Vander-Waals Gas

Many equations have been proposed which describe the *pVT* relations of real gases more accurately than does the equation of state of an ideal gas. Some of these are purely empirical, while others are derived from assumptions regarding molecular properties. Vander-Waals, in 1873, derived the following equation:

$$\left(p+\frac{a}{V^2}\right)(V-b)=RT \tag{1}$$

The quantities a and b are constants for any one gas but differ for different gases. We shall see soon that the term a/V^2 arises from the existence of intermolecular forces and that the term *b* is due to the volume occupied by the finite size molecules themselves.

This is *Vander-Waals equation of state* for real gases, that is why the real gases is also known as *Vander-Waals gases*. Various other equation of state may explain the experimental results better than Vander-Waals equation, even then we shall consider only this in great detail as it is very simple.

Deviations from Perfect Gas Equation

For every temperature a curve can be drawn which has for its abscissa the volume and for its ordinate the corresponding pressure of the enclosed substance. These curves are called *isotherm*. The equation of state for a ideal gas implies that at for a set of temperatures, these isotherm should be rectangular hyperbolas parallel to each other, but experiments show this is not true for every temperature.

Andrews using higher pressures confirmed the idea that all real gases showed considerable deviations from perfect gas equation. Andrews experiments are of fundamental importance as they reveal the actual behaviour of gases and from the basis of an important equation of state first proposed by Vander-Waals, Andrews' experiments can be described.

Andrews' Experiment on Carbon Dioxide

While engaged in the attempt to liquefy some of the imperfect gases, Andrews in 1869, was led to study the isotherms of carbon dioxide. The curves obtained by Andrews are shown in figure 1. The main conclusions are discussed below.

1. Let us consider the isotherm corresponding to low temperature 13.1ºC. As we increase the pressure, the volume decreases considerably (portion AB) and finally liquefaction of the gas begins (at point B). As long as liquefaction continues the pressure remains constant and the volume continuously decreases (horizontal portion BC), more and more gas condensed into liquid. When all the gas has condensed into liquid (at point C), after that the curve rises almost vertically (portion CD) corresponds to the fact that liquids are only slightly compressible.

2. The isotherm corresponding to temperature 21.5ºC is of the same form but the horizontal portion B'C' is shorter than BC. It means in this isotherm, the volume of the vapour when condensation begins, is smaller while volume of the liquid, when condensation has finished is greater in comparison to the isotherm at 13.1ºC. As temperature is raised further, isotherms behaves in the same manner, till at 31.4ºC.

3. At temperature 31.4ºC the horizontal portion has just disappeared and the two volumes have become the same and a kink is observed in isotherm denoted by P and known as *critical point*. This isotherm is called the

critical isotherm for carbon dioxide.

4. Above this temperature the horizontal portion is absent for all the isotherms such as for 35.5°C, and there is no formation of liquid, but volume decreases rapidly till it becomes equal to that of the liquid at that temperature.

5. This peculiar behaviour of the isotherms also disappears at higher temperature as for 48.1°C.

Figure 1 *Isotherms for Carbon Dioxide obtained by Andrews.*

Discussion of the Results

We conclude that, above the critical isotherm no liquid state is at all possible even under the greatest pressure, while below it there are three separate regions. In the region enclosed by the dotted curve whose highest point P, called the *critical point*, lies on the critical isotherm, both liquid and gaseous states coexist. To the left of the line PC and below the critical isotherm there is the *liquid region* while to the right of PB and below the critical isotherm there is the *gaseous region*. Thus, there exist a *continuity of the liquid and gaseous states*.

The Critical Constants

As we just learn about the *critical isotherm* and *critical point*, (shown in figure 2). If gaseous CO_2 is compressed above 31.4°C no liquid state is possible even under the greatest pressure. This temperature is known as critical temperature for CO_2. We may define *critical temperature T_C* as the maximum temperature at which a gas can be liquefied by pressure alone. The pressure just sufficient to liquefy the gas at the critical temperature is called the *critical pressure p_C* and the volume which the gas then occupies is called the *critical volume V_C*. These three quantities are called the ***critical constants*** of the gas.

Figure 2 *Critical Isotherm and Critical Point.*

Vander-Waals' Equation of State

The equation of state for perfect gas was deduced theoretically from the kinetic theory of gases. Two important assumptions were made in the deduction of this equation:

1. The molecules were considered to be negligibly small in size and considered as point object.

2. The gas was supposed to have only kinetic energy and have no potential energy due to intermolecular attractions.

It is now known that both these assumptions are only approximate and very nearly hold in case of extremely rarefied gases only, i.e., when the pressure is very small.

1. Clausius pointed out that the molecules, though extremely small in size, cannot be regarded as geometrical points, and account must be taken of their size in the calculation of pressure.

2. Hirn pointed out that the molecules must exert force of attraction on one another in the same way as solid or liquid does. Hence potential energy due to forces of cohesion must be taken into account.

To explain the observed temperature dependent behaviour of real gases, Vander-Waals work out a systematic theory, taking into account both these factors and proposed another equation of state.

Deduction of Vander-Waals' Equation of State

Correction for finite size: Suppose one mole of a real gas is enclosed in a vessel of volume *V*. It is evident that the space available for the free motion of the molecule becomes less when molecular size is taken into account, because one molecule cannot lie within the space occupied by other molecules. Evidently the decrease in the volume of the gas *b* must be related to the total volume *V* occupied by the molecules and *V* in the ideal gas equation has to be replaced by *V – b*. Hence, $p(V-b)=RT$

Now to find the magnitude of *b*, assume that the molecules are hard sphere of radius *r*. At the instance of collision, the centre-to-centre distance of the two colliding molecules will be *d = 2r*. This implies that around any molecule, other molecules cannot lie in a spherical volume V_s. This volume is called the *sphere of exclusion* and is eight times the volume of a molecule, V_m, i.e., $V_s = V_m$, where

$$V_s = \frac{4}{3}\pi d^3 \qquad \text{and} \qquad V_m = \frac{4}{3}\pi r^3$$

Let us imagine that the vessel is filled one by one molecule up to *N* molecules. Then,

the volume available to the first molecule $= V$

the volume available to the second molecule $= V - V_s$

and in the same way, the volume available to the Nth molecule $= V - (N - 1)V_s$.

Hence, the average volume available to each molecule, obtained by taking arithmetic mean is

$$\bar{V} = \frac{1}{N}\sum_{i=1}^{N}[V-(i-1)V_s] = V - \frac{(N-1)}{2}V_s$$

because, $\sum_{i=1}^{N}(i-1) = \frac{N}{2}(N-1)$. For large *N*, one can neglect 1 on the right hand side of the above equation and obtain

$$\bar{V} = V - \frac{N}{2}V_s = V - 4NV_m = V - b \qquad\qquad (2)$$

where $b = 4NV_m$.

Correction for intermolecular attraction: A molecule in the interior of the gas is surrounded by molecules from all sides therefore net force of attraction would be zero on it. Hence, it will behave as if there were no intermolecular attractions. However, a molecule in the outermost layer close to the surface experiences a net inward force because the molecules are distributed only on inner side. Thus whenever a molecule of this kind collides with the walls of the vessel, it will exert pressure on the wall lesser than expected for perfect gas shown in figure 3 (b). This drop in pressure is known as *cohesive pressure*.

Figure 3 *(a) Collision of two molecules of radii r.   (b) Intermolecular attraction*

This pressure will be proportional to the number of molecules per unit volume in the surface layer and the number of molecules per unit volume in the layer just below the surface layer. Thus,

$$\Delta p \propto \left(\frac{N}{V}\right)\left(\frac{N}{V}\right)$$

or,

$$\Delta p = a'\left(\frac{N^2}{V^2}\right)$$

where a' is a constant of proportionality. If we put $a' N^2 = a$, we can write

$$\Delta p = \left(\frac{a}{V^2}\right) \tag{3}$$

Hence, in the perfect gas equation we must replace p by the sum of the observed pressure for any real gas p and the drop caused by intermolecular attractions Δp. Hence, the equation of state for an ideal gas modifies to

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{4}$$

This is known as *Vander-Waals equation of state*. The quantities a and b are known as Vander Waals constants because they are considered to be constant for any gas irrespective of its temperature but differ for different gases. At sufficiently large volume, the term a/V^2 becomes negligible in comparison with p, and b becomes negligible in comparison with V. The Vander-Waals equation then reduces to the equation of state of an ideal gas, which any equation of state must do at large volumes.

Determination of Critical Constants

For liquefaction there must be two points on the curve having equal pressure. The highest isotherm for which this condition is satisfied is the one passing through the point P, in figure 2, since at P the maxima and minima have merged into one. Hence P must be identified with the *critical point* and the isotherm passing through it with the *critical isotherm*. The volume, temperature and pressure corresponds to critical point are identified as *critical volume, critical temperature* and *critical pressure*, respectively.

Since an isotherm represents those equilibrium states at which the temperature is constant, the slope of an isotherm curve is given by $(\partial p / \partial V)_T$. A study of figure 2 will show that at the critical point not only is the slope zero, but since the isotherm is concave upward at the left of this point and concave downward at the right, the critical point is also a point of inflection. Hence at critical point,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

The Vander-Waals equation may be solved for p, and hence partial derivatives of p are easily calculated. We find

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \tag{5}$$

Hence

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \tag{6}$$

and,

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \tag{7}$$

But at critical point $p \to p_c$, $V \to V_c$ and $T \to T_c$, therefore

$$p_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2} \tag{8}$$

$$-\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \tag{9}$$

and,

$$\frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \tag{10}$$

Dividing eq. (9) by (10), we get

$$V_c - b = \frac{2}{3}V_c$$

or,

$$V_c = 3b \tag{11}$$

Putting this value into eq. (9), we get

$$\frac{RT_c}{4b^2} = \frac{2a}{27b^3}$$

or,

$$T_c = \frac{8a}{27Rb} \tag{12}$$

Putting both the values into (8), we get

$$p_c = \frac{R}{2b}\left(\frac{8a}{27Rb}\right) - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{a}{9b^2}$$

or,

$$p_c = \frac{a}{27b^2} \tag{13}$$

finally combining all three values, we get

$$\frac{RT_c}{p_c V_c} = C_c = \frac{8}{3} = 2.67 \tag{14}$$

This is known as *critical coefficient*. Vander-Waals equation predicts this equal to 2.67 and is same for

all gases, irrespective of their nature. For an ideal gas, of course, C_c equals unity. Actually, however, it varies from gas to gas with an average value of 3.7 for most substances.

Determination of Vander-Waals' Constants

We observed that the critical constants are defined in terms of a and b. one can invert these relations to obtain a and b. From the expression of T_c and p_c, we combine

$$\frac{T_c^2}{p_c} = \left(\frac{8a}{27Rb}\right)^2 \frac{27b^2}{a}$$

or,
$$a = \frac{27R^2T_c^2}{64p_c} \tag{15}$$

and
$$\frac{T_c}{p_c} = \left(\frac{8a}{27Rb}\right)\frac{27b^2}{a}$$

or,
$$b = \frac{RT_c}{8p_c} = \frac{V_c}{3} \tag{16}$$

Thus, if T_c, p_c and V_c are known from experiments, one can find a and b using above relations.