

Use of Maxwell Relations:

- What is the Internal Pressure ?

$$\pi_T = \left. \frac{\partial U}{\partial V} \right|_T$$

$$dU = -PdV + TdS$$

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

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

$$dU = C_V dT + \frac{\alpha}{\kappa} T - P dV = TdS - PdV$$

- What is $\frac{\partial H}{\partial P}_T$?

$$dH = VdP + TdS$$

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

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

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

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

- Determination of $C_P - C_V$

$$C_P - C_V = \frac{\partial H}{\partial T}_P - C_V$$

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

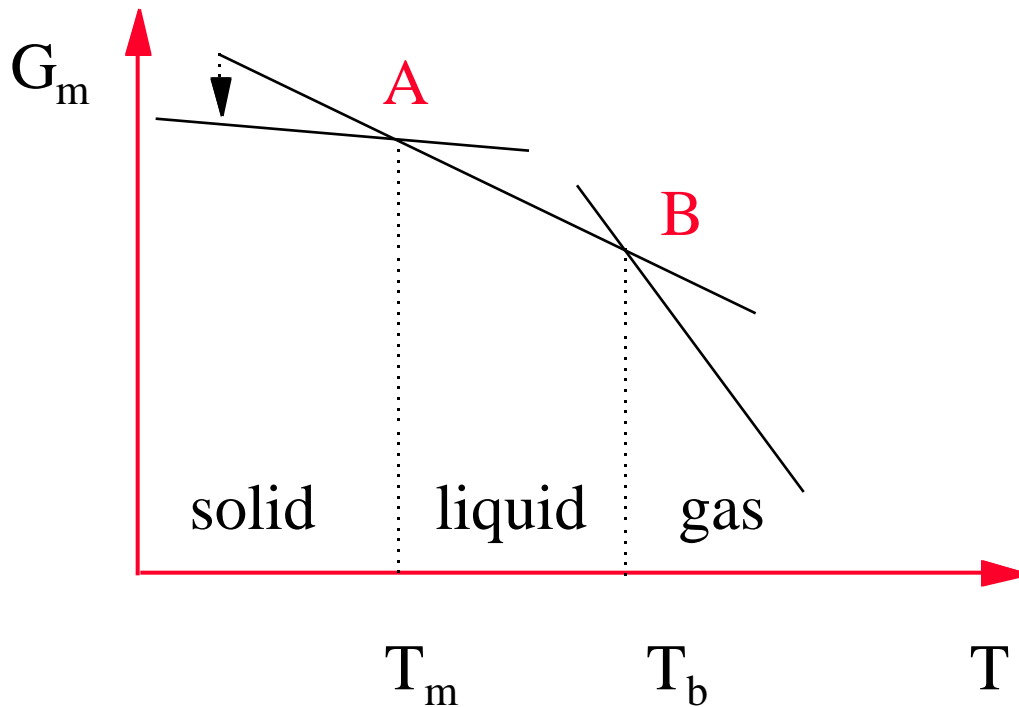
$$C_P - C_V = C_V \frac{\partial T}{\partial T}_P + T \frac{\partial P}{\partial T}_V - P \frac{\partial V}{\partial T}_P + P \frac{\partial V}{\partial T}_P - C_V$$

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

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

Properties of the Gibbs Free Energy

- Temperature Dependence of the Gibbs Free Energy



Constant Pressure
Single Component System

$$dG_m = V_m dP - S_m dT$$

$$\left. \frac{\partial G_m}{\partial T} \right|_P = -S_m$$

$$S_m(\text{S}) < S_m(\text{L}) \ll S_m(\text{V})$$

At point A the solid is in equilibrium with the liquid $G_m(\text{S}) = G_m(\text{L})$

At point B the liquid is in equilibrium with the vapor $G_m(\text{L}) = G_m(\text{V})$

- Gibbs-Helmoltz Equation:

Useful in Applications to Chemical Equilibria

$$\left. \frac{\partial G_m}{\partial T} \right|_P = -S_m = \frac{G_m - H_m}{T}$$

$$\left. \frac{\partial G_m}{\partial T} \right|_P - \frac{G_m}{T} = \frac{-H_m}{T}$$

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

$$\left. \frac{\partial \frac{G_m}{T}}{\partial T} \right|_P = \frac{-H_m}{T^2}$$

$$\left. \frac{\partial \frac{G}{T}}{\partial T} \right|_P = \frac{-H}{T^2}$$

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

$$dG_m = V_m dP$$

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

ideal gas

$$V_m = RT/P$$

$$G_m = RT \ln \frac{P_f}{P_i}$$

At low P,
 V_m is
 independent
 of P

liquids,
 solids at
 low P

liquids,
 solids at
 high P

$$G_m = V_m (P_f - P_i)$$

At high P,
 Need E.O.S.

$$V_m = f(P, T)$$

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

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 and are in equilibrium at temperature T and pressure P, if $G_m(P,T) = G_m(P,T)$
 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
 $dG_m = -S_m dT + V_m dP$ for the phase and
 $dG_m = -S_m dT + V_m dP$ for the phase

To preserve equilibrium conditions,

$$G_m + dG_m = G_m + dG_m \text{ which implies}$$

$$dG_m = -S_m dT + V_m dP = dG_m = -S_m dT + V_m dP$$

$$(S_m - S_m) dT = (V_m - V_m) dP$$

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

Clapeyron Equation

(describes the \longleftrightarrow coexistence curve)

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

- Solid - Liquid Equilibrium

$$\frac{dP}{dT} = \frac{H_{fus}(T, P)}{T V_{fus}(T, P)}$$

$$P = P^* + \frac{H_{fus}(T^*, P^*)}{V_{fus}(T^*, P^*)} \ln \frac{T}{T^*}$$

if H_{fus} and V_{fus} can be assumed independent of T and P

- Liquid - Vapor Equilibrium

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

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

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

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

- Solid - Vapor Equilibrium:

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

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

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

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

- Close to the triple point $H_{sub} = H_{fus} + H_{vap}$
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

$$X_J = \frac{\partial X}{\partial n_J} \quad n_I, P, T$$
- Chemical Potential: Partial molar Free Energy: μ_J

$$\mu_J = \frac{\partial G}{\partial n_J} \quad n_I, P, T = \mu_J^{\text{Standard State}} + RT \ln(a_J)$$

Activity: 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

$$G_{\text{mix}} = (n_A + n_B) RT (x_A \ln(x_A) + x_B \ln(x_B))$$

$$H_{\text{mix}} = 0 \quad V_{\text{mix}} = 0 \quad S_{\text{mix}} = - (n_A + n_B) R (x_A \ln(x_A) + x_B \ln(x_B))$$

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 ξ , when the reaction advances by $d\xi$, the amount of reactants changes by:

$$dn_A = -2 d\xi$$

$$dn_B = -3 d\xi$$

$$dn_C = d\xi$$

$$dn_D = 2 d\xi$$

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

At constant temperature and pressure:

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D$$

$$dG = (-2\mu_A - 3\mu_B + \mu_C + 2\mu_D) d\xi$$

In general $dG = \sum_J \mu_J dn_J = \left(\sum_J \nu_J \mu_J \right) d\xi$

- Define the Reaction Free Energy as:
$${}_R G = \frac{\partial G}{\partial \xi} \quad P, T$$
- Define the Chemical Potential of Each Species by:

$$\mu_J = \frac{\partial G}{\partial n_J} \quad n_I, P, T = \mu_J^\circ + RT \ln(a_J)$$

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

$${}_R G = {}_R G^\circ + RT \ln Q \quad (\text{Q is called the reaction quotient})$$

For the example above ${}_R G^\circ = -2\mu_A^\circ - 3\mu_B^\circ + \mu_C^\circ + 2\mu_D^\circ$

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

In general, ${}_R G^\circ = \sum_J \nu_J \mu_J^\circ$ and $Q = \prod_J a_J^{\nu_J}$

- At equilibrium, $\Delta_r G = 0$ 

$$K = \frac{a_C^1 a_D^2}{a_B^3 a_A^2} \quad eq$$

In general,

$$K = \prod_J a_J^{\nu_J} \quad eq$$

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

$$\Delta_r G^\circ = \sum_J \nu_J f^\circ G(J)$$

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

$$\left. \frac{\partial}{\partial T} \frac{G}{T} \right|_P = \frac{-H}{T^2}$$

$$\left. \frac{\partial}{\partial T} \frac{R G}{T} \right|_P = \frac{-R H}{T^2}$$

$$\left. \frac{\partial \ln K}{\partial T} \right|_P = \frac{R H}{R T^2}$$

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

$$R H = \sum_J \nu_J f H (J)$$

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).

$$\frac{K(T_1)}{K(T^*)} = \frac{1}{R} \int_{T^*}^{T_1} \frac{\Delta_r H^\circ(T)}{T^2} dT$$

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(T^*) + \int_{T^*}^T \Delta_r C_p(T) dT$$

$$\Delta_r C_p(T) = \sum_J \nu_J C_{p,m}(J, T)$$