

## Week 7

# Phase Diagrams and Critical Points

### 7.1 Virial Coefficients and Fugacity

2/21: • 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

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

- 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,

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

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

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

where we have used  $e^x = 1 + x + \dots$  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,

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

- 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  $f_{ij} \rightarrow 0$  as  $|r_i - r_j| \rightarrow \infty$ .
- Thus,

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

- 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

$$\begin{aligned} Q_u &= \frac{1}{V^N} \int \left( 1 + \sum_{i < j} f_{ij} \right) d^3 r_i \\ &= \frac{1}{V^N} \left( V^N + \frac{N(N-1)}{2} V^{N-2} \int f_{12} d^3 r_1 d^3 r_2 \right) \\ &= 1 + \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \end{aligned}$$

- It follows that

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

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

$$\begin{aligned} P &= k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \\ &= k_B T \left( \frac{\partial \ln Q_{\text{id}}}{\partial V} \right)_{N,T} + k_B T \left( \frac{\partial \ln Q_u}{\partial V} \right)_{N,T} \end{aligned}$$

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

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

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

- Thus,

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

so

$$\begin{aligned} P &= \frac{Nk_B T}{V} - \frac{Nk_B T}{V} \frac{N-1}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \\ &= \frac{RT}{\bar{V}} - \frac{RT}{\bar{V}} \frac{N-1}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \end{aligned}$$

- Consequently,

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

- Therefore, by comparison with the virial expansion,

$$\begin{aligned} B_{2V}(T) &= -\frac{N_A}{2} \int (e^{-\beta u(r)} - 1) d^3 r \\ &= -\frac{N_A}{2} \int_0^\infty (e^{-\beta u(r)} - 1) 4\pi r^2 dr \\ &= -2\pi N_A \int_0^\infty (e^{-u(r)/k_B T} - 1) r^2 dr \end{aligned}$$

- 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  $d\bar{G} = -\bar{S}dT + \bar{V}dP$ . It follows that

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

- Thus,

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

- In the ideal case,

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

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

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

- The second term in the above equation refers to the Gibbs free energy of an ideal gas at  $P_0 = 1$  bar or  $P_0 = 1$  atm. Note that even at  $P_0 = 1$  atm, however, there is too much pressure for truly ideal behavior, so  $f \neq P_0$ .
- Imagine that  $\Delta \bar{G}_1$  takes us from a real gas at  $(T, P)$  to an ideal gas at  $(T, P)$ . Then

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

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

$$\Delta \bar{G}_2 = - \int_{P \rightarrow 0}^P \bar{V} dP' \qquad \Delta \bar{G}_3 = \int_{P \rightarrow 0}^P \frac{RT}{P'} dP'$$

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

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

- We then define  $\gamma$  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  $dU = 0$ . Moreover, since  $dU = C_1 dT_1 + C_2 dT_2$ , we have that  $C_1 dT_1 = -C_2 dT_2$ .

– 3b.

- The appropriate derivation was

$$\begin{aligned} dS &= dS_1 + dS_2 \\ &= \frac{C_1 dT_1}{T_1} + \frac{C_2 dT_2}{T_2} \\ &= C_1 dT_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \end{aligned}$$

from which it follows since  $T_2 > T_1$  (and hence  $1/T_1 - 1/T_2 > 0$ ), since  $dS > 0$ , and since  $C_1 > 0$  that  $dT_1 > 0$ .

– 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  $T \rightarrow T_c$ .
- The slope of coexistence curves on  $PT$  phase diagrams.

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

$$\begin{aligned} d\bar{G}_\alpha &= d\bar{G}_\beta \\ \left( \frac{\partial \bar{G}_\alpha}{\partial T} \right)_P dT + \left( \frac{\partial \bar{G}_\alpha}{\partial P} \right)_T dP &= \left( \frac{\partial \bar{G}_\beta}{\partial T} \right)_P dT + \left( \frac{\partial \bar{G}_\beta}{\partial P} \right)_T dP \\ -\bar{S}_\alpha dT + \bar{V}_\alpha dP &= -\bar{S}_\beta dT + \bar{V}_\beta dP \\ (\bar{V}_\alpha - \bar{V}_\beta) dP &= (\bar{S}_\alpha - \bar{S}_\beta) dT \\ \frac{dP}{dT} &= \frac{\bar{S}_\alpha - \bar{S}_\beta}{\bar{V}_\alpha - \bar{V}_\beta} = \frac{\Delta \bar{S}_{\text{trans}}}{\Delta \bar{V}_{\text{trans}}} \end{aligned}$$

- Clearly, the last line above gives the slope of the coexistence curves on a phase diagram.
- Since  $T \Delta \bar{S}_{\text{trans}} = \Delta \bar{H}_{\text{trans}}$  ( $\Delta G = 0$ ), we also have

$$\frac{dP}{dT} = \frac{\Delta \bar{H}_{\text{trans}}}{T \Delta \bar{V}_{\text{trans}}}$$

- Since both  $\Delta \bar{H}_{\text{trans}}, \Delta \bar{V}_{\text{trans}} \rightarrow 0$  as  $T \rightarrow T_c$ ,  $dP/dT$  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  $\Delta \bar{V}_{\text{vap}} = \bar{V}_g - \bar{V}_l$  where  $\bar{V}_g \gg \bar{V}_l$ . Therefore, we may approximate  $\Delta \bar{V}_{\text{vap}} \approx \bar{V}_g$ .
  - Additionally, we have that  $\bar{V}_g = RT/P$ .
  - It follows that

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta \bar{H}_{\text{vap}}}{T \bar{V}_g} \\ &= \frac{P \Delta \bar{H}_{\text{vap}}}{RT^2} \\ \frac{dP}{P} &= \frac{\Delta \bar{H}_{\text{vap}}}{R} \frac{dT}{T^2} \\ \ln \frac{P}{P_0} &= \frac{\Delta \bar{H}_{\text{vap}}}{R} \left( -\frac{1}{T} + \frac{1}{T_0} \right)\end{aligned}$$

- 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

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

- Note that we take  $\Delta \bar{H}_{\text{vap}}$  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  $\Delta H_{\text{vap}}$ .
- 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,  $dP_{\text{SG}}/dT > dP_{\text{LG}}/dT$  since  $\Delta \bar{H}_{\text{SG}} = \Delta \bar{H}_{\text{SL}} + \Delta \bar{H}_{\text{LG}} > \Delta \bar{H}_{\text{LG}}$  and  $\Delta \bar{V}_{\text{SG}} \approx \Delta \bar{V}_{\text{LG}}$ .
  - Quantitatively, the ratio of the slopes is

$$\frac{dP_{\text{SG}}/dT}{dP_{\text{LG}}/dT} = \frac{\Delta \bar{H}_{\text{SG}}}{\Delta \bar{H}_{\text{LG}}} = 1 + \frac{\Delta \bar{H}_{\text{SL}}}{\Delta \bar{H}_{\text{LG}}}$$

## 7.3 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  $\bar{V}$ , 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  $\bar{V}$  (and solving for  $\bar{V}$  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<sub>2</sub>O 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  $\sigma$  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  $\sigma$  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.

## 7.4 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  $\sigma$ . *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,

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

- Thus,  $B_{2V}(T)$  is equal to 1/2 the volume of  $N_A$  hard spheres of radius  $\sigma$ .
- 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  $\sigma$  that is attractive at a consistent level from its surface up until a finite distance away. *Given by*

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

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

- Under the square-well potential,

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

- 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  $1/(1 - x) = 1 + x + x^2 + \dots$ , we have that

$$\begin{aligned} P &= \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} \frac{1}{1 - b/\bar{V}} - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} \left[ 1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots \right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a) \frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \dots \end{aligned}$$

– It follows that

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

– 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).

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

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

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

- 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.

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

## 7.5 Chapter 22: Helmholtz and Gibbs Energies

From McQuarrie and Simon (1997).

- Generalizing the equation  $\bar{G} = G^\circ + RT \ln Q$  to the case of a real gas.
- We begin by substituting the virial expansion in terms of pressure into the equation  $(\partial \bar{G} / \partial P)_T = \bar{V}$ .

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

- Note that we neglect  $P_{\text{id}}$  in every term except the first because it is so close to zero.
- Substituting  $\bar{G}(T, P^{\text{id}}) = G^\circ(T) + RT \ln P^{\text{id}}/P^\circ$  and combining the first two terms yields

$$\bar{G}(T, P) = G^\circ(T) + RT \ln \frac{P}{P^\circ} + RT B_{2P}(T)P + RT B_{3P}(T) \frac{P^2}{2} + \dots$$

- 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

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

- Fugacity must have the property that  $f(P, T) \rightarrow P$  as  $P \rightarrow 0$ , so that the above equation can reduce to  $\bar{G} = G^\circ + RT \ln P/P^\circ$ .
- By setting the above equal to the virial expansion, we learn that

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

- “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

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

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  $\gamma$ . Given by

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

- Also note the equation

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

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