

PROPERTIES OF GASES

Dilute gases behave ideally.

Equation of state for an ideal gas:

$$PV = nRT$$

Pressure (Nm^{-2})
 $\text{kg m}^{-1} \text{s}^{-2}$
→ Pascal (1 Nm^{-2})

Volume (m^3)

Temperature (K)

Universal gas constant
 $8.314 \text{ J K}^{-1} \text{ m}^{-1}$

number of moles

$$\begin{aligned} 1 \text{ atmosphere} &= 1.01325 \times 10^5 \text{ Pa} \\ &= 1.01325 \text{ bar} \\ &= 760 \text{ Torr} \end{aligned}$$

Pressure can be measured by how high a column of fluid (mercury) is supported by a gas.

$$P = \frac{F}{A} \rightarrow \text{Force (N)} = \frac{mg}{A}$$

Area (m^2)

mass (kg)

gravitational constant
 9.8 ms^{-2}

$$= \frac{\rho h A g}{A}$$

density of the fluid (kg m^{-3})

height of the column of liquid (m)

$$P = \rho h g$$

$\text{kg m}^{-3} \cdot \text{m} \cdot \text{ms}^{-2} \rightarrow \text{kg m}^{-1} \text{s}^{-2}$

Pressure exerted by a 76 cm column of Hg (density = 13.596 g cm^{-3})

$$= 13.596 \text{ g cm}^{-3} \cdot 76 \text{ cm} \cdot 980.67 \text{ cm s}^{-2}$$

$$= 1.0133 \times 10^6 \text{ g} \cdot \text{cm}^{-1} \text{s}^{-2}$$

$$= (1.0133 \times 10^6) \times (10^{-3} \text{ kg g}^{-1}) \times (100 \text{ cm} \cdot \text{m}^{-1})$$

$$= 1.0133 \times 10^5 \text{ Pa}$$

$$= 101.33 \text{ kPa}$$

The universal gas constant R

$$R = n_A k_B \leftarrow \text{Boltzmann constant } (1.38 \times 10^{-23} \text{ JK}^{-1})$$

$\nearrow$ Avogadro number
 $6.022 \times 10^{23} \text{ molecules/mol}$

Dividing both sides of the ideal gas equation by n

$$P\bar{V} = RT$$

$\nwarrow$ molar volume

Extensive quantity $\rightarrow$ proportional to the size of the system

e.g. Volume (V)

[mass, energy]

Intensive quantity $\rightarrow$ independent of the size of the system

e.g. molar volume ($\bar{V}$)

[pressure, temperature]

$$T = \lim_{P \rightarrow 0} \frac{P\bar{V}}{R}$$

No degree used $\rightarrow$ absolute temperature
 $\rightarrow$ Kelvin

Since $P \geq 0$, $\bar{V} \geq 0$, $T \geq 0$

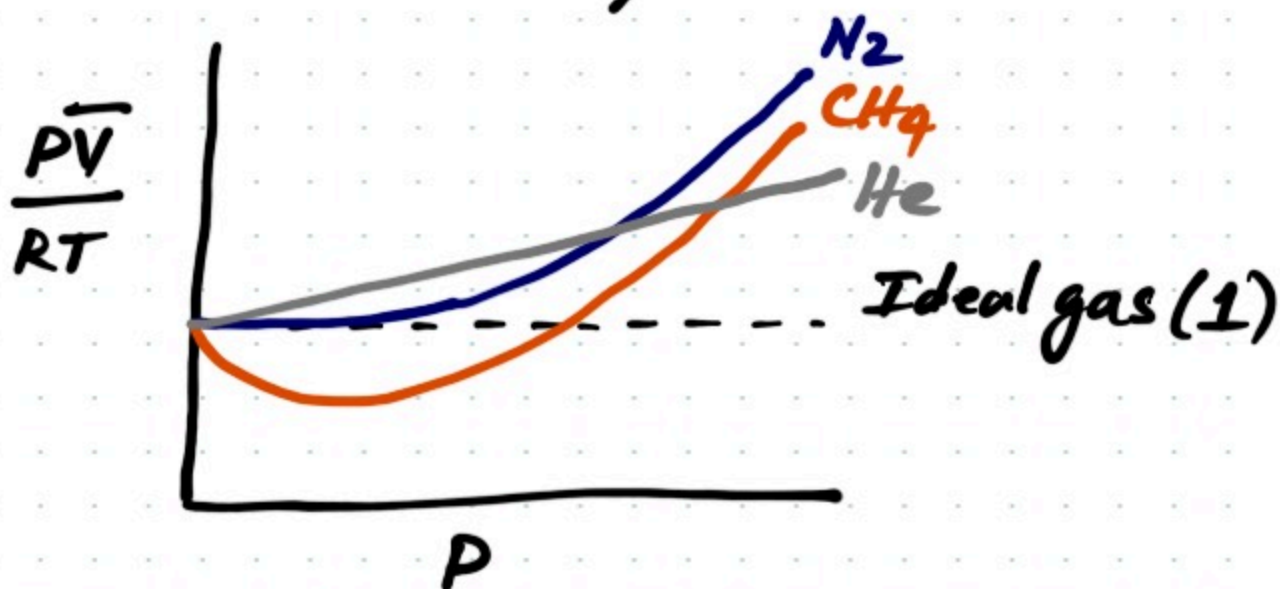
$$t(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

So absolute 0 is -273.15°C

$$\frac{C}{5} = \frac{F - 32}{9}$$

Fahrenheit

Celsius (Centigrade)



$$Z = \frac{P\bar{V}}{RT}$$



compressibility factor

$$\bar{V} < \bar{V}_{ideal}$$

Attractive forces

$$\bar{V} > \bar{V}_{ideal}$$

Repulsive forces

Non-ideality has to be taken into account

Van der Waals Equation

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

Related to
attractive
forces
between
molecules



molecular size

He

$$a = 3.46 \times 10^{-3} \text{ Pa m}^6 \text{ mol}^{-1}$$

$$b = 2.38 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

N₂

$$a = 0.137 \text{ Pa m}^6 \text{ mol}^{-1}$$

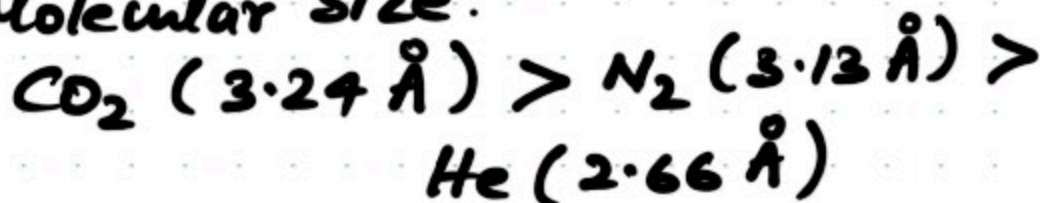
$$b = 3.87 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

CO₂ $a = 0.366 \text{ Pa m}^6 \text{ mol}^{-1}$
 $b = 4.286 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

Attractive forces:



Molecular size:



Van der Waals equation as $\bar{V} \rightarrow \infty$

$$\frac{a}{\bar{V}^2} \rightarrow 0$$

$$\bar{V} - b \rightarrow \bar{V}$$

$$P\bar{V} = RT$$

Reduces to the
ideal gas equation

Rearranging the Van der Waals equation

$$z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{\bar{V} - b} - \frac{a}{RT\bar{V}}$$

At high pressures

$\bar{V} - b \rightarrow \text{small}$

$$\frac{\bar{V}}{\bar{V} - b} > \frac{a}{RT\bar{V}}$$

: the first term dominates

At low pressures the second term dominates

Redlich-Kwong Equation

$$P = \frac{RT}{\bar{V} - b} - \frac{A}{T^{1/2} \bar{V} (\bar{V} + B)}$$

Peng-Robinson Equation

$$P = \frac{RT}{\bar{V} - \beta} - \frac{\alpha}{\bar{V}(\bar{V} + \beta) + \beta(\bar{V} - \beta)}$$

These are more accurate than the Van der Waals equation.

Rearranging the Van der Waals equation

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

Similarly, rearranging the Redlich-Kwong equation

$$\bar{V}^3 - \frac{RT}{P}\bar{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P}\right)\bar{V} - \frac{AB}{T^{1/2}P} = 0$$

Both equations have a cubic form

$$a'\bar{V}^3 + b'\bar{V}^2 + c'\bar{V} + d = 0$$

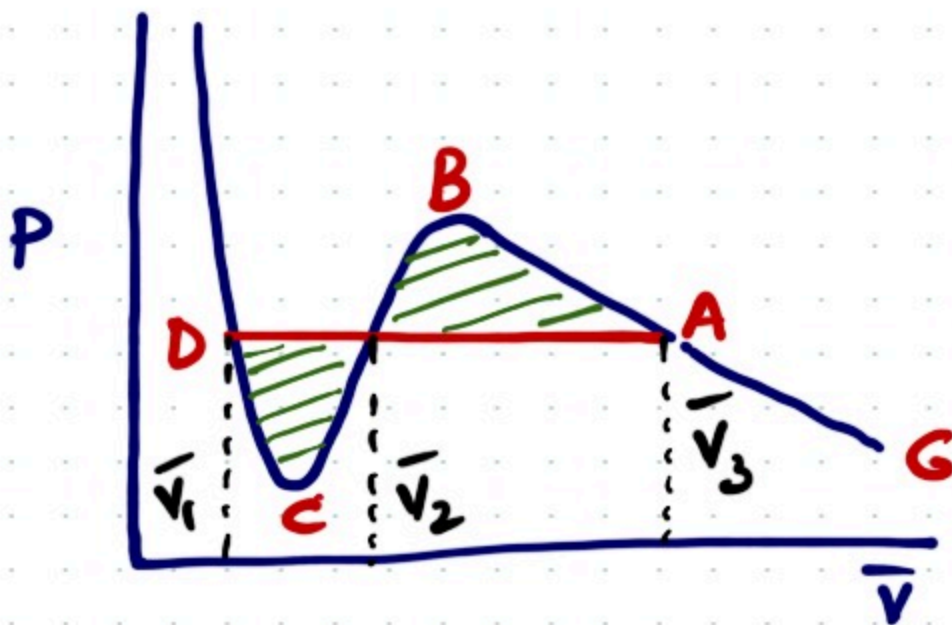
Redlich-Kwong $\rightarrow$ superior at high pressures

Peng-Robinson $\rightarrow$ superior at the liquid-vapor interface

Cubic equations can describe both the gaseous and liquid states.

Construct an isotherm $\rightarrow$
plot of P against $\bar{V}$
at constant T

$T_c \rightarrow$ Critical temperature
for $T > T_c$ the gas cannot
be liquified
no matter what
the pressure
For a VdW gas for $T < T_c$



The curve **GADL** would be seen if one compresses the gas at $T < T_c$.

The areas of the curves above and below the D-A lines are equal.

→ Maxwell equal area construction

GA → compression of the gas

AD → liquid and vapor are in equilibrium with each other

A → vapor

D → liquid

DL → change in the volume of the liquid with increasing pressure

CD → super cooled liquid
(held below its melting temperature without forming a solid)

AB $\longrightarrow$ Superheated vapor

These are metastable states.

Below the DA line, we obtain 3 values of $\bar{v}$ at a given pressure.

$\bar{v}_1 \longrightarrow$ molar volume of the liquid

$\bar{v}_3 \longrightarrow$ molar volume of the gas in equilibrium with the liquid

$\bar{v}_2 \longrightarrow$ no physical meaning

At the critical point:

$$T = T_c \quad \left(\frac{\partial P}{\partial \bar{v}} \right)_T = 0$$

$$V = V_c$$

$$P = P_c$$

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

Rewriting the cubic form of the Van der Waals equation.

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

At $T = T_c$ there is a single root.

So

$$(\bar{V} - \bar{V}_c)^3 = 0$$

$$\bar{V}^3 - 3\bar{V}_c\bar{V}^2 + 3\bar{V}_c^2\bar{V} - \bar{V}_c^3 = 0$$

Comparing,

$$3\bar{V}_c = b + \frac{RT_c}{P_c}$$

$$3\bar{V}_c^2 = \frac{a}{P_c}$$

$$\bar{V}_c^3 = \frac{ab}{P_c}$$

Thus,

$$V_c = 3b$$

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

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

We may rewrite the Van der Waals equation as

$$\left(P + \frac{3P_c \bar{V}_c^2}{\bar{V}^2}\right) \left(\bar{V} - \frac{1}{3}\bar{V}_c\right) = RT$$

Dividing through by $P_c \bar{V}_c$,

$$\left(\frac{P}{P_c} + 3 \frac{\bar{V}_c^2}{\bar{V}^2}\right) \left(\frac{\bar{V}}{\bar{V}_c} - \frac{1}{3}\right) = \frac{RT}{P_c \bar{V}_c}$$

Using

$$\frac{RT_c}{P_c \bar{V}_c} = R \left(\frac{8a}{27bR}\right) \left(\frac{27b^2}{a}\right) \left(\frac{1}{3b}\right)$$

$$= \frac{8}{3}$$

$$\frac{R}{P_c \bar{V}_c} = \frac{8}{3T_c}$$

$$\text{Thus } \frac{RT}{P_c \bar{V}_c} = \frac{8T}{3T_c}$$

The Van der Waals equation becomes

$$\left(\frac{P}{P_c} + \frac{3\bar{V}_c^2}{\bar{V}^2} \right) \left(\frac{\bar{V}}{\bar{V}_c} - \frac{1}{3} \right) = \frac{8}{3} \frac{T}{T_c}$$

Defining reduced quantities

$$T_R = \frac{T}{T_c} \quad P_R = \frac{P}{P_c} = \bar{V}_R = \frac{\bar{V}}{\bar{V}_c}$$

We have

$$\left(P_R + \frac{3}{\bar{V}_R^2} \right) \left(\bar{V}_R - \frac{1}{3} \right) = \frac{8}{3} T_R$$

No quantities related to any particular gas.

Law of corresponding states $\longrightarrow$
all gases have the same
properties when compared
under corresponding conditions.

Virial equation of state $\rightarrow$ compressibility factor is expressed as a polynomial in $\bar{V}$

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \dots$$

Second virial coefficient

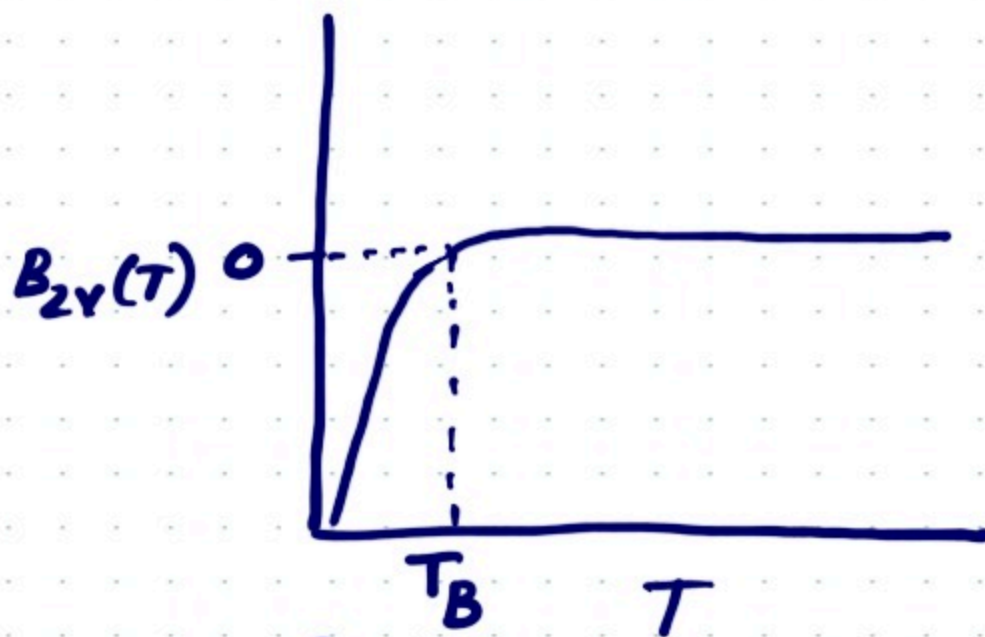
Third virial coefficient

Z can also be expressed as a polynomial in P

$$Z = \frac{P\bar{V}}{RT} = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + \dots$$

$$B_{2V}(T) = RT B_{2P}(T)$$

The second virial coefficient represents the largest deviation from ideality as the pressure increases and the volume decreases.



Boyle Temperature $\rightarrow$ Temperature where repulsive and attractive forces balance each other and the system behaves ideally.

For two molecules separated by a distance r , the potential becomes $V(r)$, and $B_{2V}(T)$ is given by

$$B_{2V}(T) = -2\pi N_A \int_0^{\infty} [e^{-V(r)/k_B T} - 1] r^2 dr$$

The most commonly used form
term is the Lennard-Jones
potential Repulsive Attractive

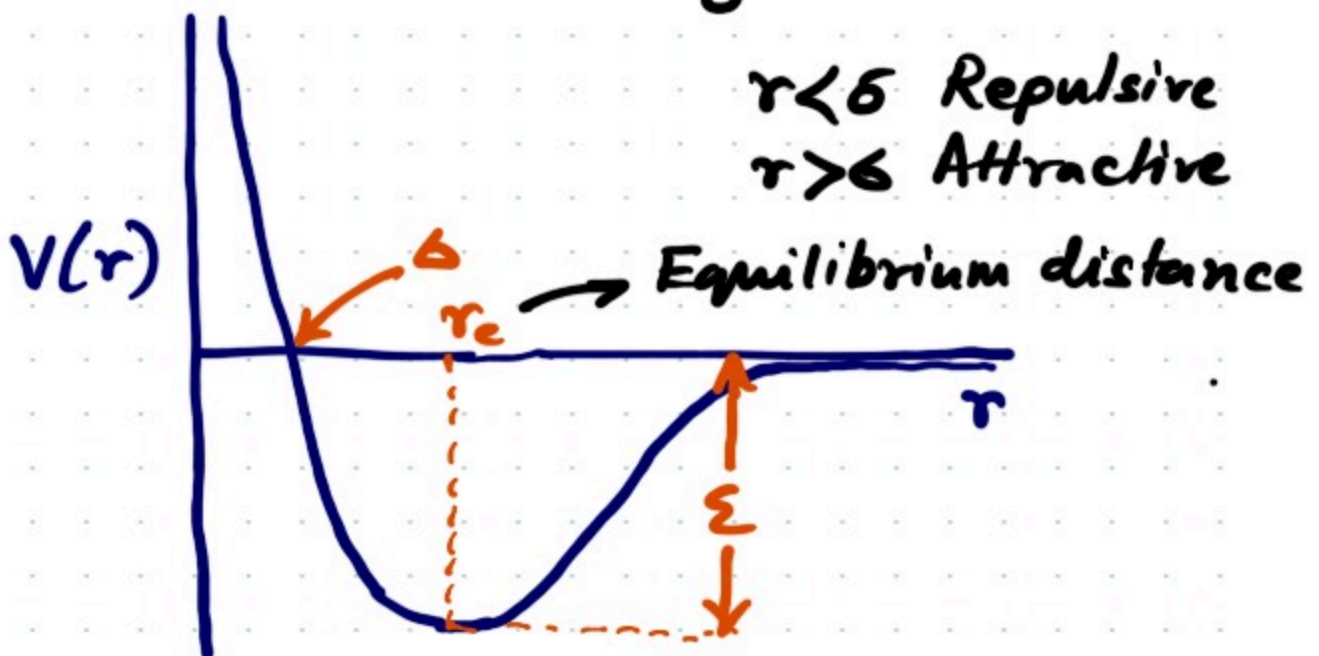
$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

well-depth

distance at
which the
potential crosses
0

$r < \sigma$ Repulsive

$r > \sigma$ Attractive



PROBLEMS

c1) Calculate the compressibility factor for a Van der Waals gas.

$$z = \frac{P\bar{V}}{RT}$$

For a Van der Waals gas

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

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

$$\frac{P\bar{V}}{RT} - \frac{Pb}{RT} + \frac{a}{\bar{V}RT} - \frac{ab}{\bar{V}^2RT} = 1$$

$$z = 1 + \frac{Pb}{RT} - \frac{a}{\bar{V}RT} + \frac{ab}{\bar{V}^2RT}$$

$$= 1 + \frac{b}{RT} \left(P + \frac{a}{\bar{V}^2}\right) - \frac{a}{\bar{V}RT}$$

$$= 1 + \frac{b}{RT} \cdot \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}RT}$$

$$= 1 + \frac{b}{\bar{V}-b} - \frac{a}{\bar{V}RT}$$

$$= \frac{\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}RT}$$

As $a \rightarrow 0, b \rightarrow 0$

$z \rightarrow 1$ as for an ideal gas

(2) Calculate the critical compressibility condition for a Redlich-Kwong gas using the equality condition of the roots at the critical point.

Starting with Redlich-Kwong equation

$$P = \frac{RT}{\bar{V}-B} - \frac{A}{T^{1/2}\bar{V}(\bar{V}+B)}$$

$$P(\bar{V} + B) \bar{V} T^{1/2} (\bar{V} - B) =$$

$$RT^{3/2} \bar{V} (\bar{V} + B) - A(\bar{V} - B)$$

$$P(\bar{V}^2 - B^2) \bar{V} T^{1/2} = RT^{3/2} \bar{V}^2 +$$

$$RT^{3/2} B \bar{V} - A \bar{V} + AB$$

$$T^{1/2} P \bar{V}^3 - PB^2 T^{1/2} \bar{V} = RT^{3/2} \bar{V}^2 + RT^{3/2} B \bar{V} - A \bar{V} + AB$$

$$T^{1/2} P \bar{V}^3 - T^{3/2} R \bar{V}^2 - \bar{V} (PB^2 T^{1/2} + RT^{3/2} B - A) - AB = 0$$

Dividing by $T^{1/2} P$

$$\bar{V}^3 - \frac{RT}{P} \bar{V}^2 - \left(B^2 + \frac{BRT}{P} - \frac{A}{T^{1/2}P} \right) \bar{V} - \frac{AB}{T^{1/2}P} = 0$$

Which gives the cubic form of the Redlich-Kwong equation

At the critical point,

$$(\bar{V} - \bar{V}_c)^3 = 0$$

$$\bar{V}^3 - 3\bar{V}_c \bar{V}^2 + 3\bar{V}_c^2 \bar{V} - \bar{V}_c^3 = 0$$

Comparing,

$$3\bar{V}_c = \frac{RT_c}{P_c}$$

$$z_c = \frac{P_c \bar{V}_c}{RT_c} = \frac{1}{3}$$

(3) The isothermal compressibility is given by

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

What is its value for an ideal gas?

$PV = nRT$ for an ideal gas

$$V = \frac{nRT}{P}$$

$$\left(\frac{\partial Y}{\partial P}\right)_T = - \frac{nRT}{P^2}$$

$$\begin{aligned}\beta &= -\frac{1}{V} \left(\frac{\partial Y}{\partial P}\right)_T = \frac{nRT}{PV \cdot P} \\ &= \frac{nRT}{nRT} \cdot \frac{1}{P} \\ &= \frac{1}{P}\end{aligned}$$

For an ideal gas,

$$\underline{\beta = \frac{1}{P}}$$

(4) For the Van der Waals equation,
Starting from

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

impose the critical conditions
and solve for a and b .

What would the compressibility
be at the critical point?

Applying the critical conditions

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

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

At the critical point

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

Thus,

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

$$\frac{2RT_c}{(\bar{V}_c - b)^3} = \frac{6a}{\bar{V}_c^4}$$

Dividing the first by the second

$$\frac{\bar{V}_c - b}{2} = \frac{\bar{V}_c}{3} \quad \text{or} \quad \underline{\bar{V}_c = 3b}$$

Substituting $\bar{V}_c = 3b$ into the first equation

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

$$\underline{T_c = \frac{8}{27} \frac{a}{bR}}$$

Substituting the $\bar{V}_c$ and T_c values into the Van der Waals equation at the critical point.

$$\left(P_c + \frac{a}{\bar{V}_c^2}\right)(\bar{V}_c - b) = RT_c$$

$$\left(P_c + \frac{a}{9b^2}\right)2b = \frac{8a}{27b}$$

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

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

$$\begin{aligned} z_c &= \frac{P_c \bar{V}_c}{RT_c} = \frac{a}{27b^2} \cdot 3b \cdot \frac{27b}{8a} \\ &= \frac{3}{8} \end{aligned}$$

- (5) Expand the van der Waals compressibility factor in powers of $\frac{1}{\bar{V}}$ and find expressions for $B_{2V}(T)$, $B_{3V}(T)$ and $B_{4V}(T)$. When does the equation converge.

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

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

Multiplying throughout by $\frac{\bar{V}}{RT}$

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

$$\text{Now, } \frac{\bar{V}}{\bar{V} - b} = \frac{1}{1 - \frac{b}{\bar{V}}}$$

Recall the geometric series

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

Thus,

$$\frac{1}{1 - \frac{b}{V}} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots$$

$$Z = 1 - \frac{a}{RTV} + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots$$

$$= 1 + \left(b - \frac{a}{RT}\right) \frac{1}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots$$

Thus,

$$B_{2V}(T) = b - \frac{a}{RT}$$

$$B_{3V} = b^2 \quad B_{4V} = b^3 \quad \text{etc.}$$

Note that only the 2nd virial Co-efficient is temperature dependent in this case.

The equation converges for $\bar{V} > b$.