

$x = \text{extensive prop}$	$x = \text{Ext}$	$x = \text{Int}$
$y = \text{extensive prop}$	$y = \text{Inten}$	$y = \text{Int}$
$x+y = \text{ext}$ ( $\Delta G = \Phi_{\text{ext}}$ )	$x+y = \text{Ext}$	$x+y = \text{Int}$
$x-y = \text{ext}$ ( $\Delta = \Delta G - \Delta H$ )	$x-y = \text{Int}$	$x-y = \text{Int}$
$\frac{x}{y} = \text{Int}$ ( $\Delta = \frac{\Delta H}{V}$ )	$x-y = \text{Ext}$	$x-y = \text{Int}$
$\frac{dx}{dy} = \text{Int}$ ( $T \cdot \Delta S = \Delta H$ )	$\frac{x}{y} = \text{Ext}$	$\frac{x}{y} = \text{Int}$
$x-y = \text{ext}$		

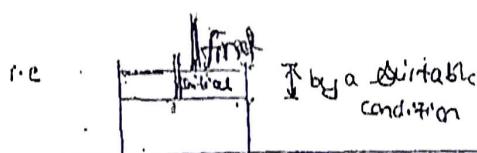
$\rightarrow$  Ext prop is additive prop  
 $\rightarrow$  Int prop is non-additive prop  
Thermodynamic equilibrium:

$\rightarrow$  When a system exists in a thermal equilibrium, chemical equilibrium & mechanical equilibrium simultaneously, then the system is said to be in Thermodynamic equilibrium.

Equilibrium	condition
Thermal eq.	$\Delta T = 0$ i.e. const. Temp
Chemical eq.	$\Delta C = 0$ i.e. concentration is constant. $\Rightarrow \Delta(\text{Conc}) \Rightarrow$
Mechanical eq.	$\Delta V = 0$ i.e. $F = 0$ i.e. $\Delta P = 0$ i.e. const. Pressure.

### Thermodynamic process:

$\rightarrow$  It is an operation by which system changes from one state to another state.



Applied at	Type of T.O process carried at	Condition	Complete change	Infinitesimal change
Thermal	Isothermal	constant temperature	$\Delta T = 0$ i.e. $T_2 - T_1 = 0$ i.e. $T_2 = T_1$	$dT = 0$
Thermo flask	Adiabatic	constant heat ( $\Delta Q = 0$ )	$\Delta Q = 0$ , $dQ = 0$	$dQ = 0$ (small del)
	Isochoric	constant pressure	$\Delta P = 0$	$dP = 0$
	Isothermal	constant volume	$\Delta V = 0$	$dV = 0$

$$(i) Q = \Delta E + W_{\text{num}} \quad \boxed{\Delta E = PAV} \quad \text{1st law TD can in expansion}$$

Resolved equation of 1st law of Thermodynamics

When both expansion & non-expansion work done on the system

$$\therefore \text{Total work done} = W_{\text{exp}} + W_{\text{non-exp}}$$

$$\Delta E = Q + W_{\text{total}}$$

$$= Q + W_{\text{exp}} + W_{\text{non-exp}}$$

$$\boxed{Q = \Delta E - (W_{\text{exp}})_{\text{num}} - (W_{\text{non-exp}})_{\text{num}}}$$

When both expansion & non-expansion work done by the system

$$\boxed{Q = \Delta E + (W_{\text{exp}})_{\text{num}} + (W_{\text{non-exp}})_{\text{num}}}$$

When expansion work done on the system & non-expansion work done by the system

$$\boxed{Q = \Delta E - (W_{\text{exp}})_{\text{num}} + (W_{\text{non-exp}})_{\text{num}}}$$

When exp. work done by the system & non-exp. work done on the system

$$\boxed{Q = \Delta E + (W_{\text{exp}})_{\text{num}} + (W_{\text{non-exp}})_{\text{num}}}$$

A system generates 450J of electric energy & has 150J of PV work done on it by the surroundings by releasing 300J of heat to the surroundings. What is the change in IE of the system?

$$\cancel{Q = \Delta E + W}$$

$$-300J = \Delta E + 50 - 150$$

$$\Delta E = -200J$$

1st law eqn in different process: [ 1st law eqn:  $Q = \Delta E + W_{\text{num}}$  in expansion]

Process	Condition	1st law eqn	$\Delta E = Q + W$
Isothermal	$\Delta T = 0$ $\therefore \Delta E = 0$	$+Q = -W$ i.e. absorbed heat is used for the expansion of gas i.e. work done by the system.	$\Delta E = Q + W$
Adiabatic	$Q = 0$	$\Delta E = +W \Rightarrow$ by work done on the system, I.E.	$\Delta E = -W \Rightarrow$ by work done by the system, I.E. system ↓
Isobaric	$\Delta P = 0$	$\Delta E = Q + P\Delta V \Rightarrow Q = \Delta E - P\Delta V$ in compression $Q = \Delta E + P\Delta V$ in expansion	$Q = \Delta H$ $Q_p = \Delta H$

Calculation of  $\Delta E$ ,  $\Delta H$ ,  $\Delta V$ ,  $\Delta T$ ,  $Q$  &  $W$  in different process:

N Isothermal process:

Condition  $\Delta T = 0$

Gas in cylinder  
type system

Chemical reactions  
at room conditions

Tie at const temp & const pressure.

(i) Gas in cyl type system:

For Isothermal process

$$\Delta \Delta T = 0$$

$$\Delta \Delta E = 0$$

3) In expansion or compression,  $\Delta P \neq 0 : P_2 - P_1$ ,

but  $P_1V_1 = P_2V_2$

$$\therefore \Delta(PV) = 0$$

$\therefore PV = \text{constant} + C + (T)$

calculation of  $\Delta H$ :

$$H = E + nRT$$

$PV = nRT$  for  $n$ -mole

$$H = E + nRT$$

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

$$\Delta H = \Delta E + nR(\Delta T)$$

when  $\Delta n_g = \text{change in gaseous mols}$

$$\Delta H = 0 + 0 + 0$$

$\Delta H = 0$

$C_V \neq 0$

$Q$  (Heat absorbed  $\Rightarrow$  evolved):

Work  $\rightarrow$  Ist law,  $+Q = -W$

$$-Q = +W$$

calculation of Work done:

① case(i): In irreversible process for intermediate expansion/compression.

$W_{irre} = -P_{ext} \cdot \Delta V$

Where  $P_{ext} = P_{final}$

② case(ii): free expansion is infinite expansion

It is a maximum in  $W_{irre}$

	Rev. (isothermal)	IR (isotermic)
$\Delta n_g$	0	0
$\Delta T$	0	0
$\Delta V$	$\neq 0$	$\neq 0$
$\Delta P$	$\neq 0$	$\neq 0$
$P, V$ relation	$P_1V_1 = P_2V_2 = \text{const}$	
$\Delta E$	0	0
$\Delta H$	0	0
$Q$	$\neq 0$	$\neq 0$
$W$	$\neq 0$ $= -Q_{rw}$	$\neq 0$ $= -Q$

$$\left. \frac{W}{\text{Rev}} \right|_{\text{NET}} = 0 \Rightarrow Q = 0 / \begin{cases} \Delta T \neq 0 \\ \Delta E = 0 \end{cases}$$

### b) Intermediate free expansion

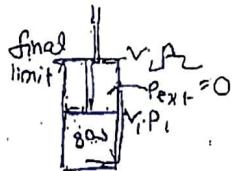
$$W_{\text{irrev}} = 0, \frac{\Delta T}{T} = \frac{\Delta E}{E} = 0$$

$$Q = 0$$

where here  $p_{\text{gas, final}} \neq 0$

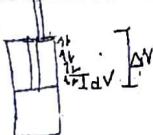
$$P_1 V_1 = P_2 V_2$$

$$P_{2, \text{final}} = \frac{P_1 V_1}{V_2}$$



### c) case (ii): Free reversible expansion (or) compression.

$$W_{\text{rev}} = \int dW$$



where  $\int dW = \text{work done in the infinitesimal change } \delta p + \delta V$ .

$$\delta W = -P_{\text{ext}} \delta V$$

but for reversible expansion  $P_{\text{gas}}$  is infinitesimally greater than  $P_{\text{ext}}$  by  $dP$  amount

$$P_{\text{gas}} = P_{\text{ext}} + dP$$

$$P_{\text{ext}} = P_{\text{gas}} - dP$$

$$\delta W = -(P_{\text{gas}} - dP) dV$$

$$= -P_{\text{gas}} dV + dP dV$$

but  $dP$  = small,  $dV$  = small  
 $\therefore dP dV$  = very small (negligible)

$$\delta W = -P_{\text{gas}} dV$$

$$W_{\text{rev}} = \int \delta W = \int nRT \cdot \frac{dV}{V} \quad (\because PV = nRT, P = \frac{nRT}{V})$$

$$W_{\text{rev}} = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$W_{\text{rev}} = 2.303 \cdot nRT \log \left( \frac{V_2}{V_1} \right)$$

but at const.  $T$   
 $PV = k$

$$P_1 V_1 = P_2 V_2$$

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

$$PV = nRT$$

### Finite free expansion

$$\Delta T = 0, \Delta E = 0, W = 0, Q = 0$$

$$\Delta H = 0, \Delta n = 0$$

$$P_1 V_1 = P_2 V_2$$

$$P_{\text{ext}} \neq P_2$$

Note:

Reversible Expansion

### Infinite free expansion

$$\Delta f = 0, \Delta E = 0, W = 0, Q = 0$$

$$\Delta H = 0, \Delta n = 0$$

$$P_1 V_1 = P_2 V_2$$

$$P_{\text{ext}} = P_2 = 0$$

Reversible Expansion

### Irrev. Isothermal

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

$$= -P_{\text{ext}} (V_2 - V_1)$$

$$\text{Usually } P_{\text{ext}} = P_2$$

$$= P_2 (V_2 - V_1)$$

Calculation

### Rev. Isothermal

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

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

$$PV = P_1 V_1 = P_2 V_2 = nRT$$

Result

### Table

$W_{rev}$  in adiabatic process: adiabatic intermediate external pressure

$$W_{rev} = nC_V \Delta T$$

$$W_{rev} = n \left( \frac{R}{\gamma-1} \right) (T_2 - T_1)$$

→ In expansion,  $T_2 < T_1 \therefore W = -ve$

→ In compression,  $T_2 > T_1 \therefore W = +ve$

$$\text{but } T_2 = \frac{P_2 V_2}{nR}, T_1 = \frac{P_1 V_1}{nR}$$

$$W_{rev} = \frac{nR}{\gamma-1} \left( \frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right)$$

$$W_{rev} = \frac{1}{\gamma-1} [P_2 V_2 - P_1 V_1]$$

\*Note 1:  $T, P, V$  relations i.e.  $T^{\gamma-1} = \text{constant}$ ,  $PV^\gamma = \text{constant}$  &  $T^{\gamma}P^{1-\gamma} = \text{constant}$  are valid only in reversible adiabatic process but not in irreversible adiabatic process.

Note 2: In  $W_{rev}$  calculation, unknown  $P$  or  $V$  or  $T$  can be calculated by using above relations.

Work done in calculation in irreversible adiabatic expansion/compression against intermediate external pressure:

where  $P_{ext} = P_2 = P_{final}$

$$W = -P_{ext} \Delta V = -P_2 \Delta V = nC_V \Delta T$$

$$W_{irre} = -P_{ext} \times (V_2 - V_1) \approx nC_V [T_2 - T_1]$$

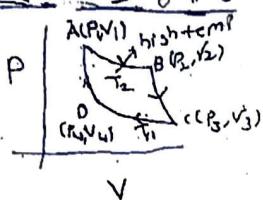
$$= -P_{ext} \left[ \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right] = nC_V [T_2 - T_1]$$

$$= -P_{ext} [V_2 - V_1] = nC_V \left[ \frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right]$$

Note:  $\begin{cases} T^{\gamma-1} = k \\ PV^\gamma = k \\ T^{\gamma}P^{1-\gamma} = k \end{cases}$  } not used here  
(is the irreversible adiabatic process)

(13)

→ Steps for 3/4 points



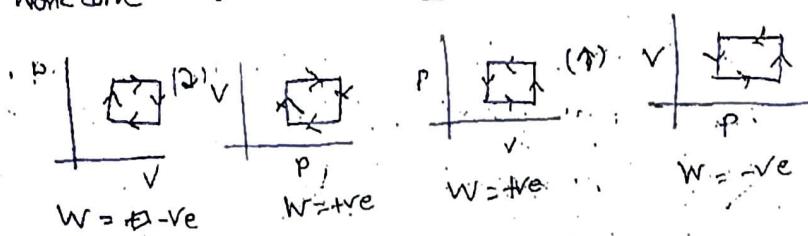
- 1) AB = Rev. Isothermal process expanding  $\Rightarrow$  different  $T$  for process
- 2) BC = Rev. Adiabatic
- 3) CD = Rev. Isothermal compression  $\Rightarrow$  same  $T$
- 4) DA = Rev. Adiabatic

$$W_{\text{net}} = W_1 + W_2 + W_3 + W_4$$

$$\neq 0$$

where  $Q_{\text{net}} \neq 0$

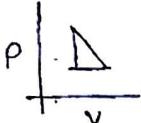
- Note: 1) In cyclic process, in P-V graph, all arrow makes in the same direction in the given cyclic figure.
- 2)  $W_{\text{rev.}}$  isothermal is a state function since it depends only on initial & final states.
- 3) Work done representation by using graph



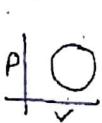
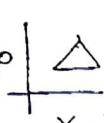
graph	direction	work done
PV	clockwise	by the system
VP	"	on the system
PV	anti-clockwise	on the system
VP	"	by the system

cal. part: For cyclic process, in P-V graph

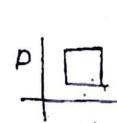
Area of cycle = work done



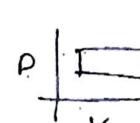
$$|\text{W.D.}| : \frac{1}{2} b h, \frac{\sqrt{3}}{4} a^2$$



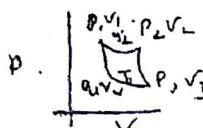
$$\pi r^2$$



$$a^2$$



$$ab$$



$$W_{\text{total}} = W_1 + W_2 + W_3 + \dots$$

if no formula, follow

$$W_{\text{total}} = W_1 + W_2 + \dots$$

$\therefore W = \text{Extensive Property}$

Note: Work done has P-V per unit, hence area of cycle should

follow P & V units

$$KV^{(1-\gamma)} = nRT$$

$$KV^{(1-\gamma)} \frac{dx}{x} = nRdT$$

$$(1-x) PdV = nRdT$$

$$\frac{PdV}{nRT} = \frac{R}{1-x}$$

$$\begin{aligned} C &= C_v + \frac{R}{1-x} \\ &= \frac{R}{\gamma-1} + \frac{R}{1-x} \end{aligned}$$

\* Joule's law:

At const temperature the change in the internal energy of the system with the change in the volume is zero i.e  $\left(\frac{\partial E}{\partial V}\right)_T = 0$

\* Comparison of  $T, W, \Delta E, \& \Delta H$  in diff. adiabatic processes

rev. adiabatic	irr. adiabatic	free expansion
$T_f$	$T_2 < T_1$	$T_2'' = T_1$
$W$	$W_1$	$W_3$
$\Delta E$	$\Delta E_1$	$\Delta E_3$
$\Delta H$	$\Delta H_1$	$\Delta H_3$

Relation:

$$\text{Temp: } T_1 = T_2'' > T_2' > T_2 \checkmark$$

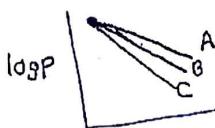
$$W = |W_1| > |W_2| > |W_3|$$

$$\Delta E = |\Delta E_1| > |\Delta E_2| > |\Delta E_3|$$

$$\Delta H = |\Delta H_1| > |\Delta H_2| > |\Delta H_3|$$

$W = nC_V(x) \rightarrow$  more distance  
more work done.

\* In a adiabatic process, graph is



Which gas has higher I.E. at given temp.?

Ans: A  $\Rightarrow$

$$\rho V^{\gamma} = \text{constant}$$

$$\log P_y = \text{const} - \gamma \log V_c - m u$$

## Isobaric

## Isobaric

Process	Isotherm	Adiabatic	Rev / Irrev	Rev / Irrev
Δq	0	0	0	0
ΔT	0	0	≠ 0	≠ 0
ΔP	≠ 0	≠ 0	= 0	≠ 0
ΔV	≠ 0	≠ 0	≠ 0	≠ 0
$P_1 V_1 = P_2 V_2 = nRT$ $P, T, V$ relations				
ΔE	0	0	ncpΔT	ncpΔT
ΔH	0	0	ncpΔT	ncpΔT
Q	0	0	0	0
W	≠ 0	≠ 0	= -PextΔV	= -PextΔV
$W = nc_v \Delta T = -P_{ext} \Delta V$ Use $P, T, V$ relations of Rev Adiabatic process				
$= -2.303nRT \log \frac{V_f}{V_i}$ $= P_{ext} \Delta V$				
$W_{rev} = nc_v \Delta T = -P_{ext} \Delta V$ $= nc_v \left[ \frac{P_2 V_2 - P_1 V_1}{nR} \right]$ $= -P_{ext} \left[ \frac{nRT_2 - nRT_1}{P_1} \right]$ do for use $P, T, V$ relations of rev process.				

Sigmas up

As T, nRT, vols. no programs change powers.

	Dq <sub>sys</sub>	ΔV	ΔQ <sub>sys</sub>	ΔH <sub>sys</sub>	ΔE <sub>sys</sub>	ΔS <sub>total</sub>	ΔS <sub>sys</sub>	ΔS <sub>sur</sub>	W
a) $H_2O(l) \xrightleftharpoons[100^\circ C]{P=1\text{ atm}} H_2O(l)$	+ve	+ve	0	+ve	+ve	0	+ve = -ve (equal)	= -ve	= -ve
b) $H_2O(l) \xrightleftharpoons[100^\circ C]{P>1\text{ atm}} H_2O(l)$	+ve	+ve	+ve	+ve	+ve	-ve	+ve < -ve	-ve	-ve
c) $H_2O(l) \xrightleftharpoons[100^\circ C]{P<1\text{ atm}} H_2O(l)$	+ve	+ve	-ve	+ve	+ve	+ve	+ve > -ve	-ve	-ve
d) $H_2O(l) \xrightleftharpoons[T+100^\circ C]{1\text{ atm}} H_2O(l)$	+ve	+ve	-ve	+ve	+ve	+ve	+ve > -ve	-ve	-ve
e) $H_2O(l) \xrightleftharpoons[T<100^\circ C]{1\text{ atm}} H_2O(l)$	+ve	+ve	+ve	+ve	+ve	-ve	+ve < -ve	-ve	-ve
f) $H_2O(s) \xrightleftharpoons[0^\circ C]{1\text{ atm}} H_2O(l)$	0	-ve	0	+ve	+ve	0	+ve = -ve (equal)	+ve	+ve
g) $H_2O(s) \xrightleftharpoons[0^\circ C]{P>1\text{ atm}} H_2O(l)$	0	-ve	-ve	+ve	+ve	+ve	+ve > -ve	+ve	+ve
h) $H_2O(s) \xrightleftharpoons[0^\circ C]{P<1\text{ atm}} H_2O(l)$	0	-ve	+ve	+ve	+ve	-ve	+ve < -ve	+ve	+ve
i) $H_2O(s) \xrightleftharpoons[T>0^\circ C]{1\text{ atm}} H_2O(l)$	0	-ve	-ve	+ve	+ve	+ve	+ve > -ve	+ve	+ve
j) $H_2O(s) \xrightleftharpoons[T<0^\circ C]{1\text{ atm}} H_2O(l)$	0	-ve	+ve	+ve	+ve	-ve	+ve < -ve	+ve	+ve

Concept: i)  $\Delta q = 0$  : equilibrium :  $\rightleftharpoons$

$\Delta q = +ve$  : non-spont. :

$\Delta q = -ve$  : spont. :

$\rightarrow \Delta S_{sys}$  &  $\Delta S_{sur}$  have opposite signs.

$\rightarrow \Delta S_{total}$  sign decides  $\Delta S_{sys}$  and  $\Delta S_{sur}$ .

2) b.p  $\propto P_{ext}$

3) m.p ice type solid  $\propto \frac{1}{P_{ext}}$  (melting,  $\Delta V = -ve$ )

4) As T  $\uparrow$ ,  $\Delta H = +ve$  side equilibrium will be shifted

5) As T  $\downarrow$ ,  $\Delta H = -ve$  side equilibrium will be shifted

6) As P  $\uparrow$ ,  $\Delta H = -ve$  side equilibrium will be shifted  
( $\Delta V = -ve$ )

7) As P  $\downarrow$ ,  $\Delta H = +ve$  side equilibrium will be shifted

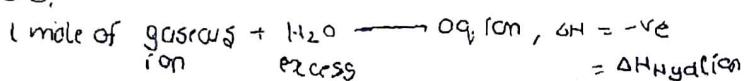
5)

Treat of hydration of ion • Heat of solution of ion(s) Heat of ion

→  $\Delta H_{\text{Hydration}}$

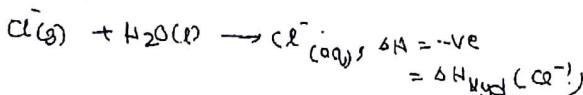
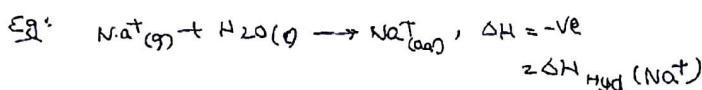
cqn:

at const.  $\text{P}$ ,  $T$ ,



Definition: It is amount of heat evolved when 1 mole of gaseous ion converts into its aqueous ion at given temperature & pressure.

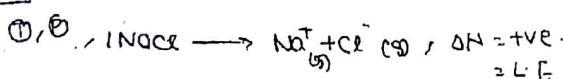
→ always exothermic



$\Delta H_s$  cal. in terms of lattice energy &  $\Delta H_{\text{Hyd}}$  ion for ionic solids:

Lattice energy: It is applicable to usually ionic, crystalline solids

eg:



→ "It is amount of heat required for the conversion of ionic crystalline solid into its constituent oppositely charged gaseous ions at given temp. & pressure"

→ Heat of solution mainly depends on two factors

(i) L.E

(ii) treat of Hydration.

Mathematically, heat of soln is calculated by

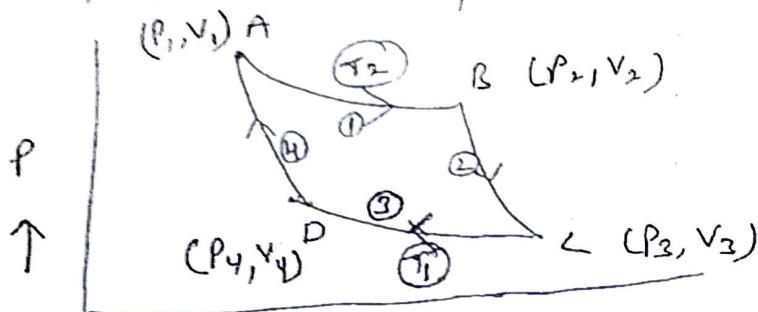
$$\Delta H_s = \Delta H_{L.E} + \Delta H_{\text{Hyd}}(\text{salt})$$

$$\Delta H_s = \Delta H_{L.E} + \Delta H_{\text{Hyd}}(+I) + \Delta H_{\text{Hyd}}(-I)$$

$\Delta H_{\text{Hyd}}$ & $\Delta H_{\text{Hyd}}$ rotation	$\Delta H_s$	Solubility	$\Delta q_s = \Delta H - \Delta H_s$
>	+ve	less soluble/insoluble	-ve/+ve
<	-ve	soluble	-ve
=	0		-ve

→ even  $\Delta H_{\text{solution}}$  is +ve, some substances are soluble :  $\Delta q_s = -\text{ve}$

PV graph for Carnot's cycle is



Step	Process	Conditions	Sign for Work done	Work
1.	Rev. isothermal expansion	$\Delta T = 0$ i.e. Temp = $T_2$ $\Delta E = 0$ $\therefore +Q_2 = -W_1$	-ve	$-2.303nRT_2 \log \frac{V_2}{V_1}$
..	Rev. adiabatic expansion	$Q = 0$ , $\Delta T = -\Delta V$ $W_2 = nC_V \Delta T = T_1 - T_2$	-ve	$nC_V(T_1 - T_2)$
	Rev. isothermal compression	$\Delta T = 0$ i.e. Temp = $T_1$ $\Delta E = 0$ $-Q_1 = +W_3$	+ve	$2.303nRT_1 \log \frac{V_3}{V_4}$
	Rev. adiabatic compression	$Q = 0$ , $\Delta T = +\Delta V$ $= T_2 - T_1$ $W_4 = nC_V \Delta T$	+ve	$nC_V(T_2 - T_1)$

$$\therefore \text{Net work done} = -W_1 - W_2 + W_3 + W_4$$

$$= -2.303nRT_2 \log \left( \frac{V_2}{V_1} \right) + nC_V(T_1 - T_2)$$

$$+ 2.303nRT_1 \log \left( \frac{V_3}{V_4} \right) + nC_V(T_2 - T_1)$$

$$\text{i.e. } W_{\text{net}} = -2.303nRT_2 \log \left( \frac{V_2}{V_1} \right) + 2.303nRT_1 \log \left( \frac{V_3}{V_4} \right)$$

but  $\frac{V_2}{V_1} = \frac{V_3}{V_4}$  according to  $TV^{k-1} = \text{const}$  in adiabatic process.

$$\therefore \Delta S_{\text{sys}} = \Delta S_{\text{Total}} - \left[ -\frac{\Delta H_{\text{sys}}}{T} \right]$$

$$\therefore (\Delta G_{\text{sys}})_{T,P} = +\Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

$$= +\Delta H_{\text{sys}} - T \left[ \Delta S_{\text{Total}} + \frac{\Delta H_{\text{sys}}}{T} \right]$$

$$\boxed{(\Delta G_{\text{sys}})_{T,P} = -T \Delta S_{\text{Total}}}$$

but spontaneity condition in terms of  $\Delta S_{\text{Total}}$  is

$$(\Delta S_{\text{Total}})_{T,P} \geq 0$$

$\therefore$  Spontaneity Condition in terms of  $(\Delta G_{\text{sys}})_{T,P}$  is

$(\Delta G_{\text{sys}})_{T,P} \leq 0$	$\rightarrow < 0$ ie -ve $\Rightarrow$ Spont. process. ie Irrev. Process
	$\rightarrow = 0$ <del>not</del> few. procs ie Equilibrium Reaction
	$\rightarrow > 0$ ie +ve $\Rightarrow$ Non Spont. Procs ie Reaction is not feasible.

The above condition is the convenient

Condition to express Spontaneity Condition  
at room Condition.

Identification of reaction Condition by  $\Delta H_{\text{sys}}$ ,  $\Delta S_{\text{sys}}$  &  $\Delta G_{\text{sys}}$   
| Signs

Gibb's Helmholtz eqn is  $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$

$\Delta H$ sign	$\Delta S$ sign	$\Delta G$ sign	Reaction conditions
{ -ve +ve }	+ve	-ve	Spont. at any temp.
	-ve	+ve	Non Spont. at any Temp.
{ +ve -ve }	+ve	-ve	Spont. only at high temp.
	-ve	+ve	Non Spont. only at high temp.
{ -ve +ve }	-ve	-ve	Spont. only at low temp.
	+ve	+ve	Non Spont. only at low temp.

and  $\Delta S_{\text{Total}} = 0$  in rev. process  
= +ve in Irrev. process.

$$\rightarrow \Delta S_{\text{sys}} = \frac{\partial Q_{\text{rev}}}{T}, \Delta S_{\text{sur}} = -\frac{\partial Q_{\text{rev}}}{T} \text{ in Rev. process}$$

$$\rightarrow \Delta S_{\text{sys}} = \frac{\partial Q_{\text{rev}}}{T}, \Delta S_{\text{sur}} = -\frac{\partial Q_{\text{irrev}}}{T} \text{ in Irrev. process}$$

<u>Process</u>	<u>Equation</u>	<u><math>\Delta H</math></u>	<u><math>\Delta S_{\text{sys}}</math></u>	<u><math>\Delta S_{\text{sur}}</math></u>	<u><math>\Delta S_{\text{Total}}</math></u>
(i) Allotropic change i.e. Transition	Allotrope <sub>1</sub> $\rightleftharpoons$ Allotrope <sub>2</sub>	+ve/-ve $= \Delta H_{\text{Transition}}$	$\frac{\Delta H}{T_b}$	$-\frac{\Delta H}{T_b}$	0
(ii) Physical change reaction					
a) sublimation	Solid $\rightleftharpoons$ gas	+ve $= \Delta H_{\text{sub}}$	$\frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$	$-\frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$	0
b) fusion	Solid $\rightleftharpoons$ liq.	+ve $= \Delta H_{\text{fusion}}$	$\frac{\Delta H_{\text{fusion}}}{T_{\text{m.p}}}$	$-\frac{\Delta H_{\text{fusion}}}{T_{\text{m.p}}}$	0
c) Vaporization	Liq $\rightleftharpoons$ gas	+ve $= \Delta H_{\text{vap}}$	$\frac{\Delta H_{\text{vap}}}{T_{\text{b.p}}}$	$-\frac{\Delta H_{\text{vap}}}{T_{\text{b.p}}}$	0

AS Calculations in gas in cylinder type systems: (long eq. b.r.s.)

a) AS expression in terms of volume & Temp. Variables:

$$\Delta S_{\text{sys}} = \frac{\partial Q_{\text{rev}}}{T}$$

i.e.  $dS = \frac{\partial Q_{\text{rev}}}{T}$  for infinitesimal change

$$\left[ \begin{array}{l} \partial Q_{\text{rev}} = \Delta E + P \Delta V \\ \partial Q_{\text{rev}} = dE + PdV \end{array} \right]$$

i.e.  $dS = \frac{dE + PdV}{T}$

$$dS = \frac{nC_V dT + nPV}{T}$$

$$\left[ P_{\text{gas}} = \frac{nRT}{V} \right]$$

$$dS = nC_V \cdot \frac{dT}{T} + nR \cdot \frac{dV}{V}$$

$$\text{in int. } T \text{ m. int. } \cdot \text{ i. r.}$$

$$\int_{S_1}^{S_2} ds = ncv \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dv}{v}$$

$$\Delta S = 2.303 ncv \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

b)  $\Delta S_{sys}$  expression in terms of Temp. and pressure Variables.  
 for infinitesimal change,  $ds = \frac{\partial q_{rw}}{T}$

$$\therefore ds = \frac{dH - Vdp}{T}$$

$$ds = ncp \frac{dT}{T} - nR \cdot \frac{dp}{p}$$

$$\left[ \frac{V}{g_m} = \frac{nRT}{p} \right]$$

Integration with limits

$$\int_{S_1}^{S_2} ds = ncp \int_{T_1}^{T_2} \frac{dT}{T} - nR \int_{P_1}^{P_2} \frac{dp}{p}$$

$$\Delta S = 2.303 ncp \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$

### (i) Cat. Part in Isothermal process

Condition :  $\Delta T=0$ ,  $\Delta E=0$ ,  $\Delta Q=W$ ,  $\frac{P_1}{P_2} = \frac{V_2}{V_1}$

$\Delta S_{sys}$	Rev. expansion	Irrrev. expansion	infiniti free expansion	finiti free expansion
$\Delta S_{sys}$	$2.303 nR \log\left(\frac{V_2}{V_1}\right)$ $(\delta)$ $2.303 nR \log\left(\frac{P_1}{P_2}\right)$	$(\Delta S_{sys})_{rw}$ $- \frac{P_{ext}(V_2 - V_1)}{T}$	+ve	$\Delta H=0, \Delta Q=0, \Delta W=0, \Delta g=0$
$\Delta S_{sur}$	$-\Delta S_{sys}$		0	0
$\Delta S_{Total}$	0	+ve ∴ $\Delta S_{sys} > \Delta S_{sur}$	+ve	+ve

NOTE : In rev. ( $\delta$ ) irrrev. process, system absorbs or lost heat in rev. manner only.

NOTE :  $S$  is state function, Hence ; Rev. ( $\delta$ ) irrrev. process have same  $\Delta S$  values.

### (i) Enthalpy part in ~~isothermal~~ Adiabatic Process

Condition:  $Q=0, \Delta T \neq 0, W = nC_V \Delta T$

$\Delta S$	Rev. expansion	Irrrev. expansion	Infinitesimal expansion	Finite expansion
$\Delta S_{sys}$	0	$= 2.303 n C_V \log\left(\frac{T_2}{T_1}\right)$ $+ 2.303 n R \log\left(\frac{V_2}{V_1}\right)$	$\Delta S_{sys} > 0$	$E=0, W=0, \Delta H=0, \Delta U=0$ $2.303 n R \log\left(\frac{V_2}{V_1}\right)$
$\Delta S_{surv}$	0	$(\delta S)_{surv} = 2.303 n C_p \log\left(\frac{T_2}{T_1}\right)$ $+ 2.303 n R \log\left(\frac{P_1}{P_2}\right)$	$= +ve$	$= +ve$
$\Delta S_{total}$	0	$= +ve$	0	0
$\Delta S_{sys}$	0	$\Delta S_{sys} = +ve$	0	$(\Delta S_{sys})_{\text{fin}} = +ve$

NOTE: all rev. adiabatic process are not isoentropic  
all irrrev. adiabatic process are isoentropic

- In Rev. adiabatic process, both temp. and volume terms are exactly compensated by  $T V^{1-1} = \text{const.}$  eqn
- In Irrrev. adiabatic process, both temp. and volume terms are not exactly compensated by one another.

### III) Ent. part in Isochoric process

Condition  $\Rightarrow \Delta P = 0, \frac{T_2}{T_1} = \frac{V_2}{V_1}$

### IV) Ent. part in Isochoric process

Condition  $\Rightarrow \Delta V = 0, \frac{T_2}{T_1} = \frac{P_2}{P_1}$

$\Delta S$	Rev. expansion	Irrrev. expansion	$\Delta S$	Rev.	Irrrev.
$\Delta S_{sys}$	$2.303 n C_p \log \frac{T_2}{T_1}$	$(\Delta S_{sys})_{\text{Rev.}}$ $= +ve$	$\Delta S_{sys}$	$2.303 n C_V \log \left(\frac{T_2}{T_1}\right)$	$(\Delta S_{sys})_{\text{Rev.}}$
$\Delta S_{surv}$	$2.303 n C_p \log \left(\frac{V_2}{V_1}\right)$ $= +ve$	$- n C_p \Delta T$	$\Delta S_{surv}$	$2.303 n C_V \log \left(\frac{P_2}{P_1}\right)$	$- (\Delta S_{sys})_{\text{Rev.}}$
$\Delta S_{total}$	0	$\Delta S_{sys} + \Delta S_{surv}$	$\Delta S_{total}$	0	$\Delta S_{sys} + \Delta S_{surv}$

Z in terms of reduced constants

$$Z = \frac{PV}{RT} \text{ for 1 mole}$$

$$Z = \frac{P_r P_c V_r V_c}{R T_r T_c}$$

$$\frac{P_c V_c}{R T_c} \cdot \frac{P_r V_r}{T_r}$$

$$Z = Z_c \times \frac{P_r V_r}{T_r}$$

Note: When  $Z_c$  is not mentioned in the problem use v.w  $Z_c$  value

$$\therefore Z_c = 3/6$$

Ans

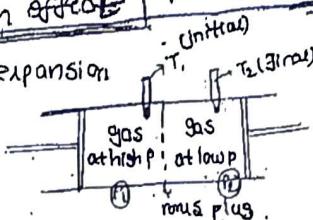
Adiabatic Process

Doule-Thomson effect

→ adiabatic expansion

Principle part of liquefaction of gases

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→ adiabatic condition ( $\Delta Q = 0$ )

↳ during the process heat change = 0 i.e. heat is not absorbed & heat is not evolved.

Observation: It is the phenomenon of observation of cooling effect when the gas is adiabatically expanded from high pressure region to lower region through porous plug.

Expt. result:

Gas	Result
Real gas	cooling effect
H <sub>2</sub> , He	warming //
Ideal gas	No effect

Explanation for experimental results

(1) Explanation of J.T. Result in terms of Net attraction & Repulsions

Gas	Net A & R	Initial temp. Final temp. relation	Reason	Result
Real gas	A > R	T <sub>2</sub> < T <sub>1</sub>	by net attractions V & T $\propto$ K.E $\propto$ T i.e. T ↓	cooling effect
H <sub>2</sub> , He	R > A	T <sub>2</sub> > T <sub>1</sub>	by net repulsions V & T $\propto$ K.E $\propto$ T ↑	warming effect
Ideal gas	A = R	T <sub>2</sub> = T <sub>1</sub>	no change v & T $\propto$ K.E $\propto$ T	No effect

pressure and

temperature