

Don't get bogged down, and show your work! If you're stuck, try another problem. Remember to put units on everything!

True or False Section [2 points each; +2 for correct, 0 for no response, -1 for incorrect!]

- i) The chemical potentials of pure substances can be measured directly in the laboratory
False
- ii) For a two-component P - x - y diagram at constant T , an azeotrope exists at compositions where $\left(\frac{\partial P}{\partial x_A}\right)_T = \left(\frac{\partial P}{\partial y_A}\right)_T = 0$ True
- iii) For any pure component, the fugacity f_i approaches zero at low pressures (i.e., $P \rightarrow 0$).
True
- iv) An azeotrope occurs at a relative volatility of zero. False
- v) The Boltzmann equation links the number of possible microstates with the enthalpy of a system.
False

Problem 1 [30 points]: (a) List three key assumptions that must be made during the derivation of Raoult's law ($y_i P = x_i P_i^{\text{sat}}$). For two of these three assumptions, show how Raoult's law can be generalized so that the assumptions are no longer necessary.

- 1) Vapor is ideal gas mixture
- 2) Liquid is ideal solution
- 3) Liquid is incompressible & pressure is low so that Poynting correction can be ignored

Generalizations

$$y_i P \rightarrow y_i P \tilde{\phi}_i$$

$$x_i P_i^{\text{sat}} \rightarrow x_i P_i^{\text{sat}} \gamma_i$$

$$x_i P_i^{\text{sat}} \rightarrow x_i P_i^{\text{sat}} \exp \left[\frac{\tilde{V}_i (P - P_i^{\text{sat}})}{RT} \right]$$

(b) A liquid mixture of 40 mole% M and 60% W is in equilibrium with a vapor consisting only of M and W. The temperature and pressure are 98°C and 1800 mm Hg. The vapor pressures of M and W at 98°C are 4533 mm Hg and 1392 mm Hg, respectively. Use the given data to provide a rationale for Raoult's law being valid or invalid for this system.

Low P) $P = 1800 \text{ mmHg} = x_1 P_1^A + x_2 P_2^A$

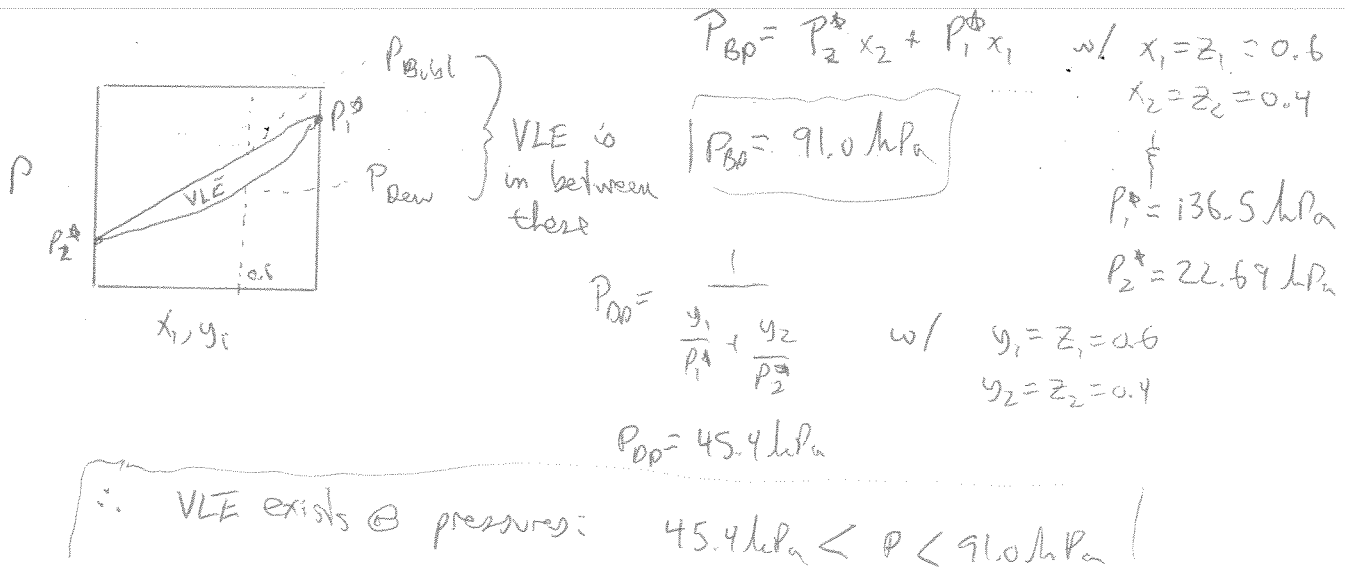
$$1800 \text{ mmHg} = (0.4)(4533 \text{ mmHg}) + (0.6)(1392 \text{ mmHg})$$

$$1800 \text{ mmHg} \neq 2648 \text{ mmHg}$$

\therefore R.L. is
invalid

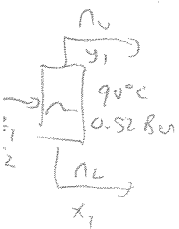
Problem 2 [30 points]: A binary mixture of benzene (1) and para-xylene (2) with a 60/40 molar ratio is kept in a tank at 90°C with adjustable pressure.

(a) Predict the range of pressures in the tank for which a vapor and a liquid phase will be observed if Raoult's law can be used to describe the system.



(b) For a pressure of 0.52 bar, predict the composition of the liquid and vapor phases, as well as the fraction of the mixture that is in the liquid phase.

VLE: $0.52 \text{ Bar} = x_1 P_1^* + (1-x_1) P_2^* \rightarrow x_1 = 0.258$ $y_1 = \frac{x_1 P_1^*}{P} = 0.676$



MB: $\frac{z}{r+z} = \frac{z_1 - y_1}{x_1 - y_1} = 0.184 = z$

Many ways to derive this

(c) The molar volume is given by the expression: $\hat{V} = 109.4 - 19.4 x_1 \left[\frac{\text{cm}^3}{\text{mol}} \right]$. Derive expressions for the partial molar volume of each component.

$\frac{d\hat{V}}{dx_1} = -19.4$
 $\bar{V}_1 = \hat{V} + x_2 \frac{d\hat{V}}{dx_1}$
 $\bar{V}_2 = \hat{V} - x_1 \frac{d\hat{V}}{dx_1}$
 $\bar{V}_1 = 109.4 - 19.4 x_2 - 19.4 x_1$
 $\bar{V}_2 = 109.4 - 19.4 x_1 - 19.4 x_1$
 $\bar{V}_1 = 90 \text{ cm}^3/\text{mol}$
 $\bar{V}_2 = 109.4 \text{ cm}^3/\text{mol}$

Problem 3 [30 points]:

(a) What is the chemical potential change of liquid ethanol going from 1 bar at 298K to 100 bar at 298K? [kJ/mol]

$$\begin{aligned} \mu_E(1 \text{ bar}) &= \bar{f}_i(T) + RT \ln \left[\frac{\hat{f}_i^L(1 \text{ bar})}{\hat{f}_i^L(1 \text{ bar})} \right] \\ \mu_E(100 \text{ bar}) &= \bar{f}_i(T) + RT \ln \left[\frac{\hat{f}_i^L(100 \text{ bar})}{\hat{f}_i^L(1 \text{ bar})} \right] \end{aligned} \quad \left. \begin{aligned} \Delta \mu_E &= \mu_E(100 \text{ bar}) - \mu_E(1 \text{ bar}) \\ &= RT \ln \left[\frac{\hat{f}_i^L(100 \text{ bar})}{\hat{f}_i^L(1 \text{ bar})} \right] \end{aligned} \right\} \quad (2)$$

$$\textcircled{D} \hat{f}_i^L(p) = \phi_i^{\text{sat}} p_i^{\text{sat}} \exp \left[\frac{\hat{V}_i^L(p - p_i^{\text{sat}})}{RT} \right] \quad \xrightarrow{p \rightarrow 100} \Delta \mu_E = RT \ln \left[\frac{\exp(\hat{V}_i^L(100 - p_i^{\text{sat}})/RT)}{\exp(\hat{V}_i^L(1 - p_i^{\text{sat}})/RT)} \right]$$

More accurate:

$$\hat{V}_E^L \approx \frac{46.04 \text{ g/mol}}{0.78 \text{ g/cm}^3} \approx 57 \text{ cm}^3/\text{mol}$$

$$\hat{V}_E^L = \hat{V}_c Z_c (1 - T_R)^{2/7}$$

$$Z_c = 0.24 \quad \hat{V}_c = 167 \text{ cm}^3/\text{mol} \quad T_c = 513.9 \text{ K}$$

$$\hat{V}_E^L = 54.8 \text{ cm}^3/\text{mol}$$

$$\Delta \mu_E = RT \left[\frac{\hat{V}_i^L(100 - p_i^{\text{sat}})}{RT} - \frac{\hat{V}_i^L(1 - p_i^{\text{sat}})}{RT} \right]$$

$$\Delta \mu_E = \hat{V}_i^L(100 \text{ bar} - 1 \text{ bar})$$

$$\Delta \mu_E = 0.543 \text{ kJ/mol}$$

$\frac{p_i^{\text{sat}}}{p_i^{\text{sat}}} = 1$
 $\frac{\phi_i^{\text{sat}}(p_i^{\text{sat}})}{\phi_i^{\text{sat}}(p_i^{\text{sat}})} = 1$

(b) What is the approximate fugacity of steam at 200°C and 700 kPa? [kPa]

Water: ω T_c /K P_c /bar Z_c \hat{V}_c (cm³/mol)

0.345	647.1	220.5	0.229	55.9
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$$f_i = \phi_i p$$

$$T_R = 0.73$$

$$P_R = 0.0317$$

$$B^0 = 0.083 - \frac{0.42}{0.73^{1.6}} = -0.613$$

$$B^1 = 0.139 - \frac{0.172}{0.73^{4.2}} = -0.502$$

$$\phi_i = \exp \left[\frac{P_R}{T_R} (B^0 + \omega B^1) \right] = 0.9665$$

$$f_i = \phi_i p = 0.9665 (700 \text{ kPa}) = 676.5 \text{ kPa}$$

Method in Ex. 11.5 work as well

(c) What is the free energy of mixing 1 mol water and 1 mol of ethanol at 298K? [kJ/mol]

$$\Delta G_{\text{mix, system}} = \Delta G_{\text{mix, product}} - \Delta G_{\text{mix, feed}} \quad \xrightarrow{p=1, p=1} \Delta G_{\text{mix, feed}} = 0$$

$$\Delta G_{\text{mix, product}} = nRT \sum x_i \ln x_i$$

$$= (2 \text{ mol}) (8.314 \text{ J/mol K}) (298 \text{ K}) [0.5 \ln(0.5) + 0.5 \ln(0.5)]$$

$$= -3434 \text{ J}$$

Exam 1, Page 3 of 3

$$\hat{\Delta G}_{\text{mix}} = \frac{-3434 \text{ J}}{2 \text{ mol}} = -1.7 \text{ kJ/mol}$$

Table B.2: Constants for the Antoine Equation for Vapor Pressures of Pure Species

$$\ln P^{\text{sat}}/\text{kPa} = A - \frac{B}{t/^\circ\text{C} + C}$$

Latent heat of vaporization at the normal boiling point (ΔH_n), and normal boiling point (t_n)

Name	Formula	Parameters for Antoine Eqn.			Temp. Range °C	ΔH_n kJ/mol.	t_n °C
		A [†]	B	C			
Acetone	C ₃ H ₆ O	14.3145	2756.22	228.060	-26 — 77	29.10	56.2
Acetic acid	C ₂ H ₄ O ₂	15.0717	3580.80	224.650	24 — 142	23.70	117.9
Acetonitrile*	C ₂ H ₃ N	14.8950	3413.10	250.523	-27 — 81	30.19	81.6
Benzene	C ₆ H ₆	13.7819	2726.81	217.572	6 — 104	30.72	80.0
<i>iso</i> -Butane	C ₄ H ₁₀	13.8254	2181.79	248.870	-83 — 7	21.30	-11.9
<i>n</i> -Butane	C ₄ H ₁₀	13.6608	2154.70	238.789	-73 — 19	22.44	-0.5
1-Butanol	C ₄ H ₁₀ O	15.3144	3212.43	182.739	37 — 138	43.29	117.6
2-Butanol*	C ₄ H ₁₀ O	15.1989	3026.03	186.500	25 — 120	40.75	99.5
<i>iso</i> -Butanol	C ₄ H ₁₀ O	14.6047	2740.95	166.670	30 — 128	41.82	107.8
<i>tert</i> -Butanol	C ₄ H ₁₀ O	14.8445	2658.29	177.650	10 — 101	39.07	82.3
Carbon tetrachloride	CCl ₄	14.0572	2914.23	232.148	-14 — 101	29.82	76.6
Chlorobenzene	C ₆ H ₅ Cl	13.8635	3174.78	211.700	29 — 159	35.19	131.7
1-Chlorobutane	C ₄ H ₉ Cl	13.7965	2723.73	218.265	-17 — 79	30.39	78.5
Chloroform	CHCl ₃	13.7324	2548.74	218.552	-23 — 84	29.24	61.1
Cyclohexane	C ₆ H ₁₂	13.6568	2723.44	220.618	9 — 105	29.97	80.7
Cyclopentane	C ₅ H ₁₀	13.9727	2653.90	234.510	-35 — 71	27.30	49.2
<i>n</i> -Decane	C ₁₀ H ₂₂	13.9748	3442.76	193.858	65 — 203	38.75	174.1
Dichloromethane	CH ₂ Cl ₂	13.9891	2463.93	223.240	-38 — 60	28.06	39.7
Diethyl ether	C ₄ H ₁₀ O	14.0735	2511.29	231.200	-43 — 55	26.52	34.4
1,4-Dioxane	C ₄ H ₈ O ₂	15.0967	3579.78	240.337	20 — 105	34.16	101.3
<i>n</i> -Eicosane	C ₂₀ H ₄₂	14.4575	4680.46	132.100	208 — 379	57.49	343.6
Ethanol	C ₂ H ₆ O	16.8958	3795.17	230.918	3 — 96	38.56	78.2
Ethylbenzene	C ₈ H ₁₀	13.9726	3259.93	212.300	33 — 163	35.57	136.2
Ethylene glycol*	C ₂ H ₆ O ₂	15.7567	4187.46	178.650	100 — 222	50.73	197.3
<i>n</i> -Heptane	C ₇ H ₁₆	13.8622	2910.26	216.432	4 — 123	31.77	98.4
<i>n</i> -Hexane	C ₆ H ₁₄	13.8193	2696.04	224.317	-19 — 92	28.85	68.7
Methanol	CH ₄ O	16.5785	3638.27	239.500	-11 — 83	35.21	64.7
Methyl acetate	C ₃ H ₆ O ₂	14.2456	2662.78	219.690	-23 — 78	30.32	56.9
Methyl ethyl ketone	C ₄ H ₈ O	14.1334	2838.24	218.690	-8 — 103	31.30	79.6
Nitromethane*	CH ₃ NO ₂	14.7513	3331.70	227.600	56 — 146	33.99	101.2
<i>n</i> -Nonane	C ₉ H ₂₀	13.9854	3311.19	202.694	46 — 178	36.91	150.8
<i>iso</i> -Octane	C ₈ H ₁₈	13.6703	2896.31	220.767	2 — 125	30.79	99.2
<i>n</i> -Octane	C ₈ H ₁₈	13.9346	3123.13	209.635	26 — 152	34.41	125.6
<i>n</i> -Pentane	C ₅ H ₁₂	13.7667	2451.88	232.014	-45 — 58	25.79	36.0
Phenol	C ₆ H ₆ O	14.4387	3507.80	175.400	80 — 208	46.18	181.8
1-Propanol	C ₃ H ₈ O	16.1154	3483.67	205.807	20 — 116	41.44	97.2
2-Propanol	C ₃ H ₈ O	16.6796	3640.20	219.610	8 — 100	39.85	82.2
Toluene	C ₇ H ₈	13.9320	3056.96	217.625	13 — 136	33.18	110.6
Water	H ₂ O	16.3872	3885.70	230.170	0 — 200	40.66	100.0
<i>o</i> -Xylene	C ₈ H ₁₀	14.0415	3358.79	212.041	40 — 172	36.24	144.4
<i>m</i> -Xylene	C ₈ H ₁₀	14.1387	3381.81	216.120	35 — 166	35.66	139.1
<i>p</i> -Xylene	C ₈ H ₁₀	14.0579	3331.45	214.627	35 — 166	35.67	138.3

Table A.2: Values of the Universal Gas Constant

$$\begin{aligned}
 R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1} \\
 &= 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} = 8.314 \text{ cm}^3 \text{ kPa mol}^{-1} \text{ K}^{-1} \\
 &= 82.06 \text{ cm}^3 (\text{atm}) \text{ mol}^{-1} \text{ K}^{-1} = 62.356 \text{ cm}^3 (\text{torr}) \text{ mol}^{-1} \text{ K}^{-1} \\
 &= 1.987 (\text{cal}) \text{ mol}^{-1} \text{ K}^{-1} = 1.986 (\text{Btu}) (\text{lb mole})^{-1} (\text{R})^{-1} \\
 &= 0.7302 (\text{ft})^3 (\text{atm}) (\text{lb mol})^{-1} (\text{R})^{-1} = 10.73 (\text{ft})^3 (\text{psia}) (\text{lb mol})^{-1} (\text{R})^{-1} \\
 &= 1.545 (\text{ft}) (\text{lb}_f) (\text{lb mol})^{-1} (\text{R})^{-1}
 \end{aligned}$$