

## PHYSICAL CHEMISTRY

CHM 100L/CHEMISTRY DEPARTMENT

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## THERMOCHEMISTRY

Thermochemistry is the branch of thermodynamics that investigates the heat flow into or out of a reaction system and deduces the energy stored in chemical bonds. As reactants are converted into products energy can either be taken up by the system or released to the surroundings. At constant temperature and constant volume, the heat that flows to the reaction system is equal to  $\Delta U$ . For a reaction that takes place at constant temperature and constant pressure, the heat that flows to the system is equal to  $\Delta H$  for the reaction. The enthalpy of formation is defined as the heat flow into the system in a reaction between pure elements that leads to the formation of 1 mol of product.

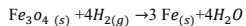
Because it is a state function, the reaction enthalpy can be written as the enthalpies of formation of the products minus those of the reactants. This property allows  $\Delta H$  and  $\Delta U$  for the reaction to be calculated for many reactions without carrying out an experiment.

Such that:

$$\Delta U = U_2 - U_1 \text{ or } U_{\text{prod}} - U_{\text{reactant}}$$

$$\Delta H_m^\circ = H_{m\text{product}}^\circ - H_{m\text{reactant}}^\circ$$

For the reaction



$$\Delta H_m^\circ = [H^\circ(3\text{Fe}(s)) + H^\circ(4\text{H}_2\text{O}(l))] - [H^\circ(\text{Fe}_3\text{O}_4(s)) + H^\circ(4\text{H}_2(g))]$$

## HESS LAW

Hess law or Hess's law of constant heat summation states that at constant temperature heat energy changes (enthalpy) accompanying a chemical reaction will remain constant, irrespective of the way the reactants react to form products. This law is based on the state function character of enthalpy and the first law of thermodynamics.

The energy (enthalpy) of a system (molecule) is a state function. So enthalpy of reactant and product molecules is a constant and does not change. According to the first law of thermodynamics the total energy of the substances before and after any (physical or chemical) change should be equal. According to the law, the total energy of the reactant should be equal to the total energy of the product. Any difference in the energy between the reactants and products is also fixed at a particular enthalpy changes of all those chemical reactions.

By illustration:- The total enthalpy change ( $\Delta H$ ) of a reaction equals to the sum of the enthalpy changes occurring in each step of the reaction, i.e.

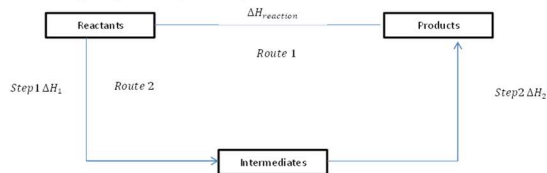


Figure 1(a).  $\Delta H_{\text{reaction}} = \Delta H_1 + \Delta H_2$

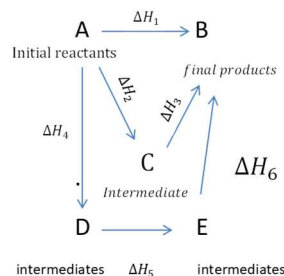
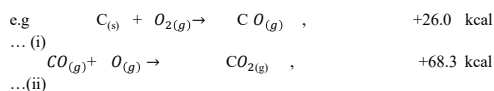


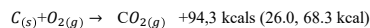
Figure b.

Reactants can form product B by following three different steps C, D and E are intermediates in the other stepwise reactions. Hess law states that the enthalpy of the reaction  $\Delta H_1$  is the same irrespective of the path. So, the enthalpy of direct single step reaction and other paths given intermediates C, D and E should be the same.

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$$



On adding the two reactions (i) + (ii)



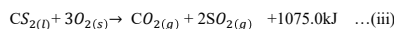
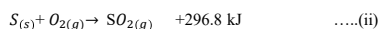
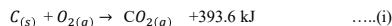
For Hess law  $\Delta H = \Delta H_1 + \Delta H_2 = (26 + 68.3 \text{ kCal})$

This means that carbon reacts with oxygen to form carbon dioxide releasing 94.3 kcal of heat in a single step. Carbon can also react in a two step process of forming an intermediate carbon monoxide, which again is converted to carbon dioxide.

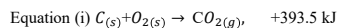
Net reaction enthalpy of both reactions is the same as that of single step formation. So, enthalpy of reaction does not change on the path followed by the reactants.

## HESS LAW AND MULTI DIFFERENT REACTIONS

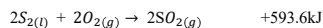
Combustion of carbon, sulphur and carbon disulphide are exothermic with an enthalpy of -393.5kJ, -296.8kJ and -1075kJ. The reactants are:



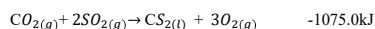
These reactions and enthalpy changes can be treated as algebraic equations to get the heat of formation of carbon disulphide even without experiments.



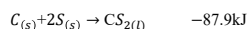
Multiply eq (ii) by 2. Gives:



Reverse equation (iii) to give



Add the three reactions



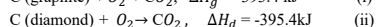
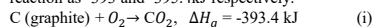
Formation of carbon disulphide is an exothermic reaction.

## APPLICATION OF HESS LAW OF HEAT SUMMATION

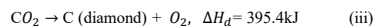
### 1. Enthalpy change in physical change

Carbon and diamond are allotropes of carbon. But measuring the energy change in the conversion of graphite to diamond cannot be determined as the process cannot be carried out. The heat changes for this hypothetical physical change can be calculated using Hess law because:

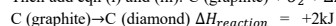
Hess law of heat summation is an efficient way to estimate heat changes that cannot be measured experimentally let's consider the combination of graphite and diamond with oxygen with the heat of reaction as -393 and -395.4kJ respectively.



Reverse equation (ii) as



Then add eqn (i) and (iii):  $C (\text{graphite}) + O_2 \rightarrow \Delta H_{gr} -393.4 \text{ kJ}$



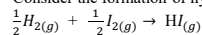
Enthalpy change in the allotrope transition of graphite to diamond is endothermic of 2KJ.

## 2. Enthalpy change of chemical reaction

The bond energy of hydrogen, iodine and hydrogen iodide are 218, 107KJ and 299KJ respectively.

Question:- Estimate the enthalpy of hydrogen iodide formation. Is the reaction endothermic or exothermic?

Consider the formation of hydrogen iodide from hydrogen and iodide:



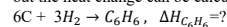
Enthalpy of formation of hydrogen iodide is the heat change occurring when one atom of hydrogen and one atom of iodine react to form one mole of hydrogen iodide in standard conditions (as gas). To get one atom of hydrogen or iodine, the molecular bond has to be broken. Heat of formation = bond energy of HI - Bond dissociation of  $H_2$  - Bond dissociation energy of  $I_2$

$$= 299 - (218 + 107) = 299 - 325 = -26 \text{ KJ}$$

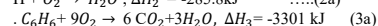
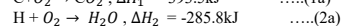
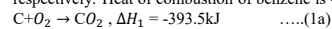
As the heat of formation is negative, the reaction is exothermic.

## 3. Enthalpy of formation

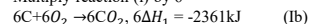
Carbon combines with hydrogen to form many hydrocarbons. Hence, the heat of formation of benzene cannot be determined experimentally but the heat change can be calculated by Hess law



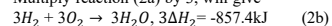
Heat of formation of  $CO_2$  and  $H_2O$  are -393.5kJ and -285KJ respectively. Heat of combustion of benzene is -330KJ such that:



Multiply reaction (i) by 6

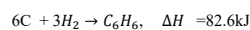


Multiply reaction (2a) by 3, will give



...(3b)

Adding the three reactions give:



The heat of formation of benzene = 82.6kJ

The heat of formation of benzene = +82.6kJ

## Assignment I

The heat of formation of carbon monoxide and steam are 111 and 244KJ respectively. Calculate the heat of the reaction:

