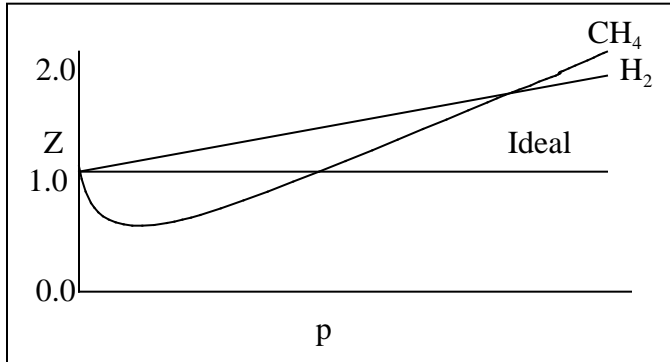


### Van der Waal's Equation:

This gives an explanation of the nonideal behavior of gases.

The plot of  $Z$  versus  $P$  shows that, gases do not conform the ideal-gas equation  $PV = nRT$ .



We saw that, the kinetic molecular theory of gases explains the ideal-gas PVT behavior based on the assumption that gases are composed of randomly moving, infinitely small particles.

Van der Waal added two more items to this model and showed that they can account for deviation of real gases from ideal behavior.

They are:

1. Volume occupied by the gas molecules.
2. The attractive forces between the molecules.

#### 1. Volume occupied by the gas molecules, i.e. Excluded Volume.

When  $n$  mol of gas is placed in a container of volume  $V$ , the volume in which the molecules are free to move is equal to  $V$  only if the volume occupied by the molecules themselves is negligible.

The presence of molecules of this nonvanishing size means there is a certain volume, called excluded volume, is not available for the molecules to move in.

If this extended volume of 1 mol of a gas sample is represented by  $b$ , then

We can write a new corrected volume as  $(V - nb)$ .

Thus, the  $PV = nRT$  equation becomes

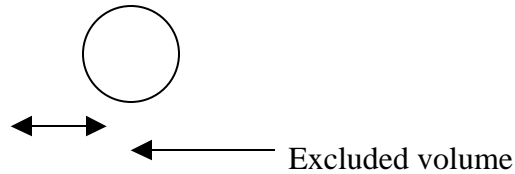
$$P(V - nb) = nRT$$

The value of  $b$  can be treated as constant and is characteristics of each gas.

### Van der Waal's Excluded Volume and Molecular Diameter:

The molecules are assumed to be spherical and to have diameter  $d$  or radius  $r$ .

A bigger circle shows the volume in which the centers of two molecules cannot move because of each others presence



Since the diameter of molecule is  $d$ .

The radius of bigger circle is also  $d$ .

Then

$$\text{Excluded Volume for a pair of molecule} = \frac{4}{3} d^3$$

Therefore,

$$\text{Excluded Volume for one molecule} = \frac{1}{2} \left( \frac{4}{3} d^3 \right)$$

$$\text{Excluded Volume for one molecule} = 4 \left( \frac{4}{3} (d/2)^3 \right)$$

$$\text{Excluded Volume for one molecule} = 4 \left( \frac{4}{3} r^3 \right) \quad \text{since } r = d/2$$

Thus the excluded volume is 4 times the volume of a molecule.

Since  $b$  is the excluded volume per mole,

Then,

$$b = 4 N_A \left( \frac{4}{3} r^3 \right) \quad \text{where } N_A = \text{avogadro's constant.}$$

## 2. The attractive forces between the molecules, i.e. Molecular Attractions

The second Van der Waal's correction term comes from the attractive forces between the molecules.

When a pressure is applied to the gas, it condenses to liquid. This can be accounted for pressure as well as the attractive forces between the molecules.

Thus the effective pressure will be less than the actual pressure required to confine the gas molecules, since the attractive forces will also help in keeping the gas molecules together.

The attraction forces of the molecules attract the nearby molecules.

So, if there is  $n$  mol of gas in volume  $V$ , then the number of molecules that are near any given molecules is proportional to  $n/V$  i.e. number of moles per unit volume.

Thus, for any given molecule which helps in holding the gas together through the molecule-molecule attractions is proportional to the number of near by molecules i.e.  $n/V$

At the same time, the other neighboring molecules will also attract its neighbors.

Thus, the total pull of gas due to these molecular interactions is proportional  $(n/V)^2$ .

We have,

$$P(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)}$$

But if we include the molecular interactions term, the equation becomes

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2} \quad \text{where } a = \text{proportionality factor.}$$

Rearranging the above equation gives Van der Waal's equation

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

For 1 mole of gas sample, the equation becomes,

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

#### Problem 1

At 200°C a pressure of 42.4 bar of pressure is required to reduce the molar volume of NH<sub>3</sub> to 0.85 L. What pressure would have been calculated on the basis of (a) ideal-gas behavior and (b) van der Waal's equation with  $a = 4.25 \text{ bar L}^2 \text{ mol}^{-1}$ ,  $b = 0.0374 \text{ L mol}^{-1}$ ,  $R = 0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1}$ .

$$T = 273 + 200 = 473 \text{ K}$$

From ideal-gas law equation:

$$PV = nRT$$

$$P = nRT / V$$

$$= (1 \text{ mol}) (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1}) (473 \text{ K}) / (0.851 \text{ L})$$

$$= 46.2 \text{ bar}$$

From Van der Waal's equation:

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$P = [ nRT / (V - nb) ] - [ an^2 / V^2 ]$$

$$= [(1.0 \text{ mol}) (0.0831 \text{ L bar K}^{-1} \text{ mol}^{-1}) (473 \text{ K}) / (0.851 \text{ L}) - (1.0 \text{ mol}) (0.0374 \text{ L mol}^{-1}) ]$$

$$- [ (4.25 \text{ bar L}^2 \text{ mol}^{-1}) (1.0 \text{ mol})^2 / (0.851 \text{ L})^2 ]$$

$$= 42.4 \text{ bar}$$

### Van der Waal's Equation and the Critical Point

The constant of Van der Waal's equation can be obtained from the critical point data.

The Van der Waal's Equation can be arranged as follow:

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad \text{-----(1)}$$

To investigate the horizontal point of inflection on a plot of P versus V, we obtain

$$\frac{dP}{dV} = \frac{-RT}{(V - b)^2} + \frac{2a}{V^3} \quad \text{----- (2)}$$

and

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} \quad \text{----- (3)}$$

At gas-liquid equilibrium, i.e. at critical-point,  
pressure is denoted as  $P_c$ ,  
volume is denoted as  $V_c$ , and  
temperature is denoted as  $T_c$ .

Also at critical point,

$$P = P_c$$

$$V = V_c$$

$$T = T_c$$

And first order and second order derivative of P with respect to V are zero.

Therefore we can write;

$$P_c = \frac{RT_c}{(V_c - b)} - \frac{a}{V_c^2} \quad \text{----- (4)}$$

and

$$0 = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} \quad \text{----- (5)}$$

and

$$0 = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} \quad \text{----- (6)}$$

These equations can be solved to get

$$a = 3P_c V_c^2 \quad \text{----- (7)}$$

$$b = V_c / 3 \quad \text{----- (8)}$$

$$R = 8 P_c V_c / 3 T_c \quad \text{----- (9)}$$

From Equation (9)

$$R = 8 P_c V_c / 3 T_c$$

$$(P_c V_c) / (R T_c) = 8/3 = 0.375$$

Thus

$Z_c = 0.375$ , which is a compressibility factor at critical point.

This value is approximately equal to the experimental values and also proves the Law of Corresponding States.

Since R is a gas constant, and the values of a and b are different for different gases. They can be calculated in terms of critical-point quantities  $P_c$  and  $T_c$  from equation (7, 8) by substituting  $V_c = 3 T_c R / (8 P_c)$ .

$$a = 27 R^2 T_c^2 / (64 P_c) \quad \text{and} \quad b = R T_c / (8 P_c)$$

### **The Law Corresponding States:**

We know the reduced pressure  $P_R$ , reduced temperature  $T_R$  and reduced volume  $V_R$  can be expressed in terms of their critical constant  $P_c$ ,  $T_c$  and  $V_c$  respectively as  $P_R = P/P_c$ ,  $T_R = T/T_c$  and  $V_R = V/V_c$ .

Also, at critical point, where  $P_R = 1$  and  $T_R = 1$ , the value for  $Z_c$ , i.e. compressibility factor at critical point, is approximately equal to 0.3

Thus the Law of Corresponding State can be expressed as:

Gases in states with the same values of  $T_R$  and  $P_R$  deviate from the ideality to the same extent; i.e. the values of  $Z = PV / (RT)$  are approximately same for different gases at the same value of  $T_R$  and  $P_R$ . In other words, the reduced volume of all gases are the same when the gases are at the same reduced pressures and temperatures.

Refer to Figure 1-12

### **Van der Waal's Equation and the Law of Corresponding States:**

If we substitute the values of  $a$ ,  $b$  and  $R$  from equation (7,8,9) and value of  $P$ ,  $T$  and  $V$  in terms of their reduced pressure  $P_R$  as  $P = P_R P_c$ , reduced temperature,  $T_R$  as  $T = T_R T_c$  and reduced volume,  $V_R$  as  $V = V_R V_c$  in Van der Waal's equation.

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

We will get

$$(P_R + (3 / V_R^2)) + (V_R - (1/3)) = 8 T_R / 3 \quad \text{----- (10)}$$

Thus, now we need only critical point data to characterize the particular gas.

Thus, the Van der Waal's equation is consistent with Law of Corresponding State.