Use of Maxwell Relations:

- What is the Internal Pressure ?

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$$

$$dU = -PdV + TdS$$

$$\frac{dU}{dV} = -P + T\frac{dS}{dV}$$

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

$$\boxed{dU = C_V\,dT + \left(\left(\frac{\alpha}{\kappa}\right)T - P\right)dV = TdS - PdV}$$

- What is $\left(\frac{\partial H}{\partial P}\right)_T$?

$$dH = VdP + TdS$$

$$\frac{dH}{dP} = V + T\frac{dS}{dP}$$

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

$$\left(\frac{\partial H}{\partial P}\right)_T = V(1 - \alpha T)$$

$$\boxed{dH = VdP + TdS = C_P\,dT + V(1 - \alpha T)dP}$$

- Determination of C_P -C_V

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - C_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial (PV)}{\partial T}\right)_P - C_V$$

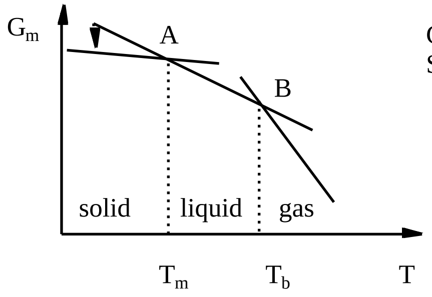
$$C_P - C_V = C_V\left(\frac{\partial T}{\partial T}\right)_P + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - C_V$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\frac{\alpha}{\kappa}\alpha V$$

$$\boxed{C_P - C_V = VT\frac{\alpha^2}{\kappa}}$$

Properties of the Gibbs Free Energy

- Temperature Dependence of the Gibbs Free Energy



Constant Pressure
Single Component System

$$dG_m = V_m dP - S_m dT$$

$$\left(\frac{\partial G_m}{\partial T}\right)_P = -S_m$$

S_m (S) < S_m (L) << S_m (V)

At point A the solid is in equilibrium with the liquid G_m(S)= G_m(L)
At point B the liquid is in equilibrium with the vapor G_m(L)= G_m(V)

- Gibbs-Helmoltz Equation:

  Useful in Applications to Chemical Equilibria

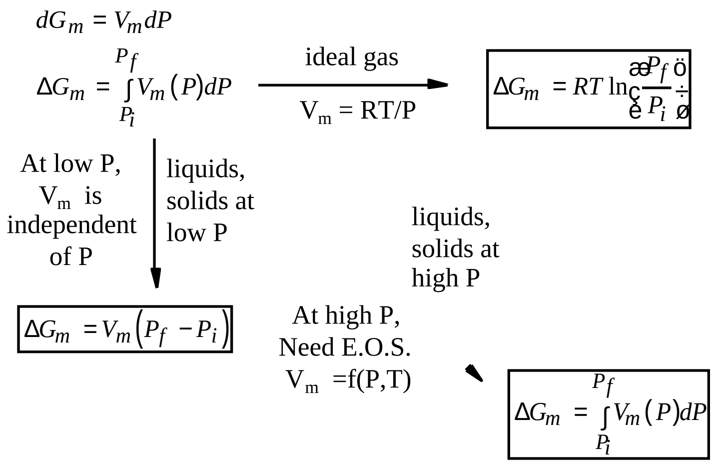
$$\left(\frac{\partial G_m}{\partial T}\right)_P = -S_m = \frac{G_m - H_m}{T}$$

$$\left(\frac{\partial G_m}{\partial T}\right)_P - \frac{G_m}{T} = \frac{-H_m}{T}$$

$$\frac{1}{T}\left(\frac{\partial G_m}{\partial T}\right)_P - \frac{G_m}{T^2} = \frac{-H_m}{T^2}$$

$$\boxed{\begin{gathered}\left(\frac{\partial\left(\frac{G_m}{T}\right)}{\partial T}\right)_P = \frac{-H_m}{T^2}\\ \left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = \frac{-\Delta H}{T^2}\end{gathered}}$$

- Pressure Dependence of the Gibbs Free Energy at cst T:



$$dG_m = V_m dP$$

$$\Delta G_m = \int_{P_i}^{P_f} V_m(P)\,dP \xrightarrow[V_m = RT/P]{\text{ideal gas}} \boxed{\Delta G_m = RT\ln\left(\frac{P_f}{P_i}\right)}$$

At low P, V_m is independent of P

liquids, solids at low P

$$\boxed{\Delta G_m = V_m\left(P_f - P_i\right)}$$

liquids, solids at high P

At high P, Need E.O.S. $V_m = f(P,T)$

$$\boxed{\Delta G_m = \int_{P_i}^{P_f} V_m(P)\,dP}$$

Phase Diagram of Single Component Materials

- **Phase Diagram: P = f(V,T)**
  - Coexistence Curves
  - Triple Point
  - Critical Point
- **Location of Phase Boundaries:**

$$\left(\frac{\partial G_m}{\partial P}\right)_T = V_m$$

  - if $V_m(L) > V_m(S)$ then T_m increases with Pressure (general)
  - if $V_m(L) < V_m(S)$ then T_m decreases with increasing pressure (water, etc..)

- Two phases α and β are in equilibrium at temperature T and pressure P, if $G_m^\alpha(P,T) = G_m^\beta(P,T)$

  Let us change P by dP and find out what is the corresponding dT required to preserve the equilibrium between the two phases.

  Changes of T by dT and P by dP lead to a change of G by dG

  $dG_m^\alpha = -S_m^\alpha\, dT + V_m^\alpha\, dP$ for the α phase and

  $dG_m^\beta = -S_m^\beta\, dT + V_m^\beta\, dP$ for the β phase

  To preserve equilibrium conditions,

  $G_m^\alpha + dG_m^\alpha = G_m^\beta + dG_m^\beta$ which implies

  $dG_m^\alpha = -S_m^\alpha\, dT + V_m^\alpha\, dP = dG_m^\beta = -S_m^\beta\, dT + V_m^\beta\, dP$

  $(S_m^\beta - S_m^\alpha)\, dT = (V_m^\beta - V_m^\alpha)\, dP$

$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}}$$

Clapeyron Equation

(describes the α ⟷ β coexistence curve)

Note at equilibrium, $\Delta G = \Delta H - T\,\Delta S = 0$ for the transition

- Solid - Liquid Equilibrium

$$\frac{dP}{dT} = \frac{\Delta H_{fus}(T,P)}{T\Delta V_{fus}(T,P)} \qquad \boxed{P = P^* + \frac{\Delta H_{fus}(T^*,P^*)}{T\Delta V_{fus}(T^*,P^*)}\ln\left(\frac{T}{T^*}\right)}$$

if ΔH_{fus} and ΔV_{fus} can be assumed independent of T and P

- Liquid - Vapor Equilibrium

$$\frac{dP}{dT} = \frac{\Delta H_{vap}(T,P)}{T\Delta V_{vap}(T,P)} \qquad \frac{\Delta H_{vap}(T,P)}{TV_{vap}(T,P)} = \frac{\Delta H_{vap}(T,P)}{\frac{TRT}{P}}$$

$$\frac{dP}{P} = \frac{\Delta H_{vap}(T,P)}{R}\frac{dT}{T^2}$$

$$\boxed{\ln\left(\frac{P}{P^*}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)}$$

if ΔH_{vap} can be assumed independent of T and P.

- Solid - Vapor Equilibrium:

$$\frac{dP}{dT} = \frac{\Delta H_{sub}(T,P)}{T\Delta V_{sub}(T,P)} \qquad \frac{\Delta H_{sub}(T,P)}{TV_{sub}(T,P)} = \frac{\Delta H_{sub}(T,P)}{\frac{TRT}{P}}$$

$$\frac{dP}{P} = \frac{\Delta H_{sub}(T,P)}{R}\frac{dT}{T^2}$$

$$\ln\left(\frac{P}{P^*}\right) = \frac{-\Delta H_{sub}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

if ΔH_{sub} can be assumed independent of T and P

- Close to the triple point $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
  Because H is a State Function

Properties of Simple Mixtures

- Partial molar value of extensive property X is an Intensive property of a component in a mixture $X_J = \left(\frac{\partial X}{\partial n_J}\right)_{n_I,P,T}$
- Chemical Potential: Partial molar Free Energy: μ_J

Activity: a_J

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{n_I,P,T} = \mu_J + RT\ln(a_J)$$

Standard State (P = 1 bar)

- Ideal Binary A-B Liquid Solution: Raoult's Law
  $P_A = x_A P_A^*$ where $a_A = x_A = n_A / (n_A + n_B)$ mole fraction of A
  $\Delta G_{mix} = (n_A+n_B)RT(x_A \ln(x_A) + x_B \ln(x_B))$
  $\Delta H_{mix} = 0$ $\Delta V_{mix} = 0$ $\Delta S_{mix} = -(n_A+n_B) R (x_A \ln(x_A) + x_B \ln(x_B))$

Phase Diagrams

- Gibbs Rule of Phase: The number of independent intensive state variables necessary to fully define the state of a system is called the variance of the system(or the # of degrees of freedom) and is given by F = C - P + 2 where
  C = # of independent constituents (# of species if no reaction)
  P = # of phases
  2 accounts for T and P
- F = 0 the system is invariant (triple point)
  F = 1 the system is monovariant (L/S, L/V, S/V coexistence)
  F = 2 the system is bivariant (single phase & single component)
  F = 3 the system is trivariant (single phase & 2 components)

Chemical Equilibrium

- Consider the reaction $2A + 3B \longrightarrow C + 2D$
  If we define the extent of reaction by ζ, when the reaction advances by $d\zeta$, the amount of reactants changes by:
  $dn_A = -2\, d\zeta$
  $dn_B = -3\, d\zeta$
  $dn_C = d\zeta$
  $dn_D = 2\, d\zeta$
  At constant temperature and pressure:
  $dG = \mu_A\, dn_A + \mu_B\, dn_B + \mu_C\, dn_C + \mu_D\, dn_D$
  $dG = (-2\mu_A - 3\mu_B + \mu_C + 2\mu_D)\, d\zeta$

In general, for a reaction written as
$\Sigma\nu_J J = 0$, then $dn_J = \nu_J\, d\zeta$

In general $dG = \Sigma\mu_J\, dn_J = (\Sigma\mu_J \nu_J)\, d\zeta$

- Define the Reaction Free Energy as: $\Delta_R G = \left(\frac{\partial G}{\partial \zeta}\right)_{P,T}$
- Define the Chemical Potential of Each Species by:

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{n_I,P,T} = \mu_J + RT\ln(a_J)$$

where a_J is $P_J/P°$ or $f_J/P°$ for gases and unity for pure liquid and pure solids.

$\Delta_R G = \Delta_R G° + RT \ln Q$ (Q is called the reaction quotient)

For the example above $\Delta_R G° = -2\mu_A° - 3\mu_B° + \mu_C° + 2\mu_D°$

and $Q = \dfrac{a_C^1 a_D^2}{a_B^3 a_A^2}$

In general, $\Delta_R G° = \Sigma\nu_J \mu_J°$ and $Q = \prod_J a_J^{\nu_J}$

- At equilibrium, $\Delta_R G = 0$ ⇨ $\boxed{K = \left(\frac{a_C^1 a_D^2}{a_B^3 a_A^2}\right)_{eq}}$

In general, $\boxed{K = \left(\prod_J a_J^{\nu_J}\right)_{eq}}$

RT ln K = - $\Delta_R G^\circ$ and K can be calculated at a given temperature from the free energies of formation for each of the reactants and products

$$\Delta_R G = \sum_J \nu_J \Delta_f G \ (J)$$

Standard Gibbs Free Energy of Formation of 1 mole of Substance J at temperature T and 1 bar found in thermodynamic tables.

Response of Chemical Equilibria to Conditions

- Pressure Dependence:
  K depends on $\Delta G^\circ(T)$ and T and **NOT** on pressure.
- Temperature Dependence:

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P = \frac{-\Delta H}{T^2}$$

$$\left(\frac{\partial\left(\frac{\Delta_R G}{T}\right)}{\partial T}\right)_P = \frac{-\Delta_R H}{T^2}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_R H}{RT^2}$$

where $\Delta_R H^\circ$ is given by:

$$\Delta_R H = \sum_J \nu_J \Delta_f H \ (J)$$

Note that the enthalpic term will also depend on T !!!

If the standard reaction enthalpy can be calculated at T* (generally at 298K) and if the molar heat capacity of reactants and products is known as a function of temperature, an expression for the temperature dependence of the reaction enthalpy can be obtained. Then the equilibrium constant can be calculated at any temperature (T_1) in terms of the equilibrium constant at T* (the latter being calculated from the standard free energy of formation of products and reactants).

$$\int_{K(T^*)}^{K(T_1)} d\ln K = \frac{1}{R}\int_{T^*}^{T_1} \frac{\Delta_R H \quad (T)}{T^2}dT$$

$$\Delta_R H \quad (T) = \Delta_R H \quad (T^*) + \int_{T^*}^{T} \Delta_R C_P(T)\,dT$$

$$\Delta_R C_P(T) = \sum_J \nu_J C_{p,m}(J,T)$$