Quiz 12
Chemical Engineering Thermodynamics
April 23, 2015

1) **DO PART (b) only for $x_1 = 0.728$. Comment on the uniqueness of this composition. DO PART (c) for $x_e = 0.4150$. Comment the uniqueness of this composition.**

11.2 In vapor-liquid equilibria the relative volatility α_{ij} is defined by Eqn. 10.32.

(a) Provide a simple proof that the relative volatility is independent of liquid and vapor composition if a system follows Raoult's law.
(b) In approximation to a distillation calculation for a nonideal system, calculate the relative volatility α_{12} and α_{21} as a function of composition for the *n*-pentane(1) + acetone(2) system at 1 bar using experimental data in problem 11.11.
(c) In approximation to a distillation calculation for a non-ideal system, calculate the relative volatility α_{12} and α_{21} as a function of composition for the data provided in problem 10.2.

See equations/tables below.

2) **DO PART (b) only for 0.0, and 0.4. Comment on Plot for part (c) given below (add comments and turn in with answer sheet).**

11.8 The liquid phase activity coefficients of the ethanol(1) + toluene(2) system at 55°C are given by the two-parameter Margules equation, where $A_{12} = 1.869$ and $A_{21} = 1.654$.

(a) Show that the pure saturation fugacity coefficient is approximately 1 for both components.
(b) Calculate the fugacity for each component in the liquid mixture at $x_1 = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0. Summarize your results in a table. Plot the fugacities for both components versus x_1. Label your curves. For each curve, indicate the regions that may be approximated by Henry's law and the ideal solution model.
(c) Using the results of part (b), estimate the total pressure above the liquid mixture at 55°C when a vapor phase coexists. Assume the gas phase is ideal for this calculation. Also estimate the vapor composition.

See equations/tables below.

3) **DO ONLY FOR 0.5199.**

11.22 Ethanol(1) + benzene(2) form azeotropic mixtures.

(a) From the limited data below at 45 °C, it is desired to estimate the constant A for the one-term Margules equation, $G^E/RT = Ax_1x_2$. Use all of the experimental data to give your best estimate.

x_1	0	0.3141	0.5199	1
y_1	0	0.3625	0.4065	1
P(bar)	0.2939	0.4124	0.4100	0.2321

(b) From your value, what are the bubble pressure and vapor compositions for a mixture with $x_1 = 0.8$?

See equations/tables below.

$$\alpha_{ij} = K_i/K_j \qquad 10.32$$

$$K_i \equiv \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P}$$ "modified Raoult's law" 11.1

$$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat} \qquad y_i = \frac{x_i\gamma_i P_i^{sat}}{P} = x_i K_i$$

$$\frac{G^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \qquad \gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} \qquad \frac{G^E}{RT} = A_{12} x_1 x_2$$

R = 8.314 MPa cm^3/(mole K°)

From problem 11.11 the *n*-pentane(1) + acetone(2) system ***at 1 bar.***

x_1	0.021	0.134	0.292	0.503	0.728	0.953
y_1	0.108	0.475	0.614	0.678	0.739	0.906
T (°C)	49.15	39.58	34.35	33.35	31.93	33.89
P_1^{sat}	1.560	1.146	0.960	0.903	0.880	0.954
P_2^{sat}	0.803	0.551	0.453	0.421	0.410	0.445

From problem 10.2 Benzene and ethanol (e) at 45°C

x_e	0	0.0374	0.0972	0.2183	0.3141	0.4150	0.5199	0.5284	0.6155	0.7087	0.9591	1.000
y_e	0	0.1965	0.2895	0.3370	0.3625	0.3842	0.4065	0.4101	0.4343	0.4751	0.8201	1.000
P	0.2939	0.3613	0.3953	0.4088	0.4124	0.4128	0.41	0.4093	0.4028	0.3891	0.2711	0.2321

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

Fugacity has units of pressure, and the fugacity coefficient is dimensionless.

$$\frac{(G - G_{ig})}{RT} = \frac{BP}{RT}$$

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

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

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

Subject to $T_r > 0.686 + 0.439P_r$ or $V_r > 2.0$ 7.10

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o}$$

11.13 Activity coefficients are commonly used for highly non-ideal solutions.

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11.13 Activity coefficients are commonly used for highly non-ideal solutions.

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P}; \quad \hat{f}_i^L \approx x_i \gamma_i P_i^{sat}; \quad \hat{f}_i^V \approx y_i P$$

11.17 Modified Raoult's law.

Modified Raoult's law.

$$y_i P = x_i \gamma_i P_i^{sat} \quad \text{or} \quad K_i = \frac{\gamma_i^L P_i^{sat}}{P}$$

11.18

The one-parameter Margules equation is the simplest excess Gibbs expression.

$$\frac{G^E}{RT} = A_{12} x_1 x_2 \qquad 11.5$$

$$\ln \gamma_1 = A_{12} x_2^2$$

$$\ln \gamma_2 = A_{12} x_1^2$$

$$\frac{G^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$$ [10] 11.33

$$\frac{1}{RT}\left(\frac{\partial G^E}{\partial n_1}\right)_{T,P,n_2} = \ln \gamma_1 = n_2\left(A_{21} + \frac{n_2}{n}(A_{12} - A_{21})\right)\left[\frac{1}{n} - \frac{n_1}{n^2}\right] + n_2\left(\frac{n_1}{n}\right)\left(\frac{-n_2}{n^2}\right)(A_{12} - A_{21}) \qquad 11.35$$

$$\ln \gamma_1 = x_2^2 \left[(A_{21} + (1 - x_1)(A_{12} - A_{21})) + (A_{21} - A_{12}) x_1\right] \qquad 11.36$$

$$\ln \gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12}) x_1\right]$$; similarly $$\ln \gamma_2 = x_1^2 [A_{21} + 2(A_{12} - A_{21}) x_2]$$ 11.37

The two parameters can be fitted to a single VLE measurement using

$$A_{12} = \left(2 - \frac{1}{x_2}\right)\frac{\ln \gamma_1}{x_2} + \frac{2 \ln \gamma_2}{x_1} \qquad A_{21} = \left(2 - \frac{1}{x_1}\right)\frac{\ln \gamma_2}{x_1} + \frac{2 \ln \gamma_1}{x_2}$$ 11.38

E.3 ANTOINE CONSTANTS

The following constants are for the equation

$$\log_{10} P^{sat} = A - \frac{B}{T + C}$$

where P^{sat} is in mmHg, and T is in Celsius. Additional Antoine constants are tabulated in Antoine.xls.

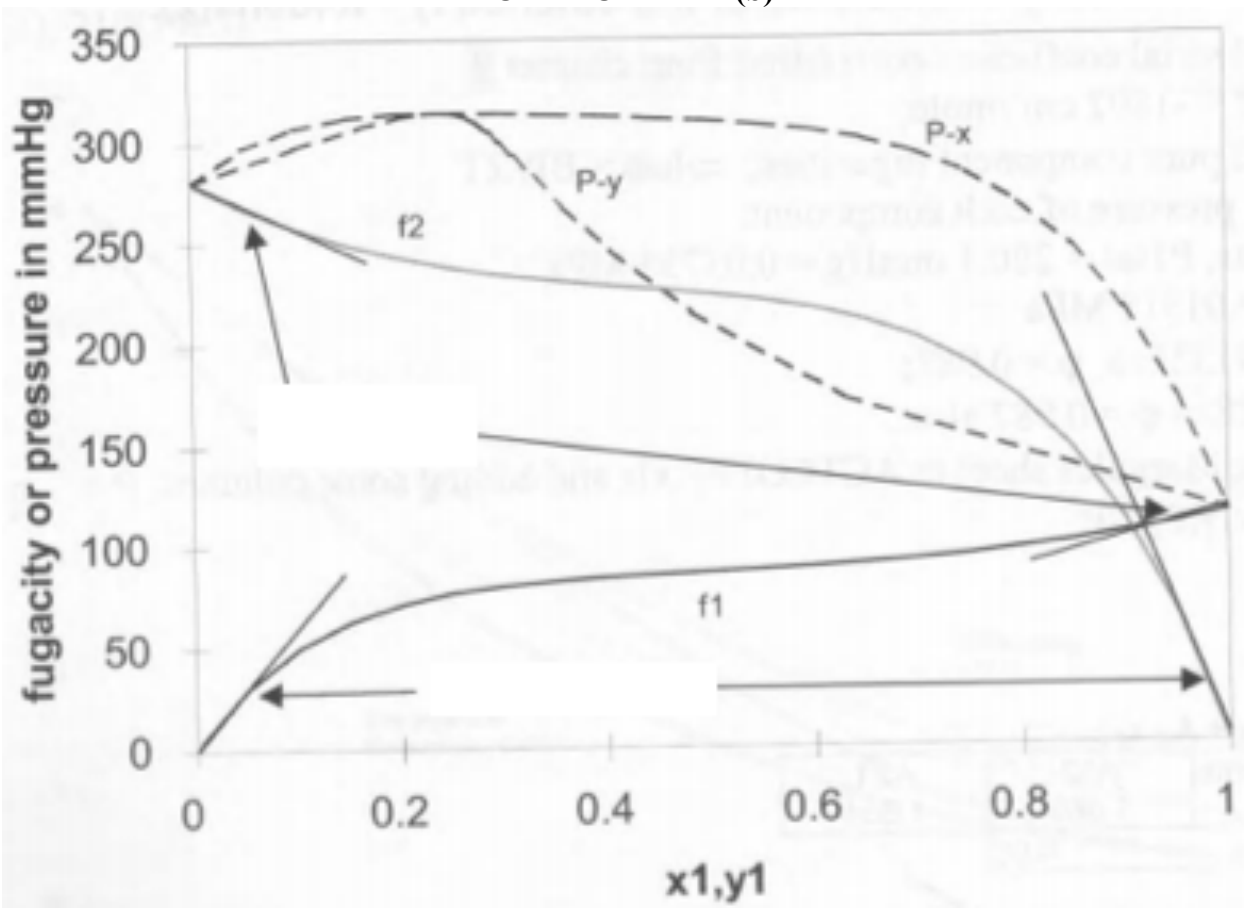
	A	B	C	T range (°C)	Source
Acetic acid	8.02100	1936.01	258.451	18–118	[a]
Acetic acid	8.26735	2258.22	300.97	118–227	[a]
Acetone	7.63130	1566.69	273.419	57–205	[a]
Acetone	7.11714	1210.595	229.664	−13–55	[a]
Acrolein (2-propenal)	8.62876	2158.49	323.36	2.5–52	[b]
Benzene	6.87987	1196.76	219.161	8–80	[a]
Benzyl chloride	7.59716	1961.47	236.511	22–180	[b]
Biphenyl (solid)	13.5354	4993.37	296.072	20–40	[c]
1-Butanol	7.81028	1522.56	191.95	30–70	[d]
1-Butanol	7.75328	1506.07	191.593	70–120	[d]
2-Butanone	7.28066	1434.201	246.499	−6.5–80	[b]
Chloroform	6.95465	1170.966	226.232	−10–60	[a]
Ethanol	8.11220	1592.864	226.184	20–93	[a]
Hexane	6.91058	1189.64	226.28	−30–170	[a]
1-Propanol	8.37895	1788.02	227.438	−15–98	[a]
2-Propanol	8.87829	2010.33	252.636	−26–83	[a]
Methanol	8.08097	1582.271	239.726	15–84	[a]
Naphthalene (solid)	8.62233	2165.72	198.284	20–40	[e]
Pentane	6.87632	1075.78	233.205	−50–58	[a]
3-Pentanone	7.23064	1477.021	237.517	36–102	[a]
Toluene	6.95087	1342.31	219.187	−27–111	[a]
Water	8.07131	1730.63	233.426	1–100	[a]

PROPERTIES OF SELECTED COMPOUNDS

*Heat capacities are values for **ideal gas at 298 K** and should be used for **order of magnitude calculations** only. See appendices for temperature-dependent formulas and constants.*

ID	Compound	T_c (K)	P_c (MPa)	ω	ρ g/cm³	MW	C_P^{ig}/R	δ (J/cm³)½	α (J/cm³)½	β (J/cm³)½
Oxygenates										
1101	METHANOL	512.6	8.096	0.566	0.79	32	5.28	29.6	17.43	14.49
1102	ETHANOL	516.4	6.384	0.637	0.79	46	7.88	26.1	12.58	13.29
1102	PROPANOL	536.7	5.170	0.628	0.80	60	10.50	24.5	11.97	10.35
1104	ISOPROPANOL	508.3	4.764	0.669	0.78	60	10.69	23.4	9.23	11.86
1105	1-BUTANOL	562.9	4.412	0.594	0.81	74	13.13	23.4	8.44	11.01
1107	ISOBUTANOL	547.7	4.295	0.589	0.80	74	13.03	22.9	3.99	3.99
1479	THF	501.1	5.190	0.217	0.88	72	16.85	19.0	0.00	10.43
1402	DIETHYL ETHER	466.7	3.590	0.281	0.71	74	13.53	15.4	0.00	6.61
1444	ETHYLENE OXIDE	469	7.100	0.200	*0.89*	44	5.80	21.7	1.17	9.38
1052	METHYL ETHYL KETONE	535.6	4.100	0.329	0.80	72	12.56	18.9	0.00	9.70
Aromatics										
501	BENZENE	562.2	4.898	0.211	0.87	78	9.82	18.7	0.63	2.24
502	TOLUENE	591.8	4.109	0.264	0.86	92	12.49	18.3	0.57	2.23
504	ETHYLBENZENE	617.2	3.609	0.304	0.86	106	15.44	18.0	0.23	1.83
505	*o*-XYLENE	630.4	3.734	0.313	0.88	106	16.03	18.4	0.10	1.80
506	*m*-XYLENE	617.1	3.541	0.326	0.86	106	15.35	18.1	0.19	1.84
507	*p*-XYLENE	616.3	3.511	0.326	0.86	106	15.26	17.9	0.27	1.87
510	CUMENE	631.2	3.209	0.338	0.86	121	18.25	17.4	0.20	2.57
558	BIPHENYL	789.3	3.847	0.366	0.99	154	19.52	19.3	0.50	4.00
563	DIPHENYLMETHANE	768	2.920	0.461	1.00	168	21.87	19.6	0.50	4.00
701	NAPHTHALENE	748.4	4.051	0.302	*0.98*	128	16.03	19.5	0.86	6.87
702	METHYLNAPHTHALENE	772	3.650	0.292	1.02	142	19.08	20.1	0.77	6.13
706	TETRALIN	720.2	3.300	0.286	0.97	132	18.63	19.3	0.60	4.82

FOR PROBLEM 2(b)



Answers Quiz 12
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1)

11.2 In vapor-liquid equilibria the relative volatility α_{ij} is defined by Eqn. 10.32.

(a) Provide a simple proof that the relative volatility is independent of liquid and vapor composition if a system follows Raoult's law.
(b) In approximation to a distillation calculation for a nonideal system, calculate the relative volatility α_{12} and α_{21} as a function of composition for the *n*-pentane(1) + acetone(2) system at 1 bar using experimental data in problem 11.11.
(c) In approximation to a distillation calculation for a non-ideal system, calculate the relative volatility α_{12} and α_{21} as a function of composition for the data provided in problem 10.2.
(d) Provide conclusions from your analysis.

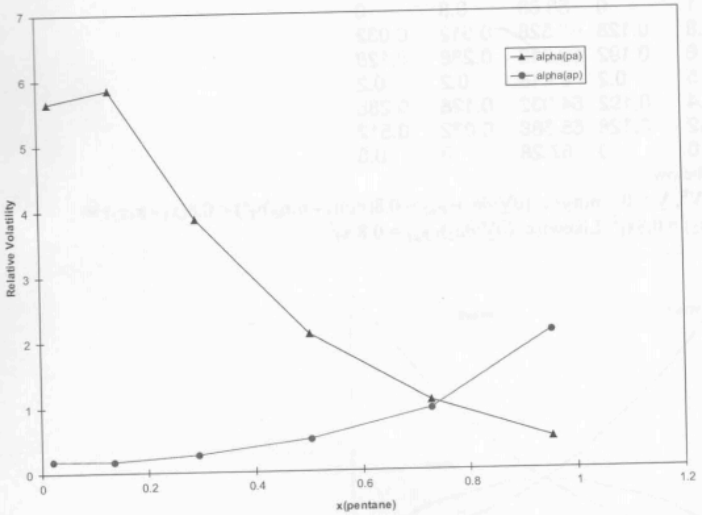
(11.02) In vapor-liquid equilibria the relative volatility is defined to be the ratio....

(a) Raoult's Law $y_i P = x_i P_i^{sat} \rightarrow K_i = y_i/x_i = P_i^{sat}/P$, therefore $\alpha_{ij} = K_i/K_j = P_i^{sat}/P_j^{sat}$, independent of composition.

(b)

x_p	y_p	K_p	K_a	α_{pa}	α_{ap}
0.021	0.108	5.14286	0.9111	5.6453	0.17716
0.134	0.475	3.544776	0.606236	5.847193	0.171022
0.292	0.614	2.10274	0.545198	3.856839	0.25928
0.503	0.678	1.347913	0.647887	2.080474	0.48066
0.728	0.739	1.01511	0.959559	1.057892	0.945276
0.953	0.906	0.950682	2	0.475341	2.103753

The relative volatility is a strong function of composition. It has a value of one for both components of a binary system at the azeotrope, and it is greater than one on one side and less than one on the other side.



2)

11.8 The liquid phase activity coefficients of the ethanol(1) + toluene(2) system at 55°C are given by the two-parameter Margules equation, where $A_{12} = 1.869$ and $A_{21} = 1.654$.

(a) Show that the pure saturation fugacity coefficient is approximately 1 for both components.

(b) Calculate the fugacity for each component in the liquid mixture at $x_1 = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0. Summarize your results in a table. Plot the fugacities for both components versus x_1. Label your curves. For each curve, indicate the regions that may be approximated by Henry's law and the ideal solution model.

(c) Using the results of part (b), estimate the total pressure above the liquid mixture at 55°C when a vapor phase coexists. Assume the gas phase is ideal for this calculation. Also estimate the vapor composition.

(d) Comment on the validity of the ideal gas assumption used in part (c).

(11.08) The liquid phase activity coefficients of the ethanol(1) + toluene(2)...

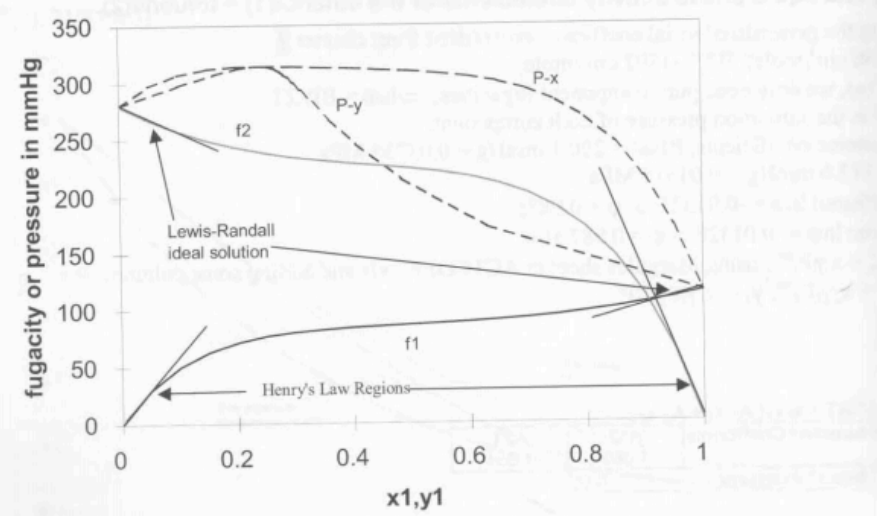
(a) Using the generalized virial coefficient correlation from chapter 7
B1 = -966 cm^3/mole; B2 = -1802 cm^3/mole;
for part (a), we only need pure component fugacities; $\Rightarrow \ln\varphi = BP/RT$
where P is the saturation pressure of each component.
From Antoine coefficients, P1sat = 280.1 mmHg = 0.03734 MPa
P2sat = 113.6 mmHg = 0.01515 MPa
$\Rightarrow$ for ethanol $\ln\varphi = -0.01321 \Rightarrow \varphi = 0.987$;
for toluene $\ln\varphi = -0.01328 \Rightarrow \varphi = 0.987$ also.
(b),(c) $f_i = x_i\gamma_i P_i^{sat}$, using Margules sheet in ACTCOEFF.xls and adding some columns, P = $x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$, $y_1 = x_1\gamma_1 P_1^{sat}/P$

Margules Equation

$G^E/RT = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$

Interaction Coefficients	A12	A21
	1.869	1.654
Table x1 increment	0.05	

x1	x2	gamma1	gamma2	f1	f2	y1	P	
0	1	6.4818113	1	0	280.1	0	280.1	
0.05	0.95	5.2982085	1.0051696	30.093824	267.4706	0.1011338	297.56442	
0.1	0.9	4.3888183	1.0206197	49.856975	257.28802	0.1623239	307.145	
0.15	0.85	3.683087	1.0464869	62.759802	249.15283	0.2012096	311.91264	
0.2	0.8	3.1302723	1.0832004	71.119787	242.72355	0.2266092	313.84333	
0.25	0.75	2.6935062	1.1314854	76.495575	237.69679	0.2434673	314.19236	
0.3	0.7	2.3457378	1.1923784	79.942746	233.78964	0.2548119	313.73239	
0.35	0.65	2.0669338	1.2672558	82.181288	230.72292	0.2626404	312.90421	
0.4	0.6	1.8421254	1.3578737	83.706177	228.20425	0.2683661	311.91043	
0.45	0.55	1.6600351	1.4664232	84.860995	225.90983	0.2730662	310.77082	
0.5	0.5	1.5121009	1.5956003	85.88733	223.46382	0.277637	309.35115	
0.55	0.45	1.3917769	1.7486932	86.958218	220.41403	0.2829085	307.37225	
0.6	0.4	1.2940282	1.9296912	88.200963	216.2026	0.2897501	304.40357	
0.65	0.35	1.2149632	2.1434169	89.712879	210.12988	0.2991998	299.84276	
0.7	0.3	1.1515628	2.3956869	91.572276	201.30957	0.3126594	292.88185	
0.75	0.25	1.1014817	2.6935062	93.846239	188.61277	0.3322473	282.45901	
0.8	0.2	1.0628989	3.0453018	96.596253	170.59781	0.361521	267.19406	
0.85	0.15	1.0344074	3.4612031	99.882383	145.42245	0.4071766	245.30483	
0.9	0.1	1.0149304	3.9533764	103.76648	110.73407	0.4837586	214.50055	
0.95	0.05	1.0036579	4.5364227	108.31476	63.5326	0.6302963	171.84736	
1	0	1	5.2278495	113.6	0	1	113.6	



Lewis-Randall and Henry's law valid at some compositions near purity, but for opposite components.
(d) The ideal gas assumption will be fine since φ is about 1 for all components.

3)

11.22 Ethanol(1) + benzene(2) form azeotropic mixtures.

(a) From the limited data below at 45 °C, it is desired to estimate the constant A for the one-term Margules equation, $G^E/RT = Ax_1x_2$. Use all of the experimental data to give your best estimate.

x_1	0	0.3141	0.5199	1
y_1	0	0.3625	0.4065	1
P(bar)	0.2939	0.4124	0.4100	0.2321

(b) From your value, what are the bubble pressure and vapor compositions for a mixture with $x_1 = 0.8$?

(11.22) Ethanol(1) + Benzene(2) form azeotropic mixtures…

a) This can be solved by fitting G^E as in Example 11.1. We can average the value of A.

x1	y1	P(bar)	gamma1	gamma2	G^E/RT	A
0.3141	0.3625	0.4124	2.050612	1.304183	0.407726	1.892518
0.5199	0.4065	0.41	1.381177	1.72454	0.42953	1.720846
					Average	1.806682

b) gamma's are calculated with Eqn. 11.6, and $P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat}$.

$\gamma_1 = \exp(1.807(0.2)^2) = 1.075$, $\gamma_2 = \exp(1.807(0.8)^2) = 3.179$

$P = 0.8(1.075)0.2321 + 0.2(3.179)0.2939 = 0.387$ bar