**Chemical reactions**

**Heat of Reaction**

When a reaction is carried out at pressure, as above, there will often be heat given off to, or absorbed from, the environment. We can easily calculate this quantity. Consider the 1st law of thermodynamics. It states that:



where H is the enthalpy, which we met before. So the heat given off is just the change in enthalpy of the system under these conditions. But is the change in enthalpy of the system equal to the sum of the enthalpy changes of the parts? This is a necessary question because in our last example, for instance, the gasses were not all at the same pressure and neither are they at the end, though the *total* final pressure is given – as p. Let’s consider our situation above initially. For the sake of discussion let us say that it was initially in mechanical equilibrium with the environment so that the pressure of each gas was also that of the environment (perhaps the environment pressure is exerted on the top of the containers). We don’t need the system to be in thermal equilibrium with the environment, or with itself. In that case we’d have: Hsys. = Usys. + psys.Vsys. = UA + UB + pA,B(VA + VB) = HA + HB. So this checks out. Maybe a more likely scenario is to have components A, B in the same volume, with their partial pressures adding up to p. Then we’d have: Hsys. = Usys. + psys.Vsys. = UA + UB + (pA + pB)V = HA + HB. And then in the final situation, we’d have all three gasses mixed and sharing the volume, their partial pressures adding up to the applied pressure. So we’d have: Hsys. = Usys. + psys.Vsys. = UA + UB + UC + psys.­­V = UA + UB + UC + (pA + pB + pC)V = HA + HB + HC. OK, so in the initial and final situations it is true that the total enthalpy is the sum of the individual enthalpies. This would not hold during the reaction, as the gasses wouldn’t be in equilibrium, and hence wouldn’t have a well-defined enthalpy. But that doesn’t matter since we only want ΔQ between initial and final states.

**Example**

What then is the heat given off in the reaction above? We need to find the enthalpy change. And this would be:



where in the last line we use the equation of state to change the pV’s into NkT’s. Of course this follows from the expression for H derived in the previous file. Note that the Φ’s are not involved, except insofar as they are needed to determine ξ. But alternatively, if we can determine Q, then we could experimentally determine ξ. Or if we knew that, then perhaps φ.

**How to find heat of reaction for general chemical reactions @ standard T, p**

Suppose instead of our particular reaction above, we have some generic chemical reaction like this:



and we want to know the heat given off for each reaction. In the cases of interest we presume to know the pressure and temperature of the reaction (both held constant), and we also know the particle number changes – because we are just looking at a single reaction: we aren’t trying to figure out how many reactions occur in this case. So the heat (input) will be:



(by the assumptions made above that the enthalpy of the system can be broken down into its constituent enthalpies). The last line is an assumption that seems to be commonly made. Certainly this isn’t true for, say entropy, though the error would be proportional to ln(a,b,c,d) rather than a,b,c,d. But it would be true for the enthalpy of an ideal gas for instance. So instead of having to measure the enthalpy of reaction for every conceivable reaction, we can reduce the requisite known enthalpies to the so-called ‘enthalpies of formation’ for each product or reactant. These are tabulated (at standard pressure p = 1 atm., and temperature T = 298K), and so the reaction enthalpies for a given reaction can be reduced to its associated enthalpies of formation. For instance consider the following example.

**Example**

So for instance consider the following reaction between propane and oxygen gas at standard temperature and pressure. What is the enthalpy of reaction?



The way this is done is to break the reactants and products into composite products and reactants.



And so we can say:



where the subscript *f* denotes ‘formation’. Looking up the values we have:



and so 2220 kJ of heat would be given off during this reaction.

**How to find heat of reaction for general chemical reactions @ arbitrary T, p**

So what if the reaction isn’t carried out at standard temperature and pressure? Let’s go back to our reaction, and see how our analysis would change. I think we can just dial the T and p back to standard values and determine the associated H change, and then replace standard T, p reaction by the formation enthalpies. Like this:



And so we’d have:



So this requires us to be able to measure enthalpy changes between standard T, p and new T, p. How may this be done? Well let’s consider the enthalpy H(T,p).



As mentioned, we can assert that the first bracket is just Cp, since this is:



So we have:



For an ideal gas this works out to:



where Cp is obviously constant, but I’m writing as Cp instead of (1+f/2)Nk so I don’t commit myself to ideal gas. For a liquid or solid, the energy and volume change with pressure (at constant T) is pretty negligible, so only the last term in the bracket will survive, leaving us with:



since U and V don’t change much with pressure. And further we can take V to be approximately constant during the change in pressure since again it doesn’t change much. I am assuming that Cp doesn’t change with pressure though, at least over the range of interest. Finally, note that we can easily accommodate different T’s and p’s on both sides of the reaction and even different T’s, p’s for individual reactants and products. But having different T’s, p’s would make Q differ from ΔH.

**How to find heat of reaction for general chemical reactions @ constant V**

What if reaction doesn’t take place at constant pressure, but at constant volume? And I’ll assume that temperature changes as well. Then go back to first law:



So heat evolved is just change in internal energy. But what is this? Perhaps we can relate it to enthalpy.



So then we’d have:



Note that as a consequence of the change in pressure due to fixed volume, implicitly included in this ΔH would be the change associated with a change away from standard pressure – supposing the reaction started at standard pressure.

**Example**

Consider following reaction at constant *volume* and standard temperature T = 298, and initially at standard pressure p = patm.?



What is the heat given off? Note that we don’t actually know what the new pressure is, nor do we know what the constant volume is. So I guess it won’t matter. We can use:



Note that ΔH[NH3(g)](Tstd., pstd.) → (T,p) = 0 because the enthalpy of a gas only depends on its temperature, not pressure.

**Example**

Since the heat given off in this case is just the internal energy change, we can also calculate Q by attempting to calculate the change in internal energy associated with the rearrangement of bonds. For instance,



looks like:



So we are breaking 2 H-H bonds, and an O-O bond, and creating a 4 H-O bonds. Examining the bond energy chart, we’d see that:



**Example**

All of our formalism applies to nuclear reactions as well. Consider the reaction



where our frame of reference is at rest with respect to the initial pair. Then,



The excess energy goes into kinetic energy of course. If the reaction takes place at constant V and T, then all of this energy will be released as heat. If at constant p and T, then some of it will do work and some released as heat so that just as before Q = Δ(U + pV) = ΔH. If it is kept adiabatically sealed, then this energy will stay manifested in kinetic energy and T will go up.