

CHEMISTRY CLASS -XI

UNIT-6

THERMODYNAMICS

MODULE -4/5

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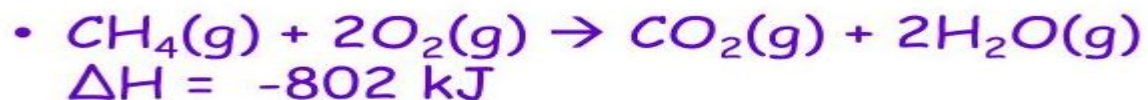


OUTLINE

- Thermochemical Equations
- Hess's Law of Constant Heat Summation.
- Limitations Of First Law of thermodynamics
- Spontaneity
- Enthalpy change and spontaneity

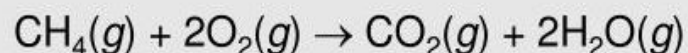
Thermochemical Equations

- ⇒ consider the balanced equation for reactants and products
- ⇒ the value and appropriate sign of enthalpy change is given on the right hand side this value is ΔH
- ⇒ the physical states of reactants and products are specified by letter s (solid) l (liquid) g (gas) and aq (aqueous) $\Delta_r H$ value refers to Physical states of substances those appear in the equation.



⇒ The given value of $\Delta_r H$ assume that the reaction occurs in a given direction . the $\Delta_r H$ for the given reaction equals in magnitude and opposite in the same to that of Forward reaction. **An exothermic reaction on reversal becomes endothermic and vice versa**

Consider



$$\Delta H^\circ_{\text{reaction}} = -802.3 \text{ kJ}$$

- Reverse thermochemical equation
- Must change sign of ΔH



$$\Delta H^\circ_{\text{reaction}} = 802.3 \text{ kJ}$$

- when the coefficients indicating the number of moles of all substances in thermochemical equation are multiplied or divided by a certain numerical factor, the corresponding ΔH need to be multiplied or divided by the same



Here, the no. of reactants and products are doubled.
Hence, enthalpy change also doubles

$$\text{Enthalpy change} = 2 \times (70 \text{ kJ}) = 140 \text{ kJ}$$

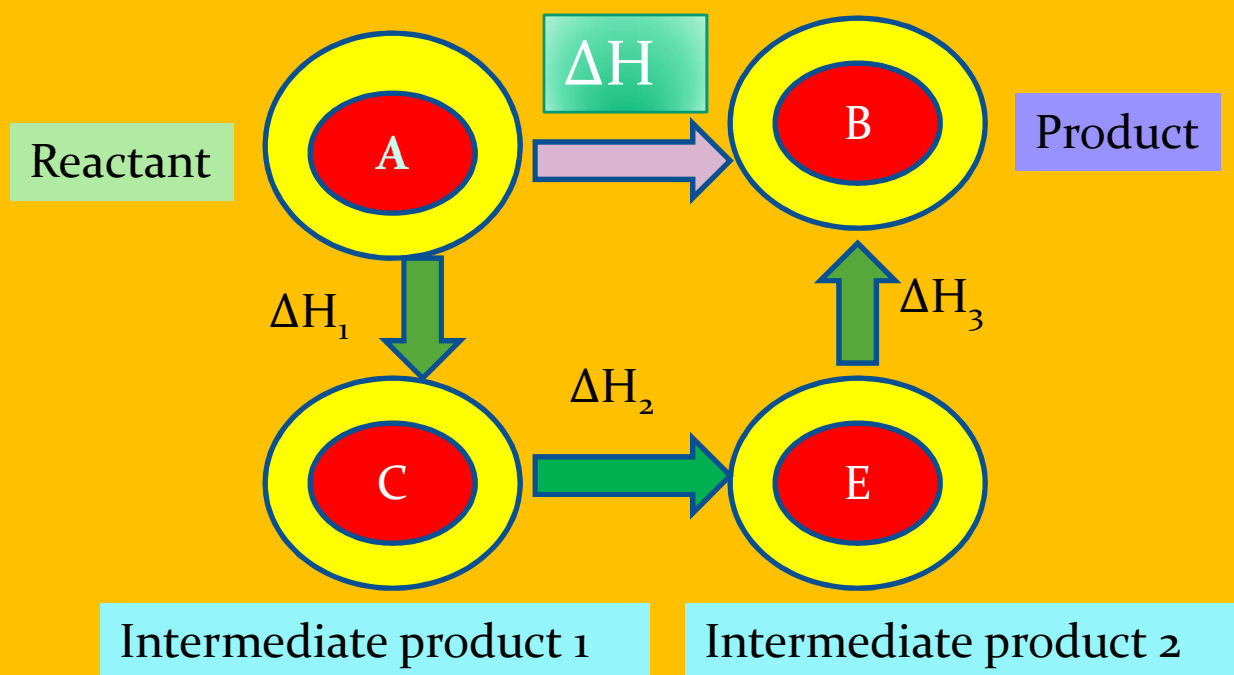
Enthalpy change of the reaction is **140 kJ**.

HESS'S LAW OF CONSTANT HEAT

SUMMATION

- Russian chemist Germain Henry Hess gave one of the most important generalization of thermochemistry in 1840 which is named after his name as Hess's law.
 - Generalization is primarily based on the fact that enthalpy is a path independent thermodynamic function. i.e enthalpy change in a chemical reaction is same whether it takes place in one step or more than one step
 - The change in enthalpy is same whether the reaction takes place in one step or series of step
- OR**
- Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction


$$\Delta H \longrightarrow \Delta H_1 \oplus \Delta H_2 \oplus \Delta H_3$$



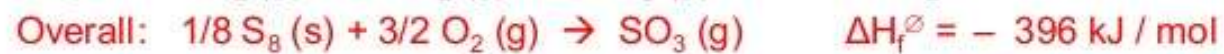
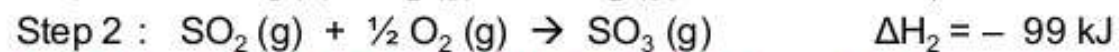
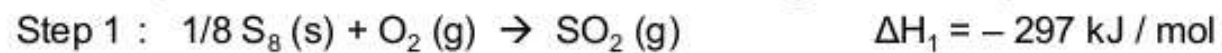


Application of Hess's Law

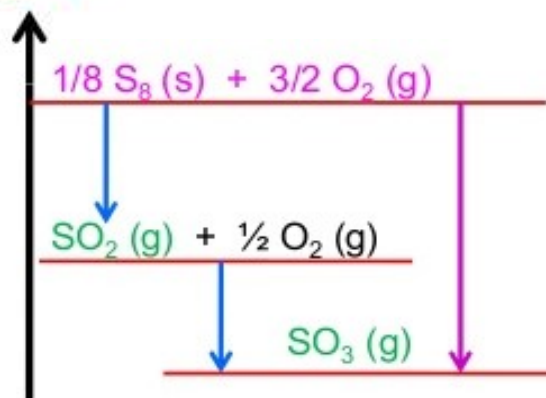
- Hess's law allow us to carry out thermochemical calculations to predict enthalpies of various reactions whose direct measurement is not possible
- The thermochemical reactions like algebraic equations can be added subtracted, multiplied or divided.
- To apply Hess's Law, all of the component steps of a chemical reaction need to occur at the same temperature.
- Hess's Law may be used to calculate entropy and Gibb's energy in addition to enthalpy.

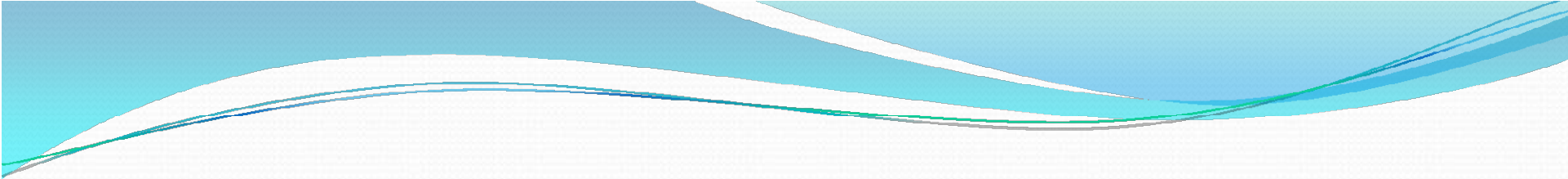
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- We can determine standard enthalpy of formation.- Large number of compounds like methane carbon dioxide benzene etc cannot be directly prepared from their elements.
 - Hence their standard enthalpies of formation cannot be determined by calorimetric method.
 - By using Hess's law we can determine the enthalpy of formation by knowing other data of the cycle

■ Example : In the reaction of formation of SO_3 , it is a 2 steps reaction.



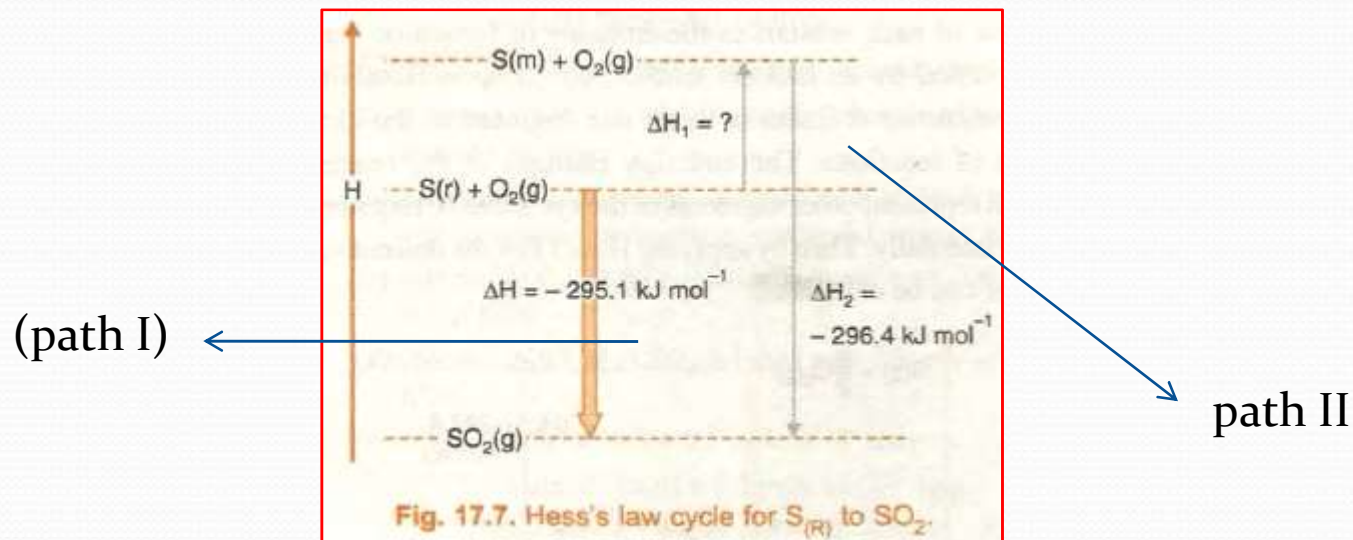
Energy / kJ



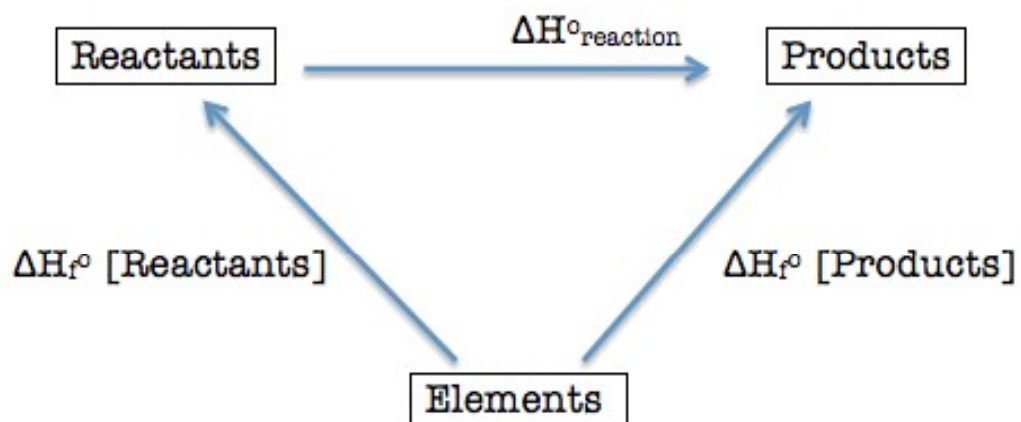
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- Using Hess's law we can calculate **Enthalpy of Transition**.
 - Changes like ..change of **graphite to diamond**, red phosphorus to yellow phosphorus, **rhombic sulphur to monoclinic sulphur** etc.
 - Such reactions are very slow and enthalpy change accompanying them cannot be calculated directly.
 - Hess's law is quite helpful in determining the enthalpy of such transition

- For example, let us calculate the enthalpy of the process S^R to S^M from the enthalpies of combustion of monoclinic sulphur (S^M) and rhombic sulphur (S^R) which have been found to be -296.4 and -295.1 kJ/mol respectively. Now Hess's law cycle is constituted as S^R to SO_2 (path I) and S^R to S^M to SO_2 (path II). These changes have been shown in Fig.

- Now according to Hess's law:
- $\Delta H = \Delta H_1 + \Delta H_2$
- $\Delta H = \Delta H_1 + \Delta H_2 = -295.4 - (-296.9) = -1.3$ KJ.



We can determine standard enthalpy of reaction using Hess's law.



$$\Delta H_o (\text{reaction}) = \sum \Delta H^{\circ}_f (\text{products}) - \sum \Delta H^{\circ}_f (\text{reactants})$$

- 1) Given:
- $\text{B}_2\text{O}_3 (\text{s}) + 3\text{H}_2\text{O} (\text{g}) \rightarrow 3\text{O}_2 (\text{g}) + \text{B}_2\text{H}_6 (\text{g})$ ($\Delta\text{H} = 2035 \text{ kJ/mol}$)
- $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{O} (\text{g})$ ($\Delta\text{H} = 44 \text{ kJ/mol}$)
- $\text{H}_2 (\text{g}) + (1/2)\text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{l})$ ($\Delta\text{H} = -286 \text{ kJ/mol}$)
- $2\text{B} (\text{s}) + 3\text{H}_2 (\text{g}) \rightarrow \text{B}_2\text{H}_6 (\text{g})$ ($\Delta\text{H} = 36 \text{ kJ/mol}$)
- Find the ΔH_f of:
- $2\text{B} (\text{s}) + (3/2) \text{O}_2 (\text{g}) \rightarrow \text{B}_2\text{O}_3 (\text{s})$
- After the multiplication and reversing of the equations (and their enthalpy changes), the result is:
- $\text{B}_2\text{H}_6 (\text{g}) + 3\text{O}_2 (\text{g}) \rightarrow \text{B}_2\text{O}_3 (\text{s}) + 3\text{H}_2\text{O} (\text{g})$ ($\Delta\text{H} = -2035 \text{ kJ/mol}$)
- $3\text{H}_2\text{O} (\text{g}) \rightarrow 3\text{H}_2\text{O} (\text{l})$ ($\Delta\text{H} = -132 \text{ kJ/mol}$)
- $3\text{H}_2\text{O} (\text{l}) \rightarrow 3\text{H}_2 (\text{g}) + (3/2) \text{O}_2 (\text{g})$ ($\Delta\text{H} = 858 \text{ kJ/mol}$)
- $2\text{B} (\text{s}) + 3\text{H}_2 (\text{g}) \rightarrow \text{B}_2\text{H}_6 (\text{g})$ ($\Delta\text{H} = 36 \text{ kJ/mol}$)
- Adding these equations and cancelling out the common terms on both sides, we get
- $2\text{B} (\text{s}) + (3/2) \text{O}_2 (\text{g}) \rightarrow \text{B}_2\text{O}_3 (\text{s})$ (**$\Delta\text{H} = -1273 \text{ kJ/mol}$**)

Limitations of First law of Thermodynamics

- For instance, the first law fails to explain why heat flows from hot end to cold end when a metallic rod is heated at one end and not on other and vice-versa.
- The first law only quantifies the energy transfer that takes place during this process.
- It is impossible to construct a machine that can continuously supply mechanical work without consuming any energy simultaneously. Such a hypothetical machine is known as the perpetual motion machine of the first kind. These types of machines violate the 1st law of thermodynamics and do not exist in reality.



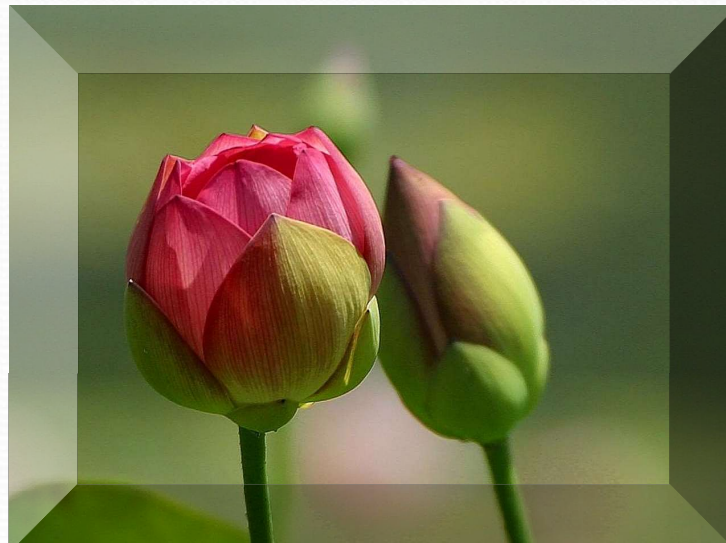
Some more examples....

- A cup of hot coffee left in a cooler room eventually cools off. The reverse of this process- coffee getting hotter as a result of heat transfer from a cooler room does not take place.
- Consider heating of a room by passage of electric current through an electric resistor. Transferring of heat from room will not cause electrical energy to be generated through the wire.
- Consider a paddle-wheel mechanism operated by fall of mass. Potential energy of mass decreases and internal energy of the fluid increases. Reverse process does not happen, although this would not violate first law.
- Water flows down hill where by potential energy is converted into K.E. Reverse of this process does not occur in nature.



So we can conclude that.....

- Processes proceed in a certain direction and not in the reverse direction. The first law places no restriction on direction.
- A process will not occur unless it satisfies both the first and second laws of thermodynamics.
- Second law not only identifies the direction of process, it also asserts that energy has quality as well as quantity.
- Before discussing Second law let us understand the meaning of **SPONTANEITY**



Spontaneous process occurring in nature



Spontaneous Process

- Process which has a natural tendency to occur either of its own or after proper initiation under given set of condition.
- Reaction may only be reversed only when external energy is applied.
- Chemical reactions which are spontaneous at given conditions can also be called feasible processes.



Examples of spontaneous process

- **Spontaneous process that need no initiation**
- Evaporation of water- $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$
- Dissolution of sugar in water to form a solution-
- $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + \text{aq} \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$
- Precipitation reactions-
- $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{BaSO}_4(\text{s})$



- **Spontaneous process that need initiation**

- Reaction of hydrogen and oxygen to form water



- Coal burns to CO_2 when ignited



- A process which has no natural tendency or urge to occur is said to be a **non spontaneous** process. these processes may made to occur when energy from external source is supplied continuously throughout the change .

- E.g-Electrolysis of Water



KEY POINTS

**SPONTANEOUS
PROCESS**

summary

- Occurs on its own

Not concerned with the rate of reaction

Proceeds in one direction

Continues till equilibrium is achieved

Enthalpy change and spontaneity

- There must be some driving force which is responsible to drag a spontaneous reaction in a forward reaction. Let us consider some spontaneous processes.
- Water flows down the hill due to its tendency to decrease its potential energy
- Heat flow from hot body to cold body to lower its energy.
- Combustion of carbon-
- $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad \Delta H = -394\text{kJ}$
- Above processes reveals that all of them proceed towards the state of lower energy.
- This leads to a conclusion that **-ve delta H may be the criterion of spontaneity**

GENERAL ASSUMPTION:-

Spontaneous reaction takes place in a direction in which energy of the system is lowered

i.e exothermic reaction

but EXCEPTIONAL CASES

ice melts by absorbing heat

NaCl dissolves in water by absorbing heat from the surrounding

i.e endothermic reactions



SECOND LAW OF THERMODYNAMICS

- The total entropy of the system and its surrounding increases in a spontaneous process
- $\Delta S_{(\text{total})} = \Delta S_{(\text{system})} + \Delta S_{(\text{surrounding})} > 0$

THANK YOU

