

Chapter 6 - Real Gases

In chapter 5, we examined the ideal gas behaviour and simple kinetic theory that explains this behaviour. The ideal gas equation of state is a good approximation of real gas behaviour only when the temperature is high and pressure is low. The assumptions used in the kinetic theory are not strictly valid in any real situation, however, at low pressures and high temperatures the errors caused by them are insignificant. These errors become larger at low temperatures and high pressures. In this section we will examine the real gas behaviour and discuss why it is different from the ideal behaviour. We will also learn about more sophisticated equations of state that give better approximations of the behaviour of real gases.

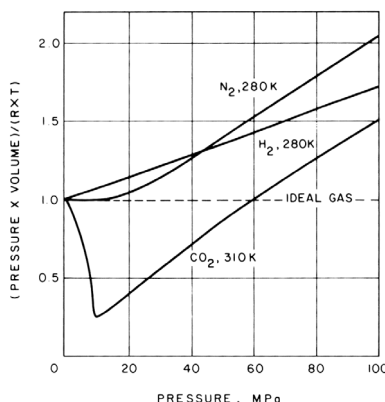


Figure 6-1 Non-Ideal Behavior of Some Gases

6.1 Deviations from ideal Gas Behaviour:

The ideal gas law states

$Pv_m = RT$ or $Pv_m/(RT) = 1$, at all pressures and temperatures. Figure 6-1 shows the value of $Pv_m/(RT)$ as a function of pressure for three different gases. All three curves converge to 1.0 at low pressure, but show varied deviations at high pressures. The ideal gas law is shown as dashed horizontal line. It is not hard to see that the deviations from the ideal behaviour are not negligible. If you were estimating the volume of N_2 at 100 MPa using the ideal gas law, the estimate will be less than half of the real volume.

Figure 6-2 shows the effect of temperature on deviation from the ideal gas law for nitrogen. The deviations become worse at lower temperatures.

These two figures show plots of $Pv_m/(RT)$ against pressure. You will get similar deviations if plots of $Pv_m/(RT)$ are made against temperature at a fixed value of high pressure. There are many reasons for such departure from ideal behaviour. These include:

- Non-zero volume of molecules (kinetic theory assumed molecules to have zero volume)
- Non-spherical shape of molecules
- Intermolecular forces
- Quantum effects

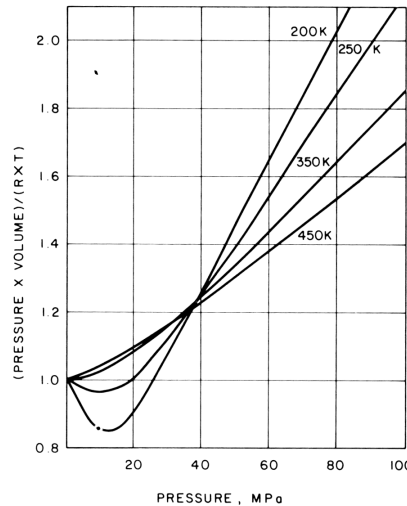


Figure 6-2 Non-Ideal Behavior of Nitrogen

These reasons for non-ideal behaviour become more prominent at high pressure and low temperatures. We will now examine an equation of state that accounts for some of the sources of non-ideal behaviour.

6.3 van der Waals Equation of State (EOS)

van der Waals developed an equation of state for the real gases that attempted to account for the size of molecules and the presence of intermolecular forces. He argued that there are two reasons for deviations from the ideal gas law.

- (1) Molecules have non-zero size
- (2) There are intermolecular forces

Effect of non-zero size

The ideal gas was assumed to have molecules that have mass but no physical size. When you are compressing the gas, you are reducing the volume of empty space. In an ideal gas, the entire volume is empty space, molecules occupying zero volume. In real gases, the molecules occupy finite volume, therefore, the empty space available for compression is reduced. He argued that since it is only the empty space that can be reduced, the correct relationship to account for the volume of molecules is

$$P(V_m - b) = RT$$

The term b accounts for the non-zero volume of molecules, and is sometimes referred to as molecular volume. Actually it is larger than the actual volume of molecules. Experimental results agree well with

$$b = 4N_A V_{\text{molecule}}$$

$$\begin{aligned} N_A &= \text{Avogadro's number} \\ V_{\text{molecule}} &= \text{actual volume of one molecule.} \end{aligned}$$

Effect of intermolecular forces:

The ideal gas is supposed to have no intermolecular forces. In real gases also, the intermolecular forces become negligible when the pressure is low and molecules are separated by large distances from each other. However, when the pressure is high the intermolecular distances become small and attractive forces become significant.

A molecule in the middle of a gas volume is attracted by molecules from all sides. Therefore, the net attraction on it would be zero.

But, at or near the wall, a molecule has to overcome the attractive forces exerted by other molecules in order to collide with the wall. This attraction slows down the molecule before it can collide with the wall. Therefore the pressure felt by the wall is less than the pressure that would exist if there were no intermolecular forces. It means that the real pressure in the interior of the gas is higher than the pressure felt by the walls. It can be argued that you have to correct the measured pressure by increasing it by a small amount (ΔP) to account for this effect of intermolecular forces. The equation of state then becomes

$$(P + \Delta P)(V_m - b) = RT$$

Now, the pressure is proportional to the number of molecules striking the wall and also to the average speed of the molecules. The attractive force reduces both of these in proportion to the molar density of the gas. Their product is proportional to the square of the molar density.

$$\Delta P \propto \rho_m^2$$

or

$$\Delta P \propto \frac{1}{v_m^2}, \text{ or}$$

$$\Delta P = \frac{a}{v_m^2}$$

The equation of state now becomes:

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

Values of constants a and b can be determined by fitting the experimental data. Later we will see how these constants can be related to the critical properties of the gas.

We have used v_m in this equation. An equation in terms of V and n can be obtained by substituting V/n in place of v_m .

$$v_m = V/n$$

$$\left[P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$$

This equation can be rearranged to make it explicit in P

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$

Or in terms of a cubic polynomial in v_m .

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

Note that being a cubic polynomial equation, it will have three roots. For a given value of P and T, the specific volume calculated by this equation can have three different values. If two values are imaginary and one is real, then the system is in single-phase region with the real root representing the value of its specific volume. If three real roots exist, the smallest one represents liquid phase and the largest will represent the vapour phase.

The use of van der Waals EOS requires values of a and b for the gas being considered. For common pure substances these values are available in handbooks. These values can also be related to the critical properties of the substance and later we will examine these relationships. Let us first see how this equation is used when the values of a and b are known.

A. Calculation of T from known P and v_m .

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

$$T = \frac{1}{R} \left[P + \frac{a}{v_m^2} \right] [v_m - b].$$

All terms on the R.H.S. are known.

B. Calculation of pressure from known values of T and v_m .

For this purpose use the form of equation that is explicit in P, i.e.

$$P = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$

Again all terms on the right hand side are known.

C. Calculation of v_m at given P and T.

This requires more work since the equation can not be written explicitly for v_m .

Generally a trial and error method is used to solve for v_m . Any form of the equation can be used. Remember that the equation is cubic in v_m . Therefore it will have three possible roots, all of which may or may not be real numbers. If only one real root exists, then that is the answer. If three real roots exist, then the smallest one is for liquid and the largest one is for vapour. The middle root does not represent any phase. Let us now look at a trial and error solution.

Example Problem:

Calculate the volume of 100 kg of pure CO₂ at 4 MPa and 50 °C by

- (a) ideal gas law and
- (b) van der Waals EOS.

Given: The molar mass of CO₂ is 44 kg/kmol and the values of the van der Waals parameters are: $a = 3.66 \times 10^5 \text{ Pa} \cdot (\text{m}^3/\text{kmol})^2$ and $b = 0.04284 \text{ m}^3/\text{kmol}$

$$P = 4 \times 10^6 \text{ Pa.}$$

$$T = 273.15 + 50 = 323.15 \text{ K}$$

$$n = m/M = 100 \text{ kg}/(44 \text{ kg/kmol}) = 2.273 \text{ kmol.}$$

$$R = 8314 \text{ J/kmol.k}$$

(a) Ideal Gas Law:

$$V = \frac{nRT}{P} = \frac{2.273 \times 8314 \times 323.15}{4 \times 10^6} = 1.527 \text{ m}^3$$

(b) van der Waals EOS

$$P = \frac{RT}{v_m - b} - \frac{a}{v_m^2}$$

We know the pressure, temperature, R, a and b. Substituting the known values:

$$4 \times 10^6 = \frac{8314 \times 323.15}{v_m - 0.04284} - \frac{3.66 \times 10^5}{v_m^2}$$

or

$$4 = \frac{2.687}{v_m - 0.04284} - \frac{0.366}{v_m^2}$$

This equation is solved by trial and error. It involves making a guess for the value of v_m and calculating the right hand side. A good starting guess is the value estimated from the ideal gas law.

From ideal gas law, $v^m = 1.527 \text{ m}^3/2.273 \text{ kmol} = 0.672 \text{ m}^3/\text{kmol}$.

V_m	0.762	0.60	0.50	0.57	0.565
R.H.S.	3.46	3.806	4.41	3.97	3.999

$$v_m = 0.565 \text{ m}^3/\text{kmol}$$

$$\text{Volume} = 0.565 \times 2.273 = 1.284 \text{ m}^3$$

Note: The experimentally determined value of v_m at these conditions is 0.557. The van der Waals equation provides a much better estimate of the experimental value.