## What sections?

Chapter 6 sections 1-7, 9, 10, 12-14. Only first page of section 3. Skip 8 and 11. We WILL cover everything – we are just skipping a few things only for exam 3.

Thermo Speak

As you venture through thermodynamics you will encounter the terms system, surroundings, and universe. You must have a good picture in your mind of what these are.

The **system** is what is currently under study. It can be incredibly tiny (a living cell or even a molecule) or emmense (an eco-system or even star system). The **surroundings** are all the things that are wrapped around the system. Sometimes the border between the system and surroundings is obvious and well defined such as the stainless steel walls of the reaction chamber of a bomb calorimeter. Sometimes the surroundings are completely mixed homogeneously with the system which is the case in solution chemistry (the solvent surrounds each of the solute molecules which are completely dispersed into the solvent). Together, the system and the surroundings make up the **universe**. For our purposes, the universe is most likely the room we are doing the experiment in. The interaction between system and surroundings is really the *immediate* surroundings.

We will generally define our systems via chemical reactions (or physical changes) shown as a balanced chemical equation. Such as the combustion of methane shown here

$$CH_{4\,(g)} \;+\; 2\,O_{2\,(g)} \;\longrightarrow\; CO_{2\,(g)} \;+\; 2\,H_2O_{\,(l)}$$
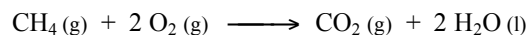
reactants	yields	products
before	change	after
initial	change	final

Below the reaction are various ways of describing the change. Realize here that when we start, only the methane and oxygen gas are our system. Anything that is not this methane and oxygen must be the surroundings. After the reaction our system is now the carbon dioxide and the water. We must quantify everything we can to get a complete description of this change. We need to measure state functions.

State functions

State functions are qualities or states of a system that are independent of the path by which the system arrived. Anything you can measure as matter "just sits there" is a state function. The main state functions that we constantly concern ourselves with are composition (formula), mass, volume, pressure, and temperature. We have very specific ways to measure each of these. Some ways are easier than others – temperature is easier than composition. In our study of thermodynamics we introduce four more state functions, all of which are pieces of the energy puzzle of matter. The four are internal energy (U), enthalpy (H), entropy (S), and free energy (G). Each of these *energy based* state functions will have a unique value for a given set of all the other state functions previously mentioned. What I mean is that if I know that I've got say exactly 30 grams of $CaCO_3$ at 25°C under 1 atm pressure then I also am aware of the fact that it also has an exact amount of internal energy, enthalpy, entropy, and free energy also. Do I know those values? Maybe, but usually not. For example, I do know a specific formula for internal energy for an ideal monatomic gas, it is simply

$$U = 3/2\,RT$$

This is a rare case where we can get the absolute value for *U*. Typically, real substances are not always gases and are certainly not "ideal". Real substances have real intermolecular attractions/repulsions that push these energetic state functions to all sorts of possibilities. So how do we get these thermodynamic state functions to reveal themselves? We initiate a *change* and in doing so we measure ΔU, ΔH, ΔS, and ΔG. All these Δ-values reveal themselves when matter undergoes change. Any physical or chemical change within matter will yield changes in these states functions (though not always). As far as exam 3 goes – you'll need to worry about the first 2 in the list: ΔU and ΔH.

Thermodynamics
FIRST LAW (3 ways of saying it)

1. The internal energy of an isolated system is constant.

2. The energy of the universe is constant.

3. Energy can neither be created nor destroyed, only converted in form.

Number 2 above comes from number 1 by assuming that the universe is a closed system. This is true because anything "outside" of the universe would by definition now be know and is part of the universe. Try to avoid some of the metaphysical stuff that finds its way into first law statements. We will be happy enough to realize that our system is typically the reaction or process what we are studying (usually in a reaction chamber of some sort), and our surroundings are the immediate surroundings wrapped around the system.

For number 3 above, realize that matter itself is one of the forms of energy ($E = mc^2$). So you could also state that the total amount of energy + matter in the universe is constant. One is often converted into the other – especially in stars, although those are NOT the systems we are concerned with.

Heat and Work

Heat (q) and work (w) are not state functions. They are very much path dependent in their values. We will only consider these two forms of energy in our studies. We will also only consider expansion work. Realize there are other forms of energy and different types of work. However, we need not concern ourselves with those until the need arises. For typical endo- and exothermic chemical reactions and physical changes, heat and expansion work are the only energies that we need to track and/or measure.

Internal Energy and Enthalpy

A system will show a change in internal energy only if heat is transferred to/from it and/or work is done on/by it. This is easier to put in equation form

$\Delta U = q + w$ where q is heat that flows in/out of the system and w is work done on/by the system

Sign convention is important, all signs (+ or –) are based on the systems point of reference

- heat flowing IN to the system is $+q$ (energy absorbed – an endothermic process)

- heat flowing OUT of the sytem is $-q$ (energy released – an exothermic process)

- work done ON the system is $+w$

- work done BY the sytem is $-w$

We define expansion work from the following

$$w = -\int_{V_i}^{V_f} P_{ext} dV$$

so if P_{ext} (external pressure your system is working against) is constant, work is simply

$$w = -P_{ext}\Delta V$$

and IF that change is due to a reaction containing gases, the Ideal Gas Law tells us that $P\Delta V = \Delta nRT$ so that work is also defined by

$$w = -\Delta n_{gas}RT$$

where Δn_{gas} is the change in the number of gases moles in the balanced equation of interest. Specifically,

$$\Delta n_{gas} = n_{final} - n_{initial}$$

where n_{final} is the total number of final state moles of gas (usually the gas products in an equation) and $n_{initial}$ is the

total number of initial state moles of gas (usually the gas reactants).

Enthalpy is defined as $H = U + PV$. The book will show you proof (p. 212) that $\Delta H = q_P$. Measure the heat flow from a system at constant pressure and you'll have the change in enthalpy, ΔH. Now we get these two equations for constant pressure processes

$$\Delta U = \Delta H - P\Delta V \qquad \text{and} \qquad \Delta U = \Delta H - \Delta nRT$$

Note how you can always get one from the other for ΔU and ΔH.

Heat Capacity

Heat capacity (C) is the ratio of how energy changes as temperature changes. There are 2 types of heat capacities that we use, one for constant volume processes (which tracks q_V) and one for constant pressure processes (which tracks q_P).

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

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

It is these equations that are used for calorimetry (see **Calorimetry** help sheet). It is also these equations (the constant pressure one in particular) that we use to track heat in ANY substance (solid, liquid, or gas). Each phase will have its own unique heat capacity. Tables will list heat capacities in 2 different ways or amounts. Many are listed on a per mole basis – these are *molar* heat capacities. Many are also listed on a per gram basis – these are *specific* heat capacities. Always look at the units on a measurement to know whether it is per mole or per gram or even per device (like an entire calorimeter). Units will tell you what to do. Once again, knowing the difference in extensive properties (heat capacity, C_P in J/K or J/°C) and intensive properties (molar heat capacity, $C_{P,m}$ in J/mol K) will always help you out. We will study some more heat capacities after exam 3 – that, of course, is another review sheet.

Thermochemistry

Do know how to calculate amount specific ΔH's when given the general ΔH of a reaction (section 14). Enthalpies of combustion are like this. If fuel A burns to yield 900 kJ of heat per mole of A, then burning 2.5 moles of A would yield 2250 kJ of heat. This is simply reaction stoichiometry with energy as another reactant (endothermic) or product (exothermic). This also applies to physical changes (melting and boiling, section 12)

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).