[Thermo dynamic]

Thermo means heat energy
dynamic means flow

→ Thermodynamics is a branch of chemistry which deals with flow of energy. The direction of their flow and change its physical and chemical behavior

⇒ Thermodynamics doesnot tell the time of reaction.

(*) Thermo chemistry

Branch of chemistry which deals with different types of enthalpies

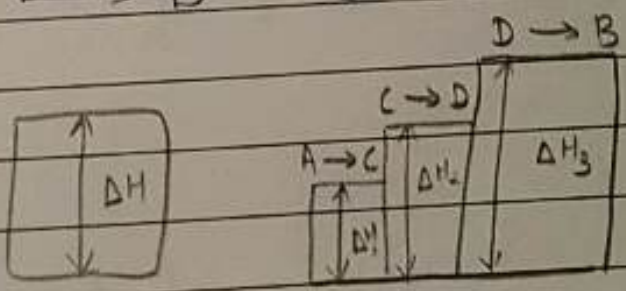
Basically enthalpy are of two types:

1. +ve (Endothermic Reaction)
2. -ve (Exothermic Reaction)

(*) Hess's Rule

According to him, the heat change in a complete chemical Reaction always remains same wheather reaction completes in one step or in multiple steps

$A \longrightarrow B = \Delta H$



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

single step $A \longrightarrow B = \Delta H$

multiple step

$A \longrightarrow C \quad \Delta H_1$

$C \longrightarrow D \quad \Delta H_2$

$D \longrightarrow B \quad \Delta H_3$

$A + C + D \longrightarrow C + D + B = \Delta H_1 + \Delta H_2 + \Delta H_3$

$A \longrightarrow B$

Unit

KJ/mole K cal/mole

(*) $\frac{J}{4.2} = Cal$

$\frac{10 J}{4.2} = 10 \text{ cal}$

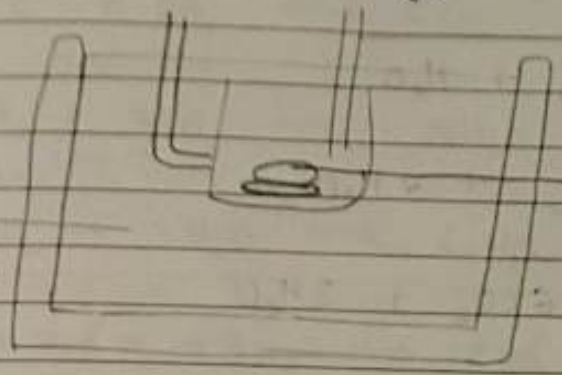
$A \longrightarrow B \quad 400 \text{ KJ}$

$B \longrightarrow A \quad -400 \text{ KJ}$

$2B \longrightarrow 2A \quad -400 \times 2 \text{ KJ/mole}$

$\frac{A}{2} \longrightarrow \frac{B}{2} \quad \frac{400}{2} \text{ KJ}$

④ Fuel Burn → Energy [Bomb calorific Meter]



$CH_4 + O_2 \longrightarrow \frac{520}{16}$ KJ/mole

12 + 4

= 16g

$= 32.5$

$H_2 + O_2 \longrightarrow \frac{120}{2}$ KJ/mole

2g

$= 60$

I Enthalpy of formation

H_2SO_4

C - same

H_2O - Half

present in elementary form

$H_2(g) + \frac{1}{8} S_8(s) + 2O_2(g) \longrightarrow H_2SO_4(l)$ $\Delta H_{f_{H_2SO_4}}$

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g)$ $\Delta H_{f_{HCl}}$

$C(s) + 2H_2(g) \longrightarrow CH_4$ $\Delta H_{f_{CH_4}}$

$\frac{1}{2} N_2 + \frac{3}{2} H_2 \longrightarrow NH_3$ $\Delta H_{f_{NH_3}}$

II Enthalpy of combustion

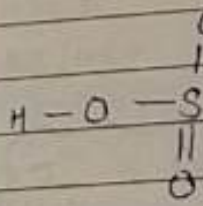
Fuel + O_2 $\longrightarrow$ CO_2 + H_2O

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$C_6H_6 + O_2 \longrightarrow 6CO_2 + 3H_2O$

$C_4H_{10} + 6.5\,O_2 \longrightarrow 4CO_2 + 5H_2O$

$H_2SO_4 \rightarrow 2H + S + 4O$



$H_2O_{(g)} \overset{100^\circ C}{\rightleftharpoons} H_2O_{(l)}$

Qu Calculate the heat of formation of Benzene (C_6H_6) if heat of combustion of C_6H_6 & CO_2 heat of CO is -393.5 and Heat of H_2O is -285.8 KJ/mole respectively

C_6H_6 ΔH_c = -3268 KJ/mole

CO_2 ΔH_f = -393.5 KJ/mole

H_2O ΔH_f = -285.8 KJ/mole

ΔH_f C_6H_6 $\quad 6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(l)}$ $\quad \Delta Hf = ?$

given (i) — $C_6H_6 + 7.5O_2 \longrightarrow 6CO_2 + 3H_2O$. ΔH_c = -3268 KJ/mol

(ii) — $C_{(s)} + O_2 \longrightarrow CO_2$ $\quad \Delta H_f$ = -393.5 KJ/mole

(iii) — $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $\quad \Delta H_f$ = -285.8 KJ/mole

6 x eq (II) + 3 x eq (III) — eq (I)

$6C + 6O_2 \longrightarrow 6CO_2$ $\Delta H = 6 \times -393.5$ ~~KJ/mole~~

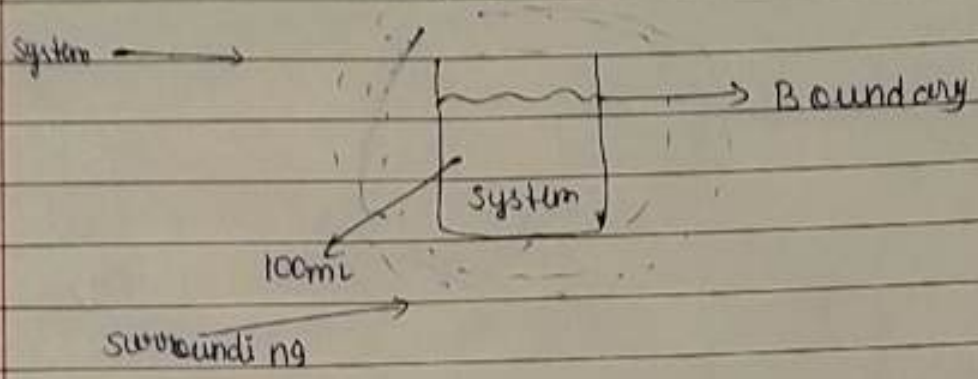
$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O$ $\Delta H = 3 \times -285.8$ ~~KJ/mole~~

$6CO_2 + 3H_2O \longrightarrow C_6H_6 + 7.2O_2$ $\Delta H = +3268$

$6C + 7.5O_2 + 3H_2 \longrightarrow 6CO_2 + 3H_2O$ $\Delta H_f = 99.6$ KJ/mole

$+ 6CO_2 + 3H_2O \quad + C_6H_6 + 7.5O_2$

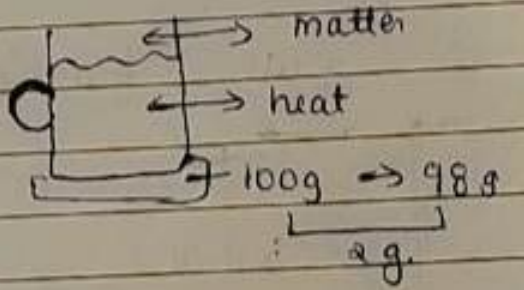
[Thermodynamics]



✱ Three types of system

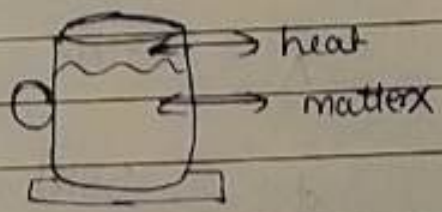
I. Open System

- a open cup of tea
- river

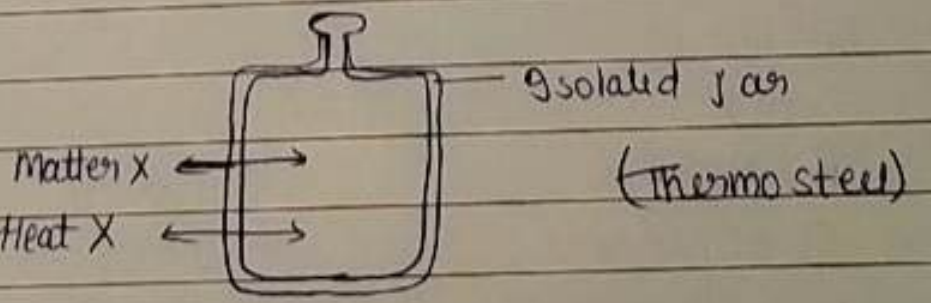


II. Close system

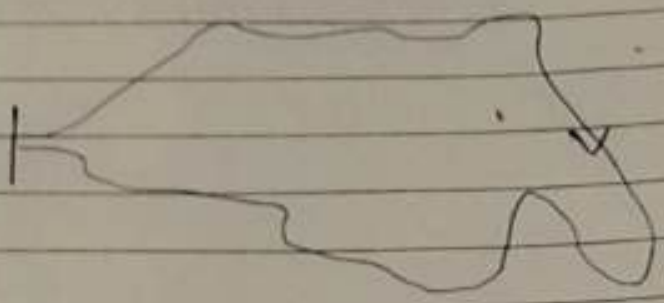
- a cup of tea with a lid



III. Isolated system



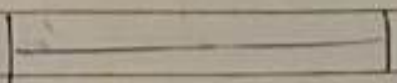
✱ Path function



→ work (w)
→ heat (q

→ petrol / energy
→ time

✱ State function



initial final

Δ → अंतर - final − initial

d → आंशिक अंतर अति सूक्ष्म

δ → अंश

$\Delta T = T_2 - T_1$
$\Delta V = V_2 - V_1$
$\Delta P = P_2 - P_1$
$\Delta S = S_2 - S_1$
$\Delta U = U_2 - U_1$
$\Delta G = G_2 - G_1$
$\Delta H = H_2 - H_1$

⇒ Intensive property

→ not depends upon matter

e.g $\frac{\text{extensive}}{\text{extensive}} = \text{intensive} = \frac{m}{vol} = P$

→ Temperature, pressure, Refractive Index, surface tension viscosity, BD, M.P, F.P, Cp Cv.

⇒ Extensive property

→ Depends upon matter

e.g Mass, volume, entropy, Gibbs free energy, heat capacity, no. of moles

✱ Ideal Gas Equation.

$PV = nRT$

P = pressure
V = volume
n = mole = $\frac{w}{Mw}$
T = Temperature

$P = \frac{n}{V} RT$ — V: volume

$P = MRT$

R (Universal Gas Constant)

- $0.0821\ L \cdot atm\ mol^{-1} K^{-1}$
- $8.314\ J\ mol^{-1} K^{-1}$
- $1.98 \approx 2\ cal\ mol^{-1} K^{-1}$

✱ Convertions

1. Pressure

S. I = N/m^2
= atm
= torr
= pascal

1 atm = 76 cm of Hg
= 760 mm of Hg
= 760 torr
= 1.013 bar
= 1.013×10^5 pascal
= 1.013×10^5 N/m^2

1 bar = 10^5 N/m^2
= 10^5 pascal

II. Temperature (K)

$$\frac{^\circ C}{100} = \frac{^\circ F - 32}{9} = \frac{K + 273}{100}$$

III. Volume = m^3

$10^3\ cm^3 = 1\ lit$
$1\ dm^3 = 10^3\ cm^3$
$1\ cm^3 = 1\ ml$
$1\ m^3 = 10^3\ lit$

(*) Heat capacity (heat holding capacity)

Amount of heat required to raise the temperature of given amount of a substance by $1^\circ C$ or $1\ K$ is called Heat capacity

$$c = \frac{q}{T} = \frac{J}{K}$$

(q = heat, T = Temperature)

↓

unit of $c = J K^{-1}$

⇒ Molar Heat capacity (holding capacity of 1 mole substance)

Amount of heat required to raise the temperature of 1 mole of substance by $1^\circ C$ or $1K$

$$C_m = \frac{q}{nT} = \frac{J}{mole\ K}$$

C_m unit $= J\ mole^{-1} K^{-1}$

⇒ Specific Heat capacity

- at constant pressure

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

$$\boxed{q_p = n C_p \Delta T}$$

$$\Delta H = n C_p \Delta T$$

(enthalpy)

- constant volume

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

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

$$\Delta U = n C_v \Delta T$$

Internal energy

⇒ Poission Ratio

$$\gamma = \frac{C_p}{C_v} \quad \frac{J K^{-1} mol^{-1}}{J K^{-1} mol^{-1}}$$

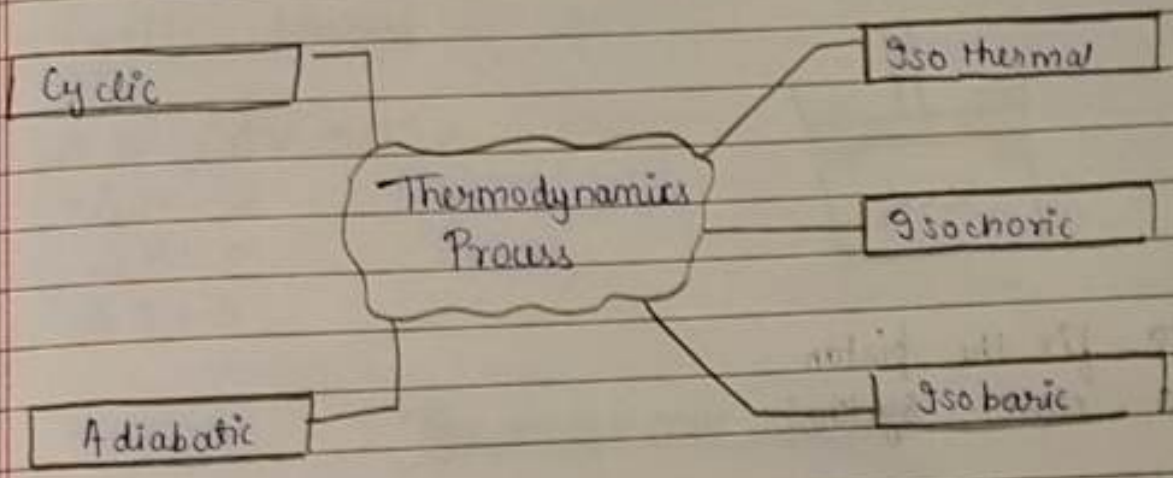
heat ratio

(unit less value)

→ Mayer's Relation

$$C_p - C_v = R$$

* Type of Thermodynamics process



I. Isothermal process

$$\Delta T = 0$$

$$T_2 - T_1 = 0$$

$$\boxed{T_2 = T_1}$$

→ q_{rev} = fully transfer

→ open system is an example of Isothermal

for Ideal gas

$$\Delta E = 0$$

$$\Delta H = 0$$

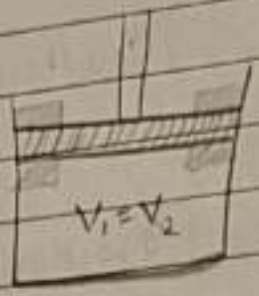
II. Isochoric process

$\Delta V = 0$

$V_2 - V_1 = 0$

$V_2 = V_1$

Work = 0



→ to fix the piston

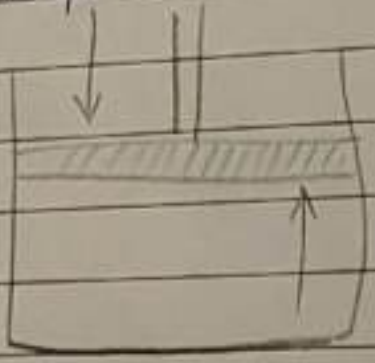
→ a close system

III. Isobaric process

$\Delta p = 0$

$p_2 - p_1 = 0$

$p_2 = p_1$



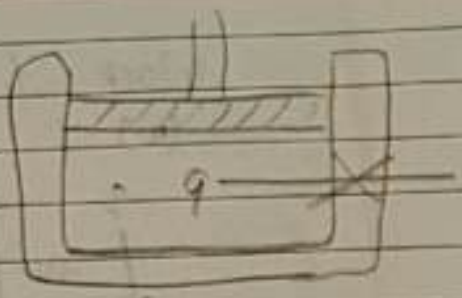
→ piston free to move

→ open system is a kind of Isobaric system

IV Adiabatic process

↓

$q = 0$



- No heat transfer

→ A isolated system is an example of adiabatic process

V Cyclic process

$\Delta E / \Delta V = 0$

$\Delta H = 0$

$\Delta P = 0$

$\Delta T = 0$

Thermodynamic process

Reversible

Irreversible

★ Quasi-static process

$P_{ext} = P_{in} \pm dP$

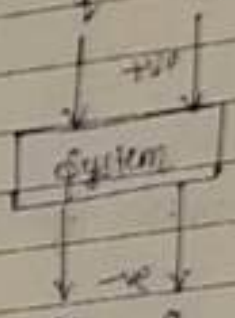
→ Ideal process

$P_{ext} = P_{in} \pm \Delta P$

→ Natural process

Work / Heat

(w) (q)



→ compression → work done on the system = +ve

→ work done by the system = -ve

Expansion → heat absorb by the system q = +ve

→ heat eliminated by the system q = -ve

Work and Heat

Heat

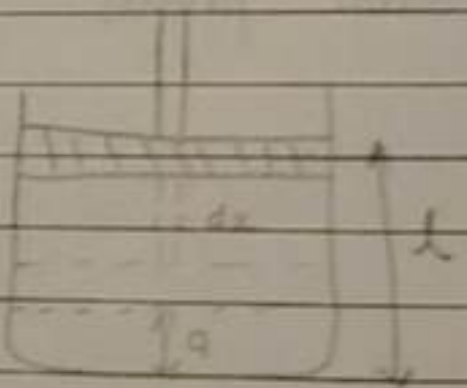
q

$q_v = n C_v \Delta T = \Delta V / \Delta E$

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

⇒ Work

→ During compression



$w = F \cdot dx$

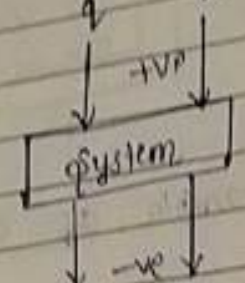
force displacement

$P = \frac{F}{A}$

$dx = l - a$

$F = P \times A$

Work / Heat
(w) (q)



w → compression → work done on the system = +ve

→ work done by the system = -ve

Expention → If q → heat absorb by the system q = +ve

→ heat eliminated by the system q = -ve

(*) Work and Heat

Heat

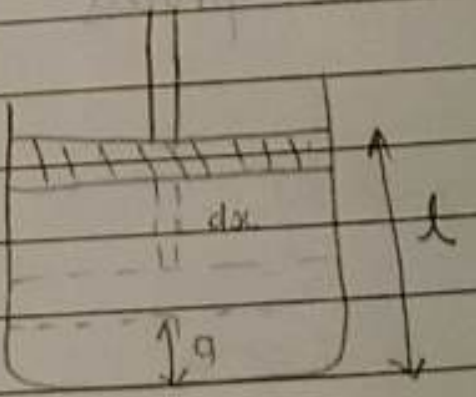
q

$q_v = n C_v \Delta T = \Delta V / \Delta E$

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

⇒ Work

→ During compression



$w = F \cdot dx$

↓ ↓

force displacement

$dx = l - q$

$P = \frac{I}{A}$

$F = P \times A$

$W = P \times A \times dx$

$W = P \times A (l_2 - l_1)$

$W = P [A \times l_2 - A \times l_1]$

A = Area of cylinder

$W = P (V_1 - V_2)$

$W = -P (V_2 - V_1)$

$W = -P \Delta V$

$\boxed{W = -P_{ext} \Delta V}$

$\Delta H = n C_p \Delta T$

$\Delta E / \Delta V = n C_v \Delta T$

$W = -P_{ext} \cdot \Delta V$

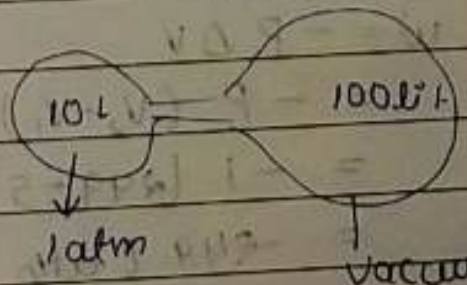
$\rightarrow C_p - C_v = R$

$\rightarrow \frac{C_p}{C_v} = \gamma$

Que 1 mole of 10 ml gas in 10 lit, 1 atm bulb it will connect to 100 lit capacity bulb at vaccume what will be the work.

$\boxed{W = 0}$

$-P \cancel{\Delta V}$



Que work during expansion of 1 mole ideal gas at constant atm pressure of 1 atm 1 lit to 5 lit

=> given = $p = 1\ atm$
$V_1 = 1\ lit$
$V_2 = 5\ lit$

$W = -P\Delta V$
$= -1 \times (5-1)$
$= -4\ L\,atm$
$\boxed{W = -4 \times 101.3\ J}$

Que 5 L contain 10 mol of O_2 gas at 27°C suddenly it break through a hole and gas escaped at the atmospheric pressure of 1 atm work during this process

$V_1 = 5\ lit$
$PV = nRT$
$V = \frac{nRT}{P}$

$W = P_{ext} = 1\ atm$
$V_2 = ?$
$R = 0.083$

$V_2 = 10 \times 0.083\ L\,atm\,mol^{-1}K^{-1} \times 300$
$\boxed{V_2 = 249\ lit}$

$W = -P\Delta V$
$= -P(V_2 - V_1)$
$= -1\,(249-5)$
$= -244\ L\,atm$

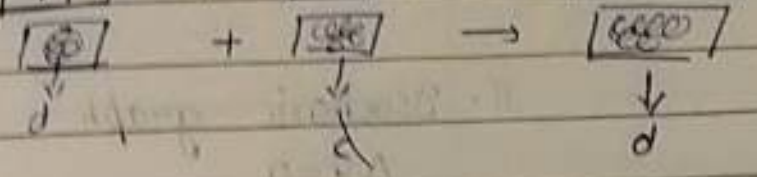
$\boxed{W = -244 \times 101.3\ J}$

⊛ Internal energy ΔE / ΔU

- → State function
- → Extension property
- → $\Delta E = E_f - E_i$
- → $E = E_{PE} + E_{KE} + E_R + E_V + E_E + E_N$

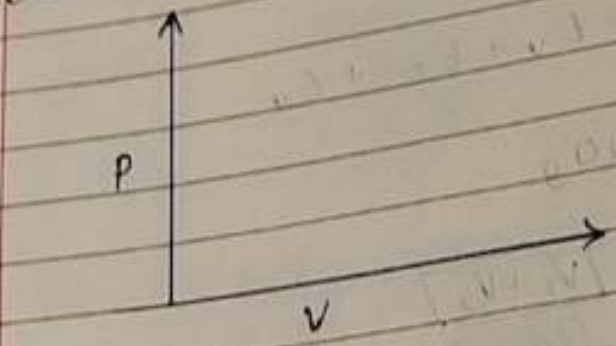
5g ✲ + 5g ✲ = 10g

V_1 + V_2 → $V_1 + V_2$



⊛ Thermodynamic graph

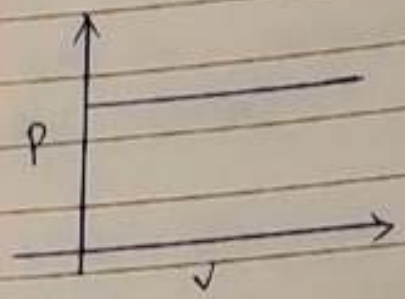
PV graph



I. Isobaric graph

$\Delta p = 0$

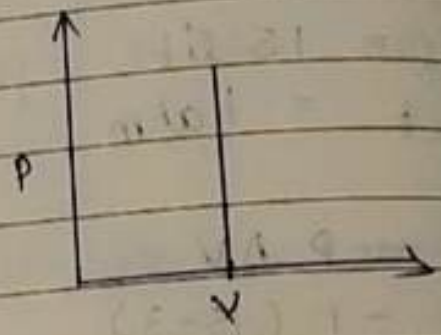
p = constant



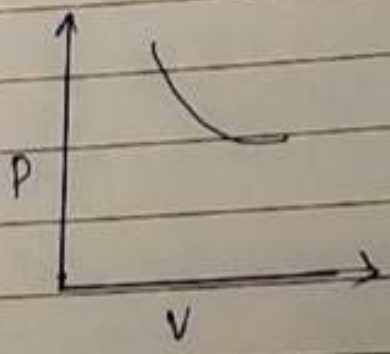
II. Isochoric graph

$\Delta V = 0$

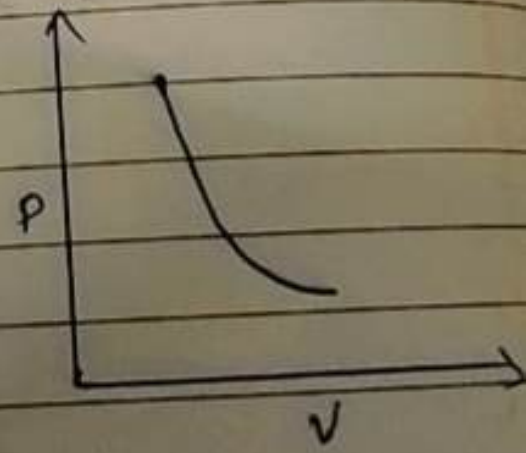
V = constant



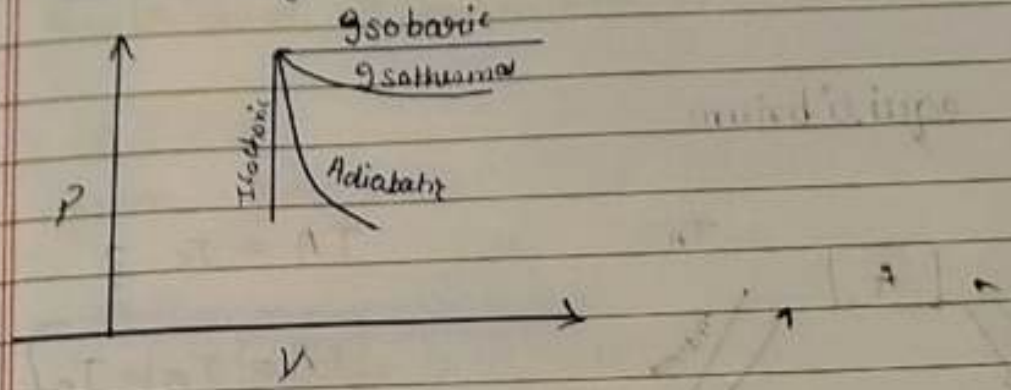
III Isothermal

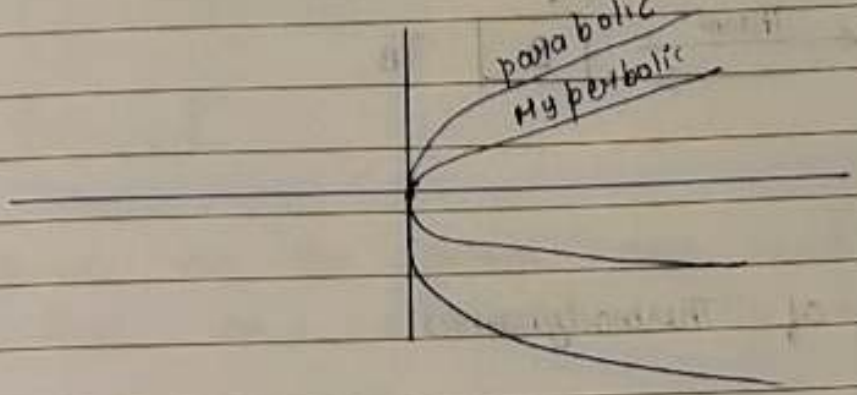


IV Adiabatic graph



Combine graph



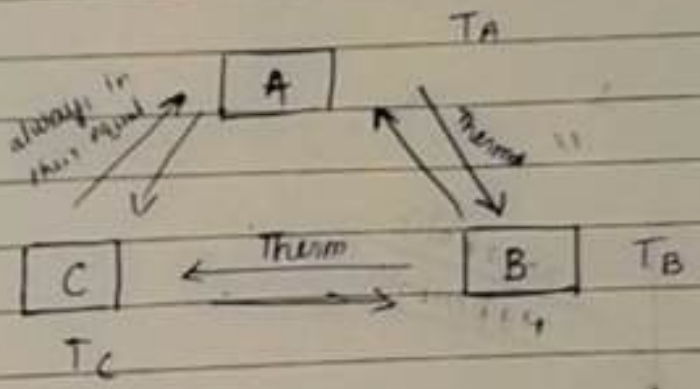


Laws of Thermodynamic

- ZLOT — Zeroth law of thermodynamic
- FLOT — First laws of thermo
- SLOT — Second law of thermo
- TLOT — Third law of thermo

ZLOT

→ Thermal equilibrium



$TA = T_C$?

$TA = T_B = T_C$

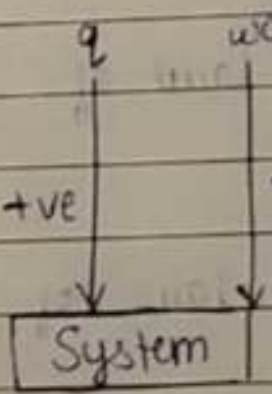
FLOT

First law of Thermodynamics

→ Based on energy conservation

→ Given By Mayer, Helmholtz

" Change in internal energy are equal to sum of heat absorbed by the system and work done on the system"



$\Delta U / \Delta E$

$$\Delta E = q + w$$

I. Isothermal Irreversible

$\boxed{\Delta E = 0}$

from Flot :-

$\Delta E = q + w$

$0 = q + w$

$\boxed{q = -w}$

$\boxed{w = -q}$

"Work done on the system are complete change into the heat and eliminated By system"

or

Heat absorb by the system get complete transfer to the workd on by the system.

II. Isochoric

$\boxed{\Delta U = 0}$

from FloT :-

$\Delta E = q + w$

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

$\Delta E = qv$

$qv = \frac{\Delta E}{\Delta U} = \boxed{nCv\,\Delta T}$

III Adiabatic (Irreversible)

$\boxed{q = 0}$

From FLOT

$\Delta E = q + w$

$\boxed{\Delta E = w}$

IV Cyclic

$\boxed{\Delta E = 0}$

From FLOT

$\Delta E = q + w$

$0 = q + w$

$\boxed{w = -q}$

V Isobaric ∵ P = const

$\Delta P = 0$

From FLOT

$\Delta E = q + w$

$\Delta E = q_p - P\Delta V$

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

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

$q_p = E_2 - E_1 + PV_2 - PV_1$

$= E_2 + PV_2 - E_1 - PV_1$

$q_p = E_2 + PV_2 - (E_1 + PV_1)$

$q_p = H_2 - H_1$

$\boxed{\Delta H = H_2 - H_1}$

↓ ↓ ↓

change in enthalpy enthalpy of

enthalpy of product Reactant

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

$PV = nRT$

$\Delta (PV) = \Delta nRT$

$\Delta H = \Delta E \quad \Delta (nRT)$

$nC_p\Delta T = nC_v\Delta T + nR\Delta T$

$C_p = C_v + R$

$\boxed{C_p - C_v = R}$

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

$$1 - \frac{1}{\gamma} = \frac{R}{C_p}$$

$$C_p = \frac{R}{1 - \frac{1}{\gamma}}$$

$$\frac{R}{\frac{\gamma - 1}{\gamma}}$$

$$\boxed{C_p = \frac{R\gamma}{\gamma - 1}}$$

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

$$\gamma - 1 = \frac{R}{C_v}$$

$$\boxed{C_v = \frac{R}{\gamma - 1}}$$

$\Delta H = \Delta E + \Delta PV$

$\Delta H = \Delta E + \Delta n_g RT$

for gas eq.

$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$

Δ = final - initial

= P - R

$\Delta n_g = 2 - 4 = -2$

$\Delta H = \Delta E - 2RT$

$\Delta H < \Delta E \rightarrow \Delta ng < 0$
$\Delta H > \Delta E \rightarrow \Delta ng > 0$
$\Delta H = \Delta E \rightarrow \Delta ng = 0$

→ $PCl_{3(g)} + Cl_{2(g)} \longrightarrow PCl_{5(g)}$

2 1

$\Delta ng = 1 - 2 = -1$

$\boxed{\Delta H < \Delta E}$

→ $H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$

2 2

$\Delta ng = 2 - 2 = 0$

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

→ $2SO_{3(g)} \longrightarrow 2SO_{2(g)} + O_{2(g)}$

2 3

$\Delta ng = 3 - 2 = 1$

$\boxed{\Delta H > \Delta E}$

for any ideal gas

$\Delta H = \Delta E + nRDT$

for P and T const

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

for gas equation

Pressure and volume Both are variable

$\Delta H = \Delta E + \Delta PV$

$\Delta H = \Delta E + (P_2V_2 - P_1V_1)$

at const Volume

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

for const pressure

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

⊛ Workdone

I. In Isothermal (irreversible)

$\Delta E = 0$

$q = -w$

$w = -P_{ext}\,\Delta V$

II. Isobaric

$P = \text{const}$

$w = -P\Delta V$

III. Isochoric

$\Delta V = 0$

$w = 0$

iv Adiabatic

$[q = 0]$

$\Delta E = w$

$[w = \Delta E = -P_{ext} \Delta V]$

(8) log

→ $\log_e = \ln$ (natural log)

→ $\log_{10} = \log$

$\ln x = 2.303 \log x$

$\log x + y$

→ $\log (x \times y) = \log x + \log y$

→ $\log \frac{x}{y} = \log x - \log y$

→ $\log x^y = y \log x$

i. $\log_{10} 1 = 1$

ii. $\log 2 = 0.3010$

iii. $\log 3 = 0.477$

iv. $\log 4 = \log 2^2 = 2 \times \log 2$
$= 2 \times 0.3010$

v. $\log 5 = 0.69$

vi $\log 6 = \log (3 \times 2)$
$= \log 3 + \log 2$
$= 0.477 + 0.3010$

vii $\log 7 = 0.84$

viii $\log 8 = \log 2^3 = 3 \log 2$
$= 3 \times 0.3010$

ix $\log 9 = \log 3^2 = 2 \log 3$
$= 2 \times 0.477$

x. $\log 10 = 1$

Work for isothermal reversible

$\Delta E = 0$

from FLOT

$q = -w$

$dw = -P\,dV$

$PV = nRT$

$P = \frac{n}{V} RT$

$$\int dw = \int_{V_1}^{V_2} -\frac{nRT}{V}\,dV$$

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V}\,dV$$

$$= -nRT \left[\ln V\right]_{V_1}^{V_2}$$

$$= -nRT \left[\ln V_2 - \ln V_1\right]$$

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

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

$$P_1V_1 = P_2V_2$$

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

$$w = -2.303\ nRT \log_{10} \left(\frac{P_1}{P_2}\right)$$

$$q = -w$$

$$\boxed{q = 2.303\ nRT \log_{10} \frac{P_1}{P_2}}$$

$$q = 2.303\ nRT \log_{10} \left(\frac{V_2}{V_1}\right)$$

Work done in Adiabatic process [for reversible, irreversible]

Adiabatic $q = 0$

from FLOT

$\Delta U = q + W$

$\Delta U = W$

$$\Delta U = W = nC_v \Delta T$$
$$= nC_v (T_2 - T_1)$$

$$PV = nRT$$
$$T_1 = \frac{P_1V_1}{nR}$$

$$T_2 = \frac{P_2V_2}{nR}$$

$$\Delta U = W = nC_v \left(\frac{P_2V_2}{nR} - \frac{P_1V_1}{nR}\right)$$

$$W = \frac{nC_v}{nR}(P_2V_2 - P_1V_1)$$

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

$$\gamma - 1 = \frac{R}{C_v}$$

$$\frac{C_v}{R} = \frac{1}{\gamma - 1}$$

$$w = \Delta U = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

PV function

PV^{γ} = constant

$TV^{\gamma-1}$ = constant

$Tp^{1-\gamma}$ = constant

only for adiabatic

FLOT

→ $\Delta U / \Delta E = q + w$

→ $w = - P_{ext} \Delta V$

→ $w_{\text{ISOTHERMAL}} = 2.303\ nRT \log_{10} \frac{V_2}{V_1}$

→ $w = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

→ $\Delta H = \Delta E + \Delta n_g RT$

→ $\Delta H = n C_p \Delta T$

→ $\Delta E / \Delta U = n C_v \Delta T$

⑧ Entropy

The thermodynamic quantity which is used to measure the degree of Randomness or disorderness is Rnown as Entropy

→ More disorder, higher is the entropy

→ The ratio of heat absorbed by the system in isothermal and reversible and temperature

→ Its unit are JK^{-1}

→ when temperature increase, entropy increase
when pressure decreases, entropy increases.

→ some famous example of entropy

→ Entropy of Universe, entropy increases

→ Entropy of graphite is higher than the entropy of diamond

→ during ionisation, ions are free to move than their entropy increases

→ On the boiling of egg, entropy decreases

→ stretching of rubber, entropy decreases

→ Precipitation of any salt, entropy decrease

→ Entropy during phase change is converted into the ΔH

gas > liq > solid

$\Delta S = \frac{q_{rev}}{\Delta T}$, $\Delta S = \frac{q_{rev}}{T}$ J/K

→ state function
→ Extensive property.

ΔS graphite > ΔS diamond

Examples: $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$\Delta n_g = P - R$
$= 2 - 4$
$= -2$

Que. $\Delta H > \Delta E$

Que. ΔS < +ve, -ve, 0

$\Delta H = \Delta E + \Delta n_g RT$

Δn_g = +ve

$\Delta H > \Delta E$

Ans. $\Delta H < \Delta E$

Ans. $\Delta S = S_{f_1} - S_{in}$

= liq - more ;

$\boxed{\Delta S = -ve}$

$N_2(g) \rightleftharpoons N_2(g)$

at 273 K — at 300 K

less — high

$\Delta S = f - i$

$= P - R$

$=$ High - low

$=$ +ve

$N_2(g) \rightleftharpoons 2N(g)$

at 900K — 900 K

ΔS = +ve

$\Delta S = \frac{q_{rev}}{900\ K}$

$AgNO_3(aq) + KCl(aq) \rightarrow AgCl \downarrow + KNO_3(aq)$

$N_2 \rightleftharpoons N_2$

5 atm — 2 atm

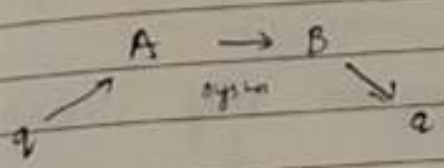
ΔS = +ve

ΔS = Adiabatic

$q = 0$

$\boxed{\Delta S = 0}$ isoentropic process

∴ In any system the total entropy are zero



Net change in entropy

$$\Delta S = + \frac{q_{in}}{T} - \frac{q_{out}}{T}$$

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

Seed → Tree

Big bang

Universe → explode

+ve

$$\Delta S = \frac{q_{rev}}{T}$$

Isothermal

$\Delta U = 0$

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

$$\Delta S = 2.303\ nR \log_{10} \frac{V_2}{V_1}$$

$$\Delta S = 2.303\ nR \log_{10} \left(\frac{P_1}{P_2}\right)$$

ΔH_{vap}

water $\rightleftharpoons$ steam

at 100°C

$\Delta S = \frac{\Delta H_{vap}}{T}$

ice $\rightleftharpoons$ water

0°C

$\Delta S = \frac{\Delta H_{fusion}}{T}$

for isothermal process

$\Delta S = \frac{q_v}{T}$

$\Delta S = \int \frac{n C_v dT}{T}$

$= n C_v \int_T^{T_2} \frac{1}{T} dT$

$\Delta S = n C_v [\ln T]_{T_1}^{T_2}$

$= n C_v [\ln T_2 - \ln T_1]$

$= n C_v \ln \frac{T_2}{T_1}$

$\Delta S = 2.303 \, n C_v \log_{10} \left(\frac{T_2}{T_1}\right)$

$\Delta S_{universal}$ = non spontaneous = -ve
spontaneous = +ve
reversible = 0

* Gibbs free energy
↓
useful work

G ⟷ state function
Extensive property

$\Delta G = G_2 - G_1$

spontaneous = ΔG = -ve
non spontaneous = Δh = +ve
Equilibrium = $\Delta G = 0$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Assume

ΔH → + Endothermic (+10)
- Exothermic (-10)

ΔS → +ve = (+1)
-ve = (-1)

Temp → high = 50
low = 5

- $\Delta H = +ve$
  $\Delta S = +ve$
  temp high

  $\Delta G = +10 - (+1) \times 50$
  $= +10 - 50 = -40$

- $\Delta H = +ve$
  $\Delta S = +ve$
  temp low

  $\Delta G = 10 - (+1) \times 5 = +5$

- $\Delta H = -ve$
  $= -10$
  $\Delta S = +ve$
  $= +1$
  temp high
  50

  $\Delta G = -10 - (+1 \times 50) = -60$

- $\Delta H = -ve$
  $= -10$
  $\Delta S = +ve$
  $= +1$
  temp low
  5

  $\Delta G = -10 - 1 \times 5$
  $= -15$

- $\Delta H = -ve$
  $= -10$
  $\Delta S = -ve$
  $= -1$
  temp high
  50

  $\Delta G = -10 - (-1 \times 50) = +40$

⊙ ΔH = -ve
= -10 temp low
ΔS = -ve
= -1

ΔG = -10 - (-1 × 50) = -5

⊙ ΔH = +ve
= +10 low temp = 50
ΔS = -ve
= -1
ΔG = 10 - (-1 × 50)
= +60

S.No	ΔH	ΔS	temp	ΔG	Condition
1.	+ve	+ve	high	-ve	spontaneous at high temp
2.	+ve	+ve	low	+ve	Non spontaneous at low temp
3.	-ve	+ve	high/low	-ve	Always spontaneous at any temp
4.	-ve	-ve	low	-ve	spontaneous at low temp
5.	-ve	-ve	high	+ve	non spontaneous at high temp
6.	+ve	-ve	high/low	+ve	non spontaneous at any temp

$\Delta G = \bullet - nFE_{cell}$ ⟶ Emf of cell

$\Delta G^\circ = -nFE^\circ_{cell}$ ⟶ Emf of standard cell

↓

Gibbs Haelmond function

$$G^\circ = -2.303\,RT \log_{10} K_s$$

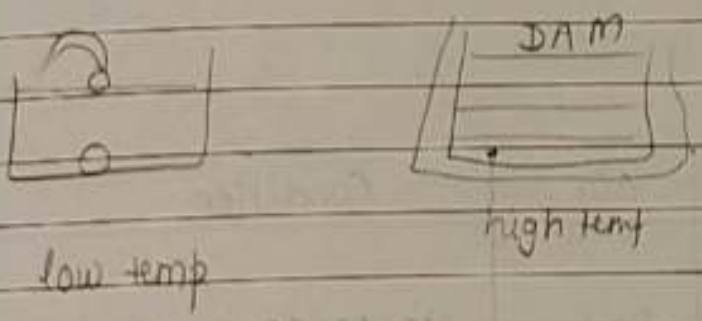


Illustration : 1 g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere. the volume increase from 1 ml to 1671 ml. The heat of vaporization at this pressure is 540 cal g^{-1}. Find the increase in internal energy of water (1L atm = 101 J)

⇒ given $P = 1$ atm

$V_1 = 1$ ml

$V_2 = 1671$ mL

$q = 540$ cal/g

$= 540 \times 4.2$

$q = +2268$ J

$W = -P\Delta V$

$= -1(1671-1)$

$= -\frac{1670}{1000}$ L atm $\times 101 = J = -168.71$ J

FIOT

$\Delta U = q + w = +2268 - 168.71$

$= +2099.33\ J$ //

Illustration 2 A gas occupies 2L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy

$V_1 = 2$ lit , $V_2 = 2.5$ l

$q = +300$, $P = 1$ atm

from FIOT

$\Delta V = q + w$

$w = -P\Delta V$

$= -1\ (2.5 - 2)$

$= -0.5$ l atm

$w = -101.3 \times 0.5$

$= -50.65$

$\Delta V = +300 - 50.65$

$\Delta V = +249.35\ J$

NW 3 A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from the volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surrounding. Calculate the change in internal energy of system

⇒ given $q = +600\,J$

$V_1 = 2L$

$V_2 = 12L$

$P = 1\,atm$

$W = -P\Delta V$

$= -1\,(12-2)$

$= -10 \times 101.3$

$W = -1013.5$

$q = +600$

$\Delta U = q + w$ — from flot

$= 600 - 1013$

$\boxed{\Delta E = -413.5}$

4 Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant pressure of 4 atm. Calculate q, w and ΔE ($R = 0.082\ L\ atm\ mol^{-1}\ K^{-1}$)

$\Delta E = 0$ isothermal

$\boxed{q = -w}$ from flot

$w = -P\Delta V$

$PV = nRT$

$V = \frac{nRT}{R}$

$n = 2\,mol$, $P = 2\,atm$, $T = 27°C + 273 = 300K$

$V_1 = \frac{2 \times 0.0821 \times 300}{2}$

$V_1 = 24.6$ Lit

$V_2 = \frac{24.6}{2} = 12.3$ lit

$w = -P\Delta V$

$= -4 \times (12.3 - 24.6)$

$= +4 \times 12.3 - 49.2$ L atm

5. A system is provided with 100 J of heat work done on the system is 20 J what is the change in internal energy

$q = +100$

$w = +20$

$\Delta E = q + w$ from flat

$\Delta E = 100 + 20$

$\boxed{\Delta E = 120 J}$

1. The heat of reaction for $C_{10}H_8(s) + 12\,O_2(g) \rightarrow 10\,CO_2(g) + 4\,H_2O(l)$ at constant volume is -1228.2 K cal at 25°C. Calculate the heat of Reaction of constant pressure and at 25°C

given $\Delta H = q_p = ?$

$\Delta E = q_v = -1228.2 \times 10^3$ cal

$\Delta H = \Delta E + \Delta ng\, RT$

$\Delta ng = P - R$

$= 10 - 12$

$= -2$

$\Delta H = -1228.2 - 2 \times 2 \times 298 \times 10^{3}$

$= 1229392$ cal

$\Delta H = 1229.392$ K cal

2. For the reaction at 25°C

$NH_3(g) \rightarrow \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$; $\Delta H^\circ = 11.04$ K cal

Calculate ΔE° of the reaction of the given temp

$\Delta H = 11.04 \times 10^{3} = 11040$ cal

$\Delta ng = \frac{3}{2} + \frac{1}{2} = 1$

$= 2 - 1 = 1$

$\Delta H = \Delta E + \Delta ng\, RT$

$+1 \quad 2 \times 298$

$\Delta E = \Delta H - \Delta ng\, RT$

$= 11040 - 1 \times 2 \times 298$

$= 10440$ cal

$= 10.44$ K cal

3. At 27°C the internal energy change of Reaction

$H_2(g) + O_2(g) \longrightarrow 2H(l)(g)$ is 2 cal what is the enthalpy change of this Reaction

Sol $T = 27\,^{\circ}C$

$= 27 + 273$

$= 300\,K$

$\Delta H = \Delta E + \Delta n_g RT$

$\Delta n_g = 0$

$\Delta H = \Delta E$

$\Delta E = 2\,cal$

$\boxed{\Delta H = 2\,cal}$

4. $\Delta U / \Delta E = -885.4 \times 10^3$

$1 CH_4(g) + 2O_2(g) \longrightarrow 1 CO_2(g) + 2H_2O(l)$

$\Delta n_g = 1 - (2+1) = -2$

$T = 298\,K / 25\,^{\circ}C$

$\Delta H = \Delta E\, \Delta n_g RT$

$= -885.4 \times 10^3 \times -2 \times 8.314 \times 298$

$= 892017$

$= 892.017\,KJ$

5. $q_v = n C_v \Delta T$

$n = 5\,mol$

$\Delta T = T_2 - T_1 = 273 + 20 - 273 + 10$

$\Delta T = 10^{\circ}$

$q_v = \Delta E = 5 \times 5.03 \times$

$= 251\,cal$

$C_p = 7.03$

$C_p - C_V = R$

$C_p - R = C_V \Rightarrow 7.03 - 2 = C_V$

$5.03 = C_V$

2. $\Delta E = q + w$ from FIOT

$\Delta E = 0$ → isothermal

$q = -w$

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

$R = 2$ cal

$n = 1$

$T = 273 + 27 = 300^\circ$

$w = -2.302 \times 1 \times 2 \times 300 \times \log_{10} \frac{2}{10} 5$

$= -2.302 \times 1 \times 2 \times 300 \times \log_{10} (5)^{-1}$

$= +2.303 \times 1 \times 600 \times 0.699$

$= 2.303 \times 600 \times 0.7$

$= 967.26$ cal

$q = -w$

$= -967.26$ cal

3. $1 dm^3 = 1$ lit

$V_1 = 3$ lit

$V_2 = 5$ lit

$P = 3$ atm

Work $= -P\Delta V$

$= -3(5-3)$

$= -3 \times 2$ latm

$= -6$ atm

$= 6 \times 101.3$ J

$= -607.8$ J

$w = nc\Delta T$

↓

$J\,mol^{-1}K^{-1}$

c for 1 mole $= 4.184 \times 18$ ← molecular mass of H_2O

$= 75.312$

$w = n\,c\,\Delta T$

$\frac{w}{nc} = \Delta T$

$\frac{607.8}{10 \times 75.312} = \Delta T$

$0.8070 = \Delta T$

$0.8070 = T_2 - T_1$

$0.8070 + T1 = T_2$

$0.8070 + 290 = T_2$

$\boxed{290.8070 = T_2}$

4. $q = 0$

$\Delta E = w$ from FLOT

$w = \Delta E = n C_v \Delta T$

$= 3 \times 27.5 \times (250 - 200)$

$= 3 \times 27.5 \times 50$

$= 15.0 \times 27.5$

$= 4125J$

$= 4.125kJ$

5. (i) $w = -2.303\, nRT \log_{10} \frac{V_2}{V_1}$

$w = -2.303 \times 10 \times 8.134 \times 300 \times \log_{10} \frac{246}{24.6}$

$= -2.303 \times 10 \times 8.134 \times 300 \times 1$

$= -57441\ J$

$= -57.441\ kJ$

(ii) $w = -P\Delta V$ $\quad w = -P\Delta V$

$= -10\ (V_2 - V_1)$

$= -10 \times (246 - 24.6)$ latm

$= -10 \times 221.4 \times 101.3$ J

$= -224278\ J$

$= -224.278\ kJ$

(iii) $w = 0$ $\quad (1\,dm^3 = 1\,lit)$

6. $w = -P\Delta V$

$= -2\ (40 - 5)$

$= -2 \times 35$

$= -70 \times 101.3$

$= -7091\ J$

(iv) $w = -2.303\, nRT \log_{10} \frac{V_2}{V_1}$

$= -2.303 \times 2 \times 8.314 \times 298 \times \log_{10} \frac{40}{8}$

$= -2.303 \times 2 \times 8.314 \times 298 \times \log_{10} 2^3$

$= -3 \times 2.303 \times 2 \times 8.314 \times 298 \times \log 2$

$= -3 \times 2.303 \times 2 \times 8.314 \times 298 \times 0.3010$

$= -10304\ J$

$= -10.304\ kJ$

1. $\Delta H_{vap} = q_{rev}$

liq $\rightleftharpoons$ gas

$\Delta S = \frac{q_{rev}}{T}$

$= \frac{40.8 \times 10^3}{373}$ J mol^{-1} K

$= 109.38$ J mol^{-1} K^{-1}

2. solid $\rightleftharpoons$ liquid

$\Delta H_{fusion} = q_{rev}$

$\Delta S = \frac{\Delta H_{fusion}}{T} = \frac{6 \times 10^3}{273}$

$\Delta S = 21.97$ J mol^{-1} K^{-1}

3. liq $\rightleftharpoons$ vap

$\Delta H_{vap} = +ve$

$q_{rev} = 26 \times 10^3$

$\Delta S = \frac{2.6 \times 10^3}{273 + 35} = \frac{2.6 \times 10^3}{308}$

$= +84.41$

vap $\rightleftharpoons$ liq

$\Delta H_{con.} = -ve$

$\Delta S = -84.41$

1. $\Delta H = 40.63 \times 10^3$
$= 40630$

$\Delta S = 100$

$T = 27^\circ C + 273$
$= 300 K$

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

$\Delta G = 40630 - 300 \times 100$
$= 40630 - 30000$

$\boxed{\Delta G = +10630 J}$

Not possible

2. $\Delta H = -11.7 \times 10^3$
$= -11700 J$

$\Delta S = -105 J$

$T = 25^\circ C + 273$
$= 298 K$

$\Delta G = \Delta H - T\Delta S$
$= -11700 - 105 \times 298$

$\Delta G = +195.90 J$

$\Delta G = +ve$ (non-spontaneous)

3. $\Delta G = -2.303 RT \log_{10} K_c$

$\Delta H = 77.2 \times 10^3$
$= 77200 J$

$\Delta S = 122 J\ mol^{-1} K^{-1}$

$T = 400$

$\Delta G = 77200 - 122 \times 400$

$\Delta G = 28400$

$28400 = -2.303\ RT \log_{10} K_c$

$$\frac{28400}{-2.303 \times 8.314 \times 400} = \log_{10} K_c$$

$-3.7 = \log_{10} K_c$

$K_c = \text{anti log}\ (-3.7)$

4. $\Delta G = -ve$

$\Delta G < 0$

$\Delta H - T\Delta S < 0$

$\Delta H < T\Delta S$

$\frac{\Delta H}{\Delta S} < T$

$\frac{+95400}{+198.3} < T$

$481\ K < T$

-273

$\boxed{208^\circ C < T}$

5 $\Delta < 0$ spontaneous

$\Delta G = 40630 - 108.8 \times 300$

$\boxed{\Delta G = +7490\ J}$ Not feasible

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

$= 40630 - 100 \times 300$

$= 40630 - 30000$

$\boxed{\Delta G = +10630}$ Not possible

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

$= -12550 - 5 \times 290$

$= -14000$

$\boxed{\Delta G = -14\ kJ}$ Spontaneous.

8. $\Delta G < 0$

$\Delta H - T\Delta S < 0$

$\boxed{\Delta H < T\Delta S}$