Gaseous State

Introduction to Postulates of kinetic theory of gases :-

① Every gas is made up of a large no. of extremely small particles called molecules. All the moles of a perticular gas are identical in mass & size & differ from gas to gas.

② The moles of a gas are separated from each other by large distances so that the actual vol of the moles is negligible as compared to the total vol of the gas.

③ The dist betn the moles are so large that the forces of attran or repuln betn them are negligible.

④ The moles are moving continuously in different diren with diff velo. Hence they collide with one another as well as on the wall of the container.

⑤ The pre exerted on the wall of container is due to the bombardment of moles on the wall of the container.

⑥ Since the moles are moving with diff velo, they possess diff KE. The avarage KE of the moles of a gas is directly prepostional to the absolute temp of the gas.

⑦ Moles are supposed to be perfectly elastic hard spheres so that no energy is lost when the moles collide with one another or with the wall of the container.

Ideal gas eqn:

$V \propto 1/p$ (at const T & n) → Boyle's law

$V \propto T$ (at const P & n) → Charle's law

$V \propto n$ (at const T & P) → Avogadro's law

combining above eqn

$$V \propto \frac{Tn}{p} = \frac{RTn}{p}$$

$$PV = nRT \quad \text{——} \; ①$$

where R is prepostionality const called as gas const. Eqn ① is ideal gas eqn.

Deviation of gases from ideal behaviour:-

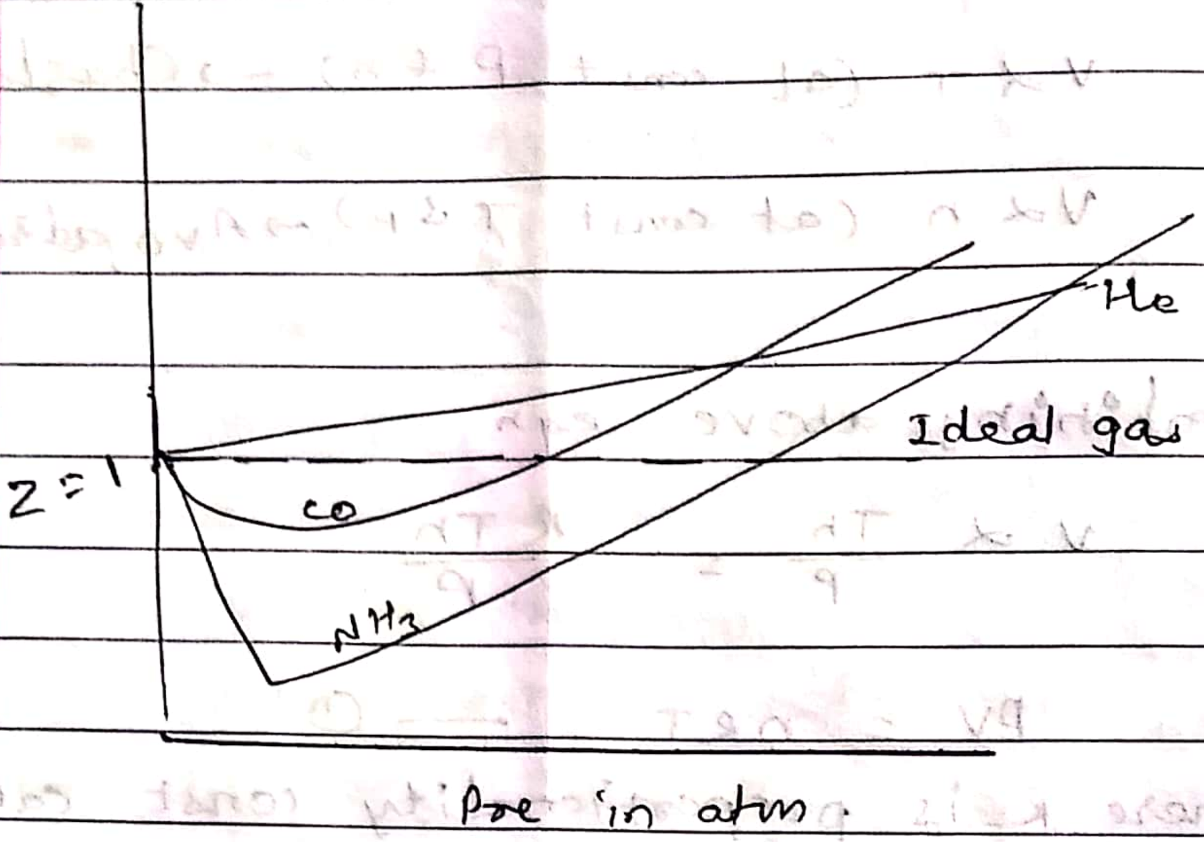
The eqn of state $PV = nRT$ is valid for an ideal gas. Real gases obey this eqn only under conditions of low pre & high temp. At high pre & low temp, the greater deviation from ideal behaviour.

The deviations from ideal behaviour are represented in terms of compressibility factor (Z)

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} = \frac{PV_m}{RT}$$

where $V_m = V/n$ is the molar vol i.e the vol occupied by one mole of the gas.

For an ideal gas, $Z = 1$ under all conditions of temp & pre. The deviation of z from unity is thus a measure of the imperfection of the gas.



Vander waals' eqn of state :

Vander Waal's show the deviation of real gases from ideal behaviour to two erroneous postulates of Kinetic theory :

i) The mole$_s$ in a gas are point masses & posses no vol.

ii) There are no intermolecular attran in gas particles.

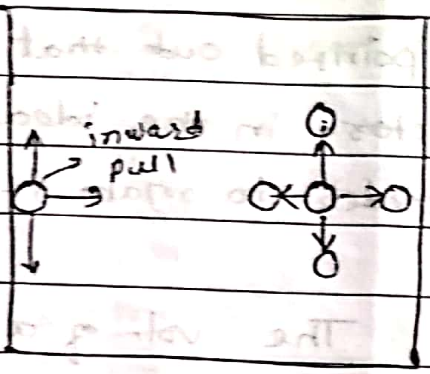
Vander Waal pointed out that both the pre (p) + vol (V) factors in the ideal gas eq^n needed correction in order to make it applicable to real gases.

Volume correction : The vol. of a gas is the free space available for free movement of gas mole$_s$ in the container. The dot mole$_s$ of ideal gas have zero vol & the entire space in the container is available for their movement. However Vander Waal assumed that mole$_s$ of a real gas are rigid spherical particles which posses a definite vol. The vol. of real gas is therefore ideal vol minus vol. occupied by gas mole$_s$.

If b is the effective vol of moles per mole of the gas, the vol. in ideal gas eqn is corrected as V-b.

For n moles of gas, the corrected vol. is (V-nb)

• Pressure correction :



A mole in the interior of gas is attracted by other mole in all sides. These attractive forces cancel out. But a mole in contact with wall of the container attracted by mole on one side only. Hence it experiences an inward pull. Therefore it strike the wall with reduced velo & actual pre of gas will decrease.

$$P_{actual} = P_{ideal} + P_{reduced}$$

& reduced pre (decrease in pre) is directly proportional to square of density of gas

$$\therefore P_{red} \propto d^2$$

$$P_{red} \propto \left(\frac{M}{V}\right)^2$$

$$P_{red} \propto \frac{1}{V^2}$$

$$P_{red} = a/V^2$$

For n moles

$$P_{red} = \frac{an^2}{V^2}$$

$$\therefore P_{actual} = P_{ideal} + \frac{an^2}{V^2}$$

$$P_{real} = P + \frac{an^2}{V^2}$$

Putting corrected values of pre & vol in ideal gas eqn

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

For 1 mole

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

a & b are vander Waal's constant.

Units of Vander Waal's const :

We know that

$$P = \frac{an^2}{V^2}$$

$$a = \frac{PV^2}{n^2} = \frac{\text{atm Lit}^2}{\text{mol}^2} = \text{atm} \cdot \text{Lit}^2\ \text{mol}^{-2}$$

& $V = nb$

$$b = V/n = \text{lit}/\text{mol} = \text{lit mol}^{-1}$$

① One mole of oxygen is confined to a 20 lit flask at 27°c. Calculate its pre using Vander Waal's eqn. [$a = 5.464$ atm lit^2 mol^{-2}, $b = 0.0305$ lit mo
$R = 0.0832$ lit atm mol^{-1} K^{-1}]

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

For $n = 1$

$$\left(\cancel{P + \frac{an^2}{V^2}}\right)$$

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

$$\left(P + \frac{5.464}{(20)^2}\right)(20 - 0.0305) = 0.0832 \times (27 + 273)$$

$$(P + 0.01366)(19.96) = 0.0832 \times 300$$

$$(P + 0.01366)(19.96) = 24.96$$

$$P + 0.01366 = 24.96 / 19.96$$

$$P + 0.01366 = 1.2505$$

$$P = 1.2368$$

$$P = 1.2368\,\text{atm}$$

② Calculate the pre exerted by 1 mole of methane in a 250 ml container at 300°K using Vander Waal's eqn. What pre will be predicted by ideal gas.
[$a = 2.253\ L^2\ atm\ mol^{-2}$, $b = 0.0428\ lit\ mol^{-1}$,
$R = 0.0832\ atm\ lit\ mol^{-1}\ K^{-1}$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad n = 1$$

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

$$\left[P + \frac{2.253}{(250 \times 10^{-3})^2}\right]\left[(250 \times 10^{-3}) - (0.0428)\right] = 0.0832 \times 300$$

$$P = 82.8\,\text{atm}$$

$$\left(P + \frac{2.25}{62500 \times 10^{-6}}\right)(0.0250 - 0.0428) = 24.96$$

$$\left(P + \frac{2.25}{0.062500}\right)(0.205) = 24.96$$

$$P + 36 = 24.96 / 0.208 = 120$$

$\therefore P = 120 - 36$

$P = 84$ atm

The ideal gas eq^n predicts that

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{0.250}$$

$$= 98.4 \text{ atm}$$

Critical phenomenon :- A gas can be liquified by lowering the temp & increasing the pre.

Andrew studied the P-T conditions of liquification of several gases. He established that for every gas there is a temp below which the gas can be liquified & above it the gas stop the liquification. This temp is called critical temp of the gas.

Critical temp (T_c) :- The critical temp of a gas may be defined as that temp above which it cannot be liquified no matter how great the pre applied.

Critical pre (P_c) :- The critical pre (P_c) is defined as minimum pre required to liquify the gas at this critical temp.

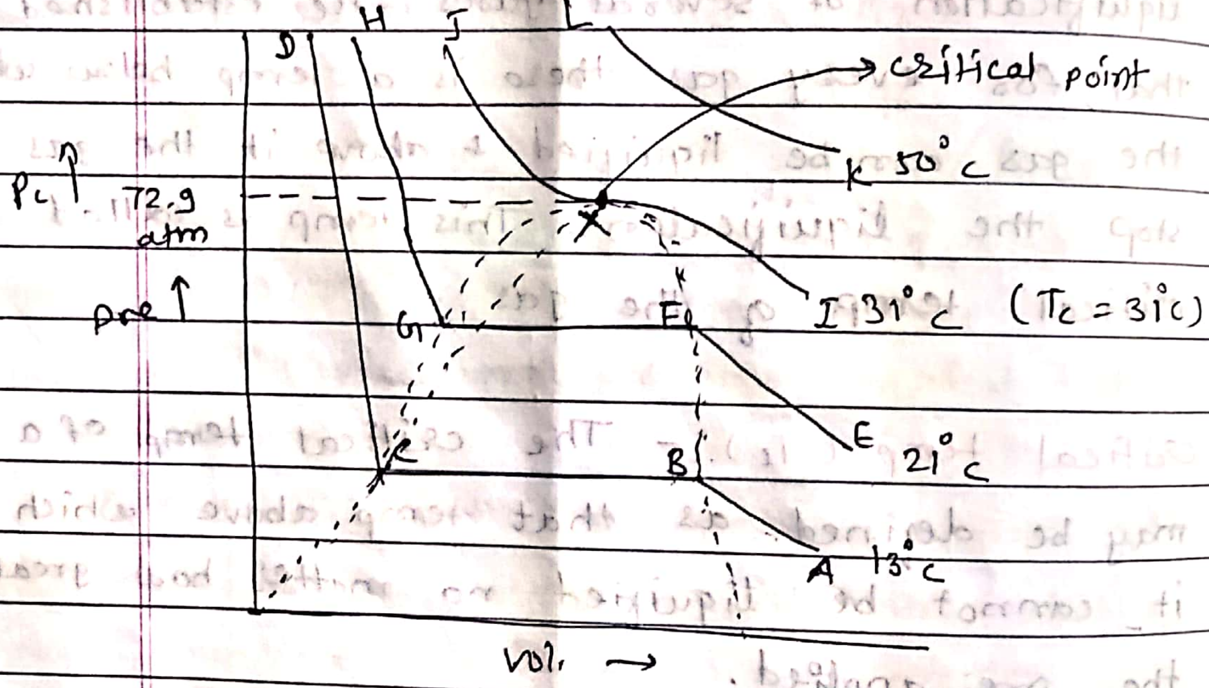
Critical vol. (V_c) :- The critical vol is defined as vol occupied by a mole of gas at critical temp & pre.

At critical temp & pre, the gas becomes identical with its liq & is said to be in critical state. The smooth merging of the gas with its liq is referred as critical phenomenon.

The p-v isotherm of CO_2.

The p-v curves of a gas at const temp are called isotherms.

Andrew plotted the isotherms of CO_2 for a series of temp as shown below:



ⓐ Isotherm at 13°c: From isotherm, CO_2 is entirely gaseous at low pre (along AB) & the vol. decreases with increasing pre & at B liquification starts, vap gets converted into liq & vol. get decrease suddenly as the vol occupied by a liq is much less than that of gas so that BC would be almost ‖el to vol axis. indicating the sudden decrease in vol occuring at same pre as more & more gas changes

changes in liq.

Liquification gets completed at c & line CD which is almost vertical represent the compressibility of a liq & reveals that the liq are much less compressible i.e increase in pre will produce a very small decrease in vol.

ⓑ Isotherm at 21°c : This isotherm is same as isotherm at 13°c with difference that horizontal portion where liquification start is short.

ⓒ Isotherm at 31°c :- As temp gets raised this horizontal portion would become less & less till at 31°c it reduces almost to point X. Beyond temp 31.1°c there occure no liquification at all when applied pre is very high.

Point X is a critical point for CO_2. The difference bet^n liq & vap state disappear at this point & CO_2 exist in a state called critical state. The critical temp for CO_2 is 31°c & critical pre is 72.9 atm.

Rel^n bet^n critical const & Vander-Waal's const :-

The Vander Waal's eq^n is

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \text{since } n=1$$

$$PV-Pb+\frac{a}{V}-\frac{ab}{V^2}-RT=0$$

multiplying by V^2 thro'out

$PV^3 - pbV^2 + aV - ab - RTV^2 = 0$

Deviding by P

$V^3 - bV^2 + \frac{aV}{P} - \frac{ab}{P} - \frac{RTV^2}{P} = 0$

$V^3 - bV^2 - \frac{RTV^2}{P} + \frac{aV}{P} - \frac{ab}{P} = 0$

$V^3 - V^2\left(b + \frac{RT}{P}\right) + \frac{aV}{P} - \frac{ab}{P} = 0$

At critical point Vander Waal's eqn given as

$V^3 - V^2\left(b + \frac{RT_c}{P_c}\right) + \frac{aV}{P_c} - \frac{ab}{P_c} = 0$ — ①

At critical point

$(V - V_c)^3 = 0$

$V^3 - 3V^2V_c + 3V_c^2V - V_c^3 = 0$ — ②

Camparing eqn ① & ②

$3V_c = b + \frac{RT_c}{P_c}$ — ③

$3V_c^2 = \frac{a}{P_c}$ — ④

$V_c^3 = \frac{ab}{P_c}$ — ⑤

Deviding eqn ⑤ by ④

$\frac{V_c^3}{3V_c^2} = \frac{ab/P_c}{a/P_c}$

$\frac{V_c}{3} = b$

$\boxed{V_c = 3b}$ — ⑥

Putting eq

Putting eq^n ⑥ into ④

$$3V_c^2 = \frac{a}{P_c}$$

$$3(3b)^2 = a/P_c$$

$$3(9b^2) = a/P_c$$

$$27b^2 = a/P_c$$

$$\boxed{P_c = \frac{a}{27b^2}} \quad — ⑦$$

Putting eq^n ⑥ + ⑦ in ⑤

$$3(3b) = b + \frac{RT_c}{a/27b^2}$$

$$9b - b = \frac{RT_c}{a/27b^2}$$

$$8b = RT_c \times \frac{27b^2}{a}$$

$$T_c = \frac{8ab}{27b^2R} = \frac{8a}{27Rb}$$

$$\therefore \boxed{T_c = \frac{8a}{27Rb}} \quad — ⑧$$

Also from eq^n ⑥

$$V_c = 3b$$

$$\boxed{\therefore b = V_c/3} \quad — ⑨$$

From eqⁿ ④

$$3V_c^2 = a/P_c$$

$$a = 3V_c^2 . P_c$$

Problems :

① Vander-Waal's const for HCl gas are $a = 3.67$ atm lit^{-2}/mol^2 & $b = 40.8$ ml/mol. Find the critical temp & critical pre of the gas.

[$R = 0.0821$ atm lit $K^{-1} mol^{-1}$]

→

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 3.67}{27 \times 0.0821 \times 40.8 \times 10^{-3}}$$

$$= 325°K$$

$$P_c = \frac{a}{27b^2} = \frac{3.67}{27 \times (40.8 \times 10^{-3})^2} = 81.6 \text{ atm}$$

② The critical const for water are $T_c = 647$ K, $P_c = 218$ atm, $V_c = 0.057$ lit/mol. Calculate Vander-Waal's const.

→

$$a = 3P_cV_c^2 = 3 \times 218 \times (0.057)^2$$

$$= 2.12 \text{ lit}^2 \text{ atm/mol}^{-2}$$

$$b = \frac{V_c}{3} = \frac{0.057}{3} = 0.019 \text{ lit/mol}$$

③ Calculate critical temp of Vander-Waal's gas for which P_c is 100 atm & b is 50 ml/mol [R = 0.0821 atm. lit/K/mol]

→

$$T_c = \frac{8a}{27Rb}$$

We know the eqn

$$P_c = \frac{a}{27b^2}$$

$$\therefore a = 27b^2 P_c$$

$$\therefore T_c = \frac{8 \times 27 b^2 P_c}{27 R b} = \frac{8 \times b \cdot P_c}{R}$$

$$= \frac{8 \times 50 \times 10^{-3} \times 100}{0.0821}$$

$$= 487.2\ ^{\circ}K$$

④ Calculate the critical temp of Vander-Waal gas for which P_c is 120 atm & b is 48 ml/mol (R = 0.0821 atm. lit/K/mol)

→ $P_c = 120$ atm $b = 48 \times 10^{-3}$ lit/mol

$$T_c = \frac{8a}{27Rb} \quad \text{but } a = 27b^2 P_c$$

$$\therefore T_c = \frac{8 \times \cancel{27} b^2 P_c}{\cancel{27} R b} = \frac{8 b P_c}{\cancel{27} R}$$

$$= \frac{8 \times 48 \times 10^{-3} \times 120}{0.0821} = 561.2\ ^{\circ}K$$

Moles velocities :-

There are diff types of moles velocities as follows :-

① Root mean square (Rms) velo ($\bar{C}$)

② Average velo ($\bar{v}$)

③ most probable velo (Vmp)

Rms velo = $\bar{C} = \sqrt{\frac{3RT}{M}}$

Avarage velo = $\bar{V} = \sqrt{\frac{8RT}{\pi M}}$

Most Pro. velo = $V_{mp} = \sqrt{\frac{2RT}{M}}$

Relⁿ betⁿ rms, avarage & most probable velo :

$$\bar{v} = 0.9213 \times \bar{c}$$

$$V_{mp} = 0.8165 \times \bar{c}$$

Numericals :-

① Calculate rms velo of CO_2 molec at 1000°C

[$R = 8.31 \times 10^7$ erg / deg / mole]

→

$T = 1000 + 273 = 1273$ K

$M = 12 + 32 = 44$

$R = 8.31 \times 10^7$ erg / deg / mole

$$\bar{c} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.31 \times 10^7 \times 1273}{44}}$$

$$= \boxed{5.47} \times 10^4 \text{ cm/sec}$$

[illegible] Calculate the temp at which the hydrogen mole will have an average speed of 17640 cm/s [R = 8.314×10⁷ erg/deg/mole]

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

$$17640 = \sqrt{\frac{8 \times 8.314 \times 10^7 \times T}{3.14 \times 2}}$$

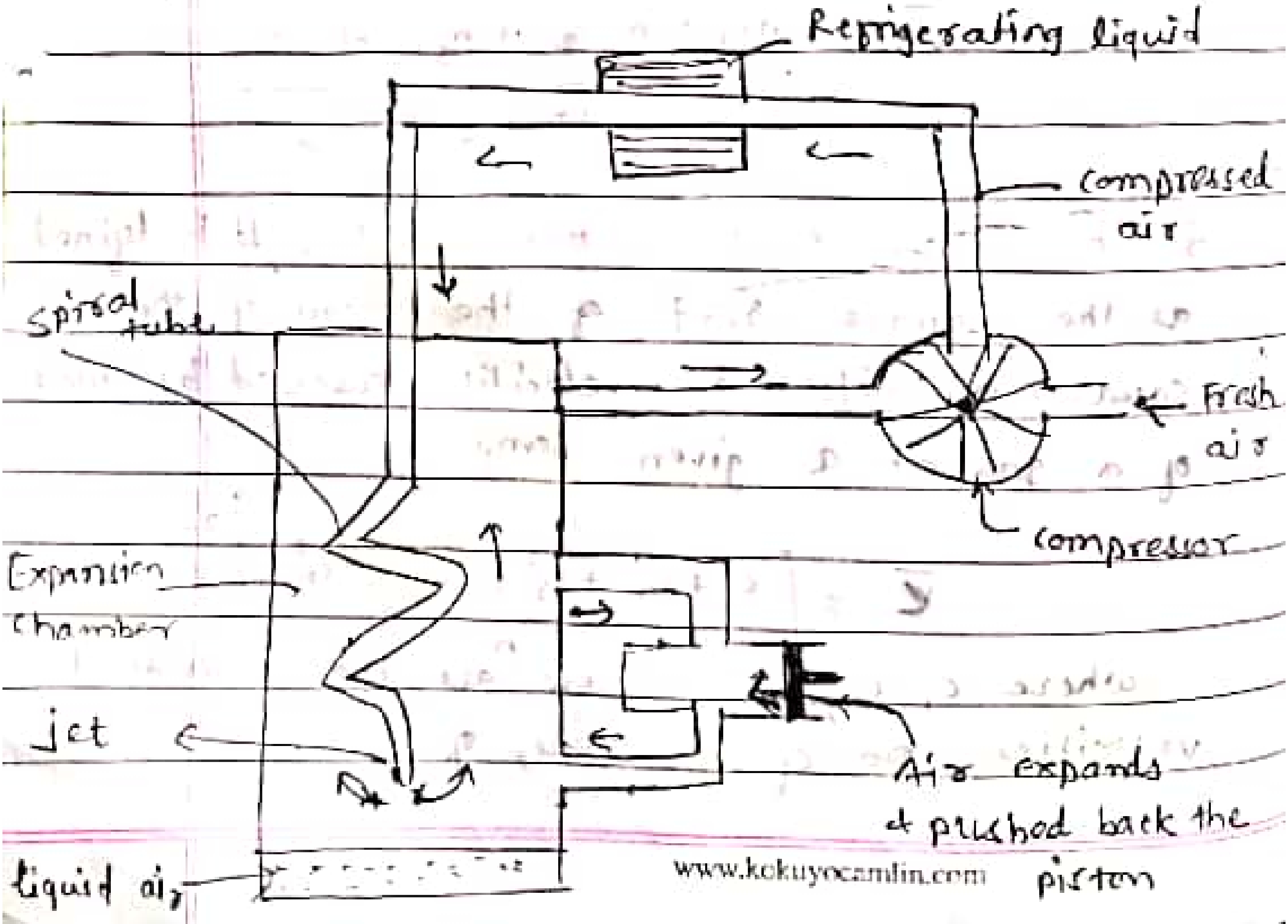
$$T = 300K \text{ or } 27^\circ C$$

Liquifaction of gases :-

If a gas is cooled below its critical temp & then subjected to adequate pre, it liquefies. The various methods employed for the liquifaction of gases depends on the tech used to attain low temp.

Claude's method :-

In Claude's method the gas is cooled not only by overcoming the intermolecular forces but also by performance of work.



Pure dry air is compressed by compressor & then passes thr' a tube cooled by refrigerating liq to remove any heat produced during the compression. The tube carrying the compressed air then enters the 'expansion chamber'. The tube bifurcates & a part of air passes thr' the side-tube into the cylinder of an engine. Here it expands & pushes back the pisten. Thus the air does mechanical work whereby it cools. The air then enters the expansion chamber & cools the incoming compressed air thr' the spiral tube. The air undergoes further cooling by expansion at the jet & liquefies. The gas escaping liquefication goes back to the compresser & the whole process is repeated over & over again.