

## → THERMODYNAMIC: -

The Branch of chemistry in which we be deals the interconversion of heat, work and various kind of energy known as Thermodynamics.

### # Thermodynamical Term ⇒

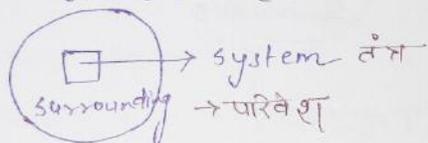
1- system ⇒ A system is defined as that part of universe which is under investigation.

2- SURROUNDING ⇒

The rest part of universe other than system is known as surrounding.

3- UNIVERSE ⇒

UNIVERSE is an collection of system and surrounding.  
Universe वैश्व



⇒ Types of system ⇒

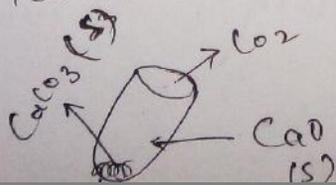
There are three's of system

- 1- OPEN system ⇒
  - 2. Closed system -
  - 3. Isolated system -
- ]= SYSTEM

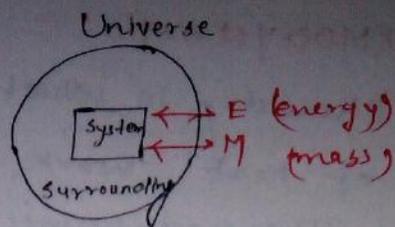
- OPEN SYSTEM ⇒ Such type of system in which we can exchange both energy and mass with surrounding known as open system.

EX - i) Making Tea in open Container

ii)



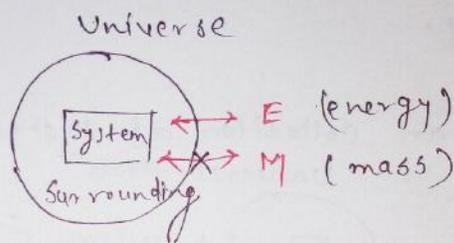
## 2) Open System



## 2) Close System (अ-व द्रव)

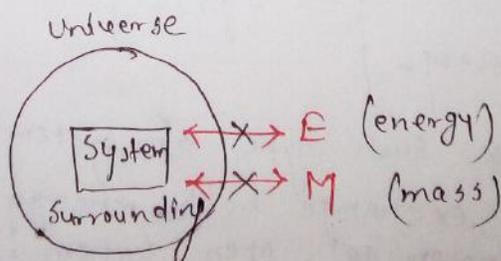
Such type of system in which only energy can exchange between system and surrounding but mass can't be exchange.

Ex- Looking rise in pressure Cooker.



## 3) ISOLATED SYSTEM

Such type of system in which neither exchange of energy nor mass take place between system and surrounding. Known as Isolated system -



Ex- Boiling water in thermoflask.

## # HOMOGENEOUS SYSTEM $\Rightarrow$

Such type of Thermodynamical system which is completely uniform through out the process known as HOMOGENEOUS SYSTEM  $\Rightarrow$ .

## \* HETEROGENEOUS SYSTEM $\Rightarrow$

Such type of Thermodynamical system which is not uniform through out the process is known as Heterogeneous system.

imp

## \* INTENSIVE AND EXTENSIVE PROPERTY $\Rightarrow$

### 1) INTENSIVE PROPERTY —

Such type of Physical Property which does not depend on the quantity of the matter present into the system is known as INTENSIVE property —

ex - Pressure, temperature, density, surface tension, viscosity, P.H., B.P., M.P., Freezing Point, Molarity, Normality, mole fraction, percentage, refractive index —

2 - EXTENSIVE Property - Such type of Physical Property which depend on the quantity of matter present into the system is known as Extensive property

ex - mass, volume, entropy, enthalpy, internal energy, no. of mole,

## \* STATE FUNCTIONS $\Rightarrow$

Such Type of Thermodynamical Property which depends only on final and initial value known as STATE function.

Ex- Temperature, pressure, Volume, entropy, internal ENERGY.

## \* PATH FUNCTIONS $\Rightarrow$

Such type of Thermodynamical property whose value depends on the path of system by which the value proceed.

Ex- work, Molar heat Capacity, specific Heat Capacity

## # THERMODYNAMICAL PROCESS $\Rightarrow$

### 1- ISOTHERMAL Process $\Rightarrow$

Such type of Thermodynamical process which proceed at constant temp - is called isotherm process -

$T$  is constant.

$$\Delta T = \text{zero}$$

NOTE in isothermal process the value of  $\Delta E = 0$

### ISO-BARIC PROCESS $\Rightarrow$

Such type of Thermodynamical process which proceed and at constant pressure is known as isobaric process.

$P$  - is constant

$\Delta P$  is zero.

### \* ISO-CORIC PROCESS $\Rightarrow$

Such type of Thermodynamical process which proceed and at constant volume known as isochoric process -

$V$  is constant

$\Delta V$  is zero

### \* ADIABATIC PROCESS $\Rightarrow$

Such type of Thermodynamical process in which no exchange of heat take place b/w system and surrounding -

$q$  is zero.

### \* CYCLIC PROCESS $\Rightarrow$

When a system undergoes different process is and finally returned to its original condition known as cyclic process.

In this process  $\Delta E$  is zero

\* RIVER SIBLE Process  $\Rightarrow$

Such type of Thermodynamical process in which all the parameter (Pressure, Volume, Temperature) come back to its original state. by applying sum ~~on~~ external condition known as Rive-sible process.

ERRIBLE SIBLE Process -

Such type of thermodynamical process in which all the parameter (Pressure, Volume, temp-) do't come back to its original state. Know as IRRIBLE SIBLE Process.

# INTERNAL ENERGY  $\Rightarrow$

The all possible types of energy present into the matter in a system is know as internal energy. it is represented By E.

$$E = E_{\text{Rotational}} + E_{\text{vibrational}} + E_{\text{translational}} + E_{\text{Kinetic}} + E_p + E_{\text{et}}$$

internal energy of system is extensive property  
" " " " system " " state function.

The SI unit of internal energy of Jule.

## \* HEAT

It is a form of energy exchange b/w system and surrounding.

Heat always flows from higher temp to lower temp.

It is represented by  $Q$  or  $q$ .

if,  $\left[ \begin{array}{l} Q \text{ is } -ve, \text{ system will be exothermic.} \\ Q \text{ is } +ve, \text{ system will be anothermic.} \end{array} \right]$

The value of depends of following two points  $\rightarrow$

$$q \propto m \rightarrow 1$$

$$q \propto \Delta T \rightarrow 2$$

$$q \propto m \cdot \Delta T$$

$$\boxed{q = cm\Delta T}$$

if.  $c$  is specific heat constant.

$$\boxed{c = \frac{q}{m \cdot \Delta T}}$$

$$m = L$$

$$\Delta T = L$$

$$\boxed{c = q}$$

Hence the amount of heat absorb or evolve when we change the temp. of unit mass object  $1^\circ$ .

Unit of specific heat  $c$  is equal.

$$\underline{\text{Jule } \text{kg}^{-1} \text{K}^{-1} .}$$

Question If a gold Ring with a mass of 5.5 gm changes its temp from  $25^{\circ}\text{C}$  to  $228^{\circ}\text{C}$  how much heat is absorb by the Ring if specific heat of gold is  $0.129 \text{ Jule gm}^{-1} \text{ K}^{-1}$ .  $\boxed{2.12}$

$$= \frac{0.129}{5.5 \times 276}$$

$$= 2.12$$

Question It has been found that 221.4 Jule heat is needed for 30 gm iron Rod to rays the temp  $15^{\circ}\text{C}$  to  $18^{\circ}\text{C}$ . Calculate the specific heat of iron.

$$Q = c m \Delta T$$

$$221.4 = c \times 30 \times 3$$

$$c = \frac{221.4}{30 \times 3}$$

$$c = \frac{221.4}{90}$$

$$\boxed{c = 2.46}$$

$\text{Jule gm}^{-1} \text{ K}^{-1}$

$$\therefore T_1 = 273 + 15 = 288$$

$$T_2 = 273 + 18 = 291$$

$$T_2 - T_1 = T$$

$$291 - 288 = 03$$

$$\boxed{T = 03}$$

next Tuesday

~~for 1 mole~~

16 Feb 2016

if we have  $n$ -mole gas

$$q = n C \Delta T$$

Here  $C$  is known as molar heat capacity.

$$C = \frac{q}{n \cdot \Delta T}$$

$$n = 1 \text{ mole}, \Delta T = 1^\circ$$

$$\boxed{C = \frac{q}{n}}$$

hence molar heat capacity is that heat for 1 mole which is used for changing the temp -  $1^\circ$ .

there are two types of molar heat capacity.

- # 1 - molar heat capacity at constant volume - ( $C_v$ )
- 2 - Molar heat capacity at constant pressure - ( $C_p$ ).

1 - Molar heat capacity at constant volume ( $C_v$ )  $\Rightarrow$

we know that  $q = n C \Delta T$

at constant volume

$$\boxed{q_v = n C_v \cdot \Delta T}$$

$$C_v = \frac{q_v}{n \cdot \Delta T}$$

Let  $n = 1$ ,

$$\boxed{C_v = \frac{q_v}{\Delta T}}$$

for 1 mole -

Molar heat capacity at constant volume is that amount of heat which is required for 1 mole substance to the temp  $1^\circ$  at constant volume. it is represented by  $C_v$ .

$C_p$  = Molar heat capacity at constant pressure  $\Rightarrow$

We know that  $q = nC\Delta T$

at constant pressure -

$$q_p = n C_p \cdot \Delta T$$

$$C_p = \frac{q_p}{n \cdot \Delta T}$$

$\therefore n = 1$

$$\boxed{C_p = \frac{q_p}{\Delta T}} \text{ for 1 mole}$$

Molar heat capacity at constant pressure is that amount of heat which is required for 1 mole substance to raise the temp  $1^\circ$  at constant pressure it is represented by  $C_p$ .

# First Law of Thermodynamic #

Statement - I<sup>st</sup>

The energy of total universe is always conserved.

Statement II<sup>nd</sup>

energy can't be created or destroyed but it can be converted from 1 form to another form

Mathematical explanation of I<sup>st</sup> Law of Thermodynamic  $\rightarrow$

Let us consider -  $E_1$  is the internal energy of the system. Let  $q$  amount of heat be supplied to the system, the new internal energy of the system is  $E_2$ .

Hence  $E_2 = E_1 + q(\text{amount}) + w$

$$E_2 - E_1 = q + w$$

$$\boxed{\Delta E = q + w}$$

If we supplied  $q$  amount of heat to the system, the one part of heat is used for changing internal energy and the remaining part of heat is used for doing work.

\* WORK \*

Exchange of energy b/w system and surrounding can occur in the form of work.

For gaseous system we will use pressure volume work (PV-work).

Work done in isothermal & reversible process -  
Such type of thermodynamical process in which all the thermodynamical parameters return to its original state.

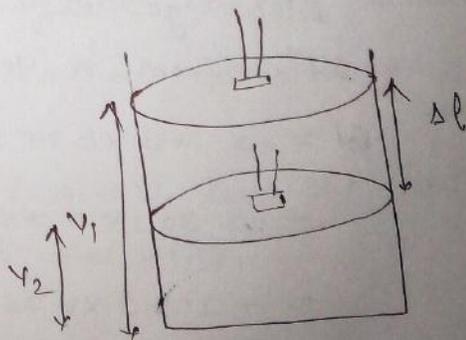
Let us consider a gas enclosed in a cylinder

$$\text{Pressure} = F/A$$

$$\text{Work} = F \times \Delta l$$

$$= P A \Delta l$$

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



If work done on the system  $W$  will be positive.  
If work by the system  $W$  will be negative.

Work done for Isothermal Reversible  $\Rightarrow$   
 Reversible process a such type of Process in which  
 all the thermodynamic parameter come to  
 it's original state.  
 this process carried out in no. of steps.

$$dw = -P \cdot dv$$

Total work

$$\int dw = - \int P dv$$

$$= - \int \frac{nRT}{v} dv$$

$$W = -nRT \int \frac{dv}{v}$$

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$W = -2.303 nRT \log_{10} \frac{V_2}{V_1}$$

Question  $\Rightarrow$  Calculate the work done when 0.75 mol of an  
 ideal gas expand isothermally Reversibly at  
 27°C from a volume of 15 L to 25 L.

Sol<sup>n</sup>

$$W = -2.303 \times 0.75 \times 8.314 \times 27 \log_{10} \frac{25}{15}$$

$$= -2.303 \times 0.75 \times 8.314 \times 27 \log 5 + \log 3$$

$$= -2.303 \times 0.75 \times 8.314 \times 27 \times 0.6990 + 0.4771$$

$$= 387.7 \times 3.9761$$

$$W = 955 \text{ Joule}$$

Question 2 mol of an ideal gas at  $27^\circ\text{C}$  at 1 atm pressure expand isothermally Reversibly till its pressure become 0.25 atm. Calculate the work done -

$$W = -2.303 \times nRT \log_{10} \frac{V_2}{V_1}$$

by Boyle's Law

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$W = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

$$W = -2.303 \times 2 \times 0.314 \times 27 \log_{10} \frac{100}{25}$$

$$W = -2.303 \times 2 \times 0.314 \times 27 \times 0.602$$

$$W = -6915 \text{ Joule}$$

Enthalpy :-

The total heat content of a system at constant pressure is equal to the sum of internal energy and PV work known as enthalpy it is represented by -H.

$$H = E + PV$$

Since internal energy of the system can not be calculated there for enthalpy of the system also can not be calculated -

let us consider  $E_1, P_1$  and  $V_1$  are the initial state of the system therefor enthalpy.

$$H_1 = E_1 + P_1 V_1 \longrightarrow \textcircled{1}$$

if the system go in state 2. the new enthalpy of the system is -

$$H_2 = E_2 + P_2 V_2 \longrightarrow \textcircled{2}$$

now can.  $\textcircled{1}$  and  $\textcircled{2}$

$$U_2 - U_1 = E_2 - E_1 + P_2 V_2 - P_1 V_1$$

Since enthalpy is calculated at constant pressure

$$\therefore P_1 = P_2 = P$$

$$\boxed{\Delta H = \Delta E + P\Delta V} \longrightarrow \textcircled{1}$$

Let us consider a system has  $n_1$  mol, at system go in state .to. The new mol will be  $n_2$ .

by ideal gas equation.

$$P V_1 = n_1 R T$$

$$P V_2 = n_2 R T$$

$$P(V_2 - V_1) = (n_2 - n_1) R T$$

$$P\Delta V = \Delta n R T$$

Putting there value in eqn  $\textcircled{1}$

$$\boxed{\Delta H = \Delta E + \Delta n R T}$$

Here  $\Delta n = n_p - n_r$   $\left. \begin{array}{l} n_p = \text{number of mol of Product} \\ n_r = \text{number of mol of Reactant} \end{array} \right\}$

$$R = 8.314 \text{ Joule/K/mole}$$

Question The enthalpy change  $\Delta H$  for the reaction



$-92.38 \text{ kJ}$  at  $298 \text{ K}$  Temp - Calculate the value of  $\Delta E$ .

$$\Delta H = \Delta E + \Delta n R T$$

$$-92.38 \times 10^3 = \Delta E - 2 \times 8.314 \times 298$$

Question  $\rightarrow 2A + 5B \rightarrow 2AB$  for this reaction if the value of  $\Delta E = -37.609 \text{ KJ}$  at  $27^\circ\text{C}$  find out  $\Delta H$ .

$$\Delta H = -37.609 - 5 \times 8.314 \times 300$$

$$= -37.609 - 7402.6$$

$$= -45171 \times 2$$

$$\Delta H = -52653 \text{ joule.}$$

NOTE [का परमाणु में हमेशा गैस के मोल ही लिखे जाते हैं।]  
Solid OR liquid के नहीं -

# Relationship b/w  $C_p$  and  $C_v$   $\Rightarrow$

We know that

$$H = E + PV$$

for 1 mole ideal gas  $PV = RT$

$$H = E + RT$$

differentiate <sup>this</sup> w.r. to  $T$ .

$$\frac{d}{dt} H = \frac{d}{dt} (E) + R \frac{d}{dt} (T)$$

$$\frac{dH}{dt} = \frac{dE}{dt} + R$$

$$C_p = C_v + R$$

$$\boxed{C_p - C_v = R}$$

### \* Atomicity of a gas $\Rightarrow$

The ratio of  $C_p$  and  $C_v$  called atomicity of the gas represented by  $\gamma$ . (gamma)

$$\gamma = C_p = C_v$$

$$\underline{\gamma = 1.6}$$

gas will be monoatomic.

$$\text{if } \underline{\gamma = 1.40}$$

gas will be diatomic.

$$\underline{\gamma = 1.33}$$

gas will be polyatomic.

### \* Heat of Combustion $\Rightarrow$

When 1 mole of the substance is completely burnt the heat evolved this known as Heat of Combustion.



$$\Delta H = -890 \text{ kJ mole}^{-1}$$

### \* Calorific value $\Rightarrow$

When 1 gm of substance is completely burnt the amount of heat produced called calorific value.

### \* Heat of Neutralization $\Rightarrow$ enthalpy of neutralization

When 1 gm equivalent of an acid is neutralized by 1 gm equivalent of a base in dil. soln. the heat evolved is known as enthalpy of neutralization.



$$\Delta H = -57.1 \text{ KJ} \quad \text{OR} \quad -13.7 \text{ Kcal}$$

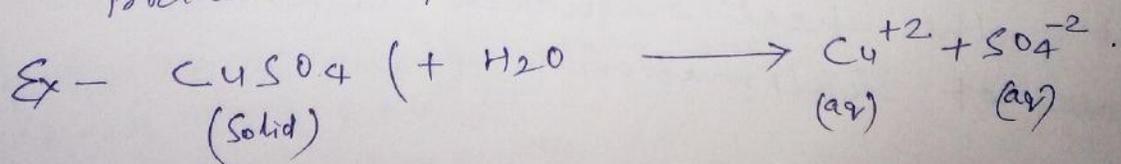
NOTE

When strong acid strong base are take part in neutralization. - the enthalpy of neutralization always 57.1 KJ OR 13.7 Kcal.

However when a strong acid and weak base, weak acid and strong base and weak acid and weak base. take part in neutralization, The heat of neutralization always smaller than 57.1 KJ OR 13.7 Kcal.

\* Heat of Solution  $\Rightarrow$

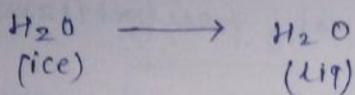
The heat of solution of a substance in a particular solvent is defined as the heat change when 1 mole of the substance. is dissolved in such a large volume of the solvent that further addition of the solvent does not produce any more heat.



$$\Delta H = -56 \text{ KJ.}$$

### \* Enthalpy of fusion or Heat of fusion $\Rightarrow$

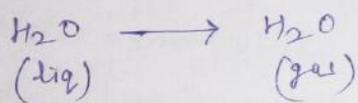
When 1 mole of a solid substance converted into its liquid state at its melting point. Known as heat of fusion.



$$\Delta H = +6 \text{ KJ.}$$

### \* Heat of vaporization $\Rightarrow$

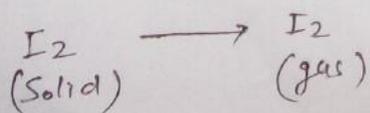
When 1 mole of a liquid directly convert into its gaseous state at its B.P. the required is known as Heat of vaporization.



$$\Delta H = 40 \text{ KJ.}$$

### # Heat of Sublimation $\Rightarrow$ (उपसर्पण)

When 1 mole of a solid substance is directly converted into a vapour state below its melting point. The heat required is known as Heat of Sublimation.



$$\Delta H = 62 \text{ KJ.}$$

$$\Delta H = +14.92 \text{ Kcal}$$

$$\Delta H = 62.425 \text{ KJ}$$

$$1 \text{ Kcal} = 4.184$$

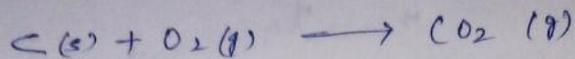
$$14.92 \text{ Kcal} = 14.92 \times 4.184$$

$$\Delta H = 62.425 \text{ KJ}$$

### Hess Law हैस का नियम

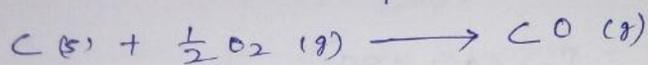
According to this the total amount of heat evolved or absorb in any thermodynamical chemical rxn. always same, whether the rxn will take place in one step or in more than one step.

Ex-

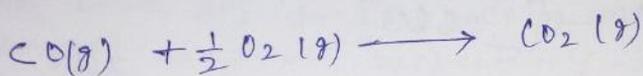


$$\Delta H = -393.5 \text{ KJ.}$$

if this rxn carried out in more than one step-



$$\Delta H = -110.5 \text{ KJ.}$$



$$\Delta H = -283.0 \text{ KJ.}$$

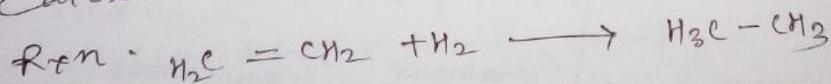
$$\text{Total heat} = -110.5 - 283.0$$

$$\text{T.H.} = -393.5 \text{ KJ} \quad \underline{\text{this is Hess Law.}}$$

### Numerical ③

Type number. 1

Calculate the heat of combustion for the following



if the bond energy data are

$$C-H = 414 \text{ KJ mol}^{-1}$$

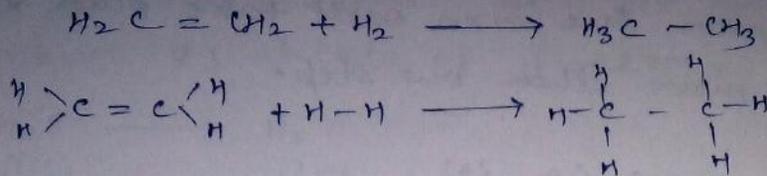
$$C=C = 619 \text{ KJ mol}^{-1}$$

$$H-H = 436 \text{ KJ mol}^{-1}$$

$$C-C = 347 \text{ KJ mol}^{-1}$$

The heat of Combustion = bond energy of the reactant

- bond energy of the product



$$[4(C-H) + (C=C) + (H-H)] - [6(C-H) + (C-C)]$$

$$[4 \times 414 + 619 + 120] - [6 \times 414 + 184]$$

$$[1656 + 619 + 120] - [2484 + 184]$$

$$[1695] - [2668]$$

$$[1695] - [2668]$$

$$\begin{array}{r} 2668 \\ -1695 \\ \hline 973 \end{array}$$

Heat of Combustion = - 973 KJ.

1 Joule = 0.2390 Calories

1 Calorie = 4.184 J

1 Kcal = 4.184 KJ

1 Joule =  $10^7$  ergs

1 erg =  $10^{-7}$  J

1 KJ = 1000 J

Bond	Bond energy
Cl-Cl	243 KJ mol <sup>-1</sup>
O=O	499.0 KJ mol <sup>-1</sup>
C-H	414.0 KJ mol <sup>-1</sup>
O-H	460.0 KJ mol <sup>-1</sup>
C=C	619 KJ mol <sup>-1</sup>
H-H	120 KJ mol <sup>-1</sup>

$\Delta E$  = internal energy

$\Delta H$  = heat content

Topic

\* Heat of Transition

$\Delta H = +3.3$  Kcal

Diamond  $\rightarrow$  C amorphous

$\Delta H = 0.016$  Kcal

S monoclinic  $\rightarrow$  S rhombic

P white  $\rightarrow$  P red

$\Delta H = -1.020$  Kcal

Bond B.E  
C-C 184 KJ mol<sup>-1</sup>

Example → Three moles of ideal gas ( $C = 5 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) at 10.0 atm and  $0^\circ$  are converted to 2.0 atm at  $50^\circ$  find  $\Delta E$  and  $\Delta H$  for the change.

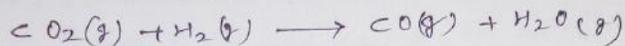
$$R = 2 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

Soln

$$\begin{aligned} \Delta E &= n C_v dT \\ &= 3 \times 5 \times (50 - 0) \\ &= 750 \text{ cal} \end{aligned}$$

$$\begin{aligned} \Delta H &= n C_p dT = n (C_p + R) dT \\ &= 3 \times (5 + 2) \times 50 \\ &= 1050 \text{ cal} \end{aligned}$$

Ex- Calculate  $\Delta H^\circ$  for the reaction -



given that  $\Delta H_f^\circ$  for  $\text{CO}_2(g)$ ,  $\text{CO}(g)$  and  $\text{H}_2\text{O}(g)$  are  $-393.5$ ,  $-111.5$  and  $-241.80 \text{ kJ mol}^{-1}$  respectively -

Soln



$$\Delta H^\circ = \Delta H_f^\circ (\text{Product}) - \Delta H_f^\circ (\text{Reactant})$$

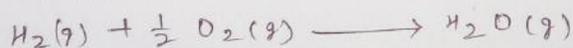
$$= [\Delta H_f^\circ [\text{CO}(g)] + \Delta H_f^\circ [\text{H}_2\text{O}(g)]] - [\Delta H_f^\circ [\text{CO}_2(g)] + \Delta H_f^\circ [\text{H}_2(g)]]$$

$$= [-111.5 + (-241.80)] - [-393.5 + 0]$$

$$= -353.3 + 393.5$$

$$\boxed{\Delta H^\circ = 40.2 \text{ kJ}}$$

Ex- Given that energies for H-H, O=O, and O-H bonds are 104, 118 and 111 kcal mol<sup>-1</sup> example -



Soln In this reaction, two O-H bonds are formed and one H-H bond is broken. Therefore we can write for  $\Delta H$

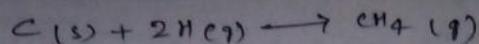
$$\Delta H = -2\Delta H(\text{O-H}) + \Delta H(\text{H-H}) + \frac{1}{2}\Delta H(\text{O=O})$$

$$= (-2 \times 111) + 104 + \left(\frac{1}{2} \times 118\right)$$

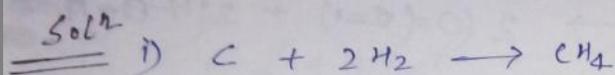
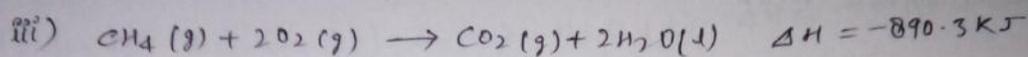
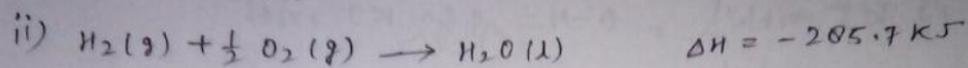
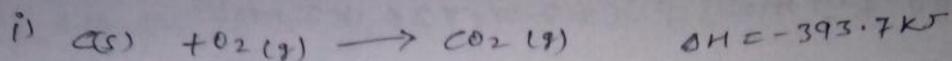
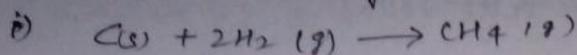
$$= -222 + 163$$

$$\Delta H = -59 \text{ kcal mol}^{-1}$$

Ques Determine of  $\Delta H$  of the reaction -



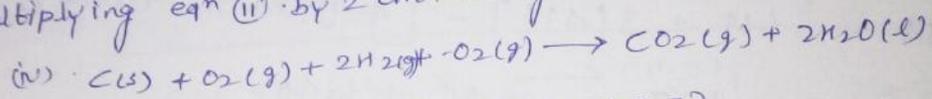
from the following data -



$$\Delta H = 1 \times (2 \times 120) = 240$$

$$-393.7 - 240 = 0$$

Multiplying eqn (ii) by 2 and adding to eqn (i) we get

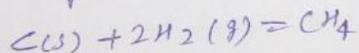


$$\Delta H = (2 \times -285.7) + (-393.7)$$

$$= -471.4 - 393.7$$

$$= -865.1 \text{ kJ}$$

On subtracting equation (iii) from equation (iv) we get.



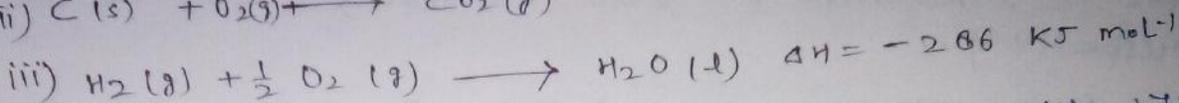
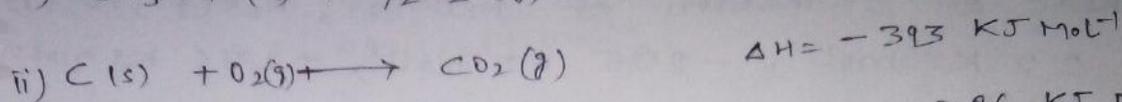
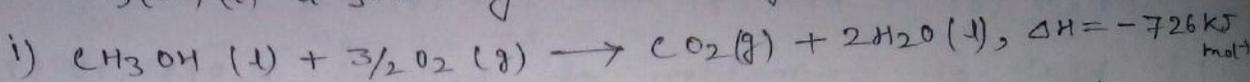
$$\Delta H = -865.1 - (-890.3)$$

$$\Delta H = -74.8 \text{ kJ}$$

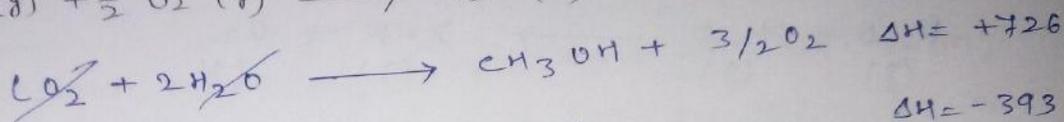
Thus the heat of formation of methane is  $-74.8 \text{ kJ}$ .

### TYPE - 2

Calculate the standard enthalpy of formation of  $\text{CH}_3\text{OH}$   
 $\text{CH}_3\text{OH}(\text{l})$  if following data are given  $\Rightarrow$

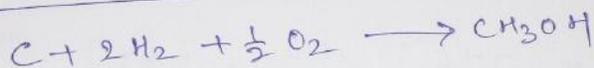


Sol<sup>n</sup>



$\Delta H = -393$

$\Delta H = -286 \times 2$

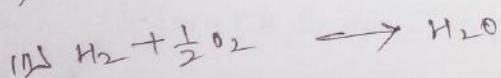
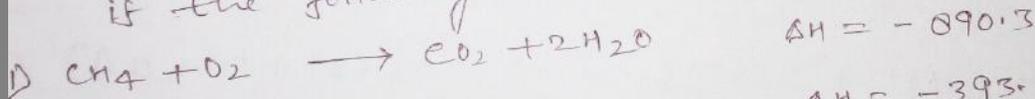


$+726 - 393 - 572$

$\Delta H = -239$

### Question

Calculate the enthalpy of combustion of  $\text{CH}_4$   
if the following data are given



$\Delta H = -393.5$

$\Delta H = -285.5$

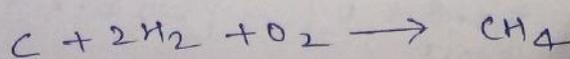
Sol<sup>n</sup>



$\Delta H = +890.3$

$\Delta H = -393.5$

$\Delta H = -285.5 \times 2$

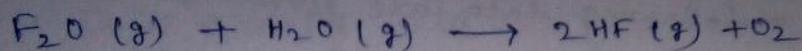


$\Delta H = +890.3 - 393.5$

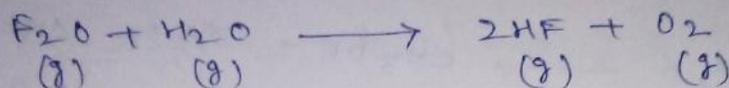
$- 285.5 \times 2$

### Type-3

Calculate the heat of the following rxn



If heat of formation of  $\text{F}_2\text{O}(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{HF}(\text{g})$  are  $22 \text{ kJ mol}^{-1}$ ,  $-285 \text{ kJ mol}^{-1}$ ,  $-276 \text{ kJ mol}^{-1}$  respectively -



$$\Delta H_R = \Delta H_{\text{Product}} - \Delta H_{\text{Reactant}}$$

$$= [2 \times \Delta H_{\text{HF}} + \Delta H_{\text{O}_2}] - [\Delta H_{\text{F}_2\text{O}} + \Delta H_{\text{H}_2\text{O}}]$$

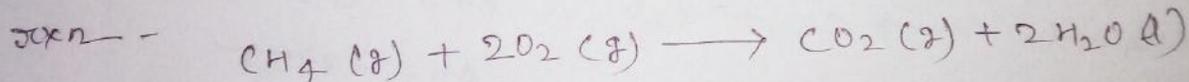
$$= [2 \times -276] - [22 - 285]$$

$$= -552 + 263$$

$$\Delta H_R = -289$$

Ques

Calculate the enthalpy change for the following



If the heat of formation of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  are  $-74.8 \text{ kJ mol}^{-1}$ ,  $-393.5 \text{ kJ mol}^{-1}$ ,  $-286.2 \text{ kJ mol}^{-1}$  respectively -

Soln



$$\Delta H_R = \Delta H_{\text{Product}} - \Delta H_{\text{Reactant}}$$

$$= [x - 393.5 + 0] - [-74.8 + 2 \cdot$$

$$= [-393.5 + 2(-206.2)] - [-74.8 + 0]$$

$$= [-393.5 - 512.4] + 74.8$$

$$= -905.9 + 74.8$$

$$= -831.1 \text{ KJ mol}^{-1}$$

Question

the standard heat of formation at 298 K for  $\text{CCl}_4(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{HCl}(\text{g})$  are  $-25.5$ ,

$-57.8$ ,  $-94.1$  and  $-22.1 \text{ Kcal mol}^{-1}$  respectively

Calculate the enthalpy of formation for the following

reaction -



Soln

$$\Delta H_R = \Delta H_{\text{product}} - \Delta H_{\text{reactant}}$$

$$= [94.1 + 4 \times -22.1] - [-25.5 + 2 \times -57.8]$$

$$= -102.5 + [-141.1]$$

$$\Delta H_R = -41.4 \text{ Kcal}$$

### Kirchhoff's equations

The equation representing the variation of heat of the rxn. with temp. known as Kirchhoff equations, at constant volume, the heat of rxn

$$\Delta E = E_2 - E_1$$

differentiate w.r. to temp at constant volume-

$$\left\{ \frac{d}{dt} (\Delta E) \right\}_V = \left\{ \frac{d}{dt} (E_2) \right\}_V - \left\{ \frac{d}{dt} (E_1) \right\}_V$$

$$\left\{ \frac{d(\Delta E)}{dT} \right\}_V = (C_V)_2 - (C_V)_1$$

$$\frac{d(\Delta E)}{dT} = \Delta C_V$$

$$d(\Delta E) = \Delta C_V \cdot dT$$

$$\int d(\Delta E) = \int_{T_1}^{T_2} \Delta C_V \cdot dT$$

$$\Delta E = \Delta C_V [T_2 - T_1]$$

$$\boxed{\Delta E_2 - \Delta E_1 = \Delta C_V [T_2 - T_1]}$$

This eqn is known as Kirchhoff's eqn at constant volume  
at constant pressure

$$\Delta H = H_2 - H_1$$

$$\left\{ \frac{d}{dT} (\Delta H) \right\}_P = \left\{ \frac{d}{dT} (H_2) \right\}_P - \left\{ \frac{d}{dT} (H_1) \right\}_P$$

$$\left\{ \frac{d(\Delta H)}{dT} \right\}_p = (C_p)_2 - (C_p)_1$$

$$\frac{d(\Delta H)}{dT} = \Delta C_p$$

$$d(\Delta H) = \Delta C_p \cdot dT$$

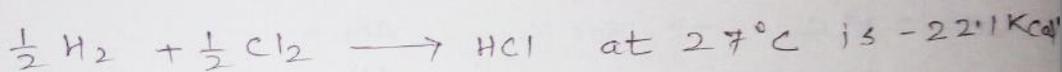
$$\int d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \cdot dT$$

$$\Delta H = \Delta C_p \cdot [T_2 - T_1]$$

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_p \cdot [T_2 - T_1]}$$

Que

The heat of rxn  $\frac{1}{2} H_2 + \frac{1}{2} Cl_2 \rightarrow HCl$



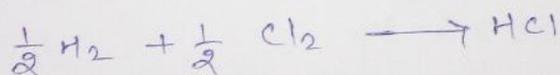
Calculate the heat of the rxn is  $77^\circ C$ .

the molar heat capacity at constant pressure at

$27^\circ C$  for Hydrogen, Chlorine, HCl, are 6.82, 7.7, 6.8

Cal/mol.

Soln



at  $27^\circ C = 300K$

$\Delta H_1 = -22100 cal$

$77^\circ C = 350K$

$\Delta H_2 = ?$

$T_1 = 300K$

$T_2 = 350K$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H_2 + 22100 = -0.46 \times 50$$

$$\Delta H_2 = \frac{-23}{22100} = -0.0010$$

$$\Delta C_p = C_p(\text{Product}) - C_p(\text{Reactant})$$

$$= 6.80 - \left[ \frac{1}{2} \times 6.82 + \frac{1}{2} \times 7.7 \right]$$

$$= 6.80 - [3.41 + 3.85]$$

$$= 6.80 - 7.26$$

$$= -0.46$$

$$\Delta H_2 + 22100 = -0.46 \times 50$$

$$\Delta H_2 + 22100 = -23$$

$$\Delta H_2 = 23 - 22100$$

$$\boxed{\Delta H_2 = -22133 \text{ cal}}$$

Question

The heat of the rxn

$\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$  at  $27^\circ\text{C}$  was found to be  $-21.976 \text{ Kcal}$ . What will be the heat of rxn at  $50^\circ\text{C}$  if the molar heat capacities at constant pressure - for  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{NH}_3$  are  $6.0, 6.77, 8.86 \text{ cal/mol}^\circ\text{C}$  respectively -



$$\text{at } 27^\circ\text{C} \quad \rightarrow \quad 300 \text{ K} \quad \Delta H_1 = -$$

$$50^\circ\text{C} \quad \rightarrow \quad 323 \text{ K} \quad \Delta H_2 =$$

$$T_1 = 300$$

$$T_2 = 323$$

$$T_2 - T_1 = 323 - 300$$

$$T = 23 \text{ K}$$

$$\Delta C_p = C_p(\text{product}) - C_p(\text{reactant})$$

$$= 2 \times 8.86 - [6.0 + 3[6.77]]$$

$$= 17.72 - [6.0 + 20.31]$$

$$= 17.72 - 27.11$$

$$\boxed{\Delta C_p = -9.39}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (23)$$

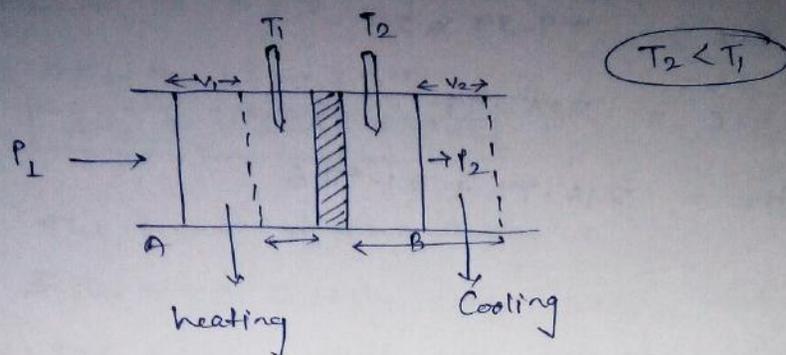
$$= 22.192$$

$$\Delta H_2 - 21.976 = +9.39 \times 23$$

$$\Delta H_2 - 21.976 = 215.97$$

$$\Delta H_2 = 215.97 + 21.976$$

## Joule Thomson Effect:-



The phenomenon of producing lowering of temp when a gas is ~~is~~ made to expand adiabatically from a high pressure to low pressure region. Known as Joule Thomson effect.

Let us consider the work done by piston A,  $W_1 = P_1 V_1$

Let the work done by the piston  $W_2 = P_2 V_2$

hence the net work done by the gas

$$W = W_2 - W_1$$

$$W = P_2 V_2 - P_1 V_1$$

According to the first law of thermodynamic

$$\Delta E = Q - W$$

$$Q = 0$$

$$\Delta E = -W$$

$$\Delta E = -(P_2 V_2 - P_1 V_1)$$

$$E_2 - E_1 = -(P_2 V_2 - P_1 V_1)$$

$$E_2 + P_2 V_2 = E_1 + P_1 V_1$$

$$H_2 = H_1$$

$$\boxed{\Delta H = 0}$$

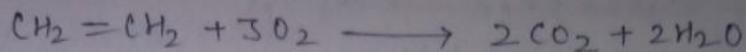
The Ratio of change in temp with change in pressure is known as Joule Thomson Coefficient, ~~dep~~ represented by  $\mu$ .

$$\mu = \frac{dt}{dp}$$

if  $\mu$  is +ve, gas expands, cooling effect.  
 $\mu$  is -ve = gas compress heating effect.

NOTE The value of  $\mu$  depends on the applied temperature.

Calculate the heat of combustion of ethene

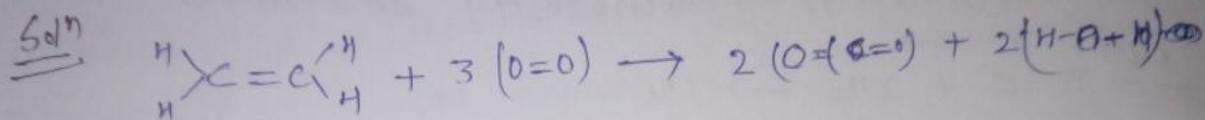


If the bond energy data's are

$$\text{C}-\text{C} = 619 \text{ kJ mol}^{-1}, \quad \text{C}=\text{O} = 724 \text{ kJ mol}^{-1}$$

$$\text{C}-\text{H} = 414 \text{ kJ mol}^{-1}, \quad \text{O}-\text{H} = 460 \text{ kJ mol}^{-1}$$

$$\text{O}=\text{O} = 419 \text{ kJ mol}^{-1}$$



$$\Delta H = [4(\text{C}-\text{H}) + \overset{(\text{C}=\text{C})}{1} + 3(\text{O}=\text{O})] - [4(\text{C}=\text{O}) + 4(\text{O}-\text{H})]$$

$$= [4(414) + 619 + 3(419)] - [4(724) + 4(460)]$$

$$= 1656 + 619 + 1257 - 2896 + 1840$$

$$= 3532 - 4736$$

$$\Delta H = -964 \text{ kJ mol}^{-1}$$

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