

Thermodynamics

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- Branch of chemistry dealing with study of Energy change taking place in CHEMICAL process
- Quantitative relationship between heat & other forms of Energy
- SYSTEM :- part of universe which is under observation Investigation or study

SURROUNDING :- part of universe excluding system
:- portion of universe interacting with system

$$\text{UNIVERSE} = \text{SYSTEM} + \text{SURROUNDING}$$

BOUNDARY - Anything ~~part of universe~~ separating system & surrounding

- Types: (a) Rigid - mostly Non-Rigid [Balloon, Piston] (b) conducting (ii) Non-conducting
- (c) (i) Real (ii) Imaginary

TYPES of SYSTEM

- ① Open System :- exchange of Heat and Mass b/w SYSTEM and SURROUNDING
- Boundary isn't sealed nor insulated → Imaginary surface
 - Total Mass isn't same throughout
 - eg: Classroom, Earth, Tea in Cup, pond
 - Living System - Human, Plant, Animals
 - Hot water in Open Glass - Earth
 - Reactants in Open Beaker

Coffee in closed glowing Bulb

- ② Closed system :- exchange of energy, No MASS change
- Boundary - sealed
 - Not insulated
 - constant with surrounding

③ Isolated

→ No eg: Coffee in

State of Sy

- In chem. sit
- certain state properties
- specified by
- if an prop

STATE fn

- depend only eg: Pressure

eg: Pressure

Balloon is of path i.e. or pump. dep on pressure w. deflated and

→ Path fn

State Variable

- fundamental
- change
- * → defining sy
- This no. dep min no. o

th study of
CHEMICAL process
of other forms of energy
is under
study

cluding System
Interacting with
System

URROUNDING

ing System

ing
conducting

Mass
and Matter

OUNDING

→ Imaginary
surface

in Cup, pond
nt, Animals
es - Earth
aker

No MASS change
constant with
surrounding

③ Isolated system : Neither Mass (sealed) nor Energy (insulated) exchange
→ No interaction

eg: Coffee in Thermos flask, WHOLE universe

State of System: [parameters / variable]

- In chem. simpler concept → Avg measurable properties
- certain state when all are dealt like P, V, T etc
properties are FIXED (defining property)
- specified by ① State fn ② State Variable
- if an property change → then system [state] changed
(macroscopic)

STATE fn (Initial & final)

→ depend only upon state and not path to attained to bring change

eg: Pressure, Volume, Temp, Internal energy [U]

Enthalpy [H], Entropy [S], Gibbs free energy

eg: Pressure in

Ballon is independent

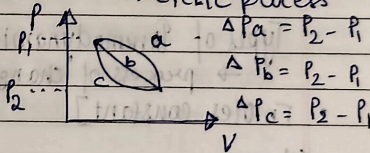
of path i.e. mouth

or pump. depends only

on pressure when ballon was

deflated and inflated

→ Path fn eg: Heat & work



State Variable

- fundamental properties determining eg: P, V, T, n
- change in system is accompanied by their change
initial → final
- * → defining system → not need to define all — becaz only few Independent
- This no. depend on nature of system
min no. of such fixed → all become definite as
Interrelated
 $PV = nRT$

Thermodynamic property

* Intensive property

- dependent on nature
- Independent of SIZE & MASS eg: P, T, density, Vapour pressure, Conc Terms, B.P, N.P, F.P, cell potential, electromotive force, μ (fugacity), Surface Tension, Refractive Index, G_m (gravity earth), Viscosity, ρ , Specific Capacity, Molar heat Capacity

* Extensive property

- dependent of Am't of substance i.e Size & Mass
- Mass, Volume, Moles, Heat capacity, $[U]$ $[H]$, $[S]$ Resistance, Heat.

Note (a) Ratio of Intensive → Extensive eg: Density, Conc Term

(b) Extensive are Additive and Vice versa

$$\frac{200 \text{ ml}}{20^\circ\text{C}} + \frac{300 \text{ ml}}{30^\circ\text{C}} \xrightarrow{\text{1g/ml}} V_{\text{total}} = 500 \text{ ml} \xrightarrow{\text{1g/ml}} [T] 20^\circ\text{C} - 30^\circ\text{C}$$

Types of Thermodynamic processes

→ process of changing state i.e change in state of system

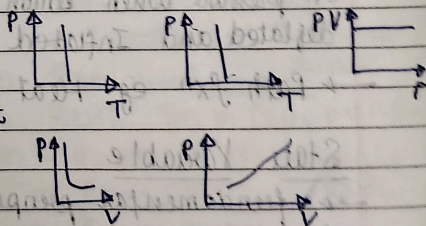
• [mole constant]

(i) Isothermal process

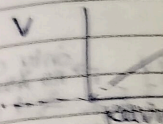
i] T constant, $dT = 0$

IGE = $PV = nRT \rightarrow \text{constant}$

$$\rightarrow P_1 V_1 = P_2 V_2$$



(i) Isothermal



(ii) Isochoric

(iv) Cyclic process
→ initial and final states are the same
thus $\Delta m = 0$
cyclic integral

Reversible

→ ∞ no. of steps

thus ΔS

→ $\Delta S_{\text{total}} = 0$

* Work

→ $P_{\text{ext}} = P_{\text{int}}$

$PV = nRT$

→ $P_{\text{ext}} = P_{\text{int}}$

Irreversible

→ initial

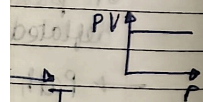
→ equilibrium

→ final

P, T, density
potential,
Surface Tension
Viscosity, ρ ,
capacity

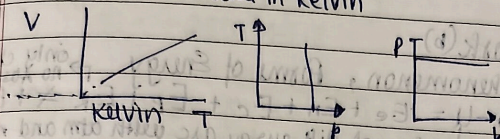
Mass
y, [U] [H], [S]
g: Density, Conc
Term
= 500 ml [E]
→ 1g/ml [I]
20°C - 30°C

In state of system



(i) Iso baric process (pressure constant)

$V \propto T$ by IGB
↳ Absolute in Kelvin



(ii) Iso choric [V. constant]

$P \propto T$

(iv) Adiabatic → Adiabatic Wall

→ No heat exchange possible

$PV^\gamma = \text{constant}$

$P_1 V_1^\gamma = P_2 V_2^\gamma$

(iv) Cyclic Process

→ initial and final state is same

thus $\Delta \text{in state fn}$ is zero

$\oint \delta q = 0$
Integral

→ ~~monotonic~~ of bringing
change → adiabatic
process

Reversible Process

→ ~~as no~~ of ~~only~~ small steps and ~~ex time~~ to occur [slow]

thus system surrounding in equilibrium [atmost] at all stages

→ ~~few~~ and ~~weightless~~ piston & Imaginary Theoretical

* Work done Reversible expansion without fr expansion

→ $P_{ext} = P_{gas} \pm dp$ approx. 0, $P_{ext} = P_{gas}$ or P

$PV = nRT$, thus $[P_{ext} = nRT/V]$

→ P_{ext} → variable if dp changes throughout

Irreversible : [no restoring when by themselves after done]

→ initial → final in single step, Real & Actual

→ equilibrium at Initial and Final only

→ other than Reversible, condition arent fulfilled

$P_{ext} = P_{gas} + \Delta P$ $\Delta P \neq 0$
 $\rightarrow$ thus $P_{ext} \neq P_{gas}$, thus I.G.E. NA
 $\rightarrow$ constant throughout process

(a) Heat & Work (b)

$\rightarrow$ boundary phenomenon, forms of Energy $\rightarrow$ only change
 $\rightarrow$ Heat $\rightarrow$ $U = E_t + E_n + E_c + E_p + E_k$ $\rightarrow$ no Δ
 $\rightarrow$ Workdone $\rightarrow$ $\rightarrow$ sum of diff energy asc with atm and mol
 $\rightarrow$ Brings change in Internal energy by Temperature difference
 $\rightarrow$ Heat $\rightarrow$ Work $\rightarrow$ flow in and out of system
 $\rightarrow$ $\neq 100\%$ efficiency
 $\rightarrow$ Thermally conducting wall $\rightarrow$ +ve $\rightarrow$ -ve

(b) Workdone when (i) P is constant $= 0$
 $\rightarrow$ on system $= +ve$ (ii) V is constant $= 0$
 $\rightarrow$ by system $= -ve$ [expansion] $\rightarrow$ system gas [IMP]
 $\rightarrow$ Force and displacement $\rightarrow$ PV = work [Mechanical]
 $\rightarrow$ Work = force $\times$ length $\times$ area $\rightarrow$ Pressure $\times$ Volume
 $\rightarrow$ 100% $\rightarrow$ Area $\rightarrow$ Note

Heat $\rightarrow$ $W = - \int P_{ext} dv$

1 cal = 4.18 of 4.2 Joule

1 Latm = 101.3 Joule

1 L-bar = 100 Joule

1 J = 10⁷ erg

R = 8.303 J

Latm > Cal > J > erg
 20.1.98 Cal or 8.314 J

Q] I.G. expansion $\rightarrow 20L \rightarrow 30L$, $P_{ext} = 2atm$
 $W = -20L \cdot atm$ cu $[30 - 20 = 10]$
 $W \text{ in J} = -20 \times 101.3 \rightarrow -2026 \text{ Joule}$

Q] I.G. 10L, $P_{ext} = 1$ constant, $W_{done} = 20L$ atmosphere
 $20L \cdot atm = -1[x - 10L] = -x + 60L$
 $-20L - 10L = -30L = -1x$
 $\rightarrow$ thus $x = 30L$

E-NA

Q) 2 mol of IGE, expanded against 280 atm ext pressure and Volume become double in L-atm
 $W = -P_{ext} [V_2 - V_1]$
 $W = -280 \times 44.8$

change
 + Eg
 1 mol
 different
 system

Internal Energy experimentally measured by Bomb Calorimetry process
 → Reaction carried at constant Volume of [liquid & known]
 → Physical
 → Chemical
 Apparatus: Calorimeter
 → dependent on Temp only for (IG)E

[Imp]
 anical]
 Nature
 volume

Therefore at Constant Temperature [Isothermal]
 $\Delta \text{Internal Energy } \Delta U = 0$ → constant
 ΔG → apparatus → Bomb → withstand High Pressure
 → steel vessel in H₂O → No heat lost
 stirrer → suspend → sealed H₂O bath → dissipate heat
 Thermometer → monitor change
 → No work done, $\Delta V = 0$

$$q = C \times m \times \Delta T$$

Enthalpy → Calorimeter → constant pressure
 → ΔT at end and start only, i.e. $[\Delta H = q_p]$
 → heat at constant pressure
 heat of reaction
 involve or absorption
 at constant Temp

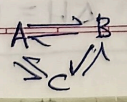
First Law → conservation of Energy → not created nor destroyed but transformed
 → T.E of universe is constant
 → of isolated system is always conserved

$$\Delta U = q + w$$

ΔE → Path fxn
 ΔU → state fxn

phore
 COL

Zeroth law: - A = B and B = C
 then C = A
 Must Thermal equilibrium



1] Isothermal

$$\Delta T \neq \text{constant} = 0, \Delta E = 0$$

$$\text{thus } [q = -W]$$

Heat absorbed = Work done by system and vice versa

2] Isochoric Process, $\Delta V = 0$

$$\Delta E = q + W = 0$$

3] Adiabatic $\rightarrow q = 0$

$$\Delta E = W$$

Heat absorbed = $\Delta E = q_v$ $\uparrow$ use in E and vice versa
Work done on system $\rightarrow \uparrow$ use E

4] Cyclic Process $\Delta E = 0$

$$[q = -W]$$

Heat absorbed " = " by system

5] Isobaric

$$\Delta E = q + W \Rightarrow \Delta E = q + -P\Delta V$$

$$[q_p = \Delta E + P\Delta V]$$

$$[q_p = \Delta H \text{ enthalpy change}]$$

Heat absorbed $\rightarrow \uparrow$ use enthalpy

- Heat $\rightarrow$ state fn : Isochoric and Isobaric for Enthalpy
- Adiabatic $\rightarrow$ work
- None : Cyclic and Isotherm } any path, fn as state

Enthalpy $[\Delta H]$

- $\rightarrow$ fn of Temperature of Process
- Heat content in system at constant pressure

$$[q_p = \Delta H]$$

- Sum of Δ internal energy and p energy

$\rightarrow$ Abs- Impossible to measure thus can calculate change

$$\Delta H = \Delta E + \Delta(pV)$$

$\rightarrow$ At Isothermal $\approx$ Cyclic

$\rightarrow$ Heat Constant $\sim$

$$\Delta H = \Delta E + \Delta(pV) \quad \text{Internal energy} \quad \Delta E = 0 \quad \text{Cuz } \Delta H = 0$$

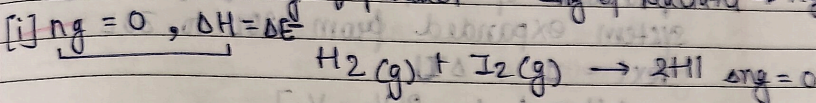
for a chemical Reactn : Temp constant

$$\Delta(PV) \rightarrow \Delta nRT$$

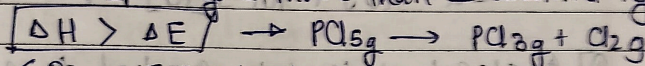
thus $\Delta H = \Delta E + \Delta nRT$

(At constant Volume) $\rightarrow$ change in Gaseous Volume $\rightarrow$ heat

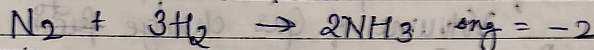
$$\Delta H = \Delta E + \Delta nRT$$



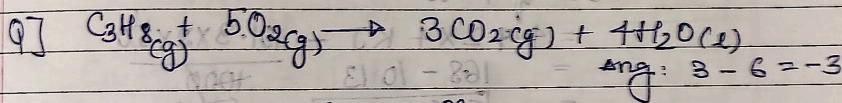
(ii) $\Delta n > 0$, product is more than reactant n_g



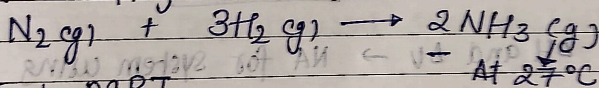
(iii) $\Delta n < 0$, reactant more



$$\Delta H < \Delta E$$



Q] Calculate ΔH for reaction



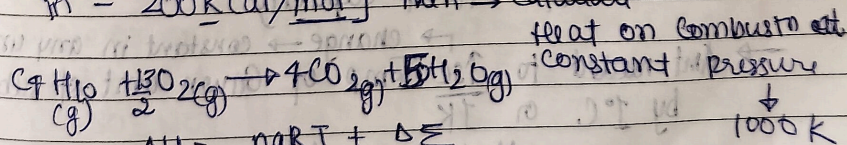
$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H = -90 kJ + \frac{-2 \times 8.314 \times 300}{1000}$$

$$\Delta H = -90 kJ - 4.988 kJ \rightarrow -94.98 kJ$$

Q] Heat on Combustion of Isobutane gas at constant Volume

In -200 K Cal/mol then $\rightarrow$ calculate



$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta H = -200 + \frac{1.5 \times 2 \times 1000}{1000}$$

$$\Delta H = -197 \text{ K Cal}$$

Q] If 10 Joules of heat is absorbed by system and 10 Calvis work down on system, calculate ΔE
 $\Delta E = q + w$
 $10 + (4.2)10 \Rightarrow \boxed{52 \text{ J}}$

Q] If 10 Joule of heat absorbed by system such that system expanded from 20L to 30L
 $P_{ext} = 1 \text{ atm}$
 $\Delta U = q + P(V_2 - V_1)$
 $\Delta U = 10 \text{ J} + 101.3 [10] \rightarrow -1003 \text{ J}$

Q] If 4KCal of heat is supplied to a Gas and Volume of Gas change from 55L to 52L
 $P_{ext} = 2 \text{ atm}$
 $\Delta E = q + w \rightarrow P(V_2 - V_1)$
 $= 4 \times 2 \times 4 \text{ KJ} - 101.3 \times 2 \times 3$
 $= 168 - 101.3$
 $= \boxed{5.67 \text{ KJ}}$

ΔH and $\Delta V \rightarrow \text{NA}$ for system using solids or liquid

Heat Capacity [C]

• Rise Temperature $\propto$ heat transfer

$$q = \text{coefficient} \times \Delta T$$

$\propto$ size, composition, nature of system
 k/a Heat Capacity

$\rightarrow$ Amt needed to rise Temp of Given amt. of substance by 1°C or 1K

$\Rightarrow$ Heat Required [transferred]
 Rise in Temperature

Unit :- J/kolvin, Calvis/Kelvin, $\text{J}/^\circ\text{C}$ or $\text{Cal}/^\circ\text{C}$

system
 n, Calculate ΔE

such that

0.3 J

Gas and
 L from 52

ids or liquid

use of system

any unit
 of substance

cal/c

[S]
 Specific Heat [Intensive]
 $\rightarrow$ Amt to raise ^{temperature} Tg of substance by $1^\circ\text{C}/1\text{kelvin}$
 Heat Capacity = mass $\times$ Specific heat
 $\left[\frac{J}{g} = S\right]$ J/g kelvin

Molar heat Capacity [Intensive] Cm/C
 $\rightarrow$ Use Temp, heat needed of 1mol by $1^\circ\text{C}/1\text{K}$
 J/mol K, cal/mol K, J/mol $^\circ\text{C}$, cal/mol $^\circ\text{C}$

$\rightarrow$ Specific Heat $\times$ Molar Mass
 $\rightarrow$ Heat Capacity $\times$ Moles $^{-1}$
 $\rightarrow$ Types ① Constant Pressure ^{isobaric} ② Constant Volume ^{isochoric}

① $C_p = \left[\frac{dq}{dt}\right]_p = \frac{dH}{dt}$ thus $dH = nC_p dt$

② $C_v = \left[\frac{dq}{dt}\right]_v = \left[\frac{dE}{dt}\right]$ thus $nC_v dt = dE$

$C_p - C_v = R$ $\rightarrow$ universal Gas Constant

$\frac{C_p}{C_v} = \gamma$ $\rightarrow$ Molar heat capacity Ratio

At constant Temp, $C_p = \infty$ and $dH = 0$ [Phase Change]

$q = -W$ $\Delta H = \Delta E + \Delta PV$

Values	C_v	C_p	γ
Gas	γ		
He, Ne, Ar, Kr, Xe	$3/2 R$	$5/2 R$	$5/3 = 1.66$
O_2, N_2, H_2	$5/2 R$	$7/2 R$	$7/5 = 1.4$
O_3, SO_2, NO_2	$3R$	$4R$	$4/3 = 1.33$

Q] If 1000 J of heat is absorbed by 180 g of H_2O such that T rise $\rightarrow 20^\circ \rightarrow 70^\circ C$ find

$C \rightarrow 1000/50 \rightarrow 20$

$S \rightarrow 20/180 \rightarrow 1/9$

$C_m \rightarrow 20/10 \rightarrow 2$

Q] If 10 moles of H_2 gas is heated such that temperature Calculate ΔH $10^\circ C \rightarrow 110^\circ C$

$\Delta H \rightarrow C_p dt$

$100 \times 10 \times 7 \times R \rightarrow 3500 R$

Q] find Molar heat Capacity during Evaporation of 1 mol of H_2O [phase change]

$\Delta H = C_p dt$

$\frac{\Delta H}{dt} = C_p - \text{then } \Delta H = \infty$

Work done Calculation

① Isothermal process: Isochoric [closed container]

$W = 0$

② Isochoric: $W = -P[V_2 - V_1]$ $W = -\int_{V_1}^{V_2} P dv$

③ Isothermal $W = -nRT \Delta \ln$

④ Reversible $\rightarrow P_{ext} = \frac{nRT}{V}$

$W = -\int_{V_1}^{V_2} \frac{nRT}{V} dv$

$= -nRT \ln V_2 - \ln V_1$

$= -nRT \log V_2/V_1$

$\ln e^x = 2.303 \log_{10} x$

$\rightarrow -2.303 \cdot nRT \log V_2/V_1$ or R/P_2

or $P_1 V_1 = P_2 V_2$

$\log_1 = 0$

$\log_2 = 0.301$

$\log_3 = 0.48$

$\log_4 = 0.602$

$\log_5 = 0.70$

$\log_6 = 0.78$

$\log_7 = 0.85$

$\log_8 = 0.903$

$\log_{10} = 1$

$\log_9 = 0.96$

② Irreversible $\rightarrow P_{ext}$ constant

$\rightarrow -P_{ext} [V_2 - V_1] = W$ or $\rightarrow -P_{ext} RT \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$

$\rightarrow [P_{ext} = P_2 \text{ when NM}]$

* Chemical reaction

$[W = \Delta n g R T]$

* free expansion $\rightarrow$ Irreversible $\rightarrow$ expansion in Vacuum
 $\rightarrow P_{ext} = 0 \rightarrow W = 0 ; \Delta H = 0, q = 0,$

Q] 1 mol of Ideal Gas is 1 by 2° Calvis at Constant P
 $1 \times 2 \times 2 \rightarrow 4 \text{ Calvis K mol,}$

Q] 10 mol of Ideal gas expanded in Reversible Isothermal
 from 10m³ to 100m³ at 27°C, find w, q, $\Delta H, \Delta E$

$\Delta H = 0$
 $\Delta E = 0$
 $W = -10 \times R \times 300 \times \log \frac{100}{10} \times 2.303$
 $W = -2.303 \times 3000 R$

Q] 1 mol of Ideal Gas at 27°C and 3atm pressure is allowed to expand in Isothermal manner against P_{ext} constant = 1 final below 1atm
 $\rightarrow -R \times 300 \times \left[\frac{2}{3} \right] \rightarrow -200 R$

Q] At 300 kelvin, 1 mol of Ideal Gas undergo pressure change from 2atm to 1atm Isothermally
 Work done

$\rightarrow P \rightarrow$ gradual $\rightarrow$ Suddenly
 $\rightarrow -2.303 \times 1 \times R \times 300 \times 0.301$
 $\rightarrow -207.27 R$
 $\rightarrow -1 \times R \times 300 \left[\frac{1}{2} \right] \rightarrow -150 R$

for expansion

$| \text{Reversible} | > | \text{Irreversible} |$

3] W in open system of 300 Kelvin, when 5kg Iron
Adiabatic react with HCl

$$q = 0$$

(1) Reversible

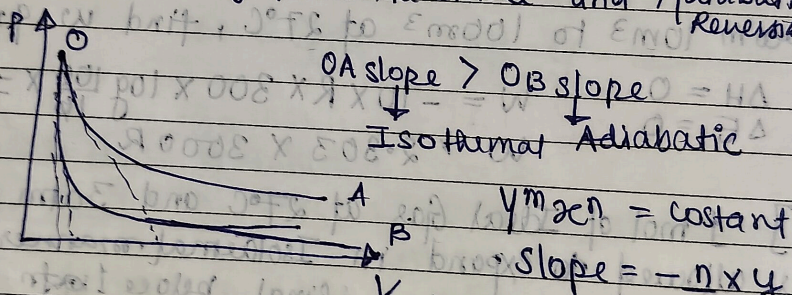
$$PV^\gamma = \text{constant}$$

$$W = n C_v [T_2 - T_1] \quad \text{or} \quad W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

(2) Irreversible

$$W = -P_{\text{ext}} [V_2 - V_1] \quad \Rightarrow \quad n R [T_2 - T_1] / \gamma - 1$$

Comparison $\rightarrow$ Isothermal Reversible and Adiabatic Reversible



$\rightarrow$ Always more than 1

$$\text{Isothermal} \rightarrow -P/V$$

$$\text{Adiabatic} \rightarrow -\gamma P/V$$

Increase of Expansion

Iso $T \rightarrow$ constant

Reversible Adiabatic

Iso > Adia, $T_o = T_A$

$T_B < T_o$

More Temp/work done $\rightarrow$ More the slope

(1)

(2)

(Feasibility)

Spontaneous & Non Spontaneous

→ Not needed to be instantaneous
Spontaneous :- Irreversible, Natural, Need some initiation
→ Natural tendency to occur in Particular Direction either own/initiate UNDER GIVEN SET of condition
→ Can be reversed by external Agency only.

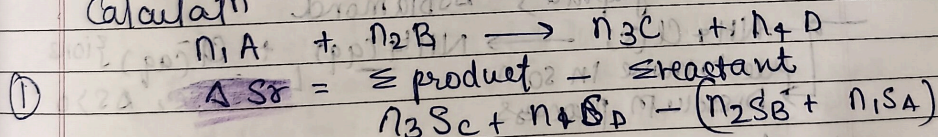
Non Spontaneous :- Not occurring own in Particular Direction
→ made occur by when energy from source [ext] is constantly applied throughout.

Criteria for Spontaneous :- $\downarrow$ min Energy, $\uparrow$ max Stability
→ attain Max Randomness more Appr

→ Reason for spontaneous process to proceed in direction
Entropy → Thermodynamic fn [Extensive property]
→ extent of disorder/Randomness; $\propto$ Randomness/Disorder
→ leads to stability

Ratio → Heat Absorbed By SYSTEM in Isothermal Exn
Temperature At which its Absorbed
 $\Delta S = \frac{q_{\text{reversible (Isothermal)}}}{T}$

Calculation



② for Ideal Gas undergoing

(i) Reversible

$$\Delta S = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{P_2}{P_1}$$

• Isothermal $T = \text{constant}$

$$\Delta S = nR \ln P_1/P_2 \left[V_2/V_1 \right]$$

• Isochoric

$$\Delta S = n C_v \ln T_2/T_1$$

• Isobaric

$$\Delta S = n C_p \ln T_2/T_1$$

• Adiabatic

→ Isoentropic process, $S \rightarrow \text{constant}$

$$\Delta S_{\text{rev}} = q_{\text{rev}}/T \rightarrow \Delta S = 0$$

Factors Affecting

(i) Physical state $S_g > S_l > S_s$

(ii) Chemical reaction

gas + gas $\Delta S \uparrow$ $\Delta n_g > 0, \Delta S > 0$ i.e. $S \uparrow$ se

gas + liq $\Delta S \uparrow$ $\Delta n_g < 0, \Delta S < 0, S \downarrow$ se

solid + solid $\Delta S \uparrow$ → particles Increased.

Phase Transition

i) Entropy of fusion → $\Delta H_{\text{fusion}} / T_{\text{melting pt}}$
 $\Delta S \rightarrow$ when 1 mol solid → liquid At melting pt

(ii) Entropy of Vaporization → $\Delta H_{\text{vap}} / T_{\text{boiling}}$ $T \rightarrow \text{Kelvin}$
 → 1 mol of liquid → Vapour at Boiling pt

→ Rust → ↑ se particle, $\Delta S +ve$
 $\Delta S_{\text{graphite}} > \Delta S_{\text{diamond}}$

→ $\text{NH}_4\text{Cl (s)} \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$ Ions
 free to move in soln. → Dissolution process
 → $S \uparrow$ se, $\Delta S > 0$

→ $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl} \downarrow$ Due to ppt
 → $[\text{AgCl}_2] + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl} \downarrow$ $S \downarrow$ se, $\Delta S < 0$

→ egg (Boiling) → Solidify egg. $\Delta S \rightarrow +ve, \uparrow S$

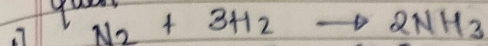
Denaturation of protein → Amino Acid → random

→ Stretching of Rubber (long, flexible macromolecule)

• $\Delta S \rightarrow -ve, S \downarrow$ se

→ stretching → Str: linear [orderly arrangement]
 Coiled

Questn



standard entropy 20, 30, 15 of N_2 , H_2 & NH_3 J/Kmol

find ΔS

Ans: -80 J/K. $(2 \times 15) - (1 \times 20 + 3 \times 30)$
 $30 - (20 + 90) \rightarrow -80$

2] Entropy of Vapourisation of liquid at 800 Kelvin

is 25 J/Kmol, then find entropy

Soln: 800×25 J/mol

3] 10 mol of Ideal Gas is Allowed to expand isothermally from 10 m³ $\rightarrow$ 100 m³ At 300 Kelvin

ΔS in cal is?

$[\Delta S = nR \ln V_2/V_1] \rightarrow 2.303 \times 10 \times 2 \times \log_{10} 10$
 $\rightarrow 23.03 \times 2 \rightarrow 46.06$ cal

Negative $\Delta S \rightarrow$ Spontaneous

ΔS and Spontaneity $\rightarrow 0 \rightarrow$ reaction Reversible/Equilibrium

$\Delta S_{total} = \Delta S_{universe} + \Delta S_{surrounding}$

$\Delta S_{surrounding} = -q_{system} / T_{surrounding}$

$\rightarrow$ Decide spontaneity of process

Q] $\Delta S_{system} = 10$ J/Kelvin at Reversible

$\Delta S_{total} = 0$, $\Delta S_{surrounding} = -10$ J/K

Second law of Thermodynamics

$\rightarrow$ states about direction of flow of heat

$\rightarrow$ Natural process $\rightarrow$ Irreversible - spontaneous

Isolated system: $\rightarrow$ The continuously ΔS rising $\&$

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

Thus $\Delta S_{system} > 0 \rightarrow$ No heat transfer from isolated system $\rightarrow$ This the universe

Gibbs free Energy (G)

- Constant Pressure is Required to predict Spontaneity of process
- Measuring Capacity of system to do useful work
part of system converted →

$$[\Delta G = [\Delta H - T\Delta S]]_{\text{system}}$$

→ Calculative; Abs not determined → Extm → State fun

Relate ΔG and ΔH

$$\Delta H_{\text{sys}} = q_{\text{system}}$$

$$\Delta G_{\text{sys}} = -q_{\text{system}}$$

$$\Delta S_{\text{surr}} = -\frac{q_{\text{surr}}}{T_{\text{surr}}} = -\frac{\Delta H_{\text{system}}}{T}$$

$$\Delta H_{\text{system}} = q_{\text{system}}$$

$$= -T\Delta S_{\text{surr}}$$

$$\Delta G_{\text{system}} = -T[\Delta S_{\text{surr}} + \Delta S_{\text{system}}]$$

$$(\Delta G_{\text{system}})_{T,P} = -T\Delta S_{\text{total}}$$

$\Delta S > 0$, then $\Delta G_{\text{system}} < 0$ → spontaneous

$\Delta S < 0$, then $\Delta G_{\text{sys}} > 0$ → Non spontaneous

Equilibrium → $\Delta S_{\text{total}} = 0$, $\Delta G_{\text{total}} = 0$ Reversible process

Sign of ΔH and ΔS Descriptors

ΔH	ΔS	Endothermic → ↑ Temp, Exo → ↓ Temp
① -ve	+ve	→ spontaneous always, $\Delta G < 0$
② +ve	-ve	→ Always Non spontaneous as $\Delta G > 0$
③ +ve	+ve	→ spontaneous At only high temp $ T\Delta S > \Delta H $
④ -ve	-ve	→ low temperature → spontaneous $\Delta H > T\Delta S$

→ The temperature at equilibrium is

→ at equi

$\Delta G = \Delta H - T\Delta S$ — true $\Delta H = T\Delta S$, $T = \Delta H / \Delta S$
 Tag Temperature > equilib → spontaneous
 Temperature < equilib → Non spontaneous
 for case 3

Ques: Predict the sign for ΔS for following

- ① $H_2O(s) \rightarrow H_2O(l)$ $\Delta S > 0$ ③ $3H_2 + N_2(g) \rightarrow 2NH_3(g)$ $\Delta S < 0$
 ② $H_2O(l) \rightarrow H_2O(g)$ $\Delta S > 0$ ④ $2SO_2(g) \rightarrow 2SO_2(g) + O_2(g)$ $\Delta S > 0$
 ⑤ $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ $\Delta S < 0$ ⑥ spreading of Ink $\Delta S > 0$

Q:- for a reactn: $\Delta H = -20 \text{ kJ/mol}$, $\Delta S = -300 \text{ J/K}^{-1}$
 at $27^\circ\text{C} \rightarrow 300 \text{ Kelvin}$

- ① $\Delta G = -20000 - (-300 \times 300) \rightarrow -20000 + 90000 = -11000$
 ② Spontaneity: - Non spontaneous

Q] for a reactn: $\Delta H = 30 \text{ kJ/mol}$ and 60 J/K^{-1} ΔS
 then at what temp reactn will be spontaneous

- a) 500 c) 300
 b) 600 d) 100

Q] for a reactn

$A(g) + B(g) \rightarrow C(g)$ at 300 K ,
 if $\Delta E = -3 \text{ kcal}$ and $\Delta S = -10 \text{ cal/K}^{-1}$
 then find ΔG

- ① $\Delta H = \Delta E + \Delta nRT$
 $= -3000 \times 2 + -1 \times 2 \times 300 = -6600$
 ② $-6600 + [10 \times 2 \times 300]$
 $\Rightarrow 600 \text{ cal}$
 $\rightarrow 600 \rightarrow \text{kcal}$

Standard Gibbs free Energy and Equilibrium Constant

$$\Delta G = \Delta G^\circ + RT \ln Q \rightarrow \text{Reaction Quotient}$$

Standard Gibbs free energy change found at standard condition

$$\Delta G = 0, Q_{\text{equilibrium}} = K_{\text{equilibrium}} [\text{constant}]$$

$$\Delta G^\circ = -RT \ln K_{eq} = -2.303 RT \log K_{eq}$$

$$\begin{matrix} K_{eq} > 1 & K_{eq} < 1 & K_{eq} = 1 \\ \Delta G^\circ < 0 & \Delta G^\circ > 0 & \Delta G^\circ = 0 \end{matrix}$$

If $K_{eq} = 10^5$ at 27°C then calculate value of ΔG° in Kcal/mol

$$\rightarrow -2.303 \times 2 \times 500 \times \log 10^5 = -2.303 \times 5 \times 10^3 = -11515$$

for a reaction ΔG° is -46.06 Kcal find value of K_{eq} at 1000 Kelvin

$$\Delta G^\circ = -2.303 \times R \times T \log K$$

Antilog m
 $0x = \log z$
 $m = z \times x$

$05 = \log P$
 $P = 10^5$

$05 = \ln e^x$
 $x = e^5$

$$\frac{-46.06}{10} = \frac{-2.303 \times 2 \times 1000}{1000} \log K_{eq}$$

$$\rightarrow 10 = \log 10 K_{eq} \rightarrow K_{eq} = 10^{10}$$

$$K_{eq} = \frac{e^{-\Delta G^\circ}}{RT}$$

Third law of Thermodynamics

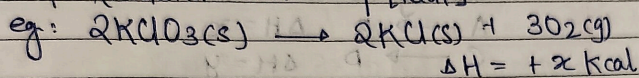
At 0 Kelvin [273.15°C] aka Absolute Temperature
 Entropy of pure perfectly crystalline solid = 0
 Exceprn: N_2O , NO , CO , CO_2

Thermochemistry

→ deal with transfer of heat b/w chemical systems

Thermochemical Reaction

→ Balanced eqn of reaction giving info abt the physical state of Reactant and Δq [Heat]



Types - Endothermic $\rightarrow \Delta H = +ve$
- Exothermic $\rightarrow \Delta H = -ve$

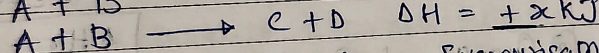
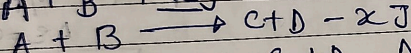
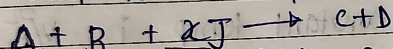
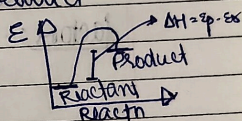
① Endothermic

→ Absorption of q

→ Stability of Reactant > Product cuz more heat is required to break the bond of reactant than product

Stable: R > or product less

Representative



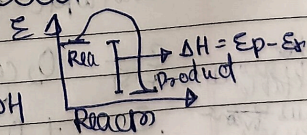
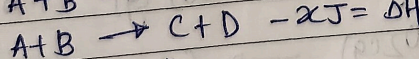
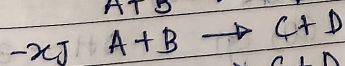
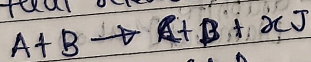
eg: fusion [combination], Phase change [vaporisation]
Photosynthesis

② Exothermic

→ evolution of heat

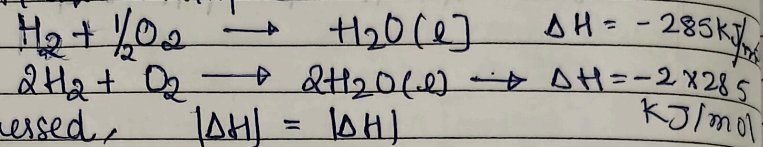
→ more stability of Product than Reactant

→ more heat released than stability of product / reactant

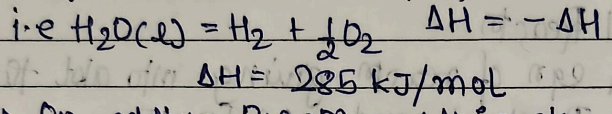


eg: Combustion, Respiration

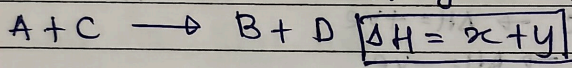
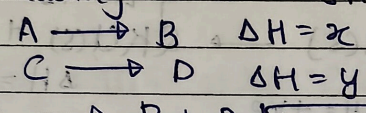
→ If Thermochemical Reactn is multiply by any No. then ΔH also multiplied



→ Reactn reversed, $|\Delta H| = |\Delta H|$



→ On adding Reactn ΔH is also added



• Heat of Reactn $\rightarrow \Delta H$ of Reactn

• Amt of heat emitted/absorbed when No. of mole of Reactant only balanced chemical reactn are completely reacted $\rightarrow \Delta H = (R)_p$

factors:- ① Condition

$\rightarrow$ constant temp i.e. V/P constant

$$\Delta E = q_v \quad \text{or} \quad q_p = \Delta H_r$$

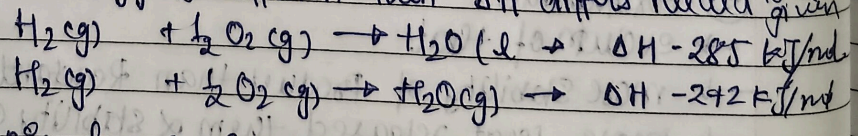
$$\boxed{\Delta H_r = \Delta E_r + \Delta n_g RT}$$

② Quantity of Substance

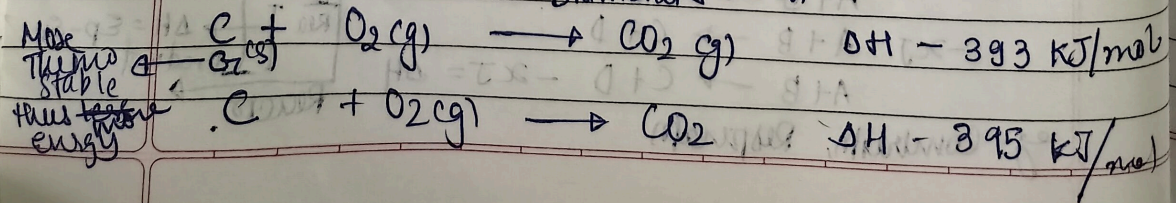
$\rightarrow$ same as Note 1:- $x(R) = x \Delta H$ when $R = \Delta H$

③ Physical state of Product

$\rightarrow$ cuz energy is different, then ΔH differs needed to be



④ Allotropic forms - Graphite, Diamond, Carbon



Temperature $\therefore$ effect by Kirchhoff's law

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p$$

$$\Delta C_p = C_{p, \text{prod}} - C_{p, \text{react}}$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

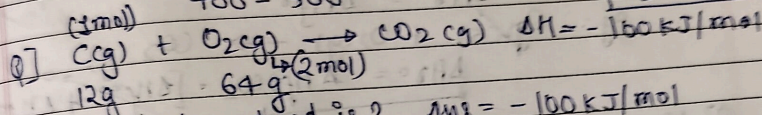
Quesn: $N_2 + 3H_2 \rightarrow 2NH_3(g)$ of 500 K.
 $\Delta H = -200 \text{ KJ}$

find ΔH at 400 Kewin. C_p for H_2 and NH_3 is 20 and 13.15

Soln
 C_p of $N_2 = 20$, C_p of $3H_2 \rightarrow 3 \times 10 = 30$, C_p of $NH_3 = 13.15$
 $\Delta C_p \rightarrow = 30 - 50 = -20$

$$30 = \frac{H_2 + 200}{400 - 500} \rightarrow -300 = \frac{H_2 + 200}{-100}$$

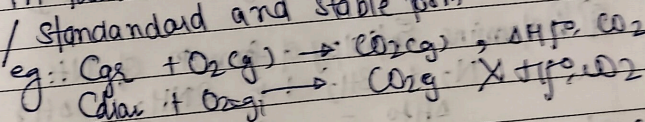
$$H_2 = -500$$



then heat produced is? Ans = -160 KJ/mol

① Enthalpy of formation [ΔH_f° or $\Delta H_{f,0}^\circ$]

- 1 mole to be formed of product
 ΔH when 1 mol. of substance is formed from its elements in their most abundant [stable] and naturally occurring / standard and stable form



Elements

C $\rightarrow$ Graphite

S $\rightarrow$ Rhombic S8

P $\rightarrow$ white P4

$H_2, O_2, N_2, F_2, Cl_2, Br_2(l), I_2(solid)$

Gas

Metals: M[solid] except Hg(l)

