Lecture 14

Let us recall a few plots and tables from the previous lectures:
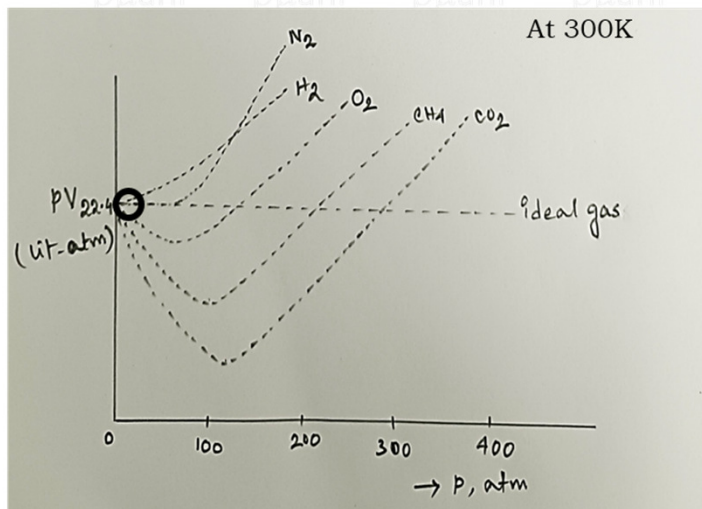
Gas	a $(lit^2\ atm\ mol^{-2})$	b $(lit\ mol^{-1})$
He	0.034	0.0237
H_2	0.244	0.0266
N_2	1.390	0.0391
O_2	1.360	0.0318
Cl_2	6.493	0.0562
NH_3	4.17	0.0371

$$T_B = \frac{a}{R\,b}$$

Gas	T_B (K)
He	22.64
H_2	110.0
N_2	327.2
O_2	405.9
CO_2	714.8
NH_3	995.0

Is it possible to have these plots irrespective of the nature of the gas?

How to do that?

How to get such an equation?

Which parameters contain the molecular parameters?

$$V_C = 3\,b, \qquad p_C = \frac{a}{27\,b^2}, \qquad T_C = \frac{8\,a}{27\,R\,b}$$

The law / principle of corresponding states:

Let us introduce a new set of parameters called "reduced variable" which is defined as the ratio of actual variable and its corresponding critical constant.

Thus, reduced pressure is defined as $p_r = \dfrac{p}{p_c}$

Similarly, $V_r = \dfrac{V}{V_c}$ and $T_r = \dfrac{T}{T_c}$

Why again another new set of parameters?

van der Waals pointed out that if one uses reduced variables to express states of gases, then to a pretty good approximation, all gases will show same p-$\overline{V}$-T behaviour.

This means, gases confined to same reduced volume (V_r) and same reduced temperature T_r would exert same reduced pressure p_r .

In other words, when gases under same reduced pressure (p_r) and same reduced temperature (T_r), then their reduced volumes (V_r) should be same.

When gases are under such conditions then they are said to be in corresponding states and the above law/principle is known as 'law/principle of corresponding states'.

Mathematically, $V_r = f(p_r , T_r)$

Assumption: Gas molecules are spherical in nature.

Let us start with the van der Waals equation:

$$\left(p + \frac{a}{V^2}\right)(V - b) = R\,T \qquad \ldots\ldots\ldots\ldots \text{(A)}$$

as $\quad p_r = \dfrac{p}{p_c}, \quad V_r = \dfrac{V}{V_c} \quad$ and $\quad T_r = \dfrac{T}{T_c}$

Equation (A) becomes,

$$\left[p_r\,p_c + \frac{a}{V_r^2 \times V_c^2}\right]\,[V_r \times V_c - b] = R\,T_r\,T_c$$

Upon substituting the critical constants, $\quad \left[p_c = \dfrac{a}{27\,b^2}, \quad V_c = 3\,b, \quad T_c = \dfrac{8\,a}{27\,R\,b}\right]$

the above equation takes the form,

$$\left[p_r \times \frac{\cancel{a}}{27\,b^2} + \frac{\cancel{a}}{V_r^2 \times 9\,b^2}\right]\,[V_r \times 3\,b - b] = \cancel{R}\,T_r \times \frac{8\,\cancel{a}}{27\,\cancel{R}\,b}$$

$$\Rightarrow \quad \left[\frac{p_r}{27} + \frac{1}{9\,V_r^2}\right]\,[3\,V_r - 1] = \frac{8\,T_r}{27}$$

$$\Rightarrow \quad \boxed{\left[p_r + \frac{3}{V_r^2}\right]\,[3\,V_r - 1] = 8\,T_r} \qquad \ldots\ldots\ldots \text{(B)}$$

This is known as van der Waals reduced equation of state.

Notice the above equation is free from a and b. Thus the above equation should provide same result for all gases. In other words same curve should be obtained using equation (B), whatever be the gas.

Let us see how is the experimental result.

When we plot Z vs. p_r for several gases the following curves were obtained:
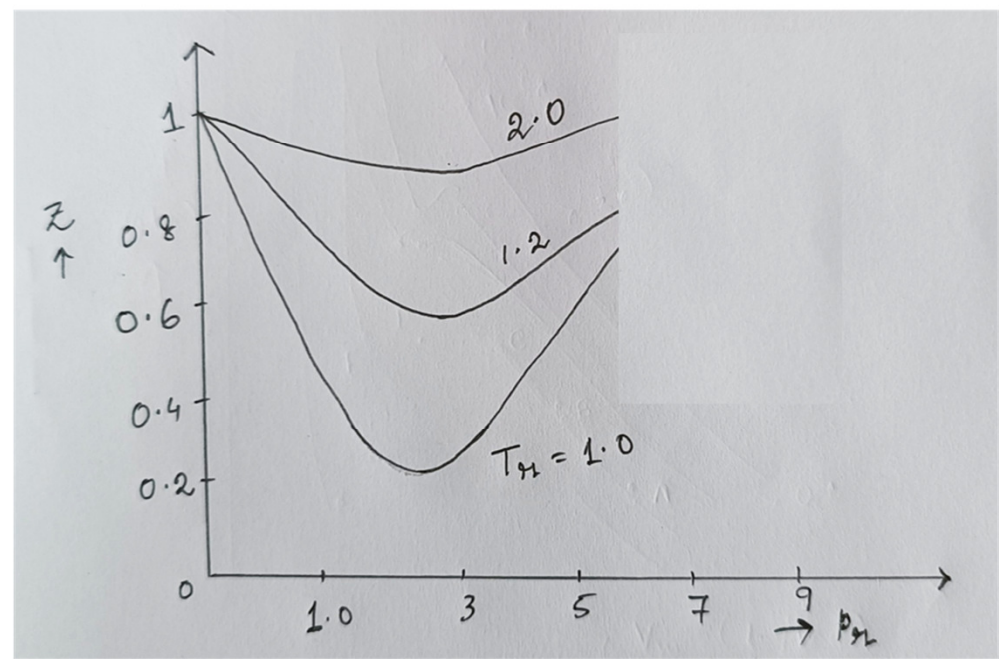
Same curves were obtained for same T_r and for gases like N_2, CH_4, propane, etc.

Thus, van der Waals reduced equation of state is quite compatible with the law/principle of corresponding states.

Exceptions:

The law/principle of corresponding states is not valid for gases with large dipole moments.

$V_r = f(p_r, T_r)$

$\Rightarrow \dfrac{p_r\,V_r}{T_r} = \dfrac{p_r}{T_r} \times f(p_r, T_r)$

The r.h.s. of the above equation is some other function of p_r and T_r

Thus, $\dfrac{p_r\,V_r}{T_r} = g(p_r, T_r)$

Function 'g' is same for all gases.

Every gas obeys $p\,\overline{V} = R\,T$ in the limit of very high volume or zero density

Thus, $\displaystyle\lim_{V \to \infty}\left(\dfrac{p\,V}{R\,T}\right) = 1$

Multiplying by $\dfrac{R\,T_c}{p_c\,V_c}$, we get,

$\lim\left(\dfrac{p_r\,V_r}{T_r}\right) = \dfrac{R\,T_c}{p_c\,V_c} = \dfrac{1}{Z_c} = K \text{ (constant)} \quad \text{and} \lim g = \dfrac{1}{Z_c} \qquad [\; Z_C = \dfrac{p_c\,V_c}{R\,T_c} = \text{critical compression factor}]$

Since 'g' is same for all gases, its limiting value as V goes to infinity must be same for all gases.

If this constant be K, then $Z_C = \dfrac{1}{K}$

Thus, law/principle of states predicts that critical compression factor should be same for all gases.

Value of Z_C for different gases are as follows:

Ar	$\rightarrow 0.29$	H_2O	$\rightarrow 0.23$
CH_4	$\rightarrow 0.29$	HF	$\rightarrow 0.12$
N_2	$\rightarrow 0.29$	HCN	$\rightarrow 0.20$
O_2	$\rightarrow 0.29$		
etc.		etc.	

Thus, the value for Z_C for non-polar gases are more or less equal where as Z_C for polar gas molecules or for molecules with H-bonding are different.

The law/principle of corresponding states can be explained by the fact that the interaction between two gas molecules is composed of only attractive and repulsive forces i.e. PE function is dependent only on distance and <u>not</u> on the relative orientation between them.

However, for polar molecules or with molecules with H-bonding ability that approximation does not hold truly. Thus we observe deviation of Z_C values for polar molecules (for molecules with H-bonding ability) from that of non-polar molecules.

Let us then go ahead with the Dieterici equation:

$$p = \frac{R\,T}{V-b} \times e^{-\frac{a}{R\,T\,V}}$$

$$\Rightarrow p_r\,p_C = \frac{R\,T_r\,T_c}{V_r\,V_c - b} \times e^{-\frac{a}{R\,T_r\,T_c\,V_r\,V_c}}$$

Substituting the values of critical constants,

$$V_C = 2\,b \quad , \quad T_C = \frac{a}{4\,b\,R} \quad , \quad p_C = \frac{a}{4\,b^2} \times \frac{1}{e^2}$$

The above equation takes the form,

$$\frac{\cancel{a}}{4\,b^2} \times \frac{1}{e^2} \times p_r = \cancel{R} \times T_r \times \frac{\cancel{a}}{4\,b\,\cancel{R}} \times \left(\frac{1}{2\,b\,V_r - b}\right) \times e^{-\frac{\cancel{a} \times 4\,\cancel{b}\,\cancel{R}}{\cancel{R} \times T_r \times \cancel{a} \times V_r \times 2\,\cancel{b}}}$$

$$\Rightarrow \frac{p_r}{4\,e^2} = \frac{T_r}{4} \times \left(\frac{1}{2\,V_r - 1}\right) \times e^{-\frac{2}{T_r \times V_r}}$$

$$\Rightarrow \boxed{\; p_r\,(2\,V_r - 1) = T_r \times e^2 \times e^{-\frac{2}{T_r \times V_r}} \;}$$

Reduced equation of state. This equation is also independent of a & b.

Question: Find out the expression for reduced equation of state corresponding to Berthelot equation.

[Berthelot equation: $p = \dfrac{RT}{V-b} - \dfrac{a}{TV^2}$]

Question: Write an expression of compressibility factor in terms of reduced parameters.

Question: Show that the area under the two shaded regions is the same.