Textbook Chapters for Exam 1

Chapter 16 sections 10 & 11. Chapter 17 sections 1-7 (no section 8 on colloids).

REMINDER! No graphing calculators for the exam. No formulas will be given on the exam. You do not get to bring a formula sheet. So KNOW your formulas. I will provide any constants that are needed.

Background Material

You must still have a basic understanding of thermodynamics which is Chapters 9 and 10. You should know the interplay between free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). This is summarized in the equation:

$$\Delta G = \Delta H - T\Delta S \quad \textit{(constant T)}$$

You should also know what it means to have a spontaneous process (reaction) and what favors a spontaneous process. Although you will not be directly tested over Chapters 9 and 10, you will need to have those concepts straight so as to answer thermodynamic questions out of Chapter 17.

Physical Equilibria

Physical equilibria are those between the different states of matter – solid, liquid, and gas. Every type change has a name:

$$\text{solid} \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftarrows}} \text{liquid}$$

$$\text{liquid} \underset{\text{condensation}}{\overset{\text{vaporization}}{\rightleftarrows}} \text{gas}$$

$$\text{solid} \underset{\text{deposition}}{\overset{\text{sublimation}}{\rightleftarrows}} \text{gas}$$

Every change has and energy cost also. All three of the changes above are endothermic as written (reading left -to-right). The liquid/gas equilibria gets a closer look.

Vapor Pressure

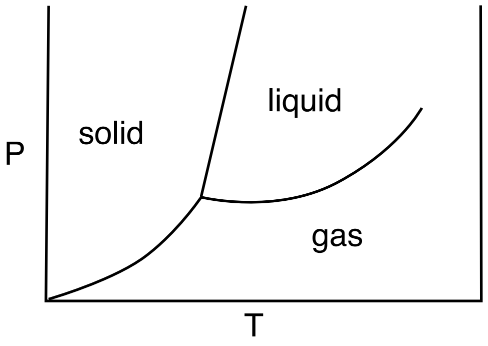
Be sure you understand what vapor pressure is. Why do we even say vapor? Is there any difference in a vapor and a gas? You can look it up and find lots of criteria for that difference. An easy and useful one is that a vapor is gas state of a substance that is normally a liquid at the given temperature. The vapor pressure of a liquid does increase with temperature, however, it is NOT linear (like ideal gases). The Clausius-Clapeyron equation is just what we need to relate 2 sets of conditions for vapor pressure. The equation is:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Any pressure units will work here. Only Kelvin temperature is valid though. Make sure your ΔH energy units and R units match. Also remember that if the normal boiling point of a substance is given in a problem, you immediately know its vapor pressure at that temperature – it's 760 torr.

Phase Diagrams

Now take a pure substance and trap it in a container that you can easily compress (high pressure) and expand (low pressure). You also must be able to control the temperature at any pressure. Now you can test numerous combinations of pressure and temperature and see what's in the container – solid, liquid, or gas or maybe combinations of them. What comes out of this experiment is a phase diagram. Here is a somewhat generic one:



Note where the solid, liquid, and gas phases are. Also note the endpoint of the liquid/gas line - that point is the *critical point*. The point where are 3 phases intersect is the *triple point*. Refer to your textbook for the phase diagram for water. What makes water rather unique in its diagram? Check out the slope of the solid/liquid line.

Dissolving Stuff

A solute dissolves into a solvent resulting in a solution. A solution is a homogeneous mixture. There is also an associated change in enthalpy when a solute goes from a pure solute to a solvated form. This process is known as solvation and the associated enthalpy change is the enthalpy of solvation, $\Delta H_{\text{solvation}}$. When the solvent is water the solvation process is hydration. The overall process is shown in your book as 3 thermodynamic steps:

1. Separation of solute molecules into the gas state. This is the input of energy to overcome the crystal lattice energy, ΔH_{cryst}. It is always a positive quantity (endothermic) because energy must be input in order to break apart the molecules or ions of the solute. Note this process is the opposite that of what we define (and most books, though not all) the lattice energy with. MOST books define lattice energies (enthalpies) as negative (making a solid from gaseous ions). We are going in the opposite direction here - pulling apart the ions or molecules.
2. Expansion of the solvent to make room for the incoming solute. This too, is endothermic.
3. Combination of the separated solute with the expanded solvent. This is always an exothermic process (negative ΔH) as attractive forces are allowed to maximize.

The first step is just the ΔH_{cryst}. Remember how I told you in class that the lattice energy could be defined two different ways and opposite in sign. So remember, to *expand* the solute, you are going UP in energy which is a positive direction. Let's call that the + ΔH_{cryst}. Now, steps 2 and 3 are really just the enthalpy of solvation or hydration, $\Delta H_{\text{hydration}}$. These 2 steps combine to give the overall enthalpy of solution:

$$\Delta H_{\text{solution}} = \Delta H_{\text{cryst}} + \Delta H_{\text{hydration}}$$

So that the way I have these, the first term is always a positive quantity (crystal lattice energy) and the second term is always a negative quantity (the hydration energy). Please note what factors affect these values most. In particular, how does charge effect the two values of crystal lattice energy (higher the charge, the higher the L.E.) and hydration energy (works just like the lattice energy)? How does size (radius) effect the energies? - think *charge density* here. Realize that the solvation process is really a tug-of-war between species in the solid (solute-solute) state and the solvated (solute-solvent) state.

Once the solute is fully solvated by the solvent, the solvent itself is now experiencing a different set of intermolecular forces. Because the chemical environment has changed, so have many of the bulk properties of the solvent. We will concentrate on 4 such properties know as colligative properties.

Colligative Properties

Bulk properties of the solution that are governed by the amount of solute and not the kind of solute are known as colligative properties. For three of these properties there is simply a shift in the normal measured value for the pure solvent. So yes, in order to calculate any of these 3 you must know the properties of the pure solvent first. The 4th is osmotic pressure which is zero for any pure solvent. You must have a solution before any osmotic pressure develops. Each of these 4 colligative properties has an equation to quantitatively calculate the amount. "A" is solvent here for Raoult's Law:

Vapor Pressure lowering	$P_A = x_A P°_A$ (aka: Raoult's Law)
Boiling Point Elevation	$\Delta T_b = k_b \cdot m$
Freezing Point Depression	$\Delta T_f = k_f \cdot m$
Membrane Osmotic Pressure	$\Pi = MRT$

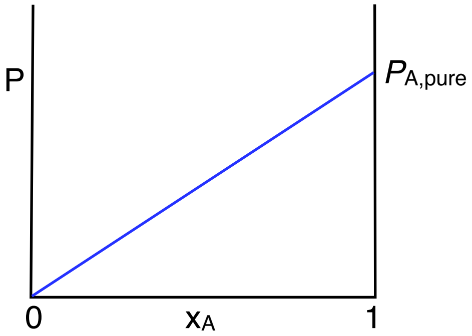
It should be noted that there are 3 different concentration terms in the equations above.

Concentration	symbol	formula
Molality	m	$m = \frac{\text{mol solute}}{\text{kg solvent}}$
Mole fraction	x	$x_A = \frac{\text{mol A}}{\text{total mol}}$
Molarity	M or [A]	$M = \frac{\text{mol solute}}{\text{L solution}}$

You should know how to convert any one of these concentrations into the other. For molality and molarity you must have the density of the solution in order to do the conversion. You can convert between molality and mole fraction without the density given. You can find these types of problems (exercises) in your book at the end of the chapter, somewhere around exercises 18-26. Now back to those colligative properties.

Raoult's Law

Vapor pressure lowing is just a linear drop from the full vapor pressure of the pure solvent. The less solvent there is in the mixture, the less vapor pressure – this is Raoult's Law. It even intersects the zero point. Think about it, if you have zero solvent ($x_{\text{solvent}} = 0$) then the vapor pressure must be zero. Here's the simple plot for Raoult's Law:



The horizontal axis is mole fraction of solvent (A) and the vertical is vapor pressure. Note that the right side of the graph intersects the pure vapor pressure and the line goes straight down to zero on the left side. The entire plot is valid only at one specific temperature. However when temperature does change the result in this graph is that $P_{A,pure}$ rises on the right side. Use the Clausius-Clapeyron equation to calculate the new value at the new temperature.

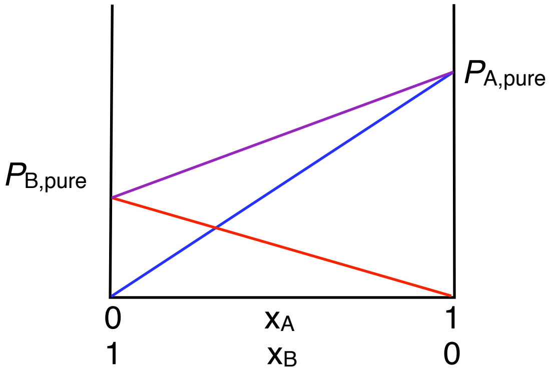
This plot assumes that your solute is non-volatile and the solution is behaving ideally. Well we CAN put a solute in that is in fact volatile. Now we have a solution with 2 volatile components. Raoult's Law still holds only now it holds for BOTH components. Let's mix liquids A and B. Raoult's Law says:

$$P_A = x_A P_{A,pure} \qquad\qquad P_B = x_B P_{B,pure}$$

Not only that but Dalton's Law of partial pressures tells us that

$$P_{\text{total}} = P_A + P_B$$

So you can calculate the overall total vapor pressure for a solution that is a mixture of 2 components. Heck, you could calculate the overall vapor pressure for 100 components using this method. Let's stick with 2 for now. You can plot 2 components easily on one plot. The horizontal axis will be BOTH x_A and x_B.



Note how the mole fractions run opposite each other for A and B. The blue line is Raoult's Law for liquid A and the red line is Raoult's Law for liquid B. The two lines combines give the upper purple line which matches the overall vapor pressure. Read all about it in your book. This is *ideal* solution behavior - realize that *real* solutions can behave with negative or positive deviations from this.

Boiling Point Elevation and Freezing Point Depression

Note the similarities of these two equations - both look alike, each using the molality of the solution and calculating for ΔT. The only difference is that the constants (k_b and k_f) are going to be different for any given substance. Also remember that the ΔT_b is ADDED to the boiling point to get the new boiling point (an elevation) and that ΔT_f. is SUBTRACTED from the freezing point to get the new freezing point (a depression).

Osmotic Pressure

This is the only one of the 4 colligative properties that was not there before the solution was made. Pure solvents don't have osmotic pressures (zero). This makes osmotic pressure the *most* sensitive of all 4 of the colligative properties. Make sure you understand the mechanism of how the osmotic pressure develops. Remember that the semipermeable membrane only allows solvent (typically water) to pass through from one side to the other. Solvent from the least concentrated side (pure solvent is the ultimate low concentration of zero) will migrate (or at least try) to the more concentrated side. The system here is trying to lower the concentration of the solute via water migration through the membrane. This will continue until the the concentrated side has matched this migration tendency with a push of its own - typically a higher column of liquid pushing back, or some device pushing back for it like in Figure 17.18. Actually that figure is showing a *greater* push back which is *reverse osmosis*.

Molecular Weight Determination

Any of the colligative properties can be used to calculate molecular weights although the most common are freezing point depression (cryoscopy) and osmotic pressure (osmometry). The idea is that you weigh (mass!) your solute and put it in a specific amount of solvent (weigh again). Now measure the colligative property and calculate the concentration. Now you know the mass of the solute, the concentration of solution, and the amount of solvent. This will get you molecular weight (g/mol) in a hurry. Refer to your book for an example (Example 17.4) of this using osmotic pressure. I will definitely put one of these type questions on the exam.

Van't Hoff Factor (*i*)

If you dissolve an electrolyte you will get more moles in solution that the straight up calculated number of moles. Why? Because the molecules ionize thus splitting into more ions. Each colligative property depends on the total number of moles of solute. Some molecules ionize 100% and you'll get a doubling or tripling (or whatever) of the stated concentration (m_{stated}). Whatever that actual factor is … is the Van't Hoff factor of i. If you dissolve NaCl in a dilute solution the value of i will be close to 2. Ideally, $i = 2$ for all 1:1 salts that are soluble. Many salts however will ion-pair in solution and keep the total number of ions from doubling. So i is really a measure of just how much ionization (or dissociation) goes on. To use i, just combine it with the stated concentration as molality (m_{stated}) or molarity (M_{stated}). Remember, that i allows you to use the actual or effective concentration ($m_{\text{effective}}$ or $M_{\text{effective}}$) which is the actual way the solute behaves - all ionizations accounted for.

$$i = \frac{m_{\text{actual}}}{m_{\text{stated}}}$$

Where m_{actual} (or $m_{\text{effective}}$) is the actual concentration of ALL species which is what the measured colligative property will reveal.

To summarize: There are 2 ways to use i. **(1)** If you know i, use it to "adjust" your stated concentration into an actual concentration which accounts for ionization. Then you can predict (calculate) the actual colligative property. **(2)** Use the colligative property measurement (typically ΔT_f, ΔT_b, or Π) to calculate the actual concentration (and therefore i). Then you can figure out the percent ionization.

Remember, when doing calculations on nonelectrolytes, $i = 1$, which is more or less the default condition. Now, here are 3 out of 4 formulas WITH the van't Hoff factor thrown in.

Vapor Pressure lowering	*not a simple formula here*
Boiling Point Elevation	$\Delta T_b = i\, k_b \cdot m$
Freezing Point Depression	$\Delta T_f = i\, k_f \cdot m$
Membrane Osmotic Pressure	$\Pi = i\, MRT$

Note that Raoult's Law for vapor pressure lowering is not given. Raoult's Law requires the mole fraction of the solvent (not solute). So simply "dropping in" the factor i will not work here. You'll have to count moles of all solutes and moles of the solvent, then get the adjusted mole fraction.

Now your turn

Now you start writing about all this stuff. Read your book. Over and over. Read other books if you need more help and insight. The more you expose yourself to the concepts the more things will make sense.

Remember, I didn't purposely leave anything out here to trick you on the exam. If I talked about it in class it is fair game on the exam. Practice working problems in the book and on the homework.