

### What Chapters and Sections?

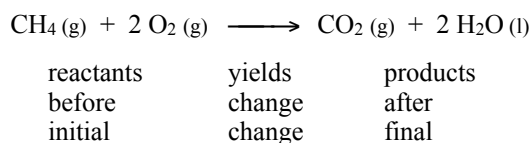
Sorry but we are covering ALL of Chapters 6 and 7 for exam number 4.

### 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 immense (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



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  $\text{CaCO}_3$  at  $25^\circ\text{C}$  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

$$U = 3/2RT$$

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  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$ . All these  $\Delta$ -values reveal themselves when matter undergoes change. Any physical or chemical change within matter will yield changes in these states functions (though not always).

### 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 known 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

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

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 system is  $-q$   
(energy released – an exothermic process)
- work done ON the system is  $+w$
- work done BY the system is  $-w$

We define expansion work from the following

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

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

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

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

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

where  $\Delta n_{\text{gas}}$  is the change in the number of gases moles in the balanced equation of interest. Specifically,

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

where  $n_{\text{final}}$  is the total number of final state moles of gas (usually the gas products in an equation) and  $n_{\text{initial}}$  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,  $\Delta H$ . Now we get these two equations for constant pressure processes

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

Note how you can always get one from the other for  $\Delta U$  and  $\Delta H$ .

## 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  $\Delta H$ 's when given the general  $\Delta H$  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)

## Heat Capacity – Another Look

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

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

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

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

Yes, 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:

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

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

Note that the heat capacity at constant pressure is always larger than 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)

$$w = -nRT \ln \frac{V_f}{V_i} \quad \text{or} \quad w = -nRT \ln \frac{P_i}{P_f}$$

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

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

which means that the equations for work ( $w$ ) above also equal heat ( $q$ ) except that the negative signs are gone.

## 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.

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

This is the equation at work when you are trying to get various reactions to add up to equal the overall reaction. Sometimes you have to “flip” a reaction, double it, half it, etc... Remember to adjust the  $\Delta H$  for the reaction when you flip it or scale it up or down.

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

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$$

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.

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_B(\text{reactants}) - \sum n\Delta H_B(\text{products})$$

Where  $\Delta H_B$  stands for the mean bond enthalpy (aka: average bond energy). Every type of bond will have an average bond energy. These are usually shown on tables. 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 system 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

$$\Delta H_{\text{rxn}}^{\circ}(T_2) = \Delta H_{\text{rxn}}^{\circ}(T_1) + \Delta C_p \Delta T$$

where

$$\Delta C_p = \sum nC_{p,m}(\text{products}) - \sum nC_{p,m}(\text{reactants})$$

For most reactions where the temperature change is small and there aren't a lot of net phase changes, the  $\Delta C_p$  term is usually small enough that we "say" that  $\Delta H$  doesn't change a lot with temperature. We say the same about  $\Delta S$ . However, looking ahead, we do NOT say that about  $\Delta G$ .

## 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 2<sup>nd</sup> law helps define what that direction is and how we can determine it through 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.
4. Energy hates being confined. - OK, so this one is really just my own spin on it - but I like it.

Any change in entropy is defined as

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

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  $\Delta S$  for isothermal changes. First, if the change is the isothermal expansion (remember,  $q = -w$  here) 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  $q_{\text{rev}}$  is the same as  $\Delta H_{\text{trans}}$  and we simply get

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

Also, like with Hess's Law and  $\Delta H_f^{\circ}$ 's, we can use table values for standard molar entropy ( $S^{\circ}$ ) and get the change of entropy for a reaction

$$\Delta S_{\text{rxn}}^{\circ} = \sum nS_m^{\circ}(\text{products}) - \sum nS_m^{\circ}(\text{reactants})$$

Note how those are absolute entropies ( $S^{\circ}$ 's not  $\Delta S^{\circ}$ '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. ALL the molecules are lined up exactly alike. This is the ultimate LOW entropy condition and is, in fact, the point at which entropy does equal zero. The energy under this condition can only be modeled in ONE way. This is the ultimate confinement of energy - no room for even the slightest jiggle of thermal motion. Nice time to consider statistical entropy.

## 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. Know the Boltzmann formula - it's easy and it's an important concept for the 2nd Law. Realize that this formula will work for any system provided you know all the microstates that are available at a given energy level. Easier said than done – but you do get the same results via a statistical consideration as you do via the heat flow over temperature method.

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**

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

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  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$  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 Clausius Inequality

The true understanding of the concept underlying the **Clausius Inequality** is quite a lot to grasp for anyone studying thermodynamics for the first time - but let's still TRY to understand it. It really lies at the heart of the 2nd Law of Thermodynamics.

The basic premise is that only  $q_{\text{rev}}$  is what is used to calculate  $\Delta S$  at a given  $T$  (whether the actual process is reversible or not - remember that  $\Delta S$  is a state function and is path independent. Also remember that  $q_{\text{rev}}$  is the maximum heat value for an isothermal change of state. You'll always get maximum work out of a system when you do it reversibly. Think  $q_{\text{rev}} = q_{\text{max}}$ . That is the same  $q_{\text{max}}$  that sets the value of  $\Delta S$ . So much for the equality part, now for the INequality. Since many processes (or dare I say, *most* processes) are in fact done irreversibly, that means that  $q$  is often LESS THAN  $q_{\text{max}}$ . Which let's us now write the Clausius Inequality:

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

Those  $q$ 's are the actual  $q$ 's, not  $q_{\text{rev}}$  which would need to be there to make the relation a straight equality (=). Now how does this get us to the 2nd Law? Now *isolate* your system! If you isolate a system, you shut down heat flowing in or out of it and  $q=0$ . Well if that is true then

$$\Delta S \geq 0$$

Do you see it? the 2nd Law? The entropy must increase (positive  $\Delta S$ ) for any spontaneous change in an isolated system. The universe is considered an isolated system and so you scale up that statement to *the entropy of the universe must increase for any spontaneous change*. I will also say that yes, you can have entropy change equal zero for a "spontaneous" change - however, that would have to be for a perfectly reversible system and heat is allowed to exchange with the surroundings. And in that very special case the system's  $\Delta S$  must exactly match the surrounding's  $\Delta S$  but opposite in sign. An entropy stalemate, if you will.

## Equilibrium

**Chemical equilibrium** 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  $\Delta S_{\text{univ}}$  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 system and the surroundings 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  $\Delta G_{\text{sys}}$  to track spontaneity. Cool! We can track spontaneity with a purely system state function. It tracks via sign the opposite of the way that  $\Delta S_{\text{univ}}$  does. There are 3 possible outcomes for  $\Delta G$ :

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

We now have a new standard to judge spontaneity and equilibrium with the added bonus that it is totally *system* based. 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:

$$\Delta G_{\text{rxn}}^{\circ} = \sum n\Delta G_f^{\circ}(\text{products}) - \sum n\Delta G_f^{\circ}(\text{reactants})$$

Most thermodynamic tables include  $\Delta G_f^{\circ}$ . However, you might NOT have  $\Delta G_f^{\circ}$  sometimes (like on an exam) and you should know how to calculate  $\Delta G$  from  $\Delta H$  and  $\Delta S$ :

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

The standard version is this:

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

And since  $\Delta H$  and  $\Delta S$  don't change much with temperature, you can use any temperature (within reason) and calculate non-standard  $\Delta G$ . That is:

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

Note how  $\Delta G$ 's sign varies with the signs on  $\Delta H$  and  $\Delta S$ . There are 4 cases here – see Figure 7.26 in your book.

Remember if you have an equilibrium process occurring,  $\Delta G = 0$  and therefore  $T = \Delta H / \Delta S$ . If you use standard values the equation is  $T \cong \Delta H^{\circ} / \Delta S^{\circ}$ . This is a Good way to get various melting points and boiling points of substances.

### 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).