



**Discipline Course-I  
Semester-II**

**Paper No: Thermal Physics : Physics-IIA**

**Lesson: Van der Waals gas equation**

**Lesson Developer: Dr. Sadhana Pandey**

**College/ Department: Physics Department,  
Maitreyi College, University of Delhi**

### Table of contents:

<b>Chapter 2:</b>	<b>van der Waal's Gas Equation</b>
	2.1 Introduction
	2.2 van der Waal's equation of state for real Gases
	2.3 Comparison of experimental curves
	2.4 Values of critical constants
	2.5 Reduced equation of state
	2.6 Law of corresponding states
	2.7 Limitations of van der Waal's gas equation
	2.8 Virial equation
	2.9 Summary
	2.10 Exercise
	2.11 Glossary
	2.12 References

### Learning Objectives:

After studying this lesson, you will be able to ;

- ✓ establish van der Waal's equation of state.
- ✓ determine van der Waal's constants a and b.
- ✓ determine critical constants.
- ✓ obtain reduced equation of state.
- ✓ define the law of corresponding states.
- ✓ discuss limitations of van der Waal's equation of state.

### 1.1 Introduction

Many gases show deviations from the behavior of ideal gases and do not resemble them even at ordinary temperatures. These deviations may be due to the assumptions which lead to the kinetic theory of gases. Different equations were proposed to show the behavior of real gases. Some of them are purely empirical while others are derived from assumptions regarding molecular properties. But the best explanation came from van der Waal, who said that the size of the molecules and the attraction between them are also significant which were not considered to play an important role in earlier attempts. Like the ideal gas, the van der Waal's gas is only a projection of real behavior and is able to describe more of the physical properties exhibited by real gases. van der Waal satisfactorily explains the general features of transition from liquid to gaseous state but fails to explain the quantitative details. However in spite of certain limitations the most commonly used equation is the van der Waal's equation because of its simplicity.

### 2.2 van der Waal's equation of state for real gases

A number of equations have been proposed which describe pressure, volume and temperature relations of the gases more accurately than does the equation of state of an

---

## Van der Waal's Gas Equation

---

ideal gas. A proper equation of state for real gases has been obtained by analyzing the two main conditions for a perfect gas which were: 1) the intermolecular force is nonexistent 2) the size of the molecules are negligible.

van der Waal modified the perfect gas equation,

$$PV = RT \text{ (for one mole of a gas) } \text{---(2.1)}$$

by applying corrections for:

1. Intermolecular force of attraction (they play a very important role!)
2. The non-zero size of the molecule (their size actually matters!!)

Considering above factors, equation (2.1) can be rewritten as:

$$(P + p)(V - v) = RT \text{---(2.2)}$$

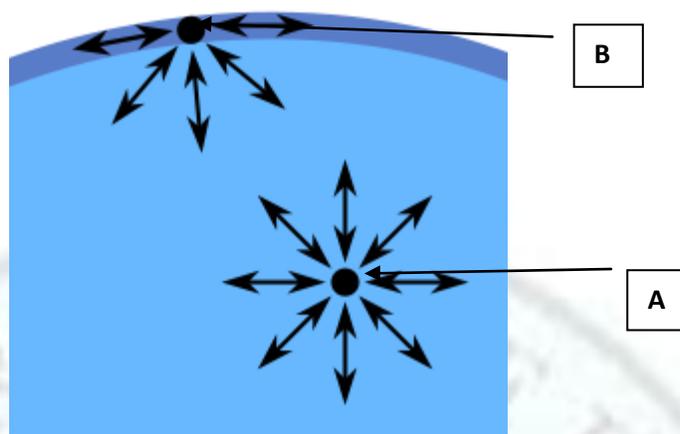
Here,  $p$ — correction for pressure;  $v$ — correction for volume

### (1) Correction for intermolecular attraction:

Molecules attract one another with a weak force which depends only upon the distance between them. The distance up to which the force of attraction is appreciable is called '**molecular range**'. A sphere surrounding a molecule and of radius equal to molecular range is called 'sphere of influence of interaction'. Molecules like **A** in fig (2.1), having its sphere of influence of interaction well inside the gas is attracted equally in all directions and hence the resultant force on it is zero. But, molecules like **B** near the boundary having their sphere of influence of interaction partially outside, experience a resultant inward pull. Due to this inwardly directed force, the impact of molecules on the wall is not as effective as its velocity and hence the momentum with which it will strike the wall would be less than the momentum with which it would strike in the absence of the force of attraction. This reduction in momentum results in decrease of pressure. This drop is known as 'cohesive pressure'. So the observed pressure is less than the actual pressure by an amount equal to the cohesive pressure. The correction for pressure **P** depends upon:

- (i) Number of molecules striking unit area per unit time of the walls of the container.
- (ii) The resultant inward pull of cohesion on each of the striking molecule.

## Van der Waal's Gas Equation



**Figure 2.1:** Intermolecular force

### Determination for the value of $p$ (correction for pressure):

Each of these factors is proportional to the density ( $\rho$ ) of the gas.

Therefore,

$$\text{Correction for pressure, } p \propto \rho^2 \text{ -----(2.3)}$$

$$\text{Putting, } \rho = \frac{1}{V}, \text{ we can write: } p = \frac{a}{V^2} \text{ -----(2.4)}$$

Here,  $a$  is a constant and  $V$  is the volume of the gas. Now, the net pressure on the gas is the sum of actual external pressure,  $P$  and the self-cohesive pressure or **co-pressure** ( $p$ ).

Therefore, the **corrected real pressure** is

$$= P + \frac{a}{V^2} \text{ -----(2.5)}$$

here,  $P$  is the observed pressure.

### (2) The non-zero size of the molecule:

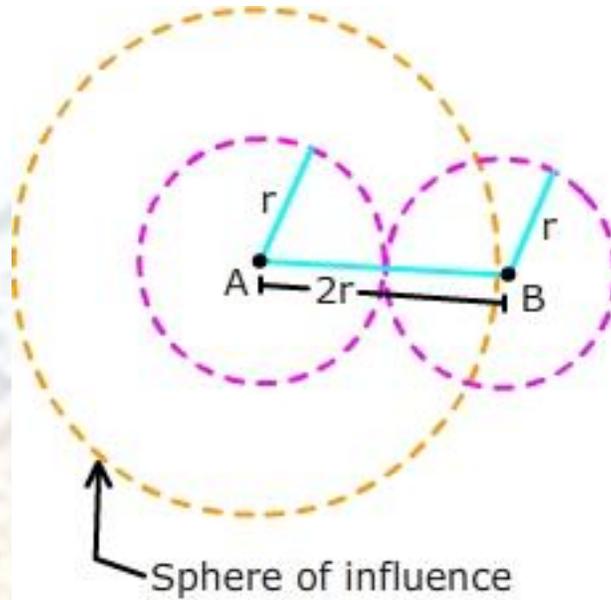
#### Determination for the value of $v$ (correction for volume):

Gas molecules have finite size and cannot be regarded as point masses. So the molecules occupy finite space and the actual space for their movement is less than the total volume of the gas.

The volume  $V$  is the volume in which each molecule is free to move about. If the size of the molecule is negligible, the entire volume of the container becomes the free volume of the gas. Due to the finite size of the gas molecule, the actual space available for the movement of the molecule is less than the volume of the vessel by an amount depending on the size and number of the molecules.

## Van der Waal's Gas Equation

Suppose that  $r$  is the radius of each molecule. Now draw a sphere of radius  $d(=2r)$  which is the diameter of each molecule. The sphere so drawn is very significant (in size) and is called "sphere of influence of collision". This represents the volume which is unavailable to the centers of other molecules. Fig (2.2).



**Figure 2.2:** Sphere of influence

Let  $x$  be the volume of each of the molecule.

Since the molecules are spherical in shape, we can write,

$$x = \left(\frac{4}{3}\right)\pi r^3 \text{ --- (2.6)}$$

The centers of any two molecules can approach each other only by a minimum distance of  $d$ .

Let  $V_s$  be the volume of sphere of influence of each molecule.

Therefore we can write,

$$\begin{aligned} V_s &= \left(\frac{4}{3}\right)\pi d^3 \\ &= \left(\frac{4}{3}\right)\pi (2r)^3 \\ &= \left(\frac{4}{3}\right)\pi 8r^3 \\ &= 8 \times \left(\frac{4}{3}\right)\pi r^3 \end{aligned}$$

Therefore, from equation (2.6);  $V_s = 8x \text{ --- (2.7)}$

Let us imagine filling that a container of volume  $V$  is being filled one by one with  $N$  molecules.

## Van der Waal's Gas Equation

For this process from the very beginning,

The volume available to the first molecule =  $V$

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

The volume available to the third molecule =  $V - 2V_s$

The volume available to the  $N^{th}$  molecule =  $V - (N - 1)V_s$

Therefore, average space available for each molecule

$$\begin{aligned}
 &= \frac{V + (V - V_s) + (V - 2V_s) + \dots + V - (N - 1)V_s}{N} \\
 &= \frac{NV}{N} - \frac{V_s}{N} [1 + 2 + 3 + \dots + (N - 1)] \\
 &= V - \frac{V_s(N-1)N}{2} \\
 &= V - \left(\frac{NV_s}{2}\right) + \left(\frac{V_s}{2}\right)
 \end{aligned}$$

As the number of molecules is very large,  $\frac{V_s}{2}$  can be neglected.

Therefore, average space available for each molecule

$$\begin{aligned}
 &= V - \left(\frac{NV_s}{2}\right) \\
 &= V - \left(\frac{N8x}{2}\right) \quad [\text{Since } V_s = 8x] \\
 &= V - 4(Nx) \\
 &= V - b
 \end{aligned}$$

Where,  $b = 4(Nx)$  ----- (2.8)

= Four times the actual volume of the molecules.

This is called the **co-volume** and depends on the nature of the gas.

Therefore, van der Waals argued that the factor  $V$  occurring in the equation for perfect gas should be replaced by  $V - b$  and  $P$  by  $P + \frac{a}{V^2}$

So, the equation of state after correction for both, size of the molecules and attraction between the molecules takes the following form ;

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ ----- (2.9)}$$

This is the required van der Waals equation of state for one mole of a gas.

[Here pressure term increases by the amount  $p = \frac{a}{V^2}$  and volume term reduces by the amount  $v = b$ .



Did you know ?

The van der Waal's equation is the second order approximation of the equation of state of a gas that works even when the density of gas is high!

**Ctrl+click** on this link <http://youtu.be/hFWWhPUDIhNY> to revise van der Waals equation for  $n$  moles of a gas:

Let us now analyse the van der Waal's gas equation in more detail.

### 2.3 Comparison of experimental curves

The van der Waal's equation of state is,

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

Or,

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

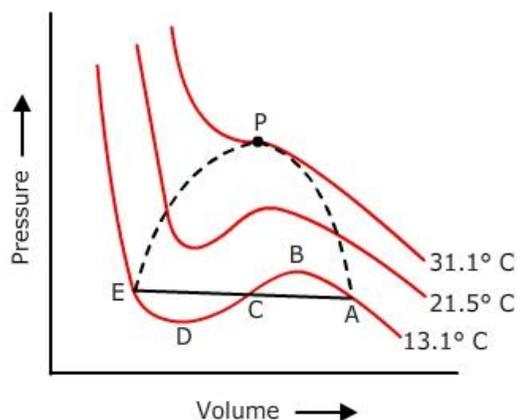
$$\text{Or, } PV^3 - (Pb + RT)V^2 - a(V - b) = 0 \text{ ----- (2.10)}$$

This is obviously a cubic in  $V$ . So, for a given value of temperature and pressure, volume will have three values.

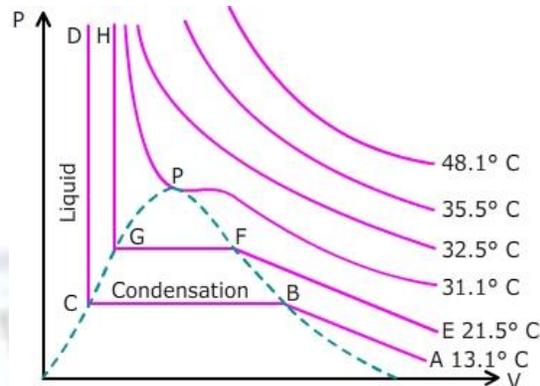
We see that for very large value of  $V$ ,  $P$  is small and in the limit  $P \rightarrow 0$ ,  $V \rightarrow \infty$ .

Again, when  $V$  is very small approaching  $b$ ,  $P$  tends to be  $\infty$ . Hence, the curve must have a concavity upward. Further,  $V$  cannot be less than  $b$  for;  $P$  would be negative which is physically impossible. With these points in view, the theoretical curves obtained are shown in Figure (2.3) along with experimental curves obtained by Andrews.

## Van der Waal's Gas Equation



**Figure 2.3a:**



**Figure 2.3b**

[Figure 2.3a: **Isotherms obeying Van der Waal's gas equation**

Figure

2.3b: **Isotherms of CO<sub>2</sub> from Andrew's experiment**]

The two sets of curve resemble apparently with a remarkable difference in one region. The horizontal part **BC** of Andrews's curves [Figure(2.3b) appears wavy in the theoretical curves [Figure(2.3a)].

### Explanation:

At temperature below  $T_c$ (critical temperature), we have maximum and minimum points on each isothermal. This enables us to get three real roots:  $V_1$ ,  $V_2$  and  $V_3$  for a single value of pressure when the pressure is around the vapor pressure. At the values away from vapor pressure, we have one real root and two imaginary. Figure (2.3a) shows that as the temperature increases, the three roots approaches each other and at  $T = T_c$ , all of them become the same. The maxima and minima points merge into one point which is the critical point.

This is not in agreement with the experimental curve for CO<sub>2</sub> as obtained by Andrews. However, the portion **AB** has been explained as due to super cooling of the vapours and the portion **ED** is due to super heating of the liquid. But the portion **BCD** cannot be explained because it shows decrease in volume with decrease in pressure which is not true in actual practice. At higher temperatures, however, both, theoretical and practical **PV** curves are similar. The portion **BCD** of the theoretical curve indicates that the volume should decrease as pressure decreases. This corresponds to a collapsible state and can never be realized in practice.

## 2.4 Values of critical constants

The equation of the locus of maxima and minima shown by the dashed curve in Figure (2.3a) can be obtained by putting  $(\frac{\delta P}{\delta V})_T$  equal to zero.

Hence, from the Van der Waal's gas equation,

## Van der Waal's Gas Equation

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

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

Or, 
$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \text{ --- (2.11)}$$

On differentiating this equation with respect to V and equating it to zero we will have,

$$\frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \text{ --- (2.12)}$$

These maxima and minima points merge into one point which is the critical point **P** at which  $T = T_c$ ,  $V = V_c$ ,  $P = P_c$ . Thus point **P** is the point of inflexion with no maxima and minima and hence, the second derivative of  $\frac{dP}{dV}$  should also vanish at the critical point.

i.e. we must have

$$\left(\frac{\delta^2 P}{\delta V^2}\right)_{T_c} = 0 \text{ --- (2.13)}$$

At the **critical point**,

From equation (2.11),

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \text{ --- (2.14)}$$

from equation (2.12),

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \text{ --- (2.15)}$$

using equation (2.13),

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \text{ --- (2.16)}$$

Dividing (2.15) by (2.16) we will get,

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

Or,

$$V_c = 3b \text{ --- (2.17)}$$

Substituting the value of  $V_c$  in equation (2.15), we get

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

$$T_c = \frac{8a}{27Rb} \text{ --- (2.18)}$$

## Van der Waal's Gas Equation

Substituting the values of  $V_c$  and  $T_c$  in equation (2.14), we get

$$P_c = \frac{8aR}{27Rb(3b-b)} - \frac{a}{(3b)^2}$$

$$P_c = \frac{a}{27b^2} \text{-----(2.19)}$$

Thus we have obtained the values of critical volume, critical temperature and critical pressure in terms of van Der Waal's constants.

Let us solve the following problem using ideal gas equation 

**Problem:** The van der Waal's constants  $a$  and  $b$  for one gram molecule of Hydrogen gas are  $a=0.245 \text{ atm}\cdot\text{litre}^2$  and  $b=2.67 \times 10^{-2} \text{ litre}\cdot\text{mole}^{-1}$ . Calculate the critical temperature.

**Solution:** From equation 2.18,  $T_c = \frac{8a}{27Rb}$

Given,  $a=0.245 \times 76 \times 13.6 \times 980 \times 10^6 \text{ dynes}\cdot\text{cm}^4\cdot\text{mole}^{-2}$

$b=2.67 \times 10^{-2} \times 10^3 \text{ cm}^3\cdot\text{mole}^{-1}$

$R=8.31 \times 10^7 \text{ erg}\cdot\text{mole}^{-1}\cdot\text{K}$

Substituting these values in the expression for  $T_c$ ,

We get,  $T_c=33.14 \text{ K}$

## Van der Waal's Gas Equation

### Determination of van Der Waal's constants:

From equations (2.17),(2.18) and (2.19) we have,

$$V_c = 3b$$

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

and  $P_c = \frac{a}{27b^2}$

### Determination of a:

Squaring eq.(2.18) and dividing it by eq.(2.19) we get,

$$\frac{T_c^2}{P_c} = \frac{64a^2 \times 27b^2}{(27)^2 R^2 b^2 \times a}$$
$$= \frac{64a}{27R^2}$$

$$a = \left(\frac{27R^2}{64}\right) \left(\frac{T_c^2}{P_c}\right) \text{ --- (2.20)}$$

### Determination of b:

Divide eq.(2.18) by eq.(2.19) and get,

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

$$b = \frac{RT_c}{8P_c} \text{ --- (2.21)}$$

The following table (2.1) shows the values of van der Waal's gas constants for some gases:

Gas	a J m <sup>3</sup> Kilomole <sup>-2</sup>	b m <sup>3</sup> Kilomole <sup>-1</sup>
He	3.44x 10 <sup>3</sup>	0.0234

## Van der Waal's Gas Equation

H <sub>2</sub>	24.8	0.0266
O <sub>2</sub>	138	0.0318
CO <sub>2</sub>	366	0.0429

**Table 2.1**

**Critical Coefficient (CC):** The ratio  $\frac{RT_c}{P_c V_c}$  is called as the critical coefficient. Substituting the values of  $T_c$ ,  $P_c$  and  $V_c$  in the expression for critical coefficient,

i.e. 
$$CC = \frac{RT_c}{P_c V_c}$$

Or, 
$$CC = \frac{R \frac{8a}{27Rb}}{\left(\frac{a}{27b^2}\right)^3 b} = \frac{8}{3} = \mathbf{2.667}$$

This value of  $CC$  is same for all the gases.

The values of critical coefficient of some gases are shown in the following table 2.2.

GAS	$RT_c/P_c V_c$
He	3.13
H <sub>2</sub>	3.28
N <sub>2</sub>	3.42
O <sub>2</sub>	3.42

## Van der Waal's Gas Equation

CO <sub>2</sub>	3.48
-----------------	------

**Table 2.2**

### 2.5 Reduced equation of state

van der Waal's gas equation can be modified by introducing reduced parameters namely, the reduced pressure  $P_r$ , reduced volume  $V_r$  and reduced temperature  $T_r$ . A reduced parameter is defined by the ratio of actual value and the corresponding critical value. Thus we can write,

$$\frac{P}{P_c} = P_r$$

$$\frac{V}{V_c} = V_r$$

$$\frac{T}{T_c} = T_r$$

Therefore,  $P = P_c P_r$  -----(2.22a)

$V = V_c V_r$  -----(2.22b)

$T = T_c T_r$  -----(2.22c)

Substituting these values of  $P$ ,  $V$  and  $T$  in the following van der Waal's equation of state,

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

We get,

$$\left(P_c P_r + \frac{a}{(V_c V_r)^2}\right)(V_c V_r - b) = R T_c T_r$$
 -----(2.23)

From equations (2.17), (2.18), (2.19), substituting the values of  $V_c$ ,  $T_c$  and  $P_c$  in equation 2.23 we get,

$$\left\{\frac{a}{27b^2} P_r + \frac{a}{(3bV_r)^2}\right\}(3bV_r - b) = R \frac{8a}{27Rb} T_r$$

Hence,  $\left\{\frac{a}{27b^2} P_r + \frac{a}{(3bV_r)^2}\right\}(3bV_r - b) = \frac{8a}{27b} T_r$

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r$$
 -----(2.24)

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \left(\frac{8}{3}\right)T_r$$

This is reduced equation of state free from van der Waal's constants

**a** and **b**.

### 2.6 Law of corresponding states

If any two of the reduced quantities are equal for two gases, the third is bound to be the same. This is known as the 'law of corresponding states'.

Thus, if any two gases have same reduced parameters, they are said to be in corresponding states. According to van der Waal, the theorem of corresponding states indicates that all fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor and all deviate from ideal gas behavior to about the same degree.



**Did you know ?**

**Negative compressibility means when you try to compress a gas it gets bigger!!**

#### Explanation:

The usefulness of the reduced variables can be investigated by seeing how the compressibility factor  $Z = \frac{PV}{RT}$  varies with the reduced pressure. At the critical point, where  $P_r$  and  $T_r$  are both equal to **1**, gases do have approximately the same value for  $Z$ . It is also approximately the same for different gases at other values of the reduced variables. These results lead to an approximate generalization known as the law of corresponding states. The law of corresponding states can be expressed in various ways. One says that gases in states with the same values of  $T_r$  and  $P_r$  deviate from ideality to the same extent, i.e. the values of  $Z = \frac{PV}{RT}$  will be approximately the same. The variables in the expression for  $Z$  can be replaced by  $P = P_r P_c$ ,  $V = V_r V_c$  and  $T = T_r T_c$  to give  $Z = \frac{P_r V_r}{T_r} \times \frac{P_c V_c}{R T_c}$ . Since  $\frac{P_c V_c}{R T_c}$  at the same  $T_r$  and  $P_r$  requires  $V_r$  to be the same for different gases. This leads to a second expression for the law of corresponding states: **different gases at the same reduced pressure and temperature have the same reduced volume.**

### 2.7 Limitations of van der Waal's gas equation

---

## Van der Waal's Gas Equation

---

### Following are the limitations:

- (i) The equation becomes invalid at very high pressures and low temperatures near the critical point.
- (ii) The values of van der Waal's constants, **a** and **b**, are temperature dependent and hence cannot be regarded as absolute constants.
- (iii) Theoretical values of the critical constants do not agree well with the experimental values. As for example the value of **V<sub>c</sub>** is equal to **2b** (experimentally), not **3b** (theoretically). Further the value of the critical coefficient is not **2.67** for all the gases but varies from gas to gas as shown in table 2.1.
- (iv) Law of corresponding state is only partially valid.

## 2.8 Virial equation

Based on the experimental facts, an empirical relation was suggested by K. Onnes of the form:

$$PV = A + BP + CP^2 + \dots \quad (2.26)$$

In this equation, A, B, C etc. are called **Virial coefficients** and can be made temperature dependent. A, B, C are constants for a given temperature depending on the nature of the gas. These coefficients are in the decreasing order of magnitude i.e. A>B>C and so on. As the constant C is always positive but very small, so this can be neglected.

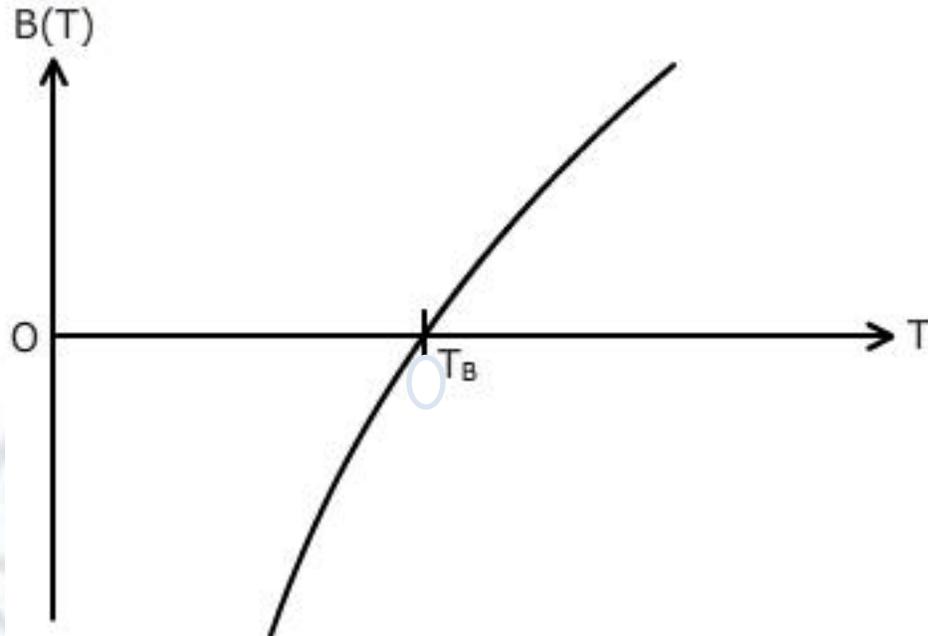
At low pressure, when  $P \rightarrow 0$ , the first Virial coefficient A will be equal to RT.

$$A = RT \quad (2.27)$$

The temperature at which the Virial coefficient B becomes zero, is called the 'Boyle's temperature' (since, it is the temperature at which Boyle's law is obeyed).

At very low temperature, the constant B has a negative value. As temperature increases, it shows a gradual rise through zero (at the Boyle's temperature) and becomes positive for all gases [fig(2.4)].

## Van der Waal's Gas Equation



**Figure 2.4:** Graph between second Virial coefficient and temperature, T

At the Boyle's temperature ( $B=0$ ), the Van Der Waal's equation reduces to the ideal gas equation,

$$PV = A = RT \text{ ----- (2.28)}$$

$$\frac{\delta(PV)}{\delta P} = B = 0 \text{ ----- (2.29)}$$

### Expression for Boyle's temperature:

From Van der Waal's equation of state

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

Solving this equation, we get

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Or, 
$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \text{ ----- (2.30)}$$

we can write, 
$$V = \frac{RT}{P}$$

Putting the value of V in equation (2.29) we get,

$$PV = RT + Pb - \frac{a}{RT}P + \frac{ab}{R^2T^2}P^2$$

or, 
$$= RT + \left(b - \frac{a}{RT}\right)P + \frac{ab}{R^2T^2}P^2 \text{ ----- (2.31)}$$

Comparing this equation with equation (2.26), we have,

## Van der Waal's Gas Equation

$$A = RT \text{ ----- (2.32a)}$$

$$B = b - \left(\frac{a}{RT}\right) \text{ ----- (2.32b)}$$

$$C = \frac{ab}{R^2T^2} \text{ ----- (2.32c)}$$

At Boyle' temperature,  $B = 0$ ,  $T = T_B$ .

Therefore from equation (2.32b),

$$b - \frac{a}{RT_B} = 0$$

$$\text{or, } \frac{a}{RT_B} = b$$

$$\text{or, } T_B = \frac{b}{RT}$$

$$\text{or, } T_B = \frac{a}{Rb} \text{ ----- (2.33)}$$

Below the Boyle's temperature ( $T_B$ ), the gases are highly compressible showing the existence of inter-molecular attraction. Beyond the Boyle's temperature Boyle's law is obeyed and inter-molecular attraction is less significant.

### 2.9 Summary

- ✓ van der Waal has modified the ideal gas equation  $P V = R T$  for one mole of a gas as,  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$
- ✓ The term  $\frac{a}{V^2}$  arises due to inter molecular forces between the molecules of a real gas and is called as the cohesive pressure.
- ✓ The term  $b$ , called as the co-volume, arises from the definite size of the molecules.
- ✓ Critical temperature ( $T_C$ ) of a gas is defined as the temperature above which it cannot be liquefied howsoever large the pressure may be.
- ✓ The minimum pressure required to liquefy a gas at critical temperature is termed as critical pressure ( $P_C$ ).
- ✓ The volume corresponding to critical temperature and critical pressure is known as critical volume ( $V_C$ ).
- ✓ The quantity  $\frac{RT_C}{P_C V_C}$  is referred as critical coefficient of a gas.
- ✓ Critical constants of a Van der Waal's gas are given by the following relations;
- ✓  $V_C = 3b, \quad P_C = \frac{a}{27b^2}, \quad T_C = \frac{8a}{27Rb}$

## Van der Waal's Gas Equation

- ✓ Reduced equation of state, free from Van der Waal's constants **a** and **b** is given by,  
$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}T_r$$
- ✓ Two gases are said to be in corresponding states if they have same reduced parameters.

### 2.10 Exercise

#### I. Fill in the blanks:

1. The isotherms passing through critical point is called \_\_\_\_\_.
2. The compressibility factor of the Van der Waal's gas is higher than that for \_\_\_\_\_.
3. Van der Waal's equation reduces to \_\_\_\_\_ at \_\_\_\_\_ pressure and \_\_\_\_\_ temperature.
4. A part of Van der Waal's isotherms consists of \_\_\_\_\_ like pattern.
5. Reduced parameters are \_\_\_\_\_.

#### II. State true /false for each of the following statements:

1. Critical coefficient  $\frac{RT_c}{P_c V_c}$  is same for all the gases.
2. Intermolecular attraction does not play an important role in case of real gases.
3. No liquefaction can occur above critical temperature how high the pressure may be after being released.
4. Virial coefficients A, B, C, D etc. depend only on the temperature and mass of the gas.

#### III. Answer the following:

- 1) Is critical coefficient  $\frac{RT_c}{P_c V_c}$  same for all the gases?
- 2) Which equation for a real gas is free from van der Waal's constants? Write an expression for it.
- 3) Using the values of **a** and **b** listed in table 2.2, find out the temperature and pressure at which each of the following gases must be liquefied by applying pressure alone:  
**H<sub>2</sub>, He, O<sub>2</sub>, CO<sub>2</sub>**

### 2.11 Glossary

**Critical point:** This is a point on the isothermal at critical temperature at which the change of state from gaseous to liquid takes place under at critical volume and critical pressure.

---

## Van der Waal's Gas Equation

---

**Molecular range:** The range in which a molecule experiences the force exerted by another molecule is called as the molecular range of the latter molecule.

**Intermolecular attraction:** The force of attraction between the molecules of a gas is called as the intermolecular attraction.

**Co pressure & co volume:** Kinetic theory of gases doesn't allow co pressure and co volume to exist as the former is due to the intermolecular attraction and the latter is due to the finite size of the molecules but they play important role in the case of real gases.

### 2.12 References

**Book cited:**

1. Thermal Physics by S. C. Garg, R. M. Bansal and C. K. Ghosh (Tata McGraw Hill Education Private Limited, 1993)
2. Concepts in Thermal Physics: by S. J. Blundell and K. M. Blundell, (Oxford University Press, 2006).
3. Statistical and Thermal physics by S. Loknathan and R.S. Gambhir (Prentice-Hall of india, 1991)
4. Thermodynamics, Kinetic Theory and Statistical Thermodynamics by Francis W. Sears and Gerhard L. Salinger. (Narosa Publishing House 1986)
5. Heat and Thermodynamics by Richard H. Dittman, Mark W. Zeemansky. (Tata McGraw Hill Education Private Limited, 2007)

**Further readings**

1. Thermodynamics by Enrico Fermi (Courier Dover Publications, 1956)
2. A Treatise on Heat: Including Kinetic Theory of Gases, Thermodynamics and Recent Advances in Statistical Thermodynamics by Meghnad Saha, B. N. Srivastava (Indian Press, 1958).
3. Thermal physics by Charles Kittle and Herbert Kroe bymer.