Chapter 5
Thermochemistry

I. Nature of Energy

Energy units

- SI unit is **joule**, **J**
- From $E = 1/2\ mv^2$, $1J = 1kg \cdot m^2/s^2$
- Traditionally, we use the calorie as a unit of energy. 1 cal = 4.184J (exactly)
- The Nutritional Calorie, Cal = 1,000 cal

Systems and Surroundings

- A system is a small part of the universe we are interested in studying. (i.e. a reaction)
- The surrounding is the rest of the universe

II. First Law of Thermodynamics

- Energy cannot be created or destroyed. (also called Law of Conservation of Energy)
- System + Surroundings = 0
- What one loses, the other gains.

Internal Energy

- The total energy of a system is called internal energy. **Absolute internal energy cannot be measured. Only changes in internal energy.**

- Change in internal energy $\Delta E = E_{final} - E_{initial}$

- Example, a mixture of H_2+O_2 has a higher internal energy than H_2O. Moving from H_2 and O_2 means the change in internal energy is negative.
     $2H_2 + O_2 \rightarrow 2H_2O$ $\Delta E< 0$
- Moving the other direction, change in internal energy is positive

     $2H_2O\rightarrow$ $2H_2 + O_2$ $\Delta E>0$
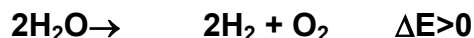
Relating ΔE to Heat and Work

- When a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or absorbed by the system plus the work done on or by the system:

   $\Delta E = q + w$

   Heat flowing from the surrounding to the system is positive (i.e. the system feels cold to the touch because it is absorbing heat from your hand) $q > 0$.

   Work done by the surroundings on the system is positive., $w > 0$.

Endothermic and Exothermic processes

- **Endothermic** absorbs heat from the surroundings (an ice pack)
- **Exothermic** transfers heat to the surroundings. (Dilution of sulfuric acid)

State functions

- Specific conditions given. (i.e. at 25°C)
- A state function depends only on the initial and final states of a system.
   - For example, the altitude difference between Colorado and Illinois does not depend on whether you fly or drive, only the elevation of the two above sea level.
- Similarly, the internal energy of 50g water at 25°C does not depend on whether we cool 50g of water at 100°C or heat 50g of water at 0°C.

III. Enthalpy

- The heat transferred between the system and surroundings during a chemical reaction carried out under constant pressure. Symbol is designated as H
- Change in enthalpy, ΔH Mathematically,

   $\Delta H = H_{final} - H_{initial} = q$

- Heat transferred from surroundings to system has a positive enthalpy ($\Delta H > 0$, endothermic reaction)
- Heat transferred from a system to surroundings has a negative enthalpy ($\Delta H < 0$, exothermic reaction)
- Enthalpy is a state function. It changes based on conditions of temperature and pressure. **Standard state** is given as 1 atm and 25°C.
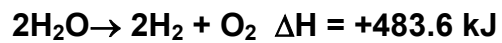
IV. Enthalpies of Reaction (ΔH_{rxn})

For a reaction, ΔH = H(products) - H(reactants)
Look at the reaction

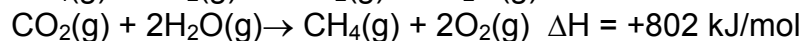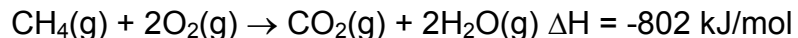$$2H_2 + O_2 \rightarrow 2H_2O \quad \Delta H = -483.6 \text{ kJ}$$

This equation tells us energy is released to surroundings therefore, exothermic reaction. In an energy diagram, the reactants have a higher energy than products.

For the reverse reaction.

$$2H_2O \rightarrow 2H_2 + O_2 \quad \Delta H = +483.6 \text{ kJ}$$

- Enthalpy is an extensive property, therefore, the *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.
- **Example, if 1 mol of CH_4 is burned in oxygen to produce carbon dioxide and water, 802 kJ of heat is released into the surroundings. If 2 mol of CH_4 is burned, then 1604 kJ of heat is released. Therefore, units of enthalpy are based on kJ/mol.**
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- The sign of ΔH depends on direction of the reaction.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ ΔH = -802 kJ/mol
$CO_2(g) + 2H_2O(g) \rightarrow CH_4(g) + 2O_2(g)$ ΔH = +802 kJ/mol

The first reaction is more probable of occurring. **Negative enthalpies represent spontaneity of a reaction**.

- Enthalpy change depends on state.

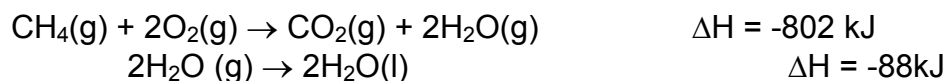$2H_2O\ (g) \rightarrow 2H_2O\ (l)$ ΔH = -88 kJ

Example 1:

Hydrogen peroxide can decompose to water and oxygen by the reaction:

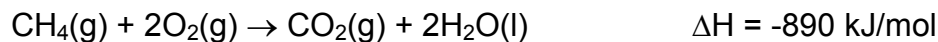$2\ H_2O_2 \rightarrow 2H_2O\ (l) + O_2(g)$ ΔH = -196 kJ
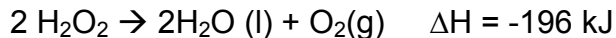
Calculate the value of q (ΔH) when 5.00 grams of hydrogen peroxide decomposes.

V. Hess's Law

- **Hess's Law**: if a reaction is carried out in a series of steps, the ΔH for the reaction is the sum of ΔH's for each step.
- The total enthalpy change is independent of the number of steps.
- Total ΔH is also independent of the path taken.
- Example

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H = \text{-802 kJ}$$
$$2H_2O\ (g) \rightarrow 2H_2O(l) \qquad \Delta H = \text{-88kJ}$$

$$CH_4(g) + 2O_2(g) + 2H_2O\ (g) \rightarrow CO_2(g) + 4H_2O(g) \qquad \Delta H = \text{-890 kJ}$$

Therefore, the reaction is

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = \text{-890 kJ/mol}$$

Notice ΔH is sensitive the states of reactants and products. BE CAREFUL!! The internal energy of water gas is different from the internal energy of water liquid.
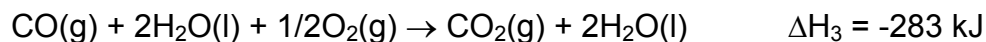

VI. Enthalpies of Formation

- Hess's Law states that if a reaction is carried out in a number of steps, ΔH for the overall reaction is the sum of the individual steps.
- Consider the formation of $CO_2(g)$ and $2H_2O(l)$ from $CH_4(g)$ and $O_2(g)$. if the reaction proceeds by one step:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = \text{-890 kJ}$$
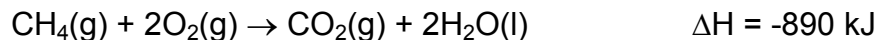
However, if the reaction proceeds through an intermediate:

$$CH_4(g) + 2O_2(g) \rightarrow CO(g) + 2H_2O(l)\ +1/2\ O_2 \qquad \Delta H_2 = \text{-607 kJ}$$
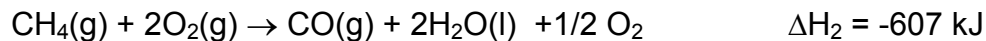
(we use $1/2\ O_2$ so we can have one mole of CH_4 in the balanced equation)

$$CO(g) + 2H_2O(l) + 1/2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_3 = \text{-283 kJ}$$

the sum of these reactions

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890 \text{ kJ}$$
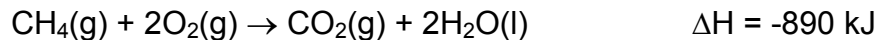
Enthalpy of Formation

- If a compound is formed from its constituent elements, it is called enthalpy of formation, ΔH_f.
- If the enthalpy of formation is said to be at **standard state**, it is at 1 atm and 25°C (298K) and designated as ΔH_f° It is based on **1 mole of substance**.
- tables are used to find standard enthalpies of formation.
- If there is more than one substance listed under standard conditions, the more stable one is used. Example, when dealing with carbon, we use graphite because it is more stable than diamond or C_{60}.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

Using Hess's Law
- *Example: Calculate ΔH_{rxn} for*

$$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O(l)$$
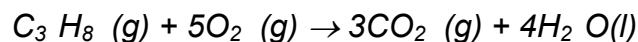
1. We start with the reactants, decompose them into elements.
(Natural state elements have a value of zero.)

2. Notice this the reverse of a formation equation

3. Write the formation equation for each product

4. Add the equations and the enthalpies to get the enthalpy for the reaction
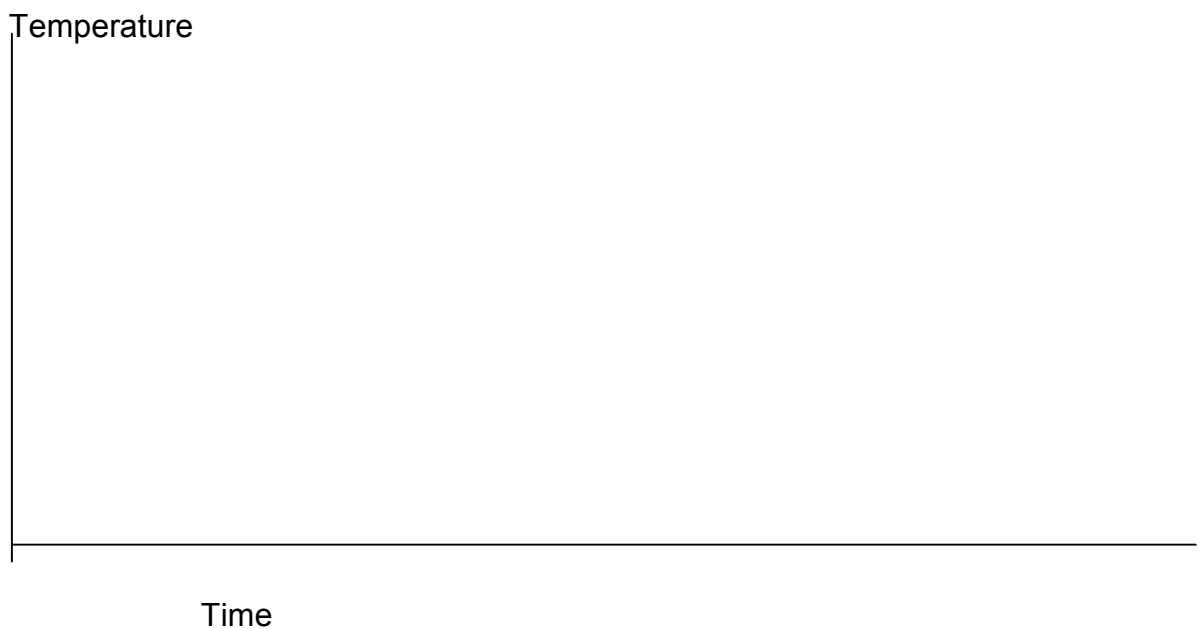*(ΔH_{rxn})*

Double check with the shortcut method:
    Where n = number of moles from the balanced equation
$\Delta H_{rxn}° = \sum n \Delta H°_f$ (products) - $\sum n \Delta H°_f$ (reactants)

$\Delta H_{rxn}° = [3(-393.5\ kJ) + 4(-285.8\ kJ)] - [-10.385kJ]$

VII. Calorimetry

Heat: heat is used to change state of a substance

                    Energy diagram for water

Temperature

            Time
What happens at the plateaus?

Where is the heat going at the plateaus?

Where is the heat going on the slope?

Heat capacity and specific heat

- Calorimetry is the measurement of heat flow

- Calorimeter is the apparatus which measures heat flow.

- Heat capacity : the amount of energy required to raise the temperature of an object. Different objects have different absorbance rates for heat based on their attractive forces.

- Molar heat capacity : heat capacity of 1 mol of substance

- specific heat = specific heat capacity = amount of heat to raise the temperature of 1 gram of a substance 1 Celsius degree

- Heat, q = (grams of substance) x (specific heat) x (ΔT)

    $q = mc\Delta T$

Be careful of the sign of q!
    Negative q means the reaction is exothermic, positive means endothermic.
    In an exothermic reaction, the reaction releases heat (negative q) and the surroundings absorb the heat (positive q)

Constant Pressure Calorimetry

Most common: atmospheric pressure
- Recall $\Delta H = q$
- Coffee cup calorimeter: a reaction or phase change occurs in a solution (usually water)
- Using a coffee cup calorimeter

$$q_{solution} = m\ c_{sol'n}\ \Delta T$$
$$q_{rxn} = m\ c_{rxn}\ \Delta T$$

$$q_{rxn} = -\ q_{sol'n}$$

Example 2:

When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21.0℃ to 27.5℃. Calculate the enthalpy change for the reaction assuming the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/ml and that its specific heat is 4.18 g/ml

Example 3:

100.0 mL of water is placed in a coffee cup calorimeter. The temperature of the water is 20.0°C. Ice is added to the water and stirred. Once no more ice can melt, the temperature of the water is recorded to be 0.0°C and the new volume is 115.0 mL. What is the heat of fusion for the ice?

Example 4

100.0 mL of water is placed in a coffee cup calorimeter. The temperature of the water is 20.0°C. 2.0 grams of ice is added to the water and stirred. Once the ice has melted, the temperature of the water is recorded to be 6.0°C.   What is the heat of fusion for the ice?
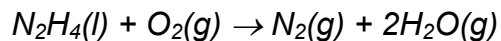
Bomb Calorimetry

- Reactions can be carried out under constant volume instead of constant pressure. A bomb calorimeter is used.
- Most common reaction studied under these conditions is combustion.
   In these cases, the q of the reaction is calculated by

$q_{rxn} = c_{calorimeter}\ \Delta T$

Example 5:
Hydrazine, N_2H_4 and its derivatives are widely used as rocket fuels. The combustion is given:

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

When 1.00g hydrazine is burned in a bomb calorimeter, the temperature of the calorimeter rises by 3.51 °C. If the calorimeter has a heat capacity of 5.510 kJ/°C, what is the quantity of heat evolved? What is the heat of reaction for the combustion of 1 mol?

answers: -19.3kJ
            -618kJ/mol hydrazine

- If the reaction is carried out in a bomb calorimeter and water is present

$$q_{rxn} = -(q_{water} + q_{bomb})$$

Example 6:
Methane is the major component of natural gas. A 1.00 gram sample of methane is burned in a bomb calorimeter containing 1225 grams water. The temperature rises from 20.00 to 29.26°C. Taking C_{bomb} = 840 J/°C, calculate

*a. $q_{reaction}$ for combustion of 1.00 g sample*
b. $q_{reaction}$ for combustion of 1.00 mole CH_4

answers: a) -55.2kJ
         b) -885 kJ

VIII. Foods and Fuels

Foods

- Fuel value = energy released when 1 g of substance is burned.
- Usually measured in Calories (1 nutritional Calorie = 1 **C**al = 1000 **c**al.
- Most energy in our bodies comes from carbohydrates and fats
- In intestines, carbohydrates are converted into glucose, $C_6H_{12}O_6$ or blood sugar

$$C_6H_{12}O_6(s) + 6\ O_2\ (g) \rightarrow 6CO_2 + 6H_2O\ (l) \quad \Delta H° = -2816kJ$$
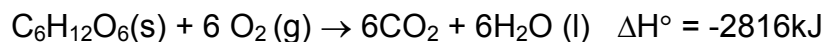
- Fats contain more energy than carbohydrates

$$C_{57}H_{110}O_6(s) + 163\ O_2\ (g) \rightarrow 114CO_2 + 110H_2O\ (l) \quad \Delta H° = -75,250kJ$$

- Fats contain more energy. they are not water soluble therefore they are a good energy source.

Fuels

- common fuels made mostly of hydrocarbons, have a typical value around 30 kJ/g
- Hydrogen has a great potential with a value of 142 kJ/g