Thermodynamics

Energy and Chemical Change

- Energy is defined as the ability to do work or produce heat
    - It exists in two basic forms
        - Kinetic Energy (KE): energy of motion
            - This is directly related to the constant random motion of its atoms or molecules and is proportional to temperature
        - Potential Energy (PE): energy due to the composition or position of an object
            - The type of atom in the substance, the number and type of chemical bonds joining the atoms and the particular way the atoms are arranged

Law of Conservation of Energy

- Energy will constantly change from one form into another
    - THE AMOUNT OF ENERGY DOES NOT CHANGE

- "In any chemical reaction or physical process, energy can be converted from one form to another, but it is neither created nor destroyed"
    - This is also known as the first Law of Thermodynamics

Chemical Potential Energy

- This is the energy stored in a substance because of its composition
    - Example: Octane (C_8H_{18})
        - This molecule holds chemical potential energy in its covalent bonds
        - In the engine, some of the energy is converted into kinetic energy and moves the pistons BUT much of the PE is converted to heat
    - Heat (q) is the energy that is the process of flowing from a warmer object to a cooler object
- Heat is measured in the metric system by use of a calorie (cal)
    - A calorie is the amount of heat energy needed to raise one gram of pure water one degree Celsius (1 °C)
        - Don't get confused with the calories you eat with food
            - Biology Recall – Your body's metabolism requires ATP energy from the carbohydrates and fats in food to run cellular respiration (mitochondria)
            - These are exothermic reactions, thus you give off heat when eating food (it makes you lose weight to eat!)
        - 1 Food calorie is actually a kilocalorie (1000x cal)
- The SI unit (metric) of heat and energy is a joule (J)
    - One joule is the equivalent of 0.2390 calories, or one calorie equals 4.184 joules
        - Be able to convert between them as we have been for other metric conversions

Specific Heat

- Since one calorie is 4.184 J and this will raise one gram of pure water by 1° C, this is water's specific heat
    - Specific Heat: amount of heat required to raise the temperature of one gram of substance by 1° C
        - **Every substance has a different composition
            - ***Thus, every substance has its own unique specific heat

    - We express specific heat (and calculate it) using the following equation:
        - $q = c \times m \times \Delta T$
            - q is the heat absorbed released
            - c is the specific heat of the substance
            - m is the mass of the sample (usually in grams)
            - ΔT is the change in the temperature ($T_{Final} - T_{Initial}$)

  - Heat changes that occur during chemical and physical processes can be measured with a calorimeter
  - It's an insulated device used for measuring the amount of heat absorbed or released during a chemical or physical process
    - A known amount of water is placed in an insulated chamber and this temperature will change with the reaction, thus being able to measure the exothermic/endothermic reaction's heat change

Thermochemistry

- Virtually every chemical reaction causes heat to be released or gained
  - Thermochemistry: the study of heat changes that accompany chemical reactions and phase changes

- $4Fe(s) + 3O_2(g) \quad 2Fe_2O_3(s) + 1625kJ$
  - Energy is found in the products, thus this is an exothermic reaction
- In thermochemistry, the system is the specific part of the universe that contains the reaction or process
  - Everything else in the universe, other than the system, is known as the surroundings
- Universe = system + surroundings

Enthalpy

- To make measuring and studying energy changes in chemical reactions, chemists have defined a property called enthalpy
  - Enthalpy (*H*): the heat content of a system at constant pressure
    - In other words… measuring the change in enthalpy is measuring the change in heat from chemical reactions

ΔHrxn – Change in enthalpy (heat) of reaction
$\Delta Hrxn = H_{\text{final}} - H_{\text{initial}}$
or
$\Delta Hrxn = H_{products} - H_{\text{reactants}}$

- Exothermic will be a negative ΔH_{rxn}
- Endothermic will be a positive ΔH_{rxn}
  - $4Fe(s) + 3O_2(g) \quad 2Fe_2O_3(s) + 1625kJ$
    - This shows that the product contains less heat than the reactants because 1625 kJ was lost to the surroundings
      - Thus its exothermic and really $\Delta H = -1625$ kJ

Thermochemical Equations

- Since the change in energy is important for chemical reactions, the change in heat (change in enthalpy), ΔH, is included in the reaction
  - A thermochemical equation is a balanced chemical reaction that includes the physical states of all reactants and products and the energy change

$C_6H_{12}O6_{(s)} + 6\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 6\ H_2O_{(l)}\ \Delta H_{comb} = -2808$ kJ

Hess's Law

- Calculating Enthalpy Change
  - **Hess's Law**: if you can add two or more thermochemical equations to produce a final equation for a reaction, then the sum of the enthalpy changes for the individual reactions is the enthalpy change for the final reaction

- So lets see Hess's Law in action, we will use acid rain from volcanic eruptions as our example
  - **$2\,S_{(s)} + 3\,O_{2(g)} \rightarrow 2\,SO_{3(g)}\ \Delta H = ?$**

a. $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}\ \Delta H = -297\ kJ$
b. $2\,SO_{3(g)} \rightarrow 2\,SO_{2(g)} + O_{2(g)}\ \Delta H = 198\ kJ$

The desired equation shows two moles of sulfur reacting, so we must take equation a. and double it (including enthalpy)

a'. $2\,S_{(s)} + 2\,O_{2(g)} \rightarrow 2\,SO_{2(g)}\ \Delta H = -594\ kJ$

Equation b shows sulfur trioxide as a reactant and we need it as a product. Thus, we switch the equation (including enthalpy)

b'. $2\,SO_{2(g)} + O_{2(g)} \rightarrow 2\,SO_{3(g)}\ \Delta H = -198\ kJ$

Now that the two equations match the desired equation, we simply add the equations together, cancel out anything that is the same on both sides and finally add the changes in enthalpy

- **$2\,S_{(s)} + 3\,O_{2(g)} \rightarrow 2\,SO_{3(g)}\ \Delta H = ?$**

a'. $2\,S_{(s)} + 2\,O_{2(g)} \rightarrow \cancel{2\,SO_{2(g)}}\ \Delta H = -594\ kJ$
b'. $\cancel{2\,SO_{2(g)}} + O_{2(g)} \rightarrow 2\,SO_{3(g)}\ \Delta H = -198\ kJ$

-594 kJ + -198 kJ = -792 kJ

Reaction Spontaneity

- Many chemical reactions, like rust on metal, will occur without intervention
  - These physical and chemical reactions are known as spontaneous processes

  - Originally, chemists thought all exothermic reactions were spontaneous and endothermic were not
  - This was, in-fact, incorrect because ice melting at room temperature is endothermic (hot to cold)

Entropy

- Entropy is the reason for the spontaneous reactions
  - If you spray perfume/cologne, recall from integrative and biology that diffusion occurs
    - Diffusion: particles freely moving from high concentration to low concentration on account of their kinetic energy

  - Another way to look at this is order
    - The particles want to mix with other gaseous molecules in a state of disorder (mixed)

- Entropy (S) is a measure of the order or randomness of the particles that make up a system

- The Law of Disorder states that everything (everything!) has a tendency toward disorder or randomness
  - Thus the spontaneous reactions occur because they are increasing entropy in the universe

*** This is also the 2nd Law of Thermodynamics

Changes in Entropy (ΔS)

1. Entropy increase with change of state because there is more KE states of matter
2. The dissolving of a gas in a solvent always decreases entropy because less movement
3. Assuming no change in state, if there are more gas particles in products than reactants then entropy increases since more random movement
4. Most solutes that are dissolved in solvents increase entropy
5. An increase of temperature of a substance is always an increase in entropy (more KE)

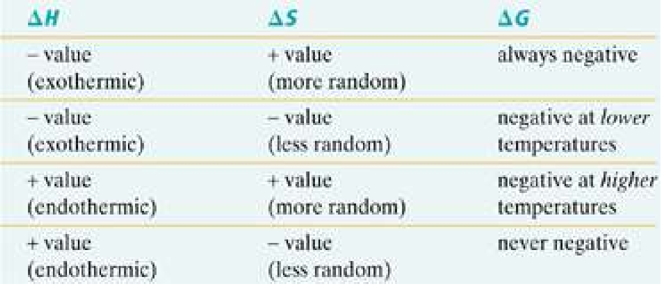
Natural Processes

- So what these means in a nutshell is that all processes in nature work toward two directions:
  1. Toward least enthalpy
  2. Toward greater entropy
- Thus a function (equation) has been designed to relate entropy and enthalpy at a given temperature and constant pressure

Gibbs Free Energy

- Combining the enthalpy and entropy into one function is known as *free energy*
  - Free energy (G) of the system simultaneously assesses the tendencies for enthalpy and entropy to change
  - **Natural process will proceed in the direction that lowers the free energy of a system

- Only the *change* in free energy can be measured and it is defined as the following:
  - ΔG of a system is the difference between the enthalpy (ΔH) and the product of the Kelvin temperature and the entropy change ($T\Delta S$): $\Delta G = \Delta H - T\Delta S$



ΔH	ΔS	ΔG
– value (exothermic)	+ value (more random)	always negative
– value (exothermic)	– value (less random)	negative at *lower* temperatures
+ value (endothermic)	+ value (more random)	negative at *higher* temperatures
+ value (endothermic)	– value (less random)	never negative