Heat of Formation

The formation enthalpy of reaction (ΔH_f°) is the enthalpy of reaction carried out at formation condition of $(25^\circ C)$ and 1atm pressure.

Unit: Cal/mole

For any reaction represented by the chemical equation

$$aA + bB = cC + dD$$

The enthalpy change can be written as

$$\Delta H = \sum \overline{H}_{\text{Pr}oducts} - \sum \overline{H}_{reactan\,ts}$$
(27)
$$\Delta H = c\overline{H}_{c} + d\overline{H}_{D} + a\overline{H}_{A} + b\overline{H}_{B}$$
(28)

Where \overline{H} = enthalpy per mole (called the molar enthalpy), and a,b,c and d are stoichiometric coefficients.

One can, for instance, choose the reaction of formation of carbon dioxide from its elements,

$$C_{(s)} + O_{2(g)} = CO_{2(g)}; \quad \Delta H_{f(25^{\circ}C)}^{\circ} = -94,052 \ cal$$

$$Here$$

$$\Delta H_{f(25^{\circ}C)}^{\circ} = \overline{H}(CO_{2}, g, 1 \ atm) - \overline{H}(C, s, 1 \ atm) - \overline{H}(O_{2}, g, 1 \ atm)$$
(29)

The subscripts represent the physical states,(s) standing for solid and (g) for gas.

 $\Delta H_{f(25\,^{\circ}C)}^{\circ}$ = the standard heat of formation of gaseous carbon dioxide

Hess's law and Heat of Combustion

It is not possible to directly measure the heats of formation of every known compound in equation (29). Incomplete or side reactions often complicate such determinations. Hess showed that because ΔH depends only on the initial and final states of system. Principle is known as Hess's law of constant heat

summation and is used to obtain heats of reaction that are not easily measured directly.

Ex.1/ Find ΔH for the reaction : $S_{(s)} + 3/2 O_{2(g)} \rightarrow SO_{3(g)}$, $\Delta H= ?$ from the following eqns.

$$\begin{split} 1. \ S_{(s)} + O_{2(g)} &\to SO_{2(g)} \\ 2 \ . \ 2 \ SO_{2(g)} + O_{2(g)} &\to 2SO_{3(g)} \\ \end{array} , \qquad \Delta H = -198.4 \ \text{kJ} \end{split}$$

Soln.

- eq.1 stay as it is because S(s) present in left for unknown eq.

- eq.2 multiply by 1/2 to get the same no. of mole in unknown eq.

$1. \ S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$,	ΔH= -296.8 kJ
2 . $SO_{2(g)} + 1/2$ $O_{2(g)} \rightarrow SO_{3(g)}$,	$\Delta H = -1/2 \text{ x} 198.4 \text{ kJ} = -99.2 \text{ kJ}$
Sum		
$S_{(s)} + 3/2 O_{2(g)} SO_{3(g)}$,	$\Delta H = -396 \text{ KJ}$

Ex.2/ Calculate ΔH for the reaction :C_(s) + 2 H_{2(g)} = CH_{4(g)}, $\Delta H(25)$ =? from eqs.

1. $CH_{4(g)} + 2 O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)}$,	$\Delta H(25) = -212.8 \text{ kJ}$
2. $C_{(s)} + O_{2(g)} = CO_{2(g)}$,	$\Delta H(25) = -94.052 \text{ kJ}$
3. $H_{2(g)} + 1/2 O_{2(g)} = H_2O_{(g)}$,	$\Delta H(25) = -68.317 \text{ kJ}$

Sol/

- eq.1 reverse, eq.2 multiple by 2, and eq.3 stay as it is.

1. $CO_{2(g)} + 2H_2O_{(l)} = CH_{4(g)} + 2O_{2(g)}$,	$\Delta H(25) = 212.8 \text{ kJ}$
2. $C_{(s)} + O_{2(g)} = CO_{2(g)}$,	$\Delta H(25) = -94.052 \text{ kJ}$
3. $H_{2(g)} + O_{2(g)} = 2 SO_{3(g)}$,	$\Delta H(25) = 2(-68.317) \text{ kJ2}$
Sum		

 $C_{(s)} + 2 H_{2(g)} = CH_{4(g)}$, $\Delta H(25) = -17.886 \text{ kJ}$

Heat of Reaction from Bond Energies.

In a chemical reaction, bonds may be broken and new bond may be formed during the reaction process.

Ex.3 : Calculate ΔH for the following reaction:

 $H_2C=\!\!CH_2 + Cl-\!\!Cl \rightarrow Cl-\!CH_2 -\!\!CH_2 -\!\!Cl$

from C=C bond is broken(requiring 130 kcal).

Cl-Cl = = = (= 57 kcal)

And C-C bond is formed (liberating 80 kcal)

2(C-Cl) = = = (= 2 x 78 or 156 kcal)

 $\Delta \mathbf{H} = \Sigma \Delta \mathbf{H}_{bond broken} - \Sigma \Delta \mathbf{H}_{bond form}$

=[130 + 57] - [80 + 156] =-49 kcal.

EX.4/A steam engine operates between the temperature 373 and 298 K.

a. what is the theoretical efficiency of the engine ?

b. If the engine is supplied with 1000 cal of Heat Q_{hot} ?

c. What is the theoretical work in ergs

Sol/

a. Efficiency = $W/Q_{hot} = T_{hot} - T_{cold}/T_{hot} = 373 - 298/373 = 0.20$ or 20%.

b. W=1000 \times 0.2 =200 cal.

c. $2000 \times 4.184 \times 10^7$ ergs/cal= 8.36×10^9 ergs

The Second law of thermodynamics:

In second law of thermodynamic the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

The Efficiency of a Heat Engine

An important consideration is that of the possibility of converting heat into work. The spontaneous character of natural processes and the limitations on the conversion of heat into work constitute <u>the second law of thermodynamics</u>. Falling water can be made to do work owing to the difference in the potential energy at two different levels, and electric work can be done because of the difference in electric potential. A heat engine (such as a steam engine) likewise can do useful work by using two heat reservoirs, a " **source**" and "**sink**" at two different temperatures. Only part of the heat at the source is converted into work, with the remainder being returned to the sink (which, in practical operations, is often the surroundings) at the lower temperature. The fraction of the heat, Q, at the source converted into work ,W, is known as the efficiency of the engine:

$$Efficiency = \frac{W}{Q}$$
(30)

Imagine a hypothetical steam engine operating reversibly between an upper temperature T_{hot} and a lower temperature T_{cold} . It absorbs heat Q_{hot} from the hot boiler or source, and by means of the working substance, steam, it converts quantity W into work and returns heat Q_{cold} to cold reservoir or sink.

Carnot, proved that the efficiency of such an engine, operating reversibly at every stage and returning to its initial stage (cyclic process), could be given by the expression:

$$\frac{W}{Q_{hot}} = \frac{Q_{hot} - Q_{cold}}{Q_{hot}}$$
(31)

Lord Kelvin used the ratios of the two heat quantities Q_{hot} and Q_{cold} of the Carnot cycle to establish the kelvin temperature scale:

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}}$$
(32)

By combining equations (30) through (32), we can describe the efficiency by:

$$efficiency = \frac{Q_{hot} - Q_{cold}}{Q_{hot}} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$
(33)

When T_{cold} reaches absolute zero on kelvin scale in reversible process ,that

$$\lim_{T_{coult} \to 0} \frac{W}{Q} = 1 \tag{34}$$