Unit 8

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Physics

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Deviation of real gas behaviour from that of an ideal gas

$PV = RT$

$$\boxed{PV = A + \boxed{B}P + CP^2 + \ldots\ldots}$$ ①

A, B, C — virial constants

$\boxed{A = RT}$

$A > B > C > D$

Andrew ✓

Onnes

Amagat

+ve at high temp

0

B -ve low temp.

$\boxed{T_B}$ → Boyle's temp.

① At infinitely low pressure ($P \rightarrow 0$)

→ gases obey Boyle's Law

② At low pressures

gases obey Boyle's Law approximately

③ At high pressure

→ Deviation

$T < T_B$

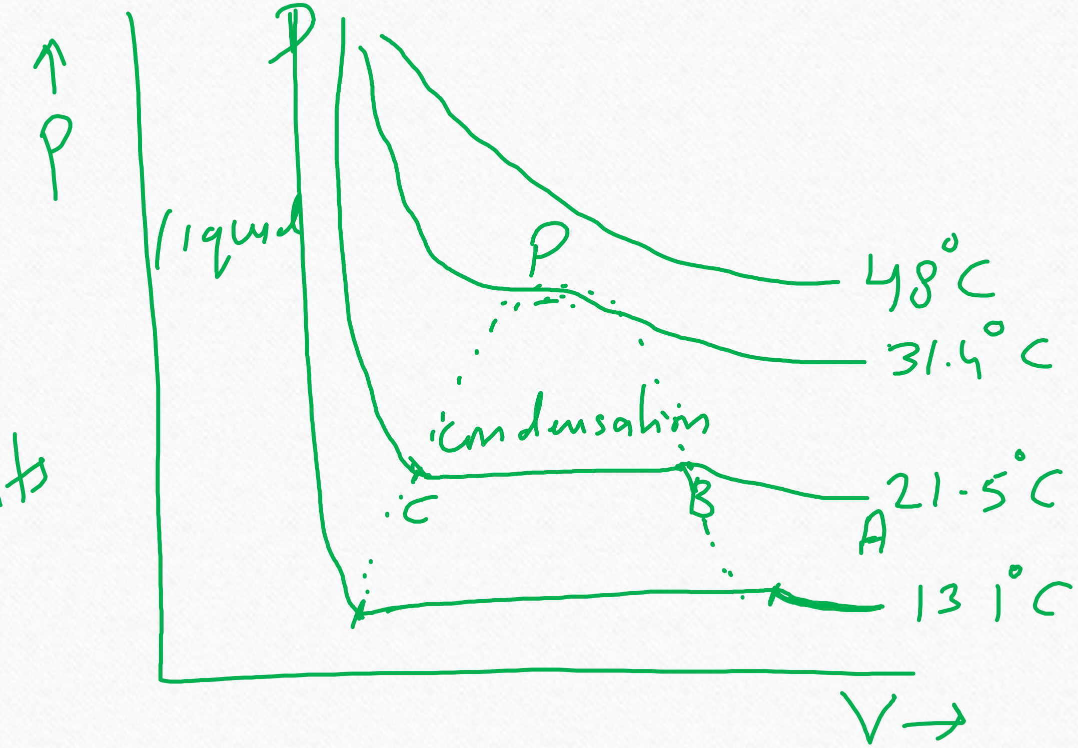
$B = -ve$

$T > T_B$ $B = +ve$

Andrew's Experiment on Carbon Dioxide

T_c
P_c
V_c

critical constants



Van Der Waal's Equation of state for real gases

$PV = RT$

① Correction due to finite size of the molecule

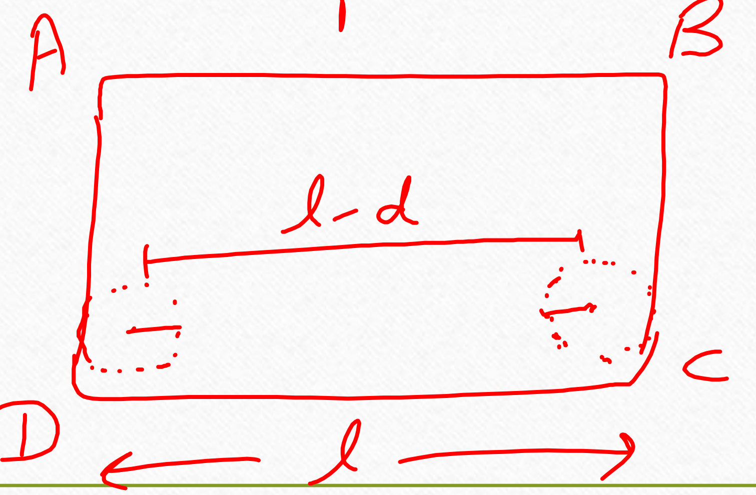
V

V

$\boxed{V - b}$ ✓

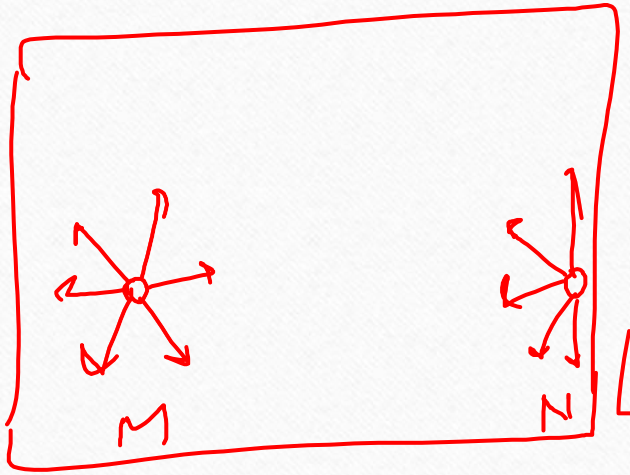
co-volume

$\boxed{b = 4V_m}$



(b) Correction due to intermolecular forces

$P + \underline{\quad}$



$$\boxed{P + \frac{a}{V^2}}$$

$\boxed{p} \propto \rho^2$

$\propto \frac{M^2}{V^2}$

$p = \frac{KM^2}{V^2}$

$= \frac{a}{V^2}$ where $a = KM^2$

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

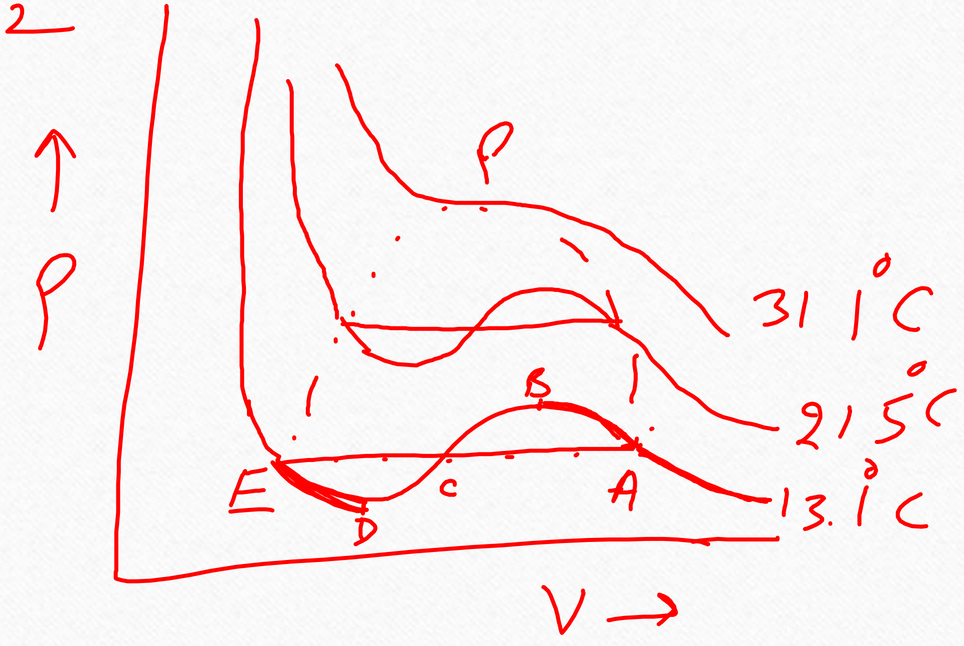
Van der Waal's Eq^n of state

Comparison with experimental results

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

BA → super cooling of vapour

DE → super-heating of liquid



BCD →

Critical Constants of a van der Waal's gas

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

$$\Rightarrow PV-bP+\frac{a}{V}-\frac{ab}{V^2}=RT$$

$$V^2 \rightarrow PV^3-bPV^2+aV-ab=RTV^2$$

$$\text{or } PV^3-V^2\cdot(bP+RT)+aV-ab=0$$

divide by P $\Rightarrow V^3-V^2\left(b+\frac{RT}{P}\right)+\frac{aV}{P}-\frac{ab}{P}=0 \quad -2$

$V = x \Rightarrow V - x = 0$

$(V-x)^3 = 0$

$\Rightarrow V^3 - V^2 3x + V 3x^2 - x^3 = 0$ — (3)

Comparing the coeff.

$3x = b + \frac{RT}{P}$ — (4)

$3x^2 = \frac{a}{P}$ — (5)

$x^3 = \frac{ab}{P}$ — (6)

$\frac{x^{\cancel{3}}}{3\cancel{x^2}} = \frac{ab/P}{a/P} = b$

$\Rightarrow \boxed{x = 3b}$

$\boxed{V_c = 3b}$ — (7)

$$3 \times 9b^2 = \frac{a}{P} \Rightarrow P = \frac{a}{27b^2}$$

$$\boxed{P_c = \frac{a}{27b^2}} \quad — 8$$

$$3 \times 3b = P + \frac{RT}{P}$$

$$\Rightarrow T = \frac{8a}{27bR}$$

$$\boxed{T_c = \frac{8a}{27bR}} \quad — 9$$

Critical coeff

$$T_c \times \frac{1}{P_c} \times \frac{1}{V_c}$$

$$= \frac{8a}{27bR} \times \frac{27b^2}{a} \times \frac{1}{3b}$$

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

$$\Rightarrow \boxed{\frac{RT_c}{P_cV_c} = \frac{8}{3} = 2.67} \quad — 10$$

$$\frac{T_c^2}{P_c} = \frac{64a}{27R^2}$$

$$\Rightarrow \boxed{a = \frac{27R^2}{64}\frac{T_c^2}{P_c}} \quad \text{— } 11$$

$$\frac{T_c}{P_c} = \frac{8b}{R}$$

$$\Rightarrow \boxed{b = \frac{RT_c}{8P_c}} \quad \text{— } 12$$

Limitations of Van der Waal's equation

① a and b are not const —

② $V_c = 3b$ but experimentally $V_c = 2b$

③ $C_c = \frac{RT_c}{P_cV_c} = \frac{8}{3} = 2.67$
experimentally about — 3.38

④ $T_B = 3\ 375\ T_c$ Theoretically
lie bet^n $2.5\ T_c$ and $3\ 7\ T_c$ experimentally

Van der Waal Equation, Virial Coefficients and Boyle Temperature

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

$$\Rightarrow PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$\Rightarrow PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}$$

$$\frac{1}{V} \rightarrow \frac{P}{RT}$$

$$PV = RT + Pb - \frac{aP}{RT} + \frac{abP^2}{R^2T^2}$$

$$PV = RT + P\left(b - \frac{a}{RT}\right) + \frac{abP^2}{R^2T^2} \quad -(1)$$

$$A = RT$$

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

(1) Below Boyle Temp

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

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

$-ve$

$PV \downarrow$

(ii) Above Boyle temp.

$\frac{a}{RT}$

$b - \frac{a}{RT} > 0$

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

$\boxed{T_B = \frac{27}{8} T_c = 3.375 T_c}$

$PV \uparrow$

(iii) At Boyle temp

$b - \frac{a}{RT} = 0$

$\Rightarrow \boxed{T_B = \frac{a}{Rb}} \quad — (2)$

Corresponding States

$$\frac{P_1}{P_{c_1}} = \frac{P_2}{P_{c_2}}$$

$$\frac{V_1}{V_{c_1}} = \frac{V_2}{V_{c_2}}$$

$$\frac{T_1}{T_{c_1}} = \frac{T_2}{T_{c_2}}$$

gas 1 and gas 2 are said to be in corresponding states.

Reduced Equation of State

P_r , V_r and T_r

$$\frac{P}{P_c} = P_r , \quad \frac{V}{V_c} = V_r \quad \text{and} \quad \frac{T}{T_c} = T_r$$

$$\Rightarrow P = P_r P_c , \quad V = V_c V_r , \quad T = T_c T_r$$

$$P_c = \frac{a}{27b^2} , \quad V_c = 3b \quad \text{and} \quad T_c = \frac{8a}{27Rb}$$

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

$$\left[\frac{a}{27b^2} P_r + \frac{a}{9b^2 V_r^2}\right](3bV_r - b) = R\,\frac{8a}{27Rb}\,T_r$$

$$\Rightarrow \frac{a}{27b^2}\left(P_r + \frac{3}{V_r^2}\right)3b\left(V_r - \frac{1}{3}\right) = \frac{8a}{27b}\,T_r$$

$$\Rightarrow \boxed{\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8}{3}\,T_r}$$

Reduced Eq^n of state

Thank you