Textbook Chapters for Exam 1

Chapter 7 sections 11-16. Chapter 8 sections 1-18.

Equilibrium

Chemical equilbrium is an example of a dynamic equilibrium and not static equilibrium. Know the difference in the two. Static equilibrium is fixed and non-changing – like balancing weights on a balance beam. Dynamic equilibrium has no NET overall change but does have some given processes still proceeding. The process itself proceeds both forwards and backwards at exactly the same rate. Any thing that you are constantly depleting via one process is simultaneously being replenished by another process. Stated chemically, equilibrium is achieved when the forward rate of reaction equals the reverse rate of reaction. That is a purely kinetic argument for equilibrium and we will study reaction kinetics in Chapter 13 in our book. A complete understanding of equilibrium requires knowledge of both arguments (definitions) for the equilibrium state. Chapter 7 focuses on the other definition of equilibrium which is based purely on thermodynamic state functions. Lets get the thermodynamic argument for equilibrium established though.

The bottom line for the thermodynamic argument lies in the spontaneity of a reaction. 2nd Law dictates what direction of change is the spontaneous direction. We know that to be universal entropy. If ΔS_{univ} is positive, you have found a spontaneous process as written. Whatever is positive one direction must be negative going the other direction. One way, spontaneous (downhill) and the other way, non-spontaneous (uphill). There IS a case right in between – neither up or downhill, flat so to speak. Both directions are equally likely to proceed forward. When conditions are met like this then you have a stalemate on universal entropy. It's that special condition where $\Delta S_{\text{univ}} = 0$. Unfortunately tracking both the sytem and the surrounding to get the universal entropy is a bit tedious. Let's get ourselves a new state function for the system that allows us to track in a relative way the universal entropy. That new state function is free energy, G, defined as:

$$G = H - TS$$

With a little math we find out that we can now switch to ΔG_{sys} to track spontaneity. It tracks via sign the opposite of ΔS_{univ}. There are 3 possible outcomes for ΔG:

$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
⊖negative	zero	⊕positive
spontaneous	equilibrium	non-spontaneous

We now have a new standard to judge spontaneity and equilibrium. ALL equilibrium processes must have a free energy change equal to zero. This is the same as saying that all the free energies (that's plain ol' G here) of the reactants must equal the free energies of the products – our "stalemate" condition for equilibrium.

Free energy is a state function and therefore can be calculated via free energies of formation for the reactants and products just like the enthalpy of reaction was:

$$\Delta G^\circ_{\text{rxn}} = \sum n\Delta G^\circ_{\text{f}}(\text{products}) - \sum n\Delta G^\circ_{\text{f}}(\text{reactants})$$

Most thermodynamic tables include $\Delta G^\circ_{\text{f}}$. However, you might not have $\Delta G^\circ_{\text{f}}$ sometimes (like on an exam) and you should know how to calculate ΔG from ΔH and ΔS:

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

The standard version is this:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

And since ΔH and ΔS don't change much with temperature, you can use any temperature and calculate non-standard ΔG. That is:

$$\Delta G \cong \Delta H^\circ - T\Delta S^\circ$$

Note how ΔG's sign varies with the signs on ΔH and ΔS.

Remember if you have an equilibrium process occurring, then $\Delta G = 0$
and therefore

$$T = \Delta H / \Delta S \quad \text{(at equilibrium)}$$

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. The liquid/gas equilibria gets a closer look.

Vapor Pressure

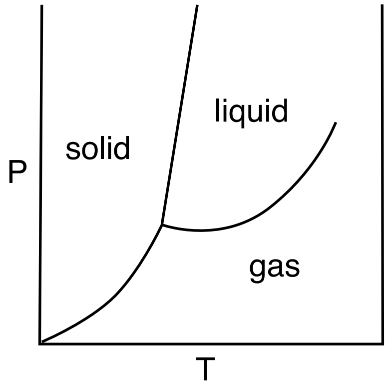
Be sure you understand what vapor pressure is. Why do we even say vapor? Is there any difference in a vapor and a gas? You can look it up and find lots of criteria for that difference. An easy and useful one is that a vapor is gas state of a substance that is normally a liquid at the given temperature. 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:

$$\ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{(see p 285)}$$

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*. See page 288 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 thought of in two 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} (ΔH_L in the book). It is always a positive quantity (endothermic) because energy must be input in order to break apart the molecules or ions of the solute.
2. Hydration of the gaseous molecules or ions. This is always an exothermic process (negative ΔH) as attractive forces are allowed to maximize. It is shown as $\Delta H_{\text{hydration}}$ (our textbook uses an abbreviated version of this designation).

These 2 steps combine to give the overall enthalpy of solution:

$\Delta H_{\text{solution}} = \Delta H_{\text{cryst}} + \Delta H_{\text{hydration}}$ (see p 299)

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.

Vapor Pressure lowering $P = x_{\text{solvent}} P_{\text{pure}}$ (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 $\Pi = cRT$

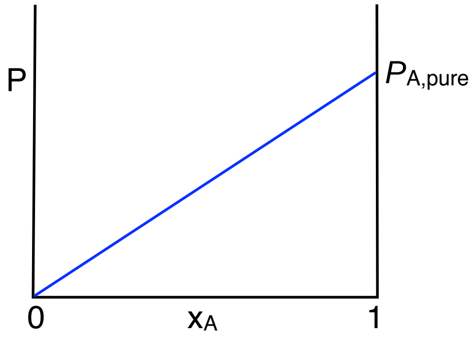
It should be noted that there are 3 different concentration terms in the equations above.

Concentration	symbol	formula
Molality	m	$m = \dfrac{\text{mol solute}}{\text{kg solvent}}$
Mole fraction	x	$x_A = \dfrac{\text{mol solute}}{\text{total mol}}$
Molarity	c_A	$c_A = \dfrac{\text{mol solute}}{\text{L solution}}$

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. All of these "tricks" are discussed in detail on page 303 in Toolbox 8.1. 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 $P_{\text{A,pure}}$ rises on the right side. Use the Clausius-Clapeyron equation to calculate the new value at the new temperature.

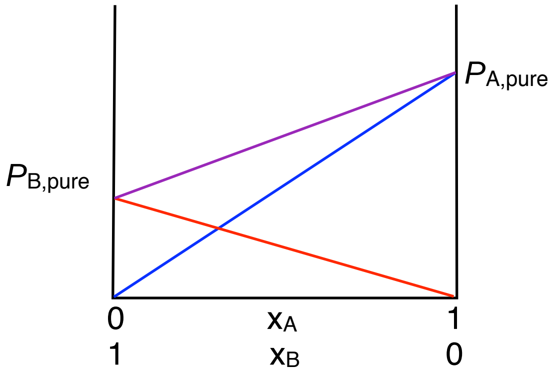
This plot assumes that your solute is non-volatile and the solution is behaving ideally. Well we CAN put a solute in that is in fact volatile. Now we have a solution with 2 volatile components. Raoult's Law still holds only now it holds for BOTH components. Let's mix liquids A and B. Raoult's Law says:

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

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 section 8.18 in your book.

Refer to your book for discussion on the other colligative properties.

Molecular Weight Determination

Any of the 3 colligative properties can be used to calculate molecular weights. 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 pages 310-312 in your book for examples. I will 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 goes on. To use i, just slip it into all four of the colligative property equations. Remember, when doing calculations on non-electrolytes, $i = 1$, which is more or less the default condition.

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. I feel I've rewritten the book here (sigh). Practice working problems in the book and on the homework.