

## Influence of Temp<sup>r</sup> on $\Delta U$ & $\Delta H$ : Kirchhoff's eq<sup>n</sup>

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

$$U_f - U_i = \Delta U$$

$$H_f - H_i = \Delta H$$

Differentiating these w.r.t.  $T$ , at constant vol<sup>m</sup> for the internal energy  $\rightarrow$  at constant pressure for the enthalpy, we have,

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

$$= C_{v,f} - C_{v,i}$$

$$= \Delta C_v$$

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

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

$$\Delta Q = \Delta C_p$$

Other way,

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

$$\Rightarrow \int \partial(\Delta H) = \int \Delta C_p dT$$

Integrating bet<sup>n</sup> the limits  $T$  &  $0K$   
we have,

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

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

$\Delta U_0$  &  $\Delta H_0$  are internal energy & enthalpy changes at  $0K$

These are called Kirchhoff's eqn<sup>s</sup>.

For chemical reactions, the eqn<sup>s</sup> (2) is more important, since most reaction takes place at const. press<sup>n</sup>.

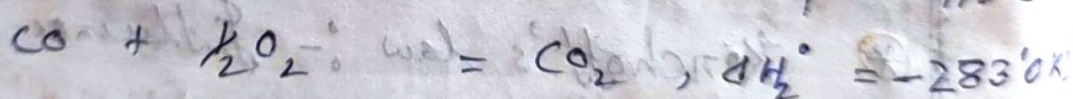
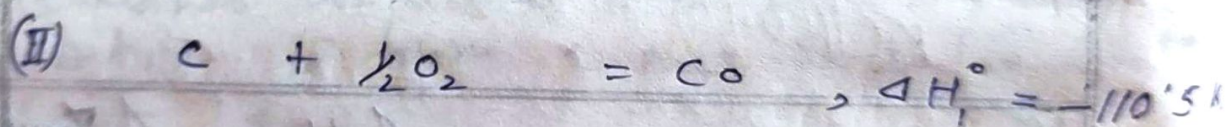
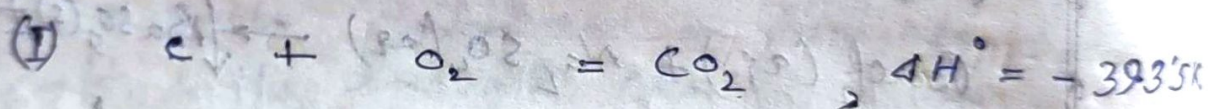
✓ Hess's law :- Law of Const. heat summation

Statement :- The law state that, for a given chemical process the net heat change ( $Q_p$  or  $Q_v$ ) will be the same whether the process occurs in one or in several stages.

Illustration :-

Carbon and oxygen can give Carbon dioxide directly (i.e. in single stage), otherwise

Carbon and oxygen can give Carbon monoxide (1st stage) firstly and then Carbon monoxide and oxygen give Carbon dioxide (2nd stage) of course, the net heat change in either case will be the same,



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

In accordance with the 1st law, if the initial and final states be fixed, the change in heat content or energy content of a system i.e.  $\Delta H_p$  and  $\Delta U_p$  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

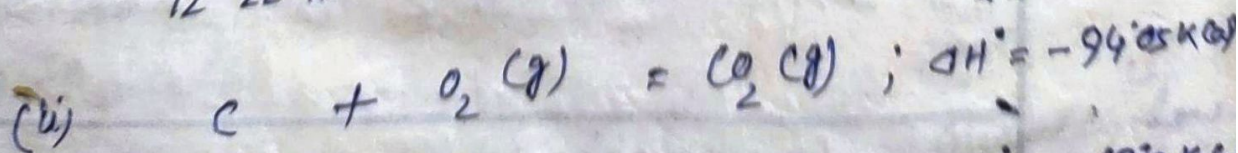
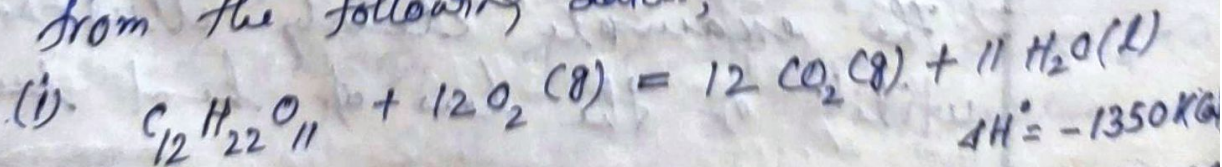
Whether the reaction takes place in a single step or in several steps.

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<sup>n</sup>.  $q_p$  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 data,



Rewriting eqn. (I)  $\Rightarrow$

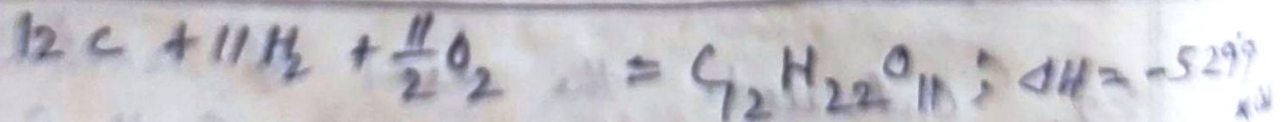
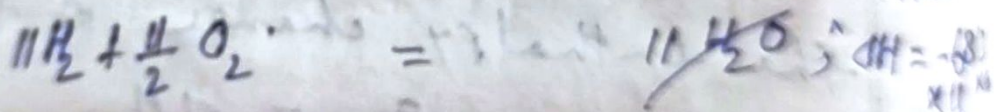
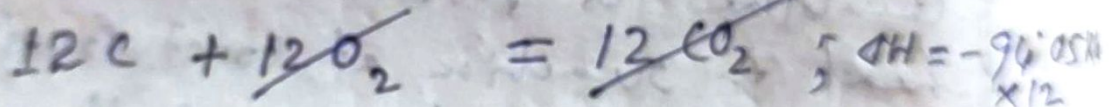


Now, (Eqn. II)  $\times 12$

(Eqn. III)  $\times 11 \rightarrow$

adding eqn. IV

$\Delta H_{II} = -1128.6 \text{ kJ}$
$\Delta H_{III} = -751.3 \text{ kJ}$
$\Delta H_{IV} = +1350.00$
<hr/>
$\Delta H = -529.9 \text{ kJ}$



The example clearly illustrated the utility of the law of heat summation.