Phase Equilibria, Mixtures, and Solutions

- Properties of phase transitions
 - Abrupt changes in physical properties under very specific conditions of P and T.
- Not satisfactorily explained until the 20th century.
 - Prior to that, there were many erroneous theories.

Why do phase transitions occur?

- Phase transitions are spontaneous processes.
 - A spontaneous process occurs when it is possible to lower the chemical potential.
- But thermodynamics tells us **nothing** about when or how quickly a spontaneous process occurs.
- Thus is it possible to find substances in unstable, metastable, states.
 - Supercooled
 - Superheated
 - Supersaturated
- Metastable states are important in metallurgy and material science.

Properties of Phases of Matter

- Thermodynamic properties may be found for any phase, regardless of whether it is thermodynamically stable at that T and P.
 - Extrapolate from observations in the absence of an established equation of state.
 - The van der Waals equation of state can describe the properties of a gas and of a liquid.
- Properties of any phase can be described through fugacity.

$$\mu(P,T) = \mu^{\circ}(1 \text{ bar},T) + RT \ln\left(\frac{Pf}{P}\right)$$

or

$$\mu(P,T) - \mu^{\circ}(1 \text{ bar},T) = RT \ln P + RT \ln \Phi$$

• Since we wish to connect this with the van der Waals equation, subtract $RT \ln(a/b^2)$ from both sides:

$$\mu(P,T) - \left[\mu^{\circ} + RT \ln\left(\frac{a}{b^{2}}\right)\right]$$
$$= RT \ln P + RT \ln \Phi - RT \ln(a/b^{2})$$
$$= RT \ln\left(\frac{Pb^{2}}{a}\right) + RT \ln \Phi$$
$$\Delta \mu = RT \ln \tilde{P}\Phi$$

• Thus:

$$\frac{\Delta\mu}{RT} = \ln\tilde{P}\Phi$$

- Now examine $\Delta \mu/RT$ for three van der Waals isotherms:
 - Above the critical temperature
 - At the critical temperature
 - Below the critical temperature
- Below the critical temperature, coexistence of liquid and vapour are possible.

- Coexistence shows up in Figure 6.1 (c) as an intersection of two curves.
- The stable phase is the one with the lower chemical potential.
- How does chemical potential relate to a van der Waals isotherm in $\tilde{P}\tilde{V}$ space?
 - Note unphysical region characterized by a negative isothermal bulk compressibility:

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

- Note also that there are regions with more than one value of V for a given value of P.
- While a phase transition is occurring, the isothermal bulk compressibility is infinite since a large volume change is occurring at constant pressure.
- For the van der Waals gas, the coexistence line is constructed such that the area above and below the line are equal.

$$P_{\Phi}(V_b - V_e) = \int_{V_e}^{V_b} P(V) dV$$

• Integrating by parts (PdV = d(PV) - VdP) gives:

$$P_{\Phi}(V_b - V_e) = \int_{V_e}^{V_b} [d(PV) - VdP]$$

= $P_{\Phi}(V_b - V_e) - \int_{P(V_e)}^{P(V_b)} V(P)dP$

• Thus

$$\int_{P(V_e)}^{P(V_b)} V(P)dP = 0$$

Some facts about phase transitions

- A spontaneous phase transition is possible when the chemical potential of an existing phase exceeds that of another phase.
- If two phases have equal chemical potential, then they may coexist in any proportion.

Phase Transitions on Isobars

- Consider a pure substance at constant pressure of 1 atm.
- Assume that the substance has
 - One solid phase
 - A single liquid phase
 - Gas phase
- Start with the substance in a solid phase and raise the temperature.
- Fusion occurs at normal melting point.
- Liquid becomes warmer.
- Vaporization occurs at normal boiling point.
- Vapour is warmed.
- This process for Zn is illustrated in Figure 6.4 as a function of μ and T.

Behaviour of Chemical Potential in Phase Transitions

- Consider a plot of chemical potential against temperature.
 - Vertical axis is the chemical potential relative to that at 300 K.
- Recall that:

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

- Therefore the slope of each section of the graph corresponds to the molar entropy of that phase.
- Note that the slope becomes steeper as the system moves from solid to liquid to gas phase.
- Changes in slope mean changes in entropy.
- Recall that:

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

- Therefore the slope (in Figure 6.4) gives information the heat capacity for each phase.
- If the heat capacity is not a constant, then the μ vs T plot will be curved.

Construction of Phase Diagrams

- Phase diagrams are constructed in (P,T) space because they are the natural variables for G.
- Consider the phase diagram for the van der Waals gas.
 - Only liquid and/or vapour are possible.
 - Only one phase can exist in any "area" of the diagram.
 - Above the critical point, the van der Waals gas can be described as being in a "fluid" state.
 - Phases are separated by a liquid-vapour coexistence curve. This means that P and T are constrained by coexistence.

The Triple Point

- For a pure substance that can exist as a solid, a liquid, and a gas, there is one unique (P,T) for the triple point.
- Recall that:

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \overline{V}$$

- Since V
 (g) >> V
 (l) ~ V
 (s), the chemical potential of a gas is very sensitive to pressure relative to that of a condensed phase.
- Reconsider figure 6.1: the slopes of the curves are proportional to the volume.
- A plot of $\mu(T)$ against P will be steeper for a gas than for a condensed phase.

The Triple Point

- There exists some pressure P for which the $\mu(T)$ curves for gas, liquid, and solid intersect in a point. This point is the triple point.
- Consider a pressure below the triple point
- The $\mu(T)$ curve for the liquid phase will be above either the gas or the solid curve.
 - Therefore the liquid phase will not be stable, either by itself or in coexistence with another phase.

- Therefore sublimation is the only phase transition possible
- Solids at pressures below the triple point pressure have vapour pressure.
- Since it is possible for substances to have more than one solid phase, it is possible for any three phases to have a triple point, if each pair can coexist at some (T, P).

Coexistence Lines

• Consider two phases in equilibrium:

$$\Phi_1(T,P) \rightleftharpoons \Phi_2(T,P)$$

• Consider the infinitesimal change in chemical potential of each phase:

$$\mu_1(T + dT, P + dP) = \mu_1(T, P) + d\mu_1$$
$$\mu_2(T + dT, P + dP) = \mu_2(T, P) + d\mu_2$$

• Since the system is at equilibrium before and after the infinitesimal change, it can be shown that:

$$d\mu_1 = d\mu_2$$

• But

 $d\mu = -SdT + VdP$

• Therefore:

$$\begin{aligned} -\overline{S}_1 dT + \overline{V}_1 dP &= -\overline{S}_2 dT + \overline{V}_2 dP \\ (\overline{S}_2 - \overline{S}_1) dT &= (\overline{V}_2 - \overline{V}_1) dP \end{aligned}$$

• Defining

$$\Delta \overline{S}_{\Phi} \equiv \overline{S}_2 - \overline{S}_1$$
$$\Delta \overline{V}_{\Phi} \equiv \overline{V}_2 - \overline{V}_1$$

• Gives the slope of a two phase coexistence line on a phase diagram as:

$$\left(\frac{dP}{dT}\right)_{\Phi} = \left(\frac{\Delta \overline{S}_{\Phi}}{\Delta \overline{V}_{\Phi}}\right)$$

This is the Clapeyron Equation

• Substituting $\Delta \overline{H}_{\Phi} = T \Delta \overline{S}_{\Phi}$ gives:

$$\left(\frac{dP}{dT}\right)_{\Phi} = \left(\frac{\Delta \overline{H}_{\Phi}}{T\Delta \overline{V}_{\Phi}}\right)$$

- Everything in this equation is a state function or a state variable and therefore is independent of the path chosen for the phase transition.
- The coexistence curve between gas and liquid ends in a critical point.
 - The properties of liquid and gas are indistinguishable at the critical point. Therefore

$$\Delta \overline{V}_{\Phi} = 0$$

- But $(dP/dT)_{\Phi}$ is not observed to be infinite.
- This is possible if only $\Delta \overline{S}_{\Phi}$ approaches zero more quickly than $\Delta \overline{V}_{\Phi}$

Is this true for the van der Waals gas?

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

• Therefore:

$$\left(\frac{dP}{dT}\right)_{\overline{V}} = \frac{R}{\overline{V} - b} = \left(\frac{dS}{d\overline{V}}\right)_T$$

• and

$$dS = \frac{Rd\overline{V}}{\overline{V} - b}$$
$$\frac{\Delta S_{\Phi}}{R} = \ln\left(\frac{\overline{V}_2 - b}{\overline{V}_1 - b}\right)$$
$$\frac{\Delta S_{\Phi}}{R} = \ln\left(\frac{\tilde{V}_2 - 1}{\tilde{V}_1 - 1}\right)$$

which approaches zero faster than $\Delta \overline{V}_{\Phi}$ as illustrated in Fig 6.9.

Using the Clapeyron Equation

• Starting with

$$\left(\frac{dP}{dT}\right)_{\Phi} = \left(\frac{\Delta \overline{H}_{\Phi}}{T\Delta \overline{V}_{\Phi}}\right)$$

- Use $\Delta \overline{V}_{\Phi} \equiv \overline{V}_2 \overline{V}_1$ and find $\overline{V} = \overline{V}(T, P)$ using the equation of state for each phase.
- Use $\Delta \overline{H}_{\Phi} \equiv \overline{H}_2 \overline{H}_1$ and find $\overline{H} = \overline{H}(T, P)$ using $(\partial H/\partial P)_T = V T(\partial V/\partial T)_P$ and the equation of state for each phase.
- and integrate:

$$\int_{T_i}^{T_f} \left(\frac{dP}{dT}\right)_{\Phi} dT = \int_{T_i}^{T_f} \left(\frac{\Delta \overline{H}_{\Phi}}{T\Delta \overline{V}_{\Phi}}\right) dT = \int_{P_i}^{P_f} dP$$

- This integration is nontrivial for most equations of state.
- But what if one phase is an ideal gas?

Vapour-Liquid Coexistence and Vapour-Solid Coexistence

- Consider a gas far enough from the critical point that $\overline{V}_g >> \overline{V}$ (condensed phase) is a valid statement.
- Therefore

$$\Delta \overline{V}_{\Phi} = \overline{V}_{a}$$

• Thus the Clapeyron Equation becomes:

$$\left(\frac{dP}{dT}\right)_{\Phi} = \frac{\Delta \overline{H}_{\Phi}}{T_{\Phi} \Delta \overline{V}_{\Phi}} \cong \frac{\Delta \overline{H}_{\Phi}}{T_{\Phi} \overline{V}_{g}} = \frac{\Delta \overline{H}_{\Phi} P}{RT_{\phi}^{2}}$$

which can be integrated if $\Delta \overline{H}_{\Phi}$ is assumed constant:

$$\int_{P_i}^{P_f} \frac{dP}{P} \cong \frac{\Delta \overline{H}_{\Phi}}{R} \int_{T_i}^{T_f} \frac{dT}{T^2}$$

$$P(T_f) = P(T_i) \exp\left[-\frac{\Delta \overline{H}_{\Phi}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i}\right)\right]$$

Coexistence of Condensed Phases

- Consider Solid-Liquid (fusion) and Solid-Solid Coexistence
 - Cannot assume that the volume of one phase is significantly greater than the other.
 - Cannot assume an equation of state that is as convenient to work with as is that of the ideal gas.

Solid-Liquid Coexistence

• Start with the Clapeyron equation:

$$\left(\frac{dP}{dT}\right)_{\Phi} = \frac{\Delta S_{\Phi}}{\Delta V_{\Phi}}$$

- Assume that ΔV_{Φ} is constant since both phases have low compressibility.
- Assume that ΔS_{Φ} is constant since the change in molecular order that occurs with fusion is not strongly dependent on T and P.
- These two assumptions imply that the coexistence line is a straight line.
- Other treatments are semiempirical, such as that of Simon and Glatzel:

$$\frac{P}{P_0} = \left(\frac{T}{T_0}\right)^a - 1$$

where a and P_0 are determined empirically for the substance of interest and T_0 is a reference temperature (usually near the critical temperature).

• Differentiation gives:

$$\left(\frac{dP}{dT}\right)_{fus} = \left(\frac{P_0a}{T_{fus}}\right) \left(\frac{T_{fus}}{T_0}\right)^a$$
$$\frac{\Delta \overline{H}_{fus}}{T_{fus}\Delta \overline{V}_{fus}} = \left(\frac{P_0a}{T_{fus}}\right) \left(\frac{T_{fus}}{T_0}\right)^a$$

which can be interpreted as

$$\frac{\Delta \overline{H}_{fus}}{\Delta \overline{V}_{fus}} \propto P_0 a$$
$$T_{fus} \propto T_{fus} \left(\frac{T_0}{T_{fus}}\right)^a$$

(i.e.) the temperature of fusion corrected by an empirical factor.

Solid-Solid Coexistence

- Coexistence lines are usually observed to be straight.
 - Sometimes nearly vertical which means that there is an entropy change with a negligible volume change.
 - Sometimes nearly horizontal which means that there is a volume change associations with a negligible entropy change.

Thermodynamics of Phase Transitions

• For equilibrium between gas and a condensed phase, it can be shown:

$$\frac{d(\Delta \overline{H}_{\Phi})}{dT} \cong \Delta \overline{C}_{P\Phi}$$

• For vaporization

$$\Delta \overline{C}_{P\Phi} = \overline{C}_P(g) - \overline{C}_P(l) < 0$$

since $\overline{C}_P(l) > \overline{C}_P(g)$ and $\Delta \overline{H}_{vap}$ decreases as T increases.

• Trouton's rule applies to vaporization and sublimation of simple condensed phase (weak intermolecular forces, no H bonds, nonpolar):

$$\Delta \overline{S}_{vap}^{\circ} \cong 10.5R$$
$$\Delta \overline{S}_{sub}^{\circ} \cong 11.5R$$

- Based on the observation of near constant entropy of vaporization or sublimation at pressure of 1 atm.
- Hildebrandt's Rule is based on observations of entropy of vaporization at a constant vapour density of 22.414 L mol⁻¹:

$$\Delta \overline{S}_{vap}^{\circ} \cong 11.1R$$

• Guggenheim's Rule is based on observation of entropy of vaporization at 1/50th of P_c ;

$$\Delta \overline{S}_{vap}^{\circ} \cong 9.0R$$

• Any of these rules may be used to estimate the vapour pressure by replacing $\Delta \overline{H}_{vap}$ with $T_{vap}^{\circ} \Delta \overline{S}_{vap}^{\circ}$ in the integrated Clapeyron equation.

Composition Variables in Mixtures

- Consider a closed system in two-phase equilibrium
 - Below T_{Φ} all in one phase
 - Above T_{Φ} all in other phase
 - But how much is in each phase at T_{Φ} ?
- Define mole fraction:

$$x(i) = \frac{n(i)}{n} = \frac{\text{amount in phase } i}{\text{total amount}}$$

• Mole fractions must add up to 1:

$$\sum_{all \ phases} x(i) = 1$$

• Define molar volume of the system:

$$\overline{V} \equiv \frac{V}{n} = \sum_{all \ phases} \overline{V}(i) \ x(i)$$

. .

• But for two phase equilibrium:

$$\overline{V} = \overline{V}[x(1) + x(2)] = \overline{V}(1)x(1) + \overline{V}(2)x(2)$$

which can be rearranged to:

$$x(2)[\overline{V} - \overline{V}(2)] = x(1)[\overline{V}(1) - \overline{V}]$$

This is the Lever Rule

• Isolating the mole fractions yields:

$$x(1) = \frac{\overline{V} - \overline{V}(2)}{\overline{V}(1) - \overline{V}(2)}$$
$$x(2) = \frac{\overline{V} - \overline{V}(1)}{\overline{V}(2) - \overline{V}(1)}$$

- Some points about notation:
 - One component system: $x(\Phi)$ is the mole fraction in phase Φ
 - Multicomponent system: $x_i(\Phi)$ is the mole fraction of compound *i* in phase Φ .

Solutions and Mixtures

- A solution has atoms randomly dispersed throughout the phase at microscopic level and is homogeneous.
 - Solutions may be solid or liquid
- A mixture has macroscopic regions of the pure constituents and is inhomogeneous.

The Ideal Mixture

- The ideal mixture consists of non-interacting components such as ideal gases that differ only mass.
- Example: a mixture of isotopes of a rare gas 83 Kr and 84 Kr
 - Initially separated in two containers of equal volume.
 - The two containers are joined by a valve.
 - Adiabatically isolated.
 - Same T and P.
 - Valve opened and mixing occurs.
 - \bullet Equilibrium is recognized by equal amounts of each isotope in each container. T and P are unchanged.
 - Spontaneous change, therefore G has decreased.
- At any point in the process:

$$G(\text{total}) = \mu_1 n_1 + \mu_2 n_2$$

where

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

• Since Kr behaves nearly ideally, f_i may be replaced with P_i , the partial pressure of component *i*. Therefore:

$$P = P_1 + P_2$$

which is known as Dalton's Law.

- But, we know pressures are intensive, not extensive.
- Partial pressure can be defined as:

$$P_i = x_i P = partial \ pressure \ of \ component \ i.$$

This is valid if there are no strong interactions between molecules.

Partial Pressure and Thermodynamics

- V is one of the natural variables of U and A.
- -P is the conjugate variable of V. Therefore:

$$\left(\frac{\partial U}{\partial V}\right)_{S,n} = \left(\frac{\partial A}{\partial V}\right)_{T,n} = -P$$

- Neither of these definitions rely on a particular equation of state.
- Consider A (since it is easier to control T than S) at constant T and P:

$$A = \sum_{i} n_i \overline{A}_i = n \sum_{i} x_i \overline{A}_i$$

• Assume that composition is constant (no chemical reactions, system closed) then:

$$\begin{pmatrix} \frac{\partial A}{\partial V} \end{pmatrix}_{T,n} = \sum_{i} x_{i} n \left(\frac{\partial \overline{A}_{i}}{\partial V} \right)_{T,n}$$

$$P = -\sum_{i} x_{i} n \left(\frac{\partial \overline{A}_{i}}{\partial V} \right)_{T,n}$$

$$P_{i} = -x_{i} n \left(\frac{\partial \overline{A}_{i}}{\partial V} \right)_{T,n}$$

and

Can partial pressure be measured?

- Consider an apparatus with two compartments separated by a fixed, rigid semipermeable membrane.
 - H_2 on one side and H_2 and N_2 on the other side.
 - The membrane (Pd foil) is perfectly permeable to ${\rm H}_2$
 - The membrane(Pd foil) is perfectly impermeable to N₂
- At equilibrium, the chemical potential of H₂ is the same on both sides of the membrane and the pressures are different on both sides.
- This method is accessible to very few combinations of membranes and gases.

Mixing

- Consider the change in an extensive quantity such as G, V, S, etc. that accompanies mixing.
- Using G as an example:

$$\Delta G_{mix} = G(x_1, x_2, \ldots)$$

 $-\sum_{i} G(\text{pure, isolated species } i)$

where $G(x_1, x_2, ...)$ is:

$$G(x_1, x_2, \ldots) = n \sum_i x_i \mu_i(x_i)$$

$$= n \sum_{i} x_i (\mu_i^\circ + RT \ln P_i)$$

Assume T, P, and n to be constant.

• For each pure component i:

$$G(\text{pure } i) = n_i \mu_i (x_i = 1) = n_i (\mu_i^{\circ} + RT \ln P)$$

• Therefore:

$$\Delta G_{mix} = n \sum_{i} x_i (\mu_i^{\circ} + RT \ln P_i)$$
$$-n \sum_{i} x_i (\mu_i^{\circ} + RT \ln P)$$

But $P_i = x_i P$. Therefore

$$\Delta G_{mix} = n \sum_{i} x_i (\mu_i^{\circ} + RT \ln P + RT \ln x_i)$$
$$-n \sum_{i} x_i (\mu_i^{\circ} + RT \ln P)$$
$$\Delta G_{mix} = nRT \sum_{i} x_i \ln x_i$$

• For a two component system where $x_2 = 1 - x_1$, this becomes:

$$\frac{\Delta G_{mix}(x_1)}{nRT} = x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)$$

• Since $\Delta S_{mix} = -(\partial \Delta G_{mix}/\partial T)_{x_i}$

$$\Delta S_{mix} = -nR\sum_{i} x_i \ln x_i$$

• Similarly

$$\Delta V_{mix} = (\partial \Delta G_{mix} / \partial P)_{x_i} = 0$$
$$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix} = 0$$
$$\Delta U_{mix} = \Delta H_{mix} - \Delta (PV)_{mix} = 0$$
$$\Delta A_{mix} = \Delta U_{mix} - T\Delta S_{mix} = \Delta G_{mix}$$

- Spontaneous ideal mixing is accompanied by:
 - An increase in entropy
 - A decrease in Gibbs free energy
 - A decrease in Helmholtz free energy
 - No change in enthalpy or internal energy

Nonideal Mixing

• Use fugacity to describe nonideal behaviour.

• Define partial fugacity using Lewis-Randall Rule

$$f_i = x_i f$$

where f is the fugacity of pure i at the T and P of the solution.

• Thus the chemical potential of component i becomes:

$$\mu_i(T, x_i) = \mu^{\circ}(\text{pure } i, T) + RT \ln f + RT \ln x_i$$

• Implicit in this is the assumption that the solution obeys Amagat's Law:

$$V = \sum_i n_i \overline{V}(\text{pure } i)$$

This is reasonable for gases, but must be examined carefully for condensed phases.

• Consider the fugacity of pure condensed phase:

$$RT\ln\left(\frac{f}{P}\right) = \int_0^P \left(\overline{V} - \frac{RT}{P}\right) dP$$

• If there is a phase transition between 0 and P then the integral should be considered as two term, one from 0 and P_{Φ} , the other from P_{Φ} to P:

$$RT \ln\left(\frac{f}{P}\right) = \int_{0}^{P_{\Phi}} \left(\overline{V} - \frac{RT}{P}\right) dP$$
$$+ \int_{P_{\Phi}}^{P} \left(\overline{V} - \frac{RT}{P}\right) dP$$

• Expanding the last integral into two terms:

$$RT \ln\left(\frac{f}{P}\right) = RT \ln\left(\frac{f_{\Phi}}{P_{\Phi}}\right)$$
$$+ \int_{P_{\Phi}}^{P} \overline{V}(\text{condensed phase}) dP - RT \ln\left(\frac{P}{P_{\Phi}}\right)$$

• Assuming that the volume of the condensed phase is constant over the interval under consideration:

$$\int_{P_{\Phi}}^{P} \overline{V}(\text{condensed phase}) dP = \overline{V}(P - P_{\Phi})$$

• Thus:

or

$$RT \ln\left(\frac{f}{P}\right) = RT \ln\left(\frac{f_{\Phi}}{P}\right) + \overline{V}(P - P_{\Phi})$$
$$f = f_{\Phi} \exp\left[\frac{\overline{V}(P - P_{\Phi})}{RT}\right]$$

which may be rewritten as:

$$f = P_{\Phi}\left(\frac{f_{\Phi}}{P_{\Phi}}\right) \exp\left[\frac{\overline{V}(P - P_{\Phi})}{RT}\right]$$

Excess Functions

- Excess functions describe deviations from ideal behaviour.
- Consider excess free energy:

$$G^E = G(\text{real}: T, P, x_i) - G(\text{ideal}: T, P, x_i)$$

- If $G^E > 0$ then deviations from ideality are positive.
- If $G^E < 0$ then deviations from ideality are negative.
- A reference or standard state must be considered and f is defined with respect to that.
- G. N. Lewis defined activity a_i as:

$$a_i(T, P, x_1, x_2, \ldots) = \frac{f_i(T, P, x_1, x_2, \ldots)}{f_i^{\circ}(T, P^{\circ}, x^{\circ})}$$

- If all species are referred to the same standard state, then the equilibrium requirement of equal fugacity in any component can be replaced by a requirement of equal activity.
- The activity coefficient is defined as:

$$\gamma_i = \frac{a_i}{x_i}$$

Therefore:

$$f_i(T, P, x) = f_i^{\circ}(T, P^{\circ}, x^{\circ})a_i(T, P, x) = f_i^{\circ}\gamma_i x_i$$

Ideal Solution

• Fugacity is directly proportional to mole fraction.

$$f_i(\text{ideal}; T, P, x_i) = K_i(T, P)x_i$$

- The definition of K_i depends on the type of ideal solution.
- Consider excess free energy:

$$\overline{G}_i^E = \overline{G}_i(\text{real}) - \overline{G}_i(\text{ideal})$$
$$= \mu_i(\text{real}) - \mu_i(\text{ideal})$$
$$= \mu_i^\circ(\text{real}) + RT \ln f_i(\text{real})$$
$$-\mu_i^\circ(\text{ideal}) - RT \ln f_i(\text{ideal})$$
$$= RT \ln \frac{f_i(\text{real})}{f_i(\text{ideal})}$$

since $\mu_i^{\circ}(\text{real}) = \mu_i^{\circ}(\text{ideal})$

• Thus

$$\overline{G}_i^E = RT \ln \frac{f_i(\text{real})}{K_i x_i}$$

- For an ideal solution $K_i = f_i^{\circ}$ and $\gamma_i = 1$
- The activity coefficient is defined by:

$$\gamma_i$$
(real or ideal) = $\frac{f_i$ (real or ideal)}{f_i^{\circ} x_i}

and

$$\overline{G}_i^E = RT \ln \frac{f_i^{\circ} \gamma_i x_i}{f_i^{\circ} x_i} = RT \ln \gamma_i$$

Thus

$$G^E = \sum_i n_i \overline{G}_i^E = nRT \sum_i x_i \ln \gamma_i$$

Phase Separation and Spontaneous Unmixing (The physical chemistry of salad dressing)

- Separation of a one-phase liquid solution into two phases observed
 - Extraction
 - Salad Dressing
 - Lava Lamps
 - Often occurs as a result of a change in composition or temperature.
- $\bullet\,$ Consider pure liquid of each component at standard T and P

$$P^{\circ} = P$$

 $x^{\circ} =$ pure compound i

- Consider only a binary solution $(x_1 + x_2 = 1)$
 - G^E goes to zero as x_1 or x_2 goes to zero.
 - The simplest empirical function that satisfies this is:

$$G^E = nAx_1x_2$$
$$\ln \gamma_1 = \frac{A}{RT}x_2^2$$

where A is empirically determined.

- What affects the value of A:
 - Temperature
 - Chemical nature of components 1 and 2 and their interaction.

• NOT the composition

- Since A contains information about non-ideal behaviour, it must be related to the activity of each component.
- Recall that:

$$G^E = \sum_i n_i \overline{G}_i^E = nRT \sum_i x_i \ln \gamma_i$$

Therefore:

$$nRT\sum_{i} x_i \ln \gamma_i = G^E = nAx_1x_2$$

 $nRT(x_1\ln\gamma_1 + x_2\ln\gamma_2) = nAx_1x_2$

$$nRT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) = nRT \frac{A}{RT} x_1 x_2 (x_1 + x_2)$$

$$= nRT\left(x_1\frac{A}{RT}x_2^2 + x_2\frac{A}{RT}x_1^2\right)$$

Thus:

$$\ln \gamma_1 = \frac{A}{RT} x_2^2$$
$$\ln \gamma_2 = \frac{A}{RT} x_1^2$$

- Spontaneous separation can occur only if it results in the lowering of the free energy at constant T and P.
 - But phase separation implies a decrease in entropy.
 - Therefore a decrease in enthalpy is implied.
- Consider excess free energy.

$$\begin{split} G(\text{real} &= G^E + G(\text{ideal}) \\ &= G^E + \sum_i n_i \mu_i(\text{ideal}) \\ &= G^E + \sum_i n_i (\mu_i^\circ + RT \ln f_i) \\ &= G^E + n \sum_i x_i (\mu_i^\circ + RT \ln f_i^\circ x_i) \\ &= G^E + n \sum_i x_i (\mu_i^\circ + RT \ln f_i^\circ) \\ &\quad + nRT \sum_i x_i \ln x_i) \\ &= G^E + n \sum_i x_i \mu_i(\text{pure } i) \\ &\quad + nRT \sum_i x_i \ln x_i) \end{split}$$

Therefore:

$$\overline{G}(\text{real}) = Ax_1x_2 + x_1\mu_1(\text{pure}) + x_2\mu_2(\text{pure})$$
$$+RT(x_1\ln x_1 + x_2\ln x_2)$$

• Recall

$$\Delta G_{mix}(\text{real}) = G^E + \Delta G_{mix}(\text{ideal})$$
$$\frac{\Delta G_{mix}(x_1)}{RT} = \frac{A}{RT} x_1 (1 - x_1)$$
$$+ x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)$$

• The larger the value of A/RT the more immiscible the mixture.

• For A/RT > 2, there exists a value for which ΔG_{mix} has a local maximum and two values which are local minima, i.e. there exists a range of x_1 such that

$$\left(\frac{\partial^2 \Delta \overline{G}_{mix}}{\partial x_1^2}\right)_{T,P,n} < 0$$

- The solution will spontaneously separate into two layers, each with composition corresponding to that of one of the local minima.
- The amount in each liquid phase will be determined by the lever rule.
- For A/RT < 2, there is one stable homogeneous phase.
- When A/RT = 2, the solution is at the critical solution temperature (or the consolute temperature).
 - Critical point for the mixture where the two phases are indistinguishable.

Activity in the Nonideal Solution

• Recall that

$$a_1 = \gamma_1 x_1$$

and that

$$\ln \gamma_1 = \frac{A}{RT} {x_2}^2$$

Therefore

$$\ln a_i = \ln \gamma_i + \ln x_i = \frac{A}{RT}(1 - x_1)^2 + \ln x_1$$

• For A/RT < 2, a_1 is a monotonic function of x_1 , but for A/RT > 2 the region of immiscibility corresponds to physical separation of the solvent mixture.

Colligative Properties

- Vapour pressure over solutions
 - Henry's Law
- Freezing point depression
- Boiling point elevation

Vapour Pressure over Solutions

- Consider a solution of two volatile components in equilibrium with the gas phase.
 - x_i is the mole fraction of component *i* in the liquid phase.
 - y_i is the mole fraction of component *i* in the gas phase.
- For an ideal solution

$$K_i = f(i)$$

where f(i) is the fugacity of pure i at the temperature of the solution and the vapour pressure of i.

- Assume that the system is sufficiently ideal that fugacity may be replaced by pressure.
 - Thus

$$P_i = P(i)x_i$$

where P_i is the partial pressure of *i* above the solution, P(i) is the vapour pressure of pure liquid *i* and x_i is the mole fraction of *i* in the liquid solution.

This is Raoult's Law

• The total pressure is a function of the solution composition. For a two component solution:

$$P(x_1) = P_1 + P_2 = P(1)x_1 + P(2)x_2$$

$$= P(1)x_1 + P(2)(1 - x_1)$$
$$= P(2) + [P(1) - P(2)]x_1$$

- But, what is the composition of the gas phase?
- From definition of partial pressure:

$$y_1 = \frac{P_1}{P}$$

• Therefore,

$$y_1(x_1) = \frac{x_1 P(1)}{P(2) + [P(1) - P(2)]x_1}$$

and the total pressure ${\cal P}$ becomes:

$$P[x_1(y_1)] = P(y_1) = \frac{P(1)P(2)}{P(1) + [P(2) - P(1)]y_1}$$

as a function of gas phase composition.

• Raoult's Law is not followed by all solutions at all compositions, but tends to work better when one component is in considerable excess.

Henry's Law and the Ideal Dilute Solution

- The ideal dilute solution consists of:
 - A solvent (the compound in excess)
 - A solute (the minor compound)
- For an ideal dilute solution of solute 2 in solvent 1, Raoult's law gives:

$$P_2 = K_{2,1}x_2$$

which is also known as Henry's Law.

- The Henry's Law coefficient $K_{2,1}$ is *specific* to that solute in that solvent and may be interpreted as the hypothetical vapour pressure of the pure solute.
- $K_{2,1}$ is often larger than the actual vapour pressure of the pure solute.
- Recalling the definition of chemical potential:

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

and assuming that

$$f_i = P_i = K_{solv,i} x_i$$

gives

$$\mu_i(\text{ideal}) = \mu_i^\circ(\text{ideal}) + RT \ln K_i + RT \ln x_i$$

where the first two terms can be considered the definition of a new reference state.

- Often concentrations expressed in terms of other than mole fraction are more convenient.
 - For example mole fraction can be related to molality by:

$$x_i = \frac{(10^{-3} \text{ kg g}^{-1})M m_i}{1 + (10^{-3} \text{ kg g}^{-1})M m}$$

where M is the molar mass of solvent in g mol⁻¹ and m_i the molality of i.

• If the solution is infinitely dilute, this becomes:

$$x_i = (10^{-3} \text{ kg g}^{-1})M m_i$$

 $x_i = (10^{-3} \text{ kg g}^{-1})M m^{\circ} \left(\frac{m_i}{m^{\circ}}\right)$

• Thus the chemical potential becomes:

$$\begin{split} \mu_i(\text{ideal}) &= \mu_i^\circ(\text{ideal}) + RT \ln K_i \\ &+ RT \ln(10^{-3} \text{ kg g}^{-1}M \ m^\circ) \\ &+ RT \ln\left(\frac{m_i}{m^\circ}\right) \end{split}$$

where the first three terms can be taken as a reference state.

Azeotropes

- A solution of azeotropic composition boils unchanged.
- Consider a mixture of two liquids with the following properties:
 - Equal vapour pressures of pure liquids.

$$P(1) = P(2) = P^{\circ}$$

• Equal Henry's Law coefficients

$$K_{1,2} = K_{2,1} = K; \frac{K}{P^{\circ}} = 2$$

• Partial pressure composition relation

$$P_i = Kx_i + (P^\circ - K)x_i^2$$

- This system
 - Has two regions of two phase behaviour.
 - Boils at a single pressure when x = .5

What is wrong with this hypothetical system?

- If one component follows Raoult's Law, the other must follow Henry's Law.
- For a binary system at equilibrium at constant T and P
 - dG(total) = 0
 - $dn_1 = dn_2 = 0$

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

• From the definition of chemical potential for each component:

$$x_1 \left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} = x_2 \left(\frac{\partial \ln f_2}{\partial x_2}\right)_{T,P}$$

• If component 1 follows Henry's Law, $f_1 = Kx_1$, then:

$$\left(\frac{\partial \ln f_1}{\partial x_1}\right)_{T,P} = \left(\frac{1}{f_1}\right) \left(\frac{\partial f_1}{\partial x_1}\right)_{T,P}$$
$$= \frac{x_1}{f_1} K = \frac{x_1}{f_1} \left(\frac{f_1}{x_1}\right) = 1$$

• Similarly:

$$\frac{x_2}{f_2}\left(\frac{f_2}{x_2}\right) = 1$$

which can be rearranged to:

$$\int_{x_2=1}^{x_2} \frac{dx_2}{x_2} = \int_{f_2^\circ}^{f_2} \frac{df_2}{f_2}$$
$$\ln x_2 = \ln\left(\frac{f_2}{f_2^\circ}\right)$$

or

or

which is Raoult's Law.

• Now reconsider the hypothetical equation:

$$P_1 = Kx_1 + (P^{\circ} - K)x_1^2$$

 $f_2 = f_2^{\circ} x_2$

- For small $x_1, P_1 \cong Kx_1$
- For large $x_1, P_1 \cong P^{\circ} x_1^2$, which is not Raoult's Law!

Freezing Point Depression and Boiling Point Elevation

• Assume

- Solute 2 is not volatile.
- Solvent 1 is volatile.
- The solute does not dissolve in solid solvent.
- Therefore gas phase and solid phase are pure solvent.
- The effect of adding the solute is to increase the boiling point and lower the freezing point.
- Consider first the freezing point:
 - Pure frozen solvent is in equilibrium with the solution:

$$\mu_1(T_{fus}, P, x_1) = \mu(T_{fus}, P, \text{pure solid } 1)$$

• Assuming the solution is ideal:

$$\mu_1(T_{fus}, P, x_1) = \mu_1^{\circ} + RT_{fus} \ln f_1^{\circ} x_1$$

• But:

$$\mu_1^\circ + RT_{fus} \ln f_1^\circ = \mu$$
(pure liquid 1)

 $\Delta \overline{G}_{fus}^{\circ} = \mu(\text{pure liquid}) - \mu(\text{pure solid})$

$$(\Delta \overline{G}_{fus}^{\circ} \neq 0 \text{ if } T \neq T_{fus}^{\circ})$$

• Differentiating gives:

$$\left(\frac{\partial \ln x_1}{\partial x_1}\right)_{T,P} = \frac{1}{x_1}$$

$$= -\frac{1}{R} \left[\left(\frac{\partial (\Delta \overline{G}_{fus}^{\circ}/T)}{\partial T}\right)_P \right]_{T_{fus}} \left(\frac{\partial T}{\partial x_1}\right)_P$$

• But from the definition of G,

$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P - \frac{H}{T^2} - \left(\frac{\partial S}{\partial T}\right)_P$$
$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

• Therefore

$$\frac{1}{x_1} = \frac{\Delta \overline{H}_{fus}^{\circ}(\text{pure } 1, T_{fus} < T_{fus}^{\circ})}{RT^2} \left(\frac{\partial T}{\partial x_1}\right)_P$$

• Isolating the variables and integrating:

$$\int_{1}^{x_1} \frac{dx_1}{x_1} = \int_{T_{fus}}^{T_{fus}} \frac{\Delta \overline{H}_{fus}^{\circ}}{RT^2} dT$$

yields (assuming $\Delta \overline{H}_{fus}^{\circ}$ is a constant):

$$\ln x_1 = \frac{\Delta \overline{H}_{fus}^{\circ}}{R} \left(\frac{1}{T_{fus}^{\circ}} - \frac{1}{T_{fus}} \right)$$

• Defining *freezing point depression* as:

$$\Delta T_{fus} = T_{fus}^{\circ}(\text{pure 1}) - T_{fus}(\text{solution})$$

• Using solute concentration in molality gives:

$$dT_{fus} = -d(\Delta T_{fus}) = \frac{RT^2}{\Delta \overline{H}_{fus}^{\circ}} \frac{dx_1}{x_1}$$
$$= \frac{RT^2}{\Delta \overline{H}_{fus}^{\circ}} \frac{1}{x_1} \left(\frac{dx_1}{dm_2}\right) dm_2$$

• For a solution with 1 kg of solvent:

$$n_1 = \frac{1000}{M_1}; n_2 = m_2$$

 $\quad \text{and} \quad$

and

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{1}{1 + \frac{M_1 m_2}{1000}}$$

• Therefore

$$\frac{1}{x_1} \left(\frac{dx_1}{dm_2} \right) = -\frac{M_1 x_1}{1000}$$

and

$$\frac{d(\Delta T_{fus})}{dm_2} = \frac{M_1 R T_{fus}^2 x_1}{1000 \Delta \overline{H}_{fus}^{\circ} (\text{pure solvent})}$$

• For a dilute solution $x_1 \cong 1$ and $T_{fus} \cong T_{fus}^{\circ}$, then:

$$\frac{d(\Delta T_{fus})}{dm_2} = \frac{M_1 R T_{fus}^2}{1000 \Delta \overline{H}_{fus}^\circ} = K_f$$

where m_2 is the molality of the solute particles.

• For small m_2

$$\Delta T_{fus} \cong \frac{d(\Delta T_{fus})}{dm_2} m_2 = K_f m_2$$

• Similarly, it can be shown that the ebulliscopic constant may be derived:

$$\Delta T_{vap} = \left(\frac{M_1 R T_{vap}^2}{1000 \Delta \overline{H}_{vap}^\circ}\right) m_2 = K_b m_2$$

Osmotic Pressure

• Consider the situation where the chemical potential of the solvent in a solution is less than the chemical potential of pure solvent.

$$\mu_1$$
(solution) < μ (pure liquid solvent)

- Consider an experimental setup consisting of two compartments.
 - Compartment A contains the pure solvent in equilibrium with its vapour.
 - Compartment B contains the solution in equilibrium with the vapour of the pure solvent.
 - The two compartments are separated by a barrier, the lower portion of which is a semipermeable membrane that is permeable only to the solvent.
- The system is allowed to reach equilibrium.
 - The semipermeable membrane is invisible to the solvent.
 - The semipermeable membrane confines the solute.
- Solvent molecules move through the membrane until the chemical potential of the solvent match on both sides of the membrane.
- This means that solvent molecules move into the solution and the level of the solution rises higher than that of the pure solvent.
 - This means that there is a pressure imbalance of the liquid on both sides of the membrane.

$$P_B > P_A$$

This is the pressure of the liquid phase, which is affected by the column of liquid above it.

• At any point of the membrane, the chemical potential is the same on both sides.

$$\mu$$
(pure 1, P_A) = $\mu_1(x_1, P_B)$

• Osmotic pressure, Π , is defined as:

$$\Pi = \text{solution pressure} - \text{solvent pressure} = P_B - P_A$$

Thus:

$$\mu(\text{pure } 1, P_A) = \mu_i(x_i, P_A + \Pi)$$
$$= \mu(\text{pure } 1, P_A + \Pi) + RT \ln x_1$$
$$= \mu(\text{pure } 1, P_A) + \int_{P_A}^{P_A + \Pi} \overline{V}(\text{pure } 1)dP + RT \ln x_1$$

and

$$-RT\ln x_1 = \int_{P_A}^{P_A + \Pi} \overline{V}(\text{pure 1})dP$$

If the osmotic pressure Π is small then the molar volume, \overline{V} may be assumed to be constant, yielding:

$$-\ln x_1 = \frac{\Pi \overline{V}}{RT}$$

• If the solution is dilute then x_1 , the mole fraction of the solvent, is close to 1. Therefore:

$$-\ln x_1 = \ln\left(\frac{1}{x_1}\right) = \ln\left(\frac{n_1 + n_2}{n_1}\right) = \ln\left(1 + \frac{n_2}{n_1}\right)$$

• This may be expanded in a power series of the form:

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 + \cdots$$

where $x = n_2/n_1$ and $n_2 < n_1$ (which is true for solute 2 dilute in solvent 1).

• For a dilute solution, the power series may be truncated after one term giving:

$$-\ln x_1 = \frac{\Pi \overline{V}}{RT} \cong \frac{n_2}{n_1}$$

• Since $\overline{V}n_1 \cong V$, the equation becomes:

$$\Pi V = n_2 R T$$

which is the van't Hoof equation.

- Although the van't Hoof equation is similar in form to the ideal gas law, it arises from very different assumptions.
- Since osmotic pressure Π depends on the the number of solute particles rather than the identity of the solute.
 - Can be used to determine molar mass of biomolecules.
- Cell walls are semipermeable membranes.

• Intravenous solutions need to be "isotonic" which means that they have the same chemical potential for water on both sides of the membrane.

Phase Diagrams

- Consider an experiment to determine the temperature of a phase transition for a pure compound at some *P*.
 - Need sample of pure substance
 - Need an energy source that provides or removes energy at a constant rate. Thus, the elapsed time is proportional to the heat transferred.
 - Phase transition occurs while heat is delivered but no temperature change occurs.
- Consider the definition of heat capacity:

$$C_P - \frac{dq_P}{dT}$$

where

$$dH = dq_P$$

• It can be shown that:

$$\frac{dT}{dt} = \frac{dq_P}{dt} \frac{1}{C_P(T)} = \frac{dH}{dt} \frac{1}{C_P(T)}$$

- Thus a slope of a temperature versus time curve is $1/C_P$
- dH/dt is a constant.
- Consider a cooling curve shown in Fig. 6.22.
 - Liquid cools to the freezing point with slope $1/C_P(l)$
 - Temperature plateaus at the freezing temperature. Heat transferred during this time is the enthalpy of the phase transition.