

Standard States :-

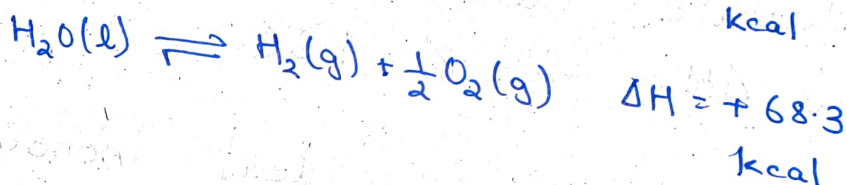
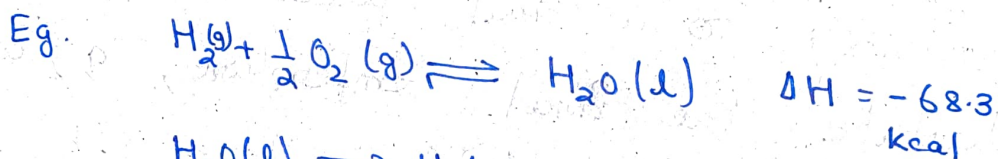
When the value of a thermodynamic function is measured at a particular temperature (T) and 1 atm pressure, the function is standard.

For e.g. $H^{\circ} = H(T, 1 \text{ atm})$

$$C_p^{\circ} = C_p(1 \text{ atm})$$

Laws of Thermochemistry :-

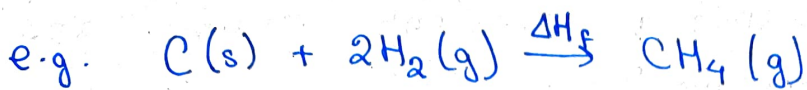
1) Law of Lavoisier and Laplace - The heat changes for a reaction in forward direction is equal in magnitude but opposite in sign for the backward reaction.



2) Hess's Law of constant heat summation - The heat change of a reaction is independent of the number of steps.

Enthalpies of reactions :-

1) Standard heat of reaction (Formation) - When 1 mole of substrate is formed from its constituent elements in their stable state, the change in enthalpy is called enthalpy of formation.



For a general reaction,



$$\left[\Delta H_f^\circ = \sum \Delta H_f^\circ(\text{Products}) - \sum \Delta H_f^\circ(\text{Reactants}) \right]$$
$$= (cH_C^\circ + dH_D^\circ) - (aH_A^\circ + bH_B^\circ)$$

If all substances are in their standard states, then $\Delta H^\circ = 0$.

2) Enthalpy of combustion - The enthalpy change involved when 1 mole of a substrate completely burns in presence of sufficient oxygen.



$$\Delta H_C^\circ = -212.81 \text{ kcal}$$

3) Enthalpy of neutralisation - The enthalpy change involved when 1 gm equivalent of an acid is exactly neutralized by 1 gm equivalent of a base.

For a strong acid and strong base, the value

is -13.7 kcal .

Heats of reaction at constant volume and
Constant pressure :-

$$\begin{aligned}\text{At constant volume, } \Delta U &= q_v \\ &= \sum U_{\text{Product}} - \sum U_{\text{Reactant}}\end{aligned}$$

$$\begin{aligned}\text{At constant pressure, } \Delta H &= q_p \\ &= \sum H_{\text{Product}} - \sum H_{\text{Reactant}}\end{aligned}$$

$$\text{Also, } [\Delta H = \Delta U + (\Delta n)RT] \text{ (at constant P)}$$

$$\text{or, } [q_p = q_v + (\Delta n)RT] \text{ (for a gaseous reaction)}$$

Kirchoff's Relations :-

(Dependence of enthalpy on ~~pressure~~ ^{temperature})

$$\Delta H^\circ = H^\circ(\text{Products}) - H^\circ(\text{Reactants})$$

$$\frac{d\Delta H^\circ}{dT} = \frac{dH^\circ}{dT}(\text{Products}) - \frac{dH^\circ}{dT}(\text{Reactants})$$

$$\text{Also, } \frac{dH^\circ}{dT} = C_p^\circ$$

$$\frac{d\Delta H^\circ}{dT} = C_p^\circ(\text{Products}) - C_p^\circ(\text{Reactants})$$

$$\left[\frac{d\Delta H^\circ}{dT} = \Delta C_p^\circ \right]$$

Integrating,

$$\int_{T_1}^{T_2} d\Delta H^\circ = \int_{T_1}^{T_2} \Delta C_p^\circ dT$$

$$\Rightarrow (\Delta H^\circ)_{T_2} - (\Delta H^\circ)_{T_1} = \int_{T_1}^{T_2} \Delta C_p^\circ \cdot dT$$

Similarly,

$$(\Delta U^\circ)_{T_2} - (\Delta U^\circ)_{T_1} = \int_{T_1}^{T_2} \Delta C_v^\circ \cdot dT$$

i) If ΔC_p° is independent of temperature, then

$$(\Delta H^\circ)_{T_2} - (\Delta H^\circ)_{T_1} = \Delta C_p^\circ (T_2 - T_1)$$

ii) If ΔC_p° is dependent on temperature, then

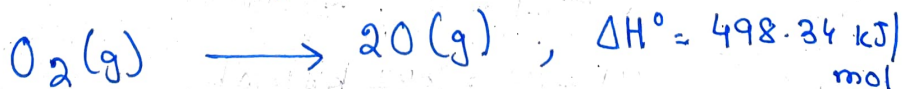
$$C_p = a' + b'T + c'T^2 + \dots$$

$$\Delta C_p^\circ = (\Delta a') + (\Delta b')T + (\Delta c')T^2 + \dots$$

$$\therefore (\Delta H^\circ)_{T_2} - (\Delta H^\circ)_{T_1} = \int_{T_1}^{T_2} [(\Delta a') + (\Delta b')T + (\Delta c')T^2 + \dots] dT$$

Bond enthalpy and bond energy :-

Consider the reaction,



Here 498.34 kJ/mol is the bond enthalpy of Oxygen.

Bond energy is the amount of energy required to break 1 mole of a particular bond in a compound.

For gases,

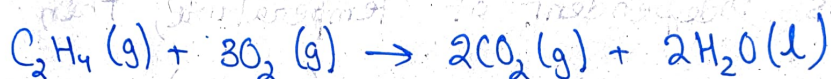
$$[\Delta U = \Delta H - (\Delta n)RT]$$

Application of Hess's Law :-

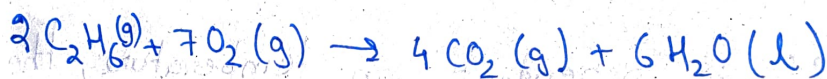
1) Calculate ΔH for the reaction



Given:



$$\Delta H = -1411 \text{ kJ}$$

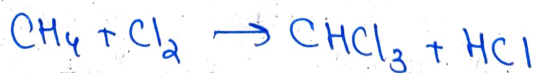


$$\Delta H = -1560 \text{ kJ}$$



$$\Delta H = -285.8 \text{ kJ}$$

2) Calculate the ΔH of the reaction-



Given: $C-H = 412 \text{ kJ/mol}$

$$C-Cl = 331 \text{ kJ/mol}$$

$$Cl-Cl = 242 \text{ kJ/mol}$$

$$H-Cl = 432 \text{ kJ/mol}$$