ECHE363 Homework 9 - Due 4/21/25 **Trevor Swan (tcs94)**

1. Determine the fugacity of pure methane at 220K and 77 bar assuming that methane obeys the Van der Waals equation of state.

$\varnothing$: $RT\,d\ln f = V_m\,dP$ 2.3 0.04301

EoS: $P = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$; $a = \dfrac{27}{64}\cdot\dfrac{(RT_c)^2}{P_c}$, $b = \dfrac{V_{m,c}}{3} = \dfrac{RT_c}{8P_c}$

$R = 8.314\times10^{-5}\ \frac{m^3\,bar}{K\,mol}$

Methane

$T_c = 190.6\,K$

$P_c = 46.00\,bar$

$$a = \frac{27}{64}\cdot\left(\frac{\left(8.314\times10^{-5}\ \frac{m^3\,bar}{\cancel{K}\,mol}\cdot 190.6\,\cancel{K}\right)^2}{46.00\,\cancel{bar}}\right) = 2.3\times10^{-6}\ \frac{m^6\,bar}{mol^2}$$

$$b = \frac{8.314\times10^{-5}\ \frac{m^3\,\cancel{bar}}{\cancel{K}\,mol}\cdot 190.6\,\cancel{K}}{8\cdot 46.00\,\cancel{bar}} = 4.3\times10^{-5}\ \frac{m^3}{mol}$$

Use $a, b, P = 77\,bar, T = 220\,K$ to get v_m $\quad V_m \approx 0.000122\ \frac{m^3}{mol}$

@ process conditions

$$RT\,d\ln f = V_m\,dP = -\left(\frac{\partial P}{\partial n}\right)_{T,P} dV = -n\left(\frac{\partial P}{\partial n}\right)_{T,P} dV_m$$

$$P = \frac{RT}{\frac{V}{n} - b} - \frac{a}{\left(\frac{V}{n}\right)^2} \Rightarrow \left(\frac{\partial P}{\partial n}\right)_{T,P} = \frac{RTV}{(V - bn)^2} - \frac{2an}{V^2}$$

$$RT\,d\ln f = -n\left[\frac{RTnV_m}{(nV_m - bn)^2} - \frac{2an}{(nV_m)^2}\right] dV_m$$

$$= -n\left[\frac{RTnV_m}{n^2(V_m - b)^2} - \frac{2an}{n^2V_m^2}\right] dV_m$$

Koretsky Example 7.2

$$\int_{P_{low}}^{f^v} RT\,d\ln f = \int_{RT/P_{low}}^{V_m} \frac{2a}{V_m^2} - \frac{RTV_m}{(V_m - b)^2}\,dV_m$$

(integrate expression, divide by RT)

$$\ln\left[\frac{f^v}{P_{low}}\right] = -\ln\left[\frac{(V_m - b)}{\frac{RT}{P_{low}} - b}\right] + b\left[\frac{1}{(V_m - b)} - \frac{1}{\frac{RT}{P_{low}} - b}\right] - \frac{2a}{RT}\left[\frac{1}{V_m} - \frac{1}{\frac{RT}{P_{low}}}\right]$$

$$\ln\left[\frac{f^v}{P_{low}}\right] = -\ln\left[\frac{(V_m - b)P_{low}}{RT}\right] + b\left[\frac{1}{(V_m - b)} - \frac{P_{low}}{RT}\right] - \frac{2a}{RT}\left[\frac{1}{V_m} - \frac{P_{low}}{RT}\right]$$

$\frac{RT}{P_{low}} \gg b$

$$\ln\left[f^v\right] = -\ln\left[\frac{V_m - b}{RT}\right] + \frac{b}{V_m - b} - \frac{2a}{RTV_m}$$

(add $\ln(P_{low})$ to both sides, let $P_{low} \to 0$)

$$f^v = \exp\left(-\ln\left[\frac{V_m - b}{RT}\right] + \frac{b}{V_m - b} - \frac{2a}{RTV_m}\right)$$

$$= \exp\left(-\ln\left[\frac{.000122 - 4.3\times10^{-5}}{(8.314\times10^{-5})(220)}\right] + \frac{4.3\times10^{-5}}{.000122 - 4.3\times10^{-5}} - \frac{2(2.3\times10^{-6})}{(8.314\times10^{-5})(220)(.000122)}\right)$$

$$f^v = 50.78\ bar$$

2. You have a pure gas at 25 bar and 300 K. The compressibility factor (z) under these conditions is 0.9. As best as you can, calculate the fugacity and fugacity coefficient. *Hint:* you may want to assume the gas obeys an equation of state expressed as a perturbation from an ideal gas's compressibility factor.

I will use: $z = 1 + B'P \rightarrow PV_m = RTz \Longrightarrow V_m = \frac{RT}{P}(1+B'P)$

$$z = 1 + B'P$$
$$0.9 = 1 + B'(25\times10^5\ Pa)$$
$$B' = -4\times10^{-8}\ \frac{1}{Pa}$$

$$V_m = \frac{RT}{P}(1+B'P) = \frac{(8.314)(300)}{25\times10^5}\left(1+(-4\times10^{-8})(25\times10^5)\right) = 8.979\times10^{-4}\ \frac{m^3}{mol}$$

$$RT\,d\ln f = V_m\,dP$$
$$\int_{P_{low}}^{f^v} RT\,d\ln f = \int_{P_{low}}^{P}\left(\frac{RT}{P} + RTB'\right)dP$$

$f \approx P$ at low P

$$\cancel{RT}\ln\left(\frac{f^v}{P_{low}}\right) = \cancel{RT}\ln\left(\frac{P}{P_{low}}\right) + \cancel{RT}B'(P-P_{low})$$
$$\ln f^v - \cancel{\ln P_{low}} = \ln P - \cancel{\ln P_{low}} + B'(P-\underbrace{P_{low}}_{\to 0})$$
$$f^v = P\exp(B'P)$$
$$f^v = (25\ bar)\exp\left(\left(-4\times10^{-8}\frac{1}{Pa}\right)(25\times10^5\ Pa)\right) = 22.62\ bar$$

$$\phi^v = \frac{22.62}{30} = 0.754$$

$f^v = 22.62$ $\quad\quad$ $\phi^v = 0.754$

3. Calculate the fugacity and the fugacity coefficient of steam at (a) 2 MPa and 400 ºC, (b) 40 MPa and 400 ºC.

↖ Superheated tables!

$$\int_{\mu^\circ}^{\mu} d\mu = \int_{f^\circ}^{f} RT\, d\ln f = v_m\, dP \qquad \text{but no EoS!}$$

$T_{(K)} = 400+273 = 673\,K$

$$\mu(T,P) - \mu(T,P^\circ) = RT \ln\left(\frac{f}{P^\circ}\right)$$

$$\mu(T,P) = g_m(T,P) = h_m(T,P) - T s_m(T,P)$$

$P_0 = 10\,kPa\ (T = 400°C)$

$\hat{h}_m^\circ = 3279.5\ \frac{kJ}{kg}$

$\hat{s}_m^\circ = 9.6076\ \frac{kJ}{kg\,K}$

$$\hat{\mu}^\circ(10\,kPa, 673\,K) = 3279.5 - 673(9.6076) = -3186.4148\ \frac{kJ}{kg}$$

$MW = 0.0180148\ kg/mol$

$\Rightarrow @\ P_{low} \rightarrow f^\circ \approx P_{low} = 10\,kPa$

a) $P = 2\,MPa\ (T = 400°C)$

$\hat{h}_m = 3247.6\ \frac{kJ}{kg}$

$\hat{s}_m = 7.1270\ \frac{kJ}{kg\,K}$

$$\hat{\mu}(2\,MPa, 673\,K) = 3247.6 - 673(7.1270) = -1548.871\ \frac{kJ}{kg}$$

$$\mu(T,P) - \mu(T,P^\circ) = \hat{\mu}(2\,MPa, 673\,K) - \hat{\mu}^\circ(10\,kPa, 673\,K)$$
$$= -1548.871 - (-3186.4148)$$
$$= 1637.5438\ \frac{kJ}{kg} = 1637543.8\ \frac{J}{kg}$$

$$MW\left(1637543.8\ \frac{J}{kg}\right) = 29500.02405\ \frac{J}{mol}$$

$$f_i^V = (10\,kPa)\exp\left[\frac{29500.02405}{8.314 \cdot 673}\right] = 1948.57\,kPa = 1.94857\,MPa$$

$$\phi_i = \frac{1.94857}{2} = 0.974$$

$f_i^V = 1.949\,MPa \quad \phi_i = 0.974$

b) $P = 40\,MPa\ (T = 400°C)$

$\hat{h}_m = 1930.8\ \frac{kJ}{kg}$

$\hat{s}_m = 4.1134\ \frac{kJ}{kg\,K}$

$$\hat{\mu}(40\,MPa, 673\,K) = 1930.8 - 673(4.1134) = -837.5182\ \frac{kJ}{kg}$$

$$\mu(T,P) - \mu(T,P^\circ) = \hat{\mu}(40\,MPa, 673\,K) - \hat{\mu}^\circ(10\,kPa, 673\,K)$$
$$= -837.5182 - (-3186.4148)$$
$$= 2348.8966\ \frac{kJ}{kg} = 2348896.6\ \frac{J}{kg}$$

$$MW\left(2348896.6\ \frac{J}{kg}\right) = 42314.90247\ \frac{J}{mol}$$

$$f_i^V = (10\,kPa)\exp\left[\frac{42314.90247}{8.314 \cdot 673}\right] = 19247.5\,kPa = 19.2475\,MPa$$

$$\phi_i = \frac{19.247}{40} = 0.481$$

$f_i^V = 19.248\,MPa \quad \phi_i = 0.481$

4. Consider a ternary system of methane (a), ethane (b), and propane (c) at 25 ºC and 15 bar. Assume this system can be represented by the virial equation truncated at the second term:

$$z = 1 + \frac{B_{mix}}{v_m} = \frac{Pv_m}{RT}$$

You can assume that the mixture obeys the following mixing rule for B_{mix}:

$$B_{mix} = y_a^2 B_{aa} + 2y_a y_b B_{ab} + 2y_a y_c B_{ac} + y_b^2 B_{bb} + 2y_b y_c B_{bc} + y_c^2 B_{cc}$$

where $B_{aa} = -42$, $B_{ab} = -93$, $B_{ac} = -139$, $B_{bb} = -185$, $B_{bc} = -274$, $B_{cc} = -399$, all in cm³/mol.

a) Develop an expression for the fugacity coefficient of methane in the mixture.

b) Estimate the fugacity and the fugacity coefficient of methane for a mixture with 20 mole % methane, 30 mole % ethane, and 50 mole % propane.

c) Repeat (a) and (b) using the Lewis Fugacity Rule.

a) $$\int_{y_a P_{low}}^{\hat f_a^v} RT\, d\ln f = \int_{\frac{nRT}{P_{low}}}^{V} -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} dV$$

$$RT\ln\left(\frac{\hat f_a^v}{y_a P_{low}}\right) = -\int_{\frac{nRT}{P_{low}}}^{V}\left(\frac{\partial P}{\partial n_a}\right)_{T,V,n_c,n_b} dV$$

write in terms of n_i

$$P = \frac{RT}{v_m}\left(1+\frac{B_{mix}}{v_m}\right) = RT\left(\frac{n_{tot}}{V} + \frac{n_{tot}^2 B_{mix}}{V^2}\right)$$

$$P = RT\left[\frac{n_a+n_b+n_c}{V} + \frac{n_a^2 B_{aa} + n_b^2 B_{bb} + n_c^2 B_{cc} + 2n_a n_b B_{ab} + 2n_a n_c B_{ac} + 2n_b n_c B_{bc}}{V^2}\right)$$

$$\left(\frac{\partial P}{\partial n_a}\right)_{T,V,n_b,n_c} = RT\left[\frac{1}{V} + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V^2}\right]$$

$$\cancel{RT}\ln\left(\frac{\hat f_a^v}{y_a P_{low}}\right) = -\int_{\frac{nRT}{P_{low}}}^{V} \cancel{RT}\left[\frac{1}{V} + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V^2}\right] dV$$

$$\ln\left(\frac{\hat f_a^v}{y_a P_{low}}\right) = -\ln V + \ln\frac{nRT}{P_{low}} + \frac{2n_a B_{aa} + 2n_b B_{bb} + 2n_c B_{cc}}{V}$$

(next, cancel $\ln(P_{low})$'s, $P_{low} \to 0$) $$- \frac{P_{low}(2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac})}{nRT}$$

$$\ln\left(\frac{\hat f_a^v}{y_a}\right) = -\ln V + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V} + \ln nRT$$

$\ln(\hat\phi_a^v)$

$$= \ln\left(\frac{nRT}{V}\right) + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V}$$ (subtract $\ln P$)

$$\ln\left(\frac{\hat f_a^v}{y_a P}\right) = \ln\left(\frac{nRT}{PV}\right) + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V}$$ $\left(\frac{nRT}{PV} = \frac{1}{z}\right)$

$$\ln\left(\frac{\hat f_a^v}{y_a P}\right) = \ln\left(\hat\phi_a^v\right) = \ln\left(\frac{1}{z}\right) + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V}$$

$$\Rightarrow \hat\phi_a^v = \left(\frac{1}{z}\right)\exp\left(\frac{2y_a B_{aa} + 2y_b B_{ab} + 2y_c B_{ac}}{v_m}\right)$$

b) $$\ln\left(\frac{\hat{f}_a^v}{y_a P}\right) = \ln\left(\hat{\phi}_a^v\right) = \ln\left(\frac{1}{z}\right) + \frac{2n_a B_{aa} + 2n_b B_{ab} + 2n_c B_{ac}}{V}$$

$$\Rightarrow \hat{f}_a^v = \left(\frac{y_a P}{z}\right) \exp\left(\frac{2y_a B_{aa} + 2y_b B_{bb} + 2y_c B_{ac}}{v_m}\right)$$

$$\begin{cases} y_a = 0.2 \\ y_b = 0.3 \\ y_c = 0.5 \end{cases} \longrightarrow B_{mix} = -42 y_a^2 + 2y_a y_b(-93) + 2y_a y_c(-139) + y_b^2(-185) + 2y_b y_c(-274) + y_c^2(-399) \quad [=] \ cm^3/mol$$

$$= -2.392 \times 10^{-4} \ \frac{m^3}{mol}$$ (converted to m^3/mol for v_m calculations)

$$z = \frac{P v_m}{RT} = 1 + \frac{B_{mix}}{v_m} \quad @ \ T = 25°C = 298\ K, \ P = 15 \ bar \approx 15 \ atm$$

$$\frac{(15\ atm)\, v_m}{(8.314 \frac{J}{mol\,K})(298\,K)} = 1 + \frac{-2.392 \times 10^{-4}}{v_m} \qquad v_m \overset{\text{wolfram}}{=} 1.36 \times 10^{-3} \ \frac{m^3}{mol}$$

$$z = \frac{(15 \times 10^5)(1.36 \times 10^{-3})}{(8.314)(298)} = 0.82339$$

$$\hat{f}_a^v = \left(\frac{y_a P}{z}\right) \exp\left(\frac{2y_a B_{aa} + 2y_b B_{bb} + 2y_c B_{ac}}{v_m}\right)$$

$$\phi_a^v = \left(\frac{1}{z}\right) \exp\left(\frac{2y_a B_{aa} + 2y_b B_{ab} + 2y_c B_{ac}}{v_m}\right)$$

Substitute
$$\begin{cases} y_a = 0.2 & P = 15 & B_{aa} = -42 \\ y_b = 0.3 & v_m = 1.36 \times 10^{-3} & B_{bb} = -185 \\ y_c = 0.5 & z = 0.82339 & B_{ac} = -139 \end{cases}$$

$$\hat{f}_a^v = 3.12 \ bar \qquad \phi_a^v = 1.04$$

c) (i) $\hat{\phi}_a(T, P_{tot}, n_b, n_c) = \phi_a(T, P_{total})$ LFR $\rightarrow y_b = y_c = 0$

$$\therefore \begin{cases} B_{mix} = B_{aa} = -42 \ \frac{cm^3}{mol} = -4.2\times10^{-5} \ \frac{m^3}{mol} \\ \text{EoS: } \frac{Pv_a}{RT} = 1 + \frac{B_{aa}}{v_a} \Rightarrow P = \frac{RT}{v_a} + RT\frac{B_{aa}}{v_a^2} \end{cases}$$

$$\left(\frac{\partial P}{\partial v_a}\right)_T = -RT\left(\frac{1}{v_a^2} + \frac{2B_{aa}}{v_a^3}\right) \Rightarrow dP = -RT\left(\frac{1}{v_a^2} + 2\frac{B_{aa}}{v_a^3}\right)dv_a$$

$$\Rightarrow \int_{P_{low}}^{f_a^v} \cancel{RT}\, d\ln f = \int_{\frac{RT}{P_{low}}}^{v_a} v_a\, dP = -\cancel{RT}\int_{\frac{RT}{P_{low}}}^{v_a} \frac{1}{v_a} + \frac{2B_{aa}}{v_a^2}\, dv_a$$

$$\ln\left(\frac{f_a^v}{P_{low}}\right) = -\left[\ln v_a - \ln\left(\frac{RT}{P_{low}}\right) - \frac{2B_{aa}}{v_a} + \frac{2B_{aa}}{\left(\frac{RT}{P_{low}}\right)}\right]$$ (cancel like terms)

$$\ln(f_a^v) = \frac{2B_{aa}}{v_a} - \ln\left(\frac{v_a}{RT}\right)$$

$$\Rightarrow f_a^v = \frac{RT}{v_a}\exp\left(\frac{2B_{aa}}{v_a}\right) \qquad \left(z_a = \frac{Pv_a}{RT}\right)$$

$$\phi_a^v = \frac{1}{z_a}\exp\left(\frac{2B_{aa}}{v_a}\right)$$

Since LFR, $\hat{\phi}_a^v = \phi_a^v$, $\hat{f}_a^v = y_a f_a^v$

(ii) $$\frac{v_a(15)}{(8.314)(298)} = 1 + \frac{-4.2\times10^{-5}}{v_a} \qquad \overset{\text{wolfram}}{v_a} = 1.61\times10^{-3} \ \frac{m^3}{mol}$$

$$f_a^v = \frac{8.314(298)}{1.61\times10^{-3}}\exp\left(\frac{2(-4.2\times10^{-5})}{1.61\times10^{-3}}\right) = 1460634.538 \text{ Pa}$$

$$\hat{f}_a^v = 0.2(14.6 \text{ bar}) = 2.92 \text{ bar}$$

$$\hat{\phi}_a^v = \phi_a^v = \frac{14.606 \text{ bar}}{15 \text{ bar}} = 0.974$$

$\hat{f}_a^v = 2.92$ bar

$\hat{\phi}_a^v = 0.974$

5. Answer the following reflection questions (5 points):

   a. What about the way this class is taught is helping your learning?

   b. What about the way this class is taught is inhibiting your learning?

(A) The posting of detailed notes was particularly helpful for my learning this past week. I was unable to make it to class for the latter half of last week, and having the notes for the rest of gas phase Fugacity and the review notes for the second midterm was great for keeping me up to date with the class. Also, posting the solutions to all assignments and exams right after they are concluded is helpful for knowing what I may have gotten wrong right away. Overall, the incredible organization of the classes materials, including scheduled assignment posting and efficient communications make learning go very smooth.

(B) There is nothing in this class currently inhibiting my learning. All of the materials are easily accessible, and I know where to go if something is particularly challenging for me to understand. This class seems to be built on supporting learning, and thus I cannot find anything that acts against that right now, and I haven't felt otherwise since the first homework assignment, but I got over that quickly.