Subject ⇒ Chemistry
Chapter → Gaseous State
Topic ⇒ 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.

$$Z = \frac{PV}{RT}$$

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 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_2 the Boyle's temp. is 332 K.

Boyle's temperature is given by

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

Derivation :-

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

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

It may be written in the form

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

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 a/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.

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

or, $$T = \frac{a}{Rb}$$

$\therefore$ Boyle's temperature $T_b = \frac{a}{Rb}$

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 critical 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

$T_c = 304\ K$

$P_c = 72.9\ atm.$

$V_c = 94\ ml/mole$

Critical State

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

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