CHAPTER III

REAL GASES

III.1. Ideal Gases and Real Gases

Careful experiments have revealed that the gas laws such as Boyle's Law, Charles' Law, etc are only approximately obeyed by different gases. Even at ordinary pressures, the deviations from the relation, $Pv = nRT$, are appreciable. Moreover, the deviations are different in different gases. It is only at very low pressures and at relatively high temperatures the gases tend to behave in accordance with the laws. The equation, $Pv = nRT$, is hence applicable for approximate calculations and is insufficient for accurate measurement. A gas, really a hypothetical one, which follows the gas-laws rigorously under all circumstances, has been named an *ideal gas* or a *perfect gas* as distinct from the *real gases* with which we carry out our experiments.

III.2. Deviations of Real Gases from Ideal Behaviour

The departure from ideal behaviour in real gases has been observed in different types of investigations. Some of these are mentioned here.

(*a*) In accordance with the Boyle's Law, $PV = $ constant, at a given temperature, the pressure of a gas plotted against its volume would give a rectangular hyperbola. At fairly high temperatures, the P-V isothermals are found to be hyperbolic, though-not exactly coinciding with the rectangular ones theoretically predicted. But at temperatures below the critical ones, the P-V curves are far from hyperbolic and really exhibit two discontinuities. The historically famous experiments of Andrews on the study of relations for carbon dioxide are represented in Fig. I.13, which indicates the wide deviations from the Boyle's Law. Similar deviations are observed with other gases too. The failure of the relation, $Pv = nRT$ to predict the change of state is its major inadequacy.

(*b*) The coefficient of thermal expansion (a) of a gas is given by,

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

Since

$$v = \frac{nR}{P}.T, \text{ hence } \left(\frac{\partial v}{\partial T}\right)_P = \frac{nR}{P}$$

or

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\cdot\frac{nR}{P} = \frac{1}{T} \qquad .....(III.1)$$

This means that α will be independent of the nature of the gas and will be a function of temperature only. But, the α-values for different gases are found to be different, contrary to the expectations from the- gas-laws. The coefficients of expansion for hydrogen and CO_2. are 2.78 × 10^{-7} and 3.49 × 10^{-7} respectively at. 0^0C and 500 atm.

(*c*) The coefficient of compressibility (β) of a gas is given by

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

Since

$$v = \frac{nRT}{P}; \text{ hence } \left(\frac{\partial v}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

or

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{-nRT}{P^2}\right) = \frac{1}{P} \qquad ....(III.2)$$

That is, β should be a function of pressure only and should be the same, for all gases. Experimentally the coefficient of compressibility has been found to be an individualistic property.

Regnault and, later on, Amagat made extensive studies on this aspect. At a given temperature, Pv should remain constant. Hence Pv plotted against P should be a straight line parallel to the P-axis. But the experimental Pv–P curves are of the nature as shown in Fig. III.1 and III.2.

At very low pressures (below 1 atmosphere), the plots of Pv versus P is linear but different for different gases and not parallel to the P-axis (Fig. III.1). For wide high ranges of pressure isothermal Pv-P curves are given in Fig. III.2. In the case of CO_2, O_2, CH_4, etc. the Pv-value first diminishes, reaches a minimum and then increases, forming a cup, with increase in pressure. In the case of hydrogen, the Pv-value begins to increase continuously from the zero-pressure. Hydrogen however is not an exception. If the temperature be made sufficiently low, hydrogen also would exhibit identical behaviour.
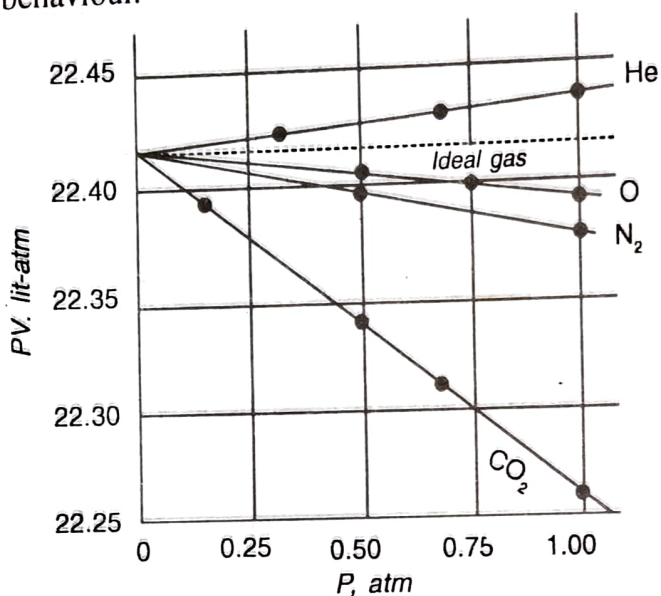

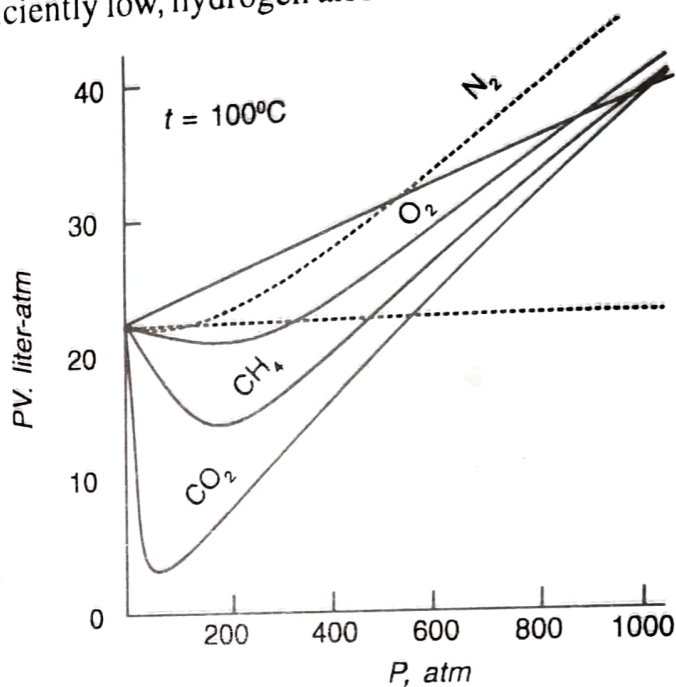| Fig. III.1	Fig. III.2
Pv-P isothermals at low pressures	Pv-P isothermals at higher pressures

It is also interesting to note the variation of the PV-P relations with temperature. In Fig. III.3 are plotted the PV-P curves of carbon dioxide at different temperatures, which are also typical of
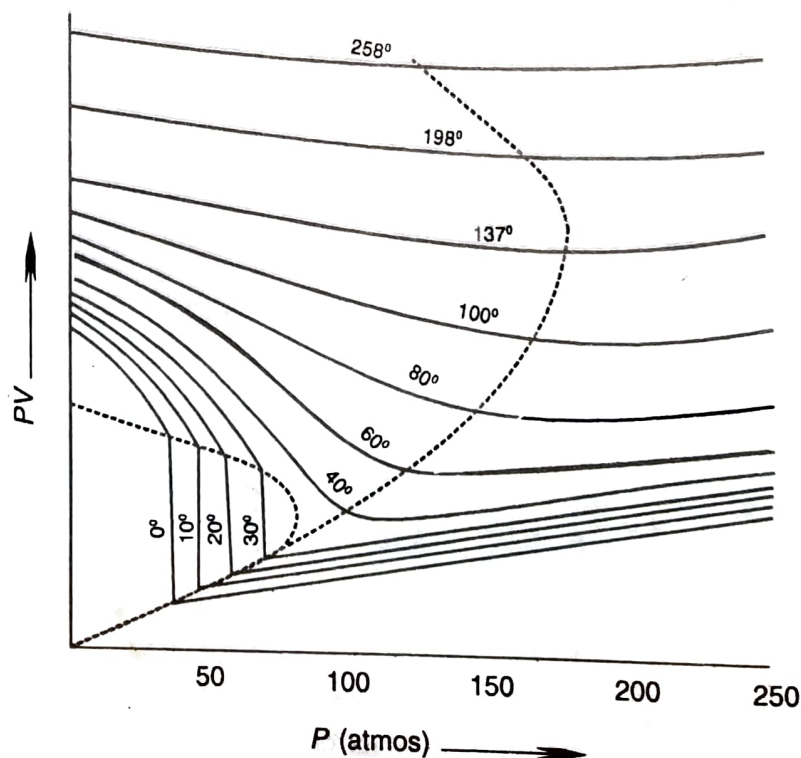

Fig. III.3. PV-P isothermals of carbon dioxide

other gases. It is seen that the extent of higher compressibility decreases with rise in temperature. As the temperature increases, the troughs of the curves become shallower and flattened. The minimal points of these curves lie approximately on a parabola, shown by the dotted line. At relatively high temperatures, the minimals gradually approach the PV-axis.

Boyle Point : There exists for every gas a characteristic temperature, where the curve (PV-P) runs sensibly parallel to P-axis from zero pressure to moderate values of pressure (P). It means that at this temperature, the value of PV remains constant for an appreciable range of pressure, i.e., Boyle's Law is obeyed. This temperature is known as the *Boyle temperature* or *Boyle Point* of the gas, T_B. Mathematically we may express the Boyle point as the temperature where

$$\frac{\partial(PV)}{\partial P} = 0, \text{ when } P \to 0.$$

The Boyle temperature for a few gases are given below.

TABLE. BOYLE TEMPERATURES

Gas	He	H_2	N_2	CH_4	NH_3
$T_B \, ^\circ K$	24	117	332	498	860

(*d*) The cooling due to Joule-Thomson effect is another evidence of the deviation of the real gases from the ideal ones in their behaviour. According to the kinetic theory, the energy of a given quantity of gas depends on the temperature only and is independent of the pressure or volume. But in fact, when a gas is allowed through a fine orifice or porous plug from a high pressure to vacuum (say), the temperature drops down generally. Under certain circumstances, there may also be temperature-rise. This is obviously contrary to the expectations from the theory.

III. 3. Reasons for Deviations

The gas laws have been derived from the postulates of the kinetic theory. Now that these laws are found to be only approximate, it is obvious that some of the postulates of the theory are inadequate and need modification. The deviations from the Ideal laws are primarily due to two factors which were not taken account of in the theory :

     (*i*) the molecules were considered as point masses, practically having no volume
    (*ii*) the existence of the forces of attraction between the molecules were ignored.

In fact, in a real gas, the volume of the bodies of the molecules may be quite appreciable even at ordinary pressure,

To *illustrate* : At N.T.P. one gm-mole of a gas, *i.e.*, 6.02×10^{23} molecules, occupy a volume, of 22400 c.c.

The diameter of a molecule may be taken as of the order 2×10^{-8} cm. So that the effective opace occupied physically by a molecule is 4/3. $\pi \, (2 \times 10^{-8})^3 \approx 3.3 \times 10^{-23}$ c.c.

Hence, the space taken up by the molecules = $6.02 \times 10^{23} \times 3.3 \times 10^{-23} = 20.46$ c.c. That is, at N.T.P. the space occupied by the molecules themselves is nearly $\approx \frac{1}{1000}$ of the volume of the gas.

If the pressure be increased to say 10 atmospheres, the volume of the gas would be approximately 2240 c.c. Then the fraction of this volume occupied by the molecule& physically = $20.46/2240 \approx 1/100$, *i.e.* nearly one percent of the volume, which is by no means negligible.

Again, in the kinetic theory it has been presumed that no inter-molecular force exists and as such the collisions are perfectly elastic, the energy is all kinetic. But, in fact, there does exist a force of attraction between the 'molecules. On cooling, the gases are converted into liquids when the molecules exhibit appreciable cohesion. This indicates that a similar attraction exists between the molecules in the gas-phase also. A more clear evidence comes from the experiments of Joule and

Thomson. When a stream of gas is allowed to pass through a porous plug of cotton or earthen-ware, there is a fall of temperature called Joule-Thomson effect. The only explanation is that the outgoing molecules have to overcome the attraction of molecules from behind and thus have to perform work. The energy thus spent causes the lowering in temperature. In an ideal gas, there is no attractive force between the molecules and hence no cooling would be expected.

Due to inter-molecular attractions, the number of impacts on the wall is restrained, *i.e.*, the number of collisions with the wall would have been greater if there were no attractive force on the colliding molecules from behind. In consequence the pressure exerted on the wall is less. Thus the pressure of one atmosphere actually exerted by oxygen, at 0^0C, would be about $(1+0.0025)$ atmospheres had it behaved as an ideal one.

It is only at very low pressures when the gas-volume is quite large the space occupied by the molecules themselves becomes negligible comparatively; and because the molecules are then far apart, the force of mutual attraction becomes too feeble. So, at very low pressures, the real gases would satisfy the postulates of the kinetic theory. That is why real gases are observed to obey $Pv = nRT$ relation at very low pressures. The expression $Pv = nRT$ is therefore a *limiting law only*.

III.4. Equations of State for Real Gases

Many attempts have been made during the last hundred years to modify the ideal gas equation and change it into a form which would represent P-V-T relations of real gasses. Corrections had to be introduced both for the pressure as well as the volume and often two or more constants entered into the form. These equations are derived on empirical or semi-empirical basis. The forms of some of these equations are :

van der Waal's $\quad : \left(P + \dfrac{a}{V^2}\right)(V - b) = RT$

Dieterici $\quad : P(V-b) = RTe^{\frac{-a}{RTV}}$

Berthelot $\quad : \left(P + \dfrac{a}{TV^2}\right)(V - b) = RT$

Clausius $\quad : \left(P + \dfrac{a}{T(V+c)^2}\right)(V - b) = RT$

Keyes $\quad : P = \dfrac{RT}{V - \beta e^{-a/v}} - \dfrac{A}{(V+l)^2}$

Beattie-Bridgeman $\quad : P = \dfrac{RT(1 - \epsilon)}{V^2}(V + B) - \dfrac{A}{V^3}$

Saha & Bose $\quad : P = -\dfrac{RT}{2b} \cdot \log\left(1 - \dfrac{2d}{v}\right)e^{\frac{-a}{RTV}}$

Wohl $\quad : P = -\dfrac{RT}{V - b} - \dfrac{a}{V(V - b)} + \dfrac{c}{V^3}$

Kammerling Onnes $\quad : PV = RT\left(1 + \dfrac{B}{V} + \dfrac{C}{V^2} + ...\right)$

etc.   etc

We shall briefly discuss here a few of these equations. One of the earliest and more widely employed equation is that of van der Waals.

III.5. van der waals' Equation

To rectify the error for neglecting intermolecular attraction and the space occupied by the molecules themselves, van der Waals introduced two correction terms in the ideal gas equation, one for the pressure and the other for the volume.

Due to intermolecular attraction, the number of impacts a molecule would make on the wall would be less than what it could if it were free from attraction. This is true for each molecule. As a result the observed pressure (P) will be less than the pressure (P_0) the gas would have if it were ideal and there were no intermolecular attraction. If the decrease in pressure be denoted by p', then the ideal pressure would be ($P + p'$).

It is also easily seen that the space available for the motion of the molecules is less than the volume the gas occupies. Suppose a molecule is moving at right angles to the opposite walls (Fig. III.4) of the containing vessel whose distance is l. If the molecules were point masses, the distance to be travelled by a molecule between two successive impacts on the same wall would be $2l$. But the molecules have dimensions, and therefore the distance actually covered by the molecules is ($2l-\sigma$), where a is the diameter of the molecule. This is true for all molecules. As a result, the space for free motion of the molecules would be measurably reduced. Suppose v' denotes the reduction in space, then the true volume for motion of the molecules would be $V - v'$ where V is the volume of the gas. We may then write the equation of state, corrected for the volume and the pressure, of a real gas in the form
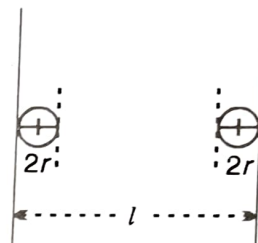

Fig. III.4

$$(P+p')(V-v') = RT \qquad \text{(for 1 gm-mole)}$$

Pressure correction, p'. During collision a molecule changes its velocity. When it approaches another molecule, there is a drop in velocity. This is followed by an acceleration on separation. Every collision therefore causes a certain loss of time τ. This time τ is a measure of the inter-molecular attraction and is therefore also a measure of p', the inward pressure.

Let us imagine that the molecule would strike the wall z times per second if there were no inter-molecular attraction. During its journey to make z bombard on the wall, suppose the molecule makes x inter-molecular collisions. The x collisions will take up $x\tau$ seconds. Now, because of the existence of inter-molecular attraction, the time needed for making z bombardments on the wall would be $1+x\tau$ seconds. That is, in 1 second it would make $\dfrac{z}{1 + x\tau}$ bombardments. The pressure is proportional to the rate of bombardments. If P is the observed pressure and P_0 the ideal pressure (the pressure corrected for inter-molecular attraction), then,

$$\frac{P_0}{P} = 1 + x\tau$$

i.e.,
$$P_0 = P(1 + x\tau) = P + Px\tau$$

Now, x, the number of molecules which the particular molecule would collide with, is proportional to its own velocity u, and the density of the gas, ρ. That is,

$$x = k'u\rho \qquad \text{(where } k'\text{=constant)}$$

So,
$$Px\tau = Pk'u\rho\tau$$

$$\approx \frac{1}{3}\cdot\frac{mN_0c^2}{V}\cdot k'u\rho\tau \qquad \left(P \approx \frac{1}{3}mN_0c^2 / V\right)$$

$$=\left[\frac{1}{3}(mN_0)^2 c^2 uk'\tau\right]\frac{1}{V^2}; \qquad \text{since } \rho = \frac{mN_0}{V}$$

It is assumed that for a definite amount of a given gas, the quantity within the parenthesis remains almost constant, and is substituted by a.

So,
$$P x \tau = \frac{a}{V^2}$$

There is no evident justification for this assumption but nevertheless the value of 'a' experimentally determined shows sensible constancy unless the temperature is widely varied. This assumption is indeed a weak point in van der Waals' treatment. The pressure of the gas, corrected for molecular attraction,

$$P_0 = P + P x \tau = P + \frac{a}{V^2}$$

The quantity a $\frac{a}{V^2}$ is the additional amount of pressure, (p') to be added to the observed pressure P. This is often called the *cohesive pressure or internal pressure*.

Volume correction, v'. Consider a gm-mol of a gas occupying a volume V. In deducing the ideal gas equation, the molecules were regarded as point-masses and hence the entire volume V was available for movement of each molecule. Since the molecules have definite size, the volume or space available for molecules to move about in real gases would be less. Assuming the molecules to be spherical, suppose r is the radius and σ $(= 2r)$ be the diameter of a molecule of the gas, so that the volume of the body of each molecule, $b_1 = \frac{4}{3} \pi r^3$.
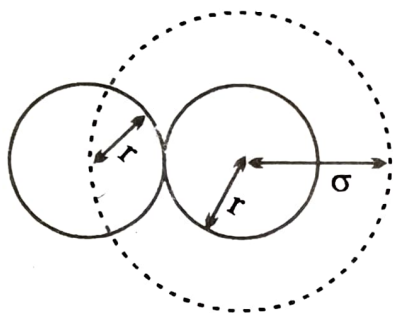

Fig. III.5. Excluded volume for a pair of molecules

When two molecules encounter each other, the distance between the centres of the two molecules would be σ. These cannot approach closer than this. In consequence, as shown in the figure, a space indicated by the dashed circle having a diameter 2σ, will be unavailable to the pair of colliding molecules. This space, often called 'excluded volume for the pair of molecules is $\frac{4}{3} \pi \sigma^3$.

Then, the excluded volume for each molecule, $\beta' = \frac{2}{3} \pi \sigma^3$. But the volume of the body of each molecule; $b_1 = \frac{4}{3} \pi r^3 = \frac{1}{6} \pi \sigma^3$.

hence,
$$\beta' = 4 b_1.$$

For a gm-mol of the gas, such excluded volume will be, $4 N_0 b_1 = b$ (say), which is a constant.

The 'volume correction v'' is thus b, which is equal to four times the actual volume of the bodies of the molecules. The observed volume should therefore be reduced by this amount (b) in computing the pressure of the gas. The volume V should be replaced by $(V-b)$.

The equation of state, corrected for the two factors, takes the form,

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \qquad \text{(for 1 gm-mol)} \qquad \text{....(III.3)}$$

This is known as van der Waals' equation.

If n gm-mols of gas be present in volume v, the volume of one gm-mol would be v/n. So, we have,

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

or
$$\left(P + \frac{n^2 a}{v^2} \right) (v - nb) = nRT \qquad \text{....(III.4)}$$

The van der Waals' constants, a and b are different for different gases. 'a' is expressed in atm-litre^2/mole^2 and 'b' is expressed in litre/mole units.

These can be evaluated from a knowledge of the pressure coefficient, $\beta' = \dfrac{1}{P}\left(\dfrac{\partial P}{\partial T}\right)_v$, for, from van der Waal's equation

$$\frac{a}{V^2} = T.P.\left(\beta' - \frac{1}{T}\right) \text{ and } b = V - \frac{R}{\beta' P}$$

The values of a and b for some gases are given here.

Gas	H_2	O_2	N_2	CO_2	NH_3	CH_4	A	He
a	0.244	1.36	1.39	3.59	4.17	2.25	1.35	0.034
b	0.027	0.032	0.039	0.043	0.037	0.043	0.032	0.024

The values of both 'a' and 'b' are actually found to vary with temperature and volume at which they are measured, With rise of temperature, the value of a diminishes, i.e., the attractive forces tend to decrease. The value of 'b' also decreases slightly with rise in temperature.

III.6. Validity of van der Waals' equation

A critical examination of the van der Waals' equation may now be made to ascertain to what extent it corresponds to the experimental observations.

(a) With knowledge of 'a' and 'b' for a given gas, its P-V isothermals are plotted at different temperatures (T) from the equation. These isothermals are then compared with the experimental P-V curves (Andrews curves). These are shown in Fig. 111.6. for CO_2; the bold lines represent the theoretical curves and the broken ones the experimental curves.
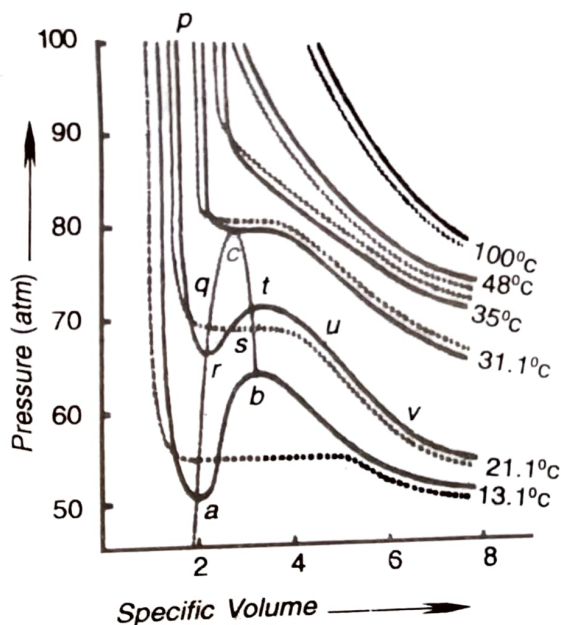
It would be readily seen that at high temperatures, the theoretical and the experimental curves coincide and the van der Waals' equation is satisfactory. But at low temperatures, there is considerable divergence between the theoretical and the experimental curves, especially in the region where liquid and gas coexist. The van der Waals' curves at low temperatures show minima and maxima, where as the experiments indicate a plateau.

Let us examine one such curve, say at 21.1°C. as represented by pqrstuv. The liquid range pq as also the gaseous range uv practically follow the experimental curve. But the portion qrstu remarkably differs from the experimental straight path qsu, where liquid and gas are present together. In fact, the system is supposed to have three volumes at the same pressure, the equation being a cubic one. [The portion qr and ut may sometimes be realised by careful superheating or 'super. cooling. But the portion rst where the curve rises from the minimum to the maximum point, that is, volumes would increase with increase in pressure, can never be realised experimentally. The equation therefore fails to represent the behaviour of gases.

Fig. III.6. P-V. isothermals of CO_2 (Dotted lines experimental ; bold lines theoretical)

With increase in temperature, the maxima and the minima of the curves come closer and closer. And at the critical isothermal, the maxima and the minima actually coalesce at the point C, which is really the critical state of the substance. Above this temperature (T_c), the maxima and the minima are not observed,

But inspite of this anomaly, van der Waals' equation is decidedly an improvement over the ideal equation of state as will be borne out from the observed and calculated values of pressure (Table A) and PV-values (Table B).

TABLE A (Temp. 100°C)

Gas	Pressure observed	Pressure calculated from			
		ideal eqn.	deviatio	van der Waals	deviation
Hydrogen	75	72.3	−3.6%	75.7	+ 0.9%
	100	95.0	−5.0%	100.8	+ 0.8%
Carbon dioxide	75	9 3	+17.3%	732	−2.3%
	100	133.5	+33.5%	95.8	−4.2%

TABLE B (Ethylene at 20°C)

Pressure (atm.)	PV (arbitrary units)	
	obs.	van der Waals
1	1.0	1.0
32	0..914	0.895
74	0.420	0.384
110	0.454	0.456
233	0.807	0.805
330	1.067	1.067

(b) At the critical point C, the maximum and the minimum points coalesce, it is thus a point of inflexion. As such the first differential $\left(\dfrac{dP}{dV}\right)_T$ and the second differential $\left(\dfrac{d^2P}{dV^2}\right)_T$ would both be zero.

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

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

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

At the critical point, $T = T_c$, when both differentials are zero. Hence,

$$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \qquad \qquad \ldots (i)$$

$$\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \qquad \qquad \ldots (ii)$$

Dividing (i) by (ii) $\dfrac{V_c-b}{2} = \dfrac{V_c}{3}$,   or $V_c = 3b$ $\qquad \ldots (iii)$

Substituting (iii) in (i) $T_c = \dfrac{2a(V_c-b)^2}{RV_c^3}$, or $T_c = \dfrac{8a}{27Rb}$

So, $P_c = \dfrac{RT_c}{V_c-b} - \dfrac{a}{V_c^2} = \dfrac{8a}{27b} \cdot \dfrac{1}{(3b-b)} - \dfrac{a}{9b^2}$, or $P_c = \dfrac{a}{27b^2}$

Thus, for a van der Waals' gas, the critical constants are given by,

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb} \qquad \text{... (III.5)}$$

It can also be shown that $RT_c/P_c V_c$, often called the 'critical coefficient' would be a constant.

$$\frac{RT_c}{P_c V_c} = \frac{8a}{27b} \times \frac{27b^2}{a} \times \frac{1}{3b} = \frac{8}{3} = 2.66 \qquad \text{... (III.6)}$$

From eqn. III. 5, the van der Waals' constants may be expressed in terms of critical constants.

$$\left.\begin{array}{ll} a = 3P_c V_c^2 = (9/8)RT_c V_c & b = \dfrac{1}{3}V_c \\[3mm] a = \dfrac{27}{64} \cdot \dfrac{R^2 T_c^2}{P_c} & b = \dfrac{1}{8}\dfrac{RT_c}{P_c} \end{array}\right\} \qquad \text{... (III.7)}$$

The van der Waals equation thus predicts that
(i) the ratio V_c/b should be equal to 3.00
and (ii) the critical coefficient $RT_c/P_c V_c$ should be equal to 2.66.

The critical constants are determined by methods mentioned earlier (Sec 1.14). The value of b is obtained from a study of P–V isothermals at different high temperatures. The experimental values for V_c/b and also for $RT_c/P_c V_c$ are given in table C and D, for some gases.

The ratio V_c/b tends approximately to a value 2.00 instead of 3.00, whereas the value of $RT_c/P_c V_c$ tends to a constant value of 3.6 instead of 2.66. The van der Waals' equation is thus quantitatively not quite accurate.

TABLE C

Gas	A	N_2	H_2	CO_2	O_2	He
V_c/b	1.41	1.76	2.80	1.86	1.46	2.50

TABLE D

Substance	$RT_c/P_c V_c$	Substance	$RT_c/P_c V_c$
Helium	3.084	Methane	3.47
Argon	3.424	Ethane	3.64
Neon	3.086	Benzene	3.75
Hydrogen	3.06	Pentane	3.76
Oxygen	3.42	Octane	3.87
Nitrogen	3.42	Chlorine	3.63
Carbon dioxide	3.49	Chlorobenzene	3.78
Sulphur dioxide	3.61	Carbontetrachloride	3.68
Water	4.39	Ether	3.81
Ethyl alcohol	4.02	Ammonia	4.12

(c) We have seen from the Amagat's curves (PV-P isothermals) that at the Boyle temperature, a real gas tends to obey Boyle's Law. The minimum of the PV-P curve is on the PV-axis (i.e., P = o).

Hence for the Boyle point, T_B, at $P = 0$ $\left[\dfrac{\partial(PV)}{\partial P}\right]_T = 0$

The van der Waals' equation, $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2}$, may be written as

$$PV = \frac{RTV}{V-b} - \frac{a}{V}$$

differentiating at constant temperature,

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T$$

$$= \left[\frac{-bRT}{(V-b)^2} + \frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T$$

So, at the Boyle point, where $\left[\dfrac{\partial(PV)}{\partial P}\right]_T = 0$, we have $\dfrac{bRT_B}{(V-b)^2} = \dfrac{a}{V^2}$, remembering $\left(\dfrac{\partial V}{\partial P}\right)_T$

cannot be zero.

Hence $$T_B = \frac{a}{Rb}\left(\frac{V-b}{V}\right)^2$$

Since when $P \rightarrow 0$, the volume V will be Infinitely large; i.e., $V - b \approx V$

$$\therefore \ T_B = \frac{a}{Rb}$$

From van der Waals' equation, we have, $T_c = \dfrac{8a}{27Rb}$

Hence, the ratio, $\dfrac{T_B}{T_c} = \dfrac{27}{8} = 3.375$

The experimental determinations, however, show that T_B/T_C is a almost constant but the magnitude of the ratio approaches 2.98 instead of 3.375. The van der Waals' equation, therefore, is only qualitatively valid.

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TABLE E

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Gas	He	Ne	A	H_2	O_2	N_2
T_B/T_c	3.65	3.00	2.73	3.21	2.56	2.72

(d) **Reduced equation of state.** Since the critical constants are definite quantities for a gas, it is possible to express its, P, V, T, the pressure, volume and temperature in any given state as multiples or sub-multiples of the critical values. Let us say,

$$P = \pi P_c, \quad V = \phi V_c \text{ and } T = \theta T_c$$

where π, ϕ and θ which are numbers called reduced pressure, reduced volume and reduced temperature. These numbers indicate how many times the critical values are greater or smaller than the respective given quantities.

The van der Waals' equation may then be changed as,

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

or

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

Substituting the critical constants by equation (111.5) we have,

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = R\theta T_c$$

or
$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$

This relation interms of the reduced parameters of the system is called the van der Waals' *reduced equation of state.* The most interesting aspect of this relation is that it would be applicable to all gases, since it is independent of the constants a, b and R.

The equation implies that *if two substances have the same reduced pressure π (i.e., their pressures are π times their respective critical pressures) and are also at the same reduced temperature θ, (i.e., their temperatures are θ times their respective critical temperatures), then their reduced volumes ϕ should be the same, (i.e., the ratio $\dfrac{V}{V_c}$ should be the same).* Substances under such conditions are said to be in corresponding states and the principle laid above is called the **law of corresponding states.**

It gives us a clue to test the validity of the van der Waals' equation from which this relation is derived. By maintainin different gases at the same π and θ, we can find out if ϕ is the same. In the table below are incorporated the data for a number of gases, which show that the law of the corresponding states is approximately obeyed. The equation can be tested in any homogeneous phase liquid or gas.

CORRESPONDING VOLUMES OF DIFFERENT SUBSTANCES

$\pi = 0.08846$	$\phi l = \dfrac{V liquid}{V_c}$		$\phi g = \dfrac{V gas}{V_c}$
Substance	θl	ϕl	ϕg
Benzene	0.7277	0.4065	28.3
Hexane	0.7476	0.4056	29.1
Octane	0.7544	0.4006	29.4
Chlorobenzene	0.7345	0.4028	28.5
Carbon tetrachloride	0.7241	0.4078	27.5
Ether	0.7380	0.4030	28.3
Ethyl acetate	0.7504	0.4001	30.25
Ethyl alcohol	0.7794	0.4061	32.15

III.7. The Dieterici Equation

Another equation of state was proposed by Dieterici in the empirical form,

$$P = \frac{RT}{V - b} \cdot e^{\frac{-a}{RTV}}$$

A theoretical basis for this equation was later developed by Jeans. The volume correction here was evidently the same as that in the van der Waals' equation. For the correction of pressure, Jeans introduced the exponential factor $e^{\frac{-a}{RTV}}$ The reasonings given by Jeans may broadly be stated as follows. A molecule in coming to the wall from the interior has to overcome the forces of attraction and thereby attains a potential energy higher than that possessed by a molecule in the bulk. In consequence, the density of molecules near the walls will be less than that in the interior. If n and n_0 denote the number of molecules per c.c. at the walls and in the interior, then, according to the distribution law,

$$\frac{n}{n_0} = e^{-\frac{A}{RT}}$$

where A is the excess energy per mole at the walls.