Week 7

Phase Equilibria and Solutions

7.1 Virial Coefficients and Fugacity

- Relation between the interaction potential and the first virial coefficient (Equation 16.25).

  – Statistical mechanics is important because it gives us the relation

  $$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1 \right) r^2 \, dr$$

  ■ We can derive this with our knowledge of statistical mechanics, but PGS will not go through this.

  – Now recall the Lennard-Jones potential

  $$u(r) = 4\epsilon \left[\left(\frac{\sigma}{\pi} \right)^{12} - \left(\frac{\sigma}{\pi} \right)^6 \right]$$

  ■ Note that the minimum is at $(2^{1/6}\sigma, -\epsilon)$.
  ■ The limiting case of the Lennard-Jones potential is hard sphere repulsion (the repulsion as you approach a hard sphere, which is zero up until you're at the surface and then infinite repulsion). Thus, with no intermolecular attraction, $a = 0$, so in this case,

  $$B_{2V}(T) = -2\pi N_A \int_0^\sigma (-1) r^2 \, dr$$
  $$= \frac{2\pi N_A \sigma^3}{3}$$
  $$= b - \frac{0}{RT}$$

  – Now consider a potential that is van der Waals (c/r^6) up until a point and then hard sphere. In this case,

  $$B_{2V}(T) = \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(e^{-c/r^6 k_B T} - 1 \right) r^2 \, dr$$
  $$= \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(-\frac{c}{r^6 k_B T} \right) r^2 \, dr$$
  $$= b + \frac{2\pi N_A c}{k_B T} \cdot -\frac{1}{3\sigma^3}$$

  where we have used $e^x = 1 + x + \cdots$ to get from the first line to the second.

■ Therefore,

$$a = \frac{2\pi N_A^2}{3} \frac{c}{\sigma^2}$$

• Derivation of the relation between $B_{2V}(T)$ and the interaction potential $u(r)$.

– Consider a system of independent, indistinguishable particles.

– The total Hamiltonian for the system has a kinetic energy part and an interaction part.

$$\hat{H}(p_i, r_i) = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_{i<j} \hat{u}(r_i, r_j)$$

– The kinetic part (which ignores intermolecular interactions) will lead to the ideal gas partition function. The nonideal part of the partition function will come from the interaction potentials. Mathematically,

$$
\begin{aligned}
Q &= \frac{1}{N!} \int e^{-\beta E(p_i, r_i)} \, d^3 p_i \, d^3 r_i \\
&= \frac{1}{N!} \int \exp\left\{ -\beta \left[\sum_i \frac{p_i^2}{2m} + \sum_{i<j} u(r_i, r_j) \right] \right\} d^3 p_i \, d^3 r_i \\
&= \frac{1}{N!} \left(\int \exp\left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3 p_i \right) \left(\int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \right) \\
&= \underbrace{\frac{V^N}{N!} \left(\int \exp\left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3 p_i \right)}_{Q_{\text{ideal}}} \cdot \underbrace{\frac{1}{V^N} \left(\int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \right)}_{Q_u}
\end{aligned}
$$

– Define

$$f_{ij} = e^{-u(r_i, r_j)/k_B T} - 1$$

– Now note that the interaction between molecules is pretty small, and in fact $f_{ij} \to 0$ as $|r_i - r_j| \to \infty$.

– Thus,

$$
\begin{aligned}
Q_u &= \frac{1}{V^N} \int \exp\left[-\beta \sum_{i<j} u(r_i, r_j) \right] d^3 r_i \\
&= \frac{1}{V^N} \int \prod_{i<j} (f_{ij} + 1) \, d^3 r_i
\end{aligned}
$$

– We can do a **cluster expansion** on this small f_{ij}:

$$\prod_{i<j}(f_{ij} + 1) = 1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{k<\ell} f_{ij} f_{k\ell}$$

– In particular, $\sum_{i<j}$ is the sum of pairwise interactions while $f_{ij} \cdot f_{k\ell}$ are binary interactions, $f_{ij} f_{k\ell} f_{mn}$ are tertiary interactions, and so on and so forth.

– But at low density, the dominant term is the pairwise interaction so we have

$$Q_u = \frac{1}{V^N} \int \left(1 + \sum_{i<j} f_{ij}\right) \mathrm{d}^3 r_i$$

$$= \frac{1}{V^N} \left(V^N + \frac{N(N-1)}{2} V^{N-2} \int f_{12} \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2\right)$$

$$= 1 + \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) \, \mathrm{d}^3 r$$

– It follows that

$$Q = Q_{\mathrm{id}} \left[1 + \frac{N(N-1)}{2V} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r\right]$$

– But now we need to extract an equation of state from the partition function. To do so, we use

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$= k_B T \left(\frac{\partial \ln Q_{\mathrm{id}}}{\partial V}\right)_{N,T} + k_B T \left(\frac{\partial \ln Q_u}{\partial V}\right)_{N,T}$$

– We know that the first term above is equal to $N k_B T/V$, but it takes a bit more work for the second one.

– We have that

$$\ln Q_u = \ln \left(1 + \underbrace{\frac{N(N-1)}{2V}}_{\substack{\text{Approximately} \\ \text{the intermolecular} \\ \text{distance } 1/\rho^3}} \underbrace{\int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r}_{\substack{\text{Approximately} \\ \text{the molecular} \\ \text{volume } a^3}}\right)$$

$$= \frac{N(N-1)}{2V} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

since the second term is a small number and the natural log of a small number plus 1 is approximately that small number.

– Thus,

$$\left(\frac{\partial \ln Q_u}{\partial V}\right)_{N,T} = -\frac{N(N-1)}{2V^2} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

so

$$P = \frac{N k_B T}{V} - \frac{N k_B T}{V} \frac{N-1}{2V} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

$$= \frac{RT}{\overline{V}} - \frac{RT}{\overline{V}} \frac{N-1}{2V} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

– Consequently,

$$Z = \frac{P\overline{V}}{RT} = 1 - \frac{N_A}{\overline{V}} \cdot \frac{1}{2} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

– Therefore, by comparison with the virial expansion,

$$B_{2V}(T) = -\frac{N_A}{2} \int \left(e^{-\beta u(r)} - 1\right) \mathrm{d}^3 r$$

$$= -\frac{N_A}{2} \int_0^\infty \left(e^{-\beta u(r)} - 1\right) 4\pi r^2 \, \mathrm{d}r$$

$$= -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1\right) r^2 \, \mathrm{d}r$$

- Free energy as a function of (T, P) for a real gas. Definition of fugacity and fugacity coefficients.

    - We want to find $\Delta G(T, P)$.
    - We have that $d\overline{G} = -\overline{S}\,dT + \overline{V}\,dP$. It follows that

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

    - Thus,

    $$\overline{G}(T, P) = \overline{G}(T, P_0) + \int_{P_0}^{P} \overline{V}\,dP$$

    - In the ideal case,

    $$\begin{aligned}
    \overline{G}_{\text{ideal}}(T, P) &= \overline{G}_{\text{ideal}}(T, P_0) + \int_{P_0}^{P} \frac{RT}{P}\,dP \\
    &= \overline{G}_{\text{ideal}}(T, P_0) + RT\ln\frac{P}{P_0}
    \end{aligned}$$

    - In the nonideal case, we define a fugacity f by

    $$\overline{G}_{\text{ideal}}(T, P) = \overline{G}_{\text{ideal}}(T, P_0) + RT\ln\frac{f}{P_0}$$

        - The second term in the above equation refers to the Gibbs free energy of an ideal gas at $P_0 = 1\,\text{bar}$ or $P_0 = 1\,\text{atm}$. Note that even at $P_0 = 1\,\text{atm}$, however, there is too much pressure for truly ideal behavior, so $f \neq P_0$.

    - Imagine that $\Delta\overline{G}_1$ takes us from a real gas at (T, P) to an ideal gas at (T, P). Then

    $$\begin{aligned}
    \Delta\overline{G}_1 &= \overline{G}_{\text{ideal}}(T, P) - \overline{G}_{\text{real}}(T, P) \\
    &= \left[\overline{G}_{\text{ideal}}(T, P_0) + RT\ln\frac{P}{P_0}\right] - \left[\overline{G}_{\text{ideal}}(T, P_0) + RT\ln\frac{f}{P_0}\right] \\
    &= -RT\ln\frac{f}{P}
    \end{aligned}$$

    - Now let $\Delta\overline{G}_2$ take us from a real gas at (T, P) to a real gas at T and $P \to 0$, which will be the same as an ideal gas at T and $P \to 0$. Then let $\Delta\overline{G}_3$ take us from this ideal gas at T and $P \to 0$ to an ideal gas at (T, P). It follows that

    $$\Delta\overline{G}_2 = -\int_{P\to 0}^{P} \overline{V}\,dP' \qquad\qquad \Delta\overline{G}_2 = \int_{P\to 0}^{P} \frac{RT}{P'}\,dP'$$

    - Thus, since $\Delta\overline{G}_1 = \Delta\overline{G}_2 + \Delta\overline{G}_3$ (G is a state function),

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

    - We then define γ to be the **fugacity coefficient** by $\gamma = f/P$. It follows that

    $$\ln\gamma = \int_0^P \frac{Z-1}{P'}\,dP'$$

- Fugacity coefficient expressed in terms of the compressibility deviation from unity.

    - At low temperature, $Z < 1$, so $\gamma < 1$ and hence $f < p$.
    - At high pressure, $Z > 1$ (excluded volume), so $\gamma > 1$ and hence $f > P$.

- Introduces phase diagrams and their notable properties.

7.2 Phase Equilibria

2/23:
- Goes over midterm answer key (and posted it to Canvas).

  – 1d.
    - We needed to say that $\max S = nk_B \ln 2$.
    - We also needed to indicate that the slope is vertical at 0 and 1.

  – Question 3.
    - Often looking for a derivation from some fundamental law of thermodynamics.
    - For example, for 3a, since this is an isolated system, we know that $\mathrm{d}U = 0$. Moreover, since $\mathrm{d}U = C_1 \, \mathrm{d}T_1 + C_2 \, \mathrm{d}T_2$, we have that $C_1 \, \mathrm{d}T_1 = -C_2 \, \mathrm{d}T_2$.

  – 3b.
    - The appropriate derivation was

$$\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2$$
$$= \frac{C_1 \, \mathrm{d}T_1}{T_1} + \frac{C_2 \, \mathrm{d}T_2}{T_2}$$
$$= C_1 \, \mathrm{d}T_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

    from which it follows since $T_2 > T_1$ (and hence $1/T_1 - 1/T_2 > 0$), since $\mathrm{d}S > 0$, and since $C_1 > 0$ that $\mathrm{d}T_1 > 0$.

  – I need a lot of help on Question 4.

- In the video of a liquid becoming a supercritical fluid, the path along the phase diagram is along the liquid-gas coexistence curve to the critical point and beyond.

- The heat of vaporization actually isn't constant; it varies with temperature.

  – At the critical temperature, it becomes zero and the line has vertical slope.

- The densities of gas and liquid also converge as $T \to T_c$.

- The slope of coexistence curves on PT phase diagrams; the Clapeyron equation.

  – Since the molar free energies $\overline{G}_\alpha, \overline{G}_\beta$ of the two phases α, β are equal when said phases are in equilibrium,

$$\mathrm{d}\overline{G}_\alpha = \mathrm{d}\overline{G}_\beta$$
$$\left(\frac{\partial \overline{G}_\alpha}{\partial T} \right)_P \mathrm{d}T + \left(\frac{\partial \overline{G}_\alpha}{\partial P} \right)_T \mathrm{d}P = \left(\frac{\partial \overline{G}_\beta}{\partial T} \right)_P \mathrm{d}T + \left(\frac{\partial \overline{G}_\beta}{\partial P} \right)_T \mathrm{d}P$$
$$-\overline{S}_\alpha \, \mathrm{d}T + \overline{V}_\alpha \, \mathrm{d}P = -\overline{S}_\beta \, \mathrm{d}T + \overline{V}_\beta \, \mathrm{d}P$$
$$(\overline{S}_\beta - \overline{S}_\alpha) \, \mathrm{d}T = (\overline{V}_\beta - \overline{V}_\alpha) \, \mathrm{d}P$$
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\overline{S}_\beta - \overline{S}_\alpha}{\overline{V}_\beta - \overline{V}_\alpha} = \frac{\Delta \overline{S}_\text{trans}}{\Delta \overline{V}_\text{trans}}$$

  – Clearly, the last line above gives the slope of the coexistence curves on a phase diagram.

  – Since $T\Delta \overline{S}_\text{trans} = \Delta \overline{H}_\text{trans}$ ($\Delta G = 0$), we also have

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta \overline{H}_\text{trans}}{T\Delta \overline{V}_\text{trans}}$$

    - Since both $\Delta \overline{H}_\text{trans}, \Delta \overline{V}_\text{trans} \to 0$ as $T \to T_c$, $\mathrm{d}P/\mathrm{d}T$ depends on the rates at which the two quantities approach zero.

- Deriving an expression for the vapor pressure (in equilibrium with liquid).

  - We know that $\Delta \overline{V}_{\text{vap}} = \overline{V}_g - \overline{V}_l$ where $\overline{V}_g \gg \overline{V}_l$. Therefore, we may approximate $\Delta \overline{V}_{\text{vap}} \approx \overline{V}_g$.
  - Additionally, we have that $\overline{V}_g = RT/P$.
  - It follows that

$$
\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta \overline{H}_{\text{vap}}}{T \overline{V}_g}
$$

$$
= \frac{P \Delta \overline{H}_{\text{vap}}}{RT^2}
$$

$$
\frac{\mathrm{d}P}{P} = \frac{\Delta \overline{H}_{\text{vap}}}{R} \frac{\mathrm{d}T}{T^2}
$$

$$
\ln \frac{P}{P_0} = \frac{\Delta \overline{H}_{\text{vap}}}{R} \left(-\frac{1}{T} + \frac{1}{T_0} \right)
$$

  - It follows that if $P_0 = 1\,\text{atm}$ and $T_0 = T_b$ (the standard boiling temperature), then the vapor pressure P at temperature T is

$$
P = P_0 \exp \left[\frac{\Delta \overline{H}_{\text{vap}}}{R} \left(\frac{1}{T_b} - \frac{1}{T} \right) \right]
$$

    - ■ Note that we take $\Delta \overline{H}_{\text{vap}}$ to be the molar heat of vaporization at temperature T, i.e., we assume it's constant from there up until T_b which it technically isn't as we mentioned earlier.
  - Note that you can also use this equation and (P, T) data to calculate ΔH_{vap}.

- Relative slopes of S-G and L-G coexistence lines at the triple point.

  - When drawing a phase diagram, you should exaggerate the discontinuity in the slopes of the S-G and L-G coexistence curves at the triple point.
  - In particular, $\mathrm{d}P_{\text{SG}}/\mathrm{d}T > \mathrm{d}P_{\text{LG}}/\mathrm{d}T$ since $\Delta \overline{H}_{\text{SG}} = \Delta \overline{H}_{\text{SL}} + \Delta \overline{H}_{\text{LG}} > \Delta \overline{H}_{\text{LG}}$ and $\Delta \overline{V}_{\text{SG}} \approx \Delta \overline{V}_{\text{LG}}$.
  - Quantitatively, the ratio of the slopes is

$$
\frac{\mathrm{d}P_{\text{SG}}/\mathrm{d}T}{\mathrm{d}P_{\text{LG}}/\mathrm{d}T} = \frac{\Delta \overline{H}_{\text{SG}}}{\Delta \overline{H}_{\text{LG}}} = 1 + \frac{\Delta \overline{H}_{\text{SL}}}{\Delta \overline{H}_{\text{LG}}}
$$

7.3 Chemical Potential and Raoult's Law

2/25:
- Today we begin the topic of solutions.

  - We'll introduce ideal solutions and then discuss nonideal solutions.
  - Today: Ideal solutions, i.e., solutions in which we negate the interactions between the solutes. The statistical entropy gives rise to boiling point elevation, freezing point depression, Raoult's law, and osmotic pressure.

- Chemical potential.

  - To discuss equilibrium, we start by discussing the energy of a solution $G(T, P, n_1, n_2)$ where n_1 is the number of moles of solute and n_2 is the number of moles of solvent.
  - The total differential is

$$
\mathrm{d}G = \left(\frac{\mathrm{d}G}{\mathrm{d}T} \right)_{P, n_1, n_2} \mathrm{d}T + \left(\frac{\mathrm{d}G}{\mathrm{d}P} \right)_{T, n_1, n_2} \mathrm{d}P + \left(\frac{\mathrm{d}G}{\mathrm{d}n_1} \right)_{T, P, n_2} \mathrm{d}n_1 + \left(\frac{\mathrm{d}G}{\mathrm{d}n_2} \right)_{T, P, n_1} \mathrm{d}n_2
$$

Labalme 6

- **Chemical potential**: The following partial derivative. *Denoted by $\boldsymbol{\mu_1}$. Given by*

$$\mu_i = \left(\frac{\mathrm{d}G}{\mathrm{d}n_i}\right)_{T,P,n_j}$$

for all $j \neq i$.

  - For a pure substance, chemical potential is the molar free energy for a given ratio of concentration.
  - μ_i is a function of $T, P, n_j \neq n_i$.

- Equilibrium in terms of relation between chemical potentials.

  - Consider a system in equilibrium between the liquid and gas phases where both phases have two components n_1^l, n_2^l and n_1^g, n_2^g.
  - We know that the free energy G is the sum of the free energies of the two systems G^l, G^g.
  - Since we are in equilibrium, $\mathrm{d}G = \mathrm{d}G^l + \mathrm{d}G^g = 0$.
  - At constant T, P, it follows that

$$\mu_1^l \, \mathrm{d}n_1^l + \mu_2^l \, \mathrm{d}n_2^l + \mu_1^g \, \mathrm{d}n_1^g + \mu_2^g \, \mathrm{d}n_2^g = 0$$

  - Furthermore, matter is conserved, i.e., $\mathrm{d}n_i^l = -\,\mathrm{d}n_i^g$.
  - Thus, we may write
$$(\mu_1^l - \mu_1^g)\,\mathrm{d}n_1^l + (\mu_2^l - \mu_2^g)\,\mathrm{d}n_2^l = 0$$
  - It follows that $\mu_1^l - \mu_1^g = 0$ and $\mu_2^l - \mu_2^g = 0$, i.e., that the chemical potentials of species in each phase are equal at equilibrium.

- **Raoult's law**: The partial pressure P_i of each component in a solution is equal to its pure vapor pressure P_i^* times its mole fraction x_i in solution. *Given by*

$$P_i = x_i P_i^*$$

for all i.

  - It's only the mole fraction of the solute that matters, not whether it's as big as a protein or as small as an ion.
  - This is only in **ideal solutions**, however.

- **Ideal solution**: A solution that has a small amount of solutes.

  - In the same way that any gas is ideal at low pressure, any solution is ideal with few enough solutes.

- Example of vapor pressure in equilibrium with an ideal solution of benzene and toluene.
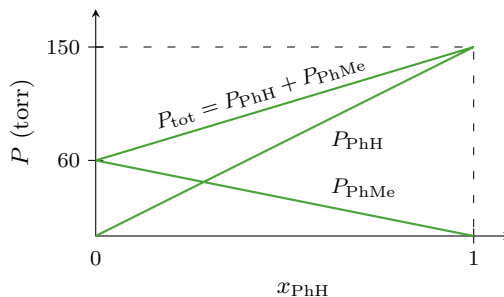

Figure 7.1: Raoult's law example.

- We'll see deviations from Figure 7.1 later, such as Henry's law.

- Chemical potential of a component in an ideal solution.

  - If the vapor is ideal, then
  $$\overline{G}^g(T,P) = \overline{G}^{\circ g}(T) + RT\ln\frac{P}{P_0}$$

  - For a pure substance, we have
  $$G^{\circ g}(T) + RT\ln\frac{P}{P_0} = G^{\circ l}(T)$$
  $$P = P_0 e^{-\Delta G/RT}$$

  where $\Delta G = G^{\circ g} - G^{\circ l}$.

  - When we have a solution,
  $$\overline{G}^l(T,x_1) = \overline{G}^g(T) + RT\ln\frac{x_1 P_1^*}{P_0}$$
  $$\overline{G}^{\circ l}(T) + ? = \overline{G}^g(T) + RT\ln\frac{x_1 P_1^*}{P_0}$$
  $$? = RT\ln\frac{x_1 P_1^*}{P_0} - RT\ln\frac{P_0}{P_1^*}$$
  $$= RT\ln x_1$$

  so
  $$\overline{G}^{\circ l}(T,x_1) = \overline{G}^{\circ l}(T) + RT\ln x_1$$

  - This result implies that the free energy of the pure substance with mole fraction x_1 in solution is equal to the free energy of the solution plus $RT\ln x_1$.

- The chemical potential for an ideal solution is a pure entropy effect.

  - For the mixing of two solutions, we have as with gases that
  $$\Delta S = k_B \ln W$$
  $$= k_B \ln\frac{(N_1+N_2)!}{N_1!N_2!}$$
  $$= k_B[(N_1+N_2)\ln(N_1+N_2) - (N_1+N_2) - (N_1\ln N_1 - N_1) - (N_2\ln N_2 - N_2)]$$
  $$= k_B\left(N_1\ln\frac{N_1+N_2}{N_1} + N_2\ln\frac{N_1+N_2}{N_2}\right)$$
  $$= -k_B N_A(n_1\ln x_1 + n_x\ln x_2)$$
  $$= -R(n_1\ln x_1 + n_x\ln x_2)$$

  - It follows that without enthalpic mixing (i.e., with $\Delta H = 0$), we have
  $$\Delta G = \Delta H - T\Delta S$$
  $$= RT(n_1\ln x_1 + n_x\ln x_2)$$

  - Thus, since $\Delta\overline{G}_1 = RT\ln x_1$, $RT\ln x_1$ is purely from entropy!
  - Note that also as before, the slope of ΔS vs x_1 is infinite at 0 and 1.
    - ■ This reflects the fact that mixing is a more purely entropic effect in the limit of very little solute (i.e., in the limit of an ideal solution).

7.4 Office Hours (PGS)

2/25:
- Plotting the coexistence curve and determining the Maxwell equal area contraction line mathematically.
  - You can do these things with Mathematica and numerical approximations.
  - PGS does not know of an easy way to do this by hand. It looks like I would have to go all the way through the cubic formula and integrals.
- I'm getting confused on treating the van der Waals equation as a cubic in $\overline{V}$, because it's graph doesn't ever cross the x-axis, and, in fact, the equation is asymptotic to both the x- and y-axes. So what are its roots, and exactly what properties of it as a cubic are preserved?
  - It is cubic because it is cubic in $\overline{V}$ (and solving for $\overline{V}$ given P, T requires solving a cubic), not because it looks like the plot of a cubic function.
- Why do intermolecular interactions behave the same way as intramolecular bonding interactions? B/c we used the Lennard-Jones potential for bond distance initially, and now we've applied it to two molecules interacting through their polarity?
  - The Lennard-Jones potential only applies to spherically symmetric distributions (e.g., not H_2O at short distances).
  - Not molecules of strong dipole or charge transfer either.
  - Thus perfect for **rare** (or inert) gases.
  - r^{-6} works well for any solids that are not charged.
- What is the σ in the hard sphere potential? Isn't it the radius of the hard sphere? Because McQuarrie and Simon (1997) says it's the diameter multiple times.
  - If the molecule centered at the origin is a hard sphere of radius $\sigma/2$ and the molecule approaching the hard sphere centered at the origin is also a hard sphere of radius $\sigma/2$, then they won't interact until their centers are a distance σ apart.
- Why can we use the ideal gas law to relate B_{iV} and B_{iP}?
- PSet 3, Question 2.
  - Use the two state model from class. Use a partition function with two states for N particles.
  - Curie's law probably isn't gonna be valid in this regime.
  - You need the heat capacity at 4 kelvin via the Debye model. You'll need the Debye temperature from the internet.

7.5 Chapter 16: The Properties of Gases

From McQuarrie and Simon (1997).

- Since the results of the Lennard-Jones potential can't be evaluated analytically, we often use other approximations that can be.
- **Hard-sphere potential**: The potential of a hard sphere of radius σ. *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

  - This is the simplest representative potential.
  - Despite its simplicity, it does account for the finite size of molecules, which turns out to be the dominant feature in determining the structure of liquids and solids.

- It does not account for intermolecular attractions, but since such attractions lessen as temperature increases, it is a good model for that condition.

- Under the hard-sphere potential,

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1\right) r^2 \, dr$$
$$= -2\pi N_A \left[\int_0^\sigma (0-1) r^2 \, dr + \int_\sigma^\infty (1-1) r^2 \, dr\right]$$
$$= \frac{2\pi \sigma^3 N_A}{3}$$

  - Thus, $B_{2V}(T)$ is equal to 1/2 the volume of N_A hard spheres of radius σ.
  - Although this formula for the second virial coefficient is not temperature dependent, it is indeed a good approximation at high temperatures, just the same way the potential is.

- **Square-well potential**: The potential of a hard-sphere of radius σ that is attractive at a consistent level from its surface up until a finite distance away. *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

  - ε is the depth of the well and $(\lambda - 1)\sigma$ is its width.

- Under the square-well potential,

$$B_{2V}(T) = -2\pi N_A \left[\int_0^\sigma (0-1) r^2 \, dr + \int_\sigma^{\lambda\sigma} (e^{\varepsilon/k_B T} - 1) r^2 \, dr + \int_{\lambda\sigma}^\infty (1-1) r^2 \, dr\right]$$
$$= -2\pi N_A \left[-\frac{\sigma^3}{3} + \frac{\sigma^3}{3}(\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1) + 0\right]$$
$$= \frac{2\pi \sigma^3 N_A}{3}[1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)]$$

- The agreement of the square-well potential with experimental data is very good, but it does have 3 adjustable parameters.

- Relating the second virial coefficient to the van der Waals constants.

  - With the help of the expansion $1/(1-x) = 1 + x + x^2 + \cdots$, we have that

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$
$$= \frac{RT}{\overline{V}} \frac{1}{1 - b/\overline{V}} - \frac{a}{\overline{V}^2}$$
$$= \frac{RT}{\overline{V}} \left[1 + \frac{b}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \cdots\right] - \frac{a}{\overline{V}^2}$$
$$= \frac{RT}{\overline{V}} + (RTB - a)\frac{1}{\overline{V}^2} + \frac{RTb^2}{\overline{V}^3} + \cdots$$

  - It follows that

$$Z = \frac{P\overline{V}}{RT} = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \frac{b^2}{\overline{V}^2} + \cdots$$

- Thus,

$$B_{2V}(T) = b - \frac{a}{RT}$$

for the van der Waals equation.

- Relating the van der Waals constants to the Lennard-Jones parameters.

  - Consider the following intermolecular potential, which is a hybrid of the hard-sphere and Lennard-Jones potentials.

  $$u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{c_6}{r^6} & r > \sigma \end{cases}$$

  - We can now calculate $B_{2v}(T)$ in terms of $u(r)$ with the help of the approximation $e^x = 1 + x$ (applicable since the argument of the exponent function will be very small).

  $$\begin{aligned} B_{2V}(T) &= -2\pi N_A \left[\int_0^\sigma (0-1)r^2 \, dr + \int_\sigma^\infty (e^{c_6/k_B T r^6} - 1)r^2 \, dr \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \int_\sigma^\infty \frac{1}{r^6} \cdot r^2 \, dr \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \left[-\frac{1}{3r^3} \right]_\sigma^\infty \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{3 k_B T \sigma^3} \end{aligned}$$

  - It follows by comparison with the result from the previous section that

  $$a = \frac{2\pi N_A^2 c_6}{3\sigma^3} \qquad\qquad b = \frac{2\pi\sigma^3 N_A}{3}$$

  - Physical interpretations: $a \propto c_6$ and b is one-half the volume of the molecules.

- In a similar fashion, we can relate $B_{2V}(T)$ to the Redlich-Kwong constants and Peng-Robinson functions.

$$B_{2V}(T) = B - \frac{A}{RT^{3/2}} \qquad\qquad B_{2V}(T) = \beta - \frac{\alpha}{RT}$$

7.6 Chapter 22: Helmholtz and Gibbs Energies

From McQuarrie and Simon (1997).

- Generalizing the equation $\overline{G} = G^\circ + RT \ln Q$ to the case of a real gas.

  - We begin by substituting the virial expansion in terms of pressure into the equation $(\partial \overline{G}/\partial P)_T = \overline{V}$.

  $$\begin{aligned} \left(\frac{\partial \overline{G}}{\partial P}\right)_T &= \overline{V} \\ &= \frac{RT}{P} \left[1 + B_{2P}(T)P + B_{3P}(T)P^2 + \cdots \right] \\ \int_{P^{\mathrm{id}}}^P d\overline{G} &= RT \int_{P^{\mathrm{id}}}^P \frac{dP'}{P'} + RT B_{2P}(T) \int_{P^{\mathrm{id}}}^P dP' + RT B_{3P}(T) \int_{P^{\mathrm{id}}}^P P' \, dP' \\ \overline{G}(T,P) &= \overline{G}(T, P^{\mathrm{id}}) + RT \ln \frac{P}{P^{\mathrm{id}}} + RT B_{2P}(T)P + RT B_{3P}(T)\frac{P^2}{2} + \cdots \end{aligned}$$

  - Note that we neglect P_{id} in every term except the first because it is so close to zero.

- Substituting $\overline{G}(T, P^{\mathrm{id}}) = G^\circ(T) + RT \ln P^{\mathrm{id}}/P^\circ$ and combining the first two terms yields

$$\overline{G}(T, P) = G^\circ(T) + RT \ln \frac{P}{P^\circ} + RTB_{2P}(T)P + RTB_{3P}(T)\frac{P^2}{2} + \cdots$$

- The above equation is exact, but complicated and different for each gas (depending on the virial coefficients).

- It will be more convenient to, especially for calculations involving chemical equilibria, to define the **fugacity**.

- **Fugacity**: A state function of P and T describing the nonideality of the energy of a system. *Denoted by f. Given by*

$$\overline{G}(T, P) = G^\circ(T) + RT \ln \frac{f(P, T)}{f^\circ}$$

- Fugacity must have the property that $f(P, T) \to P$ as $P \to 0$, so that the above equation can reduce to $\overline{G} = G^\circ + RT \ln P/P^\circ$.

- By setting the above equal to the virial expansion, we learn that

$$\frac{f(P, T)}{f^\circ} = \frac{P}{P^\circ} \exp\left[B_{2P}(T)P + B_{3P}(T)P^2 + \cdots\right]$$

- "The standard state of the real gas... is taken to be the corresponding ideal gas at one bar" (McQuarrie & Simon, 1997, p. 906).

  - Mathematically, $f^\circ = P^\circ$.
  - Note that we can also derive this from the virial expansion expression for $f(P, T)/f^\circ$ since all of the virial coefficients are equal to zero in the standard state.

- McQuarrie and Simon (1997) goes through the derivation of

$$\ln \frac{f}{P} = \int_0^P \left(\frac{\overline{V}}{RT} - \frac{1}{P'}\right) \mathrm{d}P'$$

exactly as in class.

  - The above equation allows us to calculate the ratio of the fugacity to the pressure of a gas at any pressure and temperature, given either P-V-T data or an equation of state.

- **Fugacity coefficient**: The following ratio. *Denoted by γ. Given by*

$$\gamma = \frac{f}{P}$$

- Also note the equation

$$\ln \gamma = \int_0^P \frac{Z - 1}{P'} \mathrm{d}P'$$

and that we can use this equation with the reduced pressure.

7.7 Chapter 23: Phase Equilibria

From McQuarrie and Simon (1997).

2/27:
- **Gibbs phase rule**: The number of components C and the number of phases P in a system are related to the number of degrees of freedom F by the equation

$$F = C - 2 - P$$

- Describes phase diagrams.

- **Vapor pressure**: The pressure at which solid and gas or liquid and gas are in equilibrium.

- **Solid-gas coexistence curve**: The curve separating the solid and gas regions of a phase diagram.
  - At points along this curve, the system will be in equilibrium between solid and gas.
  - As such, this curve specifies the vapor pressure as a function of temperature.

- **Triple point**: The point of intersection of the three lines in a phase diagram, at which the solid, liquid, and gaseous phases of the substance coexist at equilibrium.

- "Within a single-phase region, both the pressure and the temperature must be specified, and we say that there are two degrees of freedom within a single-phase region of a pure substance" (McQuarrie & Simon, 1997, p. 927).

- "Along any of the coexistence curves, either the pressure or the temperature alone is sufficient to specify a point on the curve, so we say that there is one degree of freedom" (McQuarrie & Simon, 1997, p. 927).

- "The triple point is a fixed point, so there are no degrees of freedom there" (McQuarrie & Simon, 1997, p. 927).

- Thus, the number of degrees of freedom f is related to the number of phases in equilibrium by the equation
$$f = 3 - p$$

- **Normal melting point**: The temperature at which a substance melts under $1\,\text{atm}$ of pressure.

- **Standard melting point**: The temperature at which a substance melts under $1\,\text{bar}$ of pressure.

- **Boiling point**: The temperature at which the vapor pressure equals the atmospheric pressure.

- **Normal boiling point**: The boiling point at $1\,\text{atm}$.

- **Standard boiling point**: The boiling point at $1\,\text{bar}$.

- **Sublime**: To pass directly from the solid to the gas phase.

- H_2O, antimony, and bismuth all expand upon freezing.

- **Orthobaric densities**: The densities of two phases that are in equilibrium with each other (i.e., of a substance along a coexistence curve).

- The orthobaric densities of the liquid and gas phases approach each other as $T \to T_c$.

- $\Delta \overline{H}_{\text{vap}}$ decreases as $T \to T_c$.
  - This is because $\Delta \overline{S}_{\text{vap}} \to 0$ as $T \to T_c$ (the phases become less distinct), so naturally $\Delta \overline{H}_{\text{vap}} = T \Delta \overline{S}_{\text{vap}} \to 0$ as $T \to T_c$.

- **Critical opalescence**: The fluctuations between the liquid and vapor state of a fluid very near its critical point which scatter light very strongly, causing the substance in question to appear milky.

- Because of the critical point, it is possible to transform a gas into a liquid (or vice versa) without ever passing through a two-phase state. To do so, just follow a path out and around the critical point along the phase diagram.

- The solid-liquid coexistence curve does not end as abruptly as the liquid-gas coexistence curve since the differences between solid and liquid are ones of intrinsically different structure as opposed to degree of motion. Thus, the solid-liquid coexistence curve of a substance either continues on indefinitely or dead ends into another solid state (some substances have multiple, such as water, which can be solid even above its normal boiling point at very high pressures).

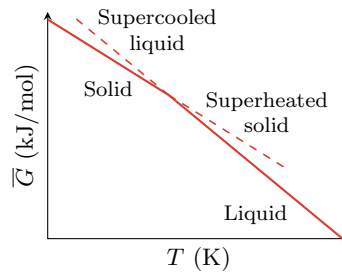- Connecting the Gibbs energy of a substance to its phase diagram.

Figure 7.2: The energetic stabilization of phase transitions.

  - Recall that the plot of $\overline{G}(T)$ for a substance is a continuous curve with two discontinuities in the slope (one for each phase transition).

  - Consider the point at one such discontinuity (say between the solid and liquid phases). If we were to extrapolate the liquid line to lower temperatures, we would be describing a **supercooled liquid** and vice versa with a **superheated solid**.

  - However, a substance does not ordinarily exist as a liquid below its melting point because its Gibbs energy is reduced by transitioning to a solid. Similarly, a substance does not ordinarily exist as a solid above its melting point because its Gibbs energy is reduced by transitioning to a liquid.

  - The influence of $G = H - TS$: At low temperatures, TS is small, so we favor a small H (and solids have the lowest enthalpy of the three phases). Likewise, at higher temperatures, a larger H can be evened out by the large TS.

  - Note that we can do the same kind of analysis for $\overline{G}(P)$. However, in this case, we have the chance that with some substances (such as water), we will go from gas to solid to liquid as pressure increases.

- **Supercooled liquid**: A liquid with temperature below its freezing point that is not nevertheless not a solid.

- **Superheated solid**: A solid with temperature above its melting point.

- **Metastable state**: A state of a substance that has greater molar Gibbs energy than the usual state encountered under some conditions.

- Consider a system consisting of the gas and liquid phases of a pure substance in equilibrium with each other.

  - If G^l is the Gibbs energy of the liquid phase and G^g is the Gibbs energy of the gaseous phase, then the total Gibbs energy G of this system is $G = G^l + G^g$.

- Now if dn moles are transferred from the liquid phase to the vapor phase at constant T, P, the corresponding change in Gibbs energy is

$$dG = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

- Since $dn^l = -dn^g$, it follows that

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

- Rewriting in terms of **chemical potentials**, we have

$$dG = (\mu^g - \mu^l)\, dn^g$$

- **Chemical potential**: The change in Gibbs energy of a substance in a phase α with respect to the change in the number of moles of the substance present. *Denoted by* $\boldsymbol{\mu^\alpha}$. *Given by*

$$\mu^\alpha = \left(\frac{\partial G^\alpha}{\partial n^\alpha}\right)_{P,T}$$

  - "Just as electric current flows from a higher electric potential to a lower electric potential, matter 'flows' from a higher chemical potential to a lower chemical potential" (McQuarrie & Simon, 1997, p. 937).
  - An equivalent definition is that since $G \propto n$ for any system, μ is the proportionality constant. Here's how we know the definitions are equivalent:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T} = \left(\frac{\partial n\mu(T,P)}{\partial n}\right)_{P,T} = \mu(T,P)$$

    ■ In other words, μ is an intensive quantity representing the same thing as Gibbs energy.

- If two phases are in equilibrium between liquid and gas, then since $dG = 0$ and $dn^g \neq 0$, $\mu^g = \mu^l$.

- "If the two phases are not in equilibrium with each other, a spontaneous transfer of matter from one phase to the other will occur in the direction such that $dG < 0$" (McQuarrie & Simon, 1997, p. 937).

  - For example, if $\mu^g > \mu^l$, we must have $dn^g < 0$ for dG to be negative, meaning that matter will transfer from the vapor phase to the liquid phase.

- McQuarrie and Simon (1997) derives the equation for dP/dT exactly as in class.

- **Clapeyron equation**: The relation between the slope of the two-phase boundary line in a phase diagram and the values of $\Delta_{\text{trs}}\overline{H}$ and $\Delta_{\text{trs}}\overline{V}$ for a transition between those two phases. *Given by*

$$\frac{dP}{dT} = \frac{\Delta_{\text{trs}}\overline{H}}{T\Delta_{\text{trs}}\overline{V}}$$

- Note that $\Delta_{\text{fus}}\overline{H}$ and $\Delta_{\text{fus}}\overline{V}$ do vary with pressure, but not always significantly.

- **Clausius-Clapeyron equation**: The relation between the vapor pressure of a liquid and its temperature. *Given by*

$$\frac{d\ln P}{dT} = \frac{\Delta_{\text{vap}}\overline{H}}{RT^2}$$

  - Two assumptions were made in the derivation of the Clausius-Clapeyron equation form the Clapeyron equation: $\overline{V}^g \gg \overline{V}^l$ and the vapor pressure is so low that the gas can be treated as ideal (so we can replace $\overline{V}^g$ with RT/P).

- – Thus, the Clausius-Clapeyron equation is easier to use, but the Clapeyron equation is more general.

- – Furthermore, if $\Delta_{\text{vap}}\overline{H}$ does not vary with temperature over the integration limits of T, then

$$\ln \frac{P_2}{P_1} = -\frac{\Delta_{\text{vap}}\overline{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- Taking the indefinite integral of the Clausius-Clapeyron equation shows that $\ln P$ and $1/T$ have a linear relation with slope $-\Delta_{\text{vap}}\overline{H}/R$.

  - – This relation can be used to experimentally measure $\Delta_{\text{vap}}\overline{H}$.

  - – By representing $\Delta_{\text{vap}}\overline{H}$ as a Taylor polynomial in T, we can also find more exact values for it based on (P, T) data.

- McQuarrie and Simon (1997) shows that the slope of the solid-gas coexistence curve is greater than the slope of the liquid-gas coexistence curve the same way PGS did in class.

- Deriving an expression for the chemical potential μ in terms of the partition function Q.

  - – We know that

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \qquad S = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

  - – It follows that

$$A = U - TS$$
$$= -k_B T \ln Q$$

  - – Additionally, the total differential of $A(T, V, n)$ is

$$dA = \left(\frac{\partial A}{\partial T}\right)_{n,V} dT + \left(\frac{\partial A}{\partial V}\right)_{n,T} dV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$
$$= -S\,dT - P\,dV + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

  and the total differential of $G(T, P, n)$ is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \left(\frac{\partial G}{\partial n}\right)_{T,P} dn$$
$$= -S\,dT + V\,dP + \mu\,dn$$

  - – But since

$$dG = dA + d(PV) = -S\,dT + V\,dP + \left(\frac{\partial A}{\partial n}\right)_{T,V} dn$$

  we have by direct comparison that

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

  - – It follows by substituting our previous expression for $A(Q)$ that

$$\mu = -k_B T \left(\frac{\partial \ln Q}{\partial n}\right)_{V,T} = -RT \left(\frac{\partial \ln Q}{\partial N}\right)_{V,T}$$

- For an ideal gas where $Q = q^N/N!$, we have by Stirling's approximation that

$$\mu = -RT \frac{\partial}{\partial N} \left(\ln \frac{q^N}{N!} \right)$$
$$= -RT \frac{\partial}{\partial N} (N \ln q - N \ln N + N)$$
$$= -RT (\ln q - \ln N - 1 + 1)$$
$$= -RT \ln \frac{q(V,T)}{N}$$

- Note that this expression for μ in terms of the partition function easily yields one for G in terms of the partition function via $G = n\mu$.

- McQuarrie and Simon (1997) discusses alternate forms of μ and $\mu°$.

7.8 Chapter 24: Solutions I — Liquid-Liquid Solutions

From McQuarrie and Simon (1997).

2/28:
- In this chapter, we consider in particular solutions of two volatile liquids.

- Having discussed the thermodynamics of one-component systems, we now move into the thermodynamics of two-component systems, though many of our results generalize to multicomponent solutions.

- McQuarrie and Simon (1997) analyzes $G(T, P, n_1, n_2)$ as in class.

- **Partial molar entropy**. The following quantity. *Denoted by $\overline{S}_j$. Given by*

$$\overline{S}_j = \left(\frac{\partial S}{\partial n_j} \right)_{T,P,n_i}$$

for all $i \neq j$.

- **Partial molar volume**. The following quantity. *Denoted by $\overline{V}_j$. Given by*

$$\overline{V}_j = \left(\frac{\partial V}{\partial n_j} \right)_{T,P,n_i}$$

for all $i \neq j$.

- In general, extensive thermodynamic properties Y have associated partial molar quantities $\overline{Y}_j$ defined analogously to the above.

- **Binary solution**: A solution composed of two different liquids.

3/1:
- Deriving a formula for G in terms of n_1, n_2 at constant T, P.

  - At constant T, P, we have that
  $$dG = \mu_1 \, dn_1 + \mu_2 \, dn_2$$

  - Now imagine that we increase the amount of each component linearly from 0 to n_i.

  - Then the amount of each component present at a given time can be represented as $n(\lambda) = n_i \lambda$ where λ varies from 0 to 1.

  - It follows that $dn_i = n_i \, d\lambda$ and, since G is extensive, $dG = G \, d\lambda$.

– Therefore, it follows from the above equation that

$$\int_0^1 G \, d\lambda = \int_0^1 n_1 \mu_1 \, d\lambda + \int_0^1 n_2 \mu_2 \, d\lambda$$

$$G \int_0^1 d\lambda = n_1 \mu_1 \int_0^1 d\lambda + n_2 \mu_2 \int_0^1 d\lambda$$

$$G(T, P, n_1, n_2) = \mu_1 n_1 + \mu_2 n_2$$

- Similarly,

$$Y = \sum_{i=1}^m \overline{Y}_i n_i$$

for any quantity Y (like entropy or volume) in an m-component system.

- Note that this implies that the final volume of a solution is not necessarily a straight sum of the component volumes, but rather depends on the partial molar volumes.

- Extending $dG = -S \, dT + V \, dP$ into multicomponent systems.

    – If we consider the Gibbs energy as $G(T, P, n_1, \dots, n_m)$, then since $G = H - TS$, we have that

    $$\left(\frac{\partial G}{\partial n_j} \right)_{T,P,n_i} = \left(\frac{\partial H}{\partial n_j} \right)_{T,P,n_i} - T \left(\frac{\partial S}{\partial n_j} \right)_{T,P,n_i}$$

    – It follows that

    $$\mu_j = \overline{G}_j = \overline{H}_j - T\overline{S}_j$$

    – Using the Maxwell relations

    $$\overline{S}_j = -\left(\frac{\partial \mu_j}{\partial T} \right)_{P,n_i} \qquad\qquad \overline{V}_j = \left(\frac{\partial \mu_j}{\partial P} \right)_{T,n_i}$$

    and the total differential of μ_j, we can determine that

    $$d\mu_j = -\overline{S}_j \, dT + \overline{V}_j \, dP$$

- Similarly, the Gibbs-Helmholtz equation for multicomponent systems is

$$\left(\frac{\partial \mu_j / T}{\partial T} \right)_P = -\frac{\overline{H}_j}{T^2}$$

- **Gibbs-Duhem equation**: The relation between the chemical potential of one component in a binary solution as a function of composition to the other. *Given by*

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

or

$$x_1 \, d\mu_1 + x_2 \, d\mu_2 = 0$$

    – Derivation: The total differential of $dG = n_1 \mu_1 + n_2 \mu_2$ is

    $$dG = \mu_1 \, dn_1 + \mu_2 \, dn_2 + n_1 \, d\mu_1 + n_2 \, d\mu_2$$

    from which we can subtract $dG = \mu_1 \, dn_1 + \mu_2 \, dn_2$ to get the former form and divide that by $n_1 + n_2$ to get the latter form.

- Note that we can also derive Gibbs-Duhem type equations for other intensive properties (such as the partial molar volume).

- $\boldsymbol{Y^*}$: A property of a pure substance.

  - For example, μ_1 denotes the chemical potential of substance 1 (which may be affected by $n_2, \ldots, n_m$) whereas μ_1^* denotes μ_1 at $x_1 = 1$.

- If one component of a binary solution obeys **Raoult's law** over the complete concentration range, the other component does, too.

  - Suppose the chemical potential of one component in a binary solution is given by

  $$\mu_2 = \mu_2^* + RT \ln x_2$$

  - Then

  $$\mathrm{d}\mu_1 = -\frac{x_2}{x_1}\,\mathrm{d}\mu_2$$
  $$= -\frac{x_2}{x_1} \cdot RT\frac{\mathrm{d}x_2}{x_2}$$
  $$= -RT\frac{\mathrm{d}x_2}{x_1}$$
  $$= RT\frac{\mathrm{d}x_1}{x_1}$$
  $$\int_1^{x_1} \mathrm{d}\mu_1 = RT \int_1^{x_1} \frac{\mathrm{d}x_1'}{x_1'}$$
  $$\mu_1 = \mu_1^* + RT \ln x_1$$

- McQuarrie and Simon (1997) derives, exactly as in class, $\mu_j^\alpha = \mu_j^\beta$ for any component j and two phases α, β in equilibrium.

- An important consequence of this is that "the chemical potential of each component in liquid solution can be measured by the chemical potential of that component in the vapor phase" (McQuarrie & Simon, 1997, p. 970).

  - If the pressure P_j of the vapor phase is sufficiently low[1], we may treat it as ideal and employ

  $$\mu_j^{\mathrm{sln}} = \mu_j^{\mathrm{vap}} = \mu_j^\circ(T) + RT \ln P_j$$

  - It follows if j is pure $(x_j = 1)$ that

  $$\mu_j^*(l) = \mu_j^\circ(T) + RT \ln P_j^*$$

  - By subtracting the above two equations, we can derive an expression for the the chemical potential of component j in solution in terms of its chemical potential as a pure substance, its vapor pressure, and its vapor pressure as a pure substance.

  $$\mu_j^{\mathrm{sln}} = \mu_j^*(l) + RT \ln \frac{P_j}{P_j^*}$$

- **Raoult's law**: The partial vapor pressure of each component of a solution is directly proportional to its mole fraction in solution. *Given by*
  $$P_j = x_j P_j^*$$

  - Note that x_j reflects the fraction of the solution *surface* that is occupied by molecules of type j (since it is these molecules that can escape into the vapor phase).

---

[1]Technically, we should use fugacities throughout, but vapor pressures under standard conditions typically are small enough so that the difference between the pressure and the fugacity is negligible.

- **Ideal solution**: A solution that obeys Raoult's law over the entire composition range.

- At a molecular level, ideal binary solutions look like two types of molecules distributed randomly throughout solution.

  - This occurs when the molecules are of similar size and shape, and the intermolecular forces are all similar.

- Between our expression for μ_j^{sln} in terms of the characteristics of the pure substance and Raoult's law, we have that

$$\mu_j^{\text{sln}} = \mu_j^*(l) + RT \ln x_j$$

- Deriving an expression for the total vapor pressure of an ideal binary solution.

$$
\begin{aligned}
P_{\text{tot}} &= P_1 + P_2 \\
&= x_1 P_1^* + x_2 P_2^* \\
&= (1 - x_2) P_1^* + x_2 P_2^* \\
&= P_1^* + x_2 (P_2^* - P_1^*)
\end{aligned}
$$

  - The above formula is a straight line that evaluates to P_1^* at $x_2 = 0$ and P_2^* at $x_2 = 1$, as we would expect (see Figure 7.1).

- Deriving an expression for the total vapor pressure of a binary solution in terms of the mole fraction y_2 of component 2 in the vapor phase.

  - By Dalton's law of partial pressures, which asserts that the partial pressure P_2 of the vapor of component 2 is equal to its mole fraction y_2 in the vapor phase, we have that

$$y_2 = \frac{P_2}{P_{\text{tot}}} = \frac{x_2 P_2^*}{P_{\text{tot}}} = \frac{x_2 P_2^*}{P_1^* + x_2(P_2^* - P_1^*)}$$

  - Solving for x_2 yields

$$x_2 = \frac{P_1^* y_2}{P_2^* - y_2(P_2^* - P_1^*)}$$

  - Therefore,

$$
\begin{aligned}
P_{\text{tot}} &= P_1^* + x_2(P_2^* - P_1^*) \\
&= P_1^* + \frac{P_1^* y_2}{P_2^* - y_2(P_2^* - P_1^*)}(P_2^* - P_1^*)
\end{aligned}
$$

- **Pressure-composition diagram**: A diagram that plots the total vapor pressure as a function of the composition of both the liquid phase and the vapor phase.
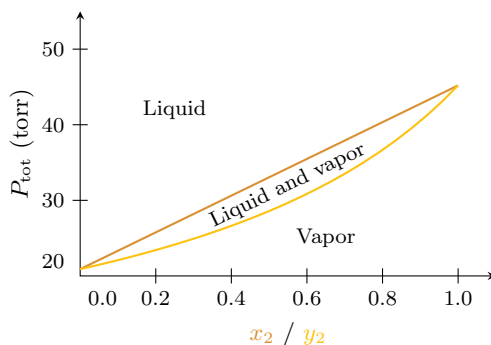

Figure 7.3: Pressure-composition diagram for a 1-propanol/2-propanol solution.

- In Figure 7.3, the brown line plots the total vapor pressure as a function of the composition of the liquid phase, and the yellow line plots the total vapor pressure as a function of the composition of the vapor phase (as per the equations derived above).

- A vertical line in Figure 7.3 corresponds to a single solution as pressure varies. If the vertical line is not at zero or 1, we see that high pressures yield exclusively the liquid phase, low pressures yield exclusively the vapor phase, and there is a region of pressures where both liquid and vapor coexist.

- **Tie line**: A horizontal line in a pressure-composition diagram that, for a given pressure, connects the concentration that will give entirely liquid to the composition that will give entirely vapor.

- Determining the relative amounts of liquid and vapor.

  - The mole fractions of component 2 in the liquid and vapor phases are, respectively,

$$x_2 = \frac{n_2^l}{n_1^l + n_2^l} = \frac{n_2^l}{n^l} \qquad\qquad y_2 = \frac{n_2^g}{n_1^g + n_2^g} = \frac{n_2^g}{n^g}$$

  - The overall mole fraction of component 2 is

$$x_a = \frac{n_2^l + n_2^g}{n^l + n^g}$$

  - It follows that

$$x_a(n^l + n^g) = x_2 n^l + y_2 n^g \frac{n^l}{n^g} \qquad\qquad = \frac{y_2 - x_a}{x_a - x_2}$$

- **Lever rule**: The balance of the number of moles in each phase and the excess fractions of liquid and vapor. *Given by* the above.

  - "Note that $n^l = 0$ when $x_a = y_2$ (vapor curve) and that $[n^g = 0]$ when $x_a = x_2$ (liquid curve)" (McQuarrie & Simon, 1997, p. 973).

- **Temperature-composition diagram**: A diagram that plots the composition of the solution and vapor phases at various temperatures.

  - Pressure is held constant in such a diagram, so choose $760\,\text{torr}$.
  - It follows that the mole percent of component 1 at this pressure is

$$760\,\text{torr} = P_2^* - x_1(P_2^* - P_1^*)$$
$$x_1 = \frac{P_2^* - 760\,\text{torr}}{P_2^* - P_1^*}$$

  - We can then find P_1^*, P_2^* at a given temperature either from a table the Clausius-Clapeyron equation (though the latter will be an approximation).

  - Lastly, we can find y_1 as before.

- Fractional distillation in a temperature-composition diagram.

  - During fractional distillation, a substance is repeatedly heated up, some vapor removed, and then heated up higher as now possible.

  - In Figure 7.4, we can see how at any given ratio, we can only heat up the liquid so much before we begin vaporizing both liquids, but by removing some vapor (increasing the concentration of the less volatile substance), we can now heat it up more.

  - The diagram also provides a pictoral representation of the law of diminishing returns (as we can never get all the way over to the top-right corner).
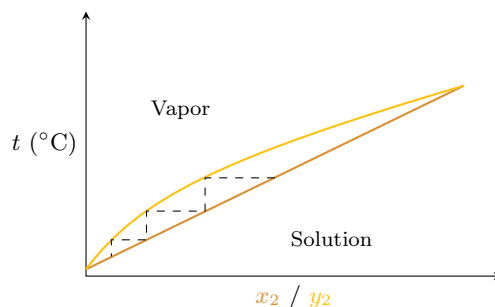
Figure 7.4: Temperature-composition diagram for a 1-propanol/2-propanol solution.

- Calculating the energy of mixing $\Delta_{\mathrm{mix}}G^{\mathrm{id}}$ of two ideal solutions of pure components.

$$\begin{aligned}
\Delta_{\mathrm{mix}}G^{\mathrm{id}} &= G^{\mathrm{sln}}(T, P, n_1, n_2) - G_1^*(T, P, n_1) - G_2^*(T, P, n_2) \\
&= n_1 \mu_1^{\mathrm{sln}} + n_2 \mu_2^{\mathrm{sln}} - n_1 \mu_1^* - n_2 \mu_2^* \\
&= n_1(\mu_1^* + RT \ln x_1) + n_2(\mu_2^* + RT \ln x_2) - n_1 \mu_1^* - n_2 \mu_2^* \\
&= RT(n_1 \ln x_1 + n_2 \ln x_2)
\end{aligned}$$

  - Since $x_1, x_2 < 1$, we know $\Delta_{\mathrm{mix}}G^{\mathrm{id}} < 1$, i.e., ideal solutions always form spontaneously from their separate components.

- The entropy of mixing of two ideal solutions of pure components.

$$\Delta_{\mathrm{mix}}S^{\mathrm{id}} = -\left(\frac{\partial \Delta_{\mathrm{mix}}G^{\mathrm{id}}}{\partial T}\right)_{P, n_1, n_2} = -R(n_1 \ln x_1 + n_2 \ln x_2)$$

  - This result is identical to that for the mixing of two ideal gases.
  - However, there are marked differences between solutions and gases, namely in the extent of intermolecular interactions. The similarity is accounted for by the fact that "in an ideal solution, the interactions in the mixture and those in the pure liquids are essentially identical" (McQuarrie & Simon, 1997, p. 977).

- We can also calculate that

$$\Delta_{\mathrm{mix}}V^{\mathrm{id}} = \left(\frac{\partial}{\partial \Delta_{\mathrm{mix}}G^{\mathrm{id}}}\right)_{T, n_1, n_2} = 0 \qquad \Delta_{\mathrm{mix}}H^{\mathrm{id}} = \Delta_{\mathrm{mix}}G^{\mathrm{id}} + T\Delta_{\mathrm{mix}}S^{\mathrm{id}} = 0$$

  - These results follow from the similarities in particles shape and size, and interaction energy, respectively, assumed for an ideal solution.