

Thoughts on Thermodynamics

In organizing your study plans for thermo, it is essential to be able to distinguish these seemingly endless stream of very similar concepts from each other. This is best done by creating a hierarchy of important facts about thermodynamics—note that the relative importance of this material doesn't run from front to back, it is more like from back to front. Thus we start with G

1. G : The most important thing about thermodynamics: Thermodynamics tells you whether a reaction is **spontaneous** or not, whether it occurs or not. To do this we look at the Gibbs' Free Energy, G and ask the following:

- If G positive (+) the reaction is not spontaneous—it doesn't happen
- If G negative (-) the reaction is spontaneous—it happens

So what is G ? It is the **free energy of a system**. It is a combination of three kinds of energy:

- heat energy, q used to calculate the **enthalpy**, H
- work, usually a change in P or V ($P \Delta V$) for a reaction involving gases
- $T \Delta S$, the **entropy**, which is a measure of the disorder in a system

We can combine these three forms of energy in a couple of ways:

- $G = H - T \Delta S$ which is a really famous equation used to calculate free energy
- $E = q + w = H - P \Delta V$ which describes all the kinds of **internal** energy in a system

Enthalpy, ΔH : The heat of reaction: Very simply, this term provides a quantitative measure of how much heat is given off in a reaction.

- **Endothermic** reaction: ΔH is +. The reaction is endothermic. The surroundings get colder.
- **Exothermic** Reaction: ΔH is -. The reaction is exothermic. The surroundings get hotter.

Calculating ΔH : There are two ways to do this.

- Experimentally: calculate $\Delta H = mC \Delta T$ using a bomb **calorimeter**. This is how they measure the calories of food products.
- **Hess' Law.** Hess' Law $\Delta H_{\text{rxn}}^{\circ} = \sum H_f^{\circ} \text{ products} - \sum H_f^{\circ} \text{ reactants}$

Because of the first Law of Thermodynamics, we know that energy is conserved. So if we want to calculate the ΔH for a reaction, we can put together any combination of reactions that cancel out to leave the ΔH_{rxn} we want. There are two ways we use Hess' Law, **heats of formation** and **bond energy**:

- **Heat of formation**, H_f° values in Appendix K. H_f° is the heat of reaction when elements in their standard state react to make an product.

- **Bond Energy:** Rather than use Appendix K, we can apply Hess' Law using average values for each and every broken and formed bond from Tables on p15-8 and 15-10 of the notes.

Work, PV (and why it often is ignored): Some reactions don't just give off heat, they produce and use up **gases** that change the pressure or volume of a system. For example, the pistons in your car do this with combusted gasoline. Very simply, this is PV work that occurs when either the pressure changes or the volume changes when a reaction of gases occurs. If a reaction involves only **liquids and solids**, or no net change in the number of moles of gas, there is no PV work and

$$E = q + w = \cancel{H} - \cancel{P} - \cancel{V} \quad \text{or} \quad \Delta E = \Delta H$$

Calculating PV work. If there is PV work it is easy to calculate from the ideal gas law:

$$P \Delta V = nRT$$

For example, for a one mole change in gas, $P \Delta V = nRT = 2.5 \text{ kJ}$ which is much smaller than most combustion reactions. It is often approximately true that

$$E = q + w = H + (\text{something small}) \quad \text{and again} \quad \Delta E = \Delta H$$

Entropy, S: Systems tend to become messy. This is because there is energy in the world above **absolute zero** that makes bonds vibrate and molecules jump around. Before you know it, the entropy, S is larger.

- When $S = -$, the system is increasingly **ordered**.
- When $S = +$, the system is increasingly **disordered**.

On the exam you will be asked to predict system that are ordered or disordered.

- Disorder occurs as phase changes happen and solids become liquids become gases
- Disorder occurs when the volume increases, when temperature increases, when the number of particles increases.
- The opposite conditions favor increased order and require that energy be removed from the system to the surroundings so all that jiggling will stop and things will freeze over.

Putting together S and H to make G:

Look at the equation

$$G = H - T S$$

Note that to make a reaction spontaneous, G must be negative. This is done by making S more positive and H more negative.

When a reactions happens:

- If H is negative and S is positive a reaction happens
- If H is positive and S is negative a reaction can't happen
- If both H and S are positive or both are negative, it is possible for a reaction to occur and depends on the **temperature**.

A Study Hint:

Everything you need to study for thermo is on these pages. When working the problems, before actually finding an answer, identify the material on this page associated with the problem. That way you know where to go for help in figuring out how to do them.