

Physical transformations

Phase diagrams

Number of phases

Gases – one single phase (even gaseous mixtures)

Solids – one solid one phase, two solids – two phases. Mixture of solids could be a single phase if the distribution of the components is uniform on a microscopic scale

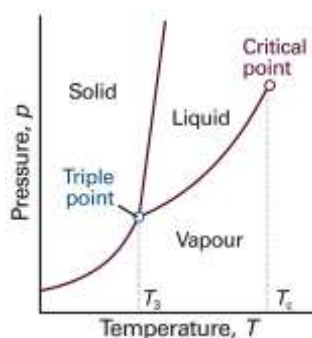
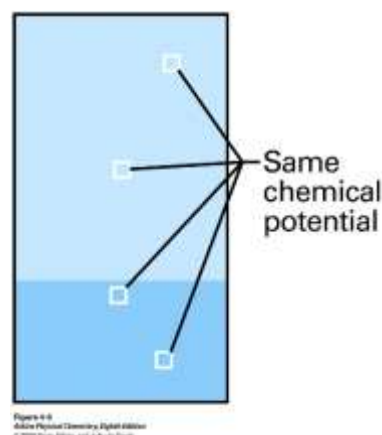
Liquids – miscible liquids form a single phase

e.g. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ is a 3-phase system.

At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present.

For a one-component system, $\mu = \bar{G}$. For more components we will define later.

At eq. ΔG must be 0. For two phases, $dG = (\mu_2 - \mu_1)dn$ implies transfer of dn moles of material from one phase to the other. $dG = 0$ will be true when $\mu_2 = \mu_1$.



The phase rule

$F = C - P + 2$; F is the degrees of freedom, C the number of components and P the number of phases.

Component: Chemically independent constituent of a system. The # of components is the minimum no. of independent species necessary to define the composition of all the phases present in the system. E.g. NaCl in water has only two components Na^+ and H_2O as no. of Cl^- ions equals the no. of Na^+ ions.

Single component, single phase system $F = 2$. We can change pressure and temperature independently of each other.

For an equilibrium between two phases (e.g. solid-liquid), if we change T , then p will follow on the s-l equilibrium curve. $\therefore F = 1$. $\mu(\text{s}, p, T) = \mu(\text{l}, p, T)$ gives one equation that relates p and T .

For an equilibrium between the three phases, $F = 0$. For example, T_3 of water occurs at 273.16 K, 611 mbar. $\mu(s, p, T) = \mu(l, p, T) = \mu(g, p, T)$ gives two independent equations which give a unique solution for p and T .

Derivation

The total no. of intensive variables: p and T , count as 2. In each phase the mole fractions of $C - 1$ components make it $P(C - 1)$. So total $P(C - 1) + 2$.

At equilibrium, the chemical potential of a component must be the same in each phase, i.e. $\mu(\alpha, p, T) = \mu(\beta, p, T) = \dots$ for P phases. Implies we need to satisfy $P - 1$ such equations for each component. For all components we need to remove $C(P - 1)$ degrees of freedom.

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

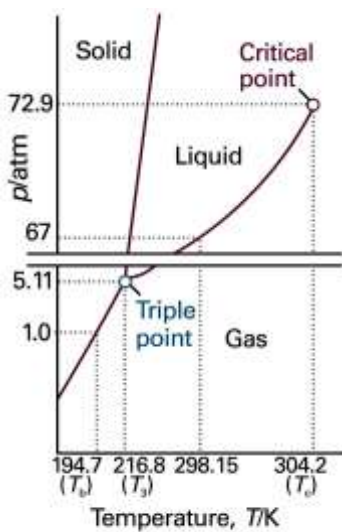


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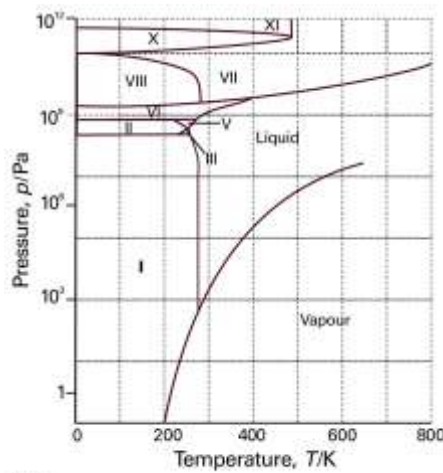


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Temperature dependence of phase stability

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m. \text{ Explains the s-l-v phase stability}$$

Response of melting to applied pressure

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m. \text{ Usually the } V_m(l) > V_m(s). \text{ So, m.p. inc. on application of pressure.}$$

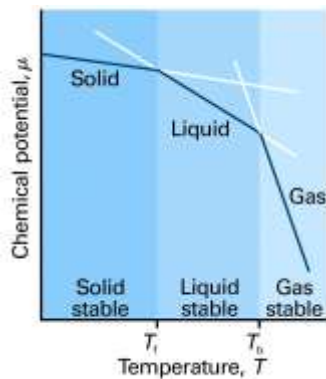


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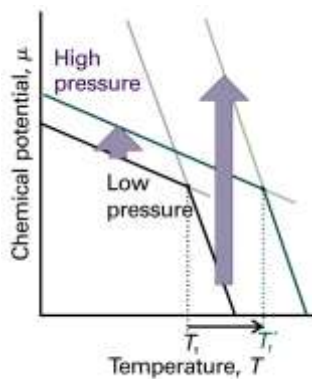


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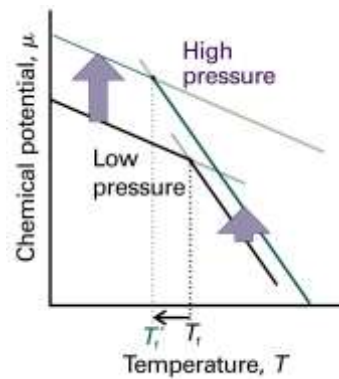


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Location of phase boundaries

At eq. the changes in chemical potential of the two phases must be equal: $d\mu(\alpha) = d\mu(\beta)$

$$\text{i.e. } -S_m(\alpha)dT + V_m(\alpha)dp = -S_m(\beta)dT + V_m(\beta)dp$$

$$\text{or } \{V_m(\beta) - V_m(\alpha)\}dp = \{S_m(\beta) - S_m(\alpha)\}dT$$

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

Solid-liquid boundary

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

ΔH_{fus} is +ve and ΔV_{fus} is usually +ve and always small. So, v. steep slope. Assume ΔH and ΔV do not change much with T .

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

For small x , $\ln(1+x) = x$, $\ln \frac{T}{T^*} = \ln(1 + \frac{T-T^*}{T^*}) = \frac{T-T^*}{T^*}$

Therefore, $p = p^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V} (T - T^*)$, a steep straight line equation.

Liquid-vapor boundary

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

Enthalpy change is +ve, volume change is large and +ve. dp/dT is +ve but small. Or dT/dp is large. i.e. the boiling temp. is more responsive to pressure than the freezing temperature.

$V_m(g) \gg V_m(l)$. Therefore, $\Delta_{vap}V \sim V_m(g)$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{TV_m(g)} = \frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} \quad (\text{for I.G.}) \rightarrow$$

$$\frac{d \ln p}{dT} = \frac{\Delta_{vap}H}{RT^2} \quad \text{Clausius Clapeyron equation}$$

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

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

Similar is the *solid-vapor boundary*

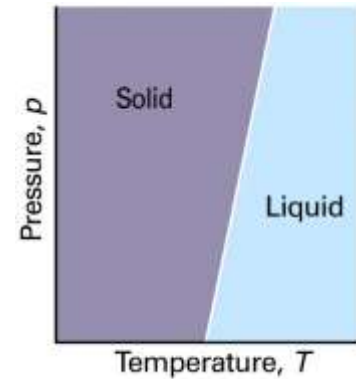


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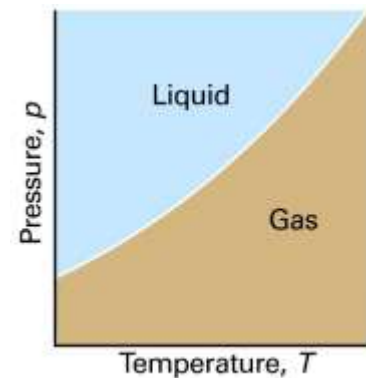


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Ehrenfest classification

First order phase transition: the first derivative of the chemical potential with respect to temperature is discontinuous.

Second order phase transition: The first derivative is continuous but not the second derivative

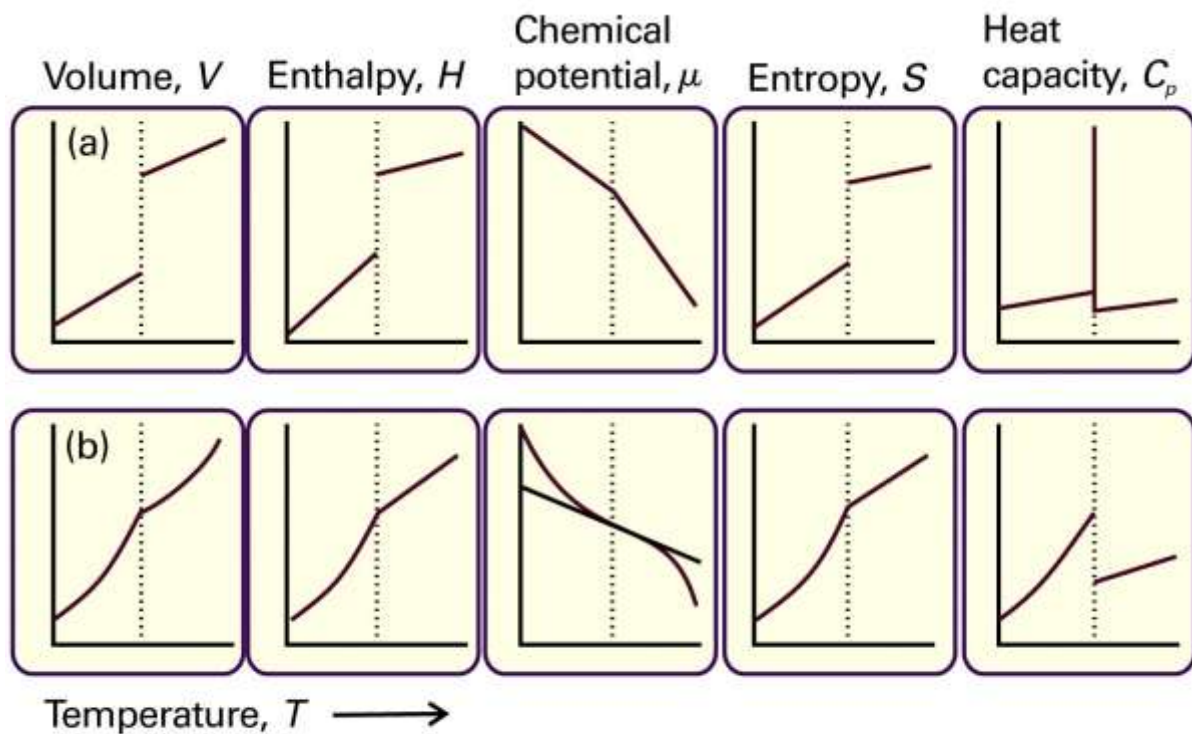


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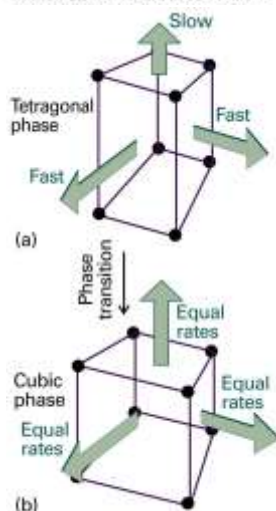


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