Study material: For B.Sc. part-I

Subject: Physical Chemistry, paper-I (A)

Topic: Gaseous State

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Compressibility factor (Z) →

for 1mol of an ideal gas $PV = RT$ —(i)

But for 1mol of real gas $PV \neq RT$

However, 1mol of a real gas we can write

$$PV = ZRT \quad \text{—(ii)}$$

where, Z → compressibility factor

$$Z = \frac{PV}{RT} \quad \text{—(iii)}$$

for an ideal gas $Z = 1$

for a real gas $Z \neq 1$ $\quad Z > 1$ or $Z < 1$

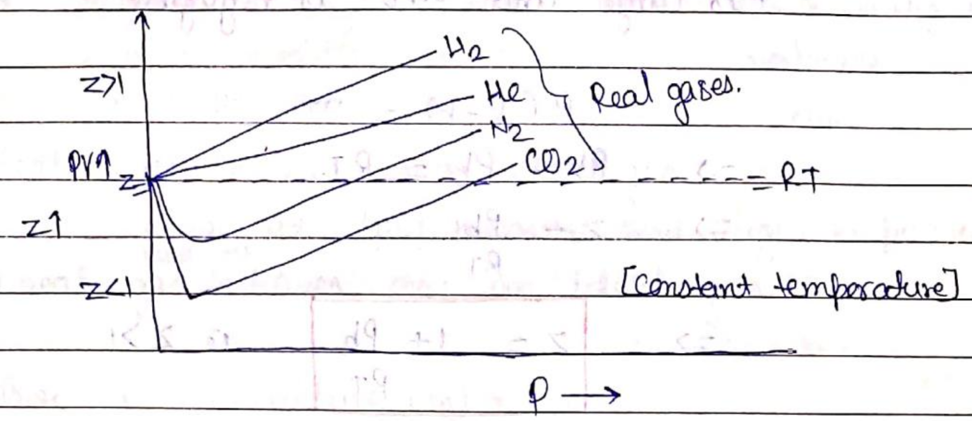
Greater the deviation of z of a real gas from unity, greater will it deviation from ideal gas behaviour.

Explanation of deviation of real gases from ideal gas behaviour with the help of van der Waals equation:→

The deviation of real gas from ideal gas behaviour can be explained nicely with the help of van der Waals equation as follows:-

The van der Waals equation for 1mol of a real gas is

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



Case I →

At very low pressure.

V is large and b can be neglected.

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

$$\Rightarrow PV + \frac{a}{V} = RT$$

$$\Rightarrow Z + \frac{a}{VRT} = 1$$

deviation $\Rightarrow$ $\boxed{Z = 1 - \frac{a}{VRT}}$ ie → $Z < 1$

For most of the gases the value of z is smaller than 1 at low pressure [except He, H_2].

The value of z.

(i) decreases with increasing in pressure.

(ii) increases with increasing temperature.

Case II →

At high pressure,
P is large and a/V^2 is negligible.

$$P(V-b) = RT$$

$$\Rightarrow PV - Pb = RT$$

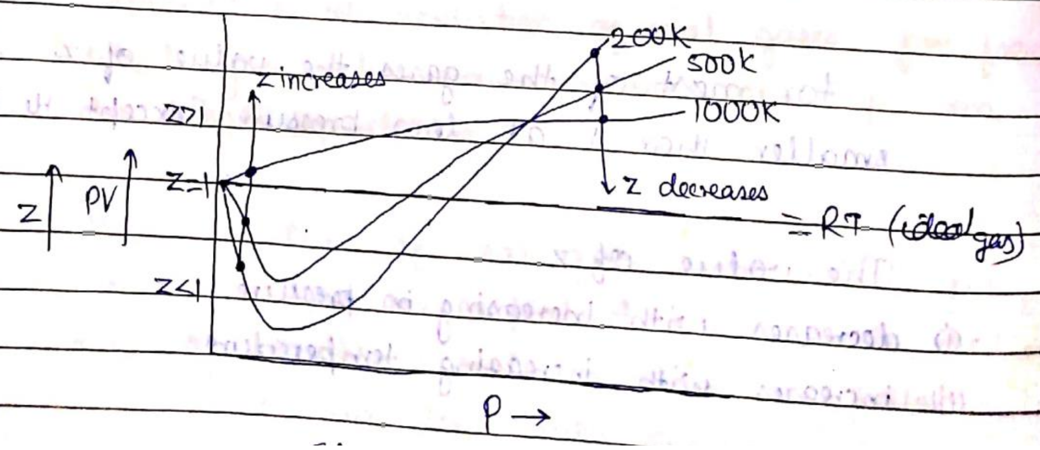
$$\Rightarrow Z - \frac{Pb}{RT} = 1$$

$$\Rightarrow \boxed{Z = 1 + \frac{Pb}{RT}} \quad \text{ie } Z > 1$$

for all gases $Z > 1$ at high pressure
The value of Z
(i) increases with increasing pressure
(ii) decreases with increasing temperature.

Exceptional behaviour of H_2 and He:→

The value of Z for H_2 and He is always greater than one even at low pressure this is due to fact that for H_2 and He, the value of 'a' is very small and it can be neglected even at low pressure



Case III →

At low pressure and high temperature both 'a' and 'b' are negligible, $\frac{1}{2}mv^2 \propto T$ — O → O ← High KE, negligible attraction

$\therefore$ $PV = RT$ and

Real gases behaves as an ideal gas.

Thus, at low pressure and high temperature a real gas tends to behaves as an ideal gas.

Boyle's temperature (T_B) →

The van der Waals equation for 1mol of a real gas is

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

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

$\because$ 'a' and 'b' are very small quantities their product even smaller so term ab/v^2 can be neglected.

$$\Rightarrow PV - Pb + \frac{a}{V} = RT$$

If $\frac{a}{v} = Pb$ then $PV = RT$

$$\Rightarrow \frac{a}{V} = \frac{RTb}{V}$$

$$\Rightarrow \boxed{T = \frac{a}{Rb}}$$

The temperature at which a real gas behaves like a ideal gas in a wide range of pressure is called Boyle's temperature

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