

## **CHM 102**

### **THERMOCHEMISTRY**

#### **The Nature and Types of Energy**

Energy is usually defined as the capacity to do work

Work = force x distance

All forms of energy are capable of doing work, however, Chemists define work as energy change resulting from a process

Kinetic Energy -----The energy produced by moving an object, it is one form of energy that is of particular interest to Chemists.

Other forms of energy include

1. Radiant energy (solar energy comes from the sun, it's the earth's primary energy source)
2. Thermal Energy – Energy associated with random motion of atom and molecules
3. Chemical Energy- stored within the structural units of chemical substances. Chemical energy is released during chemical reactions
4. Potential Energy. Energy that is available by virtue of an object's position

When one form of energy disappears some other forms of energy of equal magnitude must appear, and vice versa -----Fist law of thermodynamics ( Law of conservation of energy).

Processes which take place on their own without the external intervention of any kind are known as spontaneous processes. All the processes that takes place in nature are spontaneous in character, proceeds only in one direction and are, therefore thermodynamically irreversible. They can be reversed only with the aid of an external agency ( nonspontaneous)

#### **Energy Changes**

In an exothermic reaction, how do the strength of the bonds in the reactant compares with the strengthen of the bonds in the product?

The bonds in the products are (overall) stronger than in the reactants . The stronger the bonds that are made , the more energy is released. The reverse is true overall when the bonds in the products are weaker than in reactant

### **Energy Changes in Chemical Reactions**

Almost all chemical reactions absorb or produce energy, generally in the form of heat.

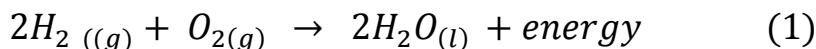
Thermochemistry is the study of heat change in chemical reactions

The energy changes that occur during chemical reactions are very important in understanding the mass relationship in reactant and product as well as thermal energy released. To analyze energy changes associated with chemical reactions, the following must be defined.

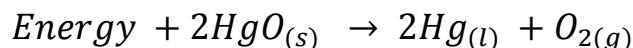
**System:** This is the specific part of the universe that is of interest, while the surroundings are the rest of the universe outside the system. Three Types of systems are identified:

1. An open system can exchange mass and energy in form of heat with its surroundings
2. A Closed System only allows the exchange of heat but not matter
3. An Isolated system is one that is totally insulated, and isolated from the surrounding, so that the transfer of mass and energy are not allowed.

**Exothermic Process:** Any process that gives out heat to its surrounding, e.g



**Endothermic Process:** In this process heat is supplied to the system by the surrounding, eg



### **The Law Of Conservation Of Energy - 1<sup>st</sup> law of thermodynamics**

The law has been stated in various forms, but the fundamental implication is that although energy may be transformed from one form into another, it can neither be created nor destroyed.

### **Mathematical formulation of the 1<sup>st</sup> law of thermodynamics**

Consider a system in site A with internal energy  $E_A$ . It absorbs heat  $q$  from the surroundings a certain amount of heat ,  $q$  and undergoes a change in its opposition to B where its energy is  $E_B$  , The change in energy of the system  $\Delta E$  is given by

$$\Delta E = E_B - E_A \quad (1)$$

Note that the change is independent of the path or manner in which the change has been brought about. If  $W$  is the work involved in this transformation, the net gain of energy is  $q + W$ , from the - 1<sup>st</sup> law

$$\Delta E = E_B - E_A = q + w \quad (2a)$$

$$\Delta E - w = q \quad (2b)$$

$$w = P\Delta V$$

$$\Delta V = \text{change in volume}$$

For an expansion work,  $w$  is negative

For a compression work,  $w$  is positive.

$q$  = heat

Eg. A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas, if it expands ; (a) against a vacuum ( $p=0$ ), and (b) against a constant pressure of 1.2 atm (Ans; ( a)=0 ( b)  $-4.9 \times 10^2 J$  ( Using 1 L atm= 101.3 J

$$w = -p\Delta v$$

Equations (2a) and (2b) are the mathematical form of the 1<sup>st</sup> law of thermodynamics..

## **Thermodynamic Functions**

Enthalpy Of Chemical Reaction.

The first law of thermodynamics can be applied to processes carried out under different conditions. Consider a situation in which the volume is kept constant, and one in which the pressure applied on the system is kept constant

If a chemical reaction is run at constant volume,  $\Delta V = 0$ , and no  $P - V$  work will result from this change . From Eq 2a.it follows that

$$\Delta E = q + P\Delta V \quad (3a)$$

$$\Delta E = q_v \quad (3b)$$

Constant-volume conditions are not common, most reactions occur under conditions of constant pressure, (usually atmospheric pressure).

For a constant pressure process

$$\Delta E = q + w \quad (3c)$$

$$\Delta E = q_p - P\Delta V \quad (3d)$$

$$q_p = \Delta E + P\Delta V \quad (3e)$$

Where subscript p denotes constant-pressure condition

$$H = E + PV \quad (4a)$$

E= internal energy of the system

$$\Delta H = \Delta E + \Delta(PV) \quad (4b)$$

If the pressure is held constant, then

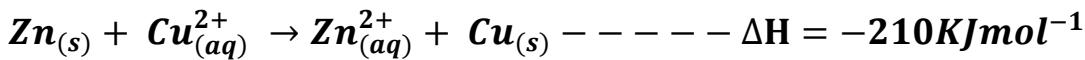
$$\Delta H = \Delta E + P\Delta V \quad (4c)$$

Considering equations 4c with 3e

$$\text{For a constant pressure process} \quad q_p = \Delta H \quad (5)$$

## **Enthalpy of Reaction**

An enthalpy change is a heat change that takes place at constant pressure



*Reactant → Product*

The difference between enthalpies of products and enthalpies of reactions is

$$\Delta H = H_{products} - H_{reactants}$$

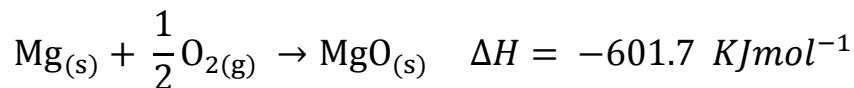
The enthalpy of reaction can be positive (endothermic reaction,  $\Delta H > 0$ ,) or negative (exothermic reaction,  $\Delta H < 0$ ).

## THERMOCHEMICAL EQUATIONS

At 0°C and 1 atm pressure, ice melts to form liquid water. Measurements show that for every mole of ice converted to liquid water under these conditions 6.01 KJ of heat energy are absorbed by the system (ice). Because the pressure is constant, the heat change is equal to the enthalpy change H. Furthermore, this is an endothermic process as expected for the energy-absorbing change of melting ice. Therefore, H is a positive quantity.

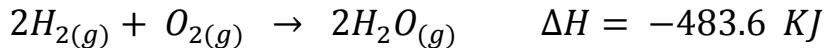


The “per mole” in the unit for  $\Delta H$  means that this is the enthalpy change per mole of the reaction. The standard heat of formation is the enthalpy change when one mole of the substance is made from its element in their standard state.



## **Thermochemical Rules**

**1-** The magnitude of  $\Delta H$  is proportional to the amount of products and reactants



According to rule 1:  $\Delta H = -\frac{483.6 \text{ KJ}}{2} = -241.8 \text{ KJmol}^{-1}$

**2.**In writing the thermochemical equations, the physical state of all reactants and products must be specified.

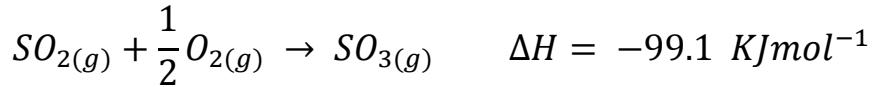
**3.** If we multiply both sides of a thermochemical equation by a factor x, then  $\Delta H$  must also change by the same factor.

**4.**If we reverse an equation, we change the roles of reactants and products.

Consequently, the magnitude of  $\Delta H$  for the equation remains the same but its sign changes.



Given a thermochemical equation:



Calculate the heat evolved when 74.6 g of  $SO_2$  (molar mass=  $64.07 \text{ gmol}^{-1}$ ) is converted to  $SO_3$  (Ans = -115.4 KJ)

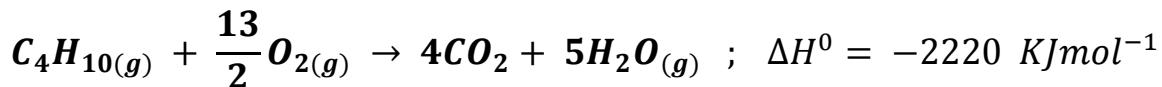
## **Standard Enthalpy of Formation and Reaction**

**Substances are said to be in their standard state at 1 atm, and 298 K hence the term standard enthalpy**

## **Standard Heat of Combustion**

**The standard heat of combustion is the enthalpy change when one mole of the substance is completely burned in oxygen**

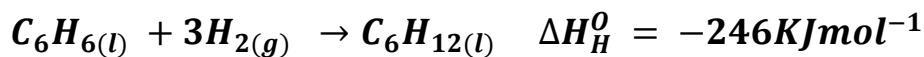
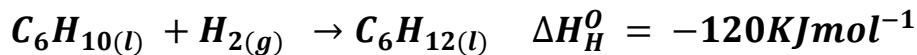
**The heat of combustion of butane is**



**The heat of hydrogenation-** The enthalpy of hydrogenation is the heat change when one mole of an unsaturated compound react with hydrogen and is completely changed into the corresponding saturated compound



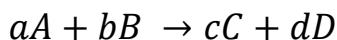
**Now compare the value of the heat of hydrogenation of cyclohexene with that of benzene**



In both cases the product is the same

The importance of the standard enthalpies of formation ( $\Delta H_{rxn}^0$ ) is that once the values are known, standard enthalpy of formation can easily be calculated

Consider an hypothetical example (**Direct Method**)



$$\Delta H_{rxn}^0 = [c\Delta H_f^0(C) + d\Delta H_f^0(D) - [a\Delta H_f^0(A) + b\Delta H_f^0(B)]$$

Where a, b, c, and d are stoichiometric coefficients

$$\Delta H_{rxn}^o = \sum n \Delta H_f^o(\text{prds}) - \sum m \Delta H_f^o(\text{rxts})$$

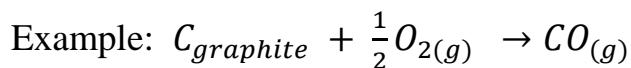
Where m and n denote the stoichiometric coefficients for the reactants and products.

By convention, the standard enthalpy of formation of any element in its most stable state is zero

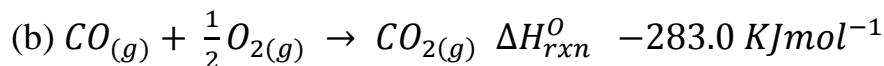
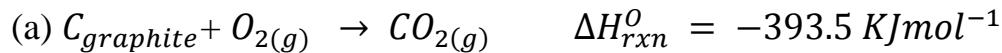
i.e substances in their stable states have  $\Delta H_f^o$  of zero ( Examples  $C_{\text{graphite}}$ ,  $O_2$  etc are stable allotropic form of the elements . The direct method works for compound that can be readily synthesized

Many compounds cannot be directly synthesized from there elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases

$\Delta H_f^o$  can be determined by an indirect approach which is based on Hess's law, it can be stated as follows. When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps



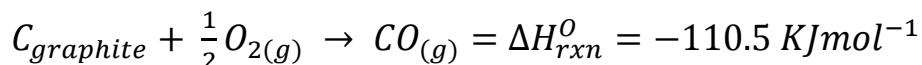
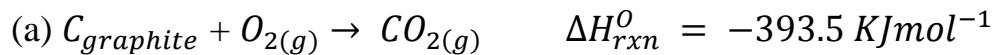
However, burning graphite also produces some  $CO_2$ . So we cannot measure the enthalpy change of  $CO_{(g)}$  directly as shown , instead the indirect route must be employed.



First, reverse equation b to get,



Because chemical equation can be added and subtracted just like algebraic equations,



Thus the  $\Delta H_f^0 (CO) = -110.5 \text{ KJmol}^{-1}$

## Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a calorimeter.

### Specific Heat (s) and Specific Heat Capacity (C)

The specific heat (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius ( $J/g^\circ\text{C}$ )

The heat capacity (C) of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius ( $J/^\circ C$ )

$$C = ms$$

M= mass of the substance (g) E.g, the specific heat of water is ( $4.184 J/g^\circ C$ ), and the heat capacity of  $60.0\ g$  of water is

$$C = ms = (60.0\ g) * 4.184\ J/g^\circ C = 251\ 04\ J^\circ C$$

Amount of heat absorbed is

$$q = ms\Delta T = C\Delta T$$

$$\Delta T = \text{temperature change} = t_{final} - t_{initial}$$

### Constant-Volume Calorimetry

Heat of combustion is usually measured by placing a known mass of a compound in a steel container called constant –volume calorimeter which is filled with oxygen at about 30 atm. of pressure . The close bomb is immersed in a known amount of water. The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the bomb. The specific design of the calorimeter enables us to assume that no heat (or mass) is lost to the surroundings during the time it takes to make measurement. Therefore, the bomb and the water can be called an isolated system. Because no heat enters or leaves the system throughout the process, the heat change of the system ( $q_{system} = q_{cal} + q_{rxn}$ ,

$$(q_{overall} = zero$$

Where  $q_{cal} + q_{rxn}$ , are the heat change for the calorimeter and the reaction respectively

$$q_{rxn} = q_{cal}$$

$$q_{cal} = C_{cal}\Delta T$$

### Constant- Pressure Calorimetry

A simple device than the constant –volume calorimeter is the constant-pressure calorimeter which is used to determine the heat changes for noncombustible reaction