Imp

State function

The thermodynamic variables which depends on initial and final state of the system but not on the path followed by the system to reach the final state is called state function.

For eg: Internal energy, potential energy, enthalpy, entropy etc.

Extensive properties

Thermodynamic properties which depends on amount of substance taken (i.e., mass of substance) are called extensive properties. For eg: internal energy, enthalpy, volume, etc.

Intensive properties

Thermodynamic properties which are independent upon amount of substance taken are called intensive properties. For eg: temp^{r}, density, refractive index, etc.

Internal energy

The sum of all kinds of energy possessed by a system is called internal energy.

$$\Delta E = \underset{\text{Final energy}}{E_2} - \underset{\text{Initial energy}}{E_1}$$

First law of thermodynamics

It states that "Energy can neither be created nor it can be destroyed but it can only be converted from one form to another form.

Suppose a system having initial internal energy E_1. If q amount of heat is supplied to the system, then final internal energy will be E_2. If W is the workdone by the system.

$$E_2 = E_1 + q - W$$

$$\Delta E = q - W$$

Enthalpy (H)

The total heat contained of a system is enthalpy. In other words, the total energy stored in a system in the form of heat is called enthalpy. It is given by

$$H = E + PV$$

Suppose a system having initial internal energy E_1 and volume V_1. If the system changes to final internal energy E_2 and volume V_2 at constant pressure then

$$H_1 = E_1 + PV_1 \text{ —— (i)}$$

$$H_2 = E_2 + PV_2 \text{ —— (ii)}$$

$$H_2 - H_1 = E_2 - E_1 + P(V_2 - V_1)$$

$$\Delta H = \Delta E + P\Delta V$$

Sign convention

* heat absorbed = +ve

* heat lost = -ve

* Workdone by the system = -ve

* Workdone on the system = +ve

Enthalpy change for reaction (Heat of Reaction)

The heat release or absorbed when all the reactants are converted to product is called enthalpy of reaction / heat of reaction.

From 1st law of thermodynamics

$$q = \Delta E + P\Delta V$$

From relation between enthalpy change and internal energy change

$$\Delta H = \Delta E + P\Delta V$$

$$\therefore q = \Delta H$$

Standard heat of reaction

The enthalpy change measured at standard condition (25°C and 1 atm pressure) is called standard enthalpy / heat of reaction

Enthalpy change in chemical change

Enthalpy of combustion (ΔH_p)

The amount of heat released when one mole of substance is completely combusted in the excess of air is called enthalpy of combustion

$$CH_4 + H_2 \longrightarrow CO_2 + H_2O, \ \Delta H = -212.8 \text{ Kcal}$$

completely $\{$ $C + O_2 \longrightarrow CO_2, \ \Delta H = -94 \text{ kcal}$

partial $\{$ $C + 1/4\, O_2 \longrightarrow CO, \ \Delta H = 20.4 \text{ kcal}$

Enthalpy of formation

Enthalpy of formation of a compound is defined as enthalpy change when 1 mole of the compound is formed from its elements.

$$H_2(g) + 1/2\, O_2(g) \longrightarrow H_2O(l),\ \Delta H = -68.3 \text{ kcal.}$$

Note: Enthalpy of formation of element is always taken as zero

$$H_2 + I_2 \longrightarrow 2HI,\ \Delta H = +12.4 \text{ kcal}$$

Enthalpy of formation of HI = $\frac{+12.4}{2} = +6.2$ kcal

↳ $(\Delta H_f)_{reaction} = \sum \Delta H_{product} - \sum \Delta H_{reactant}$

- positive ΔH_f means compound have more energy and hence less stable than elements.
- negative ΔH_f means compound have less energy and hence more stable than elements.

Enthalpy of neutralization

Enthalpy of neutralization is defined as enthalpy change when one gram equivalent of an acid (or a base) is neutralized by 1 gram equivalent of a base (or a acid).

$$HCl\,(aq.) + NaOH\,(aq.) \longrightarrow NaCl\,(aq.) + H_2O,\ \Delta H = -13.7\text{kc}$$

$$H^+Cl^- + Na^+OH^- \longrightarrow Na^+Cl^- + H_2O,\ \Delta H = -13.7 \text{ kcal}$$

$$H^+ + OH^- \longrightarrow H_2O,\ \Delta H = -13.7 \text{ kcal}$$

Therefore, enthalpy of neutralization can also be defined as heat released when 1 mole of water is formed by combination of H^+ and OH^- ion.

Enthalpy change in physical change

1. Enthalpy of fusion

The amount of heat absorb when 1 mole of solid substance is converted to its liquid form. (at melting point)

$$H_2O(s) \longrightarrow H_2O(l), \Delta H = 6\ KJ$$

2. Enthalpy of vapourization

The amount of heat absorbed when one mole of liquid substance is converted to its vapour form at boiling point is called enthalpy of vapourization.

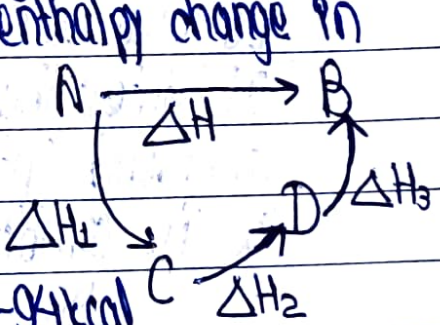
$$H_2O(l) \longrightarrow H_2O(g), \Delta H = 40.6\ KJ$$

Laws of thermochemistry

Imp # Hess's law of constant heat summation

It states that "Enthalpy change (heat change) for a reaction is same no matter whether the reaction occurs in single step/state or in a series of state."

Suppose ΔH is the enthalpy change for the reaction $A \longrightarrow B$ and $\Delta H_1, \Delta H_2, \Delta H_3$ be the enthalpy change in each steps.



Then according to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Path I: $C_{(s)} + O_2(g) \longrightarrow CO_2(g), \Delta H = -94\,kcal$

Path II: $C_{(s)} + 1/2\ O_2(g) \longrightarrow CO_{(g)}, \Delta H = -26\ kcal$

$CO_{(g)} + 1/2\ O_2(g) \longrightarrow CO_2(g), \Delta H = -68\ kcal$

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}, \Delta H = -26 - 68 = -94\,kcal$

Hess's law can be illustrated by taking example of oxidation of carbon to carbon dioxide. Carbon either directly oxidised to carbondioxide as in path I or it first converted to carbon monoxide in limited supply of oxygen and then carbon monoxide oxidised to carbondioxide as in path II.

From the above example, it is clear that enthalpy change is constant whether the reaction occurs in single step (path I) or in multiple steps (path II).

Application of Hess law.

1. Hess law can be applied to calculate enthalpy change of slow reaction.
2. It can also be applied to calculate enthalpy of formation of many compounds which can not be determined experimentally.
3. It is also applied to calculate enthalpy of combustion, entha of neutralization and enthalpy of transition.

Laplace Law

It states that," enthalpy change for the dessociation of a compound into its element is equal and opposite in sign for the combination of elements into same compound.

$$HCl \longrightarrow 1/2\ H_2 + 1/2\ Cl \quad , \Delta H = 96\ kcal$$

$$1/2\ H_2 + 1/2\ Cl_2 \longrightarrow HCl \quad , \Delta H = -96\ kcal.$$

Calculate the heat of formation of ethyl alcohol from following data.

Heat of combustion of ethyl alcohol	-330 kcal
Heat of formation of CO_2	-94 kcal
Heat of formation of H_2O	-68.5 kcal

Given, $CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$, $\Delta H_1 = -300 kcal$ —— (1)

$C + O_2 \longrightarrow CO_2$, $\Delta H_2 = -94 kcal$ —— (2)

$H_2 + 1/2\, O_2 \longrightarrow H_2O$, $\Delta H_3 = -68.5 kcal$ —— (3)

$2C + 3H_2 + 1/2\, O_2 \longrightarrow CH_3COOH$, $\Delta H = ?$

Multiplying eqⁿ(2) by 2, eqⁿ(3) by 3 and reversing eqⁿ(1)
All these equations gives

$$2C + 2O_2 \longrightarrow 2CO_2, \Delta H_2 = -188 kcal$$
$$3H_2 + 3/2\, O_2 \longrightarrow 3H_2O, \Delta H_3 = -205.5 kcal$$
$$2CO_2 + 3H_2O \longrightarrow CH_3CH_2OH + 3O_2, \Delta H_1 = +300 kcal$$

$$2C + 3H_2 + 1/2\, O_2 \longrightarrow CH_3CH_2OH, \Delta H = 330 - (188 + 205.5)$$
$$= -63.5 kcal$$

Calculate the enthalpy of formation of benzene, if enthalpy of combustion of benzene and carbon are -3280 KJ/mole and -395 KJ/mole respectively. The enthalpy of formation of water is -285 KJ/mole.

Solⁿ: $C_6H_6 + 1/2\, O_2 \longrightarrow 6CO_2 + 3H_2O$, $\Delta H = -3280 KJ/mole$ —— (1)

$C + O_2 \longrightarrow CO_2$, $\Delta H_2 = -395 KJ/mole$ —— (2)

$H_2 + 1/2\, O_2 \longrightarrow H_2O$, $\Delta H_3 = -285 KJ/mole$ —— (3)

$6C + 3H_2 \longrightarrow C_6H_6$, $\Delta H = ?$

Multiplying eqⁿ(2) by 6, eqⁿ(3) by 2 and reversing eqⁿ(1), All these equations gives.

combustion
formation x

$H_2, O_2 = 0$

$6C + 6O_2 \longrightarrow 6CO_2, \Delta H_2 = -2370$
$3H_2 + 3/2\, O_2 \longrightarrow 3H_2O, \Delta H_3 = -855$
$6CO_2 + 3H_2O \longrightarrow C_6H_6 + 15/2\, O_2, \Delta H_1 = +3280$
$6C + 3H_2 \longrightarrow C_6H_6, \Delta H = +55$

Standard enthalpy of formation of H_2O, CO_2 and C_6H_6 are -286, -393.5 and +49.02 KJ/mole respectively 298 K. Calculate the standard enthalpy of combustion of C_6H_6 at given temperature.

Soln: Given,

$H_2 + 1/2\, O_2 \longrightarrow H_2O, \Delta H_1 = -286\ KJ\, mole^{-1}$
$C + O_2 \longrightarrow CO_2, \Delta H_2 = -393.5\ KJ\, mole^{-1}$
$6C + 3H_2 \longrightarrow C_6H_6, \Delta H_3 = +49.02\ KJmol^{-1}$
$C_6H_6 + 15/2\, O_2 \longrightarrow 6CO_2 + 3H_2O, \Delta H = ?$

$\Delta H_{reaction} = \sum \Delta H_{product} - \sum \Delta H_{reactant}$
$= (6\Delta H_{CO_2} + 3\Delta H_{H_2O}) - (\Delta H_{C_6H_6} + 15/2\, \Delta H_{O_2})$
$= \{6(-393.5) + 3(-286)\} - \{+49.02 + 0\}$
$= -2361 - 858 - 49.02$
$= -3268.02$

Bond energy / Bond Enthalpy

Breaking of bond = Endothermic process
Formation of bond = Exothermic process

The amount of energy required to break 1 mole of bonds in a gaseous covalent molecule is called bond dissociation energy / bond enthalpy / bond energy.

$\Delta H_{reaction}$ = Σ Bond energy of reactant − Σ Bond energy of products.

Bond dissociation energy of H-H, O=O and O-H are 104, 118 and 111 K cal mol^{-1}. Calculate the heat of reaction.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

In H_2O, there are two OH bonds.

$\Delta H_{reaction}$ = Σ Bond energy of reactant − Σ Bond energy of products
= ΔH (bond energy of H-H) + ΔH (1/2 bond energy of O=O) − ΔH (2 bond energy of O-H)
= $(104 + 1/2 \cdot 118) - 2 \cdot 111$
= $163 - 222$
= -59 K cal mol^{-1}

Estimate the enthalpy change for the reaction

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl$$

Given, bond energy of H-H = 435 KJ mol^{-1}
bond energy of Cl-Cl = 243 KJ mol^{-1}
bond energy of H-Cl = 430 KJ mol^{-1}

$\Delta H_{reaction}$ = Σ Bond energy of reactant − Σ Bond energy of products
= ΔH (bond energy of H-H) + ΔH (bond energy of Cl-Cl) − ΔH (2 bond energy of H-Cl)
= $(435+243) - 2\times430 = -182$ KJ mol^{-1}

Spontaneous process

The process which occurs naturally by its own without external assistent is called spontaneous process. Eg: flow of heat from hoter to cooler, rusting of iron, freezing of ice below 0°C, etc.

Why enthalpy alone cannot determine whether the process is spontaneous or non-spontaneous?

Ans, For $\Delta H = -ve$, the process is always spontaneous. For eg: flow of water from hoter body to cooler body. ~~but~~

But when $\Delta H = +ve$, the process may or may not be spontaneous. For eg: evaporation of water is spontaneous process while synthesis of ammonia is non-spontaneous process.

Similarly when $\Delta H = 0$, the process may or may not be spontaneous process. For eg: dessolution of NaCl in water is neither endothermic nor endothermic but this is spontaneous process.

Therefore, enthalpy alone cannot determine whether the process is spontaneous or non-spontaneous.

Entropy

It is defined as thermodynamic function which measures disorderness or randomness of the system.

OR

Entropy is ~~nature of~~ measure of unavailable energy.

Mathematically, $S = \frac{q_{rev}}{T}$

Entropy of liquid is greater than that of solid whereas entropy of gas is greater that that of liquid.

$$S_{gas} > S_{liq} > S_{solid}$$

Entropy of phase transition

1. Entropy of fusion (ΔS_f)

Entropy of fusion $= \frac{\Delta H_f}{T_m}$, where ΔH_f = Latent heat of fusion

T_m = melting point

2. Entropy of vaporization (ΔS_v) $= \frac{\Delta H_v}{T_b}$

ΔH_v = latent heat of vaporization

T_b = boiling point

Entropy change in chemical reaction

$\Delta S_{reaction} = \sum \Delta S_{product} - \sum \Delta S_{reactant}$

Second law of thermodynamics

In terms of entropy, second law of thermodynamics states that total entropy (system + surrounding) is always increasing

i.e., $\Delta S_{system} + \Delta S_{surrounding} > 0$

From 2nd law, we can say that total entropy (system + surrounding) is always increasing for spontaneous process.

Entropy of the universe is always increasing. This statement explain about the spontanity with the help of expression

ⓐ $\Delta S_{system} > \Delta S_{surrounding}$

ⓑ $\Delta S_{system} > 0$

ⓒ $\Delta S_{system} + \Delta S_{surrounding} = \Delta G$

ⓓ $\Delta S_{system} + \Delta S_{surrounding} > 0$

Gibb's free energy / free energy function

The available energy store in a system is called free energy or Gibb's free energy. It is denoted by G and given by $G = H - TS$ where H = Enthalpy

T = Temp

S = entropy

If a system having initial enthalpy H_1 and entropy S_1 changes to final enthalpy H_2 and entropy S_2 at constant temperature

Then, $G_1 = H_1 - TS_1$ —— (1)

$G_2 = H_2 - TS_2$ —— (2)

$\therefore G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$

$\Delta G = \Delta H - T\Delta S$

this is called Gibb's Helmholtz eqn.

Standard free energy (ΔG°)

Change in free energy when 1 mole of substance is formed from its constituent elements at standard condition (25°C and 1 atm pressure) is called standard free energy of formation.

Standard free energy change for reaction:

$$\Delta G^\circ_{reaction} = \sum \Delta G^\circ_{product} - \sum \Delta G^\circ_{reactant}$$

Imp **Derivation of criteria of spontaneity in terms of free energy change**

We have, $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$ —— (1)

Again, total entropy is

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

If ΔH_{sys} is heat ~~gained by~~ loss by the system then $-\Delta H_{sys}$ will heat gain by surrounding

$$\therefore \Delta S_{total} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T}$$

$$\Rightarrow T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

$$\Rightarrow T\Delta S_{total} = -(\Delta H_{sys} - T\Delta S_{sys})$$

$$T\Delta S_{total} = -\Delta G_{sys} \text{ —— (2)}$$

On removing subscript

$$T\Delta S = -\Delta G$$

1) When $\Delta G = +ve$, ΔS will be −ve. Therefore, the process will be non-spontaneous.

2) When $\Delta G = -ve$, ΔS will be +ve, therefore the process will be spontaneous.

3) When $\Delta G = 0$, ΔS will be zero, therefore the system will be in equilibrium with surroundings.

Starting from $T\Delta S_{total} = -\Delta G_{sys}$ how would you predict whether the process is spontaneous or not.