McCord

CHAPTER 6 & 7
Exam 4 Review Topics

Fall 2005

What sections?

All of Chapter 6 and Chapter 7 sections 1-10.

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. I do know internal energy exactly for an ideal monatomic gas, it is simply

$$U = 3/2RT$$

However, 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. We will concern ourselves more with *changes* in each of these values. We are more concerned with ΔU, ΔH, ΔS, and ΔG. All these values reveal themselves when matter undergoes change. Any physical or chemical change within matter will yield changes in these states functions. We of course are concerned in CH301 that you understand the first three. We will address free energy at the start of CH302.

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 = mc2). 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 that is 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

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

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.

Some heat capacities that you should memorize for the 3 types of gases we encounter

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

$$C_P = C_V + nR$$

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

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

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

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

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.

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

Where ΔH_{B} is the mean bond enthalpy (bond energy) 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.

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

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

where

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

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

$$\mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} \qquad \text{or} \qquad \Delta S = \frac{q_{\mathrm{rev}}}{T}$$

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

$$\Delta S = nC_{P,\mathrm{m}} \ln \frac{T_{\mathrm{f}}}{T_{\mathrm{i}}}$$

A similar equation can be written for constant volume conditions using $C_{V,\mathrm{m}}$.

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

$$\Delta S = nR \ln \frac{V_{\mathrm{f}}}{V_{\mathrm{i}}}$$

Note that $P_{\mathrm{i}}/P_{\mathrm{f}}$ can be substituted for $V_{\mathrm{f}}/V_{\mathrm{i}}$ thanks to Boyle's Law. Now, if the isothermal change is due to a phase change we simply get

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

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

$$\Delta S^\circ_{\mathrm{rxn}} = \sum nS^\circ_{\mathrm{m}}(\text{products}) - \sum nS^\circ_{\mathrm{m}}(\text{reactants})$$

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.

Considering **Boltzmann's Formula**

$$S = k \ln W$$

Where W is the number of microstates for a system. If W=1 then $S = 0$. Even at ZERO Kelvin there can be more than one microstate. This 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.

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. 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.

Also know how the **Clausius Inequality** works

$$\mathrm{d}S \geq \frac{\mathrm{d}q}{T} \qquad \text{or just} \qquad \Delta S \geq \frac{q}{T}$$

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.