Gases

ideal gas eq → Vander Waals Eq. ?

i.) volume → free of particles, but particles have finite vol. actual vol. ?

ii.) attractive force ? (Wikipedia)

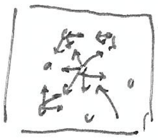
i.) $p\bar{V} = RT \rightarrow p = \frac{RT}{\bar{V}}$ ← free vol.

ideal : $\bar{V} \approx V_{container}$

real : should be smaller

$\therefore \; p = \frac{RT}{\bar{V} - b}$ small

ii.)



particle in the centre exp. no net force

particle at the edges exp. a net force away from surface

This force $\propto \rho$ (number density)

no. of mol. at surface $\propto \rho$

$\therefore \; p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$ so exert less pressure

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

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

what's the interpretation for b ?

interpretation of a ?

↳ looks at data : b ↔ size of particles ? (He, Ne, Ar, Kr)

a ↔ strength of intermolecular force ?

given $\bar{V}$, find p? $p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$

given P, find $\bar{V}$?

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

$$p\bar{V}^3 - (bp + RT)\bar{V}^2 + a\bar{V} - ab = 0$$

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

Pressure - volume isotherm :
(y) (x)

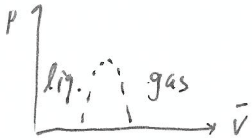
i.) how does isotherm depend on T ?

ii.) try plotting them for diff. T ; main features :

- liquid & gas phase ↔ compressibility ↔ pressure
- coexistence curve ↔ condensation !? ↔ equi. !?
- critical pt.

i.) given a $\bar{V}$, $P\uparrow$ as $T\uparrow$, so whole graph lifted

ii.)



VDW vs experimental :

remedy : Maxwell's equal area construction

i) how is this related to cubic in $\bar{V}$?

ii.) how do size of loops change with T?

iii.) what happens at the critical T?

ii) size of loops decrease (try plotting ...)

i) given $y = P$, intersect at 3 pt. below critical pt.

given P, find $\bar{V}$: $\bar{V}^3$ ↗ 3 roots ! ✓

iii) loops go "0", inflection pt.

how to find critical pt. ?

2 ways i.) inflection ⇒ $\left(\frac{\partial P}{\partial \bar{V}}\right)_T = 0$, $\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = 0$

ii.) since only single real root, we set $(V - V_c)^3 = 0$!

show that $\bar{V}_c = 3b$, $P = \frac{a}{27b^2}$, $T = \frac{8}{27}\frac{a}{Rb}$

i.)

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

$$\frac{\partial p}{\partial \bar V} = -\frac{RT}{(\bar V - b)^2} + \frac{2a}{\bar V^3} = 0 \qquad \frac{RT}{(\bar V - b)^2} = \frac{2a}{\bar V^3}$$

$$\frac{\partial^2 p}{\partial \bar V^2} = +\frac{2RT}{(\bar V - b)^3} - \frac{6a}{\bar V^4} = 0 \qquad 2\frac{1}{\bar V - b}\frac{RT}{(\bar V - b)^2} = \frac{3}{\bar V}\frac{2a}{\bar V^3}$$

$$\frac{2}{\bar V - b} = \frac{3}{\bar V} \qquad T_c = \frac{2a}{R}\frac{4b^2}{27b^3}$$

$$2\bar V = 3(\bar V - b) \qquad = \frac{8}{27}\frac{a}{Rb} \ \#$$

$$\bar V_c = 3b \ \#$$

$$P_c = \frac{\frac{8}{27}\frac{a}{b}}{2b} - \frac{a}{9b^2} = \frac{a}{27b^2} \ \#$$

ii.) $(\bar V - \bar V_c)^3 = \bar V^3 - 3\bar V^2 \bar V_c + 3\bar V \bar V_c^2 - \bar V_c^3$

comparing coeff.,

$$3\bar V_c = b + \frac{RT}{P} \qquad 3\bar V_c^2 = \frac{a}{P} \qquad \bar V_c^3 = \frac{ab}{P}$$

$$9b = b + \frac{RT(27b^2)}{a} \qquad 3\bar V_c^2 = \frac{\bar V_c^3}{b} \qquad P = \frac{a}{27b^2} \ \#$$

$$T = \frac{8}{27}\frac{a}{Rb} \ \# \qquad \bar V_c = 3b \ \#$$

$$\frac{P_c \bar V_c}{RT_c} = 3/8$$

notice: VDW : 2 parameter

RK : 3 param.

how diff. are diff. gases? what varies between them?

V.DW: assume the only diff. are the attractive forces & the effective volume.

Law of Corresponding States : "scaling"

i.) expr. VDW Eq. in terms of V_c, P_c, T_c

ii.) how to interpret?

i.)

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

$$\left(P + \frac{3P_c \bar V_c^2}{\bar V^2}\right)\left(\bar V - \frac{\bar V_c}{3}\right) = R(T/T_c)T_c \qquad \text{divide by } P_c \bar V_c$$

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

$$(P_R + 3\bar V_R)(\bar V_R - \tfrac{1}{3}) = \tfrac{8}{3} T_R \qquad \text{"relative"}$$

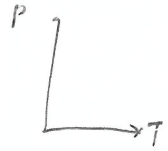
ii.) gases behave in the same way; but since they have diff a & b, the PVT at which it has a particular behavior is scaled based on these parameters.

Phase diagram (P-T) of Gas

i.) what 3 phases? Location?

ii.) what special pt.?

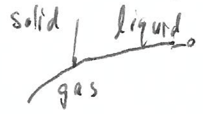
iii.) phase boundaries qualitatively? meaning?



i.) when T low, solid.; pressure low, gas

liquid, everything else.

ii.)



· Triple pt.

· critical pt.

iii.) boundaries: equilibrium of multiple phases

how does $\bar V$ come in?

$P, \bar V, T$ not independent! any 2 gives the 3rd!?

$U(S, V, \dots)$!

$\uparrow T \quad \uparrow P$