# Thermal Physics - I

## Development of Kinetic Theory:

18th century

**Anonymous theory:** 1761 J. Black : observed same temperature for ice & water & conjectured about "latent" heat.

1797 J. Watt : converted heat → work as steam engine

1797 B. Thompson, C. Rumford : work → heat

**Caloric fluid theory:** 1783 A. Lavoisier : conjectured heat as invisible fluid.

1824 S. Carnot ; Carnot engine → Thermochemistry.

19th century

**Kinetic theory:**

1738 D. Bernoulli : molecular theory of fluid.

1847 J.P. Joule, J. von Mayer, H. von Helmholtz : heat & work equivalent form of energy.

1850 R. Clausius : (a) showed that "Caloric fluid theory" is reconciled in "kinetic theory"; (b) First law of Thermodynamics, (c) defined "entropy".

1854 Thomson or Lord Kelvin → Thermodynamics

**Experimental gas laws:**

1662 Boyle's law: $P \propto V^{-1}$

1802 Charle's law: $V \propto T$

1802 Gay-Lussac's law:

## International scale of temperature

Lord Kelvin introduced lowest temperature independent of property of substance

absolute zero −273°C or 0K

ice point 0°C or 273K

steam point 100°C or 373K

Sulphur point 444.6°C

Antimony point 630.5°C

Silver point 960.8°C

Gold point 1063.8°C

Human body temperature 98.4°F ⟺ 36.9°C (remember, least count is 0.1°C)

relation between C, F, R (Reumer scale)

$$\frac{C}{5} = \frac{F-32}{9} = \frac{R}{4}.$$

## Basics of Thermometry

a) Liquid Thermometer: Hg in glass, 6's max-min, Beckmann, Index

b) Gas Thermometer: Callendar's Air, Hydrogen

c) Metal Thermometer: Platinum resistance,

d) Thermoelectric Thermometer: thermocouple generates e.m.f. $e = at + bt^2$

e) Radiation Thermometer:

principle of thermometry: let A = thermometric property

For uniform variation of A with temperature T

$A_T = A_0(1+\alpha T)$, $A_0$ = value of A at 0°C

$A_{100}$ = value of A at 100°C.

$A_{100} = A_0(1+100\alpha)$

$$\therefore \boxed{T = 100\,\frac{A_T - A_0}{A_{100} - A_0}}$$

What is A? If you take simple Hg-in glass thermometer then A = length of Hg column. For Pt-resistance thermometer A = resistance R of Pt. For constant volume gas thermometer A = pressure of air.

## Hg in glass thermometer

pros (a) liquid range [−38.87°C, 356°C]

(b) low thermal capacity & high conductivity

(c) uniform expansion, (d) shining liquid (easy to see).

cons (a) high specific gravity (less sensitive)

(b) high surface tension (motion is jerkey)

unsuitable for low T.

## Alcohol thermometer

**pros** (a) liquid range [$-112^\circ C$, $78^\circ C$]
(b) high coefficient of expansion (more sensitive)
(c) low surface tension (motion is smooth)

**cons** unsuitable for high temperature.

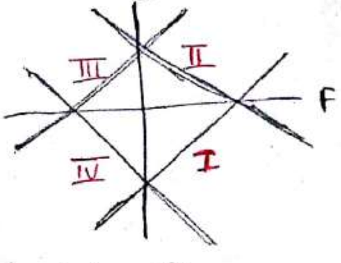
**Gas thermometer** (a) Very high coefficient of expansion (more sensitive)
(b) low thermal capacity, low specific gravity
(c) constant volume / constant pressure thermometer.

**Platinum Resistance thermometer** : Resistance smooth in range [$-200^\circ C$, $1200^\circ C$]
least count = $0.01^\circ C$ $R_t = R_0(1+\alpha T)$

| Low temperature Thermometry | High temperature thermometry |
|---|---|
| $0^\circ C$ to $630^\circ C$ → all | $630^\circ C$ to $1000^\circ C$ → liquid, gas, resistance, thermocouple. |
| $-20^\circ C$ to $0^\circ C$ → liquid, gas, resistance, thermocouple, vapour pressure. | $1000^\circ C$ to $1600^\circ C$ → gas, thermocouple. |
| $-272^\circ C$ to $-20^\circ C$ → resistance, vapour pressure, magnetic | $1600^\circ C$ to $3000^\circ C$ → thermocouple, pyrometer. |
| below $-272^\circ C$ → magnetic | |

**HW** 1. At what temperature do the Fahrenheit & celsius scale give the same reading?

2. In figure beside, which line represents $\frac{C}{5} = \frac{F-32}{9}$ ?



3. In a constant volume gas thermometer, pressure of air at $0^\circ C$ is 80 cm & at $100^\circ C$ is 109.3 cm. Calculate the temperature of a hot bath, in which when the thermometer is immersed shows a pressure 100 cm.

**Calorimetry** Definition of Calorie (heat) ⇒ quantity of heat needed to raise temperature of 1 gm of water by 1°c. But heat 5°c → 6°c ≠ 80°c → 81°c.

# Mean calorie heat [0°c → 100°c]/100.

# 15°c Calorie heat 14.5°c → 15.5°c

**B. Th. U.** quantity of heat needed to raise temperature of 1 lb of water by 1°F.

1 B. Th. U. = 252 cals

1. C. H. U. = 453.6 cals.
(centrigrad heat unit)

$$\underset{\text{heat}}{\underset{\downarrow}{H}} = \underset{\substack{\text{mass}\\ \text{of substance}}}{\underset{\downarrow}{m}} \;\; \underset{\substack{\searrow\\ \text{specific}\\ \text{heat}}}{s} \;\; \overset{\substack{\text{temperature}\\ \nearrow}}{T} = \underset{\substack{\text{thermal}\\ \text{capacity}}}{\underset{\downarrow}{c}}\, T$$

**Basic principle of Calorimetry** conservation of heat energy or sum total of (body + heat bath) is conserved.

Specific heat of solid: Method of mixture, Copper block calorimeter, Electrical method (Lindemann calorimeter), Latent heat (Bunsen ice calorimeter).

Specific heat of liquid: Method of mixture, Bunsen ice calorimeter, Method of cooling, Nernst calorimeter, continuous flow calorimeter.

Specific heat of gas: # why constant pressure or volume?

$c = \frac{dQ}{dT}$ → suppose system expands → temperature falls to prevent, dQ heat added, so $dT = 0$.

$c = \frac{dQ}{0} \rightarrow \infty$

→ suppose system compresses → temperature rise dT without the need of dQ ∴ $dQ = 0$

$c = \frac{0}{dT} = 0$.

$\therefore \quad c_p = \left(\frac{dQ}{dT}\right)_p , \quad c_v = \left(\frac{dQ}{dT}\right)_v$

definition: at P = constant, increase temperature of 1 gm of gas through 1°. If 1 gm molecule of gas is taken → molar specific heat. $C_p = Mc_p$

$C_p > C_v$? # heat transfer at V = constant, $dV = 0$. $dW = PdV = 0$
no work done by the gas.
So heat supplied transformed to thermal energy

$C_p - C_v = \frac{R}{J}$ (heat unit)

# heat transfer at P = constant, $dW = PdV \neq 0$.
So heat supplied → thermal energy + external work.

$\boxed{C_p - C_v = R}$

Isothermal transformation : T = constant $\boxed{PV = RT = \text{constant}}$

Adiabatic transformation : Q = constant, $dQ = C_v dT + PdV$ — ①

Now from PV = RT, $PdV + VdP = RdT = (C_p - C_v)dT$

put dT in ① : $dQ = C_v \frac{PdV + VdP}{C_p - C_v} + PdV = 0$ (as Q = constant)

$$\therefore \quad C_v VdP + C_p PdV = 0$$

or $\frac{C_p}{C_v}\frac{dV}{V} = -\frac{dP}{P}$, (put $\gamma = \frac{C_p}{C_v}$)

Integrating both sides, $\gamma \ln V = -\ln P + \ln C$.

$$\boxed{PV^{\gamma} = \text{Constant}}$$

**Corollary:** PT relation : put PV = RT, $P\left(\frac{RT}{P}\right)^{\gamma} = C \Rightarrow P^{1-\gamma}T^{\gamma} = \text{constan}$

VT relation: put PV = RT, $\frac{RT}{V}V^{\gamma} = C \Rightarrow V^{\gamma-1}T = \text{constant}$

**CW** Suppose dry air is enclosed in a cylinder fitted with piston. Initial temperature of air is 30°C. Find the change in temperature if the gas is compressed (a) slowly, (b) suddenly to one-half of its volume? What'll be the pressure?

(a) piston moves inwards → gas compresses

↓

no change in temperature (isothermal) ← heat goes to surrounding by conducting wall slowly ← temperature rises

$T = \underline{30°C}$

(b) Temperature rise rate >>> heat diffusion rate to surrounding

adiabatic process → no Q transfer.

So $P_1V_1^{\gamma} = P_2V_2^{\gamma}$ & given $V_2 = \frac{V_1}{2}$

$\therefore P_2 = 2^{\gamma}P_1 = 2^{1.4}P_1 = 2.6P_1 = \underline{2.6 \text{ atm}}$ when $P_1 = \underline{1 \text{ atm}}$.

compare with isothermal, $P_2 = 2P_1 = \underline{2 \text{ atm}}$.

Again from TV relation, $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$\therefore T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 2^{0.4}T_1 = 1.319 \times (273+30)K$

$= 399.7K = (399.7-273)°C = \underline{127°C}.$

HW 4. Air in a Wilson's cloud chamber at 20°C is abruptly expanded to 1.4 times its initial volume. Calculate the final temperature. Given $\gamma = 1.4$.

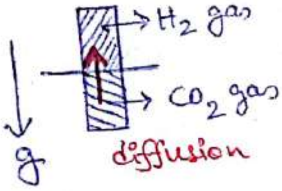
5. At $10^6$ dynes/cm$^2$ pressure, a gas ($\gamma = 1.4$) expands isothermally until its volume is double of the initial volume. Then it adiabatically expands until its volume is redoubled. Calculate the final pressure of the gas.

# Kinetic Theory of Gases (K.T.)

Rule of thumb: Every material (solid, liquid, gas, plasma, intermedial phases) are made of atoms. Them "may" attract or repel & form molecules of liquid or be restricted in definite shape of solid by huge cohesive force.

## Experimental hints in favour of K.T.

1. Diffusion and Solution:



, when slowly poured Alcohol over water, it spreads throughout.

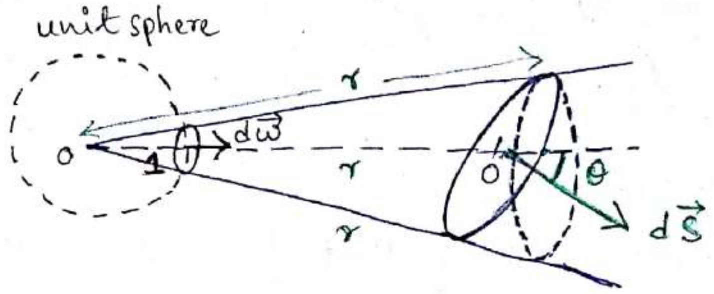
2. Expansion of substance with heat: atoms tend to move away.
3. Phenomena of evaporation & vapour pressure.
4. Brownian motion. 1827 R. Brown → incessant motion of polens on water.

## Basic assumptions & postulates of K.T.

1. A gas consists of large number of identical atoms, which are rigid, elastic & equal mass objects.
2. Atoms are in chaos → motion is fully irregular & spans in all three directions.
3. Inevitably the gas molecules collide with each other & surface of container (wall, sphere, cylinder). Total K.E. remains constant, but velocity of each atom continuously changes both in magnitude & direction. In evolving state (intermediate) density in a volume element will change but in steady state, collisions do not affect the density.
4. In between two successive collisions, molecules move in straight line following Newton's law.
5. Collisions are perfectly elastic i.e. no force of attraction/ repulsion (P.E. = 0), energy is fully kinetic.

6. Atoms are "point" mass, meaning, their total volume <<<< volume of the container.

## Concept of solid angle



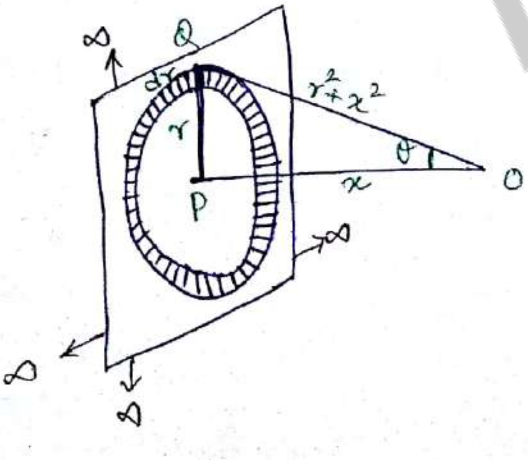
Solid angle subtended by an area at a point is defined as the area intercepted by the cone on a unit sphere (radius = 1) with its centre at the apex of the cone.

If dS is an area that makes a solid angle dω at origin O at a distance OO' = r, then from similar figures

$$\frac{d\omega}{1^2} = \frac{dS\cos\theta}{r^2} \quad \therefore \; d\omega = \frac{dS\cos\theta}{r^2}$$

unit of solid angle = steradian.

CW 1. Calculate the solid angle (a) subtended by an infinite plain at a point in front of it, (b) hemisphere and (c) full sphere at its center.



Consider the annular ring, r distance apart from P & thick dr.

Area of this ring $= \pi(r+dr)^2 - \pi r^2$

$= 2\pi r\,dr$

(N.B. we throw $O(dr^2)$ term in limit $dr \to 0$)

So solid angle subtended by that circular annulus

$$d\omega = \frac{dS\cos\theta}{OQ^2} = \frac{2\pi r\,dr\cos\theta}{r^2+x^2}$$

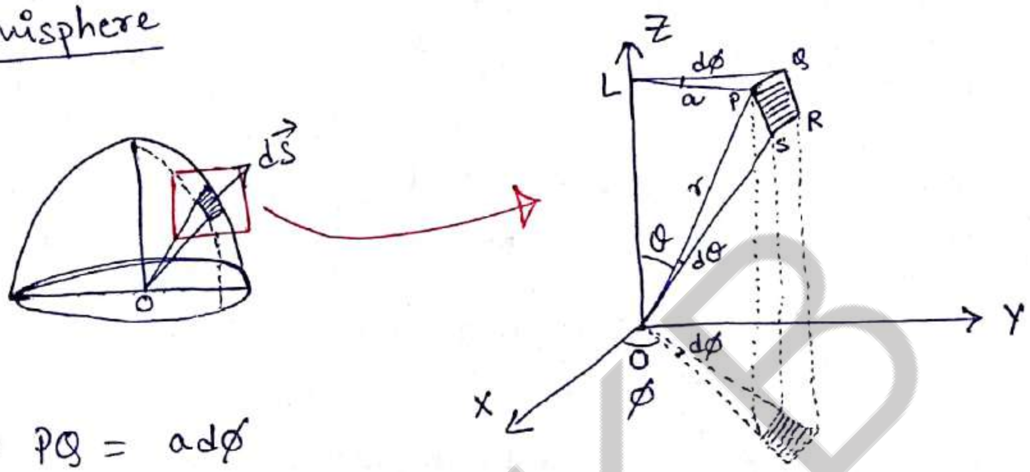
Infinite plain meaning θ going from 0 to π/2.

$$\therefore\ \omega = \int_{\theta=0}^{\pi/2} \frac{2\pi r\,dr\cos\theta}{r^2+x^2} \qquad \left[\begin{aligned} &r = x\tan\theta \\ &dr = x\sec^2\theta\,d\theta \\ &\&\ x^2+r^2 = x^2\sec^2\theta \end{aligned}\right]$$

$$= 2\pi\int_{\theta=0}^{\pi/2} \frac{x\tan\theta\; x\sec^2\theta\,d\theta\,\cos\theta}{x^2\sec^2\theta}$$

$$= 2\pi\int_0^{\pi/2}\sin\theta\,d\theta = \underline{2\pi}.$$

Hemisphere



LP = a
OP = r

$$\frac{a}{r} = \sin\theta$$

& PQ = a dφ

PS = r dθ

$$\therefore dS = \text{area } PQRS = a\,d\phi \times r\,d\theta = r^2\sin\theta\,d\theta\,d\phi.$$

$$\text{So } d\omega \text{ at point O} = \frac{r^2\sin\theta\,d\theta\,d\phi}{r^2}\times\cos 0 = \sin\theta\,d\theta\,d\phi.$$

$$\text{So solid angle subtended} = \int d\omega = \int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi}\sin\theta\,d\theta\,d\phi = \underline{2\pi}.$$

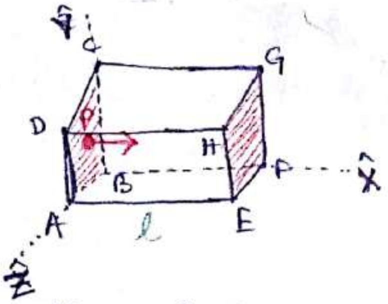
Full sphere

$$\text{solid angle subtended} = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\sin\theta\,d\theta\,d\phi = \underline{4\pi}.$$

We will find out now pressure exerted by a perfect gas from K.T. (a) collisionless atoms in a box moving in 3 directions, (b) collisionless atoms coming from all directions.

collision will be dealt in "mean free path".

Method 1 $AB = AD = AE = l$



The gas is confined within this cube of volume $l^3$. P (say) is a gas atom with velocity "c" whose components in 3-direction is $(u, v, w)$.

N = total no. of atoms or molecules.

So each of them have different velocity $c_1, c_2, c_3, c_4, \ldots$ etc so different components $(u_1, v_1, w_1), (u_2, v_2, w_2), (u_3, v_3, w_3), \ldots$

Mean square average
$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \cdots}{N} = \frac{u_1^2 + u_2^2 + u_3^2 + \cdots}{N} + \frac{v_1^2 + v_2^2 + v_3^2 + \cdots}{N} + \frac{w_1^2 + w_2^2 + w_3^2 + \cdots}{N}$$
$$= \overline{u^2} + \overline{v^2} + \overline{w^2} \quad — ①$$

mean square velocity in X-direction

Y-direction

z-direction.

Consider particle p with mass m, velocity $\vec{c} = (\vec{u}, \vec{v}, \vec{w})$.

It travels from ABCD to EFGH, makes collision to exert pressure, rebounds elastically, momentum gets changed, comes back to ABCD to make another collission.

Total distance traveled with velocity u is $2l$.

$\therefore$ Time between collission $= \frac{2l}{u}$, meaning number of collission per second $= \frac{u}{2l}$.

Momentum imparted in +X direction ~~of~~ on EFGH = mu.
Momentum obtained in −X direction after collission = −mu.

$\therefore$ Change of momentum $= mu - (-mu) = 2mu$.

Rate of change of momentum for one atom in X direction
$$= 2mu \times \frac{u}{2l} = \frac{mu^2}{l}.$$

Similarly in Y and Z direction, rate of change of momentum is $\frac{mv^2}{l}$ & $\frac{mw^2}{l}$ for one atom

∴ Total rate of change of momentum for all atoms per unit area along x direction is

$$P_x = \frac{m(u_1^2+u_2^2+u_3^2+\cdots)}{l}\times\frac{1}{l^2} = m\overline{u^2}\,\frac{N}{l^3} = mn\overline{u^2}$$

(see eqn ①)

Similarly $P_y = mn\overline{v^2}$, $P_z = mn\overline{w^2}$.

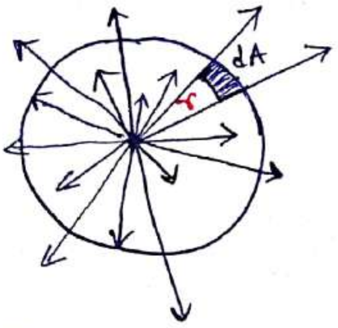
In steady state, molecules move in all directions, so no preference, meaning $\overline{u^2} = \overline{v^2} = \overline{w^2}$, & $P_x = P_y = P_z$.

Meaing $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$ (see eqn ①)

collecting all pieces together,

$$P_x = P_y = P_z = \frac{1}{3}mn\overline{c^2} \quad \text{or} \quad \boxed{P = \frac{1}{3}mn\overline{c^2}}$$

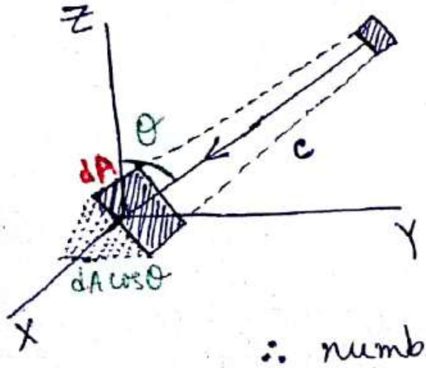
## Method 2



N no. of molecules moving in all directions with all possible velocity. How many collide with vessel & insert pressure?

number of vectors per unit area = $\frac{N}{4\pi r^2}$

∴ number of molecules at dA is $\frac{NdA}{4\pi r^2}$



We already learned that $dA = r^2\sin\theta\, d\theta\, d\phi$

$$\frac{NdA}{4\pi r^2} = \frac{N}{4\pi}\sin\theta\, d\theta\, d\phi$$

∴ number of molecules per unit volume within velocity range c & c+dc [$dn_c$], within direction $\theta$ & $\theta+d\theta$ & $\phi$ & $\phi+d\phi$

[$d\omega = \sin\theta\, d\theta\, d\phi$]

$$dn_{c,\theta,\phi} = \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi$$

Let's find now, how many of them strike dA of the wall of container. Geometrically, this is the number of molecules within the slanted prism of length cdt with edges in the direction θ & φ $= \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA\cos\theta\, dt$

∴ Total number of collisions at dA per unit time

$$\int_{c=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi}\sin\theta\, d\theta\, d\phi \times c\, dA\cos\theta$$

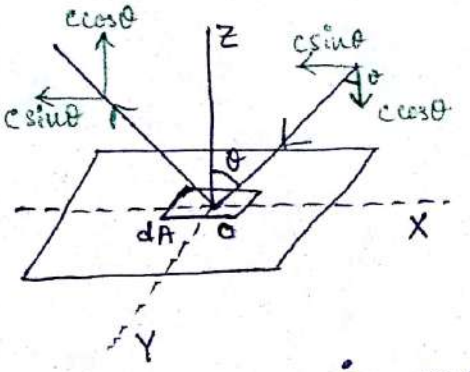
$$= \frac{dA}{4\pi}\int_0^{\infty} c\, dn_c \underbrace{\int_0^{\pi/2}\sin\theta\cos\theta\, d\theta}_{1/2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = \frac{dA}{4}\int_0^{\infty} c\, dn_c .$$

If $n_1$ atoms per unit volume moves with velocity $c_1$,
$n_2$ ″ ″ ″ ″ ″ $c_2$,
$n_3$ ″ ″ ″ ″ ″ $c_3$, . . .

average velocity $\bar{c} = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \cdots}{n_1 + n_2 + n_3 + \cdots}$

$$= \frac{\sum n_i c_i}{\sum n_i} = \frac{1}{n}\int_0^{\infty} c\, dn_c$$

∴ Number of molecules colliding at dA of the container per unit time $= \boxed{\frac{dA}{4}\, n\bar{c}}$



Now let's compute change in momentum by molecules striking area dA in unit time.

normal component of incident momentum is $mc\cos\theta$ & reflected momentum $-mc\cos\theta$.

So each atom had a change in momentum $2mc\cos\theta$.

∴ Total change of momentum experienced by all gas atoms/molecules colliding to area $dA$, per unit time is

$$\int_{c=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \frac{dn_c}{4\pi}\sin\theta\,d\theta\,d\phi \times c\,dA\cos\theta \times 2mc\cos\theta$$

$$= \frac{m\,dA}{2\pi}\int_{c=0}^{\infty} c^2\,dn_c \underbrace{\int_{\theta=0}^{\pi/2}\cos^2\theta\,\sin\theta\,d\theta}_{=1/3}\ \underbrace{\int_{\phi=0} d\phi}_{2\pi} = \frac{1}{3}\,m\,dA\int_{c=0}^{\infty} c^2\,dn_c$$

$$c_{rms}^2 = \bar{c}^2 = \frac{n_1c_1^2+n_2c_2^2+n_3c_3^2+\cdots}{n_1+n_2+n_3+\cdots} = \frac{\sum n_i c_i^2}{\sum n_i}$$

$$= \frac{\int_0^{\infty} c^2\,dn_c}{n}$$

∴ Force exerted by gas atoms on $dA$ is

$$F = \frac{1}{3}\,m\,dA\,n\bar{c}^2$$

Thus, pressure exerted $\boxed{p = \frac{F}{dA} = \frac{1}{3}mn\bar{c}^2}$

Corollary From above, $p = \frac{1}{3}\rho\bar{c}^2 \Rightarrow \bar{c} = \sqrt{\frac{3P}{\rho}}$

For Hydrogen $\rho = 8.9\times10^{-5}$ gm/cc.

1 atm pressure $P = h\rho g = 76\times13.6\times981$ dynes/cm$^2$

$$\therefore\ \bar{c} = \sqrt{\frac{3\times76\times13.6\times981}{8.9\times10^{-5}}} = 1.85\times10^{5}\ \text{cm/sec.}$$

$c_l = 3\times10^{8}$ m/s, $c_s = 300$ m/s

$= 3\times10^{10}$ cm/s. $c_s = 3\times10^{4}$ cm/s.

## Kinetic interpretation of temperature

From K.T. $p = \frac{1}{3} mn\bar{c}^2 = \frac{1}{3} m \frac{N}{V} \bar{c}^2$ But we assume!!

$\therefore PV = \frac{1}{3} mN\bar{c}^2 = RT$ [Boyle's law]

$\bar{c} = \sqrt{\frac{3RT}{mN}} = \sqrt{\frac{3RT}{M}}$ where M = molecular weight

$\therefore \bar{c} \propto \sqrt{T}$ RMS velocity of gas atom is proportional to square root of absolute temperature.

As from $T = 0$, $\bar{c} = 0$ ie. absolute zero temperature is where molecule cease to move.

Now $\bar{c}^2 = \frac{3RT}{M} \Rightarrow \frac{1}{2} M\bar{c}^2 = \frac{3}{2} RT$

divide by N, $\underbrace{\frac{1}{2} m\bar{c}^2}_{\text{mean K.E.}} = \frac{3}{2} k_B \underset{\text{abs. temp.}}{T}$, $k_B$ = Boltzmann's constant.

for a given T, there is always a K.E. & molecular collission lead to uniform T.

## Boyle's law from K.T.

$PV = \frac{1}{3} M\bar{c}^2$ & because $\bar{c}^2 \propto T$.

So if T is fixed $\bar{c}^2$ is constant so $PV$ = constant.

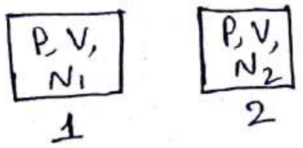
## Charle's law from K.T.

Again $\bar{c}^2 \propto T$, so $pV \propto T$.

i.e. $V \propto T$ when $p$ = constant.

## Avogadro's law from K.T.

For same T & P, equal V of gases contain equal number of atoms.



$$P = \frac{1}{3} m_1 \frac{N_1}{V} \bar{C}_1^{\,2} \qquad \therefore \; m_1 N_1 \bar{C}_1^{\,2} = m_2 N_2 \bar{C}_2^{\,2}$$
$$P = \frac{1}{3} m_2 \frac{N_2}{V} \bar{C}_2^{\,2}$$

But T is equal, so K.E. is equal.

$$\frac{1}{2} m_1 \bar{C}_1^{\,2} = \frac{1}{2} m_2 \bar{C}_2^{\,2} \Rightarrow m_1 \bar{C}_1^{\,2} = m_2 \bar{C}_2^{\,2}$$

$$\therefore N_1 = N_2$$

## Clapeyron's equation from K.T.

$$P = \frac{1}{3} m n \bar{c}^{\,2} = \frac{1}{3} \frac{n}{N} m N \bar{c}^{\,2} = \frac{n}{N} \times \frac{1}{3} M \bar{c}^{\,2}$$

$$= \frac{n}{N} RT = n k_B T \qquad \left[k_B = \frac{R}{N}\right]$$

$N = 6.023 \times 10^{23}$ atoms/mole.

## Universal gas constant R

$PV = RT$.

$$\therefore R = \frac{PV}{T} = \frac{(76 \times 13.6 \times 981) \times 22.4 \times 10^3}{273}$$

$= 8.31 \times 10^7$ dynes-cm/°K/mole or erg/degK/mole.

in heat units, $= \frac{8.31 \times 10^7}{4.18 \times 10^7} = 2$ cal/degK/mole

& $k_B = \frac{R}{N} = \frac{8.31 \times 10^7}{6.023 \times 10^{23}} = 1.38 \times 10^{-16}$ ~~ergs~~ ergs/degK/mole

## Dalton's law of partial pressure

N no. of gases with density $\rho_1, \rho_2, \rho_3$ with rms velocities $\bar{c}_1, \bar{c}_2, \bar{c}_3$ etc, $P = \frac{1}{3}\rho_1 \bar{c}_1^{\,2} + \frac{1}{3}\rho_2 \bar{c}_2^{\,2} + \frac{1}{3}\rho_3 \bar{c}_3^{\,2} = P_1 + P_2 + P_3 + \cdots$

## Relation between pressure & K.E.

$$P = \frac{1}{3}\rho \bar{c}^2 = \frac{2}{3}\,\frac{1}{2}\rho \bar{c}^2 = \frac{2}{3}E$$

so pressure of a gas is 2/3 the translational K.E. of the atoms per unit volume.

**CW** Compute the r.m.s. velocity of oxygen $(O_2)$ & ~~hydrogen~~ $CO_2$ atoms at 27°c. Given, density of oxygen at N.T.P. = 1.43 $Kg/m^3$ & molecular weight of $CO_2$ = 44 gm, (molecular weight of $O_2$ = 32 gm).

at N.T.P. $(T_0 = 273K)$ for $O_2$, $\rho_0 = 1.43\ Kg/m^3$.

[If not this supplied, then molecular weight = 32 gm
= 0.032 Kg

at N.T.P. gram molecular volume = 22.4 litre
$= 22.4 \times 10^{-3}\ m^3$
$= 0.0224\ m^3$.

Density $\rho_0 = \frac{0.032}{0.0224} = 1.43\ Kg/m^3$ ]

Similarly for $CO_2$, density $\rho_0 = \frac{0.044}{0.0224} = 1.96\ Kg/m^3$ at N.T.P.

Using K.T. we have $\rho_0 T_0 = \rho T$.

$$\therefore \rho_{27^\circ} = \frac{\rho_0 T_0}{T} = \frac{1.43 \times 273}{(27+273)} = 1.3\ Kg/m^3 \text{ for } O_2$$

$$\rho_{27^\circ} = \frac{\rho_0 T_0}{T} = \frac{1.96 \times 273}{(27+273)} = 1.79\ Kg/m^3 \text{ for } CO_2$$

pressure $P = 0.76 \times 13.6 \times 10^3 \times 9.8 = 1.013 \times 10^5\ N/m^2$.

from K.T. $P = \frac{1}{3}\rho \bar{c}^2$

So r.m.s. velocity $\bar{c}_{O_2} = \sqrt{\frac{3P}{\rho_{O_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.3}}$

$= 4.835 \times 10^2$ m/s.

$\bar{c}_{CO_2} = \sqrt{\frac{3P}{\rho_{CO_2}}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.79}}$

$= 4.12 \times 10^2$ m/s.

HW

1. Calculate the ~~ma~~ number of molecules/cc of an ideal gas at 27°C & at pressure of 20 mm of mercury. Density of mercury = 13.6 gm/cc & mean KE of a molecule at 27°C is $4 \times 10^{-21}$ Joules.

2. At what temperature will the r.m.s. velocity of a gas will become half its value at 0°C?

# Maxwell-Boltzmann law of distribution of velocity

The question is what is $dn_c$ ? Physically $dn_c$ is no. of atoms per unit volume within velocity $c$ & $c+dc$.

Can we calculate $dn_c$ ? $dn_c \overset{?}{=} f(P,T)$.

J.C. Maxwell computed it in 1859.

Let's digress & an excursion to random events & what we mean by "probability".

Random events

Exhaustive
[all events in set, coin-toss can give head or tail & no other event ]

Mutually Exclusive
[one excludes the other, coin toss, if head, no tail in one throw]

Equally Likely.
[No bias, fair coin toss: 50% chance both for head or tail]

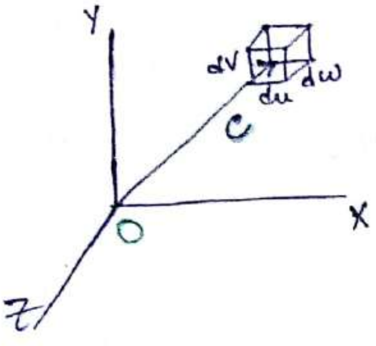
If there are N number of exhaustive, mutually exclusive and equally likely events of which M number are favourable to event A, then

$$p(A) = \frac{M}{N}$$

If two events A & B mutually exclusive, then total probability of either of them to happen in a trial is $p(A) + p(B)$

If two events A & B happen independently, then total probability of both events happening simultaneously in a trial is $p(A)\,p(B)$.

If $x$ is random variable defined by a function $f(x)$, then $f(x)\,dx$ = probability of a variate falling within $x$ & $x+dx$.



Assumptions : (a) density is uniform* & velocity in all direction is equal.

(b) isotropy → results independent of coordinate system.

(c) velocities in any 3 coordinates is independent*

If a molecule at O has velocity $\vec{c} = (u\hat{i}, v\hat{j}, w\hat{k})$ then $c^2 = u^2 + v^2 + w^2$. Components $u, v, w$ can change as $\vec{c}$ changes direction but magnitude of $c$ = constant.

$$\therefore \; dc^2 = 0 = 2u\,du + 2v\,dv + 2w\,dw$$

$$\text{So} \quad u\,du + v\,dv + w\,dw = 0 \quad \text{———} \; ①$$

This means $du, dv$ & $dw$ are not independent.

Probability that an atom has $x$ component of velocity $u$ & $u+du$ is $f(u)du$, mathematically, $P_u = \frac{dn_u}{n} = f(u)du$.

$n$ = number density.

Similarly, between $v$ & $v+dv$ is $P_v = \frac{dn_v}{n} = f(v)dv$

" " $w$ & $w+dw$ is $P_w = \frac{dn_w}{n} = f(w)dw$.

As they're independent*, the total probability is

$$P_{u,v,w} = \frac{dn_{u,v,w}}{n} = f(u)f(v)f(w)\,du\,dv\,dw$$

$$dn_{u,v,w} = n\,f(u)f(v)f(w)\,du\,dv\,dw \;, \quad \text{also means}$$

$$dN_{u,v,w} = N\,f(u)f(v)f(w)\,du\,dv\,dw$$

So in N number of molecules. $dN_{u,v,w}$ means this many of them are between u & u+du, v & v+dv, w & w+dw.

∴ Molecular density $\rho = \frac{dN_{u,v,w}}{du\,dv\,dw} = Nf(u)f(v)f(w)$

& as this is uniform, $d\rho = 0$

$$= f'(u)f(v)f(w)du + f(u)f'(v)f(w)dv + f(u)f(v)f'(w)dw$$

Divide by $\frac{1}{f(u)f(v)f(w)}$ $\Rightarrow$ $\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0$ ②

When ① & ② both are true, we invoke Lagrange's undetermined multiplier & do ① × α + ②,

$$\left[\frac{f'(u)}{f(w)} + \alpha u\right]du + \left[\frac{f'(v)}{f(v)} + \alpha v\right]dv + \left[\frac{f'(w)}{f(w)} + \alpha w\right]dw = 0$$

If we say, du is dependent, then we choose α such that

$$\frac{f'(u)}{f(u)} + \alpha u = 0$$

& because dv & dw is dependent, so

$$\frac{f'(v)}{f(v)} + \alpha v = 0, \quad \frac{f'(w)}{f(w)} + \alpha w = 0.$$

$$\therefore \frac{df(u)}{f(u)} = -\alpha u\,du.$$

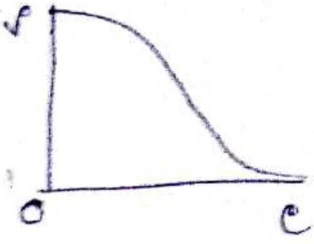
Integrating, $\ln f(u) = -\frac{\alpha}{2}u^2 + \ln A$

or $f(u) = Ae^{-\alpha u^2/2} = Ae^{-bu^2}$ $\{b = \alpha/2\}$

Similarly, $f(v) = Ae^{-bv^2}$, $f(w) = Ae^{-bw^2}$

So $\rho = NA^3 e^{-b(u^2+v^2+w^2)} = NA^3 e^{-bc^2}$

$dN_{u,v,w} = NA^3 e^{-b(u^2+v^2+w^2)} du\,dv\,dw$



What is remaining now is to find out constants A & b.

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dN_{u,v,w} = N$$

or $\cancel{N}A^3 \int_{-\infty}^{\infty} e^{-bu^2}du \int_{-\infty}^{\infty} e^{-bv^2}dv \int_{-\infty}^{\infty} e^{-bw^2}dw = \cancel{N}$

[ Now $\int_{-\infty}^{\infty} e^{-bu^2}du$

Let $bu^2 = z$

$2bu\,du = dz$

or $du = \frac{dz\sqrt{b}}{2b\sqrt{z}}$

$= \int_{-\infty}^{\infty} e^{-z}\frac{1}{2\sqrt{b}} z^{-1/2} dz$

$= \frac{1}{\cancel{2}\sqrt{b}}\cancel{2}\int_{0}^{\infty} e^{-z} z^{-1/2} dz = \frac{\Gamma(1/2)}{\sqrt{b}} = \sqrt{\frac{\pi}{b}}$ . ]

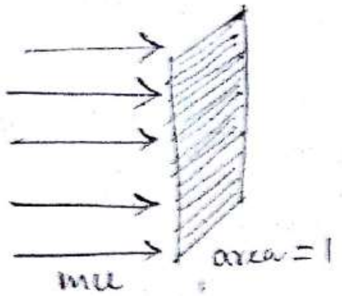
$A^3\left(\frac{\pi}{b}\right)^{3/2} = 1$ or $A = \sqrt{\frac{b}{\pi}}$

Evaluate b

Collisions per second

= area × velocity × number density at that . $n_u$

= 1 × u × $n_u$



Change in momentum = 2mu.

So pressure = rate of change of momentum per unit area.

$$P_u = \sum_{u=0}^{\infty} u n_u \times 2mu = 2m\sum_{0}^{\infty} n_u u^2 = 2m\int_{0}^{\infty} n_u u^2 f(u)\,du$$

$$= 2m n_u \int_{0}^{\infty} A e^{-bu^2} u^2 du$$

$$\therefore\ P_u = 2mn_uA\int_0^\infty e^{-z}\,\frac{z}{b}\,\frac{dz\sqrt{b}}{2b\sqrt{z}} \qquad [\text{put } bu^2 = z]$$

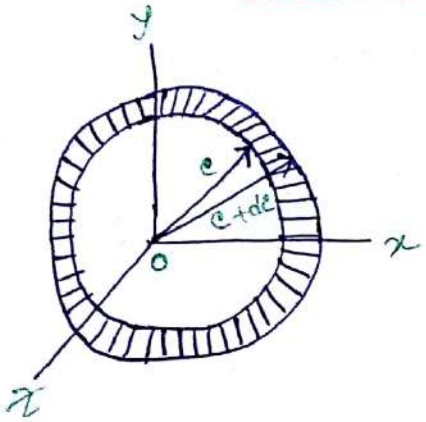
$$= \frac{mn_uA}{2b^{3/2}}\,\Gamma\left(\tfrac{1}{2}\right) \qquad \Gamma\left(\tfrac{3}{2}\right) = \tfrac{1}{2}\Gamma\left(\tfrac{1}{2}\right)$$

$$= \frac{mn_u}{2b^{3/2}}\,\frac{b^{1/2}}{\cancel{\pi^{1/2}}}\,\cancel{\pi^{1/2}} = \frac{mn_u}{2b} = n_uk_BT.$$

[from Clapeyron's equation]

$$\therefore\ b = \frac{m}{2k_BT},\quad A = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi k_BT}}$$

$$\therefore\ \boxed{dN_{u,v,w} = N\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{m}{2k_BT}(u^2+v^2+w^2)}\,du\,dv\,dw}$$



volume between c & c+dc is

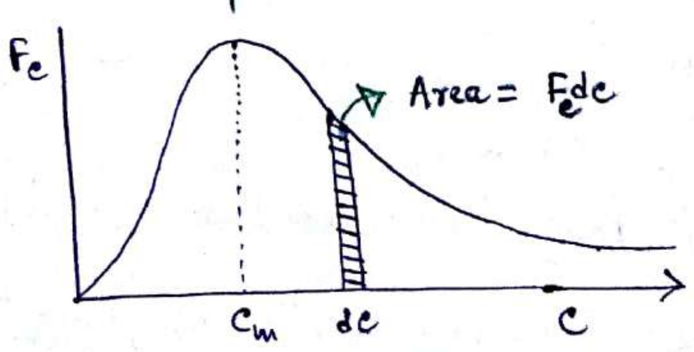
$$\tfrac{4}{3}\pi(c+dc)^3 - \tfrac{4}{3}\pi c^3$$

$$= \cancel{\tfrac{4}{3}\pi c^3} + \tfrac{4}{3}\pi\,3c^2dc + \tfrac{4}{3}\pi\,3c\,\cancel{(dc)^2}^{\,0} + \tfrac{4}{3}\pi\cancel{(dc)^3}^{\,0} - \cancel{\tfrac{4}{3}\pi c^3}$$

$$= 4\pi c^2 dc.$$

$$\therefore\ dN_c = N\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mc^2}{2k_BT}}\,4\pi c^2dc$$

$$\therefore\ P_c = \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}c^2e^{-\frac{mc^2}{2k_BT}}\,dc = F_c\,dc.$$



Remarks : (a) $c \to 0,\ F_c \to 0$

(b) $c \to \infty,\ F_c \to 0$

$$c_m = F_c^{\text{maximum}}$$

= most probable velocity

= maximum no. of atoms will possess this velocity

## Velocity component distribution

What is the number of molecules within velocity $u$ & $u+du$ but any value in $\hat{y}$ or $\hat{z}$ direction.

$$dN_{u,v,\omega} = N\left(\frac{m}{2\pi K_BT}\right)^{3/2} e^{-\frac{m}{2K_BT}(u^2+v^2+\omega^2)} du\,dv\,d\omega.$$

$$\therefore\ dN_u = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dN_{u,v,\omega}$$

$$= N\left(\frac{m}{2\pi K_BT}\right)^{3/2} du \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv \int_{-\infty}^{\infty} e^{-\frac{m\omega^2}{2K_BT}} d\omega \times e^{-\frac{mu^2}{2K_BT}}$$

$$\left[\text{Now} \int_{-\infty}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv = 2\int_{0}^{\infty} e^{-\frac{mv^2}{2K_BT}} dv\right.$$

$$\left[\text{put } z = \frac{mv^2}{2K_BT}.\quad dz = \frac{mv\,dv}{K_BT}\quad dv = \frac{K_BT\,dz\,\sqrt{m}}{m\sqrt{2K_BT}\sqrt{z}}\right]$$

$$= \frac{2\sqrt{K_BT}}{\sqrt{2}\sqrt{m}} \int_0^{\infty} e^{-z} z^{-1/2} dz$$

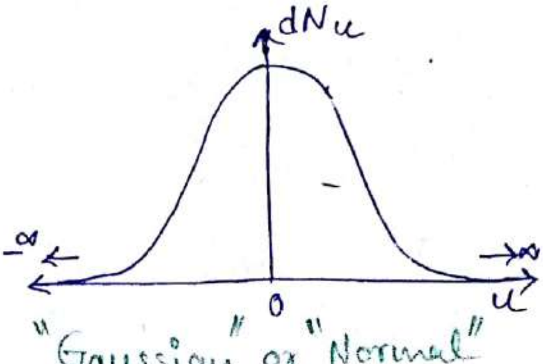
$$\left. = \sqrt{\frac{2K_BT}{m}} \times \sqrt{\pi} = \sqrt{\frac{2\pi K_BT}{m}}\ \right]$$

$$\therefore\ dN_u = N\left(\frac{m}{2\pi K_BT}\right)^{3/2}\left(\frac{2\pi K_BT}{m}\right)^{2/2} e^{-\frac{mu^2}{2K_BT}} du$$

$$dN_u = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{mu^2}{2K_BT}} du$$

Similarly, $dN_v = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{mv^2}{2K_BT}} dv$

$dN_\omega = N\left(\frac{m}{2\pi K_BT}\right)^{1/2} e^{-\frac{m\omega^2}{2K_BT}} d\omega.$



"Gaussian" or "Normal" distribution

# Average velocity, RMS velocity, Most probable velocity

Avg. velocity $$\langle c \rangle = \frac{N_1c_1 + N_2c_2 + \cdots}{N_1 + N_2 + \cdots} = \frac{\sum N_i c_i}{\sum N_i}$$

$$= \int_0^\infty c\, dN_c \Big/ N$$

$$= 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty c \cdot c^2 e^{-\frac{mc^2}{2k_BT}} dc$$

remember,

$A = \left(\frac{m}{2\pi k_B T}\right)^{1/2}$

$b = \frac{m}{2k_BT}$

$$= 4\pi A^3 \int_0^\infty c^3 e^{-bc^2} dc$$

put $bc^2 = z$

$2bc\,dc = dz$

$$= 4\pi A^3 \int \frac{z}{b} e^{-z} \frac{dz}{2b} = \frac{4\pi A^3}{2b^2} \int e^{-z} z\, dz$$

$$= \frac{4\pi A^3}{2b^2} \Gamma(2) = \frac{4\pi A^3}{2b^2} = 4\pi \frac{m}{2\pi k_BT} \left(\frac{m}{2\pi k_BT}\right)^{1/2} \times \frac{4k_B^2T^2}{2m^2}$$

$\Gamma(2) = 1$

$$= \left(\frac{8k_BT}{m\pi}\right)^{1/2}$$

$$\therefore \boxed{\langle c \rangle = \sqrt{\frac{8k_BT}{m\pi}}}$$

RMS velocity $c^2_{rms} = \frac{\sum N_i c_i^2}{\sum N_i} = \frac{1}{N}\int_0^\infty c^2 dN_c$

$$= 4\pi A^3 \int_0^\infty c^4 e^{-bc^2} dc$$

put, $bc^2 = z$

$2bc\,dc = dz$

$dc = \frac{dz\sqrt{b}}{2b\sqrt{z}}$

$$= 4\pi A^3 \int_0^\infty \frac{z^2}{b^2} e^{-z} \frac{dz\sqrt{b}}{2b\sqrt{z}}$$

$$= \frac{4\pi A^3}{2b^{5/2}} \int_0^\infty e^{-z} z^{3/2} dz = \frac{4\pi A^3}{2b^{5/2}} \Gamma(5/2)$$

$$= \frac{4\pi A^3}{2b^{5/2}} \frac{3}{\cancel{2}} \times \frac{1}{\cancel{2}} \times \sqrt{\pi} = \frac{3\pi^{3/2}}{2}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \left(\frac{2k_B T}{m}\right)^{5/2}$$

$$= \frac{3k_B T}{m}$$

$$\therefore \boxed{c_{rms} = \sqrt{\frac{3k_B T}{m}}}$$

Most probable velocity $c_m$ is $\left.\frac{df_c}{dc}\right|_{c=c_m} = 0.$

$$\therefore \left.\frac{d}{dc}\left\{4\pi A^3 c^2 e^{-bc^2}\right\}\right|_{c=c_m} = 0$$

or $\frac{d}{dc}\left\{c^2 e^{-bc^2}\right\}_{c=c_m} = 0$

or $\left\{2c\,e^{-bc^2} - c^2\, 2bc\, e^{-bc^2}\right\}_{c=c_m} = 0.$

or $\left\{2c\,e^{-bc^2}(1-bc^2)\right\}_{c=c_m} = 0.$

This can be true if $c \to \infty$ (unphysical) or $\{1-bc^2\}_{c=c_m} = 0$

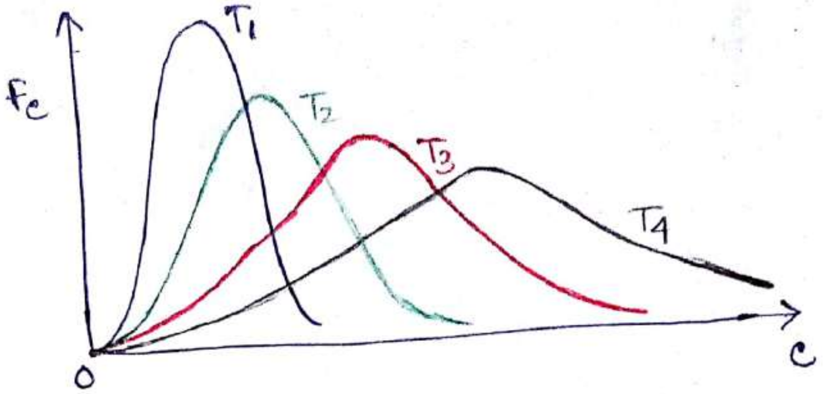
$\therefore bc_m^2 = 1$ or $c_m = \frac{1}{\sqrt{b}} = \sqrt{\frac{2k_B T}{m}}$

or $\boxed{c_m = \sqrt{\frac{2k_B T}{m}}}$

Note $c_{rms} > \langle c \rangle > c_m$

**Corollary** $\int_0^\infty F_c\,dc = 1$

$T_4 > T_3 > T_2 > T_1$



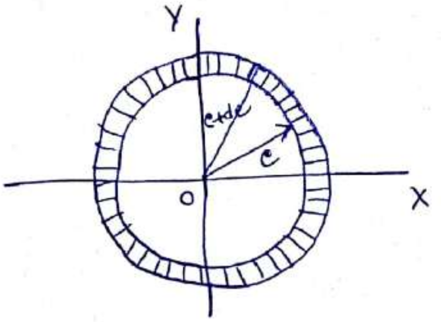
Also, no. of molecules colliding per unit area per unit time

$$dn = \frac{1}{4}n\bar{c} = \frac{1}{4}n\sqrt{\frac{8k_BT}{m\pi}} = \frac{1}{4}\frac{P}{k_BT}\sqrt{\frac{8k_BT}{m\pi}} \quad (\text{as } P = nk_BT)$$

$$\boxed{dn = \frac{P}{\sqrt{2m\pi k_BT}}}$$

CW 1. The velocity distribution in two dimension is $dn_{u,v} = n\left(\frac{m}{2\pi k_BT}\right) e^{-\frac{m(u^2+v^2)}{2k_BT}}\,du\,dv$. From this, find the distribution of molecular speed. Using that, find $c_m$, $\bar{c}$, $c^2_{rms}$.

$$c^2 = u^2 + v^2.$$



Take two concentric circles between velocity c & c+dc, area

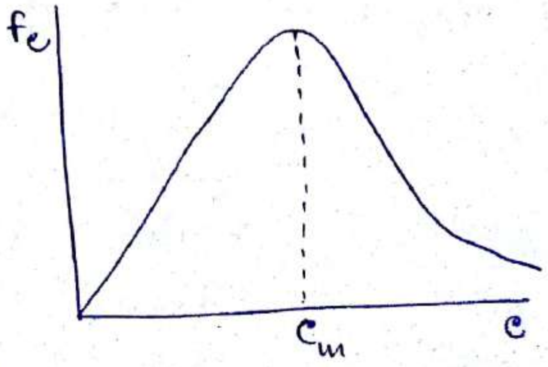
$$du\,dv = \pi(c+dc)^2 - \pi c^2 = 2\pi c\,dc.$$

$$\therefore\ dn_c = n\left(\frac{m}{2\pi k_BT}\right) e^{-\frac{mc^2}{2k_BT}}\,2\pi c\,dc = F_c\,dc.$$

$$\left.\frac{df_c}{dc}\right|_{c=c_m} = 0$$

$$\text{or } \frac{d}{dc}\left(c\,e^{-mc^2/2k_BT}\right) = 0$$

$$\text{or } 1 - c_m^2\frac{m}{k_BT} = 0 \quad \text{or } c_m = \sqrt{\frac{k_BT}{m}}$$



please also calculate $\frac{1}{n}\int_0^\infty c\,dn_c$ & $\frac{1}{n}\int_0^\infty c^2\,dn_c$.

convince yourself that $c_{rms} = \sqrt{\frac{2k_BT}{m}}$ and $\bar{c} = \sqrt{\frac{\pi k_BT}{2m}}$.

2. Using Maxwell velocity distribution, calculate the probability that the velocity of $O_2$ molecule lies between 100 m/s & 101 m/s at $-73^\circ C$.

$$dN_c = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{mc^2}{2k_BT}} c^2 dc.$$

$$\therefore \text{Probability } P = \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mc^2/2k_BT} c^2 dc. \quad — ①$$

$$\text{Now } m = \frac{M}{N} = \frac{32\ gm}{6.023\times10^{23}} = 5.31\times10^{-26}\ kg.$$

$$T = -73^\circ c = 200K, \quad c = 100\ m/s, \quad dc = 101-100 = 1\ m/s.$$

$$\therefore P = 4\pi\left[\frac{5.31\times10^{-26}}{2\pi\times1.38\times10^{-23}\times200}\right]^{3/2}\times \exp\left[-\frac{5.31\times10^{-26}\times10^4}{2\times1.38\times10^{-23}\times200}\right]\times10^4\times1$$

$$= 4\pi\times5.36\times10^{-9}\times0.9\times10^4 = 6.06\times10^{-4}. = 0.06\%$$

3. Compute the fraction of molecules of a gas possessing speeds within 1% of the most probable speed.

$$C_m = \sqrt{\frac{2k_BT}{m}}$$

fraction = probability P in equation ① above. with $c = C_m$

$$P = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\frac{\cancel{m}}{\cancel{2k_BT}}\frac{\cancel{2k_BT}}{\cancel{m}}} \frac{2k_BT}{m}\, dc_m$$

~~$dc_m$ is 1% of $C_m$~~ ~~As $C_m$~~

As c varies within 1% of $C_m \Rightarrow [0.99C_m, 1.01C_m]$.

$$\therefore dC_m = (1.01-0.99)C_m = 0.02\times\sqrt{\frac{2k_BT}{m}}.$$

$$\therefore P = \frac{4}{\sqrt{\pi}}\left(\cancel{\frac{m}{2k_BT}}\right)^{\cancel{3/2}} e^{-1}\ \cancel{\frac{2k_BT}{m}}\ \cancel{\sqrt{\frac{2k_BT}{m}}}\times0.02$$

$$= 0.016 = 1.6\%.$$

**HW** 1. At what value of speed c will the Maxwell's distribution $F_c$ yield same magnitude for a mixture of hydrogen & helium gases at 27°c ?

2. Find $\langle c^{-1} \rangle$ using $F_c$.

3. Molecular mass of an ideal gas of $O_2$ is 32. Calculate $c_m, \bar{c}, c_{rms}$ of the gas at 27°c. (Given $R = 8.3\ J/°c/mol$)

4. Convince yourself that $\frac{RT}{M} = \frac{P}{\rho}$. Using that, calculate $c_m, \bar{c}, c_{rms}$ of the molecules of gas at density $1.293 \times 10^{-3}$ gm/cc at 76 cm of Hg pressure.

5. The quantity $(c-\bar{c})^2 = c^2 - 2c\bar{c} + \bar{c}^2$ is squared deviation of atomic speed from average speed. Calculate the average value of this using Maxwell distribution & obtain the rms deviation.

Maxwell's distribution in reduced format

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc^2/2k_BT} c^2 dc$$

with respect to $C_m = \sqrt{\frac{2k_BT}{m}}$, non dimensionalized velocity $U = \frac{c}{C_m}$

Substitute $c = \sqrt{\frac{2k_BT}{m}}\, U$,

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} \frac{2k_BT}{m} U^2 \sqrt{\frac{2k_BT}{m}}\, dU\, e^{-\frac{m}{2k_BT}\frac{2k_BT}{m}U^2}$$

$$dN_U = \frac{4N}{\sqrt{\pi}} U^2 e^{-U^2} dU.$$

This distribution is independent of temperature.

# Energy distribution of the gaseous atoms

What we are after is to find the no. of atoms having K.E. between E & E + dE. As they don't have P.E.

$$E = \frac{1}{2}mc^2 \quad \text{or} \quad dE = mc\,dc.$$

$$\text{or} \quad dc = \frac{dE}{m\sqrt{\frac{2E}{m}}} = \frac{dE}{\sqrt{2mE}}.$$

From Maxwell's velocity distribution, we have

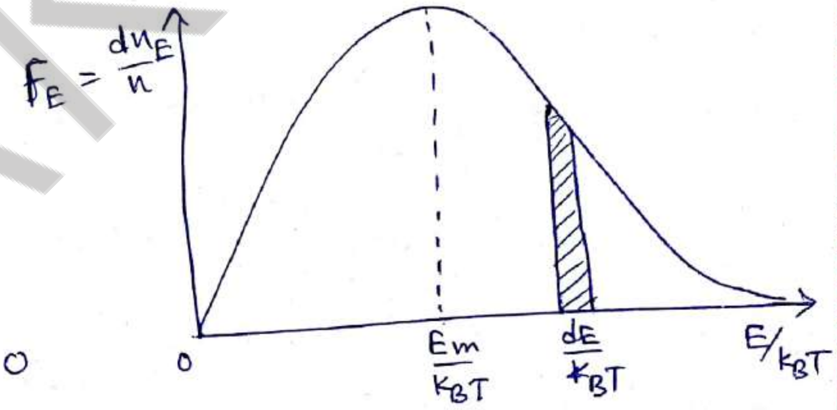
$$dn_c = 4\pi n c^2 \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mc^2/2k_BT}\,dc.$$

$$\therefore \quad dn_E = 4\pi n \,\frac{2E}{m}\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-E/k_BT}\,\frac{dE}{\sqrt{2mE}}$$

$$dn_E = 2n\sqrt{\frac{E}{\pi}}\,(k_BT)^{-3/2}\, e^{-E/k_BT}\,dE$$

( remember if V is cancelled $dN_E \sim N$)

Fraction of atoms $\frac{dn_E}{n}$ or $\frac{dN_E}{N} = \frac{2}{\sqrt{\pi}}(k_BT)^{-3/2}\sqrt{E}\,e^{-E/k_BT}\,dE = f_E\,dE$



$$F_E = \frac{2}{\sqrt{\pi}}(k_BT)^{-3/2}\sqrt{E}\,e^{-E/k_BT}$$

at $E = E_m$, $\frac{dF_E}{dE} = 0.$

$$\frac{d}{dE}\left\{\sqrt{E}\,e^{-E/k_BT}\right\}_{E=E_m} = 0$$

$$\text{or} \quad \frac{1}{2\sqrt{E_m}}e^{-E_m/k_BT} - \frac{\sqrt{E_m}}{k_BT}e^{-E_m/k_BT} = 0.$$

$$\therefore \quad \frac{1}{2\sqrt{E_m}} = \frac{\sqrt{E_m}}{k_BT} \quad \text{or} \quad E_m = \frac{k_BT}{2}.$$

Compare result with $c_m = \sqrt{\frac{2k_BT}{m}}$. Notice that

$$E_m \neq \frac{1}{2}mc_m^2 = \frac{1}{2}m\,\frac{2k_BT}{m} = k_BT.$$

## Momentum distribution of the gaseous atoms

No. of molecules in a range of momentum $p$ to $p+dp$.

$p = mc$ & $dp = mdc$.

Again, start from Maxwell's distribution

$$dN_c = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2k_BT}} dc$$

$$\therefore dN_p = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \frac{p^2}{m^2} e^{-p^2/2k_BTm} \frac{dp}{m}.$$

$$= N\sqrt{\frac{2}{\pi}}\left(mk_BT\right)^{-3/2} p^2 e^{-p^2/2mk_BT} dp = F_p dp.$$

at $p=p_m$ (most probable momentum), maximum no. of molecules lie $\left.\frac{dF_p}{dp}\right|_{p=p_m} = 0$. or $\frac{d}{dp}\left(p^2 e^{-p^2/2mk_BT}\right)_{p=p_m} = 0$

put $b = \frac{1}{2mk_BT}$

$$\text{or } \frac{d}{dp}\left(p^2 e^{-bp^2}\right)_{p=p_m} = 0$$

$$\text{or } \left(2p e^{-bp^2} - p^2 \cdot 2bp\, e^{-bp^2}\right)_{p=p_m} = 0$$

$$\text{or } \left[2p e^{-bp^2}\left(1-bp^2\right)\right]_{p=p_m} = 0 \Rightarrow p_m = \frac{1}{\sqrt{b}} = \sqrt{2mk_BT}$$

Again, $c_m = \sqrt{\frac{2k_BT}{m}}$

So $\underline{mc_m = \sqrt{2mk_BT} = p_m}$.

So most of the atoms have velocity $c_m$ are also having the momentum $mc_m$, but most of them do not have $\frac{1}{2}mc_m^2$ energy, rather most of the atoms have energy half of that.

If P.E. included in gravitational field $dN_c = 4\pi N\left(\frac{m}{2\pi k_BT}\right)^{3/2} \times e^{-(mgh+\frac{1}{2}mc^2)/k_BT} c^2 dc$

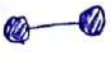
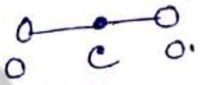
Maxwell-Boltzmann distribution.

Degrees of freedom   1D motion → 1 d.o.f.
2D (unconstrained) motion → 2 d.o.f
3D (unconstrained) motion → 3 d.o.f.

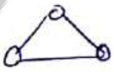
constraint reduce no. of independent variables necessary to designate the configuration of a dynamical system.

N particles in 3D coordinates $(x_1, y_1, z_1), (x_2, y_2, z_2) \dots (x_N, y_N, z_N)$
with constraint $F_j(x_1, y_1, z_1, \dots, x_N, y_N, z_N) = 0$, $j = 1, 2, 3, \dots, m$.

$\therefore K = 3N - m$ = d.o.f.

Example (1) Monoatomic atom : $K = 3$ for one atom.
(2) Diatomic ~~atom~~ molecule :  $K = 2 \times 3 - 1 = 5$ for one molecule.
(3) Triatomic molecule : (a) linear  $K = 3 \times 3 - 2 = 7$

$CO_2$

(b) Nonlinear  $K = 3 \times 3 - 3 = 6$

$H_2O$, $O_3$

So trivial case, $m = 3N$ → only one configuration.
$m > 3N$ not feasible, more constraint equation than unknowns.
$m < 3N$ is only feasible.

Generalized position & velocity coordinates

If a system has N d.o.f. then we can choose a set of N elements $q_1, q_2, q_3 \dots q_N$ that correspond to configuration & $\dot{q}_1, \dot{q}_2, \dots \dot{q}_N$ which to velocity vector at that configuration. These are generalized coordinates.

Law of equipartition of energy

Energy of a dynamical system in thermal equilibrium is equally divided amongst its d.o.f. & the value is $\frac{1}{2} k_B T$ for each d.o.f.

Suppose a system of free atoms has f d.o.f.

Every d.o.f. gets $\frac{1}{2}k_BT$ energy, then the energy per gm molecule

$$\therefore U = \frac{1}{2} N f k_B T = \frac{1}{2} R f T \qquad \left[\because k_B = \frac{R}{N}\right]$$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = Rf/2.$$

From $C_p - C_v = R$, we have $C_p = R + \frac{Rf}{2}$.

$$\therefore \frac{C_p}{C_v} = \frac{R + Rf/2}{Rf/2} = \frac{2}{f} + 1 \quad \text{or} \quad \boxed{\gamma = 1 + \frac{2}{f}}$$

For monoatomic gas, $k = 3$, $\gamma = 1 + \frac{2}{3} = 1.66$.

For diatomic gas, $k = 5$, $\gamma = 1 + \frac{2}{5} = 1.4$

For triatomic linear gas, $k = 7$, $\gamma = 1 + \frac{2}{7} = 1.28$

For triatomic not colinear gas, $k = 6$, $\gamma = 1 + \frac{2}{6} = 1.33$.

## Dulong & Petit's law

1819 Experimental investigation ⇒ product of atomic weight & specific heat of almost all solid substances are nearly equal to 6 calories.

Consider 1 mole of a solid with each atom/molecule have 3 translational d.o.f. & 2 rotational d.o.f. & 3 vibrational d.o.f. (vibration about mean equilibrium configuration). Rotation isn't allowed in crystal, as they're rigidly fixed.

∴ Number of d.o.f. of 1 mole solid is 6N.

Every d.o.f. gets $\frac{1}{2}k_BT$ energy from Equipartition theorem.

$$\therefore \text{Total energy} = U = 6N\frac{1}{2}k_BT = 3Nk_BT = 3RT$$

$$\therefore C_v = \left(\frac{dU}{dT}\right)_v = 3R = 3\times 1.98 \text{ Cal} \simeq 6 \text{ cal.}$$

Sometimes "atomicity" is also equivalent to d.o.f, $f = \frac{2}{\gamma - 1}$.

## Variation of $\gamma$ with temperature

High T, translation + rotation + vibration,

$f$ (diatomic molecule) = 7., $\gamma = 1 + \frac{2}{7} = 1.29$.

like $H_2 > 5000°c$ $\quad C_V = \frac{7}{2}R$

Medium T, translation + rotation

$f$(diatomic molecule) = 5, $\gamma = 1 + \frac{2}{5} = 1.4$.

like $H_2 \simeq 250K$ $\quad C_V = \frac{5}{2}R$.

Low T, translation

$f$(diatomic molecule) = 3, $\gamma = 1 + \frac{2}{3} = 1.66$

like $H_2 \simeq 70K$ $\quad C_V = \frac{3}{2}R$.

**CW** 1. What is the atomicity of a gas with heat capacity ratio 1.33? Given, $R = 8.31$ J/mol/K. Calculate $C_P$, $C_V$ values also.

$C_P - C_V = R$ or $C_V\left(\frac{C_P}{C_V} - 1\right) = R$ or $C_V(\gamma - 1) = R$.

$\therefore C_V = \frac{R}{\gamma - 1} = \frac{8.31}{1.33 - 1} = 25.18$ J/mol/K.

$C_P = \gamma C_V = 33.49$ J/mol/K.

$\therefore$ Atomicity $f = \frac{2}{\gamma - 1} = \frac{2}{0.33} = 6.$ (not monoatomic gas).

2. Calculate (a) K.E. of translation of $O_2$ molecule, (b) total K.E. and (c) total K.E. of a gram molecule at 27°c. Given $k_B = 1.37 \times 10^{-23}$ J/K & $N = 6.02 \times 10^{23}$.

$O_2$ = 3 translation $(x, y, z)$ + 2 rotation $(\theta, \phi)$, $f = 5$.

(a) K.E. of translation $= \frac{3}{2}k_BT = \frac{3}{2} \times 1.37 \times 10^{-23} \times 300$
$= 6.17 \times 10^{-21}$ J.

(b) K.E. ~~of~~ total $= \frac{5}{2}k_BT = 10.275 \times 10^{-21}$ J

(c) of 1 gram molecule $= \frac{5}{2}k_BT \times N = 10.275 \times 10^{-21} \times 6.02 \times 10^{23}$
$= 6185.55$ J.

## $\gamma$ for a mixture of ideal gases

At temperature T, $N_1$ moles of ideal gas with $f_1$ d.o.f.
$N_2$ moles of ideal gas with $f_2$ d.o.f.
$N_3$ moles of ideal gas with $f_3$ d.o.f.
.......
.......
$N_N$ moles of ideal gas with $f_N$ d.o.f.

Total internal energy $U = \frac{1}{2} k_B T N_1 f_1 N + \frac{1}{2} k_B T N_2 f_2 N + \cdots + \frac{1}{2} k_B T N_N f_N N$

$$\therefore C_V = \left(\frac{dU}{dT}\right)_V = \frac{1}{2} k_B N (N_1 f_1 + N_2 f_2 + \cdots + N_N f_N)$$

Also $C_P - C_V = (N_1 + N_2 + \cdots + N_n) k_B N$ $\quad [R/N = k_B]$

$$\text{or } C_P = (N_1 + N_2 + \cdots + N_n) k_B N + \frac{1}{2}(N_1 f_1 + N_2 f_2 + \cdots + N_N f_N) k_B N$$

$$= \frac{(2+f_1)N_1 + (2+f_2)N_2 + \cdots + (2+f_N)N_N}{2} k_B N$$

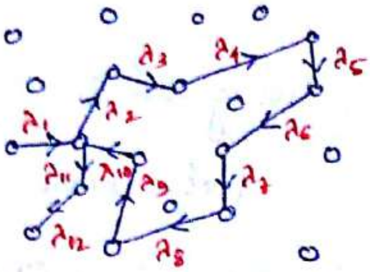
$$\therefore \gamma = \frac{C_P}{C_V} = \frac{(2+f_1)N_1 + (2+f_2)N_2 + \cdots + (2+f_N)N_N}{f_1 N_1 + f_2 N_2 + \cdots + f_N N_N}$$

**Example** 1 mole of monoatomic gas $(f=3)$ & 1 mole of diatomic gas $(f=5)$, $\gamma = \frac{(2+f_1)N_1 + (2+f_2)N_2}{f_1 N_1 + f_2 N_2} = \frac{5+7}{3+5} = 1.5$

$$\boxed{1 \le \gamma \le 1.67}$$

**Mean free path** We calculated that K.T. gives ~ 1 Km/s velocity for molecular movement. But we see clouds suspended in air holds together for hours. So there must be some factors that prevent the free escape of atoms.

Clausius showed that such discrepancy goes away if we take small & finite volume for atoms & they change velocity & direction of motion in the process of collission, zigzag path (discrete)



In between two successive collission, the traversed path is free path $(\lambda_1, \lambda_2, \cdots, \lambda_n)$.

$$\text{Mean free path} = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \cdots + \lambda_N}{\text{Number of collision}}$$

## Collision probability

Suppose collision rate is $P$, average velocity of an atom is $\bar{c}$ & in time $t$, distance covered $= \bar{c}t$ & number of collisions suffered is $Pt$. then $\lambda_{\bar{c}} = \frac{\bar{c}t}{Pt} = \frac{\bar{c}}{P}$.

Before we calculate "$\lambda$", let's compute the distibution of $\lambda$, meaning probability of an atom moving a distance $x$ without collision, say $f(x)$. This means that $f(x+dx)$ is the probability that atom traverses $x+dx$ length without collision.

If $P$ is collission probability per unit time, then for $N$ atoms number of collisions in time $t = \frac{1}{2}NPt$. (½ because each collission between 2 atoms is counted twice).

Probability that after traversing $x$, an atom will suffer a collission within $dx$ in time $dt = Pdt = P\frac{dx}{c} = \frac{dx}{\lambda}$

where $\lambda = \frac{c}{P}$ is the free path for atoms with velocity $c$.

$\therefore$ As total probability $= 1$, probability of no collision in distance $dx = \left(1 - \frac{dx}{\lambda}\right)$.

As successive collisions are independent, therefore the joint probability of no collision at $x+dx$ is $f(x)\times(1-\frac{dx}{\lambda})$

$$\therefore\ f(x+dx) = f(x)\left(1-\frac{dx}{\lambda}\right).$$

Expand LHS using Taylor's theorem.

$$f(x) + f'(x)\,dx + \cancel{\tfrac{1}{2}f''(x)(dx)^2}^{\to 0} + \cdots = f(x)\left(1-\frac{dx}{\lambda}\right) \quad \left[\lim_{dx\to 0}\right]$$

$$\text{or } f'(x) = -f(x)/\lambda. \quad \text{or} \quad \frac{f'(x)}{f(x)} = -\frac{1}{\lambda}.$$

Integrating, $\ln f(x) = -\frac{x}{\lambda} + \ln c \Rightarrow f(x) = c\,e^{-x/\lambda}.$

note that when $x=0$, $f(x)=1$. $\therefore\ c=1$.

$$\therefore\ f(x) = e^{-x/\lambda}. \Longrightarrow \text{law of distribution of free paths}$$

Method 2

Let, out of $N$ atoms, $N'$ atoms cross $x$ without collision, & after that in $dx$ distance, $dN'$ atoms are throw out due to collision. Then $dN' \propto N'$, $\propto dx$ or $dN' = -pN'dx$ (–ive for decrease)

$$\text{or } \frac{dN'}{N'} = -p\,dx$$

Integrating $\ln N' = -px + \ln c$

or $N' = c\,e^{-px}$. Now put boundary condition at $x=0$, $N'=N$.

$\therefore\ c = N$. $\therefore\ N' = N e^{-px}$

thrown out molecules are $dN' = +pNe^{-px}dx$ (+ive number)

$$\lambda = \frac{x_1 dN_1' + x_2 dN_2' + \cdots}{N} = \frac{1}{N}\int_0^\infty x\,dN'$$

$$= \frac{1}{N}\int_0^\infty x\,pNe^{-px}dx = p\int_0^\infty e^{-px}x\,dx$$

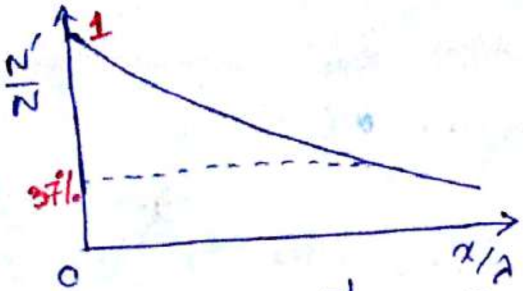
put $px = z$, $p\,dx = dz$

$$= p\,\frac{1}{p^2}\int_0^\infty e^{-z}z\,dz = \frac{1}{p}\Gamma(2) = \frac{1}{p}.$$

$$\therefore\ \boxed{N' = Ne^{-x/\lambda}} \quad \text{or} \quad f(x) = e^{-x/\lambda}$$

This is the "survival equation".

$$dN' = \frac{N}{\lambda} e^{-x/\lambda} dx \quad \text{or} \quad \boxed{\frac{dN'}{dx} = \frac{N}{\lambda} e^{-x/\lambda}}$$



(a) $P \propto 1/\lambda \Rightarrow$ collision probability is reciprocal of free path.

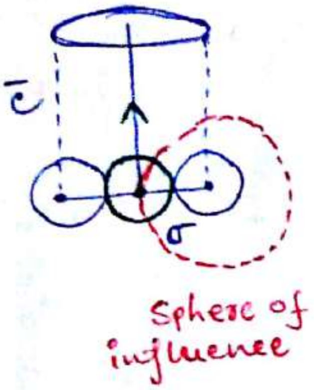
(b) Intensity of atomic beam ∝ number of atoms. $\therefore I' = I e^{-x/\lambda}$.

I' ↓ final intensity. I ↳ initial intensity

Number $> \lambda$ is $e^{-1} \sim 37\%$

$< \lambda$ is $1 - 37\% = 63\%$

## Calculation of λ



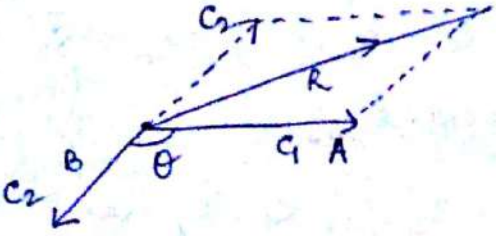
Suppose all atoms are rest but only one moves with velocity $\bar{c}$. Rigid spherical shape with diameter σ. It can only collide when they touch. & can reach distance $\bar{c}$, so it collides with $\pi\sigma^2\bar{c}n$ many atoms. This is also number of collisions per second.

$$\therefore \text{ Mean free path } \lambda = \frac{\bar{c}}{\pi\sigma^2\bar{c}n} = \frac{1}{n\pi\sigma^2}$$

This is approximate & Clausius did the first correction followed by Maxwell - Tait.

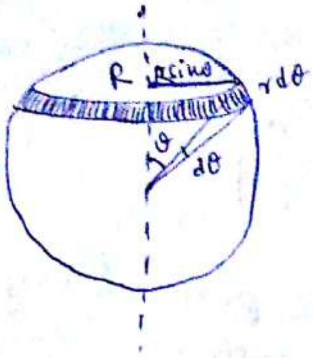
## Clausius correction

Introduction of relative velocity as all atoms are in motion.



Consider A & B atom moves with velocity $c_1$ & $c_2$ & angle θ. Making atom B observer (meaning applying equal & opposite velocity $c_2$ to B), B is in rest & relative to that A moves with relative velocity

$$R = \sqrt{c_1^2 + c_2^2 - 2c_1c_2\cos\theta}$$



Now we have to find mean relative velocity of atom A with respect to all others. If $dN_{\theta,\phi}$ is the number of atoms moving between $\theta$ & $\theta + d\theta$, $\phi$ & $\phi + d\phi$ then

$$dN_{\theta,\phi} = \frac{N}{4\pi R^2} R^2 \sin\theta \, d\theta \, d\phi = \frac{N \sin\theta \, d\theta \, d\phi}{4\pi}$$

and $$\bar{R} = \frac{\int R \, du_{\theta,\phi}}{\int du_{\theta,\phi}} = \frac{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sqrt{c_1^2 + c_2^2 - 2c_1c_2\cos\theta} \, \frac{N \sin\theta \, d\theta \, d\phi}{4\pi}}{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \frac{N \sin\theta \, d\theta \, d\phi}{4\pi}}$$

$$= \frac{\cancel{N}}{\cancel{4\pi}} \cancel{2\pi} \int_{\theta=0}^{\pi} \sqrt{c_1^2 + c_2^2 - 2c_1c_2\cos\theta} \, \sin\theta \, d\theta \Big/ \frac{\cancel{N}}{\cancel{4\pi}} \overset{2}{\cancel{4\pi}}$$

substitute $c_1^2 + c_2^2 - 2c_1c_2\cos\theta = z$ or $2c_1c_2 \sin\theta \, d\theta = dz$

$$\int^{\pi} z^{1/2} \frac{1}{2c_1c_2} dz = \frac{1}{2c_1c_2} \int_{(c_1-c_2)^2}^{(c_1+c_2)^2} \sqrt{z} \, dz = \frac{1}{2c_1c_2} \left[ \frac{z^{3/2}}{3/2} \right]_{(c_1-c_2)^2}^{(c_1+c_2)^2}$$

$$= \frac{1}{3c_1c_2} \left[ (c_1+c_2)^3 - (c_1-c_2)^3 \right]$$

$$\therefore \bar{R} = \frac{1}{6c_1c_2} \left[ (c_1+c_2)^3 - (c_1-c_2)^3 \right].$$

According to Clausius's assumption $c_1 = c_2 = \bar{c}$

$\therefore \bar{R} = \frac{1}{6\bar{c}^2} 8\bar{c}^3 = \frac{4}{3}\bar{c}$, meaning in traveling a distance $\bar{c}$, number of collision by molecule A with relative velocity $\bar{R}$ is $\pi\sigma^2\bar{R}n$ & therefore $\lambda_{cl} = \frac{\bar{c}}{\pi\sigma^2 n \bar{R}} = \frac{3}{4}\frac{1}{n\pi\sigma^2}$.

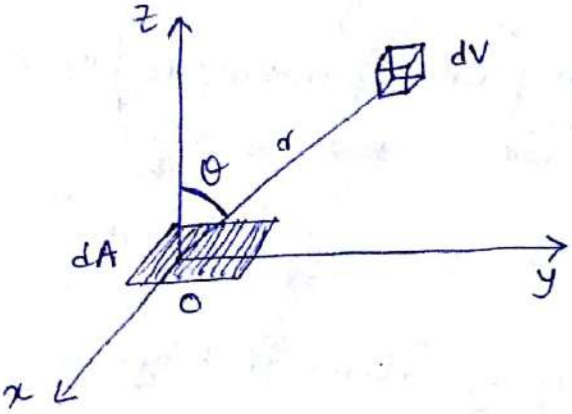
**Maxwell's correction** Clausius took $c_1 = c_2 = \cdots = c_N = \bar{c}$ but they're Maxwellian distributed in reality!

Maxwell corrected by considering both $c_1 > c_2$ & $c_1 < c_2$ case with $dN_{c_2} = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc_2^2/2k_BT} c_2^2 \, dc_2$

to obtain $\bar{R} = \sqrt{2}\,\bar{c}$ (see AB Gupta § 2.21.2 for derivation)

$$\therefore \lambda_{Maxwell} = \frac{\bar{c}}{\sqrt{2}\pi\sigma^2 n \bar{c}} = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

## Pressure of a gas using mean free path



Once again, we want to compute atoms within volume dV at distance r with inclination θ to a surface dA at origin that reach dA after collision with other atoms, using survival equation.

Number of molecules between c & c+dc in volume dV is $dn_c dV$.

If λ is mean free path of the gas atoms then number of collision suffered by one atom per unit time $= \frac{c}{\lambda}$.

As 1 → 2 & 2 → 1 collision is counted twice, so the number of collisions suffered by $dn_c dV$ number of atoms in unit time is $\frac{1}{2}\frac{c}{\lambda} dn_c dV$. But each collision results to two new paths along which atoms travel.

∴ The number of new paths or number of atoms emanating from dV per unit time $= \frac{1}{2}\frac{c}{\lambda} dn_c dV \times 2$ & fraction that are pointed towards the area dA is the solid angle subtended by dA at dV $= \frac{dA\cos\theta/r^2}{4\pi}$ ( 4π = all molecules contained)

∴ That exit from dV pointing to dA, that number is

$$N_0 = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2}$$ (per unit time).

In $N_0$, only those atoms with λ ≥ r can reach dA, which is

$$N = N_0 e^{-r/\lambda} = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2} e^{-r/\lambda}$$

$$= \frac{c\,dn_c\,dA\cos\theta\,\cancel{r^2}\sin\theta\,d\theta\,d\phi\,dr\,e^{-r/\lambda}}{\lambda\,4\pi\cancel{r^2}} \qquad (dV = r^2\sin\theta\,d\theta\,d\phi\,dr)$$

$$= \frac{dA}{\text{[illegible]}} \times \frac{c\,dn_c\,\sin\theta\cos\theta\,d\theta\,d\phi}{4\pi} \times \frac{e^{-r/\lambda}}{\lambda}\,dr$$

$\therefore$ No. of atoms striking dA is $= \frac{dA}{4\pi}\int_{c=0}^{\infty} c\,dn_c \int_{\theta=0}^{\pi/2}\sin\theta\cos\theta\,d\theta \int_{\phi=0}^{2\pi} d\phi \times \int_{r=0}^{\infty} e^{-r/\lambda}\,\frac{dr}{\lambda}$

$$= \frac{dA}{4\pi}\,n\bar{c}\,\frac{1}{2}\,2\pi \times 1 = \frac{dA}{4}\,n\bar{c}$$

So per unit area per unit time, number of atoms striking is $\boxed{\frac{n\bar{c}}{4}}$.

Again, we know one colliding atom suffers momentum change $= 2mc\cos\theta$

So change of momentum for all atom are

$$\frac{dA}{4\pi}\int_{c=0}^{\infty} 2mc^2\,dn_c \int_{\theta=0}^{\pi/2}\sin\theta\cos^2\theta\,d\theta \int_{\phi=0}^{2\pi} d\phi \int_{r=0}^{\infty} e^{-r/\lambda}\,d(r/\lambda).$$

$$dF = \frac{m\,dA}{2\pi}\,n\bar{c}^2_{rms}\,\frac{1}{3}\,2\pi = \frac{1}{3}mn\bar{c}^2_{rms}\,dA. \qquad \left[\bar{c}^2_{rms} = \frac{1}{n}\int_{c=0}^{A} c^2\,dn_c\right]$$

$$\therefore\ p = \frac{dF}{dA} = \boxed{\frac{1}{3}mn\bar{c}^2_{rms}}$$

Mean free path of a mixture of a gas

If we consider two different molecule with diameter $\sigma_1, \sigma_2$ then, $\sigma_1$ diameter molecule will collide with all molecule that are $\frac{\sigma_1+\sigma_2}{2}$ distance apart from $\sigma_1$ molecule. Hence $\lambda$ will be $1/n\pi\sigma_a^2$ where $\sigma_a = \frac{\sigma_1+\sigma_2}{2}$ & $n =$ number of molecules per unit volume of $\sigma_2$ type. But $\sigma_2$ molecules are not in rest then if $\sigma_1$ type moves with $\bar{c}_1$ & $\sigma_2$ type moves with $\bar{c}_2$ & if the molecules of $\sigma_2$ move perpendicular to $\sigma_1$ then relative velocity $R = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$ & therefore $\frac{R}{\bar{c}_1} = \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}$

So $\lambda_1$ of $\sigma_1$ type of molecules within $\sigma_2$ type molecules are

$\lambda_1 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}}$. Similarly, $\lambda_2$ of $\sigma_2$ type of molecules within $\sigma_1$ type molecules are $\lambda_2 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_2}}$. The perpendicular directionality assumption gives Maxwell's distribution with relative velocity R, & if we had assumed $\bar{c}_1 = \bar{c}_2$ & then we could get back Maxwell's expression of free path.

If we now consider $n_1$ molecule of $\sigma_1$ type with $\bar{c}_1$ & $n_2$ molecule of $\sigma_2$ type with $\bar{c}_2$ avg. velocity then no. of impact/sec by $\sigma_1$ molecules

$$\Gamma_1 = \underbrace{\sqrt{2}\,\bar{c}_1 n_1 \pi \sigma_1^2 \left(= \frac{\bar{c}_1}{\lambda_{11}}\right)}_{\sigma_1 \text{ with } \sigma_1} + \underbrace{n_2 \pi \sigma_a^2 \cancel{\bar{c}_1} \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\cancel{\bar{c}_1}} \left(= \frac{\bar{c}_1}{\lambda_{12}}\right)}_{\sigma_1 \text{ with } \sigma_2}$$

∴ Mean free path of $\sigma_1$ type molecules in the gas mixture

$$\lambda_1 = \frac{\bar{c}_1}{\Gamma_1} = \frac{\bar{c}_1}{\sqrt{2}\pi n_1 \bar{c}_1 \sigma_1^2 + \pi\sigma_a^2 n_2 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$

& Mean free path for the other

$$\lambda_2 = \frac{\bar{c}_2}{\Gamma_2} = \frac{\bar{c}_2}{\sqrt{2}\pi n_2 \bar{c}_2 \sigma_2^2 + \pi\sigma_a^2 n_1 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$

<u>HW</u> 1. Estimate the size of a He atom, assuming its mean free path is $28.5 \times 10^{-6}$ cm at N.T.P. & density is 0.178 gm/litre at N.T.P. & the mass of He atom is $6 \times 10^{-24}$ gm.

2. The diameter of a gas molecule is $3\times10^{-8}$ cm. Calculate the mean free path at N.T.P. Given $K_B = 1.38 \times 10^{-16}$ ergs/°c.

3. Find the diameter of a molecule of Benzene if its mean-free path is $2.2 \times 10^{-8}$ m & the number of Benzene molecules/unit volume is $2.79 \times 10^{25}$ molecules/m$^3$.

# Thermodynamics

Thermal Physics →
- Heat
- K.T.
- T.D.
- Stat Mech.

{ Equilibrium, Steady state, non Equilibrium.

{ Statistical T.D.

## Useful Mathematical Tools

(a) Partial differentiation : $\frac{\partial f}{\partial a_1}(a_1, a_2, \cdots, a_n)$ $a_1, \cdots, a_n$ = independent variables.

Let $z = f(x,y)$ is an explicit function (surface plot in XYZ plane)

Motion of a coordinate point on the surface → 3 choices (i) $x$ = constant $y$ varies (ii) $x$ varies $y$ = constant, (iii) both $x, y$ varies.

$x \to x + dx$, $y$ = constant, $z = f(x+dx, y)$ from $f(x,y)$.

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{dx \to 0} \frac{f(x+dx) - f(x)}{dx} = f_x$$

Similarly $f_y = \left(\frac{\partial f}{\partial y}\right)_x = \lim_{dy \to 0} \frac{f(x, y+dy) - f(x,y)}{dy}$

& higher order derivates. $f_{xx} = \frac{\partial^2 f}{\partial x^2}$, $f_{xy} = f_{yx} = \frac{\partial^2 f}{\partial x \partial y}$ etc.

(b) Total differentials :

Let $z = f(x,y)$ an explicit function where, $x, y$ are independent. means $dz \to 0$ implies $dx \to 0$ & $dy \to 0$ independently. Then $dz$ is the total differential $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$.

If an implicit function, say $f(x,y,z) = 0$ then

$$df = 0 = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = f_x dx + f_y dy + f_z dz$$

If $dx = 0$, $\left(\frac{\partial y}{\partial z}\right)_x = -\frac{f_z}{f_y}$, If $dy = 0$, $\left(\frac{\partial z}{\partial x}\right)_y = -\frac{f_x}{f_z}$ &

If $dz = 0$, $\left(\frac{\partial x}{\partial y}\right)_z = -\frac{f_y}{f_x}$. $\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$.

Also $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = M dx + N dy$ is perfect differential

if $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$.

**Example** Equation of state for hydrostatic system $f(P,V,T)=0$

substitute the variables, $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (volume expansivity)

$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (isothermal compressibility)

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = +\frac{1}{KV}\beta V = \frac{\beta}{K}.$$

Get ~~back~~ the ~~same~~ expression $P = P(V,T)$

$$\text{or } dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT = -\frac{1}{KV}dV + \frac{\beta}{K}dT.$$

(c) Line integral & exact differential :

$dz = M dx + N dy$ → required $z(x,y)$ at $(x_1,y_1)$ & $(x_2,y_2)$

means $\int_{x_1}^{x_2} M(x,y)\,dx$ , $\int_{y_1}^{y_2} N(x,y)\,dy$ be evaluated, provided

$y=f(x)$ dependency is given, meaning path in XY plane is given.

path dependent integration !! Each $f(x)$ gives different result.

However if $dz$ is total differential, then

$$M = \frac{\partial z}{\partial x}, \quad N = \frac{\partial z}{\partial y} \Rightarrow \frac{\partial M}{\partial y} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial N}{\partial x}$$

From this we can evaluate $z$ by $\iint_{x\,y}$ without using $y=f(x)$

path independent integration !!

It only depends on $(x_1,y_1)$ & $(x_2,y_2)$ ; $z$ is called "point function".

If contour integral over complete cycle $\oint dz = 0$ if $dz$ is exact or total differential.

Change of state of a system may be of different types:

**Isothermal (diathermic) :** If the change of state is such that the temperature of the system remains constant, then that state is called isothermal ($T =$ constant).

**Isobaric :** If the process is such that the pressure remains constant then it is called isobaric ($P =$ constant).

**Isochoric :** If during the change of state, the volume of the system does not change, then it is called isochoric ($V =$ constant)

**Adiabatic :** If the change is such that there is no exchange of heat then it is called adiabatic ($Q =$ constant)

**Isentropic :** If during the change, the entropy of the system remains constant, then it is called isentropic ($S =$ constant)

**Isenthalpic :** If during the change of state, the total heat content remains constant, then it is called isenthalpic process ($H = U + PV =$ constant)

<u>Thermodynamic System</u> "<u>System</u>" refers to a certain portion of the universe within some closed surface (boundary). Boundary may enclose a solid, liquid, gas, collection of magnetic dipoles, portion of liquid surface, batch of radiant energy & so forth. Boundary is not necessarily fixed in shape or size & can be real or imaginary. Like inner surface ← of tank → containing a compressed gas or surface ← enclosing certain mass of fluid.

real

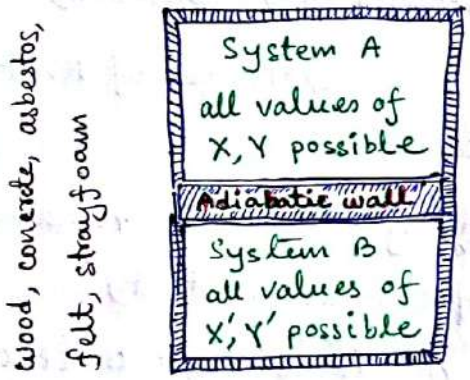
imaginary →

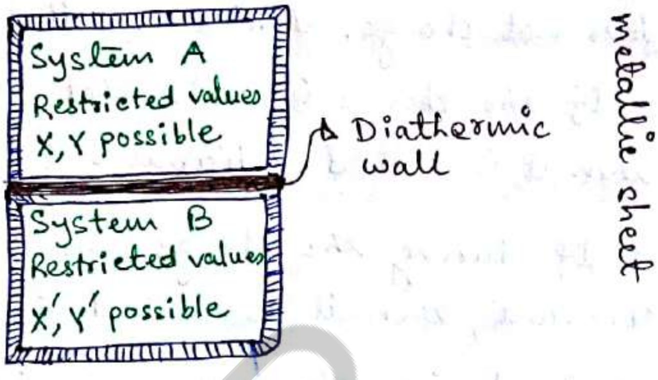
Many problems involve interchange of energy between a given system & others. Such other systems that can interchange energy with the system are called "<u>surroundings</u>". System & surrounding together constitute the universe.

When conditions are such that no energy interchange with the surroundings can take place, then the system is said to be "<u>isolated</u>". If no matter can cross the boundary, then its a "<u>closed</u>" system. But if interchange of matter between system & surrounding, then its an "<u>open</u>" system.

## Thermal Equilibrium

Consider a system having two independent coordinates X, Y (say pressure, volume or temperature). A state of the system in which X & Y have definite values that remain constant as long the external conditions are not changed is called an equilibrium state. Such equilibrium state in a system depends on the proximity of other systems & also on the nature of the separating wall.



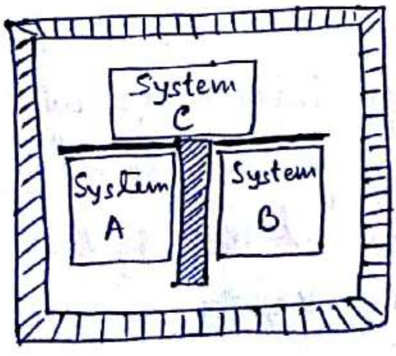


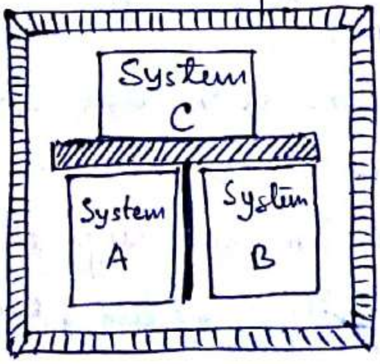
For adiabatic wall, state X, Y for system A may coexist with state X', Y' of system B as equilibrium state. But for diathermic wall, (X, Y) & (X', Y') will change spontaneously until an equilibrium state of the combined system is attained.

## Zeroth law of Thermodynamics (Fowler, 1908)

If two system A & B separated by an adiabatic wall but each of them are in contact with a third system C through diathermic wall, then A & B will come to equilibrium with C & no further change will occur if the adiabatic wall between A & B is replaced by diathermic wall.

$0^{th}$ law of T.D. : 2 systems in thermal equilibrium with third are in thermal equilibrium with each other.





## Thermodynamic equilibrium

A system is said to be in a state of thermodynamic equilibrium if (a) mechanical equilibrium, (b) chemical equilibrium & (c) thermal equilibrium is satisfied.

When there is no unbalanced force in the interior of a system & also no net force between a system & its surrounding (also net torque is zero), then the system is in a state of mechanical equilibrium.

When a system in mechanical equilibrium does not undergo a spontaneous change in its internal structure (e.g. chemical reaction & mass transfer due to diffusion) then the system is in a state of chemical equilibrium.

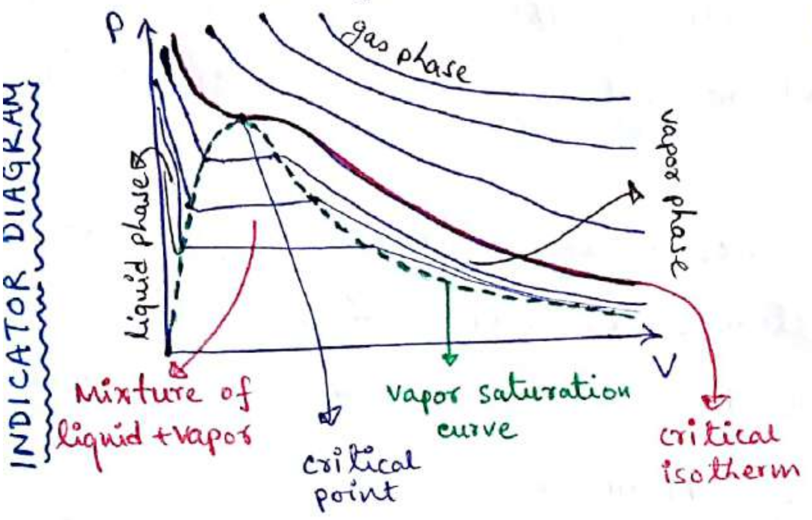
Thermal equilibrium exists when there is no spontaneous change in the (thermodynamic) coordinates (e.g. P, V, T) of a system in mechanical & chemical equilibrium when separated from surroundings by diathermic wall.

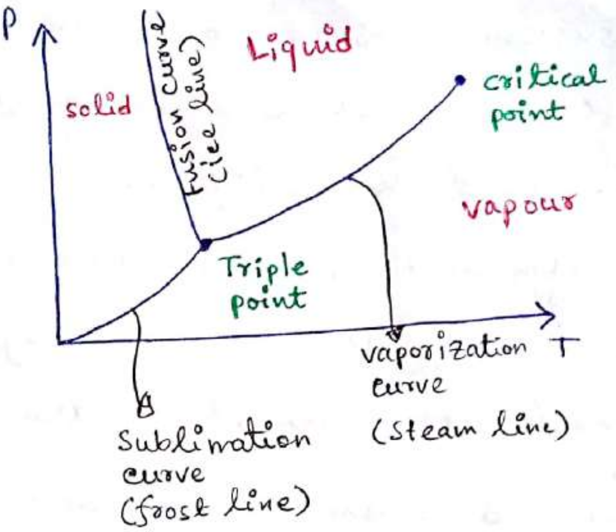
Non equilibrium states cannot be described in terms of T.D. coordinates as $P = P(x, y, z)$ that varies in space & time.

In the absence of surface, gravitational, electric, magnetic effects a constant mass system that exerts uniform hydrostatic pressure to surroundings is a "hydrostatic system". Categorically 3 systems:

1. A pure substance : 1 chemical constituent (solid, liquid, gas) mixture (s-l, l-g, s-g) or three of them (s-l-g).
2. Homogeneous mixture of different constituents : mixture of inert gases, mixture of liquids (solution)
3. Heterogeneous mixture : mixture of different gases in contact with a mixture of different liquids.

## PV & PT diagram for pure substance





## Thermodynamic description of system other than $f(P,V,T)=0$

Thermodynamics of a gaseous system is described by three thermodynamic coordinates $P, V, T$, but for other systems require different types of coordinates.

**Stretched Wire** $P, V \sim$ unchanged. Thermodynamicall equivalent coordinates (a) Tension in the wire ($\mathcal{F}$), (b) Length of the wire ($L$) (c) Ideal gas temperature ($T$). In S.I. units, $\mathcal{F}$ is Newton, $L$ is metre, $T$ in °K.

Equivalent of equation of state $f(P,V,T)=0$ is the Hooke's law at constant temperature within elastic limit.

$$\mathcal{F} = K(L-L_0) \quad , \quad L_0 = \text{length at no tension}$$

So, $L = L(\mathcal{F}, T)$ & for infinitesimal change

$$\therefore dL = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F} + \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} dT$$

Linear expansivity $\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}}$

Isothermal Young's modulus $Y = \left(\frac{\partial \mathcal{F}/A}{\partial L/L}\right)_T = \frac{L}{A}\left(\frac{\partial \mathcal{F}}{\partial L}\right)_T$

$$\therefore dL = \frac{L}{AY} d\mathcal{F} + \alpha L \, dT.$$

~~In isothermal condition.~~ ~~[illegible]~~
~~of Young's modulus [illegible],~~

for isothermal condition $dT \simeq 0$ & $dL = \frac{L}{AY} d\mathcal{F}$ &

therefore work done in expanding a wire is

$$W = \int \mathcal{F} dL = \int_0^{\mathcal{F}} \mathcal{F} \frac{L}{AY} d\mathcal{F} = \frac{L}{2AY} \mathcal{F}^2.$$

## Surface film

physical chemistry / chemical engineering / other areas.

Examples (a) Liquid- vapour interface in equilibrium,
(b) soap bubble / film → two surface films with in between liquid.
(c) thin oil film on the surface of water.

Three coordinates (a) surface tension $\mathscr{S}$ (Newton/metre), (b) area of film (A) metre$^2$, (c) ideal-gas temperature T. to describe a stretched membrane.

Equation of state $\mathscr{S} = \mathscr{S}_0 (1 - \frac{T}{T'})^n$ for surface tension

$\mathscr{S}_0$ = surface tension at 0°C, $T' \sim$ near $T_c$ & $n \sim 1$ & 2.

As T >, $\mathscr{S}$ < & $= 0$ at $T = T'$.

## Dielectric slab

Thermodynamic behaviour of a dielectric slab (whether molecules are polar or nonpolar) is described by three coordinates, (a) electric field intensity E (V/m), (b) electric polarisation (P) in Coulomb metre which is the amount of dipole moment per unit volume along the direction of the electric field.

The equation of state of the dielectric

$$P = \left(A + \frac{B}{T}\right) E$$

where A, B are constants & depends upon the nature of the dielectric material.

## Paramagnetic Rod

When a paramagnetic rod is placed within a solenoid, where the magnetic intensity is H, the rod develops a magnetic moment M. Magnetic induction B in volume V is

$$B = \mu_0 \left(H + \frac{M}{V}\right).$$

Equivalent thermodynamic coordinates are (1) Magnetic field intensity H (Ampere/metre), (2) Magnetization M (Ampere $\text{metre}^2$), (3) Ideal gas temperature T. (in °K).

The equation of state of thermodynamic equilibrium is

$$M = C\frac{H}{T} \quad (\text{Curie's law})$$

## Intensive & Extensive Parameters

If a system in equilibrium is divided into two parts, each with equal mass, then those properties of each half of the system that remain same are called intensive & those which become half are called extensive.

| | Systems | Intensive coordinates | Extensive coordinates |
|---|---|---|---|
| ⓐ | Hydrostatic system | Pressure (P) | volume (V) |
| ⓑ | stretched wire. | tension ($\mathcal{F}$) | Length (L) |
| ⓒ | surface film | Surface tension ($\mathcal{S}$) | Area (A) |
| ⓓ | Dielectric slab | Electric field Intensity (E) | Polarization (P) |
| ⓔ | Paramagnetic rod | Magnetic field Intensity (H) | Magnetization (M) |

## Equation of state for adiabatic process

Let us consider an ideal gas system of volume V at pressure P. Then for isothermal change, $PV = \mu RT = \text{constant}$ (as T = constant)

Now for an adiabatic process without any exchange of heat, using first law of thermodynamics $0 = dU + PdV$. where dU is the internal energy change & if the change in temperature for one mole of gas is dT, then $dU = C_v\,dT$ where $C_v$ is the specific heat at constant volume.

∴ $C_v dT + PdV = 0$ for adiabatic process.

From equation of state $PV = RT$ ∴ $PdV + VdP = RdT$

∴ $dT = \frac{PdV + VdP}{R} = \frac{PdV + VdP}{C_p - C_v}$ as $C_p - C_v = R$ for ideal gas.

∴ $C_v\left(\frac{PdV + VdP}{C_p - C_v}\right) + PdV = 0$

or $\frac{\cancel{C_v PdV} + C_v VdP + C_p PdV - \cancel{C_v PdV}}{C_p - C_v} = 0$ or $C_v VdP + C_p PdV = 0$

or $\frac{dP}{P} + \frac{C_p}{C_v}\frac{dV}{V} = 0$, integrating $\ln P + \gamma \ln V = \ln C$

[$\gamma = \frac{C_p}{C_v}$, $\ln C$ constant]

or $PV^{\gamma}$ = constant

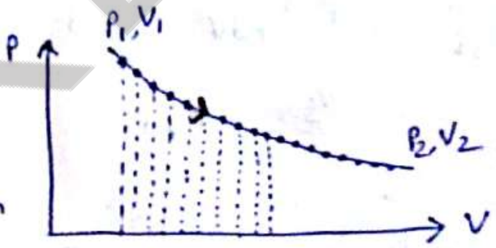
Using $PV = RT$ or $V = \frac{RT}{P}$ $\Rightarrow$ $P\left(\frac{RT}{P}\right)^{\gamma}$ = constant

or $P^{1-\gamma}T^{\gamma}$ = constant.

Again using $PV = RT$, $P = \frac{RT}{V}$ $\Rightarrow$ $\frac{RT}{V}V^{\gamma}$ = constant

or $V^{\gamma-1}T$ = constant

## Quasistatic Process

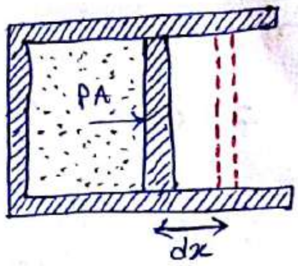


A finite unbalanced force may cause a system to pass through nonequilibrium states. Thus during a process if it is required to describe every state of the system by means of thermodynamic coordinates, the process should not conceive a finite unbalanced force, because a nonequilibrium state cannot be defined by thermodynamic coordinates. Therefore we think of an ideal situation in which external forces vary slightly so as the unbalanced force is infinitesimal. A process performed in such ideal way is "quasistatic." [ In statmech course, rethink about "local equilibrium" ]

During a quasistatic process the system is infinitesimally near a state of thermodynamic equilibrium, & all states through which the system passes can be described with equation of state with thermodynamic coordinates.

## Workdone "on" or "by" a system in a quasistatic process

### ⓐ Gaseous hydrostatic System



pressure exerted by the system on piston = PA

opposing force on the system by external agent moves piston by dx in opposite direction to PA

$(dV = Adx)$

Then $đW = -PAdx = -PdV$

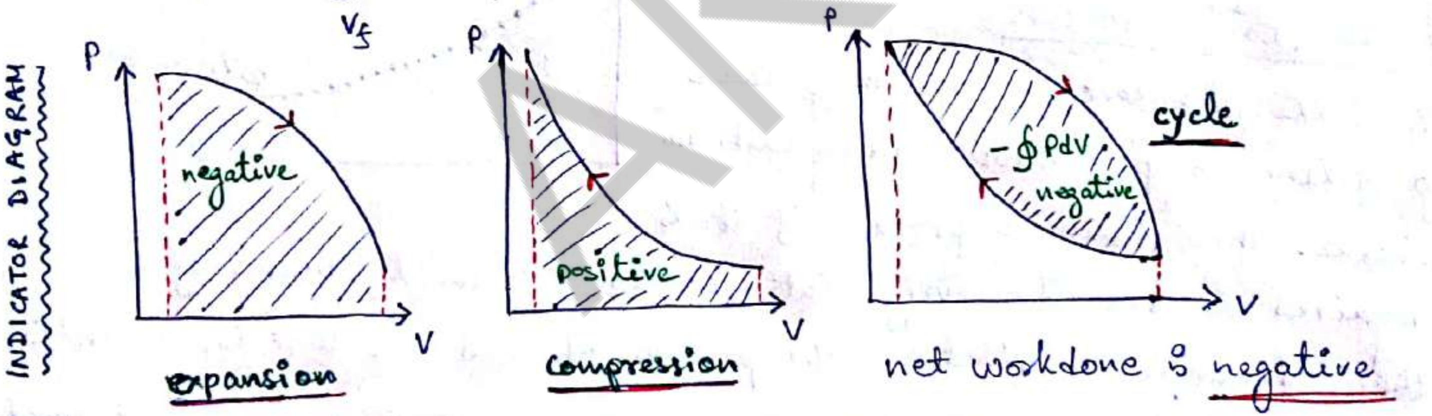
If $dV > 0$ (expansion), $đW < 0$ (negative work)

$dV < 0$ (compression), $đW > 0$ (positive work)

for finite quasistatic process $W = -\int_{V_i}^{V_f} PdV$

This depends on path because $P = P(T,V) \Rightarrow P = P(V)$ for given T.

∴ Workdone "on" a system from larger volume ($V_i$) to smaller volume ($V_f$) is $W_{if} = -\int_{V_i}^{V_f} PdV$ & for expansion, workdone "by" system is $W_{fi} = -\int_{V_f}^{V_i} PdV$ and when path is quasistatic, $W_{fi} = -W_{if}$

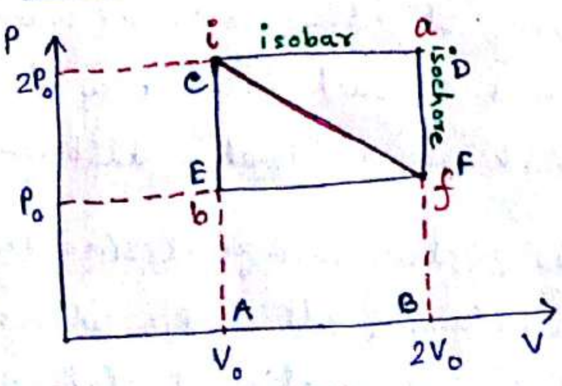


expansion

compression

net workdone is negative

### Path dependency: Exact & inexact differentials



Many route to go from $i \rightarrow f$.

ⓐ $i \rightarrow a$ (isobaric) ⇒ $a \rightarrow f$ (isochoric)

$W.D. = -\underbrace{\int PdV}_{\text{area ABDC}} = -2P_0V_0$

ⓑ $i \rightarrow b$ (isochoric) ⇒ $b \rightarrow f$ (isobar)

$W.D. = -\underbrace{\int PdV}_{\text{area ABFE}} = -P_0V_0$

ⓒ $i \to f$, W.D. $= -\int_{\text{area ABFC}} PdV = -\int_{\text{area ABEF}} PdV - \int_{\text{area EFC}} PdV = -\frac{3}{2}P_0V_0$

Infinitesimal amount of work is "inexact differential", means it is not the differential of a function of thermodynamic coordinates. That's represented with $\text{đ}W$, & it depends on the path.

Suppose if functional differential $df = 2xy^3dx + 3x^2y^2dy$
$= d(x^2y^3)$.

$\int_{x=y=1}^{x=y=3} df$ depends only on the limit & not on path. $df$ is an "exact differential".

## Isothermal quasistatic expansion/compression

Using $PV = nRT$, $W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V}dV = -nRT\ln\frac{V_f}{V_i}$

$n = 2$ kmol, $T = 273$K ($0^\circ$C), $R = 8.31$ kJ/kmol·K, $V_i = 4m^3$, $V_f = 1m^3$ (compression), $W = 6300$ kJ = positive work (work done "**on**" gas)

## Isothermal quasistatic increase of pressure on solid

$V = V(P,T)$ $\therefore dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT = \left(\frac{\partial V}{\partial P}\right)_T dP$ (isothermal)

isothermal compressibility $= \frac{1}{\text{bulk modulus}} = \frac{1}{dP/\left(\frac{dV}{V}\right)}$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$\therefore dV = -\kappa V dP$

So Work done $= \int_{P_i}^{P_f} P\kappa V dP \approx \frac{\kappa V}{2}(P_f^2 - P_i^2) = \frac{\kappa m}{2\rho}(P_f^2 - P_i^2)$

for copper, at $T = 273$K, $\rho = 8930$ kg/m$^3$, $\kappa = 7.16 \times 10^{-12}$ Pa$^{-1}$, $m = 100$ kg, $P_i = 0$, $P_f = 1000$ atm $= 1.013 \times 10^8$ Pa

$W = 0.411$ kJ. = positive work (work done "**on**" copper)

## ⓑ Isothermal stretching a wire

If tension $\mathcal{F}$ changes length of wire from L to L+dL (extension) then work done on the wire (positive work) is

$$W = \int_{L_i}^{L_f} \mathcal{F}\, dL \quad , \quad \text{remember, } L = L(\mathcal{F}, T) \text{ \& for isothermal}$$

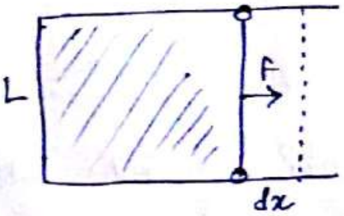
$$dL = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F} + \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} dT = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F}$$

$$= \frac{L}{AY}\, d\mathcal{F} \text{ using "isothermal Youngs modulus".}$$

$$= \int_0^{\mathcal{F}} \frac{L}{AY}\, \mathcal{F}\, d\mathcal{F}$$

$$= \frac{L}{2AY}\, \mathcal{F}^2.$$

## ⓒ Surface film

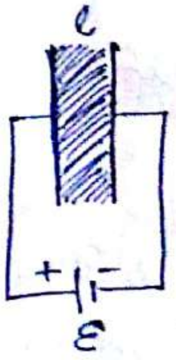


If $\gamma$ is surface tension of a double surface film with liquid in between then force exerted on both film is $2\gamma L$ & for displacement dx, work done "on" the film (positive)

$$dW = 2\gamma L\, dx = \gamma\, dA \qquad (\text{as } dA = 2L\,dx)$$

$$\therefore\ W = \int_{A_i}^{A_f} \gamma\, dA \qquad \left[\text{For soap bubble } A = 2\times 4\pi R^2,\ W = 8\pi\gamma R^2\right]$$

## ⓓ Polarization of a dielectric solid



Consider a slab of isotropic dielectric material between conducting plates of a parallel-plate capacitor, with area A & separation l connected to a battery to yield potential difference ℰ.

Uniform field intensity $E = \frac{\mathcal{E}}{l}$.

work done against the electric field to move dZ amount of charge

$$\text{is } dW = \mathcal{E}\, dZ = E l\, dZ = E l A\, dD \qquad [\text{as } Z = DA = \text{total charge \& } D = \text{electric displacement}]$$

$$= E V\, dD$$

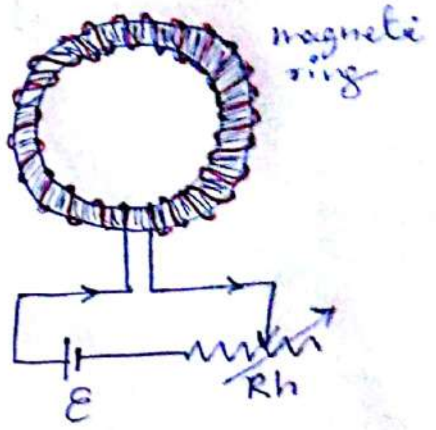
$$\text{Now } D = \epsilon E = \epsilon_0 E + \frac{P}{V} \qquad [\text{as } V = lA]$$

∴ $dD = \left(\epsilon_0 dE + \frac{dP}{V}\right)$ & then

$$\text{đ}W = EV\left(\epsilon_0 dE + \frac{dP}{V}\right) = \underbrace{V\epsilon_0 E\,dE}_{[\text{vacuum}]} + \underbrace{E\,dP}_{[\text{material}]}$$

∴ Net work on dielectric is $\text{đ}W = E\,dP$, $W = \int_{P_i}^{P_f} E\,dP$

## ⓔ Magnetization of a magnetic solid



magnetic ring cross sectional area A, circumference L. Insulated wire is wind on that (Toroidal winding)

Current in the winding initiate magnetic field with induction B (uniform). Using Rheostat if current is changed in time dt then

$$\varepsilon = -NA\frac{dB}{dt}$$ (Faraday's principle of EM induction)

N = number of turns and $H = ni = \frac{Ni}{L} = \frac{NAi}{V}$ $(V = AL)$

If dZ charge is transferred in circuit, work done "by" system to maintain current is $\text{đ}W = -\varepsilon\,dZ = NA\frac{dB}{dt}dZ$

$$= NA\frac{dZ}{dt}dB = NAi\,dB$$

$$= VH\,dB.$$

If M = total magnetic moment, then

$$B = \mu H = \mu_0 H + \mu_0\frac{M}{V} \Rightarrow dB = \mu_0 dH + \mu_0\frac{dM}{V}$$

$$\therefore \text{đ}W = \underbrace{V\mu_0 H\,dH}_{[\text{vacuum}]} + \underbrace{\mu_0 H\,dM}_{[\text{material}]}$$

Work done to change the magnetization is $\text{đ}W = \mu_0 H\,dM$

is $W = \mu_0\int_{M_i}^{M_f} H\,dM$.

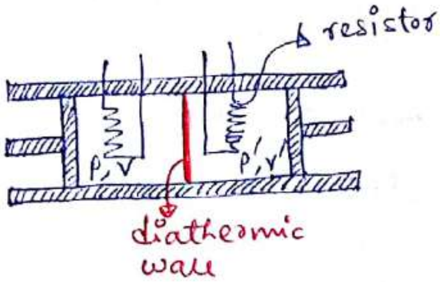
Work (extensive) = Intensive quantity × Extensive quantity

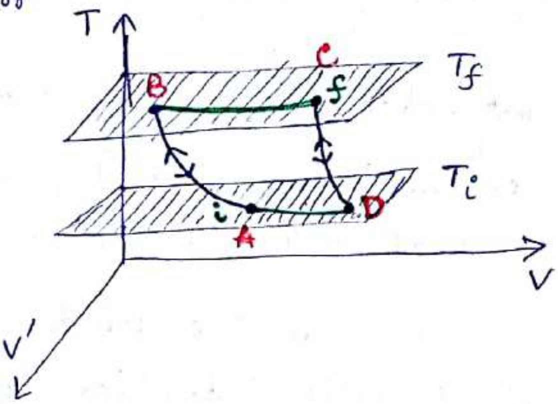
Using Curie's law $M = c\frac{H}{T}$

$$W = \mu_0 \int_{M_i}^{M_f} \frac{MT}{c} dM = \frac{\mu_0 T}{2c}(M_f^2 - M_i^2)$$

$$= \mu_0 \int_{H_i}^{H_f} H \frac{c}{T} dH = \frac{\mu_0 c}{2T}(H_f^2 - H_i^2)$$

## Adiabatic Work





System can undergo adiabatic work with surroundings ⓐ moving pistons quasistatically (slowly) $W = -\int P dV$ ⓑ non-quasistatic (free expansion) ⇒ fast so that velocity of molecules do no work at piston. Also work can be done by dissipating electrical energy on resistors

Path ABC from $i \to f$, AB is reversible quasistatic adiabatic compression between two isothermal planes. BC correspond to adiabatic irreversible dissipation of electrical energy to keep T = constant, as energy can be added to resistor but cannot be extracted.

There are many such other path (e.g. ADC), meaning adiabatic work is same along all paths.

1st law of Thermodynamics: If a system is changed from initial state to final state by adiabatic work, the work done is same for all adiabatic path connecting two states.

$W_{i\to f}$ (adiabatic) $= U_f - U_i = dU$ (perfect differential)

U = internal energy function

But if system change state nonadiabatically, then to conserve energy of heat is to be added to system (+ive) / subtracted (−ive) from the system, $U_f - U_i = Q + W$.

for infinitesimal process, $\boxed{dU = \bar{d}Q + \bar{d}W}$ & if its quasistatic then $dU$ & $\bar{d}W$ can be expressed in thermodynamic coordinates.

For hydrostatic system $dU = \bar{d}Q - PdV$

wire $dU = \bar{d}Q + \mathcal{F}\, dL$

surface film $dU = \bar{d}Q + \mathcal{S}\, dA$

paramagnetic Rod $dU = \bar{d}Q + \mu_0 \mathcal{H}\, dM$

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

$$\therefore \bar{d}Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \quad \text{——— ①}$$

$$\text{or} \quad \frac{\bar{d}Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}$$

(i) $V =$ constant, $\left(\frac{\bar{d}Q}{dT}\right)_V = \boxed{\left(\frac{\partial U}{\partial T}\right)_V = C_V}$

(ii) $P =$ constant, $\left(\frac{\bar{d}Q}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$

$$\text{or} \quad C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\beta \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{or} \quad \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V\beta} - P}$$

Cyclic process $dU = 0$, $\bar{d}Q = PdV$. heat = work.

Also, from equation ① $\bar{d}Q = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$

For ideal gas, no potential energy, free expansion do not affect heat.

$PdV = 0$, $\bar{d}Q = 0$ at constant temperature $dT = 0$, $\left(\frac{\partial U}{\partial V}\right)_T dV = 0$.

$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow$ internal energy is independent of volume.

$\therefore \boxed{\bar{d}Q = C_V dT + PdV}$ for ideal gas.

Equation of state $PV = nRT$ or $PdV + VdP = nRdT$ infinitesimal quasistatic process

$$\therefore \bar{d}Q = (C_V + nR)dT - VdP$$

or $\frac{\bar{d}Q}{dT} = C_V + nR - V\frac{dP}{dT}$, $P$ constant, $\boxed{C_P = C_V + nR}$

Also $dq = C_p dT - VdP$

## Elasticity of perfect gas

Isothermal bulk modulus $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$

Adiabatic bulk modulus $E_q = -V\left(\frac{\partial P}{\partial V}\right)_q$.

For isothermal change $PV = RT = \text{constant}$

$$PdV + VdP = 0 \quad \therefore \left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}.$$

For adiabatic change $PV^\gamma = \text{constant}$, $\gamma PV^{\gamma-1}dV + dP V^\gamma = 0$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_q = -\frac{\gamma P}{V}. \qquad \therefore \boxed{\frac{E_q}{E_T} = \gamma.}$$

## Second law of Thermodynamics

This is an extension of first law with a direction of the process → experimental development of engines.

## Reversibility & Irreversibility

reversibility = system + surroundings from changed state can restore back to initial configuration without change of universe. The opposite to that is irreversible process.

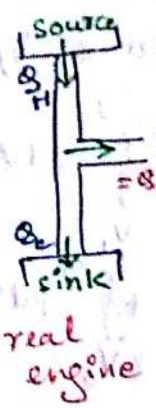
2nd law → Carnot's finding in ideal engine → Clausius statement → Kelvin's statement → birth of "entropy".

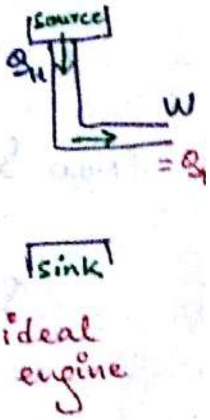
## Conversion of work to heat

In previous examples, we saw how heat can be generated indefinitely at the expense of work. To study the converse process, there may be 1 or more than 1 (series of) processes. At first it appeared that isothermal expansion may be suitable for conversion of heat into work, but its not indefinite. Thus a cycle is required that can be taken back & forth.

If in a cycle $Q_H$ amount of heat is absorbed & $Q_c$ ($Q_c < Q_H$) amount of heat is radiated & W amount of work is needed then the mechanical device is a "Heat Engine". Efficiency of such engine is defined as

$$\eta = \frac{\text{work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H}$$

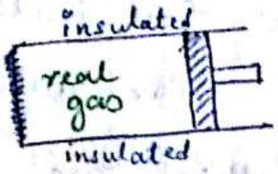


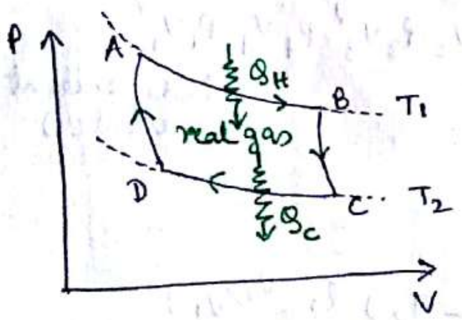


Hot reservoir of infinite heat capacity is "source" & cold reservoir is called "sink".

## Carnot cycle

It's maximum efficient engine (nearly ideal)





AB, CD = isothermal
BC, DA = adiabatic

Consists of four reversible steps.

(1) Isothermal expansion A → B :

Cylinder is placed in contact with a heat reservoir at temperature $T_1$ & gas expands isothermally from $(P_1, V_1, T_1)$ to $(P_2, V_2, T_1)$. $Q_H$ amount of heat taken from source & $-W_1$ amount of work done "by" the gas.

(2) Adiabatic expansion B → C : The gas is allowed to expand adiabatically in insulated environment. The temperature falls to $T_2$ & volume changes to $V_3$. $Q = 0$ and work done "by" the gas is $-W_2$.

(3) Isothermal compression C → D : The gas at very low pressure is now reversibly compressed in sink at temperature $T_2$ from volume $V_3$ to $V_4$. Heat rejected to sink is $Q_c$ & work done by the gas is $+W_3$ (+ive because work done "on" gas).

(4) Adiabatic compression D → A : Now the system is adiabatically restored to initial state from $V_4 \to V_1$, $T_2 \to T_1$. $Q = 0$, work done

by the gas is $+W_4$ (+ive because workdone "on" the gas).

from first law of thermodynamics $\oint_c dU = 0$

or $\oint_c dQ - \oint_c dW = 0$ or $Q_H + 0 - Q_c + 0 = -W_1 + W_2 + W_3 + W_4$

∴ Work done by engine = difference of heat absorbed & rejected.

Now $Q_H = -\int_{V_1}^{V_2} p\,dV = -RT_1 \ln\frac{V_2}{V_1} = W_1$.

$Q_c = +\int_{V_3}^{V_4} p\,dV = -RT_2 \ln\frac{V_3}{V_4} = W_3$

But for isothermal processes $P_1V_1 = P_2V_2$, $P_3V_3 = P_4V_4$

for adiabatic processes $P_2V_2^{\gamma} = P_3V_3^{\gamma}$, $P_4V_4^{\gamma} = P_1V_1^{\gamma}$

Multiplying, $P_1V_1\, P_2V_2^{\gamma}\, P_3V_3\, P_4V_4^{\gamma} = P_2V_2\, P_3V_3^{\gamma}\, P_4V_4\, P_1V_1^{\gamma}$ (independent events)

or $(V_2V_4)^{\gamma-1} = (V_3V_1)^{\gamma-1}$

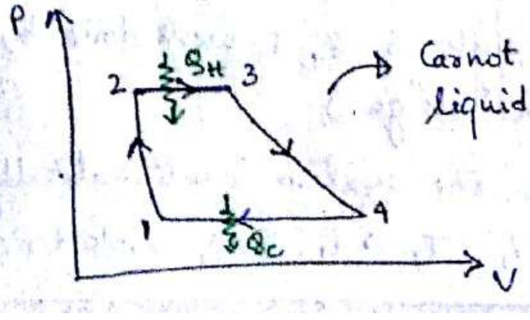
or $V_2/V_1 = V_3/V_4$

∴ Efficiency $\eta = \frac{Q_H - Q_c}{Q_H} = \frac{-R(T_1 - T_2)\ln(V_2/V_1)}{-RT_1\ln(V_2/V_1)}$

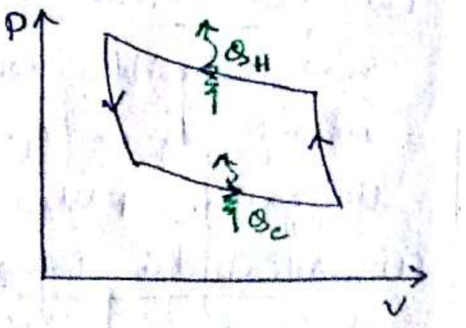
$= \frac{T_1 - T_2}{T_1} \neq 100\%$

∴ $\boxed{\frac{Q_H}{T_1} = \frac{Q_c}{T_2}}$

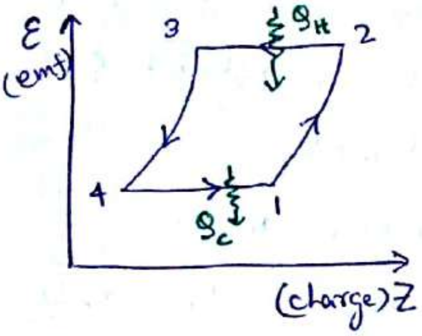
We can also reverse the cycle from any point of the indicator diagram. In that case $Q_c$ heat is removed from sink & $Q_H$ is delivered to source & work must be done to the system. The system then works as a refrigerator.



Carnot cycle of liquid+vapour



1 → 2 reversible adiabatic compression to temperature $T_H$
2 → 3 reversible isothermal isobaric vaporization
3 → 4 reversible adiabatic expansion temperature falls to $T_C$
4 → 1 reversible isothermal isobaric condensation



1 → 2 reversible adiabatic flow of charge from − to + to temperature $T_H$.
2 → 3 reversible isothermal flow of charge from + to −
3 → 4 reversible adiabatic flow of charge to temp. $T_C$
4 → 1 reversible isothermal flow of charge

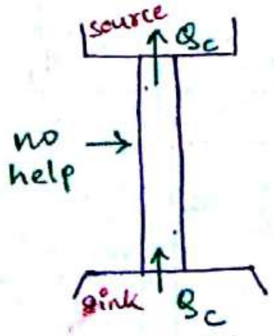
## Second low of Thermodynamics

**Kelvin's Statement** It is impossible by any inanimate object to derive mechanical work from any portion of the matter by cooling it below the temperature of the coldest of the surrounding objects.

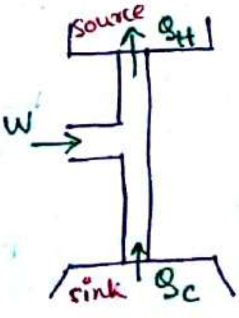
**Plank's Statement** It is impossible to fabricate an engine working in a complete cycle to produce no effect other than raising a weight & cooling of a hot reservoir.

P-K Statement → It is impossible to produce an ideal engine.

**Clausius Statement** It is impossible for a self-acting machine unaided by any external agency to convey heat from one body at lower temperature to another at a higher temperature, Heat cannot by itself transit from a colder to a warmer body or it is impossible to construct an ideal refrigerator.

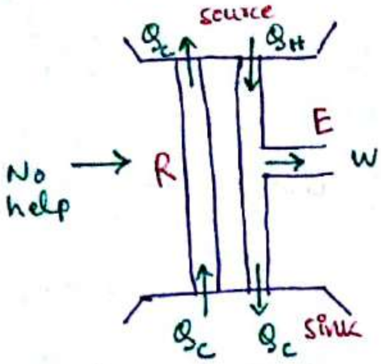


ideal refrigerator



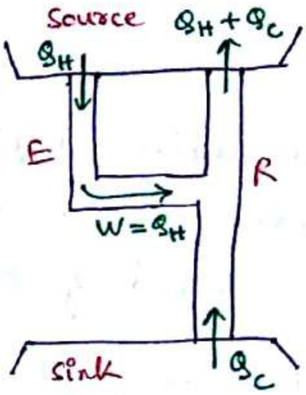
real refrigerator

## Equivalence of Kelvin-Plank & Clausius statement



Suppose we disobey Clausius's statement & make an ideal refrigerator R that transfer $Q_c$ from sink to source without any work. But engine E draws $Q_H$ from source & returns $Q_c$ to sink & delivering work $Q_H - Q_c$.

$\therefore$ Combined R-E system form a self-acting device drawing $Q_H - Q_c$ heat from hot reservoir & convert fully this heat into work without change in sink → violation of K-P statement.



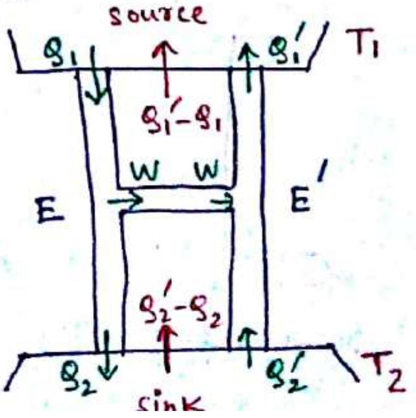
Consider again an ideal engine E that rejects no heat to sink & violate K-P statement. $Q_H$ heat is fully converted to work W which is feeded to a refrigerator R to extract $Q_c$ heat from sink. Again E-R forms a self-acting device that transfers $Q_c$ from sink to source without any change elsewhere → violation of Clausius statement.

1st law of Thermodynamics = conservation of energy

2nd law of Thermodynamics = directionality (may not be true always)

## Carnot's theorem

Efficiency of all reversible engines operating between same two temperatures is equal & no irreversible engine can have a better efficiency compared to the reversible engine between same two temperatures.



Clausius & Kelvin showed that this theorem is a consequence of the 2nd law of thermodynamics. $\eta$ is independent of working substance & depends only on $T_1, T_2$.

**proof** Suppose engine E & E' working between $T_1$ & $T_2$ differ in working substance or initial pressure or length of stroke. E runs forward & E' run backward (refrigerator). The system is so made that work done by E is exact amount of work needed for E' to function. Suppose $\eta$ (efficiency) of E > $\eta$ of E'.

$$\therefore \frac{Q_1 - Q_2}{Q_1} > \frac{Q_1' - Q_2'}{Q_1'}$$

. By construction work done per cycle be E = work needed per cycle for E'

$$\therefore W = W' \Rightarrow Q_1 - Q_2 = Q_1' - Q_2'$$

$$\therefore \frac{1}{Q_1} > \frac{1}{Q_1'} \quad \therefore Q_1' > Q_1 \quad \text{and} \quad Q_2' > Q_2 \text{ to satisfy } W = W'$$

Therefore hot source gains heat $Q_1' - Q_1$ and cold sink loses heat $Q_2' - Q_2$ and no work is done by the combined E + E' system. We've transferred heat from a cold to hot body without performing work is direct contradiction to Clausius statement.

$$\therefore \eta \ngtr \eta'$$

Similarly, by reversing the engine E backward & E' forward we can prove that $\eta' \ngtr \eta$. So the only possibility is

$$\boxed{\eta = \eta'}$$

For irreversible engine we can show by the same procedure that $\eta_{irr} \ngtr \eta_{rev}$ but due to irreversibility we "cannot" show $\eta_{rev} \ngtr \eta_{irr}$

$\therefore \eta_{irr}$ is either equal to or less than $\eta_{rev}$.

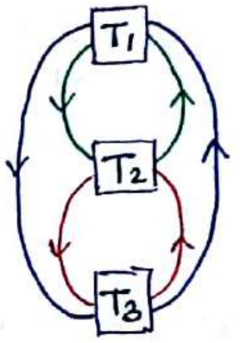
$$\therefore \boxed{\eta_{rev} \geq \eta_{irr}}$$

# Kelvin scale / Absolute scale / Thermodynamic scale of temperature

Using Carnot engine, temperature can be defined in term of energy & the scale so obtained is independent of nature of any particular substance. Efficiency of all reversible engine is a function of two temperatures only

$$\eta = \frac{W}{Q_1} = f(T_1, T_2) = \frac{Q_1 - Q_2}{Q_1} \Rightarrow \frac{Q_1}{Q_2} = \frac{1}{1-f(T_1,T_2)}$$
$$= F(T_1, T_2).$$

Suppose we have three reversible engines working between the temperature $(T_1, T_2)$, $(T_2, T_3)$ & $(T_1, T_3)$, then



$$\frac{Q_1}{Q_2} = F(T_1, T_2), \quad \frac{Q_2}{Q_3} = F(T_2, T_3)$$

$$\therefore \frac{Q_1}{Q_3} = F(T_1, T_2)\, F(T_2, T_3) = F(T_1, T_3).$$

This can satisfy if & only $F(T_1, T_3) = \frac{\psi(T_1)}{\psi(T_3)}$

$\therefore$ For any reversible engine we can write $\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)}$

Now if $T_1 > T_2$, $Q_1 > Q_2$ and therefore $\psi(T_1) > \psi(T_2)$

$\therefore$ $\psi(T)$ is a monotonically increasing function of temperature

$$\therefore \boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$

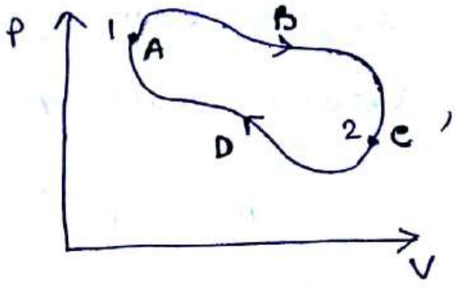
So we have defined a new scale of temperature whose ratio depends on heat absorbed & heat rejected. in a reversible engine.

$T = 0°$ in this scale is when $Q_2 = 0$ & $\therefore$ $W = Q_1$ & $\eta = 100\%$ (ideal engine). $T$ cannot be less than this as $Q_2 < 0$ mean engine would be drawing heat both from source & sink which is impossible due to direct violation of 2nd law. $\therefore$ $T = 0$ is the lowest attainable temperature when one gets an ideal engine.

**Entropy** In any reversible process, if heat Q is added at temperature T and rejects Q′ heat at temperature T′, then $\frac{Q}{T} = \frac{Q'}{T'}$

or $\frac{Q}{T} - \frac{Q'}{T'} = 0$ or $\sum \frac{Q}{T} = 0$ ( Q = +ive heat absorbed
= −ive heat rejected)

Any reversible transformation is made of a number of infinitesimal reversible isothermal & adiabatic process. ∴ for any reversible cyclic process ABCD $\oint_C \frac{\text{đ}Q}{T} = 0$. This is called "Clausius Theorem".



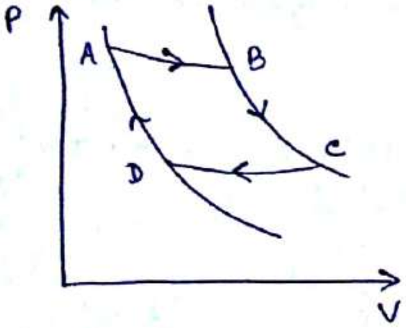
We can define a thermodynamic function "entropy" $dS = \frac{\text{đ}Q}{T}$ that has the property

$$\oint_{ABCD} \frac{\text{đ}Q}{T} = 0 \quad \text{or} \quad \oint_{ABC} \frac{\text{đ}Q}{T} + \oint_{CDA} \frac{\text{đ}Q}{T} = 0$$

$$\text{or} \quad \oint_{ABC} \frac{\text{đ}Q}{T} = \oint_{ADC} \frac{\text{đ}Q}{T}.$$

This means that $\int \frac{\text{đ}Q}{T}$ is independent of the path and depends only on the initial & final point 1 & 2.

∴ $dS = \frac{\text{đ}Q}{T}$ is an exact differential. Unit cal/°K.



To understand property of dS, consider a reversible cycle constituted by two adiabatic AD & BC & two isothermals AB & CD.

For AD & BC, $\text{đ}Q = 0$ ∴ $dS = 0$. & hence

$$\int_A^B \frac{\text{đ}Q}{T} = \int_D^C \frac{\text{đ}Q}{T}.$$

Point A & B may be taken anywhere on the adiabatic AD & BC, still the integral will remain same as $\text{đ}Q = 0$ for adiabatic process. Hence it follows that if we pass from one adiabatic to other, $\int_1^2 \frac{\text{đ}Q}{T}$ increases by a definite amount independent of the manner of transformation. We can choose any standard state n & then $\int_n^A \frac{\text{đ}Q}{T}$ on a reversible path depends only on state n & A. If my standard reference state n is fixed, integral is a function of state A only.

and termed as $S_A$ & can be different if we choose different n.

Thus the entropy is undetermined to the extent of an additive constant that represents entropy of an arbitrarily chosen standard state with respect to state with zero entropy.

$\therefore S_A = S_n + \int_n^A \frac{\bar{d}q}{T}$ . $S_n$ = entropy at state n which according to law of thermodynamics $S_n$ cannot be determined & absolute value of entropy cannot be found out. But change of entropy between states A & B can be accuratily determined,

$$S_A - S_B = S_n + \int_n^A \frac{\bar{d}q}{T} - S_n - \int_n^B \frac{\bar{d}q}{T} = \int_B^A \frac{\bar{d}q}{T}$$

This is valid for equilibrium states only & for nonequilibrium states can approach equilibrium by irreversible process in which entropy increases.

Also $\bar{d}q = dU + PdV$ is an inexact differential as $\int_1^2 (dU + PdV)$ requires a knowledge of path. But $dS = \frac{\bar{d}q}{T}$ is perfect or exact differential.

$$\boxed{\underset{(dS)}{\text{Exact differential}} = \underset{(\bar{d}q)}{\text{Inexact differential}} \times \underset{(1/T)}{\text{Integrating factor}}}$$

Example $df = 3xy\,dx + 2x^2\,dy$ = inexact $\frac{\partial^2 f}{\partial x \partial y} \neq \frac{\partial^2 f}{\partial y \partial x}$

But $\underbrace{xy}_{\text{I.F.}}\,df = d\phi = 3x^2y^2\,dx + 2x^3y\,dy = d(x^3y^2)$ = exact.

**Caratheodory's Principle** In the immediate neighbourhood of any arbitrary initial state, there exists neighbouring states which are not accessible from the initial state along adiabatic paths.

## Entropy of an ideal gas

If an ideal gas of m gm at temperature T & volume V is given heat $đQ$, then change in entropy is $mS = \int \frac{dU + PdV}{T}$

Now $dU = mC_v dT$, $P = \frac{mRT}{MV}$

$\therefore mS = m\left\{ C_v \int_{T_1}^{T_2} \frac{dT}{T} + \frac{R}{M} \int_{V_1}^{V_2} \frac{dV}{V} \right\}$ for $(P_1, V_1; T_1) \rightarrow (P_2, V_2, T_2)$

In general for monoatomic gas $C_v \neq C_v(T)$ & so

$mS = m\{C_v \ln T + R/M \ln V\} + \text{constant}$ $\therefore S = S(T, V)$.

To obtain $S = S(T, P)$, we use $C_p - C_v = R/M$.

$\therefore mS = m(C_p - R/M) \ln T + \frac{mR}{M} \ln V + \text{constant}$

$= mC_p \ln T - \frac{mR}{M} \ln (T/V) + \text{constant}$ $\left[ PV = \frac{mRT}{M} \text{ so } \right.$

$= mC_p \ln T - mR/M \ln (PM/mR) + \text{constant}$ $\left. T/V = \frac{PM}{mR} \right]$

$mS = mC_p \ln T - mR/M \ln P + \text{constant}$.

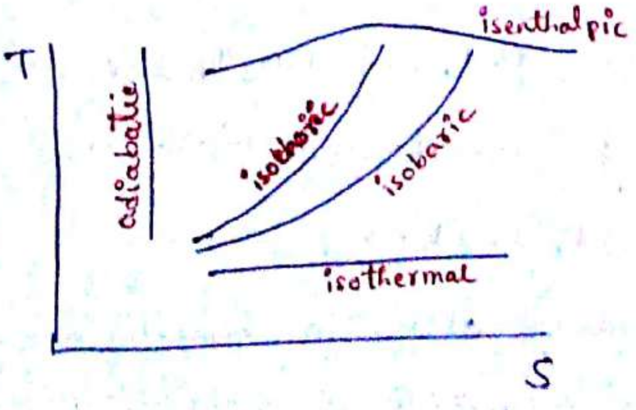
**Isothermal system** For isothermal change of state of gas $dU = 0$

$\therefore dS = \frac{PdV}{T}$ and using $PV = nRT$

$= \frac{nR\,dV}{V}$ $\therefore S = nR \ln\left(\frac{V_2}{V_1}\right)$

**Adiabatic system** for adiabatic change $đQ = 0$ & so $dS = 0$. No change in entropy of the system (isentropic process).

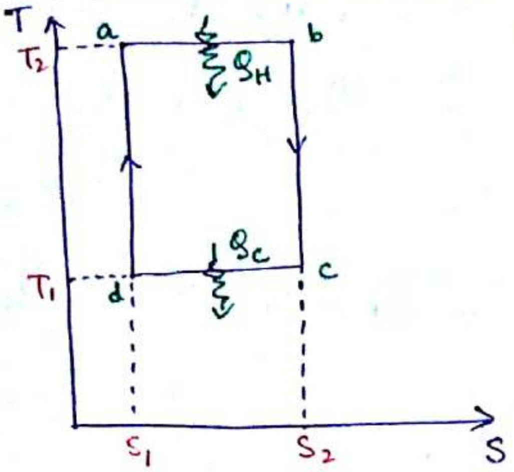
In free expansion of a perfect gas into an empty vessel in a thermally insulated environment, gain in entropy is $\Delta S = \int \frac{PdV}{T} = R \ln V_2/V_1$.



In a reversible process $Q_R = \int_i^f T dS$

So the heat is the area under a curve in T-S plane.

## Carnot's cycle in TS diagram



The carnot cycle in TS diagram is a parallelogram.

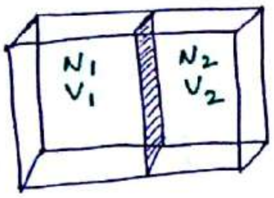
$$Q_H = T_2(S_2 - S_1)$$

$Q_c = T_1(S_2 - S_1)$ and $dQ = 0$ for bc & da lines.

$$\therefore \text{Efficiency } \eta = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H}$$

$$= \frac{(S_2 - S_1)(T_2 - T_1)}{T_2(S_2 - S_1)} = 1 - \frac{T_1}{T_2}$$

## Gibbs' Paradox



Consider an ideal gas of N particles in a container with volume V. A partition divides $N_1$ & $N_2$ particles & volume $V_1$ & $V_2$ such that

$N = N_1 + N_2$, $V = V_1 + V_2$ and $n = \frac{N_1}{V_1} = \frac{N_2}{V_2}$ (equal number density)

Using
$$S = C_V \ln T + R \ln V + \text{constant}$$
$$= \frac{3}{2} R \ln T + R \ln V + \text{constant}$$
$$= \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V + \text{constant}$$

Firstly, $T \to 0$, $S \to -\infty$ !! violating 2nd law of thermodynamics

Secondly, $S \propto N$ for a given V !! This expression from classical framework is not right. This also leads to gives paradox ⇒

In the partitioned state
$$S_1 = \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V_1 + \text{const.}$$
$$S_2 = \frac{3}{2} N_2 k_B \ln T + N_2 k_B \ln V_2 + \text{const.}$$

The partition is now removed & gas comes to well-mixed state.

$$S = \frac{3}{2}(N_1 + N_2) k_B \ln T + (N_1 + N_2) k_B \ln(V_1 + V_2)$$

Now its monoatomic gas of identical atoms, so removing the partition shouldn't increase entropy as particles are indistinguishable.

So $\Delta S = S - (S_1+S_2) = 0$ But here we find

$$\Delta S = (N_1+N_2)k_B \ln(V_1+V_2) + \cancel{\frac{3}{2}(N_1+N_2)k_B \ln T} -$$

$$N_1 k_B \ln V_1 - \cancel{\frac{3}{2}N_1 k_B \ln T} - N_2 k_B \ln V_2 - \cancel{\frac{3}{2}N_2 k_B \ln T}$$

$$= N_1 k_B[\ln(V_1+V_2) - \ln V_1] + N_2 k_B[\ln(V_1+V_2) - \ln V_2]$$

$$= N_1 k_B \ln V/V_1 + N_2 k_B \ln V/V_2 \neq 0.$$

This paradox cannot be rissolved in classical MB statistics & need statistical physics, namely quantum statmech where atoms are indistinguishable (leads to Sakkur-Tetrode formula of entropy in ideal gas) taking Stirling's approximation ($\ln N! = N\ln N - N$). Now, if we correct $S$ accordingly,

$$\boxed{S = Nk_B \ln\left(\frac{V}{N}\right) + \frac{3}{2}Nk_B \ln T + \text{constant}}$$

Then $S-(S_1+S_2) = (N_1+N_2)k_B \ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2}$

$$= N_1 k_B \ln\frac{V}{N} - N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V}{N} - N_2 k_B \ln\frac{V_2}{N_2}$$

$$= N_1 k_B \ln\left(\frac{VN_1}{NV_1}\right) + N_2 k_B \ln\left(\frac{VN_2}{NV_2}\right)$$

But $n = \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2}$ (no. density is constant)

$$\therefore \ln\left(\frac{VN_1}{NV_1}\right) = \ln\left(\frac{n}{n}\right) = \ln(1) = 0$$

$$\ln\left(\frac{VN_2}{NV_2}\right) = 0. \qquad \therefore \underline{\Delta S = 0}$$

Gibb's paradox thus gets rissolved.

## Entropy increase in Irreversible process

Consider an irreversible process in which temperature of a body at $T_1$ is increased to $T_2$ by coupling to a reservoir at $T_2$. The initial & final state of the body is same & its irreversible as heat flow from reservoir to body cannot be reversed. But change in entropy of the body is same for both reversible or irreversible process as its not path dependent.

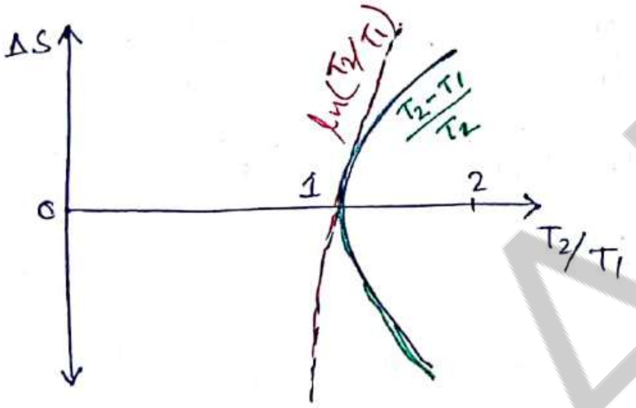
Suppose pressure remains constant, then change in entropy of the body is $\Delta S_{body} = \int_{T_1}^{T_2} C_p \frac{dT}{T} = C_p \ln(T_2/T_1) > 0$ as $T_2 > T_1$.

The reservoir temperature $T_2$ remains constant, so change in entropy is same for reversible isothermal process (heat flowing into reservoir) & irreversible isothermal process (heat only flowing out)

Heat flow into the body is $đQ = C_p(T_2 - T_1)$ & this is the heat came out from reservoir, so decrease in entropy of reservoir is $\Delta S_{reservoir} = -\frac{đQ}{T_2} = -\frac{C_p(T_2 - T_1)}{T_2}$

Total change of entropy of the composite system

$$\Delta S = \Delta S_{body} + \Delta S_{reservoir} = C_p\left[\ln(T_2/T_1) - \frac{T_2 - T_1}{T_2}\right]$$



For $T_2 > T_1$ $\ln(T_2/T_1) > \frac{T_2 - T_1}{T_2}$

∴ Increase in entropy of the body is always greater than decrease of entropy of reservoir & ∴ entropy of universe always increases in irreversible process.

Even when the body is at higher temperature than reservoir the situation is reversed but entropy of universe increases. So whenever heat flows across finite temperature difference (~~reversible~~ irreversible), entropy of universe increases. For reversible process entropy remains constant.

$S_f = S_i$ for reversible

$S_f > S_i$ for irreversible

This principle of increase in entropy can be termed as $2^{nd}$ law of thermodynamics. Clausius restated that $1^{st}$ law is energy of the universe remains constant & $2^{nd}$ law is entropy of universe tends to be the maximum.

## Entropy flow & entropy production

Consider heat conduction along a copper wire that are held between two reservoirs at $T_1$ & $T_2$ $(T_1 > T_2)$. If heat current or rate of flow of heat is $I_Q$ then in unit time, hot source decreases its entropy by $I_Q/T_1$, sink increases entropy by $I_Q/T_2$ & copper wire at steady state suffers no change in entropy. So $\Delta S_{universe} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} > 0$.

We can see it from the perspective of wire that the hot source lost entropy to the wire & there is a flow of entropy into the wire of $I_Q/T_1$ per unit time. The sink gained entropy so there was a flow of entropy out of the wire. $I_Q/T_2$.

Entropy production in wire $\frac{dS}{d\tau} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} = I_Q \frac{T_1 - T_2}{T_1 T_2}$

& if $T_1 = T + \Delta T$, $T_2 = T$, $T_1 T_2 \approx T^2$

$$\therefore \frac{dS}{d\tau} = I_Q \frac{\Delta T}{T^2} = \frac{I_Q}{T} \frac{\Delta T}{T} = I_S \frac{\Delta T}{T}$$

$\frac{dS}{d\tau}$ ↓ entropy production

$I_S$ ↓ entropy current

CW 1. A reversible engine in Carnot cycle between 100°C & 0°C does work 1200 Kg-metre / cycle. Find the amount of heat drawn from source. $J = 4.18 \times 10^7$ ergs/cal.

$$Q_1/T_1 = Q_2/T_2 = \frac{Q_1 - Q_2}{T_1 - T_2} = \frac{W}{T_1 - T_2} \qquad W = mgh$$

$$\therefore Q_1 = \frac{W T_1}{T_1 - T_2} = \frac{1200 \times 10^3 \times 980 \times 373}{100 \times 4.18 \times 10^7} = 10494 \text{ cal.}$$

2. A body of constant heat capacity $C_p$ at temperature $T_i$ is put in contact with reservoir at $T_f$. At constant pressure, body comes to equilibrium. Show that entropy change of universe is $C_p[x - \ln(1+x)]$ where $x = -\frac{T_f - T_i}{T_f}$.

Gain in entropy of the body $\Delta S_{body} = \int_{T_i}^{T_f} \frac{C_p\, dT}{T} = C_p \ln(T_f/T_i)$

Loss of entropy of reservoir $\Delta S_{reservoir} = -\frac{dQ}{T_f} = -\frac{C_p(T_f - T_i)}{T_f}$

∴ Total change in entropy of the universe $\Delta S = C_p \ln\frac{T_f}{T_i} - C_p \frac{T_f - T_i}{T_f}$

$$= \left(C_p \ln(1+x)^{-1} + C_p x\right) = C_p(x - \ln(1+x))$$

3. According to Debye's law, the molar heat capacity at constant volume of Diamond varies with temperature as

$C_V = 3R\frac{4\pi^4}{5}\left(\frac{T}{\Theta}\right)^3$. What is the entropy change in units of R of a diamond of 1.2 gm when it's heated at constant volume from 10 to 350K. Atomic weight of Carbon is 12 gm & $\Theta = 2230$ K.

$$\Delta S = \frac{1.2}{12}\int_{10}^{350} \frac{C_V\, dT}{T} = \frac{1.2}{12}\, 3R \frac{4\pi^4}{5}\frac{1}{\Theta^3}\int_{10}^{350} T^2 dT$$

$$= 0.03R.$$

4. m gms of water at $T_1$ is isobarically & adiabatically mixed with an equal mass of water at $T_2$, so that they attain a common final temperature $T_c$. Show that entropy change of the universe is $2mC_V \ln\frac{\left(\frac{T_1+T_2}{2}\right)}{\sqrt{T_1T_2}}$. What would be the loss of available energy?

$T_c$ will attend when $mC_V(T_1 - T_c) = mC_V(T_c - T_2)$

or $T_c = \frac{T_1+T_2}{2}$.

$$\Delta S_1 = mC_V\int_{T_1}^{T_c}\frac{dT}{T} = mC_V \ln\frac{T_c}{T_1}$$

$$\Delta S_2 = mC_V\int_{T_2}^{T_c}\frac{dT}{T} = mC_V \ln\frac{T_c}{T_2}$$

$$\Delta S_{universe} = \Delta S_1 + \Delta S_2 = mC_V \ln\frac{T_c^2}{T_1T_2} = mC_V \ln\left(\frac{T_c}{\sqrt{T_1T_2}}\right)^2$$

$$= 2mC_V \ln\frac{T_1+T_2}{2\sqrt{T_1T_2}}$$

If $T_0$ is the lowest attainable temperature, then unavailable amount of energy is $Q_{unattain} = T_0\Delta S_{universe} = 2mC_V T_0 \ln\frac{T_1+T_2}{2\sqrt{T_1T_2}}$.

HW 1. The equation of state of a new matter is $PV = AT^3$, $A$ = constant. Internal energy of this matter is $U = BT^n \ln(V/V_0) + f(T)$. Using first law of thermodynamics, find $B$ and $n$.

2. Suppose an engine works between two reservoirs at $T_1$ & $T_2$ ($T_2 > T_1$) until both reservoirs attain final temperature $T_C$. Show that $T_C > \sqrt{T_1 T_2}$. What is the maximum amount of work obtainable from this engine?

## Entropy & Unavailable energy

Suppose that $Q$ amount of heat is extracted from a reservoir at temperature $T_1$ & it is desired to convert this heat into work as much as possible. If $T_0$ is the temperature of sink, then using a reversible engine, $W^{r}_{max} = Q(1 - \frac{T_0}{T_1})$.

Consider an irreversible conduction of heat $Q$ along a metal bar under finite temperature gradient from a region at temperature $T_1$ to a region at temperature $T_2$. After conduction has taken place, $Q$ amount of heat is available at lower temperature $T_2$ or the maximum amount of available work is $W^{irr}_{max} = Q(1 - \frac{T_0}{T_2})$.

As $T_1 > T_2$, so maximum work obtained in $W^{irr}_{max}$ is less than $W^{r}_{max}$.

∴ The amount of energy that is unavailable for work is,

$$E = Q(1 - \frac{T_0}{T_1}) - Q(1 - \frac{T_0}{T_2}) = T_0 Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = T_0 \Delta S$$

where $\Delta S$ is the entropy change of the universe due to the irreversible process. Since irreversible process is continually happening in nature, so energy is continually becoming unavailable for work. This is known as "Principle of degradation of energy."

Thus according to this principle, we are always losing available energy & then a day will come when we will have no available energy for work. This is called "heat death" of the universe.

Disorder & entropy.

Whenever work is dissipated within the system because of friction, viscosity, inelasticity, electric resistance or magnetic hysteresis, the molecules are more disordered. We learned that irreversible process is associated with an increase in entropy of the universe. Thus, entropy must be related with the disorder.

Disorder of a system depends on the number of microstates accessible to the system. This is called "Thermodynamic probability" ($\Omega$) & we can write $S = f(\Omega)$. To obtain the functional form, consider two systems having thermodynamic probability $\Omega_1$ and $\Omega_2$ with entropy $S_1 = f(\Omega_1)$ and $S_2 = f(\Omega_2)$ respectively.

If these systems are mixed then the total entropy is $S = S_1 + S_2$ and the total number of microstates of the system will be $\Omega = \Omega_1 \Omega_2$. $\therefore \; S_1 + S_2 = f(\Omega_1 \Omega_2)$

$$\therefore \; f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \Omega_2)$$

$$\therefore \; \frac{\partial f(\Omega_1)}{\partial \Omega_1} + 0 = \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_1} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)} \frac{\partial (\Omega_1 \Omega_2)}{\partial \Omega_1}$$

$$= \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$$

Multiplying with $\Omega_1$, $\Omega_1 \frac{\partial f(\Omega_1)}{\partial \Omega_1} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$

Similarly, $0 + \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_2} \Rightarrow \Omega_2 \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$

$\therefore \Omega_1 \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_2)}{d\Omega_2}$ or $\Omega \frac{df(\Omega)}{d\Omega}$ = constant (K say)

or $df(\Omega) = K \frac{d\Omega}{\Omega}$ or $f(\Omega) = K \ln \Omega + C$

But if $\Omega = 1$, $f(\Omega) = 0$ as the system is in perfect ordered state.

$\therefore C = 0$. $\boxed{S = K \ln \Omega}$

## Entropy and Information

Since the disorder of a system is related to the available information, therefore the entropy of a system should also have a relation with information.

Suppose we are called upon to guess a persons first name. The number of choices of names of men & women is huge. So there is a great disorder without any information. But given an information that the person is a man, the number of choices of names is reduced. Information is reduced further that man is a physicist and this reduces the disorder. The disorder in choosing names is further reduced if given an information that the physicist is a Nobel laureate. ∴ Fewer the number of ways a particular state of a system is achieved, the greater is the information.

A measure of the information when the number of choices is reduced from $\Omega_0$ to $\Omega_1$ is $I = K \ln \frac{\Omega_0}{\Omega_1} = S_0 - S_1$. The bigger the reduction, the bigger the information. Also, $\boxed{S_1 = S_0 - I}$.

∴ Entropy measures the lack of information about the exact state of a system.

## Entropy & 2nd law of Thermodynamics

The 2nd law provides proper direction to all natural processes while the Kelvin-Planck statement gives a direction for the conversion between heat and work, Clausius statement gives a direction for heat flow between two bodies at different temperature. Combining the 2nd law can be defined in terms of entropy as

"A natural irreversible process will always proceed in a direction in which the entropy of universe increases. In a reversible process, entropy does not change."

This means in approaching equilibrium, the entropy of the universe must increase. $S_f - S_i = \int_i^f \frac{dQ}{T}$. The principle of unavailable energy is a replacement of Kelvin-Planck's statement of 2nd law since both suggest a definite rejection of heat energy if some work is to be obtained from heat. The concept of entropy with reference to disorder shows that the direction of all natural processes are governed by probability laws. Thus 2nd law is a statistical law which is defined as the probability of a process to occur is more if the direction of the process gives an increment in entropy of the universe.

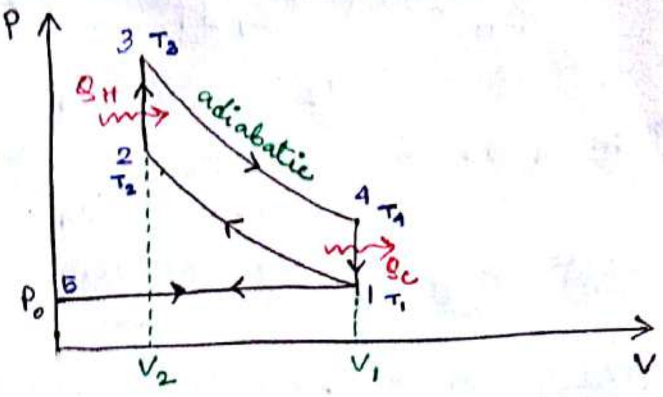
## Practical Engines

We learned, engine is a device that converts heat into work. Practical engines are of two types ⓐ Internal-combustion engine (Gasoline & Diesel engine)

ⓑ External-combustion engine. (Steam & stirling engine)

In internal combustion engine, burning of fuel & oxygen with air takes place in confined combustion chamber to rise P, & T of the system. In external combustion engine, high temperature surroundings transfer heat to the combustion chamber.

# Otto Cycle & Gasoline Engine



The cycle involves performance of 6 process, 4 of which require "stroke" (vertical motion) of the piston

**1. Intake stroke:**

A mixture of gasoline vapour and air is drawn into the combustion chamber at constant pressure by the sucssion of the piston, represented by 5→1, & according to equation

$P_0V = nRT_1$ , $P_0$ = atmospheric pressure, V = vol. of chamber,

$T_1$ = temperature of air outside & n moles of atom.

**2. Compression stroke:** The mixture is compressed in quasistatic adiabatic stroke until its pressure & temperature rise considerably. No friction & no loss of heat at the cylinder wall. 1→2 process is represented as. $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

**3. Ignition or combustion:** Process 2→3 represents quasistatic isochoric increase of temperature from $T_2$ to $T_3$ where combustion takes place very rapidly by an electric spark.

**4. Power stroke:** The hot combustion product expands and push the piston out. 3→4 represents quasistatic adiabatic process so that temperature falls down to $T_4$ with equation $T_3V_2^{\gamma-1} = T_4V_1^{\gamma-1}$

**5. Valve Exhaust:** The combusted product at the end of power stroke are still at a higher pressure and temperature than outside. An exhaust valve allows the gas mixture to escape, that is 4→1.

**6. Exhaust Stroke:** The piston pushes all the remaining combustion product out of the chamber by exerting a sufficiently large pressure 1→5 represents this isobaric exhaust.

If the specific heat $C_v$ of the gas mixture is constant then heat absorbed in process 2→3 is

$Q_H = \int_{T_2}^{T_3} C_V\, dT = C_V(T_3 - T_2)$ and the heat rejected in $4 \to 1$ is $Q_C = -\int_{T_4}^{T_1} C_V\, dT = C_V(T_4 - T_1)$. Thus the thermal efficiency of the gasoline engine is $\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$

Also for the two adiabatic process we know

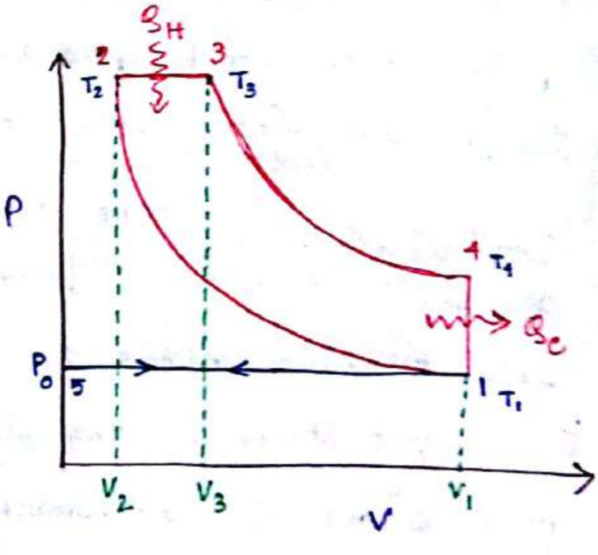
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$$

$$\therefore (T_4 - T_1) V_1^{\gamma-1} = (T_3 - T_2) V_2^{\gamma-1} \Rightarrow \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$\therefore \boxed{\eta = 1 - \left(\frac{1}{r}\right)^{\gamma-1}}$ where $r = \frac{V_1}{V_2}$ is the compression ratio.

In actual gasoline engine $r \leq 10$. If $r$ is large then temperature of the gasoline-air mixture upon compression is huge enough to cause combustion before the advent of spark. This is called "Preignition." Taking $r = 9$, $\gamma = 1.4$, we obtain $\eta = 67\%$. In actual engine however due to turbulence, heat conduction etc, the efficiency is less than 67%.

**Diesel Engine**



Rudolf Diesel in 1897 designed this air-standard Diesel cycle where only air is admitted on intake stroke. The air is compressed adiabatically until temperature reaches high to ignite oil after compression stroke. Combustion stroke happens isobarically & piston moves out. Process 4, 5, 6 happen like the Otto cycle. Only change is $2 \to 3$ is horizontal.

Quasistatic isobaric heat absorption $(2 \to 3)$ $Q_H = \int_{T_2}^{T_3} C_p\, dT = C_p(T_3 - T_2)$

and valve exhaust releases (4→1) $Q_c$ heat as in Otto engine,

$Q_c = -\int_{T_4}^{T_1} C_V \, dT = C_V (T_4 - T_1)$. Thus the thermal efficiency of an idealized diesel engine is $\eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_4 - T_1}{\gamma(T_3 - T_2)}$.

We want to calculate the ratio in terms of adiabatic expansion ratio $\rho = \frac{V_1}{V_2}$ and combustion expansion ratio $e = \frac{V_3}{V_2}$. So we've to evaluate $\frac{T_4 - T_1}{T_3 - T_2}$ in that.

For path 1→2, adiabatic

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

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

For path 2→3 isobaric

$$\frac{T_3}{V_3} = \frac{T_2}{V_2}$$

$$\text{or } T_3 = T_2 \frac{V_3}{V_2} = T_2 e$$

For path 3→4, adiabatic

$$T_4 V_4^{\gamma-1} = T_3 V_3^{\gamma-1}, \text{ as } V_1 = V_4$$

$$\text{or } T_4 = T_3 \left(\frac{V_3}{V_1}\right)^{\gamma-1} = T_3 \left(\frac{V_3}{V_2}\right)^{\gamma-1} \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$= T_3 e^{\gamma-1} \frac{1}{\rho^{\gamma-1}} = T_2 e^{\gamma} \frac{1}{\rho^{\gamma-1}}$$

$$\therefore \eta = 1 - \frac{1}{\gamma}\left[\frac{T_2 e^{\gamma} \frac{1}{\rho^{\gamma-1}} - T_2 \frac{1}{\rho^{\gamma-1}}}{T_2 e - T_2}\right] = 1 - \frac{1}{\gamma}\frac{1}{\rho^{\gamma-1}}\left[\frac{e^{\gamma} - 1}{e - 1}\right]$$

if $e = 5$, $\gamma = 1.4$, $T_1 = 300K$, $T_2 = 990K$, $\eta = 54\%$

Efficiency of Diesel engine < Efficiency of Otto engine

Q 1. Find the efficiency of a Carnot's engine working between the steam point and the ice point.

$T_1 = 100°c = 373K$, $T_2 = 0°c = 273K$.

$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{100}{373}$. ∴ % efficiency $= \frac{100}{373} \times 100$
$= 26.81\%$

2. Find the efficiency of a Carnot's engine working between 127°c and 27°c. It absorbs 80 cals of heat. How much heat is rejected?

$T = 400K$, $T_2 = 300K$, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$

$\% \eta = 25\%$, $W = \eta Q_1 = 0.25 \times 80 = 20$ cals.

Heat rejected $Q_2 = Q_1 - W = 80 - 20 = 60$ cals.

HW 1. A Carnot engine has an efficiency of 30% when the sink temperature is 27°c. What must be the change in temperature of the source to make its efficiency 50%?

2. An inventor claims to have developed an engine working between 600K and 300K to deliver an efficiency of 52%. Is this claim valid? [Hint: use Carnot's theorem].

3. Two Carnot engines X & Y are operating in series. X receives heat at 1200K & rejects to a reservoir at temperature TK. The 2nd engine Y receives the heat rejected by X & inturn rejects to a heat reservoir at 300K. Calculate the temperature T for the situation when,

(i) The work outputs of two engines are equal.

(ii) The efficiency of two engines are equal.

4. A Carnot's refrigerator takes heat from water at 0°c and discards it to a room temperature at 27°c. 1kg of water at 0°c is to be changed into ice at 0°c. How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the coefficient of performance $\left(P = \frac{Q_2}{Q_1 - Q_2}\right)$ of the machine? [1 Cal = 4.2 Joule].

## Third law of Thermodynamics : Nernst's Heat Theorem

In 1906, Nernst proposed a general principle on atomic heat of solids at low temperature. The third law of thermodynamics states that The heat capacities of all solids tend to zero as the absolute zero of temperature is approached & the internal energies and entropies of all substances become equal there, approaching their common value ymptotically tending to zero. In terms of entropy, at absolute zero temperature, the entropy tends to zero & the molecules of a substance are in perfect order.

We cannot have less than zero K temperature because if $T_2 < 0K$ then efficiency $\eta = 1 - \frac{-T_2}{T_1} = 1 + \frac{T_2}{T_1} > 1$. So we cannot make more than 100% efficient engine.

## Maxwell's Thermodynamical Relationship

From the 1st law of thermodynamics, Maxwell derived 6 fundamental thermodynamic relations using P, V, T, S with any two pair as dependent & other as independent variable.

from 1st law, $dQ = dU + PdV$ & from 2nd law, $dQ = TdS$

$$\therefore \ dU = dQ - PdV = TdS - PdV \quad \text{—} ①$$

Here $dU, dS, dV$ are all exact differentials. Considering $U, S, V$ as function of two independent variables $x$ & $y$ where $\{x, y\}$ = {combination of P, V, T, S any two}. Then,

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy, \quad dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

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

Substituting in ①, $$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$= \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right]dx + \left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right]dy$$

Comparing the coefficients of $dx$ & $dy$, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y, \quad \left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x$$