

GASES

ABOUT CRITICAL CONSTANTS

→ Andrews Isotherm

→ In 1869, Thomas Andrews carried out an experiment of P-V relations of CO_2 gas at various temperatures. Such that other real gases also show the same types of isotherms.

Observations from isotherm

1) At high temperatures, T_4 , the isotherms look like those of an ideal gas.

2) At low temps:

a) A curve 'abcd':-

→ As pressure increases the volume of gas decreases (curve a → b).
→ At point 'b' liquification commences and volume decreases rapidly as gas converted to a liquid with a much higher density.
→ At point 'c', liquification is complete, thus line 'cd' represents the variation of 'v' with 'p' of liquid state.

→ 'AB' represents the gaseous state

'BC' liquid & vapour in equilibrium.

'CD' shows liquid state only.

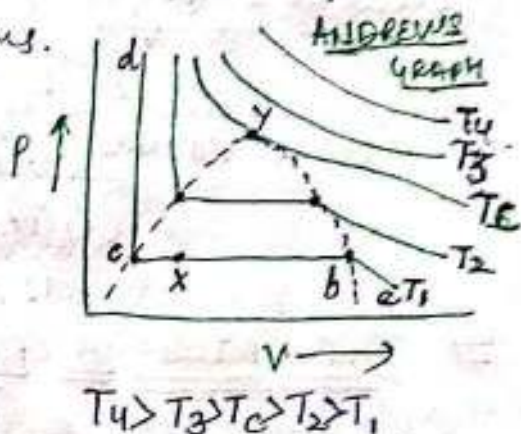
→ Liquification commences at 'b' and is complete at 'c'

→ At a point 'x' between b and c, ratio of liquid and gas is equal to $\frac{bx}{cx}$. Pressure corresponding to line 'bc' is known as 'vapour pressure' of liquid

3) At temperature T_c , the horizontal portion is reduced to a mere point 'y'.

→ At temperature higher than T_c there is no liquification of gas at all.

* therefore, for every gas, there is limit of temperature above which it can't be liquified no matter what the pressure is



Definitions of Critical Constants

- Critical temperature; T_c : The maximum temperature at which a gas can be liquified i.e. temperature above which a liquid can't exist.
- Critical pressure; P_c : The maximum pressure required to cause liquification at the temperature T_c
- Critical volume; V_c : Volume occupied by 1 mole of a gas at critical temperature T_c and at critical pressure P_c .

CALCULATION OF CRITICAL CONSTANTS FOR VANDER WAALS EQN:

1 mole of Van der Waals Equation

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

may be written as:

$$V_m^3 - \left(b + \frac{RT}{P}\right)V_m^2 + \frac{a}{P}V_m - \frac{ab}{P} = 0 \quad \text{--- (a)}$$

Equation has three roots; either all three roots are real or one is real and other two are imaginary.

→ Expressions of Critical Constants in Terms of Van der Waals Constants

At very high temperatures, eqn (a) may be written in general format of cubic eqn as:

$$(V_m - V') (V_m - V'') (V_m - V''') = 0$$

which at critical points ($V' = V'' = V''' = V_c$) becomes.

$$(V_m - V_c)^3 = 0$$

on expanding;

$$V_m^3 - V_c^3 - 3V_c V_m^2 + 3V_c^2 V_m = 0 \quad \text{--- (b)}$$

where at critical situation; $P = P_c$, $T = T_c$.

Comparing (a) & (b);

$$3V_c = b + \frac{RT_c}{P_c}, \quad 3V_c^2 = \frac{a}{P_c}, \quad V_c^3 = \frac{a}{P_c}$$

Solving these equations for P_c , V_c & T_c in terms of a , b , and R ;

$$V_c = 3b; \quad P_c = \frac{a}{27b^2}; \quad T_c = \frac{8a}{27Rb}$$

thus, a & b values may be written

$$b = \frac{1}{3} \left(\frac{3RT_c}{8P_c} \right) = \frac{RT_c}{8P_c}$$

$$a = 8P_c V_c^2 = 8P_c \left(\frac{3RT_c}{8P_c} \right)^2 = \frac{27(RT_c)^2}{64P_c}$$

→ Value of Gas Constant at Critical state

Value of $P_c V_c / RT_c$ at critical state (Experimentally obtained)

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375$$

* MAXWELL DISTRIBUTION OF MOLECULAR SPEEDS

- Distribution of Molecular speeds

The speed of molecule of gas changes continuously with collisions with walls of containers and other gas molecules. Thus, the net speed of individual molecule is not possible to determine. Therefore, a statistical average of the speeds of the whole collection of gas molecules is estimated.

⇒ Law of distribution of molecular speeds

J.C. Maxwell using the theory of probability describes how the molecules of gas are distributed over the possible ranges, from zero to very high values. Which may be represented by the law of distribution of molecular speeds

$$dN_u = 4\pi N \left(\frac{M}{2\pi RT} \right)^{3/2} \exp \left(-\frac{Mu^2}{2RT} \right) u^2 du$$

$$dN_u = 4\pi N \left(\frac{m}{2\pi RT} \right)^{3/2} \exp \left(-\frac{mu^2}{2KT} \right) u^2 du. \quad \text{--- (I)}$$

M = Molar Mass

m = mass of single molecule, m

→ Consequences of distribution of speeds

→ Distribution of speeds states that the average kinetic energy of a gas is also constant for a given temperature.

Average kinetic energy

$$\begin{aligned} \overline{KE} &= \frac{1}{N} \left(\frac{1}{2} m u_1^2 + \frac{1}{2} m u_2^2 + \dots + \frac{1}{2} m u_N^2 \right) \\ &= \frac{1}{N} m \left(u_1^2 + u_2^2 + \dots + u_N^2 \right) = \frac{1}{2} m \overline{u^2} \end{aligned}$$

OR
$$\overline{KE} = \frac{1}{N} \left(\frac{1}{2} m \sum_i dN_i u_i^2 \right) = \frac{1}{2} m \left(\sum_i \frac{dN_i}{N} u_i^2 \right) =$$

Thus, it states that the average kinetic energy of gas has constant value at a given temperature.

Derivation of some expressions from the Maxwell distribution

Average speed

The average speed given by relation

$$\bar{u} = \frac{u_1 + u_2 + \dots + u_N}{N} = \frac{1}{N} \sum u_i$$

$$\bar{u} = \frac{1}{N} \int_0^{\infty} u dN_u = \int_0^{\infty} u \frac{dN_u}{N}$$

Substituting dN_u/N value from eqn (1);

$$\bar{u} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^{\infty} u^3 \exp \left(-\frac{Mu^2}{2RT} \right) du$$

$$\bar{u} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \left\{ 2 \left(\frac{RT}{M} \right)^2 \right\} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

$$\therefore \boxed{\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}}$$

Root Mean Square Speed

The mean square speed is given by

$$\bar{u}^2 = \frac{u_1^2 + u_2^2 + \dots + u_N^2}{N} = \frac{1}{N} \sum_i u_i^2 = \frac{1}{N} \int_0^{\infty} u^2 dN_u$$

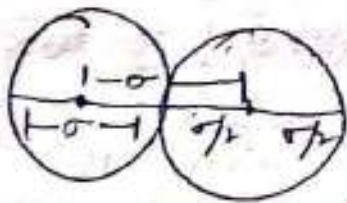
$$\bar{u}^2 = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^{\infty} u^4 \exp\left(-\frac{Mu^2}{2RT}\right) du = \frac{3RT}{M}$$

$$u_{rms} = \sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

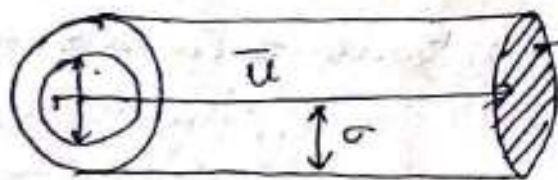
⇒ Molecular Collisions in a Gas

We assume molecules to be rigid, non-interacting and spherical with diameter σ . It is also assumed all molecules move with same speeds, thus, the average speed, \bar{u} .

Collision Cross Section of molecules:



two identical molecules with diameter, σ such that distance separating their centers is σ . The quantity $(\pi\sigma^2)$ is called collision cross-section for the rigid spherical molecule.



collision cross section

Volume swept by a molecule \Rightarrow in unit time

$$V = (\pi\sigma^2) \bar{u}$$

N^* No. of molecules per unit volume, v .

$$N = VN^* = (\pi\sigma^2 \bar{u}) N^*$$

No. of collisions made by a single molecule in unit time

$$Z_1 = N = (\pi\sigma^2 \bar{u}) N^*$$

⇒ Effect of Temperature and Pressure on Mean free path and molecular collisions

→ Dependence of N^* on P & T

Ideal gas equation

$$PV = nRT = \frac{N'}{N_A} RT$$

$$P = \left(\frac{N'}{V}\right) \left(\frac{R}{N_A}\right) T = \left(\frac{N'}{V}\right) K T$$

NO. of molecules per unit volume;

$$N^* = \frac{N'}{V} = \frac{P}{KT}$$

Thus; $N^* \propto \frac{P}{T}$

→ Dependence of \bar{u}

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8KT}{\pi m}}$$

Thus; $\bar{u} \propto \sqrt{T}$

⇒ Dependence of λ on P & T

mean free path, $\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 N^*}$

Thus; $\lambda \propto \frac{1}{N^*}$

therefore; $\lambda \propto \frac{T}{P}$; $\lambda \propto T$ provided $P = \text{constant}$
 $\lambda \propto \frac{1}{P}$ provided $T = \text{constant}$

According to Gay Lussac's law, $P \propto T$ at constant 'V'

∴ $\lambda \propto \text{constant}$

∴ there is no effect of changing T or P on λ if the volume of the gas is constant.

→ Dependence of Molecular Collisions

$$Z_1 = \sqrt{2} \pi \sigma^2 \bar{u} N^*$$

$$Z_1 \propto \bar{u} N^*$$

$$Z_1 \propto (\sqrt{T}) \left(\frac{P}{T}\right)$$

$$Z_1 \propto \frac{P}{\sqrt{T}}$$

$\therefore Z \propto P$; $T = \text{constant}$, $Z_1 \propto \frac{1}{\sqrt{T}}$ when $P = \text{constant}$

Effect of changing P or T at constant volume, described by Gay-Lussac's law

$$Z_1 \propto \frac{1}{\sqrt{T}} \propto \sqrt{T}$$

$$Z_1 \propto \frac{P}{\sqrt{T}} \propto \sqrt{P}$$

$$\therefore Z_{11} = \frac{\sqrt{P}}{\sqrt{2}} \pi \sigma^2 \bar{u} N^*$$

$$Z_{11} \propto (\sqrt{T}) \left(\frac{P}{T}\right)^2$$

$$\boxed{Z_{11} \propto \frac{P^2}{T^{3/2}}}$$

$$\rightarrow Z_{11} \propto \frac{P^2}{T^{3/2}} \propto \frac{T^2}{T^{3/2}} \propto T^{1/2} \quad (\text{volume constant})$$

$$\cdot Z_{11} \propto \frac{P^2}{T^{3/2}} \propto \frac{P^2}{P^{3/2}} \propto P^{1/2} \quad (\text{volume constant})$$

⇒ Viscosity of Gases

The internal friction which opposes the relative motion of adjacent layers of a fluid is known as viscosity.

Viscosity coefficient

The tangential force f , required to maintain uniform velocity will depend on:

(a) Area of contact A between two layers

(b) velocity gradient, dv/dx

$$f \propto A \frac{dv}{dx}$$

$$\boxed{f = \eta A \frac{dv}{dx}}$$

$\eta = \text{coefficient of viscosity}$
units = Nm^{-2}sec

Expression for viscosity of gases

→ viscosity of gas arises due to the transfer of momentum across layers of gases.

(1) The flow velocity u_z is very small compared to mean gas velocity, u_{av} .

(2) The only molecules reaching plane P-P' are those which on average, have just made their collision at a distance λ from the height z .

(3) The number of molecules passing downwards or upwards through a unit area per unit time = $\frac{N^* u_{av}}{4}$, No. of molecules per unit time = N^*

amount of momentum coming up through a unit area per unit time

$$(mu)_{\uparrow} = m \left(\frac{1}{4} N^* u_{av} \right) \left(u_z - \lambda \frac{du}{dz} \right)$$

amount of horizontal momentum

$$(mu)_{\downarrow} = m \left(\frac{1}{4} N^* u_{av} \right) \left(u_z + \lambda \frac{du}{dz} \right)$$

∴ net downward flow

$$(mu)_{\downarrow} - (mu)_{\uparrow} = \frac{1}{2} N^* u_{av} m \lambda \frac{du}{dz}$$

$$f = \frac{1}{2} m N^* u_{av} \lambda \frac{du}{dz}$$

$$\eta = \frac{1}{2} m N^* u_{av} \lambda = \frac{1}{2} \rho u_{av} \lambda \quad \rho = \text{density of medium}$$

Effect of Pressure and Temperature on Viscosity of Gas

$$u_{av} = \sqrt{\frac{8KT}{\pi m}} \quad \text{and} \quad \lambda = \frac{1}{\sqrt{2} \pi \sigma^2 N^*}$$

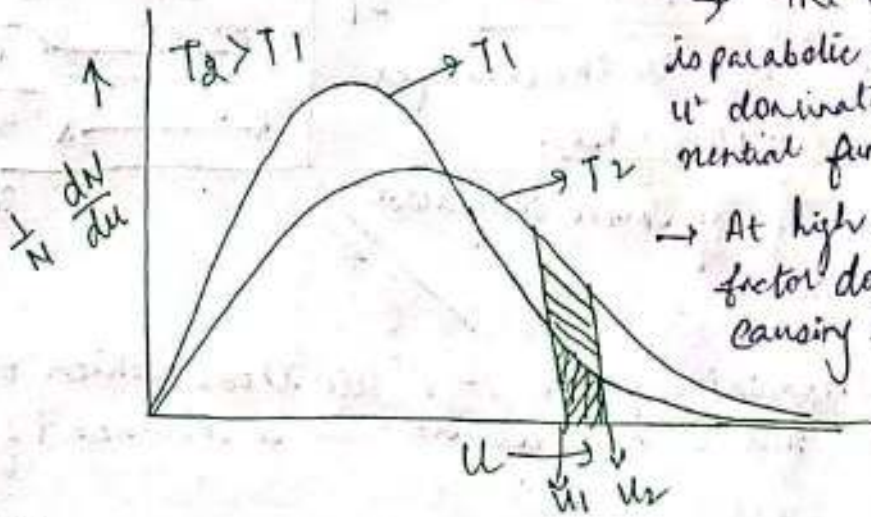
$$\therefore \eta = \frac{1}{2} m N^* \left(\sqrt{\frac{8KT}{\pi m}} \right) \left(\frac{1}{\sqrt{2} \pi \sigma^2 N^*} \right)$$

$$\boxed{\eta = \frac{(mKT)^{1/2}}{\pi^{3/2} \sigma}}$$

η = independent of pressure
 $\eta \propto T^{1/2}$
 η independent of density.

(5)

Maxwell-Boltzmann distribution laws



→ The curve at any temperature is parabolic near the origin, as factor u^2 dominates in this region, the exponential function ≈ 1 (approx).

→ At high values of u , exponential factor dominates the behavior function causing it to decrease rapidly.

1)