Chemical Engineering Thermodynamics
Quiz 11
April 7, 2016

An azeotrope of isopropanol (1) and toluene (2) forms at atmospheric pressure (760 mmHg), 80.6°C, and at 42 weight percent toluene (2). (You will need to convert to mole fraction by considering one gram of the solution has 0.42 grams of toluene and 0.58 grams of isopropanol and that the molecular weights are 60 g/mole for (1) and 92 g/mole for (2).

The boiling point at atmospheric pressure for isopropanol is 82.5°C and for toluene is 111°C. The saturated pressures for isopropanol (1) and toluene (2) at 80.6°C are 716 and 300 mmHg from the Antoine equation.
The saturated pressures at 25°C are 44.6 and 28.7 mmHg also from the Antoine equation.

a) Use the azeotrope conditions to calculate the one-parameter Margules constant. (Use the isopropanol activity coefficient for the rest of the calculations, but compare with the toluene value.)
b) Why do you think the two values are different? Would it be better to use a two-parameter Margules model? (Remember that the one-parameter model is symmetric in composition.)
c) Make a rough sketch of the P versus composition plot for 80.6°C.
-Note if it is a positive or negative deviation from Raoult's Law,
-the two vapor pressures and
-the azeotrope conditions.
-Indicate the bubble point and dew point lines and
-one tie line below the azeotrope and one above the azeotrope in composition indicating the y and x that are in equilibrium.
d) Make a rough sketch of the T versus composition plot for atmospheric pressure.
-Note if it is a maximum boiling or minimum boiling azeotrope.
-Note the boiling points of the components and of the azeotrope.
e) Determine the bubble point at 25°C for an equimolar mixture (pressure and composition).
f) Determine the dew point at 25°C for an equimolar mixture. Proceed only to the second iteration and then indicate how the iterations would proceed after that point.
g) Sketch the pressure versus composition diagram at 25°C using the values you have for saturate pressure, BP and DP, as well as the value of the activity coefficient to determine the shape of the curve.

Modified Raoult's law.

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

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

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

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

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

$$\frac{G^E}{RT} = x_1x_2(A_{21}x_1 + A_{12}x_2) \qquad 11.33$$
[10]

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

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

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

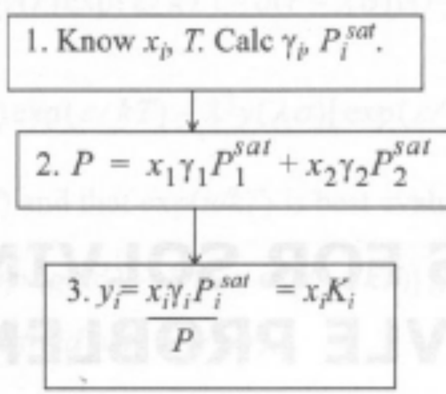
The two parameters can be fitted to a single VLE measurement using

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

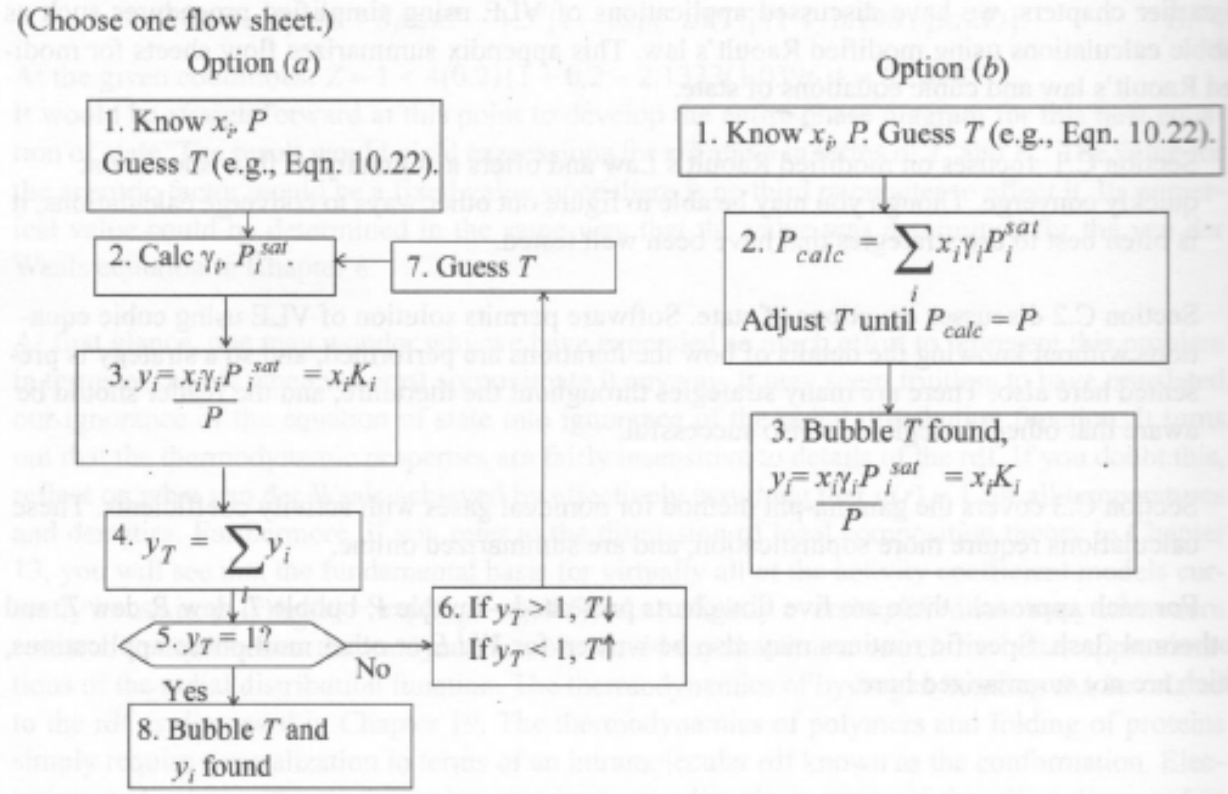
C.1 MODIFIED RAOULT'S LAW METHODS

The equation that must be solved is: $y_iP = x_i\gamma_iP_i^{sat}$

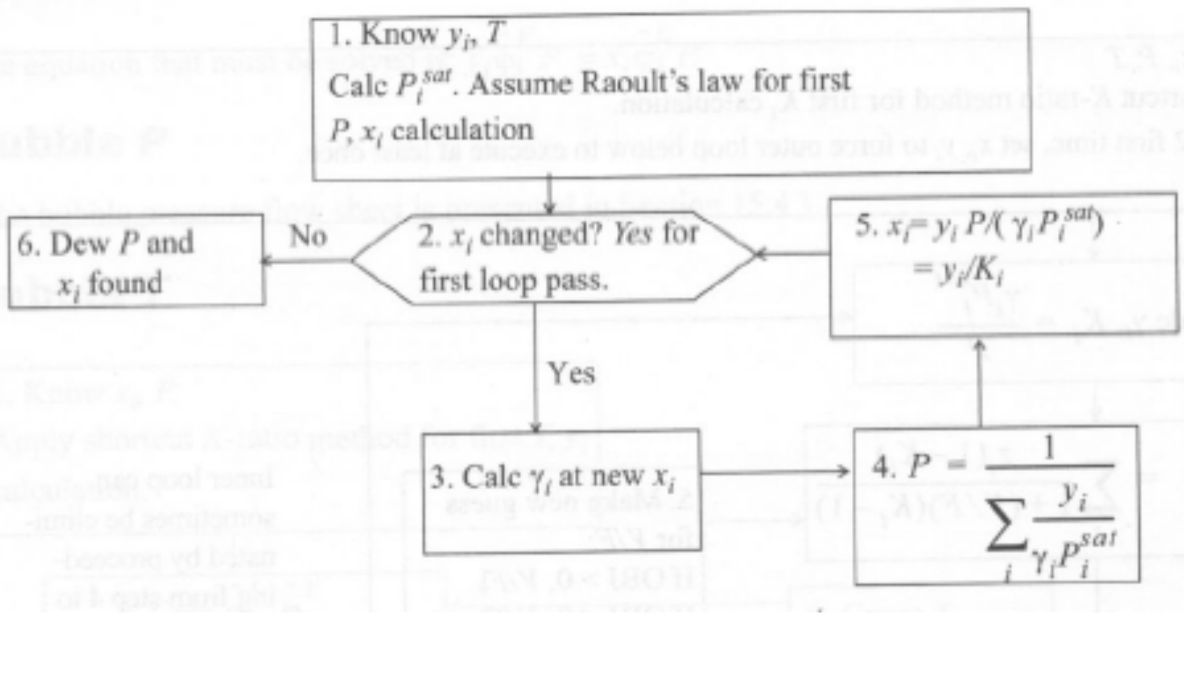
Bubble *P*



Bubble T



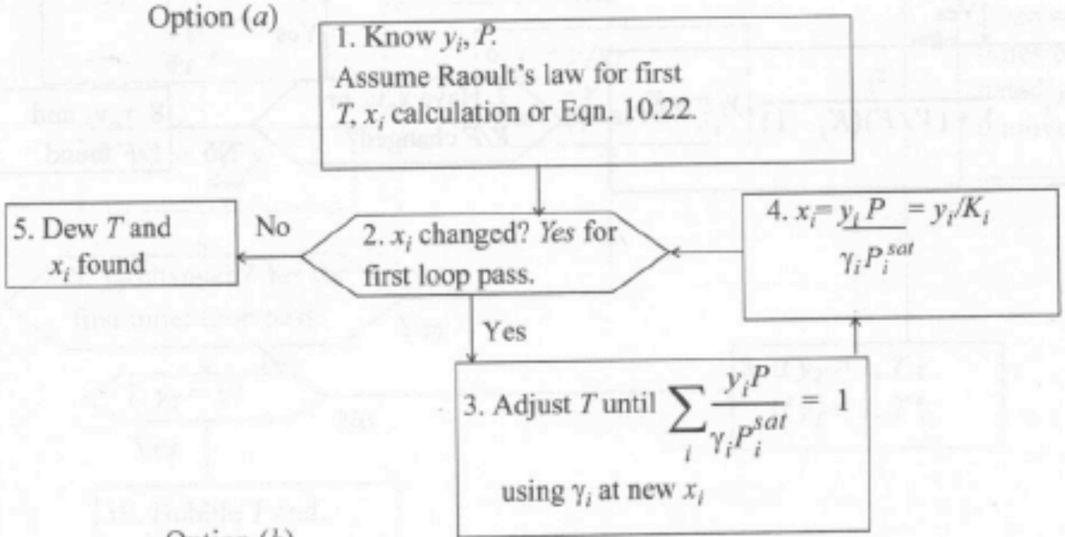
Dew P



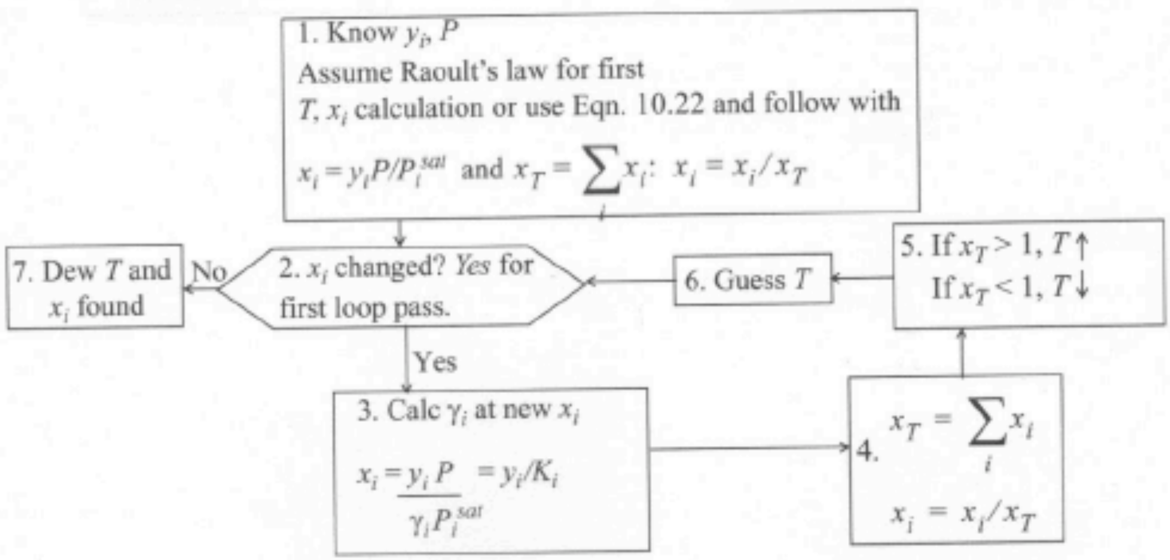
Dew T

(Choose one flow sheet.)

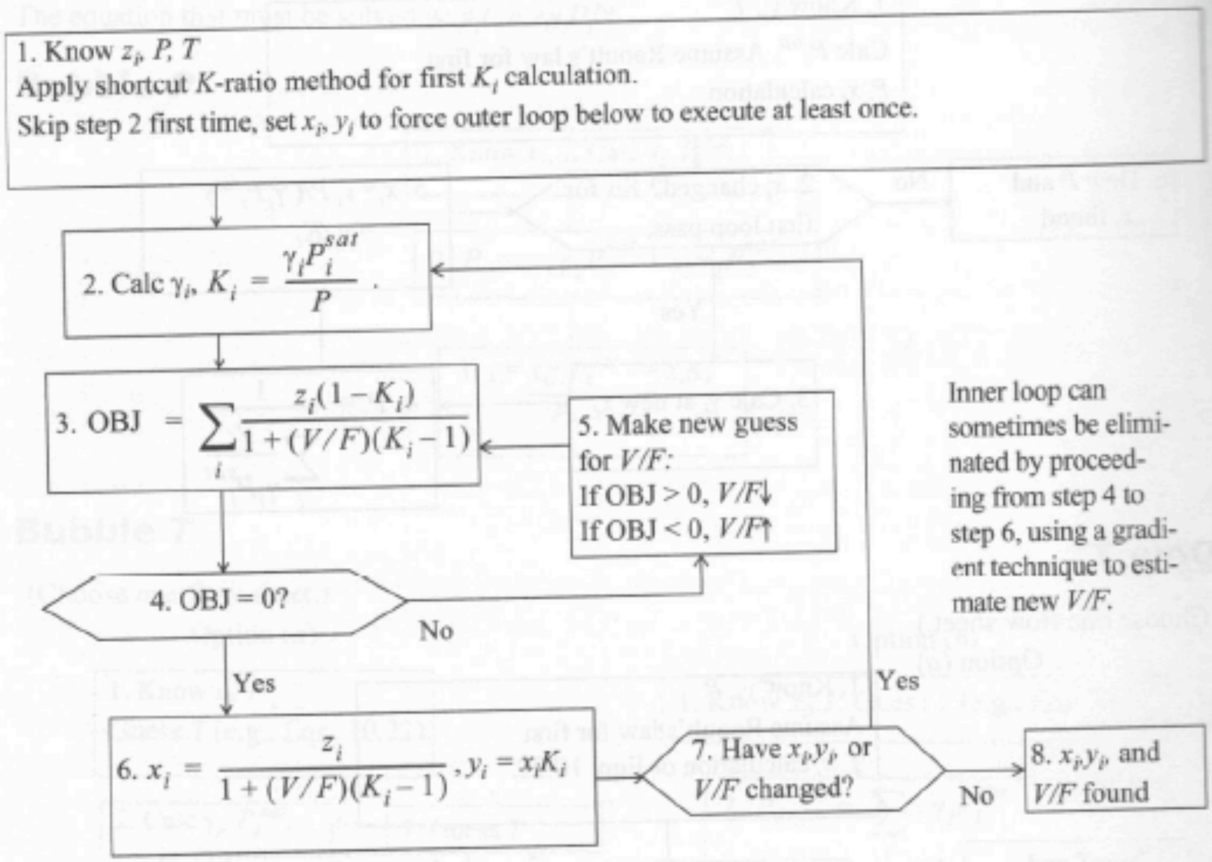
Option (a)



Option (b)



Isothermal Flash



ANSWERS QUIZ 11

(1)

a) At azeotrope $x_1 = y_1$ so

$$\gamma_1 = \frac{P}{P_1^{sat}} = \frac{760 \text{ mm Hg}}{716 \text{ mm Hg}} = 1.06$$

Positive deviation from Raoult's Law

$$\gamma_2 = \frac{760 \text{ mm Hg}}{300 \text{ mm Hg}} = 2.53$$

$$A_{12} = \frac{\ln \gamma_1}{x_2^2} = \frac{\ln \gamma_2}{x_1^2}$$

x_1 is mole fraction & we have weight fraction

Say for 1 g

$$\frac{0.42 \text{ g toluene}}{92 \text{ g/mole}} = 0.457 \text{ mole toluene}$$

$$\frac{0.58 \text{ g isopropanol}}{60 \text{ g/mole}} = 0.967 \text{ mole isoprop}$$

$$x_{toluene\,(2)} = \frac{0.457 \text{ mol}}{0.457 + 0.967 \text{ mol}} = 0.321 \text{ toluene (2)}$$

$$x_{isoprop\,(1)} = \frac{0.967 \text{ mol}}{0.457 + 0.967 \text{ mol}} = 0.679 \text{ isopropanol (1)}$$

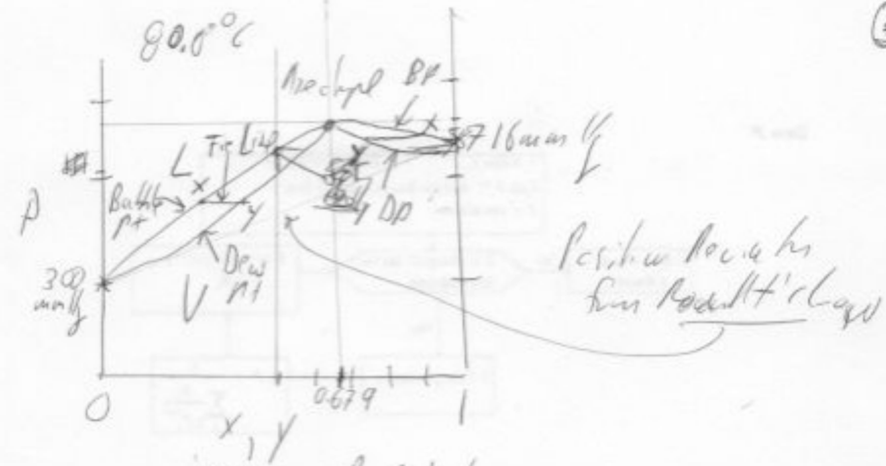
use isopropanol γ_1: $A_{12} = \frac{\ln(1.06)}{(0.321)^2} = 0.565$

$A_{12} = \frac{\ln(2.53)}{(0.679)^2} = 2.01$ — should be same

(2)

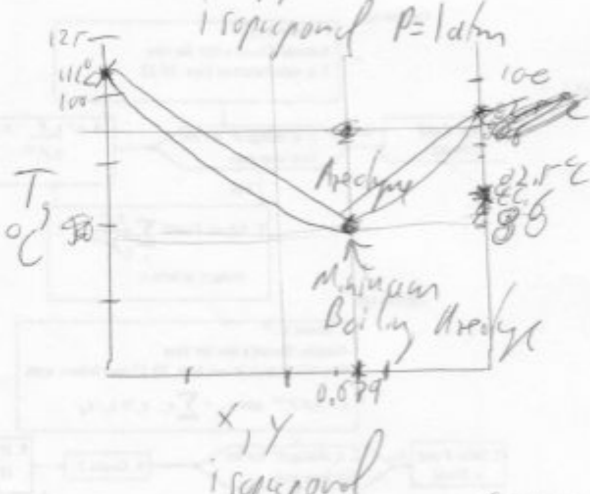
b) The Margules 1-parameter Model would predict an azeotrope at $z = 0.5$ not at 0.679. So it's an approximation good to about ±1.5 for A_{12}. The 2-parameter model is really needed for this system.

c)



isopropanol P=1atm

d)



e)

$x_1 = 0.50 \quad \gamma_1 = \exp(0.565(0.5)^2) = 1.15$

$\gamma_2 = \exp(0.565(0.5^2)) = 1.15$

$P_{BP} = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$

$= 0.5(1.15)\,44.6\ (\text{~~716~~}) + 0.5(1.15)\,28.7\ (\text{~~300~~})$

$=$ ~~585 mmHg~~ 42.0 mmHg

$y_1 = \dfrac{x_1 \gamma_1 P_1^{sat}}{P} = \dfrac{0.5(1.15)\,44.6}{42} = 0.610$

$y_2 = 0.390$

(4)

f) $y_1 = 0.50$

① $\gamma_{initial} = 1$ Raoult's Law

② $P_{initial} = \dfrac{1}{\dfrac{0.5}{\gamma_1 P_1^{sat}} + \dfrac{0.5}{\gamma_2 P_2^{sat}}} = \dfrac{1}{\dfrac{0.5}{44.6} + \dfrac{0.5}{28.7}} = 34.9 \text{ mmHg}$

(with $\gamma_1 = 1$, $\gamma_2 = 1$)

③ Calculate x_1 x_2

$x_1 = \dfrac{0.5\ P}{\gamma_1\ 44.6 \text{ mmHg}} = 0.391$ (with $\gamma_1 = 1$)

$x_2 = \dfrac{0.5\ P}{\gamma_2\ 28.7} = 0.608$ (with $\gamma_2 = 1$)

④ Calculate γ_i's

$\gamma_1 = \exp(A_{12}\ x_2^2) = e^{(0.565(0.608)^2)} = e^{(0.209)} = 1.23$

$\gamma_2 = \exp(A_{12} x_1^2) = \exp(0.565(0.391)^2) = 1.09$

⑤ Get $P = \dfrac{1}{\dfrac{0.5}{1.23(44.6)} + \dfrac{0.5}{1.09(28.7)}} = 39.8 \text{ mmHg}$

(Like ②)

⑥ redo 3 $x_1 = \dfrac{0.5(39.8)}{1.23\ (44.6)} = 0.363$ $x_2 = \dfrac{0.5(39.8)}{1.09\ (28.7)} = 0.636$

→ ④, ⑤, ⑤, ⑥ until change P or repeat

	A	B	C
Isopropanol	8.88	2010	253
Toluene	6.95	1340	219

10^{A – b/(t+c)}

Azeotropes of isopropanol, b.p.=82.5 °C

2nd Component	b.p. of comp. (°C)	b.p. of mixture (°C)	% by weight	spef. grav
with various esters				
ethyl acetate	77.1	75.3	75	0.869
isopropyl acetate	91.0	81.3	40	0.822
with various hydrocarbons				
benzene	80.2	71.9	66.7	0.838
toluene ‡[10]	110.8	80.6	42	

a) Determine the Azeotrope pressure and composition at 25°C using $P_{sat1}/P = \exp(A_{12}(1-x_1)^2)$ and $P_{sat2}/P = \exp(A_{12} x_1^2)$. (Two equations and two unknowns, P and x1, solve by trial and error. For the quiz, P is 256.4 mmHg and just find x_1.)