Properties Of Gases

Dilute gases behave ideally.

Equation of state for an ideal gas:

$$PV = nRT$$

- P: Pressure ($N m^{-2}$) = $kg\, m^{-1} s^{-2}$ → Pascal ($1\ N m^{-2}$)
- V: Volume (m^{-3})
- n: number of moles
- R: Universal gas constant $8.314\ J K^{-1} m^{-1}$
- T: Temperature (K)

1 atmosphere = 1.01325×10^5 Pa
= 1.01325 bar
= 760 Torr

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

$$P = \frac{F}{A} = \frac{mg}{A}$$

- F: Force (N)
- m: Mass (kg)
- A: Area (m^{-2})
- g: gravitational constant $9.8\ ms^{-2}$

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

ρ → density of the fluid (kg m^{-3})

h → height of the column of liquid (m)

$$P = \rho h g$$

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

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

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

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

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

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

$= 101.33\ kPa$

The universal gas constant R

$R = n_A k_B$ ← Boltzmann constant (1.38×10^{-23} JK^{-1})

↗ Avogadro number 6.022×10^{-23} molecules/mol

Dividing both sides of the ideal gas equation by n

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

↖ molar volume

Extensive quantity → proportional to the size of the system
e.g. Volume (V)
[mass, energy]

Intensive quantity → independent of the size of the system
e.g. molar volume ($\bar{V}$)
[pressure, temperature]

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

No degree used → absolute temperature → Kelvin

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

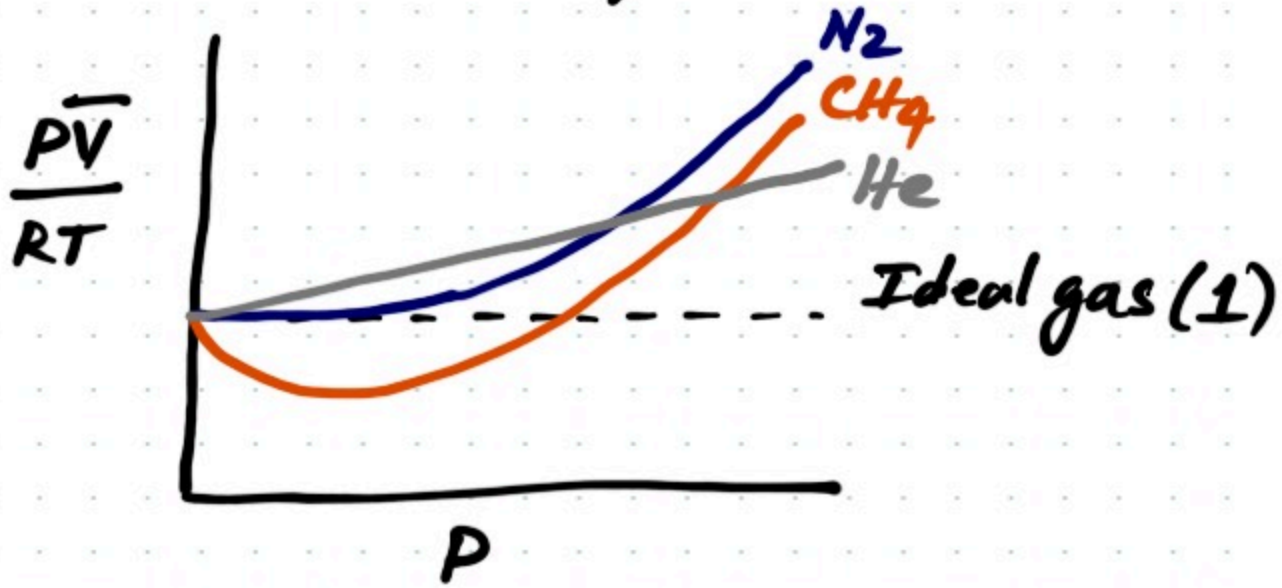
$$t(^\circ C) = T(K) - 273.15$$

So absolute 0 is $-273.15\ ^\circ C$

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

C → Celcius (Centigrade)

F → Fahrenheit



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

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

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

$\frac{a}{\bar{V}^2}$: Related to attractive forces between molecules

b: molecular size

He

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

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

N_2

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

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

CO_2 $a = 0.366\ Pa\ m^6\ mol^{-1}$

$b = 4.286 \times 10^{-5}\ m^3\ mol^{-1}$

Attractive forces :

$CO_2 \gg N_2 \gg He$

Molecular size:

CO_2 (3.24 Å) > N_2 (3.13 Å) > He (2.66 Å)

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

$$\frac{a}{\bar{V}^2} \to \infty$$

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

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

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

$\bar{V} - b \longrightarrow$ 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 → superior at high pressures

Peng-Robinson → superior at the liquid-vapor interface

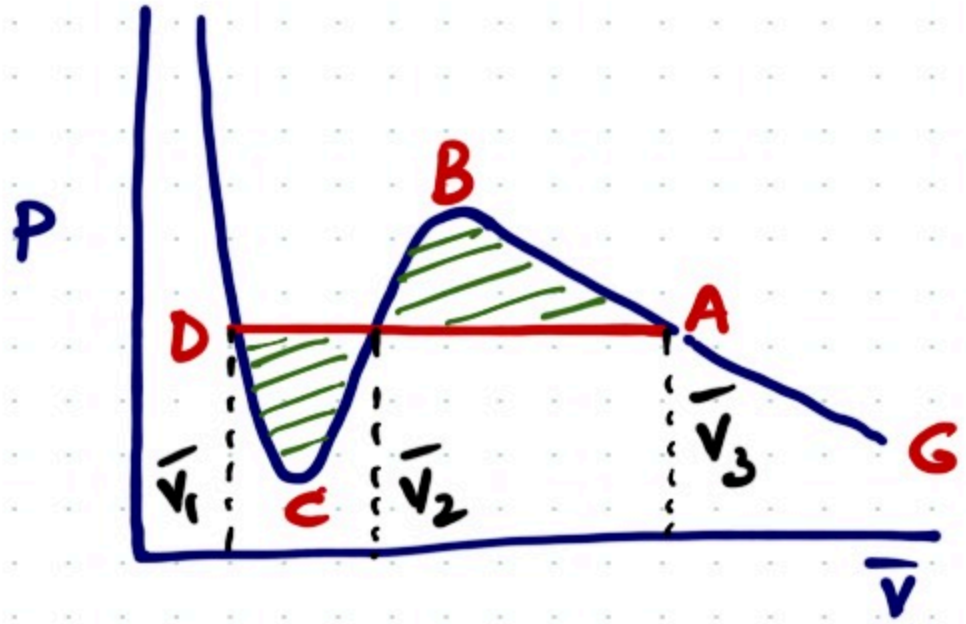
Cubic equations can describe both the gaseous and liquid states.

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

T_c ⟶ 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 ⟶ supercooled liquid (held below its melting temperature without forming a solid)

AB ⟶ Superheated vapor

These are metastable states.

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

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

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

$\bar{v}_2$ ⟶ no physical meaning

At the critical point:

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

$$V = V_c$$

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

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 recorite 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

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

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

$$\frac{R}{P_cV_c} = \frac{8}{3T_c}$$

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

The Van der Waals equation becomes

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

Defining reduced quantities

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

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 ⟶ all gases have the same properties when compared under corresponding conditions.

Virial equation of state → compressibility factor is expressed as a polynomial in $\frac{1}{\bar{V}}$

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

Second virial coefficient

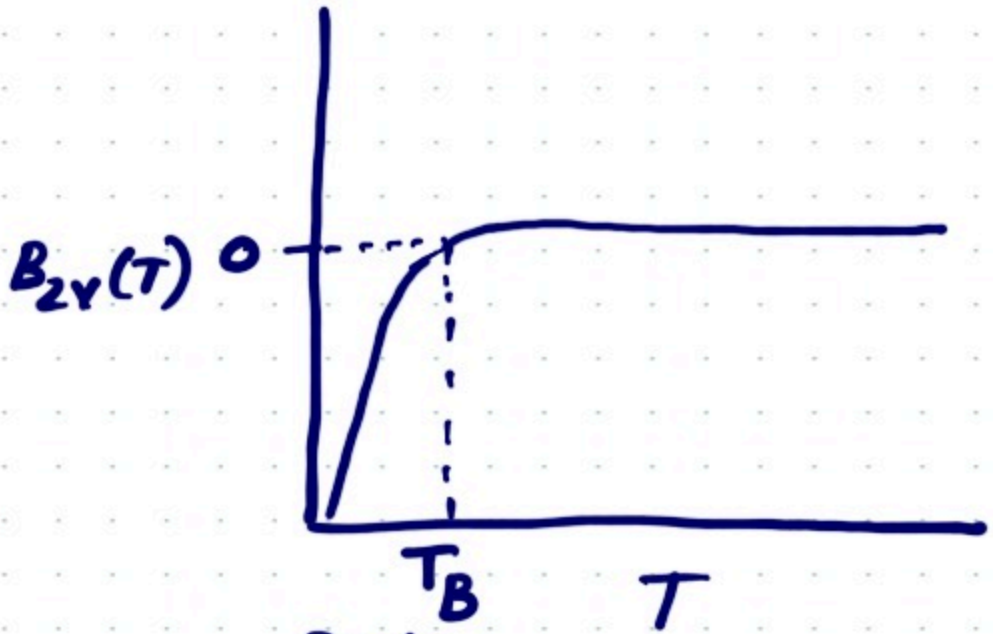
Third virial coefficient

Z can also be expressed as a polynomial in P

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

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

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



Boyle Temperature → 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

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

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

Repulsive Attractive

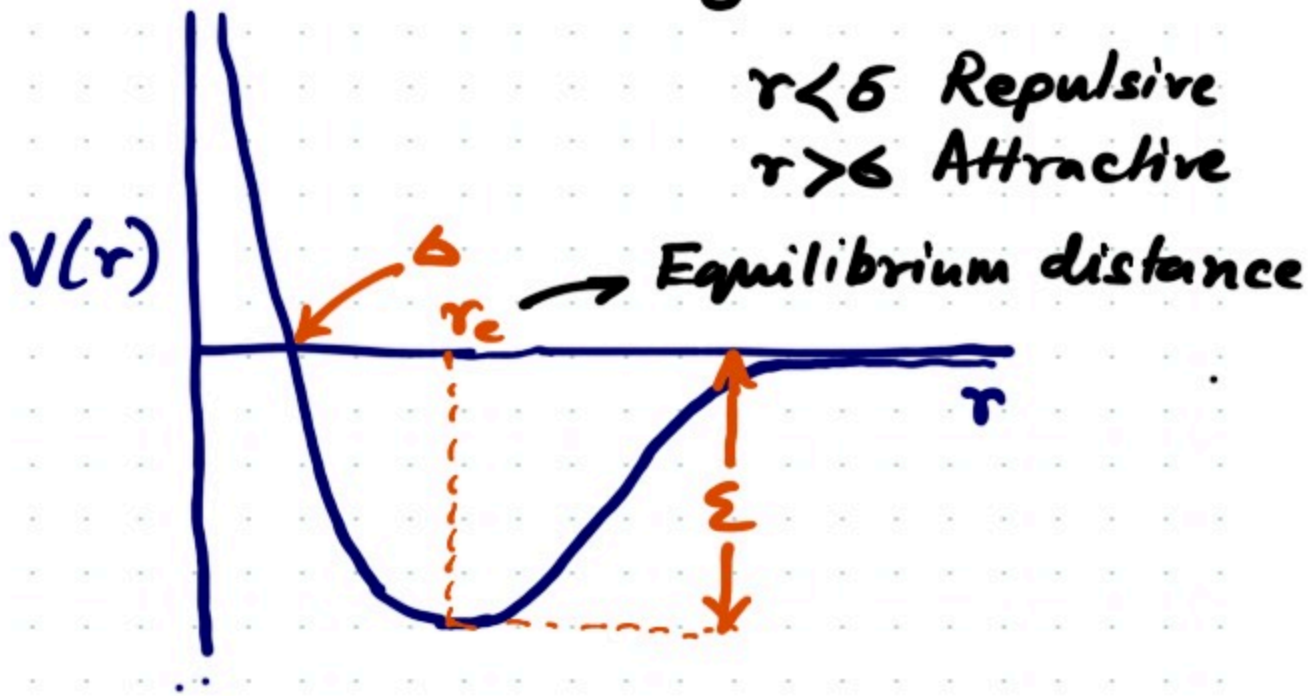
$$V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

ε : well-depth

σ : distance at which the potential crosses 0

$r < \sigma$ Repulsive

$r > \sigma$ Attractive



PROBLEMS

(1) 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 $a \to 0$, $b \to 0$

$Z \to 1$ 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

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

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

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

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

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

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

$$-A\bar{V} + AB$$

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

$$-A) - AB = 0$$

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

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

What is its value for an ideal gas?

$PV = nRT$ for an ideal gas

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

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

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

$$= \frac{nRT}{nRT} \cdot \frac{1}{P}$$

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

For an ideal gas,

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