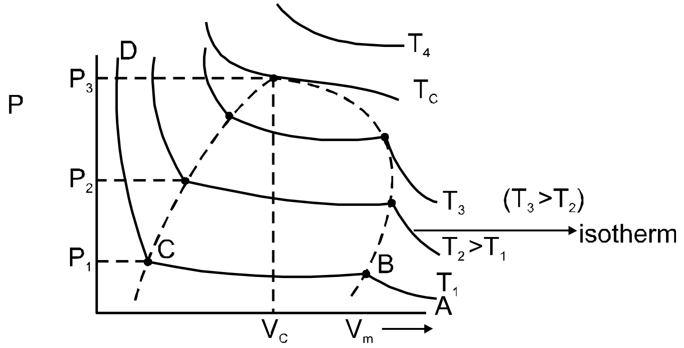
Real Gases

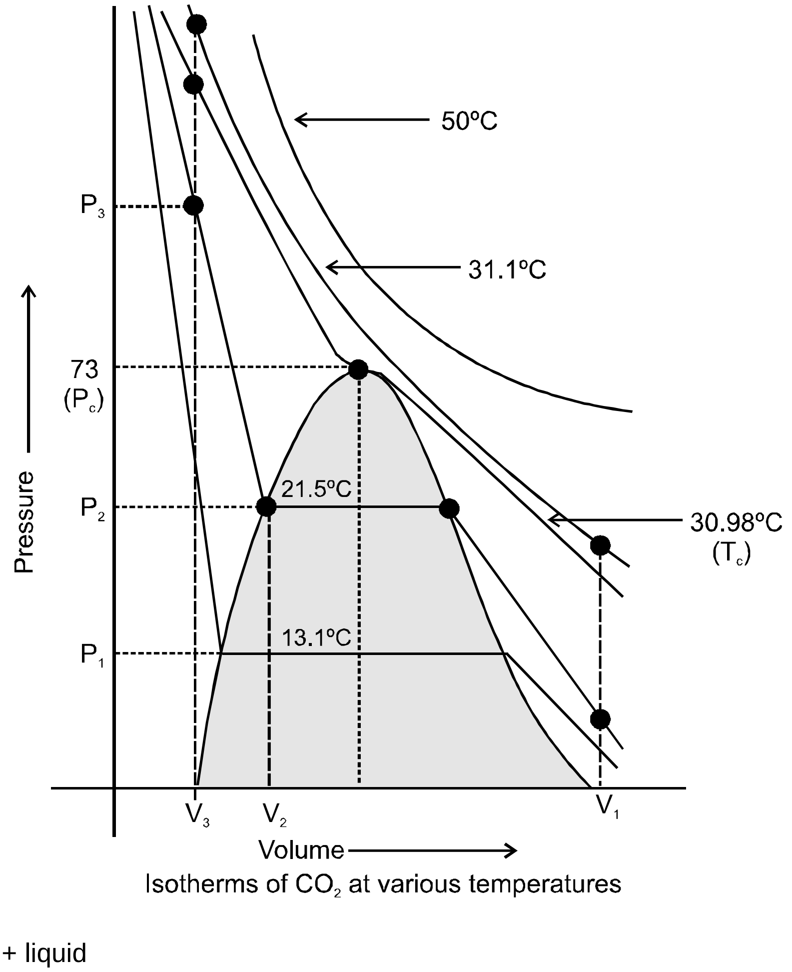
Section (A) : Experimental Observation and critical state

Th1 Critical constant of a gas:

When pressure increases at constant temperature volume of gas decreases



$T_4 > T_C > T_3 > T_2 > T_1$



Isotherms of CO_2 at various temperatures

AB → gas

BC → vapour + liquid

CD → liquid

Critical point: At this point, all the physical properties of liquid phase will be equal to physical properties in vapour such that density of liquid = density of vapour

T_C or critical temp: Temperature above which a gas can not be liquified

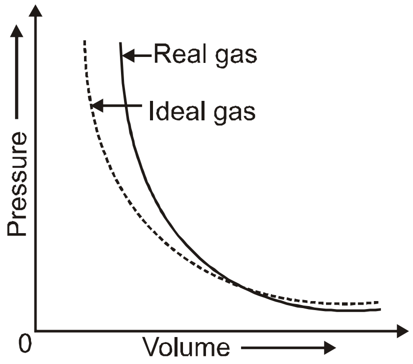
P_C or critical pressure: Minimum pressure which must be applied at critical temperature to convert the gas into liquid.

V_C or critical volume: Volume occupied by one mole of gas at T_C & P_C.

Section (B) : Vander waal equation and virial equation of state

Th2 Real Gases:

- Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure.
- Real gases deviates from ideal behaviour because
  - Real gas molecules have a finite volume.
    {Since on liquefaction real gases occupy a finite volume}
  - Inter molecular attractive forces between real gas molecules is not zero.
    {Real gases can be converted into liquid where as ideal gases cant be}
- Deviation of real gases from ideal behaviour can be measured by using compressibility factor: (Z)



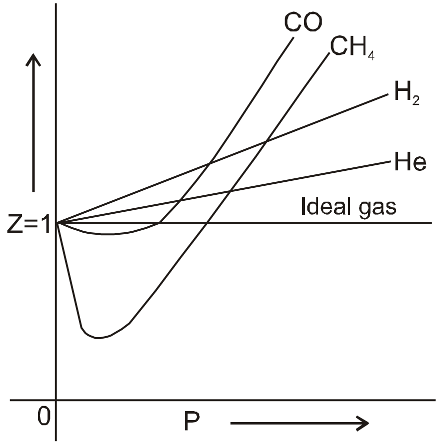
F1 $Z = \frac{(PV)_{real}}{(PV)_{ideal}}$ $(PV)_{ideal} = nRT$

F2 $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$,

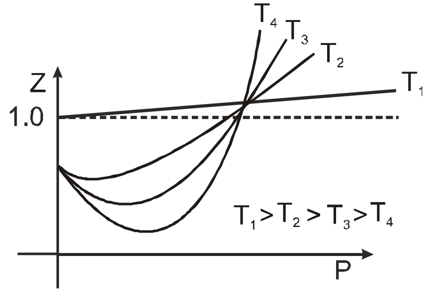
V_M is volume of one mole of gas or molar volume.

F3 $Z = \frac{V_{m\ real}}{V_{m\ ideal}}$

Variation of Z with pressure at constant temperature :



Variation of Z with pressure at different temperature (for same gas) :



Conclusions :

Z = 1 for ideal gas ;
Z < 1 at low pressure (for all other gases) ;

Z > 1 at all pressures for He/H_2
Z > 1 at high pressure (for all other gases)

Th3 Vander Waal Equation of real gases:

The ideal gas equation does not consider the effect of attractive forces and molecular volume. Vander Waal's corrected the ideal gas equation by taking the effect of

(a) Molecular volume **(b)** Molecular attraction

Der.1 ● Volume orrection :

Ideal gas equation :

$P_i\ V_i = nRT$; In the equation 'V_i' stands for the volume which is available for free movement of the molecules.

V_{ideal} = volume available for free movement of gaseous molecule

Hence, $V_i = V$ – {volume not available for free movement}

For an ideal gas $V_i = V$ {V = volume of container}

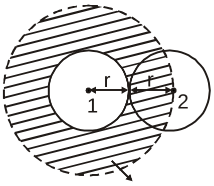
But for a real gas $V_i \neq V$, as all the volume is not available for free movement

Molecules have finite volume :

Excluded volume per molecule = $\frac{1}{2}\left\{\frac{4}{3}\pi(2r)^3\right\}$ = Co-volume per molecule.

The volume that is not available for free movement is called excluded volume.

let us see, how this excluded volume is calculated.



Excluded volume
(not available for free momement)

For above example, the entire shaded region is excluded, as its centre of mass cannot enter this region.

If both molecules were ideal, then they would not have experienced any excluded volume but not in the case, of real gas as the centre of mass of '2' cannot go further.

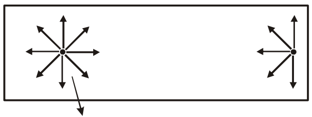
Hence for this pair of real gas molecules, excluded volume per molecule = $\frac{1}{2}\left\{\frac{4}{3}\pi(2r)^3\right\} = 4\left\{\frac{4}{3}\pi r^3\right\}$

F4 Excluded volume per mole of gas (b) = $N_A \times 4 \times \left\{\frac{4}{3}\pi r^3\right\} = 4 \times N_A \times$ Volume of individual molecule

for n moles, excluded volume = nb

$V_i = V - nb$ volume correction

- **Pressure correction or effect of molecular attraction forces :**



Molecule in the middle of container

Due to these attraction, speed during collisions will be reduced

Momentum will be less

Force applied will be less

Pressure will be less.

$P_{ideal} = P$ + {correction term}

Correction term α no. of molecules attracting the colliding molecule $\propto$ (n/v).

Correction term α density of molecules $\propto$ (n/v).

no. of collision α density of molecules $\propto \left(\frac{n}{v}\right)$

F5 net correction term $\propto \left(\frac{n}{v}\right)\left(\frac{n}{v}\right) = \frac{an^2}{v^2}$

'a' is constant of proportionality and this is dependent on force of attraction

Stronger the force of attraction greater will be 'a' (Constant)

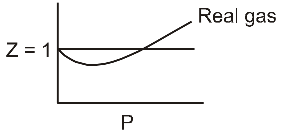
$$P_i = P + \frac{an^2}{v^2}$$

Vander waal's equation is

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

VERIFICATION OF VANDER WAAL'S EQUATIONS:

Th4 Variation of Z with P for vander waals' equation at any temperature.



Vander waal equation for 1 mole

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

V_m = volume of 1 mole of gas

- **AT LOW PRESSURE** (at separate temp.)
  At low pressure V_m will be high.

  Hence b can be neglected in comparision to V_m. but $\frac{a}{V_m^2}$ can't be neglected as pressure is low

  Thus equation would be

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

  $$PV_m+\frac{a}{V_m}=RT$$

  $$\frac{PV_m}{RT}+\frac{a}{V_mRT}=1$$

F6 $Z=1-\frac{a}{V_mRT}$ $\quad$ $Z<1$

Real gas is easily compressible as compared to an ideal gas.

- **At high pressure** (moderate temp.)
  V_m will be low
  so b can't be neglected in comparision to V_m

  but $\frac{a}{V_m^2}$ can be neglected as compared to much higher values of P.

  Then vander Waals' equation will be
  $P(V_m-b)=RT$
  $PV_m-Pb=RT$

  $$\frac{PV_m}{RT}=\frac{Pb}{RT}+1$$

F7 $Z=\frac{Pb}{RT}+1$ $\quad$ $(Z>1)$

If Z > 1, then gas is more difficult to compress as compared to an ideal gas.

- At low pressure and very high temperature.
  V_m will be very large

  Hence 'b' can't be neglected and $\frac{a}{V_m^2}$ can also be neglected as V_m is very large

  $PV_m=RT$ (ideal gas condition)

- For H_2 or He a ≈ 0 because molecules are smaller in size or vander Wall's forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.

$$P(V_m - b) = RT \qquad \text{so} \qquad Z = 1 + \frac{Pb}{RT}$$

- 'a' factor depends on inter molecular attractive forces.
  - 'a' factor for polar molecule > 'a' factor for non polar molecule.

Solved Examples

Ex-1. Arrange following in decreasing 'a' factor (H_2O, CO_2, Ar)

Sol. H_2O > CO_2 > Ar

Polar

- **For non polar molecules:** Greater the size or surface area, greater will be vander waals' forces, so greater will be 'a' constant.

Gas	a, liters^2 atm mole^{-2}	b, liters mole^{-1}
He	0.0341	0.0237
H_2	0.244	0.0266
N_2	1.39	0.0391
CO	1.49	0.0399
Ar	1.35	0.0330
O_2	1.36	0.0318
CH_4	2.25	0.0343
CO_2	3.60	0.0427
NH_3	4.17	0.0371
$n\text{–}C_5H_{12}$	19.01	0.1460
CH_3OH	9.52	0.0670
CCl_4	20.4	0.1383
C_6H_6	18.0	0.1154
H_2O	5.46	0.0305

Ex-2. Arrange following gases according to 'a' (He, Ar, Ne, Kr).

Sol. $a_{Kr} > a_{Ar} > a_{Ne} > a_{He}$

- More 'a' factor means high boiling point.
- **liquification pressure (LP) :** Is the pressure required to convert gas into liquid.

For easy liquefaction a↑ and LP↓

When $Z < 1$, $V_m < V_{m,\ ideal}$ ⇒ easily liquifiable

$Z > 1$, $V_m > V_{m,\ ideal}$ ⇒ more difficult to compress.

Ex-3. Arrange the following according to liquification pressure (n-pentane; iso-pentane, neo pentane).

Sol. $a_{n\text{-pentene}} > a_{iso\text{-pentane}} > a_{neo\text{-pentane}}$

liquification pressure = LP

$LP_{n\text{-pentene}} < LP_{iso\text{-pentane}} < LP_{neo\text{-pentane}}$

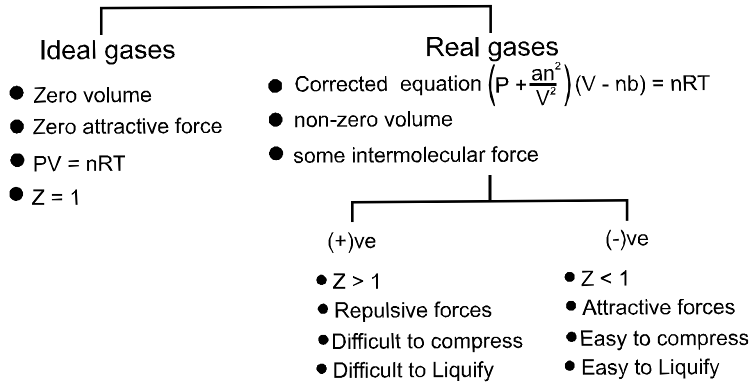
- **b** is roughly related with size of the molecule. (Thumb rule)

$$b = N_A\, 4\left\{\frac{4}{3}\pi r^3\right\}$$

Ex-4. Two vander waals gases have same value of b but different a values. Which of these would occupy greater volume under identical conditions ?

Sol. If two gases have same value of 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume. This is because the gas with a larger value of 'a' will have larger force of attraction and hence lesser distance between its molecules.

Real Gases



$$\left(P + \overset{\text{Correction term for intermolecular attraction}}{\frac{an^2}{V^2}}\right)(V - \overset{\text{Correction term for molecular volume}}{nb}) = nRT$$

Der.2 **Virial Equation of state:** It is a generalised equation of gaseous state. All other equations can be written in the form of virial equation of state.

Z is expressed in power series expansion of P or $\left(\frac{1}{V_m}\right)$

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

B – second virial coefficient, C – third virial coefficient, D – fourth virial coefficient.
The coefficients B, C...depend on the temperature but not the density and are known as virial coefficients. Both B and C are negatige at low temperature and positive at high temperature.
The virial coefficients are determined by the intermolecular potential.
B represents the effects of interactions between pairs of molecules, C interactions among triplets of molecules, and so forth.

Vander waals' equation in virial form:

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

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

$$Z = \frac{PV_m}{RT} = \frac{V_m}{(V_m - b)} - \frac{a}{V_mRT} = \frac{1}{(1 - b/V_m)} - \frac{a}{V_mRT}$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots\ldots\ldots\ldots$$

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

comparing vander waals equation with virial equation

$$B = b - \frac{a}{RT},\ C = b^2,\ D = b^3$$

At low pressure : V_m will be larger

Hence $\frac{1}{V_m^2}, \frac{1}{V_m^3}$ .... can be neglected

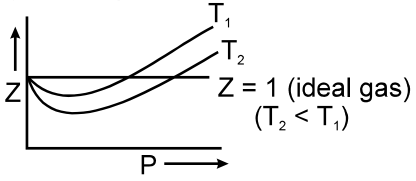
$$Z = 1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right)$$

If $\left(b - \frac{a}{RT}\right) = 0 \Rightarrow$ at $T = \frac{a}{Rb}$; $Z = 1$

So at $T = \frac{a}{Rb}$, gas will behave as an ideal gas (or follows Boyles law)

But at constant temperature, ideal gas equation is obeying Boyles law as $T = \frac{a}{Rb}$,

so the temperature is called Boyles' temperature.



F8 $T_B = \frac{a}{Rb}$

$Z = 1 - \frac{a}{V_mRT}$

For a single gas, if we have two graphs as above, we must conclude $T_2 < T_1$.
At Boyles' temperature 'a / RT' factor is compensated by 'b' factor, so Z = 1.

Der.3 Critical constant using vander waals' equations :

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

$(PV_m^2 + a)(V_m - b) = RT\,V_m^2$

$PV_m^3 + aV_m - PbV_m^2 - ab - RTV_m^2 = 0$

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

Given equation is cubic, hence there will be three roots of equation at any temperature and pressure.
At critical point, all three roots will coincide and will give single value of $V = V_C$
At critical point, Vander Waals' equation will be

$$V_m^3 - V_m^2\left(b + \frac{RT_C}{P_C}\right) + \frac{a}{P_C}V_m - \frac{ab}{P_C} = 0 \qquad ...(1)$$

But, at critical point, all three roots of the equation should be equal, hence equation should be:

$$V_m^3 - 3V_m^2V_C + 3V_mV_C^2 - V_C^3 = 0 \qquad ...(2)$$

Comparing with equation (1)

$$b + \frac{RT_C}{P_C} = 3V_C \qquad ....(i)$$

F9

$$\frac{a}{P_C} = 3V_C^2 \qquad ...(ii)$$

$$\frac{ab}{P_C} = V_C^3 \qquad ...(iii)$$

$$\left.\begin{matrix}(ii)\\(iii)\end{matrix}\right\} V_c = 3b$$

F10 $P_C = \frac{a}{3V_C^2}$ On substituting value of V_C $P_C = \frac{a}{3(3b)^2} = \frac{a}{27b^2}$

by (i) $\frac{RT_C}{P_C} = 3V_C - b = 9b - b = 8b$

F11 $T_C = \dfrac{8a}{27Rb}$

At critical point, the slope of PV curve (slope of isotherm) will be zero

$$\left(\frac{\partial P}{\partial V_m}\right)_{T_C} = 0 \qquad \text{...(i)}$$

At all other point slope will be negative 0 (zero) is the maximum value of slope.

$$\frac{\partial}{\partial V_m}\left(\frac{\partial P}{\partial V_m}\right)_{T_C} = 0 \qquad \text{....(ii)}$$

{Mathematically such points are known as point of inflection (where first two differentiation becomes zero)}

Using the two, T_C, P_C and V_C can be calculated by $\underbrace{V_c \quad \rlap{$\overbrace{}^{\substack{a\\ \Uparrow}}$}T_c}_{\substack{\Downarrow\\ a}} \quad \& \quad P_c$.

By any two a can be calculated but a calculated by V_C and T_C and a calculated by T_C and P_C may differ as these values are practical values and V_C can't be accurately calculated. So when we have V_C T_C & P_C given, use P_C & T_C to deduce 'a' as they are more reliable.

Der.4 **Reduced Equation of state:**

Reduced Temp : Temperature in any state of gas with respect to critical temp of the gas

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

Reduced pressure : $P_r = \dfrac{P}{P_C}$

Reduced volume : $V_r = \dfrac{V_m}{V_C}$

Vander waals' equation, $\left(P + \dfrac{a}{V_m^2}\right)(V_m - b) = RT$

Substitute values : $\left(P_rP_C + \dfrac{a}{V_r^2V_C^2}\right)(V_r\,V_C - b) = R\,T_r\,T_C$

Substitute the value of P_C, T_C and V_C

$$\left(P_r\frac{a}{27b^2} + \frac{a}{V_r^2(3b)^2}\right)(3b\,V_r - b) = RTr\,\frac{8a}{27Rb}$$

$$\left(\frac{P_r}{3} + \frac{1}{V_r}\right)(3\,V_r - 1) = \frac{8\,RT_r}{3}$$

F12 $\left(P_r + \dfrac{3}{V_r^2}\right)(3V_r - 1) = 8\,T_r$ (Reduced equation of state)

Above equation is independent from a, b and R, so will be followed by each and every gas, independent of its nature.

Solved Examples

Ex-5. The vander waals constant for HCI are a = 371.843 KPa.dm^6 mol^{-2} and b = 40.8 cm^3 mol^{-1} find the critical constant of this substance.

Sol. The critical pressure, $P_C = \dfrac{a}{27b^2} = \dfrac{371.843 \times 10^3}{27 \times (40.8)^2 \times 10^{-6}} = \dfrac{371.843 \times 10^9}{27 \times (40.8)^2}$ = 8.273 × 10^6 Pa = 8.273 MPa

The critical pressure, $T_C = \dfrac{8a}{27Rb}$

R = 8.314 KPa dm^3 K^{-1} mol^{-1}

$$T_C = \frac{8a}{27Rb} = \frac{8 \times 371.843}{8.314 \times 27 \times 40.8 \times 10^{-3}} = 324.79 = 324.8 \text{ K}$$

The critical volume, $V_C = 3b = 3 \times 40.8 = 122.4$ cm^3

Ex-6. The vander waals constant for gases A, B and C are as follows:

Gas	**a/dm^6 KPa mol^{-2}**	**b/dm^3 mol^{-1}**
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has

(i) Highest critical temperature

(ii) The largest molecular volume

(iii) Most ideal behaviour around STP ?

Sol. $T_C = \dfrac{8a}{27Rb}$ Since, R is constant, higher the value of a/b, higher will be critical temperature.

$V_C = 3b$ and $V_C \propto V_m$ (for a particular gas) therefore higher the value of V_C, higher will be molar volume of the gas.

If the critical temperature is close to 273 K, gas will behave ideally around the STP. Let us illustrate the result in a tabular form.

Gas	**a/dm^6 KPa mol^{-2}**	**b/dm^3 mol^{-1}**	**T_C**	**V_C**	**a/b**
A	405.3	0.027	534.97 K	0.081	1.501 × 10^4
B	1215.9	0.030	1444.42 K	0.09	4.053 × 10^4
C	607.95	0.032	677.07 K	0.096	1.89 × 10^4

(i) B gas has the largest critical temperature.

(ii) C gas has the largest molecular volume.

(iii) A gas has the most ideal behaviour around STP

Ex-7. Under critical states of a gas for one mole of a gas, compressibility factor is :

(A) 3/8 (B) 8/3 (C) 1 (D) 1/4

Sol. For 1 mole of gas $Z = \dfrac{P_C V_C}{RT_C}$ (Under critical condition)

But, $P_C = \dfrac{a}{27b^2}$, $V_C = 3b$, $T_C = \dfrac{8a}{27Rb}$

$$Z = \left(\frac{a}{27b^2}\right) \times \frac{3b}{R} \times \frac{27Rb}{8a} = \frac{3}{8}$$

Hence, Ans. (A)

CHECK LIST

Theories (Th)

Th-1 Critical constant of a gas ☐

Th-2 Real Gases ☐

Th-3 Vander Waal Equation of real gases ☐

Th-4 Verification of Vander Waal's Equations ☐

Formulae (F)

F-1. $Z = \frac{(PV)_{real}}{(PV)_{ideal}}$ ☐

F-2. $Z = \frac{PV}{nRT} = \frac{PV_m}{RT}$ ☐

F-3. $Z = \frac{V_{m\ real}}{V_{m\ ideal}}$ ☐

F-4. Excluded volume per mole of gas (b) = $N_A\ 4\left\{\frac{4}{3}\pi r^3\right\}$ ☐

F-5. net correction term $\propto \left(\frac{n}{v}\right)\left(\frac{n}{v}\right) = \frac{an^2}{v^2}$ ☐

F-6. $Z = 1 - \frac{a}{V_m RT}$ ☐

F-7. $Z = \frac{Pb}{RT} + 1$ ☐

F-8 $T_c = \frac{8a}{27Rb}$ ☐

F-9 $V_c = 3b$ ☐

F-10 $P_c = \frac{a}{27b^2}$ ☐

F-11 $T_c = \frac{8a}{27Rb}$ ☐

F-12 $\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8\ T_r$ ☐

Derivation (Deri.)

Deri-1. Derivation of Vander Waal Equation of real gases ☐

Deri-2. Derivation of Virial Equation of state ☐

Deri-3. Derivation of Critical constant using vander waals' equations ☐

Deri-4. Derivation of Reduced Equation of state ☐