Influence of Temp^r. on ΔU & ΔH : Kirchhoff's Eqn.

If a system undergoes a change from a given state to another given state both the internal energy and heat content would alter, we have

$$U_f - U_i = \Delta U$$

$$H_f - H_i = \Delta H$$

differentiating these wrt. T, at constant vol^m. for the internal energy and at constant Press^r. for the enthalpy, we have,

$$\left[\frac{\partial(\Delta U)}{\partial T}\right]_V = \left[\frac{\partial U_f}{\partial T}\right]_V - \left[\frac{\partial U_i}{\partial T}\right]_V$$

$$= C_{V_f} - C_{V_i}$$

$$= \Delta C_V$$

and $$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \left[\frac{\partial H_f}{\partial T}\right]_P - \left[\frac{\partial H_i}{\partial T}\right]_P$$

$$= C_{P_f} - C_{P_i}$$

$$\boxed{= \Delta C_P}$$

Otherway,

$$\int \partial(\Delta U) = \int \Delta C_v \, dT$$

and $$\int \partial(\Delta H) = \int \Delta C_P \, dT$$

Integrating betn. the limits T K and 0 K we have,

$$\Delta U_T = \Delta U_0 + \int_0^T \Delta C_v \, dT \rightarrow (1)$$

$$\Delta H_T = \Delta H_0 + \int_0^T \Delta C_p \, dT \rightarrow (2)$$

ΔU_0 and ΔH_0 are internal energy and enthalpy changes at 0 K

These are called Kirchhoff's equn.

For chemical reactions, the equn (2) is more important, since most reaction takes place at Const. Pressr.

✓ * Hess's law :- law of Const. heat Summatio

Statement :- The law state that, "for a given chemical process the net heat-chan (qp or qv) will be the same whether the process occurs in one or in several stages."

Illustration :-

Carbon and oxygen can give carbon di oxide directly (i.e. in single stage), otherwise carbon and oxygen can give carbon monoxide (Ist stage) firstly and then carbon monoxide and oxygen give carbon di oxide (2nd stage). Of course, the net heat change in either case will be the same,

(I) $C + O_2 = CO_2 \;,\; \Delta H^\circ = -393.5\,K$

(II) $C + \frac{1}{2}O_2 = CO \;,\; \Delta H_1^\circ = -110.5\,K$

$CO + \frac{1}{2}O_2 = CO_2 \;,\; \Delta H_2^\circ = -283.0\,K$

$$\therefore \; \Delta H^\circ = \Delta H_1^\circ + \Delta H_2^\circ$$

In accordance with the Ist law, if the initial and final states be fixed, the change in heat content or energy content of a system i.e. ΔH_p and ΔU_p would be independent of the path. Hence q_p and q_v will be independent of the path. i.e, heat change of a reaction will be the same whether the reaction takes place in a single step or in several steps.

The advantage of this principle is that we can add or subtract the heat changes in the process. Thus applying Hess's law we can compute the heat of a reaction in the formation of a compound though the elements would not directly combine to produce the compound. The heat of reaction at const. press^{r}. q_p is really the enthalpy change of the process, i.e.

$$q_p = \Delta H$$
$$= H_{\text{Prod.}} - H_{\text{React.}}$$

Eg. calculate the heat of reaction of
$$C + H_2 + O_2 = C_{12}H_{22}O_{11} \; ; \; \Delta H = ?$$
from the following datas,

(i) $C_{12}H_{22}O_{11} + 12\,O_2\,(g) = 12\,CO_2\,(g) + 11\,H_2O\,(l)$
$\Delta H^\circ = -1350\,KC$

(ii) $C + O_2\,(g) = CO_2\,(g) \; ; \; \Delta H^\circ = -94.05\,KC$

(iii) $H_2 + \frac{1}{2}O_2 = H_2O\,(l) \; ; \; \Delta H^\circ = -68.3\,KC$

Rewriting equn. (I) ⇒

(IV) $12CO_2(g) + 11H_2O(l) = C_{12}H_{22}O_{11} + 12O_2$; $\Delta H' = 135$

Now, (Equn. II) × 12

(Equn. III) × 11 ⟶

adding equn. IV

$\Delta H_{II} = -1128.6$ kJ

$\Delta H_{III} = -751.3$ kJ

$\Delta H_{IV} = +1350.00$

$\Delta H = -529.9$ kJ

$$12C + \cancel{12O_2} = \cancel{12CO_2} \;;\; \Delta H = -94.05\text{ kJ} \times 12$$

$$11H_2 + \frac{11}{2}O_2 = \cancel{11H_2O} \;;\; \Delta H = -68 \times 11\text{ kJ}$$

$$\cancel{12CO_2} + \cancel{11H_2O} = C_{12}H_{22}O_{11} + \cancel{12O_2} \;;\; \Delta H = 1350\text{ kJ}$$

$$12C + 11H_2 + \frac{11}{2}O_2 = C_{12}H_{22}O_{11} \;;\; \Delta H = -529.9\text{ kJ}$$

The example clearly illustrates the utility of the law of heat summation #