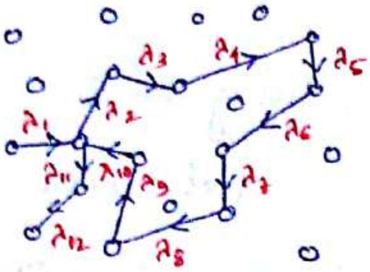
Mean free path

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 "λ", let's compute the distibution of λ, 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 $t = \frac{1}{2}NPt$. ($\frac{1}{2}$ because each collission between 2 atoms is counted twice).

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

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 $f(x) \times \left(1-\frac{dx}{\lambda}\right)$

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

Expand LHS using Taylor's theorem.

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

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

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

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

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

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)

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

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)

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

$$= \frac{1}{N}\int_0^\infty x P N e^{-Px}\,dx = P\int_0^\infty e^{-Px}\,x\,dx$$

put $Px = z$

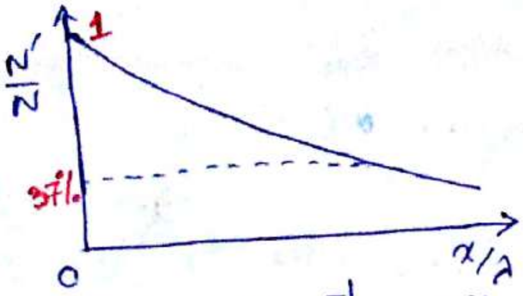
$P\,dx = dz$

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

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

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 $\propto$ number of atoms. $\therefore I' = I e^{-x/\lambda}$.

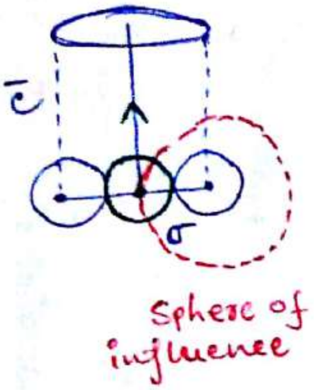
↳ initial intensity

final intensity.

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

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

Calculation of λ



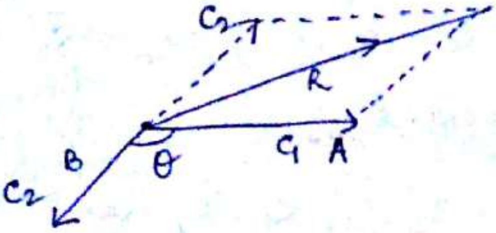
Suppose all atoms are rest but only one moves with velocity $\bar{c}$. Rigid spherical shape with diameter σ. It can only collide when they touch. & can reach distance $\bar{c}$, so it collides with $\pi\sigma^2\bar{c}n$ many atoms. This is also number of collisions per second.

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

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

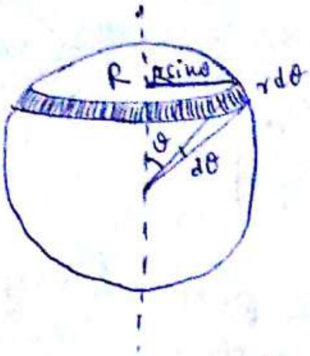
Clausius correction

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

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

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 $\lambda_{cl} = \frac{\bar{c}}{\pi\sigma^2 n\bar{R}} = \frac{3}{4}\frac{1}{n\pi\sigma^2}$.

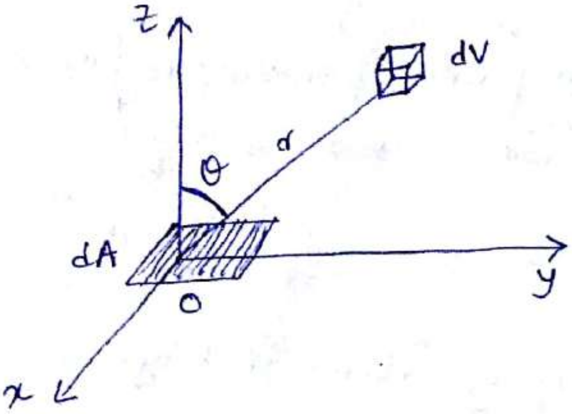
Maxwell's correction Clausius took $c_1 = c_2 = \cdots = c_N = \bar{c}$ but they're Maxwellian distributed in reality!

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 $\lambda \geq r$ can reach dA, which is

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

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

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

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

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

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

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

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

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

Mean free path of a mixture of a gas

If we consider two different molecule with diameter σ_1, σ_2 then, σ_1 diameter molecule will collide with all molecule that are $\frac{\sigma_1+\sigma_2}{2}$ distance apart from σ_1 molecule. Hence λ will be $1/n\pi\sigma_a^2$ where $\sigma_a = \frac{\sigma_1+\sigma_2}{2}$ & m = number of molecules per unit volume of σ_2 type. But σ_2 molecules are not in rest then if σ_1 type moves with $\bar{c}_1$ & σ_2 type moves with $\bar{c}_2$ & if the molecules of σ_2 move perpendicular to σ_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 λ_1 of σ_1 type of molecules within σ_2 type molecules are

$\lambda_1 = \dfrac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_1}}$. Similarly, λ_2 of σ_2 type of molecules within σ_1 type molecules are $\lambda_2 = \dfrac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2 + \bar{c}_2^2}}{\bar{c}_2}}$. 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 σ_1 type with $\bar{c}_1$ & n_2 molecule of σ_2 type with $\bar{c}_2$ avg. velocity then no. of impact/sec by σ_1 molecules

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

$\therefore$ Mean free path of σ_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

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

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

2. The diameter of a gas molecule is 3×10^{-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 2.2×10^{-8} m & the number of Benzene molecules/unit volume is 2.79×10^{25} molecules/m^3.

(Nonequilibrium) Transport Phenomena in Gases

(i) **Viscosity** : velocity varies from layer to layer & momentum is transferred from layer to layer leading to kinetic interpretation of viscosity in gases. In 1860, Maxwell interpreted that if two layer have relative velocity, viscous force acts along the surface of contact retarding the faster moving layer & making the slower moving layer to move faster. Retarding force is proportional to area of contact & velocity gradient.

$$F \propto A \quad \text{or} \quad F = \eta A \frac{dv}{dz} \quad \text{or} \quad \underset{\text{stress}}{\underset{\downarrow}{\sigma}} = \underset{\text{coeff}^n\text{ of viscosity}}{\underset{\downarrow}{\eta}}\,\dot{\gamma} \longrightarrow \text{strain rate}$$

$$\propto \frac{dv}{dz}$$

Newton's law of viscosity

(ii) **Thermal conductivity** : Taken a solid rod & heated in one end, after sufficiently long time when measured temperature at different distances then amount of heat conducted (rate) is proportional to temperature gradient, area of face of slab.

$$Q \propto A \quad \text{or} \quad Q = \underset{\text{thermal conductivity}}{\underset{\downarrow}{K}} A \frac{dT}{dz}$$

$$\propto \frac{dT}{dz}$$

Fourier's law of heat conduction

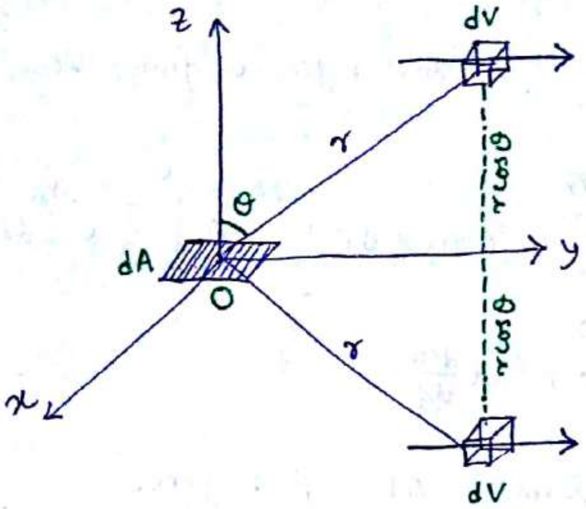
(iii) **Diffusion** : Whenever there is difference in concentration, mass transfer results to an equilibrium distribution of concentration. In monodisperse system, diffusion to concentration gradient is called self-diffusion & if two gases diffuse into each other, called inter-diffusion. Number of molecules crossing is proportional to

$$N \propto \frac{dn}{dz} \quad \text{or} \quad N = DA\frac{dn}{dz}$$

$$\propto A$$

Fick's law of diffusion

General method for obtaining coefficient of viscosity & conduction



In a reference frame, consider an elementary volume dV at coordinate (r, θ). The layer that contains dV is at a vertical height $r\cos\theta$ from XY plane at origin O. If the physical entity has a value $\mathcal{H}$ (energy, momentum etc) on the XY plane at origin, then the value at the upper layer is $\mathcal{H} + r\cos\theta \frac{d\mathcal{H}}{dz}$. For an identical layer beneath at same distance, the value is $\mathcal{H} - r\cos\theta \frac{d\mathcal{H}}{dz}$

The number of molecules within c & c+dc in dV is $dn_c dV$. If λ is the mean free path, then the number of collison suffered in unit time is $\frac{c}{\lambda} \frac{1}{2} dn_c dV$. Factor ½ is because collision between two molecules are identical & counted twice. But each collision results in 2 paths. So the number of molecule coming out of dV in all possible direction is $2 \times \frac{1}{2} \frac{c}{\lambda} dn_c dV$.

Number of molecules which are headed towards area dA at origin is $\frac{dA\cos\theta}{4\pi r^2} \frac{c}{\lambda} dn_c dV$. Due to collisions some of them cannot reach dA & the number that reaches dA in unit time is

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

If the molecule carry the physical entity characteristic of the layer when they last suffered collisions then the transport of physical entity downwards through area dA per unit time is

$$L\downarrow = \frac{dA}{4\pi} \int_{c=0}^{\infty} \int_{r=0}^{\infty} \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} c \, dn_c \sin\theta \cos\theta \, d\theta \, d\phi \, e^{-r/\lambda} \frac{dr}{\lambda} \left(\mathcal{H} + r\cos\theta \frac{d\mathcal{H}}{dz}\right)$$

Considering an identical volume below the reference frame, the transport of physical entity upwards is

$$L\uparrow = \frac{dA}{4\pi}\int_{c=0}^{\infty}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} c\,dn_c \sin\theta\cos\theta\, d\theta\, d\phi\; e^{-r/\lambda}\,\frac{dr}{\lambda}\left(\mathcal{H} - r\cos\theta\frac{d\mathcal{H}}{dz}\right)$$

∴ The net transfer of physical entity to the reference frame via area dA in unit time :

$$\Delta L = L\downarrow - L\uparrow = \frac{2\,dA}{4\pi}\frac{d\mathcal{H}}{dz}\int_0^{\infty} c\,dn_c \int_0^{\pi/2}\cos^2\theta\sin\theta\, d\theta \int_0^{2\pi} d\phi \int_0^{\infty}\frac{r}{\lambda}e^{-r/\lambda}\,dr$$

$$= dA\frac{d\mathcal{H}}{dz}\,\frac{1}{3}\lambda\int_0^{\infty} c\,dn_c \quad = \frac{1}{3}n\bar{c}\lambda\, dA\frac{d\mathcal{H}}{dz}$$

(i) Viscosity : $\mathcal{H} = mv$ = momentum , $\Delta L = F$ = force

$$\therefore F = \frac{1}{3}n\bar{c}\lambda\, dA\, m\frac{dv}{dz} = \eta\, dA\frac{dv}{dz}$$

$$\therefore \boxed{\eta = \frac{1}{3}mn\bar{c}\lambda = \frac{1}{3}\rho\bar{c}\lambda}$$

(ii) Thermal conductivity : $\mathcal{H} = E$ = thermal energy, $\Delta L = Q$ = heat

$$\therefore Q = \frac{1}{3}n\bar{c}\lambda\, dA\frac{dE}{dz} = \frac{1}{3}n\bar{c}\lambda\, dA\frac{dE}{dT}\frac{dT}{dz} = K\, dA\frac{dT}{dz}$$

$$\therefore K = \frac{1}{3}n\bar{c}\lambda\frac{dE}{dT}$$

If C_v = specific heat of molecules, $E = mC_vT$ ∴ $\frac{dE}{dT} = mC_v$

$$\therefore \boxed{K = \frac{1}{3}n\bar{c}\lambda mC_v = \eta C_v}$$

Variation of $K/\eta C_v$ with the atomicity of molecules

$K/\eta C_v = 1$ was not matching with experiments, because many factors are omitted to reach the expression. In general $K/\eta C_v = \epsilon = [1, 2.57]$

For a polyatomic molecule, the energy transfer is not only translational but also internal energy (rotational, vibrational etc) In rigorous calculation, Chapman found total energy transferred per unit time is $\frac{1}{3}n\bar{c}\lambda\, dA\left(\frac{5}{2}\frac{dE_T}{dz} + \frac{dE_R}{dz}\right)$ E_T = Translational energy & E_R = Rotational energy.

∴ $K\,dA\frac{dT}{dz} = \frac{1}{3}n\bar{c}\lambda\,dA\frac{dT}{dz}\left\{\frac{5}{2}\frac{dE_T}{dT}+\frac{dE_R}{dT}\right\}$

or $K = \frac{\eta}{m}\left(\frac{5}{2}\frac{dE_T}{dT}+\frac{dE_R}{dT}\right)$ — ①

From the principle of equipartition of energy, total energy associated with 1 gm molecule of gas is $\frac{3+\beta}{2}RT$, β = # of d.o.f. for rotational motion. ∴ Molar specific heat $C_V = \frac{dE}{dT} = \frac{3+\beta}{2}R$.

Using $C_P - C_V = R$, $C_P = \frac{5+\beta}{2}R$

or $\gamma = C_P/C_V = \frac{5+\beta}{3+\beta} = 1+\frac{2}{3+\beta}$. — ② or $\beta = \frac{2}{\gamma-1}-3$

But $E_T = \frac{3}{2}k_BT$, $E_R = \frac{\beta}{2}k_BT$ or $\frac{dE_T}{dT} = \frac{3}{2}k_B$, $\frac{dE_R}{dT} = \frac{\beta}{2}k_B$

putting in ①, $K = \frac{\eta}{m}\left(\frac{15k_B}{4}+\frac{\beta k_B}{2}\right)$

But $c_v = \frac{3+\beta}{2}\frac{k_B}{m}$ (molecular specific heat)

$= \frac{k_B}{m(\gamma-1)}$ [using ②] or $k_B = m(\gamma-1)c_v$

∴ $K = \frac{\eta}{m}m(\gamma-1)c_v\left(\frac{15+2\beta}{4}\right) = \eta c_v(\gamma-1)\left(\frac{15}{4}+\frac{\beta}{2}\right)$

$= \eta c_v(\gamma-1)\left[\frac{15}{4}+\frac{1}{\gamma-1}-\frac{3}{2}\right] = \eta c_v(\gamma-1)\left(\frac{9}{4}+\frac{1}{\gamma-1}\right)$

$= \eta c_v\left(\frac{9\gamma-5}{4}\right)$. ∴ $\epsilon = \frac{9\gamma-5}{4}$

monoatomic gas $\gamma = 1.66$, $\epsilon = 2.5$
diatomic gas $\gamma = 1.4$, $\epsilon = 1.9$

Variation of η with temperature & pressure

$\eta = \frac{1}{3}mn\bar{c}\lambda = \frac{1}{3}m\cancel{n}\bar{c}\frac{1}{\sqrt{2}\pi\sigma^2\cancel{n}} = \frac{1}{3}\frac{m\bar{c}}{\sqrt{2}\pi\sigma^2}$

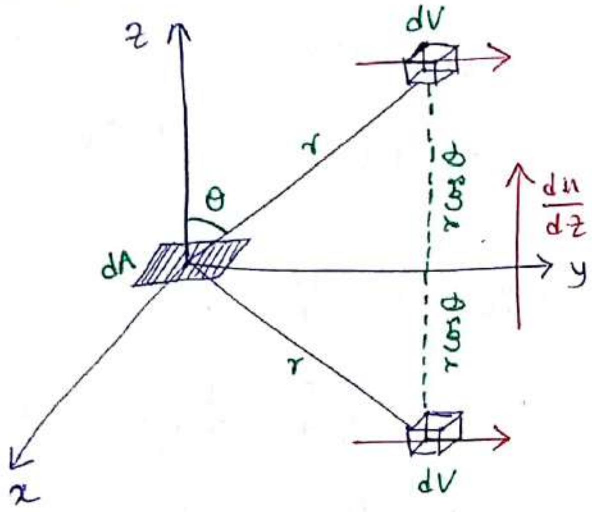
η is independent of concentration, that Maxwell found at moderate pressure. At very high pressure, η increases & at low pressure, η decreases with pressure. At very high pressure, mean free path of molecules are comparable to the molecular dimension. Hence $\eta \propto p$ as λ = constant At low pressure, mean free path is comparable to the dimension of the container

f again is constant. So reducing pressure n decreases & hence η.

as $\bar{c} = \sqrt{\frac{8K_BT}{m\pi}}$, so $\eta \propto \sqrt{T}$ but in reality η varies more rapidly. This is because in K.T. molecular interaction is not taken care of. The molecular force field in K.T. is zero but in reality increase in temperature impinges the molecules to penetrate into each other & thus effective size of molecule decreases or increase in η.

Sutherland found that $\eta = \frac{A\sqrt{T}}{1+ b/T}$ holds for hydrogen, helium, argon etc.

General Method for obtaining Diffusivity



If there is a concentration gradient $\frac{dn}{dz}$ along z-direction, then the number of molecules that flows through dA per unit time is $N = D\,dA\frac{dn}{dz}$

Let the concentration in XY plane is n & concentration gradient increases in z direction,

No. of molecules within c & $c+dc$ contained at dV located at (r, θ) is $4\pi A^3 e^{-bc^2} c^2 dc \left(n + r\cos\theta \frac{dn}{dz}\right) dV$, $A = \sqrt{\frac{m}{2\pi K_BT}}$, $b = \frac{m}{2K_BT}$

Due to collision, number of new paths emanating in unit time is $2 \times \frac{1}{2} \frac{c}{\lambda} \left(n + r\cos\theta \frac{dn}{dz}\right) 4\pi A^3 e^{-bc^2} c^2 dc\, dV$ & out of them, the number that will head towards dA is

$$\frac{dA\cos\theta}{\cancel{4\pi r^2}} \frac{c}{\lambda}\left(n + r\cos\theta\frac{dn}{dz}\right) \cancel{4\pi} A^3 e^{-bc^2} c^2 dc\, dV (= \cancel{r^2} \sin\theta d\theta d\phi)$$

Taking collision into account, total number of molecules crossing area dA in downward direction

$$N\downarrow = A^3 dA \int_{c=0}^{\infty}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \left(n + r\cos\theta\frac{dn}{dz}\right)\cos\theta \sin\theta\, d\theta\, d\phi\, dr \frac{e^{-r/\lambda}}{\lambda} c^3 e^{-bc^2} dc$$

Similarly the number of molecules crossing dA in upward direction

$$N\uparrow = A^3 dA \int_{c=0}^{\infty}\int_{r=0}^{\infty}\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi} \left(n - r\cos\theta \frac{du}{dz}\right) \sin\theta\cos\theta\, d\theta\, d\phi\, dr\, \frac{e^{-r/\lambda}}{\lambda} c^3 e^{-bc^2} dc$$

∴ Net number of molecules moving through dA in unit time

$$\Delta N = N\downarrow - N\uparrow = 2A^3 dA \int_0^{\infty} c^3 e^{-bc^2} dc \int_0^{\infty} r e^{-r/\lambda} \, dr/\lambda \int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta \times$$

$$\int_0^{2\pi} d\phi \times \frac{du}{dz}$$

$$= \frac{2\pi}{3} \lambda\, dA \frac{du}{dz} A^3/b^2 = \frac{1}{3} dA\, \lambda \frac{du}{dz} \sqrt{\frac{8KT}{m\pi}} = \frac{1}{3}\lambda \bar{c}\, dA \frac{du}{dz}$$

From Fick's law, $\Delta N = D\, dA \frac{du}{dz}$

$$\therefore \boxed{D = \frac{1}{3}\lambda\bar{c} = \frac{\eta}{\rho}}$$

$$= \frac{1}{3}\frac{1}{\sqrt{2}\pi\sigma^2 n}\sqrt{\frac{8KT}{m\pi}} \qquad \therefore D \propto \frac{1}{n} \propto \frac{T^{3/2}}{P}$$

$$\propto \frac{1}{\sqrt{m}} \quad \text{(Graham's law)}$$

Brownian motion

First observed by R. Brown in 1827 on suspended polen grains on water. Perpetual, random motion of big solute particle in solvent is the Brownian motion.

Features: (i) Motion of Brownian particle is completely irregular. No two particle execute the same motion.

(ii) Motion ~~of~~ is continuous & based on discrete collisional steps.

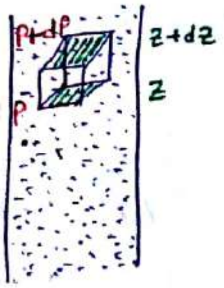
(iii) Smaller particles are more agitated than larger particles, but motion is independent of the nature of suspended particles. Two particles of same weight & size move equally fast at same temperature.

(iv) The motion is vigorous with increasing temperature, & in lower viscosity.

(v) Motion is not modified due to shaking of container.

Basis fluctuation + dissipation

Law of Atmosphere



Brownian particles form a gas in equilibrium under the gravitational force. Consider a vertical cylinder of unit cross-section in a gas having end face at z & $z+dz$ & corresponding pressure P & $P+dP$ then

Force of gravity in layer vertically downward $= 1 \times dz \times \rho g = \rho g dz$

As cylinder is in equilibrium, net force on layer $= 0$.

$$(P+dP) - P + \rho g dz = 0$$

$$\text{or} \quad dP = -\rho g dz \quad \text{—①} \quad (-\text{ive sign means } P \text{ decreases with } z)$$

$m =$ mass of single molecule, $n =$ average number of molecules per unit volume.

$$\rho = mn.$$

Using Clapeyron's equation $P = nK_BT$, $dP = dnK_BT$. —②

Equating ① & ②, $dnK_BT = -mngdz$

$$\text{or} \quad \frac{dn}{n} = -\frac{mg}{K_BT}dz = -\frac{mgN}{RT}dz \qquad \left(K_B = \frac{R}{N}\right)$$

Integrating $\ln n = -\frac{mgN}{RT}z + \ln c$

at $z = z_0$, $n = n_0$ $\qquad \ln n_0 = -\frac{mgN}{RT}z_0 + \ln c$

$$\text{or} \quad \ln n = -\frac{mgN}{RT}z + \ln n_0 + \frac{mgN}{RT}z_0$$

$$\text{or} \quad \ln\frac{n}{n_0} = -\frac{mgN}{RT}(z - z_0)$$

$$\text{or} \quad \boxed{n = n_0\, e^{-\frac{mgN}{RT}(z-z_0)}}$$

Exponential decrease of no. density of Brownian particles with height.

For colloidal solution, particles have downward force due to gravity & upward force due to the buoyancy of liquid. If ρ' is the density of particle then effective mass of particle $m = \frac{4}{3}\pi r^3(\rho' - \rho)$

$$\therefore \ln\frac{n}{n_0} = -\frac{4\pi r^3(\rho'-\rho)gN}{3RT}(z - z_0)$$

$$\text{or} \quad N = \frac{3RT}{4\pi \underset{\uparrow}{r^3}(\underset{\uparrow}{\rho'}-\rho)g(z-z_0)}\ln\frac{n_0}{n}$$

Thus Avogadro number can be calculated if r, ρ' are known.

Langevin equation of Brownian motion

Equation of motion $\quad m\frac{d\vec{v}}{dt} = \underset{\substack{\downarrow \\ \text{viscous}}}{-\vec{F}_v} + \underset{\substack{\downarrow \\ \text{Brownian}}}{\vec{F}_B(t)}$

Time average over sufficiently long time $t \gg \tau$, $\quad m\frac{d\langle\vec{v}\rangle}{dt} = -\langle\vec{F}_v\rangle$

For colloidal fluid $\quad m\frac{dv}{dt} = -\alpha v + F_B(t)$

From hydrodynamics, Stokes calculated that $\alpha = 6\pi\eta a$ for a spherical object of size a moving at velocity v through a liquid with viscosity η. This is known as Stokes law.

Clearly $\langle x\rangle = 0$ but $\langle x^2\rangle \neq 0$. $\quad \langle F_B(t)\rangle = 0$

Magnitude of fluctuations

$$m\frac{d^2x}{dt^2} = -\alpha\frac{dx}{dt} + F_B(t)$$

$$\text{or} \quad m x\frac{d^2x}{dt^2} = -\alpha x\frac{dx}{dt} + xF_B(t)$$

$$\text{or} \quad m\left[\frac{d}{dt}(x\dot{x}) - \dot{x}^2\right] = -\alpha x\frac{dx}{dt} + xF_B(t)$$

Now $\langle xF_B(t)\rangle = \langle x\rangle\langle F_B(t)\rangle = 0$ "statistical independence"

and from equipartition theorem, $\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_BT$

$$\therefore m\left\langle\frac{d}{dt}(x\dot{x})\right\rangle = m\langle\dot{x}^2\rangle - \alpha\left\langle x\frac{dx}{dt}\right\rangle + \cancelto{0}{\langle xF_B(t)\rangle}$$

or $m\frac{d}{dt}\langle x\dot{x}\rangle = k_BT - \alpha\langle x\dot{x}\rangle$

or $$\frac{d\langle x\dot{x}\rangle}{dt} + \frac{\alpha}{m}\langle x\dot{x}\rangle = \frac{k_BT}{m}$$

integrating factor $= e^{+\alpha/m\, t}$

particular integral $= e^{-\alpha/m\, t}\int e^{\alpha/m\, t'}\frac{k_BT}{m}\,dt'$

$$= e^{-\alpha/m\, t}\frac{k_BT}{m}\left(\frac{m}{\alpha}e^{\alpha/m\, t} + c'\right)$$

$$\langle x\dot{x}\rangle = \frac{k_BT}{\alpha} + c\,e^{-\alpha/m\, t}$$

at $t=0$, $\langle x\dot{x}\rangle = \langle x\rangle\langle\dot{x}\rangle = 0$ $\therefore$ $c + \frac{k_BT}{\alpha} = 0$

$\therefore$ $\langle x\dot{x}\rangle = \frac{k_BT}{\alpha}\left(1 - e^{-\alpha/m\, t}\right)$

or $\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = \frac{k_BT}{\alpha}\left(1 - e^{-\alpha/m\, t}\right)$

or $$\boxed{\langle x^2\rangle = \frac{2k_BT}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-\alpha/m\, t}\right)\right]}$$

Case I $\quad \frac{m}{\alpha} \gg t$, $\quad e^{-\alpha/m\, t} \simeq 1 - \frac{\alpha}{m}t + \frac{1}{2}\frac{\alpha^2}{m^2}t^2 - \cdots$

$\therefore$ $\langle x^2\rangle = \frac{k_BT}{m}t^2$. Therefore for a short time interval the particle moves ballistically with constant velocity $v = \sqrt{\frac{k_BT}{m}}$

Case II $\quad \frac{m}{\alpha} \ll t$, $\quad e^{-\alpha/m\, t} \simeq 0$, $\; t - \frac{m}{\alpha} \gg 0$.
$\simeq t$

$\langle x^2\rangle = \frac{2k_BT}{\alpha}t$. Therefore the Brownian particle diffuses

as $\langle x^2\rangle = 2Dt = \frac{2k_BT}{\alpha}t = \frac{k_BT}{3\pi\eta a}t = \frac{RT}{3\pi N\eta a}t$

or $\boxed{D = \frac{RT}{6\pi N\eta a}}$ $\qquad D \propto \frac{1}{a}$ but independent of mass.

Einstein's argument

τ = time interval << observation time scale

>> large enough than individual collision

that two consecutive intervals of τ are mutually independent.

For N solute (Brownian) particle in time interval τ, x coordinate increase by Δ (both ±ive) due to thermal motion, no. of solute particles that are between Δ & $\Delta + d\Delta$ is

$$dN = N\phi(\Delta)\,d\Delta \quad \text{with the property} \quad \phi(\Delta) = \phi(-\Delta) \;\&$$

$$\int_{-\infty}^{\infty}\phi(\Delta)\,d\Delta = 1. \quad (\text{normalized})$$

If $f(x,t)$ is the no. of particles at time t at position x

$$\text{Then} \quad f(x, t+\tau)\,dx = dx\int_{-\infty}^{\infty} f(x+\Delta, t)\,\phi(\Delta)\,d\Delta$$

Kramers - Moyal Expansion : $f(x+\Delta, t) = f(x,t) + \Delta\frac{\partial f(x,t)}{\partial x} + \frac{\Delta^2}{2}\frac{\partial^2 f(x,t)}{\partial x^2} + \cdots$

$$f(x, t+\tau) = f(x,t) + \tau\frac{\partial f(x,t)}{\partial t} \quad \text{as } \tau \text{ is short.}$$

$$\therefore \; f + \tau\frac{\partial f}{\partial t} = f\underbrace{\int_{-\infty}^{\infty}\phi(\Delta)\,d\Delta}_{=1} + \frac{\partial f}{\partial x}\overset{0}{\underbrace{\cancel{\int_{-\infty}^{\infty}\Delta\phi(\Delta)\,d\Delta}}_{\text{odd function}}} + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)\,d\Delta + \cdots$$

$$\text{Equating} \quad \frac{\partial f}{\partial t} = \frac{1}{\tau}\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\phi(\Delta)\,d\Delta\,\frac{\partial^2 f}{\partial x^2} = D\frac{\partial^2 f}{\partial x^2}$$

$$\text{So} \quad \boxed{D = \frac{1}{\tau}\int_{-\infty}^{\infty}\Delta^2/2\;\phi(\Delta)\,d\Delta} \qquad \boxed{\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2}} \quad \text{Diffusion equation}$$

CW Observation on Brownian movement in water showed that the horizontal displacement for a test particle in 11 successive intervals of 33 secs were $[0, 5.6, -1.7, -10.8, 6.6, -9.8, -11.2, -4.0, 15.0, 19.1, 16.0] \times 10^{-4}$ cm, radius of particle 1.15×10^{-5} cm & $T = 20^\circ C$ & $\eta_{water} = 0.01$ cgs unit, $R = 8.32 \times 10^7$, ergs/deg/mole. Obtain N.

$$\langle x^2 \rangle = \frac{RT}{N} \frac{1}{3\pi\eta a} t$$

$$\langle x^2 \rangle = \frac{x_1^2 + x_2^2 + x_3^2 + \cdots + x_{11}^2}{11} = 1.18 \times 10^{-6} \text{ cm}^2$$

$$\therefore \quad N = \frac{RTt}{\langle x^2 \rangle 3\pi\eta a} = \frac{8.32 \times 10^7 \times 293 \times 30}{1.18 \times 10^{-6} \times 3 \times 3.14 \times 0.01 \times 1.15 \times 10^{-5}}$$

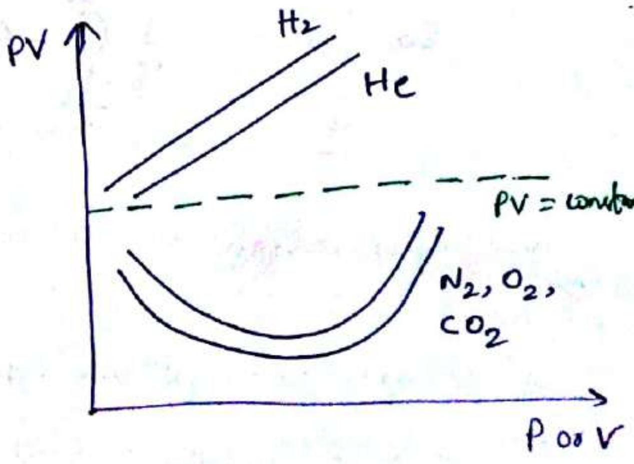
$$= 5.72 \times 10^{23}.$$

Equation of State for Real Gases

To define the state of a gaseous system completely, we need to know three parameters P, V & T. By equation of state we mean the mathematical relation that express functional form of P, V, T as $f(P,V,T) = 0$. The equation of state of a perfect gas $PV = RT$ is the most simple form of equation of state.

Insufficiency of the perfect gas equation

Boyle found that that the perfect gas equation $PV = RT$ does not fit the experimental results and works only at ideal condition i.e. at very high temperature & very low pressure. In indicator diagram (P vs. V) one can obtain isothermals. Experiment by Regnault showed that no gas obeys $PV =$ constant but either increases with pressure or they decrease & increase with pressure. So modification of perfect gas laws is necessitated.



To explain the gradual increment of PV with P for H_2, He etc consider the modified equation $P(V-b)$ = constant or PV = constant $+ Pb$. which increases with P. On the other hand to explain the initial drop of curves for O_2, N_2, CO_2 we take $(P+P_i)V$ = constant

∴ In combined form $(P+P_i)(V-b)$ = constant was noted in 1860.

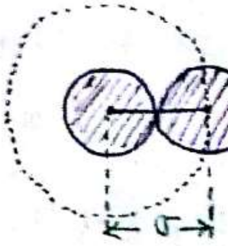
Semiderivation of Vanderwaal's equation

To obtain heuristically an expression for real gas, in 1909, Vanderwaal made a few simplifying assumptions that

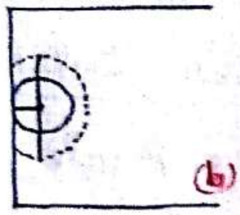
(i) The molecules are rigid spherical objects of diameter σ

(ii) They attract each other with a weak force that depends only on the intermolecular distance & independent of the orientation of the molecules. To derive, first he considered the effect of finite size of molecules & then considered the weak attractive force & then superposed them which cannot be rigorously justified.

Volume Correction


(a)

We know that $\frac{4}{3}\pi\sigma^3$ is the sphere of influence of a molecule, so that center of no other molecule can penetrate it. So if the total space contains N molecules then $(N-1)\frac{4}{3}\pi\sigma^3$ is excluded from the center of others.


(b)

∴ The actual free volume is $V-(N-1)\frac{4}{3}\pi\sigma^3$

$\simeq V-\frac{4}{3}\pi N\sigma^3$ as $N \sim 10^{23} >> 1$.

∴ The actual number density is $n_r = \frac{N}{V-2b}$ where $b = \frac{2}{3}\pi N\sigma^3$.

As in figure (b), if we consider the gas to be enclosed in a vessel, then the molecule may approach only to a distance $\sigma/2$ from the wall, as then the surface of the molecule will touch the wall. But since the sphere of influence is of radius σ meaning when a molecule is at a distance σ, its sphere of influence extends to the wall & therefore the center of no other molecule can lie within the hemisphere $\frac{2}{3}\pi\sigma^3$.

$\therefore$ If we consider an elementary volume dV in the neighbourhoo of the wall, then $\frac{2}{3}\pi n_r \sigma^3$ is the fraction of volume unavailab for the center of other molecules. So if dV_a is the amount of dV existing as free space, then

$$dV_a = dV - \frac{2}{3}\pi\sigma^3 n_r\, dV = dV\left(1 - \frac{2/3\,\pi N\sigma^3}{V-2b}\right) = dV\left(1 - \frac{b}{V-2b}\right)$$

The actual number of molecules in dV is $n_r\, dV_a$

$$= \frac{N}{V-2b}\left(1 - \frac{b}{V-2b}\right)dV = \frac{N\,dV}{V-2b}\,\frac{\left(1-\frac{b}{V-2b}\right)\left(1+\frac{b}{V-2b}\right)}{\left(1+\frac{b}{V-2b}\right)}$$

$$= \frac{N\,dV}{V-2b}\,\frac{1}{1+\frac{b}{V-2b}} \quad \left(\text{as } \frac{b^2}{(V-2b)^2} << 1\right)$$

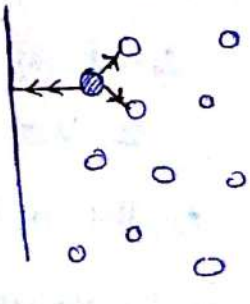
$$= \frac{N\,dV}{V-b}$$

If we would've considered the molecules as geometrical point mass objects, then the number of molecules in dV would be $\frac{N}{V}dV$

So finite size correction is V−b and volume correction is

$$b = \frac{2}{3}\pi\sigma^3 N = 4 \times \frac{4}{3}\pi N\left(\frac{\sigma}{2}\right)^3 = 4 \times \text{Total volume of all molecules.}$$

Pressure Correction



The molecule attract with a cohesive force that varies inversely as some power of the distance between them, which is negligible at long distance. On average, molecule get zero force due to isotropicity except near a surface. Parallel to surface forces will still balance but not pependicular to it, so uncompensated inward force $\perp^r$ to boundary. Force on single molecule $\propto$ number of attracting molecule / cc.

Also force acting / unit area of surface $\propto$ number of molecules in that area of surface. Hence cohesive force / unit area of the surface is $\propto n^2 = \left(\frac{N}{V}\right)^2$ where N is the total number of molecules & V is the total volume. $\therefore$ $P_1 \propto \frac{1}{V^2} = \frac{a}{V^2}$. This cohesive pressure is called internal pressure or intrinsic pressure & acts only in the boundary layer of any solid or fluid giving rise to surface tension in liquids & tensile force in solids. It opposes the kinetic pressure but assists the external pressure in keeping the substance together. So it opposes the outward motion & decreases the momentum & hence the pressure. So P is replaced by $P + \frac{a}{V^2}$ as if the external pressure is increased.

$\therefore$ for one mole gas $\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT}$ Vanderwaal's equation of state.

Constant volume method of finding "a" and "b"

From VW equation, $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{or} \quad \boxed{b = V - \frac{R}{\left(\frac{\partial P}{\partial T}\right)_V}}$$

$$\boxed{a = V^2\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}}$$

Therefore "a" and "b" can be obtained by observing the rate of increase of pressure with temperature as in constant volume gas thermometer very accurately. But they vary with temperature.

At N.T.P.

Gas	a in atm cm^6 $(\times 10^{-5})$	b in cc $(\times 10^{-5})$
He	6.8	106
Ar	268.0	143
O_2	273.0	143
N_2	272.0	173
CO_2	717.0	191
NH_3	833.0	168

Vander Waal's equation from Clausius virial theorem

In an entirely different approach, Clausius deduced rigorously the equation for a real gas, using Newtonian concept of classical dynamics. If x, y, z denote the coordinate of a molecule in an arbitrary reference frame and f_x, f_y, f_z denote the force components, then

$$m\frac{d^2x}{dt^2} = f_x , \quad m\frac{d^2y}{dt^2} = f_y , \quad m\frac{d^2z}{dt^2} = f_z$$

as $\frac{d^2}{dt^2}(x^2) = 2\frac{d}{dt}\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2}$

$\therefore \; x\frac{d^2x}{dt^2} = \frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2$, similarly for y and z.

$\therefore \; mx\frac{d^2x}{dt^2} = f_x x \Rightarrow m\left\{\frac{1}{2}\frac{d^2}{dt^2}(x^2) - \left(\frac{dx}{dt}\right)^2\right\} = f_x x$

or $\frac{m}{2}\left(\frac{dx}{dt}\right)^2 = \frac{m}{4}\frac{d^2}{dt^2}(x^2) - \frac{1}{2}f_x x$, similarly for y and z.

Adding all components, we get the K.E. of a molecule.

$$\frac{1}{2}m\left\{\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right\} = \frac{m}{4}\frac{d^2}{dt^2}(x^2+y^2+z^2) - \frac{1}{2}(xf_x + yf_y + zf_z)$$

Summing over all molecule and taking average over sufficiently long interval τ, we get

$$\frac{1}{2}\overline{\sum_i mv^2}^{\tau} = \frac{m}{4}\sum_i \overline{\frac{d^2}{dt^2}(r^2)}^{\tau} - \frac{1}{2}\sum_i \overline{xf_x + yf_y + zf_z}^{\tau} \qquad \left[\overline{X}^{\tau} = \frac{1}{\tau}\int_0^{\tau} X\,dt\right]$$

In steady state, $\overline{\frac{1}{2}\sum_i mv^2}^{\tau}$ and $\overline{\frac{1}{2}\sum_i \vec{r}\cdot\vec{f}}^{\tau}$ are approximately constant throughout the motion. But $\frac{m}{4}\frac{1}{\tau}\int_0^{\tau}\sum_i \frac{d^2}{dt^2}(r^2)\,dt = \frac{m}{4\tau}\int_0^{\tau}\sum_i \frac{d}{dt}\left(2r\cdot\frac{dr}{dt}\right)dt$

$= \frac{m}{2\tau}\sum_i \vec{r}\cdot\frac{d\vec{r}}{dt}\Big|_0^{\tau} = 0$ as $\vec{v} = \frac{d\vec{r}}{dt}$ fluctuates irregularly with time and using the Brownian motion concept, $\overline{r\cdot\frac{dr}{dt}}^{\tau} = \overline{r}^{\tau}\cdot\overline{\frac{dr}{dt}}^{\tau} = 0$. Remember in Einstein's theory (Langevin equation)

$$\underbrace{m\frac{dv}{dt}}_{\text{inertial}} = \underbrace{-\alpha v}_{\text{Viscous}} + \underbrace{f_B(t)}_{\text{Brownian}} , \qquad \begin{array}{ll} \overline{x f_B}^{\tau} = 0 & \text{(Markovian)} \\ \overline{v f_B}^{\tau} \neq 0 = \alpha k_B T & \text{(non-Markovian)} \end{array}$$

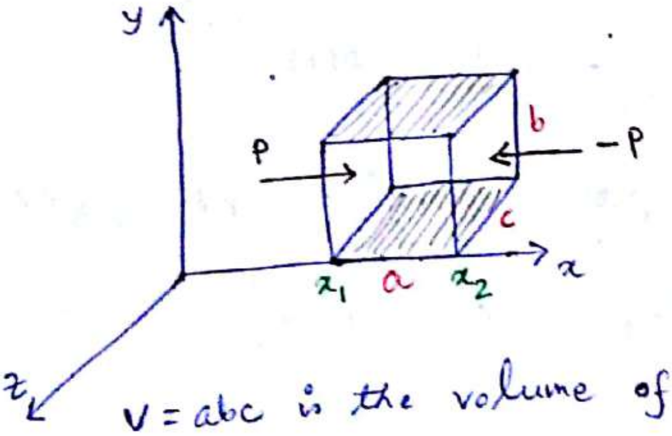
$$\therefore \boxed{\underbrace{\frac{1}{2}\overline{\sum_i m v^2}^{\tau}}_{KE} = \underbrace{-\frac{1}{2}\overline{\sum_i \vec{r}\cdot\vec{F}}^{\tau}}_{virial}}$$

Virial theorem states that average Kinetic energy of translation of the molecules of a gas in the steady state is equal to its virial.

Now, F_x, F_y and F_z include all the forces that act on the molecule. These forces can be broadly categorized as.

1. The force of impact on the molecule due to collision with the walls of the vessel.
2. The force due to collision between two molecules.
3. The force of attraction between molecules within some distance.

We consider the contribution of 1 to the virial. Imagine the gas confined in a box of dimension a, b, and c with faces cutting x axes at x_1 & x_2. If the pressure exerted by the gas is P, then



$$\sum F_x \text{ at } x_1 = Pbc$$
$$\sum F_x \text{ at } x_2 = -Pbc.$$
$$\therefore -\frac{1}{2}\sum F_x x = \frac{1}{2}Pbc(x_2 - x_1)$$
$$= \frac{1}{2}Pabc = \frac{1}{2}PV.$$

where $V = abc$ is the volume of the box. Similarly $-\frac{1}{2}\sum F_y y = \frac{1}{2}PV$ and $-\frac{1}{2}\sum F_z z = \frac{1}{2}PV$ for two other faces. ∴ Total contribution by the forces acting on the wall is $\frac{3}{2}PV$.

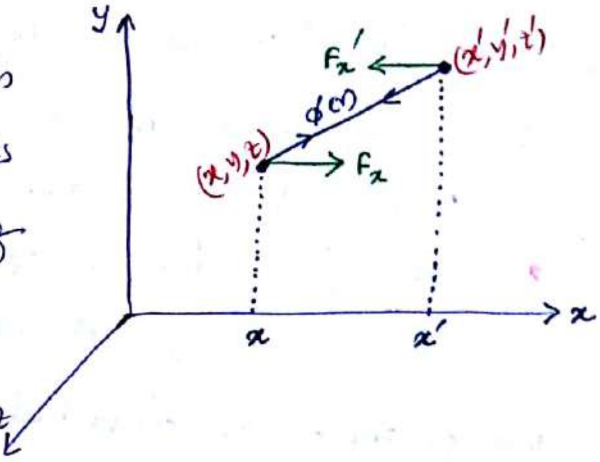
For an ideal gas, contribution form 2 and 3 is neglected, because there is no cohesive force, nor they've a finite size, then,

$$\frac{1}{2}mN\bar{c}^2 = \frac{3}{2}PV = \frac{3}{2}RT \quad \text{(using Virial theorem)}$$

or $\boxed{P = \frac{1}{3}mn\bar{c}^2}$

Equation of state for real gases

Now we incorporate point 2 and 3 but we do not know the nature of forces. For simplicity, let's assume isotropicity so that the force is fully radial, say $\phi(r)$, with $\phi(r) = -\frac{dE}{dr}$ where E is the P.E. due to intermolecular force. Let the coordinates of the center of two molecules be (x, y, z) and (x', y', z'). Then the components (F_x, F_y, F_z) and (F_x', F_y', F_z') of the forces acting are



$$F_x = \phi(r)\left(\frac{x-x'}{r}\right)$$

$$F_x' = \phi(r)\left(\frac{x'-x}{r}\right),$$ Therefore the contribution to $\Sigma F_x x$ by these forces is $F_x x + F_{x'} x' = \frac{\phi(r)}{r}(x-x')^2$ similarly for the y and z components. So the total contribution is

$$-\frac{1}{2}\sum \frac{\phi(r)}{r}\underbrace{\left[(x-x')^2 + (y-y')^2 + (z-z')^2\right]}_{r^2} = -\frac{1}{2}\sum r\phi(r).$$

Hence from the virial theorem, we get $\frac{1}{2}mN\bar{c}^2 = \frac{3}{2}PV - \frac{1}{2}\Sigma r\phi(r)$

But $\frac{1}{2}m\bar{c}^2 = \frac{3}{2}k_BT$, $\therefore$ $\boxed{PV = Nk_BT + \frac{1}{3}\Sigma r\phi(r)}$

Evaluation of $\Sigma r\phi(r)$

According to MB distribution with P.E. we know

$$N_c = N_0\left(\frac{m}{2\pi k_BT}\right)^{3/2} 4\pi c^2 e^{-(\frac{1}{2}mc^2 + E)/k_BT} dc.$$

$\hookrightarrow$ no. of molecules when P.E. = 0. $\simeq N_0 e^{-E/k_BT}$

Let us calculate the contribution of one molecule to the virial. Average number of other molecules lying within r and r+dr from this molecule is $4\pi r^2 dr n$ & the force exerted by them is $\phi(r)$. So the contribution of one molecule to $r\phi(r)$ is

$\int_0^\infty 4\pi r^3 n_0\, e^{-E/k_BT}\, \phi(r)\, dr$ and so the contribution of N molecules is $\frac{N}{2}\int_0^\infty 4\pi r^3 n_0\, \phi(r)\, e^{-E/k_BT}\, dr$ where division by 2 is to avoid the double-counting. Substituting $n_0 = \frac{N}{V}$ and $\phi(r) = -\frac{\partial E}{\partial r}$ we have

contribution of N molecules $= \frac{2\pi N^2}{V}\int_0^\infty r^3 e^{-E/k_BT}\, dr\, \phi(r)$.

Now $\int e^{-E/k_BT}\phi(r)\, dr = -\int e^{-E/k_BT}\frac{\partial E}{\partial r}\, dr = -k_BT\int e^{-E/k_BT}\, d(E/k_BT)$

$= k_BT\, e^{-E/k_BT} + \text{Constant}$, $(\text{constant} = -k_BT)$

∴ Integrating by parts $\left[\int u\, dv = uv - \int v\, du\right]$

$$\frac{2\pi N^2}{V}\left[\overset{0}{\left\{r^3 (k_BT\, e^{-E/k_BT} + \text{constant})\right\}_0^\infty} - \int_0^\infty 3r^2 (k_BT\, e^{-E/k_BT} + \text{constant})\, dr\right]$$

$$= \frac{2\pi N^2}{V}\, 3k_BT\int_0^\infty r^2 (1 - e^{-E/k_BT})\, dr = \sum r\phi(r).$$

Substituting this to real gas equation of state, we obtain

$$PV = Nk_BT + \frac{2\pi N^2}{V}k_BT\int_0^\infty r^2 (1 - e^{-E/k_BT})\, dr.$$

To evaluate the integral, we assume that molecules are rigid spheres of diameter σ, so $E = \infty$ for $r < \sigma$

$= \text{small}$ for $r > \sigma$

$$\therefore \int_0^\sigma r^2\, dr + \int_0^\infty r^2 (1 - e^{-E/k_BT})\, dr = \frac{1}{3}\sigma^3 + \int_0^\infty \frac{r^2 E\, dr}{k_BT}$$

$$\therefore \boxed{PV = RT + \frac{RT}{V}\left(b - \frac{a}{RT}\right)} \quad \text{with} \quad \boxed{\begin{aligned} b &= \frac{2}{3}N\pi\sigma^3 \\ a &= -2\pi N^2\int_0^\infty E r^2\, dr \end{aligned}}$$

Note that "b" is identical to VW constant and "a" is positive (as E is negative). Thus the second virial coefficient obtained from virial theorem is $\frac{RT}{V}\left(b - \frac{a}{RT}\right)$

from VW equation $\left(p + \frac{a}{V^2}\right)(V - b) = RT$ we have

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

$$\therefore \boxed{PV = RT + \frac{RT}{V}\left(b - \frac{a}{RT}\right) + RT\left(\frac{b}{V}\right)^2 + \cdots}$$

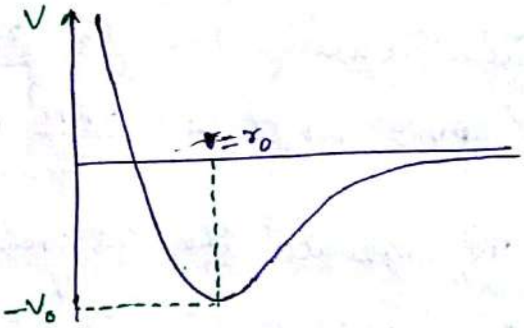
This equation agrees with the earlier obtained expression (using virial theorem) upto second virial coefficient. Third virial coefficient isn't correct & do not agree with Clausius's virial theorem. So VW equation is theoretically correct upto $\frac{1}{V}$ term & no further.

Nature of molecular force

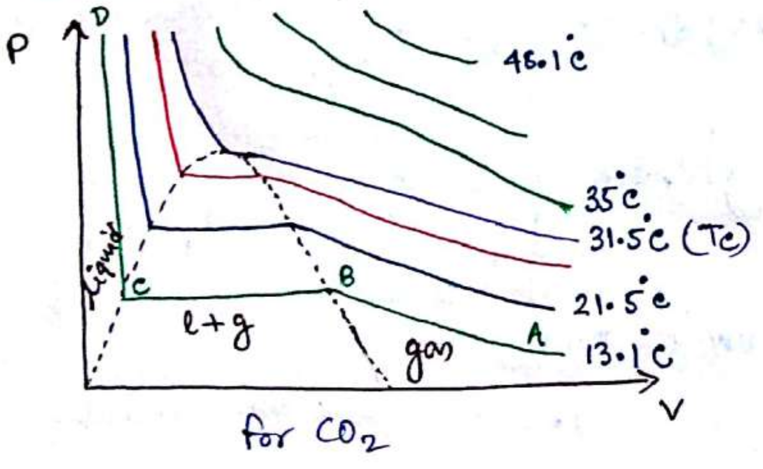
The force of interaction between the molecules of a gas is a very complicated phenomena. It is found that the force is attractive when the molecules are far apart & strongly repulsive when they are closeby. Lennard & Jones showed by taking fluctuating dipole-dipole interaction that the P.E. without any charge is

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

where r is intermolecular distance and A & B are constants.



Andrew's Experiments & inferences



for CO_2

Isothermals:

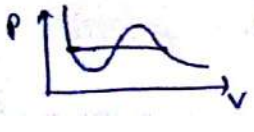
AB → P increases, V decreases

BC → V decreases without P changing (Lever rule)

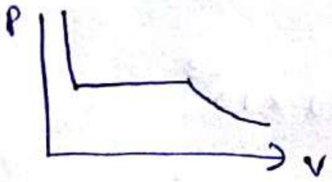
CD → almost negligible change of V, P shoots up

"Critical Opalescence" 1910 Einstein's final theoretical investigation on Brownian motion.

liquifaction of gas. Vanderwaal's equation gives a curve as



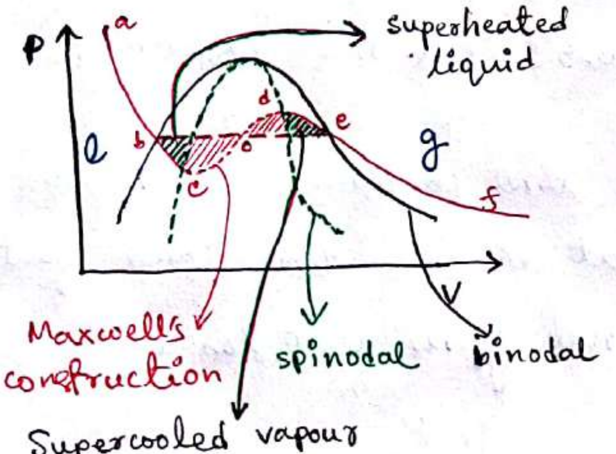
Thomson hypothesized but Maxwell's construction was

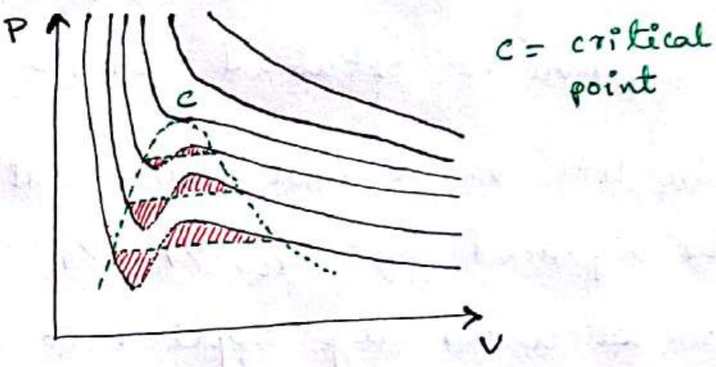


so that ambiguity can be removed, $\frac{\partial P}{\partial V} > 0$.

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

or $$\frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \quad \frac{\partial^2 P}{\partial V^2} = -\frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$





Critical constants & the law of corresponding states

From pictures above we find that there are three points b, o, e where P is same for three values of V which becomes one at point C. So the temperature at which maximum & minimum coalesce is the critical temperature & corresponding pressure & volume is the critical pressure & critical volume. To evaluate P_c, V_c, T_c we see that at C, $\frac{\partial P}{\partial V} = 0$

Equation for the points of maxima-minima (dotted graph) is:

$$\frac{RT}{(V-b)^2} = \frac{2a}{V^3} \quad \text{or} \quad T = \frac{2a(V-b)^2}{RV^3} \quad \text{— ①}$$

$$\therefore P = \frac{R}{V-b}\,\frac{2a(V-b)^2}{RV^3} - \frac{a}{V^2} = \frac{2a(V-b)}{V^3} - \frac{a}{V^2} \quad \text{— ②}$$

At the critical point, $$\left.\frac{dP}{dV}\right|_{V=V_c} = 0 = \frac{2a}{V_c^3} - \frac{6a(V_c-b)}{V_c^4} + \frac{2a}{V_c^3}$$

or, $2aV_c - 6aV_c + 6ab + 2aV_c = 0$ or $\boxed{V_c = 3b}$

from ①, $T_c = \frac{2a\cdot 4b^2}{R\times 27b^3} = \frac{8a}{27Rb}$, or $\boxed{T_c = \frac{8a}{27Rb}}$

from ②, $P_c = \frac{2a\times 2b}{27b^3} - \frac{a}{9b^2} = \frac{a}{27b^2}$, or $\boxed{P_c = \frac{a}{27b^2}}$

At 1 cc at STP, $a = 0.00874$ atm-cm^6, $b = 0.0023$ cc for CO_2
($T = 273K$), $P = 1$atm, $V = 1$cc.

Using VW equation $(P + \frac{a}{V^2})(V-b) = RT$,

$$\left(1 + \frac{0.00874}{1^2}\right)(1 - 0.0023) = 273R, \quad \therefore R = 3.687 \times 10^{-3}$$

$$\therefore T_c = \frac{8a}{27Rb} = \frac{8 \times 0.00874}{27 \times 3.687 \times 10^{-3} \times 0.0023} = 305.5\,^\circ K = 32.5\,^\circ C.$$

Experiments obtained 31.1 °C & 30.9 °C (Andrews experiment).

In 1881, van der Waal found that the three constants a, b, R can be replaced by P/P_c, V/V_c, T/T_c so that the non-dimensional equation can be universally applied to all real gases that has an indicator diagram of VW.

If $P/P_c = P^*$, $V/V_c = V^*$, $T/T_c = T^*$ are reduced (P, V, T) then

$$(P + \frac{a}{V^2})(V-b) = RT \Rightarrow \left(P^* P_c + \frac{a}{V^{*2} V_c^2}\right)(V^* V_c - b) = R T_c T^*$$

Substituting P_c, V_c, T_c, $\left(\frac{a}{27b^2} P^* + \frac{a}{9b^2 V^{*2}}\right)(3bV^* - b) = RT^* \frac{8a}{27Rb}$

$$\text{or} \quad \boxed{\left(P^* + \frac{3}{V^{*2}}\right)\left(V^* - \frac{1}{3}\right) = \frac{8}{3} T^*}$$

The states of two substances for which their values of (P^*, V^*, T^*) are equal are called "corresponding states." Clearly critical states of all bodies are their corresponding states. If two reduced parameters of any two substances are same, then the third reduced parameter must be identical for them. This is called the "law of corresponding states."

$$(P^*)_{CO_2} = (P^*)_{SO_2} \ \& \ (V^*)_{CO_2} = (V^*)_{SO_2} \ \text{then} \ (T^*)_{CO_2} = (T^*)_{SO_2}$$

HW 1. Calculate VW constants "a" and "b" for a gm-mole of He gas using $T_c = 5.3\,K$, $P_c = 2.25$ atm & $R = (273)^{-1}$ ~~ke~~ litre atmosphere /°.

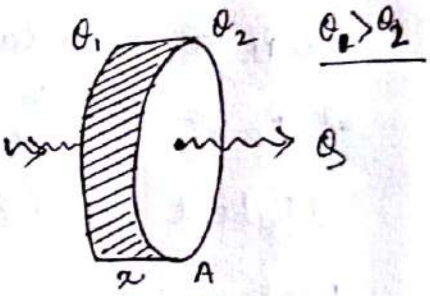
2. Calculate P_c & T_c of He gas using $a = 6.15 \times 10^{-5}$ atm-cm^6, $b = 9.95 \times 10^{-}$ cc per gm-molecule, where pressure is 1 atm & volume is volume of gas at S.T.P.

Conduction

Transmission of Heat : CONDUCTION, CONVECTION, RADIATION

In conduction, heat is transmitted from one point to other through the substance without actual motion of particles. Air or vacuum is poor conductor of heat, hence woolen fabric keeps us warm or thermos flask keeps thing isolated. In convection, heat is transmitted by the actual motion of particles. Hot water circulation in heated kettle. Heat radiation is transmitted directly without any intervening medium. Like sun radiation into earth by EM spectrum.

Coefficient of Thermal Conductivity



If we have a plane slab of area A, thickness x having temperature θ_1 & θ_2 at its two faces then if Q amount of heat is transmitted in time t, then,

$$Q \propto A$$
$$\propto (\theta_1 - \theta_2)$$
$$\propto 1/x$$
$$\propto t$$

$$\therefore \boxed{Q = \frac{KA(\theta_1-\theta_2)t}{x}}$$

K = coeff.^{n} of thermal conductivity

$$\therefore \underset{\text{heat current}}{q} = \frac{Q}{t} = \frac{KA(\theta_1-\theta_2)}{x} = \frac{\theta_1-\theta_2}{x/KA} = \frac{\theta_1-\theta_2}{\underset{\text{thermal resistance}}{R_{Th}}}$$

This equation is similar to Ohm's law $I = \frac{V}{R}$, redefined in terms of thermal resistance & heat current. We know $R = \rho\frac{l}{A} = \frac{l}{\sigma A}$ where $\sigma = \frac{1}{\rho}$ is the electrical conductivity. Comparing with $R_{Th} = \frac{x}{KA}$ we can define the proportionality constant as coeff.^{n} of thermal conductivity.

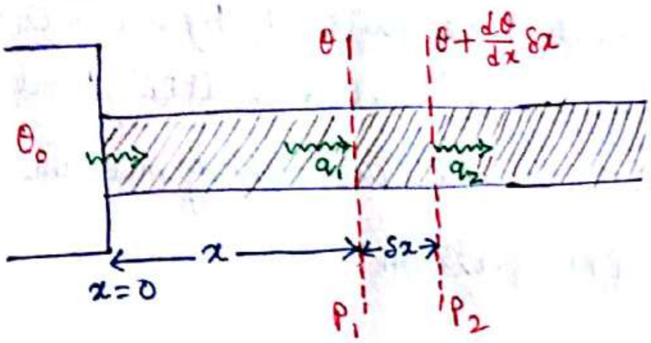
Dimension of $[Q] = [ML^2T^{-2}]$, $[x] = [L]$, $[A] = [L^2]$, $[\theta] = [\theta]$,

$[t] = [T]$

$$\therefore [K] = [MLT^{-3}\theta^{-1}]$$

Thermal diffusivity is defined as the ratio of thermal conductivity to thermal capacity per unit volume. If ρ = density & S = specific heat then $h = \frac{K}{\frac{mS}{V}} = \frac{K}{\rho S}$ = "Thermometric conductivity"

Rectilinear Propagation of heat along a bar



Consider a bar of uniform area of cross-section A contact with an oven at temperature θ_0 at $x=0$. If θ is the excess temperature above the surroundings of the bar at P_1 at a distance x from the point of contact, then excess temperatu

at P_2 = $\theta + \frac{d\theta}{dx}\delta x$.

If heat flowing through P_1 in one second $q_1 = -KA\frac{d\theta}{dx}$ &

heat flowing through P_2 in one second $q_2 = -KA\frac{d}{dx}(\theta + \frac{d\theta}{dx}\delta x)$

∴ Heat gained per second by the rod between P_1 & P_2

$$q = q_1 - q_2 = -KA\frac{d\theta}{dx} + KA\frac{d}{dx}(\theta + \frac{d\theta}{dx}\delta x)$$

$$= KA\frac{d^2\theta}{dx^2}\delta x$$

This amount of heat is used in two ways before steady state is reached. ① A part will increase the temperature, ② Rest part is lost due to radiation from the exposed surface of the slab.

If rate of rise of temperature is $\frac{d\theta}{dt}$ then heat used per second

$= \underbrace{(A\delta x)\rho}_{\text{mass}} \times \underbrace{S}_{\text{specific heat}} \times \frac{d\theta}{dt}$ & heat lost per second due to radiation

$= Ep\,\delta x\,\theta$ where E = emissive power of surface, p = perimeter

& θ = average excess of temperature within P_1 & P_2.

$$\therefore q = A\delta x \rho S\frac{d\theta}{dt} + Ep\,\delta x\,\theta = KA\frac{d^2\theta}{dx^2}\delta x$$

$$\boxed{\frac{K}{\rho S}\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \frac{PE}{A\rho S}\theta}$$ Fourier's differential equation

Special Cases1: when heat lost by radiation is negligible:

When rod is covered by insulating materials, heat lost $E p \delta x \theta = 0$ & total heat gained by rod is to raise the temperature, using

$$\frac{K}{\rho S}\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} \quad \text{or} \quad h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt}$$

Special Cases 2: after the steady state is reached:

$$\frac{d\theta}{dt} = 0 \quad \text{and} \quad \frac{d^2\theta}{dx^2} = \frac{PE}{KA}\theta = \mu^2\theta$$

This is a second order homogeneous linear differential equation

If $\theta = e^{mx}$ is the trial solution then $m^2 = \mu^2$ or $m = \pm\mu$

$$\therefore \quad \theta = \underbrace{A_1 e^{\mu x} + A_2 e^{-\mu x}}_{\text{Boundary conditions}}$$

If the bar is sufficiently long, we can assume that under steady state no heat is lost from free end of the bar, as whole of the heat is lost from ~~free end~~ sides as radiation & free end will be at the temperature of the surroundings.

(a) **when bar is of infinite length:**

Boundary condition, $x = 0, \ \theta = \theta_0$ (Dirichlet B.C.)

$x = \infty, \ \theta = 0$

we see that $0 = A_1 e^{\infty}$ can be true only if $A_1 = 0$. and $\theta_0 = A_2$. $\therefore \boxed{\theta = \theta_0 e^{-\mu x}}$

Thus after steady state is reached, temperature is exponentially distributed. This is useful in Ingen-Hausz experiment.

(b) **When bar is of finite length:** $x = 0, \ \theta = \theta_0$

$x = L, \ \frac{d\theta}{dx} = 0$ (Neumann B.C.)

In this case $A_1 = \frac{\theta_0}{1+e^{2\mu L}}$, $A_2 = \frac{\theta_0}{1+e^{-2\mu L}}$

∴ Solution $\boxed{\theta = \theta_0 \left[\frac{e^{\mu x}}{1+e^{2\mu L}} + \frac{e^{-\mu x}}{1+e^{-2\mu L}} \right]}$

Special Cases I at steady state Ideal case when there is no loss of heat by radiation i.e. rod is thermally lagged & in steady state

$$h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} = 0 \quad \text{or} \quad \frac{d^2\theta}{dx^2} = 0 \quad (\text{as } h \neq 0)$$ [Laplace equation in electrostatics]

Solving $\frac{d}{dx}\left(\frac{d\theta}{dx}\right) = 0$ or $\frac{d\theta}{dx}$ = constant = A

or $\theta = Ax + B$.

Find A & B using B.C. that $x=0,\ \theta = \theta_0$

$x = l,\ \theta = \theta_m$ (say)

at unknown distance l, the temperature is θ_m.

$\theta_0 = B$. and then $\theta_m = Al + \theta_0$ or $A = \frac{\theta_m - \theta_0}{l}$

$$\therefore \boxed{\theta = \theta_0 - \frac{\theta_0 - \theta_m}{l} x}$$

The decrement is linear, as "solution of Laplace equation is always a straight line".

In steady state length upto which wax melts in wax coated bar

from $\theta = \theta_0 e^{-\mu x}$, $\ln\frac{\theta}{\theta_0} = -\mu x$ we see that if we have number of bars with conductivities $K_1, K_2, K_3, \dots$ etc & wax melts upto length $l_1, l_2, l_3, \dots$ etc then at these length the temperature would be melting point of wax (say θ_m).

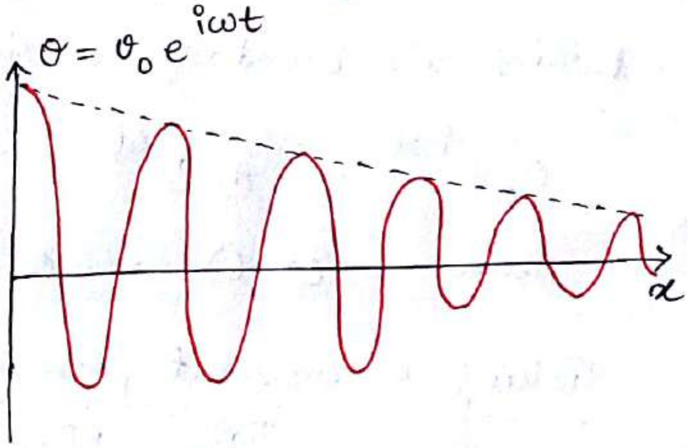
$$\therefore \ln\frac{\theta_m}{\theta_0} = -\mu_1 l_1 = -\mu_2 l_2 = -\mu_3 l_3 = \cdots$$

$$\therefore \sqrt{\frac{PE}{K_1 A}}\, l_1 = \sqrt{\frac{PE}{K_2 A}}\, l_2 = \sqrt{\frac{PE}{K_3 A}}\, l_3 = \cdots$$

or $l/\sqrt{K}$ = constant or $l \propto \sqrt{K}$

Hence in a steady state the length upto which the wax melts along a wax coated bar is proportional to the square root of the coefficient of thermal conductivity of the material.

Periodic flow of heat : Propagation of heat wave in an insulated rod with one end heated sinusoidally.



Consider a system of infinite length, well insulated (no loss due to radiation) whose one end is connected to an heat source from where heat is supplied not continuously but periodically. with θ_0 amplitude and ω being the angular frequency.

Using fourier's equation $h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \cancelto{0}{\frac{PE}{A\rho S}\theta}$ without radiation loss, the unidirectional heat equation is $h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt}$, $h = \frac{K}{\rho S}$ is the thermal diffusivity of the rod.

Let $\theta = u(x) + v(x,t)$ is a trial solution. then separating the variables, $\frac{d^2u}{dx^2} = 0$, $h\frac{d^2v}{dx^2} = \frac{dv}{dt}$

The solution of v-equation can be $v = F(x)e^{i\beta t}$

$\therefore hF''(x) = i\beta F(x)$ $\therefore F''(x) = \frac{i\beta}{h}F(x) = \left(\sqrt{\frac{i\beta}{h}}\right)^2 F(x).$

Taking the trial solution as $F(x) = Ae^{mx}$ we obtain,

$m^2 = \frac{i\beta}{h}$ or $m = \pm\sqrt{\frac{i\beta}{h}}$ $\therefore F(x) = A_1 e^{\sqrt{i\beta/h}\,x} + A_2 e^{-\sqrt{i\beta/h}\,x}$

As $x \to \infty$ yields $F(x) \to \infty$ (unphysical), so $A_1 = 0$.

$\therefore F(x) = A_2 e^{-\sqrt{\frac{i\beta}{h}}x}$

Now $(1+i)^2 = 2i$ or $i = \frac{1}{2}(1+i)^2$ or $\sqrt{i} = \pm\frac{1}{\sqrt{2}}(1+i)$

$\therefore F(x) = A_2 e^{-(1+i)\sqrt{\frac{\beta}{2h}}x} + A_3 e^{(1+i)\sqrt{\frac{\beta}{2h}}x}$

$$\therefore \vartheta = F(x)\, e^{i\beta t} = \left[A_2 e^{-\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t - \sqrt{\frac{\beta}{2h}}x)} + A_3 e^{\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t + \sqrt{\frac{\beta}{2h}}x)} \right]$$

Here also, as $x \to \infty$, $\vartheta \to \infty$ (unphysical), hence $A_3 = 0$.

$$\text{So } \vartheta(x,t) = A_2 e^{-\sqrt{\frac{\beta}{2h}}x} e^{i(\beta t - \sqrt{\frac{\beta}{2h}}x)}$$

Putting the boundary condition for $\theta = \theta_0 e^{i\omega t}$ at $x = 0$, we see

$$\theta_0 e^{i\omega t} = A_2 e^{i\beta t} \qquad \therefore A_2 = \theta_0,\ \beta = \omega.$$

$$\text{Hence } \vartheta(x,t) = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} e^{i(\omega t - \sqrt{\frac{\omega}{2h}}x)}$$

Taking a constant phase factor ϕ from the solution of u, we have

$$\boxed{\theta = \theta_0 e^{-\sqrt{\frac{\omega}{2h}}x} e^{i[\omega t - \sqrt{\frac{\omega}{2h}}x - \phi]}}$$

This represents a progressive wave traveling with velocity

$$V = \frac{\omega}{K} = \frac{\omega}{\sqrt{\frac{\omega}{2h}}} = \sqrt{2\omega h} = \sqrt{\frac{2\omega K}{\rho S}} = \sqrt{\frac{2K}{\rho S}\frac{2\pi}{T}} = \sqrt{\frac{4\pi K}{T\rho S}}$$

$$\text{damping factor} = \sqrt{\frac{\omega}{2h}}$$

$$\text{As } \frac{\lambda}{T} = \vartheta = \sqrt{\frac{4\pi K}{T\rho S}} \quad \text{or} \quad K = \frac{\lambda^2 \rho S}{4\pi T}$$

CW In a periodic flow of heat along an iron bar, the periodic time is 4 minute. If the temperature travels maximum 6 cm in 1 minute, calculate the thermal conductivity of iron. Density of iron = 7.8 gm/cm³, specific heat of iron = 0.11 cal/gm°C.

$$\vartheta = \sqrt{2\omega h} = \sqrt{\frac{4\pi K}{T\rho S}} \quad \text{or} \quad \vartheta^2 = \frac{4\pi K}{T\rho S}$$

Here $\vartheta = 6\text{cm/min} = 0.1\ \text{cm/sec}$, $T = 4\ \text{min} = 4 \times 60 = 240\ \text{sec}$

$S = 0.11\ \text{cal/gm}^\circ\text{C}$, $\rho = 7.8\ \text{gm/cm}^3$

$$\therefore K = \frac{\vartheta^2 T\rho S}{4\pi} = \frac{0.1^2 \times 240 \times 7.8 \times 0.11}{4 \times 3.14} = 0.1639\ \text{cal cm}^{-1}\text{sec}^{-1}\,{}^\circ\text{C}^{-1}$$

Heat flow in three dimensions

We have learned Fourier's law in one dimension,

$$h\frac{d^2\theta}{dx^2} = \frac{d\theta}{dt} + \mu^2 h\theta .$$

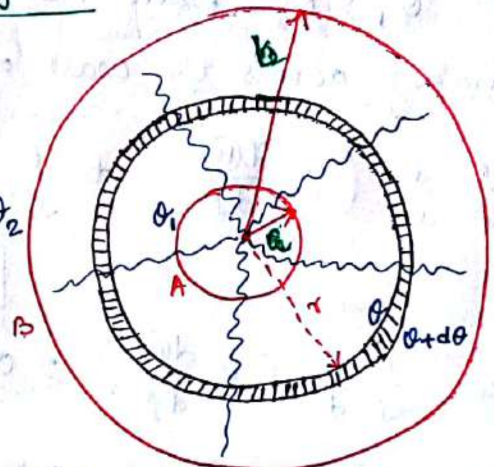
In three dimensions, we have

$$h\nabla^2\theta = \frac{d\theta}{dt} + \mu^2 h\theta.$$

In steady state, $\frac{d\theta}{dt} = 0$ and without radiation loss, $\mu^2 = 0$ yields $\boxed{\nabla^2\theta = 0}$ This is called "Laplace equation" of heat flow. Compare with Electrostatics, Laplace equati

ⓐ Spherical shell Method (Radial flow)

Consider a spherical shell of inner radius a and outer radius b. Let θ_1 & θ_2 are the temperature at inside & outside the sphere. We wont to find out temperature at $a<r<b$.



In spherical polar coordinates, Laplace eqn is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Theta}{\partial r}\right) + \cancelto{0}{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)} + \cancelto{0}{\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Theta}{\partial\phi^2}} = 0$$

$$\left[\text{as } \Theta \neq \Theta(\theta,\phi)\right]$$

$$\text{or } \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Theta}{\partial r}\right) = 0$$

$$\text{or } r^2\frac{d\Theta}{dr} = \text{constant} = C_1 \text{ (say)}$$

$$\text{or } d\Theta = \frac{C_1}{r^2}dr \quad \text{or} \quad \Theta = -\frac{C_1}{r} + C_2$$

Now we use Dirichlet Boundary condition $\Theta = \theta_1$ at $r=a$
$\Theta = \theta_2$ at $r=b$.

$$\therefore \theta_1 = -\frac{C_1}{a} + C_2$$
$$\theta_2 = -\frac{C_1}{b} + C_2$$

$$\text{or } (\theta_1 - \theta_2) = C_1\left(\frac{1}{b} - \frac{1}{a}\right)$$

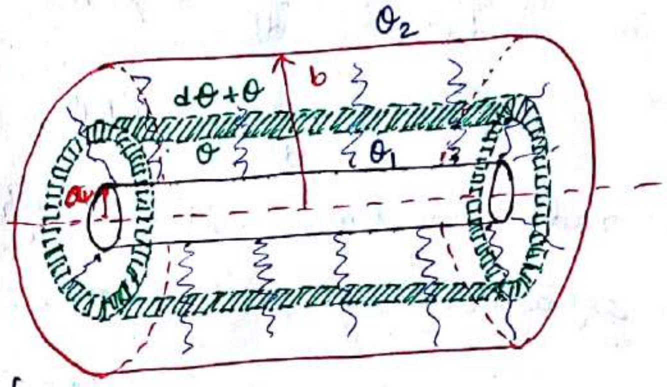
$$\text{or } C_1 = \frac{ab(\theta_1-\theta_2)}{a-b}$$

$$\therefore C_2 = \theta_1 + \frac{C_1}{a} = \theta_1 + \frac{(\theta_1-\theta_2)b}{a-b} = \frac{a\theta_1 - b\theta_2}{a-b}.$$

∴ The temperature at any distance r is

$$\Theta = \left[\frac{ab(\theta_1-\theta_2)}{b-a}\right]\frac{1}{r} + \frac{a\theta_1 - b\theta_2}{a-b}$$

ⓑ Cylindrical flow of heat



Consider a cylindrical tube of length l, inner radius a & outer radius b with temperature of inner surface θ_1 & outer surface θ_2 with $\theta_1 > \theta_2$ where heat is conducted radially across the wall of the tube. Laplace eqⁿ becomes

$$\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{\partial\Theta}{\partial\rho}\right) + \frac{1}{\rho^2}\cancelto{0}{\frac{\partial^2\Theta}{\partial\theta^2}} + \cancelto{0}{\frac{\partial^2\Theta}{\partial\phi^2}} = 0$$

$$\left[\Theta \neq \Theta(\theta,\phi)\right]$$

or $\frac{1}{\rho}\frac{d}{d\rho}\left(\rho\frac{d\Theta}{d\rho}\right) = 0$ or $\rho\frac{d\Theta}{d\rho} = \text{constant} = c_1$

or $d\Theta = \frac{c_1}{\rho}d\rho$ or $\Theta = c_1 \ln\rho + c_2$

We use Dirichlet boundary condition, $\Theta = \theta_1$ at $\rho = a$
$\Theta = \theta_2$ at $\rho = b$.

∴ $\theta_1 = c_1 \ln a + c_2$ or $\theta_1 - \theta_2 = c_1 \ln a/b$.

$\theta_2 = c_1 \ln b + c_2$ or $c_1 = \frac{\theta_1-\theta_2}{\ln a/b}$.

∴ $c_2 = \theta_1 - c_1\ln a = \theta_1 - \frac{(\theta_1-\theta_2)}{\ln a/b}\ln a = \frac{\theta_1(\ln a - \ln b) - (\theta_1-\theta_2)\ln a}{\ln a/b}$

$= \frac{\theta_2\ln a - \theta_1 \ln b}{\ln a/b}$. So the temperature at any distance r is, $\Theta = \frac{\theta_1+\theta_2}{\ln a/b}\ln\rho + \frac{\theta_2\ln a - \theta_1\ln b}{\ln a/b}$

Using Fourier's law at unit time, $Q = K\,2\pi r l\,\frac{d\theta}{dr}$

or $Q\int_a^b \frac{dr}{r} = 2\pi K l\int_{\theta_1}^{\theta_2} d\theta = 2\pi K l\,(\theta_2-\theta_1)$.

∴ $Q_r \ln \frac{b}{a} = 2\pi K l(\theta_2-\theta_1)$ ∴ $Q_r = \frac{2\pi K l(\theta_1-\theta_2)}{\ln a/b}$

or $K = \frac{Q_r \ln a/b}{2\pi l(\theta_1-\theta_2)}$

Wiedemann-Franz law The law states that ratio of thermal and electrical conductivities for all metals is directly proportion to the absolute temperature of the body.

$\frac{K}{\sigma} \propto T$ or $\frac{K}{\sigma T} = \text{constant} = 2\sqrt{\frac{6}{\pi}}\,\frac{K_B^2}{e^2} = L$ (Loretz number)

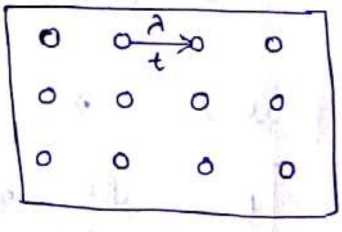
Physically this means that substances which are good conductor of heat are also good conductor of electricity.

Drude's theory of electrical conduction

Drude in 1900 introduced the concept of free electron gas model of metals, & obtained the electric conductivity of the metal. All metals (conductors) contain a huge number of nearly free electrons that behave as gas atoms in Kinetic theory. If m is mass of electron & v is velocity at temperature T,

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}K_BT \quad \text{or} \quad v_{rms} = \sqrt{\frac{3K_BT}{m}}$$

If we apply an electric field E & then electron will experience a force eE and accelarate with $\frac{eE}{m}$. Now as the electron moves to hit an atom or ion, if λ is the mean interatomic distance that is gone in time t then average drift velocity of the electron



is $v_d = \frac{eE}{2m}t = \frac{eE}{2m}\frac{\lambda}{v}$

∴ The current density $J = nev_d = \frac{ne^2\lambda}{2mv_{rms}}E = \sigma E$

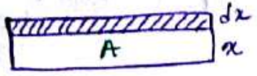
and Thermal conductivity $K = \frac{1}{3}n\bar{c}\lambda\frac{dE}{dT}$ & for only translational energy case, $E = \frac{3}{2}K_BT$, $K = \frac{1}{3}n\bar{c}\lambda\frac{3}{2}K_B = \frac{1}{2}n\bar{c}\lambda K_B$

$$\therefore \frac{K}{\sigma} = \frac{\frac{1}{2} n\bar{c}\lambda k_B}{ne^2\lambda} 2m\sqrt{\frac{3k_BT}{m}}$$

$$= 2\sqrt{\frac{8k_BT}{\cancel{m}\pi}} \frac{\cancel{n}\cancel{\lambda} k_B}{2\cancel{n}e^2\cancel{\lambda}} \cancel{m}\sqrt{\frac{3k_BT}{\cancel{m}}} = 2\sqrt{\frac{6}{\pi}} \frac{k_B^2}{e^2} T.$$

$\therefore \frac{K}{\sigma T}$ = constant = Loretz number L.

Heat conduction through a slab of varying thickness

✓ 

To form ice, 80 cals of heat are given out at 0°C when some thick ice layer has formed, heat given out has to conduct through this thickness. Let us find out the time required to increase the icelayer from x_1 to x_2. If at t, ice formed is x then within time dt, dx thickness of ice is formed, then the heat liberated is $Q = A\,dx\,\rho L$. This heat flows in dt from 0°C to outside temperature $-\theta$°C.

$$\therefore Q = \frac{KA[0-(-\theta)]dt}{x} = \frac{KA\theta}{x}dt$$

$$\therefore A\,dx\,\rho L = \frac{KA\theta}{x}dt \quad \text{or} \quad x\,dx = \frac{K\theta}{\rho L}dt$$

Integrating, $\frac{1}{2}x^2 = \frac{K\theta}{\rho L}t + c$

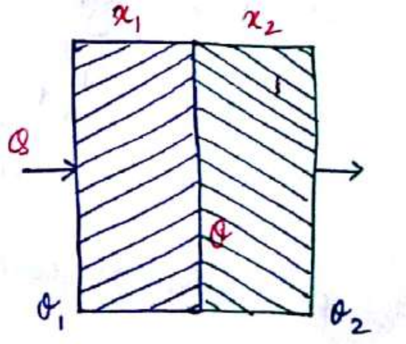
Now at $t=0$, $x=x_1$, $t=t_2$, $x=x_2$

$$\therefore \frac{1}{2}x_1^2 = c \quad \& \quad \frac{1}{2}x_2^2 = \frac{K\theta}{\rho L}t_2 + \frac{1}{2}x_1^2$$

$$\text{or} \quad t_2 = \frac{\rho L}{2K\theta}(x_2^2 - x_1^2)$$

If at $t=0$, $x=0$ then time required to form a layer of thickness x is

$$\boxed{t = \frac{\rho L}{2K\theta}x^2}$$



Heat conduction through a composite slab

Consider a slab made of two materials of thickness x_1 and x_2 and conductivities K_1 and K_2. At steady state, heat enters at θ_1

crossing interface at θ & leaves out of the second face θ_2.

$$Q = \frac{K_1 A(\theta_1-\theta)}{x_1} = \frac{K_2 A(\theta-\theta_2)}{x_2}$$

$$\text{or } Q = \frac{A(\theta_1-\theta)}{\frac{x_1}{K_1}} = \frac{A(\theta-\theta_2)}{\frac{x_2}{K_2}} = \frac{A(\theta_1-\theta_2)}{\frac{x_1}{K_1}+\frac{x_2}{K_2}}$$

If the composite slab can be replaced by a single slab of thickness x_1+x_2 such that it will conduct in unit time heat Q under temperature difference $\theta_1-\theta_2$, then the equivalent conductivity be K., then

$$Q = \frac{KA(\theta_1-\theta_2)}{x_1+x_2} = \frac{A(\theta_1-\theta_2)}{\frac{x_1}{K_1}+\frac{x_2}{K_2}} \qquad \therefore \frac{x_1+x_2}{K} = \frac{x_1}{K_1}+\frac{x_2}{K_2}$$

If we have $n \geq 2$ slabs then $\frac{x_1+x_2+x_3+\cdots}{K} = \frac{x_1}{K_1}+\frac{x_2}{K_2}+\frac{x_3}{K_3}+\cdots$

$$\text{or } \sum_{i=1}^{N} x_i \frac{1}{K} = \sum_{i=1}^{N} \frac{x_i}{K_i} \qquad \therefore \boxed{K = \frac{\sum_{i=1}^{N} x_i}{\sum_{i=1}^{N} \frac{x_i}{K_i}}}$$

HW ① One end of a metal rod is in contact with a source of heat at 100°C. In the steady state the temperature at a point 10 cm from the source is 60°C. Find the temperature at a point 20 cm from the source.

② Suppose 10 cm of ice has already formed on a pond so that the air outside is at −5°C. How long will it take for the next milimeter to form? Given for ice $L = 80$ cal/gm, $\rho = 0.917$ gm/cc & $K = 0.005$ cgs unit.

③ A lake is covered with ice 2 cm thick. Temperature of air is −15°C. Find the rate of thickening of ice in cm/hour. For ice given $K = 0.004$ cgs unit, $\rho = 0.9$ gm/cc, $L = 80$ cal/gm.

④ Two equal bars of copper & aluminium are welded end to end and lagged. If the free ends of the copper & aluminium are maintained at 100°C and 0°C respectively. Find the temperature of welded surface. K of Cu & Al are 0.92 and 0.5 cgs unit respectively.

Radiation

According to Maxwell, thermal radiation is defined as the transfer of heat from hot to cold body without any heating of the intervening medium. Thermal radiation, e.g. heat, has the same nature as light with properties:

(i) Electromagnetic wave nature to travel in Ether/vacuum at velocity of light.

(ii) travels in a straight line like light & exhibit reflection, refraction, interference, diffraction & polarisation.

These are not visible radiation but usually in UV, X ray or γ-ray. These can be detected using Thermopiles, Balometer etc.

Blackbody radiation If heat is transferred through matter, a fraction of incident radiation is absorbed (say a), a fraction reflected (say b) and rest transmitted (say c) then $a+b+c=1$ and if $b=c=0$ then the body appears black because nothing is reflected or transmitted. When heated, such blackbody radiates energy of all wavelengths. These principles are used for instance ⓐ White clothes are trendy in summer but dark coloured clothes in winter, as white clothes reflect maximum light & is least warm. Converse is true with dark shades. ⓑ Utensils are polished atop & blackened bottom so that maximum heat is absorbed & minimal heat flows out from above, ⓒ Hot water pipes are painted black inside room & white outside to provide heating to room in winter & prevent radiation at outside. ⓓ thermocouple junctions that has to be heated is painted black and so on.

Spectral Emissive Power e_λ : It is the radiant energy emitted normally from unit area of the blackbody surface per unit time in unit solid angle within a unit wavelength range.

If spectral energy density is u_λ then $u_\lambda d\lambda$ is radiated energy from area dS in solid angle $d\omega$ in time dt, then

$$e_\lambda d\lambda = \frac{u_\lambda d\lambda}{dS\, d\omega\, dt} \longrightarrow [\lambda, \lambda + d\lambda]$$

Absorptive power a_λ : It is the fraction of incident to absorbe radiation, so if Q_λ is incident & Q_λ' is absorbed then

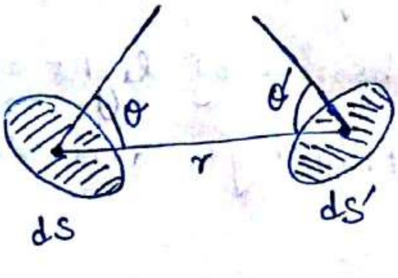
$a_\lambda = \frac{Q_\lambda'}{Q_\lambda}$ and total heat absorbed by all $\lambda = \int_0^\infty a_\lambda Q_\lambda d\lambda$.

Total Emission from dS

$$dQ_\lambda = \frac{u_\lambda d\lambda}{dt} = e_\lambda d\lambda\, dS\, d\omega.$$ So the total emission on one side $= \int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} e_\lambda d\lambda\, dS\, d\omega \cos\theta$

$$= e_\lambda d\lambda\, dS \int_0^{\pi/2} \sin\theta \cos\theta\, d\theta \int_0^{2\pi} d\phi = \pi e_\lambda d\lambda\, dS.$$

Mutual radiation between two surfaces



The solid angle subtended by dS' at dS is $d\omega' = \frac{dS' \cos\theta'}{r^2}$. So the amount of radiatio incident on dS is $e_\lambda d\lambda\, dS \cos\theta\, d\omega'$

$= e_\lambda d\lambda\, dS \cos\theta \frac{dS' \cos\theta'}{r^2}$ and the energy absorbe is $a_\lambda e_\lambda d\lambda\, dS \cos\theta \frac{dS' \cos\theta'}{r^2}$ and energy reflected will be

$(1 - a_\lambda) e_\lambda d\lambda\, dS \cos\theta \frac{dS' \cos\theta'}{r^2}$.

Kirchhoff's law Ratio of emissive to absorptive power for a given wavelength at a given temperature for all bodies is same & equal to the emissive power of a perfect black body.

By definition, a_λ = absorptive power of a body, if dQ heat is incident on unit area in unit time within λ & $\lambda + d\lambda$, then heat absorbed $= a_\lambda dQ$ and $dQ - a_\lambda dQ$ will be transmitted or reflected. If e_λ = emissive power then $e_\lambda d\lambda$ is the energy emitted per unit area per unit time within λ & $\lambda + d\lambda$.

$\therefore$ Total emitted energy $= (1 - a_\lambda) dQ + e_\lambda d\lambda$ and in equilibrium, $\cancel{dQ} = (\cancel{1} - a_\lambda) dQ + e_\lambda d\lambda \Rightarrow a_\lambda \underline{\underline{dQ}} = e_\lambda d\lambda.$

For a perfect blackbody $e_\lambda = E_\lambda$ (notation) & $a_\lambda = 1$.

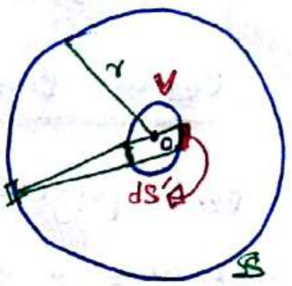
$\therefore \underline{\underline{dQ}} = E_\lambda d\lambda.$ $\qquad \therefore a_\lambda E_\lambda d\lambda = e_\lambda d\lambda$

or $\boxed{E_\lambda = \frac{e_\lambda}{a_\lambda}}$ Kirchhoff's law

It also means not only radiation is independent on the shape or nature of wall of a hollow radiator & good absorbers are also good emitters. Na vapour that emit yellow D_1 & D_2 lines of λ 5890 Å & 5896 Å is also a good absorber of light of these two wavelengths. This explains the Fraunhofer dark lines in Sun's spectrum.

Pressure of diffuse radiation

When radiation falls normally to a surface then the radiation pressure is the sum of incident & reflected waves energy density. Larmor calculated it using Kepler's observation of radiation pressure of tail of comets rotating around so as to be always opposite to sun. Inside a heated container such radiation is diffuse.



Consider volume V at a very large distance from container wall so that radiation through V is the radiation coming from surface of sphere of radius r. As by construction $ds << V$, we can divide solid angle subtended by V at ds into many cones of solid angle $d\omega$ with area ds', so that $d\omega = \frac{ds'}{r^2}$.

If the volume V intersects infinitesimal cone of length l then time taken by radiation to travel is $dt = \frac{l}{c}$. If K is specific intensity or radiation emitted per unit area per unit time per unit solid angle then energy coming from $dS = K\,dS\,d\omega\,dt$

$$= K dS \frac{ds'}{r^2}\frac{l}{c}$$

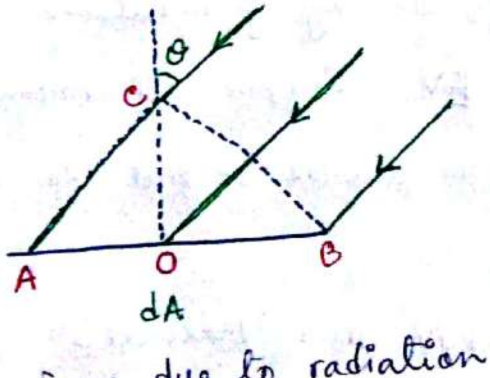
So the radiation contained in $V = \sum_V K ds \frac{ds'}{r^2}\frac{l}{c} = \frac{Kds}{cr^2}\sum_V l\,ds'$

$$= \frac{Kds}{cr^2} V$$

∴ Total radiation in V from the whole surface is $= \sum_S \frac{Kds}{cr^2} V$

$$= \frac{KV}{cr^2}\sum_S ds = \frac{KV}{cr^2} 4\pi r^2 = \frac{4\pi K}{c} V, \quad E = \frac{4\pi K}{c}$$

∴ energy density of diffuse radiation is $\frac{4\pi K}{c}$. Suppose a parallel beam of radiation is incident on dA at angle θ so that, pressure on BC is



$$p = \frac{\text{intensity of radiation}}{\text{speed of radiation}} = \frac{K}{c}\sin\theta\,d\theta\,d\phi$$

Force due to radiation on BC $= \frac{K}{c}\sin\theta d\theta d\phi\, BC$ & the normal component is $= \frac{K}{c}\sin\theta\,d\theta\,d\phi\, BC\cos\theta = \frac{K}{c}\sin\theta d\theta d\phi\, AB\cos^2\theta$

∴ Total radiation pressure on AB $= 2\int_{\theta=0}^{\pi/2}\int_{\phi=0}^{2\pi}\frac{K}{c}\sin\theta d\theta d\phi\cos^2\theta$

also reaction pressure ←

$$= \frac{2K}{c}\int_{\theta=0}^{\pi/2} \cos^2\theta \sin\theta d\theta \int_{\phi=0}^{2\pi} d\phi = \frac{1}{3}\frac{4\pi K}{c} = \frac{1}{3}E.$$

$$\therefore \boxed{P = \frac{1}{3}E}$$

Stefan - Boltzmann law

For a perfect blackbody, the rate of emission of radiant energy by unit area is proportional to the fourth power of its absolute temperature.

$E = \sigma T^4$, σ = Stefan's constant $= 5.67 \times 10^{-8}\ W m^{-2} K^{-4}$

In other words, if a black body at absolute temperature T is surrounded by another blackbody at absolute temperature T_0 then the net rate of loss of heat energy per unit area of the surface per unit time is $E = \sigma(T^4 - T_0^4)$.

Note that this is in accordance with "Prevost's theory of heat exchange" that states, "the net loss of heat is the difference in the heat radiated by the hot body and the heat absorbed by it from its surroundings." Stefan's law refers to the emission of heat radiation only by the blackbody and not to the net loss of heat by the blackbody after heat exchange with its surroundings.

In 1884, Boltzmann theoretically proved Stefan's law using Thermodynamics. Suppose an encloser of volume V is filled with radiation at uniform temperature T. E is the energy density of radiation so that total internal energy is $U = EV$. Suppose dQ amount of heat is flowed into the enclosure from outside so that the volume changed to $V + dV$.

Using first law of T.D. $dQ = dU + PdV$ and Maxwell's thermodynamic relation $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$ we have

$$\left(\frac{\partial U + PdV}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

using $P = \frac{1}{3}E$ and $U = EV$, we have $\left(\frac{\partial U}{\partial V}\right)_T = E$, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\left(\frac{\partial E}{\partial T}\right)_V$

$$\therefore E = \frac{T}{3}\frac{dE}{dT} - \frac{E}{3} \quad \text{or} \quad \frac{4E}{\cancel{3}} = \frac{T}{\cancel{3}}\frac{dE}{dT}$$

$$\text{or} \int \frac{dE}{E} = 4\int\frac{dT}{T} + \text{constant} \quad \text{or} \quad \ln E = 4\ln T + \ln\sigma$$

$$\text{or} \quad E = \sigma T^4$$

Newton's law of cooling

Stefan's law is applicable for all temperatures but Newton's law is applicable when temperature difference between blackbody & surrounding is small. If T_1 is hotbody's temperature which is placed in an enclosure at T_2 then from Stefan's law

$$E = \sigma(T_1^4 - T_2^4) = \sigma(T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3).$$

while $(T_1 - T_2)$ is small, $T_1 \approx T_2$ so that $T_1^2T_2 \sim T_2^3$ & so on

$$\therefore E = \sigma(T_1 - T_2)(T_2^3 + T_2^3 + T_2^3 + T_2^3)$$

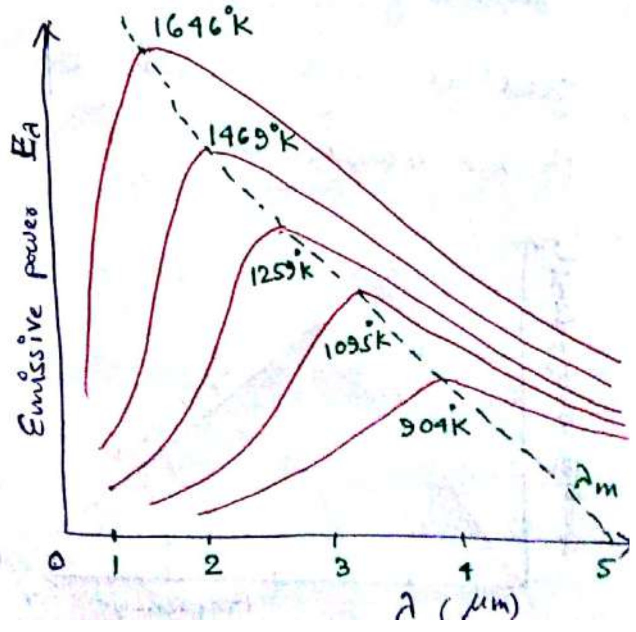
$$= \underbrace{4\sigma T_2^3}_{K}(T_1 - T_2). = K(T_1 - T_2).$$

$$\therefore E \propto (T_1 - T_2)$$

Distribution of Energy in Blackbody Spectrum

Energy is not uniformly distributed for isothermals, and exhibits a maxima at a particular wavelength. If λ_m is the wavelength for which the emitted energy is maximum, then Wien's displacement law states that

$$\lambda_m T = \text{constant}.$$



for all wavelengths, increase in temperature leads to increase in energy emission. Area under each curve represents total energy emitted & is found to be directly proportional to T^4, or $E \propto T^4$ which is the Stefan-Boltzmann's law.

Wien's Displacement law

When an electric wire is heated, at 500°C it is dull red, at 900°c its cherry red, at 1100°c its orange red, at 1250°c its yellow and at > 1600°c becomes white. So as the temperature is raised, the maximum intensity of emission is displaced towards the shorter wavelength. Wien's law is $\lambda_m T$ = constant = 0.2892 cmK

$$E_m \propto T^5 \quad \text{or} \quad E_m T^{-5} = \text{constant}$$

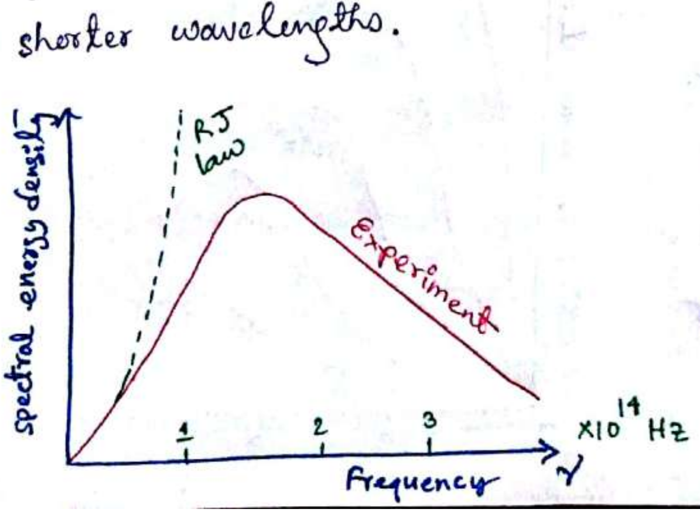
This can be combined with Stefan's law in one form as

$$E_\lambda = C \lambda^{-5} f(\lambda T)$$

Wien derived that $E_\lambda d\lambda = K\lambda^{-5} e^{-a/\lambda T} d\lambda$. This law holds good only at shorter wavelength & lower temperature, but do not hold good at longer wavelengths & higher temperature.

Rayleigh - Jeans law & the UV Catastrophe :

According to RJ law, $E_\lambda d\lambda = \frac{8\pi k_B T}{\lambda^4} d\lambda$. This law holds good at longer wavelengths at higher temperatures and not good at shorter wavelengths.



Writing $\lambda = \frac{c}{\nu}$ or $d\lambda = \frac{c}{\nu^2} d\nu$

using RJ law we can write

$$dE = E_\lambda d\lambda = \frac{8\pi k_B T}{c^4} \nu^4 \frac{c}{\nu^2} d\nu$$

$$= \frac{8\pi \nu^2 k_B T}{c^3} d\nu$$

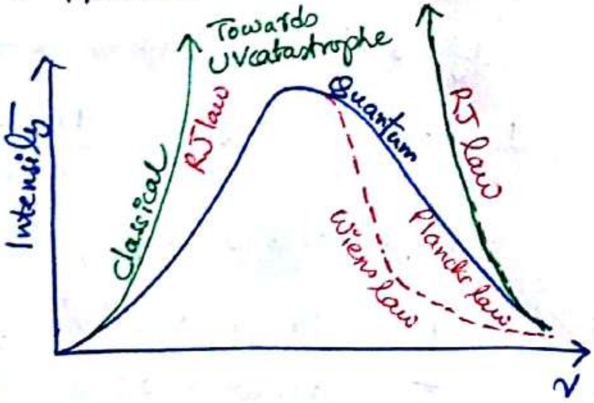
for $\nu \to \infty$, $dE \to \infty$ is a direct contradiction to experimental observations → "ultraviolet Catastrophe". Again,

$$E = \int_0^\infty \frac{8\pi\nu^2 k_B T\, d\nu}{c^3} \to \infty$$ which is contradiction to Stefan's law.

Thus before 1900, UV catastrophe was the biggest failure of classical physics until Max Planck, who used quantum mechanics idea to treat radiation as emitted quanta of energy $h\nu$. According to his treatment

$$\boxed{\begin{aligned} E_\nu\, d\nu &= \frac{8\pi h}{c^3}\,\frac{\nu^3 d\nu}{e^{h\nu/k_BT}-1} \\ E_\lambda\, d\lambda &= \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{hc/\lambda k_BT}-1} \end{aligned}}$$

, $h = 6.626 \times 10^{-34}$ Js = Planck's constant.



This is called Planck's Radiation law, that agrees perfectly with experiments.

Planck's quantum postulates say that (a) A radiation enclosure can be imagined as a collection of resonators (simple harmonic oscillators) that can vibrate at all frequencies. (b) Resonators cannot radiate/absorb energy continuously but in the form of quanta-packets (photons). Each photon has energy $h\nu$ so that energy emitted/absorbed is $0, h\nu, 2h\nu, \ldots, nh\nu$ or "quantum".

① $\lambda <<$ (short wavelengths) Planck's Radiation law

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{hc/\lambda k_BT}-1} \simeq \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{hc/\lambda k_BT}}$$

$$= \frac{8\pi hc}{\lambda^5}\, e^{-hc/\lambda k_BT}\, d\lambda$$ ⟹ "Wien's displacement law."

② $\lambda >>$ (larger wavelengths) $e^{hc/\lambda k_BT} \simeq 1 + \frac{hc}{\lambda k_BT}$

Planck's radiation law $$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{1+\frac{hc}{\lambda k_BT}-1} = \frac{8\pi k_BT}{\lambda^4}\, d\lambda$$

⟹ "Rayleigh-Jeans law."

Solar Constant

It is the amount of radiation absorbed per unit time per unit area of a black body placed at a mean distance between sun & earth in the absence of atmosphere with the surface held normal to the sun rays.

If mean distance between sun & earth $= R$, solar constant $= S$

$\therefore$ Total amount of radiation received by the sphere in 1 minute $= 4\pi R^2 S$.

If $r =$ sun's radius then radiation by 1 square cm surface in 1 minute $E = \frac{4\pi R^2 S}{4\pi r^2}$

$r = 6.928 \times 10^5$ Km, $R = 148.48 \times 10^7$ Km, $S = 1.94$ cals/cm^2/minute

$$\underline{\underline{E}} = \frac{(148.48 \times 10^7)^2}{(6.928 \times 10^5)^2} \times \frac{1.94}{60} \text{ cals/second.}$$

But from Stefan's law $\underline{\underline{E}} = \sigma T^4 = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} T^4$ as

$$\sigma = 5.75 \times 10^{-5} \text{ Ergs/cm}^2\text{/deg}^4 = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} \text{ cals/cm}^2\text{/deg}^4$$

Equating,
$$\frac{(148.48 \times 10^7)^2}{(6.928 \times 10^5)^2} \frac{1.94}{60} = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} T^4$$

$$\therefore T = \underline{5730 K}.$$

The photosphere of sun (outer surface) is approximately $\underline{6000K}$. Calculated value yields the effective temperature when sun acts as a blackbody radiator.

This can also be calculated from Wien's displacement law

$\lambda_m T = 0.2892$. $\lambda_m = 4900 \times 10^{-8}$ cm (maximum in spectrum)

$\therefore T = \underline{5902 K}.$

CW 1. (a) Two large closely spaced concentric spheres (blackbody radiator) are kept at temperature 200K & 300K & the in between space is vacuum. Calculate the net rate of energy transfer between the two spheres. (b) Calculate the radiant emittance of a blackbody at temperatures 400K & 4000K. Given $\sigma = 5.672 \times 10^{-8}$ M.K.S. units.

(a) $T_1 = 300K$, $T_2 = 200K$ ∴ from Stefan's law, net rate of energy transfer $E = \sigma(T_1^4 - T_2^4)$

$= 5.672 \times 10^{-8} (300^4 - 200^4) = 368.68$ watts/m^2

(b) for $T = 400K$, $E = 5.672 \times 10^{-8} \times 400^4 = 1452$ watts/m^2

for $T = 4000K$, $E = 5.672 \times 10^{-8} \times 4000^4 = 1452 \times 10^4$ watts/m^2

$= 14520$ Kilowatts/m^2.

2. An aluminium foil is placed between two concentric spheres (blackbody radiators) at temperatures 300K & 200K. Calculate the temperature of the foil in the steady state. Also calculate the rate of energy transfer between one of the spheres and the foil.

If x is the temperature of foil in steady state then we have using Stefan's law, $\sigma(T_1^4 - x^4) = \sigma(x^4 - T_2^4)$

here $T_1 = 300K$, $T_2 = 200K$. or $300^4 - x^4 = x^4 - 200^4$

or $x = 263.8$ K.

∴ Rate of energy transfer $E = \sigma(T_1^4 - x^4)$

$= 5.672 \times 10^{-8} (300^4 - 263.8^4)$

$= 185$ watts/m^2.

[N.B. If relative emittance is mentioned (say $e = 0.1$) then

$E = e\sigma(T_1^4 - x^4) = 18.5$ watts/m^2]

3. Obtain the number of modes of vibration per unit volume in the wavelength range 4990 Å to 5010 Å for a cubic shaped cavity of a blackbody.

Number of modes/volume within λ & $\lambda + d\lambda$

$$n = \frac{E_\lambda d\lambda}{k_B T} = \frac{8\pi d\lambda}{\lambda^4}$$ using Rayleigh-Jean's law.

$\lambda = 5000\ \text{Å} = 5000 \times 10^{-8}$ cm, $d\lambda = (5010 - 4990) = 20\text{Å} = 20 \times 10^{-8}$ cm

$$\therefore\ n = \frac{8 \times 3.14 \times 20 \times 10^{-8}}{(5000 \times 10^{-8})^4} = 8.038 \times 10^{11}\ /\text{cc}.$$

[Same thing, if asked frequency range say 4×10^{14} & 4.01×10^{14} sec^{-1} for a chamber of volume 50 cc, then $n = \frac{8\pi \nu^2 d\nu}{c^3} = 1.5 \times 10^{11}$ /cc and total number of modes in $V = 50$ cc is $= 1.5 \times 10^{11} \times 50$

$= 7.5 \times 10^{12}$]

HW 1. If a black body at a temperature 6174 K emits 4700 Å with maximum energy, calculate the temperature at which it will emit a wavelength of 1.4×10^{-5} m with maximum energy.

2. Using Stefan's law, calculate the total radiant energy emitted by Sun/second. Also calculate the rate at which energy is reaching the top of earth's atmosphere. Given radius of sun $= 7 \times 10^{8}$ m & distance of earth's atmosphere from sun $= 1.5 \times 10^{11}$ m and sun (blackbody) temperature $= 5800$ K.

3. The order of magnitude of the energy received from sun at earth's surface is 10^{-1} Joule/cm^2 sec. Calculate the order of magnitude of the total force due to solar radiation on the earth (perfectly absorbing). Given earth's diameter $= 10^{7}$ metre, & radiation pressure $P = \frac{E}{C}$.

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, $dQ = TdS$

$$\therefore \; dU = dQ - PdV = TdS - PdV \quad — ①$$

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

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y, \quad \left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x$$

Since dU is a perfect differential, $\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$, so

$$\left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x + \cancel{T\frac{\partial^2 S}{\partial x \partial y}} - \cancel{P\frac{\partial^2 V}{\partial x \partial y}} =$$

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y + \cancel{T\frac{\partial^2 S}{\partial x \partial y}} - \cancel{P\frac{\partial^2 V}{\partial x \partial y}}$$

or $$\left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y$$

This is the general expression for Maxwell's T.D. relation, which can be written in determinant form

$$\begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial T}{\partial y}\right)_x \\ \left(\frac{\partial S}{\partial x}\right)_y & \left(\frac{\partial S}{\partial y}\right)_x \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial x}\right)_y & \left(\frac{\partial P}{\partial y}\right)_x \\ \left(\frac{\partial V}{\partial x}\right)_y & \left(\frac{\partial V}{\partial y}\right)_x \end{vmatrix} \quad \text{or,} \quad \boxed{\frac{\partial(T,S)}{\partial(x,y)} = \frac{\partial(P,V)}{\partial(x,y)}}$$

There are ${}^4C_2 = 6$ combinations (S,V), (T,V), (S,P), (T,P), (P,V), (T,S).

1^{st} Relation: Let $x = T$, $y = V$, then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_V & \left(\frac{\partial S}{\partial V}\right)_T \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial P}{\partial V}\right)_T \\ 0 & 1 \end{vmatrix} \quad \text{or} \quad \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

So the first relation says, increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant.

2^{nd} Relation: Let $x = T$, $y = P$, then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \quad \text{or} \quad \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

This means decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase in volume per unit increase in temperature when the pressure remains constant.

3rd Relation: Let $x = S,\ y = V$, $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial S}\right)_V & \left(\frac{\partial P}{\partial V}\right) \\ 0 & 1 \end{vmatrix}$

$$\therefore \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

4th Relation: Let $x = S,\ y = P$, $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_P & \left(\frac{\partial T}{\partial P}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial S}\right)_P & \left(\frac{\partial V}{\partial P}\right)_S \end{vmatrix}$

$$\therefore \boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

5th Relation: Let $x = P,\ y = V$, $\begin{vmatrix} \left(\frac{\partial T}{\partial P}\right)_V & \left(\frac{\partial T}{\partial V}\right)_P \\ \left(\frac{\partial S}{\partial P}\right)_V & \left(\frac{\partial S}{\partial V}\right)_P \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$

$$\therefore \boxed{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1}$$

6th Relation Let $x = T,\ y = S$, $\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_S & \left(\frac{\partial P}{\partial S}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_S & \left(\frac{\partial V}{\partial S}\right)_T \end{vmatrix}$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1}$$

Applications of Maxwell's Thermodynamic Relations

from the relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ after multiplying by T we obtain $T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$ or $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

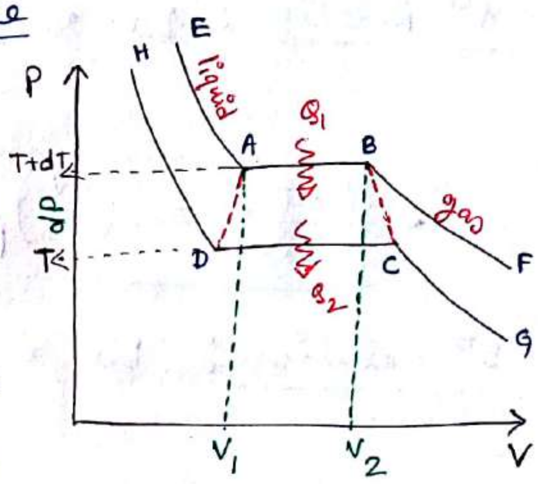
$\left(\frac{\partial Q}{\partial V}\right)_T$ represents heat absorbed or liberated per unit change in volume at constant temperature. This heat represents latent heat when substance changes from solid to liquid (melting) or liquid to vapour (boiling) state at constant temperature. If L is the heat required to change unit mass of substance, V_2 & V_1 be specific volume (volume per unit mass) then $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1}$

$$\therefore \frac{L}{V_2 - V_1} = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{or} \quad \boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$$

Clausius - Clapeyron's latent heat equation.

Latent heat equation using Carnot's cycle



Consider two isothermals FBAE and GCDH with a cycle ABCD where Carnot's theorem can be applied. At point A, volume is V_1 & temperature T+dT & pressure is just below its saturation pressure & liquid begins to evaporate tile point B at volume V_2 where its in the vapour state. If mass of liquid at B is 1 gm, the amount of heat absorbed is $Q_1 = L + dL$ is latent heat at T+dT.

At B, pressure decreases by dP & vapour expands & temperature falls to point C at temperature T. Here the gas starts to condense & changes to liquid state at point D. The amount of heat rejected for C→D is $L = Q_2$. Increasing the pressure, reversibly A point is restored.

From Carnot's theorem, $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ or $\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$

Here $Q_1 - Q_2 = dL$, $T_1 - T_2 = dT$, $Q_2 = L$, $T_2 = T$.

So $\frac{dL}{L} = \frac{dT}{T}$. Now $dL = Q_1 - Q_2 = dP(V_2 - V_1)$ = area of ABCD

So $\frac{dP(V_2 - V_1)}{L} = \frac{dT}{T}$ or $\boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$.

Using this, lets calculate the change in freezing point of a substance by pressure. Consider the melting of ice to water at 0°C, where $T = 273.16K$ & $L = 79.6 \times 4.2 \times 10^7$ Ergs, V_2 = volume of unit mass of water = 1.0001 cc & V_1 = volume of unit mass of ice = 1.0908 cc

$\therefore \left(\frac{dP}{dT}\right)_{\text{Saturation}} = \frac{79.6\times 4.2\times 10^{7}}{273.16\times(1.0001-1.0908)}$. If $dP = 1$ atm $= 1.01\times 10^{6}$ dynes/cm^2

then we obtain $dT = -0.0075°C$. $\therefore$ To reduce $\underline{1°C}$ temperature of the melting point of ice, one has to apply $\Delta P = \frac{1}{0.0075} \approx \underline{133}$ atm of pressure.

Consider the other extreme i.e. boiling point of water at 100°C where $L = 537.6\times 4.2\times 10^{7}$ ergs, $V_1 = 1.0001$ cc & $V_2 = 1674$ cc.

In this case, $\frac{dP}{dT} > 0$ meaning there will be an increase in boiling point if the pressure on the water is increased.

$\therefore$ Ice will melt at lower than 0°C at a higher pressure than 76 cm of Hg. Also water will boil at a lower temperature under reduced pressure or boiling point increases with increase in pressure.

Adiabatic Stretching of wire using Maxwell's relations

From 1st & 2nd law, using $dQ = dU + PdV$, we have

$TdS = dU + PdV$. In case of stretching a wire, $dW = +\vec{F}\cdot d\vec{l}$

$\therefore dU = TdS + Fdl$

$$\boxed{\left.\begin{array}{l} P \leftrightarrow -F \\ V \leftrightarrow l \end{array}\right\} \text{replacement.}}$$

we get from $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$, $\left(\frac{\partial T}{\partial l}\right)_S = \left(\frac{\partial F}{\partial S}\right)_l = T\left(\frac{\partial F}{T\partial S}\right)_l$

$$= T\left(\frac{\partial F}{\partial Q}\right)_l$$

$$\therefore \left(\frac{\partial T}{\partial l}\right)_S = T\left(\frac{\partial F}{\partial T}\right)_l\left(\frac{\partial T}{\partial Q}\right)_l . \quad \text{— ①}$$

Now $l = l(F,T)$ $\therefore$ $dl = \left(\frac{\partial l}{\partial F}\right)_T dF + \left(\frac{\partial l}{\partial T}\right)_F dT$

Under no elongation $dl = 0$, $0 = \left(\frac{\partial l}{\partial F}\right)_T dF + \left(\frac{\partial l}{\partial T}\right)_F dT$

$$A \quad \therefore \left(\frac{\partial F}{\partial T}\right)_l = -\frac{\left(\frac{\partial l}{\partial T}\right)_F}{\left(\frac{\partial l}{\partial F}\right)_T}$$

Substituting this in equation ①, we get $\left(\frac{\partial T}{\partial l}\right)_S = -T\frac{\left(\frac{\partial l}{\partial T}\right)_F}{\left(\frac{\partial l}{\partial F}\right)_T}\left(\frac{\partial T}{\partial Q}\right)_l$

Coefficient of linear expansion $\beta = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_F$

Isothermal Young's modulus $Y_T = \frac{l}{A}\left(\frac{\partial F}{\partial l}\right)_T$

Specific heat at constant length $C_l = \left(\frac{\partial Q}{\partial T}\right)_l$

$$\therefore \left(\frac{\partial T}{\partial l}\right)_S = -T\frac{\beta l}{\left(\frac{l}{Y_T A}\right)}\frac{1}{C_l} = -\frac{T\beta Y_T A}{mC}$$, m = mass/unit length, C = sp. heat of wire

Using $Y_S = \frac{l}{A}\left(\frac{\partial F}{\partial l}\right)_S$, we have $\left(\frac{\partial T}{\partial F}\right)_S = \left(\frac{\partial T}{\partial l}\right)_S\left(\frac{\partial l}{\partial F}\right)_S$

$$= -\frac{T\beta Y_T A}{mC}\frac{1}{Y_S A} \approx -\frac{T\beta}{mC}$$

$$\therefore dT = -\frac{T\beta}{mC}\,dF \quad (Y_T \sim Y_S)$$

for solids

If $\beta > 0$, then increase in tension should cool the wire. for an adiabatic stretching.

Adiabatic stretching of a liquid film using Maxwells relations

$dQ = dU + dW$ (1^{st} law) yields $dU = dQ - dW$

$$= dQ + 2\mathcal{S}\,dA$$

where $-2\mathcal{S}\,dA$ is the work done by the surface film with surface tension $\mathcal{S}$. Comparing with PdV, $P \leftrightarrow -2\mathcal{S}$

$V \leftrightarrow A$

From $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ $\therefore$ $T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

or $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$. Substituting, $\left(\frac{\partial Q}{\partial A}\right)_T = -2T\left(\frac{\partial \mathcal{S}}{\partial T}\right)_A$

$\therefore$ for a finite change of area dA we have

$dQ = -2T\left(\frac{\partial \mathcal{S}}{\partial T}\right)_A dA$. for a liquid, surface tension decreases with temperature so $\left(\frac{\partial \mathcal{S}}{\partial T}\right)_A < 0$, or $dQ > 0$. $\therefore$ To keep temperatur constant of the film, dQ amount of heat is to be supplied when stretch

In adiabatic stretching, the fall in temperature is

$$\Delta T = \frac{\partial T}{C}\left(\frac{\partial S}{\partial T}\right)_A dA$$ where C is the heat capacity for the liquid film

Clausius latent heat equation

For a change of state from liquid to vapour, $S_v - S_l = \frac{L}{T}$.

Differentiating with respect to T, we have

$$\frac{dS_v}{dT} - \frac{dS_l}{dT} = -\frac{L}{T^2} + \frac{1}{T}\frac{dL}{dT}$$

or $$T\left(\frac{dS_v}{dT}\right) - T\left(\frac{dS_l}{dT}\right) = -\frac{L}{T} + \frac{dL}{dT}$$

∴ $$\boxed{C_v - C_l = \frac{dL}{dT} - \frac{L}{T}}$$ *(See page 10)

More applications of Maxwells relations

Using $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ we have $T\left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$

∴ $\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$. But the coefficient of volume expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ ∴ $\left(\frac{\partial V}{\partial T}\right)_P = V\alpha$.

∴ $\left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$. If $\alpha > 0$ or if the sustance expands on heating then $\left(\frac{\partial Q}{\partial P}\right)_T < 0$, meaning heat must be withdrawn from the substance to keep temperature constant when the pressure is increased. On other hand if $\alpha \ngtr 0$, the substance contracts on heating, $\left(\frac{\partial Q}{\partial P}\right)_T > 0$ meaning heat must be added to keep its temperat constant, when the pressure is increased.

∴ Increase in pressure heats a body that expands on rise of temperatu Cooling is produced when a substance, which contracts on heating, is suddenly compressed.

Energy Equations of Pure Substances

Energy on volume

From first law of T.D. $dU = Tds - PdV$ — ①

or $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$. Using Maxwell's relation

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}$ 1st Energy equation

For Ideal Gas $PV = nRT$ ∴ $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$

∴ from energy equation, $\left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V} - P = 0$. So U is a function T only and does not depend on V.

For Van der Waals Gas $\left(P + \frac{a}{v^2}\right)(v-b) = RT$

or $P = \frac{RT}{v-b} - \frac{a}{v^2}$

∴ $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$ ∴ Using 1st Energy equation

$$\left(\frac{\partial U}{\partial v}\right)_T = \frac{RT}{v-b} - P = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$$

∴ $du = C_v dT + \frac{a}{v^2} dv$ or $u = \int C_v dT - \frac{a}{v} + \text{const.}$

So the internal energy increases with increasing volume at constant temperature.

Energy on pressure

Again, using ①, $\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$.

using Maxwell's relation, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ we obtain

$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T}$ 2nd Energy equation

Using equation of state $f(P,V,T) = 0$, $df = 0$

or $\left(\frac{\partial f}{\partial P}\right) dP + \left(\frac{\partial f}{\partial V}\right) dV + \left(\frac{\partial f}{\partial T}\right) dT = 0$.

For isobaric process, $\left(\frac{\partial f}{\partial V}\right) dV = -\left(\frac{\partial f}{\partial T}\right) dT$ or $\left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial V}\right)}$

for isochoric process, $\left(\frac{\partial f}{\partial P}\right) dP = -\left(\frac{\partial f}{\partial T}\right) dT$ or $\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial P}\right)}$

for isothermal process, $\left(\frac{\partial f}{\partial P}\right) dP = -\left(\frac{\partial f}{\partial V}\right) dV$, or $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{\left(\frac{\partial f}{\partial V}\right)}{\left(\frac{\partial f}{\partial P}\right)}$

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

Using this, we can rewrite 1st Energy equation as

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left[-V\left(\frac{\partial P}{\partial V}\right)_T\right]\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right] = \frac{\beta}{K}$$

where K = isothermal compressibility & β = volume expansivity.

$$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\beta}{K} - P}$$

$\left(\frac{\partial U}{\partial V}\right)_T$ is known as "internal pressure" that arises due to the intermolecular attraction. Fact that gases condense to form liquid & solids shows that their exist intermolecular attraction that pulls the gas atoms together even without any external pressure. When the temperature is increased, the pressure diminishes till it becomes zero at the perfect gas stage.

T-dS Equations

Entropy of a pure substance is

$$S = S(T,V) \quad \text{or} \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\text{or } TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \because \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$= \left(\frac{\partial q}{\partial T}\right)_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\boxed{TdS = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \qquad \text{1}^{\text{st}} \text{ T-dS Equation}$$

Similarly, $S = S(T, P)$, $ds = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

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

$$\because \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left(\frac{\partial Q}{\partial T}\right)_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

or $\boxed{Tds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$ 2^{nd} T-ds Equation

Equating the first & second T-ds equation, we obtain

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

or $(C_P - C_V)\, dT = T\left(\frac{\partial V}{\partial T}\right)_P dP + T\left(\frac{\partial P}{\partial T}\right)_V dV$

or, $dT = \dfrac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V} dP + \dfrac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V} dV$

Also, $T = T(P, V)$ or $dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$

$\therefore$ Equating the coefficients, we see, $\left(\frac{\partial T}{\partial P}\right)_V = \dfrac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$

or $C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$

Using $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$, we have $C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$

$$= TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2 \left[-V\left(\frac{\partial P}{\partial V}\right)_T\right] = \frac{TV\beta^2}{K_T}$$

or $\boxed{C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T = \frac{TV\beta^2}{K_T}}$

This is one of the important equations of Thermodynamics which shows that ⓐ As $\left(\frac{\partial P}{\partial V}\right)_T < 0$ always for most substances, therefore $C_P - C_V > 0$ or $C_P > C_V$. ⓑ As $T \to 0$, $C_P \to C_V$ or at absolute zero the two heat capacities are equal. ⓒ When $\left(\frac{\partial V}{\partial T}\right)_P = 0$, we obtain $C_P = C_V$. Water at 4°C have maximum density & minimum volume so that heat capacities become equal.

If $K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ and $k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ then using 1st & 2nd Tds equation at constant S, we have

$$T ds = 0 = C_P\, dT_S - T\left(\frac{\partial V}{\partial T}\right)_P dP_S \quad \therefore\ C_P\, dT_S = T\left(\frac{\partial V}{\partial T}\right)_P dP_S$$

$$T ds = 0 = C_V\, dT_S + T\left(\frac{\partial P}{\partial T}\right)_V dV_S \quad \therefore\ C_V\, dT_S = -T\left(\frac{\partial P}{\partial T}\right)_V dV_S$$

$$\therefore\ \frac{C_P}{C_V} = \gamma = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V}\left(\frac{\partial P}{\partial V}\right)_S = +\frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{-\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_S}{-\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T} = \frac{K_S}{K_T}$$

$$\left(\text{using } \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V = -1\right)$$

$$\therefore\ \boxed{\gamma = \frac{C_P}{C_V} = \frac{K_S}{K_T}} = \frac{\text{adiabatic compressibility}}{\text{isothermal compressibility}}$$

HW ① Consider a metal (say Copper) at 300K with the following values, $V = 7.06\ \text{cm}^3/\text{mol}$, $K_T = 7.78 \times 10^{-12}\ \text{N/m}^2$, $\beta = 50.4 \times 10^{-6}\ \text{K}^{-1}$, $C_P = 24.5\ \text{J/mol K}$. Determine C_V.

② Prove that ratio of adiabatic $\left(\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S\right)$ to isobaric $\left(\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right)$ coefficient of expansion is $\frac{1}{1-\gamma}$. Also prove that adiabatic $\left(E_S = -V\left(\frac{\partial P}{\partial V}\right)_S\right)$ to isothermal $\left(E_T = -V\left(\frac{\partial P}{\partial V}\right)_T\right)$ elasticities is equal to ratio of specific heats.

③ Prove that adiabatic $\left(\beta_S = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S\right)$ to isochoric $\left(\beta_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V\right)$ pressure coefficient of expansion is $\frac{\gamma}{\gamma-1}$.

Variation of C_V with V and C_P with P

From 1st T-ds equation, $ds = \frac{C_V\, dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$

As ds is a perfect differential $\frac{\partial}{\partial V}\left(\frac{C_V}{T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V$

$\therefore\ \frac{\partial C_V}{\partial V} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$. If $\left(\frac{\partial P}{\partial T}\right)_V = 0$ then C_V is independent of volume (initial).

Similarly from the 2nd Tds equation $ds = \frac{C_p\, dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$

& ds being exact differential, $\frac{\partial}{\partial P}\left(\frac{C_p}{T}\right) = -\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P$

or $\frac{\partial C_p}{\partial P} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

Negative specific heat of Steam *

Clausius latent heat equation between two arbitrary states 1 & 2 is

$c_2 - c_1 = \frac{dL}{dT} - \frac{L}{T}$ where c is the specific heat. of substance in states 1 and 2 which is neither at constant volume nor at constant pressure. The vapour always remain in equilibrium with the evaporating liquid, so vapour is in saturated state called "specific heat of saturated vapour." from $S = S(T,P)$, $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

or $\left(\frac{\partial S}{\partial T}\right)_{saturation} = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{saturation}$

Using Clausius-Clapeyron latent heat equation, $\left(\frac{\partial P}{\partial T}\right)_{saturation} = \frac{L}{T(V_2-V_1)}$

and Maxwells relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, we obtain

$$\left(\frac{\partial S}{\partial T}\right)_{saturation} = \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2-V_1)}$$

or $$\boxed{C_S = C_p - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2-V_1)}}$$

For evaporation of water at 100°c, $V_1 = 1$ cc, $V_2 = 1674$ cc, $L = 537.5$ cal $c_p = 0.47$, $\left(\frac{\partial V}{\partial T}\right)_P = 4.813$ gives $C_S = -1.07$ cal/K. Thus the specific heat of saturated water vapour at 100°c is negative. Though its a paradoxical result but it holds true because specific heat may vary from $+\infty$ to $-\infty$ depending on external condition, which is saturation here & Saturated water vapour exerts pressure of 760 mm of Hg at 100°c & 787.6 mm of Hg at 101°c. i.e. the specific volume of saturated water vapour at 100°c decreases with increasing temperature. When heated, to 101°C at constant pressure, vapour becomes unsaturated & to satisfy the condition of saturation it is to be compressed tile the pressure becomes 787.6 mm. The compression gnerated heat is large that has to be extracted out to Keep the temperature fixed at 101°C. Thus the specific heat of saturated vapour sometimes become negative.

Properties of van der Waals gas

VW equation of state $(P+\frac{a}{V^2})(V-b) = RT$.

Using T-ds equation & exact differentiability of S we know

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad \text{Now} \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{or} \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

$$\therefore \left(\frac{\partial C_V}{\partial V}\right)_T = 0$$

or C_V is independent of volume for VW gas & function of temperature only.

To calculate the variation of entropy of VW gas use T-ds equation

$$dS = \frac{C_V dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV = \frac{C_V}{T}dT + \frac{R}{V-b}dV$$

$$\text{or} \quad S = C_V \ln T + R\ln(V-b) + S_0 = \text{constant for adiabatic process.}$$

$$\text{or} \quad \ln T^{C_V} + \ln(V-b)^R = \text{constant}$$

$$\text{or} \quad \ln T^{C_V}(V-b)^{C_P-C_V} = \text{const.} \quad \text{or} \quad T(V-b)^{\frac{C_P-C_V}{C_V}} = \text{constant}$$

$$\text{or} \quad \boxed{T(V-b)^{\gamma-1} = \text{constant}}$$

To calculate the change in internal energy $U = U(V,T)$

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

$$= C_V dT + \left(\frac{RT}{V-b} - P\right)dV \qquad P + a/V^2 = \frac{RT}{V-b}$$

$$\text{or,} \quad \frac{RT}{V-b} - P = a/V^2$$

$$= C_V dT + \frac{a}{V^2}dV$$

$$\text{or} \quad \left[U = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2}\frac{a}{V^2}dV = \underline{C_V(T_2-T_1) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}\right]$$

So internal energy of a VW gas depends on the VW pressure coefficient "a" and not on volume coefficient "b". This is because "a" is a measure of the force of attraction between the molecules (Potential energy) that changes as the specific volume of the gas changes & the intermolecular separation changes. "b" is proportional to volume occupied by molecules & it affects the entropy because entropy is volume dependent & occupation of molecules of container volume makes the available volume less than the volume of the container.

Finally lets calculate $C_P - C_V = TV\beta^2/K_T = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$

Now $\left(P + \frac{a}{V^2}\right)(V-b) = RT$ so $\left(\frac{\partial V}{\partial T}\right)_P\left(P+\frac{a}{V^2}\right) + (V-b)\left(-\frac{2a}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_P = R$

so $\left(\frac{\partial V}{\partial T}\right)_P\left[P + \frac{a}{V^2} - \frac{2a}{V^3}(V-b)\right] = R$

or $$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^3}(V-b)} = \frac{R}{\frac{RT}{V-b}\left[1 - \frac{2a}{RTV^3}(V-b)^2\right]}$$

Now from $P = \frac{RT}{V-b} - \frac{a}{V^2}$, $$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$
$$= -\frac{RT}{(V-b)^2}\left[1 - \frac{2a(V-b)^2}{RTV^3}\right].$$

$$\therefore C_P - C_V = \cancel{T}\frac{R^{\cancel{2}}}{\left(\frac{\cancel{RT}}{V-b}\right)^{\cancel{2}}\left[1 - \frac{2a}{RTV^3}(V-b)^2\right]^{\cancel{2}}}\frac{\cancel{RT}}{(V-b)^2}\cancel{\left[1 - \frac{2a(V-b)^2}{RTV^3}\right]}$$

$$= \frac{R}{1 - \frac{2aV^2}{RTV^3}\left(1-\frac{b}{V}\right)^2} \simeq \frac{R}{1 - \frac{2a}{RTV}} \quad \left[\text{as } \frac{b}{V} << 1\right]$$

$$= R\left(1 - \frac{2a}{RTV}\right)^{-1} \simeq R\left(1 + \frac{2a}{RTV}\right) \quad \left[\text{as } \frac{2a}{RTV} << 1\right]$$

$$\therefore \boxed{C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)}$$

Finally work done by VW gas, $W = -\int P\,dV = -\int_{V_1}^{V_2}\frac{RT}{V-b}dV + \int_{V_1}^{V_2}\frac{a}{V^2}dV$

$$\boxed{W = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - RT\ln\left[\frac{V_2 - b}{V_1 - b}\right]}$$

Liquefaction of Gases

Different methods of liquefaction of gases : (a) Method of freezing mixture, (b) Adiabatic expansion of gas, (c) Joule-Thomson expansion, (d) Throttling process & regenerative cooling, (e) Adiabatic demagnetisation of paramagnetic salt. Adding salt to ice is the well known example of method (a) thereby reducing temperature (eutectic temperature) significantly.

Enthalpy It has been found that a term U+PV appeared several times in describing various properties of gas, that is termed as Enthalpy $H = U + PV$. To study its properties, consider change in enthalpy for an infinitesimal process from initial to fina equilibrium state,

$dH = dU + PdV + VdP$. But from 1st law of thermodynamics,

$\text{đ}q = dU + \text{đ}W = dU + PdV$. $\therefore\ dH = \text{đ}q + VdP$.

At constant pressure, $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial q}{\partial P}\right)_P + \cancel{V\left(\frac{\partial P}{\partial T}\right)_P}^{\,0} = C_p$

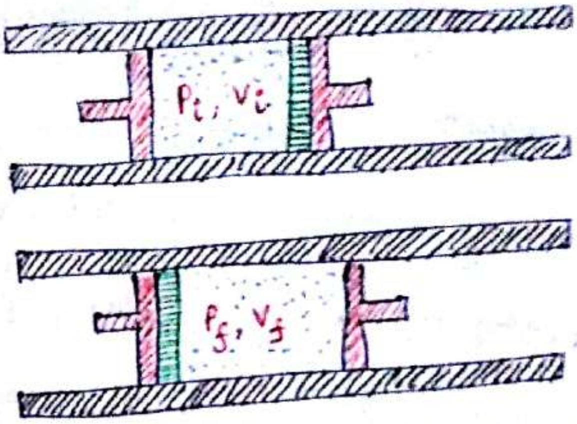
Since $dH = \text{đ}q + VdP$, the change in enthalpy during an isobaric process is equal to the heat transferred, so the latent heat measured during a phase transition at constant pressure (e.g. melting boiling, sublimation) is the change in enthalpy.

$$\therefore\ H_f - H_i = q = \int_i^f C_p\, dT.$$

Isobaric processes are more important than isochoric process in Scienc & technology, so enthalpy plays important role.

from $dH = TdS + VdP$, $\left(\frac{\partial H}{\partial S}\right)_P = T$, $\left(\frac{\partial H}{\partial P}\right)_S = V$. So on a three dimensional diagram $H = H(S,P)$, slopes of the tangent to the surface at a point determines (T, V).

Throttling process



Suppose a cylinder (thermally insulated) with two nonconducting pistons at two sides of a porous wall contains a gas. The wall (horizontal green lines) is a porous plug made of small holes on a narrow constriction. Initially the gas is at (P_i, V_i) with right hand piston against the wall to prevent seeping of gas, retaining equilibrium. If we now move both pistons simultaneously so that constant pressure P_i (left side of wall) and constant lower pressure P_f (right side of wall) then in final equilibrium state, all gas is sipped to the right side of wall. This is called a "throttling process."

Though its a nonequilibrium process but initial & final equilibrium states can be described, by applying 1st law

$$Q = U_f - U_i - W.$$

No heat transfer happens, so $Q = 0$ and $\underset{\text{(flow work)}}{W} = -\int_0^{V_f} P_f \, dV - \int_{V_i}^{0} P_i \, dV$

(as pressure remains constant) $= -P_f V_f + P_i V_i$

$$\therefore \; 0 = U_f - U_i + P_f V_f - P_i V_i$$

$$\Rightarrow \; U_i + P_i V_i = U_f + P_f V_f \quad \Rightarrow \quad \boxed{H_i = H_f}$$

So in a throttling process, final & initial enthalpies are equal although intermediate nonequilibrium states cannot have any information about enthalpy & thus cannot be plotted in an indicator diagram as continuous lines/surfaces but points.

Comparison of Internal Energy U & Enthalpy H

Internal Energy (U)	Enthalpy (H)
# $dU = \text{đ}Q - PdV$, $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	# $dH = \text{đ}Q + VdP$, $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
# Isochoric process $U_f - U_i = Q = \int_i^f C_V dT$	# Isobaric process, $H_f - H_i = Q = \int_i^f C_P dT$
# Adiabatic process $U_f - U_i = -\int_i^f PdV$	# Adiabatic process, $H_f - H_i = \int_i^f VdP$
# Free expansion, $U_i = U_f$	# Throttling process, $H_i = H_f$
# For an ideal gas $U = \int C_V dT +$ constant	# For an ideal gas, $H = \int C_P dT +$ constant
# Nearby equilibrium states $dU = TdS - PdV$, $T = \left(\frac{\partial U}{\partial S}\right)_V$, $P = -\left(\frac{\partial U}{\partial V}\right)_S$	# Nearby equilibrium states $dH = TdS + VdP$, $T = \left(\frac{\partial H}{\partial S}\right)_P$, $V = \left(\frac{\partial H}{\partial P}\right)_S$

Joule - Thomson/Kelvin effect : Adiabatic Throttling of gases

Gay-Lussac & Joule's experiments independently showed that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for perfect gases but with real gases slight cooling was found, meaning $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. To find out the relation, Lord Kelvin modified the Gay-Lussac-Joule's experiments, known as "Porous plug experiment." A highly compressed gas is continuously forced at constant pressure through a constricted nozzle to throttle & thus to expand in volume. We already learned that $H_i = H_f$. Now we calculate the change in temperature.

$$\because \; H = U + PV \quad \text{or} \quad dH = dU + PdV + VdP = \text{đ}Q + VdP = TdS + Vd$$

$$\text{or} \quad 0 = T\left[\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT\right] + VdP$$

$$\text{or} \quad 0 = -T\left(\frac{\partial V}{\partial T}\right)_P dP + \left(\frac{\partial Q}{\partial T}\right)_P dT + VdP \qquad \left[\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\therefore \quad C_P\, dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V \right] dP = 0$$

$$\therefore \quad \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V \right] = \mu, \quad \text{or } \Delta T = \int_{P_1}^{P_2} \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

$$\boxed{\mu = \frac{T^2}{C_P}\frac{\partial}{\partial T}\left(\frac{V}{T}\right)}$$

for perfect gas, $T\left(\frac{\partial V}{\partial T}\right)_P - V = T\frac{V}{T} - V = 0$ $\quad \left[PV = RT, \; \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \frac{V}{T}\right]$

Hence the J-T effect vanishes for ideal gas.

Again, $C_P\, dT = -\left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right] dP$

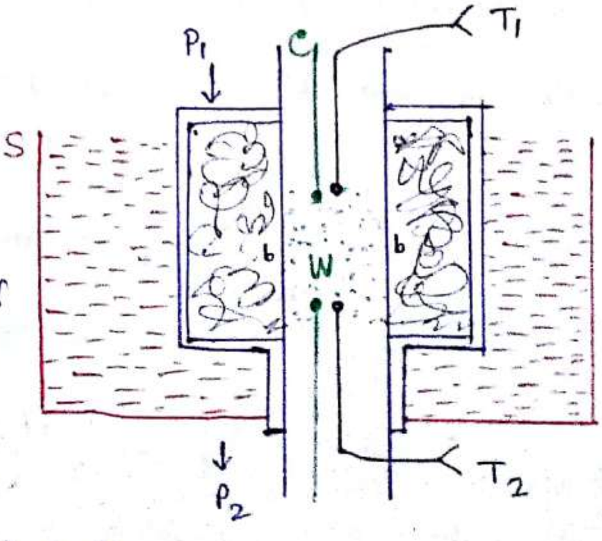
$$\therefore \quad \underbrace{C_P\left(\frac{\partial T}{\partial P}\right)_H}_{\text{J-T effect}} = \underbrace{-\left(\frac{\partial U}{\partial P}\right)_T}_{\text{Deviation from Joule's law}} \underbrace{- \frac{\partial}{\partial P}(PV)}_{\text{Deviation from Boyle's law}} \qquad \text{as } TdS = dU + PdV$$

Now $\left(\frac{\partial U}{\partial P}\right)_T < 0$ because internal energy decreases with decreasing volume (or increase of pressure). ∴ Due to deviation from Joule's law, J.T. effect will be a cooling effect $\left(\frac{\partial T}{\partial P}\right)_H > 0$ means fall of temperature per unit fall in pressure. The effect of deviations from Boyle's law can be a cooling $\left(\frac{\partial (PV)}{\partial P} < 0\right)$ or heating $\left(\frac{\partial (PV)}{\partial V} > 0\right)$ effect.

$[O_2, N_2$ etc$]$

$[H_2, He]$

The porous plug Experiment



Joule & Thomson employed a cylindrical plug where the compressed gas flows through a copper tube immersed in a thermostat to the porous plug, which consists of silk, cotton wool or other porous materials W between two piece of wire gauge & enclosed in a cylinder of (nonconducting) wood bb. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder so that no heat reaches from the bath. The temperature drop is measured by the thermocouples. They worked with O_2, N_2, CO_2 within 4°c & 100°c with initial pressure 4.5 atm & final pressure 1 atm.

A small cooling effect on expansion is seen for gases while for H_2, He (surpricingly) heating on expansion is seen. This paradox was rissolved by applying van der Waal's equation of state.

We have $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$. Using VW equation of state

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \quad \text{or} \quad P + \frac{a}{V^2} = \frac{RT}{V-b}$$

$$\text{so} \quad -\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b} - \frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\text{or} \quad \left[-\frac{2a}{V^3} + \frac{RT}{(V-b)^2}\right]\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b}.$$

$$\therefore \quad \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[\frac{RT}{V-b}\,\frac{1}{\left\{-\frac{2a}{V^3}+\frac{RT}{(V-b)^2}\right\}} - V\right]$$

$$= \frac{1}{C_p}\left[\frac{\cancel{RT/V-b}}{\cancel{\frac{RT}{(V-b)^2}}\left\{1-\frac{2a(V-b)^2}{RTV^3}\right\}} - V\right] = \frac{1}{C_p}\left[\frac{V-b-V\left\{1-\frac{2a}{RTV^3}(V-b)^2\right\}}{1-\frac{2a}{RTV^3}(V-b)^2}\right]$$

$$= \frac{1}{C_p}\left[\frac{\frac{2a}{RT}\left(1-\cancelto{0}{\frac{b}{V}}\right)^2 - b}{1-\cancelto{0}{\frac{2a}{RTV^3}}(V-b)^2}\right] \simeq \frac{1}{C_p}\left(\frac{2a}{RT}-b\right)$$

$\therefore$ $\mu > 0$ if $\frac{2a}{RT} > b$ or $T < \frac{2a}{Rb}$ and this gives cooling effect. At $T > \frac{2a}{Rb}$, the gas is heated on suffering J-T expansion. The temperature $T = \frac{2a}{Rb}$ is called the "temperature of inversion". One can show that $T_i = \frac{2a}{Rb} = \frac{27}{4}T_c$ with T_c = critical temperature of the gas and this relation is approximately true because vander Waal's equation isn't accurate for real gases.

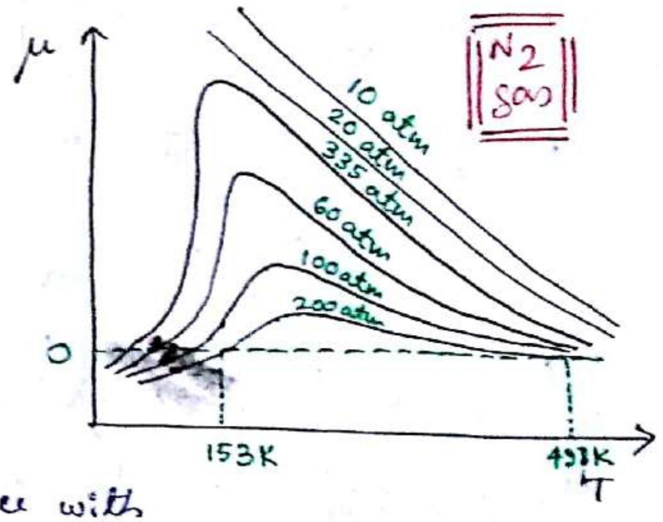
For N_2, O_2, CO_2 etc, T_i is greater than the temperature at which J-T expansion was carried out, hence a cooling effect was obtained.

for H_2, He, $T_i < 300K$, so heating effect was found. It was found later that if H_2, He are sufficiently precooled then they exhibit cooling on J-T expansion.

If we donot neglect $\frac{b}{V}$ and $\frac{2a}{RTV}$ term in μ, then for very high pressures, $\boxed{\mu \simeq \frac{1}{C_P}\left[\frac{2a}{RT} - b - \frac{6ab}{R^2T^2}P\right]}$

and for vander Waals gas, $C_P = C_{P_0} + \frac{2a}{RT^2} - \frac{3ab}{R^2T^3}P^2$

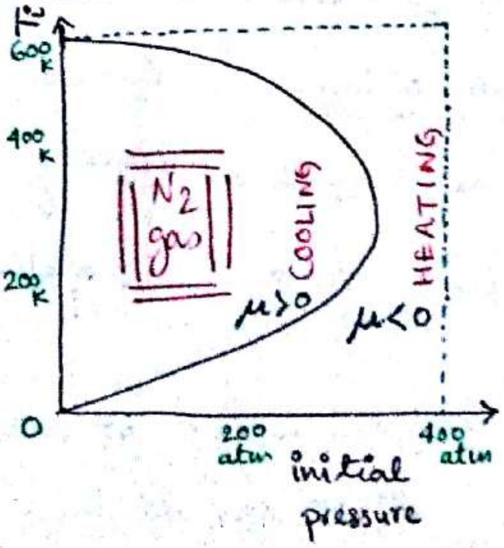
Combination of above gives $\mu = \mu(P, T)$. The experimental results of J-T effect on N_2 is shown for different initial pressures.



Observations

(a) For equal temperature, μ is greater at lower initial pressures in accordance with $\mu = \frac{1}{C_P}\left(\frac{2a}{RT} - b - \frac{6ab}{R^2T^2}P\right)$, (b) for a definite pressure, μ passes through a maximum & decreases to zero on both sides. $\therefore$ There exist two inversion temperatures for J-T effect corresponding to an initial pressure. For example at 200 atm for N_2 $\mu = 0$ happens at $-120°C$ = 153°K & other at 225°C = 498°K.

Curve of inversion



Temperature of inversion depends on the initial pressure. Inversion curve gives inversion temperature at different initial pressure. Roebuck & Osterberg obtained the experimental graph shown beside.

To have a cooling effect, the J-T expansion should be carried out at points to the left of the inversion curve. This can be explained by considering the reduced equation of state of vanderWaal gas.

In term of p^*, V^*, T^*, $\mu = \frac{1}{C_p}\left[T^*\left(\frac{\partial V^*}{\partial T^*}\right)_{p^*} - V^*\right]$ and

$\frac{8}{3}T^* = \left(p^* + \frac{3}{V^{*2}}\right)\left(V^* - \frac{1}{3}\right)$, differentiating,

$$\frac{8}{3}\left(\frac{\partial T^*}{\partial V^*}\right)_{p^*} = p^* + \frac{3}{V^{*2}} - \frac{6}{V^{*3}}\left(V^* - \frac{1}{3}\right)$$

$$\therefore \mu = \frac{1}{C_p}\left[\frac{T^*}{\frac{3}{8}\left(p^* + \frac{3}{V^{*2}} - \frac{6}{V^{*2}} + \frac{2}{V^{*3}}\right)} - V^*\right] = \frac{1}{C_p}\frac{\left[\frac{8}{3}T^* - V^*\left(p^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}}\right)\right]}{\left(p^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}}\right)}$$

$$= \frac{\left(\cancel{p^*} + \frac{3}{V^{*2}}\right)\left(\cancel{V^*} - \frac{1}{3}\right) - \cancel{V^*}\left(\cancel{p^*} - \frac{3}{V^{*2}} + \frac{2}{V^{*3}}\right)}{C_p\left(p^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}}\right)} = \frac{\left(-\frac{p^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}}\right)}{C_p\left(p^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}}\right)}$$

$$= \frac{\left(-\frac{p^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}}\right)}{\left[\frac{8}{3}C_p\left(\frac{\partial T^*}{\partial V^*}\right)_{p^*}\right]}$$

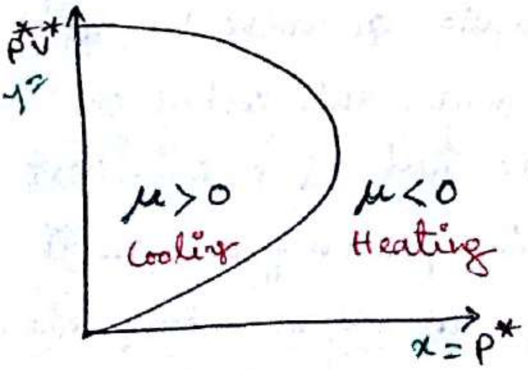
. Here the denominator is always positive because $\left(\frac{\partial T^*}{\partial V^*}\right)_{p^*} > 0$.

$$\therefore \left[\begin{array}{ll} \mu > 0 \text{ if } \frac{p^*}{3} < \frac{6}{V^*} - \frac{3}{V^{*2}} \text{ or } p^* < \frac{9(2V^*-1)}{V^{*2}} \\ \mu < 0 \text{ if } \qquad p^* > \frac{9(2V^*-1)}{V^{*2}} \end{array}\right] \begin{array}{l} \to \text{Cooling} \\ \to \text{Heating} \end{array}$$

Thus inversion occurs at $\boxed{p^* = \frac{9(2V^*-1)}{V^{*2}}}$ and in that state the gas cannot undergo a change in temperature.

Setting $p^* = x$, $p^*V^* = y$ we have $p^*V^{*2} = 9(2p^*V^* - p^*)$

or $y^2 = 9(2y - x)$ representing a parabola. Here $\mu > 0$ means $9x < 18y - y^2$ which are points inside the curve with cooling effect & for points outside, $\mu < 0$ and heating effect takes place. The temperature of inversion is obtained by putting p^* in reduced VW state

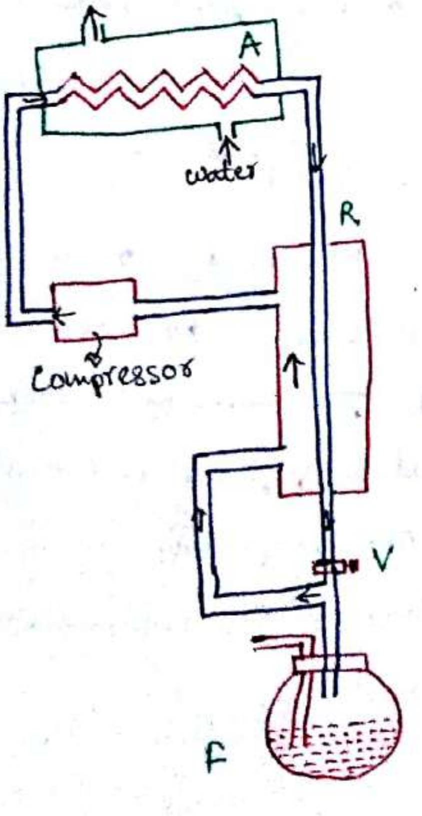


$$\boxed{T_i = \frac{3}{4}\left(3 - \frac{1}{V^*}\right)^2}$$

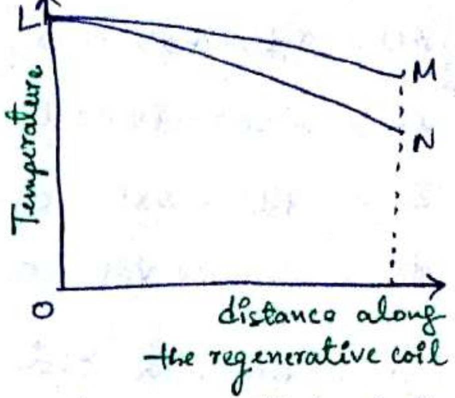
Principle of Regenerative cooling

Joule-Thomson cooling that depends on the pressure difference on the sides of the porous plug is observed to be very small for most of the gases. For air at 20°c temperature with pressure on two sides at 50 atm & 1 atm, Joule-Thomson found that the temperature falls by 11.7°c only. Even using a pressure of 210 atm instead of 50 atm, the cooling was only 42°c. However the cooling effect can be intensified by employing regenerative cooling.

A portion of the gas which first suffers J-T expansion and becomes cooled is employed to cool other portions of the incoming gas before the later reaches the nozzle. The incoming gas becomes more cooled after traversing the nozzle. In this way the cooling effect can be cumulatively rendered. In this method the extra advantage is the lower the temperature, the greater is the J-T cooling.



The high pressure gas from compressor enters the spirals contained in the water cooled jacket A where the heat of compression is removed. The gas enters the regenerator R and suffers J-T expansion at valve V & gets cooled by small amount. This cooled gas returns by the outer tube & absorbs heat from the incoming high pressure gas before it reaches the compressor at the same temperature as the incoming gas at R. The gas is again compressed, cooled by A and reenters at R. In a time interval, the gas approaching V becomes cooled more & more till the J-T cooling at V is sufficiently to liquefy the gas. A portion of the escaping gas then condenses inside the Dewar flask F. At this stage the temperature throughout the apparatus become steady. LM represents the continual decrease of temperature of the gas as we approach the nozzle V through the inner tube, while MN represents the J-T cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high pressure gas at each point of the coil. Thus, the low pressure gas extracts heat from the incoming gas.



Thermodynamic Potentials : Helmholtz & Gibbs free energy

There are 4 thermodynamic potentials

① Internal Energy : U

② Helmholtz free Energy : F

③ Enthalpy : H

④ Gibbs function : G

We know internal energy is the total energy of the system. Using 1st & 2nd law we know

$$dU = TdS - PdV \quad \text{——} ①$$

The function $F = U - TS$ is known as Helmholtz free energy function. While TS is the energy associated with disorder & unavailable from the system to do work. so $U - TS$ energy can be extracted from the system to do work. Hence the term "free".

Any small change is $dF = dU - TdS - SdT$

and we know $dQ = TdS = dU + PdV$. ∴ $dF = TdS - PdV - TdS - SdT$

$$\text{or } dF = -PdV - SdT \quad \text{——} ②$$

Similarly total heat content is $H = U + PV$

$$\therefore dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP \quad \text{——} ③$$

Similarly Gibbs function is $G = U - TS + PV = H - TS$

$$\therefore dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT \quad \text{——} ④$$

$dU = TdS - PdV = 0$, isochoric adiabatic process, $U =$ constant

$dF = -SdT - PdV = 0$, isochoric isothermal process, $F =$ constant

$dH = TdS + VdP = 0$, isobaric adiabatic process, $H =$ constant

$dG = -SdT + VdP = 0$, isobaric isothermal process, $G =$ constant

A mechanical system is in stable equilibrium when potential energy is minimum. In thermodynamics, U, F, H, G plays the role of P.E. The direction of isothermal-isochoric process is to make F minimum. In isothermal-isobaric process G tends to be minimum & for isobaric-adiabati process, H tends to be minimum.

Relation of T.D. potentials with their variables

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad , \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad , \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad , \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad , \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dU is a perfect differential

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

$$\text{so} \quad \underline{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

Similarly dF being a perfect differentia

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V$$

$$\text{so} \quad \underline{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

Similarly dH is a perfect differential,

$$\text{so} \quad \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P \qquad \text{so} \quad \underline{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

So as dG a perfect differential, $\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$

$$\text{so} \quad \underline{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$$

Four Maxwell's T.D. relation.

Relation amongst T.D. potentials, $U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

Chemical potential and Gibbs-Duhem equation

Just like U and S, thermodynamic quantities F, H, G have the additivity property, if P & T remains constant. This means that when the amount of matter (N number of particles) is changed by a given factor, T.D. changes similarly or the T.D. quantity is a homogeneous function of first order with respect to the additive variable.

$$\therefore\ U = N U\left(\frac{S}{N}, \frac{V}{N}\right), \quad F = N F\left(\frac{V}{N}, T\right), \quad H = N H\left(\frac{S}{N}, P\right)$$

$$G = N G(P, T).$$

So we have essentially regarded N as a parameter then for a change dN, we can write

$$dU = TdS - PdV + \mu dN$$
$$dF = -SdT - PdV + \mu dN$$
$$dH = TdS + VdP + \mu dN$$
$$dG = -SdT + VdP + \mu dN$$

where the "chemical potential" is defined to be

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial H}{\partial N}\right)_{T,V} = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

and the general equation

$$\boxed{U(S, \{x_i\}, \{N_j\}) = TS + \sum_i \underbrace{X_i}_{\text{Generalized force}} \underbrace{x_i}_{\text{Generalized displacement}} + \sum_j \mu_j N_j}$$

is called "Gibbs-Duhem" equation

This is a very important equation in Chemical Thermodynamics.

For any single valued function $\phi(x_1, x_2, \cdots, x_n)$ $\frac{\partial}{\partial x_i}\left(\frac{\partial \phi}{\partial x_j}\right) = \frac{\partial}{\partial x_j}\left(\frac{\partial \phi}{\partial x_i}\right)$ we recover Maxwell relations with additional Maxwell relations

$$\left(\frac{\partial S}{\partial N}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial T}\right)_{V,N}, \quad \left(\frac{\partial P}{\partial N}\right)_{V,T} = -\left(\frac{\partial \mu}{\partial V}\right)_{T,N}$$

from Helmholtz free energy

Similarly

$$\left(\frac{\partial V}{\partial N}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N}, \quad \left(\frac{\partial S}{\partial N}\right)_{P,T} = -\left(\frac{\partial \mu}{\partial T}\right)_{P,N}$$

from Gibbs free energy

Gibbs Duhem equation for a single component PVT system reduces to

$$U = TS - PV + \mu N \quad \text{or} \quad \boxed{G = \mu N.}$$

We will use this results to discuss the phase equilibria & phase transitions.

Phase Equilibria

In most of the daily encountered phase transition, e.g. melting of ice, vaporization of water or sublimation, we can write down the Clausius-Clapeyron's equation $\left(\frac{\partial P}{\partial T}\right)_{saturation} = \frac{L}{T(V_2 - V_1)}$.

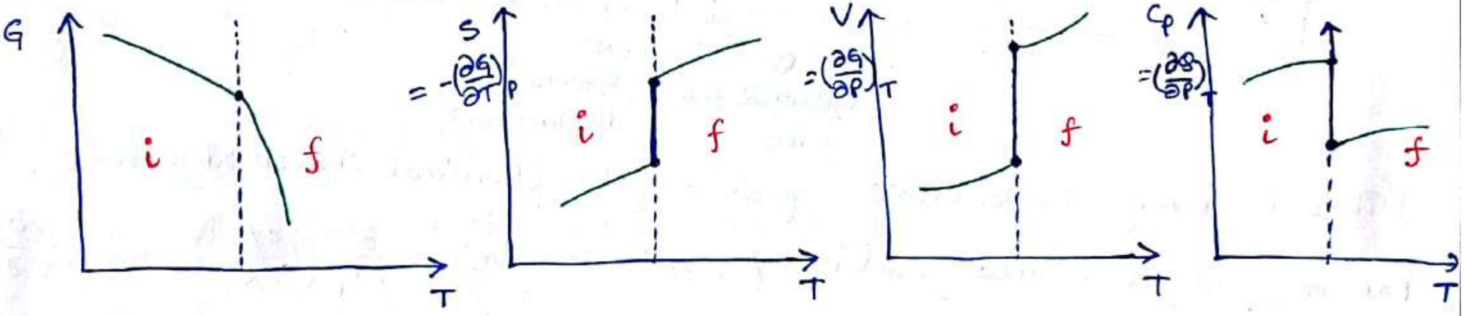
This is classified as 1^{st} order phase transition. This takes place at constant T and P while there is a transfer of latent heat that change the entropy and volume. As $dG = -SdT + VdP = 0$, so G is equal at two states $G^i = G^f$ and $S = -\left(\frac{\partial G}{\partial T}\right)_P$,

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

As T & P is constant, $dT = 0$ when $P = \text{constant}$

$dP = 0$ when $T = \text{constant}$

So $C_P = T\left(\frac{\partial S}{\partial T}\right)_P \to \infty$, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \to \infty$, $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \to \infty$.



A 1^{st} order phase transition is where the 1^{st} order derivative of the Gibbs function changes abruptly at the transition point.

Using $G = \mu N$ and $dG = -SdT + VdP + \mu dN$ we obtain

$$\mu dN + Nd\mu = -SdT + VdP + \mu dN$$

$$\text{or } d\mu = -\frac{S}{N}dT + \frac{V}{N}dP.$$

$\therefore$ Along an isotherm $dT = 0$ means $\mu_{liquid} - \mu_{gas} = \int_{gas}^{liquid} \frac{V}{N}dP = 0$

$$\therefore \mu_l = \mu_g.$$

Note that T-ds equation $Tds = C_P dT - TV\beta \, dP$ gives indeterminate result because $C_P \to \infty$, $dT \to 0$, $\beta \to \infty$, $dP \to 0$. However the other T-ds equation $Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ can be integrated along the phase transition.

$$\therefore \; T(S^f - S^i) = T\left(\frac{\partial P}{\partial T}\right)_V (V^f - V^i) = T\frac{dP}{dT}(V^f - V^i)$$

$$\text{or } H^f - H^i = T\frac{dP}{dT}(V^f - V^i)$$

$$\text{or } \boxed{\frac{dP}{dT} = \frac{H^f - H^i}{T(V^f - V^i)}}$$

Clausius- Clapeyron's equation for 1st order transition

[One can reach to this conclusion starting from the fact that at constant temperature & pressure, G = constant.

So applying, $G^i = G^f$ and for a change of phase from (T, P) to (T+dT & P+dP) we have $G^i + dG^i = G^f + dG^f$

$$\text{or } dG^i = dG^f \quad \text{or} \quad -S^i dT + V^i dP = -S^f dT + V^f dP$$

$$\text{or } \frac{dP}{dT} = \frac{T(S^f - S^i)}{T(V^f - V^i)} = \frac{H^f - H^i}{T(V^f - V^i)} \quad]$$

2nd order Phase Transition

In 1st order phase transition (sublimation, vaporization, fusion) happening at a constant temperature & pressure, there is a transfer of (latent) heat & hence a change in entropy & volume. G remains fixed and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$ or the first order derivative of G changes abruptly. at the transition point.

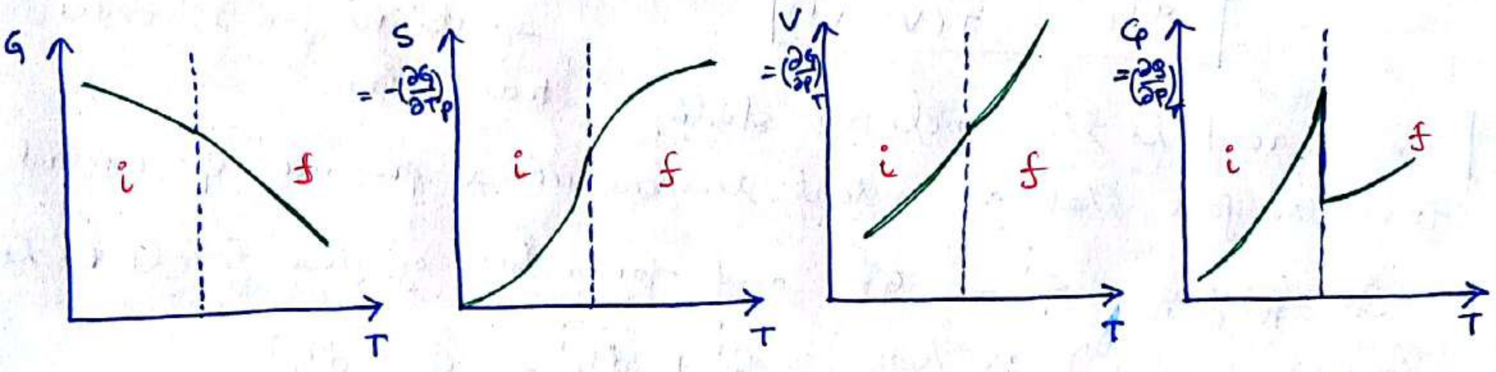
However investigation on some liquid showed no evolution of latent heat or change in volume. T, P, G, S, V remain unchanged and therefore U, H, G etc remain unchanged. However, finite change is seen in C_P, K and β, which are,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = +\frac{\partial}{\partial T}\left(-\frac{\partial G}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial P}\right)_T\right]_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P\partial T}\right)_{T,P}.$$

This led Ehrenfest to conclude that in a 1st order phase transition the 1st order derivative of G changes discontinuously while in a 2nd order phase transition, the 2nd order derivative of G changes discontinuously



Second order phase transition is an example of continuous phase transition

As S = constant, we have $dS^i = dS^f$

from $S = S(T,P)$, $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$$= \frac{C_P}{T}dT - \left(\frac{\partial V}{\partial T}\right)_P dP = \frac{C_P}{T}dT - V\beta\, dP$$

we have, $\frac{C_P^i}{T}dT - V\beta^i dP = \frac{C_P^f}{T}dT - V\beta^f dP$

$$\therefore\ (C_P^i - C_P^f)\frac{dT}{T} = VdP(\beta^i - \beta^f)$$

$$\therefore\ \boxed{\frac{dP}{dT} = \frac{C_P^i - C_P^f}{TV(\beta^i - \beta^f)}}$$

Ehrenfest's first equation for 2nd order phase transition

Similarly V = constant yields $dV^i = dV^f$

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

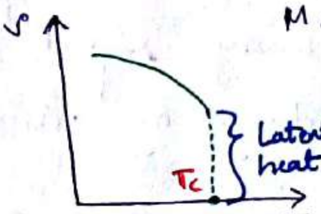
$$= \beta V dT - \kappa V dP$$ we have

$$\beta^i\cancel{V}dT - \kappa^i\cancel{V}dP = \beta^f\cancel{V}dT - \kappa^f\cancel{V}dP$$

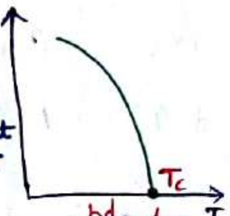
or $(\beta^i - \beta^f)\,dT = (\kappa^i - \kappa^f)\,dP$

or $\boxed{\frac{dP}{dT} = \frac{\beta^i - \beta^f}{k^i - k^f}}$: Ehrenfest's second equation for 2nd order phase transition.

Paramagnetic to ferromagnetic transition is an example of 2nd order P.T. Ehrenfests classification gave birth to "<u>critical phenomena</u>" that phase transition can be classified as n^{th} order if n^{th} derivative of the free energy with respect to any of its arguments yields a discontinuity at the phase transition. It was found that $\rho_{lg} \propto (T - T_c)^{\beta}$ and $M_{pf} = \frac{1}{N}\sum_{i=1}^{N} S_i \propto (T_c - T)^{\beta}$



1st order
Liquid-gas

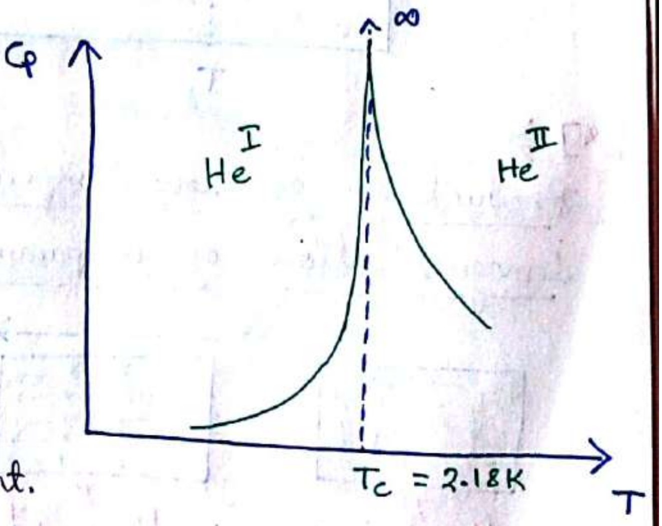


2nd order
para-ferro.

The fact that two apparently different physical systems may share precisely the same set of critical exponents is known as "<u>universality</u>." These led to many Nobel prizes including <u>Landau's theory of 2nd order phase transition</u>, <u>Bragg-Williams theory of 1st order phase transition</u>, <u>Widom's scaling laws</u> & <u>Kadanoff's renormalisation group (RG)</u> with two variant → <u>GellMan-Low RG</u> and <u>Wilson-RG</u>. which made the last significant contribution in the list of Nobel prizes in Statistical physics.

λ - Transition in He^4

By far the most interesting higher order phase transition that is found in Helium is the Lambda Transition, which is characterized by:



(a) T, P, G remains constant.

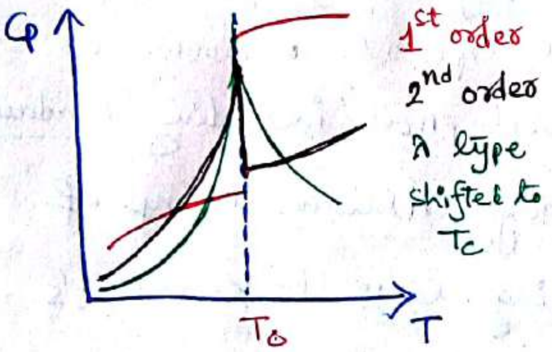
(b) S, V (also U, H, F) remains constant.

(c) C_p, β, K tends to infinity at transition temperature.

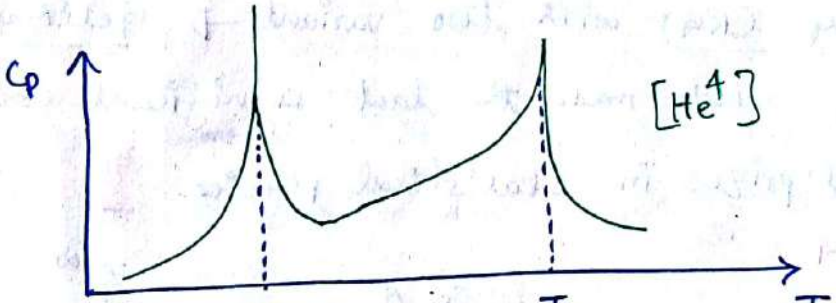
Examples of "λ"-type phase transition is

(1) Order disorder transformation in alloys.
(2) Onset of ferroelectricity in Rochelle salt.
(3) Ferro to paramagnetism at the Curie point.
(4) Ordinary liquid Helium-I to superfluid liquid helium-II.
(5) A change of orientation of an ion in a crystal lattice.

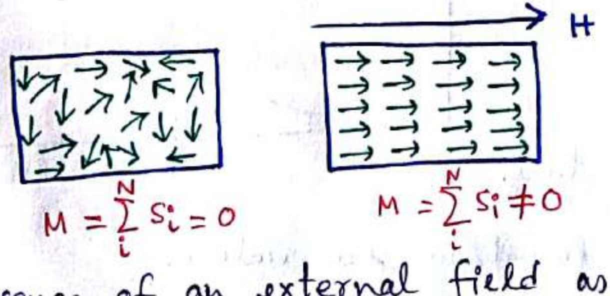
To note that as a substance in any one phase approaches the temperature at which 1st order phase transition occurs, C_p remains finite upto the transition temperature. It becomes infinite only when a small amount of the other phase is present and its behaviour before this takes place shows no evidence of the happening of the event.



But in case of λ-type transition, C_p starts to rise before the transition point is reached and the substance anticipates the outcome of the phase transition.



[*] ⇒ [Production of low temperature using the method of adiabatic demagnetisation of a paramagnetic substance.

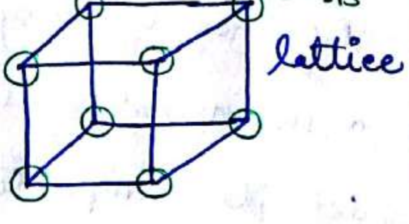


The atoms of a paramagnetic material possess a permanent magnetic moment 2ml. In the absence of an external field as a result of the thermal (Brownian) motion of the atoms, the orientation of magnetic moments is almost random. Quantitatively disorder is confined in entropy $S = K_B \ln \Omega$ where Ω is the thermodynamic probability i.e. the number of ways N number of atoms of the paramagnetic sample can be distributed among the $(2J+1)$ sublevels into which every atomic level splits in a magnetic field. So $\Omega = (2J+1)^N$ and $\therefore S = K_B N \ln(2J+1)$

When the magnetic field is applied and its intensity is increased, more & more number of magnetic moments are oriented in the direction of the field, and the entropy is reduced. At the state of magnetic saturation, all moments are ordered & the entropy vanishes.

This process of magnetisation of a paramagnetic sample upto saturation is accompanied by the decrease of entropy. At a constant temperature T with a decrease in entropy ΔS, heat $\Delta Q = T\Delta S$ is generated & transmitted to the surrounding (immersing on a liquid Helium bath). After equilibriated, the bath is removed & the sample is left thermally insulated.

In such condition, the sample will quasistatically & adiabatically demagnetize with an increase in entropy ΔS. Heat is required to increase the entropy that is supplied by the thermal vibrations of the lattice. As the sample is thermally insulated, its temperature drops. Using this principle, it is possible to obtain temperature down to millikelving $\sim 10^{-3}$ °K.



Gibbs Phase Rule

Gibbs published a series of papers on the equilibrium of heterogeneous substance. Phase : A homogeneous, physically distinct part of a system that is separated from other parts by definite bounding surfaces is called a phase. E.g. ice-water-vapour constitute a three-phase system. Component : The smallest number of independently variable constituents by means of which the composition of each phase can be expressed. In above example, density is that variable, so the water phases is one component system. Variance or d.o.f. : The number of variable factors (e.g. pressure, temperature, concentration etc) that need to be fixed in order that the condition of system at equilibrium may be completely defined is called degree of freedom (d.o.f.).

If the equilibrium between any number of phases is not influenced by external forces (electromagnetic, gravity) but only influenced by pressure, temperature and concentration, then Gibb's phase rule provides the relation between number of d.o.f. F of the system to the components C and phases P as

$$\boxed{F = C - P + 2}$$

E.g. for water system, $C = 1$, $P = 3$. $\therefore F = 1 - 3 + 2 = 0$ or it is a nonvariant system. So the three phases can only exist in contact at definite temperature & pressure, which is the "triple point."

[Read more about phase rule for heterogeneous substance from Wikipedia].