Deviations of Real Gases from Ideal Behaviour:-

$$PV = nRT$$

is valid for ideal gas only.

Real gas obeys such laws only under approximations. The condition of low pressure or high temperature are ideal for gases to follow ideal gas equation.

The most easily liquifiable and highly soluble gases show larger deviations.

CO_2, SO_2 and NH_3 show more deviation than H_2, O_2 and N_2.

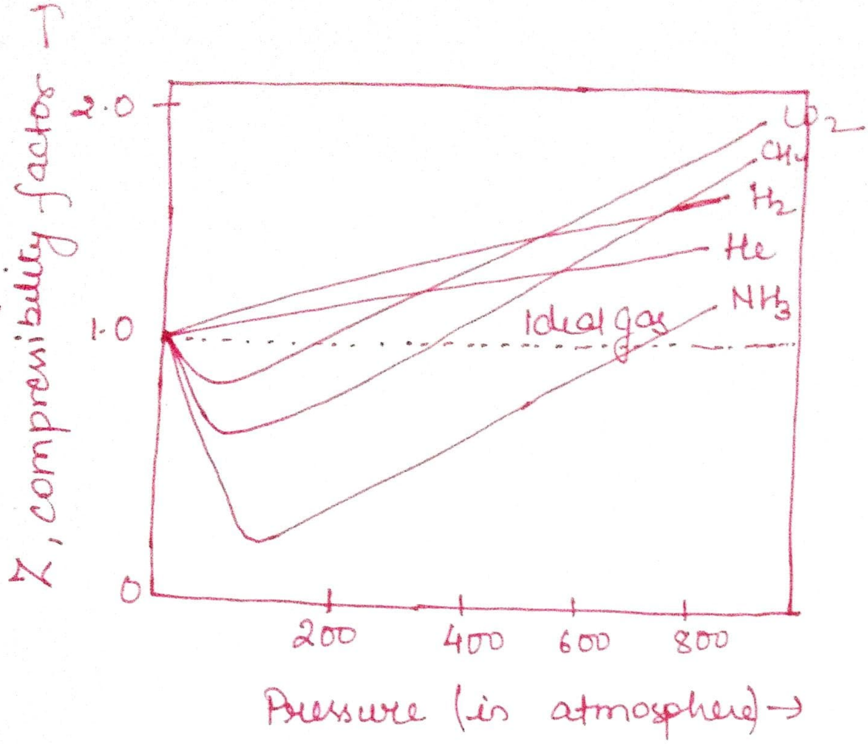
The deviations from ideal behaviour are best represented in terms of compressibility factor (also called compression factor) Z, which is best defined as

$$Z = \frac{PV}{(PV)_{ideal}} = \frac{PV}{nRT} = \frac{PV_m}{nRT} \quad \text{--- (1)}$$

where $V_m = V/n$ is the molar ~~mass~~ volume i.e. volume occupied by one mole of gas.

For an ideal gas, $Z = 1$ under all conditions of temperature and pressure.

The deviation of Z from unity is measure of imperfection of gas under consideration.



Deviations of real gases from ideal behaviour

The graph plotted for the compressibility factors determined for a number of gases over a range of pressures at a constant temperature (0°C) are shown as above.

→ At extremely low pressures, all the gases are known to have Z close to unity which means that the gases behave almost ideally.

→ At very high ~~temperature~~ pressure, all the gases have Z more than unity indicating that the gases are less compressible than ideal gas. This is due to fact that high pressure, the molecular repulsive forces are dominant.

→ At moderately low pressures CO, CH_4 and NH_3 are more compressible than an ideal gas i.e. PV is less than $(PV)_{ideal}$ so that $Z<1$.

This is due to fact that at low pressure the long range attractive forces are dominant and favor compression.

→ The compressibility factor Z goes on decreasing with increase in ~~temperature~~ pressure, passes through a minimum at certain stage and then begins to increase with increase in pressure.

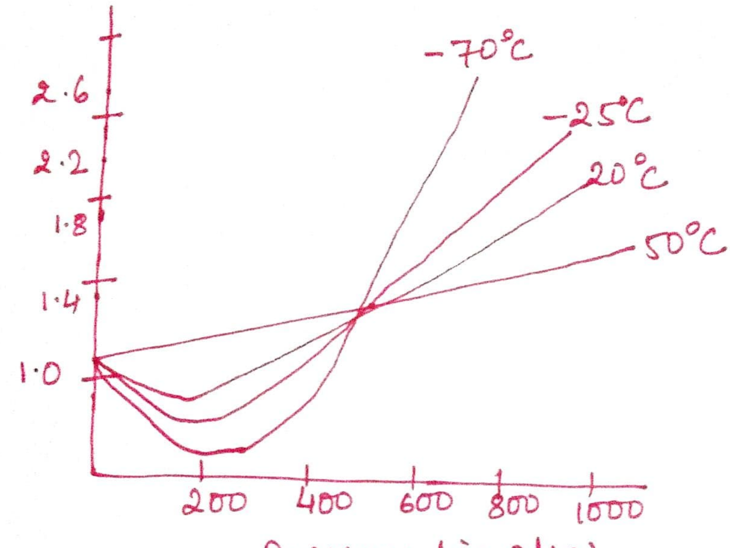
→ The gases now become less compressible than an ideal gas i.e. (PV) is more than $(PV)_{ideal}$ so that $Z > 1$. While CO and CH_4 exhibit marked deviations from ideal behaviour only at high pressures, ammonia shows large deviation even at low pressure.

→ At $0°C$, H_2 and He are less compressible, than the ideal gas at all pressures i.e. $Z > 1$.
If the temperature is sufficiently low (eg. below $-48°C$ for H_2 and $-242°C$ for Helium).
The Z-P plot is almost similar between H_2 & He as well as NH_3, CH_4 and CO at $0°C$.

→ If the temperature is sufficiently high, the Z-P plots of NH_3, CH_4 and CO will be similar to that of H_2 and He at $0°C$ i.e. the value of Z will increase continuously with increase in pressure.

Effect of temperature on deviation from Ideal gas equation:-

The Z-P plots of nitrogen at different temperatures varying between −70°C and 50°C can be shown as below:-



As the temperature is raised the dip in the curve becomes smaller and smaller.

→ At 50°C, the curve seems to remain almost horizontal and for an appreciable range of pressure varying between 0 and about 100 atmospheres, showing thereby the compressibility factor Z almost becomes unity under these conditions.

→ PV remains constant and Boyle's law is obeyed within this range of pressure at 50°C. This temperature is called Boyle point or Boyle temperature.