

Date 22.12.2023

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## Chapter - Thermodynamics

### System and Surrounding

- System is the part of universe, <sup>which is under investigation</sup>
- The rest of the universe excluding system is called surrounding.

$$\text{Universe} = \text{System} + \text{Surroundings}$$

### # Types of system

Open	Closed	Isolated
↓	↓	↓
Energy & mass can change	Only Energy can Exchange	Neither heat nor mass can exchange
$\Delta E \neq 0$	$\Delta E \neq 0$	$\Delta E = 0$
$\Delta m \neq 0$	$\Delta m = 0$	$\Delta m = 0$
	$\Delta m = m_2 - m_1$	
	$= m_2 - m_1$ [m <sub>2</sub> = m <sub>1</sub> ]	
	$\Delta m = 0$	

Note:- No system in the world is completely isolated

⇒ Intensive & Extensive properties

- Intensive = The properties which are independent of amount of substance present in the system.

Ex:- Colour, taste, density, temperature, viscosity, surface tension, freezing point, boiling point, Molarity, Mole fraction



⇒ Extensive:- depends upon the amount of substance.

Ex- Mass, Volume, Enthalpy, Entropy, heat capacity, Internal Energy

Heat Capacity

Types of process

1. Isothermal:- In this process the temp. is constant.

$$\Delta T = T_2 - T_1$$

$$\Delta T = 0$$

2. Isobaric:- In this process the pressure is constant.

$$\Delta P = 0$$

3. Isochoric:- In this process the volume is constant.

$$\Delta V = 0$$

4. Adiabatic:- In this process change in heat is constant

$$\Delta Q = 0$$

# State function & ~~path~~ path function

1. State function in which value does not depend upon the path followed but depends upon state only initial & final

2. Path function in which value depends on state and path.

# Internal Energy:- Every substance is associated with a definite amount of Energy, which depends upon its chemical nature as well as temp., pressure & volume. This energy is known as internal energy. It is the sum of diff. types of energies like electronic energy, chemical bond energy, vibrational energy, etc.



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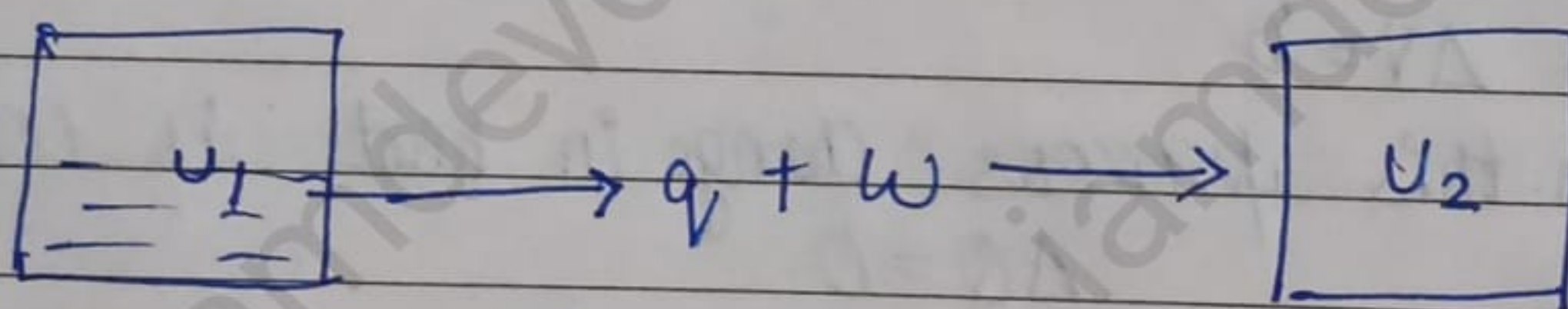
The exact value of the energy cannot be determined but we can calculate the change in internal energy.

$$U = E_e + E_B + E_v + E_R + \dots \infty$$

## # First law of Thermodynamics

It is also called law of conservation of energy. It can neither be created nor be destroyed. Although it may be converted from one form to another form.

## # Formulation of first law



$$U_2 = U_1 + q + w$$

$$U_2 - U_1 = q + w$$

$$\Delta U = q + w$$

## Sign Convention for first law

If heat is absorbed by the system  $\Rightarrow +q$

If heat is released by the system  $\Rightarrow -q$

If work is done by the system  $\Rightarrow -w$

If work is done on the system  $\Rightarrow +w$

Ques Calculate the internal energy change in each of the following cases

System absorbs

(i) System absorbs 15 KJ heat and does 10 KJ of work



(ii) 5 kJ work is done on the system & 55 kJ heat is given by the system

(i)  $15 \text{ kJ} - 10 \text{ kJ}$   
 $5 \text{ kJ}$

(ii)  $5 \text{ kJ} - 55 \text{ kJ}$   
 $-50 \text{ kJ}$

### → Limitations of First Law

- It does not tell about the direction of flow of heat.
- It does not tell about spontaneity or feasibility of the reaction.

### Enthalpy of a system

Suppose the change of a state of system is carried out at constant pressure.

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

but if this process is carried out at constant pressure volume

$$\Delta V = 0$$

$$\boxed{q_v = \Delta U}$$

Internal Energy change  $\Delta U$  is amount of heat is absorbed or released at constant volume but this process is carried out at constant pressure

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

$$q_p = [U_2 - U_1] + P[V_2 - V_1]$$



$$q_p = \left[ \underset{H_2}{U_2 + P V_2} \right] - \left[ \underset{H_1}{U_1 + P V_1} \right]$$

$$q_p = H_2 - H_1$$

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

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

$$\Delta H = \Delta U + P \Delta V \quad \text{--- (1)}$$

$$\Delta H = \Delta U + \Delta n_g \cdot R T$$

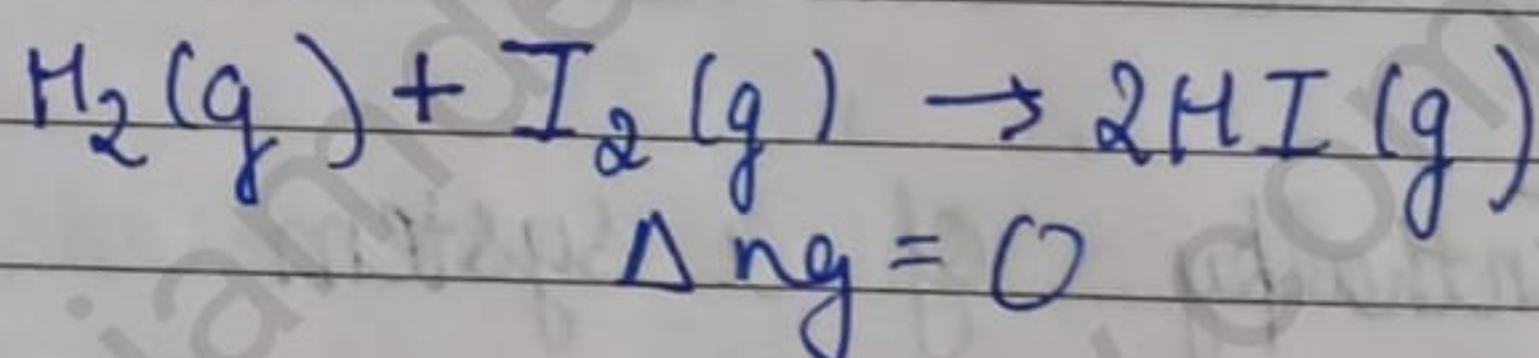
for ideal gas

$$P \Delta V = \Delta n_g \cdot R T$$

↓  
no. of moles of gas

Condition:-

1.  $\Delta V = 0$
2.  $\Delta n_g = 0$ 
  - Solid liq.
  - Change = 0



Is heat capacity of a system

⇒ Heat Capacity

Heat Capacity of a system is amount of heat to raised the temp. from  $T_1$  to  $T_2$

formula ⇒  $C = \frac{q}{T_2 - T_1}$  or  $\frac{dq}{dt}$

It mainly divided into two parts:-

- (i) Heat capacity at ~~to~~ Constant Volume
- (ii) Heat Capacity at Constant pressure

$C_v$

1. Acc. to first law at Constant volume  $C_v$

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

$$dq = dU + P dV$$



$$\left(\frac{dq}{dt}\right)_v = \frac{dQ}{dt}$$

$$C_v = dv/dt - \text{①}$$

Heat capacity at constant pressure

A/C FLOT

$$dq = dU + Pdv$$

diff. w.r.t  $(t)$

$$\left( \frac{dq}{dt} \right)_p = \frac{dU}{dt} + \frac{PdV}{dt}$$

$$\left(\frac{dq}{dt}\right)_p = \frac{dU + PdV}{dt}$$

$$\left( \frac{dQ}{dt} \right)_P = \frac{dH}{dt} \quad (11)$$

$$C_p = \frac{dH}{dT} \quad - (11)$$

$$\therefore dH = (du + PdV)$$

$$2q^n \text{ (11) - (1)}$$

$$C_p - C_v = \frac{dH}{dt} - \frac{dU}{dt}$$

$$= \cancel{\frac{du}{dt}} + \frac{P dv}{dt} - \cancel{\frac{du}{dt}}$$

$$C_p - C_v = \frac{PdV}{dT} \left[ \text{for 1 mol of ideal gas} \right]$$

$$PdV = RdT$$



$$C_p - C_v = \frac{R dt}{dt}$$

$$[C_p - C_v = R]$$

## Spontaneity of the Reaction

A process which proceeds by its on without any outside resistance is called spontaneous process & the driving forces for spontaneous rxn are:-

- Tendency of a system to ~~require~~ acquire min. energy or max. stability for ex:- heat flows from hot system to cold system
- Tendency to attain max. randomness for ex:- When a drop of ink is put in the beaker full of water it spreads uniformly.  
for ex:- Solid  $\rightarrow$  liquid  $\rightarrow$  gas

## Criteria of Spontaneity

- Spontaneous Change is unidirectional
- Increase in randomness favours spontaneous process.  
Ex:- melting of ice

## → II<sup>nd</sup> Law of Thermodynamics

- Entropy of universe is always increasing
- It is impossible to construct a machine working in cycle which ~~may~~ will transfer heat to ~~low~~ lower temp to higher temp. without any need of external agency (Clausius statement)
- Kelvin-Planck's statement  $\rightarrow$  Heat cannot be completely



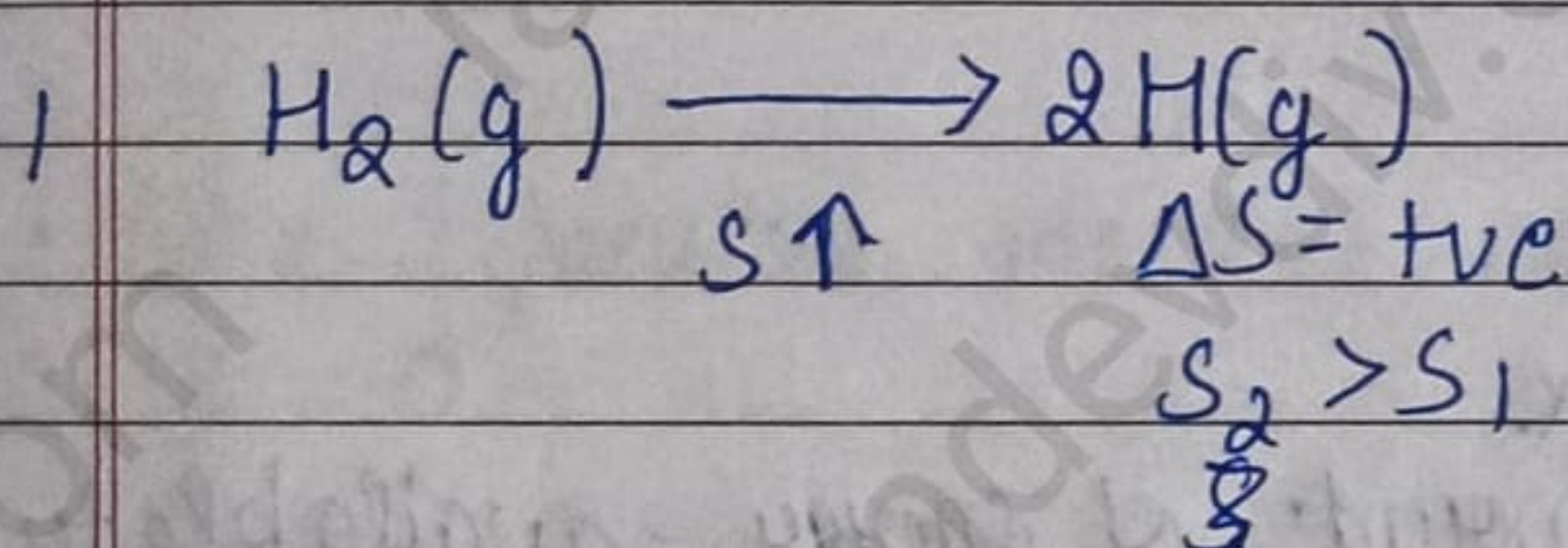
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converted into work without leaving any changes either in the system or the surrounding.

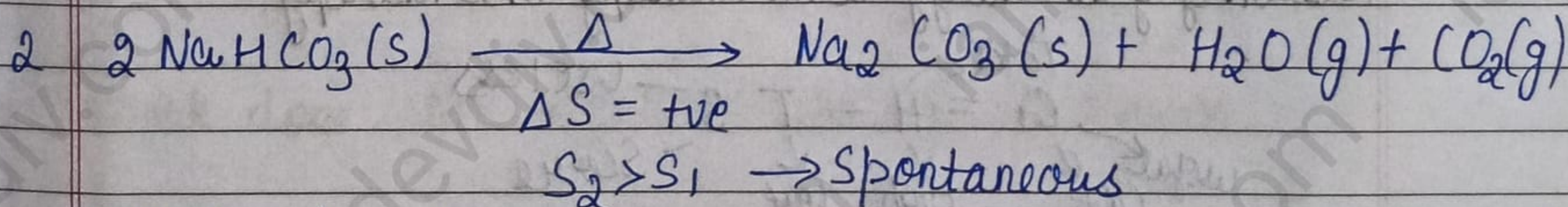
## Entropy

- Entropy is the measure of degree of randomness or disorder of the molecules.
  - It is denoted by 'S'.
- $$\Delta S = S_2 - S_1$$

Predict in which of the following Entropy decreases or increases



This can be explained on the basis of increase in the no. of moles i.e. increment in intermolecular interaction. Hence, Entropy increases.



Entropy is increasing

This can be explained on the basis of concept of states of matter in which  $S_{solid} < S_{liq} < S_{gas}$

- ③ Temp. of crystalline solid is raised from 0 Kelvin to 115 K  
 Entropy increases because constituent particles began to oscillate



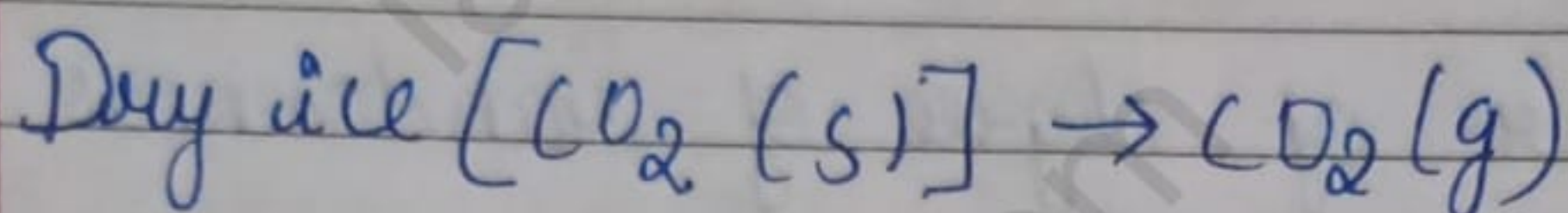
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## Formula of Entropy

$$S \propto \frac{q_{\text{reversible}}}{T}$$

heat  
T → initial temp.

Ex:-



Entropy ↑  
 $\Delta S = +ve$

Normal egg → Boiled egg  
The entropy increases +ve because Albumin (protein) gets denatured after boiling

## Gibbs free energy

It can be defined as <sup>max.</sup> amount of energy available to the system during the process for doing useful work under constant temp. & pressure

## Relation of free energy with Enthalpy and Entropy

$$G = H - TS$$

Total ←  
useful ← G ← High test ← Source  
Get

$$\Delta G = G_2 - G_1$$

$$\Delta G = [H_2 - TS_2] - [H_1 - TS_1]$$

$$= [H_2 - H_1] - T[S_2 - S_1]$$

$$\Delta G = \Delta H - T\Delta S \text{ Gibbs equation}$$



Gibbs free energy and Spontaneity

$$\therefore \Delta S = +ve \text{ spont.}$$

$$\Delta S = -ve \text{ Non Spont.}$$

$$\Delta S = 0 \text{ Eq}^m$$

$$\Delta G = -ve \text{ Spont.}$$

$$\Delta G = +ve \text{ non Spont.}$$

$$\Delta G = 0 \text{ Eq}^m$$

Exothermic

 $\Delta H$ 

-ve

$$\Delta S > 0$$

-ve Spont.

-ve

$$\Delta S < 0$$

- Free expansion means expansion of gas in vacuum

$$W = 0$$

$q = 0$  and acc. to 1<sup>st</sup> law of thermodynamics

$$\Delta U = q + w$$

$$\Delta U = 0 + 0$$

$$\Delta U = 0$$

$$U_1 = U_2$$

Work done in different type of processes

In Isochoric process volume remains constant  $dv = 0$

$$W = -Pdv$$

$$W = 0$$

$$W = F \cdot dx$$

$$= -P \cdot A \cdot dx$$

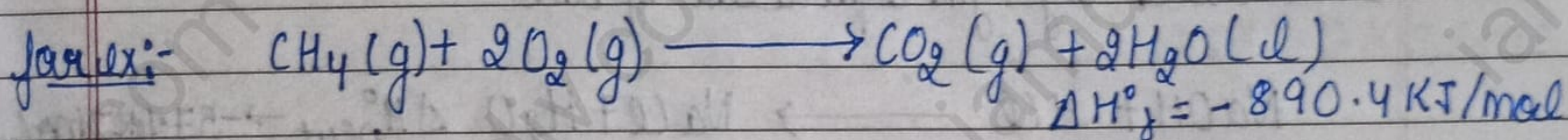
$$= -Pdv$$

In Isobaric process pressure is constant



Thermochemistry

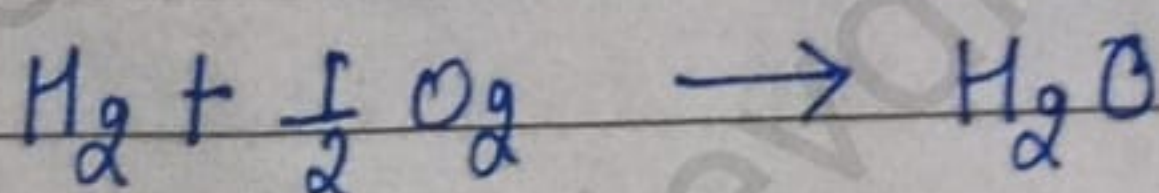
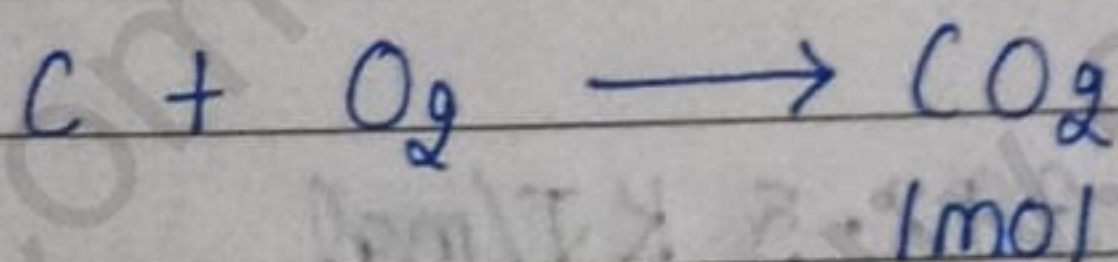
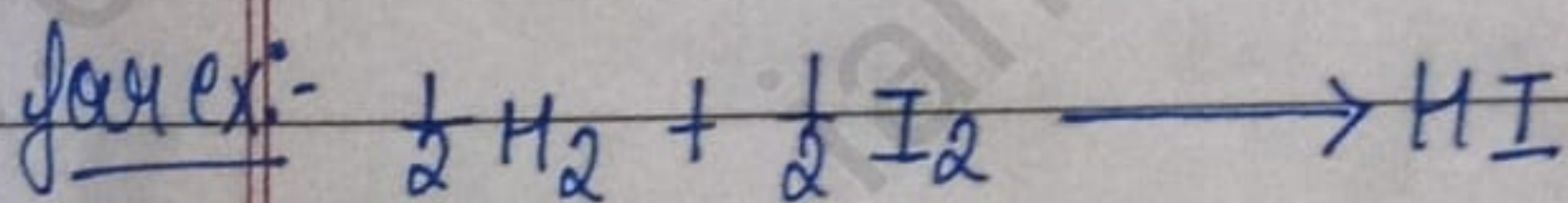
1. Heat of reaction:- The amount of heat involve in a chemical rxn when the no. of moles of reactants as represented by Chemical rxn have completely reacted.



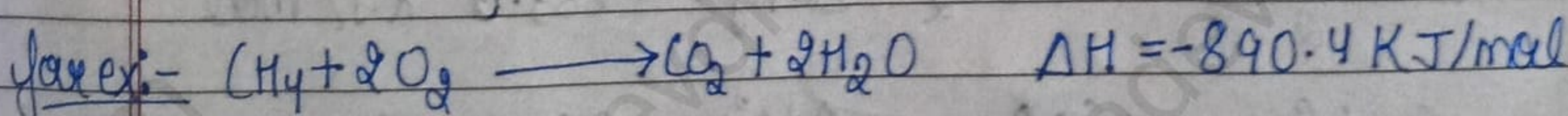
Heat of reactions = Sum of enthalpies of products - Sum of enthalpies of reactants

$$\Delta H^\circ_r = [(x+2y) - (b+2a)]$$

2. Heat of formation:- The amount of heat involved in the formation of a compound from its constituent atoms or molecules at standard STP.



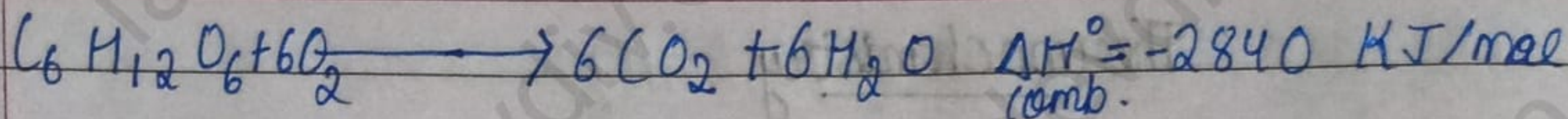
3. Heat of Combustion:- It is the heat released when 1 mole of substance is completely burnt in oxygen.



Ex:- Human eat Carbohydrate first it decomposes into glucose then glucose undergoes oxidation by oxygen that we inhale to produce energy.

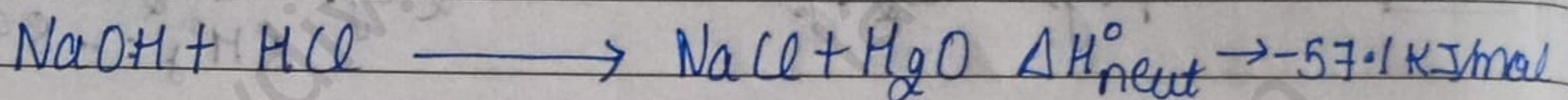


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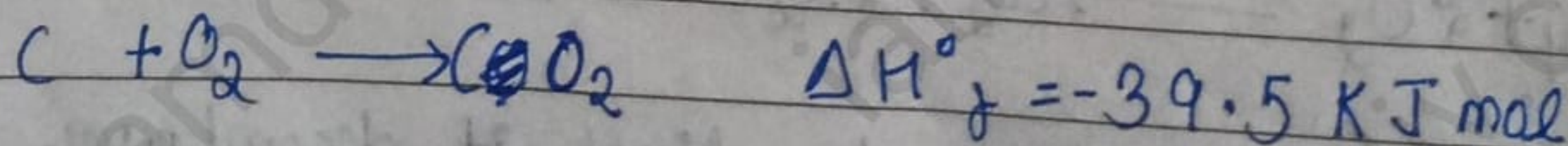
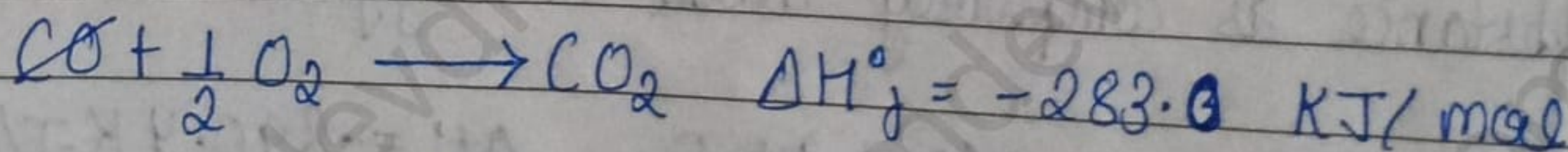
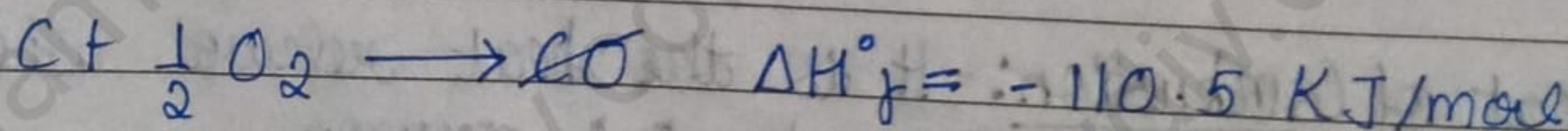
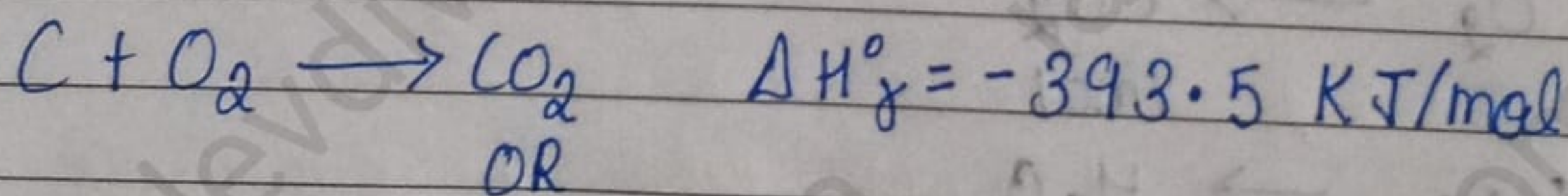
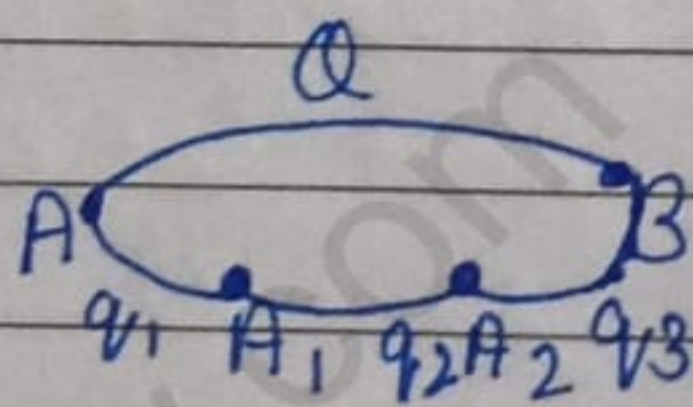
### 3. → Heat of neutralisation:-

Heat of neutralisation of an acid by a base is defined as heat released when 1 gm equivalent of an acid is neutralised by 1 gm equivalent of base



★ Hess Law:- Total amount of heat change in a rxn depends only upon the nature of initial reactant and the nature of final product.

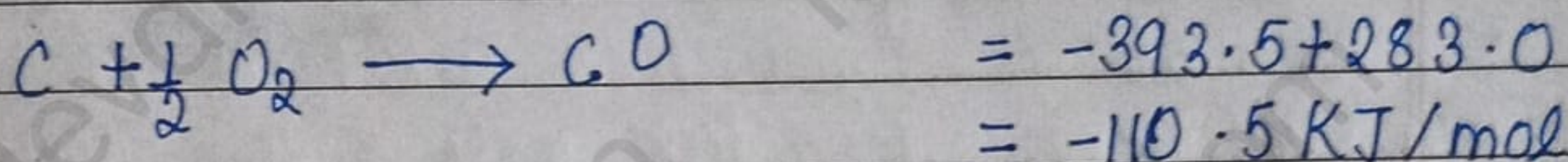
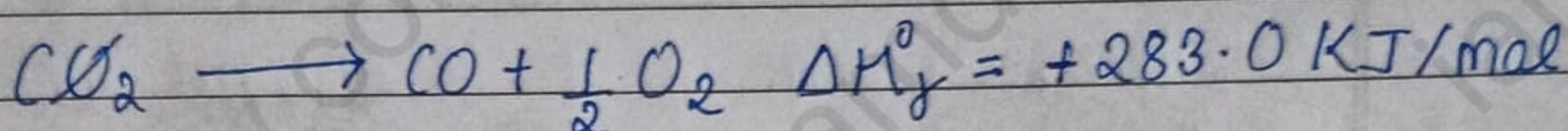
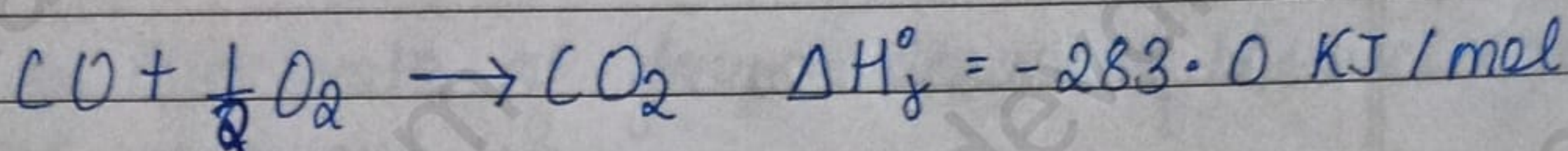
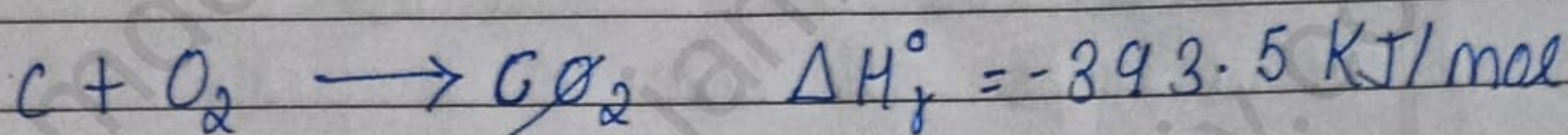
Amount of heat absorbed or released is whether the process takes place in one step or several steps





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Q- Calculate the enthalpy of formation of Carbon monoxide from the following data



Q- Calculate the enthalpy of formation of  $CH_4$  from the following data

