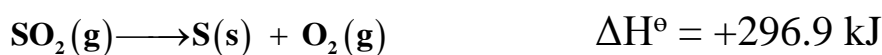


Laplace's Law

L.Lavoisier and P.S.Laplace gave this law in 1780 which states that **"the enthalpy of a reaction is exactly equal but opposite in sign for the reverse reaction."**

For example, if ΔH is the enthalpy change in going from A to B then the enthalpy change for the process B to A would be $-\Delta H$. Thus, the enthalpy of formation of a compound is numerically equal but opposite in sign to the enthalpy of decomposition of the compound.



Whenever a thermochemical equation is reversed the sign of ΔH also gets reversed.

Methods of determining ΔH

1. **Calorimetry** (experimental)
2. **Hess's Law**: using Standard Enthalpy of Reaction (ΔH_{rxn}) of a series of reaction steps (indirect method).
3. **Standard Enthalpy of Formation** (ΔH_f) used with Hess's Law (direct method)
4. **Bond Energies** used with Hess's Law

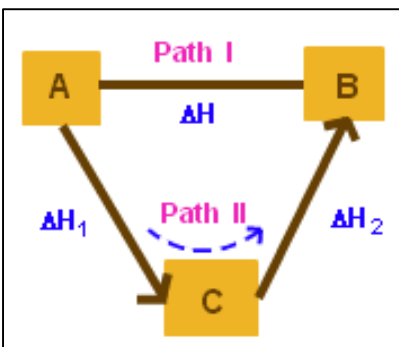
Hess's Law

G.H.Hess proposed a law regarding the heat or enthalpies of reaction in 1840 called the Hess's law. This law states that

"The heat change in a particular reaction is the same whether it takes place in one step or several steps."

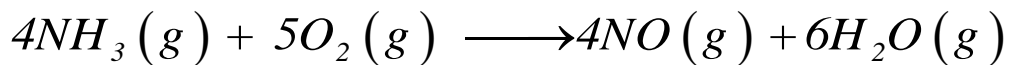
By other words, total **enthalpy change** for a reaction is **independent of the route** by which the chemical change takes place.

For example, a reactant 'A' changes to a product 'B' in one step and the heat change during this process is ΔH . If the reaction is carried out in two steps where 'A' first changes to 'C' an intermediate stage and then 'C' changes to 'B' in the following step then let the heat change during the formation of 'A' to 'C' be ΔH_1 and that from 'C' to 'B' be ΔH_2 . From Hess's law the heat change for the reaction is given as



$$\Delta H = \Delta H_1 + \Delta H_2$$

Q) Determine the heat of reaction for the reaction:

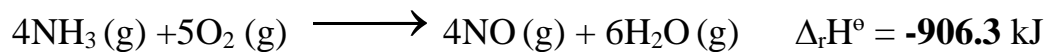
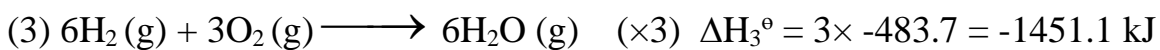
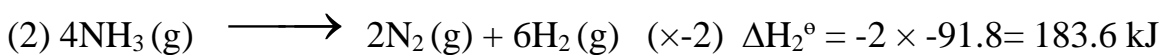
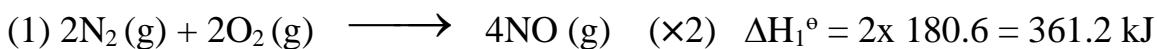


Using the following sets of reactions:



Sol/

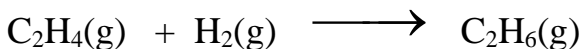
(eq.2) Reverse and multiply $\times 2$, (eq.1) multiply $\times 2$ and (eq.3) multiply $\times 3$



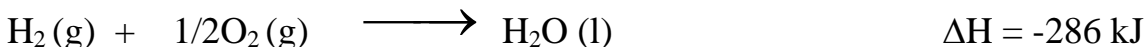
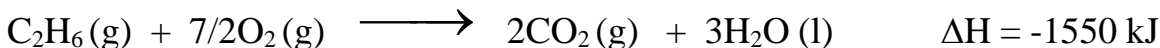
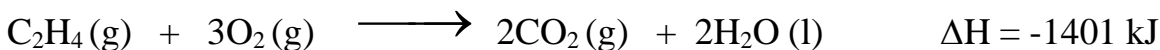
$$\Delta_r H^\circ = \Delta H_1^\circ + \Delta H_2^\circ + \Delta H_3^\circ$$

$$\Delta_r H^\circ = (361.2 + 183.6 + (-1451.1)) \text{ kJ} = \mathbf{-906.3 \text{ kJ}}$$

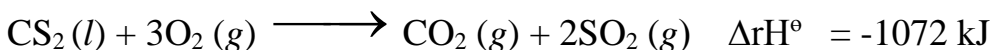
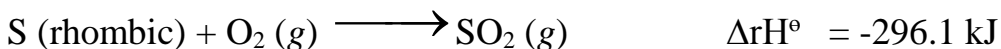
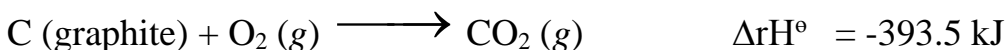
H.W) Determine the heat of reaction for the reaction:



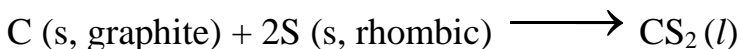
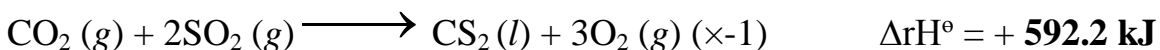
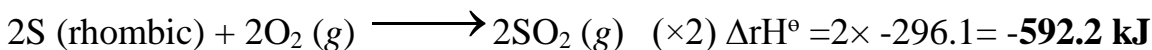
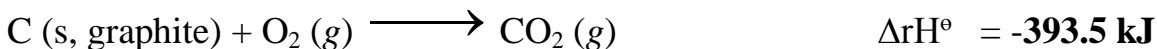
Use the following reactions:



Calculate the standard enthalpy of formation of $\text{CS}_2(\text{l})$ given that:

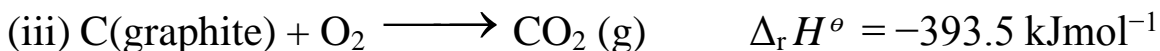
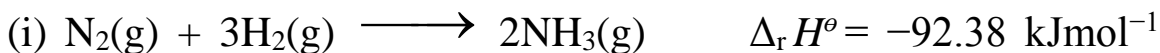


Sol/ (eq.3) Reverse and (eq.2) multiply $\times 2$



$$\Delta_f\text{H}^\ominus = (-393.5 + (-592.2) + 592.2) \text{ kJ} = 86.3 \text{ kJ}$$

Q) Calculate $\Delta_r U^\theta$ for the following reactions at 1 atm and 298K.

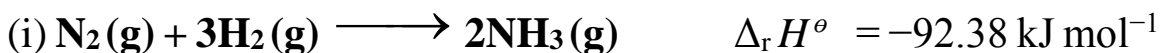


Solution:

$$\Delta_r U = \Delta_r H - RT\Delta n$$

$$R = 8.314 \text{ J K}^{-1}\text{mol}^{-1} \quad T = 298 \text{ K}$$

$$RT = 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K} = 2477 \text{ J mol}^{-1} = 2.477 \text{ kJ mol}^{-1}$$



$$\Delta n = 2 - (1+3) = -2$$

$$\Delta_r U = -92.38 \text{ kJ mol}^{-1} - (-2 \times 2.477 \text{ kJ mol}^{-1}) = -87.426 \text{ kJ mol}^{-1}$$



$$\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$$

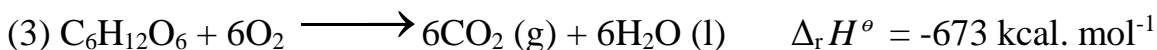
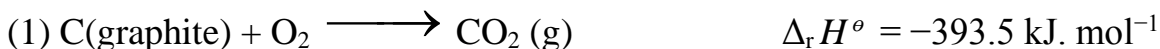
$$\Delta_r U = -110.5 \text{ kJmol}^{-1} - (\frac{1}{2} \times 2.477 \text{ kJ mol}^{-1}) = -111.738 \text{ kJ mol}^{-1}$$



$$\Delta n = 1 - 1 = 0$$

$$\Delta_r U = \Delta_r H = -393.5 \text{ kJ mol}^{-1}$$

H.w) for the following reactions at 1 atm and 298K.



Calculate $\Delta_f H^\ominus$ and $\Delta_f U^\ominus$ of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)

The reaction enthalpy in terms of enthalpies of formation

For a given reaction, the overall enthalpy change is equal to the difference between the algebraic sum of enthalpies of formation of products and the algebraic sum of enthalpies of formation of reactants.

$$\Delta_r H^\ominus = \sum n_p \Delta_f H^\ominus (\text{products}) - \sum n_r \Delta_f H^\ominus (\text{reactants})$$

Where n_p and n_r are stoichiometric numbers

Note/ **The standard enthalpies** of formation of **elements** in their reference states are **zero** at **all** temperatures

Q) Calculating enthalpy of combustion of diborane, B_2H_6 , using the molar enthalpy of formation data:

Given:

- (1) $\frac{1}{2} B (s) + \frac{3}{2} O_2 (g) \rightarrow B_2O_3 (s); \quad \Delta_f H_{(1)} = -1273 \text{ kJ}$
- (2) $2B(s) + 3H_2(g) \rightarrow B_2H_6(g); \quad \Delta_f H_{(2)} = 36.4 \text{ kJ}$
- (3) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O (g); \quad \Delta_f H_{(3)} = -241.85 \text{ kJ}$

Calculate ΔH for the following combustion reaction:



Sol/

$$\Delta_r H^\ominus = \sum n_p \Delta_r H^\ominus (\text{products}) - \sum n_r \Delta_r H^\ominus (\text{reactants})$$

$$\Delta_r H^\ominus = [\Delta_f H^\ominus (B_2O_3) + 3 \times \Delta_f H^\ominus (H_2O)] - [\Delta_f H^\ominus (B_2H_6) + 3 \times \Delta_f H^\ominus (O_2)]$$

$$\Delta_r H^\ominus = [-1273 + 3 (-241.85)] - [36.4 + 3 (0)]$$

$$\Delta_r H^\ominus = -2034.95 \text{ kJ}$$

H.W) calculate heat of reaction using molar enthalpy of formation:

Given: $\Delta_f H^\ominus [C_3H_8(g)] = -104 \text{ kJ/mol};$

$\Delta_f H^\ominus [H_2O(g)] = -242 \text{ kJ/mol},$ and

$\Delta_f H^\ominus [CO_2(g)] = -394 \text{ kJ/mol};$

Calculate $\Delta_r H^\ominus$ for the following combustion of $C_3H_8(g)$:

