

UG SEM II (MJC - 2T), Physical Chemistry

1. Gaseous State

Deviation of Real Gases from Ideal Behaviour:

An ideal gas is one which obeys the gas laws for the equation $PV = RT$ (for 1 mole of gas) at all pressures and temperatures. However, no gas is ideal. They approach perfection as the temperature gets farther from their boiling points. Thus, the gases H_2 , N_2 and CO_2 which fail to obey the ideal-gas equation are termed as non-ideal or real gases.

The extent to which a real gas departs from ideal behaviour may be depicted in terms of a function called Compressibility factor, denoted by Z ,

$$\text{It is defined as } Z = \frac{PV}{RT}$$

- The deviation from ideality may be shown by a plot of Compressibility factor, Z against P .
- For an ideal gas, $Z = 1$. For real gases, the deviation from ideal behaviour will be determined by the value of Z being greater or less than unity.
- Temperature and pressure have no effect on an ideal gas, which has a Z value of 1 at all temperatures and pressures.
- For non-ideal or real gases, $Z > 1$ or $Z < 1$. Thus, the value of Z determines the difference between ideal and real gas behaviour.
- The degree of gas non-ideality is represented by the

Difference between unity and Z .

- Pressure and temperature cause deviations from ideal behaviour in a real gas.
- when $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour. when $Z > 1$, it is a positive deviation, it shows that the gas is less compressible than expected from ideal behaviour.

If $Z \neq 1$ then $PV \neq nRT \Rightarrow$ non-ideal behaviour.

$$Z < 1$$

$$V_{\text{real}} < V_{\text{ideal}}$$

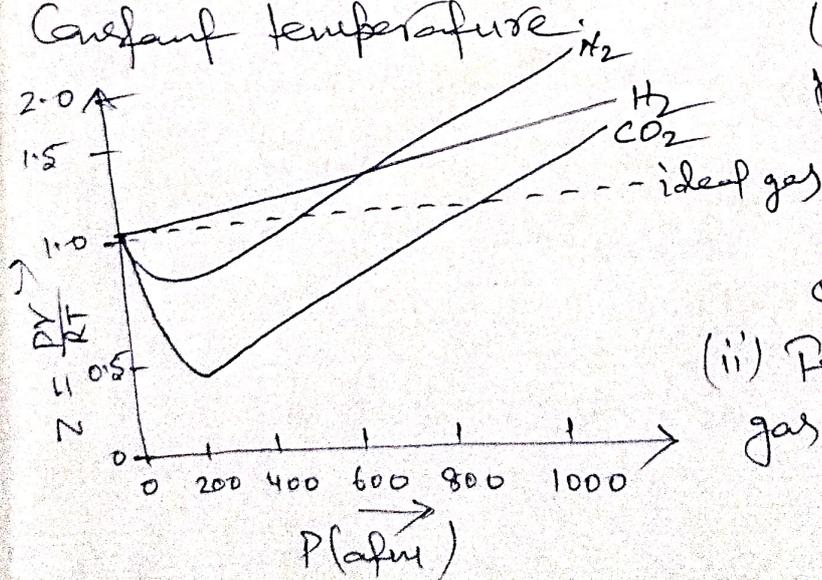
i.e. Attractive forces dominates. (-ve deviation from ideal behaviour).

$$Z > 1$$

$$V_{\text{real}} > V_{\text{ideal}}$$

i.e. Repulsive force dominates (+ve deviation from ideal behaviour).

→ Effect of pressure: Fig. below shows the Compressibility factor Z , plotted against pressure for H_2 , N_2 and CO_2 at constant temperature.



(i) At very low ~~temperature~~ pressure for all these gases Z is approximately one. This indicates that all real gases exhibit ideal behaviour (up to 100 atm).

(ii) For H_2 , curve lies above ideal gas curve at all pressure.

(iii) For N_2 and CO_2 , Z first decreases. It passes to a minimum then increases continuously with increase of pressure.

(iv) For gas like CO_2 , the dip in the curve is greatest as it is most easily liquefied.