Unit-6
THERMODYNAMICS

- **Definition:** It is branch of chemistry which deals with exchange of energy between system and surrounding and the effects of that change on system parameters.

  In other words - Flow of heat is called thermodynamics.

- **Importance:**
  - It tells us about feasibility of process.
  - It tells about transformation of heat.

- **Limitation:**
  - It does not involve time variable
  - Nuclear reactions are not part of thermodynamics.
  - It does not deal with mechanism of reaction.

- **Heat (q):** It is process of energy transfer due to temperature difference or it is energy in transit.

- **Work (ω):** It is process of energy transfer due to pressure difference.

* Some basic Definitions :-

1. **System :** It is part of universe which is under thermodynamics consideration. It can be as small as 1 ml of water or it can be as large as Indian ocean.

2. **Surrounding :** Everything around system except system. It is always considered as infinitaly large.

Note: Any process can be slow or fast reversible with respect to system. But for surrounding it is always considered as reversible.

System + Surrounding = Universe

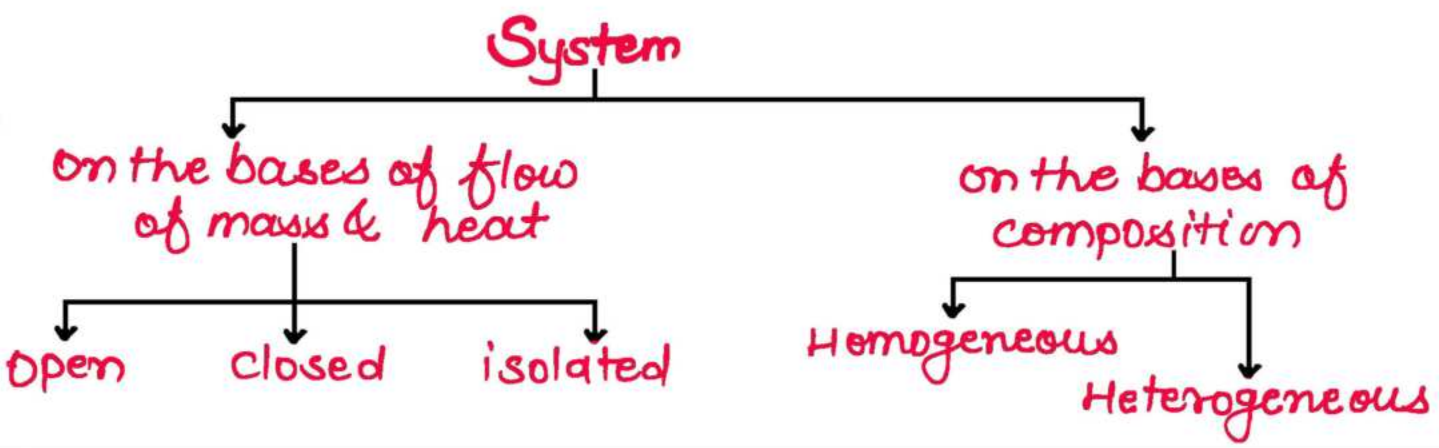
3. **Boundary :** It is the layer which separates system from surrounding.

Types :

(a) Real or imaginary boundary
(b) Rigid or flexible
(c) Permeable or impermeable
(d) Diathermic or adiabatic

Types of systems :-

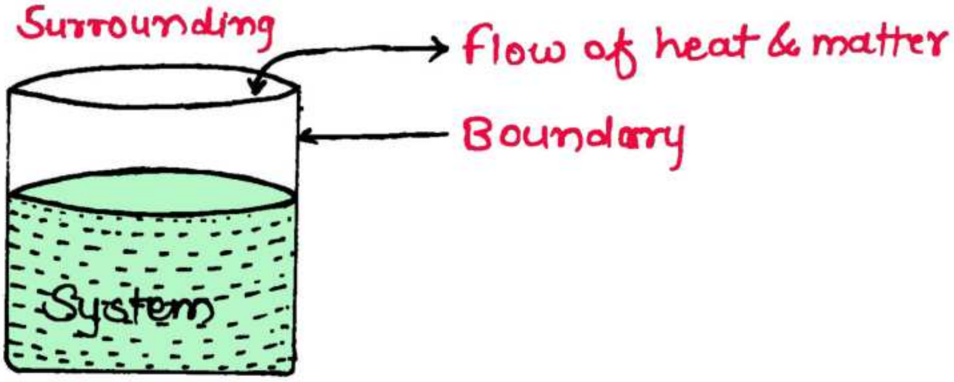
System can be classified on following bases –



- **On the bases of flow of heat & mass :**

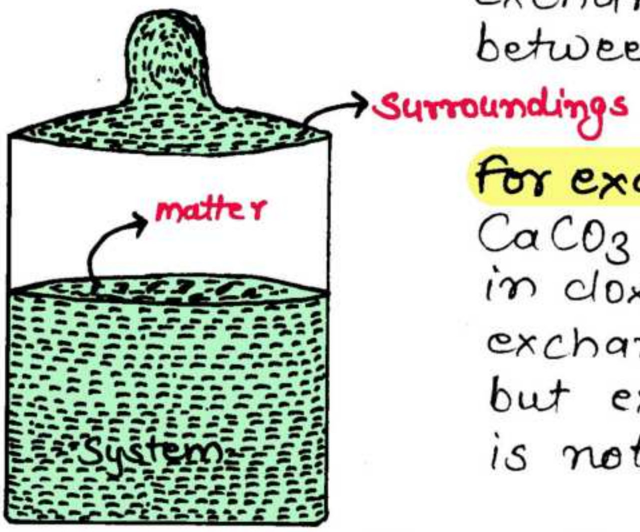
1. **Open system :** In this type of system energy as well as matter transfer takes place between system & surroundings.

for example : If reaction of $CaCO_3$ & HCl is furnished in open test tube, there may be exchange of CO_2 & energy produced during reaction.



open system

2. **Closed system :** In a closed system, there is no exchange of matter but exchange of energy is possible between the system & surrounding.



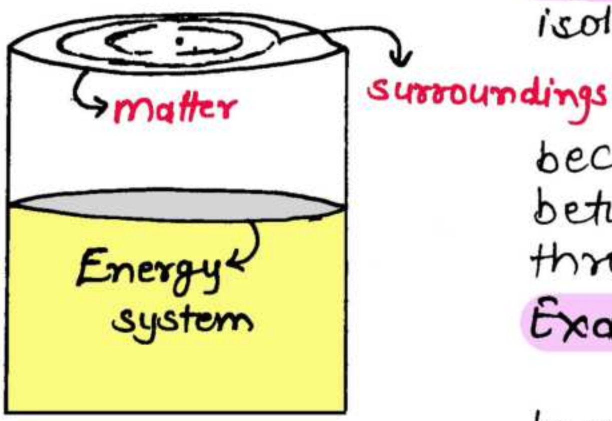
for example : If a reaction of $CaCO_3$ and HCl is carried out in closed test tube, then exchange of energy is possible but exchange of matter is not possible.

Note: In thermodynamics all laws are applied only for closed system.

3. **Isolated system:** In this type of system neither energy nor matter transfer can take place

For example: Tea or coffee in thermos flask

Note: Any system can not be isolated 100 percent



isolated system

because some energy exchanges between system and surroundings through radiation

Example:

The Tea in thermas flask lose its temperature after sometime and becomes cold.

On the basis of composition:

Homogeneous	Heterogeneous
If system is having uniform composition and phase throughout then it is called homogeneous. for eg. sugar solution	A system having non-uniform composition is called heterogeneous. For eg. - chalk powder sol^n.

Q. A closed system can not interact with sun. → False

Q. Atlantic ocean is an open system. → True

Q. A homogeneous system must be pure. → False

Q. A pure system must be homogeneous. → false

Universe is considered as isolated system.

× Thermodynamic Properties :

Any directly or indirectly measurable quantity is called property of system.

For eg.- pressure, volume, temperature, concentration

These are of **two types :**

(a) Intensive	(b) Extensive
Intensive	Extensive
- These are the prop. which on division of system remain unchanged. Eg: Density, temperature	- These are the prop. which get changed on division of system. Eg. mass, volume, mole
- They are non-additive	- They are additive
1 m HCl 100 g + 2 m HCl 100g	1 m HCl 100 g + 2 m HCl 100g
~~3 m HCl 300g~~	3 m HCl 300g
- Generally ratio of two extansive quantity is intensive.	- Generally product of intensive & extensive quantity is extensive.

Properties	Intensive/Extensive
P	I
V	E
T	I
n	E
H	E
U	E
G	E
S	E
A (Helmheltz free Energy)	E
Vapour pressure	I
EMF	I
Resistance	E
Boiling point	I
Surface tension	I
Refractive index	I
Heat capacity	E
molarity	I
Volume strength	I
Concentration	I

- If extensive quantity are divided by amount than they become intensive for example- molar heat capacity, specific volume, specific heat capacity.

- Heat (q), work (w) & time (t) are neither intensive nor extensive.

* **State Parameters :** These are properties or parameters which depend only on initial & final state of system.

If out of given parameters even a single parameters changes, then we call it change of state.

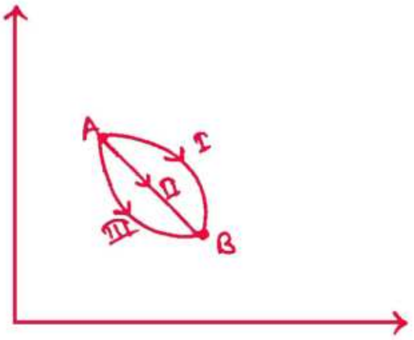
$\boxed{P_1\ V_1\ T_1\ ⓝ} \longrightarrow \boxed{P_2\ V_1\ T_2\ ⓝ}$

State I State II

Note:- A state parameter like P,V,T,U,H,G,S should characterise state of a system.

* **Path parameters:-** These are parameters which depend on path followed when system changes its state.

for eg., work, heat, heat capacity etc.



$\Delta H_{I} = \Delta H_{II} = \Delta H_{III} - H_B - H_A$

$\Delta V_1 = \Delta V_{II} = \Delta V_{III} = V_B - V_A$

$q_{I} \neq q_{II} \neq q_{III}$

$w_1 \neq w_2 \neq w_3$

Note: Here U & H are state f:n, ΔU & ΔH are not state f:n, These simply represent change when state of system is changed.

* Conditions for a function to be state f:n :-
(f:n) (↓ function)

(i) if ϕ is a state f:n, then.

$$\int_A^B d\phi = \phi_B - \phi_A$$

(ii) if ϕ is a state f:n, then

$$\oint_A^B d\phi - 0$$

(iii) A state f:n should characterise state of a system. for eg. - H, U, G, S etc. but $\Delta H, \Delta U, \Delta G, \Delta S$ are not state f:n they are path independent parameters.

(iv) if $\phi = f(x, y)$ is a state parameter then it should satisfy euler's theorem.

$$\left\{ \frac{\partial}{\partial y} \left(\frac{\partial \phi}{d x} \right)_y \right\}_x = \frac{\partial}{\partial x} \left\{ \left(\frac{\partial \phi}{\partial y} \right)_x \right\}_y$$

eg. P.T. $f(x, y) = x^2 y + x y^2$ is a state f:n.

$$2x + 2y = 2x + 2y$$

(v) if $\phi = f(x, y)$ is a state f:n, then it can be written as

$$d\phi = \left(\frac{\partial \phi}{\partial x} \right)_y dx + \left(\frac{\partial \phi}{\partial y} \right)_x dy$$

eg. $H = f(P, T)$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

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

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Q. Prove that pressure is intensive property.

$$\rightarrow P = \frac{nRT}{V} \begin{matrix}\longrightarrow E \\ \longrightarrow E\end{matrix}$$

- **Process :-** It is the path followed when system changes its state.

  Types of process:

  (a) Physical process

  (b) chemical process

- **Physical Process:** These are process during which chemical identity of system remains unchange. for example. melting, vapourisation etc.

Physical Process

- Isobaric ($n, P \rightarrow$ constant)
- Isochoric ($n, V \rightarrow$ constant)
- Isothermal ($n, T \rightarrow$ constant)
- Adiabatic ($n \rightarrow$ cons., $q = 0$, $P, V, T \rightarrow$ variable)
- Cyclic ($\Delta(SP) = 0 = \Delta H = \Delta V = \Delta G$)
- Polytropic

- During isobaric process pressure remains constant throughout.

• Chemical Process :

During it one type of substance gets convert into chemically other type of substance.

During a chemical rxn temp. is always kept constant and out of pressure & volume one par will be constant at a time.

$$A \xrightarrow{P, T} B + 200\,kJ \qquad q_p = \Delta H = -200\,kJ/$$

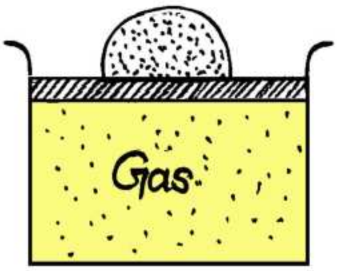
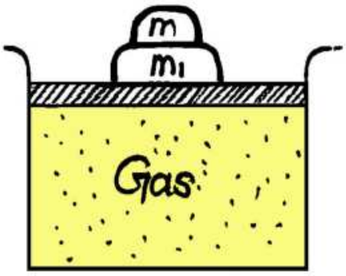
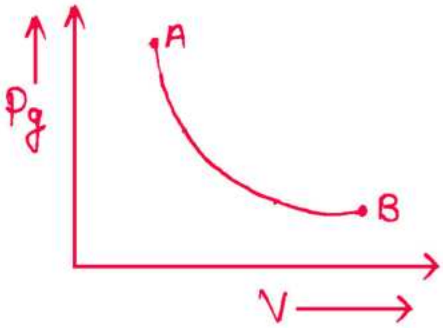
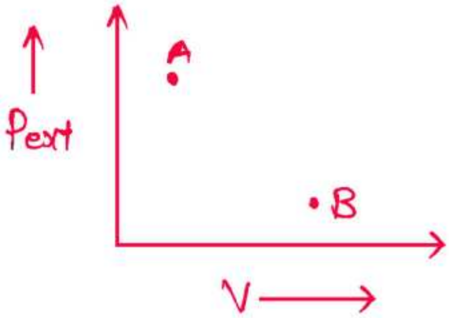
$$A \xrightarrow{V, T} B + 100\,kJ \qquad q = \Delta U = -100\,kJ/mol$$

Note: Although phase transformations are physical processes but still we will apply all laws for phase transformation which we use for chemical Rx^n:

$$H_2O(s) \xrightarrow{P, T} H_2O(l) \qquad \Delta_{transformation}H = +ve$$

Any process can be carried out in two ways:

(i) Reversibly (ii) Irreversibly

	Reversible Process	Irreversible process
1.		
2.	In it external forces change gradually	External forces change suddenly
3.	This process will be slow (Hypothetical)	This process will be fast (real)
4.	Ext. pressure changes at every constant $P_{gas} = P_{ext} \pm \underset{\to 0}{dP}$ $P_{gas} \approx P_{ext}$	Here process takes place at constant pressure $P_{gas} = P_{ext} \pm \Delta P$ $P_{gas} \neq P_{ext}$
5.	Here we can plot Pgas V/s V 	We can not plot Pgas V/s V so we plot Pext V/s V 
6.	If process is reversed then it will follow the same path.	If process is reversed then it will follow a different path.

7.	We can apply $PV = nRT$ anywhere	We can apply $PV = nRT$ at initial & final points only.
8.	In reversible cyclic process system as well as surrounding are restored to their original position	In irreversible cyclic process system is restored to its original position but not surrounding.

Note: A process can be reversible or irreversible with respect to system but it is always considered as reversible for surrounding.

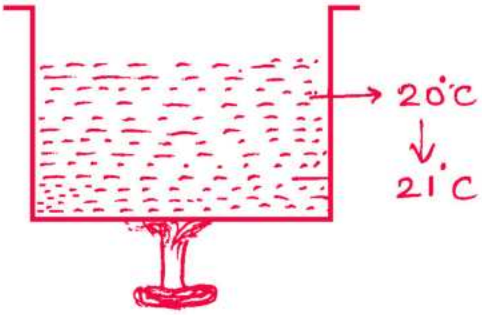
* Heat Capacity (C):

Amount of heat required to raise the temperature of 'm' gm of substance by 1°C. is called heat capacity.

$$\boxed{C = \frac{q}{\Delta T} \ (J/K)}$$

Where,

$C \rightarrow$ heat capacity
$q \rightarrow$ heat exchanged
$\Delta T \rightarrow$ Change in temp.



- It is extensive quantity.

- C is a path function.

* Molar heat Capacity :

Amount of heat required to raise the temp of one mole of substance by 1°c.

$$\boxed{C_m = \frac{q}{n\Delta T} \ -(J/_{K\text{-}mol})}$$

Where,

C_m → molar heat Capacity
q → Heat exchanged
ΔT → Change in temperature
n → no. of moles.

→ It is an intensive quantity.
→ Path function.

* Specific Heat Capacity :

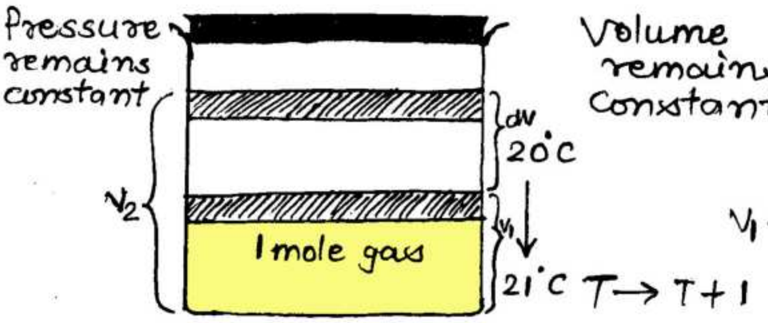
Amount of heat required to raise the temperature of one gm of substance by 1°c.

$$\boxed{\frac{C}{m} = C_s = \frac{q}{m\Delta T} \ (J/_{K\text{-}Kg})}$$

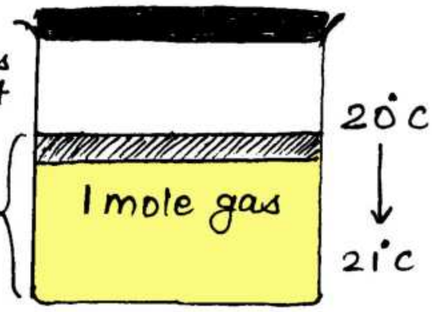
- Intensive quantity
- Path function

*** In case of gases heat capacities are of two types.**

(i) Molar heat capacity at constant pressure (C_{pm})
(ii) Molar heat capacity at constant volume (C_{vm})



C_p for gases



C_v for gases

$$C_{pm} > C_{vm}$$

- State function
- Intensive quantity

• for an ideal gas

$$C_p - C_v = nR$$

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

$$C_{pm} - C_{vm} = R$$

$$\frac{C_{p.m}}{C_{v.m}} = \gamma = \text{adiabatic coefficient}$$

$$\frac{C_{p.m}}{C_{vm}} - 1 = \frac{R}{C_{v.m}}$$

$$\gamma - 1 = \frac{R}{C_{vm}}$$

$$\boxed{C_{vm} = \frac{R}{\gamma-1} \quad C_{pm} = \frac{\gamma R}{\gamma-1}}$$

for ideal gas

$$c = f(T) \text{ only}$$

$$c = a + bT + cT^2 + \cdots$$

for solids & liquids

$$C_{p,m} \approx C_{v,m} \approx C_m$$

* Heat capacities for various processes:

1) for Isobaric process

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

2) for Isochoric process

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

3) for adiabatic process

$$C = \frac{q}{\Delta T} = 0$$

4) for isothermal process

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

* Degree of freedom:

It represents the no. of ways there which a system can change from its current state.

Types:

1) Translational (K.E) → at all temperature
II) Rotational (K.E) → at moderate temperature
III) Vibrational (K.E + P.E) → very high temp.

Total Degree of freedom = 3N

N → no. of atoms in a given molecule.

Q. Find total degree of freedom for

(a) He ⟶ 3N ⟶ 3×1 = 3
(b) H_2 ⟶ 3N ⟶ 3×2 = 6
(c) CO_2 ⟶ 3N ⟶ 3×3 = 9
(d) H_2O ⟶ 3N ⟶ 3×3 = 9
(e) NH_3 ⟶ 3N ⟶ 3×4 = 12
(f) C_2H_6 ⟶ 3N ⟶ 3×8 = 24

Translation Degree of freedom → 3 (for all)

Rotational D.o.f. → 0 (for mono atomic)
2 (for, Di, Tri ((linear) atomic)
3 (for Polyatomic)

Vibrational D.o.f. → 0 (mono atomic)
→ 3N-5 (for Di, tri (linear) atomic)
→ 3N-6 (for polyatomic)

* Law of equipartition of Energy:

According to it, energy is distributed among various degrees of freedom equally for translational Degree of freedom.

Energy associated with each trans D.of. = $\frac{1}{2}KT$ J/molecule

Energy associated with each trans. Dof per molecule $= \frac{1}{2}RT$ J/mol

If translational Dof are f_T

Then total energy associated with f_t no. of trans D.of. per molecule =

$$f_t \frac{RT}{2} \text{ J/mole}$$

for Rotational degree of freedom.

same as above.

for vibrational degree of freedom.

Energy associated with each vibration degree of freedom per molecule = KT J/molecule

Energy associated with each vibration degree of freedom per mole = RT J/mol.

- Internal energy for 1 mol.

$$U = f_t \frac{RT}{2} + f_R \frac{RT}{2} + f_{vb} RT$$

$$U = (f_t + f_R + 2f_{vb}) \frac{RT}{2}$$

$$C_{v,m} = \left(\frac{f_t}{2} + \frac{f_R}{2} + f_{vb}\right) R$$

$$C_{p,m} = C_{v,m} + R$$

$$\gamma = \frac{C_{p,m}}{C_{v,m}}$$

Q. find out $C_{p,m}$, $C_{v,m}$ & γ for

		$C_{p,m}$	$C_{v,m}$	γ
a)	$He(g)$ ⇒	$5R/2$	$3R/2$	$5/3$
b)	$H_2(g)$ ⇒	$7R/2$	$5R/2$	$7/5$
c)	$CO_2(g)$ ⇒	$7R/2$	$5R/2$	$7/5$
d)	$H_2O(g)$ ⇒	$4R$	$6R/2$	$4/3$
e)	$NH_3(g)$ ⇒	$4R$	$3R$	$4/3$

Atomicity		f_t	f_R	f_{vib}	C_v		C_p		γ	
					ex vib	inc vib	ex vib	inc vib	exc. vib	inc vib
mono		3	0	0	$\frac{3R}{2}$	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5R}{2}$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5R}{2}$	$3R$	$\frac{7R}{2}$	$4R$	$\frac{7}{5}$	$\frac{4}{3}$
Tri	Linear	3	2	4	$5R/2$	$9R/2$	$7R/2$	$11R/2$	$7/5$	$11/9$
	non. Linear	3	3	3	$3R$		$4R$		$4/3$	

Note: As atomicity ↑,

* Parameters Related to I^{st} Law of thermodynamics.

1) Work (w): It is transfer of energy due to pressure difference.

- Neither intensive nor extensive
- It is path function

Types of work :-

a) PV or expansion work

b) Non PV work (eg. muscle work, electrical work)

In first law, we will mainly deal with PV or expansive work.

Sign convention :-

- Work done by system or work of expansion is taken as -ve.
- Work done on the system or work of compression is taken as +ve.

$$w = -20J$$

⇒ work done by the system = 20J.

Calculation of work :-

$$|dw| = |f_{ext}\ dx|$$

$$|dw| = \left|\frac{F_{ext}}{A} . A dx\right|$$

$$|dw| = |P_{ext} \cdot dv|$$

$$\int dw = -\int P_{ext}\ dv$$

$$\Rightarrow \boxed{w = -\int_{V_1}^{V_2} f_{ext}\ dv}$$

Applicable for all kind of process & for all types of fluid in closed vessel.

1) If $P_{ext} = 0 \Rightarrow$ free expansion will taken place

$$w = -\int P_{ext}\, dv = 0$$

2) If process is irreversible

$$P_{ext} = \text{constant}$$

$$w = -P_{ext} \int_{v_1}^{V_2} dv$$

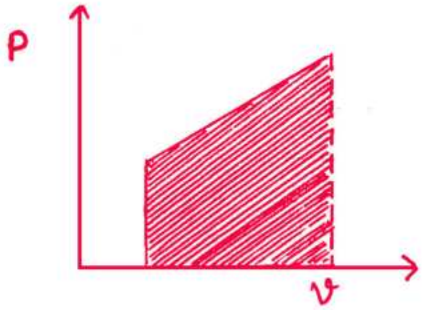
$$\Rightarrow w = -P_{ext}(v_2 - v_1)$$

3) If process is reversible

$$P_{ext} \cong P_{gas} = \frac{nRT}{V}$$

$$w = -\int P_{ext}\, dv = -\int_{v_1}^{v_2} nRT \frac{dv}{v}$$

4) Area under the PV curve will give magnitude of work done.



5) If $P = f(v)$ eg. $P = a + bv$

$$w = -\int_{v_1}^{v_2} (a + bv)\, dv$$

Q. Calculate work done for exp. of a substance $3m^3$ to $5m^3$ against.

a) Constant pressure = 10^5 Pa ⇒ $-10^5(2)$ J

b) Variable pressure = $(10+5V)$ Pa ⇒ $-(10\times2+40)$ J

c) free exp. ⇒ 0

d) for 1 mol of ideal gas following $T=4V^2$

$$\Rightarrow -4nR\left(\frac{V_2^2-V_1^2}{2}\right)$$

Q. Derive an expression for work done for n mol of vanderwall gas. (constant temperature).

$$\rightarrow \left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \Rightarrow P=\frac{nRT}{(V-nb)}-\frac{an^2}{V^2}$$

$$w=-\int P\,dv$$

$$\Rightarrow w=-\left[\int_{V_1}^{V_2}\frac{nRT}{(V-nb)}\,dv+\int_{V_1}^{V_2}\frac{an^2}{V^2}\,dv\right]$$

$$w=-nRT\ln\frac{V_2-nb}{V_1-nb}-an^2\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$$

Unit conversion:

1 bar L = 100 J

1 atm L = 101.3 J

* Heat (q) :-

- It is transfer of energy due to temp. difference
- It is neither extensive nor intensive
- It is path function.

Sign convention:

- Heat lost by the system is taken as -ve
- Heat gained by system is taken as +ve

Heat exchanged at constant volume (q_v) = ΔU

Heat exchanged at constant pressure (q_p) = ΔH

$$dq = nC_m\,dT$$

$$dq_v = nC_{v,m}\,dT$$

$$\Rightarrow \frac{dq_v}{dT} = nC_{v,m} = C_v$$

$$\left(\frac{\partial U}{\partial T}\right)_V = nC_{v,m} = C_v$$

$$\left(\frac{\partial H}{\partial T}\right)_P = nC_{pm} = C_p$$

3) Internal energy (U or E):-

It is sum of all kind of energies present in the system.

$$U = KE + PE + \overbrace{BE + \cdots\cdots}^{\text{negligible effect of change in } P, V, T}$$

We cannot determine absolute value of U

- It is extensive quantity.
- State function

In thermodynamics we consider system at rest & except gravitational feilds, all other fields are assumed to be absent.

If internal energy is changed,

$$\Delta V = \Delta KE + \Delta PE$$

In case of ideal gas there are no interactions between particles $\Rightarrow PE = 0$

$$\Delta V = \Delta KE$$

for an ideal gas, $KE \propto f(T)$ only

$$U = f(T)$$

for an ideal gas, v is a function of temperature only for real gas & other substances.

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

In case of gases, if eq^n of state is known then state parameters can be determined using two variables at a time.

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

for an ideal gas,

$$\left(\frac{\partial U}{\partial v}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

$$\left(\frac{\partial U}{\partial T}\right)_V = nC_{V,m} = C_V$$

We know that V is a state function

$$dU = \left(\frac{\partial V}{\partial P}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_P dV$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_P dT$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial V}{\partial T}\right)_V dT$$

Applicable only for physical process

All three differentiable eq^n are correct but we will use third eq^n extensively.

Calculation of ΔU for physical process:

1) for an ideal gas undergoing any process

$$dU = \underset{\longrightarrow 0}{\left(\frac{\partial U}{\partial V}\right)_T} dV + \left(\frac{\partial V}{\partial T}\right)_V dT$$

$$\Rightarrow \boxed{\int dU = n \int C_{V,m}\, dT}$$

if $C_{V,m}$ is independent of temp.,

$$\boxed{\Delta U = n C_{V,m} (T_2 - T_1)}$$

2) Real gas undergoing isochoric process

$$dV = 0$$

$$\int_{U_1}^{U_2} dU = n \int_{T_1}^{T_2} n C_{pm} \cdot dT$$

3) for solids & liquids.

Change in volume is negligible.

$$dv \cong 0$$

$$\int_{U_1}^{U_2} dU = n\int_{T_1}^{T_2} C_m \, dT$$

4) for a real gas undergoing any process.

$$\boxed{dU = nC_{v,m}\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV}$$

* first law of thermodynamics:

This law is based on conservation of energy.

According to it,

Energy can neither be created nor destroyed it can just be transferred from one body to another.

- Suppose a system has internal E 'U', it exchanges some heat with surrounding & W.D is 'W'. so,

$$U_2 = U_1 + q + W$$

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

or

$$dU = dq + dW$$

Applicable for all kinds of process & for all types of fluids in closed system.

* ENTHALPY :-

- Represented by 'H'.
  Mathematically it is defined as,

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

- Extensive property & state function
- Absolute value of 'H' cannot be determined

$H = U + PV$

$H + dH = U + du + (P + dp)(V + dv)$

$dH = dq + dw_{PV} + dw_{non-PV} + Pdv + Vdp$

$dH = dq + dw_{non-PV} + Vdp$

At constant pressure.

$dH = dq_p + dw_{non-PV}$

if $dw_{non-PV} = 0$

$dH = dq_p$ or $\Delta H = q_p$

Note: $\boxed{\Delta H = \Delta U + (P_2V_2 - P_1V_1)}$

Calculation of ΔH,

a) for physical process

$H = U + PV$

$\Delta H = \Delta U + \Delta PV$

for an ideal gas.

$H = U + nRT$

$H = f(T)$

for real gas & other substance.

$$H = f(P, V, T)$$

$$H = f(P, V) = f(V, T) = f(P, T)$$

for ideal gas,

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \quad \left(\frac{\partial H}{\partial V}\right)_T = 0 \quad \left(\frac{\partial H}{\partial T}\right)_P = nC_{pm} = C_p$$

∵ H is a state function.

$$dH = \left(\frac{\partial H}{\partial P}\right)_V dp + \left(\frac{\partial H}{\partial V}\right)_P dv \quad \text{———} \ ①$$

$$= \left(\frac{\partial H}{\partial V}\right)_T dv + \left(\frac{\partial H}{\partial T}\right)_V dT \quad \text{———} \ ②$$

$$= \left(\frac{\partial H}{\partial P}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_P dT \quad \text{———} \ ③$$

Out of given eqn we will use (III) eqn extensively.

- **Case I :** for an ideal gas undergoing any process

$$dH = \underbrace{\left(\frac{\partial H}{\partial P}\right)_T}_{\longrightarrow 0} dp + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$\Delta H = n\int_{T_1}^{T_2} C_{P,m}\, dT$$

- **Case II :** for real gas undergoing isobaric process.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T \overset{dP}{\longrightarrow} 0$$

$$\Delta H = n\int_{T_1}^{T_2} C_{p,m}\, dT$$

- **Case III:** A real gas undergoing any process

$$dH = nC_{p,m}\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\Delta H = n\int_{T_1}^{T_2} C_{p,m}\, dT + \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP$$

Now using def^n:-

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

for an ideal gas

$$\Delta H = \Delta U + nR\Delta T$$

for solids & liquids,

$$\Delta H \cong \Delta U$$

- **Calculation of ΔH for chemical process.**

$R \xrightarrow{V,T} P$ $\qquad q_v = \Delta U$

$R \xrightarrow{P,T} P$ $\qquad q_p = \Delta H$

- **Case I :** if only gaseous reactants & products are present.

$$aA(g) + bB(g) \longrightarrow cC(g)$$

We have asssumed that all gases are ideal

$$\boxed{\Delta H = \Delta U + (\Delta n_g) RT}$$

Δn_g = moles of gaseous product - moles of gas reactant

- **Case II :** If along with gases, solids & liquids are also present

$$aA(g) + bB(s) \longrightarrow cC(l) + dD(g)$$

due to solids & liquids $\Delta(PV) \approx 0$

$$\Delta H = \Delta V + (\Delta n_g) RT$$

$$\Delta n_g = d - a$$

Work done during a chemical reaction:

$$A(g) + B(g) \xrightarrow{V, T} 4C(g)$$

$$w = 0$$

$$A(g) + B(g) \xrightarrow{P, T} 4C(g)$$

$$w = -\int_{V_1}^{V_2} P\,dV = -P_{ext}[V_2 - V_1]$$

$$= -P_{ext}\left[\frac{n_f RT}{\cancel{P}} - \frac{n_i RT}{\cancel{P}}\right]$$

$$= \boxed{-\Delta n_g RT}$$

* CALORIMETRY :

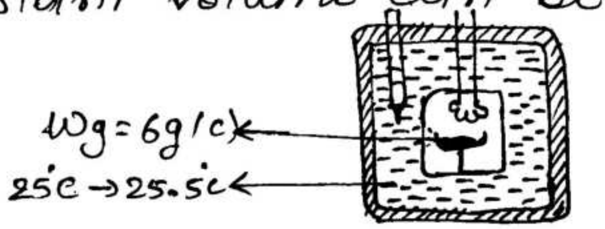
It is branch of chemistry which deals with measurement of energy exchange during physical or chemical processs because it is carried out in vessel called calorinuter thats why it is called calbrimetry.

Measurements are done under,

(i) At constant V & T (q_v or ΔU)
(ii) At constant P & T (q_p or ΔH)

A) At constant V & T :-

This process is carried out in a close rigid vessel called bomb calorimeter. In this processs small amount of substance undergoes combustion, As a result temperature outside system / water + calorimeter) changes & heat exchanged at constant volume can be calculated using.



$$q_v = C\Delta T$$

where,

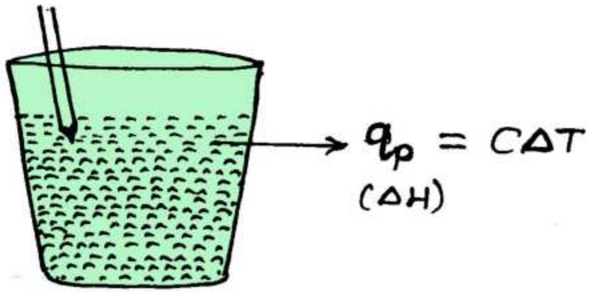
q_v = Heat exchanged at constant volume
C = Heat capacity of water + calorimeter

$$C_{(s)} + O_2 \longrightarrow CO_{2(g)} \qquad \Delta U = -\frac{m}{w} q_v$$

Bomb calorimeter is generally used when gaseous components are involved.

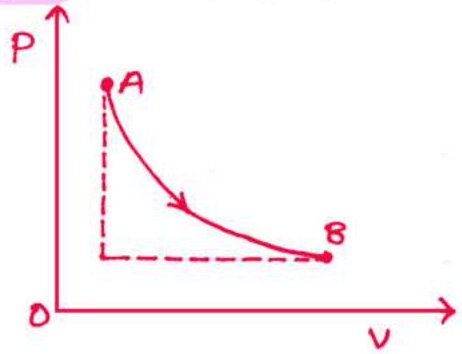
B) At constant P & T :-

Generally reactions involving solids & liquids are carried out at constant P & T in open styofoam cups.



• Calculation of $q, w, \Delta H$ & ΔU :→

1) for isothermal processs :-



- $T, n =$ const. $\Rightarrow \Delta T = 0$
- $\Delta U = n C_{v,m} \; \Delta T = 0$
- $\Delta H = n C_{p,m} \; \Delta T = 0$

from FLT

$$\Delta U = q + w$$

$$\Rightarrow \boxed{q = -w}$$

Magnitude of work will depend on whether process is reversible or irreversible.

Case I. for reversible process.

$$w = -\int_{V_1}^{V_2} P\,dw = \boxed{-nRT \ln V_2/V_1}$$

$$= \boxed{-nRT \ln P_1/P_2}$$

Case II. for irreversible process

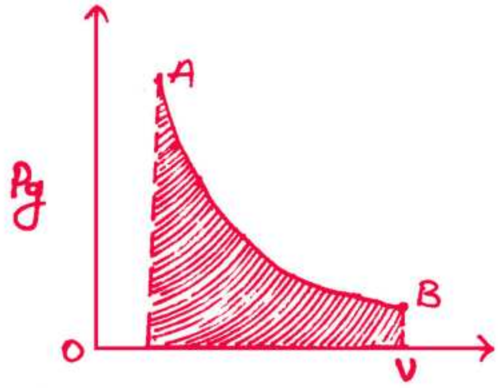
$$\boxed{w = -\int_{V_1}^{V_2} P_{ext}\,dV = -P_{ext}(V_2 - V_1)}$$

Note: If Pext is not given then final pressure of system is considered as ext. pressure.

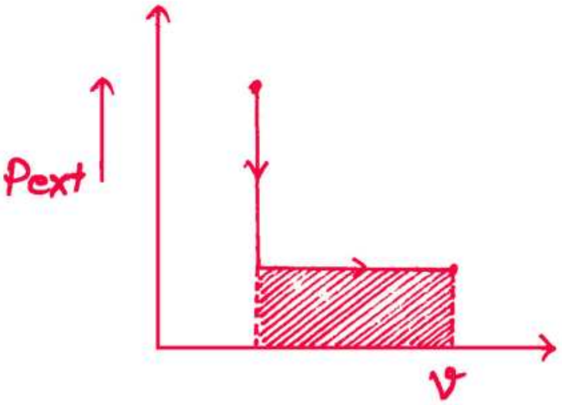
* Graphical analysis of work:
(Isothermal process

for expansion

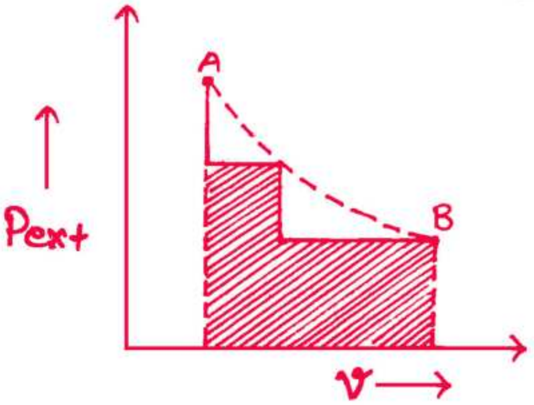
Reversible



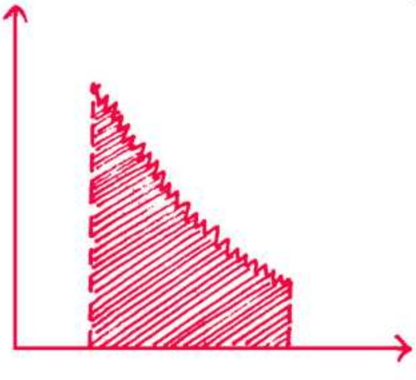
Irreversible (single stage)



Irreversible (Two stage),



Irreversible (n stages)

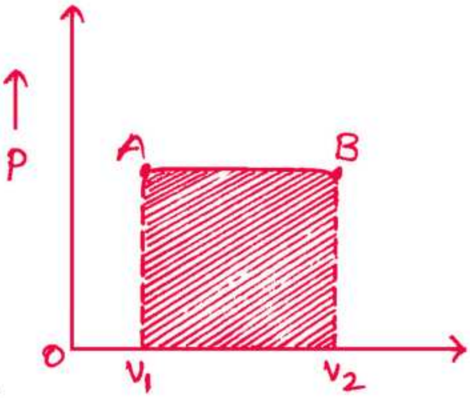


if n → ∞ then process becomes reversible

$$|w|_{rev} > |w_{irr}|_{m.s} > |w_{irr}|_{s.s.}$$

- Reversible processes are more efficient with respect to work because we have to do minimum work during compression & we can extract maximum work during expansion from the system three reversible process.

2) For Isobaric process :-



$\Delta P = 0$

$\Delta U = nC_{v,m}\Delta T$

$\Delta H = nC_{p,m}\Delta T$

from FLT

$\Delta V = q + w$

$$\boxed{w = -P_{ext}\cdot(V_2 - V_1) = -nR\Delta T}$$

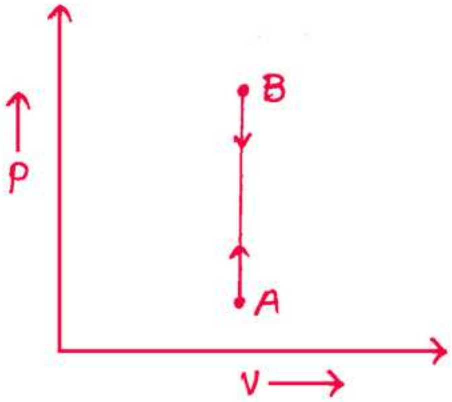
$nC_{v,m}\Delta T = q_p - nR\Delta T$

$$\boxed{\therefore\ q_p = nC_{p,m}\Delta T}$$

$$\frac{\Delta H}{\Delta U} = \frac{C_{p,m}}{C_{v,m}} = \gamma$$

Note: Magnitude of work done will be same irrespective of reversible or irreversible isobaric process.

3) Isochoric Process :



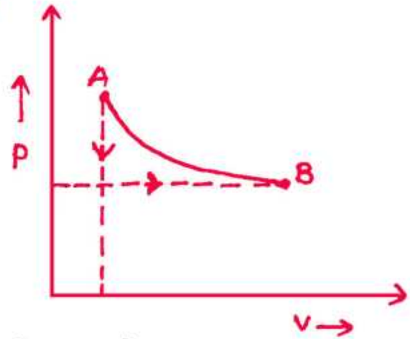
$\Delta V = 0$

$q_v = \Delta U = nC_{vm}\Delta T$

$\Delta H = nC_{p,m}\Delta T$

$$w = -\int P\,dV = 0$$

4) for Adiabatic Process :-



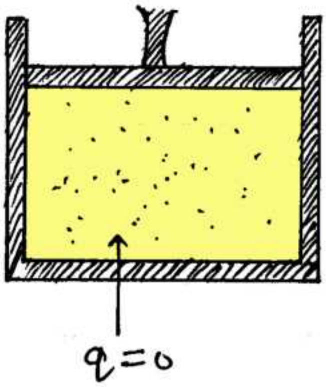
$q = 0$

$\Delta U = n C_{v m} \Delta T$

$\Delta H = n C_{p,m} \Delta T$

$$w = \Delta U = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

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



Between two states of an ideal gas only one adiabatic process is possible.

Adiabatic process are unique between two states.

$$P_1V_1T_1 \xrightarrow[\text{adiabatic}]{\text{reversible}} P_2V_2T_2$$

$$P_1V_1T_1 \xrightarrow[\text{adiabatic}]{\text{Irreversible}} P_2V_3T_3$$

If we move from A $(P_1V_1T_1)$ to B $(P_2V_2T_2)$ reversibly then we cant achive $(P_2V_2T_2)$ by adiabatic irreversible process and vice versa.

To calculate final parameters. we should know whether process is reversible or irreversible

for reversible adiabatic process:

from FLT,

$$dU = \underset{\longrightarrow 0}{dq} + dw$$

$$dU = -P_{ext}\ dV$$

$$\cancel{n}\, C_{v,m}\ dT = \cancel{n} RT\ \frac{dV}{V}$$

Case I: If $C_{v,m}$ is independent of temperature

$$\frac{R}{\gamma-1}\ dT = RT\ \frac{dV}{V}$$

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

$$\Rightarrow \boxed{TV^{\gamma-1} = K}$$

$$\Rightarrow \boxed{PV^{\gamma} = K}$$

Case-II If $C_{v,m}$ is $f(T) = a+bT^2$

$$\int_{T_1}^{T_2} \left(\frac{a+bT^2}{T}\right) dT = -R\int_{V_1}^{V_2} \frac{dV}{V}$$

for irreversible process:

$$dU = dq + dw$$

$$n\, C_{v,m}\,(T_2 - T_1) = -P_{ext}\,(V_2 - V_1)$$

$$\Rightarrow \boxed{\frac{nR(T_2-T_1)}{\gamma-1} = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT}{P_1}\right)}$$

from FLT

$$\Delta U = q + w$$

for adiabatic , $q = 0$

$$\Rightarrow \Delta U = w$$

If work is done by the system.

$$w = -20\ kj$$

$$\Delta U = -20\ kj$$

work is done at the expense of internal energy.

If work is done on the system.

$$w = 20\ kj$$

$$\Delta U = 20\ kj$$

increase in internal energy.

if expansion is free

$$w = 0$$

$$\Delta U = 0$$

$$\Delta T = 0 \longrightarrow \text{Ideal gas}$$

- free expansion of real gas

from PLT

$$\Delta U = \underset{\rightarrow 0}{q} + \underset{\rightarrow 0}{w}$$

$$\Delta U = 0$$

$$\Delta U = KE + PE = 0$$

$$KE = f(T)$$

If attractive forces are do inating ($z<1$),

Gas molecules will want to shrink but gas is expanding, as a result, stability will decrease, means PE↑, KE↓ & T↓. Gas is showing cooling effect.

If repulsive forces are do ($z>1$)

Gas molecules will try to expand due to rep^n. so on free expansion stability will increase, means PE↓, KE↑ ⇒ T↑. Gas is showing heating effect.

- Most of the gases will show cooling effect on free expansion. (except H_2 & He)
- If vanderwal gas is mentioned then we have to consider only attractive forces.
- If free expansion takes place at inversion temperature. then there will be no heating or cooling.

$$\text{Attractive forces dominate (Cooling effect)} \xleftarrow{T<T_i} T_i = \frac{2a}{bR} \xrightarrow{T>T_i} \text{Repulsive forces dominate (heating effect)}$$

$$\downarrow$$

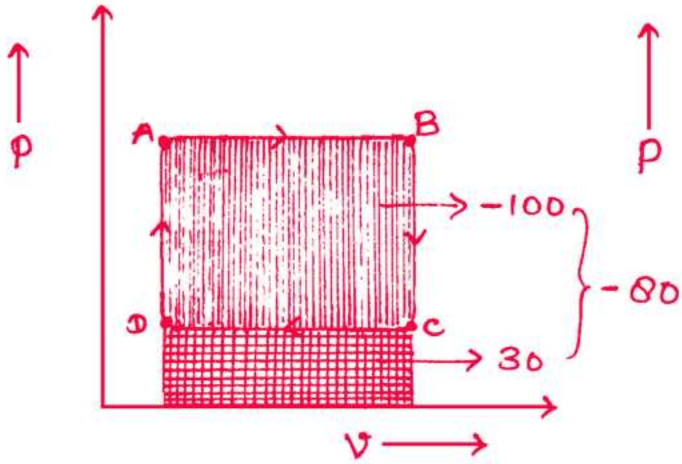
attractive force of = force of rep^n

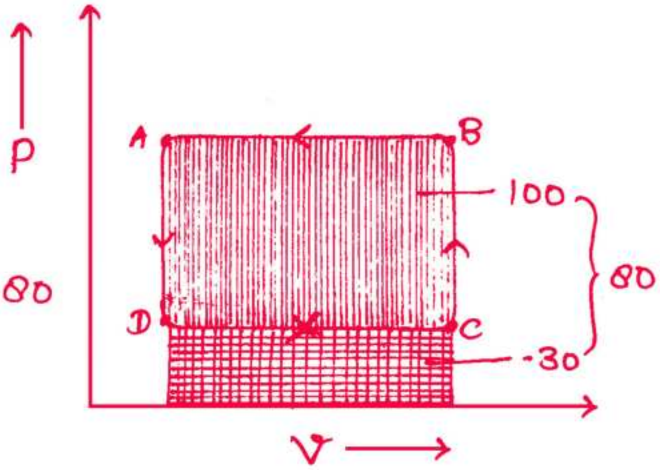
($\Delta T=0$)

* Cyclic Process :-

Sign convention.

Anticlockwise work is taken as +ve & clockwise work is taken as -ve because in anticlockwise work expansion occurs at low pressure & compression occurs at high pressure.





- $\Delta(SF) = 0 = \Delta H = \Delta U = \Delta G = \Delta S$
- From FLT

$$\underset{\longrightarrow 0}{\Delta U} = q + w$$

$$q = -w$$

$$w = w_{AB} + w_{BC} + w_{CD} + w_{DA}$$

Note : In case of standard processs like isobaric, isochoric, isothermal we can directly use formula. But if processs is not standard then

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

* Polytropic Process :-

It is a general process represented by $PV^{x} = K$

if $x = 1 \Rightarrow PV = K \Rightarrow$ Isothermal

$x = 0 \Rightarrow P = K \Rightarrow$ Isobaric

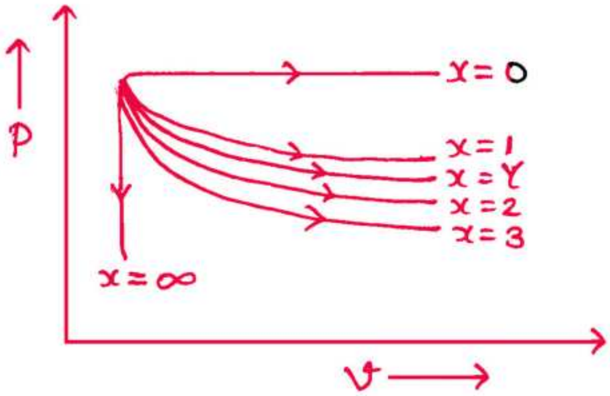
$x = \gamma \Rightarrow PV^{\gamma} = K \Rightarrow$ Adiabatic

$x = \infty \Rightarrow V = K \Rightarrow$ Isochoric

$$PV^{x} = K$$

$$V^{\gamma} dp + x\,V^{x-1}\,dP = 0$$

$$\frac{dP}{dV} = -\frac{xP}{V}$$



• Work done :-

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

$$P_1V_1^{x} = P_2V_2^{x} = K$$

$$= -\int_{V_1}^{V_2} \frac{K}{V^{x}}\,dV$$

$$= \frac{-K(x-1)}{V^{x-1}}\Bigg|_{V_1}^{V_2} \qquad = \frac{-K(x-1)}{V_2^{x-1}} + \frac{K(x-1)}{V_1^{x-1}}$$

$$= P_2V_2(1-x) + P_1V_1(x-1)$$

$$= \frac{nR\Delta T}{x-1}$$

• Molar heat capacity for polytropic processs :-

$$C_m = \frac{q}{n\Delta T}$$

$$\Delta U = q + w$$

$$n C_{v,m} \Delta T = q + \frac{nR\Delta T}{x-1}$$

$$q = n C_{v,m} \Delta T - \frac{nR\Delta T}{x-1}$$

$$\boxed{C_m = C_{vm} + \frac{R}{1-x}}$$

• Graphical comparison between reverssible & irreversible adiabatic processs :-

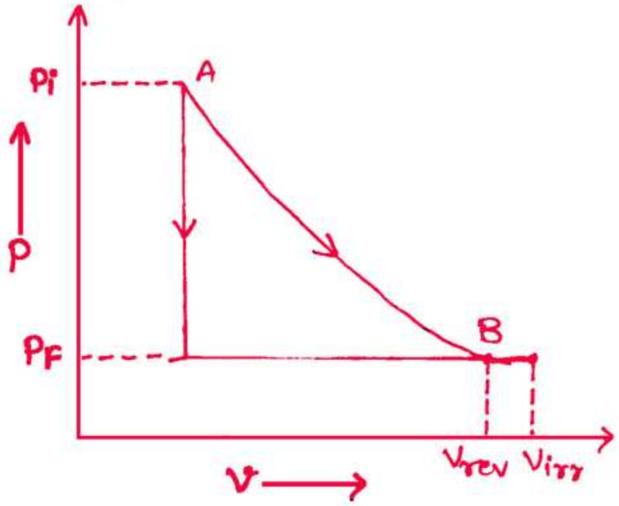
A) for same final pressure :

	U_i	w	U_f
rev.	100	-60	40
irre.	100	-40	60

$$(U_f)_{irr} > (U_f)_{rev}$$

$$T_{irr} > T_{rev}$$

$$\therefore\ V_{irr} > V_{rev}$$



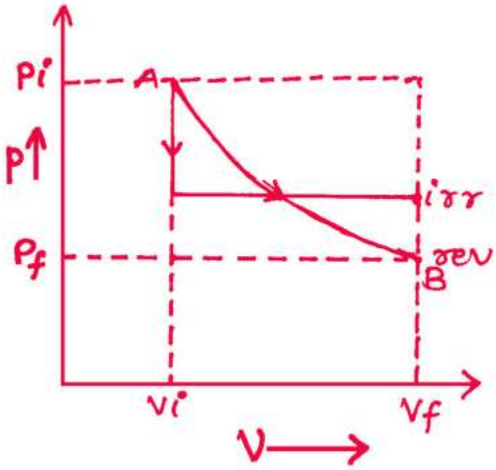
B) for same final volume :

	U_i	w	U_f
rev	100	−60	40
irr	100	−40	60

$(U_f)_{irr} > (U_f)_{rev}$

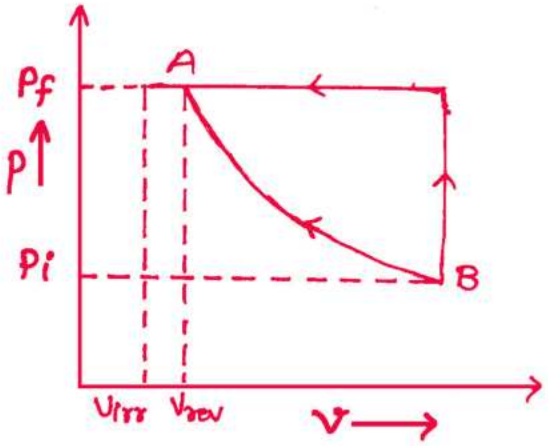
$T_{irr} > T_{rev}$

$\therefore P_{irr} > P_{rev}$

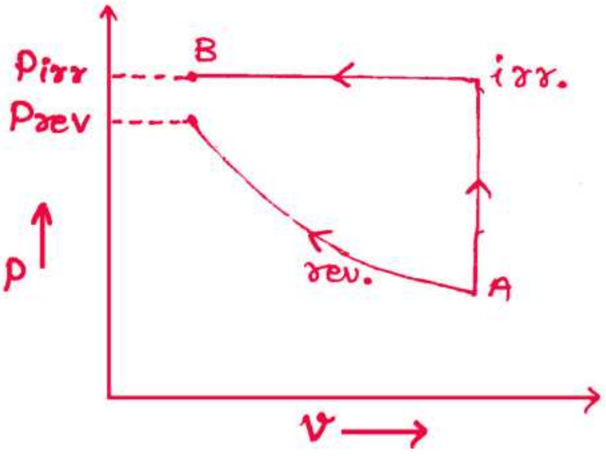


COMPRESSION :-

A) for same pressure :



B) for same final volume.



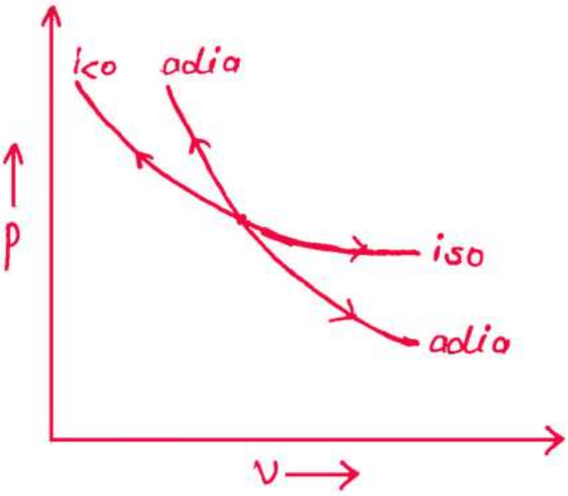
Comparison between Isothermal & Adiabatic process :-

$$pV^{\gamma} = K$$

$$V\,dp + \gamma V^{\gamma-1}\,dV\,p = 0$$

$$\frac{dp}{dV} = -\gamma \frac{p}{V}$$

$$|\gamma| > 1$$



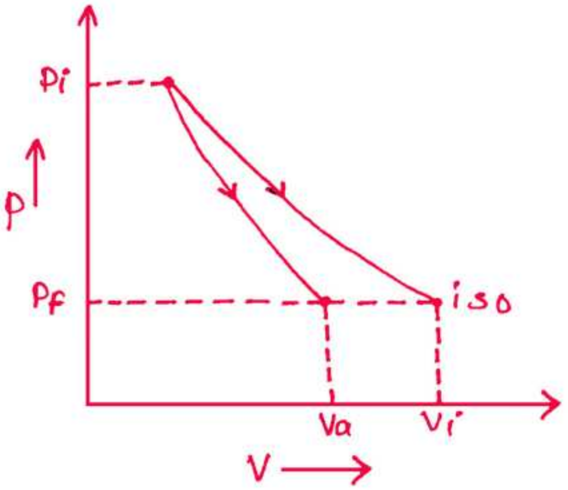
Case-I: for same final pressure.

Expansion:

As in isothermal process $\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow U =$ Constant.

But in adia. exp. wD is -ve, hence $\Delta U \downarrow$ so $T_f \downarrow$

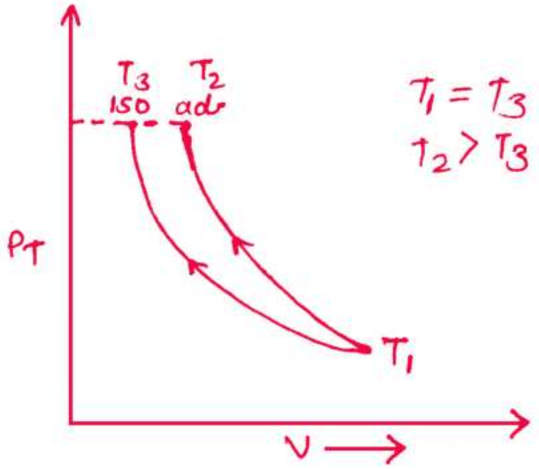
$\therefore V_f \downarrow$.



Compression:

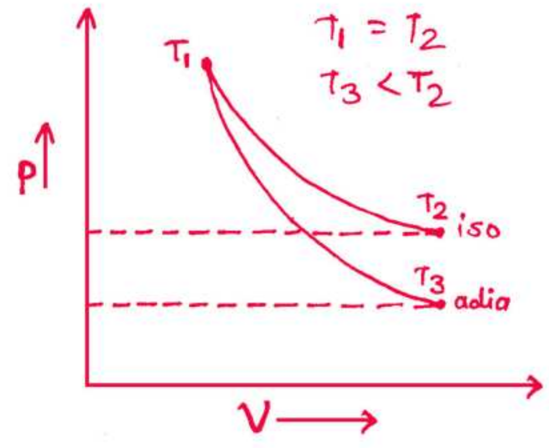
$V_{ad.} > V_{iso} \Rightarrow T_{ad.} > T_{iso}$. in case of compression, $w = +ve$ hence $\Delta V \uparrow$

$\therefore T_f \uparrow$ (adia.) where as in isothermal $T_i = T_f$

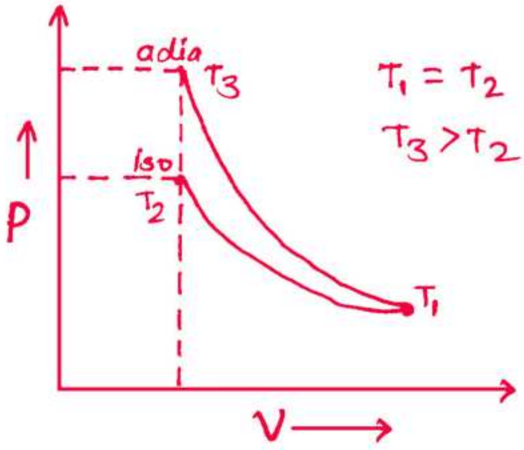


Case II : for same final volume

Expansion



Compression



* Limitation of FLT :-

1) FLT helps in determination of energy exchanges in terms of heat and work, but it does not tell anything about:

   a) feasibility of a process

   b) entent of a process

* SECOND LAW OF THERMODYNAMICS :

According to it is impossible to build a cyclic machine operating between two temperature which can convert 100% heat given to it at high temperature into work without liberating some amount of heat at low temperature.

OR

There is a natural asymmetry between heat & work. 100% work can be converted to heat but 100% heat can not be converted to work cyclically.

- Engine is best example of cyclic processs. So now we will consider cannot engine based on carnot cycle.

* Carnot cycle:-

It consists of 4 reverssible processs, out of which two are reverssible isothermal (C & E) & two are reverssible adiabatic (C & E).

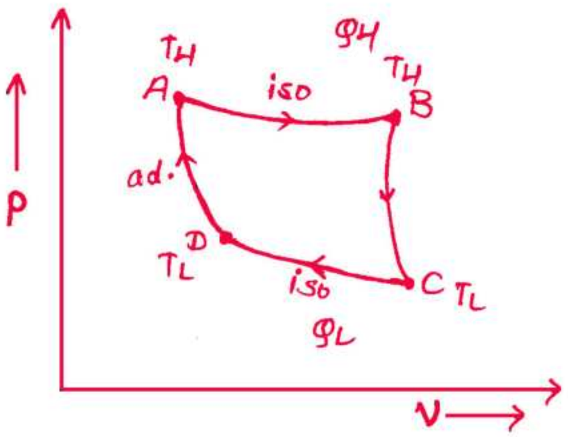
$$\eta = \frac{\text{work done}}{\text{heat supplied}} = \frac{-w}{q_H} = \frac{|w|}{q_H} = \frac{q_H + q_L}{q_H}$$

where,

q_H = Heat supplied to system
q_L = Heat rejected at sink
w = work done per cycle.

- Rfficiency of carnot cycle is independent of working substance.

But we will consider ideal gas as working substance



for isothermal exp. (AB) :

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

$$Q_H = -w$$

$$= nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$w_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

for adiabatic exp. (BC) :

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

$$w_{BC} = nC_{v,m}(T_L - T_H)$$

for isothermal comp. (CD) :

$$Q_L = -w = -(-nRT_L \ln\left(\frac{V_D}{V_C}\right)$$

for adiabatic comp. (DA) :

$$w_{DA} = \Delta U = nC_{v,m}(T_H - T_L)$$

$$\eta = \frac{Q_H + Q_L}{Q_H} = 1 + \frac{Q_L}{Q_H} = 1 + \frac{T_L \ln V_D/V_C}{T_H \ln V_B/V_A}$$

for BC

$$\frac{T_B}{T_C} = \frac{T_U}{T_L} = \left(\frac{V_C}{V_B}\right)^{\gamma-1} \text{——} ①$$

for DA

$$\frac{T_A}{T_D} = \frac{T_H}{T_L} = \left(\frac{V_D}{V_A}\right)^{\gamma-1} \text{——} ②$$

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} = \frac{V_D}{V_C} = \frac{V_A}{V_B}$$

$$\boxed{\eta_{carnot} = 1 - \frac{T_L}{T_H}}$$ for ideal gas & carnot cycle

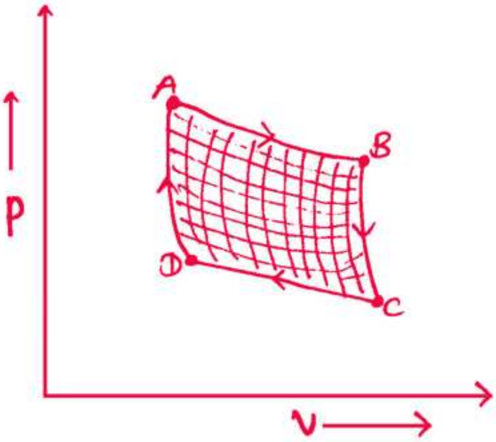
In order to have 100% efficiency either T_L should be 0K or $T_H \rightarrow \infty$ & practically both conditions are impossible so we can say 100% efficiency is not possible, in case of carnot cycle.

* For reversible cycle process:

$$1 - \frac{T_L}{T_H} = 1 + \frac{Q_L}{Q_H}$$

$$\Rightarrow -\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

$$\frac{(Q_L)_{rev}}{T_L} + \frac{(Q_H)_{rev}}{T_H} = 0$$



If cycle divided into n parts

$$\oint \frac{dq_{rev}}{T} = 0$$

$$\oint ds = 0$$

ds ⟶ Entropy

$$ds = \frac{dq_{rev}}{T}$$

- **for irreversible cyclic process:**

$$(\eta_{rev}) > (\eta_{irr})$$

$$1 - \frac{T_L}{T_H} > 1 + \frac{(Q_L)_{irr}}{(Q_H)_{irr}}$$

$$\Rightarrow \frac{(Q_L)_{irr}}{T_L} + \frac{(Q_H)_{irr}}{T_H} < 0$$

for n steps

$$\oint \frac{dq_{irr}}{T} < 0$$

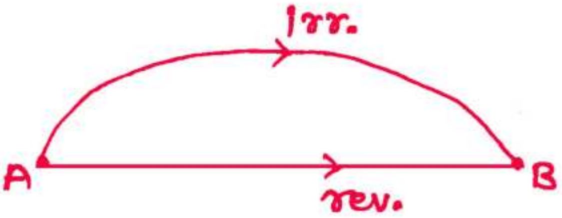
In general

$$\oint \frac{dq}{T} \leq 0$$

* Claussius Inequality:

- **Non cyclic process:**

Suppose we can move from A to B by two paths one is reversible & another is irreversible.



$$dU_{rev} = dq_{rev.} + dw_{rev.} \text{ ——— } ①$$

$$dU_{irr} = dq_{irr} + dw_{irr} \text{ ——— } ⑪$$

$\because$ U is a state function,

$$dq_{rev.} + dw_{rev.} = dq_{irr} + dw_{irr}$$

$$\Rightarrow dq_{rev} - dq_{irr} = -P_{ext}\,dV + P_g\,dV$$

$[\because$ for rev. $P_{ext} = P_g]$

$$\Rightarrow dq_{rev} - dq_{irr} = (P_g - P_{ext})\,dV$$

Case I : If $P_{ext} > P_{gas} \Rightarrow$ Compression

$$dq_{reve} - dq_{irr} = \frac{(P_g - P_{ext})}{P_g}\,\frac{dV}{P_{ext.}}$$

$$dq_{rev} - dq_{irr} > 0$$

Case II : if $P_g > P_{ext} \Rightarrow$ Expension

$$dq_{rev} - dq_{irr} > 0$$

$$Tds > dq_{irr}$$

$$\boxed{ds > \frac{dq_{irr}}{T}} \longrightarrow \text{non cyclic}$$

In general, $ds \geqslant \frac{dq}{T}$

If system is isolated

$$dq = 0$$

$$ds > 0$$

* Introduction to entropy :-

$$ds = \frac{dq_{rev}}{T}$$

$$\int ds = \int \frac{dq_{rev}}{T}$$

$$\Delta S = \int \frac{dq_{rev}}{T} \quad JK^{-1}$$

$S \rightarrow$ state function

• Calculation of ΔS :

Case I: for rev. wating/cooling of solids/liquids

$$ds = dq_{rev}$$

$$\int ds = n \int C_m \frac{dT}{T}$$

If C_m is independent of temperature

$$\boxed{\Delta S = n C_m \ln \frac{T_2}{T_1}}$$

Case II: In case of real gas undergoing isobaric rever process

$$dS = \left(\frac{dq_{rev}}{T}\right)_P = n C_{P,m} \frac{dT}{T}$$

$$\boxed{\Delta S = n C_{P,m} \ln \frac{T_2}{T_1}}$$

Case III: In case of real gas undergoing isochoric rev. process

$$dS = \left(\frac{dq_{rev}}{T}\right)_V = n C_{v,m} \frac{dT}{T}$$

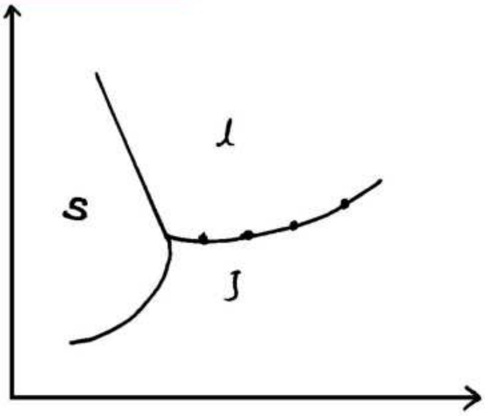
$$\boxed{\Delta S = n C_{v,m} \ln \frac{T_2}{T_1}}$$

Case IV: If phase transformation occurs at BP, MP or sublimation point, then process is considered as rev.

$$A(l) \longrightarrow A(g) \qquad \Delta_{vap} H = q_{(rev)P}$$

$$\Delta S_{vap} = \frac{q_{rev}}{T} = \frac{\Delta H_{vap}}{T_{BP}}$$

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_{mp}}$$



Case V: for an ideal gas undergoing any process

$$\Delta S = \int \frac{dq_{rev}}{T}$$

$$\Rightarrow \Delta S = \int \frac{dU - dw}{T} = \int \frac{n C_{v,m} dT}{T} - \int \frac{P dV}{T}$$

$$= n C_{v,m} \ln \frac{T_2}{T_1} \rightarrow nR \ln \frac{V_2}{V_1}$$

$$\Delta S = n C_{v,m} \ln\left(\frac{P_2 V_2}{P_1 V_1}\right) + nR \ln \frac{V_2}{V_1}$$

$$\boxed{\Delta S = n\, C_{v,m} \ln\left(\frac{T_2}{T_1}\right) + nR \ln \frac{P_1}{P_2}}$$

for isobaric

$$\Delta S = n\, C_{v,m} \ln\left(\frac{T_2}{T_1}\right)$$

for isochoric

$$\Delta S = n C_{v,m} \ln \frac{T_2}{T_1}$$

for isothermal

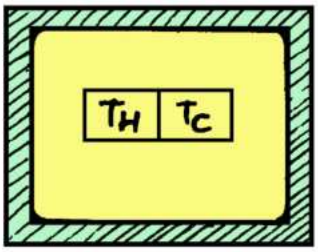
$$\Delta S = nR \ln \frac{V_2}{V_1}$$

* Using entropy to find out direction :-

Suppose we have taken an adiabatic rigid vessel & inside it we have taken two rods at different temperature.

Where,

T_H & T_C → temp. of hot & cold rods respec.



$Q_H \cdot Q_C$ → Heat exchanged by hot & cold rod resp.

$$Q_H + Q_C = 0$$

$$\Delta S_T = \Delta S_H + \Delta S_C$$

$$\Delta S_T = \frac{-Q_C}{T_H} + \frac{Q_C}{T_C}$$

$$\Delta S_T = Q_C \left(\frac{T_H - T_C}{T_H T_C}\right)$$

Case I :- if heat flows from cold to hot rod.

$$\Delta S = Q_c \left(\frac{T_H - T_c}{T_H T_c} \right)$$

$$\underbrace{\ominus \qquad \oplus}_{\ominus}$$

$$\Delta S_T < 0 \quad \Rightarrow \quad S_f < S_i$$

Case II: If heat flows from hot to cold

$$\Delta S_T = Q_c \left(\frac{T_H - T_c}{T_H T_c} \right)$$

$$\Delta S > 0$$

$$\Rightarrow S_f > S_i$$

for an isolated system,

if $\Delta S > 0 \Rightarrow$ Process is spontaneous

if $\Delta S < 0 \Rightarrow$ Process is non-spontaneous

if $\Delta S = 0 \Rightarrow$ Process is rev. or at equilibrium

Conclusion:

In an isolated system increase in entropy represents direction of natural change.

Generally we deal with closed system and not with isolated because system interack with surrounding.

System + Surrounding = Universe

$$\Delta S_{Uni/Total} = \Delta S_{sys} + \Delta S_{surr.}$$

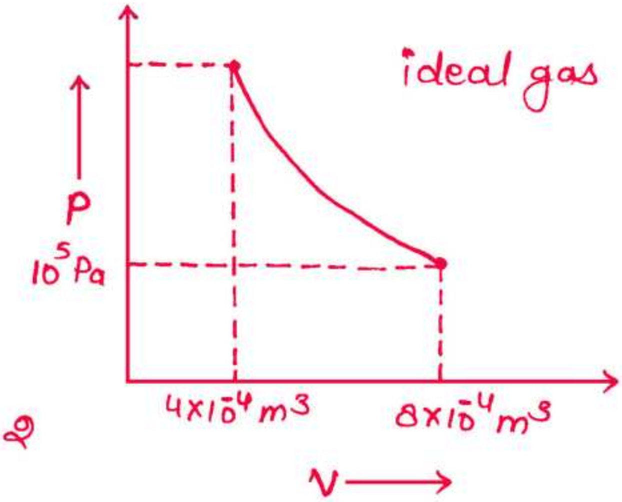
if $\Delta S_{Total} > 0$ = Process is spontaneous

$\Delta S_{Total} < 0$ = Process is non-spontawous

$\Delta S_{Total} = 0$ = Process is reversible or at equilibrium

All natural process are spontaneous and irreversible it means entropy of universe is increasing continuously from about points. it is clear that entropy of universe can be created but it cannot be destroyed while energy can neither be created not be destroyed.

Q. for an isothermal process at 300K calculate ΔS
(i) if process is reversible
(ii) if process is irreversible



→ $P_1 = 10^5 \times 2$ Pa ; $V_1 = 4\times10^{-4}$ m^3

$P_2 = 10^5$ Pa ; $V_2 = 8\times10^{-4}$ m^3

(i) $\Delta S = nR\ln\frac{V_2}{V_1} = \frac{80}{300}\ln 2$

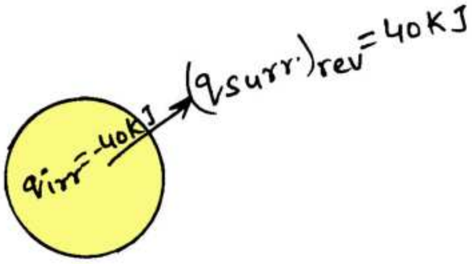
(ii) $\Delta S = -nR\ln\frac{P_2}{P_1} = \frac{80}{300}\ln 2$

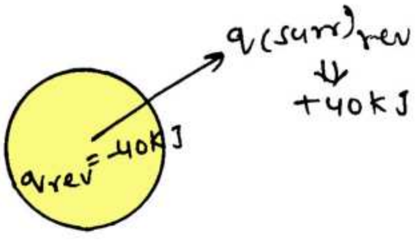
In irreversible isothermal process, heal exchange will be irreversible & we know that $\Delta S \neq \frac{q_{irr}}{T}$.

In such a scenario we will connect initial state to final state through a reversible path & calculate ΔS for that. In irreversible we will use q_{rev} for path we have assured so q_{rev} is not actual heat exchange.

• Calculation of $\Delta S_{surr.}$:

Surrounding is always considered as infinitely large and exch. between system & surrounding cannot change pressure & temp. of surr. as a result P&T of surrounding will remain constant.





$$\boxed{\Delta S_{surr.} = \frac{q_{surr.}}{T} = \frac{-q_{sys}}{T}}$$

Note: Sometimes if temperature of surrounding is not mentioned then we have to take final temp. of system as temp. of surrounding.

• Calculation of ΔS for various processes:

Isothermal

Reversible

$\Delta S_T = \Delta S + \Delta S_S$

$\Delta S_T = 0$

$\Delta S = nR \ln V_2/V_1$

$\Delta S = -\Delta S_S$

Irreversible

$\Delta S_T = \Delta S + \Delta S_S$

$\Delta S = nR \ln V_2/V_1$

$\Delta S_S = -\dfrac{P_{ext}(V_2 - V_1)}{T}$

Free- Expansion

It will also be adiabatic

$\Delta S_S = 0$

$\Delta S_T = \Delta S = nR \ln V_2/V_1$

Adiabatic

Reversible

$\Delta S_T = \Delta S + \Delta S_S$

$\Delta S_S = 0$

$\Delta S_T = 0$

$\Delta S = 0$

Irreversible

$\Delta S_S = 0$

$\Delta S = nC_{v,m} \ln \dfrac{T_2}{T_1} + nR \ln V_2/V_1$

Free- Expansion

$\Delta S_S = 0$

$\Delta S = nR \ln V_2/V_1$

Isochoric

Reversible

$\Delta S_T = 0$

$\Delta S + \Delta S_{surr} = 0$

$\Delta S = nC_{v,m} \ln \dfrac{T_2}{T_1}$

Irreversible

$\Delta S = nC_{v,m} \ln T_2/T_1$

$\Delta S_S = -\dfrac{nC_{v,m}\,\Delta T}{T}$

$\Delta S_T = \Delta S + \Delta S_{surr}$

Isobaric

$\Delta S_T = 0$

$-\Delta S = \Delta S_{surr}$

$= -nC_{p,m}\ln\frac{T_2}{T_1}$

$\Delta S = nC_{p,m}\ln\frac{T_2}{T_1}$

$\Delta S_{surr.} = -\frac{[nC_{v,m}\Delta T - P\Delta V]}{T}$

$= -\frac{nC_{p,m}\Delta T}{T}$

×

* Physical significance of entropy :

- It represents extent of randomness.

$$S_g >> S_l > S_s$$

- On ↑ temperature, randumness will increase

-

Sr. No.	Processs	ΔS
1	Sublimation	+ve
2.	Vaporisation	+ve
3	Melting	+ve
4	Melting of ice	+ve
5	Boiling of egg	+ve

- During chemical reaction.

$$aA_{(g)} + bB_{(g)} \longrightarrow cC_{(g)}$$

$$\Delta n_g = c - a - b$$

if

$\Delta n_g > 0 \Rightarrow \Delta S = +ve \Rightarrow$ entropy will ↑

$\Delta n_g < 0 \Rightarrow \Delta S = -ve \Rightarrow$ entropy will ↓

$\Delta n_g = 0 \Rightarrow \Delta S$ can be +ve or −ve.

- As atomicity ↑, randomness or entropy ↑ as molecule becomes complex.

$He < H_2 < CO_2 < NH_3 < CH_4 < N_2H_4 < C_2H_6$

- If atomicity is same then entropy ↑ with molar mass.

$S_{O_2} > S_{N_2}$

$S_{N_2} > S_{H_2}$

$S_{(2 mol\ O)} > S_{(1 mol\ O_2)}$

$S_{(graphite)} > S_{(diamond)}$

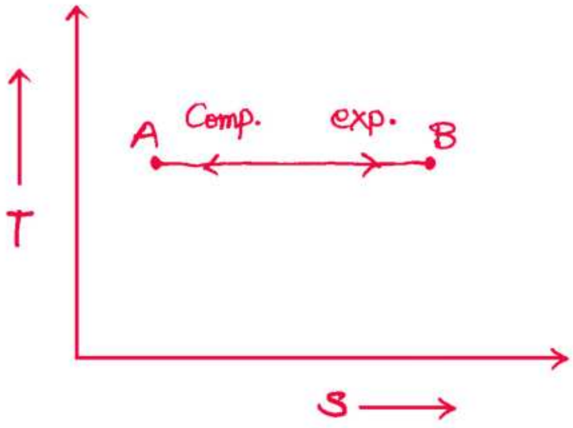
$S_{(p-red)} < S_{(p-white)}$

* T- S diagram :-

1) For reversible isothermal process.

$$dS = \frac{dq_{rev}}{T}$$

$$dq_{rev} = TdS$$



Area of T-S curve will give magnitude of heat exchanged during reversible isothermal process.

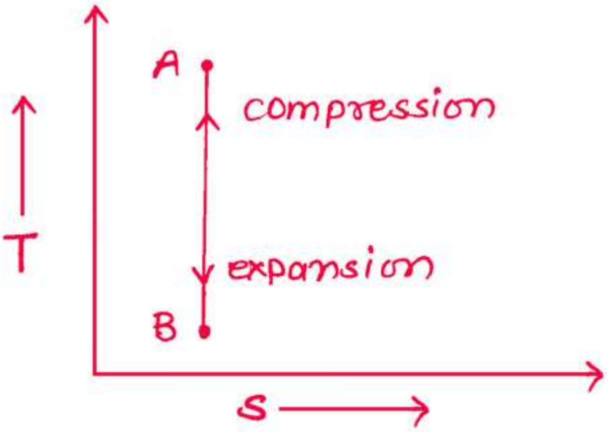
2) for reversible adiabatic process :

$$ds = \frac{dq_{rev}}{T}$$

for adiabatic process

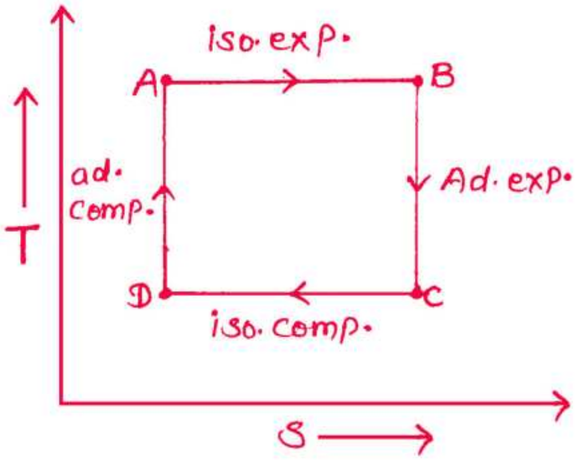
$$dq = 0$$

$$\therefore ds = 0$$



3) for carnot cycle :

Area of this diagram will give net heat exchanged or net work done during the cycle.



* Third law of thermodynamics :

According to it, entropy of substance at 0K will be zero.

It means at 0K every substance will be perfect crystal. But still there are certain substances which have some entropy even at 0K & that entropy is called residual entropy.

eg.,

CO & NO

CO CO CO CO CO
CO CO CO CO CO
CO CO $\boxed{OC}$ CO CO
CO CO CO CO CO

S_m (0K) $\neq 0$
∞

HCl

HCl HCl HCl HCl HCl
HCl HCl HCl HCl HCl
HCl HCl HCl HCl HCl
HCl HCl HCl HCl HCl

S_m (0K) $= 0$
∞

• Standard state :-

For gases
$P = 1$ bar
$T = T$ K

For solution (liquid)
Conc. = 1m
$T = T$ K

Pure solids or pure liquids are considered to be in their standard state.

Note: Sometimes at standard state, temperature is not gives & we need temperature for calculation then we will use $T = 298$ K

Standard enthalpy change = ΔH°

Standard entropy charge = ΔS°

• Application of third law of thermodynamics:

1) It is used to calculate absolute entropy of a substance.

$$\Delta S^\circ_{TK} = S^\circ_m(TK) - S^\circ_m(0K)$$

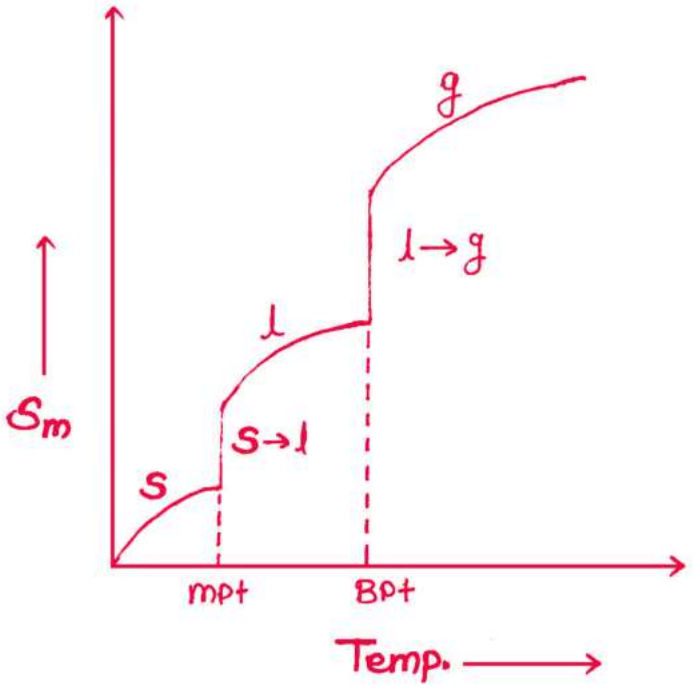
Suppose we want to calculate amt./absolute entropy of A(g) at TK.

$$\underset{(0K)}{A(s)} \xrightarrow{\Delta S_1} \underset{(mpt)}{A(s)} \xrightarrow{\Delta S_2} \underset{(mpt)}{A(l)} \longrightarrow \underset{(BPt)}{A(l)} \longrightarrow \underset{(BPt)}{A(g)} \longrightarrow \underset{(TK)}{A(g)}$$

for $n = 1$ mol

$$\Delta S^\circ_m = S^\circ_m(TK) - S^\circ_m(0K) = \int_0^{mpt} \frac{C_m dT}{T} + \frac{\Delta H}{T_{m.pt}} + \int_{mpt}^{Bpt} \frac{C_m dT}{T}$$

$$+ \frac{\Delta H_v}{T_{B.pt}} + C_{p,m} \ln \frac{T_2}{T}$$



Note: Absolute entropy of all substances will be positive above 0 K.

* Gibbs free energy (G):

- G is extensive qty. and state function.

Till now to predict spontanily we have to do calculation for system as will as surrounding. If we want to find out spontainity without doing any calculation for surrounding then we need a thermodynamics parameter for system which is G.

$$G = H - TS$$

for spontaincity

$$dS_{Total} \geq 0$$

$$dS_{sys} + dS_{surr.} \geq 0$$

$$dS_{sys} - \frac{dq_{sys.}}{T} \geq 0$$

At constant P & T

$$dS - \frac{dq_P}{T} \geq 0$$

$$dq_p = dH \quad (\text{when } W_{nonPV} = 0)$$

$$dS - \frac{dH}{T} \geq 0$$

$$TdS - dH \geq 0$$

$$d(H - TS) \leq 0 \Rightarrow (dG)_P \leq 0$$

$$dS_{Total} \geq 0$$

$$dS_{sys} - \frac{dq_{sys}}{T} \geq 0$$

At constant P & T

$$H = U + PV$$

$$dH = dU + PdV + Vdp$$

$$dH = dq_p + dW_{non\,PV}$$

$$dq_p = dH - dW_{non\,PV}$$

$$dS - \frac{dq_p}{T} \geq 0$$

$$dS - \left(\frac{dH - dW_{non\,PV}}{T}\right) > 0$$

$$(dG)_{P,T} \leq dW_{non\,PV}$$

if non PV work is zero

$$(dG)_{P,T} \leq 0$$

* Relationship between ΔS_{Total}, $\Delta G_{P,T}$ & temp. :

$$\Delta S_{Total} = \Delta S + \Delta S_{surr.}$$

$$\Delta S_{Total} = \Delta S - \frac{q_p}{T}$$

At constant P & T

$$\Delta S_{Total} = \Delta S - \frac{q_p}{T}$$

$$\Delta S_{Total} = \Delta S - \frac{\Delta H}{T}$$

$$T\Delta S_{Total} = -(\Delta H - T\Delta S)$$

$\therefore$ $\boxed{T\Delta S_T = -\Delta G_{P,T}}$ when

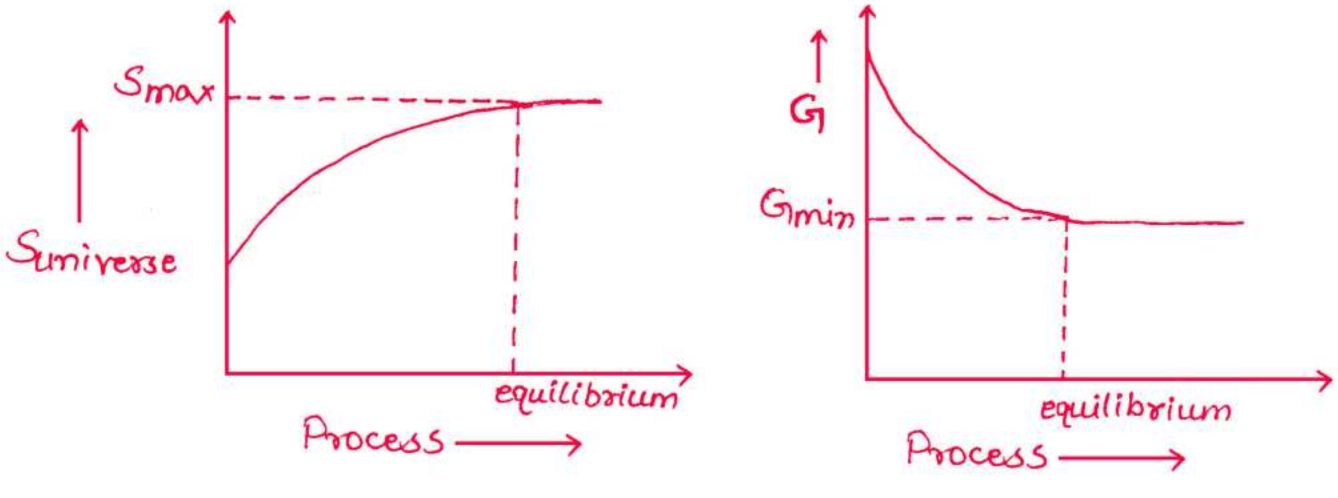
if $\Delta S_T > 0 \Rightarrow \Delta G_{P,T} < 0 \Rightarrow$ Processs is spontaneous

if $\Delta S_T < 0 \Rightarrow \Delta G_{P,T} > 0 \Rightarrow$ Processs is non spontaneous

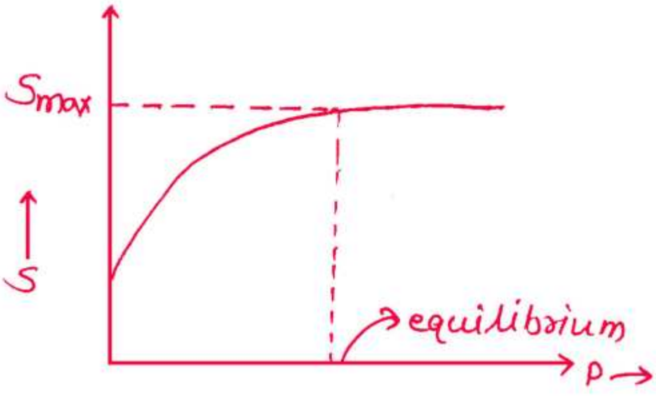
if $\Delta S_T = 0 \Rightarrow \Delta G_{P,T} = 0 \Rightarrow$ Processs is reversible or at equilibrium

Still ΔS_T is ultimate criterion of spontaineity & G is defined for system.

For closed system :



for isolated system :



* Predicting spontancity at constant P & T for chemical Rx^n :-

$$R \xrightarrow{P,T} P$$

$$\underset{\ominus}{\Delta G} = \underset{\ominus}{\Delta H} - T \underset{\oplus}{\Delta S}$$

There are two criterion for spontaneity

i) Tendency to have min. energy ($\Delta H < 0$)

ii) Tendency to have max. entropy ($\Delta S > 0$)

Sr. No.	ΔH	ΔS	ΔG	process
1	$\ominus$	$\oplus$	$\ominus$	Spontaneous
2	$\oplus$	$\ominus$	$\oplus$	non- spontaneous
3	$\oplus$	$\oplus$	$\ominus$	spontaneous at ↑T
4	$\oplus$	$\oplus$	$\oplus$	non-spontaneous at ↓T
5	$\ominus$	$\ominus$	$\oplus$	non-spontaneous at ↑T
6	$\ominus$	$\ominus$	$\ominus$	spontaneous at ↓ T

* Calculation of ΔG:

1) for Physical Process:

In physical processs, P & T cannot be constant simultaneously, As a result sign of ΔG will not predit anything about spontaneity.

$$G = H - TS$$

$$G = V + PV - TS$$

$$dG = dU + PdV + Vdp - Tds - SdT$$

$$dG = \cancel{dq} - P\cancel{dV} + P\cancel{dV} + Vdp - T\cancel{dS} - SdT$$

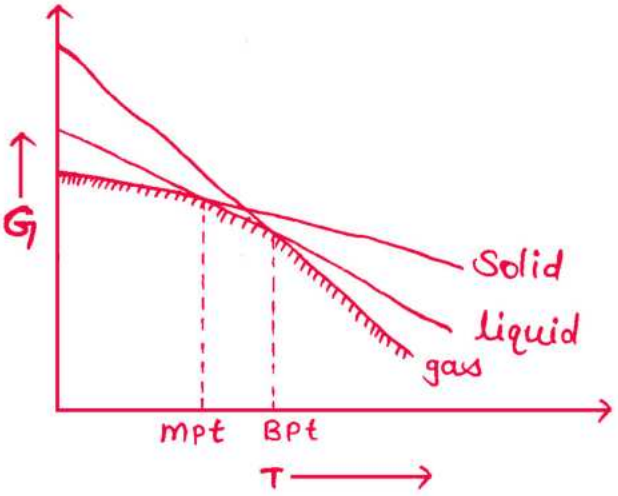
$$\boxed{dG = Vdp - SdT}$$ Applicable only for physical process.

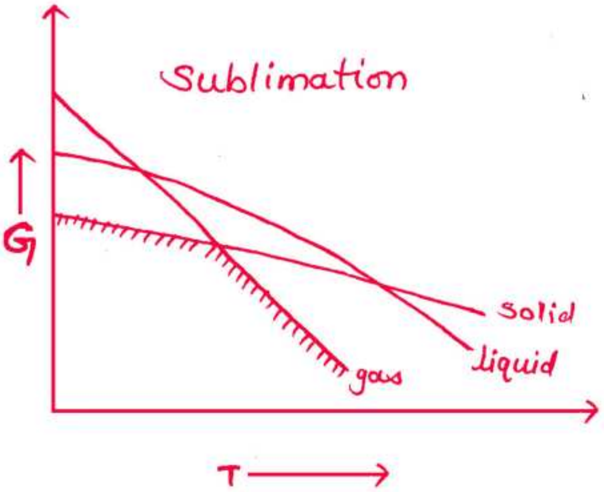
At low pressure, G of gas is lowest whereas at high pressure all substances except water tend to be in solid state which has lowest G.

Case II : Variation of G with T at constant pressure

$$dG = -SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_T = -S$$





At low temp. solid is more stable & at ↑ T, gas is more stable.

2) for chemical reaction :

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G_f^* \quad \Delta_f G^* \qquad \Delta_f G^* \quad \Delta_f G^*$$

$$\Delta_f H^* \quad \Delta_f H^* \qquad \Delta_f H^* \quad \Delta_f H^*$$

$$\Delta_{rxn} G^* = d\,\Delta G_f^*(D) + c\,\Delta_f G^*(C) - a\,\Delta_f G^*(A) - b\Delta_f G^*(B)$$

$$\Delta_{rxn} H^* = \Sigma(\nu_i \Delta_f H_i)_{product} - \Sigma(\nu_i \Delta_f H_i)_{reactants}$$

for any elements in their reference state, gibbs free energy of formation is taken as 0.

$$\Delta_f G^* (H_{2(g)}) = 0$$

$$\Delta_f G^* (O_{2(g)}) = 0$$

$$\Delta_f G^\circ (Co_{2(g)}) \neq 0$$

$$\Delta_f G^* (O_3(g)) \neq 0$$

$$\Delta_f G^* (C_{(graphic)}) = 0$$

(a) Variation of $\Delta_{rxn} H^\circ$ with temperature :

$$aA + bB \xrightarrow{T_1, P} cC + dD \qquad \Delta_{rxn} H^0$$

$$aA + bB \xrightarrow{T_2\, P} cC + dD \qquad \Delta_{rxn} H_2^\circ$$

$$dH = n C_{P,m}\, dT$$

for 1 mol of rxn.

$$\int_{\Delta H_{T_1}}^{\Delta H_{T_2}} d(\Delta H) = \int_{T_1}^{T_2} \Delta_{rxn} C_p \, dT$$

$$\boxed{\Delta H_{T_2} = \Delta H_{T_1} + \Delta_{rxn} C_p (T_2 - T_1)}$$

↳ Kirchoff eqn.

Similarly,

$$\Delta U_{T_2} = \Delta U_{T_1} + \Delta_{rxn} C_p (T_2 - T_1)$$

b) Variation of ΔG° with temperature:

$$aA + bB \xrightarrow{T_1 P} cC + dD \quad \Delta G^\circ T_1$$

$$aA + bB \xrightarrow{T_2 P} cC + dD \quad \Delta G^\circ T_2$$

$$\boxed{\Delta G^\circ_{T_2} = \Delta H^\circ_{T_2} - T_2 \Delta S^\circ_{T_2}}$$

where,

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta_{rxn} C_p (T_2 - T_1)$$

$$\Delta S_{T_2} = \Delta S_{T_1} + \Delta_{rxn} C_p \ln \frac{T_2}{T_1}$$

* Relationship between G, ΔrxnG° & Keq :

$$dG = Vdp - SdT$$

At constant temp.

$$dG = Vdp$$

$$dG = vdp$$

for 1 mol of an ideal gas

$$\int_{G^\circ}^{G} dG = 1 \times RT \int_{P=1bar}^{P\,bar} \frac{dP}{P}$$

$$\Rightarrow G - G^\circ = 1 \times RT \ln P$$

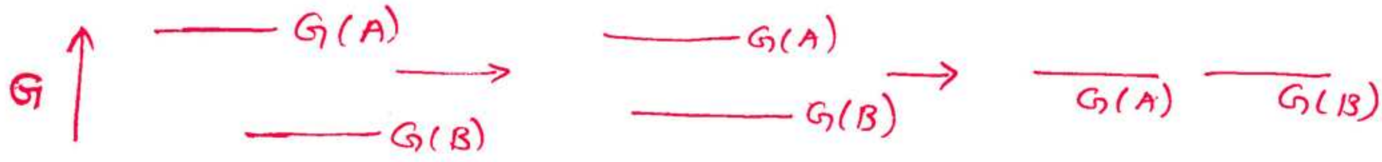
$$\therefore \boxed{G(A) = n\left(G^\circ(A) + RT \ln P\right)}$$

Suppose we take A at 1 bar (std. state)

$$\begin{array}{lcc} & A(g) \longrightarrow & B(g) \\ t = 0 & 1\,mol & 0 \\ t = t & 1-x & x \end{array}$$

$$G_A = \left(G_A^\circ + RT \ln P_A\right) n_A$$

$$G_B = \left(G_B^\circ + RT \ln P_B\right) n_B$$



$$\Delta_{ran} G = G_B - G_A$$

At equilibrium,

$$\Delta_{ran} G = 0 \Rightarrow G_A = G_B$$

$$G_A^\circ + \ln P_A (RT) = G_B^\circ + RT \ln P_B$$

$$\Rightarrow \boxed{\Delta_{ran} G^\circ = RT \ln K^\circ}$$

$$G_{system} = G_A + G_B$$

A process will move in a direction where it can ↓ or minimize gibbs free energy of a system (its).

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

$$\Delta G = 2G_{(NH_3)} - 3G_{(H_2)} - G_{(N_2)}$$

At eqⁿ,

$$\Delta_{rxn} G = 0 = 2G(NH_3) - 3G_{(H_2)} - G_{(N_2)}$$

$$2G_{(NH_3)} = 3G_{(H_2)} + G_{(N_2)}$$

eg. $aA + bB \longrightarrow cC + dD$

$$\Delta_{rxn} G = dG_{(D)} + cG_{(c)} - aG_{(A)} - bG_{(B)}$$

$$= d(G^\circ_{(D)} + RT \ln P_D) + c(G^\circ_{(c)} + RT \ln P_C) - a(G^\circ_{(A)} + RT \ln P_A) - b(G^\circ_{(B)} + RT \ln P_B)$$

$$\Delta_{rxn} G = \Delta_{rxn} G^* + RT \ln Q$$

At equilibrium,

$$\Delta_{rxn} G = 0 \quad \& \quad Q^\circ = K^*$$

$$\Delta_{rxn} G^* = -RT \ln K$$

$$\Delta G^* = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ - T\Delta S^\circ = -RT\ln K$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T}$$

Variation of K°_{eq} with temp.

we are assuming ΔH° & ΔS° as temp. independant.

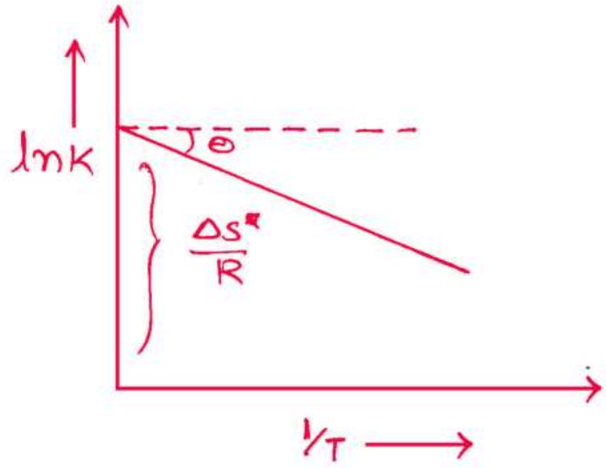
$$\ln K^\circ_{T_1} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T_1} \text{ ——— ①}$$

$$\ln K^\circ T_2 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T_2} \text{ ——— ②}$$

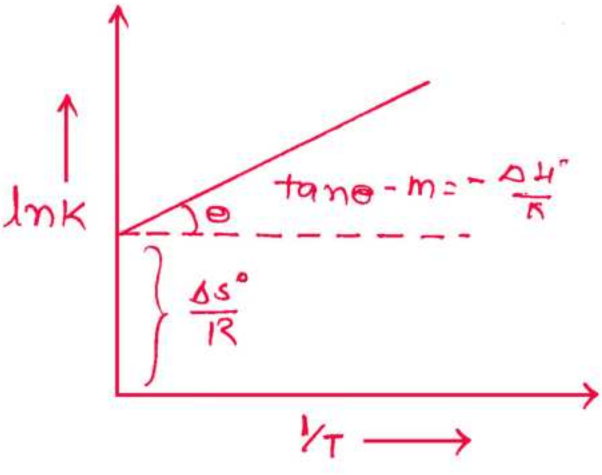
eqⁿ ② − ①

$$\ln \frac{K T_2}{K T_1} = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Endothermic



Exothamic



Q. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

$\Delta G^\circ = -482.5$ KJ/mol

find K at 300K·

$\rightarrow +482.5 \times 10^2 = +8.3 \times 300 \ln K$

$\frac{48250}{249} = \ln K \Rightarrow K = e^{194}$

for rxn,:

$R \longrightarrow P \qquad K_{eq} = 10^{-36}$

ΔG° (KJ/mol)	K°_{eq}	
+200	8.7×10^{-36}	non-spontaneous
+100	3×10^{-18}	
+50	1.7×10^{-9}	
+10	6.7×10^{-1}	
+1	0·95	
0	1	
−1	1·5	Spontaneous
−10	5.7×10^{1}	
−50	5.8×10^{8}	
−100	3.4×10^{17}	
−200	1.1×10^{35}	

✶ Physical Significance of gibbs free Energy(G) :-

- It is amount of energy which is available freely for doing non- PV work or useful work like electrical work or muscle work

$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6O_2(g) + 6H_2O(l)$

$\Delta H^\circ = -500$ kJ

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

$$\Rightarrow \Delta G^\circ = -300\,KJ$$

$$R \longrightarrow P \quad \Delta G^\circ = +300\,Kg$$

It means if 300 kj of non PV work is done then one mole of 'R' can be converted into 1 mol of P.

- **Photosynthessis Rx^n :-**

$$CO_{2(g)} + H_2O + \text{Photon} \longrightarrow (C_6H_{12}O_6)_{1/6} + O_{2(g)}$$

$$\Delta G^\circ = +480\,KJ$$

- Diamond ⟶ Graphite $\Delta G^\circ = -3\,kj/mol$

- $dW_{non\,PV} \geq dG_{P,T}$ if $\Delta G = -300\,KJ$
  $dW_{by\,non\,PV} \leq 300\,kj$

$$dW_{non\,pv} = -dW_{by\,non\,PV}$$

for rev.,
$dW_{by\,non\,pv} = 300\,kj$

$$dW_{by\,non\,pv} \geq dG_{P,T}$$

$$\boxed{dW_{by\,non\,pv} \leq -(dG)_{PT}}$$

for irrev.,
$dW_{non\,pv} < 300\,KJ$

Decrease in G at const. P & T will be equal to maximum non PV work that can be extracted from the system^{rl} rev. process.

• Driving non spontaneous Rx^n :-

Decomposition of Cu_2S to its elements is non spontaneous rx^n :-

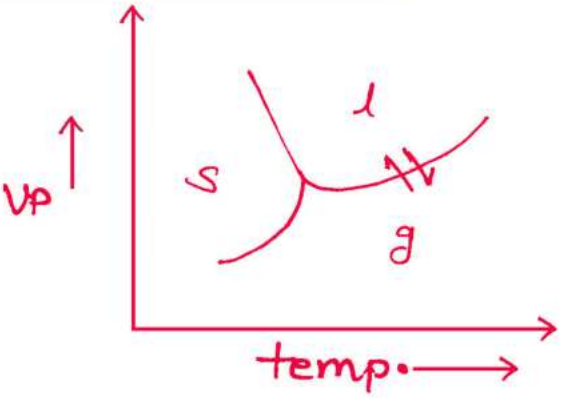
$$Cu_2S(s) \rightarrow 2Cu(s) + S(s)$$
$$\Delta G^\circ = +86.2\ KJ/mol$$

It means we cannot get pure copper directly but we can couple it with another rx^n :-

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$\Rightarrow Cu_2S(s) + O_2(g) \longrightarrow 2Cu(s) + 2(SO_2)g$$
$$\Delta G^\circ = -214.2\ KJ/mol$$

★ Clapeyron requation :-



$$A(l) \rightleftharpoons A(g) \qquad K = p = VP$$

At equilibrium,

$$G_A(l) = G_A(g)$$
$$dG_A(l) = dG_A(g)$$
$$N_l dp - S_l dT = V_g dp - S_g dT$$
$$(V_l - V_g)\ ap = (S_l - S_g)\ dT$$
$$\frac{dp}{dT} = \frac{S_g - S_l}{V_g - V_l} = \frac{\Delta S}{\Delta V}$$

$$\boxed{\frac{dP}{dt} = \frac{\Delta S}{\Delta V}}$$ Clapeyron eq.

$\Delta S = \frac{\Delta H}{T}$ during phase change

$$\frac{dP}{dt} = \frac{\Delta H}{T\Delta V}$$

if we take liquid gas eq.

$$\Delta H = \Delta vap.\ H$$

$$\frac{dP}{dt} = \frac{\Delta vap H P}{RT^2}$$

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{dT}{T^2} \cdot \frac{\Delta H}{R}$$

$$\Rightarrow \ln\frac{P_2}{P_1} = \frac{\Delta vap.\ H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

for normal B. Pt.

$$\ln\frac{P_2}{1} = \frac{\Delta vap.\ H}{R}\left[\frac{1}{T_t} - \frac{1}{T_2}\right]$$

- In case of water, Ga & Bi slope of S - l line is negative.
- Scope for solid - liquid line is very steap coz ΔV for solid - liquid is very small.

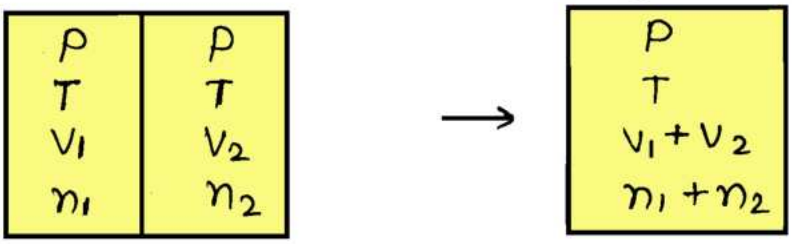
★ Trouton's Rule:-

$A_{(l)} \longrightarrow A_{(g)}$ $\Delta_{vap} S = \frac{\Delta vap H}{T_{Bpt}} = 10.5R$ or 88 J/mole.

According to it entropy of vapourisation (molar) of normal liquids at their B.Pt. is constant (10.5R or 88J)

- This rule is not applicable where H-bonding takes place like in water, ethanol etc.
- It is just an observation.

★ Entropy of mixing for ideal gases :-



Initially both gases have pressure P & on mixing final pressure also remains P.

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= + n_1 R \ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R \ln\left(\frac{V_1 + V_2}{V_2}\right)$$

$$\Delta_{rxn} S = - n_1 R \ln \frac{V_1}{V_1 + V_2} - n_2 R \ln \frac{V_2}{V_1 + V_2}$$

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{PV_1/RT}{\frac{PV_1}{RT} + \frac{PV_2}{RT}} = \frac{V_1}{V_1 + V_2}$$

$$\Delta_{rxn} S = -(n_1 + n_2) R \left[x_1 \ln x_1 + x_2 \ln x_2\right]$$

$$= - n_T R \left[x_1 \ln x_1 + x_2 \ln x_2\right]$$

↳ we can apply it for ideal sol.

Questions & Answers

1. Enthalpy is an extensive property. Suppose that $\Delta_r H$ is the enthalpy for the reaction $A \rightarrow B$. While enthalpies of other intermediate paths are $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$ etc. Then what is the relation among them?

→ According to Hess's law

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots$$

2. What is the primary requirement for fuel to be a good quality?

→ for a good quality of fuel, it should have high calorific value.

3. Why air of atmosphere becomes colder when it goes to upward?

→ In upper layer of atmosphere, the pressure is low. Hence, on moving upward the air expands in which air works by spending its internal energy. So its temperature decreases and it becomes colder.

4. When an ideal gas expands in vaccum then heat is neither released nor absorbed. Why?

→ In ideal gas, there is no intermolecular force. Hence, when volume of gas expands then neither energy is absorbed nor released.

5. Why $\Delta U = 0$ for isothermal expansion of ideal gas?

→ Since internal energy and change in internal energy are related to temperature. In isothermal process, the temperature remains constant. So, ΔU will be zero.

6. Identify the exothermic and endothermic reactions out of the following:
(i) Lighting of match box.
(ii) Melting of ice.
(iii) When melted metal becomes solid.
(iv) Reaction of potassium with water.
(v) Evaporation of either.

→(i) Lighting of match box - Exothermic
(ii) Melting of ice - Endothermic
(iii) When melted metal becomes solid - Exothermic
(iv) Reaction of potassium with water - Exothermic
(v) Evaporation of Ether - Endothermic.

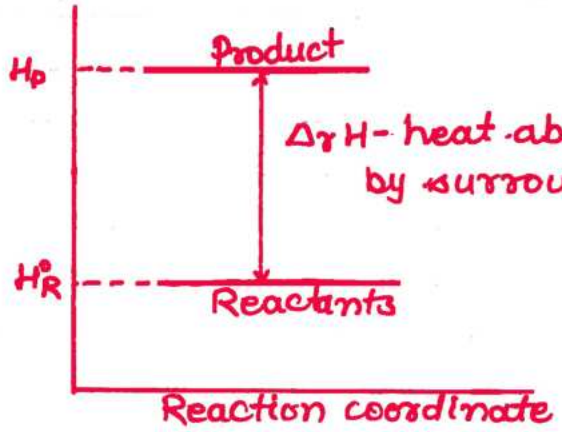
7. Why, increase in enthalpy of solid to liquid is less than Increase in enthalpy of liquid to gas?

→ Because. In gaseous state, the disorderness in molecule is more than liquid. So increase in entropy during solid → liquid is less than that of increase in enthalpy during liquid to gas.

8. Why temperature of gas increased on compression?

→ Because during compression work increases internal energy of molecules of gas. So temperature of gas is increased compression.

9. for a certain reaction, enthalpy graph is given as follow. It is possible to determine the spontaneity of reaction through this curve?



→ No, only enthalpy is not responsible for spontaneity of any reaction since this reaction is endothermic i.e., the value of energy is increasing. The other factors like entropy etc. are also considered for determining the spontaneity of reaction.

10. 5.0 mol of ideal gas is compressed reversibly upto its half of the volume at 25°C and 1 atm pressure. Calculate the work done and heat?

→ Given, $T = 25 + 273 = 298\ K$

$n = 5\ mol$

$R = 8.314 J K^{-1} mol^{-1}$

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

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

$= -2.303 \times 5 \times 8.314 \times 298 \times \log \frac{V_1/2}{V_1}$

$= 8587.3 J$

$w = 8.59 KJ$

∵ Process is isothermal so $\Delta U = 0$
from first law of thermodynamics,

$\Delta U = q + w$

$q = -w$

$q = -8.59 KJ$