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:

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

- 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 $\overline{V}(\mathrm{g}) >> \overline{V}(\mathrm{l}) \sim \overline{V}(\mathrm{s})$, 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:

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

- 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

$$dS = \frac{R d\overline{V}}{\overline{V} - b}$$

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

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

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
$$\Delta\overline{V}_\Phi = \overline{V}_g$$
- Thus the Clapeyron Equation becomes:
$$\left(\frac{dP}{dT}\right)_\Phi = \frac{\Delta\overline{H}_\Phi}{T_\Phi \Delta\overline{V}_\Phi} \cong \frac{\Delta\overline{H}_\Phi}{T_\Phi \overline{V}_g} = \frac{\Delta\overline{H}_\Phi P}{R T_\phi^2}$$

  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:

$$\left(\frac{dP}{dT}\right)_{fus} = \left(\frac{P_0 a}{T_{fus}}\right)\left(\frac{T_{fus}}{T_0}\right)^a$$

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

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):

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

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

  - 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}:

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

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

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

- Any of these rules may be used to estimate the vapour pressure by replacing $\Delta\overline{H}_{vap}$ with $T^{\circ}_{vap}\Delta\overline{S}^{\circ}_{vap}$ 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.
  - 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:

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

  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:

$$\left(\frac{\partial A}{\partial V}\right)_{T,n} = \sum_i x_i n \left(\frac{\partial \overline{A}_i}{\partial V}\right)_{T,n}$$

$$P = -\sum_i x_i n \left(\frac{\partial \overline{A}_i}{\partial V}\right)_{T,n}$$

and

$$P_i = -x_i n \left(\frac{\partial \overline{A}_i}{\partial V}\right)_{T,n}$$

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 H_2
  - The membrane(Pd foil) is perfectly impermeable to N_2

- At equlibrium, the chemical potential of H_2 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:

$$\begin{aligned}\Delta G_{mix} &= G(x_1, x_2, \ldots) \\ &\quad - \sum_i G(\text{pure, isolated species } i)\end{aligned}$$

where $G(x_1, x_2, \ldots)$ is:

$$\begin{aligned}G(x_1, x_2, \ldots) &= n \sum_i x_i \mu_i(x_i) \\ &= n \sum_i x_i (\mu_i^\circ + RT \ln P_i)\end{aligned}$$

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:

$$\begin{aligned} RT \ln\left(\frac{f}{P}\right) &= \int_0^{P_\Phi} \left(\overline{V} - \frac{RT}{P}\right) dP \\ &+ \int_{P_\Phi}^{P} \left(\overline{V} - \frac{RT}{P}\right) dP \end{aligned}$$

- 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:

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

or

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

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:

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

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:

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

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.

- Consider pure liquid of each component at standard T and P

$$P^\circ = P$$

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

- 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:

  $$nRT \sum_i x_i \ln \gamma_i = G^E = nAx_1x_2$$

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

$$nRT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) = nRT\frac{A}{RT}x_1x_2(x_1 + x_2)$$

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

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.

$$G(\text{real} = G^E + G(\text{ideal})$$

$$= G^E + \sum_i n_i \mu_i(\text{ideal})$$

$$= G^E + \sum_i n_i(\mu_i^\circ + RT \ln f_i)$$

$$= G^E + n \sum_i x_i(\mu_i^\circ + RT \ln f_i^\circ x_i)$$

$$= G^E + n \sum_i x_i(\mu_i^\circ + RT \ln f_i^\circ)$$

$$+nRT \sum_i x_i \ln x_i)$$

$$= G^E + n \sum_i x_i \mu_i(\text{pure } i)$$

$$+nRT \sum_i x_i \ln x_i)$$

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

$$\Delta G_{mix}(\text{real}) = G^E + \Delta G_{mix}(\text{ideal})$$

$$\begin{aligned}\frac{\Delta G_{mix}(x_1)}{RT} &= \frac{A}{RT} x_1(1 - x_1) \\ &\quad + x_1 \ln x_1 + (1 - x_1)\ln(1 - x_1)\end{aligned}$$

- 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 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:

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

  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
  - $dG(\text{total}) = 0$
  - $dn_1 = dn_2 = 0$

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

  - 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:

  $$\int_{x_2=1}^{x_2} \frac{dx_2}{x_2} = \int_{f_2^\circ}^{f_2} \frac{df_2}{f_2}$$

  or

  $$\ln x_2 = \ln\left(\frac{f_2}{f_2^\circ}\right)$$

  or

  $$f_2 = f_2^\circ x_2$$

  which is Raoult's Law.

- Now reconsider the hypothetical equation:

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

  - 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:

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

and

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

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

- Differentiating gives:

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

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

- 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

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

- Isolating the variables and integrating:

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

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

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

- Defining *freezing point depression* as:

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

- Using solute concentration in molality gives:

$$dT_{fus} = -d(\Delta T_{fus}) = \frac{RT^2}{\Delta \overline{H}^\circ_{fus}} \frac{dx_1}{x_1}$$

$$= \frac{RT^2}{\Delta \overline{H}^\circ_{fus}} \frac{1}{x_1} \left(\frac{dx_1}{dm_2} \right) dm_2$$

- For a solution with 1 kg of solvent:

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

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.

$$\mu_1(\text{solution}) < \mu(\text{pure liquid solvent})$$

- 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.

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

- 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:

$$\Pi V = n_2 RT$$

  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.