

student of 2<sup>nd</sup> year to 3<sup>rd</sup> year class  $\Rightarrow$  B.Sc. (Hons) - Part-1  
Subject  $\Rightarrow$  Chemistry  
Chapter  $\Rightarrow$  Gaseous State

Topic  $\Rightarrow$  Compressibility factor,  
Boyle's temperature, critical Phenomenon

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## Compressibility factor

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called Compressibility factor.

compressibility factor is denoted by  $z$ .

①

$$z = \frac{PV}{RT} \quad V = VH = VV$$

The deviations from ideality may be shown by a plot of the compressibility factor,  $z$  against  $P$ .

For an ideal gases  $z=1$  and it is independent of temperature and pressure.

The deviations from ideal behaviour of a real gas will be determined by the value of  $z$  being greater or less than 1.

The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of nonideality of the gas.

## Boyle's Temperature

The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range

(2)

is called Boyle's temperature or Boyle's point because at this temperature Boyle's law is obeyed over a range of pressures.

Obviously above the Boyle's temperature a gas shows positive deviations only.

The Boyle's temperature of each gas is characteristic.

e.g. for N<sub>2</sub> the Boyle's temp. is 332 K.

Boyle's temperature is given by

$$T_B = \frac{q}{Rb}$$

Derivation  $\Rightarrow$

It may be derived from the van der waal's equation as follows

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

It may be written in the form

$$PV = RT - \frac{q}{V} + \frac{ab}{V^2} \quad (1)$$

As both  $a$  and  $b$  are small and if the pressure is not too high so that  $V$  is not so small,  $ab/V^2$  can be neglected.

further  $V$  in the correction term  $q/V$  may be replaced by  $RT/P$ .

Then equation (1) reduces to

$$PV = RT - \frac{ap}{RT} + bp$$

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

Since the gas behaves ideally at Boyle's temp;

$$PV = RT$$

Hence the second term on R.H.S. should be zero since  $P$  has a finite value.

$$\frac{b-a}{RT} = 0$$

$$\text{OR, } T = \frac{q}{Rb}$$

$\therefore$  Boyle's temperature

$$\frac{T_B}{R_B} = 9$$

## Critical Phenomenon

The smooth merging of the gas with its liquid is called critical phenomenon.

Andrews demonstrated the critical phenomenon in gases by taking example of  $\text{CO}_2$ .

## critical temperature

The temperature above which it cannot be liquefied no matter how great the pressure applied is called critical temperature.

Critical temperature is denoted by  $T_c$ .

## Critical pressure

The minimum pressure required to liquefy the gas at its critical temperature is called critical pressure.

critical pressure is denoted by  $P_c$ .

## Critical volume

The volume occupied by a mole of the gas at the critical temperature and pressure is called critical volume. Critical volume is denoted by  $V_c$ .

## Critical constants

Critical temperature, critical pressure and critical volumes are collectively called critical constants.

All real gases have critical characteristic constants:

e.g. critical constant of  $\text{CO}_2$

$$P_c = 72.9 \text{ atm}$$

$$T_c = 304 \text{ K}$$

$$V_c = 94 \text{ ml/mole}$$

## Critical state

At critical temperature and critical pressure, the gas becomes identical with its liquid and is said to be in critical state:

It is the point where  $P_c$  and  $T_c$  are coincident

## Critical points

It is the point where  $P_c$  and  $T_c$  are coincident

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## Critical pressure

It is the pressure at which the gas becomes liquid at its critical temperature

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## Critical density

It is the density of the liquid formed by compressing the gas at its critical temperature