Real Gases

$$PV = nRT$$

The gas which obeys this equn. under all conditions of temp. and Pr. is called ideal gas. The gas which does not obey this equn. at all temp.s and Pr.s is called Real gas.

A number of points can be discussed to compare these two types of gases.

Ideal gas:

① The ideal gas cannot be liquefied. As the gas has no intermolecular attraction, so the molecules will not be condensed.

② co-efficient of thermal expansion (α) depends solely on temp (T) and does not depend on the nature of the gas.

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

For one mole ideal gas, $PV = RT$

Hence, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

So, $\alpha = \frac{1}{V} \times \frac{R}{P} = \frac{R}{RT} = \frac{1}{T}$

i.e. $\alpha = \frac{1}{T}$

This shows that all gases have the same co-efficient of thermal expansion at a given temp.

③ The coefficient of compressibility (β) similarly is defined as $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

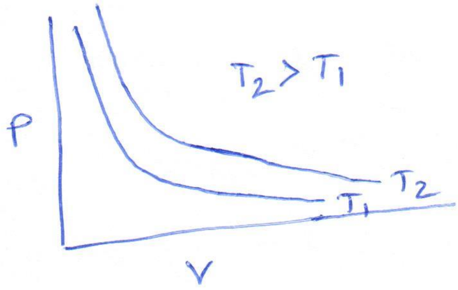
For ideal gas, $PV = RT$, so, $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$

Thus, $\beta = -\frac{1}{V}\left(-\frac{RT}{P^2}\right) = \frac{RT}{PV \times P} = \frac{PV}{PV} \times \frac{1}{P} = \frac{1}{P}$

$\Rightarrow \beta = \frac{1}{P}$

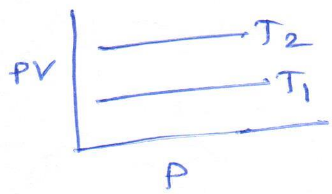
Thus, β also depends only on P of the gas and same for all gases.

④ when P is plotted against V at const. temp, a rectangular hyperbola curve is obtained as demonstrated by Boyles law, PV = const. at a given T.



The hyperbola curve at each T is called one isotherm and at diff. temp.s we have diff. isotherms. Two isotherm will never intersect.

⑤ when PV is plotted against P at const. T, a st. line parallel to P- axis is obtained.



At diff. temp.s there will be diff. parallel lines.

⑥ when an ideal gas passes through a porous plug, from higher Pr. to lower Pr. under insulated enclosure, there will be no change of temp. of the gas (J-T expansion). This confirms that ideal gas has no intermolecular attraction.

Real gas :

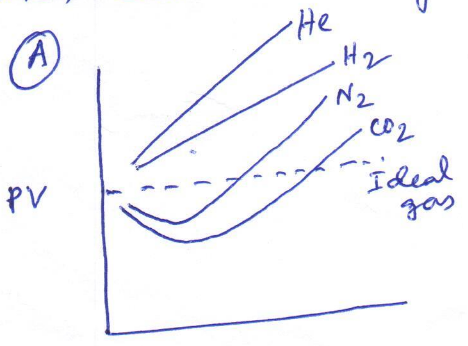
① This gas could be liquefied since it has intermolecular attraction which helps to coalesce the gas molecules.

② The co-efficient of thermal expansion (α) is found to vary from gas to gas at a given temp. and hence it depends on the nature of the gas.

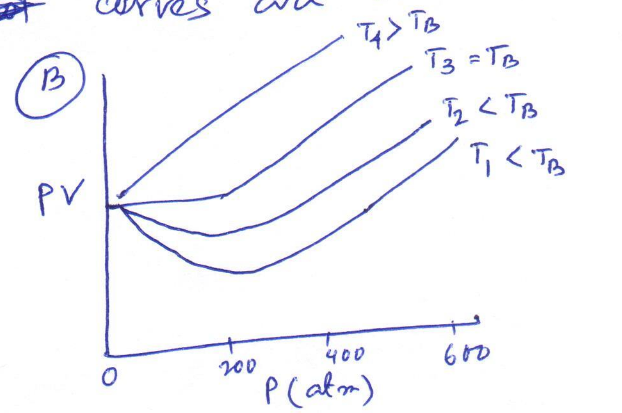
③ The co-efficient of compressibility (β) also is found to depend on the nature of the gas at a given Pr.

④ when P is plotted against V at a const. temp, a rectangular hyperbola is obtained only at high T (above a certain T, called critical temp, T_c of the gas). T_c is defined as the temp above which the gas could ~~be~~ not be liquefied whatever the Pr. is applied. But at temp. below T_c, the gas is liquefied after certain Pr. depending on Temp. we will discuss later when we will learn critical phenomena.

⑤ when PV is plotted against P for real gas, the following plots; called Amagat's ~~plot~~ curves are obtained.



Amagat curves for different gases at 0°C.



Amagat curve for CO_2 at diff. temp.s.

Fig A → shows for most gases, the value of PV decreases, attains minimum and then increases with increase of pr. only H_2 and He baffle this trend and the curve rises with increase of P from the beginning.

Fig B → shows that for CO_2 gas, the depth of the minimum shifts towards the PV axis with increas of T. At T_3 temp., PV curve runs parallel to P-axis up to certain range of P at low pr. region ($P \to 0$). This temp. is called Boyle temp (T_B) at which real gas also obeys Boyle's law up to certain range of Pr. at the low Pr. region. The minimum coincides with the PV axis. The mathematical condition for calculation of Boyle temp (T_B) is :

$$\left[\frac{\partial (PV)}{\partial P}\right]_T = 0 \quad \text{when } P \to 0.$$

The curves obtained for H_2 and He at 0°C is above their Boyle temp. and so with increase of P, the value of PV increases from beginning.

An important single parameter, called compressibility factor (Z) is used to measure the extent of deviation of the real gases from ideal behavior.

It is defined as, $Z = \frac{PV}{RT}$; V = Molar vol. of the gas.

$Z = 1$; the gas is ideal or there is no deviation of the gas from the ideal behavior.

$Z \neq 1$; the gas is non-ideal and departure of the value of Z from unity is a measure of the extent of non-ideality of the gas.

when $Z < 1$, the gas is more compressible than the ideal gas
when $Z < 1$, the gas is less " " " " ".

Since V is a function of T and P, Z is also a function of T and P, so Z may be defined as

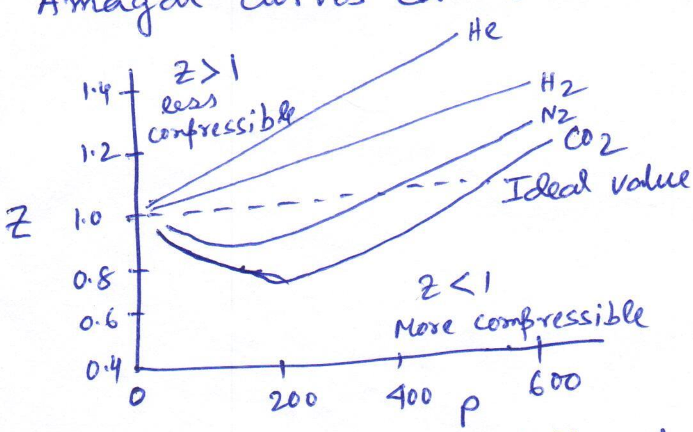
$$Z = \frac{V}{V_{ideal}} \quad \text{and} \quad Z = \frac{P}{P_{ideal}}$$

where, V_{ideal} is the molar volume of an ideal gas at the same T and P as the real gas.
Similarly, P_{ideal} is the Pr. of an ideal gas at the same T and V as the real gas.

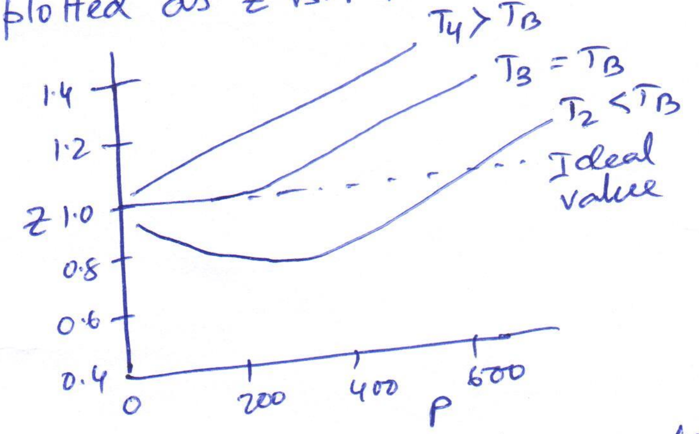
when $Z < 1$, the gas exerts lower Pr. than the ideal gas would and the volume of the gas becomes also lower than that of the ideal gas i.e. the gas becomes more compressible.

when $Z > 1$, the gas exerts higher Pr. than the ideal gas would and the volume of the gas becomes higher than that of the ideal gas i.e the gas becomes less compressible.

Amagat curves can also be plotted as Z vs. P:



Amagat curves for different gases at a given temp.



Amagat curves for a gas (CO_2) at diff. temperatures.

For N_2 gas at 50°C, Z remains close to 1 up to nearly 100 atm.

(6) when real gases pass through porous plug from higher Pr. to lower Pr. within insulated enclosure, there occurs a change of Temp. This is due to the fact that real gases have intermolecular attraction and when the gas expands, the molecules have to spend energy to overcome intermolecular attraction and so the temp. of the gas drops down.