**Thermochemistry**

Chemical rxns are always accompanied by energy changes.

Most of our societal needs are met by chemical energy: i.e.. gas, coal, oil, etc.

Future energy needs will be a problem for us since our fossil fuel resources are limited. There are other associated problems as well, such as pollution and global warming.

**6.1 The Nature the Energy**

The study of energy and the changes it causes is called **thermodynamics.**

**Energy is the ability to do work or transfer heat.**

**In normal chemical processes, energy is conserved (Law of Conservation of Energy).**

It is possible to explain a lot with just a few theories and principles. We will frequently deal with heat, pressure and volume in our discussion.

• **Mechanical work: work = force x distance, w = fd** (and f = ma)

• **Potential energy**: the energy of position, **Ep = fd**

• **Kinetic energy**: the energy of motion, **Ek = 1/2mv2**

Other types of energy include light, chemical and electrical. (Chemical and electrical are essentially the same; they simply deal with the transfer of electrons from one place to another.)

**Units of energy:**

• **1 joule (J) = 1kgm2/s2**  The joule is the standard unit of energy in the SI.

• **1 calorie (cal)** = the heat needed to raise the temperature of 1g of water from 14.5 - 15.5ºC.

= 4.184J

The calorie is still used occasionally to measure heat energy, but we will not deal with it very often. Perhaps its most frequent use is with reference to diet. One dietetic calorie (Cal.) = 1000 cal. or 1 kcal.

• British Thermal Unit (BTU) = 1.05 kJ.

We will use J or kJ.

Two terms that are also pertinent to the discussion are *system* and *surroundings*.

• **System: a well-defined part of the universe.**

• **Surroundings: the rest of the universe.**

There are 3 laws of thermodynamics (TD). We will eventually discuss all of them, but will only consider the first law for now. Also, the laws are sometimes expressed in different ways and using different terms depending on the situation.

**1st Law of Thermodynamics: Energy cannot be created or destroyed.**

Energy lost by the system must be gained by the surroundings and *vice versa*.

These exchanges may be in the form of: **1) heat or 2) work**.

**Thermal or Internal Energy:**  energy of an object by virtue of the Ek of its atoms or molecules that are in constant motion.

Thermal energy increases as temperature increases.

**Heat refers to the flow of thermal energy from a warmer body to a cooler one.**  Mass is not important in determining which direction the heat will flow, temperature is.

Energy is delivered from the system to the surroundings in the form of mechanical work or heat. Mechanical work is often referred to as pressure-volume or **PV work**.

• Ex. System: hot gases of gasoline combustion in the cylinder of a car engine.

**Mechanical work: (PV work)** 🡪 expanding gases force the piston down.

**Heat**: Temp. difference- the gases are hotter than the metal cylinder- heat flows to the cylinder and the engine block.

The source of both work and heat flow is the internal energy of the gases ( the Ek of their molecules.)

Change in Internal Energy: Δ**E = Efinal - Einitial** or Ef - Ei

• Δ**E = q + w q** = heat **added to** the system

**w** = work **done to** the system.

**Heat added = +q** and **Heat lost = -q**

Work done to the system = +w. Work done by the system to the surroundings = -w.

**PV Work**

**w = -PV**

Example problem: A gas expands from 46L to 64L at a constant pressure of 15 atm. How much work is done?

V = Vfinal – Vinitial = 64L – 46L = 18L. w = -15 atm (18L) = **-270 L atm**

Since the **gas is expanding**, it is doing **work on the surroundings**. The **system is losing energy** and **w is negative**.

If heat is added to the system and work is done on the system, both increase the internal energy of the system, and ΔE = + value.

If heat is lost to the surroundings and work is done by the system, ΔE = - value.

• Ex. If 50 J of heat is added (causing system temperature to rise) and 20 J of work are done on the system:

ΔE = +50 J + (+20 J) = +70 J 🡪 increase in system internal energy.

Rxns. which release heat are **exothermic**. Those which absorb heat are **endothermic**.

It is impossible to know the exact internal energy of a system, but we do know that it is fixed for a given set of circumstances.

**Internal energy is a state function\*,** that is a property of the system **determined by specifying its physical state** (temperature, pressure, phase, location, etc.)

**\***Work hard at understanding this concept of state vs. non-state functions. It always seems to serve as a source of confusion to those new to discussions of thermodynamics.

A state function does not depend on the previous history of the system.

• Ex. 50g of 25ºC water are in a beaker on a bench. The water may have been at 100ºC and cooled to 25ºC, or perhaps the water started out as ice at 0ºC and warmed to 25ºC. The end result is the same, no matter how it got there.

Work done by a system is **not** a state function. The type and amount of work done by a system during an energy change can vary greatly.

• Ex. System: a D-cell battery which is discharging completely.

In a flashlight, heat and light are produced, but no mechanical work is done.

In a toy car, heat is produced and mechanical work is done.

In both cases, ΔE (state function) is the same, but work (non-state function) is very different.

\*Usually, state function variables are represented by a capital letter, non-state variables with lower case.

**6.2 Enthalpy and Calorimetry**

In chemistry most of our concern will be with electrical work and that due to expanding gases. Of these, we will concentrate on the latter.

• Ex. Consider an imaginary system with a cylinder and a weightless piston. 1 mol of water at 100ºC will be converted from liquid to gas at 1 atmosphere of pressure.

Added heat increases the internal energy of the system by a certain amount and does work against the force of the atmosphere pushing down on the piston. The piston moves up as the liquid is converted to gas (and the temp. remains the same.)

The work is P-V work. At constant pressure w = -PΔV. Substituting into ΔE = q + w, we get

ΔE = qp - PΔV, and qp = ΔE + PΔV (The subscript "p" = constant pressure).

Heat added to a system = internal energy + PV work done on the system.

\*\***P**Δ**V is only significant when gases are involved**. This means that for the chemical rxn, there must be a **differing number of moles of gas** between the reactant and product sides of the equation.

This is because as temperature changes, solids and liquids do not expand or contract as much as gases. Therefore, PΔV is very small and q is the only thing available to cause ΔE and so ΔE = qp, when no gases are involved.

**Enthalpy.**

Since most rxns occur under more or less constant pressure (usually about 1 atm.), a new state function, enthalpy (H) can be defined.

• H = E + PV and for processes under constant pressure, ΔH = ΔE + PΔV

• Since qp = ΔE + PΔV also, then ΔH = qp . Because of this, enthalpy is often called "heat of rxn."

Enthalpy change at constant pressure = the heat change for the system.

***+ΔH = endothermic change.***

***-ΔH = exothermic change.***

**Calorimetry**

The measurement of heat flow is calorimetry.

The temperature change of a body when it absorbs a certain amount of heat energy is determined by its **heat capacity.**

Heat capacity is the heat needed to raise the temperature of a body by 1ºC or 1K.

Heat capacity = q/ΔT for the entire body.

Molar heat capacity (C) = the heat needed to raise the temperature of 1 mol of a substance by 1ºC = **change in heat/change in temperature**. For gases (and some other substances) P or V must sometimes be specified: Cp (constant pressure calorimetry) or Cv (constant volume calorimetry).

q = nCΔT where n = number of moles of material.

Molar heat cap. is not used very often.

Used much more frequently is **Specific Heat Capacity (s):** the heat required to raise the temp. of 1 **gram** of a substance by 1ºC or 1K.

**q = msΔT** where m = mass in grams of the body. Or sometimes **H = msΔT**.

There is also an energy change when a substance changes phase. These energies are typically reported as molar heat of fusion, Hfus and molar heat of vaporization, Hvap and are reported in kJ/mole of heat needed to melt or vaporize (boil) one mole of substance.

A simple type of physics/chemistry problem involves the heat needed to take a substance from solid to gas in steps.

For example: How much heat is needed to change ice from -45°C to steam at 135°C. The necessary steps would be

1. Warm the ice from -45° to 0°. Use DH = msT.
2. Melt the ice. Use (grams of ice/18.0g/mol) x Hfus.
3. Warm the water from 0° to 100°. Use DH = msT.
4. Vaporize the water. Use (grams of ice/18.0g/mol) x Hvap.
5. Warm the steam to 135°. Use DH = msT.
6. Add all the heat values together (Hess’s Law).

**Calorimeter** = an insulated container. Usually the ΔT of water is measured, but often the heat capacity of the entire calorimeter is known and used, since the calorimeter itself also absorbs some heat as well as the water in the device. A sophisticated version is the "bomb" calorimeter.

qevolved = -CpΔT .

• Ex. 1g of hydrazine is burned in pure O2. The bomb calorimeter's temp. rises by 1.17ºC.

1. If the heat capacity of the calorimeter is 16.53kJ/ºC, how much heat is evolved?

2. What is the heat of combustion of 1 mol of hydrazine (N2H4)?

Solution:

q = -CpΔT = -16.53kJ/ºC (1.17ºC) = -19.3kJ So -19.3kJ/g (32.0g/mol) = -619kJ/mol

ΔE = q + w: In a calorimeter, there is no V change, so PΔV = 0, no work is done; and ΔE = qv, where

qv = heat absorbed by the calorimeter at constant volume. In a calorimeter, qv and ΔE are usually negative.

If volume changes do occur, ΔE can be easily converted to ΔH: ΔH = ΔE + PΔV and ΔH = heat of combustion.

Usually ΔH's are given for rxns that produce CO2(g) and H2O(l)

In simple calorimeters, P is constant.

**6.3 Hess's Law**

ΔH, as a state function, depends on the amount of matter reacting, and the states of the reactants and products.

Many rxns appear as a single step process, however, in reality, most are really 2 or more simpler steps.

**Hess's Law states that if a particular rxn is carried out as a series of steps,** Δ**H for the overall rxn will be equal to the sum of the enthalpy change values for each of the single steps.**

• Ex. CH4(g) + 2 O2(g) 🡪 CO2(g) + 2H2O(g) ΔH = -802kJ **Two**

2H2O(g) 🡪 2H2O(l) ΔH = -88kJ **Steps**

CH4(g) + 2 O2(g) + ~~2H2O(g)~~ 🡪 CO2(g) + ~~2H2O(g)~~ + 2H2O(l) ΔH = -890kJ

Net CH4(g) + 2 O2(g) 🡪 CO2(g) + 2H2O(l) ΔH = -890kJ **One Step**

The enthalpy change results are the same, whether the rxn is represented as 1 step or 2. **The number and nature of the steps is not important.**  As you will see, many Hess's law examples have several steps.

ΔH values are often difficult to measure directly but can be done as a series of steps and calculated, using Hess's law. We will be doing a lab of this type involving the combustion of Mg.

**\*It is impossible to get more energy from a rxn by changing the pathway or number of steps to the product.**

There are several examples of sample and practice exercises on pp. 244-6 in the text. Look these over.

Hints for using Hess’s Law:

* Work backward from the net (final) reaction. Use the reactants and products in this reaction to decide whether the reactions above are going in the proper direction.
* Reverse any reactions that are going in the wrong direction.
* Multiply reactions by whole number factors if necessary to produce the correct number of moles of each reactant and product.
* A little practice goes a long way.

**Enthalpies of Reaction**

For chemical rxns, the enthalpy of rxn products is generally different than that of the reactants.

• ΔH = Hproducts - Hreactants

• Ex. Combustion of Mg ribbon: 2Mg(s) + O2(g) 🡪 2MgO(s) (old fashioned flash bulb rxn.)

This process is highly *exothermic*. System enthalpy is *reduced*.

Insert diagram here:

At constant pressure, the enthalpy of the products is *less* than that of the reactants, and Δ**H is (-)**.

• Heat absorbing processes are *endothermic*. Δ**H is (+)**.

• Ex. E + 2H2O(l) 🡪 2H2(g) + O2(g)

Insert diagram here:

* To return to our earlier example, the combustion of methane can be viewed in two steps.

Insert diagram here:

**Enthalpy** has 3 important characteristics:

1. Enthalpy is an extensive property: that is, ΔH depends directly on the amount of reactants and products.

Ex. CH4(g) + 2 O2(g) 🡪 CO2(g) + 2H2O(g) ΔH = -802kJ (exothermic)

Burning 1 mol of methane gas produces 802kJ of heat energy. Burning 2 mols of gas produces 1604kJ.

Twice as much reactant, twice as much energy released. Common sense, right?

1. The enthalpy change for a reverse rxn has the same value, but opposite sign as that for the forward rxn.

Ex. CO2(g) + 2H2O(g) 🡪 CH4(g) + 2 O2(g) ΔH = +802kJ (endothermic)

1. The enthalpy change for a rxn depends on the state of the reactants and products (i.e., as we mentioned earlier, enthalpy is a state function.)

Ex. You know that it requires heat energy input to convert liquid water to steam (boil it.)

If the product of methane combustion was 2H2O(l) rather than 2H2O(g), ΔH would have a value of -890kJ rather than -802kJ. This suggests that for 2H2O(g) 🡪 2H2O(l), ΔH = -88kJ

**\*\*Therefore, when writing thermodynamic chemical rxns and using** Δ**H, it is very important to indicate the states of reactants and products.**

**\*Unless otherwise specified, we will assume that both reactants and products are at the same temperature. STANDARD THERMODYNAMIC TEMP. = 25°C.** This is about room temperature. **Be careful not to confuse this with standard temp. for work with gases, which is 0°C.**

ΔH is a very important quantity to chemists. It helps explain a lot about the energy changes that accompany rxns, how that energy might be used to do work, or how much energy will be required to make a certain desirable rxn go. It also gives insight into rxn mechanisms, which we will discuss later.

ΔH can be determined either directly (by experiment) or it can be calculated indirectly based on associated changes and the 1st Law of TD.

**6.4 Standard Enthalpies (or Heats) of Formation**

We can calculate the enthalpy changes for many rxns from a few standard values. It is simply a matter of combining the standard rxn values in different ways, much like combining the 26 letters of our alphabet in different ways makes many different words.

S**tandard Enthalpy** (Heat ) **of Formation =** Δ**H°f**

ΔHf = the energy involved in forming 1 mol of a specific compound **from its elements**. Please remember this. It frequently trips people up. The compound must be formed from its **elements**, not from other compounds.

The Standard Enthalpy Change = ΔH° = one that takes place when all constituents are in their standard states, that is, their most stable form at standard thermodynamic temperature and pressure (25°C and 1 atm).

\*\*When used in conjunction with a state function variable, please note that the "°" symbol means "standard states."

**Standard conditions are**:

1. 25°C or 298 K
2. 1 atmosphere of gas pressure
3. 1 molar solutions

**Standard states** are defined as the state an element or compound is in at standard consitions.

ΔHºf is in kJ/mol.

• Ex. ΔHºf for ethanol (C2H5OH)

2C(graphite\*) + 3H2(g) + 1/2 O2(g) 🡪 C2H5OH(l) ΔHºf = -277.7kJ/mol

\*Note: C(graphite) 🡪 C(diamond) ΔHº = +1.88kJ/mol

\*Table 6.2, p. 247 gives a few standard ΔHºf values. Appendix A 20 is more complete.

**\*\* The** Δ**Hºf value for free elements in their standard state is reported as zero.**

The standard enthalpy change ΔHºrxn for any rxn can be found as follows:

**ΔHºrxn = Σ npΔHºf (products) - Σ nrΔHºf (reactants)\*\*\* This equation is very important.**

Σ = summation or the sum of, np and nr are stoichiometric moles from a balanced eq.

* Ex. C6H12O6(s) + 6O2(g) 🡪 6CO2(g) + 6H2O(l)

ΔHºrxn = [ 6ΔHºf (CO2) + 6ΔHºf (H2O)] - [ΔHºf (C6H12O6) + 6ΔHºf (O2)]

ΔHºrxn = [ 6 mol (CO2)(-393.5kj/mol) + 6 mol (H2O)(-285.9kJ/mol] -

[ 1 mol (C6H12O6)(-1260kj/mol)+ 6 mol (O2)(0kJ/mol)]

= **-2816kJ**

**What important reaction is this?**

**6.5 Present Sources of Energy**

Please read this short section

Conventional fuels make use of the enthalpy of combustion (Hcomb). Burning such fuels has impacts on our environment.