

student assigned to section class \Rightarrow B.Sc. (Hons.) Part-1
in Dept. of subject \Rightarrow Chemistry
assigned Chapter \Rightarrow Gaseous State
student assigned 9th topic \Rightarrow Compressibility factor,
plan & notes involve 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 .

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$$Z = \frac{PV}{RT} \quad V - fV = v$$

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 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

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

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 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

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

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

Since the gas behaves ideally at Boyle's temp;

$$PV = RT \quad \text{and} \quad \frac{RT}{V} = P$$

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

$$b = \frac{a}{RT} \quad \text{or} \quad b = \frac{a}{RT_0}$$

$$\text{or, } T = \frac{a}{bR}$$

i.e. Boyle's temperature

$$T_b = \frac{a}{bR}$$

$$\therefore \text{Boyle's pressure} = \frac{a}{b} \quad \text{and} \quad T_b = \frac{a}{bR}$$

critical phenomenon

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

Andrews demonstrated the critical phenomena 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 .

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10

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

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

$$T_c = 310 \text{ K}$$

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

Critical state

At critical temperature and critical pressure,

the gas becomes identical with its liquid and is said to be in critical state;

In critical state it becomes a supercritical fluid

so no separate phase exist b/w solid & liquid

superfluid

is formed at higher temperature & it

is separated with two distinct regions

• superfluid & liquid

at low temperature

• superfluid

at higher temperature & it is

separated into two distinct regions

• superfluid & liquid

gradual transition

to see at large a number of superfluid

below a certain temperature