

gas tension of
using deep number method.

Requirements:- of chemical required \rightarrow Ethanol &
Water

force inward. So as to reduce the force entered by the impact the measured pressure P is less than ideal pressure.

$$\text{Ideal pressure} = P + P_a$$

The inward force P_a is directly related to

to (1) no. of molecules striking the wall at any given instant, which is proportional to the density of the gas.

(2) The number of molecules in the interior which are attracting the striking molecules, which is also proportional to the density of the gas.

$$P_a \propto d^2$$

$$\text{Density} \propto \frac{1}{\text{Volume}}$$

$$\therefore P_a \propto \frac{1}{V^2}$$

$$P_a = \frac{a}{V^2}$$

a is proportionality constant, called Co-efficient of attraction.

Ideal pressure = $(P + \frac{a}{V^2})$

Hence now the modified gas equation is

$(V-b) (P + \frac{a}{V^2}) = RT$ — (1)

Called as Van der Waal's equation

which was given in 1873.

For n number of gas molecules

$(P + \frac{n^2 a}{V^2}) (V-nb) = nRT$

Units of Van der Waal's Constant

$$P_a = \frac{a n^2}{V^2} \quad a = \frac{P_a V^2}{n^2}$$

$$= \frac{\text{Pressure} \times (\text{Volume})}{(\text{moles})^2} = \text{atm L}^2 \text{mol}^{-1}$$

Requirements:- a) Chemical Required \rightarrow Ethanol

(91)

$$\begin{aligned} V &= nb \\ b &= \frac{V}{n} = \frac{\text{Volume}}{\text{moles}} \\ &= \text{L mol}^{-1} \end{aligned}$$

Significance of Van der waal's Constant :-

The gases such as CO_2 , NH_3 , HCl which can be liquified easily have high values of a and b .

\rightarrow The Van der waal's constant a is measure of strength of the Van der waal's force between the molecules of the gas. Greater the magnitude of a , stronger are the Van der waal's forces.

\rightarrow The constant b represents effective volume of gas molecules. It has been observed that its value remains constant over a wide range of temp. and pressure for a gas.

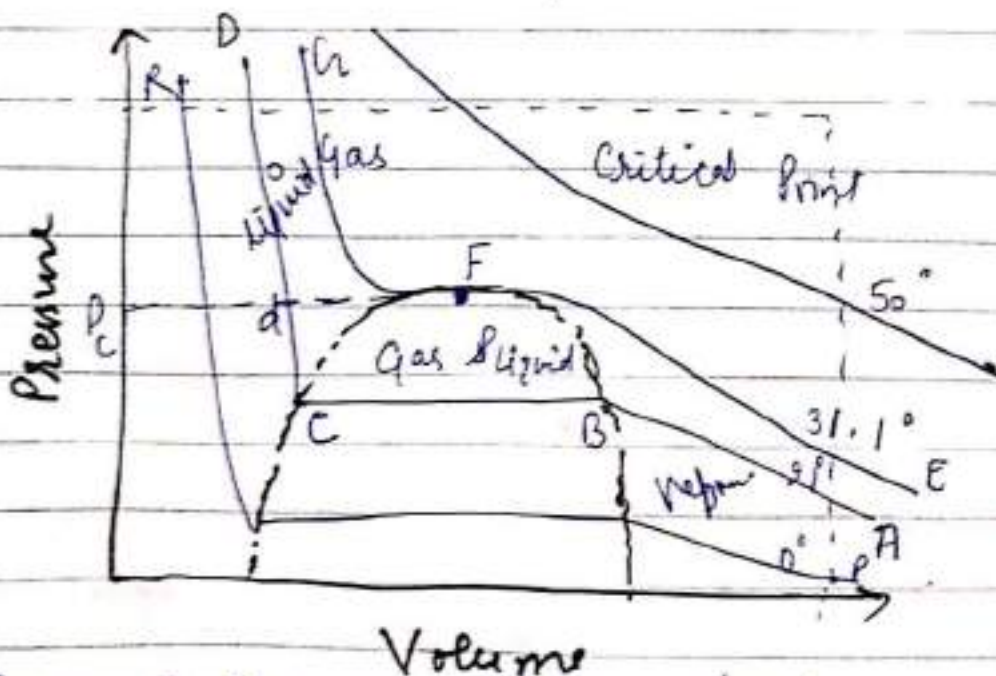
Isotherms of CO_2 - Critical Phenomenon

The curves representing the variation of volume and pressure at constant temp. are called isotherms.

In 1869, T. Andrews studied the effect of pressure on volume of CO_2 at different temperatures. It is known as Isotherm.

→ The curve should be rectangular, hyperbolas like that expected for an ideal gas.

→ Various isotherms of CO_2



Isotherm of CO_2 at different temp.

① Isotherm at 0°C ; CO_2 is entirely gaseous at low pressure and volume decreases with increasing pressure.

② Isotherm below at 31°C ; below 31°C isotherm is not continuous.

→ Point A represents gaseous CO_2 at certain pressure

→ At low pressure, volume get decreased by BA

→ At Point B liquification occurs
vapour is converted into liquid

→ at point C liquification is complete
CD shows a small effect of pressure on liquid. Liquids are less compressible

→ In total

- AB curve - vapour state
- CD curve - liquid
- BC curve - liquid and vapour co-exist

③ Isotherm at 31°C :- F is critical point of CO_2 . Distinction between liquid and vapour state disappears. The isotherm

passing through critical point is called critical ~~point~~ isotherm.

(4) Isotherm above \bullet 31°C :- Beyond this temperature CO_2 could not be liquified.

Hence it shows that is the temp of CO_2 is above 31.1°C CO_2 can not be liquified.

Critical Constants

(1) Critical temperature :- It is the minimum pressure which must be reached before the gas can be liquified by applying the pressure.

Represents $T_c = \text{CO}_2$ is 31.1°C

(2) Critical pressure :- Minimum pressure essential for the liquefaction of a gas at critical temp e.g. $P_c = \text{CO}_2$ is 72.9

Requirements:- a) Chemical Reagents
Water
Apparatus:-
Densimetry method.

③ Critical Volume : Volume occupied by one mole of a gas or liquid under critical pressure and critical temp. $V_c = 95.65 \text{ ml}$.

Relationship b/w Van der waal's Constants and Critical Constants

The Van der waal's equation

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

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

Multiplying with V^2 we get

$$PV^3 + aV - PbV^2 - ab = RTV^2$$

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

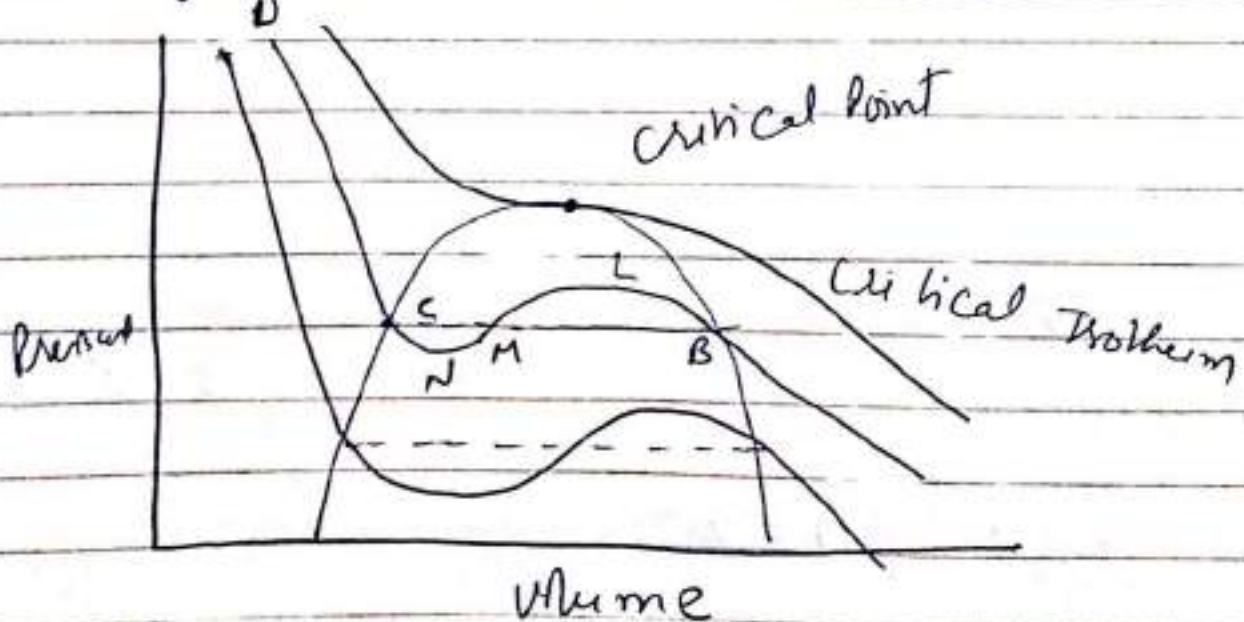
$$PV^3 - PbV^2 + ~~RTV^2~~ RTV^2 + aV - ab = 0$$

Divide by P

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

$$V^3 - V^2 \left(b + \frac{RT}{P} \right) + \frac{aV}{P} - \frac{ab}{P} = 0 \quad (1)$$

This is a third-degree equation in terms of V



The three real unequal roots corresponds to Point B, M and C

Requirements:-
 1. Order
 2. Absence

using deep number method

Surface Tension of

B and C \rightarrow Represents Vapour and liquid

M has no significance

Three roots of the van der waal is equation at critical point.

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

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

Critical Conditions $T = T_c$ $P = P_c$

Putting in eq (1)

$$V^3 - V^2 \left(b + \frac{RT_c}{P_c} \right) + \frac{V a}{P_c} - \frac{a b}{P_c} = 0 \quad \text{--- (3)}$$

From (2) and (3)

$$3V_c = b + \frac{RT_c}{P_c} \quad \text{--- (4)}$$

$$3V_c^2 = \frac{a}{P_c} \quad \text{--- (5)}$$

$$V_c^2 = \frac{ab}{P_c} \quad \text{--- (6)}$$

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Dividing (6) by (5) we get

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

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

$$\boxed{V_c = 3b} \quad \text{--- (7)}$$

Putting the value of V_c from (7) to (6)

$$3 \times (3b)^2 = \frac{ab}{P_c}$$

$$9b^2 \times 3 = \frac{a}{P_c}$$

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

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

...determine the surface Tension of
 given liquid using drop number method

Requirements:- a) Chemical Re
 Water
 b) Apparatus :-

Putting the value of V_c ~~from~~ and P_c
 in the equation (4)

$$3 \times 3b = b + RT_c \times \frac{27b^2}{a}$$

$$9b = b + RT_c \times \frac{27b^2}{a}$$

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

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

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

Important Questions

Q1. What are the causes of deviation from ideal behaviour shown by real gas.

Ans The ideal gas behaviour will be

shown only if the assumptions of kinetic theory are correct. However the assumptions are not correct

- ① The actual volume of occupied by molecules is negligible
- ② The molecules exert no appreciable attraction on one another

Q2. When does a real gas behave as ideal gas

Ans. At its Boyle's temp.

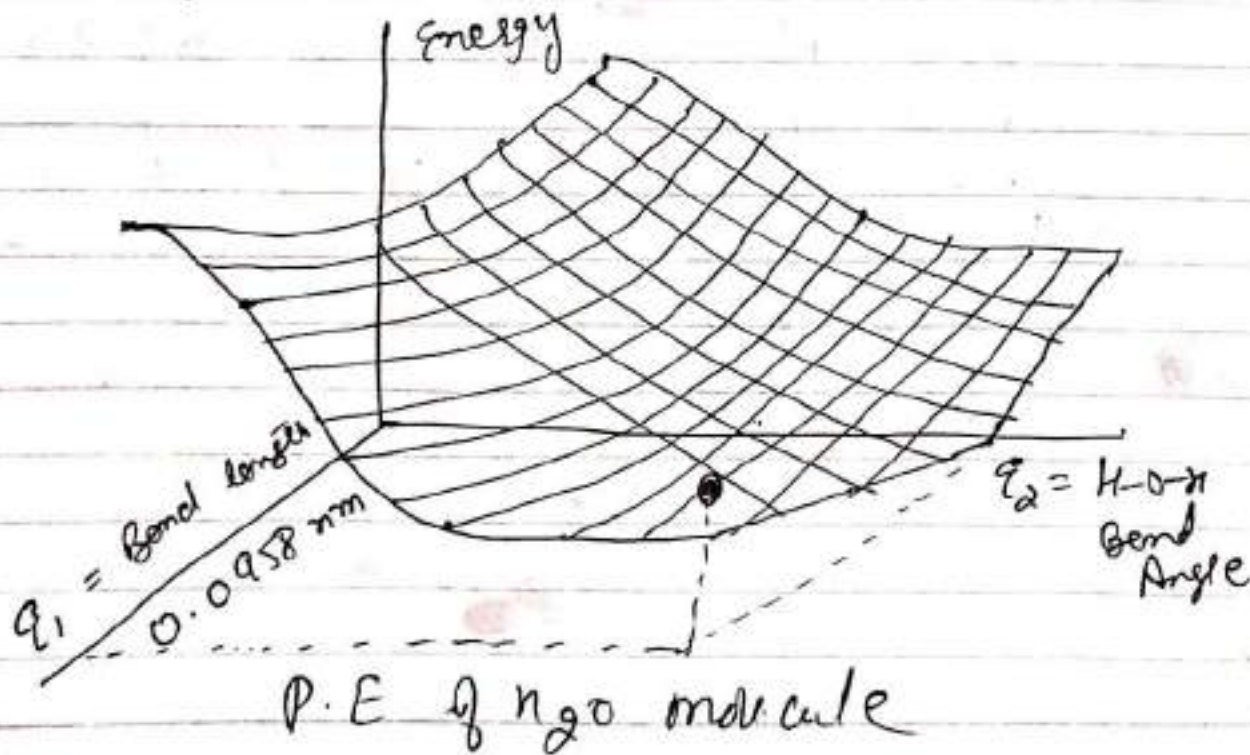
Q3. Can we liquefy a gas by increasing pressure alone? why.

Ans. No. unless the

Potential energy surface

It describes the energy of a system in terms of the position of the atoms. Energy as a function of one or more co-ordinates is defined. If there is only one co-ordinate, the surface is called Potential energy curve or energy profile.

For a system with two degrees of freedom the value of energy is a function of two co-ordinates.



perpendicularly per unit area on the surface of any liquid is known as surface

Due to surface tension drops are spherical in nature.

$$O-H \text{ Bond length} = 0.0958$$

$$H-O-H = 104.5^\circ$$

It finds application in Chemistry, Physics and mathematics

Minima in the PEC represents the bond angle of the molecule which defines the shape of the molecule as helping in the rate determination.

In maths, Geometry of a molecule is determined by vector \vec{r}

It finds application in finding the analysis of molecular shapes and chemical kinetics.

Classification

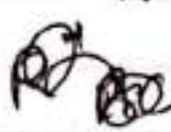
PES are of two types $\begin{matrix} \swarrow & \searrow \\ \text{Attractive} & \text{Repulsive} \end{matrix}$
① $A + B - C \longrightarrow AB + C$

Bond length extension is

$$R_{AB} = R_{AB} - R^0_{AB}$$

R_{AB} represents A-B Bond length in the transition state.

R_{AB}° is the Bond of the product molecule

 R_{AB}° = Bond length of the ~~product~~ AB molecule reactant

Similarly for $R_{BC}^{\ddagger} = R_{BC} - R_{BC}^{\circ}$

where R_{BC} represents B-C Bond length in transition state

R_{BC}° = BC Bond length in reactant

R_{BC}° = B.C of the ~~broken~~ molecule (product)

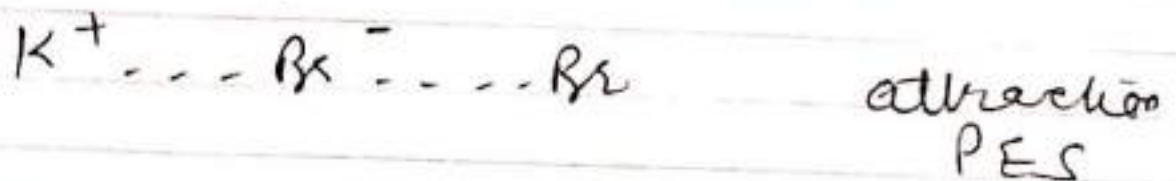
For Endothermic $R_{AB}^{\ddagger} > R_{BC}^{\circ}$ PES is attractive

→ Reactants are approaching to each other

→ Vib. energy is responsible

$$R_{KBr}^{\ddagger} > R_{Br}^{\ddagger}$$

It means the Extension in Bond length in the reaction molecule must be greater than product.



is Repulsive PES

$$R_{HCl}^{\ddagger} < R_{Cl}^{\ddagger}$$

for Endothermic

Here translational energy is most effective for attractive force, while vib. excitation is more effective for repulsive

