

$$P = \frac{m}{V} = \nu \left(\frac{\rho}{\rho_0} \right) + \nu \left(\frac{T}{T_0} + \alpha \right) = \nu P'$$

① Study Material - Sem. 3 - C6 T-

Theory of Kinetic Theory of Gases -

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3.11. DISCUSSION ON VAN DER WAALS' EQUATION

From van der Waals' equation we get

$$\begin{aligned} \left(P + \frac{a}{V^2} \right) (V - b) &= RT \\ \text{or, } (PV^2 + a)(V - b) &= RTV^2 \\ \text{or, } PV^3 + aV - PV^2b - ab &= RTV^2 \\ \text{or, } V^3 - \left(b + \frac{RT}{P} \right)V^2 + \frac{aV}{P} - \frac{ab}{P} &= 0 \end{aligned} \quad \dots (3.4)$$

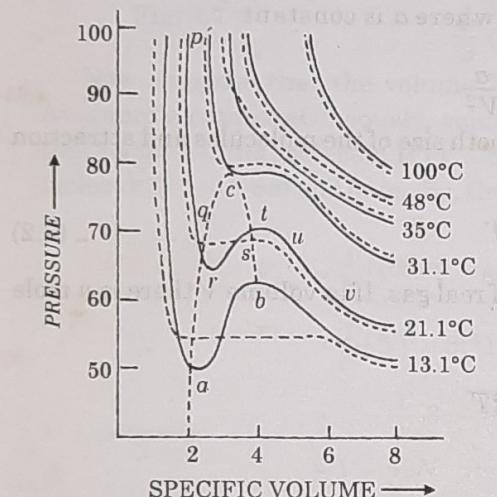


Fig. 3.9

For a given value of P and T , the equation (3.4) is a cubic equation in volume V . Solving the above equation, we get three values of V , all of them may be real or one of them may be real and the other two imaginary. If the values of a and b are known for a gas, then, for a particular temperature, different values of P may be found out from the above equation corresponding to different values of V . Hence, for a given mass of a gas, we can draw theoretical P - V isothermal at different temperatures. These isotherms are called *van der Waals' isotherms*. Fig. 3.9 shows van der Waals' isotherms (continuous curves) and Andrews' experimental isotherms for carbon dioxide (shown by dotted lines) meant for comparison.

Comparing the theoretical isotherms with the experimental isotherms of Andrews, the following remarks can be made :

- The two sets of curves are fairly similar. There is a good general agreement between the two.
- At higher temperatures, the two sets of isotherms are identical, e.g., the isotherms above 31.1°C for carbon di-oxide are identical.
- Some portions of the theoretical isotherms below critical temperature are wavy and not horizontal as is found in the isotherms of Andrews' experiment. So, these two sets of curves are not similar in the region, where liquid and vapour co-exist. Below the critical temperature, maxima and minima are observed in van der Waals' isotherms. But the corresponding portions in Andrews' isotherms are horizontal.
- Now consider the isothermal ($pqrstuv$) corresponding to the temperature 21.1°C (below critical temperature). The liquid portion pq and gaseous portion uv are similar to the experimental curve. But in the portion $qrstu$, the two types of curves are not similar. On the theoretical curve, this part is wavy; but is horizontal in the Andrew's curves. In the portion rst the curve passes from minimum to maximum point. So, along this portion, volume increases along with pressure, which is not possible in practice.
- With increase of temperature the maxima and minima approach each other. These two points meet at c . Above critical temperature T_c , curves do not have any maxima or minima.

From the above discussions we see that van der Waals' theoretical curves and Andrews' experimental curves coincide and hence similar in major part of the curves. So, van der Waals expresses the behaviour of real gas fairly accurately.

Critical Constants In Terms of van der Waals Constant:

From van der Waals Eqn. we get,

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

$$\text{or, } PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT \quad \text{for first}$$

$$\text{or, } PV^3 - PbV^2 + \frac{aV^2}{V} - ab = RTV^2 \quad \text{for first}$$

$$\text{or, } V^3 - bV^2 + \frac{a}{P}V - \frac{ab}{P} = \frac{RT}{P}V^2$$

$$\text{or, } V^3 - bV^2 - \left(\frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \frac{ab}{P} = 0$$

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

→ (1)

Evidently, for given values of P and T,
The volume V will have three roots. But
at the critical points, they are identical.

Because at critical point, pressure,
volume and temperature cannot have
more than one value.

At critical point, $V = V_c$

$$\therefore V - V_c = 0$$

$$\text{or, } (V - V_c)^3 = 0$$

$$\text{or, } V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \rightarrow (2)$$

Now comparing coefficients of V_c^2 , V_c and the constant terms in eq. ① and ② and putting $P = P_c$ and $T = T_c$, we get,

$$3V_c = b + \frac{RT_c}{P_c} \rightarrow ③$$

$$3V_c^2 = \frac{a}{P_c} \rightarrow ④$$

$$V_c^3 = \frac{ab}{P_c} \rightarrow ⑤$$

From, eq. ④ & ⑤ we get,

$$V_c (V_c^2) = \frac{ab}{P_c}$$

$$\text{or, } V_c \left(\frac{a}{3P_c} \right) = \frac{ab}{P_c}$$

$$\text{or, } V_c = 3b \rightarrow ⑥$$

$$\text{From ④, } 3(3b)^2 = \frac{a}{P_c}$$

$$\text{or, } P_c = \frac{a}{27b^2} \rightarrow ⑦$$

$$\text{From ③, } 3(3b) = b + \frac{RT_c}{\left(\frac{a}{27b^2}\right)}$$

$$\text{or, } 9b = b + \frac{27b^2 RT_c}{a}$$

$$\text{or, } 8b = \frac{27b^2 RT_c}{a}$$

$$\text{or, } T_c = \frac{8a}{27bR} \rightarrow ⑧$$

The quantity $\frac{RT_c}{P_c V_c}$ is called critical coefficient. For an ideal gas, its value is 1. For a real gas obeying van der Waals equation, its value is —

$$\frac{RT_c}{P_c V_c} = \frac{R \left(\frac{8a}{27bR} \right)}{\left(\frac{a}{27b^2} \right) (3b)} = \left(\frac{8a}{27b} \right) \left(\frac{27b}{3a} \right) \\ = \frac{8}{3} = 2.67$$

So, critical coefficient is a number and its value does not depend on the values of the constants a and b .

Defects of van der Waals Equation

van der Waals equations is considered to be one of the most useful and satisfactory equation of state for real gases. Still it has some drawbacks as indicated below —

1. The isotherms that are obtained theoretically from van der Waals

equation do not tally with those obtained experimentally by Andrews. Below critical temperature T_c , Andrews' curves do not show any maxima or minima as are shown by van der Waals' curves.

2. In van der Waals' equation a and b are supposed to be constants.

But they are found to vary with different substances and even for a particular substance, a and b are found to vary with temperature.

3. The value of $V_c = 3b$ according to van der Waals' equation, but practically it is found to be equal to $2b$.

4. The critical coefficient $\frac{RT_c}{P_c V_c}$ according to van der Waals' equation should be 2.67. But experimentally it is found to be equal to 3.75 on average.

5. According to van der Waals' equation, The Boyle temperature (T_B) is equal to $\frac{27}{8} T_c$. But it is found to vary from gas to gas — 3.65 for He and 2.65 for N_2 .

Boyle Temperature for a van der Waals' gas

Boyle temperature is the temperature at which $PV \propto P$ isothermal will be parallel to P axis. At this temperature, a real gas obeys ideal gas equation.

From van der Waals' equation —

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

$$\therefore P + \frac{a}{V^2} = \frac{RT}{V - b}$$

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

$$\therefore PV = \frac{RTV}{V - b} - \frac{a}{V} \rightarrow (1)$$

At Boyle temperature, i.e., when $T = T_B$,

The real gas obeys ideal gas equation. So, $PV = RT_B$

From ①,

$$RT_B = \frac{RT_B V}{V-b} - \frac{a}{V}$$

$$\therefore RT_B \left[\frac{V}{V-b} - 1 \right] = \frac{a}{V}$$

$$\therefore \frac{RT_B b}{V-b} = \frac{a}{V}$$

$$\therefore T_B = \left(\frac{a}{V} \right) \left(\frac{V-b}{bR} \right)$$

$$\leq \frac{a}{bR}$$

$V-b \approx V$ as b is negligible compared to V

$$\therefore T_C = \frac{8a}{27bR}$$

$$T_C = \frac{8}{27} T_B$$

$$T_B = \frac{27}{8} T_C$$

Reduced Equation of State

We know that physical state of a gas can be expressed correctly if pressure, volume and temperature of the gas are known. Sometimes actual pressure, volume and temperature of a gas is not given. Instead its critical pressure,

volume and temperature is used to form an equation. The form to which an equation of state reduces when we express the actual pressure, volume and temperature as functions of critical pressure, volume and temperature, is called a reduced equation of state.

We make the following substitutions:

$P = \pi P_c$, $T = \theta T_c$ and $V = \phi V_c$ in the van der Waals' equation.

π , θ , and ϕ are called reduced pressure, reduced temperature and reduced volume respectively.

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

$$\therefore \left[\pi P_c + \frac{a}{\phi^2 V_c^2} \right] [\phi V_c - b] = R \theta T_c$$

①

$$\text{Now, } P_c = \frac{a}{27b^2}, V_c = 3b \text{ & } T_c = \frac{8a}{27bR}$$

From ①, we get,

$$\left[\frac{\pi a}{27b^2} + \frac{a}{\phi^2 (3b)^2} \right] [3b\phi - b] = R \theta \frac{8a}{27bR}$$

$$\therefore \left[\frac{\pi a}{27b^2} + \frac{a}{9b^2 \phi^2} \right] b [3\phi - 1] = \frac{8a \theta}{27b}$$

$$a) \left(\frac{a}{b^2}\right) \left[\frac{\pi}{27} + \frac{1}{9\phi^2}\right] b (3\phi - 1) = \frac{8a\phi}{27b}$$

$$b) \left(\frac{\pi}{27} + \frac{1}{9\phi^2}\right) (3\phi - 1) = \frac{80}{27}$$

$$c) \left(\pi + \frac{3}{\phi^2}\right) (3\phi - 1) = 80$$

$$d) \boxed{\left(\pi + \frac{3}{\phi^2}\right) \left(\phi - \frac{1}{3}\right) = \frac{80}{3}} \rightarrow ②$$

The above equation is van der Waals' reduced equation of state. It is to be noted that, it does not contain the constants a and b which are the characteristics of a particular gas. So, This equation is equally applicable to all gases.

Law of Corresponding State

It follows from the above reduced equation of state that if two gases have same reduced pressure and volume, They will have the same reduced temperature. This is known as The law of corresponding states.

If any two of the quantities π , ϕ

and δ (i.e., the reduced pressure, volume and temperature) are same for two gases, then the third will also be the same.

It also follows that a set of isotherms for a gas may be made to hold for another gas by adjusting the scales for p and V .

Also if for two gases, the values of T , P and δ be equal, the gases are said to be in corresponding state.