Quiz 9
Chemical Engineering Thermodynamics March 28, 2019

a) The fugacity and fugacity coefficient are defined by equation 9.22,

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi} \qquad 9.22$$

Use the Arrhenius equation to explain the meaning of the fugacity in terms of a probability.

Determine the fugacity (MPa) for octane at (1) 450 K and 0.1 MPa and (2) 450 K and 0.8 MPa using the virial equation and the shortcut vapor pressure method. **Put your answers in the chart on page 2 below. (Show your work, i.e. write the equations with values, units and answers.)**

T_c =569 K, P_c =2.49 MPa, V_c =755 cm^3/mol, ω = 0.396, R=8.31 J/(mol K) or cm^{3}MPa/(mol K)

b) For condition (1) determine if the short-cut method is appropriate.
Calculate the vapor pressure.
Determine the state of matter at this condition.
c) For condition (1) determine if the virial equation is appropriate.
Calculate the fugacity.
d) For condition (2) determine if the short-cut method is appropriate.
Calculate the vapor pressure.
Determine the state of matter at this condition.
e) For condition (2) calculate the fugacity.
Test to see if the virial equation works for f^{sat}. In case the viral equation is not appropriate do the calculation using the virial equation and compare the result with the "*correct*" result from PREOS.xls of f^{sat} = 0.888 P^{sat}. Use **your calculated** value of f^{sat} if it is within 10% of the "*correct*" result.

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1 - \frac{1}{T_r}\right) \quad 9.11$$

Shortcut vapor pressure equation. Use care with the shortcut equation below $T_r = 0.5$.

$$\ln \varphi = \frac{BP}{RT} \quad 9.31$$

$$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \quad 7.6$$

$$\text{where } B(T) = (B^0 + \omega B^1)RT_c/P_c \quad 7.7$$

$$B^0 = 0.083 - 0.422/T_r^{1.6} \quad 7.8$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \quad 7.9$$

$$\text{Subject to } T_r > 0.686 + 0.439P_r \text{ or } V_r > 2.0 \quad 7.10$$

Poynting Correction

$$f = f^{sat} \exp\left(\frac{V^L\left(P - P^{sat}\right)}{RT}\right)$$

$$V^{satL} = V_C Z_C^{(1-T_r)^{0.2857}}$$

$$Z_c = P_c V_c/(RT_c)$$

	Part (1)	Part (2)
T, K	450	450
P, MPa	0.1	0.8
T_r		
P_r		
P^{sat}, MPa		
f^{sat}, MPa		
State of Matter		
f, MPa		

ANSWERS: Quiz 9
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a) The Arrhenius Equation is:
Probability = $\exp(-E_a/RT)$ for a thermally activated process.
E_a is the molar activation energy for an event whose probability of occurrence is calculated.
For fugacity equation 9.22 can be rearranged to:
$\phi = f/P = \exp((G-G^{ig})/RT)$
Where ϕ expresses the probability of a molecule ***escaping*** from the phase whose Gibbs energy is $(G-G^{ig})$. G = H – TS where H reflects the cohesive energy which opposes ***escape*** and TS reflects the thermal energy driving ***escape***. Lower f means a lower probability of ***escape***. This means the phase is ***more stable***.

	Part (1)	Part (2)
T, K	450	450
P, MPa	0.1	0.8
T_r	0.791	0.791
P_r	0.0402	0.321
P^{sat}, MPa	0.343	0.343
f^{sat}, MPa	0.306	0.306
State of Matter	Vapor	Liquid
f, MPa	0.0967	0.322

b) Is $T_r > 0.5$? Yes $T_r = 0.791$ so SCM works.
$P^{sat} = P_c\, 10\text{^}(7/3\,(1 + w)(1 - 1/T_r)) = 2.49\text{ MPa}\, 10\text{^}(7/3\,(1 + 0.396)(1 - 1/0.791)) = 0.343\text{ MPa}$
P = 0.1 MPa so this is a **Vapor**.

c) Does Virial Eqn. Work?
$T_r = 0.745 > 0.686 + 0.439P_r = 0.686 + (0.439)\, 0.0402 = 0.704$ **Yes it works**
$B_0 = 0.083 - 0.422/T_r^{1.6} = -0.531$
$B_1 = 0.139 - 0.172/T_r^{4.2} = -0.321$
$B = (B_0 + wB_1)RT_c/P_c = -1250\text{ cm}^3\text{/mole}$
$f = P_1 \exp(-1250\text{ cm}^3\text{/mole } 0.1\text{ MPa}/(8.31\text{ cm}^3\text{MPa/(K mole) } 450\text{K}))$ = **0.0967 MPa**

d) Same as b, 0.791>0.5 so **Yes SCM is OK**.
Same T so P_2sat is same 0.343 MPa
P= 0.8 MPa so this is a **<u>Liquid</u>**

e) For a liquid calculate f^{sat} then use the Poynting Method to get f.
Get $f^{sat} = P^{sat} \exp(BP^{sat}/(RT^{sat}))$ if
Does Virial Eqn. Work?
$T_r = 0.745 > 0.686 + 0.439P_r^{sat} = 0.686 + (0.439)\ 0.343\text{MPa}/2.49\text{MPa} = 0.837$ **This doesn't work also;** $V_r^{sat} = V^{sat}/V_c = 419\ \text{cm}^3/\text{mole}/755\ \text{cm}^3/\text{mole} = 0.555 < 2$ so **it doesn't work by the volume test either.**
Do the virial calculation which shouldn't work and compare with PREOS.xls solution.
$f^{sat} = 0.343\ \text{MPa}\ \exp(-1250\text{cm}^3/\text{mole}\ 0.343\ \text{MPa}/(8.31\ \text{MPa cm}^3/(\text{mole K})\ 450\text{K})) = 0.306\ \text{MPa}$
The PREOS.xls result would be $f^{sat} = 0.888\ (0.343\ \text{MPa}) = 0.305\ \text{MPa}$ so the result is well within 10%, **use f^{sat} = 0.306 MPa**.
$V^{satL} = V_c Z_c\text{^}(1-T_r)\text{^}(0.2857) = 755\ \text{cm}^3/\text{mole}\ 0.398\text{^}(1-0.791)\text{^}0.2857 = 419\ \text{cm}^3/\text{mole}$
$Z_c = P_c V_c/(RT_c) = 2.49\ \text{MPa}\ 755\ \text{cm}^3/\text{mole}/(8.31\ \text{MPa cm}^3/(\text{mole K})\ 569\text{K}) = 0.398$
$f = f^{sat} \exp(V^{satL}(P-P^{sat})/RT)$
$= 0.306\ \text{MPa}\ \exp(419\ \text{cm}^3/\text{mole}\ (0.8\ \text{MPa} - 0.343\ \text{MPa})/(8.31\ \text{MPa cm}^3/(\text{mole K})\ 450\text{K}))$
$=$ **0.322 MPa**