Chap. 4. <u>Physical transformations</u>

Phase - form of matter that is uniform throughout in chemical composition and physical state

e.g.) liquid, gas, different types of crystals, glasses

**Phase transition - spontaneous conversion between two phases, which occurs at the transition temperature T_{tr} for a given pressure.**

Metastable phase - thermodynamically unstable phase that persists because the transition is kinetically hindered.

e.g. Diamond, Glass
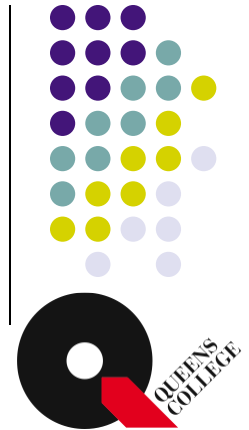
Phase diagram - shows regions of pressure and temperature at which various phases are thermodynamically stable
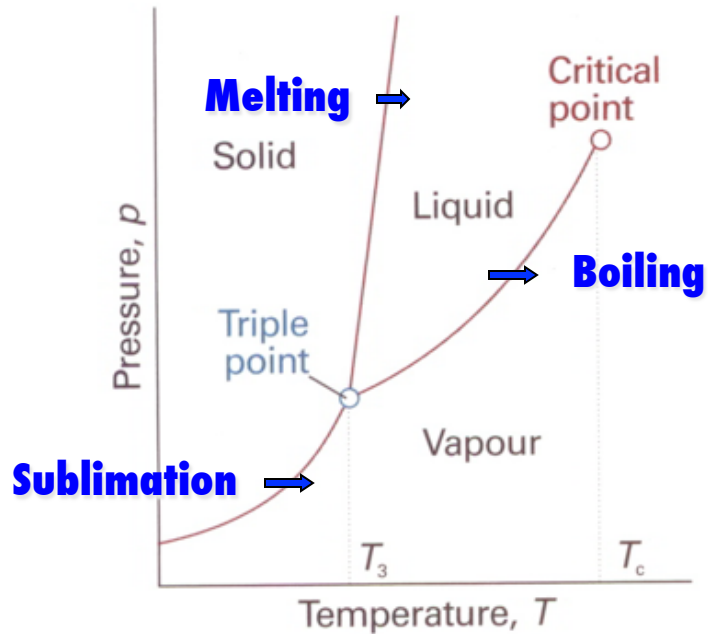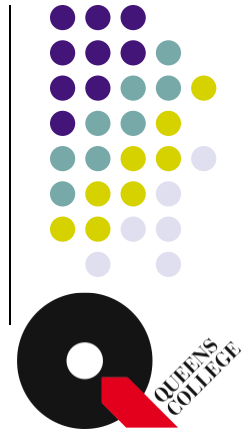

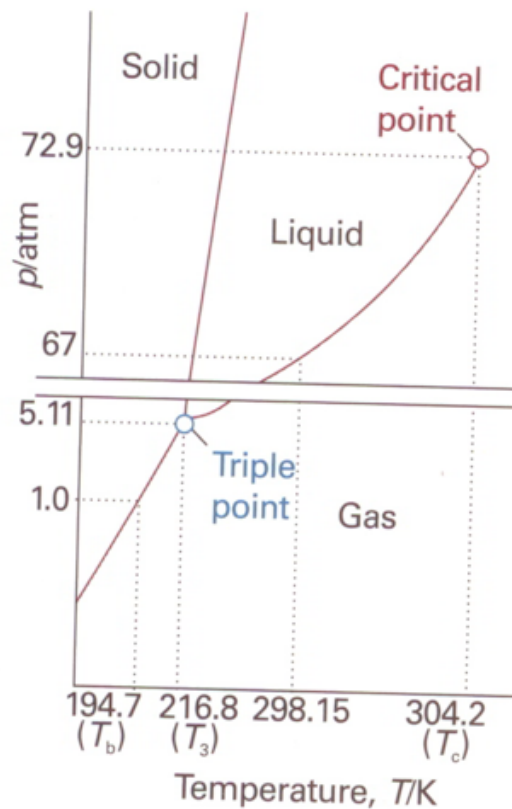**Vapour pressure** - the pressure of a vapour in equilibrium with the liquid

Sublimation vapour pressure - the pressure of a vapour in equilibrium with the solid

Normal boiling temperature - boiling temperature at 1 atm

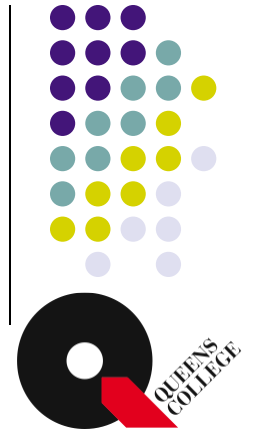**Standard boiling temperature** - boiling temperature at 1 bar
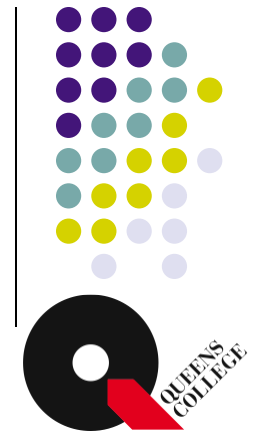
Phase diagram of CO$_2$

Positive slope of solid-liquid :
high pressure favors solid

Triple point pressure > 1 atm :

liquid cannot exist at normal atmosphereic pressure
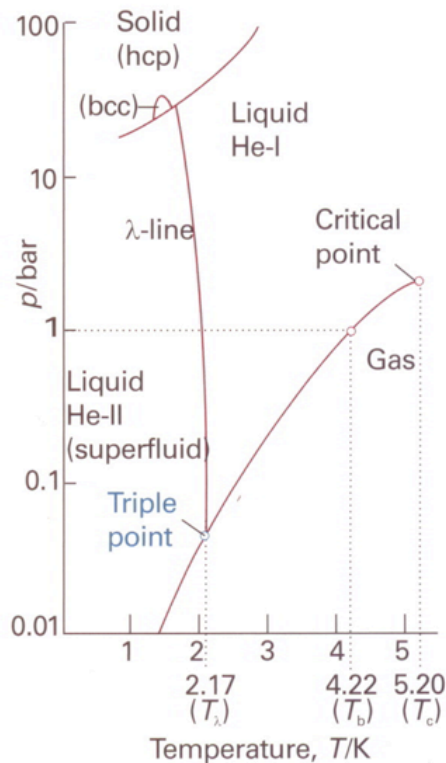
Phase diagram of H₂O
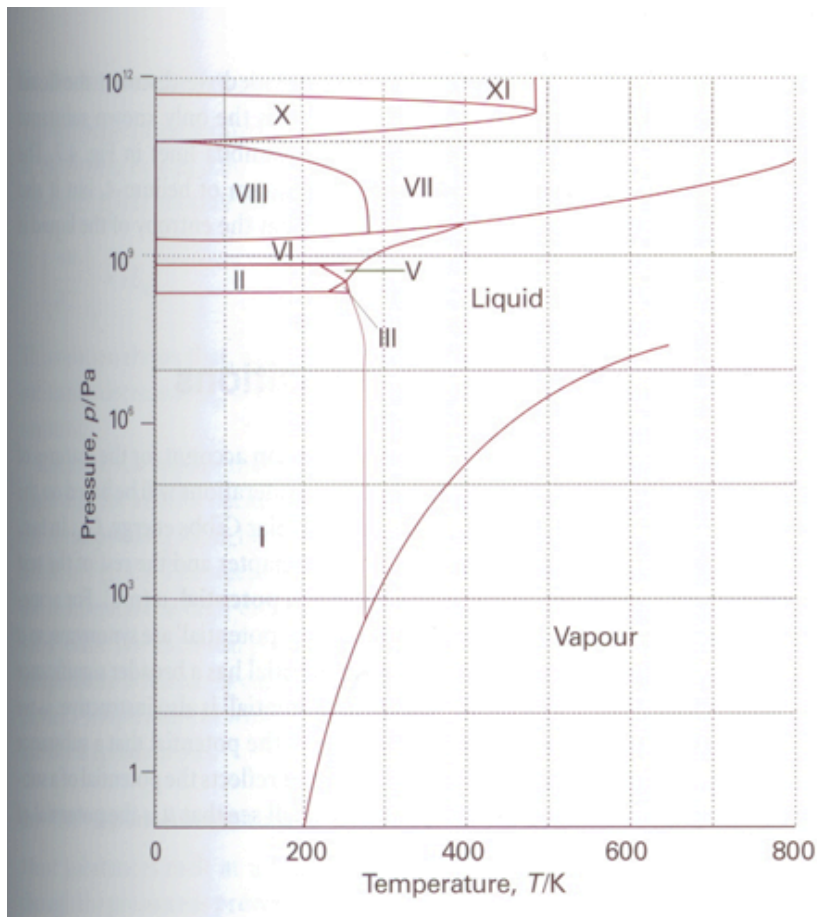
Steep negative slope of solid-liquid phase line (up to 2k bar) :

high pressure favors liquid (liquid is denser than solid)

Ice VII melts at 100 ºC, exists above 25 kbar

**Different solid phases (polymorphs) represent different arrangement of water molecules**

Helium

Solid and gas phases of helium are never in equilibrium
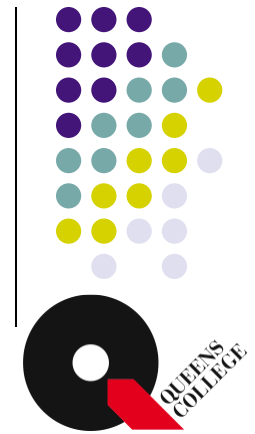
Solid phase is obtained only at very high pressure

^{4}He becomes superfluid at low temperature, zero viscosity

^{3}He - different from ^{4}He, but possesses a superfluid phase

Entropy of liquid is lower than that of the solid
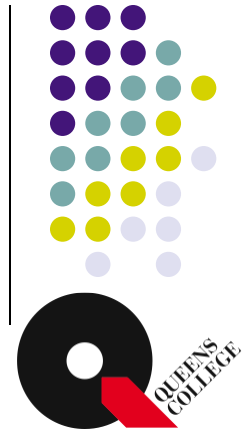
Phase stability and phase transitions

For one component system, $\mu = G_m = G/n$

Same for all the phases at equilibrium

Condition of equilibrium: $dG = (\mu_2 - \mu_1)dn = 0$ **for any** dn.

$$\mu_2 = \mu_1$$

$S_m(l) > S_m(s)$ **almost always**
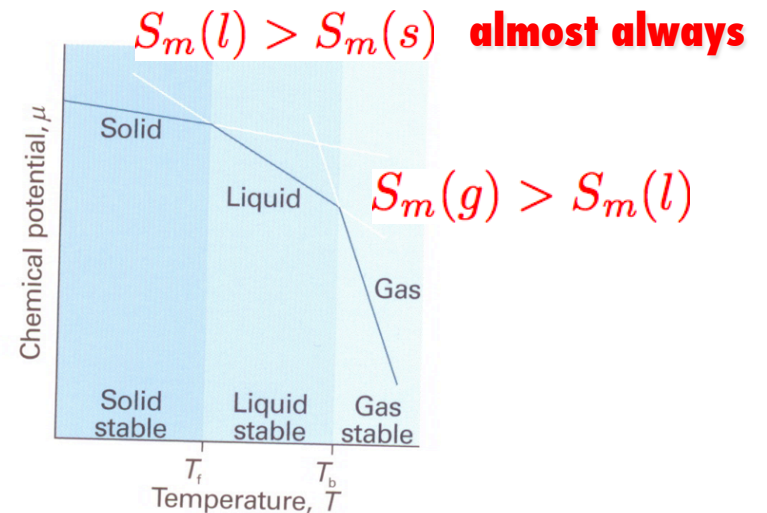
Temperature dependence

$$\left(\frac{\partial \mu}{\partial T}\right)_p = \frac{1}{n}\left(\frac{\partial G}{\partial T}\right)_p = -\frac{S}{n} = -S_m$$

$S_m(g) > S_m(l)$

μ **decreases as temperature increases**

Steeper negative slope for larger entropy

Chemical potential, μ

Solid

Liquid

Gas

Solid stable | Liquid stable | Gas stable

T_f T_b
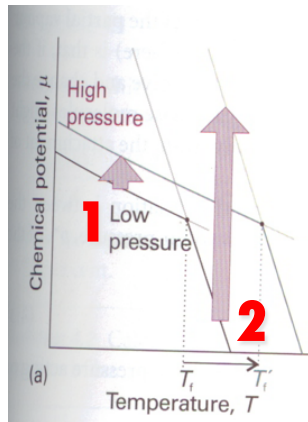
Temperature, T

Pressure dependence

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{1}{n}\left(\frac{\partial G}{\partial p}\right)_V = \frac{V}{n} = V_m$$

Increase of pressure results in increase of μ
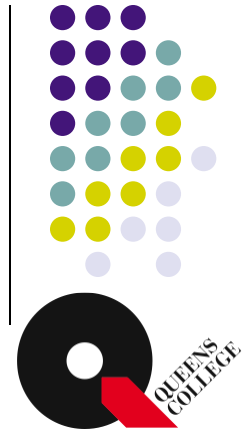
$V_m(1) < V_m(2)$

Increase of pressure increases the transition temperature
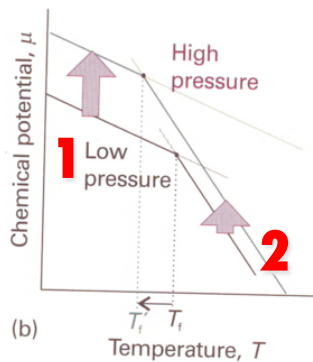
$V_m(1) > V_m(2)$

Increase of pressure decreases the transition temperature

Effect of external pressure on vapour pressure

$$d\mu(l) = d\mu(g)$$

Any change in liquid chemical potential should result in the same change in vapour chemical potential
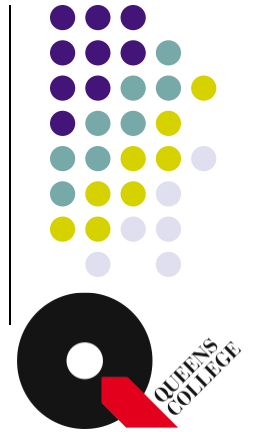
Effect of external pressure on vapour pressure

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Any change in liquid chemical potential should result in the same change in vapour chemical potential

At constant temperature

pressure applied to vapor

$$V_m(l)dP = V_m(g)dp = \frac{RT}{p}dp$$

pressure applied to liquid

$$\int_{p^*}^{p+\Delta P} V_m(l)dP = RT \int_{p^*}^{p} \frac{dp}{p} = RT \ln\left(\frac{p}{p^*}\right)$$

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Effect of external pressure on vapour pressure

$$d\mu(l) = d\mu(g)$$ **Any change in liquid chemical potential should result in the same change in vapour chemical potential**
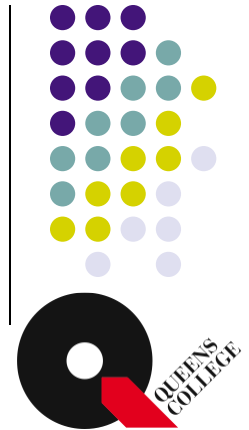
At constant temperature

$$V_m(l)dP = V_m(g)dp = \frac{RT}{p}dp$$

$$\longrightarrow \quad \int_{p^*}^{p+\Delta P} V_m(l)dP = RT\int_{p^*}^{p}\frac{dp}{p} = RT\ln\left(\frac{p}{p^*}\right)$$

Pressure to liquid in addition to the vapor pressure

Assume $V_m(l)$ is insensitive to pressure

$$(p + \Delta P - p^*)V_m(l) = RT\ln\left(\frac{p}{p^*}\right)$$

Assume $\Delta P \gg (p - p^*)$ $\quad\Longrightarrow\quad$ $\Delta P V_m(l) \approx RT\ln\left(\frac{p}{p^*}\right)$

$$\Longrightarrow \quad p \approx p^* e^{\frac{\Delta P}{RT}V_m(l)}$$
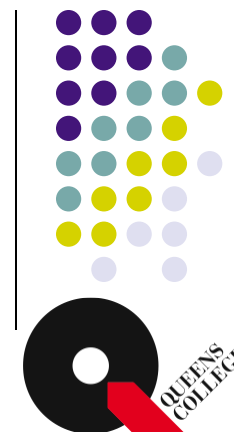
Determining boundaries in phase diagram

If phases α and β are in equilibrium, $\mu_\alpha(p,T) = \mu_\beta(p,T)$

$$\longrightarrow \quad d\mu_\alpha(p,T) = d\mu_\beta(p,T)$$

Determining boundaries in phase diagram

If phases α and β are in equilibrium, $\mu_\alpha(p,T) = \mu_\beta(p,T)$

$$\longrightarrow \quad d\mu_\alpha(p,T) = d\mu_\beta(p,T)$$

$$d\mu_\alpha(p,T) = -S_{\alpha,m}dT + V_{\alpha,m}dp = -S_{\beta,m}dT + V_{\beta,m}dp = d\mu_\beta(p,T)$$

$$(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT$$

Determining boundaries in phase diagram

If phases α and β are in equilibrium, $\mu_\alpha(p,T) = \mu_\beta(p,T)$

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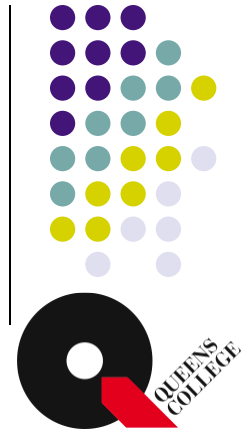$$(V_{\beta,m} - V_{\alpha,m})dp = (S_{\beta,m} - S_{\alpha,m})dT$$

$$\uparrow \qquad\qquad\qquad \uparrow$$

$$\Delta_{trs}V \qquad\qquad\qquad \Delta_{trs}S$$

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

Solid-liquid transition (fusion)

positive except for ³He

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T} \qquad \longrightarrow \qquad \frac{dp}{dT} = \frac{\Delta_{fus}H}{T\Delta_{fus}V}$$
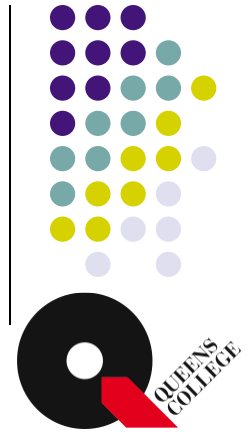
positive and small in general

If $\quad \dfrac{\Delta_{fus}H}{T\Delta_{fus}V} \quad$ is insensitive to p and T,

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

$$\longrightarrow \quad p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln\left(\frac{T}{T^*}\right) = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln\left(1 + \frac{T-T^*}{T^*}\right)$$

$$\approx p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V} \frac{T-T^*}{T^*} \qquad \text{for } T - T^* << T^*$$

Liquid-vapor transition

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

⟵ **positive**

⟵ **positive, much larger than that of the solid-liquid transition**

Boiling temperature is more sensitive to pressure

Liquid-vapor transition

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

← positive

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Boiling temperature is more sensitive to pressure

$$\Delta_{vap}V \approx V_m(g) = \frac{RT}{p}$$

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

Clausius-Clapeyron equation

Liquid-vapor transition

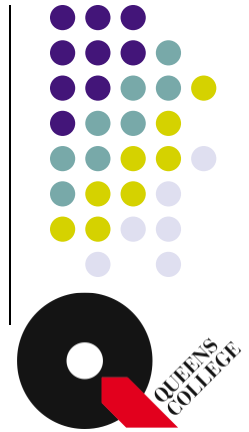$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V}$$

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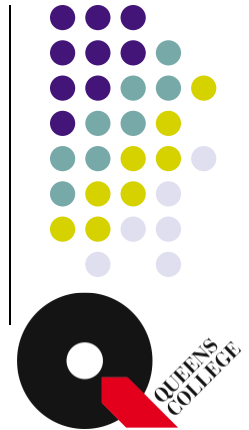
$$\Delta_{vap}V \approx V_m(g) = \frac{RT}{p}$$

⟶ $$\frac{dp}{pdT} = \frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$ **Clausius-Clapeyron equation**

$$\int_{p^*}^{p} dp\ln p = \ln(p/p^*) = \int_{T}^{T^*} dT\,\frac{\Delta_{vap}H}{RT^2} \approx -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$\Delta_{vap}H$ **is assumed to be independent of temperature**

$$p = p^*e^{-\chi}$$ **where** $$\chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

Classification of phase transition (Ehrenfest)

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

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

(i) First order phase transition (boiling,melting,...)

$\Delta_{trs}V$ and $\Delta_{trs}H$ are finite.

$\left(\frac{\partial \mu}{\partial T}\right)_T$ and $\left(\frac{\partial \mu}{\partial p}\right)_T$ are discontinuous.

C_p is infinite.

(ii) Second order phase transition (conducting-superconducting,...)

$\Delta_{trs}V$ and $\Delta_{trs}H$ are zero.

$\left(\frac{\partial \mu}{\partial T}\right)_T$ and $\left(\frac{\partial \mu}{\partial p}\right)_T$ are continuous.

C_p is discontinuous.