

## Thermochemistry (chapter 5)

### Basic Definitions:

- Thermochemistry = the study of the energy changes that accompany physical and chemical changes of matter.
- Energy is defined as the ability to do work or the capacity to produce change. The forms of energy that are chemistry related include:

(1) Potential Energy

(2) **Thermal Energy** = the energy available from a substance as a result of the motion of its molecules.

(3) Chemical Energy

(4) Nuclear Energy

(5) Radiant Energy

- During chemical reactions, chemical energy may be *stored*, *released* as heat, or *converted* to other forms of energy. Regardless of the change, energy is always conserved (**Law of Conservation of Energy**).
- When studying the transfer of energy, a distinction between the **chemical system** and the **surroundings**

**Chemical System:** the set of reactants and products that are being studied (usually represented by a chemical equation)

**Surroundings:** all matter around the system being studied that is capable of absorbing or releasing energy.

*For example? What would the surroundings be in this case?*

## Types of Systems

**Closed system** = one in which there is no transfer of matter between the system and the surroundings

**Open system** = one in which there is a transfer of matter and energy between the system and the surroundings (e.g. a reaction taking place in an open beaker)

**Isolated system** = one in which no matter nor energy is transferred between the system and the surroundings

## Calorimetry

- A process of measuring the energy changes in a chemical system
- Done using a calorimeter (which we assume provides an isolated system, but in reality, is only a closed system)
- Process depends on three important things: mass (m); temperature change ( $\Delta T$ ), and the types of substance:

$$q = m c \Delta T$$

Here “c” is the *specific heat capacity* = the quantity of heat required to raise the temperature of one gram of a substance by one degree Celcius or one kelvin. See Table 1 on page 301 for the specific heat capacities of certain substances. Water has a “c” of 4.18 J/g.<sup>0</sup>C)

### **Ex1:**

When 600 ml of water in an electric kettle is heated from 20<sup>0</sup>C to 85<sup>0</sup>C to make a cup of tea, how much heat flows into the water?

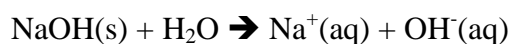
### **Ex2:**

If water is heated from 0<sup>0</sup>C to 50<sup>0</sup>C, calculate the mass of water that could be warmed by the addition of 8.00 kJ of heat?

## Classification of Changes

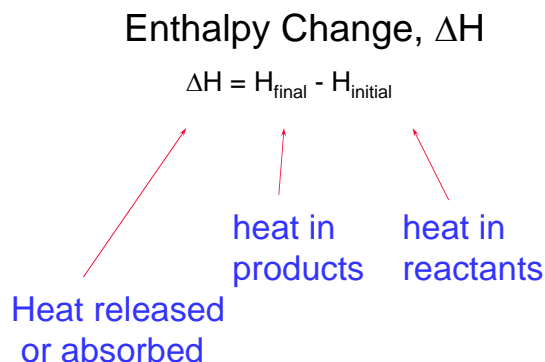
- Energy changes are classified into endothermic or exothermic based on how energy flows between the chemical system and its surroundings.
- If energy is lost from the system to the surroundings, the change is EXOTHERMIC.
- In an exothermic change, the value of  $q$  will be negative and the temperature of the system will decrease. Why
- If energy is absorbed from the surroundings into the system, the change is ENDOTHERMIC.
- In an endothermic change, the value of  $q$  will be positive and the temperature of the system will increase. Why?

e.g. which of the following changes is endothermic/exothermic?



## Enthalpy:

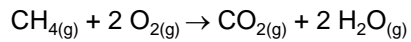
- Internal Energy of the System,  $E$  = sum of potential and kinetic energies of all species in system; for a change
- It is difficult to measure the sum of all the different types of potential and kinetic energies of a system
- What is usually measured is the enthalpy change ( $\Delta H$ )



- $\Delta H$  = enthalpy after the change in the system – enthalpy before change  
or
- Enthalpy change = quantity of heat that flows from a system to its surroundings or from the surroundings to the system:

$$\Delta H_{\text{system}} = +/-!q_{\text{surroundings}}!$$

for example...



$$\Delta H = -890.3 \text{ kJ/mol}$$

reactants  $\rightarrow$  products + heat

i.e. less H in products than reactants

i.e. heat is released!!!

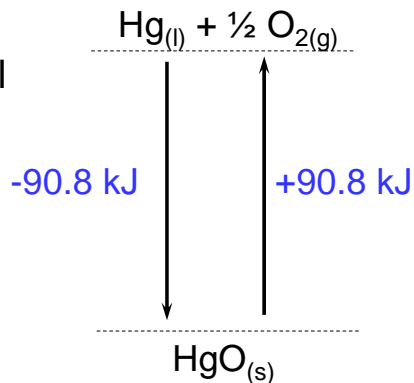
Enthalpy,  $\Delta H$ , is ultimately the change in potential energy of the system. The potential energy is associated with the attractive forces in a system

*If the attractive forces are greater after the change has taken place, then:*

- A) potential energy has decreased
- B) heat is evolved
- C) the change is exothermic
- D) the enthalpy of the system has decreased
- E) the  $\Delta H$  has a negative value

*If the attractive forces are less after the change has taken place, then ?:*

Reversing  
a Chemical  
Reaction



**Observing Enthalpy Changes:** Enthalpy changes may occur when:

- a) A *physical change* occurs (change in the form of the substance, but involves no breakage of chemical bonds e.g phase changes or dissolution)
- b) *Chemical change* = a change in the chemical bonds between atoms, resulting in the rearrangement of atoms for form new substances
- c) *Nuclear change* = a change in the protons or neutrons in an atom resulting in the formation of new atoms

**N.B**

In thermochemistry, the state of the substances in the system must be shown:

See Table 2 & Figure 7 on page 304 for more details of the above changes

### **Molar Enthalpies: (5.2)**

**Molar Enthalpy,  $\Delta H_x$**  = the enthalpy change per mole of a substance, where x indicates the type of change. The unit is then kJ/mol. See table 1 & 2 on page 306/307 for different types of molar enthalpies.

- A - sign in front of  $\Delta H$  = an exothermic change
- A + sign in front of  $\Delta H$  = an endothermic change

You can find the molar enthalpies for a number of substances in Reference books. Note that a linear relationship exists between enthalpy and moles. 2 mole will have 2x the enthalpy change than 1 mole  $\rightarrow \Delta H = n\Delta H_x$

### **Using Molar Enthalpies in Heat Calculations:**

#### **Ex 1:**

Freon, a common refrigerant (molar mass is 120.91g/mol) is alternately vaporized in tubes inside a refrigerator, hence absorbing heat, and condensed in tubes outside the refrigerator, thus releasing heat. This results in energy being transferred from inside to the outside of the refrigerator. The molar enthalpy of vaporization of freon is 34.99 kJ/mol. If 500.0 g of refrigerant is vaporized, what is the expected enthalpy change?

$$\Delta H_{\text{vap}} = 34.99\text{kJ/mol}$$

$$\Delta H = ?$$

#### **Steps:**

$$1) n_{\text{freon}} = m/M$$

$$2) \Delta H = n\Delta H$$

$\Delta H = +$  because heat is absorbed by the system during vaporization

Ex2: Calculate the enthalpy change,  $\Delta H$ , for the vaporization of 100.0 g of water at 100°C

Steps:

- 1)  $\Delta H_{\text{vap}}$  of water =
- 2)  $n_{\text{water}}$
- 3)  $\Delta H = n\Delta H$

### Using Calorimetry to Determine Molar Enthalpies

- Requires a calorimeter → consists of an insulated container for the chemical system (nested Styrofoam cups are perfectly OK)
- Involves some underlying assumptions:
  - a) No heat is transferred between the calorimeter and the outside environment
  - b) Any heat absorbed or released by the calorimeter materials is negligible
  - c) Dilute aqueous solutions is assumed to have a density and specific heat capacity equal to that of pure water
- Water is often then the **surrounding**, thus energy changes between the chemical system and the surrounding are monitored by changes in temperature of the water.

### **EX1:**

In a calorimetry experiment, 7.46g of potassium chloride is dissolved in 100 ml (100 g) of water at an initial temperature of 24.1°C. If the final temperature of the solution is 20°C, what is the molar enthalpy of solution for potassium chloride?

**Since:**

$$\Delta H = q$$

$$\Delta H = n\Delta H_{\text{sol}}$$

$$q = mc\Delta T$$

Then:

$$n\Delta H_{\text{sol}} = mc\Delta T$$

**EX 2:** What mass of lithium chloride must have dissolved if the temperature of 200.0 g of water increased by 6.0°C? The molar enthalpy of solution of lithium chloride is -37 kJ/mol

*The above changes dealt with solubility changes; chemical changes can be approached the same way by dissolving small amounts of the reactants in water*

**Representing Enthalpy Changes:** (5.3)

**Method 1** = Writing thermochemical Equations with energy terms

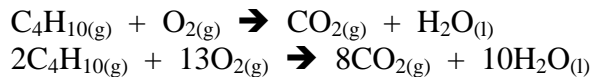
**Method 2** – Thermochemical Equations with  $\Delta H$  values

**Method 3** – Molar Enthalpies of Reactions = the energy change associated with the reaction of one mole of a substance. If the molar enthalpy was determined at SATP conditions, it is called a standard molar enthalpy of reaction and given the symbol,  $\Delta H_r^\circ$ . A lot of these values are summarized in reference textbooks.

**Method 4** – potential energy diagrams

EX1:

Write a thermochemical equation to represent the exothermic reaction that occurs when two moles of butane burn in excess oxygen gas. The molar enthalpy of combustion of butane is  $-2871 \text{ kJ/mol}$ .



$$\Delta H = n\Delta H_{\text{com}}$$



### Hess's Law of Additivity of reaction Enthalpies (5.4)

Many reactions occur in steps:

Ex. The formation of  $\text{CO}_2$

1. Directly in the presence of lots of oxygen



2. A two step process when oxygen is limited



Notice that the overall enthalpy change  $[(-110.5 \text{ kJ}) + (-280.0 \text{ kJ}) = -395.5 \text{ kJ}]$  in the production of one mole of  $\text{CO}_2$  in the two step method is the same as in that of the one-step method.

This illustrates **Hess's Law**: The value of  $\Delta H$  for any reaction that can be written in several steps = the sum of the values of  $\Delta H$ s for each of the individual steps

#### **Another version of Hess's law:**

If two or more reactions with known enthalpies are added together to form a new "target" equation, then the sum of their enthalpies will give the enthalpy change of the target equation

$$\Delta H_{\text{target}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \dots$$

or

$$\Delta H_{\text{target}} = \Sigma \Delta H_{\text{known}}$$

Hess's Law allows chemists to determine enthalpy change of a reaction without direct calorimetry (some reactions can't be done due to safety or expense reasons). Two rules must be followed when using Hess's Law:

- a) If a chemical equation is reversed, the sign of  $\Delta H$  must also be reversed
- b) If the coefficients of a chemical equation are altered by multiplying or dividing by a factor, the  $\Delta H$  must be altered the same way

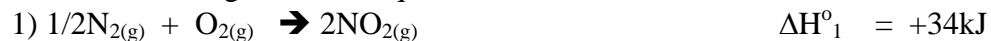


**Ex 1:** Determine the enthalpy change involved in the formation of two moles of liquid propanol, according to the following equation:  $6\text{C}_{(s)} + 8\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow \text{C}_3\text{H}_7\text{OH}_{(l)}$  .

The standard enthalpies of combustion for propanol, carbon, and hydrogen gas at SATP are –2008, –394, and –286 kJ/mol, respectively.

**EX2:** What is the enthalpy change for the formation of two moles of nitrogen monoxides from its elements?  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{(g)}$   $\Delta\text{H}_f^\circ = ?$

Use the following reference equations:

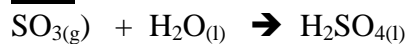


### **Standard Enthalpies of Formation (5.5)**

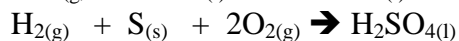
Calorimetry and Hess's Law are two ways of determining enthalpies of reaction. A third way method uses tabulated enthalpy changes, i.e. **standard enthalpies of formation** = the energy associated with formation of one mole of a substance from its elements in their standard states.



### **N.B:**



$\Delta\text{H}$  = heat of reaction

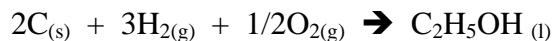
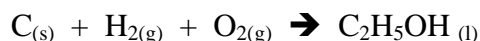


$\Delta\text{H}$  = heat of formation

**Writing formation Equations:**

1. Write one mole of the product in the state specified
2. Write the reactant elements in their standard states
3. Choose coefficients for the reactants to give a balanced equation which has one mole of the product

**EX 1.** Write the formation equation for liquid ethanol

**NOTE:**

- 1) The  $\Delta H_f^\circ$  of any element is 0
- 2)  $\Delta H = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$ ; “n” in this case is the coefficient of the balanced equation

**EX2:**

What is the thermochemical equation for the reaction of calcium oxide and water?

The Target equation:

**Steps:**

- 1) Write the standard enthalpy of formation for each of the products in the above equation, look up their enthalpy values @ the back of the book.



**EX3:** The main component in natural gas used in home heating or laboratory burners is methane. What is the molar enthalpy of combustion of methane fuel?

Steps:

- 1) Write balanced equation for the reaction
- 2) Use  $\Delta H = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$

**EX4:** One way to heat water in a home or cottage is to burn propane. If 3.20 g of propane burns, what temperature change will be observed if all of the heat from combustion transfers to the 4.0 kg of water?

Steps:

- 1) Work out  $\Delta H$
- 2) Use  $n\Delta H_{\text{com}} = mc\Delta T$