

Going to 1st year to 2nd 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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$$P = \text{RT}$$

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 .

$$\textcircled{1} \quad Z = \frac{PV}{RT} \quad V - TV = V_0$$

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 N₂ the Boyle's temp. is 332 K.

Boyle's temperature is given by

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

Derivation \Rightarrow

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

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

It may be written in the form

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

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

Further V in the correction term a/V may be replaced by RT/Pr where r is the reduced pressure.

Then equation (1) reduces to

$$PV = RT - \frac{a}{RT} + bP$$

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

Since the gas behaves ideally at Boyle's temp.,

$$PV = RT$$

(3)

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

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

$$RT = a \quad \text{or, } T = \frac{a}{R}$$

$$\text{OR, } T = \frac{a}{R}$$

\therefore Boyle's temperature $T_B = \frac{a}{R}$

$$\therefore \text{Boyle's law } T_B = \frac{a}{R}$$

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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 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 CO_2

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

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

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

Critical State

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

critical point \rightarrow no
two states can't coexist

critical point

critical point is defined under following conditions
i) mixture composed of deep and shallow gas
ii) isothermal compression follows
iii) heat loss is negligible

critical conditions

critical conditions are defined as those conditions which are same for all gases at which they become identical with their liquids

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