Thermodynamics.

Thermo = heat   dynamic = motion.

heat change in physical and chemical processes is studies in thermodynamics.

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \qquad \Delta H = +ve \qquad \text{Endothermic.}$$

$$H_2O_{(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -ve \qquad \text{Exothermic.}$$

⟹ We study about various form of energy.
- ⟹ Heat   ⟹ Work
- ⟹ internal energy   ⟹ enthalpy.
- ⟹ Gibbs free energy   ⟹ Helmholtz free energy.

⟹ feasibility. – whether the process proceed or not.

⟹ spontaneous – which takes place on it's own withount any external force.

Ex. Expansion of gas from high pressure to low pressure.

⟹ efficiency of <u>heat engine</u>

↳ heat energy $\xrightarrow{\text{converted to}}$ Work energy.

Drawbacks
- → ~~Draw~~ Rate of reaction – X
- → mechanism – X.

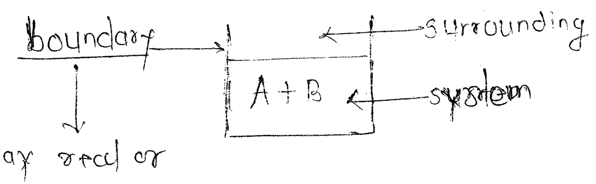
$\Delta H = +ve$ – stronger bond going to <u>break</u> – endothermic reaction

stronger bonds going to <u>form</u> – <u>exothermic</u> reaction = $\Delta H = -ve$.

Terms used in thermodynamics.
⟹ system – part of universe which is under thermodynamic observation

⟹ surrounding – other than system, remaining part is called surrounding.

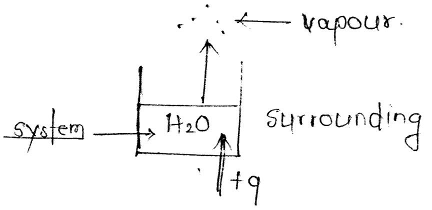
syt + surrounding = universe.



it may real or imaginary.

Systems types – depending upon nature of boundary.
- → open system
- → closed system
- → isolated system

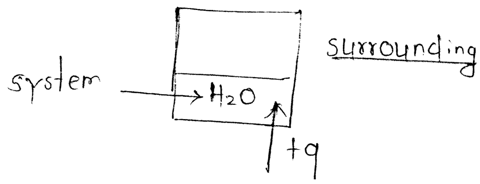
open system



Heat exchange ✓ } open system.
Matter exchange ✓ }

Ex - boiling of water in open beaker.

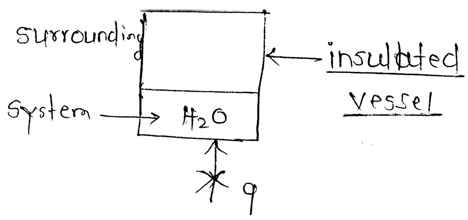
Closed system.



Heat exchange ✓ } closed system
Matter exchange × }

Ex- boiling of water in closed vessel.

Isolated system



Heat exchange × } isolated system.
Matter exchange × }

state of system :- The system is said to be in a particular state. if all its properties —not changing with time.

10 AM	11 AM	11.30 AM.
25°C	25°C	25°C.
1 atm	1 atm	1 atm
2L	2L	1 L.

$\underbrace{10\text{ AM},\ 11\text{ AM}}_{\text{same state}}$ — thermodynamic properties — initial → final.

Thermodynamic properties

↓

amount of substance

- Extensive (✓)
  ⇒ length, mass, area, volume, internal energy, enthalpy, G, A, C
- Intensive (×)
  ⇒ conc.,

Extensive properties : E/U - internal energy

m - mass
l - length
A - Area
C - heat capacity

H - enthalpy
G - Gibbs free energy
A - Helmholtz free energy
C - heat capacity.
n - amount of substance
V - volume
F - force.

Intensive properties

- concentration $c = n/V$
- density $\rho = m/V$
- pressure $P = \frac{F}{A}$
- temperature.
- B.P, M.P, Freezing point.
- pH (depend upon conc.).
- electrode potential (depends upon conc.)

{Ratio of two extensive properties is intensive property.}

- C_n : molar heat capacity
- C_s : specific heat capacity.

⟹ Extensive properties are said to be additive.

Example 1 mol, U = 10 unit.

2 mol, U = 10×2 = 20 Unit.

⟹ If a properties are expressed per mole, per unit area, per gram, per unit area are intensive properties.

Example $C_s = \frac{C}{m}$ — specific heat capacity

$C_n = \frac{C}{n}$ — molar heat capacity

molar internal energy

Examples 2 mole, U = 10 unit 10/2 = 5 unit

10 mole, U = 50 unit. 50/10 = 5 unit

Path function and state function.

path function - change in properties depends on path followed.

{Heat & Work are two path function}

Example process A ⟶ D.

path-I A ⟶ C ⟶ D.

path-II A ⟶ B ⟶ D.

} give different changes in energy.

State function - change in properties depends only on initial & final state whatever may be the path followed by the system.

Example E/U

H

S

G

A

T

P

Work & heat

Work : ordered form of energy

$\boxed{\text{system}} \longleftrightarrow \boxed{\text{surrounding}}$

energy ~~Heat~~ exchange depends upon pressure difference

$P_{system} > P_{surrounding}$ $\Rightarrow$ Expansion take place.

$\Rightarrow$ Work done by the system on surrounding

$\Rightarrow$ $W = -ve$

$\Rightarrow$ system energy (E/U) decreases.

$P_{system} < P_{surrounding}$ $\Rightarrow$ compression

$\Rightarrow$ Work done on the system by the surrounding

$\Rightarrow$ $W = +ve$

$\Rightarrow$ system's energy (E/U) increases.

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

$\Rightarrow$ Expansion $\quad \Delta V = +ve. \quad \therefore W = -ve \quad U\downarrow \quad$ W done by system

$\Rightarrow$ compression $\quad \Delta V = -ve \quad \therefore W = +ve. \quad U\uparrow \quad$ W done on system.

Heat : disordered form of energy.

$\boxed{\text{system}} \longleftrightarrow \boxed{\text{surrounding}}$.

~~heat~~ energy exchange depend upon temp difference.

$T_{sys} > T_{surrounding}$ $\Rightarrow$ heat is evolved by the system

$\Rightarrow$ $q = -ve$.

$\Rightarrow$ system internal energy decrease. $E/U \downarrow$

$T_{sys} < T_{surrounding}$. $\Rightarrow$ heat is absorbed by the system

$\Rightarrow$ $q = +ve$

$\Rightarrow$ system's internal energy increases. $E/U \uparrow$

Internal energy — sum of all forms of energy of the system.

$U = R.E + V.E + T.E + K.E + P.E + \underline{E.E} + \ldots$

↳ electronic energy.

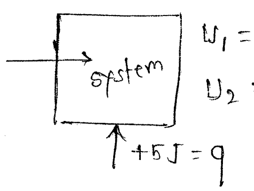
{ All thermodynamic properties, exact value of these are not possible to calculate experimentally but change in them can be calculated. }

	Exact value		Change in Energy		
unable to calculate exact values experimentally	U	×	ΔU	✓	change may be calculated experimentally.
	H	×	ΔH	✓	
	G	×	ΔG	✓	
	A	×	ΔA	✓	
	S	×	ΔS	✓	

$\underline{\Delta U}$ - change in heat content during a process at $\underline{\text{constant volume}}$.

$\boxed{q_V = \Delta U}$ —— closed system.

closed system (V = constant).



$U_1 = 10\,J$

$U_2 = 15\,J$

$\Delta U = 15 - 10 = 5\,J.$

$\Delta V = 0$

V = constant

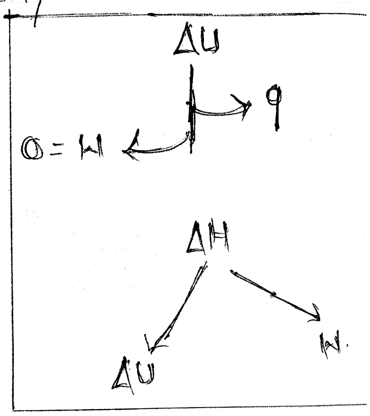
$\boxed{W = 0}$

⟹ $R \longrightarrow P + \text{heat } (q)$ [Exothermic]
$\Delta U = -ve$ $q = -ve$

⟹ $R + \text{heat} \longrightarrow P$ [endothermic]
$\Delta U = +ve$

⟹ Extensive property.

⟹ state function.



Enthalpy, H: heat content of system at $\underline{\text{constant pressure}}$.

$\boxed{q_p = \Delta H}$

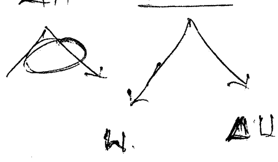
$\boxed{H = U + PV}$ $\boxed{\Delta H = \Delta U + P\Delta U}$

$\boxed{q_p = q_v + P\Delta V}$ $\boxed{q_p = q_v - W}$

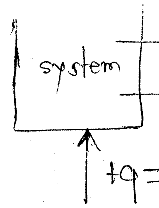
$\underline{\Delta H}$ - change in heat content during a process at constant pressure

$\boxed{q_p = \Delta H}$ —— open system.

$\Delta H = \underline{10\,J}$



open system →



$H_1 = 15\,J$

volume change.

$H_2 = 25\,J$

$R \xrightarrow[\text{pressure}]{\text{constant}} P + \text{heat}$ [~~endoth~~ exothermic]

$\Delta H = -ve.$

$R + \text{heat} \xrightarrow[\text{pressure}]{\text{constant}} P$ [endothermic]

$\Delta H = +ve.$

☆☆☆ { ΔU, internal energy change occurs only in the form of heat whereas, ΔH, enthalpy change occurs in the form of heat as well as work }

heat capacity → amount of heat require ~~the~~ to raise the temperature of a substance by 1°c.

substance 25°c → substance 26°c

1°c.

$q = C$

25°c → 26°c. $q = C$

25°c → 27°c $q = 2C$

t_1°c → t_2°c $q = (t_2 - t_1)C.$

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

$\boxed{C = \frac{q}{\Delta T}}$ ⟹ unit : J/K , cal/K.

⟹ extensive property

Cs/S − q require to rise the temp. of 1 gram of substance by 1°c. is called specific heat capacity.

1 gram substance

25°c → 26°c.	$q = C_s$	∴	$q = S$
25°c → 28°c	$q = 3C_s$		$q = 3S$
t°c → t_2°c	$q = (t_2 - t_1)\,C_s$		$q = (t_2 - t_1)S$
	$q = C_s\,\Delta T$		$\boxed{q = S\Delta T}$

specific heat capacity → $\boxed{S = \frac{q}{\Delta T}}$

2 gram t_1 c $\longrightarrow$ t_2 c $q = 2S\Delta T$ S = specific heat capacity.

m gram. t_1°c $\longrightarrow$ t_2°c. $\boxed{q = mS\Delta T}$

$\boxed{S = \frac{q}{m\Delta T}}$ $\Longrightarrow$ unit : $J\ K^{-1}\ gram^{-1}$
: $cal \cdot K^{-1} \cdot gram^{-1}$

{m - mass of substance in grams.

$\Longrightarrow$ intensive property

Molar heat capacity at constant volume [C_V/$C_{V,m}$] $\Longrightarrow$ intensive property.

volume constant

$\Delta V = 0$ 1 mol substance $\xrightarrow{\text{constant "V"}}$ substance

25 °c 26 °c

1°c

$q_V = C_V$ — {q required to raise the temp. of 1 mole of substance by 1°C at constant volume. is called molar heat capacity $C_{V,m}$}

closed vessel. 1 mole $\longrightarrow$ $\Delta V = 0$ $C = \frac{q}{\Delta T}$

At constant volume $q_V = \Delta U$

$$C_V = \frac{\Delta U}{\Delta T}$$

$\boxed{\Delta U = nC_V\Delta T}$

$\boxed{\Delta U = C_V\Delta T}$ —— for one mole of substance. at constant 'V'

2 mole $\Delta U = 2C_V\Delta T$

12 mole $\Delta U = 12C_V\Delta T$

n mole $\boxed{\Delta U = nC_V\Delta T}$ —— for ~~one~~ "n" mole of substance at constant volume..

C_p / $C_{p,m}$ - molar heat capacity at constant pressure.

pressure = constant 1 mol sub $\xrightarrow[\text{volume}]{\text{at constant}}$ sub

open system $\longrightarrow$ 1mole

(P = constant)

25 °C 26 °C

$q_p = C_p$.

for n mole
t_1°c $\longrightarrow$ t_2°c
$\boxed{\Delta H = nC_p\Delta T}$

$C = \frac{q}{\Delta T}$ At constant P , $q_p = \Delta H$

$$\boxed{C_p = \frac{\Delta H}{\Delta T}}$$

$\rightarrow q_v = \Delta U$

$\rightarrow q_p = \Delta H$

$\rightarrow W = -P\Delta V$

$\rightarrow C = \frac{q}{\Delta T}$

$\boxed{C_p - C_v = R}$

$\boxed{C_p > C_v}$

R = gas constant
= 8.314 J. K^{-1}. mol^{-1}
= 1.987 ~~2~~ cal K^{-1} mol^{-1}
= 0.0821 L. atm K^{-1}. mol^{-1}

{heat require to rise temp. of open system at constant pressure is more than heat require to rise temp. of closed system at constant volume}

$\rightarrow C_s/s = \frac{q}{m\Delta T}$

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

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

$C_p - C_v = R$

$\cancel{\Delta U} + P\Delta V - \cancel{\Delta U} = R$

$\boxed{W = R}$ — {Work done by 1 mole of ideal gas at constant pressure is called gas constant}

Note :

Atomicity	C_v	C_p	$\gamma = C_p/C_v$
monoatomic (He, Ne)	$\frac{3}{2}R$ to	$\frac{3}{2}R + R = \frac{5}{2}R$	$5/3 = 1.66$ — monoatomic
diatomic (O_2, N_2)	(trans) (rotational) $\frac{3}{2}R + \frac{2}{2}R = 5/2$	$7/2\ R$	$7/5 = 1.4$ — diatomic
tri/polyatomic. (NH_3, SO_3)	$\frac{3}{2}R + \frac{3}{2}R = 3R$	4R	$4/3 = 1.33$ — triatomic. or polyatomic

$\rightarrow \Delta U = nC_v\Delta T$

$\rightarrow \Delta H = nC_p\Delta T$

$\rightarrow C_p - C_v = R$ $\longrightarrow C_p > C_v$

{C_v constitute translational degree of freedom as well as rotational degrees of freedom.}

Thermodynamic process

process A $\xrightarrow{\text{condition.}}$ B

A: initial state; B: final state.

{A - finite change
d - infinitesimally change / small change.}

1) isothermal process : constant temp.

25°C

A 25°C — B 25°C.

$\Delta T \neq dT = 0$

$\boxed{q \neq 0}$

$\Delta T = 0$

$\Delta U = 0$

Example $\Rightarrow$ isothermal expansion of gas $\quad q \neq 0$.

$\downarrow$

some energy ~~q~~ required for expansion.

get from internal energy

$\not\downarrow$

expansion doesn't used internal energy

because $\quad \Delta U = nC_v \Delta T$

$\Delta U \propto \Delta T$

if ΔU is used

$\Delta T \neq 0$.

temp. $\neq$ constant

get from surrounding.

$\downarrow$

q required is obtained from surrounding.

$\downarrow$

$\therefore \boxed{q = +ve}$ $\because$ heat is absorbed by the system from the surrounding.

$\Rightarrow$ Isothermal compression of a gas – some energy is ~~required~~, released

$\downarrow$

some energy is released.

remains in the system

$\not\downarrow$

if remains in system

$\Delta U \uparrow \quad \Delta U \neq 0$

also $\quad \Delta T \uparrow \quad \boxed{\Delta T \neq 0}$

$\downarrow$

remain no longer as isothermal change

leaves the system & goes to surrounding.

$\downarrow$

$\Delta U = 0$ remains constant

$\boxed{\Delta T = 0}$ — become isothermal change.

$\downarrow$

$\therefore$ energy released goes to surrounding.

Adiabatic process – No exchange of heat between system and surrounding.

$q = 0$

$\Delta T \neq 0$.

$\Delta U \neq 0$.

$\Rightarrow$ Adiabatic expansion of gas : some energy is required

from internal energy

↓

if U/E is used internal energy ↓

↓

temp. decrease ↓ ($\because \Delta U \propto \Delta T$)

↓

gas is said to be cooled.

from surrounding

↓

for adiabatic process $q = 0$.

Adiabatic processes takes place in thermally insulated system.

$\Rightarrow$ Adiabatic compression of gas : some energy is released

~~from~~ to surrounding

↓

$\therefore q = 0$.

↓

doesnot follow this path

to internal energy or remains in system.

↓

if energy released in system

↓

internal energy ↑

↓

temp ↑

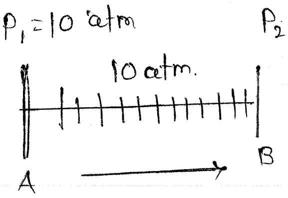
↓

gas is said to be heated.

isobaric process.

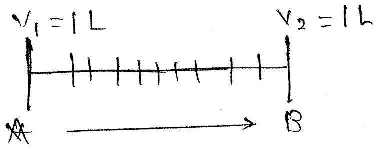
$p =$ constant

$\Delta P / dP = 0$.



isochoric process

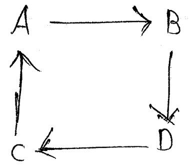
$V =$ constant $\quad \Delta V / dV = 0$.



Cyclic process : initial & final state are same.

$\oint$ — indicated cyclic process.

initial & final state



{change in state function for cyclic process $= 0$.

$\Delta U = \Delta H = \Delta G = \Delta S = 0 = \Delta A$.

$\oint dU = 0 \qquad \oint dH = 0$.}

{only heat & work energy can changes between system & surrounding}

Que-1 When freezing of a liquid takes in a system.

1) may have $q > 0$ or $q < 0$

2) $q > 0$

3) $q < 0$

4) $q = 0$.

Freezing liquid $\longrightarrow$ solid.

$-q$

$\boxed{q < 0}$

stronger bonds are going to form.

Ans :- $q < 0$

Que-2 A sample of liquid is thermally insulated continuously stirred for 2 hrs by the mechanical linkage to a motor in surrounding for this prosess

(a) $w < 0$, $q = 0$, $\Delta U = 0$

(b) $w > 0$, $q > 0$, $\Delta U > 0$

(c) $w < 0$, $q > 0$, $\Delta U = 0$

(d) $w > 0$, $q = 0$, $\Delta U > 0$.

$\longrightarrow$ thermally insulated system.

$q = 0$

$\longrightarrow$ continuous stirring $\quad U \uparrow$

$\Delta U = +ve \quad \Delta U > 0$.

$\longrightarrow$ work is done on the system.

$W = +ve \quad W > 0$

Ans : for thermally insulated system , $q = 0$

due to mechanical stirring , temp. ↑ $\therefore$ internal energy also ↑ $\Delta U > 0$

work is on the system by motor $\therefore$ $W = +ve$ $W > 0$.

$\Longrightarrow$ option 4 is the correct answer.

Que - 3 The heat capacity of 10 moles of an ideal gas at certain temp. is 300 J/K at constant pressure. The heat capacity of the same gas at the same temp and at constant volume would be.

1) 383 $J.K^{-1}$

2) 217 $J.K^{-1}$

3) 134 $J.K^{-1}$

4) 466 $J.K^{-1}$

$\Longrightarrow$

10 mol $\therefore$ $C_p = 300 \; J.K^{-1}$

1 mol $C_p = 30 \; J.K^{-1}$

$C_p - C_v = R$ ——— 1 mol

$300 - C_v = 8.3 \times 10$ ——— for 10 mol.

$C_v = 300 - 83$

$\boxed{C_v = 217 \; J.K^{-1}}$

$\boxed{C_{p,m} - C_{v,m} = R}$ ——— for 1 mole

$\boxed{C_{p,m} - C_{v,m} = nR}$ ——— for n mole

Que - 4 Among the following the system that could require the least amount of thermal energy to bring it's temp to 80°c is

i) 200 gm of H_2O at 40°c

ii) 100 gm 20°c

iii) 150 gm 50°c

iv) 300 gm 30°c.

$\boxed{C_{water} = 1 \text{ cal}}$

$\Longrightarrow$ $\boxed{q = mS\Delta T}$

i) $q = 200 \times 1 \times 40 = 8000$ cal.

ii) $q = 100 \times 1 \times 60 = 6000$ cal

iii) $q = 150 \times 1 \times 30 = 4500$ cal

iv) $q = 300 \times 1 \times 50 = 15000$ cal.

Ans :- iii) 150 grams of water at 50°c.

Que-5 Find the amount of workdone in L.atm on the the surrounding when 1L of ideal gas initially at pressure of 10 atm, is allowed to expand at constant temperature to 10 L by.

(a) reducing external pressure to 1 atm. in single step.

(b) reducing external pressure first to ~~5f~~ 5 atm and then to 1 atm

(c) Allowing the gas to expand to an evacuated space so that it's vacuum

→ isothermal process constant - Temp $\Delta T = 0$ $\Delta U = 0$. $q \neq 0$.

→ adiabatic process constant = q $\Delta T \neq 0$ $\Delta U \neq 0$ $q = 0$.

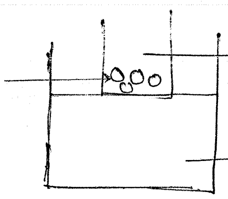
Reversible processes → occur very very slowly

→ difference betn driving & opposing force is very very small

→ infinite number of steps.

→ difference betn internal & external pressure is very very small

sand particle



$P_{ex} = 10$ atm

$P_{int} = 10$ atm.

if one sand particle is removed $P_{ex} = 9.99$.

then

P_{int} → toward 9.99 by expanding.

$$P_{ex} = 10 \text{ atm} \xrightarrow[\text{particle}]{-\text{sand}} 9.99 \text{ atm}$$

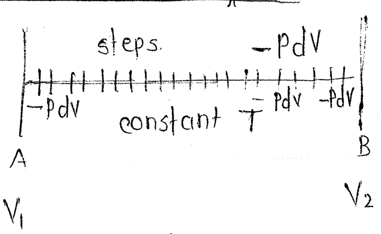
$$\Downarrow\Uparrow \qquad\qquad \Downarrow\Uparrow$$

$$P_{int} = 10 \text{ atm} \xrightarrow[\text{gas expand}]{\text{tend toward}} 9.99 \text{ atm}$$

→ system is said to at equilibrium at every step.

→ ideal/reference process

Workdone in isothermal reversible process



net, workdone $W = \int_{V_1}^{V_2} -PdV$.

$\int$ - sum of all step taking place.

~~from~~ for ideal gas

$PV = nRT$

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

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

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

$$\left\{ \begin{aligned} \int \frac{1}{x} \cdot dx &= \ln x \\ \int_{x_1}^{x_2} \frac{dx}{x} &= \ln x_2 - \ln x_1 \\ &= \ln \frac{x_2}{x_1} \end{aligned} \right\}$$

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

$$\boxed{W = -2.303\, nRT \log \frac{V_2}{V_1}} \qquad \{\because \ln x = 2.303 \log x\}$$

For 1 mole of Ideal gas.

Isothermal reversible expansion. $V_2 > V_1 \Rightarrow W = -ve$. Work done by the system : $U \downarrow$

Isothermal reversible compression $V_1 > V_2 \Rightarrow W = +ve$ Work done on the system : $U \uparrow$

At constant temperature, 'T', a/c Boyle's law.

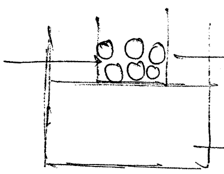
$$P \propto \frac{1}{V}.$$

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

$$\boxed{W = -2.303\, nRT \log \frac{P_1}{P_2}}$$ — for "n" mole of gas.

Irreversible process - very fastly
- difference between driving & opposing force is very large.
- difference between $P_{internal}$ & $P_{external}$ is very large such that $P_{internal}$ become negligible.

sand particle



$P_{ex} = 10$ atm $\longrightarrow$ 5 atm $\longrightarrow$ 0 atm

$\upharpoonleft\downharpoonright$

$P_{int} = 10$ atm $\xrightarrow{\text{tend toward}}$ 5 atm $\longrightarrow$ 0 atm

$$\text{if} \quad \left\{ \begin{aligned} P &= 0 \\ \boxed{W} &\boxed{= 0} \end{aligned} \right\}$$

Example : Naturally occuring process & are spontaneous.

flow of water : Uphill $\longrightarrow$ downfield

Expansion of gas : High Pressure $\longrightarrow$ low pressure

flow of current :

Isothermal irreversible processes takes place in two ways.

(i) $\rightarrow$ isothermal irreversible ~~expansion~~. free expansion.

: $P_{ex} = 0$.

: expansion again vacuum / expansion in evacuated vessel.

: $\boxed{W = 0. = -P\Delta V}$

(ii) $\rightarrow$ isothermal irreversible intermediate expansion.

: expansion against constant external pressure Pex or constant atmosphere pressure. Pex.

: $\boxed{W = -P\Delta V}$

V_1 — V_2

T = constant

P = constant

{ This indicates that work is a path function and not a state function }

$$\because W = -\int_{V_1}^{V_2} P\,dV$$

$$= -P\int_{V_1}^{V_2} dV \qquad \left\{ \because \int dx = x, \quad \int_{x_1}^{x_2} dx = x_2 - x_1 \right.$$

$$= -P(V_2 - V_1)$$

$$W = -P\Delta V$$

work : ordered form of energy

$$W \xrightarrow{100\%} q$$

$$W \xleftarrow[100\%]{\times} q$$

$\rightarrow$ { Workdone in reversible process is more compared to workdone in irreversible process since opposing pressure (Pex) is more in reversible process. }

$W_{rev} > W_{irreversible}$

$q_{rev} > q_{irreversible}$.

heat - disordered form of energy.

at constant T but not at constant P A ++++++++ B V_1 $\quad$ V_2	Reversible
A ———— B V_1 $\quad$ V_2 constant T & constant P	irreversible

$\rightarrow$ { Workdone obtained in reversible process is called maximum work. }

Note : Relation between pressure & volume for an adiabatic process

PV^{γ} = constant where $\gamma = \frac{C_p}{C_v}$: heat capacity ratio

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

relation between T & V for adiabatic process.

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

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

relation between T & P for adiabatic process

$$\boxed{TP^{\frac{1-\gamma}{\gamma}} = \text{constant}}$$

$$\frac{T_1}{T_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1-\gamma}{\gamma}}$$

$\gamma = \frac{C_p}{C_v}$ = heat capacity ratio.

$$\boxed{\gamma = \frac{C_p}{C_v} = \frac{f+2}{f}}$$

f - degrees of freedom.

monoatomic gas $f = 3$

diatomic & colinear molecule (CO_2) $f = 5$

tri & polyatomic molecules $f = 6$

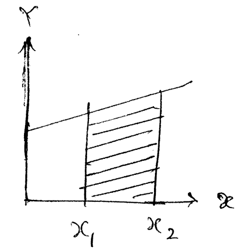
calculation of workdone by graphical method.

→ for adiabatic process

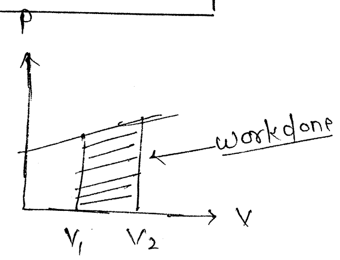
$PV^{\gamma} = \text{constant}$

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

$TP^{\frac{1-\gamma}{\gamma}} = \text{constant}.$



$$\int_{x_1}^{x_2} y\,dx = \text{Area under shaded portion}$$



$$W = -\int_{V_1}^{V_2} P\,dV$$

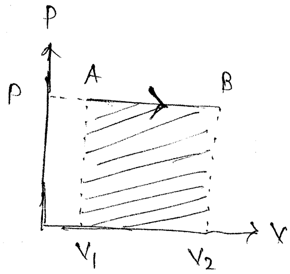
→ isothermal reversible process

$W = -2.303\, nRT \log \frac{V_2}{V_1}$

$W = -2.303\, nRT \log \frac{P_1}{P_2}$

→ irreversible process

$W = -P\Delta V$



Workdone = -shaded area

$= -(V_2 - V_1)(P - 0)$

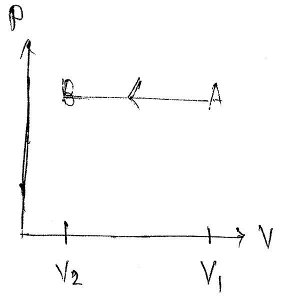
$= -P\Delta V$ $(\because V_2 > V_1)$

W = -ve

volume increases

↓

expansion.



Workdone = -shaded area.

$= -(P-0)(V_2 - V_1)$

$= -P(\Delta V)$

$= +P\Delta V$ — $\because \boxed{V_2 > V_1}$

W = +ve.

↓

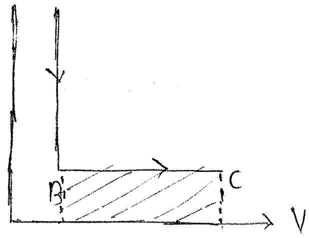
Volume decreases

↓

compression.

Work of compression, $W_{compre} = +ve$ $(\because \Delta U \uparrow)$

Work of expansion, $W_{expansion} = -ve$ $(\because \Delta U \downarrow)$

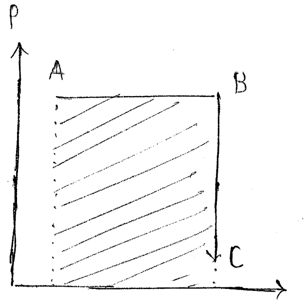


$$\text{Workdone} = W_{A\to B} + W_{B\to C}.$$

$$= 0 + W_{B-C}$$

$$= W_{B-C}.$$

$\because W_{A\to B} = 0$ because volume = constant, $\Delta V = 0$

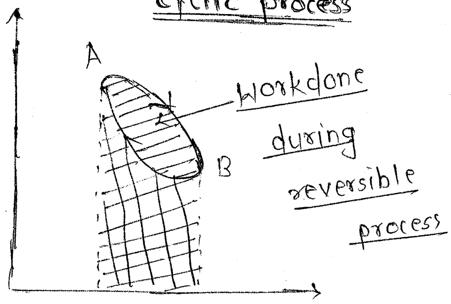


$$\text{Workdone} = W_{A\to B} + W_{B\to C}.$$

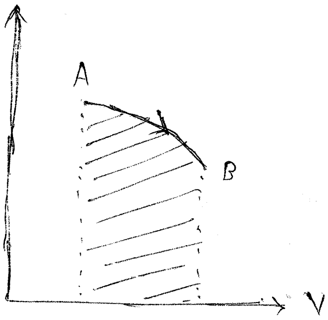
$$= W_{A\to B} + 0$$

$$= W_{A\to B}.$$

Cyclic process

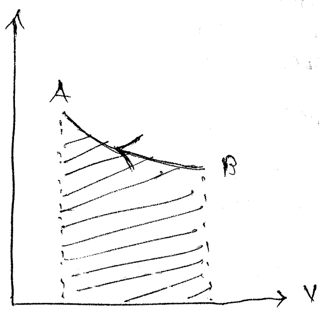


cyclic process.



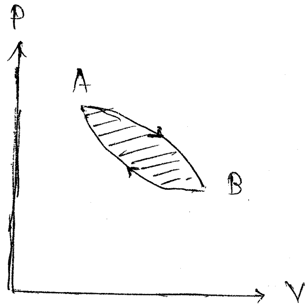
$W = -ve$

— expansion



$W = +ve$

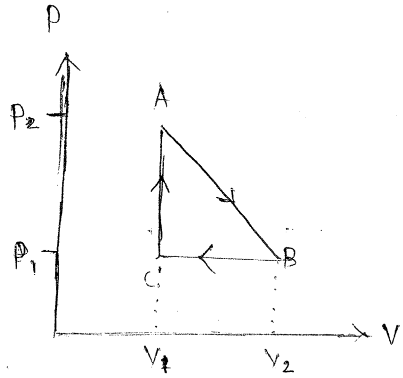
— compression.



cyclic process

Net work done $W = -ve$.

$W =$ Area of curve $= l \times b$.



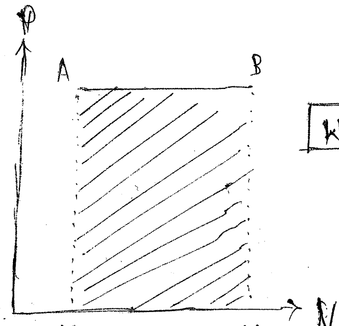
net work done = Area of triangle

$$= \frac{1}{2}\,\text{base} \times \text{height}$$

$$= \frac{1}{2}(V_2 - V_1)(P_2 - P_1)$$

Isobaric process

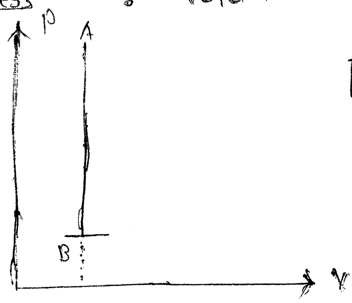
P = constant



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

isochoric process

: volume = constant



$$\boxed{W = 0}$$

$\because \Delta V = 0$

$W = 0$

isothermal ~~therm~~ process

$P \propto \frac{1}{V}$

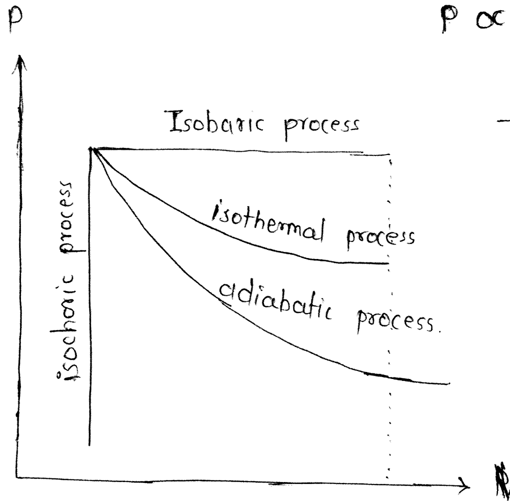
$PV = \text{constant}$

— carried out in open or closed system

Isothermal Adiabatic process. ∵ $PV^{\gamma} = \text{constant}$

$P \propto \frac{1}{V^{\gamma}}$ $[\gamma > 1]$

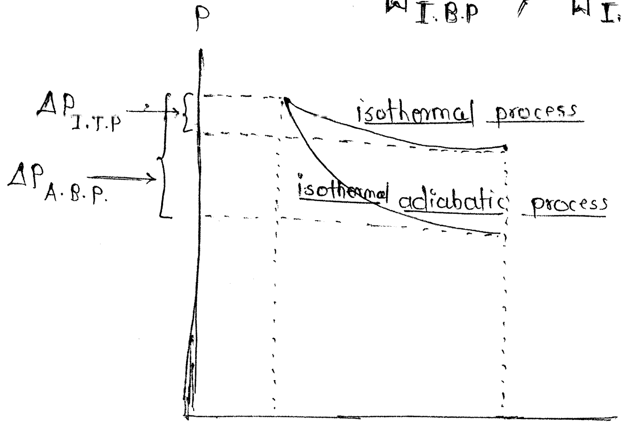
— carried out in thermally insulated system.



important snapshot point

{ decreasing order of workdone during various process.

$W_{I.B.P} > W_{I.T.P} > W_{I.A.B.P} > W_{I.C.P}$ }



$\Delta P_{I.A.B.P} > \Delta P_{I.T.P}$

I.A.B.P – isothermal adiabatic process

I.T.P – isothermal process

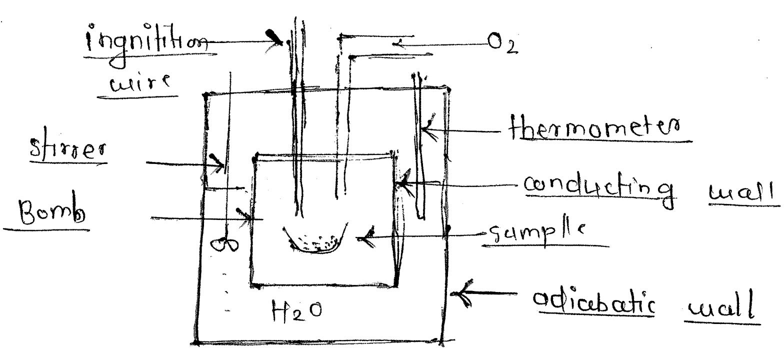
I.B.P – isobaric process

I.C.P – isochoric process.

calorimetry : Bomb calorimeter.

→ to determine heat changes during various processes.

→ Bomb calorimeter : used to calculate ~~d~~ ΔU.



Bomb calorimeter. (ΔU) calculation.

for m gram of sample.

$\boxed{q = mC_s\Delta T}$ $\quad \because C_s = \frac{q}{\Delta T}$

for 1 mole of sample (molar mass = M)

$\boxed{q = \Delta U = \frac{M}{m} \times C_V\Delta T}$ $\quad \because V = \text{constant}$, $q = \Delta U$.

combustion - exotherimic.

$\Delta U = -ve$

$\boxed{\Delta U = \frac{M}{m} C_V \Delta T}$ $\quad \cancel{\boxed{\Delta U = \frac{m}{M} \times C_V\Delta T}}$

$\cancel{\Delta U = \frac{m}{M} C_V \Delta T}$

ΔT - rise in temperature.

C_V - Heat capacity of substance at constant volume.

Determination of ΔH.

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

$\Delta H = \Delta U + RT\Delta n_g.$

$\left\{ \begin{array}{l} \because PV = nRT \\ P\Delta V = RT\Delta n \end{array} \right\}$ — for gaseous reaction

i) considering the reactn involving solid/liquid.

$\Delta V \approx 0.$ since ΔV-negleable for solid/liquid.

$\Delta H \approx \Delta U.$

ii) considering reaction involving gases.

considerable change in vol. take place.

$\Delta H = \Delta U + \Delta n \cdot RT$

$\Delta n_g = n_{product} - n_{reactant}$

Example

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

$\Delta n_g = 1$

$\therefore \Delta H = \Delta U + RT.$

Bomb calorimeter - Enthalpy of combustion of gas.

$\left\{ \begin{array}{l} Q = n_{bomb} C_{bomb} \Delta T + n_{H_2O} C_{H_2O} \Delta T \\ Q = m_{bomb} S_{bomb} \Delta T + m_{H_2O} S_{H_2O} \Delta T. \end{array} \right\}$

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

at constant volum

$q_V = \Delta U = nC_V\Delta T = \frac{M}{M} C_V\Delta T$

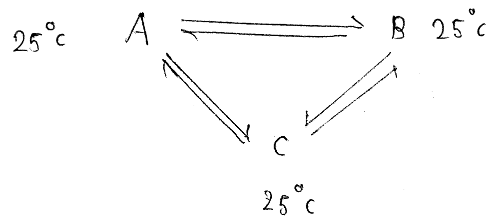
Zeroth law of thermodynamic - If two systems are in thermal equilibrium with third one seperately then all the systems are said to be under thermal equilibrium.

— it introduce the concept of temperature.

mechanical equilibrium

↓

equilibrium at constant pressure



thermal equilibrium

↓

equilibrium at constant temperature.

1st law of thermodynamics. - law of conservation of energy.

create energy ×

destroy energy ×

Energy one form ⟶ another form.

% conservation a/c 1st law = 100% energy conservation

→ Energy of universe remain constant.

→ Energy of isolated system remains constant.

100 J ⟶ 100 J

one form ⟶ another form

% conversion = 100%.

→ mathematical expression.

change in internal energy

↓

occurs in two way. → heat, → work.

: heat &

: work

i) by absorption/ evolution of heat

ii) work done by the system/ on the system.

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

$$\boxed{\Delta U = q - P\Delta V}$$ — for finite changes

$$\boxed{\begin{gathered} dU = dq + dw \\ dU = dq - Pdv \end{gathered}}$$ — for infinitesimally small changes

Application of 1st law to various process.

→ isothermal process

$T = \text{constant}$

$\Delta T/dT = 0.$

$\because \Delta U \propto \Delta T$

$\therefore \Delta U = 0. = nC_v \Delta T$

From 1st law.

$\Delta U = q + W.$

$\boxed{q = -W}$ $\{\because \Delta U = 0\}$

{ workdone by the system = heat absorbed by the system. $\boxed{-W = q}$

workdone on the system = heat evolved by the system $\boxed{W = -q}$

→ isothermal free expansion.

$\Delta T/dT = 0$

$\Delta U = 0.$

$P_{ex} = 0$

$\therefore \Delta U = nC_v \Delta T = 0.$

$\Delta H = \cancel{\Delta U}\ nC_p \Delta T = 0.$

$W = -P\Delta V = 0$ $(\because P_{ex} = 0).$

$\Delta U = q + W$

$0 = q + 0$

$\therefore \boxed{q = 0}$

$\boxed{q = W = \Delta U = \Delta H = 0.}$

→ $W = -2.303\, nRT \log \frac{P_1}{P_2}$

→ $W = -2.303\, nRT \log \frac{V_2}{V_1}$

→ $W = -P\Delta V.$

→ $PV^{\gamma} = \text{constant}$

→ $TV^{\gamma-1} = \text{constant}$

→ $TP^{\frac{1-\gamma}{\gamma}} = \text{constant}$

} adiabatic process

→ $q_v = \Delta U = \frac{M}{m} C_v \Delta T$

→ $q = \Delta U = \frac{M}{m} C_v \Delta T.$

→ $\Delta H = \Delta U + RT.\Delta n_g.$

→ adiabatic process

$q = 0.$

$\Delta U = q + W$

$\Delta U = 0 + W$

$\therefore \boxed{\Delta U = W}$ or $\boxed{-\Delta U = -W}$

$\Delta U = W$: workdone on the system = ~~change~~ ↑ ΔU internal energy

$-\Delta U = -W$: workdone by the system = ↓ internal energy

→ Adiabatic free expansion.

$q = 0$

$W = 0.$ $(\because P_{ex} = 0).$

$\Delta U = q + W$

$\boxed{\Delta U = 0}$

$\boxed{q = W = \Delta U = \Delta H = 0}$

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

$\Delta H = 0 + 0$

$\boxed{\Delta H = 0}$

→ isochoric process.

V - Constant $\Delta V = 0.$

$\Delta U = q + W = q - P\Delta V$ — first law.

$\boxed{\Delta U = q_v}$

$\therefore \boxed{\Delta U = q_v}$ — heat content of system at constant volume

→ isobaric process

P- constant

$\Delta H = \Delta U + P\Delta V$ — at constant pressure.

$\Delta U = q + W$ — 1st law

$q = \Delta U - W.$

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

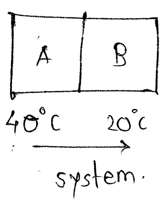
$\boxed{\Delta H = q_p}$

$\boxed{q_p = \Delta H}$ — heat content of system at constant pressure

Limitation of 1st law of thermodynamic.

→ feasibility of process is not explained

→



A/c $A \longrightarrow B$, $B \longrightarrow A$ } A/c first law

but in practice $B \longrightarrow A$ is not possible

heat transfer $A \longrightarrow B$

The direction in which heat transfer takes place is not explained.

→ heat engine : Heat energy 100 J ⟶ Work energy 100 J

It doesn't contradicts the existance of 100% efficiency of heat engine.

but In practice this is not possible

→ self acting refrigeration : Low temp → high temp.

refrigerator.

In practice ✗ }

a/c to 1^{st} law ✓ } to construct self acting refrigerator.

Que-1 In a bomb calorimeter, the combustion of 0.5 grams of compound A (Molar mass = 50 gram/mole) increased the temp. by 4 K. the heat capacity of calorimeter is 2.5 kJ. K^{-1}, the molar internal energy of combustion is.

1. 1000 2. −1000 3. 20 4 = −20.

⟹ m = 0.5 gram $C_V = 2.5$ kJ. K^{-1} = 2500 J. K^{-1}

M = 50 gram.

$$\Delta U = -\frac{M}{m} C \Delta T$$

$\Delta U = n C_V \Delta T$

$\Delta U = \frac{m}{M} C_V \Delta T$

$$= -\frac{50}{0.5} \times 2.5 \times 4$$

$$= -100 \times 2.5 \times 4$$

$$= -100 \times 10$$

$$= -1000 \text{ kJ. mol}^{-1}$$

Que-2 Work (w) involved in isothermal reversible expansion from V_i to V_f of n moles of an ideal gas is.

i) $w = -nRT \ln\left(\frac{V_i}{V_f}\right)$

ii) $w = -nRT \ln\left(\frac{V_f}{V_i}\right)$

iii) $w = -nRT (V_f/V_i)$

iv) $w = nRT \log (V_f/V_i)$.

→ isothermal reversible condition

$W_{max} = -nRT \ln\left(\frac{V_f}{V_i}\right)$

∴ option (iii) is the correct answer.

Que-3 Further reaction $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$, the value of $\Delta H - \Delta U$ in kJ at 300 K and 1 bar is.

1. −5.0 2. 00 3. 2.5 4. 5.0.

⟹ $$\Delta H = \Delta U + RT\Delta n_g$$

$\left\{ \begin{array}{c} \text{at } 298/300 \text{ K} \\ RT \approx 2.5 \text{ kJ} \end{array} \right\}$

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

$\Delta n_g = (n_g)_{products} - (n_g)_{reactants}$

at 300 K/29 K $\quad RT = 2.5\ kJ$ $\quad$ $\left\{ \begin{array}{c} \text{if temp } T = 300\ k/298\ k \\ RT = 2.5\ kJ \end{array} \right\}$

$$\Delta H - \Delta U = \Delta n_g \cdot RT$$
$$= -2 \times 2.5 = \underline{-5\ kJ}$$

Que-4 The value of $\Delta U - \Delta H$ further reaction. $Fe_2O_{3(s)} + 3C_{(s)} \longrightarrow 2Fe_{(s)} + 3CO_{(g)}$

1. $-3RT$ $\quad$ 2. $+3RT$ $\quad$ 3. $+RT$ $\quad$ 4. $-RT$

$\Rightarrow$

$$\Delta H = \Delta U + RT.(\Delta n_g).$$
$$\Delta U - \Delta H = -RT.\Delta n_g.$$

option 1 is the correct answer.

$\Delta n_g = 3$ $\quad$ $\therefore \Delta U - \Delta H = -3RT.$

Que-5 5 moles of ideal gas at 27 °c expands isothermally & reversibly from a volume of 6 L $\longrightarrow$ 60 L. workdone in calories is

$\Rightarrow$ isothermal reversible expansion.

$$W = -2.303\ nRT \log \frac{V_f}{V_i} = -2.303 \times 5 \times 2 \times 300 \times \log\left(\frac{60}{6}\right)$$
$$= -2.303 \times 3000 \times 1 \quad \left(\because \log \frac{60}{6} = \log 10 = 1\right)$$
$$= -2303 \times 3$$
$$= -6909\ cal.$$

Que-6 Calculate the maximum workdone for expanding 16 gm of gas at 300 K and occuping volume of 5 dm^{-3} untill the volume become 50 dm^{-3}

$\Rightarrow$ <u>isothermal</u> <u>reversible</u> <u>expansion</u> – <u>maximum work is obtained</u>

$$W_{max} = -2.303\ nRT \log\left(\frac{V_f}{V_i}\right)$$
$$= -2.303 \times \frac{16}{32} \times 2 \times 300 \times \log\left(\frac{50}{5}\right)$$
$$= -2.303 \times 0.5 \times 600 \times 1$$
$$= -690\ cal.$$

Que-7 During expansion of gas the absorbed heat is 800 cal and the decreases in internal energy 400 cal then calculate the work

$\Longrightarrow$

$q = +800$ cal.

$\Delta U = -400$ cal.

$W = ?$

$\Delta U = q + W.$

$\therefore W = \Delta U - q = -400 - 800$

$= -1200$ cal. (-ve value indicates work-done by the system)

Que.8 If an electric motor produced 15 kJ of energy each second has mechanical work & lost 2 kJ as heat to the surrounding then the change in internal energy each second.

$\longrightarrow$

$W = -15$ kJ. work is done by the system $W = -ve$ value

$q = -2$ kJ

By the system

$W = -ve$
$q = -ve$

$\Delta U = q + W.$

$= -15 - 2$

$= -17$ kJ.

On the system.

$W = +ve$
$q = +ve$

Que.9 : Calculate q, W, ΔU, ΔH (in Joule) for the reversible isothermal expansion of one mole of ideal gas at 27°c from volume of 10 $dm^3 \longrightarrow$ 20 dm^{-3}.

$\Longrightarrow$

$n = 1$ mol.

$T = 27°c = 300K.$

$V_1 = 10\ dm^{-3}$

$V_2 = 20\ dm^{-3}$

$\left.\begin{array}{l}\Delta U = nC_v\Delta T = 0 \\ \Delta H = nC_p\Delta T = 0\end{array}\right\}$ ($\because$ T = const)

$W_{max} = -2.303\, nRT \log\left(\frac{V_f}{V_i}\right)$

$= -2.303 \times 1 \times 8.3 \times 300 \times \log 2$

$= -2.303 \times 1 \times 8.3 \times 300 \times 0.3010$

$= -0.693 \times 8.3 \times 300$

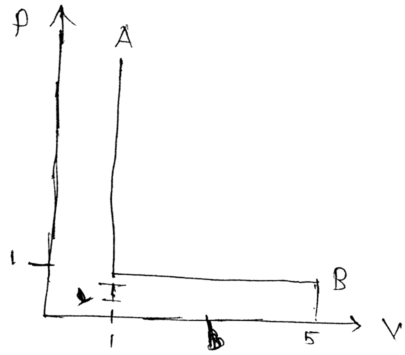
$W_{max} = -1725.57$ J

A/c 1st law $\Delta U = q + W$

but $\Delta U = 0$ $\therefore W = -q.$

$q = +1725.57$ J.

Que-9 The figure below represents the path followed by a gas during expansion from A $\longrightarrow$ B, the workdone in litre . atm is.



1. 0
2. 9
3. 5
4. 4

$\Longrightarrow$ $W_{A-B} = W_{A-I} + W_{I-B}$.

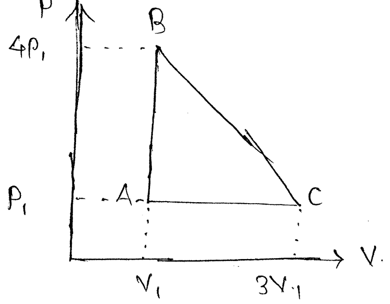
$= 0 + \text{shaded area } (l \times b)$

$= (5-1)(1-0)$

$= 4 \times 1$

$= 4$

Que-10 The workdone by an ideal gas around the cycle. ABCA is.



Net work done = Area of triangle.

$= \frac{1}{2} \times \text{base} \times \text{height}$

$= \frac{1}{2} \times (3V_1 - V_1)(4P_1 - P_1)$

$= \frac{1}{2} \times 2V_1 \times 3P_1$

$= 3P_1V_1$

Que-11 During expansion of an ideal gas for a given volume change, the change in pressure in adiabatic process (ΔP_{ad}) is ___ that of isothermal process $(\Delta P_{isothermal})$

1) equal to
2) exactly half
3) smaller than
4) larger than

$\Longrightarrow$ For isothermal process

$P \propto \frac{1}{V}$

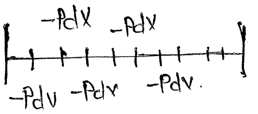
For addiabatic process

$P \propto \frac{1}{V^{\gamma}}$ $(\gamma > 1 \text{ always})$

$\therefore \Delta P_{ad} > \Delta P_{isothermal}$.

option (4) is the correct answer.

Workdone in isothermal reversible ~~process~~ # Expansion of an ideal gas



isothermal : T - constant

expansion : $W = -PdV$

→ reversible process involves infinite number of steps and in every step $-PdV$ work is done by an ideal gas during isothermal expansion.

→ the total workdone during isothermal reversible expansion process is equal to summation or collection of $-PdV$ work done by the system in every step.

$$\therefore \int dW = -\int_{V_1}^{V_2} PdV.$$

$$W_{max} = -\int_{V_1}^{V_2} \frac{nRT}{V} . dV. \qquad (\because PV = nRT, \text{ for ideal gas})$$

$$W_{max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \qquad (\because \text{for isothermal process T also constant.})$$

$$W_{max} = -nRT \int_{V_1}^{V_2} d(\ln V) \qquad \left(\because \frac{dx}{x} = d(\ln x)\right)$$

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

$$W_{max} = -nRT(\ln V_2 - \ln V_1)$$

$$W_{max} = -nRT. \ln\left(\frac{V_2}{V_1}\right) \qquad \left(\because \ln x - \ln y = \ln \frac{x}{y}\right)$$

$$W_{max} = -2.303\, nRT. \log\left(\frac{V_2}{V_1}\right) \qquad (\because \ln x = -2.303 \log x$$

The workdone ~~obtain~~ by the system during isothermal reversible expansion of an ideal gas is <u>maximum</u> than the irreversible isothermal expansion of an ideal gas.

Workdone in adiabatic reversible expansion of an ideal gas

adiabatic process : $q = 0$

: there is no heat exchange b/w system and surrounding.

reversible process : involves infinite number of steps

expansion : work is done by the system.

for adiabatic process

$$q = 0.$$

A/c to 1st law

$$\Delta U = q + w.$$

$$\therefore \Delta U = w \quad \text{—— (1)} \quad (q = 0 \text{ for adiabatic process})$$

or

$$-w = -\Delta U.$$

but

$$U = f(T, V).$$

$$\cancel{dU = \left(\frac{dU}{dT}\right)_V \cdot dT + \left(\frac{dV}{dT}\right)}$$

$$dU = \left(\frac{dU}{dT}\right)_V \cdot dT + \left(\frac{dU}{dV}\right)_T \cdot dV.$$

$$dU = C_V \cdot dT + 0$$

$\left(\because \left(\frac{dU}{dV}\right)_T = 0\right.$ because for this term $T =$ constant $\therefore dU = 0$)

$$\therefore dU = C_V \cdot dT \quad \text{—— (2)}$$

integrating equation (2) on both side within particular limit

$$\int_{U_1}^{U_2} dU = C_V \int_{T_1}^{T_2} dT$$

$$U_2 - U_1 = C_V \cdot (T_2 - T_1)$$

$$\boxed{\Delta U = C_V \Delta T} \quad \text{—— (3)}$$

(for one mole of an ideal gas)

for 'n' mole of an ideal gas

$$\boxed{\Delta U = W = nC_v\Delta T}$$

this is expression for workdone ~~by the system~~ in adiabatic reversible expansion of an ideal gas.

Relationship between T, P and V for adiabatic reversible expansion of an ideal gas.

ⓐ relation between pressure and volume.

for adiabatic reversible expansion of an ideal gas

$$dU = C_v \cdot dT = W = -PdV.$$

$$\therefore C_v \cdot dT = -PdV$$

$$C_v \cdot dT = -nRT\left(\frac{dV}{V}\right) \quad \left\{ \because PV = nRT \ \& \ P = \frac{nRT}{V} \text{ for an ideal gas} \right\}$$

$$\therefore C_v \cdot dT = -nRT \cdot d(\ln V) \quad \text{——} (1) \quad \left(\because \frac{dx}{x} = d(\ln x)\right)$$

but for 'n' mole of an ideal gas, we have

$$PV = nRT. \quad \text{——} (2)$$

differentiating equation (2) on both side.

$$PdV + VdP = nR \cdot dT.$$

$$\therefore dT = \frac{P}{nR} \cdot dV + \frac{V}{nR} \cdot dP.$$

$$\therefore dT = \frac{\cancel{n}RT}{\cancel{n}RV} \cdot dV + \frac{\cancel{n}RT}{\cancel{n}RP} \cdot dP \quad \left\{ \because P = \frac{nRT}{V} \ \& \ V = \frac{nRT}{P} \right\}$$

$$\therefore dT = T \cdot \left(\frac{dV}{V}\right) + T \cdot \left(\frac{dP}{P}\right)$$

$$\therefore dT = T \cdot d(\ln V) + T \cdot d(\ln P) \quad \text{——} (3) \left\{ \because \frac{dx}{x} = d \cdot (\ln x) \right)$$

putting value of equation ③ in equation ①

$$C_v \cdot \left\{ T \cdot d(\ln V) + T \cdot d(\ln P) \right\} = -nRT \cdot d(\ln V)$$

$$\therefore C_v \cdot T \cdot d(\ln V) + C_v \cdot T \cdot d(\ln P) = -nRT \cdot d(\ln V)$$

$$\therefore C_v \cdot T \cdot d(\ln P) = -C_v \cdot T \cdot d(\ln V) - nRT \cdot d(\ln V)$$

$$C_v \cdot \cancel{T} \cdot d(\ln P) = -(C_v + nR)\, \cancel{T} \cdot d(\ln V)$$

$$C_v \cdot d(\ln P) = -C_p \cdot d(\ln V) \qquad \{\because C_v + nR = C_p\}$$

$$d(\ln P) = -\frac{C_p}{C_v} \cdot d(\ln V)$$

$$d(\ln P) = -\gamma \cdot d(\ln V) \quad \text{—— ④} \qquad \left\{\because \frac{C_p}{C_v} = \gamma \text{ – heat capacity ratio}\right\}$$

Integrating equation ④ on both side within particular limit.

$$\int_{P_1}^{P_2} d(\ln P) = -\gamma \int_{V_1}^{V_2} d(\ln V)$$

$$\ln P_2 - \ln P_1 = -\gamma (\ln V_2 - \ln V_1)$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\gamma \cdot \ln\left(\frac{V_2}{V_1}\right) \qquad \left\{\because \ln x - \ln y = \ln\left(\frac{x}{y}\right)\right\}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \gamma \cdot \ln\left(\frac{V_1}{V_2}\right) \qquad \left\{\because -\ln\left(\frac{x}{y}\right) = +\ln\left(\frac{y}{x}\right)\right\}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{\gamma} \qquad \left\{\because x \cdot \ln m = \ln m^{x}\right\}$$

$$\boxed{\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}}$$

or

$$\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma}}$$

(b) Relationship between temperature and volume : For adiabatic reversible expansion of an ideal gas, the workdone is given by.

$$dU = dw = C_v . dT = -P.dV. = -nRT\left(\frac{dV}{V}\right) = -nRT. d(\ln V)$$

$$C_v . dT = -nRT. d(\ln V). \quad \text{—— (1)}$$

$$\frac{C_v}{nR}\left(\frac{dT}{T}\right) = -d(\ln V)$$

$$\frac{C_v}{nR} . d(\ln T) = -d(\ln V) \qquad \left\{\because \frac{dx}{x} = d(\ln x)\right\}$$

$$d(\ln T) = -\frac{nR}{C_v} . d(\ln V)$$

$$d(\ln T) = -\frac{(C_p - C_v)}{C_v} . d(\ln V) \qquad \left\{\because nR = C_p - C_v\right\}$$

$$d(\ln T) = \frac{C_v - C_p}{C_v} . d(\ln V)$$

$$d(\ln T) = \left(\frac{C_v}{C_v} - \frac{C_p}{C_v}\right) . d(\ln V)$$

$$d(\ln T) = (1-\gamma) . d(\ln V) \quad \text{—— (2)}$$

Integrating equation (2) on both side.

$$\int_{T_1}^{T_2} d(\ln T) = (1-\gamma)\int_{V_1}^{V_2} d(\ln V)$$

$$\ln T_2 - \ln T_1 = (1-\gamma)(\ln V_2 - \ln V_1)$$

$$\ln\left(\frac{T_2}{T_1}\right) = (1-\gamma)\ \ln\left(\frac{V_2}{V_1}\right) \qquad \left\{\because \ln x - \ln y = \ln\left(\frac{x}{y}\right)\right\}$$

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

$$\therefore \boxed{\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}}$$

$$\boxed{T_1 V_2^{1-\gamma} = T_2 . V_1^{\gamma-1}}$$

or

$$\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{1-\gamma} = \ln\left(\frac{V_2}{V_1}\right)^{-1(\gamma-1)} = -1 . \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\therefore \quad \ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\therefore \quad \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

$$\therefore \quad \boxed{T_1 V_1^{\gamma-1} = T_2 . V_2^{\gamma-1}}$$

(c) **Relationship between temperature and pressure :** For an adiabatic reversible expansion of an ideal gas, the workdone is given by.

$$dU = dw = C_v.dT = -PdV = -nRT\left(\frac{dV}{V}\right) \qquad \left\{\because P = \frac{nRT}{V}.\right\}$$

$$\therefore \quad C_v.dT = -nRT.\ d(\ln V) \qquad \left\{\because \frac{dx}{x} = d.(\ln x)\right\}$$

~~but~~

$$C_v.dT = -P.dV \quad \text{——— ①}$$

but for an ideal gas,

$$PV = nRT \quad \text{——— ②}$$

differentiating equation ② on both side

$$P.dV + VdP = nRdT.$$

$$\therefore \quad -P.dV = -nR.dT + V.dP \quad \text{——— ③}.$$

putting value of equation ③ in equation ①.

$$\therefore \quad C_v.dT = -nR.dT + V.dP.$$

$$\therefore \quad V.dP = C_v.dT + nR.dT$$

$$nRT\left(\frac{dP}{P}\right) = (C_v + nR)\,dT \qquad \left\{\because V = \frac{nRT}{V} \ \&\ C_p - C_v = nR\right\}$$

$$nRT.\left(\frac{dP}{P}\right) = C_p.dT \qquad \left\{\because C_p - C_v = nR \ \&\ C_v + nR = C_p\right\}$$

$$\frac{dP}{P} = \frac{C_p}{nR}\left(\frac{dT}{T}\right)$$

$$d(\ln P) = \frac{C_p}{C_p - C_v}.d(\ln T). \qquad \left\{\because \frac{dx}{x} = d.(\ln x)\right\}$$

$$d(\ln P) = \frac{(1/C_V)}{\left(\frac{C_P - C_V}{C_V}\right)} \cdot d(\ln T)$$

$$d(\ln P) = \frac{\gamma}{\gamma - 1} \cdot d(\ln T) \quad \text{——} (5) \qquad \left\{ \because \frac{C_P}{C_V} = \gamma \ \& \ \frac{C_V}{C_V} = 1 \right\}$$

integrating equation (5) on both side, we get.

$$\int_{P_1}^{P_2} d(\ln P) = \left(\frac{\gamma}{\gamma-1}\right) \int_{T_1}^{T_2} d(\ln T)$$

$$\ln P_2 - \ln P_1 = \left(\frac{\gamma}{\gamma-1}\right)(\ln T_2 - \ln T_1)$$

$$\ln\left(\frac{P_2}{P_1}\right) = \left(\frac{\gamma}{\gamma-1}\right) \cdot \ln\left(\frac{T_2}{T_1}\right) \qquad \because \ln x - \ln y = \ln\left(\frac{x}{y}\right)$$

$$\ln\left(\frac{P_2}{P_1}\right) = \ln\left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}$$

$$\therefore \boxed{\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}}$$

Hence for adiabatic reversible expansion of an ideal gas.

(i) $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$

(ii) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$

(iii) $\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}$

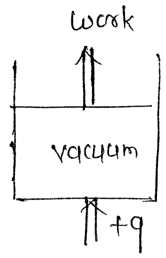
2nd law of thermodynamics. - The flow of heat : High temp $\xrightarrow{}$ low temp.
spontaneously

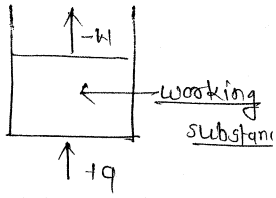
→ The flow of heat low temp → high temp.
non-spontaneous (by using some external energy).

Example : Refrigerator
electrical energy → used to lower the temp.

→ heat engine.

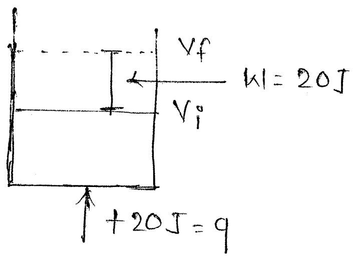
heat energy → work energy





{ without using working substance, heat energy cannot be converted to work energy }

→



Without changing the state of ~~stat~~ system, complete conversion of heat energy → work energy is not possible.

→ It is not possible to construct 100% efficient heat engine.

Heat engine : convert heat energy → work energy.

$$\eta, \text{ efficiency of heat engine} = \frac{\text{workdone } (w)}{\text{amount of heat absorbed } (q)} = \frac{w}{q}$$

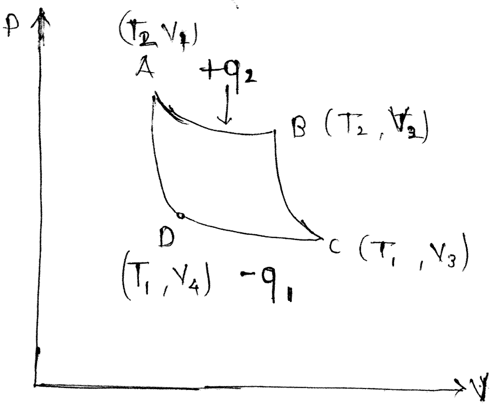
$$\boxed{w < q}$$

$$\boxed{\eta \nless 1}$$

Carnot heat engine : ideal / reference heat engine by which ~~we~~ we can calculate maximum conversion of heat energy → work energy.

→ system : 1 mole of ideal gas
: undergo 4 successive operation.

i) isothermal reversible expansion.
ii) adiabatic reversible expansion.
iii) isothermal reversible compression.
iv) adiabatic reversible compression.



i) **isothermal reversible expansion.** (A → B)

⇒ some energy is required

⇒ required energy is taken from surrounding.

q_2 = amount heat absorbed from surrounding.

= energy reservior.

ii) adiabatic **reversible expansion.** B → C

⇒ some energy in required

⇒ it used from system's internal energy.

⇒ system's Internal energy ↓

⇒ temperature ↓ $(T_2 > T_1)$

iii) **isothermal reversible compression** C → D.

⇒ some energy is released

⇒ required energy released to surrounding.

q_1 - amount of heat released to surrounding -

- sink.

iv) **adiabatic reversible compression** D → A

⇒ Some energy is released

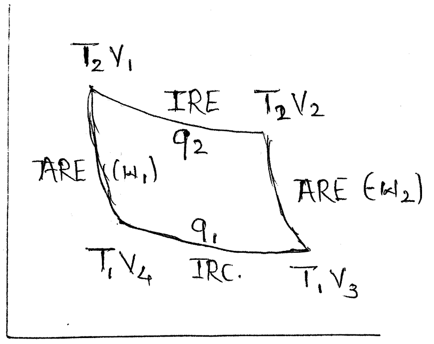
⇒ released energy remains in system

⇒ system's internal energy ↑

⇒ temp ↑ $(T_2 > T_1)$

Expression for workdone during Carnot's Cycle and efficiency of heat engine

(i) Isothermal Reversible ~~process~~ Expansion.



- T : constant , expansion : W = -ve valued
- $dT/\Delta T = 0$ $\because \Delta U = 0$
- A/c first law

$$\Delta U = q + W$$

$$\therefore q = -W$$

- for IRE

$$q_2 = -W_1 = -(-PdV)$$

$$= +PdV.$$

$$= \frac{RT_2}{V} dV. \qquad \left\{\because PV = nRT \text{ \& } P = \frac{nRT_2}{V}\right\}$$

$$= RT_2 \int_{V_1}^{V_2} \frac{dV}{V}. \qquad \{\text{for } n = 1\}$$

$$= RT_2 \int_{V_1}^{V_2} d(\ln V) \qquad \left\{\because \frac{dx}{x} = d(\ln x)\right\}$$

$$= RT_2 (\ln V_2 - \ln V_1)$$

$$q_2 = -W_1 = RT_2 \ln\left(\frac{V_2}{V_1}\right) \text{ —— (1)} \qquad \left\{\because \ln x - \ln y = \ln\left(\frac{x}{y}\right)\right\}$$

(ii) Adiabatic Reversible expansion (-W)

- for expansion W = -ve valued
- q = 0 , no exchange of heat b/w system & surrounding.
- A/c to first law.

$$\Delta U = W$$

$$\text{or} \quad -W = -dU = -C_v dT \qquad \{\because n = 1\}$$

- for ARE,

$$-W_2 = -C_v (T_1 - T_2)$$

$$-W_2 = C_v (T_2 - T_1) \text{ —— (2)}$$

iii) Isothermal Reversible Compression.

- T constant , $dT/\cancel{\Delta T} = 0$ $\therefore \Delta U/dU = 0$.

- ~~A/c~~ ~~to~~ ~~1st~~ ~~law~~. For compression (+W)

$W = +ve$ valued $\quad W = -RT_1 \frac{dV}{V}$

- but for isothermal process,

$$q = -W$$

- For IRC

$$q_1 = -W_3 = RT_1 \frac{dV}{V}$$

$$= RT_1 \int_{V_3}^{V_4} \frac{dV}{V}$$

$$= RT_1 \int_{V_3}^{V_4} d(\ln V) \qquad \left\{\because \frac{dx}{x} = d(\ln x)\right\}$$

$$= RT_1 (\ln V_4 - \ln V_3)$$

$$q_1 = -W_3 = RT_1 \ln\left(\frac{V_4}{V_3}\right) \quad \text{—— (3)} \qquad \left\{\because \ln x - \ln y = \ln\left(\frac{x}{y}\right)\right\}$$

or $\quad -q_1 = W_3 = +RT_1 \ln\left(\frac{V_4}{V_3}\right)$

iv) Adiabatic Reversible Compression (+W)

- $q = 0$, no heat exchange occur b/w system & surrounding

- A/c to 1st law

$$\Delta U = W.$$

- for compression $W = +ve$ valued (+W)

- For ARC

$$W_4 = dU = -C_v (T_2 - T_1)$$

$$W_4 = -C_v (T_2 - T_1) \quad \text{—— (4)}$$

But for adiabatic processes, we know that

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

Now ARE curve BC

$$T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$$

$$\therefore \frac{T_2}{T_1} = \frac{V_3^{\gamma-1}}{V_2^{\gamma-1}} \quad \text{—— (5)}$$

for ARC curve CD,

$$T_1 V_4^{\gamma-1} = T_2 V_1^{\gamma-1}$$

$$\therefore \frac{T_2}{T_1} = \frac{V_4^{\gamma-1}}{V_1^{\gamma-1}} \quad \text{——— } (6)$$

Now from equation (5) and equation (6), we get.

$$\frac{V_3^{\gamma-1}}{V_2^{\gamma-1}} = \frac{V_4^{\gamma-1}}{V_1^{\gamma-1}}$$

$$\therefore \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\therefore \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \text{——— } (7)$$

Now net workdone obtained during Carnot's Cycle or by Carnot heat engine.

$$W_{net} = -W_1 - W_2 - W_3 + W_4 \qquad \{\text{from equation 1 to 4}\}$$

$$= q_2 - W_2 + q_1 + W_4$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) + \cancel{C_v(T_2 - T_1)} + RT_1 \ln\left(\frac{V_4}{V_3}\right) - \cancel{C_v(T_2 - T_1)}$$

$$\{\because \text{from eq}^n \text{ 1 to 4}\}$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_3}{V_4}\right) \qquad \left\{\because \ln\left(\frac{x}{y}\right) = -\ln\left(\frac{y}{x}\right)\right\}$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right) \qquad \{\because \text{from equation 7}\}$$

$$\boxed{W_{net} = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right)} \quad \text{——— } (8)$$

Net heat absorbed by the Carnot heat engine.

$$Q_{net} = q_2 - q_1$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_3}{V_4}\right)$$

$$Q_{net} = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right) \qquad \left\{\because \text{from eq}^n\ 7\right\}$$

$$Q_{net} = R(T_2 - T_1) \ln\left(\frac{V_2}{V_1}\right) = W_{net} \quad \text{—— (9)}$$

A/c to defination of efficiency of heat engine.

$$\eta = \frac{\text{net workdone by the heat engine}}{\text{amount of heat energy absorbed}} = \frac{\text{net heat absorbed by the system}}{}$$

$$\eta = \frac{W_{net}}{q_2} = \frac{Q_{net}}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{\cancel{R}(T_2 - T_1) \cancel{\ln\left(\frac{V_2}{V_1}\right)}}{\cancel{R}T_2 \cancel{\ln\left(\frac{V_2}{V_1}\right)}}$$

$$\boxed{\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}}$$

$$\boxed{\eta = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}}$$

$$\frac{W_{net}}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\boxed{W_{net} = q_2\left(\frac{T_2 - T_1}{T_2}\right) = q_2 \times \eta = q_2 \times \text{efficiency}}$$

$$\frac{q_h}{q_c} = \frac{q_2}{q_1} = \frac{RT_2 \ln\left(\frac{V_2}{V_1}\right)}{RT_1 \ln\left(\frac{V_4}{V_3}\right)} = \frac{RT_2 \ln\left(\frac{V_2}{V_1}\right)}{-RT_1 \ln\left(\frac{V_3}{V_4}\right)}$$

$$\frac{q_h}{q_c} = \frac{q_2}{q_1} = \frac{-\cancel{R}T_2 \cancel{\ln\left(\frac{V_2}{V_1}\right)}}{\cancel{R}T_1 \cancel{\ln\left(\frac{V_2}{V_1}\right)}} \qquad \left\{\because \text{from eq}^n\ 7\right\}$$

$$\therefore \quad \boxed{\frac{q_h}{q_c} = -\frac{T_2}{T_1}}$$

~~amount~~ heat absorbed / heat supplied / heat of reservoir $= q_h = q_2 = -q_c\left(\frac{T_2}{T_1}\right)$

heat released / heat rejected / heat of sink $= q_c = q_1 = -q_h\left(\frac{T_1}{T_2}\right)$

$$= -q_2\left(\frac{T_1}{T_2}\right)$$

efficiency $\eta = \frac{[illegible]}{Q_2/q_2} = \frac{[illegible]}{q_2}$

q_2 - reservoir

q_1 - sink.

$\eta = \frac{T_2 - T_1}{T_2}$

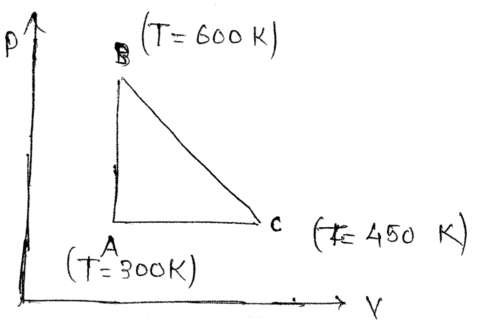
$\eta = \frac{\text{net heat absorbed}}{q_2} = \frac{q_2 - q_1}{q_2}$

$$\boxed{\eta = \frac{W}{-q_2} = 1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2}}$$

$$\boxed{\eta = \frac{W}{q_2} = 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}}$$

Carnot theorem $\Rightarrow$ { From the above equation efficiency of heat engine. not depends on nature of working substance. but it depends on temperature where it is working it is called the Carnot theorem }

Que-1 A heat engine carries 1 mole of ideal monoatomic gas around the cycle as shown in the figure, the amount of heat added in process $A \longrightarrow B$ and the heat removed process $C \longrightarrow A$.



$\Rightarrow$ $q_{AB} = ?$

$q_{CA} = ?$

For monochromatic gas

$C_p = 5/2\ R$

$C_v = 3/2\ R$.

$A \longrightarrow B$ isochoric process V= constant

$\Delta U = q_v$.

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

$= 1 \times 3/2\ R \times 300$

$= 450\ R$.

$C \longrightarrow A$ constant pressure, isobaric.

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

$= 1 \times \frac{5}{2} R\ (-150)$

$= -375\ R$

1. $450\ R$, $-450\ R$
2. $450\ R$, $-225\ R$
3. $450\ R$, $-375\ R$
4. $375\ R$, $-450\ R$

$\therefore$ option (3) is the correct answer.

Que-1 A mixture of 2 moles of CO & 1 mole of O_2, in a closed vessel is ignited to convert the CO into CO_2. If ΔH is the enthalpy change & ΔU is internal energy change, then.

i> $\Delta H < \Delta E$ ii> $\Delta H > \Delta E$ iii> $\Delta H = \Delta E$

iv> The relationship depends on heat capacity of vessel.

⟹ closed vessel - V = constant

$\Delta V = 0$.

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

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

but $2CO_{(g)} + O_{2\,(g)} \longrightarrow 2CO_{2\,(g)}$

$\Delta n = -1$

$\therefore \Delta H = \Delta U - RT\Delta n_g$

$\therefore \boxed{\Delta H < \Delta U}$

Que-2 - At constant T & P, which one of the following statement is correct.

$$CO_{(g)} + \frac{1}{2} O_{2\,(g)} \longrightarrow CO_{2\,(g)}.$$

A] ΔH is independent of the physical state of the reactant of that compound.

B] $\Delta H < \Delta E$ C] $\Delta H > \Delta E$ D] $\Delta H = \Delta U$

⟹ For above reaction.

$\Delta n_g = 1 - 1\frac{1}{2} = -\frac{1}{2}$.

option (B) is the correct answer

$\therefore \Delta H = \Delta U + RT\Delta n_g$

$\therefore \Delta H = \Delta U - \frac{1}{2}RT$

$\therefore \boxed{\Delta H < \Delta U}$

Que-3 If ΔH & ΔU is change in enthalpy & the change in internal energy respectively, accompanying a gaseous reaction.

(A) ΔH is always greater than ΔU

(B) $\Delta H < \Delta E$ only if the number of moles of product is greater than the number of moles of reactant.

(C) ΔH is always less than ΔU.

(D) $\Delta H < \Delta E$ if $n_{product} < n_{reactant}$.

⟹ $\Delta H = \Delta U + RT\Delta n_g$.

$\Delta n_g = -ve$ when $n_{product} < n_{reactant}$

$$\Delta H = \Delta U - xRT$$

$\therefore$ $\boxed{\Delta H < \Delta U}$ only if $n_{product} < n_{reactant}$.

hence option (D) is the correct answer.

$$\boxed{Q/q = C\Delta T = nC_n\Delta T = mC_s\Delta T}$$

→ isochoric process — V = constant — $C = C_V$.

→ isobaric process — P = constant — $C = C_p$.

$\boxed{C = \infty}$ → **isothermal process** — T = constant — $\therefore \Delta T = 0$ — $C = \frac{Q}{0} = \infty$

$\boxed{C = 0}$ → **adiabatic process** — $q = 0$. — $C = \frac{q}{\Delta T} = \frac{0}{\Delta T} = 0$.

→ q : disordered form of energy.

→ w : order form of energy.

$W \xrightarrow{100\%} q$

$q \rightarrow W$: not 100%

Work
- PV - work → expansion or compression
- non - PV work → electrical work

Work

→ **isobaric process.** P = constant.

$$W = -\int P\,dV = -P\int_{V_1}^{V_2} dV = -P[V_2 - V_1] = -P\Delta V.$$

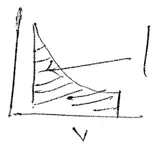
$\boxed{W_{irreversible} \neq W_{reversible}}$ ($\because$ W - path function)

$\boxed{W_{reversible} > W_{irreversible}}$

→ **reversible isothermal process.**

T - constant

infinite step.



|Work| = shaded area.

$$W = -\int_{V_1}^{V_2} P\,dV. \quad \text{—— isothermal irreversible process}$$

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$$

$$W = -2.303\,nRT\log\frac{V_2}{V_1} = -2.303\,nRT\log\frac{P_1}{P_2}$$ —— for reversible process only.

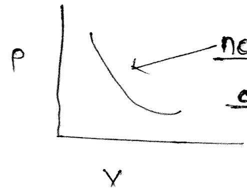
→ isothermal irreversible process.

P_{ex} = constant

$P_{ex} = P_{system}$.

definite step

$\Delta T = 0$.



not possible for irreversible process & only possible for reversible process

↓

against constant ~~press~~ external pressure

$$W_{irreversible} = -\int P_{ex} \cdot dV$$

$$\boxed{W_{irr} = -P_{ex}\,\Delta V.}$$ — similar to formula of isobaric process

→ irreversible adiabatic process.

$$\boxed{W_{irr} = -P_{ex}\,\Delta V}$$

Example 10 mole of an ideal gas is expanded reversibly from 1L to 10 L at 227°c.

→ (a) reversible isothermal expansion.

$n = 2$ mol.

$V_1 = 1$ L

$V_2 = 10$ L.

$T = 227°c + 273 = 500$.

$$W = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303 \times 10 \times 8.3 \times 500 \times \log \frac{10}{1}$$

$$= -2303 \times 8.3 \times 5 \times 1$$

$$= 95,574.5$$

$$= 95.6 \text{ kJ}.$$

Example : 2 moles of an ideal gas expands reversibly from 1L to 10 L at 227°c find the workdone by the gas on the system.

→ $n = 2$ mole $V_1 = 1$ L $V_2 = 10$ L $T = 500$ K. (227°c)

process : isothermal reversible expansion.

$$W = -2.303\, nRT \log \frac{V_2}{V_1} = -2.303 \times 2 \times R \times 500 \log \frac{10}{1}$$

$$= 2303\, R.$$

① if $R = 2$ cal/mol. K

$W = 2303 \times 2$

$= 4606$ cal.

$= 4.606$ kcal.

② if $R = 8.3$ J/mol. k

$W = 2303 \times 8.3$

$= 19,115$ J

$= 19.115$ kJ

Pressure unit.

$1\ atm = 760\ mm/Hg.$

$= 760\ torr.$

$1\ bar = 10^5\ N/m^2$

$= 10^5\ Pascal.$

$1\ atm = 1.013 \times 10^5\ N/m^2 = 1.013 \times 10^5\ Pa$

$\boxed{1\ atm = 1.013\ bar}$

$1\ atm.L = 1.013 \times 10^5\ N/m^2 \times 10^{-3}\ m^3$

$= 101.3\ N.m = 101.3\ J$

$\boxed{1\ atm.L = 101.3\ J}$

$\boxed{1\ bar.L = 100\ J}$

Q. Example ③ 2 mole of an ideal gas expands from 1 L to 10 L at 227 °c. against 2 atm constant external pressure.

→ $n = 2$ mole. $T = 500\ K\ (227°c.)$ — isothermal.

$V_1 = 1L.$ $P_{ex} = 2\ atm$ — constant ; irreversible process

$V_2 = 10l.$

∴ $W = -P_{ex}\ \Delta V.$ — for isothermal irreversible expansion process

$W = -2 \times 9$

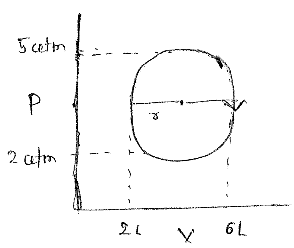
$= -18.\ atm.L.$

$= -18. \times 101.3\ J$ $\boxed{1\ cal = 4.184\ J}$

$= 1823.4\ J$

$= 1.823\ kJ.$

→ Work for clockwise cyclic process $= \underline{-ve}.$



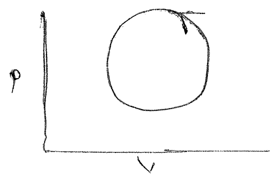
radius, $r = 2$

Work $= \pi r^2$

$= 4\pi$

$\boxed{W = -4\pi}$ — work done by the gas

→ Work for. anticlockwise cyclic process $= \underline{+ve}$



→ For clockwise cyclic work $\boxed{W = -ve}$ & For anticlowise cyclic work $\boxed{W = +ve}$

→ $W \xrightarrow{100\%} q$, $W \xleftarrow{\text{not } 100\%} q$

→ $C = \frac{q}{\Delta T}$

i) isothermal process

$\Delta T = 0$.

$\boxed{C_v = \infty}$

ii) isochoric process.

V = constant

$\boxed{C = C_v}$

iii) adiabatic process

$q = 0$.

$\boxed{C = 0}$

(iv) isobaric proce.

P = constant

$\boxed{C = C_p}$

→ For irreversible process.

P_{ex} is always constant.

→ For reversible process

P_{ex} changes very infinitesimally for each step.

Que - 1 If Q, E & W denotes respectively heat added, change in internal energy and work done in a close cyclic system, then :

1) $Q = 0$.
2) $W = 0$
3) $Q = W = 0$
4) $E = 0$

→ for cyclic closed system,

changes in all state function is equal to 0.

$\therefore E = 0$

option 4 is the correct answer.

Que - 2 In thermodynamic processes which of the following statement is ~~true~~ not true ?

1) In adiabatic process, PV^{γ} = constant
2) In adiabatic process, system is insulated from surrounding.
3) In isochoric process, pressure remains constant.
4) In isothermal process, temperature remains constant.

→ In isochoric process $V = \text{constant}$

$\Delta V = 0.$

but $P = \text{constant}$ in isobaric process where $\Delta P = 0$

Que-3 Pick out one that is not a state function.

1) temperature

2) heat.

3) volume

4) internal energy

→ only q & W are path functions and all others are state function.

∴ heat is not a state function.

option ② is correct answer

$$\left.\begin{array}{l} PV^{\gamma} = \text{constant.} \\ TV^{\gamma-1} = \text{constant} \\ TP^{\frac{1-\gamma}{\gamma}} = \text{constant} \end{array}\right\} \leftarrow \text{for adiabatic process}$$

~~Que-4 Solid benzoic acid is combusted in bomb calorimeter at 27°c.~~

Concept of entropy

→ carnot heat engine

efficiency of heat engine, $\eta = \frac{W}{q_2} = 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$.

$\therefore \quad 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$

$\therefore \quad \frac{q_1}{q_2} = \frac{T_1}{T_2}$.

Q_1 & Q_2 represent the amount of heat exchange.

q_1 = amount of heat evolved. = -ve value.

q_2 = amount of heat absorbed = +ve value.

$\frac{T_1}{T_2} = \frac{-q_1}{+q_2}$.

$\therefore \quad \frac{q_2}{T_2} = \frac{-q_1}{T_1}$

$\therefore \quad \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$.

→ for finite change.

$$\boxed{\Sigma \frac{Q}{T} = \frac{q_1 + q_2}{T_1 + T_2} = 0.}$$

→ for infinitesimal / small changes.

$$\boxed{\Sigma \frac{dq}{T} = 0}$$

Clausius theorem.

$$\boxed{\Delta S = \frac{Q}{T} = \frac{q_{rev}}{T}}$$ → for finite changes

$$\boxed{dS = \frac{dq}{T}}$$ → for small changes.

$\Delta S \Rightarrow$ { Ratio of amount of heat exchange in reversible process to absolute temperature is called change in entropy. }

$\Delta S = \frac{Q_{rev}}{T} = \frac{Q}{T} = \frac{q_1 + q_2}{T_1 + T_2}$

$dS = \frac{dq}{T} = \frac{dq_1 + dq_2}{T_1 + T_2}$

→ { At particular absolute temperature 'T' $Q \uparrow$ then $\Delta S \uparrow$ } → { at constant 'q' or 'Q' $T (\uparrow)$ then $\Delta S (\downarrow)$ }

unit ⟹ cal/K or J/K

Example   System - 1   System - 2

10°c   40°c.

↑   ↑ $\Delta S_{40°c} < \Delta S_{10°c}$

q/Q.   10 J   10 J

→ Clausius put forth the concept of 'entropy' & 'change in entropy'

Entropy - It is a measure of disorderness and/or randomness
or it is a measure of dispersion energy in the system.

randomness ↑
disorderness ↑ → ↑es the entropy
dispersion energy ↑

Example ① solid → liquid.
→ disorderness increases ⇒ ∴ entropy increases ⇒ $\Delta S = +ve$. / $\Delta S > 0$
⇒ spontaneous process

② liquid → solid.
⇒ disorderness ↓ ⇒ ∴ entropy ↓ ⇒ $\Delta S = -ve$ / $\Delta S < 0$.
⇒ non-spontaneous process.

→ some important orders..
i) order of entropy (S) → gas > liq. > solid
ii) order of internal energy (U) → gas > liq > solid.
iii) order of enthalpy (H) → gas > liq > solid.

Example ③ solid ⇌ liquid.
→ equilibrium ⇒ $\Delta S = 0$

some physical processes.
→ fusion   s → l. $\Delta S = +ve$.
→ freezing   l → s $\Delta S = -ve$.
→ evaporation   l → g $\Delta S = +ve$
→ condensation   g → l $\Delta S = -ve$.

→ sublimation.
s → g $\Delta S = +ve$.
g → s $\Delta S = -ve$.

Driving forces for spontaneous processes.
1) Tendancy to attain minimum energy
low energy ⇒ high stability.
high energy ⇒ low stability

Energy of system $\propto \frac{1}{\text{stability of that system}}$

{System always move ~~from~~ spontaneously from high energy to low energy state}

Example ① flow of water uphill (high P.E) ⟶ downhill (low P.E) P.E↓ during this process

Example ② flow of heat hot boby (high q) ⟶ cold body (low q) heat energy ↓ in this process

Both processes above moves spontaneously

⟶ For exothermic processes, there is decrease in energy.

$C + O_2 \longrightarrow CO_2 + \text{heat}$ E ↓ ⟹ spontaneous

$R \xrightarrow{\text{const}^n \text{"V"}} P + \text{heat}$. $\Delta U \downarrow$ ⟹ spantaneous

$R \xrightarrow{\text{const}^n \text{"p"}} P + \text{heat}$ $\Delta H \downarrow$ ⟹ spontaneous.

{As energy decreases during all exothermic or exergonic process. they are spontaneous in nature}

② ⟶ At room temperature.

VVIP case

Exceptional case

ice ⟶ water $\Delta H = +ve$.

endothermic ⟹ but it is spontaneous process.

The spontaneoity of this ~~required~~ reaction is explained by entropy change.

2) Tendancy to attain maximum randomness..

{system always move spontaneously from more order state to less order state

more order state ⟶ less order state.

: spontaneous process}

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

Example ① 3 coins ⟹ 8 probability.

{HHH, TTT} {HHT, HTH, THH, TTH, THT, HTT}

2/8 6/8

important example

⟶ at room temp. ice ⟶ water $\Delta S = +ve$ ($\Delta H = +ve$) ⟹ spontaneous

↳ endothermic.

⟶ below 0° C ice ⟶ water $\Delta S = +ve$ ⟹ but non-spontaneous

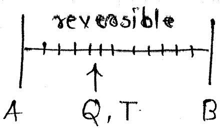
⟶ at 0°c ice ⇌ water $\boxed{\Delta S = 0}$

characteristic of entropy (S).

- → state function.
- → extensive property.
- → Entropy (S) is not possible to calculate but change in entropy (ΔS) can be calculated experimentally.

Entropy change of universe in reversible/equilibrium process.

reversible process :



$$\Delta S_{syst} = \frac{q}{T} = +\frac{q_{rev}}{T} \qquad \Delta S_{surrounding} = -\frac{q}{T} = -\frac{q_{rev}}{T}$$

$$\therefore \Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} = \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right)$$

$$\therefore \boxed{\Delta S_{universe} = 0}$$ — for reversible/equilibrium processes.

Example ① At 0°c. ice $\rightleftharpoons$ water. $\boxed{\Delta S_{uni} = 0}$ } important example.

Entropy change of universe in irreversible/spontaneous process.

spontaneous process : $\boxed{\text{system}} \xrightarrow{Q} \boxed{\text{surrounding}}$

T_1 T_2

$$\boxed{T_1 > T_2}$$

$$\Delta S_{system} = -\frac{Q}{T_1} \qquad \Delta S_{surrounding} = \frac{+Q}{T_2}$$

$$\therefore \Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} = -\frac{Q}{T_1} + \frac{Q}{T_2}$$

$$= Q\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = Q \times \left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\therefore \Delta S_{universe} = Q\left[\frac{T_1 - T_2}{T_1 T_2}\right] = +ve. \quad \left(\because T_1 > T_2 \ \& \ \frac{T_1 - T_2}{T_1 T_2} > 0\right)$$

$$\therefore \boxed{\Delta S_{universe} = +ve \ \& > 0}$$ — for irreversible/spontaneous process

{ In nature always spontaneous processes takes place in which entropy increases, so entropy of the universe always tends towards maximum }

Entropy as a function of temperature (T) & volume (V) for an ideal gas.

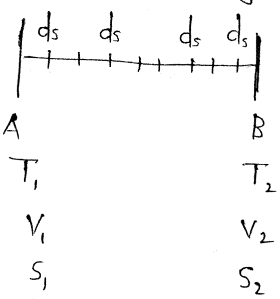
→ According to I[st] law , for one mole of an ideal gas.

$\Delta U = q + w = q - P\Delta V.$

— for finite change.

$dU = dq + dw = dq - pdv$

— for infinitesimal change



$\boxed{\Delta S = S_2 - S_1}$

→ for infinitesimal change.

$$dQ = dU + pdV.$$

$$\frac{dQ}{T} = \frac{dU}{T} + p\frac{dV}{T}$$

$$ds = \frac{dU}{T} + \frac{P}{T}dV \quad \left(\because ds = \frac{dq}{T}\right) \qquad \text{— (1)}$$

for 'n' moles of gas.

$$q_v = dU = nC_v dT \qquad \& \qquad PV = nRT.$$

for 1 mole of gas

$$q_v = dU = C_v dT \qquad \& \qquad PV = RT.$$

$$\therefore \quad ds = \frac{C_v dT}{T} + R\frac{dV}{V} \quad \left(\because PV = RT \;\&\; \frac{P}{T} = \frac{R}{V}\right) \qquad \text{— (2)}$$ for 1 mole

integrating equation (2).

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dV}{V}$$ — for '1' mole of gas

$$\Delta S = C_v . \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$$ — for 1 mole of gas.

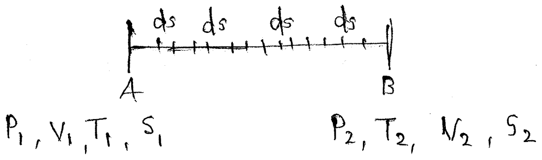
∴ for 'n' moles of ideal gas

$$\boxed{\Delta S = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}} \qquad \text{— (3)}$$

$$\boxed{\Delta S = 2.303\, nC_v \log\frac{T_2}{T_1} + 2.303 nR \log\frac{V_2}{V_1}}$$

Entropy as a function of T and P for an ideal gas.

$$\Delta S = nC_v . \ln\frac{T_2}{T_1} + nR . \ln\frac{V_2}{V_1} \qquad \text{— (3)}$$



A/c. KTG $PV = nRT$

initial state $P_1V_1 = nRT_1$

final state $P_2V_2 = nRT_2$.

$$\frac{P_2V_2}{P_1V_1} = \frac{nRT_2}{nRT_1} \qquad \therefore \frac{V_2}{V_1} = \frac{T_2}{T_1} \times \frac{P_1}{P_2}$$

$$\rightarrow \Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln\left(\frac{T_2}{T_1} \times \frac{P_1}{P_2}\right) \qquad \left(\because \frac{V_2}{V_1} = \frac{T_2}{T_1} \times \frac{P_1}{P_2}\right)$$

$$= nC_v \ln \frac{T_2}{T_1} + R \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{P_1}{P_2}.$$

$$= (nC_v + R) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}.$$

$$\boxed{\Delta S = nC_p \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{P_1}{P_2}} \qquad (\because nC_p - nC_v = R \;\&\; nC_v + R = nC_p).$$

$$\boxed{\Delta S = 2.303\, nC_p \ln \frac{T_2}{T_1} + 2.303\, nR \log \frac{P_1}{P_2}} \quad \text{—— (4)}$$ — for 'n' moles of ideal gas.

Entropy changes during various thermodynamic processes.

1. Isothermal process $\quad A \longrightarrow B$

$T_1 = T_2. \qquad T_1 \quad T_2$

→ at constant volume condition. (V = constant)

$$\Delta S = 2.303\, nC_v \log\left(\frac{T_1}{T_1} \text{ or } \frac{T_2}{T_2}\right) + 2.303\, nR \log \frac{V_2}{V_1} \qquad (\because T_1 = T_2)$$

$$= 2.303\, nC_v \log 1 + 2.303\, nR \log \frac{V_2}{V}$$

$$\boxed{\Delta S = 2.303\, nR \log \frac{V_2}{V_1}} \qquad (\because \log 1 = 0)$$

→ at constant pressure condition.

$$p \propto \frac{1}{V} \qquad \because \frac{P_1}{P_2} = \frac{V_2}{V_1}.$$

$$\therefore \boxed{\Delta S = 2.303\, nR \log \frac{P_1}{P_2}} \qquad \left\{\because \log \frac{T_2}{T_1} = \log 1 = 0 \text{ because } T_1 = T_2\right\}$$

2. Isochoric process.

V = constant

$V_1 = V_2$.

$$\therefore \boxed{\Delta S = 2.303\, nC_v \log \frac{T_2}{T_1}}$$

3. Isobaric process.

$$P = \text{constant}$$

$$P_1 = P_2.$$

$$\therefore \quad \boxed{\Delta S = nC_p \cdot \ln \frac{T_2}{T_1} = 2.303\, nC_p \cdot \log \frac{T_2}{T_1}}$$

4. Adiabatic process

→ **Adiabatic Reversible process**

No heat q/Q exchange takes place between system & surrounding

$$\boxed{Q = 0}$$

$$\therefore \quad \Delta S = \frac{Q}{T}$$

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

→ **Adiabatic irreversible process.**

→ Irreversible process are spontaneous & entropy always tends to maximum for spontaneous process.

$$\therefore \quad \boxed{\Delta S > 0}$$

Entropy increases during a spontaneous processes. like. adiabatic irreversible processes.

Entropy change on mixing of ~~gas~~ ideal gases.

Ideal gas 1	+	ideal gas -2	→	P_1° P_2° $V_1 + V_2$
n_1		n_2		mixture of two ideal gas:
V_1		V_2		
P_1		P_2		
ΔS_1		ΔS_2		$\Delta S_{mix} = \Delta S_1 + \Delta S_2$

at isothermal process condition.

$$\Delta S_1 = n_1 R \ln \frac{V_1 + V_2}{V_1} = n_1 R \ln \frac{P_1^\circ}{P_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_1 + V_2}{V_2} = n_2 R \ln \frac{P_2^\circ}{P_1}$$

total ~~and~~ entropy change on mixing of gas.

$$\Delta S_{mix} = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2}$$

A/c Avogadro's law $\boxed{V \propto n}$

$$\Delta S_{mix} = R\left[n_1 \ln\left(\frac{n_1+n_2}{n_1}\right) + n_2 \ln\left(\frac{n_1+n_2}{n_2}\right)\right]$$

$\because \left(x_1 = \frac{n_1}{n_1+n_2} \text{ \& } x_2 = \frac{n_2}{n_1+n_2}\right)$

$\because \frac{n_1+n_2}{n_1} = \frac{1}{x_1}$ & $\frac{n_1+n_2}{n_2} = \frac{1}{x_2}$

$$= R\left[n_1 \ln\left(\frac{1}{x_1}\right) + n_2 \ln\left(\frac{1}{x_2}\right)\right]$$

$$\boxed{\Delta S_{mix} = -R\left[n_1 \ln x_1 + n_2 \ln x_2\right]}$$

$\left(\because \ln \frac{1}{x} = -\ln x\right)$ — ~~for~~ two two gases of n_1 & n_2 mol.

→ for 'i' number of gases.

$$\boxed{\Delta S_{mix} = -R \sum_i n_i \ln x_i = -2.303 R \sum n_i \log x_i}$$

$$\boxed{\Delta S_{mix} = +ve} \text{ — positive..}$$

$(\because \ln x_i = -ve)$

Two component system

$x_1 + x_2 = 1$

x_1 & $x_2 < 1$

$\ln x_i$ or $\ln x_2$

or $\ln x_i < 0$.

i.e. $\ln x_i = -ve$

$\therefore$ {mixing of two or "i" ideal gases occurs spontaneously}

$$\Delta S_{mix} = -2.303 R \sum_i n_i \log x_i$$

$$\Delta S_{mix} = -2.303 RN \sum \frac{n_i}{N} \log x_i$$

$$\boxed{\Delta S_{mix} = -2.303 NR \sum x_i \log x_i}$$

{N = total no. of moles $= n_1 + n_2 + \dots + n$

x_i – mole fraction

⇒ another method.

$$\Delta S_{mix} = n_1 R \cdot \ln\left(\frac{P_1^\circ}{P_1}\right) + n_2 R \cdot \ln\left(\frac{P_2^\circ}{P_2}\right)$$

$$= R\left[n_1 \cdot \ln\left(\frac{P_1^\circ}{P_1}\right) + n_2 \ln\left(\frac{P_2^\circ}{P_2}\right)\right]$$

Now according to Raoult's law

$$\boxed{P_i = P_i^\circ x_i}$$

P_i° = partial vapour pressure

x_i – mole fraction of 'i' component.

$P_1 = P_1^\circ x_1$ & $P_2 = P_2^\circ x_2$

$\therefore \frac{P_1^\circ}{P_1} = \frac{1}{x_1}$ & $\frac{P_2^\circ}{P_2} = \frac{1}{x_2}$

$\left(\because \ln \frac{1}{x} = -\ln x\right)$

$$\therefore \Delta S_{mix} = R\left[n_1 \cdot \ln\left(\frac{1}{x_1}\right) + n_2 \cdot \ln\left(\frac{1}{x_2}\right)\right] = -R\left[n_1 \ln x_1 + n_2 \ln x_2\right]$$

$\therefore \Delta S_{mix} = -NR \sum_i \frac{n_i}{N} \ln x_i$ — for 'i' number of gases.

$$\therefore \boxed{\Delta S_{mix} = -NR \sum_i x_i \ln x_i}$$

N = total number of moles of gases

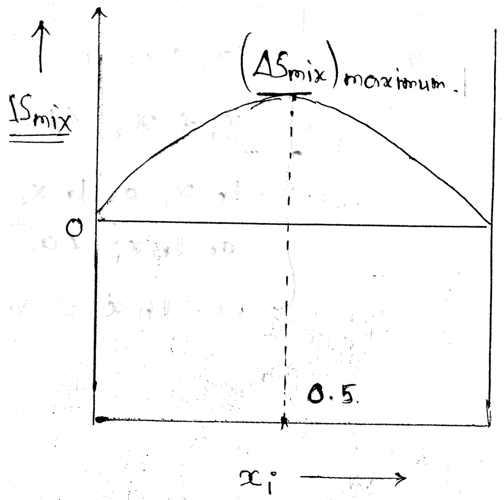
$N = n_1 + n_2 + \ldots + n_i$

$$\therefore \boxed{\Delta S_{mix} = -2.303\ NR \sum x_i \log x_i}$$

$\frac{n_i}{N} = x_i$ = mole fraction of 'i' compon.

$\boxed{\Delta S_{mix} = +ve.}$ $(\because \log x_i < 1 = -ve)$

↳ mixing of ideal gases occurs spontaneously



→ For 2 component system, ΔS_{mix} is maximum when $x_1 = x_2 = \frac{1}{2}$ or 0.5.

→ For 3 component system. ΔS_{mix} is maximum when. $x_1 = x_2 = x_3 = \frac{1}{3}$ or. 0.33.

→ For 'i' component system. ΔS_{mix} is maximum when. $x_i = \frac{1}{i}$ → snapshot point

Entropy change during phase transition.

1. Fusion

$$\text{1 mole of solid} \xrightarrow[+q]{\text{fusion}} \text{liquid.}$$

+q = molar heat of fusion. or

$\Delta_f H$ = latent heat of fusion.

$$\boxed{\Delta_f S = S_l - S_s = \frac{Q}{T_m} = \frac{\Delta H_f}{T_m} = \frac{\Delta_f H}{T_m}}$$

T_m - melting temp.

Latent heat of fusion, $\Delta_f H$ — It is the amount of heat required for the conversion of 1 mole of solid to liquid. or also called molar heat of fusion.

Entropy of fusion, $\Delta_f S$ - Entropy change for 1 mole of substance during fusion is called entropy of fusion.

2. Vaporization.

$$\text{1 mole of liquid} \xrightarrow[+q]{\text{vaporizat}^n} \text{gas}$$

$+q$ = molar heat of vaporization or.
$\Delta_v H$ = latent heat of vaporization.

$$\boxed{\Delta S = S_{gas} - S_{liquid} = \frac{Q}{T_b} = \frac{\Delta_v H}{T_b}}$$

T_b - boiling temp.

$\Delta_v S$ = Entropy of vaporization.

→ fusion : $s \rightarrow l$.	$q = +ve$	$\Delta S = +ve$.	spontaneous.
→ freezing : $l \rightarrow s$	$q = -ve$	$\Delta S = -ve$	exothermic
→ vaporization : $l \rightarrow g$	$q = +ve$	$\Delta S = +ve$	
→ condensation : $g \rightarrow l$	$q = -ve$	$\Delta S = -ve$	exothermic.

Importance of Entropy.

→ measure of disorderness / ~~red~~ randomness / dispersion energy

→ gives feasibility of a process.

$s \rightarrow l \rightarrow g$	$\Delta S = +ve$	spontaneous.	} irreversible.
$g \rightarrow l \rightarrow s$	$\Delta S = -ve$	non-spontaneous	
$g \rightleftharpoons l \rightleftharpoons s$	$\Delta S = 0$	equilibrium/reversible	

→ Entropy, S - function of probability where the probability ↑ entropy ↑

$S \propto f(W)$. W = probabilility.

$$\boxed{S = K \cdot \ln W}$$ — Maxwell - Boltzmann's law.

$W = e^{S/K_B}$

K = Boltzmann constant $= R/N = \dfrac{8.314 \text{ J/K.mol}}{6.02 \times 10^{23}}$

$\therefore K = 1.38 \times 10^{-23} \text{ J. K}^{-1} \text{ mol}^{-1}$.

→ Entropy is also referred as unavailable energy ~~per~~ for unit temperature

$$\therefore \boxed{S = \frac{\text{unvailable energy (U.A.E)}}{T}}$$

T: temp.

$$\therefore \boxed{U.A.E. = T. S}$$

{ unavailable energy — energy that is not available to do useful work. }

Important formulaes for entropy

$\Rightarrow$ $\Delta S = Q/T$: Clausius theorem $\Rightarrow$ reversible / equilibrium process $\Delta S_{uni} = 0$

$\Rightarrow$ $dS = dq/dT$: Clausius theorem $\Rightarrow$ irreversible / spontaneous process $\Delta S_{univ} = +ve$

$\Delta S_{uni} > 0$

$\Rightarrow$ process.

$$\Delta S = nC_v \cdot \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_p \cdot \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$$

$\Rightarrow$ isothermal process.

$$\Delta S = \cancel{nC_v}\ nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nR \cdot \ln\left(\frac{P_1}{P_2}\right)$$

$\Rightarrow$ Adiabatic rev. process.

$\Delta S_{syst} = \Delta S_{surr} = \Delta S_{universe} = 0.$

$\Rightarrow$ Adiabatic irreversible process.

$\Delta S_{system} = +ve$ $\quad \Delta S_{surrounding} = 0.$

$\Delta S_{universe} = +ve$

$\Rightarrow$ isobaric process.

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

$\Rightarrow$ isochoric process

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

$\Rightarrow$ $\Delta S_{mix} = -R\sum_i n_i \ln x_i = -RN\sum_i x_i \ln x_i = -2.303\ NR\sum_i x_i \log x_i > 0$

$\Delta S_{mix} = +ve$ — spontaneous.

$\Rightarrow$ $\Delta_f S = \dfrac{\Delta_f H}{T_m}$

$\Rightarrow$ $\Delta_v S = \dfrac{\Delta_v H}{T_b}.$

$\Rightarrow$ $\Delta_{sub} S = \dfrac{\Delta_{sub} H}{T_{sub}} = \dfrac{\Delta_f H + \Delta_v H}{T_{sub}}.$

$\Rightarrow$ $S = K \cdot \ln W = 2.303\ K \cdot \log W.$

$\Rightarrow$ $S = \dfrac{U.A.E}{T}$

Third law of thermodynamics

Statement ① $\Rightarrow$ As the temperature increases, rotational, translational and vibrational motion is also increases.

$\rightarrow$ Temp. $\uparrow$ $\Rightarrow$ K.E $\uparrow$ $\Rightarrow$ $\left\{\begin{array}{l}\text{rotational motion.}\\ \text{vibrational motion}\\ \text{translational motion}\end{array}\right\}\uparrow$ $\Rightarrow$ disorder $\uparrow$ $\Rightarrow$ S $\uparrow$

$\Rightarrow \Delta S > 0$

$\Rightarrow \Delta S = +ve.$

$\rightarrow$ Temp. $\downarrow$ $\Rightarrow$ K.E $\downarrow$ $\Rightarrow$ $\left\{\begin{array}{l}\text{rotational motion}\\ \text{translational motion}\\ \text{vibrational motion}\end{array}\right\}\downarrow$ $\Rightarrow$ orderness $\uparrow$ $\Rightarrow$ S $\downarrow$

$\Rightarrow \Delta S < 0$

$\Rightarrow \Delta S = -ve$

$\rightarrow$ $T = 0$ (absolute zero) $\Longrightarrow$ All the motion stopped $\Longrightarrow$ No orderness & no disorderness $\Longrightarrow$ $\boxed{S \rightarrow 0}$

Statement ③ - The entropy of pure crystalline substance is zero at absolute zero temperature.

$$\left\{ \begin{array}{l} \lim S \longrightarrow 0 \\ T = 0 \text{ (absolute zero).} \end{array} \right\}$$

important point

- $\rightarrow$ zeroth law : temperature concept.
- $\rightarrow$ 1^{st} law : internal energy concept
- $\rightarrow$ 2^{nd} law : Entropy concept.
- $\rightarrow$ 3^{rd} law : puts limitation on the value of entropy.

Application $\longrightarrow$ It is useful to determine absolute entropy of solid, liquid and gases at any temperature.

$\longrightarrow$ It is useful to determine standard entropy change of a chemical reaction.

Determination of absolute entropy of solid.

Example ① consider a solid having entropies at two different temp.

T 10 K $\longrightarrow$ 20 K.

$S_{10K} \longrightarrow S_{20K}$

$\therefore$ $\boxed{\Delta S = S_{20K} - S_{10K}}$

T 0 K $\longrightarrow$ 20 K

$S_{0K} \longrightarrow S_{20K}$

$\therefore$ $\boxed{\Delta S = S_{20K}}$ $(\because S_{0K} = 0)$ — for solid.

Example ② Temp. 0 K $\longrightarrow$ T K.

entropy $S_{0K} \longrightarrow S_{TK}$

According to second law of thermodynamics

$$dS = \frac{dQ}{T}$$

$$\therefore \frac{dS}{dT} = \frac{dQ}{T\,dT} = \frac{dQ}{dT} \times \frac{1}{T} = C_p / C_v \times \frac{1}{T}$$

$\because Q = C\Delta T$

$\therefore C = \dfrac{dQ}{\Delta T}$

$$\therefore \boxed{dS = C_p \cdot \frac{dT}{T}}$$

→ taking integration on both side

$$\int_{S_{OK}}^{S_{TK}} ds = \int_{OK}^{TK} C_p \cdot \frac{dT}{T}$$

$$[S_{TK} - S_{OK}] = \int_0^T C_p \cdot \frac{dT}{T} = \Delta S = S_T \qquad (\because S_0 = 0)$$

$$\therefore \boxed{\Delta S = S_T = \int_0^T \frac{dT}{T} C_p = \int_0^T d(\ln T) C_p} \qquad (\because S_{OK} = 0 \text{ III}^{rd} \text{ law})$$

$$\frac{dx}{x} = \ln x.$$

$$\frac{d(\ln x)}{dx} = \frac{1}{x}$$

Determination of absolute entropy of liquid.

Consider a ~~gas~~ liquid whose entropy is determined at TK

Temp. limits tends to $0\,K \longrightarrow 1\,K$.

$$\underset{0\,K}{\text{solid}} \xrightarrow{\Delta S_1} \underset{T_m}{\text{solilid}} \xrightarrow{\Delta S_2} \underset{T_m}{\text{liquid}} \xrightarrow{\Delta S_3} \underset{T\,K.}{\text{liquid}}$$

phase transition

total entropy change, $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$[S_T - S_0] = \int_0^{T_m} C_p \cdot (d \ln T) + \frac{\Delta_f H}{T_m} + \int_{T_m}^{T} C_p \cdot d(\ln T).$$

According to 3rd law, $S_0 = 0$

$$\therefore \boxed{S_T = \int_0^{T_m} C_{p(s)} \cdot d(\ln T) + \frac{\Delta_f H}{T_m} + \int_{T_m}^{T} C_{p(l)} \cdot d(\ln T)}$$

Determination of absolute entropy of gas :-

Consider a gas whose entropy is determined at T, then

gas limit: $S_0 \longrightarrow S_T$

Temp. limit $0\,K \longrightarrow T\,K$.

$$\underset{OK}{\text{solid}} \xrightarrow{\Delta S_1} \underbrace{\underset{T_m}{\text{solid}} \xrightarrow{\Delta S_2} \underset{T_m}{\text{liquid}}}_{\text{phase transition}} \xrightarrow{\Delta S_3} \underbrace{\underset{T_b}{\text{liquid}} \xrightarrow{\Delta S_4} \underset{T_b}{\text{gas}}}_{\text{phase transition}} \xrightarrow{\Delta S_5} \underset{T\,K}{\text{gas}}$$

total entropy change $= \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 = S_T - S_0$.

$$\therefore \boxed{[S_T - S_0] = \int_0^{T_m} C_{P(s)} \cdot d(\ln T) + \frac{\Delta_f H}{T_m} + \int_{T_m}^{T_b} C_{P(l)} \cdot d(\ln T) + \frac{d_v H}{d_b} + \int_{T_b}^{T} C_{P(g)} \cdot d(\ln T) = S_T}$$

$\left(\begin{array}{l} \text{because } S_T - S_0 = S_T \\ \because S_0 = 0 \quad a/c \ 3^{rd} \text{ law} \end{array} \right)$

Determination of standard entropy change of a chemical reaction.

Standard entropy (S°) - Entropy of 1 mole of pure substance measured at 1 atm pressure & 25°c.

For a reaction. $A + B \longrightarrow C + D$.

standard entropy change $\Delta S^\circ = \Sigma (S_P^\circ - S_R^\circ)$.

$$\therefore \Delta S^\circ = (S_C^\circ + S_D^\circ) - (S_A^\circ + S_B^\circ)$$

$\longrightarrow$ Similarly for reaction.

$$aA + bB \longrightarrow cC + dD.$$

$$\Delta S^\circ = \left[c.S_c^\circ + d.S_d^\circ\right] - \left[a.S_a^\circ + b.S_b^\circ\right]$$

Que-1 Heat capacity of a species is independent of T if it is ——

ⓐ tetraatomic ⓑ triatomic.

ⓒ monoatomic ⓓ diatomic

option ⓒ is correct answer

$\longrightarrow$ Due to only translation motion possible for monoatomic species

$$K.E \propto T$$

Whatever T supplies, i.e. utilizes & increases translational motion. whereas for polyatomic gases in add^n to translational motion, rotational and vibrational motions are also possible.

At particular temp. T, after increasing T, rotational motions start so then increasing T is more ~~important~~. because some heat is used for increasing T & some heat is used to rotationational motion. In the same way to observe vibration motion, more amount of heat is required.

Que-2 The criteria for spontaneity of a process is.

(i) $\Delta S_{syst} > 0$ ii) $\Delta S_{surrounding} > 0$

(iii) $\Delta S_{syst} + \Delta S_{surrounding} > 0$ (iv) $\Delta S_{system} - \Delta S_{surrounding} > 0$

$\Rightarrow$ $\Delta S_{uni} > 0$ i.e. +ve — criterion for spontaneity of reaction.

$\therefore$ $\Delta S_{syst} + \Delta S_{surrounding} > 0$ & hence option ③ is the correct answer

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Que-3 The number of configurations of state according to Boltzmann formula is

(i) e^{S/K_B} (ii) e^{-S/K_B}

(iii) e^{-E/K_B} (iv) $e^{-\Delta G/K_B}$

$\Rightarrow$ $S = K_B \cdot \ln W$. $\therefore$ option (i) is the correct answer

$\therefore$ $\boxed{W = e^{S/K_B}}$ Entropy is a function of probability.

Que-4 The direct conversion of $A \longrightarrow B$ is difficult, hence it is carried out, by the following path shown : ~~A → C → B~~ → D. $A \rightarrow C \rightarrow D \rightarrow B$

given, $\Delta S_{(A\rightarrow C)} = 50$ units $\Delta S_{(C\rightarrow D)} = 30$ units $\Delta S_{(B \rightarrow D)} = 20$ unit.

then $\Delta S_{(A\rightarrow B)}$ is :

i) 60 units ii) 100 units.

iii) −60 units iv) −100 units

$\Rightarrow$ $A \xrightarrow{50} C \xrightarrow{30} D \xleftarrow{20} B$

option ① 60 unit is the correct answer

$\therefore \Delta S_{(A\rightarrow B)} = 50+30-20 = \underline{60 \text{ unit}}$

Que-5 1 mole of CO_2, 1 mole of N_2, 2 moles of O_2 were mixed at 300 K, then entropy of mixing is. —

$\Rightarrow$ $\Delta S_{mix} = -2.303\, NR \sum x_i \log x_i$

$= -2.303 \times 4 \times 2 \left(0.25 \log \frac{1}{4} + 0.25 \log \frac{1}{4} + 0.50 \log 0.50\right)$

$= -2.303 \times 8 \left(0.25 \times -0.6 + 0.25 \times -0.6 + 0.50 \times -0.30\right)$

$= -2.303 \times 8 \left(-0.150 - 0.150 - 0.150\right) = -18.42 \times (-0.75)$

$= +13.815$ cal/ K =

$\Delta S_{mix} = -R \sum n_i \ln x_i$

$= -R\left(1 \cdot \ln\frac{1}{4} + 1 \cdot \ln\frac{1}{4} + 2\ln\frac{2}{4}\right)$

$= -R\left(2 \ln\frac{1}{4} + 2\ln\frac{1}{2}\right)$

$= -R\left(-2\ln 4 - 2\ln 2\right)$

$= -R\left(-4\ln 2 - 2\ln 2\right)$

$= \underline{6R \cdot \ln 2}$

Que-6 When two moles of an ideal gas heated $\left(C_p = \frac{5}{2}R\right)$ from 300K to 600 K at constant P, the change in entropy of gas is —

(i) $\frac{3}{2} R \ln 2$ (ii) $-\frac{3}{2} R. \ln 2.$

(iii) $5\, R. \ln 2$ (iv) $3R \cdot \ln 2.$

$\Delta S = n C_p \ln \frac{T_2}{T_1}$

$\Delta S = 2 \times \frac{5}{2} R \ln\left(\frac{600}{300}\right)$

gas : monoatomic $C_v = \frac{3}{2}R$ $C_p = \frac{5}{2}R.$

$\Longrightarrow$ At isobaric condition.

$\Delta S = nC_p \cdot \ln \frac{T_2}{T_1}$

$= 2 \times \frac{5}{2} R \ln \left(\frac{600}{300}\right)$

$\therefore \boxed{\Delta S = 5R\ln 2}$

$\boxed{\Delta S = 5R\ln 2}$

$C_p = 5/2\, R$. correct answer.

$T_1 = 300$ $T_2 = 600K$.

Que-7 For the same data given in above problem, the process is carried out at constant volume. Calculate the entropy change.

$\Longrightarrow$ $C_v = 3/2\, R$, isobaric process.

$\therefore \Delta S = nC_v \ln \frac{T_2}{T_1} = 2 \times \frac{3}{2} R \cdot \ln \left(\frac{600}{300}\right) = 3R \cdot \ln 2.$

$\boxed{\Delta S = 3R \cdot \ln 2}$

Que-8 When one mole of an ideal gas is compressed to half of it's initial volume and simultaneously heated to twice it's initial temperature, the change in entropy of the gas.

i) $C_p \ln 2$ (ii) $C_v \cdot \ln 2$ (iii) $R \cdot \ln 2$ (iv) $(C_v - R) \ln 2$.

$\Longrightarrow$ $n = 1$ mole.

$V_1 = x$

$V_2 = x/2$

$T_1 = m$

$T_2 = 2m$.

$\Delta S = nC_v \cdot \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

$= C_v \ln \frac{2\cancel{m}}{\cancel{m}} + R \ln \frac{\cancel{x}/2}{\cancel{x}}$

$= C_v \ln 2 + R \cdot \ln \frac{1}{2}$

$\therefore \Delta S = C_v \cdot \ln 2 - R \ln 2$

$\because \ln \frac{1}{x} = -\ln x$

$\therefore \Delta S = (C_v - R) \ln 2$

is the correct answer.

Que-9 Calculate entropy change when 2 moles of an ideal gas expands reversibly from initial volume of 2 dm^3 to final volume of 20 dm^3 at constant T. of 298 K.

$\Longrightarrow$ condition : isothermal reversible expansion.

$n = 2$

$V_1 = 2\ dm^3$

$V_2 = 20\ dm^3$

$\therefore \Delta S = nR \cdot \ln \frac{V_2}{V_1}$

$= 2 \times 2 \ln \frac{20}{2} = 2.303 \times 4 \times \log 10$

$\therefore \Delta S = 2.303 \times 4$

$= 9.212$ cal/K

or $\Delta S = 9.212 \times 4.184$ J/K

$= 38.54$ J/K

Que-10. Calculate ΔS when 5 moles of an ideal gas expands from initial pressure of 10 atm to final pressure of 1 atm. at constant temp.

$\Longrightarrow$ $n = 5$ mol.

T - constant.

$P_1 = 10$ atm.

$P_2 = 1$ atm.

isothermal expansion.

$\therefore \Delta S = nR \cdot \ln \frac{P_1}{P_2}$

$= 2.303\, R \log 10$

$= 2.303 \times 2 \times 5 \times 1$

$\therefore \Delta S = 23.03$ cal/K.

$\Delta S =$

$= 23.03 \times 4.184$ J/K

$= 96.36$ J/K

Que-11 The latent heat of vaporization of water is 9720 cal/mol. what is the entropy change in the vaporization of 1 gram of water at it's boiling point.

$\Rightarrow$

$\Delta_{vap} H = 9720$ cal/mol.

$T_b = 373$ K

$$\Delta S = \frac{\Delta_{vap} H}{T_b} = \frac{9720}{373} = 26.05 \text{ cal/K} \text{ — for 1 mole.}$$

$n = \frac{m}{M} = \frac{1}{18} = 0.056$

$\therefore \Delta S_{vap} = 26.05 \times 0.056$

$= 1.44$ cal/K. gram.

Que-12 The latent heat of fusion of ice is 80 cal/gram. What is ΔS_f for 1 mole of ice at it's melting point..

1 gram. solid $\longrightarrow$ liquid $\Delta_f H = +ve$.

$\Rightarrow$

$$\Delta S = \frac{\Delta_{fus} H}{T_m} = \frac{80}{273} = 0.29 \text{ Kal/K. gram.}$$

$$\Delta_{fus} S = 0.29 \times 18 = 5.27 \text{ cal/K. mol}^{-1}.$$

Que-13 The latent heat of fusion of ice is 180 cal/gram. What is the change in entropy of fusion for 1 mole of ice at it's melting point.

$\Rightarrow$

$\Delta_f H = 180$ cal/gram. $T_m = 273$ K.

$$\Delta_f S = \frac{\Delta_f H}{T_m} = \frac{180}{273} = 0.66 \text{ cal/gram. J}$$

$$\Delta_f S = 0.66 \times 18 \text{ cal. J}^{-1}\text{. mol}^{-1} = 11 \text{ cal. J}^{-1}\text{. mol}^{-1}$$

Que-14 5 moles of each H_2 & N_2 are mixed at 25°C at 1 atm pressure. Calculate the entropy of mixing.

$\Rightarrow$

$$\Delta S_{mix} = -R \sum n_i \ln x_i$$

$$= -R\left(5 \ln \frac{1}{2} + 5 \ln \frac{1}{2}\right)$$

$$= -R(-5 \ln 2 - 5 \ln 2)$$

$$= 10 R \cdot \ln 2.$$

$$\Delta S_{mix} = 10 \times 8.314 \times 2.303 \times 0.3010$$

$$= 57.63 \text{ J/K}$$

Que-15. What amount of ice will remain when 52 grams of ice is added to 100 grams of H_2O at 40°c [specific heat capacity of H_2O at 40°c is 1 cal/gm or 4.18 J/gram] and latent heat of fusion of ice is 80 cal/gram.

Que-1 Which of the following pair has the higher entropy per mole of substance.

(a) H_2 at 25°c in volᵐ of 10 L (or) ×

H_2 at 25°c in volᵐ of 50 L. ✓

(b) O_2 at 25°c and 1 atm pressure (or) ✓

O_2 at 25°c and 10 atm pressure. ×

(c) H_2 at 25°c and 1 atm pressure (or) ×

H_2 at 100°c and 1 atm pressure. ✓

(d) CO_2 at STP (or) ×

CO_2 at 100°c and 0.1 atm. ✓

Que-2 For water, $\Delta_{vap}H = 41$ kJ/mol, the molar entropy of vaporization at 1 atm is approximately $\Delta_{vap}S = ?$

1) 410 $J.K^{-1}.mol^{-1}$

2) 110 $J.K^{-1} mol^{-1}$

3) 41 $J.K^{-1} mol^{-1}$

4) 11 $J.K^{-1}.mol^{-1}$.

$\Rightarrow$

$$\Delta S_{vap} = \frac{\Delta_{vap}H}{T_b} = \frac{41000}{373} = 109.91 \approx 110.\ J.K^{-1}.mol^{-1}.$$

Que-3 $n_{CO_2} = 1$ mol, $n_{N_2} = 1$ mol, $n_{O_2} = 2$ mole. are mixing at 300 K. The entropy of mixing is, $\Delta_{mix}S = ?$

i) 6 R ln 2

ii) 8 R. ln 2

iii) 8 R. ln(2/300)

(iv) 16 R. ln 2

$\Rightarrow \quad \Delta_{mix} S = -R\left(1 \cdot \ln\frac{1}{4} + 1 \cdot \ln\frac{1}{4} + 2 \cdot \ln\frac{1}{2}\right)$

$= -R\left(2 \ln\frac{1}{4} + 2 \ln\frac{1}{2}\right)$

$= -R\left(-2 \ln 4 - 2 \ln 2\right)$

$= -R\left(-4 \ln 2 - 2 \ln 2\right)$

$\Delta_{mix} S = -R(-6 \ln 2) = 6 R \cdot \ln 2$

$= 6 \times 8.314 \times 2.303 \times 0.3010$

$= 34.57$

Que-4 When 2 moles of an ideal gas heated from 400 K to 1200 K at constant pressure. The change in entropy of the gas is.

(i) $\frac{3}{2}$ R. ln 3 (ii) $-\frac{3}{2}$ R. ln 3

(iii) 5 R. ln 3 (iv) $\frac{5}{2}$ R. ln 3.

$\Rightarrow \quad \Delta S = nC_p \ln\frac{T_2}{T_1} = 2 \times \frac{5}{2} R \ln\frac{1200}{400} = \underline{5R \cdot \ln 3}$

Que-5 The latent heat of fusion of ice is 80 cal/gram. What is the entropy change in fusion of 1 mole of ice at it's melting point.

i) 10.6 cal. K^{-1}. mol^{-1} ii) -5.3 cal. K^{-1}. mol^{-1}

iii) 5.3 cal. K^{-1}. mol^{-1} iv) -10.6 cal. K^{-1}. mol^{-1}

$\Rightarrow$

Que-6 Which of the following is correct for endothermic process.

(a) $\Delta H < 0$, $\Delta S_{syst} < 0$, $\Delta S_{surr} > 0$.

(b) $\Delta H > 0$, $\Delta S_{system} > 0$, $\Delta S_{surr} < 0$.

(c) $\Delta H > 0$, $\Delta S_{system} > 0$, $\Delta S_{surr} > 0$.

(d) $\Delta H > 0$, $\Delta S_{system} > 0$, $\Delta S_{surr} = 0$

$\Rightarrow$

Que-7 For the reaction $Cl_2(g) \longrightarrow 2Cl(g)$, which is true ?

	ΔH	ΔS
i)	+ve	+ve
ii)	−ve	−ve
iii)	+ve	−ve
iv)	−ve	+ve.

$\Longrightarrow$ $Cl_2(g) \longrightarrow 2Cl_{(g)}$ $\Delta H = +ve$, $\Delta S = +ve$

$\therefore$ option (i) is the correct answer

Que-8 When solid NH_4NO_3 is dissolved in water at 25 °c. The temp. of solution decreases, Then ΔH, ΔS.

Have to solve later

i) −ve, −ve. ii) −ve, +ve

iii) +ve, −ve iv) +ve, +ve.

$\Longrightarrow$ $NH_4NO_3 \xrightarrow{aq.} NH_4^+ + NO_3^-$ $\Delta H = -ve$ (heat is evolved by system)

$\Delta S = +ve$ $\therefore$ option (ii) is the correct answer.

Que-9. How much energy must be supplied to change 36 gram of ice at 0°c to water at 25°c. C_p (liq.) $= 4\ J \cdot K^{-1} \cdot gm^{-1}$ & $\Delta_{fus}H = 6.01\ kJ.mol^{-1}$.

i) 12 kJ ii) 15.62 kJ.

iii) 9.54 kJ iv) 22 kJ.

Trucant's rule.

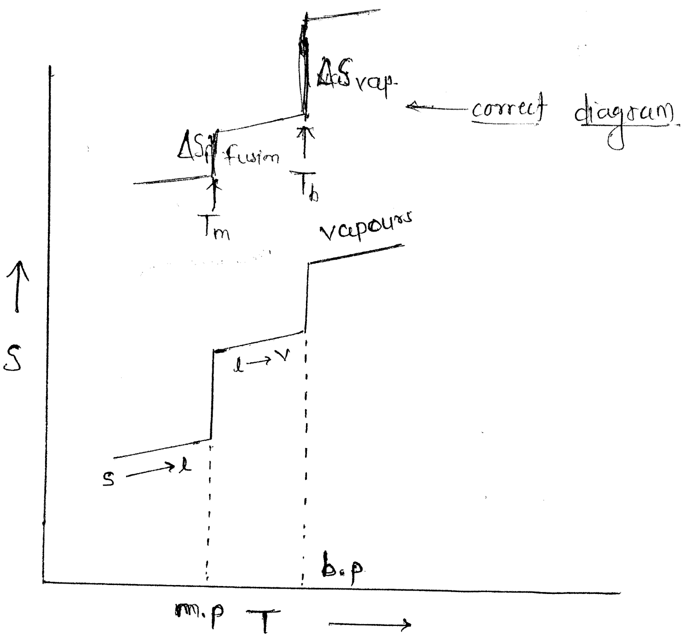
Liq	$\Delta_{vap} S^{\ominus}$
cyclohexane	88.1
CCl_4	85.8
C_6H_6	87.2
H_2S	87.9
H_2O	109.1 (H-bonding)

→ This data shows that almost all the liquids have same standard entropy of vaporization. This empirical experimental observation is called "Trucant's rule". It is due to same change in volume take place when liquid evaporates & converts to gas.

→ Water show deviation due to presence of H-bonding in liquid state.

Tephigraph

Graph of entropy (S) Vs (T) is called tephigraph.



i) $T \uparrow \Rightarrow$ all degrees of freedom $\uparrow$.
$\Rightarrow$ disorderness $\uparrow$
$\Rightarrow S \uparrow$ & $\Delta S > 0$. or +ve.

ii) $T \downarrow \Rightarrow$ all degrees of freedom $\downarrow$.
$\Rightarrow$ orderness $\downarrow$.
$\Rightarrow S \downarrow$ & $\Delta S < 0$ or −ve.

iii) $T = 0K \Rightarrow$ disorderness stopped.
$\Rightarrow S = 0$.

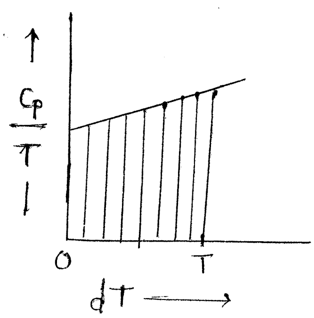
Problem with determination of absolute entropy of solid. ✡

Temp $0 \longrightarrow T$ K.

entropy $S_0 \longrightarrow S_T$

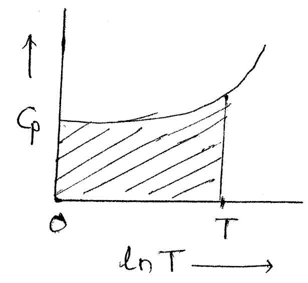
we get.

$$\boxed{S_T = \int_0^T C_p \cdot d(\ln T)}$$



The integral can be evaluated by a pot of C_P/T Vs T.

→ The area in between 0 & T gives the value of integral.

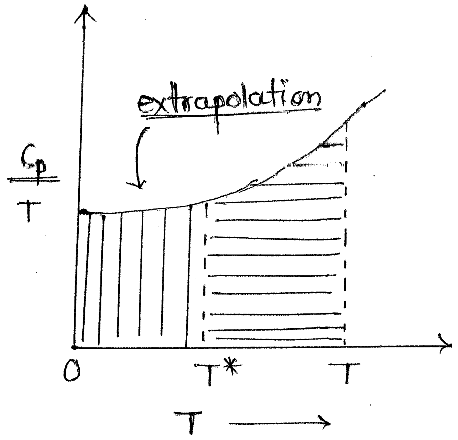


→ It is impossible to calculate exact value of C_p near 0 K so we can calculate C_p value upto as low to T^* as possible [usually upto 15 K] and C_p at 0 absolute zero is obtained by with extrapolation

$$S_T = \int_0^T \frac{C_p}{T}\, dT.$$

$$S_T = \int_0^{T^*} \frac{C_p}{T}\, dT + \int_{T^*}^{T} \frac{C_p}{T}\, dT$$

$$\boxed{0 < T^* < 15\,K}$$



→ First integral can be can be calculated by Debye T^3 law.

i.e. $\boxed{C_p = aT^3}$ ⟶ near absolute zero : at Debye law

where a = constant.

{ Debye law / Debye model, correctly predicts the ~~depen~~ low temperature dependence of the heat capacity (C_p) which is proportional to T^3 - Debye T^3 law }

$$S_T = \int_0^{T^*} \frac{aT^3}{T}\, dT + \int_{T^*}^{T} \frac{C_p}{T}\, dT. = \int_0^{T^*} aT^2 dT + \int_{T^*}^{T} \frac{C_p}{T}\, dT$$

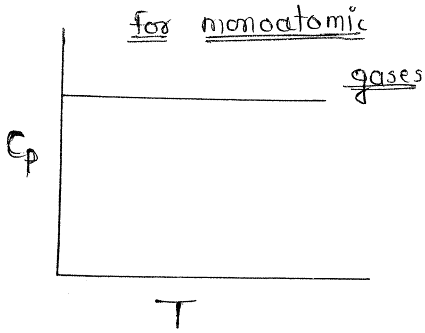
$$= a\int_0^{T^*} T^2 dT + \int_{T^*}^{T} \frac{C_p}{T}\, dT$$

$$= a\left[\frac{T^3}{3}\right]_0^{T^*} + \int_{T^*}^{T} \frac{C_p}{T}\, dT.$$

$$= a.\left[\frac{T^{*3}}{3} - 0\right] + \int_{T^*}^{T} \frac{C_p}{T}\, dT.$$

$$\therefore \boxed{S_T = \frac{a.T^{*3}}{3} + \int_{T^*}^{T} \frac{C_p}{T}\, dT}$$

→ It is observed in monoatomic gases that. C_p is independent of temperature T



→ For diatomic molecules, supplied temp. T causes translational, rotational & vibrational motion to take place.

→ Tra~~s~~lational, vibrational & rotational motions takes place at a particular temperature after only.

Que-1 IIIrd law of thermodynamic leads to

(a) concept of entropy.

(b) concept of internal energy.

(c) concept of free energy.

(d) The limitation on the value of entropy of a crystalline solid (pure)

$\Rightarrow$ At absolute zero $\rightarrow$ all motion stopped $\rightarrow$ no orderness or disorderness $\rightarrow$ $\Delta S \rightarrow 0$.

This is 3rd law.

$\therefore$ option (d) is the correct answer.

Que-2 $A + B \rightarrow C + D$ reaction haves standard entropies of A, B, C & D are 40, 60, 70 and 50 ~~respectively~~. cal / K. mol respectively. In terms of entropy change predict the reaction is spontaneous or not?

$\Rightarrow$

$$\Delta S = (70 + 50) - (40 + 60)$$

$$\Delta S = 120 - 100$$

$$\boxed{\Delta S = 20} \text{ cal/K. mol}$$

$\because$ $\Delta S = +20$ cal/K . mol^{-1}

$\boxed{\Delta S > 0}$

indicates that the reaction is spontaneous

Que-3 How much heat is required to change 10 grams of ice at 0°C to steam at 100°C. $\Delta_{fus} H = 8$ cal/gm & $\Delta_{vap} H = 540$ cal/gram respectively with given that C_s for water is 1 cal / K. gram.

$\Rightarrow$

Que-4 For a perfectly crystalline solid $C_p = aT^3$ where 'a' is constant if $C_p = 0.42$ J/K. mol. at 10 K, molar entropy at 20 K is ______

⟨i⟩ 0.42 J. K^{-1} mol^{-1} ⟨ii⟩ 0.14 J. K^{-1}. mol^{-1}

⟨iii⟩ 1.12 J. K^{-1}. mol^{-1} ⟨iv⟩ zero.

$\rightarrow$

$$\Delta S = S_{20K} = \frac{aT^3}{3} + \int_{10}^{20} \frac{C_p}{T} dT$$

$$= \frac{C_p}{3} + \int \frac{aT^{\cancel{3}2}}{\cancel{T}} dT$$

$$= \frac{C_p}{3} + \int_{10K}^{20K} aT^2 dT$$

$$S_{20K} = \frac{C_p}{3} + \frac{2aT^3}{3}$$

$$= \frac{C_p + 2C_p}{3}$$

$$= \frac{3C_p}{3}$$

$$= C_p$$

$S_{20K} = 0.42$ J/K . mol

$\therefore$ option (i) is the correct answer.

Some important point

→ At absolute zero,

$\lim S \longrightarrow 0$. 3rd law — for pure crystalline solid.

→ absolute entropy of solid.

$$\Delta S = S_T = \int_0^T \frac{C_p}{T}\, dT = \int_0^T C_p \cdot d(\ln T)$$

→ absolute entropy of liquid.

$$\Delta S = S_T = \int_0^{T_m} C_{p(s)} \cdot \frac{dT}{T_m} + \frac{\Delta_{fus} H}{T_m} + \int_{T_m}^{T} C_{p(l)} \frac{dT}{T}$$

→ absolute entropy of gas.

$$\Delta S = S_T = \int_0^{T_m} C_{p(s)} \cdot \frac{dT}{T_m} + \frac{\Delta_{fus} H}{T_m} + \int_{T_m}^{T_b} C_{p(l)} \cdot \frac{dT}{T} + \frac{\Delta_{vap} H}{T_b} + \int_{T_b}^{T} C_{p(g)} \cdot \frac{dT}{T}$$

→ standard entropy change for a chemical reaction.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta_r S^\theta = \left[cS^\circ_C + dS^\circ_D\right] - \left[aS^\circ_A + bS^\circ_B\right]$$

→ problem with calculation of absolute entropy of solid.

C_p cannot be calculate exactly at ~~0°C~~ absolute zero

C_p can be calculated upto T^* temp & gives exact value &

below T^*, C_p calculation is extrapolated.

$$S_T = \frac{aT^{*3}}{3} + \int_{T^*}^{T} C_p \cdot \frac{dT}{T}$$

Gibb's free energy (G) and Helmholtz free energy (A)

(T.E) $\frac{\text{total}}{\text{energy}} = \frac{\text{Available}}{\text{energy}}$ (A.E) + $\frac{\text{unavailable}}{\text{energy}}$ (U.A.E)

Available energy (A.E) = T.E. − U.A.E.

at constant pressure. A.E = H − TS. = G — Gibb's free energy

at constant volume A.E. = U − T.S. = A. — Helmholtz free energy.

$\therefore$ ~~A = U~~ $\boxed{A = U - T.S}$ & $\boxed{G = H - TS}$

$\downarrow$ Helmholtz free energy $\downarrow$ Gibb's free energy

⇒ **Relation between A & G**

$G = H - TS = U + PV - TS$

$\therefore G = (U - TS) + PV.$

$\therefore \boxed{G = A + PV.}$

⇒ properties of A & G

→ exact values of A & G are impossible to calculate but ΔA & ΔG are.

→ extensive properties

→ state functions.

→ free energies to do useful work. at constant volume & at constant pressure

⇒ **Variation of G with temperature (T) and pressure (P).**

dG = ?

$G = H - TS$

$G = U + PV - TS.$

differentiating on both sides

$dG = dU + d(PV) - d(TS)$

$dG = dU + PdV - TdS + Vdp - SdT$

According to Ist

$dU = dQ - PdV.$

$\therefore dU + PdV = dQ.$ —— ①

According to 2nd law.

$dS = \frac{dQ}{T}$ $\therefore -dQ = -TdS$ —— ②

$\therefore dG = \cancel{dQ} - \cancel{dQ} + Vdp - SdT$

$\therefore \boxed{dG = Vdp - SdT}$ i.e. $G = f(p, T)$

At constant 'p' ⇒ $\boxed{dP = 0}$

$\therefore dG = -SdT$

$\therefore \boxed{\frac{dG}{dT} = -S}$ — complete change

$\therefore \boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$ — partial change

- At constant 'T' ⇒ ~~dV~~ $\boxed{dT = 0}$

$\therefore dG = Vdp.$

$\therefore \boxed{\frac{dG}{dP} = V}$ — complete change

$\therefore \boxed{\left(\frac{\partial G}{\partial P}\right)_T = V}$ — partial change

⟹ Variation of A with T and V

$$G = A + PV.$$

$$dA = ?$$

$$dG = dA + d(PV).$$

$$\cancel{VdP} - SdT = dA + PdV + \cancel{VdP}$$

$$\therefore \boxed{dA = -PdV - SdT}$$

$$\boxed{A = f(T, V)}$$

1) at contant temperature 'T' $\Rightarrow dT = 0$

$$dA = -PdV.$$

$$\therefore \left(\frac{dA}{dV}\right)_T = -P. \quad \text{— complete change}$$

$$\text{or} \quad \boxed{\left(\frac{\partial A}{\partial V}\right)_T = -P} \quad \text{— partial change.}$$

2) at constant volume 'V' $\Rightarrow dV = 0.$

$$\therefore dA = -SdT$$

$$\therefore \left(\frac{dA}{dT}\right)_V = -S \quad \text{— complete change}$$

$$\therefore \boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S} \quad \text{— partial change}$$

⟹ Change of G at constant 'T' for an ideal gas.

$$G = H - TS$$

i.e. $\Delta G = \Delta H - T\Delta S.$

A ———— B

const. T

$\Delta G = ?$

at constant temp. (T)

$$\Delta G = 0 - T\Delta S. \quad (\because \Delta H = nC_p \Delta T = 0 \text{ at } T = \text{constant}).$$

$$\therefore \boxed{\Delta G = -T\Delta S} \quad \text{— at constant 'T'}$$

$$\therefore \Delta G = -TnR \ln \frac{V_2}{V_1} \quad \left(\because \Delta S = nR \ln \frac{V_2}{V_1}\right) \quad \text{— at constant T}$$

$$\therefore \boxed{\Delta G = -nTR \ln \frac{V_2}{V_1} = -2.303\, nRT \log \frac{V_2}{V_1}}$$

OR

$$\boxed{\Delta G = -nRT \ln \frac{P_1}{P_2} = -2.303\, nRT \log \frac{P_1}{P_2}}$$

⟹ Change of 'A' at constant 'T' for an ideal gas.

$$A = U - T.S.$$

$$\Delta A = \Delta U - T\Delta S$$

at constant T $\Delta A = \Delta U - T\Delta S$

$\Delta A = 0 - T\Delta S$ $\quad (\because \Delta U = nC_V\Delta T = 0$ at const 'T')

$\Delta A = -T\Delta S$

$\therefore \Delta A = -TnR \ln \frac{P_1}{P_2}$

$$\boxed{\Delta A = -nRT \ln\left(\frac{V_2}{V_1}\right) = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)}$$

$$\boxed{\Delta A = -nRT \ln\left(\frac{P_1}{P_2}\right) = -2.303\, nRT \log\left(\frac{P_1}{P_2}\right)}$$

Some important formulaes.

→ $G = H - TS$ $\quad \Delta G = \Delta H - T\Delta S.$

→ $A = U - TS$ $\quad \Delta A = \Delta U - T\Delta S$

→ $G = A + PV$ $\quad \Delta G = \Delta A + P\Delta V + V\Delta P.$

→ variation of G with T & P.

$dG = VdP - SdT$ $\quad G = f(T, P)$

at constant 'T'

$\left(\frac{dG}{dP}\right)_T = V$ or $\left(\frac{\partial G}{\partial P}\right)_T = V$

at constant 'P'

$\left(\frac{dG}{dT}\right)_P = -S$ or $\left(\frac{\partial G}{\partial T}\right)_P = -S$

→ variation of A with T & V.

$dA = -PdV - SdT$ $\quad A = f(T, P)$

at constant 'T'

$dA = -PdV$

$\left(\frac{dA}{dV}\right)_T = -P$ or $\left(\frac{\partial A}{\partial V}\right)_T = -P$

at constant 'V'

$dA = -SdT$

$\left(\frac{dA}{dT}\right)_V = -S$ or $\left(\frac{\partial A}{\partial T}\right)_V = -S$

→ change of G at constant T for an ideal gas.

$\Delta G = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT.\ln\left(\frac{P_1}{P_2}\right) = -2.303\, nRT. \log\left(\frac{V_2}{V_1}\right) = -2.303\, nRT \log\left(\frac{P_1}{P_2}\right)$

→ change of A at constant T for an ideal gas.

$\Delta A = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right) = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right) = -2.303\, nRT \log\left(\frac{P_1}{P_2}\right)$

Clausius inequality theorem.

↳ criteria for reversible and irreversible process.

→ Consider a small change of state in the system reversibly by absorption of dQ amount of heat from surrounding. then,

$$dS = \frac{dQ_{rev}}{T} \quad \text{——— (1)}$$

→ consider some change of state is brought irreversible.

$$W_{rev} > W_{irr}$$

$$dQ_{rev} > dQ_{irr}.$$

$$\therefore \frac{dQ_{rev}}{T} > \frac{dQ_{irr}}{T}$$

$$\left.\begin{array}{c} \therefore \boxed{dS > \frac{dQ_{irr}}{T}} \\ \text{or} \\ \boxed{TdS > dQ_{irr}} \end{array}\right\} \text{— Clausius inequality}$$

→ According to first law,

$$dU = dQ + dW.$$

$$dU = dQ - PdV.$$

$$dQ = dU + PdV.$$

$$\Longrightarrow \boxed{TdS \geq dU + PdV} = dH$$

$>$: indicates irreversible/ spontaneous process.

$=$: indicates reversible / equilibrium process.

Conditions for spontaneity and equilibrium w.r.t. U, H, S, G, A.

Clausius unequality $\Longrightarrow$ $TdS \geq dU + PdV$.

1) At constant S & V.

$$0 \geq dU. \quad \text{i.e.} \quad \boxed{dU \leq 0} \quad \text{i.e.} \quad \boxed{(dU)_{S,V} \leq 0}$$

$dU < 0$: spontaneous $\qquad dU = 0$: equilibrium

2) at constant U & V.

$$TdS \geq 0. \quad \text{i.e.} \quad \boxed{dS \geq 0} \quad \text{i.e.} \quad \boxed{(dS)_{U,V} \geq 0.}$$

$dS > 0$: spontaneous $\qquad dS = 0$: equilibrium.

3) at constant 'P' & 'S'

$$dH = dU + PdV. \qquad \text{i.e.} \quad TdS \geq dH.$$

$$dH \leq 0 \qquad \text{i.e.} \quad (dH)_{P,S} \leq 0$$

$dH < 0$: exothermic/spontaneous $\quad$ $dH = 0$ equilibrium.

4) at constant 'H'

$$TdS \geq dH.$$

$\therefore$ $ds \geq 0$ $\quad$ i.e. $\boxed{(ds)_{H,P} \geq 0}$

$ds > 0$: spontaneous $\quad$ $ds = 0$ equilibrium.

5) at constant 'T'

$$Tds \geq dH$$

$$0 \geq dH - Tds$$

$$0 \geq dG.$$

$$\boxed{(dG)_{T,P} \leq 0}$$

$dG < 0$: spontaneous

$dG = 0$: equilibrium.

6) at constant V.

$$Tds \geq dU + PdV.$$

$\therefore$ $Tds \geq dU$

$\therefore$ $0 \geq dU - Tds.$

$\therefore$ $0 \geq dA$

$$\boxed{(dA)_{T,V} \leq 0}$$

$dA < 0$: spontaneous

$dA = 0$: equilibrium.

condition for spontaneity	condition for equilibrium	At constant	
$dU < 0$	$dU = 0$	S & V.	$(dU)_{S,V} \leq 0$
$dH < 0$	$dH = 0$	S & P	$(dH)_{S\,\&\,P} \leq 0$
$ds > 0$	$ds = 0$	U & V	$(ds)_{U,V} \geq 0$
$ds > 0$	$ds = 0$	H & P	$(ds)_{H,P} \geq 0$
$dG < 0$	$dG = 0$	P & T	$(dG)_{P,T} \leq 0$
$dA < 0$	$dA = 0$	V & T	$(dA)_{V,T} \leq 0$

#

$$T.ds \geq dU + PdV$$

Condition for spontaneity and relative sign of ΔH, ΔS & ΔG

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
0	+ve	−ve, spontaneous.
−ve	0	−ve, spontaneous
−ve	+ve	−ve, spontaneous
+ve	−ve	+ve, non-spontaneous.
−ve	−ve	at low temp : −ve, spontaneous. at high temp : +ve, non-spontaneous.
+ve	+ve	at low temp : +ve, non-spontaneous. at high temp : −ve, spontaneous.

important case

Example ① Ice ⟶ water $\Delta H = +ve$, $\Delta U = +ve$.

$\Delta G = +ve \rightarrow$ at low temp $\Delta H > -T\Delta S$
$\rightarrow$ non-spontaneous.

$\Delta G = -ve \rightarrow$ at high temp. $\Delta H < -T\Delta S$
$\rightarrow$ spontaneous.

Importance of G and A.

$\rightarrow (dG)_{T,P} < 0$: spontaneous. $\quad \rightarrow (dA)_{T,V} < 0$ spontaneous

$(dG)_{T,P} > 0$: nonspontaneous. $\quad (dA)_{T,V} > 0$ non-spontaneous.

$(dG)_{T,P} = 0$: equilibrium. $\quad (dA)_{T,V} = 0$ equilibrium.

→ We know that $A = U - TS$.

at constant temp. $\Delta A = \Delta U - T\Delta S$ ——①

From I law : $\Delta U = q + W \implies \Delta U = Q_{rev} + W_{max}$.

II^{nd} law : $\Delta S = \frac{Q_{rev}}{T} \implies \therefore T\Delta S = Q_{rev}$

Now.

$$\Delta A = \Delta U - T\Delta S = \cancel{Q_{rev}} + W_{max} - \cancel{Q_{rev}}$$

$\therefore \boxed{\Delta A = W_{max}}$ ⟵ work done on the system.

If work is done by the system $W = -ve$.

$$\therefore \boxed{-\Delta A = W_{max}}$$

{Decrease in helmholtz free energy gives the maximum work-done by the system. So A is also called as <u>work function</u>}

$$\therefore \boxed{-A = W_{max}}$$

→ According to

$$G = H - TS$$

At constant temp.

$$\Delta G = \Delta H - T\Delta S = \Delta U - T\Delta S + P\Delta V.$$

$$\therefore \Delta G = \Delta A + P\Delta V.$$

$$\therefore \boxed{\Delta G = -W_{max} + P\Delta V}$$ — net workdone by the system.

i.e. $$\boxed{-\Delta G = W_{max} - P\Delta V.}$$

{The decrease in Gibbs free energy gives maximum work other than expansion work or volume – pressure work, work which is done is called net-work done by the system, and 'G' is also net work function / non-PV work.

$$\boxed{-\Delta G = W_{max} - P\Delta V}$$}

→ Bridging equation between thermodynamic and electrochemistry.

$\Delta G = -nFE_{cell}$
$-\Delta G = nFE_{cell}$

$$\Delta G = -nFE_{cell}.$$

If $E_{cell} = +ve \Rightarrow \Delta G = -ve$, spontaneous.

If $E_{cell} = -ve \Rightarrow \Delta G = +ve$, non-spontaneous.

Que – 1 The free energy change of ΔG of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm. is.

⇒ $\Delta G = -nRT\ln\left(\frac{P_1}{P_2}\right)$

$\Delta G = -1RT\ln\left(\frac{1}{2}\right)$

$$\therefore \boxed{\Delta G = +RT\ln 2}$$

Que-2 A reversible expansion of 1 mole of an ideal gas is carried out from 1.0 litre to 4.0 litre under isothermal condition at 300 K. ΔG

for this process is ——

⟨i⟩ $300\ R \ln 2$ ⟨ii⟩ $-600\ R \ln 2$

⟨iii⟩ $600\ R \ln 2$ ⟨iv⟩ $-300\ R \ln 2$.

$\Rightarrow$ $V_1 = 1\,L$. $V_2 = 4\,L$.

$\Delta G = -nRT \ln\left(\frac{V_2}{V_1}\right)$

$\Delta G = -1 \cdot R \cdot 300 \ln\left(\frac{4}{1}\right)$

$\Delta G = -300 R \ln(4)$

$\Delta G = -300 R \ln(2^2)$

$\boxed{\Delta G = -600 R \ln 2}$

$\therefore$ option (ii) is the correct answer

Que-3 ΔH of a reaction is equal to the slope of the plot of ——

i) ΔG Vs $\frac{1}{T}$ ⟨ii⟩ ΔG vs T

⟨iii⟩ $\frac{\Delta G}{T}$ Vs T iv) $\frac{\Delta G}{T}$ Vs $\frac{1}{T}$.

$\Rightarrow$ $\Delta G = \Delta H - T\Delta S$. ($\Delta H$: slope)

$\therefore \frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S$ (slope = ΔH)

graph b/w $\frac{\Delta G}{T}$ Vs $\frac{1}{T}$

$\therefore$ option (iv) is the correct answer.

Que-4 The value of $\Delta U - \Delta H$ for the following reaction

$Fe_2O_{3(s)} + 3C_{(s)} \longrightarrow 2Fe_{(s)} + 3CO_{(g)}$ is ——

⟨i⟩ $-3RT$ ⟨ii⟩ $+3RT$ ⟨iii⟩ $+RT$ ⟨iv⟩ $-RT$

$\Rightarrow$ $\Delta n_g = (n_g)$ product $- n_g$(reactant)

$= 3 - 0$

$= 3$

$\Delta H = \Delta U + RT\Delta n_g \Rightarrow \Delta U - \Delta H = -RT\Delta n_g$

$\therefore \boxed{\Delta U - \Delta H = -3RT}$ $\because \Delta n_g = 3$

$\therefore$ option (i) is the correct answer.

Que-5 In an irreversible process, the change in Gibbs free energy (dG) and the change in entropy (ds), satisfy the criteria.

i) $(ds)_{V,U} = 0$, $(dG)_{T,P} = 0$. ⟨iii⟩ $(ds)_{V,U} = -ve$, $(dG)_{T,P} = -ve$.

ii) $(ds)_{V,U} = 0$ $(dG)_{T,P} = +ve$ ⟨iv⟩ $(ds)_{U,V} = +ve$, $(dG)_{T,P} = -ve$.

$\Rightarrow$ $TdS \geq \Delta U + P\Delta V$.

$\therefore \boxed{(ds)_{U,V} = +ve}$

$dG \lneq VdP - SdT$.

$(dG)_{P,T} < 0$

$\boxed{(dG)_{P,T} = -ve}$

$\therefore$ option (iv) is the correct answer.

Que-6 In view of the sign of ΔG for the following reactions.

$PbO_2 + Pb \longrightarrow 2PbO$ $\Delta G < 0$

$SnO_2 + Sn \longrightarrow 2SnO$ $\Delta G > 0$.

Which of the state are more stable for Pb & Sn.

⟨i⟩ +4, +2 ⟨ii⟩ +2, +2

⟨iii⟩ +4, +4 ⟨iv⟩ +2, +4.

⟹ (i) $PbO_2 + Pb \longrightarrow 2PbO$

$\boxed{\Delta G < 0}$ — spontaneous

↓

forward reactⁿ is favourable

product is stable ∴ Pb^{2+} is stable

(ii) $SnO_2 + Sn \longrightarrow 2SnO$

$\Delta G \not> 0$ — non-spontaneous

↓

~~forward~~ backward reactⁿ is favourable

↓

reactant is stable ∴ Pb^{4+} is stable

∵ option (iv) is the correct answer

Que-7 Calculate change in Gibbs free energy in cal. during compression of 2 moles of an ideal gas from 1 atm to 10 atm at 300 K.

⟹ n = 2 mole T = 300 K

$P_1 = 1$ atm $P_2 = 10$ atm.

$\Delta G = -nRT \times 2.303 \log\left(\frac{P_1}{P_2}\right)$

∴ $\Delta G = -2 \times 2.303 \times 8.3 \times 300 \log\left(\frac{1}{10}\right)$

$\Delta G = +5 \times 2.303 \log 10.$

$\Delta G = 11.515 \times 1$

∴ $\boxed{\Delta G = 11.5 \text{ kJ/mol}}$

Que-8 Calculate the change in Gibbs free energy during expansion of 5 moles of an ideal gas from 10 litre to 100 litre at 27°C.

⟹ n = 5, T = 27°C = 300 K R = 8.3 J/K.mol.

∴ RT = 2.5 kJ/mol., $V_1 = 10$ L, $V_2 = 100$ L

∴ $\Delta G = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right) = -2.303 \times 2.5 \times 5 \log\left(\frac{100}{10}\right)$

$\Delta G = -2.303 \times 12.5$ ~~k~~ $\log 10$

$\Delta G = -2.303 \times 12.5$

$\boxed{\Delta G = -27.75 \text{ kJ/mol}}$

Que-9 Sign of ΔG for melting of ice is −ve at. ___

⟨i⟩ 265 K ⟨ii⟩ 270 K.

⟨iii⟩ 271 K ⟨iv⟩ 274 K.

⟹ ΔG < 0 above 273 K. ⟹ spontaneous

ΔG > 0 below 273 K ⟹ nonspontaneous

∴ option (iv) is the correct answer.

Que-10 Consider the freezing of liquid H_2O at +10°C for this process what are the signs of ΔH, ΔS & ΔG ___

⟨i⟩ +ve, −ve, 0 ⟨ii⟩ −ve, +ve, 0

⟨iii⟩ +ve, −ve, +ve ⟨iv⟩ −ve, −ve, +ve.

⟹ $H_2O_{(s)} \longrightarrow H_2O_{(l)}$

above 0°C ⟹ nonspontaneous

below 0°C ⟹ spontaneous.

s ⟶ l : ΔH = +ve

but l ⟶ s : ΔH = −ve

∴ option (iv) is the correct answer.

Que-11 For $A \longrightarrow B$ $\Delta H = 4$ kcal · mol^{-1} K^{-1}, $\Delta S = 10$ cal · mol^{-1} · K^{-1}, the reaction is spontaneous when temperature can be ——

⟨i⟩ 400 K ⟨ii⟩ 300 K.

⟨iii⟩ 500 K ⟨iv⟩ 100 K.

$\Longrightarrow$ $\Delta H = 4$ kcal/mol.k $= 4000$ cal. K^{-1}.mol^{-1}

$\Delta S = 100$ cal . mol^{-1}. K^{-1}

for reaction to be spontaneous, $T\Delta S > \Delta H$

$\therefore$ $\Delta G = \Delta H - T\Delta S$
$= 4000 - 500 \times 10$
$= -1000$ cal/K. mol

$\therefore$ option ③ is the correct answer

Que-12 Consider the following spontaneous reaction $3X_{2}(g) \longrightarrow 2X_{3}(g)$, what are the sign of ΔH, ~~ΔG~~ ΔS and ΔG for the reaction.

⟨i⟩ +ve, +ve, +ve ⟨ii⟩ +ve, +ve, −ve.

⟨iii⟩ −ve, +ve, −ve. ⟨iv⟩ −ve, −ve, −ve.

$\Longrightarrow$ $\Delta S = -ve$.

$3X_2 \longrightarrow 2X_3$ (spontaneous)

$\Delta H = -ve$. , $\Delta G = -ve$

the reaction must carried out at low temp. to to be spontaneous

$\therefore$ option (iv) is the correct answer.

Que-13 A process is carried out at constant V ant at constant entropy S. It ~~is~~ will be spontaneous if ——.

⟨i⟩ $\Delta G < 0$ ⟨ii⟩ $\Delta H < 0$ ⟨iii⟩ $\Delta U < 0$ ⟨iv⟩ $\Delta A < 0$.

$\Longrightarrow$ A/c Clausius inequality theorem
$TdS \geq dU + PdV$.

at constant 'V' & 'S', $\boxed{dU \leq 0}$

$\therefore$ For reaction occurs to be spontaneous $\boxed{dU < 0}$

$\therefore$ option (iii) is the correct answer.

Que-14 In a reaction change in enthalpy is 3 kcal . K^{-1}. mol^{-1} and ΔS is 10 cal · K^{-1} . mol^{-1}. at what temperature reaction attains equilibrium.

$\Longrightarrow$ $\Delta H = 3$ Kcal· mol^{-1} K^{-1} $= 3000$ cal· mol^{-1}. K^{-1}

$\Delta S = 10$ cal . K^{-1}, mol^{-1}.

For reaction to be spontaneous, $\boxed{\Delta G < 0}$

at 300 K $\boxed{\Delta G = 0}$ - equilibrium

For $\Delta G < 0$ temp. must be greater than 300 K.

Que-15 Which of the following thermodynamic properties must be associated wit a reaction found to be spontaneous at high temperature, but not spontaneous at low temperature.

⟨i⟩ $\Delta H < 0$; $\Delta S < 0$ ⟨ii⟩ $\Delta H > 0$, $\Delta S > 0$

iii⟩ $\Delta H < 0$; $\Delta S > 0$ iii⟩ $\Delta H > 0$, $\Delta S < 0$

option ② is the correct answer

Que-16 The maximum non P-V work that a system can perform is ____.

<i> ΔH <ii> ΔG <iii> ΔS <iv> ΔA.

$\Rightarrow$ $\Delta A = -W_{max}$ or $-\Delta A = W_{max}$.

$\Delta G = \Delta A + P\Delta V$.

$\Delta G = -W_{max} + P\Delta V$.

$\boxed{-\Delta G = W_{max} - P\Delta V}$

$\therefore$ maximum non- P/V work that a system can perform is ΔG

$\therefore$ option (ii) is the correct answer

Que-17 Although the dissolution of NH_4Cl in water is an endothermic reaction even though it is spontaneous because. ____

i> $\Delta S = +ve$ <ii> $\Delta S = 0$.

<iii> $T\Delta S < \Delta H$ <iv> $T\Delta S > \Delta H$ & $\Delta S = +ve$.

$\Rightarrow$ For endothermic reaction

$\Delta H = +ve$ or

$\Delta H > 0$

For the reaction to be spontaneous.

$\boxed{\Delta G < 0}$

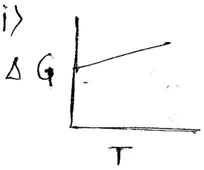
ΔG become less than 0 for $\Delta H > 0$

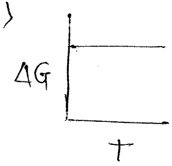
if $T\Delta S > \Delta H$ & $\Delta S = +ve$.

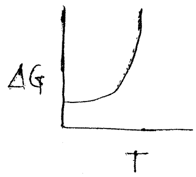
$\therefore$ option (iv) is the correct answer.

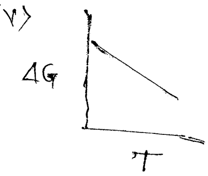
Que-18 Which of the following diagram best describes the relationship between ΔG and temp. for the following reaction.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

<i>


<ii>


<iii>


<iv>


$\Rightarrow$ $\Delta G = VdP - SdT$

$\Delta G = -nRT \ln\left(\frac{V_2}{V_1}\right)$

$\Delta n = 2 - 3 = -1$.

$\therefore \Delta G = +RT \ln\left(\frac{V_2}{V_1}\right)$

$\therefore$ slope, $m = R \ln\left(\frac{V_2}{V_1}\right)$

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

$\Delta S = -ve$

$y = c + mx$.

$m = -\Delta S$

$m = -(-ve)$

$\boxed{m = +ve}$

$\therefore$ option (i) is the correct answer.

Que-19 1 mole of an ideal gas initially present in a 2 litre insulated cylinder at 300 K is allowed to expand against vacuum to 8 litre. determine W, ΔU, ΔH, $\Delta S_{universe}$ & ΔG.

→ $n = 1$ mole. $V_1 = 2$ Litre $V_2 = 8$ L. $T = 300K$. $q = 0$.

$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$ —— isothermal process

$\Delta S = R\ln\left(\frac{8}{2}\right)$

$\Delta S = R\ln 4 = R.\ln 2^2$

$\boxed{\Delta S = 2R.\ln 2}$

$W = -P\Delta V$

but expansion against vacuum

$P_{ex} = 0$

$\therefore \boxed{W = 0}$

$\Delta G = -T.\Delta S = -300 \times 2R.\ln 2$

$\boxed{\Delta G = -600\,R.\ln 2}$

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

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

$= -600R\ln - 300 \times 2R\ln 2$

$\boxed{\Delta H = -1200\,R\ln 2}$

expansion against vacuum.

$P_{ex} = 0.$

$\boxed{\Delta H = \Delta U = -1200R\ln 2}$

Que-20 For the reaction $X_2O_4\,(l) \longrightarrow 2XO_{2\,(g)}$ at 298 K, Given that

$\Delta U = 9.$ kJ, $\Delta S = 84$ J/K, $\Delta G = ?$

i) -11.08 kJ (iii) -13.55 kJ

ii) $+11.08$ kJ (iv) $+13.55$ kJ.

Que-21 The entropy change ΔS in $J \cdot g^{-1} \cdot K^{-1}$ for $H_2O_{(l)} \longrightarrow H_2O_{(g)}$, $\Delta H = 2270$ J/gram at 1 atm, 100°c is

⟨i⟩ $2270/373$ ⟨ii⟩ $373/2270$

⟨iii⟩ 2270×373 ⟨iv⟩ $(2270 \times 373)^{1/2}$.

$\Longrightarrow$

Some important formulae.

→ $TdS \geq dU + PdV$

→ $(dU)_{S,V} \leq 0$

→ $(dH)_{S,P} \leq 0$

→ $(dS)_{U,V} \geq 0$

→ $(dS)_{H,P} \geq 0$

→ $(dG)_{P,T} \leq 0$

→ $(dA)_{V,T} \leq 0$

→ Work done by the system.

$$\boxed{-A = W_{max}}$$

→ Net work done / non-PV work done by the system.

$$-G = W_{max} - P\Delta V.$$

→ bridging equation between thermodynamic and electrochemistry

$$\Delta G = -nFE_{cell}$$

$$-\Delta G = nFE_{cell}.$$

Gibb's equation (for closed, equilibrium system)

The expression that gives the relation between G, H, A, U [dependent variable] and T, P, V, S [independent variables] is called Gibb's equation.

U, H, G, A : dependent variables.

T, P, V, S : independent variables.

→ A/c 1^{st} law.

$$dU = dQ + dW = dq - PdV.$$

A/c 2^{nd} law

$$ds = \frac{dQ}{T} \quad \because \; dq/dQ = T.ds.$$

$$\therefore \boxed{dU = Tds - PdV} \quad \text{———} (1).$$

$$U = f(S, V)..$$

(2) $H = U + PV.$

$$\therefore dH = dU + PdV + VdP.$$

$$dH = Tds \cancel{-PdV} \cancel{+PdV} + VdP \qquad \text{(from eq}^n\text{ (1))}$$

$$\therefore \boxed{dH = Tds + VdP} \quad \text{———} (2).$$

$$H = f(S, P)$$

(3) $dG = dH - Tds - SdT$

$$= \cancel{Tds} - VdP \cancel{-Tds} - SdT \qquad \text{(from eq}^n\text{ (2))}$$

$$\boxed{dG = +Vdp - SdT} \quad \text{———} (3)$$

$$G = f(P, T)$$

(4)

$$dA = dU - d(TS)$$

$$dA = \cancel{Tds} - PdV \cancel{-Tds} - SdT$$

$$\boxed{dA = -PdV - SdT}$$

$$A = f(V, T).$$

——— (4)

i) $dU = Tds - PdV$. $U = f(S, V)$

ii) $dH = Tds + VdP$. $H = f(S, P)$

iii) $dG = VdP - SdT$ $G = f(T, P)$

iv) $dA = -PdV - SdT$. $A = f(T, V)$

These are four Gibbs equation

→ $dU = Tds - PdV$. $U = f(S, V)$ $\left(\frac{\partial U}{\partial S}\right)_V = T$ & $\left(\frac{\partial U}{\partial V}\right)_T = -P$

→ $dH = Tds + Vdp$ $H = f(S, P)$ $\left(\frac{\partial H}{\partial S}\right)_P = T$ & $\left(\frac{\partial H}{\partial P}\right)_S = V$.

→ $dG = VdP - SdT$ $G = f(T, P)$ $\left(\frac{\partial G}{\partial P}\right)_T = V$ & $\left(\frac{\partial G}{\partial T}\right)_P = -S$

→ $dA = -PdV - SdT$ $A = f(T, V)$ $\left(\frac{\partial A}{\partial V}\right)_T = -P$ & $\left(\frac{\partial A}{\partial T}\right)_V = -S$.

From the above equation.

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = V.$$

$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -P \qquad \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial A}{\partial T}\right)_V = -S$$

→ U, H, G, A → All are extensive properties → depends on no. of moles.

Now,

for closed equilibrium system.

$\boxed{A \rightleftharpoons B}$

↓

there is no change in number of moles so far.

↓

hence, U, H, G, A are not depends on above system.

→ For open system.

$A \rightleftharpoons B$ 'n' doesn't remains constant.

U, H, G, A depends on 'n' for open system.

Exact and inexact differentials

→ **Exact differentials** : The functions ~~betw~~ which is integrated between appropriate limit is called exact differentials.

Example : all state functions. – U, G, H, A, ...

① $\int_{U_1}^{U_2} dU = U_2 - U_1$ (only.

path I : $\int_{U_1}^{U_2} dU = \int_{U_1}^{U_3} dU + \int_{U_3}^{U_2} dU = U_2 - U_1$

path II : $\int_{U_1}^{U_2} dU = \int_{U_1}^{U_4} dU + \int_{U_4}^{U_2} dU = U_2 - U_1$

→ definite value : exact differentials.

→ **Inexact differentials** : The functions which are not integrated in between appropriate limits is called path functions

Example : all path functions are inexact differentials : q or W.

① $\int_{q_1}^{q_2} dQ = Q_2 - Q_1$ (it's values depends on path).

path I : $\int_{Q_1}^{Q_2} dQ = \int_{Q_1}^{Q_3} dQ + \int_{Q_3}^{Q_2} dQ = (Q_2 - Q_1)_1$

path II : $\int_{Q_1}^{Q_2} dQ = \int_{Q_1}^{Q_4} dQ + \int_{Q_4}^{Q_2} dQ = (Q_2 - Q_1)_2$

different values : Inexact differentials

Euler's reciprocal rule.

Whether a given function is exact or inexact differential that can be obtained by Euler's reciprocal rules.

$$dz = M dx + N dy$$

$$\Longrightarrow \boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y}$$

state functions : exact differential : definite value : U, G, H, A ....

path functions : inexact differential : different values : Q, W,

Maxwell Relations.

$\longrightarrow \quad dU = +TdS - PdV.$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$\longrightarrow \quad dH = TdS + VdP.$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$\longrightarrow \quad dG = VdP - SdT$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$\longrightarrow \quad dA = -PdV - SdT$

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$\longrightarrow$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S = V$$

$\longrightarrow$

$$\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial A}{\partial T}\right)_V = -S.$$

$\longrightarrow$

$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S = -P$$

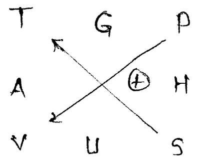
$\longrightarrow$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T.$$

Que-1 For a given system, of constant composition. The pressure is given by.

(i) $-\left(\frac{\partial U}{\partial S}\right)_V$ (ii) $-\left(\frac{\partial U}{\partial V}\right)_S$ (iii) $\left(\frac{\partial U}{\partial S}\right)_T$ (iv) $\left(\frac{\partial U}{\partial V}\right)_T$

$\Longrightarrow$



$dU = -PdV + TdS$

$dA = -PdV - SdT$

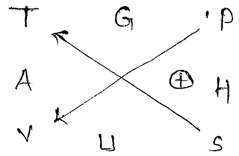
$$-\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial A}{\partial V}\right)_T = P$$

$\therefore$ option ② is the correct answer

Que-2 For a process in a closed system, temperature is equal to

a. $\left(\frac{\partial H}{\partial P}\right)_S$ b. $\left(\frac{\partial A}{\partial V}\right)_T$ c. $\left(\frac{\partial G}{\partial P}\right)_T$ d. $\left(\frac{\partial H}{\partial S}\right)_P$.

$\Longrightarrow$



$dU = TdS - PdV$

$dH = VdP + TdS$

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T$$

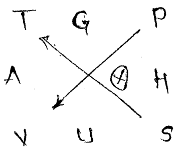
$\therefore$ option ④ is the correct answer

Que-3 The correct thermodynamic relation among the following is

ⓐ $\left(\frac{\partial U}{\partial V}\right)_S = -P$ (ii) $\left(\frac{\partial H}{\partial V}\right)_S = -P.$

(iii) $\left(\frac{\partial G}{\partial U}\right)_S = -P$ (iiii) $\left(\frac{\partial A}{\partial V}\right)_S = -P.$

⟹



$dU = TdS - PdV$

$dA = -SdV - PdT$

$dG = VdP - SdT$

$\left(\frac{\partial U}{\partial V}\right)_S = -P$

∴ option ① is the correct answer.

Que-4 Using the fundamental equation $dA = -SdT - PdV$, The maxwell relation is ____

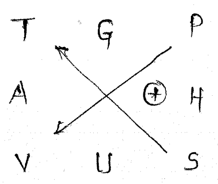
(a) $\left(\frac{\partial A}{\partial P}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V$

(b) $\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V$

(c) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_T$

(d) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

⟹



$dA = -SdT - PdV$

$dG = -SdT + VdP$

$dU = TdS - PdV$

$dH = VdP + TdS$

∴ option ④ is the correct answer

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Que-5 The maxwell relationship derived from equation $dG = Vdp - SdT$ is

(a) $\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$

(b) $\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial T}{\partial S}\right)_P$

(c) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

(d) $\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial S}\right)_P$

⟹

$dG = VdP - SdT$

$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

∴ option ⓒ is the correct answer.

Que-6 Identify which of the following is not correct

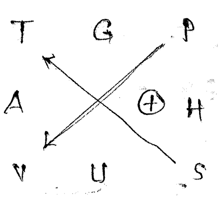
(a) $-\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$

(b) $-\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(c) $-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$

(d) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

⟹



$dH = VdP + TdS$

$dU = TdS - PdV$

$dA = -PdV - SdT$

$dG = VdP - SdT$

$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

∴ option ⓑ is the correct answer

Que-7 $\left(\frac{\partial U}{\partial S}\right)_P = ?$

ⓐ $T - P\left(\frac{\partial T}{\partial P}\right)_S$ ⓑ $T + P\left(\frac{\partial T}{\partial P}\right)_S$

ⓒ $T - P\left(\frac{\partial P}{\partial T}\right)_S$ ⓓ $T + P\left(\frac{\partial P}{\partial T}\right)_S$

$\Longrightarrow$

$$\begin{array}{ccc} T & G & P \\ A & & H \\ V & U & S \end{array}$$

$-dA = PdV + SdT$

$$\left(\frac{\partial U}{\partial S}\right)_P = \frac{\partial}{\partial S}\{TdS - PdV\}$$

$dH = VdP + TdS$

$$= T - P\left(\frac{\partial V}{\partial S}\right)_P$$

$dU = -PdV + TdS$

$dG = VdP - SdT$

$$= T - P\left(\frac{\partial T}{\partial P}\right)_S \quad (\because dH = VdP + TdS)$$

$\therefore$ option ⓐ is the correct answer

Que-8 $\left(\frac{\partial U}{\partial V}\right)_T = ?$

a. $T\left(\frac{\partial P}{\partial T}\right)_V + P$ ⓑ $T\left(\frac{\partial P}{\partial T}\right)_V - P$

ⓒ $T\left(\frac{\partial T}{\partial P}\right)_V + P$ ⓒ $T\left(\frac{\partial T}{\partial P}\right)_V - P$

$\Longrightarrow$

$dH = VdP + TdS$

$dU = -PdV + TdS$

$dG = VdP - SdT$

$-dA = PdV + SdT$

$\therefore$ option ⓑ is the correct answer.

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\partial}{\partial V}\{TdS - PdV\}$$

$$= T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Que-9 $\left(\frac{\partial H}{\partial P}\right)_T = ?$

ⓐ $V + T\left(\frac{\partial U}{\partial T}\right)_P$ ⓑ $V - T\left(\frac{\partial V}{\partial T}\right)_P$

ⓒ $T\left(\frac{\partial V}{\partial T}\right)_P - V$ ⓓ $-T\left(\frac{\partial T}{\partial V}\right)_P + V$

$\Longrightarrow$

$\frac{\partial H}{\partial P}$ $dH = VdP + TdS$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{\partial}{\partial P}\{VdP + TdS\} = V + T\left(\frac{\partial S}{\partial P}\right)_T = V + T\left\{-\left(\frac{\partial V}{\partial T}\right)_P\right\}$$

$$= V - T\left(\frac{\partial V}{\partial T}\right)_P$$

∴ option (b) is the correct answer

Trick to solve Maxwell relations and some important formulae.

$\longrightarrow dU = TdS - PdV$

$\longrightarrow dH = TdS + VdP$

$\longrightarrow dG = VdP - SdT$

$\longrightarrow dA = -PdV - SdT$

$\longrightarrow \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P = T$

$\longrightarrow \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = -P$

$U = f(S, V)$

$H = f(S, P)$

$G = f(P, T)$

$A = f(V, T)$.

$\longrightarrow \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = V$.

$\longrightarrow \left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial A}{\partial T}\right)_V = -S$.

$\longrightarrow$ Euler's reciprocal rule

$dz = Mdx + Ndy$.

$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$.

Thermodynamic square method.

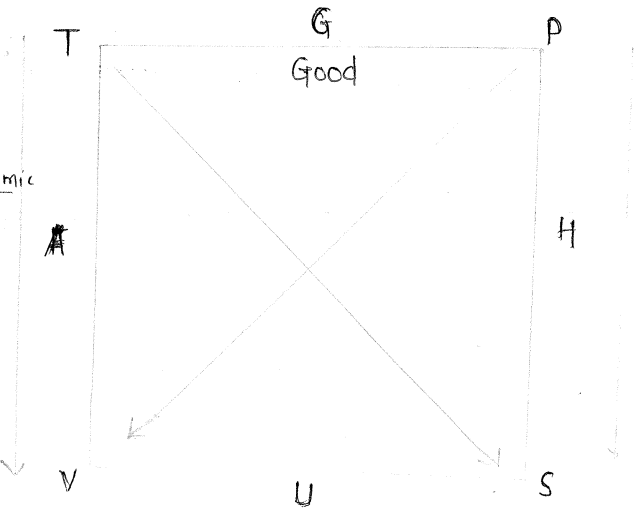
trick : Good Professor Have Studied Under Very Antique Teacher

G - Gibb's free energy P - Pressure H - Enthalpy S - Entropy U - internal energy

V - Volume T - temperature. A - HelmHolt free energy

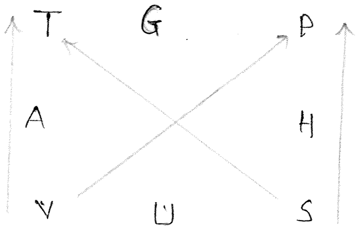
T, P, V, S - thermodynamic state variable

G, H, U, A - thermodynamic state function

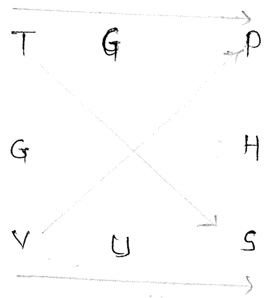


$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

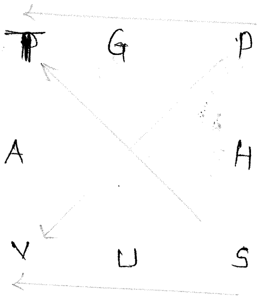
whenever P, & S come together add -ve sign to it.



$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

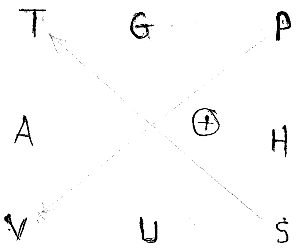


$$+\left(\frac{\partial T}{\partial P}\right)_S = +\left(\frac{\partial V}{\partial S}\right)_P$$



$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

Trick for various thermodynamic relations.



$$\left.\begin{aligned}
&\text{(i)}\ dH = VdP + TdS \\
&\text{(ii)}\ dG = VdP - SdT \\
&\text{(iii)}\ -dA = SdT + PdV \\
&\text{(iv)}\ dU = TdS - PdV
\end{aligned}\right\}\ \text{Gibb's equation.}$$

$\longrightarrow \left(\frac{dH}{dS}\right)_P = \left(\frac{dU}{dS}\right)_V = T$ $\qquad$ $\longrightarrow \left(\frac{dA}{dT}\right)_V = \left(\frac{dG}{dT}\right)_P = -S$

$\longrightarrow \left(\frac{dH}{dP}\right)_S = \left(\frac{dG}{dP}\right)_T = V$ $\qquad$ $\longrightarrow \left(\frac{dU}{dV}\right)_S = \left(\frac{dA}{dV}\right)_T = -P$

{ Good Professors Have Studied Under Very Antique Teacher.
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Cyclic rules # — Applicable to state functions only and not to the path functions.

If $z = f(x, y)$

then $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \partial y$

For a process at constant $z \Rightarrow dz = 0$

$$\left(\frac{\partial z}{\partial x}\right)_y \cdot dx + \left(\frac{\partial z}{\partial y}\right)_x \cdot \partial y = 0.$$

$$\left(\frac{\partial z}{\partial x}\right)_y \cdot dx = -\left(\frac{\partial z}{\partial y}\right)_x \partial y$$

$$\boxed{\left(\frac{\partial z}{\partial x}\right)_y \cdot \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x = -1}$$

$\Downarrow$

{ it is called cyclic rule which is applicable to state functions only & not to path functions }

Example For 1 mole of ideal gas $PV = nRT \Rightarrow PV = RT$

$$d(PV) = d(RT)$$

$$PdV + VdP = RdT \quad \text{——} (1)$$

at constant temperature 'T' $\quad PdV = -VdP \quad$ —— (2) $\quad \left(\frac{\partial V}{\partial P}\right)_T = \frac{-V}{P}$

at constant pressure 'P' $\quad PdV = RdT \quad$ —— (3) $\quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}$

at constant volume 'V' $\quad VdP = RdT \quad$ —— (4) $\quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

A/c cyclic rule.

$$\left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial T}{\partial V}\right)_P \cdot \left(\frac{\partial P}{\partial T}\right)_V = \frac{-V}{P} \times \frac{P}{R} \times \frac{R}{V} = -1$$

$\Longrightarrow G = f(T, P) \cdot \quad \left(\frac{\partial G}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_G \left(\frac{\partial P}{\partial G}\right)_T = -1$

$\Longrightarrow A = f(T, V) \quad \left(\frac{\partial A}{\partial T}\right)_V \left(\frac{\partial V}{\partial A}\right)_T \left(\frac{\partial T}{\partial V}\right)_A = -1$

Que-1 For an ideal gas,

(i) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = 0$ (iii) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$

(ii) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = 1$ (iv) $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -2$

$\Rightarrow$ option (ii) is the correct answer.

Que-2 Non-spontaneous process among the following is

1. The vaporization of superheated water at 105 °c & 1 atm pressure
2. Expansion of gas into vacuum.
3. Freezing of super-cooled water at −10°c & 1 atm pressure
4. Freezing of water at 0°c & 1 atm pressure.

$\Longrightarrow$ At 0°C.

Ice $\rightleftharpoons$ water (equilibrium process)

$\downarrow$

so freezing of water $\longrightarrow$ ice.

is not spontaneous i.e. it is non-spontaneous

$\therefore$ option (4) is the correct answer

{ super heated water – above 100°c exist as liquid.
super cooled water – below 0°c exist as liquid }

Que-3 Very whether $dz = (5x^2y + 3y^4)\,dx + (5/3\, x^3 + 12y^3x)\,dy$ is an exact differential or not.

$\Longrightarrow$ If $dz = M dx + N dy \Longrightarrow \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

given $dz = (5x^2y + 3y^4)\,dx + \left(\frac{5}{3}x^3 + 12y^3x\right)dy$.

$$\left\{\frac{\partial(5x^2y+3y^4)}{\partial y}\right\}_x = \text{ or } \neq \left\{\frac{\partial\left(\frac{5}{3}x^3 + 12y^3x\right)}{\partial x}\right\}_y$$

$$5x^2 + 3\times4y^3 = \text{ or } \neq 5/\cancel{3} \times \cancel{3}x^2 + 12y^3$$

$\therefore \quad 5x^2 + 12y^3 = 5x^2 + 12y^3$

$\therefore$ given dz is an exact differential.

Que-4 The exact differential dF of a state function $f(x, y)$ among the follow[ing] is

(i) $dx - \frac{x}{y} dy$

(ii) $\frac{1}{y} dx - \frac{x}{y^2} dy$

(iii) $x dy$.

(iv) $y dx - x dy$.

$dF = f(x, y)$

$$\left(\frac{\partial F}{\partial x}\right)_y = \left(\frac{\partial F}{\partial y}\right)_x.$$

$\Rightarrow$ (i) $dx - \frac{x}{y} dy$. $\quad M = 1 \quad N = -\frac{x}{y}$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial 1}{\partial y}\right)_x = 0. \quad \& \quad \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial \frac{-x}{y}}{\partial x}\right)_y = -\frac{1}{y} x^2 = \frac{-x^2}{y}$$

$$\therefore \left(\frac{\partial M}{\partial y}\right)_x \neq \left(\frac{\partial N}{\partial x}\right)_y$$

i.e. given function is not exact differential.

(ii) $\frac{1}{y} dx - \frac{x}{y^2} dy \qquad M = \frac{1}{y} = y^{-1} \quad N = -x/y^2$.

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial y^{-1}}{\partial y}\right)_x = -y^{-2} = -\frac{1}{y^2} \quad \& \quad \left(\frac{\partial N}{\partial x}\right)_y = \left\{\frac{\partial\left(-\frac{x}{y^2}\right)}{\partial x}\right\}_y = -\frac{1}{y^2}\left(\frac{\partial x}{\partial x}\right)_y = -1/y^2$$

$$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$\therefore$ given function is an exact differential.

$\therefore$ option (ii) is the correct answer.

Mathematical formulae

$\rightarrow \ln x = 2.303 \log x \qquad \rightarrow \ln x = a \Rightarrow x = e^a \qquad \rightarrow \log x = a \Rightarrow x = 10^a$

$\rightarrow \ln(a.b) = \ln a + \ln b \qquad \rightarrow \ln(a/b) = \ln a - \ln b$

$\rightarrow \ln e^x = x = \log 10^x \qquad \rightarrow \ln m^n = n \ln(m) \qquad \ln e = 1 = \log 10$

$\rightarrow \log 10^x = x \qquad \rightarrow \log 1 = 0, \quad \log 2 = 0.3010, \quad \log 3 = 0.447, \quad \log 4 = 0.6$

$\rightarrow \log 5 = 0.699 \qquad \rightarrow \log\left(\frac{1}{x}\right) = -\log x \qquad \rightarrow (a^m)^n = a^{mn}$

$\rightarrow a^m = a^n \Rightarrow (m = n) \qquad \rightarrow a^0 = 1 \qquad \rightarrow \pi = 22/7 = 3.14$

$\longrightarrow \frac{d}{dx}(x^n) = n.x^{n-1}$ $\longrightarrow \frac{d}{dx}(\text{constant}) = 0$ $\longrightarrow \frac{d}{dx}(U+V) = \frac{dU}{dx} + \frac{dV}{dx}$

$\longrightarrow \frac{d}{dx}(U.V) = U\frac{dV}{dx} + V\frac{dU}{dx}$ $\longrightarrow \frac{d}{dx}\left(\frac{U}{V}\right) = \frac{V.\frac{dU}{dx} - U\frac{dV}{dx}}{V^2}$

$\longrightarrow \frac{d}{dx}f(x) = f'(x)$ $\longrightarrow \frac{d}{dx}(k.f(x)) = k.f'(x)$ $\longrightarrow \frac{d}{dx}(\sin x) = \cos x.$

$\longrightarrow \frac{d}{dx}(\sin ax) = a\cos x$ $\longrightarrow \frac{d}{dx}(\cos x) = -\sin x$ $\longrightarrow \frac{d}{dx}(\cos ax) = -a.\sin x.$

$\longrightarrow \frac{d}{dx}e^x = e^x$ $\longrightarrow \frac{d}{dx}e^{ax} = a.e^x$ $\longrightarrow \frac{d}{dx}(\ln x) = \frac{1}{x}$

$\longrightarrow \frac{d^2}{dx^2} = \frac{d}{dx}\cdot\frac{d}{dx}$ $\longrightarrow$ If $z = f(x,y)$, then $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \cdot dy.$

$\longrightarrow$ If $z = f(x,y,z)$, then $dz = \left(\frac{\partial z}{\partial x}\right)_{y,z} dx + \left(\frac{\partial z}{\partial y}\right)_{x,z} dx + \left(\frac{\partial z}{\partial z}\right)_{x,y} dz.$

Integration

$\longrightarrow \int dx = x$ $\int_{x_1}^{x_2} dx = [x]_{x_1}^{x_2} = x_2 - x_1$

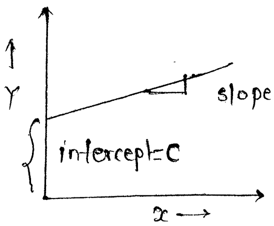
$\longrightarrow \int\frac{dx}{x} = \ln x \implies \int_{x_1}^{x_2}\frac{dx}{x} = [\ln x]_{x_1}^{x_2} = \ln x_2 - \ln x_1$

$\longrightarrow \int\frac{1}{T^2}dT = \frac{-1}{T}$ $\longrightarrow \int x^n dx = \frac{x^{n+1}}{n+1}$

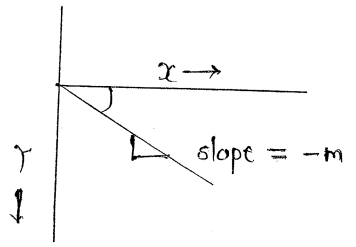
straight line equations.

$\rightarrow y = mx + c.$

m = slope , c = intercept



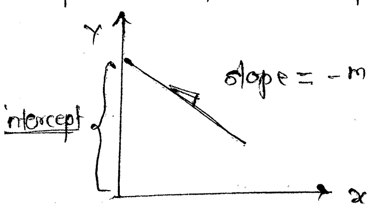
$\longrightarrow y = mx.$ $m = -ve$



$m = \text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{dy}{dx} = \tan\theta$

$\rightarrow y = -mx + c$

slope $= -m$, intercept $= c$.



Standard Gibb's free energy. (ΔG)

$G^\circ \Rightarrow$ 1 mole of pure ~~of~~ substance. at $T = 25^\circ c$ & $P = 1$ atm.

Example ① $R \longrightarrow P.$

$$\Delta G^\circ = \Sigma G^\circ(P) - \Sigma G^\circ(R).$$

→ standard Gibbs free energy of a compound is calculated from the formation of given compounds from it's element in stable form. For this purpose standard free energy of elements in it's stable form is assummed to be zero.

Example ① : $G^\circ_{(NH_3)} = ?$

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \longrightarrow 1\,NH_3$$

$$\Delta_f G^\circ = [G^\circ(NH_3)] - [G^\circ(N_2) + G^\circ(H_2)]$$

$$= [G^\circ(NH_3)] - [\tfrac{1}{2}\times 0 + \tfrac{3}{2}\times 0]$$

$$\Delta_f G^\circ = [G^\circ(NH_3)]$$

Example ② $G^\circ_{(HCl)} = ?$

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \longrightarrow HCl.$$

$$\Delta_f G^\circ = [G^\circ(HCl)] - [G^\circ(H_2) + G^\circ(Cl_2)]$$

$$= [G^\circ(HCl)] - [\tfrac{1}{2}\times 0 + \tfrac{1}{2}\times 0]$$

$$\Delta_f G^\circ = G^\circ(HCl)$$

∴ {Standard Gibbs free energy of a compound, G°, is nothing but standard free energy of formation from it's element in stable form.}

→ $\Delta_f G^\circ$ of an element $= 0$.

Example $H_2 \longrightarrow H_2$. $\Rightarrow$ Null reaction (No change) **Null reaction**

→ For a reaction.

$$R \longrightarrow P$$

$$\boxed{\Delta_{reac^n} G^\circ = \Sigma G^\circ(\text{product}) - \Sigma G^\circ(\text{reactant})}$$

Que-1 Will the reaction, $I_{2(s)} + H_2S_{(g)} \longrightarrow 2HI_{(g)} + S_{(s)}$ proceeds spontaneously in the forward direction at 298 K

$\Delta_f G^\circ(HI) = 1.8$ kJ/mole $\qquad \Delta_f G^\circ(H_2S) = 33.8$ kJ/mole.

$\Rightarrow$ For a reaction, $\Delta H^\circ = \Sigma H^\circ(P) - \Sigma H^\circ(R)$.

$\rightarrow$ For a compound if $\Delta_f H^\circ = +ve$, it is called endothermic compound and is less stable than reactants.

$\rightarrow$ For a compound if $\Delta_f H^\circ = -ve$, it is called exothermic compounds and is more stable than reactants.

$\therefore$ reaction is spontaneous

$\Delta G^\circ = \Delta_f G^\circ(\text{product}) - \Delta_f G^\circ(\text{reactant}) = 2(1.8) - 33.8 = 3.6 - 33.8 = -30.2$ kJ/mol

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Que-1 The compound A, B, C have $\Delta_f H^\circ$ values equal to $-10, -20, +15$ respectively. Give decreasing order of stability.

$\Rightarrow$ increasing order of stability.

	C	< A	< B
$\Delta_f H^\circ$	+15	−10	−20

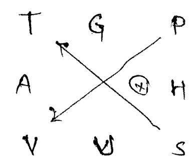
Que-2 For a closed system, the correct statement is.

i) $dU = TdS - PdV$.

(ii) $dU = VdP + SdT$

(iii) $dU = TdS + PdV$.

(iv) $dU = VdP - SdT$



$\Rightarrow$ $dU = TdS - PdV$.

$\therefore$ option (i) is the correct answer.

Que-3 $\left(\frac{\partial H}{\partial P}\right)_S$ has a dimension of.

i) Pressure

(ii) Volume

(iii) temperature

(iv) Heat capacity.

$\Rightarrow$ $dH = TdS + VdP$.

$\left(\frac{\partial H}{\partial P}\right)_S = V$.

$\therefore$ option (ii) is the correct answer

Que-4 The parameter which always decreases during a spontaneous process at constant S & V is

(i) U

(ii) H

(iii) G

(iv) Q.

$\Rightarrow$ $dU = TdS - PdV$.

at $U = f(S, V)$

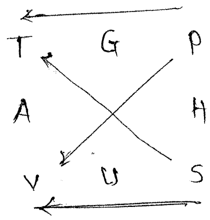
$\therefore$ option (i) is the correct answer

Que-5 Which of the following Maxwell relation is not correct.

⟨1⟩ $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$ ⟨2⟩ $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

⟨3⟩ $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ ⟨4⟩ $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$

$\Rightarrow$



$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

∴ option (iv) is the correct answer.

Que-6 Which of the following reactions occurs spontaneously.

ⓐ $A \longrightarrow B$; $\Delta H = -40$ kJ, $T\Delta S = -100$ kJ

ⓑ $P \longrightarrow Q$; $\Delta H = -80$ kJ, $T\Delta S = 10$ kJ.

ⓒ $X \longrightarrow Y$; $\Delta H = 30$ kJ, $T\Delta S = 120$ kJ.

ⓓ $M \longrightarrow N$; $\Delta H = -50$ kJ, $T\Delta S = -150$ kJ.

ⓔ $C \longrightarrow D$; $\Delta H = 100$ kJ, $T\Delta S = 40$ kJ.

⟨1⟩ a, d, e ⟨2⟩ a, d ⟨3⟩ b, c (4) a, e.

$\Rightarrow$ ⓐ $\Delta G = \Delta H - T\Delta S = -40 + 100 = 60$ kJ, non-spontaneous

ⓑ $\Delta G = -80 - 10$ kJ $= -90$ kJ, spontaneous

ⓒ $\Delta G = 30 - 120 = -90$ kJ, spontaneous

ⓓ $\Delta G = -50 - (-150) = -50 + 150 = 100$ kJ, non-spontaneous

ⓔ $\Delta G = 100 - 40 = 60$ kJ, non-spontaneous

∴ option ③ is the correct answer.

Que-7 For the determination of absolute entropy (S_T) of a solid between T_1 and T_2, The property of solid is measured in this temp. range and plotted. The area under the curve give the measure of S_T. What are the variables plotted.

⟨i⟩ $\ln T$ (x-axis), C_p (Y-axis) ⟨ii⟩ T (x-axis), C_p (Y-axis)

⟨iii⟩ $\ln \frac{1}{T}$ (x-axis), C_p (Y-axis) ⟨iv⟩ C_p (x-axis), $\ln T$ (Y-axis).

$\Rightarrow$

Que-8 Identify the correct equation for entropy change of 1 mole of an ideal gas with initial volume V_1 and temp. T_1, it's change to final volume V_2 and temperature T_2.

1) $\Delta S = C_v \ln \frac{T_1}{T_2} + R \ln \frac{V_1}{V_2}$

option ③ is the correct answer

$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$

2) $\Delta S = \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

3) $\Delta S = C_v \cdot \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

4) $\Delta S = C_v \cdot \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

Que-9 At 300 K, 1 mole of an ideal gas expanded reversibley from a volume 10 L to 100 L. The ΔS in J/K is ($R = 8.314$ J. K^{-1}. mol^{-1}).

⟨i⟩ 19.417 ⟨ii⟩ −19.147 ⟨iii⟩ 1.9147 ⟨iv⟩ −1.9417.

$\Rightarrow$ $\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$ at constant T.

$\Delta S = 2.303 \times 8.314 \times 1 \times \log\left(\frac{100}{10}\right)$

$\Delta S = 2.303 \times 8.314 \times \log 10$

$\therefore \Delta S = 19.147 \times 1$

$\boxed{\Delta S = 19.147 \text{ J/K}}$

$\therefore$ option ⓘ is the correct answer.

Que-10 The free energy change of 1 mole of an ideal gas that is compressed isothermally from 1 atm to 2 atm. is.

⟨i⟩ RT ln 2 ⟨ii⟩ −2RT

⟨iii⟩ −RT ln 2 ⟨iv⟩ RT

$\Rightarrow$ $\Delta G = -nRT \ln\left(\frac{P_1}{P_2}\right)$

$\Delta G = -1 \times RT \ln\left(\frac{1}{2}\right)$

$\boxed{\Delta G = +RT \ln 2}$

$\therefore$ option ① is the correct answer.

Que-11 A reversible expansion of 1 mole of an ideal gas is carried out from 1 litre to 4 litre under isothermal condition at 300 K. ΔG

for this reaction is.

⟨i⟩ 300 R . ln 2 ⟨ii⟩ 600 R . ln 2.

⟨iii⟩ −600 R ln 2 ⟨iv⟩ −300 R ln 2.

$\Rightarrow$

Que - 12 The non-spontaneous reaction among the following is.

⟨i⟩ The vaporization of superheated water at 105°c & 1 atm.

⟨ii⟩ Expansion of the gas into the vacuum.

⟨iii⟩ Freezing of supercooled water at −10°c. & 1 atm. pressure.

⟨iv⟩ Freezing of water at 0°c & 1 atm.

$\Rightarrow$

Que-13 $\left(\frac{\partial G}{\partial P}\right)_T = ?$

⟨i⟩ V ⟨ii⟩ S ⟨iii⟩ −S ⟨iv⟩ −V.

$\Rightarrow$

Que - 14 ΔH of a reaction is equal to the slope of plot.

⟨i⟩ ΔG V/s $1/T$ ⟨ii⟩ ΔG V/s T

⟨iii⟩ $\frac{\Delta G}{T}$ V/s T ⟨iv⟩ $\frac{\Delta G}{T}$ V/s $\frac{1}{T}$

$\Rightarrow$

Que - 15 The standard free energy of formation of H_2S gas & CdS ~~at~~ is -49.0 kJ. mol^{-1} & -121.2 kJ. mol^{-1}. Use this data to predict whether H_2S gas will reduced $CdS_{(s)}$ to metallic Cd at this temp.

i) $\Delta G = -78.2$ kJ. mol^{-1} & H_2 reduces CdS

ii) $\Delta G = -39.1$ kJ. mol^{-1} & H_2 reduces CdS.

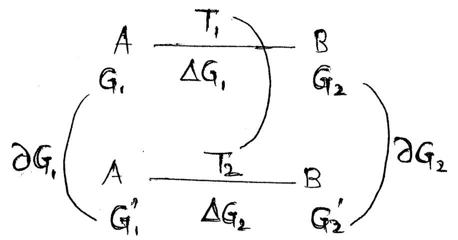
iii) $\Delta G = 0$ k.J. mol^{-1} & reaction is at equilibrium.

iv) $\Delta G = 78.0$ kJ. mol^{-1} & the reaction is not feasible.

$\Longrightarrow$

Temperature dependence of Gibbs Helmholtz equation.

$\longrightarrow$ Consider a process which takes place at two different temperature T_1 and T_2.



$$dG = Vdp - SdT$$

At constant pressure $\Longrightarrow dp = 0$

$$\therefore \quad dG = -SdT$$

$$\Longrightarrow \left(\frac{dG}{dT}\right)_P = -S.$$

$$G = f(T, P).$$

For initial state, $\left(\frac{\partial G_1}{\partial T_1}\right)_P = -S_1$ ——— ①

For final state, $\left(\frac{\partial G_2}{\partial T_2}\right)_P = -S_2$. ——— ②

subtracting equation ① from ②.

$$\left(\frac{\partial G_2}{\partial T_2}\right)_P - \left(\frac{\partial G_1}{\partial T_1}\right)_P = -S_2 + S_1 = S_1 - S_2 = -(S_2 - S_1) = -\Delta S.$$

$$\therefore \boxed{\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S} \quad ——— ③$$

Now, we know that

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

$$\therefore \boxed{\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p} \quad \text{—— (4)}$$

Gibb's - Helmholtz equation, gives temperature dependence of Gibb's free energy change at constant pressure condition

or

$$-\Delta H = -\Delta G + T\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

$$\longrightarrow \boxed{-\frac{\Delta H}{T^2} = \left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_p} \quad \text{—— (5)}$$

Gibb's Helmholtz equation at constant ~~volume~~. pressure

as

$$\left\{ \begin{aligned} -\frac{\Delta H}{T^2} &= -\frac{\Delta G}{T^2} + \frac{1}{T}\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \\ \& \quad \frac{d}{dx}\left(\frac{u}{v}\right) &= \frac{v \cdot \frac{du}{dx} - u \cdot \frac{dv}{dx}}{v^2} \end{aligned} \right\}$$

Similarly, Equation (3), (4) and equation (5) are three different form of Gibbs - Helmholtz equation at constant pressure.

→ Similarly, Gibb's - Helmholtz equation at constant volume are.

$$\boxed{\Delta A = \Delta U + T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V}$$

$$\boxed{-\frac{\Delta U}{T_2} = \left[\frac{\partial}{\partial T}\left(\frac{\Delta A}{T}\right)\right]_V}$$

Gibb's equation for non-equilibrium for open / non-equilibrium system

$\updownarrow$

1, 2, 3 ......, i

$\downarrow \quad \downarrow \quad \downarrow \qquad \downarrow$

$n_1 \quad n_2 \quad n_3 \qquad n_i$

open - system

n = not constant

no. of moles changes

⇓

U, G, H, A also changes.

$A \rightleftharpoons B$

n = constant ⟹ no change in extensive properties

closed system.

⇓

$dU = TdS - PdV$

$dH = TdS + VdP$

$dG = VdP - SdT$

$dA = -PdV - SdT$

→ consider a non-equilibrium / open system.

matter exchange between system and surrounding.

$n \neq$ constant.

Number of molecules/moles changes and hence extensive properties also changes.

$G = f(T, p)$ — for closed, equilibrium system.

$G = f(T, P, n)$ — for open / non-equilibrium system.

where n = no. of moles

$$G = f(T, P, \underbrace{n_1, n_2, \ldots n_i}_{n_j})$$

$$G = f(T, P, n_1, n_2, n_j\}$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T, n_j} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_j} \cdot dT + \left(\frac{\partial G}{\partial n_1}\right)_{T, P, n_j \neq 1} \cdot n_i + \left(\frac{\partial G}{\partial n_2}\right)_{T, P, n_j \neq 2} \cdot n_2$$

$$+ \ldots\ldots + \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j \neq 1} \cdot dn_i$$

$$\therefore\ dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots + \mu_i dn_i$$

$$\left[\because \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j \neq i} = \overline{G}_i / \mu_i = \text{chemical potential}\right]$$

$$\therefore \boxed{dG = Vdp - SdT + \sum_i \mu_i dn_i}$$

or

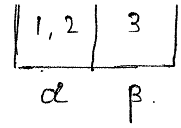
$$\boxed{dG = Vdp - SdT + \sum_i \overline{G}_i dn_i}$$

similarly

$$\left\{\begin{aligned} dU &= TdS - PdV + \sum_i \overline{U}_i \cdot dn_i \\ dH &= TdS + VdP + \sum_i \overline{H}_i \cdot dn_i \\ dA &= -PdV - SdT + \sum_i \overline{A}_i\, dn_i \\ dG &= V \cdot dp - SdT + \sum_i \overline{G}_i \cdot dn_i \end{aligned}\right\} \longrightarrow$$

Gibb's equation for open / non-equilibrium systems.

→ For multiphase system



$$dG = Vdp - SdT + \sum_i^{\alpha} \mu_i^{\alpha}\, dn_i^{\alpha} + \sum_i^{\beta} \mu_i^{\beta}\, dn_i^{\beta}$$

$$dG = Vdp - SdT + \sum_i \left[\mu_1^{\alpha} dn_1^{\alpha} + \mu_2^{\alpha} dn_2^{\alpha} + \mu_3^{\beta} dn_3^{\beta}\right]$$

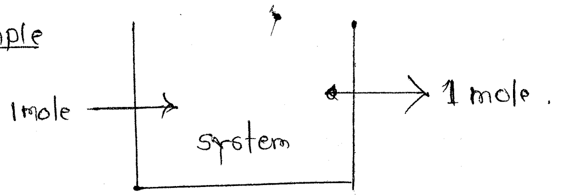
Chemical potential and it's importance.

μ – chemical potential is an intensive property.

$$\bar{G}_i / \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq i}$$

→ The change in Gibb's free energy per mole is called as chemical potential.

Example



G - changes } chemical potential.

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$dG = Vdp - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \dots\dots + \mu_i dn_i$$

at constant pressure (P) and temp (T).

$$dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots\dots + \mu_i dn_i.$$

on integrating the both sides. $\left(\because \int dx = x\right)$

$$G = \mu_1 n_1 + \mu_2 n_2 + \dots\dots + \mu_i n_i$$

→ For pure substance of 1 mole.

$$G = \mu_1 n_1 \text{ or } \mu \quad (\because n = 1)$$

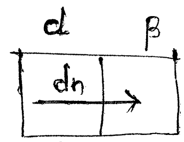
$\therefore$ $\boxed{G_{1m} = \mu}$ — chemical potential for 1 mole.

but μ is intensive property

$\therefore$ { For pure substance, chemical potentials is equals to the molar free energy i.e. $G_m = \mu$ }

Importance of μ_i

→ consider a component 'i' present in two region α & β. and dn amount of i is transferring from α → β



→ We know that

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

at constant T & p

$$dG = \sum_i \mu_i dn_i = \mu_1 n_1 + \mu_2 n_2 + \dots + \mu_i n_i$$

→ change in free energy in α- region.

$$dG = \mu_i^{\alpha}(-dn)$$ no. of moles decreases.

change in free energy in β - region.

$$dG = \mu_i^{\beta}(+dn)$$ no. of moles increases.

→ The total free energy change.

$$dG = dG^{\alpha} + dG^{\beta}$$

$$= \mu_i^{\alpha}(-dn) + \mu_i^{\beta}(+dn)$$

$$\boxed{dG = dn(\mu_i^{\beta} - \mu_i^{\alpha})}$$

{ if $\mu_i^{\alpha} > \mu_i^{\beta}$ then $dG = -ve$ the process is spontaneous }

snapshot point ⟨i⟩ $\mu_i^{\alpha} > \mu_i^{\beta}$ ⟹ matter transfer from α- region to β-region spontaneously.

⟨ii⟩ $\mu_i^{\beta} > \mu_i^{\alpha}$ ⟹ matter transfer occurs from β region to α-region spontaneously.

⟨iii⟩ $\mu_i^{\alpha} = \mu_i^{\beta}$ ⟹ system under equilibrium.

{ Where the chemical potential is more from such place matter escapes spontaneously. So chemical potential is a measure of ~~opposing tendancy~~. escaping tendancy }

Example

below 0°c $\overset{\alpha}{\text{water}} \longrightarrow \overset{\beta}{\text{ice}}$ ⟹ spontaneously.

$\therefore \mu_W > \mu_I$

at room temp. $\overset{\alpha}{\text{ice}} \longrightarrow \overset{\beta}{\text{water}}$ ⟹ spontaneously

$\therefore \mu_I > \mu_W$

Que-1 The chemical potential μ_i of the ith component is defined as.

a. $\mu_i = \left(\frac{\partial U_i}{\partial n_i}\right)_{T,P}$ b. $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P}$

c) $\mu_i = \left(\frac{\partial A_i}{\partial n_i}\right)_{T,P}$ d) $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$

$\Rightarrow$ chemical potential $\mu_i / \bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq 1}$

$\therefore$ option (d) is the correct answer.

Que-2 Two phases α & β are in equilibrium. The correct relations observed among the variables T, P & H are.

(a) $P_\alpha = P_\beta$, $T_\alpha \neq T_\beta$, $\mu_\alpha = \mu_\beta$

(b) $P_\alpha \neq P_\beta$, $T_\alpha = T_\beta$, $\mu_\alpha = \mu_\beta$

(c) $T_\alpha = T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha = \mu_\beta$.

d) $T_\alpha = T_\beta$, $P_\alpha = P_\beta$, $\mu_\alpha \neq \mu_\beta$.

$\Rightarrow$ when system reaches the equilibrium.

$\mu_\alpha = \mu_\beta$, $P_\alpha = P_\beta$

✡✡✡✡✡✡ **some important formulae.** ✡✡✡✡✡✡

$\rightarrow$ Gibb's Helmholtz's equation at constant pressure.

(i) $\left(\frac{\partial \Delta G}{\partial T}\right)_T = -\Delta S$ (ii) $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$. (iii) $\boxed{-\frac{\Delta H}{T^2} = \frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)_P}$

$\rightarrow$ Gibb's Helmholtz's equation at constant volume

(i) $\left(\frac{\partial \Delta A}{\partial T}\right)_V = -\Delta S$ (ii) $\Delta A = \Delta U + T\left(\frac{\partial \Delta A}{\partial T}\right)_V$ (iii) $-\frac{\Delta U}{T^2} = \frac{\partial}{\partial T}\left(\frac{\Delta A}{T}\right)_V$.

$\rightarrow$ Gibb's equation for closed or equilibrium system

(i) $dG = VdP - SdT$

(ii) $dA = -PdV - SdT$

(iii) $dH = VdP + TdS$

(iv) $dU = -PdV + TdS$.

$\rightarrow$ Gibb's equation for open or non-equilibrium system

(i) $dG = VdP - SdT + \Sigma \bar{G}_i dn_i$

(ii) $dA = -PdV - SdT + \Sigma \bar{A}_i dn_i$

(iii) $dH = VdP + TdS + \Sigma \bar{H}_i dn_i$

(iv) $dU = -PdV + TdS + \Sigma \bar{U}_i dn_i$

$\rightarrow$ Chemical potential.

$\left(\frac{\partial \Delta G}{\partial n_i}\right)_{T,P,n_j \neq 1} = \bar{G}_i / \mu_i$

$\rightarrow$ G at constant P, & T

$G = \Sigma \mu_i n_i$

$\rightarrow$ For 1 mole pure substance.

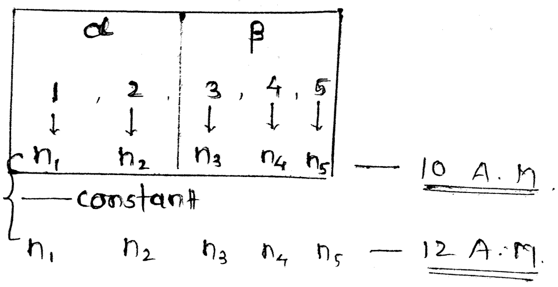
$G_m = \mu_i$ $(n = 1$

$\rightarrow$ $dG = dn(\mu_i^\beta - \mu_i^\alpha)$

$\alpha \; \boxed{dn \rightarrow} \; \beta$

$\rightarrow$ μ_i / chemical potenti[al] is a measure of escapi[ng] power.

Material equilibrium.



→ The number of moles of each component in each phase of the system remains constant with time, then the system is said to be under material equilibrium.

→ It is of two ~~ways~~. types.

1) Chemical / reaction equilibrium. – Equilibrium w.r.to conversion of 1 set of species to another set is called chemical equilibrium

$$A + B \rightleftharpoons C + D$$

At equilibrium rate of forward reaction = rate of backward reaction.

{ Even at equilibrium, reaction takes place, but no net reaction. This is called chemical / reaction equilibrium }

2) Physical equilibrium / phase equilibrium.

The equilibrium with respect to transfer of matter from one phase to another phase is called physical / phase equilibrium.

$$\text{solid} \rightleftharpoons \text{liquid}.$$

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}.$$

{ Even at equilibrium, transfer of matter takes place but no net transfer. }

→ condition for material equilibrium.

$$dG = Vdp - SdT + \Sigma \mu_i dn_i$$

at constant T & P,

$$dG = \sum_i \mu_i dn_i$$

$$\because \boxed{dG = 0} \text{ — at equilibrium.}$$

$$\boxed{\sum_i \mu_i dn_i = 0} \text{ — condition for material equilibrium}$$

Phase equilibrium – Clapeyron equation.

It gives the relation between P & T. It is useful in the construction of phase diagrams. It is applicable to one component two phase system.

H_2O (Ice) $\rightleftharpoons$ H_2O (water) : 1 component, 2 phases.

→ consider two phases A & B are in equilibrium at a given temp and pressure.

$$\text{phase } A \rightleftharpoons \text{phase } B.$$

At equilibrium.

$$dG = 0$$

$$G_A - G_B = 0.$$

$$G_A = G_B. \quad \text{——} (1)$$

→ By changing the temperature and pressure.

$$T \longrightarrow T + dT$$

$$P \longrightarrow P + dP$$

then

$$G_A \longrightarrow G_A + dG_A$$

$$G_B \longrightarrow G_B + dG_B.$$

At equilibrium.

$$\cancel{G_A} + dG_A = \cancel{G_B} + dG_B \quad \text{——} \text{ from equation (1).}$$

$$dG_A = dG_B.$$

but

$$dG = VdP - SdT.$$

$$\therefore \quad V_A\, dp - S_A\, dT = V_B\, dP - S_B\, dT$$

$$S_B\, dT - S_A\, dT = V_B\, dP - V_A\, dP$$

$$dT(S_B - S_A) = dP(V_B - V_A).$$

$$dT.\Delta S = dP.\Delta V.$$

$$\therefore \boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V}} \quad \text{——} \text{ Clapeyron equation for any phase equilibrium.}$$

OR

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T.\Delta V}}$$

$$s \longrightarrow l. \qquad \Delta S = \frac{\Delta_{fus} H}{T_{fus}}$$

$$l \longrightarrow g \qquad \Delta S = \frac{\Delta_{vap} H}{T_b}$$

Clausius - Clapeyron equation.

On applying Clapeyron equation to liquid - vapour equilibrium to get Clausius - Clapeyron equation.

at equililibrium liquid $\rightleftharpoons$ vapour.

Clapeyron equation $\Longrightarrow$ $\frac{dP}{dT} = \frac{dH}{T\Delta V}$.

$$\Longrightarrow \frac{dP}{dT} = \frac{\Delta_{vap.} H}{T_b (V_g - V_l)}.$$

volume occupied $V_g >> V_l$. Hence V_l can be neglected.

$$\frac{dP}{dT} = \frac{\Delta_{vap} H}{T \cdot V_g}.$$

by using ideal gas equation $V_g = \frac{RT}{P_g}$ — for 1 mole.

$$\therefore \frac{dP}{dT} = \frac{P_g \cdot \Delta_{vap} H}{RT^2}$$

$$\therefore \boxed{\frac{dP}{P_g} = \frac{\Delta_{vap} H}{R} \cdot \frac{dT}{T^2}.}$$

— ① This is called Clausius - Clapeyron equation.

→ Now integrated on both sides.

$$\int \frac{dP}{P} = \int \frac{\Delta_V H}{R} \cdot \int \frac{dT}{T^2}.$$

$$\ln P = \frac{\Delta_V H}{R} \times -\frac{1}{T} + c \qquad \because \int \frac{dx}{x^2} = -\frac{1}{x}.$$

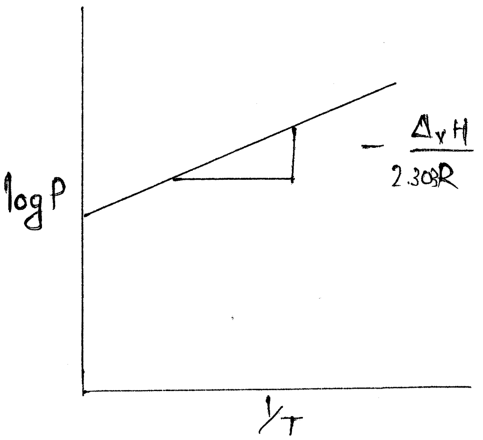
$$Y = m \; x + c.$$

$$\boxed{\ln P = -\frac{\Delta_V H}{R} \times \frac{1}{T} + c}$$

$$\boxed{\log P = \frac{-\Delta_V H}{2.303 R} \times \frac{1}{T} + c.}$$

for exothermic ~~ΔH.~~ $\Delta_V H = -ve$

for endothermic $\Delta_V H = +ve.$



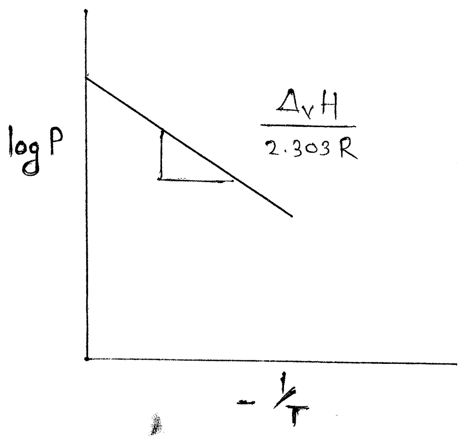
For exothermic reaction..

$\Delta H = -ve$.

$$\Rightarrow \log P = \left(-\frac{\Delta_v H}{2.303 R}\right) \times \frac{1}{T} + c.$$

$$y = mx + c.$$

vap $\longrightarrow$ liquid



For endothermic reaction.

$\Delta H = +ve$.

$$\Rightarrow \log P = \left(\frac{\Delta_v H}{2.303 R}\right)\left(-\frac{1}{T}\right) + c.$$

$$y = mx + c.$$

liquid $\longrightarrow$ gas

$\longrightarrow$ $P_1 \longrightarrow P_2$ and $T_1 \longrightarrow T_2$. and from Clausius - Clapeyron equation

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta_v H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \text{— from equation (1).}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta_v H}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\boxed{\ln \frac{P_2}{P_1} = \frac{\Delta_v H}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]}$$

$$\boxed{\log \frac{P_2}{P_1} = \frac{\Delta_v H}{2.303 R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]}$$

} Clausius - Clapeyron equation. within finite limit of T & P condition. and is used to calculate $\Delta_{vap} H$

Some important formulae.

$\longrightarrow$ condition for material equilibrium.

$$\boxed{\sum_i \mu_i dn_i = 0}$$

$\longrightarrow$ Clapeyron equation.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}.$$

$\longrightarrow$ $s \rightarrow l$: $\Delta S = \frac{\Delta_{fus} H}{T_m}$

$l \rightarrow g$: $\Delta S = \frac{\Delta_{vap} H}{T_b}$

$\longrightarrow$ Clausius - Clapeyron equation $l \rightleftharpoons v$ eq^m

$$\frac{dP}{dT} = \frac{P_g \cdot \Delta_{vap} H}{RT^2}$$

→ Differential form of Clausius-Clapeyron equation.

$$\frac{dP}{P_g} = \frac{\Delta_{vap}H}{R} \cdot \frac{dT}{T^2}.$$

→ exothermic reaction, $\Delta H = -ve$.

$$\log P = \frac{-\Delta_{vap}H}{2.303\,R} \cdot \left(\frac{1}{T}\right) + c.$$

~~l → gas~~ gas → liquid.

→ Integral form of Clausius-Clapeyron equation.

$$\log P = \frac{\Delta_{vap}H}{2.303\,R} \cdot -\left(\frac{1}{T}\right) + c$$

→ endothermic reaction, $\Delta H = +ve$.

$$\log P = \left(\frac{\Delta_{vap}H}{2.303\,R}\right) \cdot \left(-\frac{1}{T}\right) + c.$$

liquid → gas.

Que-1 Sign of ΔG for the melting of ice is $-ve$ at.

1> 265 K 2> 270 K 3> 271 K 4> 274 K.

⟹ solid ⇌ liquid.

at 0°c	equilibrium
below 0°c	nonspontaneous
above 0°c	spontaneous

above 273K reaction melting of ice is spontaneous, $\Delta G = -ve$

∴ option 4 is the correct answer.

Que-2 Which of the following thermodynamic properties must be associated with a reaction found to be spontaneous at high temp. but not spontaneous at low temp.

i> $\Delta H < 0$, $\Delta S < 0$ <iii> $\Delta H > 0$, $\Delta S > 0$

ii> $\Delta H < 0$, $\Delta S > 0$ <iv> $\Delta H > 0$, $\Delta S < 0$.

⟹ For reaction to be spontaneous at High temp.

$\Delta G = -ve$

at high temp., spontaneous reaction have

$\Delta H = +ve$, $\Delta S = +ve$.

i.e. $\Delta H > 0$, $\Delta S > 0$

∴ option 2 is the correct answer

Que-3 Consider freezing of water at +10°c for this process

	ΔH	ΔS	ΔG
i>	−	+	0
ii>	+	−	+
iii>	−	+	−
iv>	−	−	+

$\Longrightarrow$ above 0°C melting of ice → spontaneous.

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

ice → water $\boxed{\Delta S = +ve}$

∴ Option (iii) is the correct answer

Que-4 Combustion of octane takes place in an engine

$$C_8H_{18}(g) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g).$$

The sign of ΔH, ΔS and ΔG are.

(i) +ve, +ve, −ve (ii) −ve, +ve, −ve

(iii) −ve, −ve, −ve (iv) +ve, −ve, +ve.

$\Longrightarrow$ For combustion reaction.

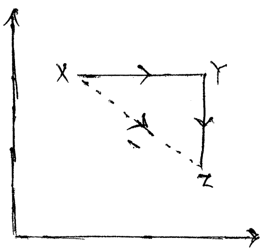
$\boxed{\Delta S = +ve}$

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

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

∴ option (ii) is the correct answer.

Que-5 For an ideal gas, going from initial state X to final state Z. The final state Z can be reached by either of the two path. shown in figure. Which of the following is correct.



1) $\Delta S_{x\to z} = \Delta S_{x\to y} + \Delta S_{y\to z}$

2) $W_{x\to z} = W_{x\to y} + W_{y\to z}$

3) $W_{x\to y\to z} = W_{x\to y}$

4) $W_{x\to y\to z} = \Delta S_{x\to y}$

$\Longrightarrow$

Que-6 For a system of constant composition, the pressure is given by.

1) $-\left(\frac{\partial U}{\partial S}\right)_V$ (2) $-\left(\frac{\partial U}{\partial V}\right)_S$

3) $\left(\frac{\partial U}{\partial S}\right)_T$ (4) $\left(\frac{\partial U}{\partial V}\right)_T$

$\Longrightarrow$

Que-7 The correct thermodynamic relation among the following is

(1) $\left(\frac{\partial U}{\partial V}\right)_S = -P$ (2) $\left(\frac{\partial H}{\partial V}\right)_S = -P.$

(3) $\left(\frac{\partial G}{\partial V}\right)_S = -P$ (4) $\left(\frac{\partial A}{\partial V}\right)_S = -S$

$\Rightarrow$

Que-8 Gibb's - Helmhottz equation is expressed as.

(1) $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_V = \frac{-\Delta E}{T^2}$ (2) $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$

(3) $dG = Vdp - SdT$ (4) $dH = Tds + VdP.$

$\Rightarrow$ Gibb's Helmholtz equation.

$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -S$ or $\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$ or $\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right]_P = \frac{-\Delta H}{T^2}$

$\therefore$ option 2 is the correct answer.

Que-9 The chemical potential μ_i of ith component is defined as

(1) $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{T,P}$ (2) $\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{T,P.}$

(3) $\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,P}$ (4) $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P.}$

$\Rightarrow$

$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i} = \bar{G}_i$ or μ_i (chemical potential).

$\therefore$ option 4 is the correct answer.

Que-10 In an open system, which one of the following is an intensive property.

(1) G (2) S (3) μ (4) V.

$\Rightarrow \mu_i = \frac{G}{n_i}$ $\therefore$ μ is intensive property $\therefore$ option 3 is the correct answer

Que-11 A vapour pressure of Et_2O is 100 mm at 270°C. and 200 mm at 127 °C, the molar enthalpy of vaporization is

(1) 1663.2 J. mol^{-1} (2) 1663.2 cal. mol^{-1}

⟨3⟩ 16.63 cal. mol   ⟨4⟩ 632 cal. mol

$\Rightarrow$

Que – 12 Standard Enthalpies of formation of O_3, CO_2, NH_3 and HI are 142.2, −3992, −46.2 and +25.9 kJ. mol^{-1}. The order of their increasing stability will be.

$\Rightarrow$

Que - 13 For liquid – vapour equilibrium of a substance, $\frac{dP}{dT}$ at 1 bar and 400 K is 8×10^{-3} bar. K^{-1}. The molar volume of vapor form is 200 L. ~~atm~~ mol^{-1}. The molar volume of liquid form is negligible. The molar enthalpy of vaporization is

⟨1⟩ 1,640 kJ. mol^{-1} ⟨2⟩ 100 kJ. mol^{-1}

⟨3⟩ 80 kJ. mol^{-1} ⟨4⟩ 64 kJ. mol^{-1}

$\Rightarrow$

Condition for reaction equilibrium.

reaction : $2A \rightleftharpoons 3B$.

$\longrightarrow$ condition for material equilibrium.

$$\sum \mu_i dn_i = 0.$$

$$\mu_1 dn_1 + \mu_2 dn_2 + \ldots\ldots + \mu_i dn_i = 0.$$

$\therefore$ For $2A \rightleftharpoons 3B$

$$\mu_A dn_A + \mu_B dn_B = 0.$$

$$\because \frac{1}{2}\left(-\frac{d[A]}{dt}\right) = \frac{1}{3}\left(+\frac{d[B]}{dt}\right)$$

$$\frac{1}{2}(-dn_A) = \frac{1}{3}(dn_B)$$

$$\therefore dn_A = -\frac{2}{3} dn_B.$$

$$\therefore \mu_A \times \left(-\frac{2}{3} dn_B\right) + \mu_B dn_B = 0.$$

$$\therefore -2\mu_A dn_B + 3\mu_B dn_B = 0.$$

$$\therefore dn_B(-2\mu_A + 3\mu_B) = 0$$

$$\left\{ \begin{array}{l} \because A.B = 0 \\ A \neq 0 \Longrightarrow B = 0 \\ B \neq 0 \Longrightarrow A = 0. \end{array} \right\}$$

$\therefore dn_B \neq 0.$;

$\Downarrow$

$\boxed{-2\mu_A + 3\mu_B = 0}$ $\longleftarrow$ under equilibrium

$3A \rightleftharpoons 2B$. $\quad 3A \rightarrow 2B$

$\downarrow$

$\boxed{-3\mu_A + 2\mu_B = 0}$ — also in equilibrium.

In general, $aA + bB \rightleftharpoons cC + dD$.

$\boxed{-a\mu_A - b\mu_B + c\mu_C + d\mu_D = 0.}$ $\longrightarrow$ reaction is under chemical equilibrium

$\Longrightarrow$ $\boxed{\sum_i \nu_i \mu_i = 0}$

$\nu_i \longrightarrow$ stoichiometric coefficient

reactant (-ve)

product (+ve).

Example ①

$$A + 2B \longrightarrow 4C + 3D$$

if $-\mu_A - 2\mu_B + 4\mu_C + 3\mu_D = 0$ — therefore reactⁿ is under equilibrium

then: $A + 2B \rightleftharpoons 4C + 3D.$

Chemical potential (μ) of pure ideal gas

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

intermolecular forces are negligible $\approx$ absent in ideal gas

→ At constant T & composition. $dT = 0$ $dn_i = 0$.

$$\therefore \quad dG = VdP$$

→ for one mole of an gas.

$$dG_m = V_m \, dP$$

$\because dG_m = d\mu$ (G_m replaced by μ).

$V_m = \frac{RT}{P}$

$$\therefore \quad d\mu = \frac{RT}{P} dP \quad \text{——} ①$$

→ $P_1 \longrightarrow P_2$ & $\mu_1 \longrightarrow \mu_2$

Now integrating equation ①

$$\int_{\mu_1}^{\mu_2} d\mu = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\therefore (\mu_2 - \mu_1) = RT \ln \frac{P_2}{P_1} = RT \ln \frac{P_2}{P_1} = 2.303 \, RT \log \frac{P_2}{P_1}$$

Since initial state is considered as standard state.

$\therefore \mu_1 = \mu^\circ =$ for pur substance → initial state ↓ standard state.

$P_1 = 1$ atm , at and temp(T) $\doteq 25°c$.

$$\therefore \quad \mu_2 - \mu_o^\circ = RT \ln \frac{P_2}{1} = RT \ln P_2$$

$$\therefore \quad \boxed{\mu_f = \mu^\circ + RT \ln P_f}$$

μ_f - final chemical potential

μ° - standard chemical potential

P_f - final pressure.

→ for mixture of ideal gases.

$$\mu_1 = \mu_1^\circ + RT \ln P_1$$

$$\mu_2 = \mu_2^\circ + RT \ln P_2$$

$$\vdots$$

$$\boxed{\mu_i = \mu_i^\circ + RT \ln P_i}$$

value $P_i \Longrightarrow$ partial vapour pressure of i^{th} ideal gas.

Relation between ΔG° & equilibrium constant (K) :-

$$\Delta G = \Delta G^\circ + RT\ln K.$$

At equilibrium

$$\Delta G = 0.$$

$$\therefore \quad \Delta G^\circ + RT\ln K = 0.$$

$$\left\{ \begin{array}{l} aA + bB \longrightarrow cC + dD. \\ K = \dfrac{[C]^c [D]^d}{[A]^a [B]^b} \end{array} \right\}$$

$$\therefore \quad \boxed{\Delta G^\circ = -RT\ln K}$$ —— Van't Hoff Reaction Isotherm.

where K - equilibrium constant

If

$$\left\{ \begin{array}{lll} K > 1 ; & \Delta G^\circ = -ve & \longrightarrow \text{spontaneous} \\ K < 1 ; & \Delta G^\circ = +ve & \longrightarrow \text{non-spontaneous.} \\ K = 0 ; & \Delta G^\circ = 0 & \longrightarrow \text{equilibrium.} \end{array} \right\} \leftarrow \text{at standard condition}$$

$$\Longrightarrow \quad \Delta G^\circ = -RT\ln K.$$

$$\Delta H^\circ - T\Delta S^\circ = -RT\ln K.$$

$$\boxed{\ln K = \frac{-\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R}} \Longrightarrow y = mx + c.$$

slope : $m = \dfrac{-\Delta H^\circ}{R}$ constant $c = \dfrac{\Delta S^\circ}{R} \Rightarrow$ intercept.

$$\Longrightarrow \quad \Delta G^\circ = -RT\ln K.$$

$$\therefore \quad \ln K = \frac{-\Delta G^\circ}{RT}$$

$$\therefore \quad \boxed{K = e^{-\Delta G^\circ / RT}} \Longrightarrow$$ equilibrium constant, K ⟶ depends only on temperature

Van't - Hoff equation.

⟹ It shows the temperature dependence of K.

$$\Delta G^\circ = -RT\ln K$$

$$\therefore \quad \frac{\Delta G^\circ}{T} = -R\ln K.$$

$$\therefore \left\{ \frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right\}_p = -R\left(\frac{\partial}{\partial T} \ln K\right)_p \quad \text{—— (1)}$$

But a/c Gibb's - Helmholtz equation.

$$\left\{ \frac{\partial}{\partial T}\left(\frac{\Delta G^\circ}{T}\right)\right\}_p = -\frac{\Delta H^\circ}{T^2} \quad \text{—— (2)} \longrightarrow \text{at standard condition.}$$

from equation (1) and equation (2).

$$\cancel{-} R\left(\frac{\partial}{\partial T} \ln K\right)_p = \cancel{-} \frac{\Delta H^\circ}{T^2}$$

$$R\left(\frac{\partial}{\partial T} \ln K\right)_p = \frac{\Delta H^\circ}{T^2}.$$

or $$\boxed{\therefore \left(\frac{\partial}{\partial T} \ln K\right)_p = \frac{\Delta H^\circ}{RT^2}}$$ —— for infinitesimally small change.

$$\boxed{\left(\frac{d}{dT} \ln k\right)_p = \frac{\Delta H^\circ}{RT^2}}$$ —— for large changes.

$\longrightarrow$ Now $T_1 \longrightarrow T_2$ & $K_1 \longrightarrow K_2$.

$$d(\ln k) = \frac{\Delta H^\circ}{R} \times \frac{dT}{T^2}$$ $\quad \frac{k_2}{k_1}$

taking integration on both side.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\boxed{\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]}$$

$$\therefore \boxed{\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]}$$

from above equation..

$\Longrightarrow$ For **exothermic reaction** ; $\Delta H^\circ = -ve$ and $T \Longrightarrow T_1 \rightarrow T_2$

$$\ln \frac{K_2}{K_1} = -ve.$$

$\therefore \boxed{K_2 < K_1}$

for exothermic reaction
Temp ↑ &
equilibrium constant K ↓

⟹ for endothermic reaction. $\therefore \Delta H^\circ = +ve$ & $T \Rightarrow T_1 \longrightarrow T_2$.

$$\ln \frac{K_2}{K_1} = +ve.$$

$$\boxed{K_2 > K_1}$$

for endothermic reaction.
Temp ↑ &
equilibrium constant K ↑

Example K at 25°c = 100 units.
at 50°c = 150 units.

& if $\Delta H^\circ = +ve$ —— endothermic reaction

$\Delta H^\circ = -ve$
$\Delta H^\circ = 0$ —— not a endothermic reaction.

⟹ For a reaction where equilibrium constant is independent of temperature.

$$K \xrightarrow{\times} T.$$

$$\Delta H^\circ = ?$$

$$\frac{d}{dT}(\ln K) = \frac{\Delta H^\circ}{RT^2}$$

⟹ K = constant K = 0.

$$\therefore \frac{\Delta H^\circ}{RT^2} = 0.$$

$$\Delta H^\circ = RT^2 \times 0$$

$$\therefore \boxed{\Delta H^\circ = 0}$$

Que ⟹ For a spontaneous ~~reqi~~ reaction. ΔG, equilibrium constant, E_{cell} be.

i) +ve , > 1 , − ve

ii) −ve , < 1 , −ve

iii) −ve , > 1 , +ve.

iv) −ve , < 1 , +ve.

⟹ $\boxed{\Delta G^\circ = -RT\ln K}$ ∴ option 3 is the correct answer

for spontaneous reaction

$\Delta G^\circ = -ve.$

$K = > 1$

$\boxed{\Delta G^\circ = -nFE^\circ_{cell}}$

∴ for spontaneous reaction E°_{cell} = +ve

Que ⟹ A chemical potential of component one, of A binary mixture is $\mu_1 = \mu_1^\circ + RT\ln P_1$, where P_1 is the partial vapour pressure of the component one, in vapour phase A standard state μ is

i) independent of T & P.

ii) depends on both T & P

iii) depends on T only

iv) depends on P only.

⟹ P = 1 atm at any Temp. T.

$\boxed{\mu = \mu^\circ}$

∴ μ° ~~only~~ depends ~~upon~~ only on temperature in the standard state.

Que ⟹ The variation of equilibrium constant K of such a reaction of the temperature T is $\ln K = 3 + \frac{2.0 \times 10^4}{T}$ given R = 8.3 J. mol⁻¹

The value of ΔH° & ΔS° are.

i) 166 $kJ.mol^{-1}$ & 24.9 $J.K^{-1}.mol^{-1}$

ii) 166 $kJ.mol^{-1}$ & 249 $J.K^{-1}.mol^{-1}$

iii) −166 $kJ.mol^{-1}$ & 249 $J.K^{-1}.mol^{-1}$

iv) −166 $kJ.mol^{-1}$ & −24.9 $J.K^{-1}.mol^{-1}$.

$\Longrightarrow$

$$\Delta G^\circ = -RT\ln K.$$

$$\Delta H^\circ - T\Delta S^\circ = -RT\ln K.$$

$$\therefore \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}.$$

$$\frac{\Delta S^\circ}{R} = 3.0$$

$$\Delta S^\circ = 3.0 \times 8.3$$

$$\Delta S^\circ = 24.9\ J.K^{-1}.mol^{-1}$$

$$-\frac{\Delta H^\circ}{R\cancel{T}} = \frac{2.0\times10^4}{\cancel{T}}$$

$$\therefore \Delta H^\circ = -8.3\times 2\times10^4$$

$$\Delta H^\circ = -16.6\times10^4$$

$$\Delta H^\circ = -166\ kJ.mol^{-1}$$

Que $\Longrightarrow$ For a closed system, the correct statement is

i) $dU = TdS - PdV$ ii) $dG = VdP + SdT$

iii) $dU = TdS + PdV$ iv) $dU = VdP - SdT$

$\Longrightarrow$ $dU = TdS - PdV$ is the correct statement, for a closed system.

$\therefore$ option ① is the correct answer.

Que $\longrightarrow$ Identify the correct statement from the following

a) At the melting point, the chemical potential of substance in solid phase and in liquid phase are same.

b) At the boiling point, the chemical potential of substance in liquid phase and in gaseous phase are same

c) partial molar free energy is designated as chemical potential.

i) a, b ii) b, c iii) a, c (iv) ~~abc~~ a, b, c.

$\Longrightarrow$

$$\Delta \bar{G}_{m,i} = \mu_i$$

All statement are correct option (iv) is the correct answer

Que → The equilibrium constant becomes 10 times on increasing temp from 400 K to 600 K. What is ΔH° in kJ/mol = ?

$R = 8.314\ J.\ K^{-1}/mol$

⟨i⟩ 23 ⟨ii⟩ 0.016

⟨iii⟩ 0.000016 ⟨iv⟩ 230.

$$\Longrightarrow \quad \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.3RT^2} = \frac{\Delta H^\circ}{2.3R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad \log \frac{10K_1}{K_1} = \frac{\Delta H^\circ}{2.3 \times 8.3}\left[\frac{600-400}{24 \times 10^4}\right]$$

$$= \frac{\Delta H^\circ}{8.3 \times 2.3} \times \frac{200}{24 \times 10^4}.$$

$$\Delta H^\circ = \frac{8.3 \times 2.3 \times 24 \times 10^4}{200} = \frac{458.16 \times 10^4}{200} = 2.29 \times 10^4$$

$$\therefore \quad \Delta H^\circ = 22.9 \times 10^3 \approx 23 \times 10^3 \approx \underline{23\ kJ/mol}$$

∴ option ① is the correct answer

Que → Enthalpy is equal to = ?

i) $TS + PV + \Sigma \mu_i n_i$

2) $TS + \Sigma \mu_i n_i$

3) $\Sigma \mu_i n_i$

4) $PV + \Sigma \mu_i n_i$

$$\Longrightarrow \quad dH = TdS + PdV + \Sigma \mu_i dn_i$$

$$\therefore \quad H = TS + PV + \Sigma \mu_i n_i$$

Hence, option ① is the correct answer.

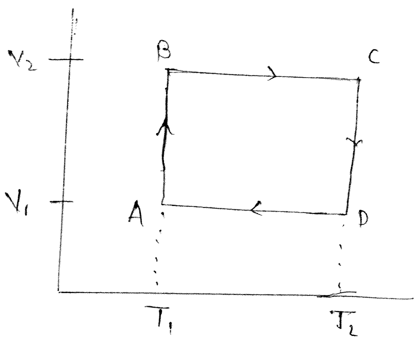
Que → 1 mole of an ideal gas undergo a cyclic process ABCDA starting from point A through four reversible steps as shown in figure. The total work done in the process is.

1) $R(T_1 - T_2)\,\frac{V_2}{V_1}$

2) $R(T_1 + T_2)\,\frac{V_2}{V_1}$

3) $R(T_1 + T_2)\ln\frac{V_2}{V_1}$

4) $R(T_2 - T_1)\ln\frac{V_2}{V_1}$



$\Longrightarrow$ $W = -RT\ln\frac{V_f}{V_i}$ for 1 mole.

$$W = W_{A\rightarrow B} + W_{B\rightarrow C} + W_{C\rightarrow D} + W_{D\rightarrow A}$$

$$= -RT_1\ln\frac{V_2}{V_1} + 0 + -RT_2\ln\frac{V_1}{V_2} + 0.$$

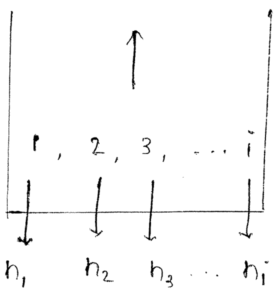
$$= -RT_1\ln\frac{V_2}{V_1} + RT_2\ln\frac{V_2}{V_1}$$

$\because$ option 4 is the correct answer.

$$\therefore \boxed{W = R(T_2 - T_1)\ln\frac{V_2}{V_1}}$$

Thermodynamics of open system. – partial molar properties.

For open system. – Number of moles (n) changes.



$\therefore X = f(T, P) \longrightarrow$ for closed system.

$\therefore X = f(T, P, n_1, n_2, n_3, \ldots n_i) \longrightarrow$ for open system.

$$\therefore dX = \left(\frac{\partial X}{\partial T}\right)_{P, n_j} + \left(\frac{\partial X}{\partial P}\right)_{T, n_j} + \left(\frac{\partial X}{\partial n_1}\right)_{T, P, n_j \neq 1} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{T, P, n_j \neq 1} dn_2$$

$$\ldots\ldots + \left(\frac{\partial X}{\partial n_i}\right)_{T, P, n_j \neq i} dn_i$$

$$\therefore \left(\frac{\partial X}{\partial n_i}\right)_{T, P, n_j \neq 1} = \overline{X}_i = \text{partial molar properties}$$

$\therefore$ at constant temperature T & constant pressure P

$$dX = \overline{X}_1\,dn_1 + \overline{X}_2\,dn_2 + \ldots\ldots \overline{X}_i\,dn_i$$

$$\therefore X = \overline{X}_1 n_1 + \overline{X}_2 n_2 + \ldots + \overline{X}_i n_i$$

$\therefore \boxed{X = \sum x_i n_i}$

$\therefore$ Hence extensive properties are $U, G, A, S, H \Longrightarrow X$.

& intensive properties are $\bar{U}, \bar{G}, \bar{A}, \bar{S}, \bar{H} \Longrightarrow \bar{X} \rightarrow$ P.M.P

intensive properties $\longleftarrow$ partial molar properties

partial molar properties : change in extensive properties per mole is called partial molar properties (P.M.P) and these are intensive properties.

$\rightarrow$ partial molar entropy $(\bar{S}_i)$

$$\bar{S}_i = \left(\frac{\partial S}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

$$S = \sum_i \bar{S}_i n_i$$

$\rightarrow$ partial molar enthalpy $(\bar{H}_i)$

$$\bar{H}_i = \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

$$H = \sum_i \bar{H}_i n_i$$

$\rightarrow$ partial molar Gibb's free energy $(\bar{G}_i)$

$$\bar{G}_i / \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

$$\therefore G = \sum \bar{G}_i n_i = \sum \mu_i n_i$$

$\rightarrow$ partial molar volume $(\bar{V}_i)$

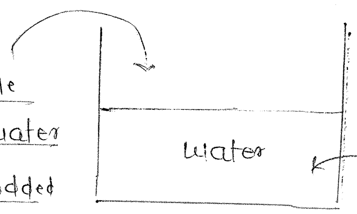
$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

$$V = \sum_i \bar{V}_i n_i$$

partial molar properties are intensive properties.

Example $\longrightarrow$ partial molar volume

1 mole of water is added



$\longleftarrow (V_m^*, H_2O = 18\ ml)$ — added. — before adding

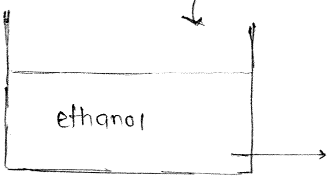
large amount of water $V_i = 1000\ ml.$ — before addin

$V_f = 1018\ ml.$ — after adding

change in volume $= 18\ ml.$

$\therefore$ partial molar volume of water $\left(\bar{V}^*_{H_2O}\right) = 18\ ml$ after adding

1 mole of H_2O is added (18 ml) $(V^*_{m, H_2O}) = 18$ ml. before adding.



V_i (ethanol) — 1000 ml.

V_f (C_2H_5OH + H_2O) — 1014 ml.

change in volume = 14 ml.

∴ partial molar volume of water $(\bar{V}^*_{m, H_2O}) = 14$ ml after adding

some important formulae

→ condition for reaction equilibrium.

$$\sum_i \nu_i \mu_i = 0.$$

ν_i — stoichiometric coefficient → product (+ve); → reactant ~~(+ve)~~. (−ve)

→ chemical potential of pure ideal gas.

$\mu = \mu^\circ + RT \ln P_f$ μ° — standard chemical potential — depends only on T & P = 1 atm P_f - final ~~vapour~~ pressure

$\mu_i = \mu_i^\circ + RT \ln P_i$ P_i — partial vapour pressure of i^{th} ideal gas.

→ relation betn ΔG° & equilibrium constant K.

i) $\Delta G^\circ = -RT \ln K = -2.303\, RT \log K.$

⟨iii⟩ $K = e^{-\Delta G^\circ / RT}$

ii) $\ln K = \dfrac{-\Delta H^\circ}{R} \times \dfrac{1}{T} + \dfrac{\Delta S^\circ}{R}$

⟨iv⟩ $\Delta G^\circ = -nFE^\circ_{cell}$

→ van't Hoff equation - temperature dependence of K.

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{or} \quad \frac{d}{dT}(\ln K) = \frac{\Delta H^\circ}{RT^2}$$

$K_2 > K_1$ — T↑ K↑ — endothermic

$K_2 < K_1$ — T↑ K↓ — exothermic

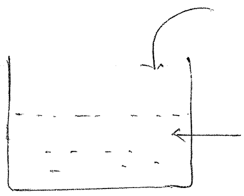
→ partial molar properties - explains thermodynamics of open system

i) $X = \sum_i \bar{x}_i n_i$ ⟨ii⟩ $S = \sum \bar{S}_i n_i$ ⟨iii⟩ $G = \sum_i \bar{G}_i n_i = \sum_i \mu_i n_i$

partial molar properties are

For partial molar volume. (P.M.V.)

1 mole of water added (18 ml) $(V^*_{m,H_2O} = 18 \text{ mol})$.



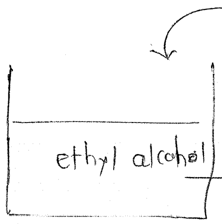
large ~~amount~~ amount of water — $V_i = 1000$ ml.

$V_f = 1018$ ml

change in vol^m = 18 ml.

$\therefore$ P.M.V of water in water $(\overline{V}^*_{H_2O}) = 18$ ml.

1 mole of H_2O (added (18 ml) = V^*_m, H_2O



$V_i = 1800$ ml.

$V_f = 1014$ ml

change in volume = 14 ml.

$\therefore$ P.M.V. of water in ethyl alcohol. $(\overline{V}^*_{water}) = 14$ ml.

→ due to H-bonding intermolecular interaction between $H_2O - C_2H_5OH$ so the packing get changed. with the change in size and shape.

partial molar volume indicated change in volume after addition or removal of ~~water~~ 1 mole of water $(V^*_{m}, H_2O = 18 \text{ ml})$.

→ For adding water to water.

$$V^*_{m}, H_2O = \overline{V}^*_{H_2O}.$$

$$S^*_{m}, H_2O = \overline{S}^*_{H_2O}$$

$$H^*_{m}, H_2O = \overline{H}^*_{H_2O}.$$

→ 50 ml H_2O + 50 ml. C_2H_5OH = 95 ml $(\overline{V}^*_{H_2O})$ — partial molar volume.

→ Note :

G, H, A, U, S, V — extensive properties — depends on T, P, n (no. of moles

partial molar properties: $\overline{G}, \overline{H}, \overline{A}, \overline{U}, \overline{S}, \overline{V}$ — intensive properties — depends on T, P, composition but not of n (no. of moles)

1 mole A

2 mole A
2 mole B

change in volume ($\bar{V}$) = 10 ml

I

1 mole A

4 mole A
4 mole B

change in volume ($\bar{V}$) = 10 ml

II

no change in composition

↓

no change in volume.

1 mole A

2 mol A
3 mol B

$\bar{V} \neq 10$ ml.

III

—— for this case,

composition change occurs.

↓

hence volume also changes ($\bar{V}$ — partial molar volume change from I)

Variation of μ with P.

$$\frac{\partial \mu}{\partial P} = ?$$

$$dG = VdP - SdT + \sum_i \mu_i \, dn_i$$

at constant T & composition

$$dG = V.dP$$

$$\frac{dG}{dP} = V.$$

or $$\left(\frac{\partial G}{\partial P}\right)_{T, n_j} = V.$$

We know that

$$\bar{G}_i / \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

Applying $\frac{\partial}{\partial n_i}$ to both side.

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T, n_j}\right]_{T, P, n_j \neq 1} = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j \neq 1}$$

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq 1}\right]_{T, n_j} = \bar{V}_i$$

$$\boxed{\left(\frac{\partial \mu}{\partial P}\right)_{T, n_j} = \bar{V}_i}$$

Variation of μ with T.

$$\frac{\partial \mu}{\partial T} = ?$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

at constant P & composition.

$$dG = -SdT$$

$$\frac{dG}{dT} = -S$$

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_j} = -S.$$

We know that.

$$\bar{G}_i / \mu_i \; \left(\frac{\partial G}{\partial T}\right)_{P, V, n_j \neq i}$$

Applying $\frac{\partial}{\partial n_i}$ to both side.

$$\left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_{P, n_j}\right]_{P, V, n_j \neq 1} = -\left(\frac{\partial S}{\partial n_i}\right)_{P, V, n_j \neq 1}$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{P, V, n_j \neq 1}\right]_{P, V, n_i} = -\bar{S}_i$$

$$\left(\frac{\partial \mu}{\partial T}\right)_{P, V, n_j} = -\bar{S}_i$$

Gibb's - Duhem equation : relation between μ and composition.

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

at constant T, & P.

$$dG = \sum_i \mu_i dn_i \quad \text{——— (1)}$$

$$X = \sum_i \bar{X}_i n_i$$

$$G = \sum_i \bar{G}_i \bar{n}_i / \sum_i \mu_i n_i \quad \text{——— (2)}$$

differentitating equation (2)

$$dG = d\left(\sum_i \mu_i n_i\right)$$

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i) \quad \text{——— (3).}$$

~~from~~ equation (1) & (3).

$$\sum_i \cancel{\mu_i dn_i} = \sum_i \cancel{\mu_i dn_i} + \sum_i n_i d\mu_i$$

$$\boxed{\sum_i n_i \, d\mu_i = 0}$$ —— Gibb's – Duhem equation.

or

$$\sum \frac{n_i}{n_1 + n_2 + \dots n_i} \, d\mu_i = 0.$$

$$\sum_i x_i \, d\mu_i = 0.$$

For any partial molar properties $(\bar{X}_i)$

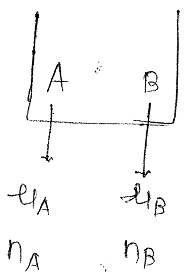
$$\boxed{\sum x_i \, d\bar{X}_i = 0}$$ x_i – mole fraction of ith component.

or

$$\boxed{\sum_i n_i \, d\bar{X}_i = 0}$$

<u>Significance of Gibb's – Duhem equation.</u>

→



Gibb's Duhem equation.

$$\sum n_i \, d\mu_i = 0.$$

$$n_A \, d\mu_A + n_B \, d\mu_B = 0.$$

$$n_A \, d\mu_A = -n_B \, d\mu_B.$$

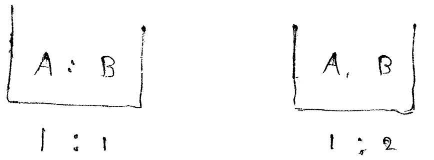
$$\therefore \; d\mu_A = -\frac{n_B}{n_A} \, d\mu_B.$$

→

$$\boxed{\begin{array}{l} \mu_A \uparrow \; \Longrightarrow \; \mu_B \downarrow \\ \mu_B \uparrow \; \Longrightarrow \; \mu_A \downarrow \end{array}}$$

∴ chemical potential <u>can't vary</u> independently that means one component's chemical potential changes, chemical potentials of all other remaining components also changes.

<u>Example</u> →



1 : 1   1 ; 2

Not only composition of A changes ...

composition also changes.

mixing properties : difference betn actual properties & expected (unmixed) properties.

Example   50 ml H_2O + 50 ml C_2H_5OH

expected (unmixed) volume = 100 ml.

actual (observed) volume = 96 ml.

mixing volume, $\Delta V_{mix} = -4$ ml $= V_f - V_i$)

	1	+ 2 + ...	i
no. of moles	n_1	n_2	n_i
molar volume of pure component	$V^*_{m,1}$	$V^*_{m,2}$	$V^*_{m,3}$
volume occupied by each component.	$n_1 \times V^*_{m,1}$	$n_2 \times V^*_{m,2}$	$n_i \times V^*_{m,i}$

volume expected on mixing

$$V^* = n_i V^*_{m,1} + n_2 V^*_{m,2} + \ldots\ldots n_i V^*_{m,i}$$

$$V^* = \sum_i n_i V^*_{m\,i}$$

Actual volume after mixing $\{ X = \sum n_i \bar{X}_i \}$

$$V = \sum_i n_i \bar{V}_i$$

$$\Delta V_{mix} = V - V^*$$

$$\Delta V_{mix} = \sum_i n_i \bar{V}_i - \sum_i n_i V^*_{m,i}$$

$$\therefore \boxed{\Delta V_{mix} = \sum_i n_i \left(\bar{V}_i - V^*_{m,i}\right)}$$

$*$ — indicates values of pure component

— (bar) — indicates actual value after mixing similarly,

$$\Delta S_{mix} = S - S^* = \sum_i n_i \left(\bar{S}_i - \bar{S}^*_{m,i}\right)$$

$*$ — indicates pure component

$$\Delta H_{mix} = H - H^* = \sum_i n_i \left(\bar{H}_i - S^*_{m,i}\right)$$

$$\Delta G_{mix} = G - G^* = \sum_i n_i \left(\bar{G}_i - \bar{G}^*_{m,i}\right)$$

variation of ΔG_{mix} with T & p for ideal solution.

$$\left[\frac{\partial(\Delta_{mix} G)}{\partial p}\right]_{T, n_j} = ? \quad \& \quad \left[\frac{\partial(\Delta_{mix} G)}{\partial T}\right]_{p, n_j} = ?$$

i)
$$\left[\frac{\partial(\Delta_{mix} G)}{\partial p}\right]_{T, n_j} = \left[\frac{\partial}{\partial p} \sum n_i (\mu_i - \mu_i^*)\right]_{T, n_j}$$

$$= \sum n_i \left[\left(\frac{\partial \mu_i}{\partial p}\right)_{T, n_j} - \left(\frac{\partial \mu_i^*}{\partial p}\right)_{T, n_j}\right]$$

$$= \sum_i n_i \left(\bar{V}_i - \bar{V}_i^*\right)$$

but $\bar{V}_i^* = V^*_{m, i}$

$$\therefore \boxed{\left[\frac{\partial(\Delta_{mix} G)}{\partial p}\right]_{T, n_j} = \sum_i n_i \left(\bar{V}_i - V^*_{m, i}\right)}$$

$$\boxed{\left[\frac{\partial(\Delta_{mix} G)}{\partial p}\right]_{T, n_j} = \Delta V_{mix}.}$$

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

$$\boxed{\left[\frac{\partial(\Delta_{mix} G)}{\partial T}\right]_{p, n_j} = -\sum n_i \left(\bar{S}_i - S^*_{m,i}\right)}$$

$$\boxed{\left[\frac{\partial(\Delta_{mix} G)}{\partial T}\right]_{p, n_j} = - \Delta_{mix} S}$$

XV Ideal Solution

Liq A + liq B ⟶ solution
↓
ideal solution - ?

⟶ ideal solution condition.

⟹ i) same intermolecular forces.

$$A - A = B - B = A - B.$$

ii) for same intermolecular forces, non-polarity & polarity of mixing components must be same.

⟹ iii) size and shape of both A & B must be same so that we get same packing.

Example : Benzene + toulene (non-polar) — ideal solution)

C_2H_5I + C_2H_5Br (polar) — ideal solution).

Thermodynamic properties of ideal solution.

⟶ Vapour pressure : Raoult's law.

⟶ mixing properties.

⟶ partial molar properties.

i) Vapour pressure - Raoult's law.

$$P_i = P_i^* x_i$$

P_i^* = pressure of pure component i

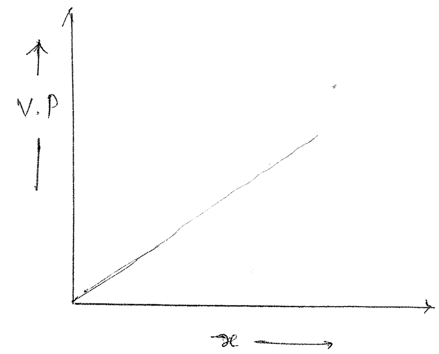
x_i = mole fraction of 'i'

$$\frac{P_i}{P_i^*} = x_i$$

P_i = partial vapour pressure of compon 'i'

{ The ration P_i to P_i^* is equal to x_i in it's liquid phase }

$$P_i = P_i^* x_i$$
$$y = m x$$



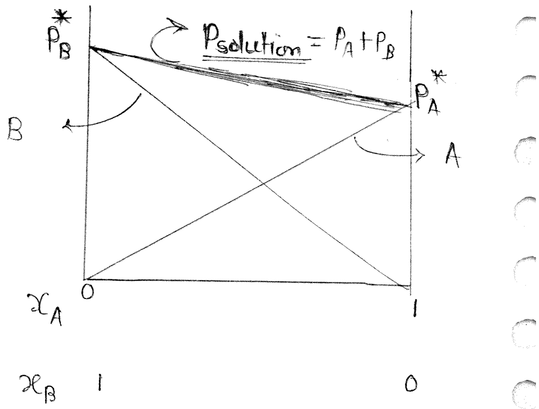
The solutⁿ which follows Raoult's law at all temp, pressure, compositions are called <u>ideal</u> <u>solution</u>.

<u>Example</u> $A + B \longrightarrow$ ideal solution.

$$P_A = P_A^* x_A \qquad P_B = P_B^* x_B.$$

$$P_{soln} = P_A + P_B$$

$$P_{soln} = P_A^* x_A + P_B^* x_B.$$



→ chemical potential of component 'i' in mixture of ideal gases

$$\mu_i = \mu_i^\circ + RT \ln P_i$$

'i' in any solution (ideal / or non-ideal soln) : $\mu_i = \mu_i^* + RT \ln \frac{P_i}{P_i^*}$

'i' for ideal solution : $\mu_i = \mu_i^* + RT \ln x_i$ from Raoult's law

ii) <u>Mixing properties of ideal solution.</u>

→ $\Delta_{mix} G = \left(\sum_i n_i (\mu_i - \mu_i^*) \right)$

for ideal solution.

$$\mu_i = \mu_i^* + RT \ln x_i$$

$$\mu_i - \mu_i^* = RT \ln x_i$$

$$\therefore \Delta_{mix} G = \sum_i n_i (RT \ln x_i)$$

⇓

−ve ($\because x_i < 1 \ \therefore \ln x = -ve$)

⇓

$\Delta_{mix} G = -ve$ — spontaneous mixing.

$$\boxed{\Delta_{mix} G = RT \sum_i n_i \ln x_i}$$

$$= NRT \sum_i \frac{n_i}{N} \ln x_i$$

$$(N = n_1 + n_2 + \cdots + n_i)$$

$$\boxed{\Delta_{mix} G = NRT \sum_i x_i \ln x_i} \longrightarrow \Delta_{mix} G = -ve$$

$\downarrow$

since $\ln x_i = -ve$ because x_i is less than 1

$\rightarrow$ $\Delta_{mix} V$

$$\left\{ \frac{\partial(\Delta_{mix} G)}{\partial P} \right\}_{T,\, n_j} = \Delta_{mix} V$$

$$\therefore \quad \Delta_{mix} V = \left\{ \frac{\partial}{\partial P} \left[RT \sum_i n_i \ln x_i\right] \right\}_{T,\, n_j}$$

$RT \sum_i n_i \ln x_i$ = constant for ideal solution.

$$\therefore \quad \boxed{\Delta_{mix} V = 0}$$

for ideal solution.

expected volume = actual volume.

V^* $\qquad$ V.

Example $\quad C_6H_6$ + toulene.

50 ml. $\qquad$ 50 ml

$V^* = 100$ ml.

$V = 100$ ml.

$\therefore \quad \Delta_{mix} V = 0.$

$\rightarrow$ $\Delta_{mix} S$

$$\left\{ \frac{\partial(\Delta_{mix} G)}{\partial T} \right\}_{P,\, n_j} = -\Delta_{mix} S$$

$$-\Delta_{mix} S = \left[\frac{\partial}{\partial T}\left(RT \sum_i n_i \ln x_i\right)\right]_{P,\, n_j} = R \sum_i n_i \ln x_i$$

$$\therefore \quad \boxed{\Delta_{mix} S = -R \sum_i n_i \ln x_i}$$

$\Downarrow$

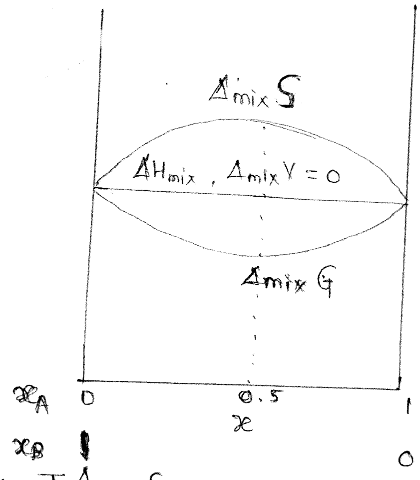
+ve $\quad$ ($\because \ln x_i = -ve$ because $x_i < 1$)

$\Downarrow$

$\Delta_{mix} S = +ve$

$$\Delta_{mix} S = -RN \sum \left(\frac{n_i}{N} \ln x_i \right)$$

$$\boxed{\Delta_{mix} S = -RN \sum x_i \ln x_i}$$



→ $\underline{\Delta_{mix} H}$

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

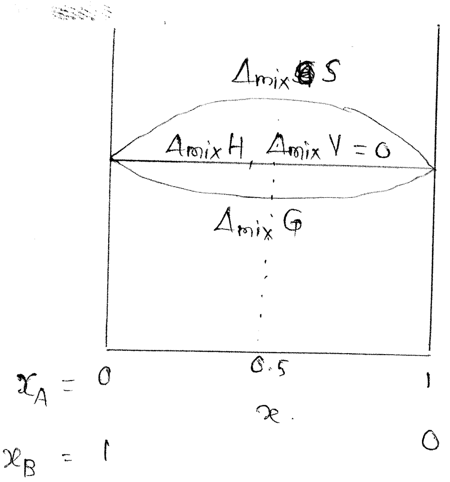
$$\Rightarrow \quad \Delta_{mix} G = \Delta_{mix} H - T\Delta_{mix} S.$$

$$\therefore \quad \Delta_{mix} H = \Delta_{mix} G + T\Delta_{mix} S.$$

$$\Delta_{mix} H = NRT \sum x_i \ln x_i - NRT \sum x_i \ln x_i$$

$$\boxed{\Delta_{mix} H = 0}$$

III) partial molar properties.



2 component system – $\Delta_{mix} S$ – max. value – mole fraction of each component $= \frac{1}{2}$

3 — " — – ΔS_{mix} – " – " $= \frac{1}{3}$

n — " — – $\Delta_{mix} S$ – " – " $= \frac{1}{n}$

$$\bar{G}_i / \mu_i, \quad \bar{V}_i, \quad \bar{S}_i, \quad \bar{H}_i$$

$$\rightarrow \quad \mu_i = \mu_i^* + RT \ln x_i$$

$$\rightarrow \quad \bar{V}_i = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, n_j} = \left\{ \frac{\partial}{\partial P} (\mu_i^* + RT \ln x_i) \right\}_{T, n_j}$$

$$= \left(\frac{\partial \mu_i^*}{\partial P} \right)_{T, n_j} + RT \left(\frac{\partial \ln x_i}{\partial P} \right)_{T, n_j}$$

$$= \bar{V}_i^* + 0 \qquad \left(\frac{\partial RT \ln x_i}{\partial P} \right) = \text{constant} = 0.$$

$$\boxed{\bar{V}_i = \bar{V}_{m,i}^*} \longrightarrow \text{for } \underline{\text{ideal}} \ \underline{\text{solution}}$$

$\Delta_{mix} V = 0$

$$\therefore \boxed{\bar{V}_i = V^*_{m,i}}$$

$\bar{V}^*_i = V^*_{m,i}$

→ $\Delta_{mix} H = 0$

$$\therefore \boxed{\bar{H}_i = H^*_{m,i}}$$

→ $\bar{S}_i$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, n_j} = -\bar{S}_i$$

$$-\bar{S}_i = \left\{\frac{\partial}{\partial T}\left(\mu_i^* + RT \ln x_i\right)\right\}_{P, n_j}$$

$$= \left(\frac{\partial}{\partial T} \mu_i^*\right)_{P, n_j} + \left(\frac{\partial\, RT \ln x_i}{\partial T}\right)_{P, n_j}$$

$$-\bar{S}_i = -\bar{S}_i^* + R \ln x_i$$

$$\therefore \boxed{\bar{S}_i = \bar{S}^*_{m,i} - R \ln x_i}$$

entropy after mixing $(\bar{S}_i)$ is maximum or increase than before mixing ideal solution.

Ideally dilute solution : Henry's law.

Real solⁿ :- doesn't follows Raoult's law at all composition.

Real solⁿ under dilute condition — 99% A + 1% B

(solvent) (solute)

A has negligible interaction with B & doesn't show nearly ideal behaviour.

$x_A = 0.99$ $\quad$ $x_B = 0.01$.

$x_A \rightarrow 1$ $\quad$ $x_B \rightarrow 0$

A follow Raoult's law.

$P_A = P_A^* \cdot x_A$.

B doesn't follow Raoult's law

B follows Henry's law

$$\boxed{P_B = K_B \cdot x_B \ (x_B \rightarrow 0)}$$

$$\boxed{P_B = K_B \cdot x_B \quad (x_B \to 0)}$$

where K_B - Henry's ~~law~~. constant

In a binary solution, if one component follows (solvent) Raoults law & another component (solute) follows Henry's law are called ideally diluted solution

Raoult's law is special case Henry's law.

→ Component whose mole fraction $(x \to 0)$ follows Henry's law and is called ideally diluted solution

→ component whose mole fraction $(x \to 1)$ follows Raoult's law.

Que ⇒ Entropy of a perfect gas is

i) Independent of V

ii) proportional of V

iii) proportional to ln V.

iv) proportional to V^2.

option (iii) is the correct answer.

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V}$$

at const T

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

∴ Entropy depends on ln V.

$$\therefore \Delta S \propto \ln V.$$

Que → A thermodynamic equation that relates the chemical potential to the composition of a mixture is known as.

i) Gibb's - Helmholtz eq^n.

ii) Joule - Thomson eq^n

iii) Debye - Huckel eq^n

iv) Gibb's - Duhem eq^n.

⇒ $\sum n_i \, d\mu_i = 0$ — Gibb's - Duhem equation

n_i - composition

μ_i - chemical potential

gives relation between

→ chemical potential (μ_i) &

→ chemical composition (n_i)

Que $\Rightarrow$ Given the following two statements

1. $x_i\, d\mu_1 + x_2\, d\mu_2 = 0.$

2. $x_1\, dV_1 + x_2\, dV_2 = 0$

for a binary liquid, the true statement is.

i) Both the relation are correct.

ii) ① ✓ ② ×

iii) ① × ② ✓

iv) both the relation are incorrect.

$\Rightarrow$ $\sum_i n_i\, d\bar{X}_i = 0.$ or $\sum_i x_i\, d\bar{X}_i = 0$

$\therefore$ Both relations are true.

Que $\rightarrow$ 78 grams of benzene is mixed with 92 grams of toulene at 25°. Calculate ΔS_{mix} & ΔG_{mix}. (assume ideal behaviour)

$W_A = 78$ gram

$W_B = 92$ gram.

$T = 25°C = 298\ K.$

$\Rightarrow$ $n_{C_6H_6} = \frac{72}{72} = 1$ mole.

$n_{toulene} = \frac{92}{92} = 1$ mole.

$\Delta_{mix} G = 2.303\ RT \sum_i n_i \log x_i$

$= 2.303 \times 8.3 \times 298 \left\{1. \log \frac{1}{x} + 1. \log \frac{1}{2}\right\}$

$= 5688.2 \left\{\log \frac{1}{4}\right\}$

$= -5688.2 \times 2 \log 2$

$= -5{,}688.2 \times 2 \times 0.30$

$= -3412.92$

$= -3.4$ kJ/mol^{-1}.

$\Delta_{mix} S = -2.3\ R \sum n_i \log x_i$

$= -2.3 \times 8.3 \left(1. \log \frac{1}{2} + 1 \times \log \frac{1}{2}\right)$

$= -2.3 \times 8.3 \left(\log \frac{1}{4}\right)$

$= +19.09 (\log 4)$

$= 19.09 \times 2 \log 2$

$= 38.18 \times 0.3010$

$= 11.49$ J. K^{-1}. mol^{-1}

Que → At 27°c, 1 mole of pure liquid A is mixed with 1 mole of pure liquid B to form an ideal solution. what is $\Delta_{mix}S$ (in $J \cdot K^{-1}$) of the solution ?

⟨i⟩ 5.763 ⟨ii⟩ − 1729.159 ⟨iii⟩ 1729.159 ⟨iv⟩ 0.0.

⟹ A → 1 mole B → 1 mole $\Delta_{mix}S = ?$

$$\Delta_{mix}S = -R\sum_i n_i \ln x_i = -2.3 \times 8.3\left(1\times\log\frac{1}{2} + 1\times\log\frac{1}{2}\right) = -19.09\left(\log\frac{1}{4}\right)$$

$$= -19.09(-\log 4) = +38.18 \times \log 2 = 38.18 \times 0.3010$$

$$= 11.49 \ J.K^{-1}.mol^{-1}$$

Que → The mole fraction of CO_2 in 1 litre aqueous solution is 1.423×10^{-5}. The partial pressure of CO_2 over the sol^n is 760 mm/Hg. What is the Henry's constant.

⟨i⟩ 5.34×10^5 ⟨ii⟩ 5.34×10^{-1}

⟨iii⟩ $5.34 \times \cancel{10}\ 10^7$ ⟨iv⟩ 1.87×10^{-8}.

⟹ Henry's law ⟹ $P_i = K_i x_i$

$$K_i = \frac{P_i}{x_i} = \frac{760}{1.423 \times 10^{-5}} = 534.08 \times 10^5$$

$$= 5.34 \times 10^7.$$

∴ option (iii) is the correct answer.

Que → 1 mole of liquid A is mixed with 1 mole of liquid B to form an ideal solution. The correct state of $\Delta_{mix}H$, $\Delta_{mix}V$, $\Delta_{mix}G$, $\Delta_{mix}S$ for this solution.

⟨i⟩ 0, +ve, −ve, −ve ⟨ii⟩ 0, 0, −ve, +ve.

⟨iii⟩ +ve, 0, +ve, −ve ⟨iv⟩ 0, −ve, −ve, +ve.

⟹ $\Delta_{mix}H = \Delta_{mix}V = 0.$

$\Delta_{mix}S = -R\sum n_i \ln x_i$

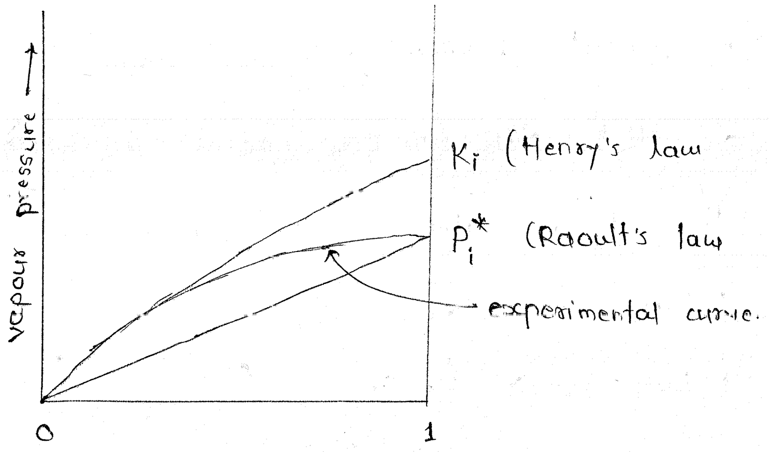
$\Delta_{mix}S = +ve \quad (\because x_i < 1)$

$\Delta_{mix}G = RT\sum n_i \ln x_i$

$\Delta_{mix}G = -ve \quad (\because x_i < 1)$

∴ option 2 is the correct answer.

→ Henry's law is not applicable to electrolytic solutions since, in these solutions even at high dilution interionic interactions are presents.



Solubility of Gases in liquids

solution of gases in liquid : follows Henry's law.

Consider the solubility of sparingly soluble gas in a given liquid Since it's solubility is low (dilute sol^n) it follows Henry's law

sparingly soluble gas ⟹ solubility is extremely low in liquid

⇓

gas ($x \longrightarrow 0$)

⇓

follows Henry's law.

A/c Henry's law

$$P_i = K_i x_i$$

$$x_i = \frac{P_i}{K_i}$$

$$\boxed{x_i \propto P_i} \quad \text{or} \quad \boxed{m \propto P} \quad \text{or} \quad \boxed{\frac{m_1}{m_2} = \frac{P_1}{P_2}}$$

⇓

{ The amount of gas dissolve in a certain amount of liquid at a given temperature is proportional to the pressure of the gas. }

→ As temperature ↑es, solubility of gas ↓es, Henry's constant ↑es

because $x_i = \left(\frac{1}{K_i}\right) P_i$ K_i : Henry's constant

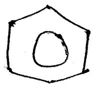
x_i : indicates solubility.

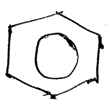
→ Most of gases follows Henry's law.

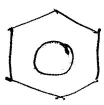
1. The pressure is not too high i.e. low P.
2. The temperature is not too low i.e. high T.
3. There is no reactn between gas and liquid.

Ex : solubility of HCl, NH_3 & CO_2 gases in water doesn't follow Henry's law but they follow Henry's law in benzene.

$$\left.\begin{array}{l} HCl + HOH \longrightarrow H_3\overset{\oplus}{O} \\ NH_3 + HOH \longrightarrow \overset{+}{N}H_4\overset{-}{O}H \\ CO_2 + HOH \longrightarrow H_2CO_3 \end{array}\right\} \text{solubility} \uparrow\text{es} \Longrightarrow \text{doesn't obey Henry's law.}$$

HCl +  ⟶ N.R.

NH_3 +  ⟶ N.R.

CO_2 +  ⟶ N.R.

} No solubility ⟹ obeys Henry's law.

Applications

→ Aquatic species are more confortable in cold H_2O (T ↓es ⟹ solubility ↑es) (more O_2 dissolved) than warm water (T ↑es ⟹ solubility ↓es) (less O_2 dissolved

→ In soft drink's or soda water to increase the solubility of CO_2 gas, the bottles are sealed under very high pressure. (P ↑es ⟹ sol ↑es)

→ The tankers carried by Scuba drivers filled with O_2 is diluted with He. Since the solubility of He is less than N_2, in blood, to avoid bends

→ People living at high altitude contain less conc. of O_2 in blood. So they are unable to think properly (situation is called anaxia)

Non-Ideal Gases – Non ideal gases are studied by taking the reference of ideal gases.

For ideal gas $\mu_i^{ideal} = \mu_i^* + RT\ln P_i$ ——— ①

for non-ideal gas $\mu_i^{NIG} = \mu_i^* + RT\ln f_i$ ——— ②

f_i = fugacity or corrected pressure

Concept of fugacity (f) & fugacity coefficient (ϕ).

fugacity (f) & fugacity coefficient (ϕ) = used to study non-ideal gases
&
~~non-ideal solution~~

non-ideal gases are studied by taking reference of ideal gases.

→ for ideal gas

$$\mu_i^{IG} = \mu_i^{\circ} + RT \ln P_i \quad \text{——} ①$$

$$\mu_i^{NIG} = \mu_i^{\circ} + RT \ln (f_i) \quad \text{——} ②$$

↳ fugacity
↳ pressure only
↳ pressure shown by non-ideal gas.

IG - ideal gas.
NIG - nonideal gas.
} μ_i° = same at same T

because μ_i° depends only on temp. T.

$\boxed{\mu_i^{\circ},\ P = 1 \text{ atm at any temp.}}$

$f_i \Rightarrow$ fugacity of gas 'i'

$\Rightarrow$ pressure of non-ideal gas (NIG).

$\Rightarrow$ corrected pressure.

{ standard state μ of a component 'i' of non-ideal gas (NIG) is defined as chemical potential produced at $f_i \rightarrow 1$ atm. }

by subtracting ① from ②

$$\mu_i^{NIG} - \mu_i^{IG} = RT (\ln f_i - \ln P_i)$$

$$\mu_i^{NIG} - \mu_i^{IG} = RT \ln \frac{f_i}{P_i}$$

$$\boxed{\mu_i^{NIG} - \mu_i^{IG} = RT \ln \phi_i}$$

$\phi_i = \frac{f_i}{P_i}$ — fugacity coefficient.

→ if $\phi_i = 1$

$\mu_i^{NIG} = \mu_i^{IG}$ given gas is ideal gas

→ if $\phi_i \neq 1$

$\mu_i^{NIG} \neq \mu_i^{IG}$ given gas is non-ideal gas

$\phi_i > 1$ +ve deviation.

$\phi_i < 1$ -ve deviation.

→ At high P,

repulsive forces dominate over attractive forces.

$P_{NIG} > P_{IG}$

$f > P.$

$\frac{f}{P} > 1.$

$\boxed{\phi > 1}$ —— indicates $\underbrace{\text{repulsive forces}}_{\text{(dominant)}}$ > $\underbrace{\text{attractive forces}}_{\text{occurs at high pressure}}$

→ at low P,

attractive forces dominate over repulsive forces.

$P_{NIG} < P_{IG}.$

$f < P.$

$\frac{f}{P} < 1$

$\boxed{\phi < 1}$ —— indicates $\underbrace{\text{attractive forces}}_{\text{(dominant)}}$ > $\underbrace{\text{repulsive forces}}_{\text{occurs at low pressure}}$

Favourable condition for a gas to show ideal behaviour.

→ high temp.

→ low pressure.

→ at constant T.

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

$$\Delta G = -T\Delta S \quad \text{(isothermal condition)}.$$

$$\Delta G = -T \cdot nR \ln \frac{P_1}{P_2} = +nRT \ln \frac{P_2}{P_1}$$

concept of activity (a) & activity coefficient (γ)

activity (a) & activity coefficient (γ) — used to study deviation shown by non-ideal solution (NIS) with reference to ideal solution (IS).

$$\mu_i^{IS} = \mu_i^{\circ} + RT \ln x_i$$

$$\left\{ \begin{array}{c} \boxed{\mu_i^{\circ}, \text{ pure at any } T \;\&\; P} \\ \mu_i^{\circ} = \mu^*(T,P) \text{ or } \mu^* \end{array} \right\}$$

$$\mu_i^{IS} = \mu_i^{\circ} + RT \ln x_i \quad \text{——} (1)$$

$$\mu_i^{NIS} = \mu_i^{\circ} + RT \ln a_i \quad \text{——} (2)$$

→ activity of component 'i' of non-ideal solution

↓

a_i - corrected mole fraction / activity of component "i"

subtracting (1) from (2).

$$\mu_i^{NIS} - \mu_i^{IS} = RT\left(\ln a_i - \ln x_i\right).$$

$$= RT \ln \left(\frac{a_i}{x_i}\right).$$

$$\boxed{\mu_i^{NIS} - \mu_i^{IS} = RT \ln \gamma_i}$$

$$\boxed{\gamma_i = \frac{a_i}{x_i} = \text{activity coefficient}}$$

→ if $\gamma_i = 1$

$\mu_i^{NIS} = \mu_i^{IS}$ given solution is ideal solution (IS)

→ if $\gamma_i \neq 1$

$\mu_i^{IS} \neq \mu_i^{NIS}$ given solution is non-ideal solution (NIS).

{ activity & activity coefficient are the concept applicable during study of Debye-Huckel equation in electrochemistry. }

Note :

$$\mu_i^{IG} = \mu_i^{\circ} + RT\ln P_i \qquad \phi = \frac{f_i}{P_i} = 1$$

$$\mu_i^{\text{any mixture}} = \mu_i^{*} + RT\ln\left(P_i/P_i^{*}\right)$$

$$\mu_i^{IS} = \mu_i^{*} + RT\ln x_i \quad , \qquad \gamma_i = \frac{a_i}{x_i} = 1$$

$$\mu_i^{NIG} = \mu_i^{\circ} + RT\ln f_i \qquad \phi \neq 1$$

$$\mu_i^{NIS} = \mu_i^{\circ} + RT\ln a_i \qquad \gamma_i \neq 1.$$

NIS showing +ve deviation from Raoult's law.

Example : Binary solution of A & B.

→ Nature of intermolecular forces.

i) A – B interaction < A–A or B–B interaction.

→ vapour pressure → $P_{NIS} > P_{IS}$

↳ easy to evaporate

due to weak A–B interaction $\therefore P_{NIS} > P_A^{*} x_A + P_B^{*} \cdot x_B$.

→ $\Delta_{mix} V = +ve$.

→ This solution is less stable. than ideal soln.

→ $\Delta_{mix} H = +ve$ (endothermic).

NIS showing –ve deviation from Raoult's law.

→ Nature of intermolecular force.

A – B interaction > A-A or B – B interaction

→ $P_{NIS} < P_{IS}$

$P_{NIS} < P_A^{*} x_A + P_B^{*} \cdot x_B$

→ $\Delta_{mix} V = -ve$ → This NIS is more stable than IS.

→ $\Delta_{mix} H = -ve.$ (exothermic)

Hess's law.

Heat of reaction doesn't depend on path followed, but depends on initial reactants & final products, so heat of reaction is state function.

$R \longrightarrow P$

P-I $\quad R \longrightarrow X \longrightarrow P. \quad \Delta H_I$

$\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad ||$

P-II $\quad R \longrightarrow Y \longrightarrow P \quad \Delta H_{II}$

Enthalpy of combustion. ($\Delta_{com} H$).

- Amount of heat evolved during complete oxidation of 1 mole of a substance.
- it is always exothermic ($\Delta_{com} H^\circ$ = −ve).

Example

$$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O. + x \text{ kJ/mol}$$

$$\Delta_{com} H_{(CH_4)} = -x \text{ kJ. mol}^{-1}.$$

$$2CH_4 + 4O_2 \longrightarrow 2CO_2 + 2H_2O + 2x \text{ kJ/mol}.$$

$$\Delta_{com} H = -\frac{2x}{2} \text{ kJ/mol} = -x \text{ kJ./mol}$$

{ partial oxidation is not considered to give enthalpy of combustion.
but
complete oxidation is considered to give enthalpy of combustion }

→ For a reaction

$R \longrightarrow P.$

$$\boxed{\Delta_{reaction} H = \sum(\Delta_{com} H)_R - \sum(\Delta_{com} H)_P}$$

used when enthalpy of combustion of both reactants & products is given

but $R \longrightarrow P.$

$$\boxed{\Delta_{reaction} H^\circ = \{\sum \Delta_f H^\circ\}_P - \{\sum \Delta_f H^\circ\}_R}$$

— used when std. enthalpy of formation is given

Bond enthalpies.

Bond dissociation energy = − (enthalpy of formation of bond).

Example

$H_{(g)} + Cl_{(g)} \longrightarrow H-Cl_{(g)} + x\ kJ/mol$ (exothermic).

$HCl \xrightarrow{+x\ kJ/mol} H_{(g)} + Cl_{(g)}$ (endothermic).

Bond dissociation energy.

$\Delta H\ (B.D.E) = +ve.$

→ for a reaction,

R ⟶ P.

Bond dissociation energy data is given.

$$\boxed{\Delta_{reactn} H = \Sigma(\Delta_{B.D.E} H)_R - \Sigma(\Delta_{B.D.E} H)_P}$$

Enthalpy of Neutralization.

1 gram eq acid + 1 gram eq base ⟶ salt + HOH + x kJ/mol

$\Delta_{neut} H = -x\ kJ/mol$

Ex ①

HCl (1 gm. eq) + $NaOH$ (1 gm. eq). ⟶ $HOH + NaCl + 13.7$ kcal

$\Delta_{neutr} H = -13.7$ kcal

$$\left\{ n_{gram.\ eq.} = \frac{W}{eq.\ wt} = \frac{W}{mol.\ wt} \times valency = n_{mole} \times valency \right\}$$

$N = M \times valency.$

Example ②

$\frac{1}{2} H_2SO_4$ ($\frac{1}{2}$ gm. eq.) ($\frac{1}{2}$ mole). + $NaOH$ (1 gm. eq.) ⟶ $\frac{1}{2} Na_2SO_4 + H_2O. + 13.7$ kcal

$\Delta_{neut} H = -13.7\ kcal/mol.$

general

$$\left\{ \begin{array}{l} S.A\ vs\ S.B \text{ — } \Delta_n H \text{ — same.} \\ \Delta_n H = -13.7\ kcal / -57\ kJ.mol^{-1} \end{array} \right\}$$

Example(3)

$$CH_3COOH + NaOH \longrightarrow CH_3CO\overset{\ominus}{O}\overset{\oplus}{Na} + HOH + 12.3\ kcal.mol^{-1}$$

W.A S.B

$\Delta_n H = -12.3\ kcal.mol^{-1}$

$\therefore$ 1.4 kcal is required for complete ionization of CH_3COOH.

Kirchoff's equation.

↳ effect of temperature on enthalpy of reaction.

$A \xrightarrow[T_1]{\Delta H_1} B$ at temp T_1

$A \xrightarrow[T_2]{\Delta H_2} B$ at tem T_2

$$\boxed{\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_p(\text{Product}) - C_p(\text{reactant})}$$ — at constant P

$$\boxed{\Delta C_v = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = C_v(\text{product}) - C_v(\text{reactant})}$$ — at constant V.

Joule - Thomson's effect / Joule - Thomson's Expansion.

↳

real gas is expanded adiabatically from high pressure region to low pressure region } — experiment.

⇓

Temp. T of gas ↓es (decreases) ⟶ gas is cooled.

⟶ at room temp.

↳ all gases ⟹ shows same behaviour.

exception H_2 & He. ⟹ Temp ↑ — gas is heated (H_2 & He

→ Temp below which Joule - Thomson effect is observed is called inversion temp. (T_i)

$T_i(H_2) = -42°C.$ T_i - inversion temp.

$T_i(He) = -248°C.$

→ for all other gases other than H_2 & He, inversion temperature is above room temp.

→ isoenthalpic process H = constant

→ Ideal gas ⟹ similar experimental observation

↓

no. change in ~~temp~~. inversion temperature.

→ J. T experiment.

below T_i - cooling of gas. occurs

above T_i - heating of gas. occurs

at T_i - neither heating or cooling of gas takes place.

Joule-Thomson coefficient (μ).

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H}$$

constant H ⟹ isoenthalpic process

i) if μ = +ve,

→ cooling of gas.

$$+ve = \frac{dT}{-ve\ (P\downarrow)} \Longrightarrow dT = +ve \times -ve$$

$$\boxed{dT = -ve}$$

∴ cooling of gas occurs

ii) if μ = −ve.

$$-ve = \frac{dT}{-ve\ (P\downarrow)} \Longrightarrow dT = -ve \times -ve$$

$$\boxed{dT = +ve}$$

↳ heating of gas occurs.

iii) $H \quad U = 0$

$\Longrightarrow dT = 0$

neither heating nor cooling takes place.

Que $\longrightarrow$ The B.D.E. of gaseous H_2, Cl_2 & HCl are 104, 58 & 103 kcal.mol respectively. Calculate $\Delta_f H$ of HCl.

$\Longrightarrow$

$$\Delta H_{H-H} = 104 \text{ kcal. mol}^{-1}$$

$$\Delta H_{Cl-Cl} = 58 \text{ kcal. mol}^{-1}$$

$$\Delta H_{H-Cl} = 103 \text{ kcal. mol}^{-1}.$$

$$\Delta_f H_{H-Cl} = ?$$

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g), \quad \Delta_f H(HCl).$$

$$\Delta_f H(HCl) = \Sigma(B.D.E)_R - \Sigma(B.D.E)_P$$

$$= \left(\frac{1}{2}\Delta H_{H-H} + \frac{1}{2}\Delta H_{Cl-Cl}\right) - \left(\Delta H_{HCl}\right)$$

$$= \left(\frac{1}{2} \times 104 + \frac{1}{2} \times 58\right) - 103$$

$$= 52 + 29 - 103$$

$$= -22 \text{ kcal/mol.}$$

Que $\longrightarrow$ The $\Delta_{com} H^\circ$ at 25°C. of H_2, C_6H_{10} and C_6H_{12} are -241, -3800 & -3920 kJ. mol^{-1} respectively. Calculate heat of hydrogenation of cyclohexene (C_6H_{10})

$\Longrightarrow$

$$\Delta_c H^\circ(H_2) = -241. \text{ kJ. mol}^{-1}$$

$$\Delta_c H^\circ(C_6H_{10}) = -3800 \text{ kJ. mol}^{-1}$$

$$\Delta_c H^\circ(C_6H_{12}) = -3920 \text{ kJ. mol}^{-1}$$

$C_6H_{10} + H_2 \longrightarrow C_6H_{12}.$

$$\Delta H^\circ = \Sigma(\Delta_c H^\circ)_R - \Sigma(\Delta_c H^\circ)_p.$$

$$= \{-3800 + (-241)\} - \{-3920\}$$

$$= -4041 + 3920.$$

$$= -121 \text{ kJ. mol}^{-1}.$$

Que $\longrightarrow$ $\Delta_f H^\circ$ of ethane, CO_2 and water are -21.1, -94.1 & -68.3 kcal. mol^{-1} respectively. Calculate $\Delta_c H^\circ (C_2H_6)$

$\Longrightarrow$

$$\Delta_f H^\circ (C_2H_6) = -21.1 \text{ kcal. mol}^{-1}$$

$$\Delta_f H^\circ (CO_2) = -94.1 \text{ k.cal . mol}^{-1}$$

$$\Delta_f H^\circ (H_2O) = -68.3 \text{ kcal. mol.}$$

$$C_2H_6 + \frac{7}{2} O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$\Delta_c H^\circ (C_2H_6) = \Sigma(\Delta_f H^\circ)_p - \Sigma(\Delta_f H^\circ)_R$$

$$= \{2\times(-94.1) + 3\times(-68.3)\} - \{-21.1 + 0\}$$

$$= -188.2 - 214.9 + 21.1$$

$$= -403.1 - 21.1$$

$$= -372.0 \text{ kcal/mol.}$$

Que $\longrightarrow$ A hypothetical reaction proceeds via following steps.

$$A \longrightarrow 2B$$

$$A \longrightarrow C \quad \Delta H = q_1 \quad \text{—— (1)}$$

$$C \longrightarrow D \quad \Delta H = q_2 \quad \text{—— (2)}$$

$$\tfrac{1}{2} D \longrightarrow B \quad \Delta H = q_3 \quad \text{—— (3)}$$

The heat of reaction is

(i) $q_1 - q_2 + 2q_3$ (ii) $q_1 + q_2 + 2q_3$

iii) $q_1 + q_2 - 2q_3$

$\Rightarrow$ $\frac{1}{2} D \rightarrow B$

$\therefore$ $D \rightarrow 2B$.

$$
\begin{array}{lll}
 & A \longrightarrow \cancel{C} & \Delta H = q_1 \\
+ & \cancel{C} \longrightarrow \cancel{D} & \Delta H = q_2 \\
+ & \cancel{D} \longrightarrow 2B & \Delta H = 2q_3 \\
\hline
 & A \longrightarrow 2B & \Delta H = q_1 + q_2 + 2q_3
\end{array}
$$

(Hess law)

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some important formulae