Rubric for VLE calculations

1) For a given T, P, use EOS to calculate $\underline{V}$ (use a computer)

in matlab.

roots

for vapor

2) Choose the low density (biggest) $\underline{V}$

bigger $\underline{V}$ is, the more ideal gas-like it is.

max( )

3) Use the value of $\underline{V}$ and sub into your equation for fugacity.

$$\ln\left(\frac{f^V(T,P)}{P}\right) = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=Z^V RT/P}\left(\frac{RT}{\underline{V}} - P\right)d\underline{V} - \ln Z^V + (Z^V - 1)$$

for liquid

$$\ln\left(\frac{f^L(T,P)}{P}\right) = \frac{1}{RT}\int_{\underline{V}=\infty}^{\underline{V}=Z^L RT/P} \left(\frac{RT}{\underline{V}} - P\right) d\underline{V} - \ln Z^L + (Z^L - 1)$$

Vapor, no problem $\underline{V}$ goes from ∞ to some $\underline{V}$ and no phase changes

For liquid, $\rightarrow$ goes through vapor phase, condenses so there is a phase change

Same procedure for f^V, or f^L but how do we handle the phase change?

$$RT \ln\left(\frac{f^L}{P}\right) = \underline{G}(T,P) - \underline{G}^{IG}(T,P)$$

$$= \underbrace{\int_{P=0}^{P_{vap}} \left(\underline{V} - \frac{RT}{P}\right) dP}_{①\ \text{Vapor}} + \underbrace{RT\, \Delta \ln\left(\frac{f}{P}\right)}_{②\ \text{trancition}} + \underbrace{\int_{P_{vap}}^{P} \left(\underline{V} - \frac{RT}{P}\right) dP}_{③\ \text{liquid.}}$$

② what is $RT\,\Delta \ln\left(\frac{f}{P}\right)$?

fugecity between phases @ equilibrium.

<u>same in both!</u> so

$$\Delta \ln\left(\frac{f}{P}\right) = 0$$

① $$\int_0^{P_{vap}} \left(\underline{V} - \frac{RT}{P}\right) dP = RT \ln\left(\frac{f}{P}\right)_{sat}$$

③ $$\int_{P_{vap}}^{P} \left(\underline{V} - \frac{RT}{P}\right) dP = \int_{P_{vap}}^{P} \underline{V}\, dP - RT \int_{P_{vap}}^{P} \frac{1}{P}\, dP$$

$$= \int_{P_{vap}}^{P} \underline{V}\, dP - RT \ln\left(\frac{P}{P_{vap}}\right)$$

So, now

$$1 + \cancel{2}^{\,0} + 3$$

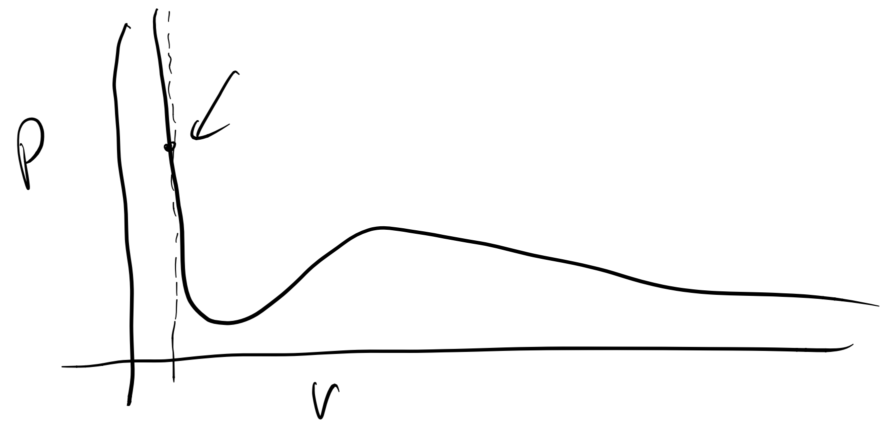
$$f^L(T,P) = \underbrace{P^{vap}(T) \left(\frac{f}{P}\right)_{sat}}_{f_{sat}} \underbrace{\exp\left[\frac{1}{RT}\int_{P_{vap}}^{P} \underline{V}\, dP\right]}_{\text{Poynting correction factor}}$$

Most of the time.

$$\boxed{f^L(T,P) \approx P_{vap}(T)}$$

$$f^L(T,P) = f^L_{sat}(T) = f^V(T, P_{vap})$$

$$= P_{vap}\left(\frac{f}{P}\right)_{sat.}$$



if you assume liquid is incompressible,

then the fugacity is

$$f^L(T,P) = P^{vap}(T)\left(\frac{f}{P}\right)^{sat,T} \exp\left[\frac{\underline{V}(P-P_{vap})}{RT}\right]$$

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