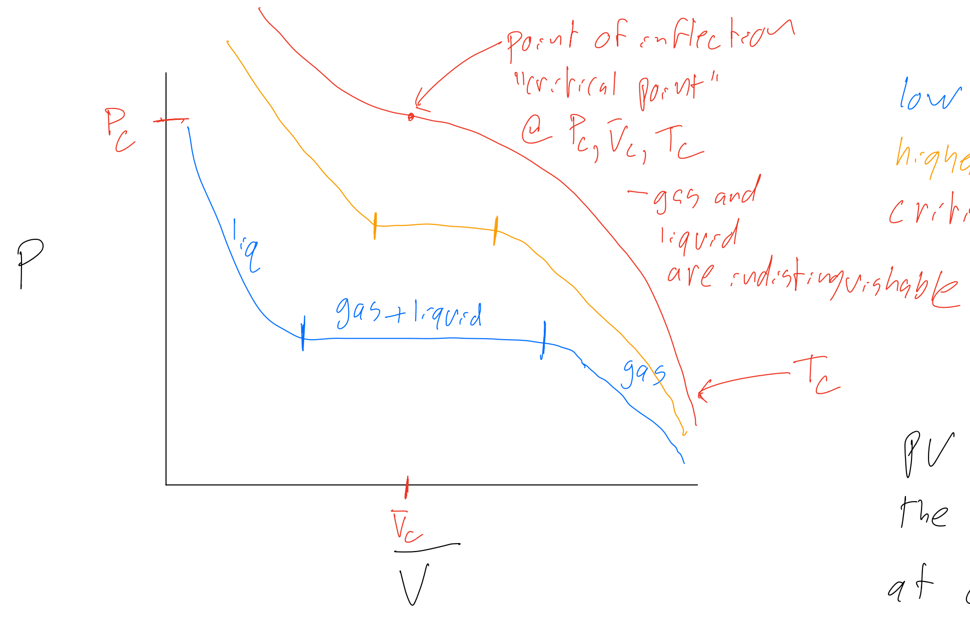
Non ideal gas parameters came from experiments — measurement of Pressure-Volume Isotherm



low temp
higher temp
critical temp

PV isotherm is just the graph of the gas law at constant temp

* At a point of inflection 1st and 2nd deriv = 0

For VDW $\longrightarrow$ $P = \dfrac{RT}{\bar{V}-b} - \dfrac{a}{\bar{V}^2}$ at $T = T_c$

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

when $P = P_c$ and $\bar{V} = \bar{V}_c$ 1st + 2nd deriv = 0

$$\frac{dP}{d\bar{V}} = RT_c(-1)(\bar{V}-b)^{-2}) - (-2\bar{V}^{-3})(a)$$

— this = 0 when $\bar{V} = \bar{V}_c$ and $T = T_c$

$$\boxed{\frac{-RT_c}{(\bar{V}_c-b)^2} + \frac{2a}{\bar{V}_c^3} = 0} \times \frac{3}{\bar{V}_c} \rightarrow \frac{-3RT_c}{\bar{V}_c(\bar{V}_c-b)^2} + \frac{6a}{\bar{V}_c^4} = 0$$

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

$$\frac{2RT_c}{(\bar{V}_c-b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

Add

$$\frac{2RT_c}{(\bar{V}_c-b)^3} - \frac{3RT_c}{\bar{V}_c(\bar{V}_c-b)^2} = 0 \qquad \frac{2}{\bar{V}_c-b} = \frac{3}{\bar{V}_c}$$

$$2\bar{V}_c = 3\bar{V}_c - 3b$$

$$3b = \bar{V}_c$$

$$\boxed{b = \frac{\bar{V}_c}{3}}$$

$$\frac{-RT_c}{(\bar{V}_c-b)^2} + \frac{2a}{\bar{V}_c^3} = 0$$

$$\frac{-RT_c}{\left(\bar{V}_c - \left(\frac{\bar{V}_c}{3}\right)\right)^2} + \frac{2a}{\bar{V}_c^3} = 0 \qquad \frac{-RT_c}{\left(\frac{2\bar{V}_c}{3}\right)^2} + \frac{2a}{\bar{V}_c^3} = 0$$

$$\frac{-RT_c \cdot 9}{4\bar{V}_c^2} + \frac{2a}{\bar{V}_c^3} = 0$$

$$2a = \cancel{\bar{V}_c^3}\left(\frac{9RT_c}{4\cancel{\bar{V}_c^2}}\right)$$

$$\boxed{a = \frac{9}{8}RT_c\bar{V}_c}$$

If you know a, b you can calculate $T_c, \bar{V}_c, P_c$

since $b = \frac{\bar{V}_c}{3} \rightarrow \boxed{\bar{V}_c = 3b}$

$$a = \frac{9}{8}RT_c(3b) \longrightarrow \frac{8a}{9R \cdot 3b} = \boxed{T_c = \frac{8a}{27Rb}}$$

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \qquad P_c = \frac{R\left(\frac{8a}{27Rb}\right)}{2b} - \frac{a}{9b^2}$$

$$P_c = \frac{8a\cancel{R}}{54\cancel{R}b^2} - \frac{a}{9b^2} \qquad P_c = \frac{8a}{54b^2} - \frac{6a}{54b^2} = \boxed{\frac{a}{27b^2} = P_c}$$

$$Z = \frac{P\bar{V}}{RT} = 1 \text{ ideal}$$

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

$$Z_c = \frac{\cancel{a}\cdot 3\cancel{b}\cdot \cancel{27}\cancel{R}\cancel{b}}{\cancel{27}\cancel{b^2}\cdot\cancel{R}\cdot 8\cancel{a}} = \frac{3}{8}$$

Z_c for <u>any</u> gas described by VDW $= \frac{3}{8}$

Can use an infinite series to describe non-ideal behavior

Virial equation $\qquad Z = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \frac{B_{4V}(T)}{\bar{V}^3} + \ldots$

virial coeff

$B_{2V}(T)$

volume expansion

2nd

fxn of temp

Usually we only need $B_{2V}(T)$ to get good results

$$Z = 1 + B_{2P}(T)P + B_{3P}(T)P^2 + B_{4P}(T)P^3 + \ldots$$

Since virial coefficients are functions of temp there is often a temp at which the virial coeff $= 0 \Rightarrow$ gas behaves ideally

Boyle temperature $\rightarrow$ where gas behaves ideally