## *6.4 Applicability of the van der Waals EOS*

### At very low pressures:

Although the van der Waals equation of state does not describe the exact behaviour at all T and P, it does a much better job than the ideal gas law. When the pressure is low it becomes equivalent to the ideal gas law.

$$\left[P + \frac{a}{v_m^2}\right][v_m - b] = RT$$

This can be written as:

$$Pv_m - bP + \frac{a}{v_m} - \frac{ab}{v_m^2} = RT$$

$$Pv_m = RT + bP - \frac{a}{v_m} + \frac{ab}{v_m^2}$$

When P is very small, $v_m$ is very large since the volume increases with decreasing pressure. The last three terms on the right hand side become negligible compared to RT and the equation is essentially:

$Pv_m = RT$, the ideal gas law.

### At very high pressures:

$V_m$ is now relatively small and the magnitude of b is comparable to $v_m$.

$$\frac{a}{v_m} \approx \frac{ab}{v_m v_m}$$

Therefore, $PV_m = bP + RT$, or $\dfrac{Pv_m}{RT} = 1 + \dfrac{bP}{RT}$

The value of z increases linearly with pressure at high P. In figure 6-2, we see that PV/RT increases linearly at high pressures.

### At Relatively Low Pressures

Now $(V_m)^2$ is large compared to ab and the product bP is also very small. Therefore,

$$Pv_m = RT - \frac{a}{v_m} \quad \text{or}$$

$$\frac{Pv_m}{RT} = 1 - \frac{a}{v_m RT}$$

The value of z is less than 1.0 at moderate pressures. Look at the $N_2$ curve in Figure 6-2 -> there are dips at 200 K and 250 K. Thus the van der Waals equation of state can describe some of the deviations from ideal gas behaviour quite well.

### *6.5 van der Waals EOS and the Critical Point*

The cubic polynomial form of the vdW EOS is

$$v_m^3 - \left(b + \frac{RT}{P}\right)v_m^2 + \frac{a}{P}v_m - \frac{ab}{P} = 0$$

Note that a cubic equation in x can be written as
$(x-x_1)(x-x_2)(x-x_3) = 0$, where $x_1$, $x_2$ and $x_3$ are the three roots.

At a given P & T the van der Waal's equation will have three roots for $v_m$.

At $T < T_c$, three real roots, highest and lowest correspond to dew point and bubble pt. $V_m$.

At $T > T_c$, only one real root and two imaginary roots.

At T = Tc, three real roots exist but they are identical since the liquid and gas properties are the same. Therefore all three roots become ($v_m = v_c$). For a cubic equation, this happens when the equation can be written as,

$$(v_m - v_c)^3 = 0$$
or
$$v_m^3 - 3v_c v_m^2 + 3v_c^2 v_m - v_c^3 = 0$$

At the critical point $P = P_c$ and $T = T_c$. Therefore the cubic form of vdW EOS at critical point can be written as.

$$v_m^3 - \left(b + \frac{RT_c}{P_c}\right)v_m^2 + \frac{a}{P_c}v_m - \frac{ab}{P_c} = 0$$

Comparing these two equations we can say,

$$3v_c = b + \frac{RT_c}{P_c}$$

$$3v_c^2 = \frac{a}{P_c}$$

$$v_c^3 = \frac{ab}{P_c}$$

These equations can be solved for $V_c$, $P_c$ and $T_c$ in terms of a, b and R.

Dividing #3 by #2, we get,

$$v_c = 3b$$

Now from # 2 we can write,

$P_c = a/(27\ b^2)$

Substituting the values of $v_c$ and $P_c$ in # 1,

$$3(3b) = (b + \frac{RT_c}{a} 27b^2)$$

*or*

$$T_c = \frac{8a}{27Rb}$$

Alternatively, one could solve for a and b in terms of the critical properties.

$$b = \frac{RT_c}{8P_c}$$

*and*

$$a = \frac{27R^2T_c^2}{64P_c}$$

## Critical Compressibility Factor:

The term $\frac{P_c v_c}{RT_c} = z_c$, is called critical compressibility factor. Its value for the van der Waals equation of state can be determined by substituting the relationships for the critical properties ($P_c$, $V_c$, $T_c$) in terms of a, b, and R that we developed earlier.

$$\frac{P_c v_c}{RT_c} = \frac{a}{27b^2} \frac{3b}{R} \frac{27Rb}{8a} = \frac{3}{8} = 0.375$$

Table 6-3 lists the values of critical compressibility factors for different gases. All are lower than the value determined above from van der Waals equation of state. The main reason for this failure of van der Waals equation of state is the simple form used for the attractive force. In reality, the attractive force is much more complicated.

## Two Other Characteristics of the Critical Point

The critical isotherm has a point of inflection at the critical point, i.e. the slope of the pressure curve becomes zero without the point being a minimum or maximum.

Therefore,

$$\left( \frac{\partial P}{\partial V} \right)_T = 0$$

And

$$\left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0$$

These derivatives can be evaluated using the pressure explicit form of the vdW EOS and the resulting equations can be solved to relate the values of a and b to critical properties. You get the same relationship derived earlier.

<u>Coming back to the b term</u>
We mentioned previously that $b = 4N_A V_{molecule}$
But, $v_c = 3b$
Therefore,
$v_c = 12 N_A V_{molecule}$

For a spherical molecule,
$$V_{molecule} = \frac{4\pi}{3} r^3 = \frac{\pi}{6} \sigma^3$$

In chapter 5, the mean distance between the molecules (separation distance) was given by Eq. 5-64 (p149) as

$$\delta = \left[ \frac{kT}{P} \right]^{1/3}$$

When the molecules are separated by this distance, each molecule can be considered to occupy a cubic cell of volume $\delta^3$. The critical volume for one mole of the gas will be this volume multiplied by Avogadro's number (evaluated at $T_c$).

$$v_c = N_A \delta^3 = 12 N_A V_m$$

Or, $\delta^3 = 12 (\pi/6) \sigma^3$

Or $\delta = (2\pi)^{1/3} \sigma = 1.85\sigma$

Thus at the critical point, the molecules are separated by less than two molecular diameters (centre to centre distance). The gas is highly compacted at its critical point. The molecular diameter, the separation distance and the mean free path are of the same order of magnitude at the critical point.

At standard conditions, the separation distance is about 30 molecular diameters and the mean free path is of the order of 300 molecular diameters.

## *6.6 Other Equations of State*

Many other equations of state have been proposed to overcome the deficiencies of vdW EOS. However, none is totally accurate at all temperatures and pressures. New equations are still being developed to improve the accuracy of existing equations. Table 6-4 lists some of the popular EOS's.