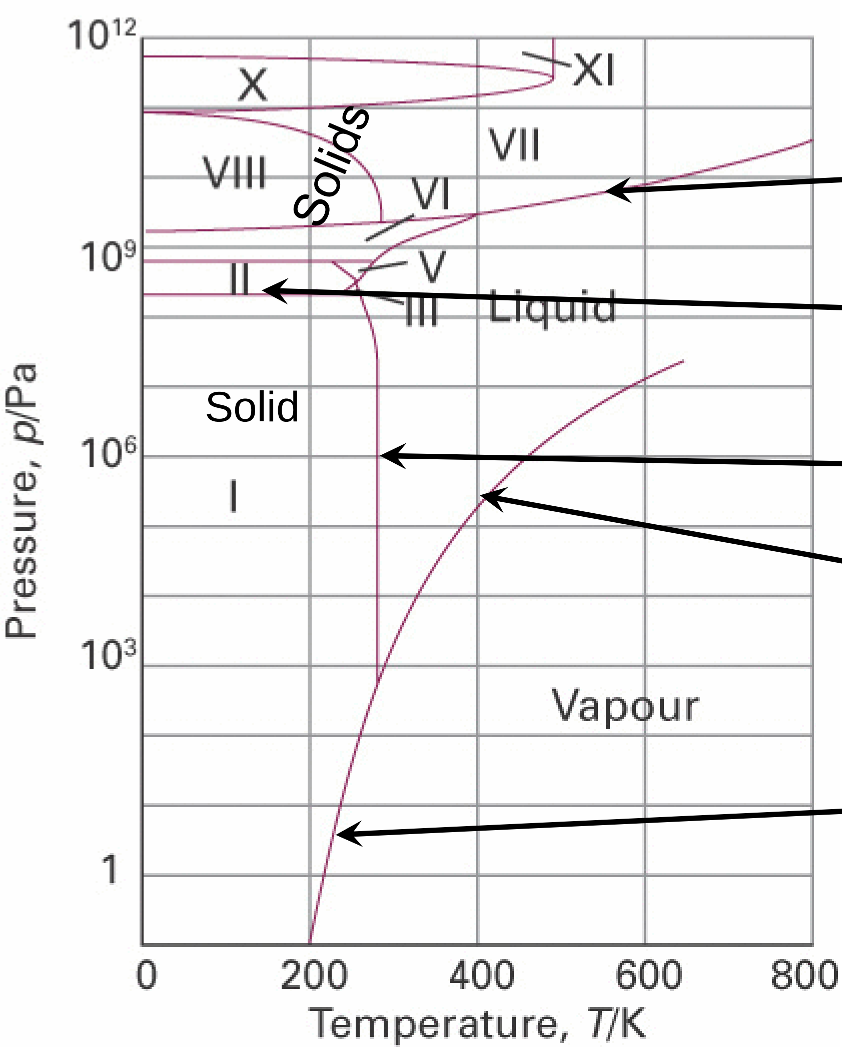
(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



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

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

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

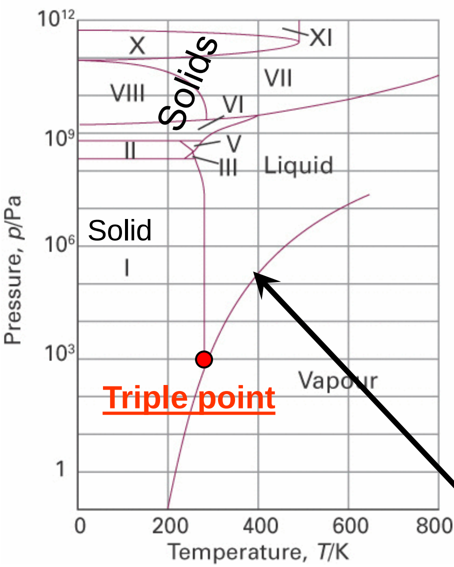
$$G_{l,\mathrm{m}} = G_{g,\mathrm{m}}$$

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

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

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

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

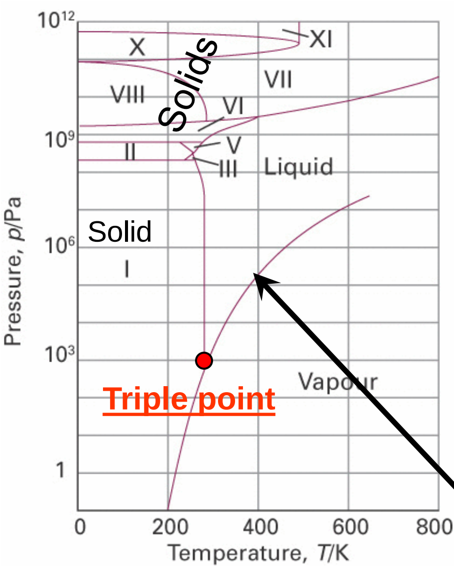
$$dG_{i,\mathrm{m}} = V_{i,\mathrm{m}} dP - S_{i,\mathrm{m}} dT$$

$$V_{l,\mathrm{m}} dP - S_{l,\mathrm{m}} dT = V_{g,\mathrm{m}} dP - S_{g,\mathrm{m}} dT$$

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

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

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

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

$$V_{l,\mathrm{m}} dP - S_{l,\mathrm{m}} dT = V_{g,\mathrm{m}} dP - S_{g,\mathrm{m}} dT$$

Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta_{l\leftrightarrow g} S_\mathrm{m}}{\Delta_{l\leftrightarrow g} V_\mathrm{m}}$$

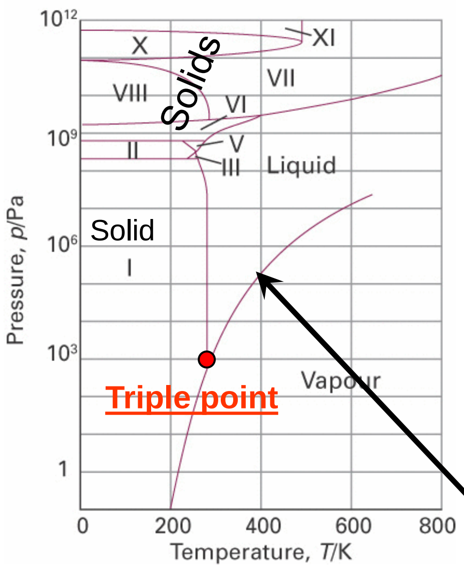
$$\Delta_{l\leftrightarrow g} G_\mathrm{m} = 0$$

$$\frac{dP}{dT} = \frac{\Delta_{l\leftrightarrow g} H_\mathrm{m}}{T_{l\leftrightarrow g} \Delta_{l\leftrightarrow g} V_\mathrm{m}}$$

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

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

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

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

$$V_{l,\mathrm{m}}dP - S_{l,\mathrm{m}}dT = V_{g,\mathrm{m}}dP - S_{g,\mathrm{m}}dT$$

Let's work this out in detail

Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta_{l\leftrightarrow g}S_\mathrm{m}}{\Delta_{l\leftrightarrow g}V_\mathrm{m}}$$

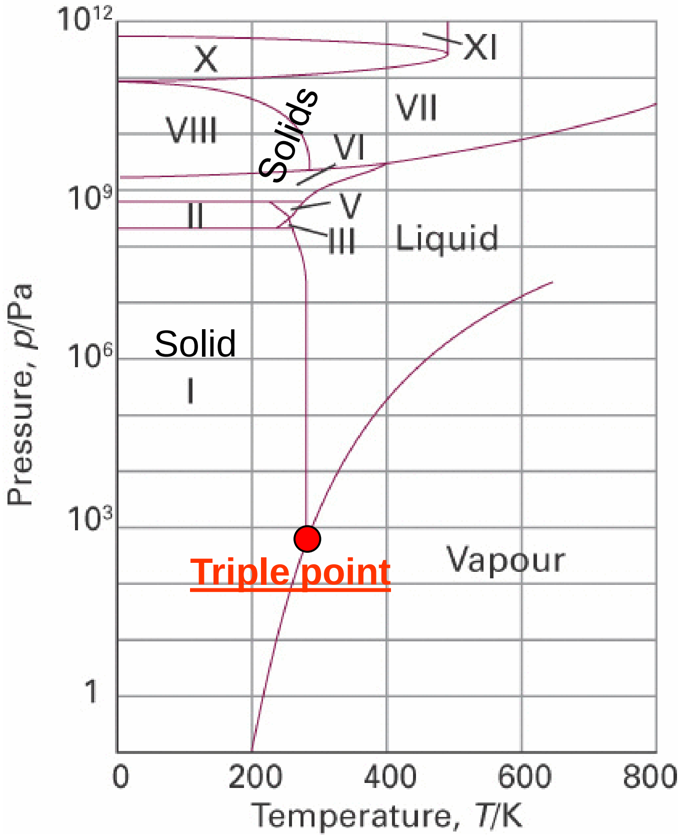
$$\Delta_{l\leftrightarrow g}G_\mathrm{m} = 0$$

$$\frac{dP}{dT} = \frac{\Delta_{l\leftrightarrow g}H_\mathrm{m}}{T_{l\leftrightarrow g}\Delta_{l\leftrightarrow g}V_\mathrm{m}}$$

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

(Equilibrium) Phase Diagram H_2O

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

Clapeyron equation:

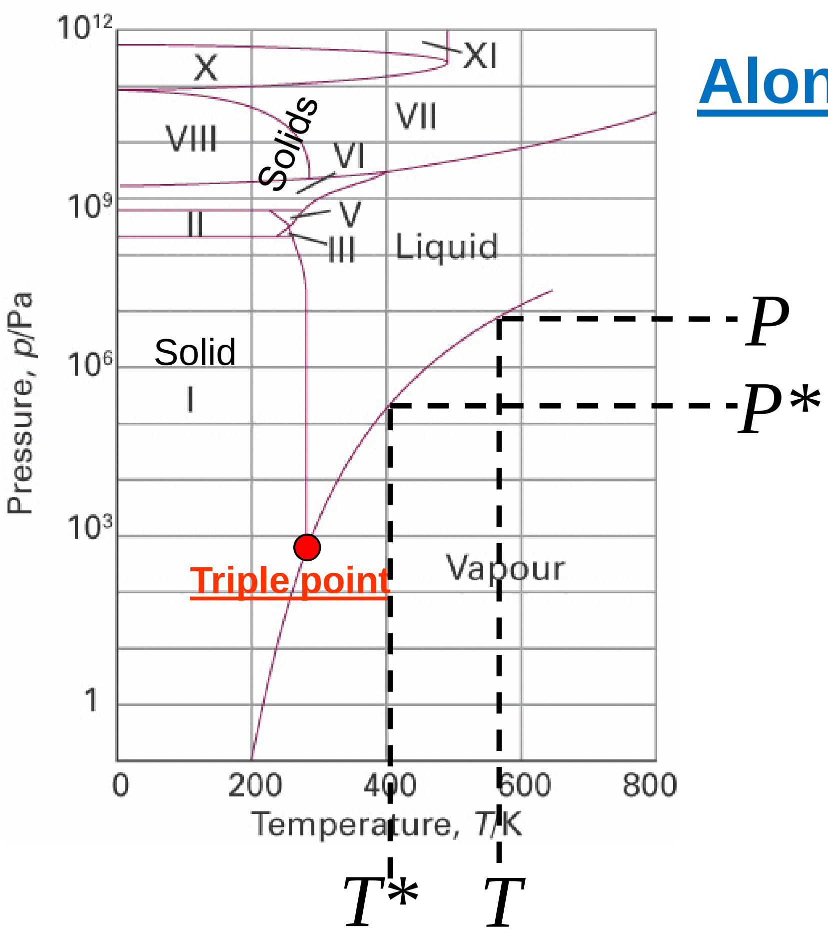
$$dP = \frac{\Delta_{l\leftrightarrow g} H_{\mathrm{m}}}{T_{l\leftrightarrow g} \Delta_{l\leftrightarrow g} V_{\mathrm{m}}} dT$$

Perfect gas: $PV_{\mathrm{m}} = RT$

$$\Delta_{l\leftrightarrow g} V_{\mathrm{m}} \approx V_{g,\mathrm{m}} = \frac{RT}{P}$$

$$\frac{dP}{P} = \frac{\Delta_{l\leftrightarrow g} H_{\mathrm{m}}}{RT^2_{l\leftrightarrow g}} dT \Rightarrow \int \frac{dP}{P} = \int \frac{\Delta_{l\leftrightarrow g} H_{\mathrm{m}}}{RT^2_{l\leftrightarrow g}} dT$$

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

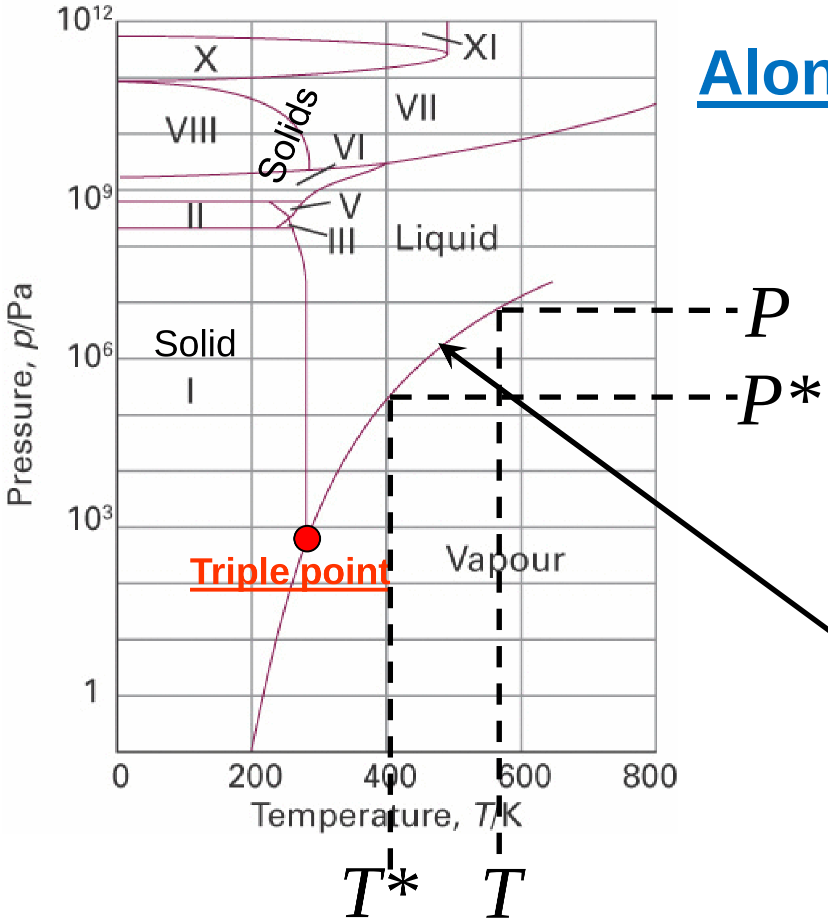
$$\int_{P^*}^{P} \frac{dP}{P} = \int_{T^*}^{T} \frac{\Delta_{l\leftrightarrow g} H_m}{RT^2_{l\leftrightarrow g}} dT$$

$$\Delta_{l\leftrightarrow g} H_m(T) \approx \Delta_{l\leftrightarrow g} H_m$$

$$\int_{P^*}^{P} \frac{dP}{P} = \frac{\Delta_{l\leftrightarrow g} H_m}{R} \int_{T^*}^{T} \frac{dT}{T^2}$$

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

Phase boundary lines in diagrams of unary systems



Along phase boundary line:

Clausius-Clapeyron equation:

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

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

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

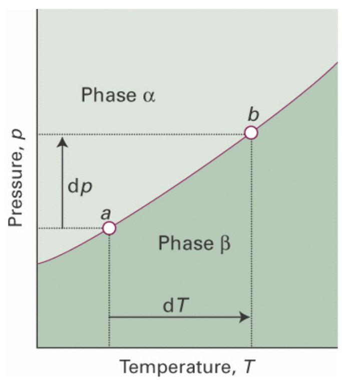
Clausius-Clapeyron equation

Phase boundary lines in phase diagrams of unary systems

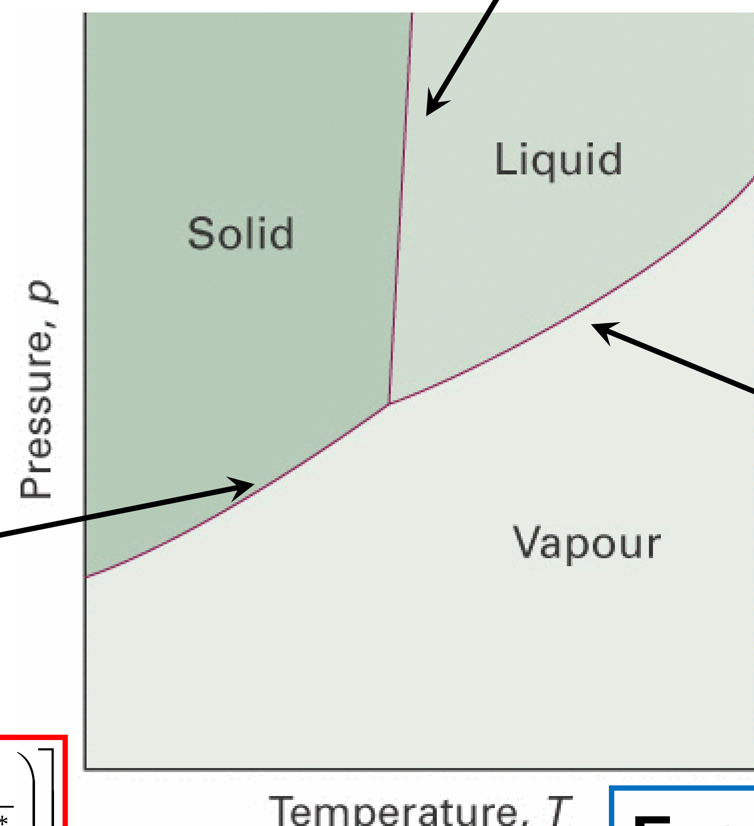
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{trs}} S}{\Delta_{\mathrm{trs}} V} = \frac{\Delta_{\mathrm{trs}} H}{T_{\mathrm{trs}} \Delta_{\mathrm{trs}} V}$$

Clapeyron

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}} H}{T_{\mathrm{fus}} \Delta_{\mathrm{fus}} V}$$



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



$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}} H}{T_{\mathrm{vap}} \Delta_{\mathrm{vap}} V}$$

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} \approx \frac{\Delta_{\mathrm{vap}} H}{\mathrm{R} T^2}$$

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

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sub}} H}{T_{\mathrm{sub}} \Delta_{\mathrm{sub}} V}$$

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} \approx \frac{\Delta_{\mathrm{sub}} H}{\mathrm{R} T^2}$$

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

Clausius-Clapeyron

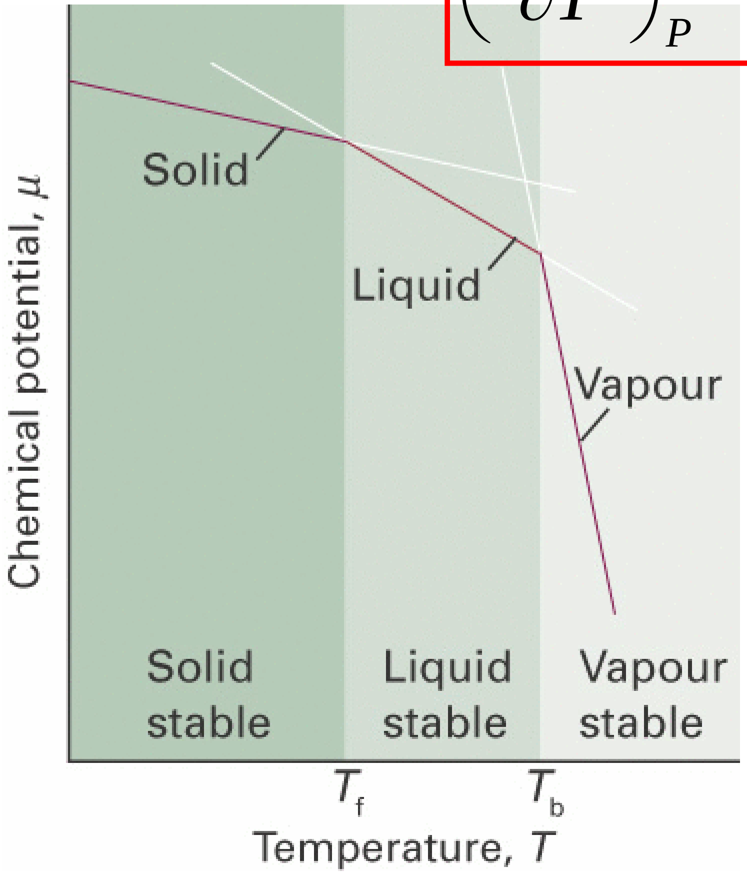
Exercise 5-8

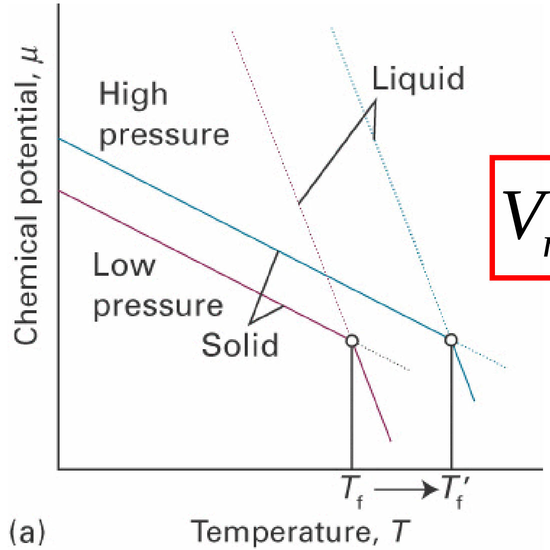
Phase transitions in phase diagrams of unary systems

Phase transitions in phase diagrams of unary systems

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

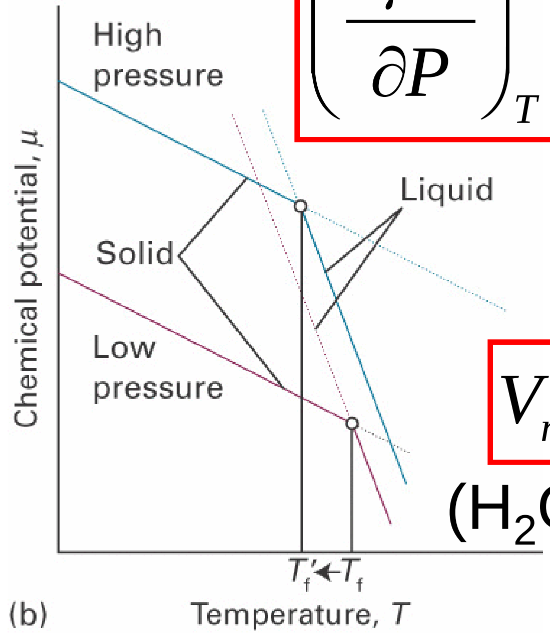
$$\left(\frac{\partial \mu^\alpha}{\partial T}\right)_P = -S_m^\alpha$$





$$V_m^l > V_m^s$$

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



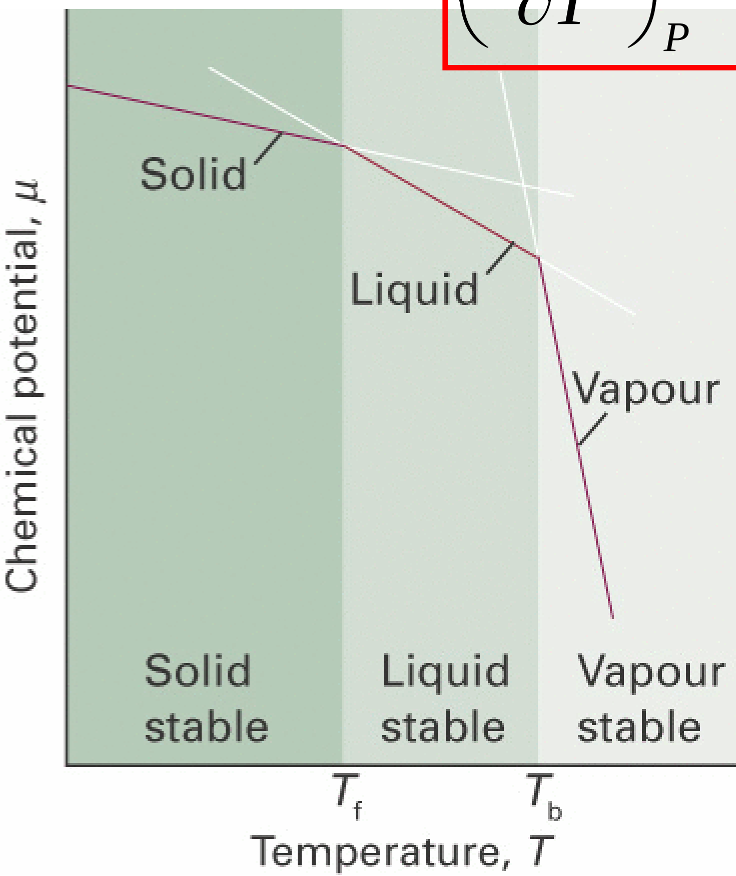
$$V_m^l < V_m^s$$

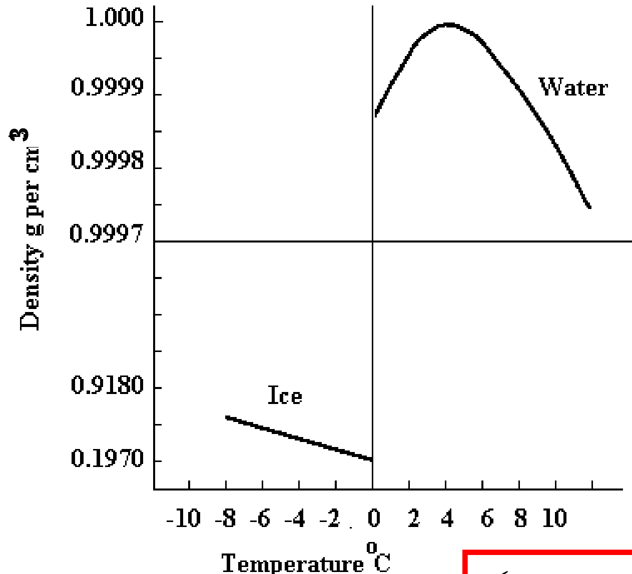
(H_2O)

Phase transitions in phase diagrams of unary systems

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

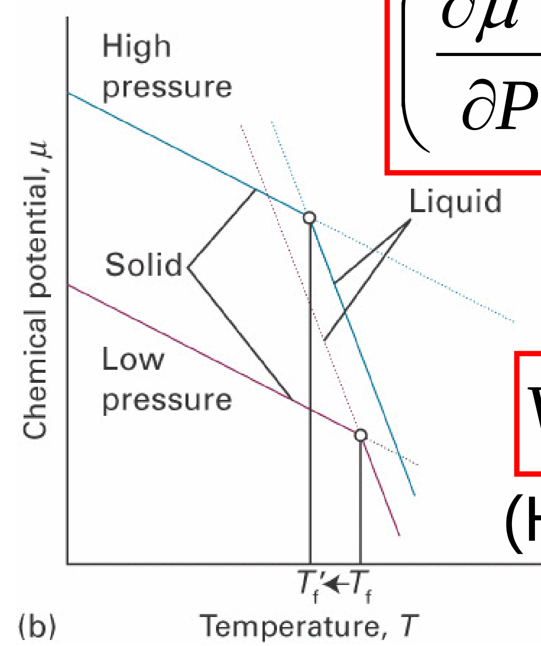
$$\left(\frac{\partial \mu^\alpha}{\partial T}\right)_P = -S_m^\alpha$$





(H_2O)

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

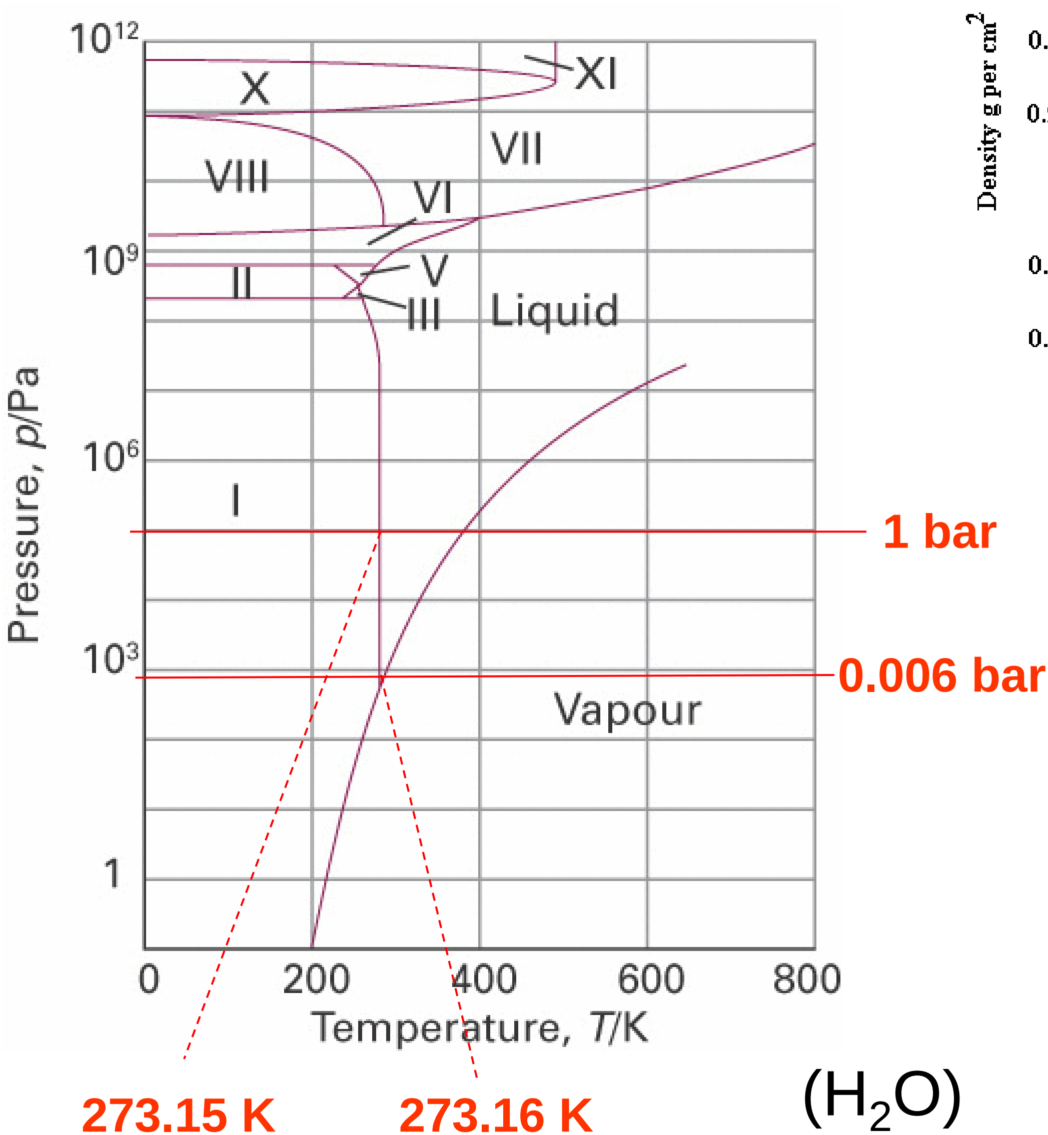


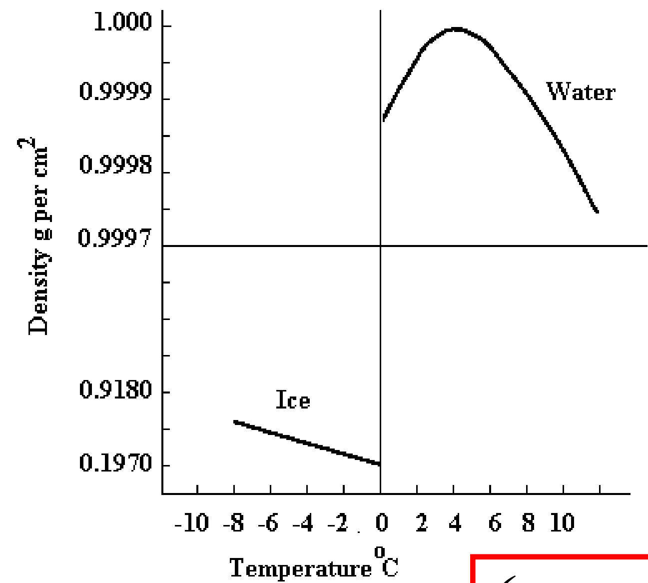
$$V_m^l < V_m^s$$

(H_2O)

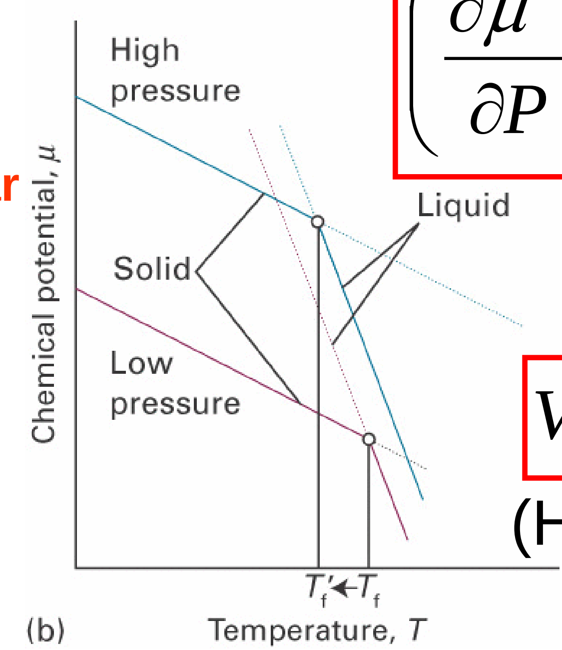
Phase transitions in phase diagrams of unary systems

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





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



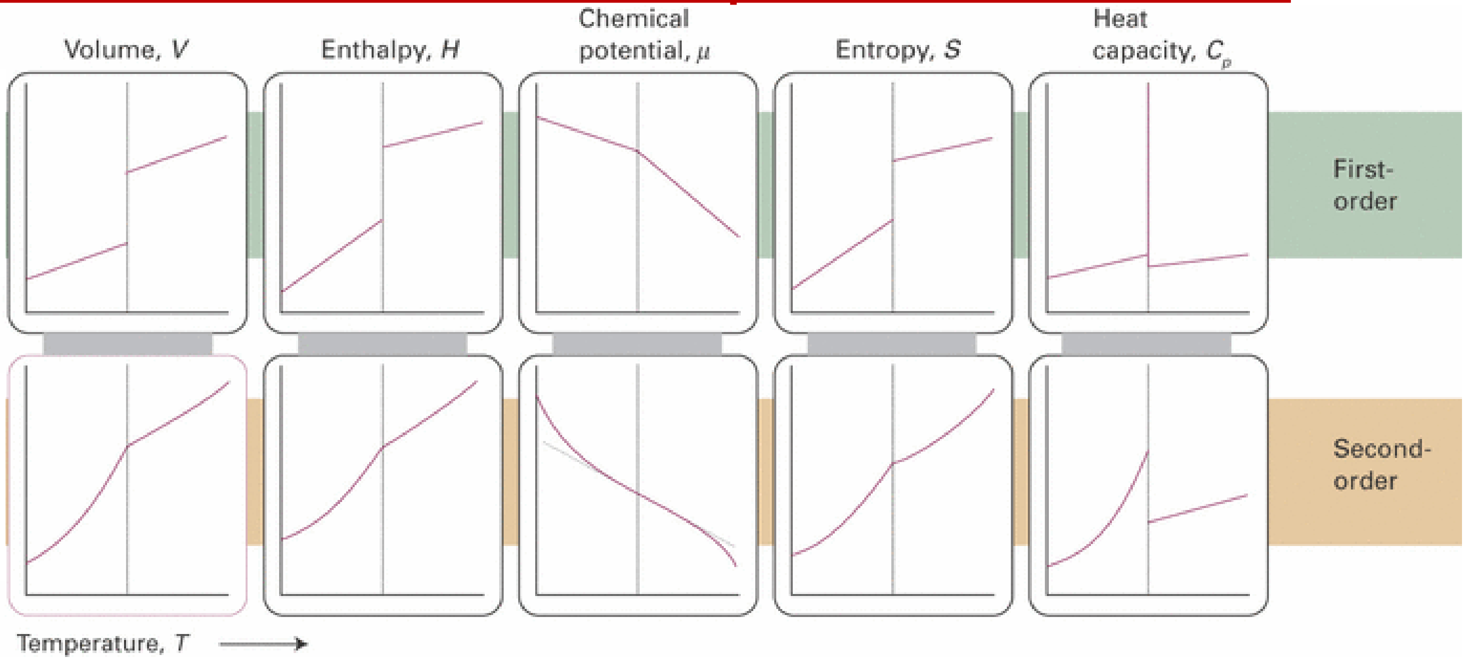
$$V_m^l < V_m^s$$

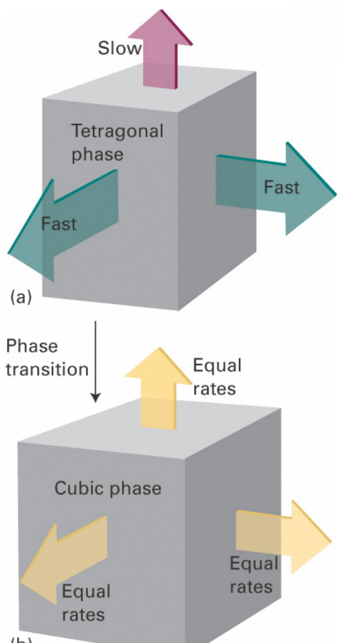
(H_2O)

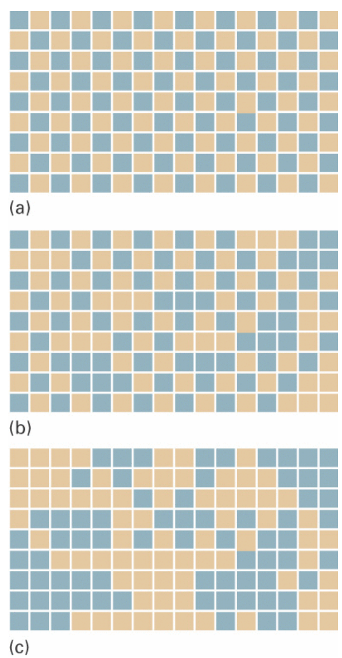
Ehrenfest classification of phase transitions

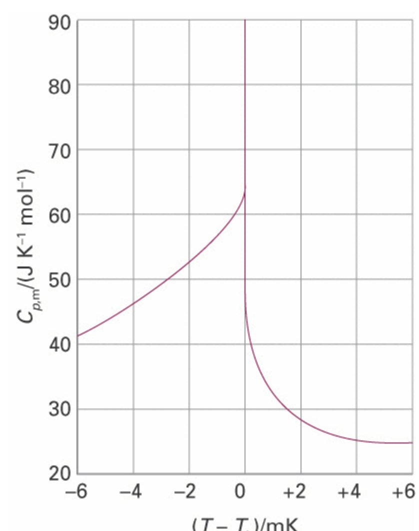
$$\left(\frac{\partial \mu}{\partial T}\right)_P (T) =$$

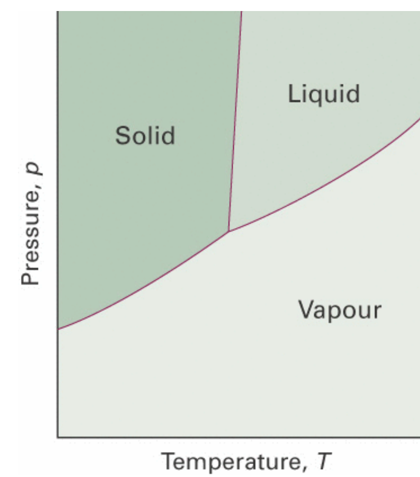
$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P (T) =$$









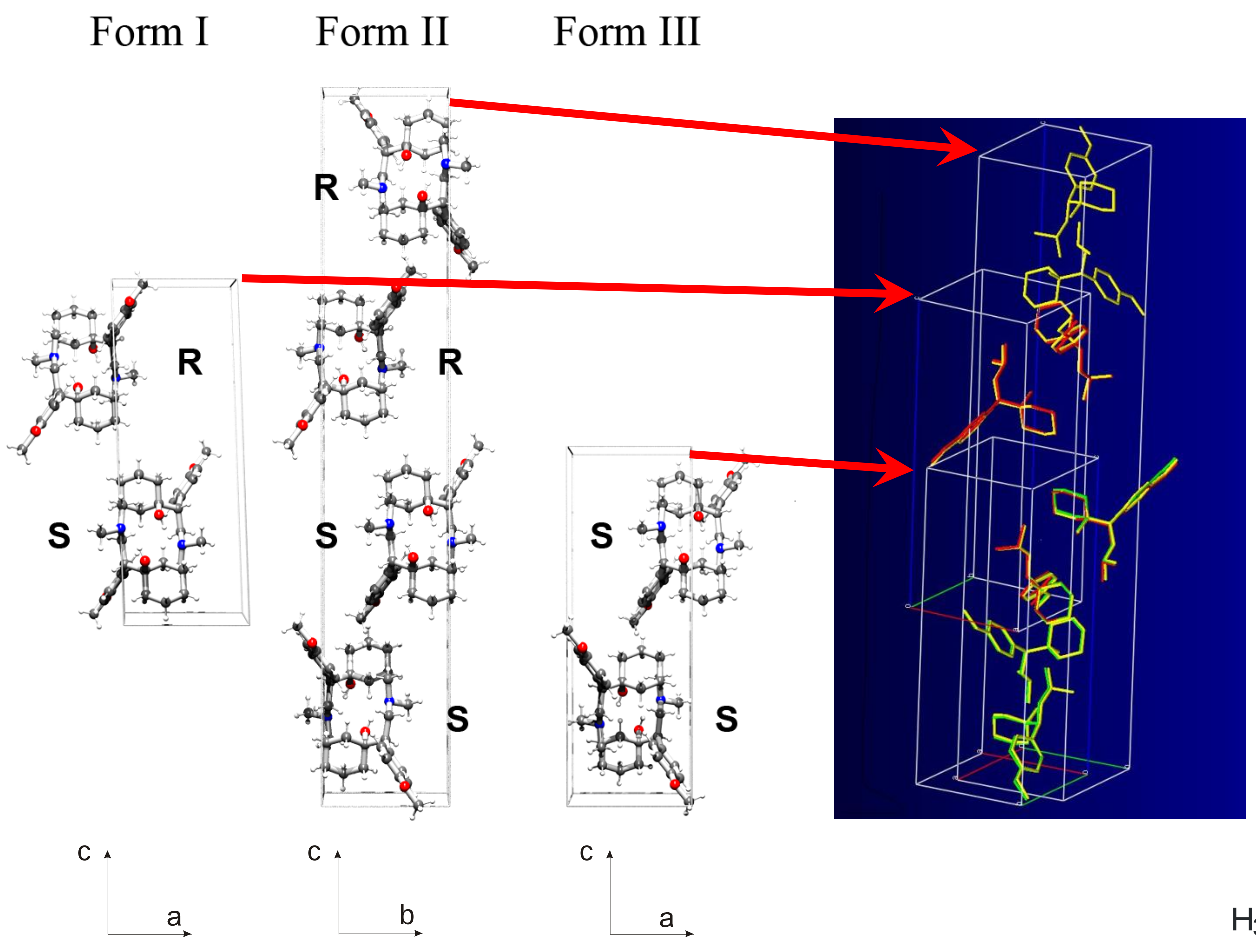


Second order

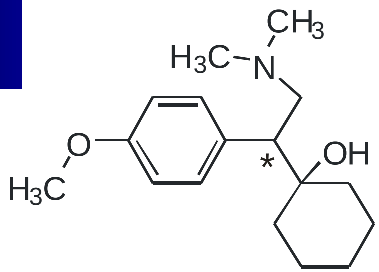
Exercise 9

First order

Polymorphic (solid state) phase transitions

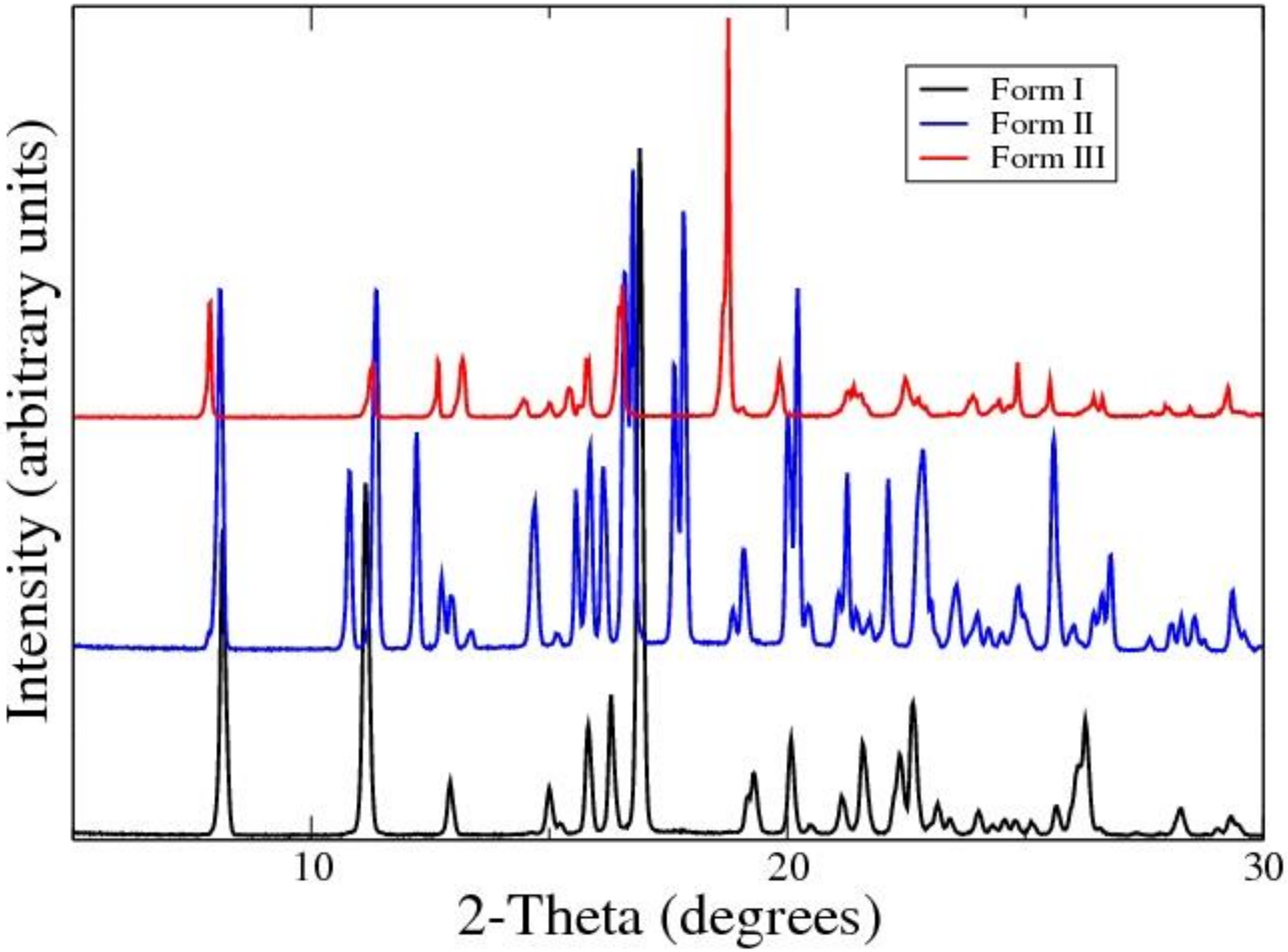


T < 40 ºC   T > 40 ºC   T > 60 ºC   (T_{fus} = 70 ºC)



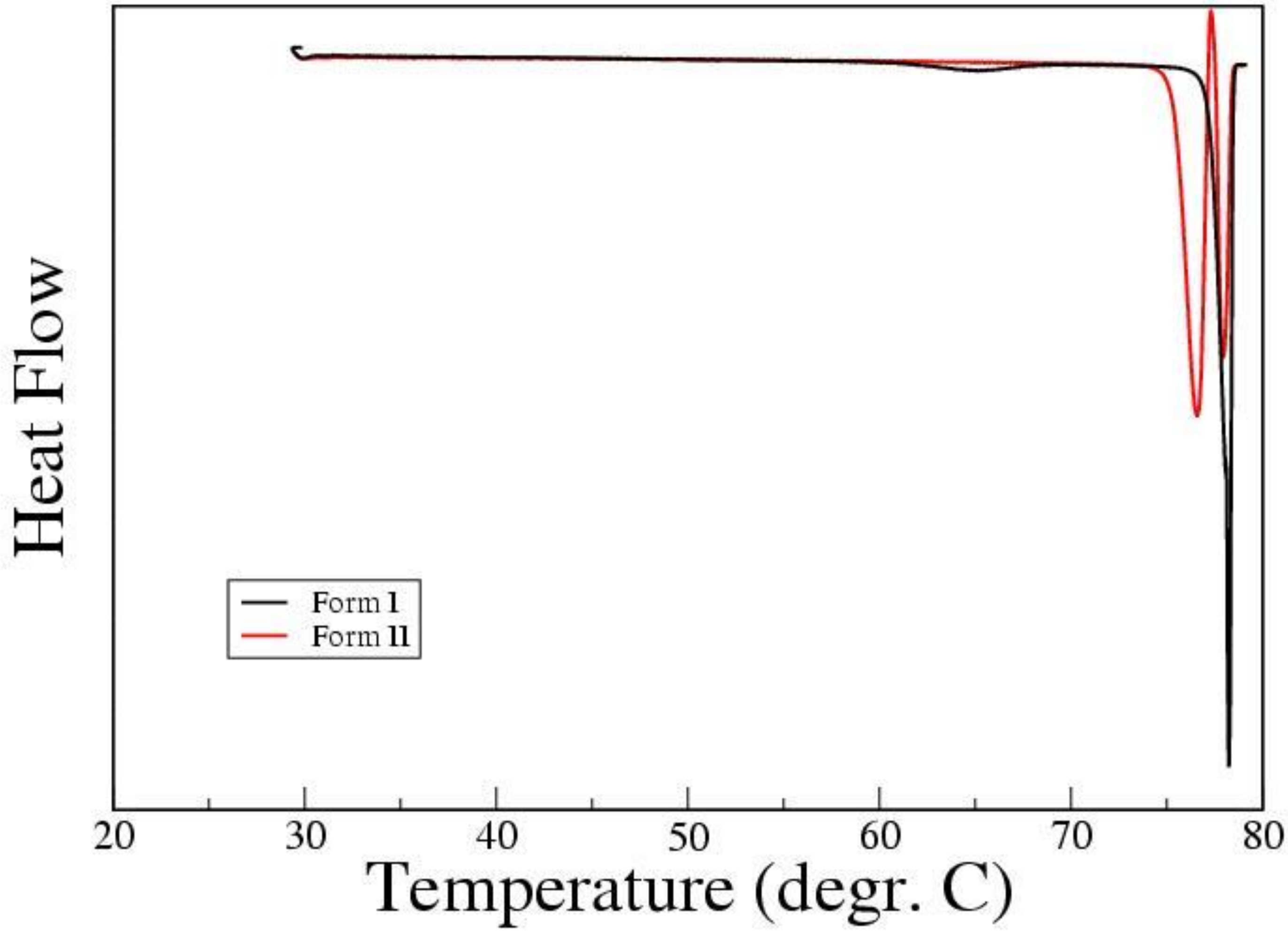
Venlafaxine

Polymorphic solid state phase transitions



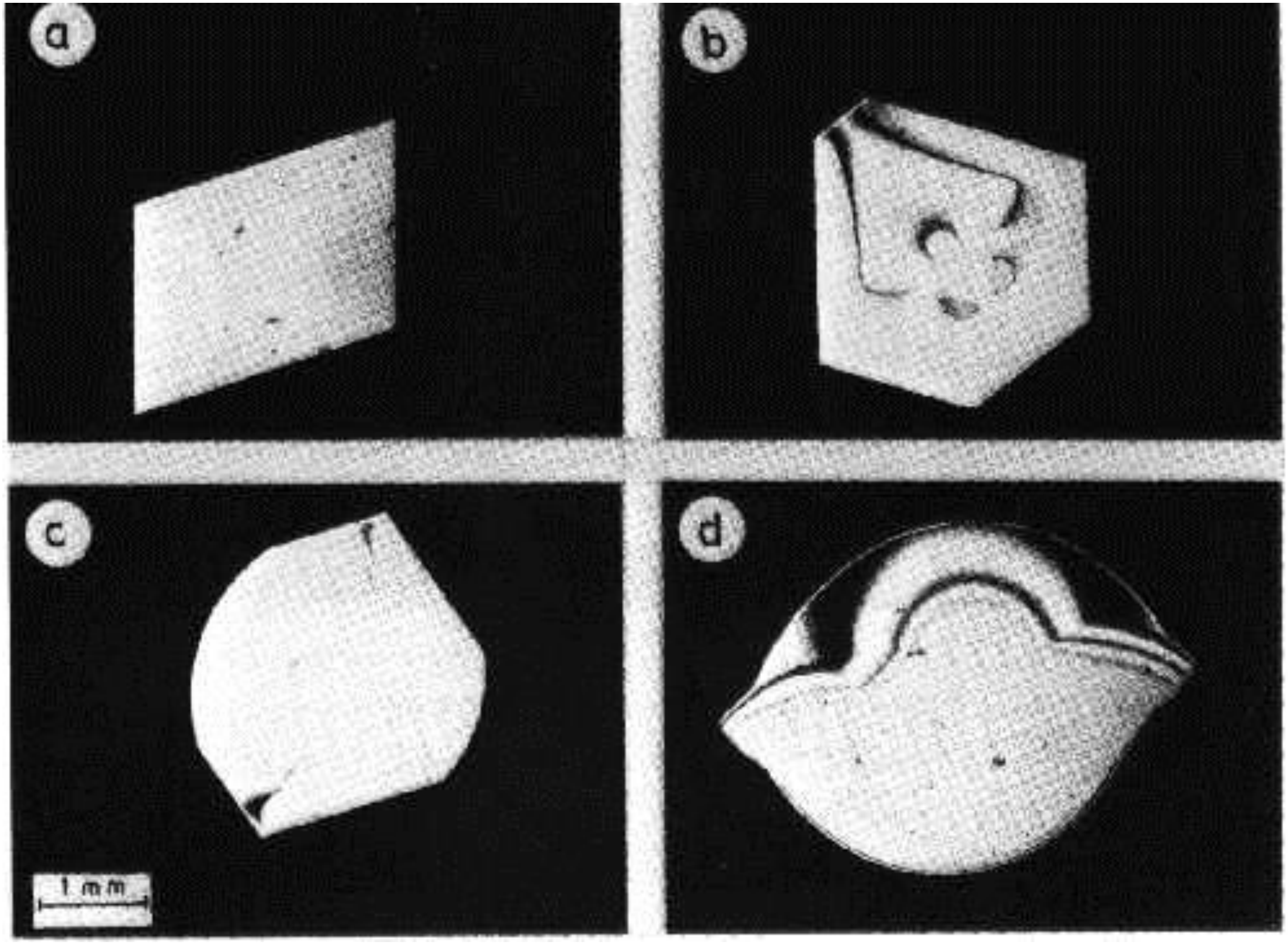
Polymorphic forms characterized using X-Ray Powder Diffraction

Polymorphic solid state phase transitions



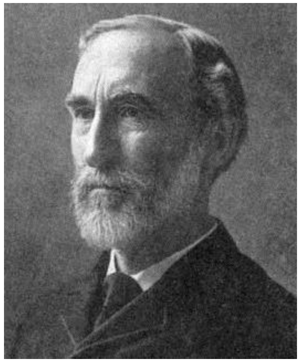
Characterized using Differential Scanning Calorimetry

Kinetic roughening transition for naphthalene crystals in a toluene solution

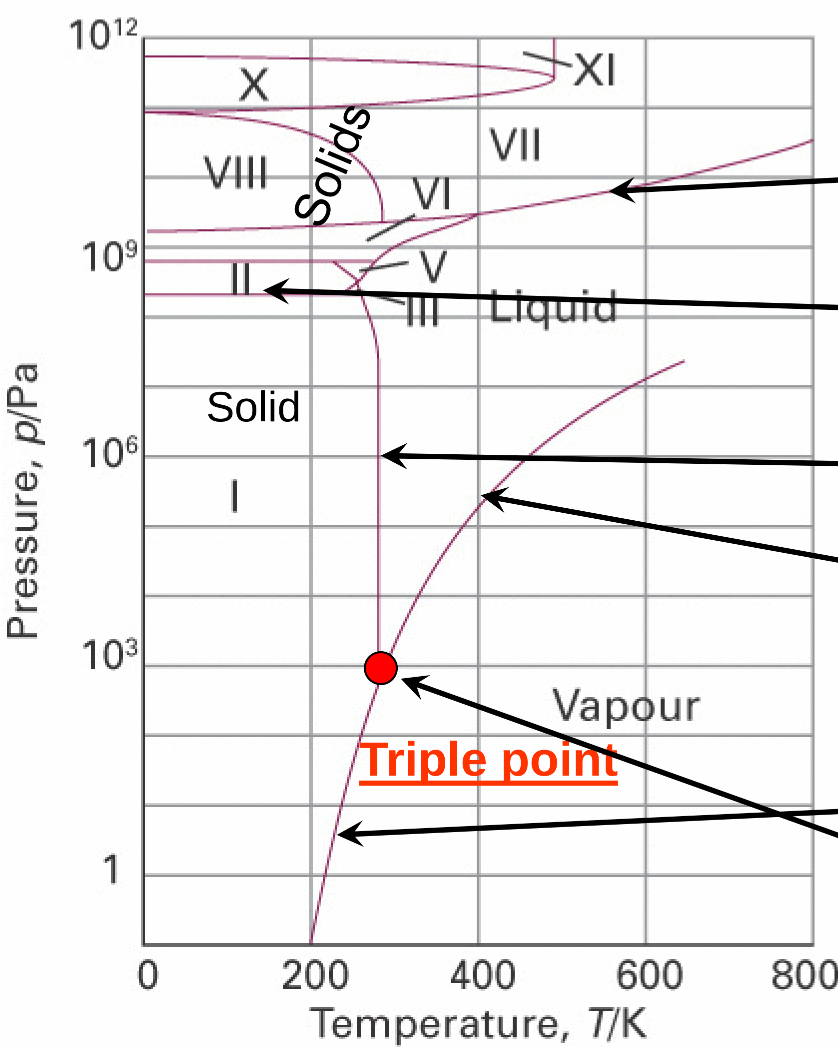


a→d: increasing driving force for crystallization

Gibbs phase rule: multicomponent phases



Phase boundary lines in diagrams of unary systems



(**Equilibrium**) Phase Diagram H_2O

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

$$\mu_{s_I} = \mu_{s_{II}}$$

$$\mu_{s_I} = \mu_l$$

$$\mu_l = \mu_g$$

$$\mu_{s_I} = \mu_g$$

$$\mu_{s_I} = \mu_l = \mu_g$$

What about mixtures of compounds in the phases?

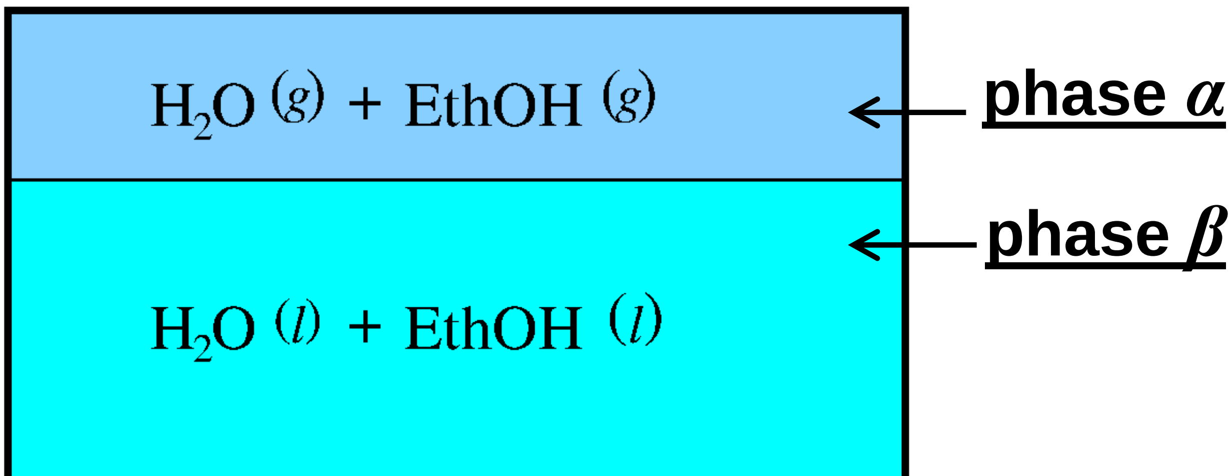
Gibbs phase rule: multicomponent phases

Importance of the chemical potential:

Equilibrium between phases $H_2O(\alpha) \leftrightarrow H_2O(\beta)$

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

Equilibrium between phases of components *i* in mixtures

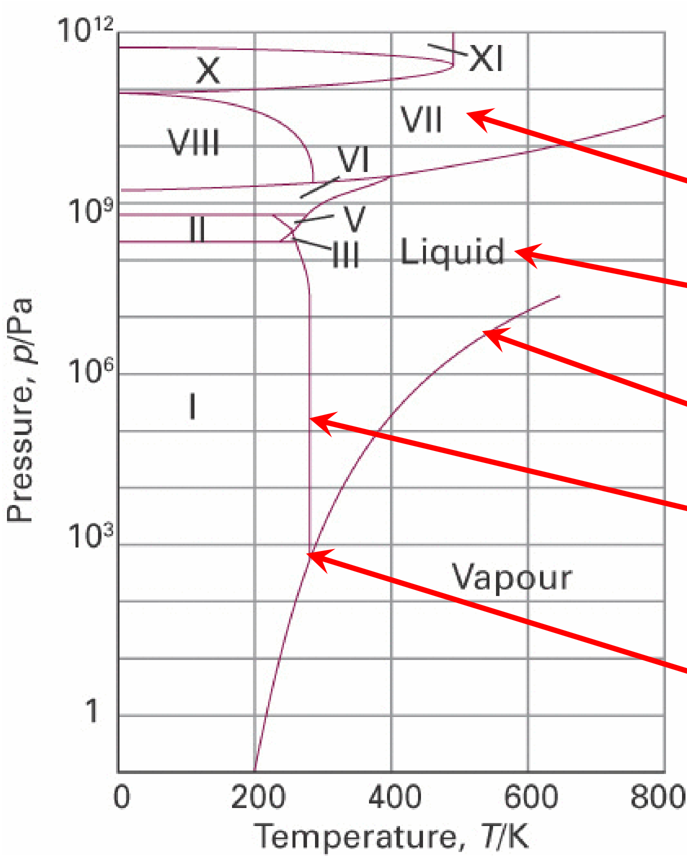


in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases α, β**; **components *i*** }

Gibbs phase rule: multicomponent phases

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

***P* phases in mutual equilibrium**



$P=1$

$P=2$

$P=3$

unary phase diagram

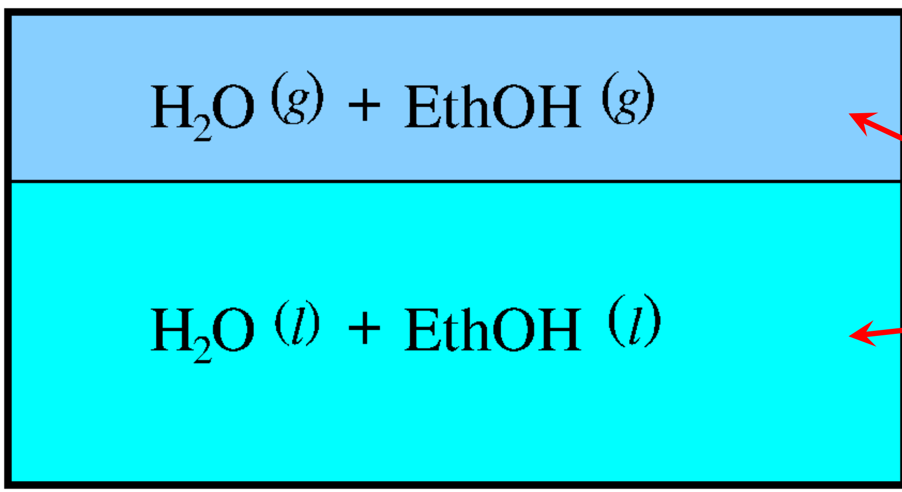
Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$

- **phases α, β , γ, ...**
- **components i =1, 2**

C components in each phase ⇒ $x_i \equiv \dfrac{n_i}{\sum_j n_j}$

mole fraction of component i



$C = 2$

binary phase diagram

Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases $\alpha, \beta, \gamma, \ldots$** / **components $i = 1, 2, 3, \ldots$**

Equilibrium between P phases of components i in mixtures

C components in each phase

P phases in mutual equilibrium } ⇒

 # independent variables $F \to P, T, x_1 \cdots x_C \to 2 + PC$

(P, T: **whole system**; $x_1 \cdots x_C$: **for each phase**)

$$dG = VdP - SdT + \sum_{j=\alpha}^{P} \sum_{i=1}^{C} \mu_{i,j} dn_{i,j}$$

Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases α, β, γ, ...** / **components i = 1, 2, 3, ...** }

Equilibrium between P phases of components i in mixtures

C components in each phase
P phases in mutual equilibrium
→ $F \rightarrow 2 + PC$

for each phase
mole fraction
$$x_i \equiv \frac{n_i}{\sum_j n_j}$$
→ $\sum_i x_i = 1$

→ **# independent variables** $F \rightarrow 2 + P(C-1)$

Gibbs phase rule: multicomponent phases

in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ — **phases** $\alpha, \beta, \gamma, \ldots$; **components** $i = 1, 2, 3, \ldots$

Equilibrium between phases of components *i* in mixtures

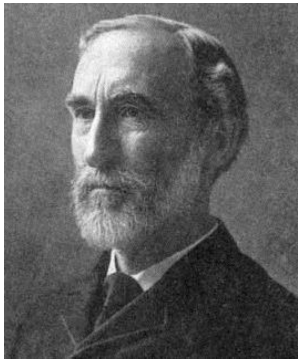
***P* phases in mutual equilibrium**

$$\begin{aligned}
\mu_{1,\alpha} &= \mu_{1,\beta} = \cdots \mu_{1,P} \\
\mu_{2,\alpha} &= \mu_{2,\beta} = \cdots \mu_{2,P} \\
\cdot &= \cdot = \cdot \\
\cdot &= \cdot = \cdot \\
\mu_{C,\alpha} &= \mu_{C,\beta} = \cdots \mu_{C,P}
\end{aligned}$$

$(P-1)C$ times an "=" sign

$$F \rightarrow 2 + P(C-1) - (P-1)C = C - P + 2$$

Gibbs phase rule: multicomponent phases



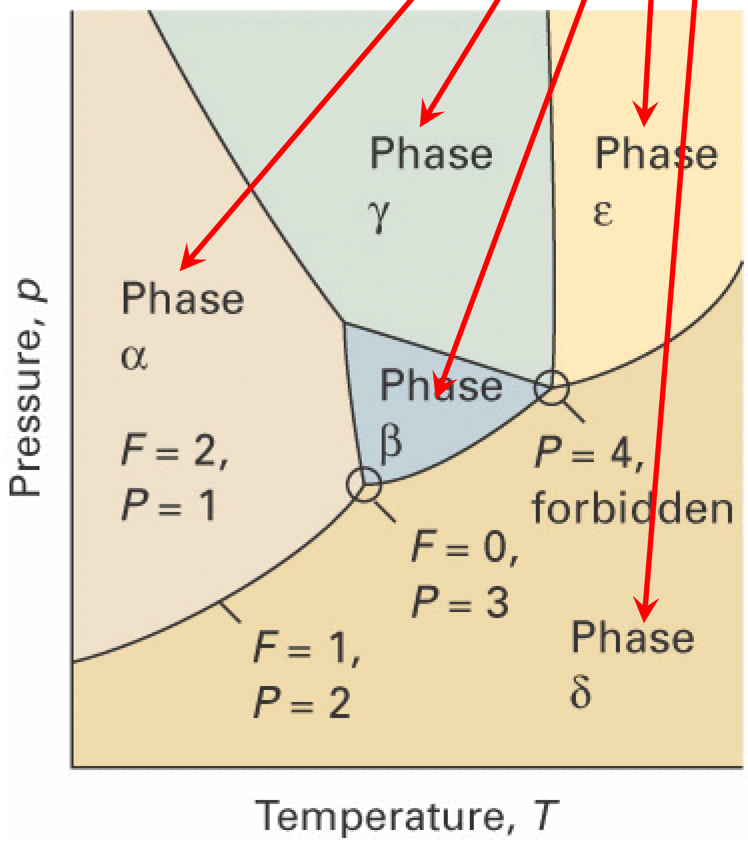
in equilibrium: $\mu_{i,\alpha} = \mu_{i,\beta}$ { **phases α, β**; **components i** }

Equilibrium between P phases of C components in mixtures

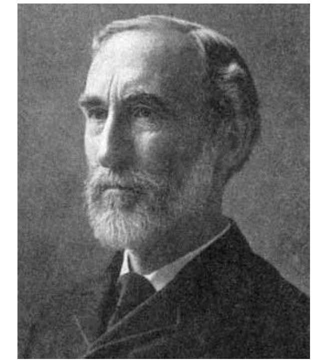
C components in the mixtures
P phases in mutual equilibrium } ⇒ $F = C - P + 2$

Gibbs phase rule: unary phase diagrams

$C = 1$, $P = 1$ → $F = 2$



unary phase diagram



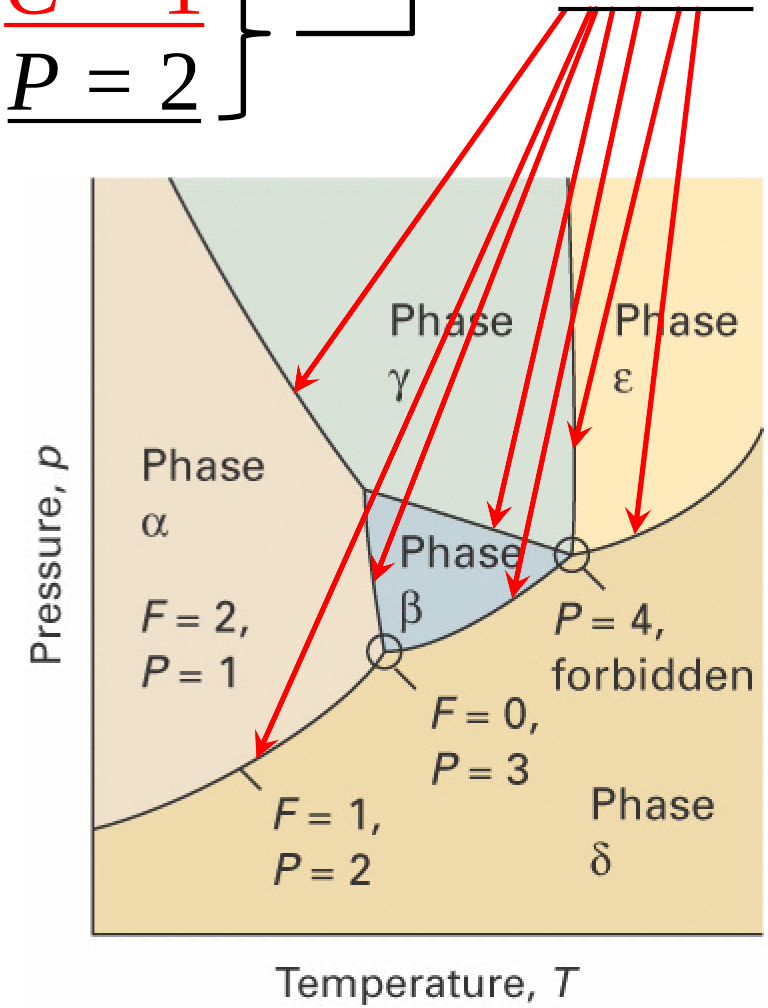
Gibbs phase rule

$$F = C - P + 2$$

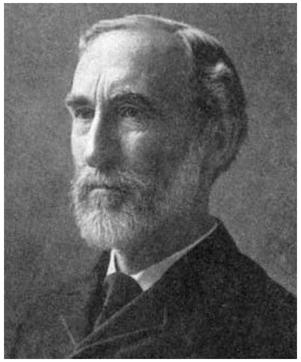
F: # degrees of freedom
C: # components
P: # phases

Gibbs phase rule: unary phase diagrams

$\underline{C = 1}$
$\underline{P = 2}$ → $\underline{F = 1}$



unary phase diagram

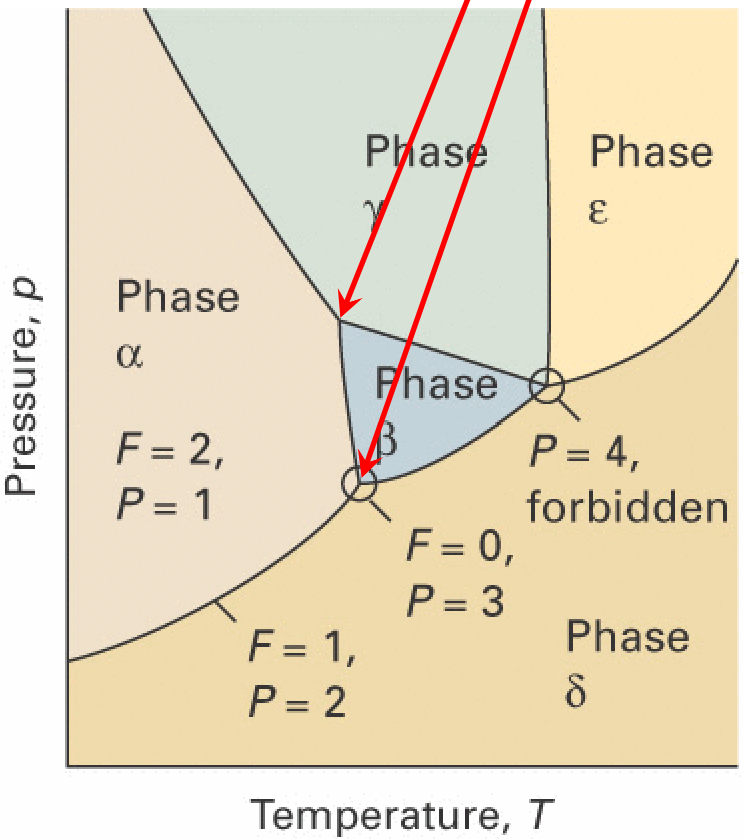


Gibbs phase rule

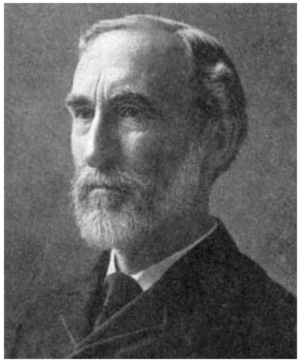
$$F = C - P + 2$$

Gibbs phase rule: unary phase diagrams

$C = 1$
$P = 3$
→ $F = 0$



unary phase diagram

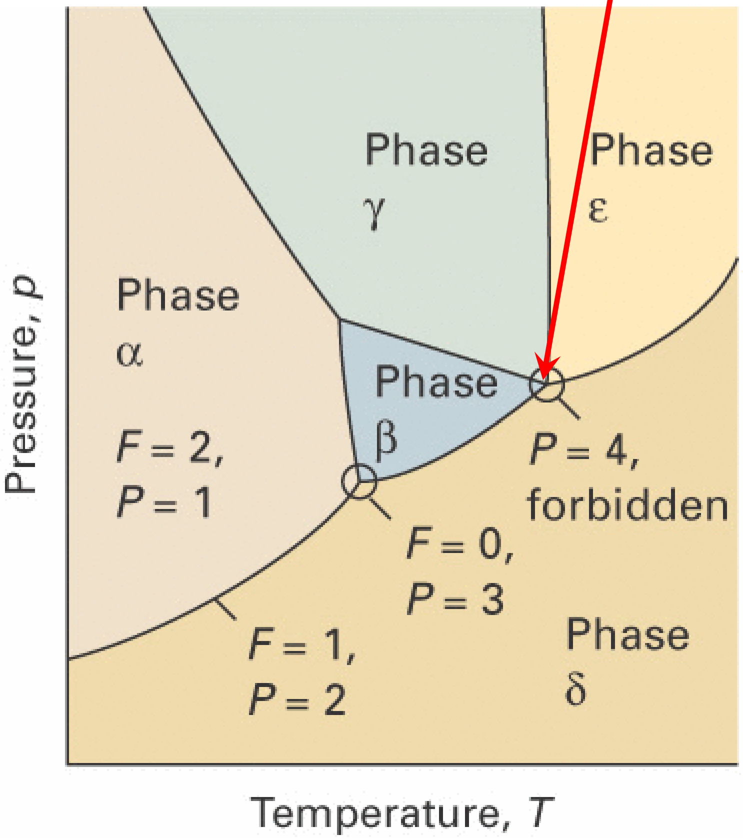


Gibbs phase rule

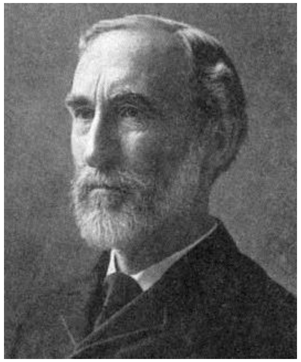
$$F = C - P + 2$$

Gibbs phase rule: unary phase diagrams

$$\left.\begin{array}{l} C = 1 \\ P = 4 \end{array}\right\} \rightarrow F = -1$$



unary phase diagram



Gibbs phase rule

$$F = C - P + 2$$