Quiz 11
April 9, 2020
Chemical Engineering Thermodynamics

Vacuum distillation of ethanol from an ethanol (1)/water (2) mixture can lead to a lower energy load and a higher concentration of ethanol compared to distillation at atmospheric pressure. Data for the equilibrium concentrations of vapor and liquid ethanol at 190 mmHg are given in the attached excel sheet. [Beebe A.H.; Coulter K.E.; Lindsay R.A.; Baker E.M. *Equilibria in Ethanol-Water System at Pressures Less Than Atmospheric.* Ind.Eng.Chem. Ind.Ed. **34** 1501-1504 (1942).]

a) Use this data to obtain the one-parameter Margules coefficient by adding to the table columns for $P_{sat,1}$, $P_{sat,2}$, γ_1, γ_2, calculated $y_{calc,1}$ for the bubble point, and the calculated P values, the calculated $(P_{calc}-P)^2$, and a cell containing the sum of the $(P_{calc}-P)^2$ values.
b) Using solver find the **minimum** of the sum of $(P_{calc}-P)^2$ by varying the Margules coefficient, A_{12} (*P is 190mmHg*). (*This is the least-squares method.*)
After solving for A_{12} make a plot of $y_{calc,1}$ and y_1 versus x_1. *Why do y_{1calc} and y_1 disagree?*
c) Use the Margules coefficient to calculate the dew pressure, P_{dew}, for $T = 50.5°C$; $y_1 = 0.6925$.
d) Does an azeotrope exist at $T = 50.5°C$ for this system (use the Margulis model)?
At the azeotrope $x_1 = y_1$, and $x_2 = y_2$.
Using expressions for y_1 in terms of x_1, for y_2 in terms of x_2, and $x_1 + x_2 = 1$, solve for $x_{1,azeotrope}$ at the azeotrope for $T = 50.5°C$.
Use this value of $x_{1,azeotrope}$ to calculate $P_{azeotrope}$ at the azeotrope.
Calculate $y_{1,azeotrope}$ at the azeotrope.
Is this a maximum boiling or a minimum boiling temperature azeotrope (remember P vs x_1 and T vs x_1 plots are different)?
e) Make a scatter plot of T versus x_1 and T versus y_1 on the same chart with the x/y range 0 to 1 and the T range from 45 to 65 °C. On the same plot add your T versus $y_{calc,1}$. Does this plot support your prediction of an Azeotrope?

A_{12}	3.49
P_{dew}	77.2 mmHg
$x_{1,azeotrope}$	0.422
$P_{azeotrope}$	173 mmHg
$y_{1,azeotrope}$	0.422
Max or Min?	Minimum Boiling Temperature

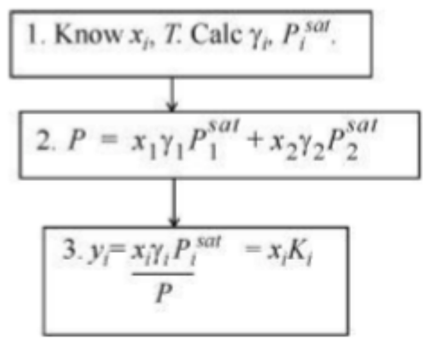
$$\ln \gamma_1 = A_{12} x_2^2$$

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

Modified Raoult's law.

$$\boxed{y_i P = x_i \gamma_i P_i^{sat}} \quad \text{or} \quad \boxed{K_i = \frac{\gamma_i^L P_i^{sat}}{P}} \qquad 11.18$$

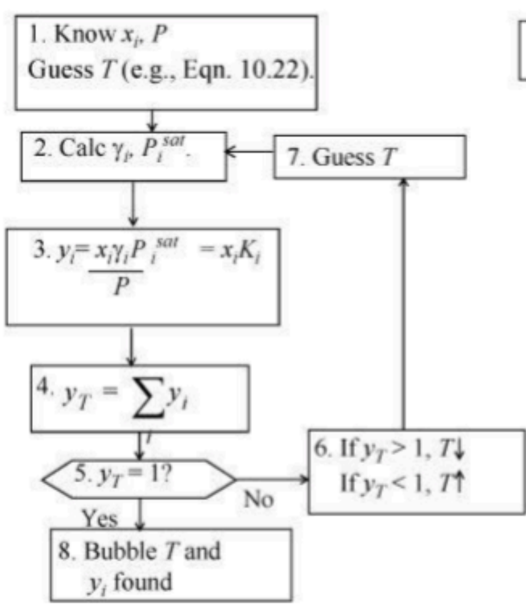
Bubble *P*



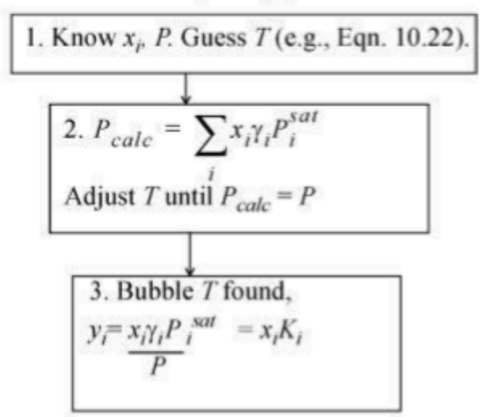
Bubble *T*

(Choose one flow sheet.)

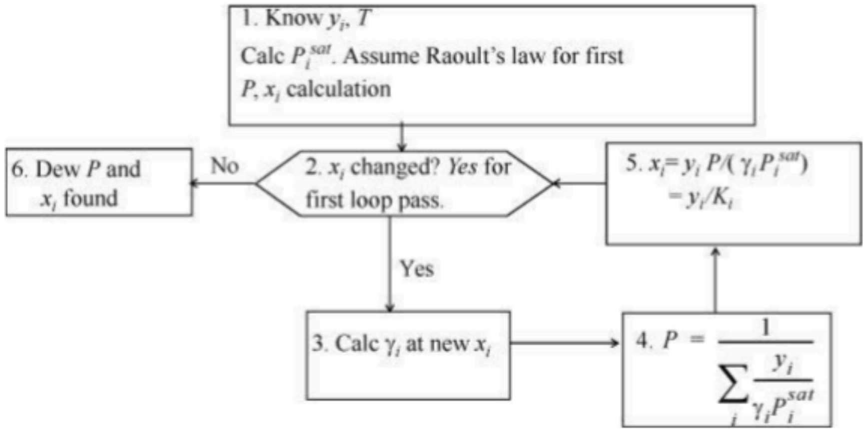
Option (*a*)



Option (*b*)



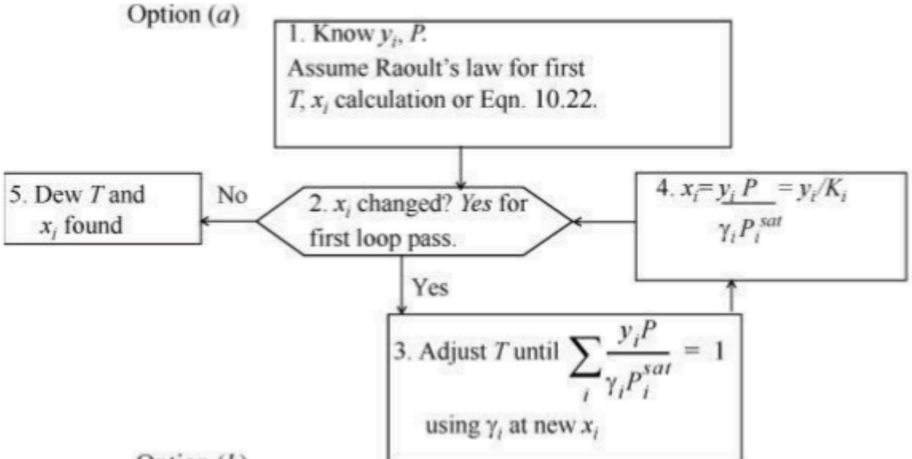
Dew *P*



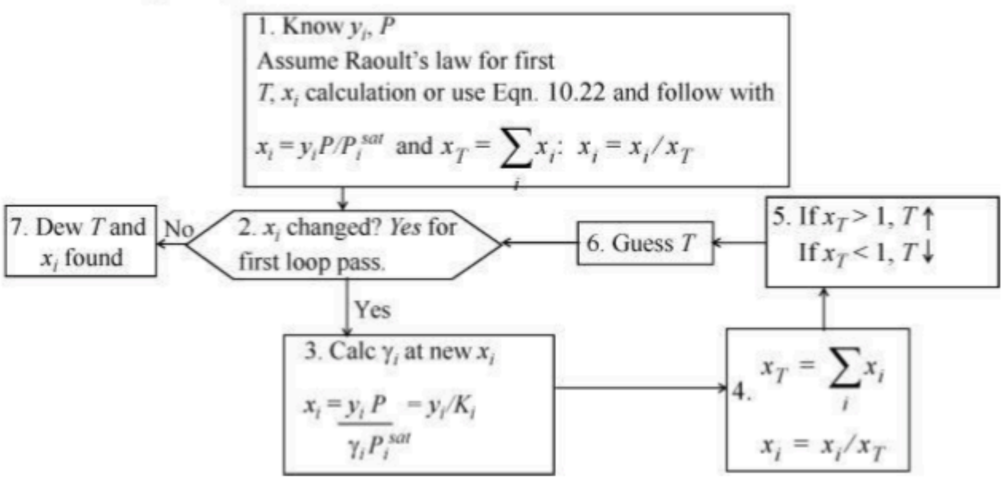
Dew *T*

(Choose one flow sheet.)

Option (*a*)



Option (*b*)

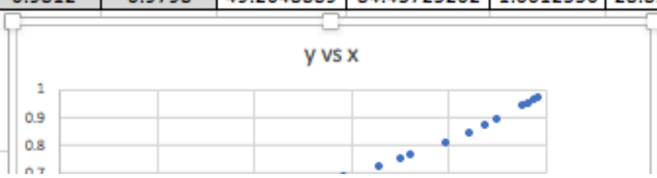


ANSWERS

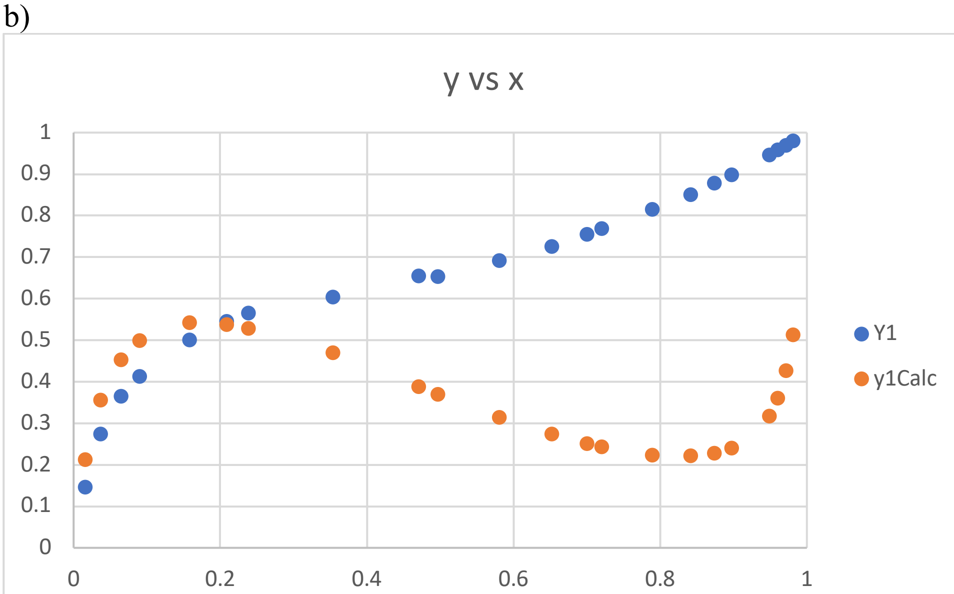
a)

				Adjustable Parameters						
	P, mmHg		A12	3.493845679						B
	190									

T, °C	x1 ethanol	y1 ethanol	Psat1, mmHg	Psat2, mmHg	γ1	γ2	Pcalc	y1,calc	(Pcalc-190)^2
62	0.016	0.146	90.6775965	160.5436825	29.457161	1.0008948	200.85402	0.2127798	117.809674
60	0.037	0.275	83.056011	146.4074377	25.535871	1.0047945	220.13993	0.3564714	908.415147
57.2	0.065	0.365	73.3124385	128.4085888	21.20861	1.014871	222.91304	0.4533856	1083.26831
55.3	0.09	0.4125	67.27472	117.3022326	18.051948	1.0287044	219.10866	0.4988373	847.314206
52.2	0.158	0.5015	58.3405262	100.9441944	11.905623	1.0911371	202.4849	0.5419846	155.872713
53	0.209	0.5455	60.5421553	104.9660733	8.8998361	1.164876	209.32991	0.5379661	373.645317
52.4	0.2385	0.565	58.8843655	101.9370745	7.5838356	1.2198621	201.19868	0.5293613	125.410529
50.1	0.3535	0.6045	52.8862861	91.00916482	4.3072326	1.5474351	171.57211	0.4693363	339.586992
49.8	0.4705	0.6545	52.1441963	89.66078687	2.6633118	2.1671945	168.22968	0.3884052	473.947015
48.9	0.497	0.654	49.9715374	85.71799644	2.4205007	2.3702877	162.31289	0.3703662	766.576335
50.5	0.5805	0.6925	53.8898895	92.83403579	1.8493752	3.2457842	184.25758	0.3139852	32.9754149
48.5	0.6525	0.726	49.0312633	84.01400483	1.5248617	4.4261345	178.00515	0.2740637	143.876348
49.8	0.7	0.755	52.1441963	89.66078687	1.3695005	5.5399439	199.00277	0.2511927	81.0499368
48.7	0.72	0.7685	49.4994743	84.86232869	1.3151063	6.1178431	192.23873	0.2438109	5.01189531
50.2	0.7895	0.8152	53.1356641	91.46247258	1.1674398	8.8264229	218.90861	0.2237226	835.707707
49.1	0.8416	0.8502	50.4474787	86.58106023	1.0916197	11.877643	209.24168	0.2214973	370.242362
49	0.8735	0.879	50.2090216	86.14860056	1.0575019	14.379623	203.0857	0.2283739	171.235439
49.8	0.897	0.899	52.1441963	89.66078687	1.0377617	16.629524	202.11426	0.2401591	146.75522
49.5	0.9485	0.9466	51.4111017	88.32958596	1.0093096	23.178987	154.658	0.3182338	1249.05699
47.5	0.96	0.958	46.7470813	79.88073785	1.0056058	25.026323	125.09362	0.36076	4212.83871
50.3	0.9719	0.97	53.3860551	91.91771581	1.0027626	27.119427	122.07568	0.4262048	4613.71283
48.6	0.9812	0.9798	49.2648889	84.43725202	1.0012356	28.896253	94.268938	0.5134081	9164.43623
								Sum P mean square difference = minimum	26218.7453



b)



$y_{1\text{calc}}$ and y_1 disagree because this is optimized for pressure not y. If we had used $(y\text{-}y_{\text{calc}})^2$ for the least squares optimization this plot would look better but P would be wrong.

c)

dew pressure for T = 50.5°C; y_1 = 0.6925.							Antoine Equation Constants			P mmHg	T,°C
							A	B	C	tMin[oC]	tMax[oC]
	P, mmHg		A12	3.49384568		Ethanol (1)	8.02	1940	258	20	93
	190					Water (2)	8.07	1730	233	1	100
	Psat1 mmHg	Psat2 mmHg									
	53.8898895	92.8340358									
			g1	g2	P mmHg						
	x1	x2	1	1	60						
	0.77101661	0.242368	1.22781523	7.98028889	91.9030001						
	0.961854	0.04651951	1.00758956	25.3398228	77.6144356						
	0.98985442	0.01237266	1.00053499	30.6708023	77.211712						
	0.99166135	0.01016909	1.00036137	31.0568899	77.2064271						
	0.99176557	0.01004198	1.00035239	31.0793294	77.2061988						
	0.99177154	0.0100347	1.00035188	31.0806152	77.206186						
	0.99177188	0.01003429	1.00035185	31.0806888	77.2061853						
	0.9917719	0.01003426	1.00035184	31.080693	77.2061852						
	0.99177191	0.01003426	1.00035184	31.0806932	77.2061852						

d) $x_1 = y_1 P/(P^{sat}_1\ \gamma_1)$ and $x_1 = y_1$ at the azeotrope so,

$$P = P^{sat}_1\ \gamma_1 = P^{sat}_2\ \gamma_2$$

$$\gamma_1 = \exp(x_2^2 A_{12})$$

$$P^{sat}_1/P^{sat}_2 = \gamma_2/\ \gamma_1 = \exp((x_2^2 - x_1^2)A_{12}) = \exp((1-2x_1^2)A_{12})$$

Solve for x_1; calculate P; calculate y_1

Azeotrope at 50.5°C							Antoine Equation Constants			P mmHg	T,°C
							A	B	C	tMin[oC]	tMax[oC]
	P, mmHg		A12	3.49384568		Ethanol (1)	8.02	1940	258	20	93
	190					Water (2)	8.07	1730	233	1	100
		yi = xi Psati gi/P		Psat1 mmHg	Psat2 mmHg	at 50.5°C					
				53.8898895	92.8340358						
		gi = f(xi)									
		Psati = f(T)			g1	3.21093472					
		P= 190 mmHg			g2	1.86393833					
			x1,azeo =	0.42216736	g1 Psat1	g2 Psat2					
			P =	173.036917	173.036917	173.036917					
				Minimum Boiling Azeotrope							
			y1,azeo =	0.42216736							

e)