Units of 'a' and 'b' in the Equn:-

From the VDW Equn: ; $P_a = \frac{an^2}{V^2} \Rightarrow a = \frac{P_a \times V^2}{n^2}$

So, unit of a $= \frac{atm \times L^2}{mol^2} = atm\ L^2\ mol^{-2}$

Again, nb = unit of vol.

So, $b = L\ mol^{-1}$

Significance of 'a' and 'b':-

Since, 'a' term originates from the intermolecular attraction, thus 'a' is a measure of internal pr. of the gas and it measures the attractive forces betwn. the molecules. Higher the value of 'a', greater is the intermolecular attraction and more easily the gas could be liquefied.

$a_{CO_2} = 3.95\ atm\ L^2\ mol^{-2}$ and $a_{H_2} = 0.22\ atm\ L^2\ mol^{-2}$.

So, CO_2 is more easily liquefied than H_2 gas.

Another const., 'b' measures the molecular size and also a measure of repulsive forces. The value of 'b' can be utilized to calculate the molecular diameter, σ. The greater the value of b, larger is the size of the gas molecule. Thus, $b_{CO_2} = 0.04\ L\ mol^{-1}$ and $b_{H_2} = 0.02\ L\ mol^{-1}$.

Let us consider two hypothetical cases to show the size effect and attraction effect on the Pr. of the gas.

(a) For the real gas, $a = 0$ (i.e, no intermolecular attraction exist) but $b \neq 0$ (size is considered).

VDW Equn: $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$, but $a = 0$,

So, $P = \frac{nRT}{V - nb} > P_{id}$ Since, $P_{id} = \frac{nRT}{V}$

It means that the molecular size (repulsive attraction) creates higher pr. than that observed by the ideal gas where molecules have no vol.

(b) For the real gas $a \neq 0$ (intermolecular attraction exists but $b = 0$, i.e, no size of the molecule.

The VDW Equn:, $P = \frac{nRT}{V} - \frac{an^2}{V^2} < P_{id}$, Since $b = 0$ and $P_{id} = \frac{nRT}{V}$

Thus, intermolecular attraction effect reduces the Pr. of the real gas.

Calculation of Boyle Temp, T_B:

We know, at T_B, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$ when $P \to 0$

VDW Equⁿ: $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$PV = \frac{RTV}{V-b} - \frac{a}{V}$$

Thus, $\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{\partial(PV)}{\partial V}\right]_T \times \left[\frac{\partial V}{\partial P}\right]_T$

$$= \left[-\frac{RTb}{(V-b)^2} + \frac{a}{V^2}\right] \times \left(\frac{\partial V}{\partial P}\right)_T$$

when $T = T_B$, $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$ but $\left(\frac{\partial V}{\partial P}\right)_T \neq 0$

Hence, $\frac{RT_B b}{(V-b)^2} = \frac{a}{V^2}$

$$\Rightarrow T_B = \frac{a}{Rb}\left(\frac{V-b}{V}\right)^2$$

Since, $P \to 0$, V is large and $\frac{V-b}{V} \simeq 1$

Therefore, $T_B = \frac{a}{Rb}$

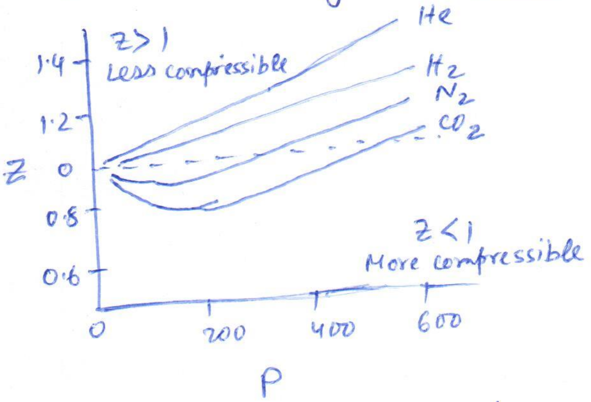
This is the expression of Boyle temp. for a gas obeying VDW equation.

⊛ Calculate a/b for a gas for which $T_B = 500\,K$.

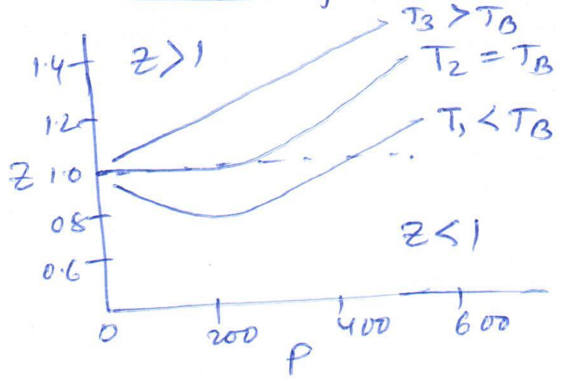
$T_B = \frac{a}{Rb} \Rightarrow \frac{a}{b} = RT_B = 0.082\ L\ atm\ mol^{-1}K^{-1} \times 500K$

$= 41\ L\ atm\ mol^{-1}$

Explanation of Amagat's curves in the light of VDW Equⁿ.:



For diff. gases at const. T.



For CO_2 at diff. T

VDW Equⁿ. for 1 mole real gas:

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

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

$$\Rightarrow PV = RT + Pb - \frac{a}{V} \quad \left[\text{Neglecting the small term } \frac{ab}{V^2}\right]$$

$$\Rightarrow \frac{PV}{RT} = 1 + \frac{Pb}{RT} - \frac{a}{VRT}, \quad \text{Since } Z = \frac{PV}{RT}$$

$$\Rightarrow Z = 1 + \frac{1}{RT}\left(Pb - \frac{a}{V}\right)$$

$$= 1 + \frac{1}{RT}\left(Pb - \frac{aP}{RT}\right)$$

$$= 1 + \frac{P}{RT}\left(b - \frac{a}{RT}\right)$$

$PV = RT$
$aPV = aRT$
$\frac{aP}{RT} = \frac{a}{V}$

This shows that $Z = f(T, P)$

This equⁿ. can be used to explain Amagat's curves quantitatively at low P to moderate P region.

Fig A: For CO_2 gas, 'a' is very high as we have seen that the gas is easily liquefiable.

Thus, $\frac{a}{RT} > b$ in the equⁿ. and $b - \frac{a}{RT} = -ve$. Intermolecular attraction dominates over the size effect.

Thus, the slope of Z vs. P curve is −ve for CO_2 at moderate Pr. region. This shows that the value of Z decreases with increase of P and it is found also in the curve.

For. H_2 gas, 'a' is small as it is not easily liquefied. $\frac{a}{RT} < b$ and the slope of Z vs. P curve for H_2 is +ve. The value of Z increases with increase of P.

Fig. B: (i) when $T < T_B$, $T < \frac{a}{Rb}$, or $b < \frac{a}{RT}$,

thus $b - \frac{a}{RT} = -ve$.

It means that when $T < T_B$, the value of Z decreases with increase of P at the moderate Pr. The effect is due to intermolecular attraction dominates over the size effect. So, for CO_2, $Z < 1$ and the gas is more compressible.

(ii) when $T = T_B = \frac{a}{Rb}$ or $b = \frac{a}{RT}$, or $b - \frac{a}{RT} = 0$, so, $Z = 1$.

The gas shows ideal behavior. The size effect compensates the effect due to intermolecular attraction of the gas. Z runs parallel to P-axis up to certain range of Pr. at low Pr. region.

(iii) when, $T > T_B$ means $T > \frac{a}{Rb}$, or $b > \frac{a}{RT}$.

Thus, $b - \frac{a}{RT} = +ve$. Thus, Z increases with increase of P when $T > T_B$. The size effect dominates over the effect due to intermolecular attraction and $Z > 1$ and the gas is less compressible.

(*) For H_2 and He, $0°C$ is greater than their T_B values and so Z vs. P slope becomes +ve.

(*) At very low P ($P \to 0$) and at high T, volume is very large and both the size effect and attraction effect becomes negligible. Thus Pb and $\frac{aP}{RT}$ are negligibly small and $Z = 1$. The gas behaves ideal.