Lecture 22  Chapter 11 section 6 and Chapter 8 Sections 1-4 from Atkins
Announce:

• Outline:
  - osmotic pressure
  - electrolyte solutions
  - phase diagrams of mixtures
    - Gibbs phase rule
  - liquid-vapor distillation
  - azeotropes

Review

activity

\[ a_A = \gamma_A X_A \quad (\gamma_A \text{ is not constant}!!) \]

as \( X_A \rightarrow 1 \), \( \gamma_A \rightarrow 1 \) and therefore \( a_A \rightarrow X_A \)

(Note that activity could also be defined in terms of \( M \) or \( m \).)

\[ \Delta G_{\text{mix}} = \Delta G_{\text{ideal}} + \Delta G_{\text{excess}} \]

\[ \Delta G_{\text{mix}} = n_{\text{tot}}RT \left( X_A \ln X_A + X_B \ln X_B + X_A \ln \gamma_A + X_B \ln \gamma_B \right) \]

ideal mixing  excess Gibbs energy of mixing

colligative properties depend only on amount of solute, not identity
assume that solute affects only liquid

boil pt elevation
\[ \Delta T = \left( \frac{RT^2}{\Delta_{\text{cap}} H} \right) X_B \]

freeze point depression

\[ \Delta T = \left( \frac{RT^2}{\Delta_{\text{fus}} H} \right) X_B \]

OK, one last colligative property that we will look at.

**Osmotic pressure**

osmosis: the passage of a pure solvent into a solution separated from it by a semipermeable membrane (impermeable to the solute).

osmotic pressure: the pressure that must be applied to the solution to stop the transfer of solvent.

\[ \downarrow p \quad \downarrow p + \Pi \]

\[ \mu_A^*(p) \quad \rightarrow \quad \mu_A(p + \Pi) \quad \rightarrow \quad \mu_B(p + \Pi) \]

The pure solvent is thermodynamically driven to the solution side because of the lower chemical potential for A in solution.

Because we are at equilibrium, it must be that the change in the chemical potential for mixing is exactly equal to the change in chemical potential for additional pressure:

\[ \Delta_{\text{mix}} G \quad \text{from our above} \quad \mu_A(l) = \mu_A^*(l) + RT \ln X_A \]

\[ \Delta_{\text{press}} G \quad \text{from} \quad dG = Vdp - SdT \quad \text{(constant T)} \]

\[ -RT \ln X_A = \int_{p}^{p+\Pi} V_m dp \]

If we make two additional assumptions:

1) \( V_m \) doesn't change for the pressure range of interest
2) \( \ln X_A = \ln (1 - X_B) \sim -X_B \) for small \( X_B \)
\[ RTX_B = \Pi V_m \]

For small \( X_B \), \( X_B = n_B/(n_A+n_B) \approx n_B/n_A \). And \( n_A V_{Am} = V \),

Thus, we can rewrite this equation in a very tantalizing form:

\[ \Pi V = n_B RT \]

The practical use for this arrangement is the determination of molecular masses of large biochemical molecules.

i.e. put a known mass of stuff in solution, measure \( \Pi \), this gives \( n \).

**Electrolytes**

dissolve CA in water

\[ C_{v+}A_{v-}(s) \rightarrow v_+C^{z+}(aq) + v_-zA^{z-}(aq) \]

\[ \text{NaCl (s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \]

Total solute chemical potential

\[ \mu_2 = v_+\mu_+ + v_-\mu_- \]

\[ a_2 = a_v^+a_v^- = a_v^- \quad (\text{where } v = v_+ + v_-) \]

Activity is defined similarly to before, but in terms of molality instead of mole fraction (why not use molarity? it is temp dependent)

\[ a_+ = m_+\gamma_+ \]

This leads to

\[ a_2 = a_\pm = a_v^+a_v^- = m_+\gamma_+m_-\gamma_- = m_\pm\gamma_\pm \]

Book does several examples

Note that because many ions have \( v > 1 \), electrolytes are often non-ideal even at low concentrations.

We have spent the last several days talking about how understanding condensed phases will help us understand intermolecular interactions. We have finally ended up showing how the activity coefficient tells us about \( \Delta_{\text{mix}}G \). But, \( \gamma \) is still just an empirical factor. We would really like to understand things well enough to be able to derive \( \gamma \) for a solute.

**Debye-Hückel Theory**

We will derive (actually just show) the activity for electrolytes in (dilute) solution.

We assume:

1) the solvent is a perfect continuum dielectric (\( \varepsilon \sim 80 \) for water, \( \varepsilon = 1 \) for vacuum)
2) the solutes interact only Coulombically – otherwise their distribution is random.
Note that we are dealing now with the activity coefficient in terms of molarity, not mole fraction of molality.

\[
\ln \gamma_j = -\frac{\kappa q_j^2}{8 \pi \varepsilon_0 \epsilon k_B T}
\]

\[
\ln \gamma_\pm = -|q_+ q_-| \frac{\kappa}{8 \pi \varepsilon_0 \epsilon k_B T}
\]

\[
\kappa^2 = \sum_{j=1}^{s} \frac{q_j^2}{\epsilon_0 \epsilon k_B T} \left( \frac{N_j}{V} \right)
\]

\[
q_+ = z_+ e \quad q_- = z_- e
\]

(s is the number of ionic species)

Ionic Strength

\[
I_c = \frac{1}{2} \sum_{j=1}^{s} \left( z_j^2 c_j \right)
\]

(note that \(c\) is in molarity here)

this allows us to rewrite the equation for \(\kappa\) and \(\gamma\)

\[
\kappa^2 = \frac{2e^2 N_j (1000 \text{ m}^{-1})}{\epsilon_0 \epsilon k_B T} I_c
\]

\[
\ln \gamma_\pm = -1.173 |z_+ z_-| I_c
\]

(aqueous solution at 25 °C)

Note that \(\kappa\) has units of meters\(^{-1}\)

\(\kappa^{-1}\) is the Debye screening length. It describes the volume required to contain a neutralizing amount of counter ion.

if \(\kappa R < 1\) (or \(R \approx 1/\kappa\)) \(\rightarrow\) pos and neg ions are closely paired

if \(\kappa R >> 1\) (or \(R >> 1/\kappa\)) \(\rightarrow\) ions are screened from each other

(where \(R\) is the separation of the ions)

OK, so we have formed a connection between fundamental molecular properties like dielectric constant (really only defined for bulk, not molecules) and ionic charge.

Note that if we allowed \(\varepsilon\) to be variable, we would have the Poisson-Boltzmann equation. This is often used to describe solvation free energies in contemporary research problems.
Phase Diagrams for Mixtures

Information available:
1) As for phase diagrams for pure substances, it is a mapping of physical changes as pressure and temperature are varied.
2) However, we have an additional variable: composition ($z_A$).
3) Indicator of possible equilibria between the various phases.

Gibbs Phase rule: $F = C - P + 2$

**Phase (P):** a state of matter that is uniform throughout in chemical composition (this does not necessarily mean a pure chemical composition) and physical state.
- Ice: $P = 1$
- Ice/water: $P = 2$
- Water at the triple point: $P = 3$

**Component (C):** the minimum number of independent chemical species necessary to define the composition of all the phases present in the system. Not as simple as it sounds – please read this part of handout carefully. But, basically salt water should be $C = 2$.

**Degrees of Freedom (F):** the number of intensive variables ($T$, $p$, composition) that can be changed independently without disturbing the number of phases in equilibrium.

Let’s try it out:

- liquid water: $F = 1 - 1 + 2 = 2$ (temperature and pressure are independent)
- boiling water: $F = 1 - 2 + 2 = 1$ (temperature and pressure are coupled)
- water at triple point: $F = 1 - 3 + 2 = 0$ (temperature and pressure are both fixed)

When $F = 2$, the single phase that is mapped out by the temperature and pressure, is represented by an **area** on the phase diagram.

When $F = 1$, the phase boundary (the coupled dependence of the temperature and pressure) is represented by a **line** on the phase diagram.

When $F = 0$, both the temperature and pressure are each confined to a fixed value, with this condition being represented by a **point** (the triple point) on the phase diagram.

**Show Diagram 8.3** as water is cooled at constant pressure, we lose control of the temperature at the phase boundaries (this is why substances have well-defined phase transition temperatures)
Two-Component Systems:

We have talked about this quite a bit already, so we’ll go quickly

Binary mixture of volatile liquids → Raoult’s law

With two components, the phase rule is \( F = 4 - P \)
If the temperature is constant, there are still, at most, two remaining degrees of freedom \( (F' = 3 - P) \). Therefore, a phase diagram could be constructed with the pressure and composition as the independent variables.

Alternatively, the pressure could be held constant, and a phase diagram could be constructed as a function of temperature and composition (this is more common).

**Pressure-composition diagram (holding temperature constant)**

From Raoult’s law:

\[
p_A = X_A p_A^* \quad \text{and} \quad p_B = X_B p_B^*
\]

**Equation for total vapor pressure with respect to liquid phase composition**

\[
p = p_A + p_B = X_A p_A^* + X_B p_B^* = p_B^* + (p_A^* - p_B^*) X_A \quad (\text{where } X_B = 1 - X_A)
\]

This gives our familiar dependence of the vapor pressure on composition

![Diagram of binary mixture obeying Raoult's Law](image)

Liquid and vapor phase compositions are not the same. One would expect that the gas phase is more rich in the more volatile component (i.e. this why the head on a glass of beer is more alcoholic).
From Dalton’s law for the mole fractions in the gas phase (note we are using $X$ for the composition of the liquid phase and $Y$ for the gas phase):

$$Y_A = \frac{p_A}{p} \quad Y_B = \frac{p_B}{p}$$

By combining our two equations above for $p_A$ and $p_{\text{tot}}$, we can solve for $Y_A$ and $Y_B$:

$$Y_A = \frac{X_A p_A^*}{p_B^* + (p_A^*-p_B^*)X_A} \quad Y_B = 1 - Y_A$$

So, our hypothesis that the more volatile component will have a larger mole fraction in the gas phase can be easily proved by plotting $X_A$ (liquid comp.) vs. $Y_A$ (gas comp.) for differing vapor pressure ratios ($p_A^*/p_B^*$) \textbf{Show Fig 8.7}

$p_A^*/p_B^*$ for ethanol/water is about 3, so the enhancement of ethanol in a head of beer is not really enough to change one’s drinking habits…

Above, we had $p_{\text{tot}}$ as a function of $X_A$. We can also express $p_{\text{tot}}$ as a function of $Y_A$. Even for an ideal solution, they are different. (show Figure 8.9)

$$p = \frac{p_A^* p_B^*}{p_A^* + (p_B^*-p_A^*)Y_A}$$

\textbf{Pressure composition diagrams}

\textbf{Draw diagram 8.10}

We can follow an \textbf{isopleth} (constant composition) as the pressure is dropped. We will go through this example methodically so as to understand the mechanics and principles involved.
1) Starting at point a, the pressure is high enough that substance exists in the liquid phase only. C = 2, P = 1, so F = 3 (but T implicitly fixed, so F' = 2)

2) After depressurization to p₁, the mixture is now at the line for which the liquid is in equilibrium with the gas. The composition of the liquid is a₁ which is essentially equal to a, our beginning composition. Drawing a horizontal line (called the tie line) over the gas line, we get the composition of the gas, a₁'. At this pressure, basically all of substance A is still a liquid. F' = 1 (F = 2) **Which component is more volatile?**

3) After additional depressurization to p₂, a horizontal line is drawn to both the liquid and gas curves to find the representative compositions. We can see that the composition of A drops in the liquid - the mixture must vaporize some of substance A to achieve the new composition (because we have only one degree of freedom, the composition must adjust for the change in pressure). By the same token, the composition of the gas is richer in A than the overall composition. We can quantify the amounts of liquid and gas through the lever rule: \( n_\alpha l_\alpha = n_\beta l_\beta \) Usually we use this in the form \( n_\alpha / n_\beta = l_\beta / l_\alpha \)

4) After another depressurization to p₃, we are at the point where everything has been converted to gas. Necessarily, the gas phase composition is now equal to the overall composition. The last drop of liquid was composition a₃'.

5) A final depressurization to p₄ results in the presence of the gas phase only at the overall composition we started with for the liquid. F' = 2 again.

With this example, we can see how the phase rule “forces” the change in composition as one of the independent variables (in this case, pressure) is changed in a way that a phase boundary is crossed.

**Temperature-composition diagrams (holding pressure constant)**

This is a more common way of looking at the physical properties of mixtures, since it is usually easier to control the temperature than the pressure in a typical laboratory setting. Again we will look at the case where A is the more volatile substance.

**Figure 8.14**
The **liquid is now**? on the bottom of the graph and the gas on the top. This liquid line represents the boiling pt as a function of temperature at a fixed pressure (of usually 1 atm). Again the region between the lines has $F' = 1$, while the regions above and below have $F' = 2$.

1) Beginning at point $a_1$, we have the liquid phase only and because $F' = 2$, we are free to change both the composition and the temperature.

2) If the temperature is increased to point $a_2$ on the liquid line, our liquid will start to boil (at temp $T_2$) and the composition of the gas phase is $a_2'$. As in the case of decreasing the pressure, increasing the temperature leads to an enrichment of the gas phase amount of the more volatile substance (A).

3) If the vapor were drawn off and condensed (point $a_3$ at temperature $T_3$), the liquid would have the same composition as the gas did at the higher temperature $T_2$. Thus we can see the principle behind distillation. Heating, collecting and cooling will lead to an enrichment of the more volatile substance.

4) Now let’s heat up our first sample from the first distillation and do the same procedure. Once point $a_3$ is reached (temperature $T_3$), the new gas composition is $a_3'$. This fraction can be collected and condensed (point $a_4$ at temperature $T_4$) and it may be seen that more volatile substance has been concentrated further still.

This is the basis for **fractional distillation** - repeated boiling and condensation cycles.

This is accomplished in practice by building a distillation column with a very high surface area to allow many condensation and vaporization events before the vapor is collected and condensed.
Draw a column with plates and a column with glass wool.
Depending on the substance being distilled, the column will need to allow more or less condensation steps (called theoretical plates). This is the reason why petroleum refining distillation columns are so high - it takes many steps to separate the very similar longer chain hydrocarbons (octane, nonane, etc.) from each other.

Non-ideal effects in temperature-composition phase diagrams (azeotropes)
Not all phase boundaries show a smooth temperature dependence with respecting to changing composition. This dependence on composition has to do with the non-ideal effects that are expected when the A-B interactions are different than the A-A or B-B interactions.

There are two possible situations:
1) The A-B interactions are much stronger than the A-A and B-B interactions, thus stabilizing the liquid. Therefore, we would expect a maximum in the boiling curve in this case. Chloroform-acetone is a case of this.
2) The A-B interactions are much weaker than the A-A and B-B interactions, thus destabilizing the liquid. Therefore we would expect a minimum in the boiling curve in this case. Ethanol-water is a case of this.

Show Figures 8.16 and 8.17
This possibility of strong non-ideal effects can have important ramifications for distillation.

Discuss a distillation procedure for diagram 8.16 and show how it is impossible to purify the liquid. All distillation procedures will lead to the minimum or maximum in the phase diagram and that corresponding mole fraction.

These mixtures are called azeotropes - meaning that boiling can take place without any change in composition.

Ethanol-water is a low boiling azeotrope. At 96 % ethanol, it will boil at a fixed composition at 78 °C.

Immiscible liquids
We can think of an immiscible mixture as two totally separate substances occupying the same container. For this case, the total pressure is simply the sum of the pure vapor pressures: \( p_A^* + p_B^* \). However, because the boiling point is defined for a total vapor pressure of one atmosphere, the immiscible mixture will boil at a lower temperature than would either of the two pure components \( \rightarrow \) basis for steam distillation. Show Figure 8.18

Take a look at Sections 8.5, 8.6, and 8.8 in Atkins (liquid-liquid, liquid-solid diagrams and 3 component systems, respectively)