The Gaseous State

Ideal gas: An ideal gas is one which obeys the equation of state, $PV = nRT$ under all conditions of temperature and pressure.

Practically no gas is ideal, real gases deviate from ideal behaviour.

Deviation from ideal behaviour: As a measure of the deviation from ideality of the behaviour of a real gas, compressibility factor or compression factor, Z of a gas is defined.

Compression factor, Z: The compression factor, Z, of a gas is the ratio of its molar volume, V_m to the molar volume of a perfect gas, V_m^0 at the same temperature and pressure:

$$Z = \frac{V_m}{V_m^0}$$

Again, for a perfect gas,

$$PV = nRT$$

$$\Rightarrow P\frac{V}{n} = RT$$

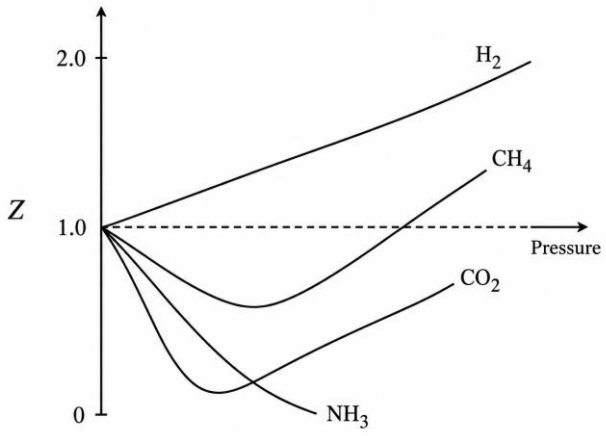
$$\Rightarrow PV_m^0 = RT$$

$$\therefore Z = \frac{PV_m}{RT}$$

For an ideal gas, $Z = 1$ for all temperatures and pressures; deviation of Z from 1 is a measure of departure from ideal/perfect behaviour.

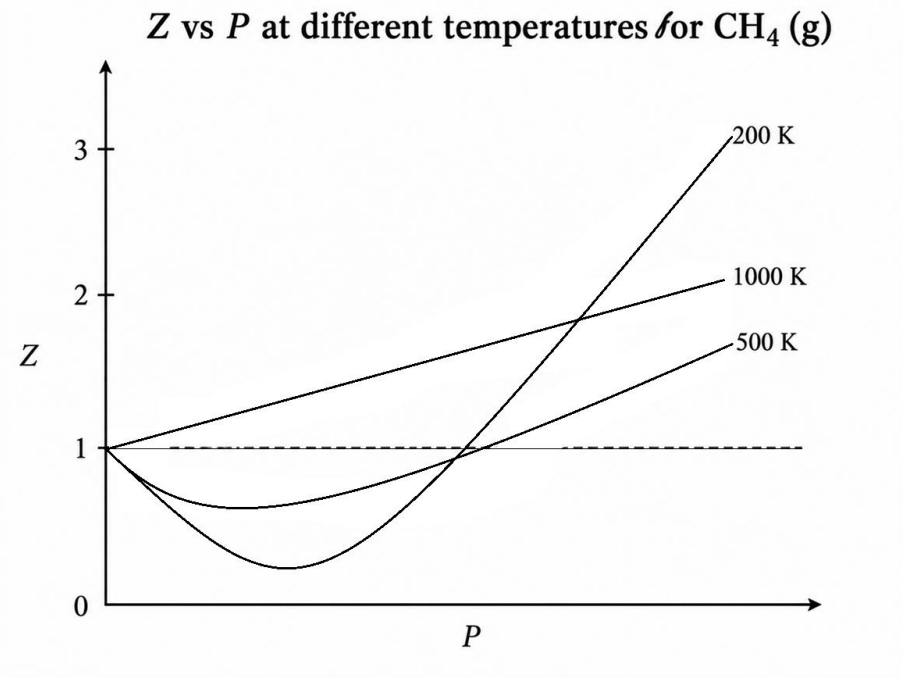
Effect of pressure on Z: The variation of Z with pressure for several gases at 0°C are shown below: (Fig 1)

Fig. 1: Z vs P for several gases at 0 °C



At low pressure all the gases shown have Z = 1 i.e., behave nearly ideally. At high pressures, all the gases have Z > 1, indicating that they have a larger molar volume than a perfect gas. At intermediate pressures, most gases have Z < 1, indicating that they have a smaller molar volume than a perfect gas.

Effect of temperature on Z: The plot of Z vs P at different temperatures for $CH_4(g)$ is shown below:



At lower temperature dip in the curve is large and the slope of the curve is negative. As T is increased, dip in the curve decreases and the position of the minimum moves to the left. For a gas, there exists a particular temperature at which Z = 1 for an appreciable range of pressure i.e, at this temperature the gas behaves ideally. This is called Boyle temperature, T_B.

Thus, real gases approach ideal behaviour under two conditions:

(i) at low pressures ($p \rightarrow 0$) and

(ii) at high temperature ($T \rightarrow \infty$).

Causes of deviations: Deviations from ideality are due to

(i) the presence of intermolecular forces and

(ii) the non-zero volume of the molecules.

At low pressure, when the gas occupies a large volume, the molecules are so far apart that the intermolecular forces play no significant role. The gas behaves perfectly ideal, i.e.

$$Z = \frac{V_m}{V_m^0} = 1$$

Also, at infinite volume, volume of the molecules themselves is negligible compared with the infinite volume the gas occupies.

At moderate pressure, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. Thus, attractive forces reduce the molar volume relative to a perfect gas

$$Z = \frac{V_m}{V_m^0} < 1$$

At high pressure, where the average separation of the molecules is small, the repulsive forces dominate, as a result of which gases have a larger volume than a perfect gas.

$$Z = \frac{V_m}{V_m^0} > 1$$

Q: Why the most easily liquefiable gases show larger deviations?

Equation of state for real gases

van der Waals equation of state for real gases: The van der Waals equation is

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

or

$$(V - nb)(p + a\left(\frac{n^2}{V^2}\right) = nRT$$

In terms of molar volume $V_m = \frac{V}{n}$

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

or

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

The constants a and b are van der Waals coefficients. They are characteristics of gas but independent of temperature.

Q. Find out the units of a and b. Write about their significance.

Derivation: Ideal gas equation was modified by van der Waals introducing following corrections into it-

(i) Volume correction: When n moles of a gas are placed in a container of volume V, due to the non-zero volume of the molecules, they are restricted to a smaller volume $V - nb$, where nb is approximately the total volume taken up by the molecules themselves. Therefore, the perfect gas law $p = \frac{nRT}{V}$ should be replaced by

$$p = \frac{nRT}{V - nb} \cdots\cdots (1)$$

(ii) Pressure correction: The pressure of a gas depends on both the frequency of the collision of the molecules with the walls and the force of each collision. Both the frequency of the collision and their force are reduced by the intermolecular attractive forces. The attractive forces are proportional to the molar concentration, $\frac{n}{V}$, of molecules in the sample. Therefore,

$$frequency\ of\ collision \propto \frac{n}{V}$$

$$force\ of\ collision \propto \frac{n}{V}$$

and hence,

$$reduction\ in\ pressure \propto \left(\frac{n}{V}\right)^2$$

or

$$\text{reduction in pressure} = a\left(\frac{n}{V}\right)^2$$

where a is a positive characteristic of the gas.

Due to this reduction in pressure eqn (1), becomes

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

This is the van der Waals equal for real non-ideal gases.

Effect of molecular size and intermolecular interaction on pressure: Higher is the molecular size, higher will be the value of b, the excluded volume per mole of the gas. Therefore, molecular size tends to increase the pressure as is evident from the following relation:

$$p = \frac{nRT}{V - nb}$$

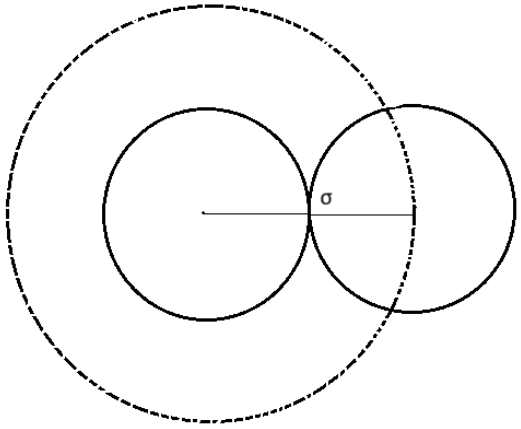
The pressure of a gas depends on frequency of the collisions of the molecules with the walls and the force of each collision, which in turn is reduced by intermolecular attraction. Thus, intermolecular attraction tends to decrease the pressure of a gas. Reduction in pressure due to intermolecular attraction is given by

$$a\left(\frac{n}{V}\right)^2$$

where a is a positive constant.

Excluded volume: Gas molecules have non-zero volume, so, the volume available for the molecules to move is less than V. The corrected volume is $V - nb$ for n moles of a gas. The volume b is roughly the same as the molar volume of the solid or liquid, where the molecules are close together.

The gas molecules are impenetrable and incompressible spheres due to the repulsive forces when they are close together. Let us consider such a pair of spheres with diameter σ.



For this pair of molecules, a sphere of radius σ constitutes 'excluded volume'. This excluded volume equals to $\frac{4}{3}\pi\sigma^3$. Thus, excluded volume per molecule is $\frac{2}{3}\pi\sigma^3$

where $\sigma = 2r$.

The actual volume of one gas molecule of radius r is $\frac{4}{3}\pi r^3$.

$\therefore \frac{2}{3}\pi\sigma^3 = \frac{2}{3}\pi(2r)^3 = 4 \times (\frac{4}{3}\pi r^3)$

Thus, excluded volume per molecule is 4-times the actual volume of the gas molecule.

Thus, excluded volume per mole of the gas would be,

$$b = N_a \times 4 \times \frac{4}{3}\pi r^3$$

Q: The van der Waals constant b has a value of 0.0319 L mol^{-1} for oxygen gas. Calculate the molecular diameter of oxygen molecules.

Virial equation of state: Virial equation is a common procedure in which a simple law is treated as the first term in a series in powers of a variable. In the virial equation of state, compressibility factor Z is expressed as

$$Z = \frac{pV_m}{RT} = 1 + B'p + C'p^2 + \cdots\cdots (i)$$

$$Z = \frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m{}^2} + \cdots\cdots (ii)$$

These two expressions are two versions of the virial equation of state. The coefficients B, C, ⋯, which depend on T are the second, third, ... virial coefficients.

van der Waals equation in virial form and determination of Boyle temperature:

For one mole of a real gas

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}\cdots\cdots\cdots (1)$$

multiplying (1) with V_m/RT, we get

$$\frac{pV_m}{RT} = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

But,

$$Z = \frac{pV_m}{RT}$$

Therefore, compressibility factor for a van der Waals gas is given by

$$Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

or

$$Z = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m}\cdots\cdots\cdots (2)$$

Since b is approximately the liquid's molar volume, $b < V_{\mathrm{m}}$ for the gas and $\frac{b}{V_m} < 1$.

Therefore, we can use

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots \quad for\ |x| < 1$$

Deriving (2) as a Taylor series with

$$x = \frac{b}{V_{\mathrm{m}}}$$

We get,

$$Z = 1 + \frac{b}{V_{\mathrm{m}}} + \left(\frac{b}{V_{\mathrm{m}}}\right)^2 + \left(\frac{b}{V_{\mathrm{m}}}\right)^3 + \cdots\cdots - \frac{a}{RTV_m}$$

or

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_{\mathrm{m}}} + \frac{b^2}{{V_{\mathrm{m}}}^2} + \frac{b^3}{{V_{\mathrm{m}}}^3} + \cdots\cdots (3)$$

Now the van der Waals equation has the same form as the virial equation:

$$Z = 1 + \frac{B}{V_{\mathrm{m}}} + \frac{C}{{V_{\mathrm{m}}}^2} + \cdots\cdots (4)$$

Comparing (3) and (4), the second virial coefficient

$$B = b - \frac{a}{RT}$$

Putting

$$V_{\mathrm{m}} = \frac{RT}{p}$$

as an approximation in eqn (3),

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \left(\frac{b}{RT}\right)^2 p^2 + \cdots\cdots (5)$$

Differentiating w.r.t. p at constant T,

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right) + 2p\left(\frac{b}{RT}\right)^2 + \cdots\cdots$$

As $p \to 0$ all the higher terms drop out:

$$\left(\frac{\partial Z}{\partial p}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

At the Boyle temperature(T_B), initial slope of Z vs P plot is zero, hence

$$\frac{1}{RT_B}\left(b - \frac{a}{RT_B}\right) = 0$$

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

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

At the Boyle temperature, a real gas behaves ideally over an appreciable range of pressure. At Boyle temperature, repulsive interaction and attractive interaction between the molecules roughly compensate each other.

Implications of van der Waals equation:

van der Waals equation for 1 mole of a gas is given by

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \cdots\cdots\cdots (1)$$

(i) The first term on right side takes the effect of molecule size into account. The finite molecular size (impenetrable sphere) indicates repulsive interactions between gas molecules.

The 2nd term on right side takes the effect of intermolecular forces into account. Intermolecular attractive forces reduce the pressure below the ideal value.

(ii) The compressibility factor Z for a van der Waals gas is given by

$$Z = \frac{V_m}{V_m - b} - \frac{a}{RTV_m}$$

$$\Rightarrow Z = \frac{1}{1 - \frac{b}{V_m}} - \frac{a}{RTV_m} \cdots\cdots\cdots (2)$$

$\therefore$ $b < V_m$ and hence $b/V_m < 1$, expanding the first term in Taylor series, we get

$$Z = 1 + \frac{b}{V_m} + \left(\frac{b}{V_m}\right)^2 + \left(\frac{b}{V_m}\right)^3 + \cdots\cdots - \frac{a}{RTV_m}$$

$$\Rightarrow Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m} + \frac{b^2}{V_m{}^2} + \frac{b^3}{V_m{}^3} + \cdots\cdots (3)$$

(a) At low pressures, V_m is much larger than b and the b^2/V_m^2, b^3/V_m^3, $\cdots$ terms can be neglected to give

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V_m}$$

At low temperature (and low pressure), we have

$$\frac{a}{RT} > b$$

So,

$$b - \frac{a}{RT}$$

is negative, making $Z < 1$.

Thus, at low pressure and low temperature $Z < 1$ and pressure of the gas is lower than the ideal pressure.

At low temperature, intermolecular attractions (van der Waals a) are more important than intermolecular repulsions (van der Waals b) in determining P.

At high temperature and (low pressure), we have

$$\frac{a}{RT} < b$$

and hence

$$b - \frac{a}{RT}$$

is positive, making $Z > 1$.

Thus, at low pressure and high temperature $Z > 1$ and the pressure of the gas is higher than the ideal pressure.

At high temperature (and low p), the molecules smash into each other harder than at low T, which increases the influence of repulsions on p.

(b) At extremely low pressure and high temperature:

As $p \to 0$,

$$\frac{1}{V_{\mathrm{m}}} \to 0 \quad (i.e. V_{\mathrm{m}} \to \infty)$$

eqn (3) gives

$$Z = 1$$

van der Waals equation, under these conditions, reduces to the perfect gas equation:

$$p = \frac{RT}{V_{\mathrm{m}}}$$

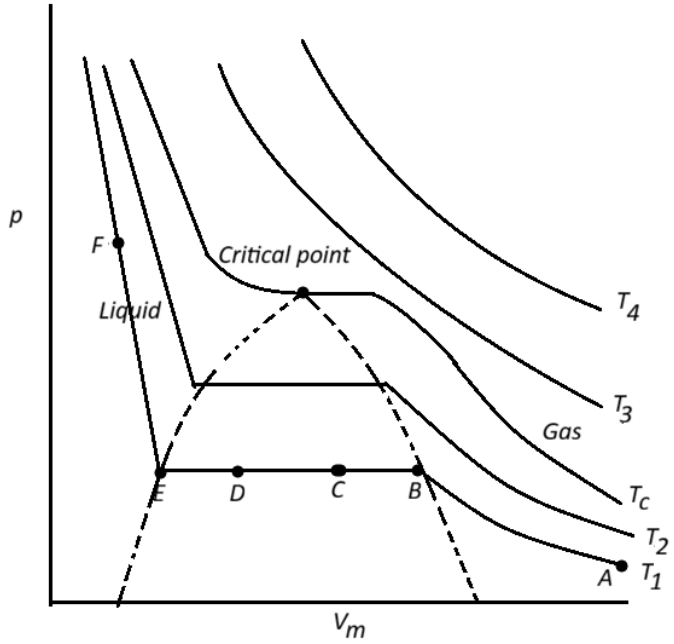
As $T \to \infty$, also $V_{\mathrm{m}} \to \infty$ (since $V_{\mathrm{m}} \propto T$) and we get the same result

$$Z = 1$$

Thus, at extremely low p and high T real gases tend to approach ideal behaviour.

Critical Phenomenon

Isotherms of a real gas (Andrew's isotherms): P−V_m isotherms of a real gas measured at various temperatures (isotherms) are shown below:



Let us consider the isotherm at T_1. To go from A to B, we slowly push in the piston, decreasing V_m and increasing p, while keeping the gas in a constant temperature bath. From A to B, pressure of the gas rises in approximate agreement with the Boyle's law. At *B*, deviations from Boyle's law begin to appear and volume decreases rapidly as the gas is converted into the liquid. At point *E*, the gas has been completely liquified. Along *BCDE*, pressure remains constant and both the gas and liquid phases are in equilibrium. Beyond the point *E*, for a very small decrease in volume shows sharp rise in pressure. Along *EF*, the system is completely liquid, therefore any further reduction in volume requires the exertion of considerable pressure. At a higher temperature T_2, the curve shows a similar behaviour except that liquefaction starts at higher pressure and the horizontal portion is shorter. At the critical temperature T_C, the horizontal portion reduces to a point, known as *critical point*. At this point, the boundary between the two phases disappears indicating that both the liquid and gaseous phases have identical characteristics at the critical point.

Above T_C, there is no indication of liquefaction. So, at a temperature above T_C, the gas can't be liquified howsoever high the pressure may be.

At the critical temperature and pressure, physical properties of a gas are indistinguishable from its liquid form and no distinction can be observed between the two. The phenomenon of smooth merging of a gas with its liquid form is called critical phenomenon.

Critical Constants of a Gas

1. Critical temperature, T_C:

The critical temperature of a gas is the highest temperature at which the gas can be liquefied by applying pressure, however high the pressure may be.

2. Critical pressure, P_C:

The critical pressure is the minimum pressure required to liquefy a gas at its critical temperature.

3. Critical volume, V_C:

The critical volume is the molar volume of a gas at its critical temperature and critical pressure.

Gas	Critical Temperature (°C)
CO_2	31.1
H_2	−240
O_2	−118.8

The van der Waals isotherm:

For 1 mol of a gas,

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

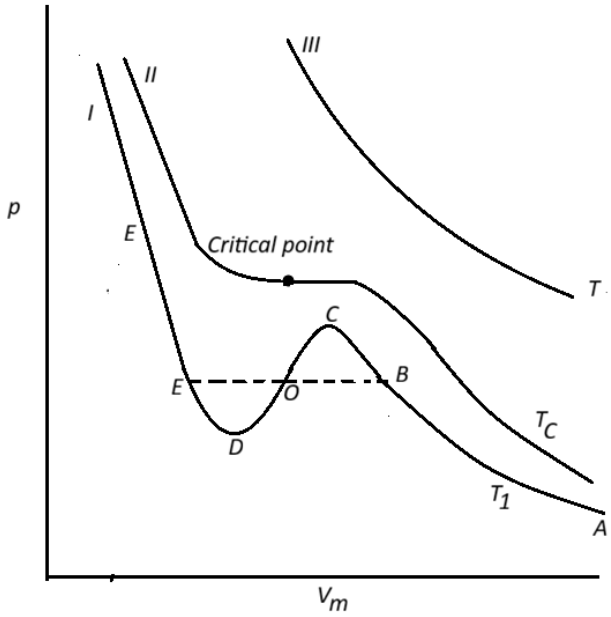
$$\Rightarrow pV_m - pb + \frac{a}{V_m} - \frac{ab}{V_m^2} - RT = 0$$

Multiplying by V_m^2 and dividing by p and rearranging

$$V_m^3 - \left(b + \frac{RT}{p}\right)V_m^2 + \left(\frac{a}{p}\right)V_m - \frac{ab}{p} = 0 \cdots\cdots (1)$$

This is a cubic equation in V_m. At a given T and pressure p, there should be three values of V_m.

If we plot p against V_m at a given temperature, we obtain the theoretical isotherms according to equation (1):



Isotherm (I) at temperature T_1, for a certain pressure shows three values of V_m marked as B, O and E. With increase in temperature, three values move closer to one another. At the critical temperature, T_c, the three values merges into a single point known as the critical point of the gas.

Validity of van der Waals equation:

The reliability of the equation can be judged by comparing the isotherms it predicts with the experimental isotherms. At and above T_c, van der Waals isotherms resemble quite well with the experimental isotherms (marked II and III). Below T_c, isotherms of van der Waals show oscillations, known as van der Waals loop (BCOED). Experimental isotherms exhibit plateau (marked by EOB). The van der Waals loop are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume.

Critical Constants from van der Waals equation: van der Waals isotherm at the critical temperature shows a flat inflection indicating a zero slope, i.e.,

$$\left(\frac{\partial P}{\partial V_m}\right)_T = 0 \cdots\cdots (1)$$

The slope is negative on both sides of the critical point, indicating that $\left(\frac{\partial P}{\partial V_m}\right)_T$ is negative on both sides and has a maximum at the critical point.

For $\left(\frac{\partial P}{\partial V_m}\right)_T$ to be maximum $\left(\frac{\partial^2 P}{\partial V_m{}^2}\right)_T$ has to be zero at that point, i.e.,

$$\left(\frac{\partial^2 P}{\partial V_m{}^2}\right)_T = 0 \cdots\cdots (2)$$

Differentiating the van der Waals equation for 1 mol of a real gas:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \cdots\cdots\cdots (3)$$

we get,

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

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

Application of conditions (1) and (2) gives

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

$$\Rightarrow \frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \cdots\cdots (4)$$

and

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

$$\Rightarrow \frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c{}^4} \cdots\cdots (5)$$

$$\frac{(4)}{(5)} \Rightarrow \mathrm{V_c} - \mathrm{b} = \frac{2\mathrm{V_c}}{3}$$

$$\Rightarrow V_c = 3b \cdots\cdots (6)$$

Putting V_c=3b in equation (4), we get

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

$$\Rightarrow T_c = \frac{8a}{27Rb} \cdots\cdots (7)$$

Moreover, the van der Waals equation itself gives at the critical point:

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{{V_c}^2} \cdots\cdots (8)$$

Substitution of (6) and (7) into (8) gives

$$P_c = \frac{R8a}{27Rb.2b} - \frac{a}{9b^2}$$

$$\Rightarrow P_c = \frac{4a}{27b^2} - \frac{a}{9b^2}$$

$$\Rightarrow P_c = \frac{a}{27b^2} \cdots\cdots (9)$$

Solving (7) and (9) for a and b, we get

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

$$\Rightarrow 1 = \frac{8P_c\,b}{RT_c}$$

$$\Rightarrow b = \frac{RT_c}{8P_c}$$

Now,

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

$$\Rightarrow a = P_c \times 27b^2$$

$$\Rightarrow a = P_c \times 27\left(\frac{RT_c}{8P_c}\right)^2 = \frac{27R^2{T_c}^2}{64P_c}$$

Now, the critical compression factor, Z_c is predicted to be:

$$Z_c = \frac{P_cV_c}{RT_c} = \frac{a \times 3b \times 27Rb}{27b^2 \times 8a} = \frac{3}{8} = 0.375$$

for all gases.

The law of corresponding states: It was shown by van der Waals that instead of using volume, pressure and temperature of a gas, the ratio of these quantities to the corresponding critical quantities could be used. Thus, defining reduced pressure, reduced volume, and reduced temperature as

$$p_{\mathrm{r}} = \frac{p}{p_c}$$

$$V_{\mathrm{r}} = \frac{V_{\mathrm{m}}}{V_c}$$

$$T_{\mathrm{r}} = \frac{T}{T_c}$$

and replacing p, V_m and T with

$$p = p_{\mathrm{r}} p_c$$

$$V_{\mathrm{m}} = V_{\mathrm{r}} V_c$$

$$T = T_{\mathrm{r}}\, T_c$$

we can rewrite the van der Waals equation:

$$\left(p + \frac{a}{{V_{\mathrm{m}}}^2}\right)(V_{\mathrm{m}} - b) = RT$$

$$\Rightarrow \left(P_{\mathrm{r}} P_c + \frac{a}{{V_c}^2 {V_{\mathrm{r}}}^2}\right)(V_c V_{\mathrm{r}} - b) = RT_c T_{\mathrm{r}}$$

Now putting $P_c = a/(27b^2)$, $V_c = 3b$ and $T_c = 8a/(27Rb)$, we get:

$$\left(P_{\mathrm{r}} \frac{a}{27b^2} + \frac{a}{9{V_{\mathrm{r}}}^2 b^2}\right)(3V_{\mathrm{r}} b - b) = RT_{\mathrm{r}} \frac{8a}{27Rb}$$

$$\Rightarrow \frac{a}{27b^2}\left(P_{\mathrm{r}} + \frac{3}{{V_{\mathrm{r}}}^2}\right)(3V_{\mathrm{r}} - 1)b = \frac{8a \times T_{\mathrm{r}}}{27b}$$

$$\Rightarrow \frac{a}{27b}\left(P_{\mathrm{r}} + \frac{3}{{V_{\mathrm{r}}}^2}\right)(3V_{\mathrm{r}} - 1) = \frac{a \times 8T_{\mathrm{r}}}{27b}$$

$$\Rightarrow \left(P_{\mathrm{r}} + \frac{3}{{V_{\mathrm{r}}}^2}\right)(3V_{\mathrm{r}} - 1) = 8T_{\mathrm{r}}$$

This is known as reduced equation of state. It follows from this equation that "if two or more substances have the same reduced temperature and the same reduced pressure, they would have the same reduced volume." This statement is known as the principle of corresponding states.

Dieterici Equation: Dieterici proposed the following relationship to account for the behaviour of real gases:

For 1 mole of gas:

$$p\, e^{\frac{a}{RTV_m}} (V_m - b) = RT$$

or

$$p\,(V_m - b) = RTe^{-\frac{a}{RTV_m}}$$

This equation differs with van der Waals equation in the pressure correction term. Dieterici introduced an exponential term to account for the effect of molecular attraction on the pressure.

This equation gives results identical with van der Waals equation at moderate pressure, but differs appreciably at high pressure. At high pressure Dieterici equation gives more satisfactory agreement with the experimental data than the van der Waals equation does.

Berthelot equation: For 1 mol of a real gas, the following equation was proposed by Berthelot:

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

where a and b are called Berthelot constants.

For n mole of a real gas,

$$\left(P + \frac{an^2}{TV^2}\right)(V - nb) = nRT$$