Thermo-chemistry

Thermo-chemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

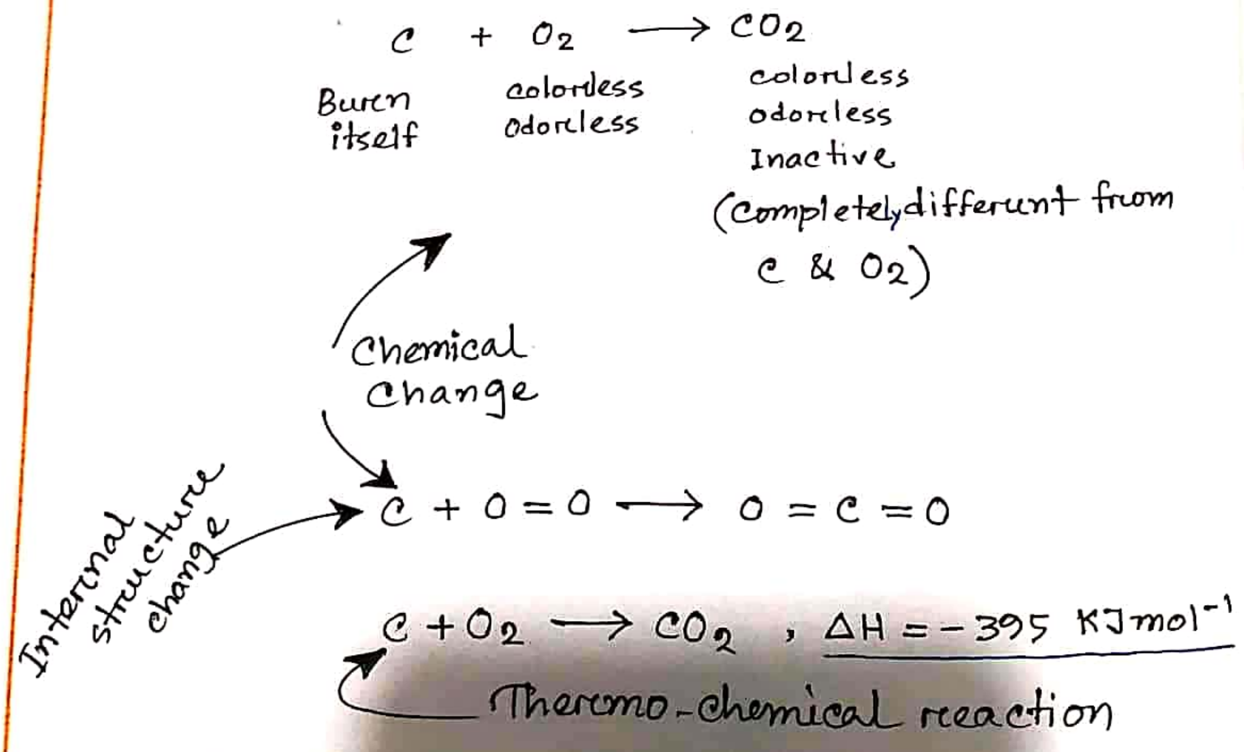
Two types of change.

1) Physical change
2) Chemical change

Physical change & Chemical change :

A chemical change results from a chemical reaction, while a physical change is when matter changes forms but not chemical identity.

Chemical changes occur when a substance combines with another to form a new substance.



The chemical change which includes the enthalpy change, ΔH is called thermo-chemical change.

Thermo-chemical reaction : A thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change, ΔH.

Every chemical bond carries a definite amount of enthalpy which is different from the enthalpy of other chemical bonds.

Bond length or bond distance is defined as the average distance between nuclei of two bonded atoms in a molecule.

Bond enthalpy or bond energy is defined as the amount of energy required to break one mole of the stated bond.

$$C + O \underset{\sigma}{\overset{\pi}{=}} O \longrightarrow O \underset{\sigma}{\overset{\pi}{=}} C \underset{\sigma}{\overset{\pi}{=}} O$$

Difference of bond energy = Heat energy (ΔH)

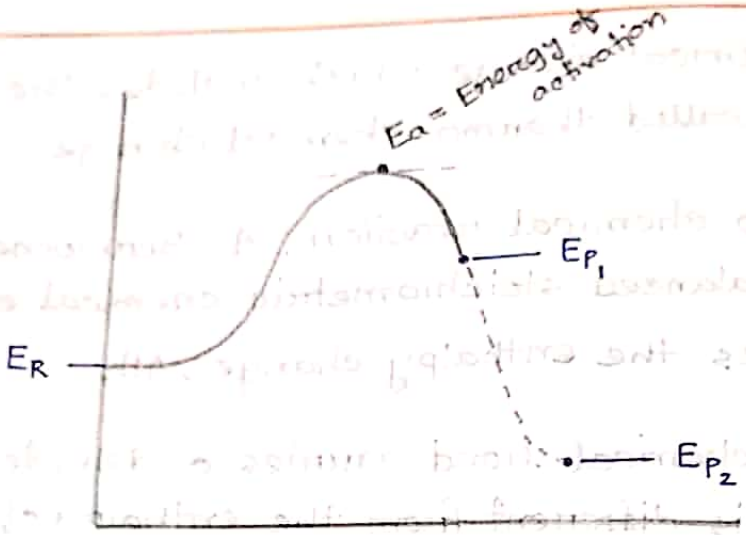
Bond energy of reactant = Bond energy of product

Enthalpy of reactant = Enthalpy of product

$$H_R = H_P$$

If i) $H_R >> H_P$, then it is exothermic (তাপউৎপাদী) react

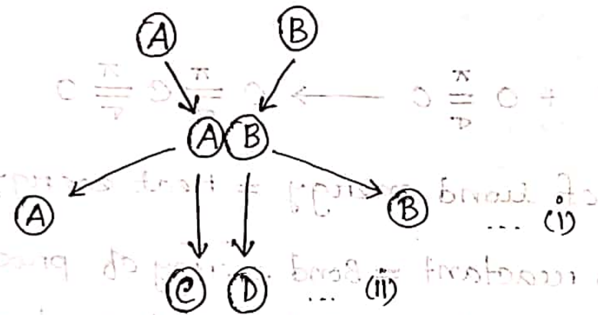
ii) $H_P >> H_R$, then it is endothermic reaction (তাপগ্রাহী)



1. $E_R << E_{P_1}$
Endotheremic
Heat alusorebed

2. $E_R >> E_{P_2}$
Exotheremic
Heat released

$A + B \rightleftharpoons C + D$

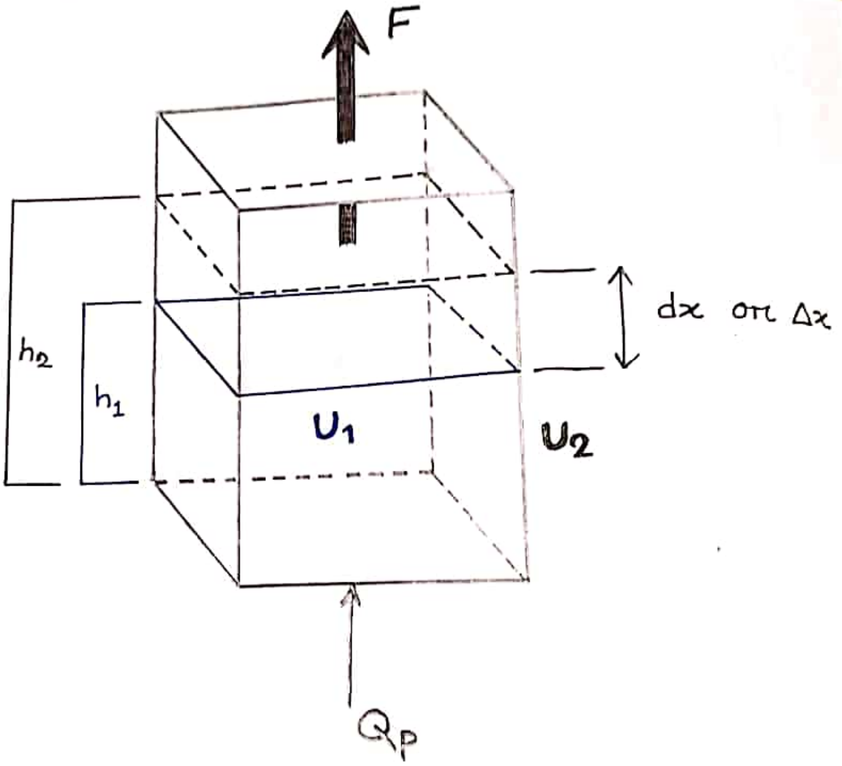


Conditions: * Collision energy must be greater than E_a

* The collision must occur in proper orientation

* The collision frequency must be greater than the frequenc factor for the reaction

Mother equation of Thermochemistry :



প্রথমে পিস্টনের মাধ্যমে চাপ প্রয়োগ করে গ্যাসকে h_1 height এ নিয়ে আসতে হবে। এরপর আর কোনো চাপ এই গ্যাসপাত্রে প্রয়োগ করা যাবে না। এইজন্য এটাকে সমচাপীয় প্রক্রিয়া বলা যায়।

তারপর Q_p পরিমান heat গ্যাসপাত্রে প্রয়োগ করা হবে।
আমরা জানি, heat দিলে volume বাড়বে।
exception : Ice, tetragonal structure এর steel
তাপ দেয়ার পর গ্যাসের আয়তন বাড়বে। তাই পিস্টনটি h_1 হতে h_2 height এ উঠবে। তাই পিস্টনের উপরের দিকে একটা বল কাজ করবে।

Let, the force is F.

If the cross section area is A, then

$$\text{Pressure}, \; P = \frac{F}{A}$$

$$\therefore \boxed{F = PA} \quad \text{——— (1)}$$

এইখানে P কে thrust / ধাক্কা বলা হয়।

Total area তে যে পরিমান বল কাজ করে

Thrust is a force or push. When a system pushes or accelerates mass in one direction, there is a thrust just as large in the opposite direction.

Thrust is used to describe how strongly an engine pushes.

Displacement, $\boxed{\Delta x = h_2 - h_1}$ ——— (2)

Work done by the system, $\boxed{\Delta w = F(\Delta x)}$ ——— (3)

Initial volume, $V_1 = A \times h_1$

Final volume, $V_2 = A \times h_2$

From (3),

$$\begin{aligned} \Delta w &= F(\Delta x) \\ &= PA(h_2 - h_1) \\ &= P(Ah_2 - Ah_1) \\ &= P.(V_2 - V_1) \\ &= P.\Delta V \end{aligned}$$

$$\therefore \boxed{\Delta W = P\Delta V}$$

কোনো system এ constant pressure এ heat দিলে volume বৃদ্ধির কারণে কাজ সম্পাদিত হয়।

Q_P পরিমান heat এর একাংশ আয়তন বৃদ্ধিজনিত কাজে ব্যবহৃত হয়।

Internal Energy change, $\Delta U = U_2 - U_1$

According to the law of conservation of energy,

$$\boxed{Q_P = \Delta U + \Delta W}$$

Q_P heat এর একাংশ আয়তন বৃদ্ধিজনিত কাজে use হয়। বাকিটা internal energy এর change এ ব্যবহৃত হয়।

$$Q_P = \Delta U + \Delta W$$

$$\boxed{Q_P = \Delta U + P\Delta V}$$

- Isobaric process : সমচাপীয়। $P = \text{constant}$

  $$Q_P = \Delta U + P\Delta V$$

- Isothermal process : সমোষ্ণ প্রক্রিয়া।

  Temp change হবে না।

  $$\Delta U = 0$$

  $$Q_T = P\Delta V$$

- Adiabetic process : রুদ্ধতাপীয় প্রক্রিয়া।

  তাপের আদান-প্রদান হবে না।

  $$Q_P = 0$$

  $$\Delta U = -P\Delta V$$

- Isocoric process : সমআয়তন প্রক্রিয়া

$$\Delta V = 0$$

$$\therefore \Delta W = 0$$

$$Q_V = \Delta U$$

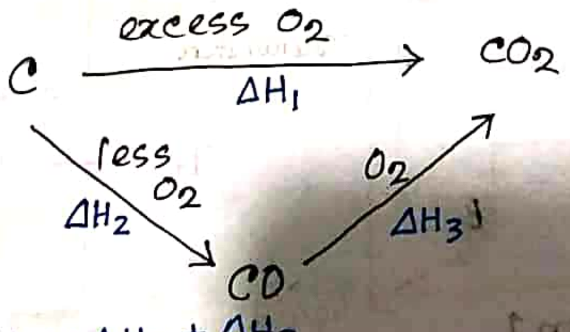
এইক্ষেত্রে সব heat internal energy এর ক্ষেত্রে ব্যয় হবে।

Hess's Law :

If a chemical change can be made to take place in two or more different ways. whether in one step or two or more steps, the amount of total heat change (ΔH) is ~~a~~ same no matter what method the change is brought about.

$$\begin{tikzcd}
A \arrow[rrr, "Q_1"] \arrow[dr, "q_1"'] & & & Z \\
& B \arrow[r, "q_2"'] & C \arrow[ur, "q_3"'] &
\end{tikzcd}$$

$$\therefore \quad Q_1 = q_1 + q_2 + q_3$$



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

Lavoisier and Laplace's law :

The heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction.

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \; ; \; \Delta H = -285.85 \text{ KJ/mol}$$

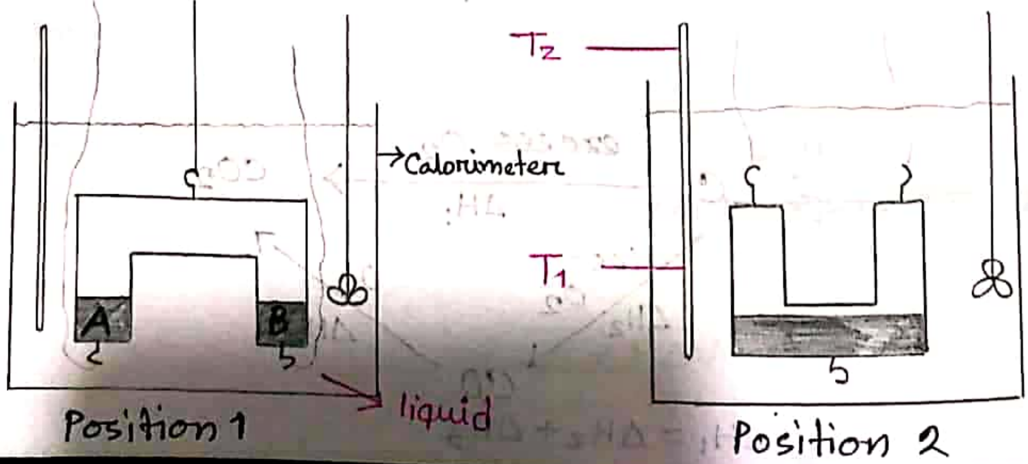
$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2 \; ; \; \Delta H = +285.85 \text{ KJ/mol}$$

If the reaction is an exothermic reaction, then its reverse reaction will be an endothermic reaction.

Experimental Procedure :

Enthalpy of reaction :

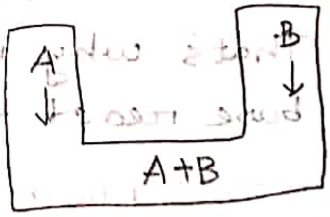
The experimental measurement of the heat of reaction or enthalpy change is known as calorimetry. The heat given out or absorbed in a chemical reaction is measured in a suitable apparatus called a calorimeter.



The apparatus consists essentially of a liquid - bath with thermally insulated walls. A reaction chamber consisting of two limbs is suspended in the liquid bath. Through the lid of the wal bath pass thermometer that records the temperature variations and stirrer that stirs the liquid so that the liquid share the absorbed or released heat equally.

A known quantity of liquid is taken in the liquid bath or calorimeter ~~at~~ and its temperature is noted. The reacting substances are filled in the two limbs as shown in the position no. 1. The reacting chamber is now turned upside down (Position 2) to allow the substances to mix. Then the temp. is noted again.

mass of calorimeter $= m_1$
Specific heat of calorimeter $= S_1$
Initial temperature $= T_1$
mass of liquid $= m_2$
Specific heat of liquid $= S_2$
Final temperature $= T_2$



$A+B \longrightarrow C+D$

We know, $Q = ms\Delta\theta$

$$Q_1 = m_1 s_1 (T_2 - T_1) \quad [\text{Calorimeter}]$$

$$Q_2 = m_2 s_2 (T_2 - T_1) \quad [\text{liquid}]$$

$$\therefore \Delta H = Q_1 + Q_2 = (m_1 s_1 + m_2 s_2)(T_2 - T_1)$$

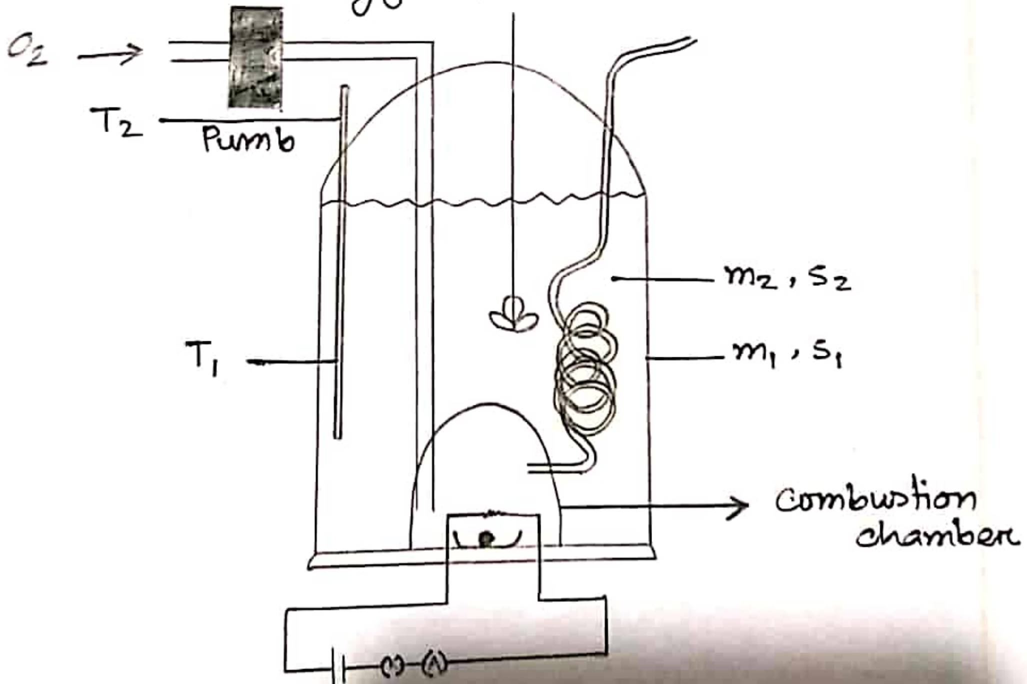
ΔH = Enthalpy of reaction

The enthalpy for this reaction is always same. But as the acid and base are weak, then some of the heat is used to help the acid and base to dissociation completely. So, total enthalpy of the reaction between weak acid and weak base is less than −57.34 KJ/mol

Thus the heat or enthalpy of neutralization of an acid and a base is merely the heat of formation of water from hydrogen and hydroxil ions.

Enthalpy of combustion:

Enthalpy change of combustion is the energy released when 1 mole of a compound is burned in excess of oxygen.



$$C_xH_4 + O_2 \longrightarrow CO_2 + H_2O$$

$$Q = ms\Delta\theta$$

$$Q_1 = m_1 s_1 (T_2 - T_1)$$

$$Q_2 = m_2 s_2 (T_2 - T_1)$$

Enthalpy of neutralisation : প্রশমন এনথ্যালপি

If the chemical substances A & B are acid and base respectively, then the enthalpy is called enthalpy of neutralisation.

In the case of strong acid, the dissociation of acid in solution is 100% complete.

$$NaOH \longrightarrow Na^+ + OH^-$$

$$HCl \longrightarrow H^+ + Cl^-$$

The main reaction is happened between H^+ and OH^- ion. They produce water.

$$H^+ + OH^- \longrightarrow H_2O$$

The enthalpy of this reaction is always −57.34 KJmol^{-1}

That's why when a strong acid and a ~~basic~~ strong base react together, the enthalpy of the reaction is −57.34 KJmol^{-1}

That's why if one of them is weak, the enthalpy changes.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The main reaction,

$$H^+ + OH^- \longrightarrow H_2O \quad , \quad \Delta H = -57.34 \text{ KJmol}$$

$$\Delta H = Q_1 + Q_2$$

$$= (m_1 s_1 + m_2 s_2)(T_2 - T_1)\ J$$

$$= (m_1 s_1 + m_2 s_2)(T_2 - T_1)\frac{M}{W}\ J/mol$$

mass = W

molecular weight = M

mole, $n = \frac{W}{M}$

$= (m_1 s_1 + m_2 s_2)(T_2 - T_1)\frac{\;}{W}$ J/mol

mass = W

molecular weight = M

$$\text{mole}, n = \frac{W}{M}$$

Caloritic value

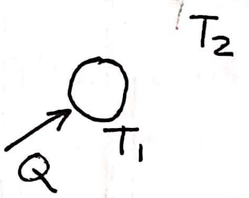
Kirechoff's equation :

$$\begin{matrix} \text{Reactant} & \longrightarrow & \text{Product} \\ H_R & & H_P \\ T_1 & & T_2 \end{matrix}$$

$\Delta H = H_P - H_R$ ...... (i)

Heat capacity

$\Delta T = T_2 - T_1$



$\Delta T \longrightarrow Q$

$\therefore 1 \longrightarrow \frac{Q}{\Delta T}$

$$C = \frac{Q}{\Delta T}$$

$$\begin{tikzcd} & \text{Heat capacity} \arrow[dl] \arrow[dr] & \\ C_P & & C_V \end{tikzcd}$$

$$Q_P = \Delta H = \Delta U + P\Delta V$$

$$C_P = \frac{Q_P}{\Delta T} \qquad C_V = \frac{Q_V}{\Delta T}$$

$$\Delta H = H_P - H_R$$

$$\frac{\partial(\Delta H)}{\partial T} = \frac{\partial H_P}{\partial T} - \frac{\partial H_R}{\partial T}$$

$$= (C_P)_P - (C_P)_R$$

$$= \Delta C_P$$

$$\therefore \frac{\partial(\Delta H)}{\partial T} = \Delta C_P$$

Again, $\Delta U = U_P - U_R$

$$\therefore \frac{\partial(\Delta U)}{\partial T} = \frac{\partial U_P}{\partial T} - \frac{\partial U_R}{\partial T} = (C_V)_P - (C_V)_R = \Delta C_V$$

$$\Rightarrow \frac{\partial(\Delta U)}{\partial T} = \Delta C_V$$

$$\Rightarrow \partial(\Delta U) = \Delta C_V \, \partial T$$

$$\Rightarrow \int_{\Delta U_1}^{\Delta U_2} \partial(\Delta U) = \Delta C_V \int_{T_1}^{T_2} \partial T$$

$$\Rightarrow \int_{\Delta H_1}^{\Delta H_2} \partial \Delta H = \Delta C_P \int_{T_1}^{T_2} \partial T$$

★ Proof $\Delta H = Q_P = \Delta U + P\Delta V$

We know,

$$Q_P = \Delta U + P\Delta V = (U_2 - U_1) + PV_2 - PV_1 = (U_2 + PV_2) - (U_1 + PV_1)$$

$$= H_2 - H_1 = \Delta H$$

$$\therefore \Delta H = Q_P = \Delta U + P\Delta V$$