What sections?

All of Chapter 6 (mainly sections 11-22 though) and all of Chapter 7.

Heat Capacity – Another Look

On the last review sheet (Review Exam 3 – Chapter 6) internal energy and enthalpy were defined as such:

$$\Delta U = q_V = C_V \Delta T = n C_{V,m} \Delta T$$

$$\Delta H = q_P = C_P \Delta T = n C_{P,m} \Delta T$$

We use these equations for calorimetry. Review that section from that old review sheet again.

Now, unlike on exam 3, on exam 4 I DO want you to know the general heat capacities of ideal gases (3 types: monatomic, linear, and non-linear). Memorize the C_V ones and then the C_P ones are just a modification (add R) on those. Here they are spelled out for you:

$$C_{V,m} = \tfrac{3}{2}R \qquad C_{V,m} = \tfrac{5}{2}R \qquad C_{V,m} = 3R$$
monatomic   diatomic/linear   polyatomic/non-linear

$$C_{P,m} = C_{V,m} + R$$

Note that the heat capacity at constant pressure is always larger that the heat capacity at constant volume. Why? Heating a gas at constant pressure leads to expansion and therefore work. That work energy cost must be paid – it is paid with one more R unit of energy per mole of gas.

Isothermal Expansion

If a gas is allowed to expand isothermally and reversibly then the work done is shown to be (p. 203)

$$w = -nRT \ln\!\left(\frac{V_f}{V_i}\right) \quad \text{or} \quad w = -nRT \ln\!\left(\frac{P_i}{P_f}\right)$$

Also remember that the internal energy of a gas is directly tied to temperature so that for isothermal expansion

$$\Delta U = 0 \qquad \text{and therefore} \qquad q = -w$$

Hess's Law (3 versions)

The first version listed here is the "true" version of Hess's Law. This would work for any state function but it is especially useful for enthalpies.

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \cdots$$

Once you understand what an "of formation" reaction is (see help sheet) then you can see how the following is just an extension of Hess's Law

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

The standard enthalpies of formation will be given in tables.

And finally, we can also think of a reaction as going about via the breaking of reactant bonds and the making of product bonds giving us yet another way to calculate enthalpies of reaction.

$$\Delta H^\circ_{rxn} = \sum n B.E.(\text{reactants}) - \sum n B.E.(\text{products})$$

Where *B.E.* stands for bond energy. Your book uses the term ΔH_B and is the mean bond enthalpy for a specific type of bond. You will be given a bond energy table much like that on pages 234 and 235 in your book or one where you look up one half of the bond in a column and the other half in a row – where they intersect is the bond energy of that type of single bond. Most multiple bonds are given in separate tables.

IMPORTANT: Just remember you must ADD energy to the system (+, endothermic) to break bonds (reactants) and then the sytem releases energy (-, exothermic) when new bonds are formed (products). It is this reason that the reactants are listed first in the equation above and the products last. This is *unlike* all the other equations we use.

Temperature and Enthalpy change

If you know how all the reactants and products respond to temperature change (know the heat capacities), then you can calculate how a temperature change will affect the overall enthalpy change for the reaction via Kirchhoff's Law

$$\Delta H^\circ_{rxn}(T_2) = \Delta H^\circ_{rxn}(T_1) + \Delta C_P \Delta T$$

where

$$\Delta C_P = \sum n C_{P,m}(\text{products}) - \sum n C_{P,m}(\text{reactants})$$

For most reactions where the temperature change is small and there aren't a lot of net phase changes, the ΔC_P term is usually small enough that we "say" that ΔH doesn't change a lot with temperature. We say the same about ΔS. However, looking ahead, we do NOT say that about ΔG.

SECOND LAW (3 ways of saying it)

The second law is all about spontaneous change and what drives it forward. A spontaneous change has the tendency to occur. Spontaneity must always have direction associated with it. The 2nd law helps define what that direction is and how we can determine it though entropy.

1. Any spontaneous change is accompanied by an increase in universal entropy.

2. Heat flows spontaneously from a hot object to a cold one (never the opposite).

3. Energy spontaneously disperses from being localized to becoming spread out if it is not hindered from doing so.

Entropy is defined as

$$dS = \frac{dq_{rev}}{T} \quad \text{or} \quad \Delta S = \frac{q_{rev}}{T}$$

If we are simply heating a substance (or group of substances) under constant pressure from one temperature to another without going through any phase changes then the change in entropy can be defined as

$$\Delta S = nC_{P,m} \ln \frac{T_2}{T_1}$$

Note that is just the integrated form of the previous dS equation. Note also that a similar equation can be written for constant volume conditions using $C_{V,m}$.

There are 2 basic equations for ΔS for isothermal changes. First, if the change is isothermal expansion of a gas you get

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

Note that P_1/P_2 can be substituted for V_2/V_1 thanks to Boyle's Law. Now, if the isothermal change is due to a phase change, then q_{rev} is the same as ΔH_{trans} and we simply get

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

Also, like with Hess's Law and ΔH_f's, we can use table values for standard molar entropy ($S°$) and get the change of entropy for a reaction

$$\Delta S°_{rxn} = \sum nS°_m(\text{products}) - \sum nS°_m(\text{reactants})$$

Note how those are absolute entropies (S's not ΔS's). Absolute entropies are possible due to the 3rd law which establishes conditions for true ZERO entropy.

The 3rd Law. The entropy is zero for a *perfectly crystalline solid* at absolute zero.

It is under these conditions that there can only be ONE single energy microstate for all the molecules in a solid. That is the energy is *confined* to only one possible arrangement. This is the ultimate LOW entropy condition and is, in fact, the points at which entropy does equal zero.

Considering **Boltzmann's Formula**

$$S = k \, ln \, W$$

Where W is the number of microstates for a system and k is the Boltzmann constant – really just the same as R except for single molecules instead of moles of molecules. If $W=1$ then $S = 0$. Even at ZERO kelvin there can be more than one microstate (this would NOT be a *perfectly crystalline substance*, BTW). This non-zero entropy at zero kelvin is called residual entropy. You can use the Boltzmann formula to calculate residual entropy if you know how many ways a molecule can be oriented in its lattice. See example 7.8 on page 255 for an example. I'll give you this formula if you need it.

One more thing, it turns out that for most liquid to gas phase changes (vaporization) the increase in entropy is about the same for most substances with typical intermolecular forces. This observation is known as **Trouton's Rule**

$$\Delta S_{vap} \approx 85 \ \text{J K}^{-1} \text{mol}^{-1}$$

This estimate comes in handy sometimes for quick calculations.

Do look at the logic of how absolute entropies are actually measured via C_P/T vs T plots and measured areas (integrations). See page 258 for details.

We discussed $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ in class. You should realize the importance of each part (system and surroundings) when discussing universal entropy – which is the ultimate determining factor for spontaneity.

The true understanding of the concept underlying the **Clausius Inequality** is quite a lot to grasp for anyone studying thermodynamics for the first time. The inequality itself is somewhat trivial:

$$dS \geq \frac{dq}{T} \quad \text{or just} \quad \Delta S \geq \frac{q}{T}$$

What this equation tells us is far more involved though. Just know that it is part of the argument and partly the

proof of the 2nd Law of Thermodynamics. Specifically, the entropy of an isolated system cannot decrease.

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 (that's CH302). 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 indicator 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 $\Delta S_{univ} = 0$. 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:

$$G = H - TS$$

First notice that G made up from 3 other state functions. Also check out how G will change with T (see Figures 7.23 and 7.24). Now, with a little math (top of page 268) we find out that we can now switch to ΔG_{sys} to track spontaneity. Cool! We can track spontaneity with a purely system state function. It tracks via sign the opposite of the way that ΔS_{univ} does. There are 3 possible outcomes for ΔG:

$\Delta G < 0$	$\Delta G = 0$	$\Delta G > 0$
$\ominus$negative	zero	$\oplus$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 and products just like the enthalpy of reaction was:

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

Most thermodynamic tables include ΔG°_{f}. However, you might NOT have ΔG°_{f} sometimes (like on an exam) and you should know how to calculate ΔG from ΔH and ΔS:

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

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 (within reason) 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. There are 4 cases here – see Figure 7.26 in your book.

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

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

Read the book.

Once again I'm asking you to READ. Yes, read your book. You must read over and over to get things straight. Read everything in context. If our book is not getting through to you, go to the chemistry library and read another one.

Standard Disclaimer: Any mistakes on this review sheet are NOT intentional. You should crosscheck all stated information. You should double check your book too (see errata).