We've moved from IG to cubic EOS

but there are many more options

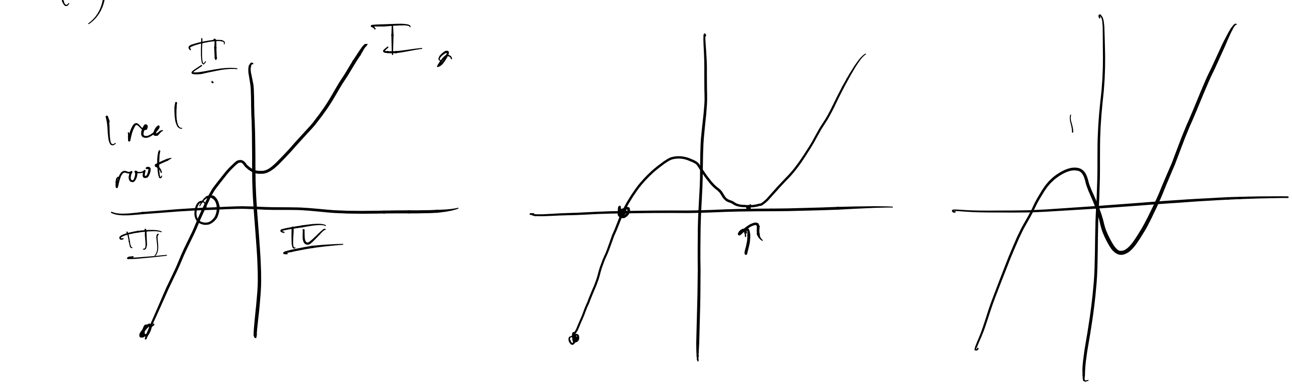
$$P = \frac{T}{\underline{V}}\left[R + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \frac{D}{\underline{V}^3} + \dots\right]$$

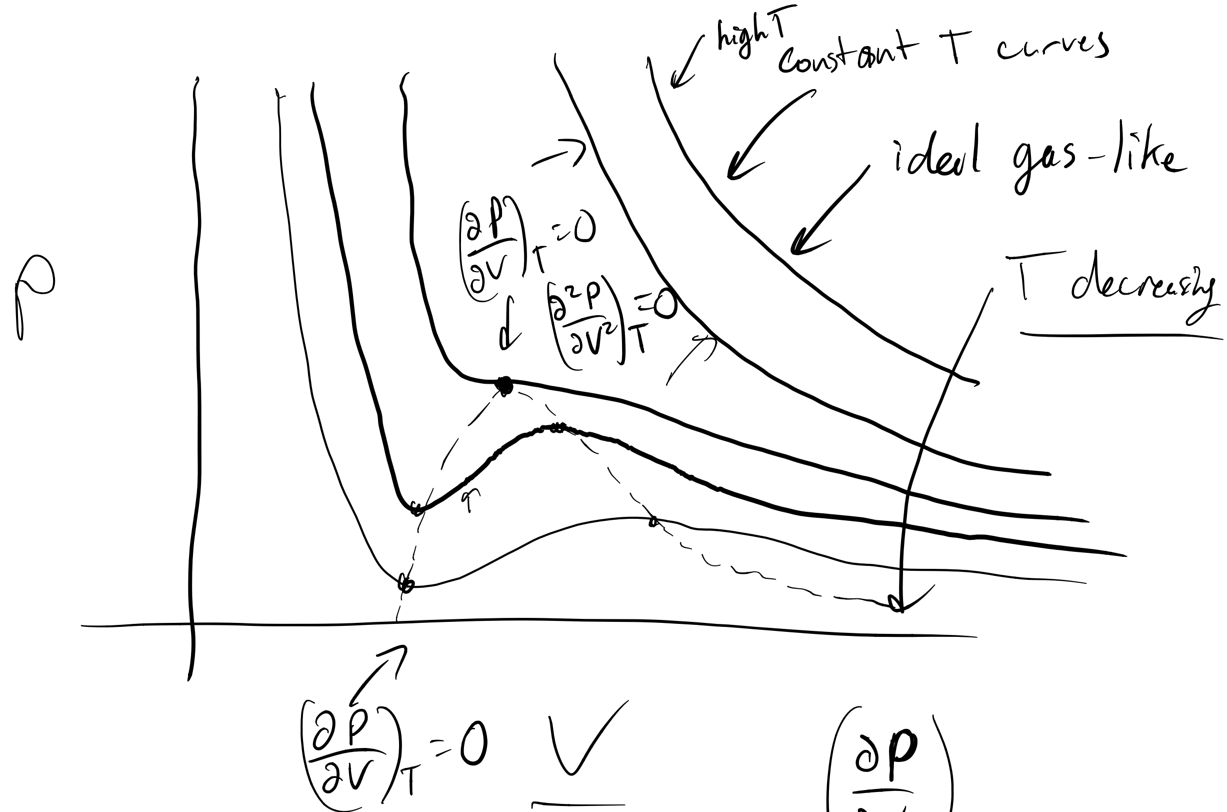
But - we will only do cubic EOS

$$Z \equiv \frac{PV}{RT}$$

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$$

1) 2 real roots 3 real roots





$$\left(\frac{\partial P}{\partial V}\right)_T$$

for $\left(\frac{\partial P}{\partial V}\right)_T < 0 \rightarrow$

a small increase in V leads to a small decrease in P

T_c = critical temperature.

for $T < T_c$ there are 2 points where $\left(\frac{\partial P}{\partial \underline{V}}\right)_T = 0$

@ $T = T_c$, the min, max, + inflection converge to a sigle point

T_c, P_c, $\underline{V}_c$

looking @ T_c, P_c, $\underline{V}_c$ is impor tant because the EOS has a similar behaviour

$T > T_c$ - P monotone decreasing function of $\underline{V}$ — like <u>an ideal gas</u>

1) Real fluids obey cubic like behaviour
2) <u>All</u> materials of interest have T_c, P_c, $\underline{V}_c$

Using VanderWaal's EOS

$$\boxed{\begin{gathered} P_c = \frac{RT_c}{\underline{V}_c - b} - \frac{a}{\underline{V}_c^2} \\ 1)\ \left(\frac{\partial P}{\partial \underline{V}}\right)_T \Bigg|_{T_c, P_c, \underline{V}_c} = 0 \\ 2)\ \left(\frac{\partial^2 P}{\partial \underline{V}^2}\right)_T \Bigg|_{T_c, P_c, \underline{V}_c} = 0 \end{gathered}}$$

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

$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T = \boxed{0 = -RT_c\left(\underline{V}_c-b\right)^{-2} + 2a\left(\underline{V}_c\right)^{-3}}$$

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

solve for a, b

3) $$\boxed{a = \frac{9\underline{V}_c RT_c}{8} \qquad b = \frac{\underline{V}_c}{3} \qquad P_c = \frac{a}{27b^2}}$$

You can sub in + calc. compressibility factor @ critical point

$$Z_c = \frac{P_c \underline{V}_c}{RT_c} = \frac{3}{8} = 0.375$$

$Z_c = 1$ for I. G.

VW is better but Real materials have $Z_c \approx 0.31$

what if you can't measure T_c, $\underline{V}_c$?
but you can measure T_c, P_c

$$\boxed{\begin{gathered} a = \frac{27 R^2 T_c^2}{64 P_c} \\ b = \frac{R T_c}{8 P_c} \end{gathered}}$$

with T_c, $\underline{V}_c$, P_c, we can now non-dimensionalize our EOS.

Rewrite VW EOS as:

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

· Define dimensionless variables:

*2)

$$\frac{P}{P_c} \equiv \underline{P_r} \qquad \frac{\underline{V}}{\underline{V_c}} \equiv \underline{\underline{V_r}} \qquad \frac{T}{T_c} = \underline{T_r}$$

$$P = P_r \cdot P_c \qquad \underline{V} = \underline{V_r} \cdot \underline{V_c} \qquad T = T_r \cdot T_c$$

5 minute break.

Take 1, sub in 2) and 3) →

get new <u>Dimensionless EOS</u>

To get new equation with

$$\frac{P}{P_c} \quad \frac{\underline{V}}{\underline{V_c}} \quad \frac{T}{T_c}$$

$$\frac{8}{T_c}\left[\left(P + \frac{\frac{9V_cRT_c}{8}}{V^2}\right)\left(V - \frac{V_c}{3}\right) = RT\right]$$

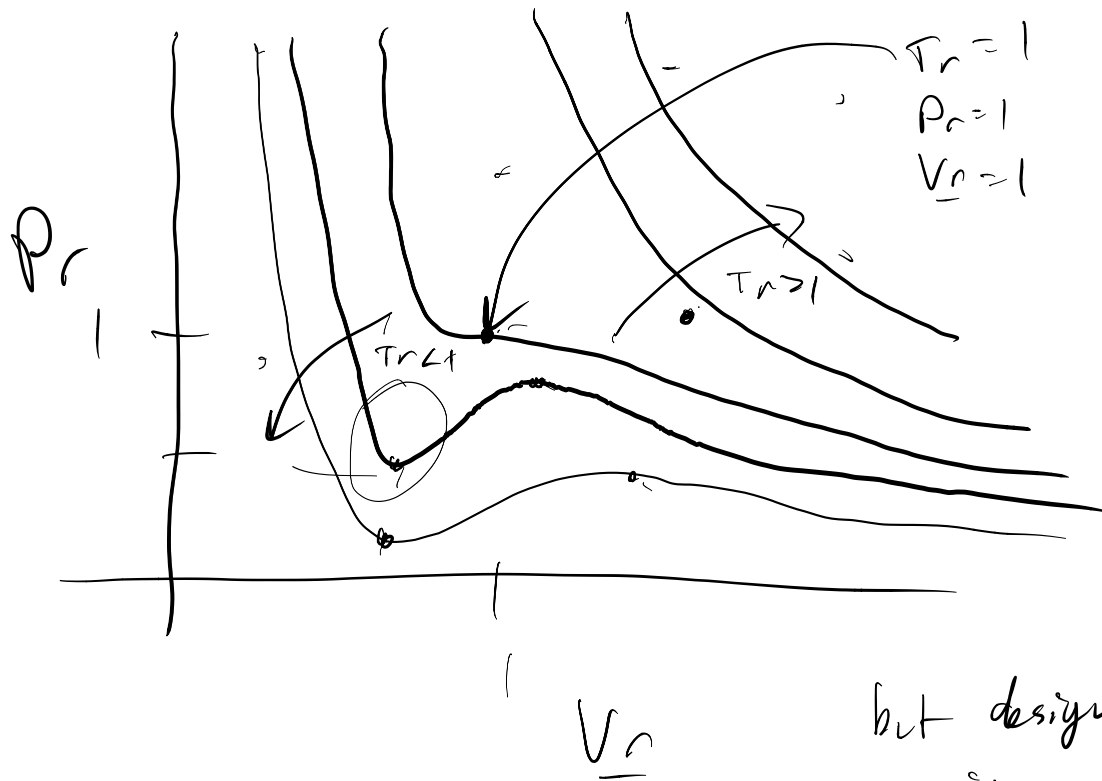
$$\left(\frac{8P}{RT_c} + \frac{9V_c\cancel{R}}{V^2}\right)\left(V - \frac{V_c}{3}\right) = \cancel{R}\,8\frac{T}{T_c}$$

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

$$\boxed{\left[\underbrace{\frac{P}{P_c}}_{P_r} + \underbrace{3\left(\frac{V_c}{V}\right)^2}_{\frac{3}{V_r^2}}\right]\left[3\left(\underbrace{\frac{V}{V_c}}_{V_r} - 1\right)\right] = 8\underbrace{\frac{T}{T_c}}_{T_r}}$$

$$\boxed{\left[P_r + \frac{3}{V_r^2}\right]\left[3V_r - 1\right] = 8T_r}$$

new graph



suppose YFM is $T_c = 100K$
$P_c = 2MPa$

but design is $T = 50K$
$P = 1MPa$

This in nice - very nice.

But not perfect.

The correspondence between the idealized case here and reality needs some correction factor

It gets insanely more difficult for mixtures of multiple components.

To account for differences in real materials, there is a new variable taken in to account:

It is called the acentric factor

omega

$$\boxed{\omega = -1.0 - \log_{10}\left(\frac{P^{vap}_{Tr=0.7}}{P_c}\right)}$$

acentric factor is like a bridge between microscopic properties & macroscopic properties.

accounts for some structure.

e.g. spherical vs. rod-like molecules