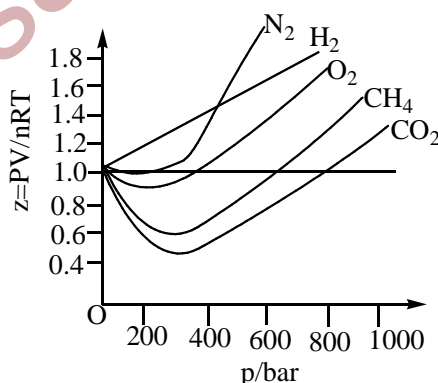# Real Gases

1. Gases (N2, CO_2) which don't obey gas laws or gas equation PV=RT at all pressure and temperatures are called real gases.

2. Real gases obey gas laws at extremely low pressure and high temperature. Real gases deviated from ideal behavior at high pressure and low temperature.

3. Compressibility factor (Z): The extent to which a real gas deviated from ideal behavior may be expressed in terms of Compressibility factor (Z).

$$Z = \dfrac{Molar\,volume\,of\,given\,gas\,(PV)}{Molar\,volume\,of\,ideal\,gas\,(RT)}$$

   i. For an ideal gas, Z=1 and it is independent of temperature and pressure.

   ii. The deviation from ideal behavior of a real gas will be determined by the value of Z being grater or less than one. The difference between unity and the value of Z of a gas is a measure of degree of non-ideality of the gas.

   iii. For a real gas the deviation from ideal behavior depends on pressure and temperature. This may be illustrated by examining the compressibility curves of some gases.

iv. At very low pressure, for all these gases Z is approximately equal to one this indicates that at low pressures, real gases exhibit nearly ideal behavior.

v. As the pressure is increased H_2 shows a continuous increase in Z. Thus H_2 curve lies above the ideal gas curve (positively deviated) at all pressures. In this case the repulsive forces dominant.

vi. For N2 , CO2, Z first decreases (Z<1).It passes through a minimum and then increases continuously with pressure (Z>1). In this case the forces of attraction are dominant.

4. Effect of temperature on deviations

It is clear from the shape of the curves that thedeviations from ideal gas behavior becomesless and less with increase of temp.

At low temperatures Z<1. While at high temperatures Z>1.

At particular temperature, PV/RT is almost unity and the Boyles law is obeyed for an appreciable range of pressure is called Boyles temperature.

The Boyles temperature of each gas is characteristic for example for N_2 it is 332K.

5. Explanation for deviation from ideal gas behavior: The deviation of real gases from the ideal behavior is mainly due to two faulty assumptions of kinetic theory of gases.

i. The molecules is a gas are point masses and posses no volume.

ii. There are no intermolecular attractions in a gas.

There fore ideal gas equation PV=nRT derived from kinetic theory could not hold for real gas.

6. Equation of state for real gas

Vander walls pointed out that both the pressure (P) and volume (V) factors are the ideal gas equation needed correction in order to more it applicable to real gases.

i. The volume of real gas =volume of ideal gas –volume occupied by gas molecules

 Thus corrected volume = (V-b)

 Here 'b' is co-volume or excluded volume or prohibited volume.

For 'n' mole of gas, Co-volume is (V-nb)

Excluded volume is four times the actual volume of molecules (b=4v).

ii. Corrected pressure $P = P + \dfrac{a}{v^2}$ for one mole.

For 'n' mole of gas P= $P + a.\left(\dfrac{n}{V}\right)^2$.

iii. Van der Waals equation for one mole of a Real gas is (p+$\dfrac{a}{V^2}$) (v-b)=RT

For 'n' mole of gas is $\left(P + \dfrac{n^2 a}{V^2}\right)\left(V - nb\right)$ =nRT

Here 'a' and 'b' are constants known as Van der Waals constants, which vary from gas to gas.

iv. Units of a & b

The value of 'a' is given by the relation.

a= $\dfrac{pv^2}{n^2} = \dfrac{pressure(volume)^2}{mole^2} = atm \times lit^2.mole^{-2}$

The excluded volume b= $\dfrac{volume}{n} = \dfrac{litre}{mole} = litre \; mole^{-1}$

* 'a'is a measure to the magnitude of attractive forces, greater the value of 'a'. more is the ease of liquification of gas.

7. Interpretation of deviations from Van der Waals equations:

i. Case 1: At extremity low pressure volume becomes very large hence 'b' and $\dfrac{a}{V^2}$ can be neglected.

Therefore the Vander Waals equations reduces to PV=RT

ii. Case 2: At low pressure volume will be large; 'b' can be neglected, hence

$\left(P + \dfrac{a}{V^2}\right)(V) = RT (or) PV = RT - \dfrac{a}{V}$, dividing both sides with RT, we get

PV/RT =1- a/RTV, Z= 1-a/RTV i.e. Z<1

Hence the gas shows negative deviation from ideal behaviour.

iii. **Case 3**.At high pressure volume will be small, therefore $\dfrac{a}{V^2}$ can be neglected.

Hence   P(V-b) =RT or   PV=RT+ Pb or PV/RT =1+ Pb/RT i.e Z>1The gas shows positive deviation from ideal behaviour

iv. **Case 4**.At high temperature volume will be large and pressure will be small, the state equation becomes 'PV=RT'

8. In case of H_2 and He attraction between the molecules is negligible because of small mass. So $\dfrac{a}{V^2}$ can be neglected, the state of equation becomes

 P (V-b) = RT or PV=RT+Pb, dividing both sides with RT, we get

Z=1+Pb/RT i.e Z>1

Hence both hydrogen and helium always show positive deviation from ideal behavior

**Liquefaction of Gases and Critical Point**

A gas can be liquefied by lowering the temperature and increasing pressure (or) rapid evaporation and doing mechanical work in adiabatic conditions.

9. Isotherms

The graph drawn between pressure and Volume at constant temperature is called isotherm.

The perfect gas isotherms are obtained from Van der Waals equation at high temperature and low pressure.

Andrews plotted isotherms of carbon dioxide at various temperatures as shown in the following
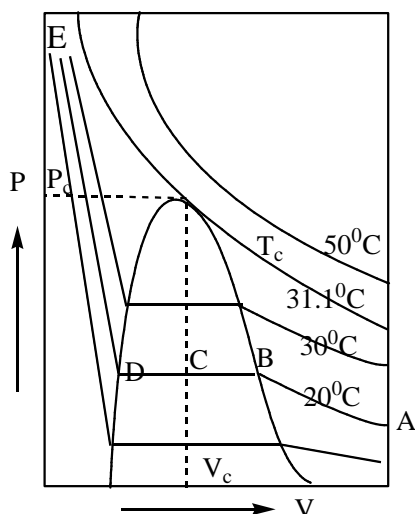
Fig.25. Isotherms of carbondioxide at various temperatures

It was noticed that at high temperatures isotherms look like that of an ideal gas. The gas can not be liquified even at very high pressure. As the temperature is lowered, shape of the curve changes and shows considerable deviation from ideal behaviour.

In the isotherm of CO_2 at 20^0C, at a point A it is a gas. When the gas is compressed, the pressure increases upto a point B. The piston can be pushed in from point B to D through C without any further increase in pressure. The gas begins to condense from point B and condensation completes at a point D. At a point C the vessel contains both the liquid and gas. At point D the molecules are in liquid state.

A very large pressure is required to decrease the volume from D to E. It is because when the pressure is increased from D the repulsive forces between the molecules increases. So the decrease in volume is less from D to E even though the pressure increase is very high.

At 31.1^0C, carbondioxide remains as gas up to 73 atm pressure. At 73 atm, liquid carbondioxide appears for the first time. 31.1^0C is called critical temperature of carbondioxide.

The temperature above which the gas can't be liquified by the application of pressure is called critical temperature (T_c).

Volume of one mole of gas at critical temperature (T_c) is called critical volume (V_c) and pressure at this temperature is called critical pressure (P_c). T_c, P_c and V_c are called critical constants and are obtained using the Van der Waals' constants 'a' and 'b'.

Critical temperature $T_c = \dfrac{8a}{27Rb}$

Critical volume, $V_c = 3b$

Critical pressure, $P_c = \dfrac{a}{27b^2}$

At critical condition, the compressibility factor for one mole of a gas,

$$z = \frac{PV}{RT} = \frac{P_c V_c}{RT_c} = \frac{3}{8}$$

Liquefaction of Gases

All real gases upon compression at constant temperature show the same behaviour as shown by carbon dioxide. Gases cooled only below their critical temperatures, can be liquified easily. This is because gases deviates much from ideal gas behaviour and intermolecular attractions are considerably high.

A gas liquefies if it is cooled below its boiling point at a given pressure. At 1 atm chlorine can be liquefied by cooling it to -34^0C in a dry ice bath. To liquify gases like nitrogen and oxygen simple cooling to bring down temperature to -196^0C and -183^0C is not possible. To liquify such type of gases the technique based on intermolecular forces called Joule Thomson effect is used.

When a gas is allowed to expand from a high pressure to low pressure adiabatically through a narrow opening, the cooling effect of gas takes place. It is called *Joule - Thomson effect.*

In *Joule - Thomson effect,* the gas is allowed to expand from high pressure to low pressure through a narrow opening (throttle), without supplying heat from outside. In expanding, the molecules require certain energy to overcome the attractions of their neighbouring molecules. For this some of their kinetic energy converted into potential energy. So the average velocity of molecules decreases and hence the temperature of the gas decreases and the gas gets cooling effect.

Under normal conditions when hydrogen is subjected to *Joule - Thomson effect* it warms up. Because it's Z is greater than 1. It can be condensed to a liquid only when the temperature of a gas is below the inversion temperature.

The temperature above which gases get heated up and below which gases get cooled due to Joule Thomson experiment is called inversion temperature, T_i . Where $T_i = 2a/Rb$

Liquefaction of gases like helium and hydrogen is difficult. They are called permanent gases. Liquefaction of permanent gases requires cooling as well as compression.