

CE 407 Notes
Binary batch distillation examples

1. considering distilling an equimolar solution of methanol and water. He has in his possession a batch still fitted with a rectifying column that offers the equivalent of two ideal stages.

- Plot x_D as a function of x_B for operation at a constant reflux ratio $R = 2.0$.
- Plot the reflux ratio R required to maintain a distillate composition $x_D = 0.90$ as a function of x_B .

Equilibrium data are given in Table 21.5 on p. 731.

2. 600 cm^3 of a $25 \text{ }^\circ\text{C}$ equimolar liquid mixture of tetramethylbenzene and pentamethylbenzene is charged to a batch still operating at atmospheric pressure. Heating occurs at the rate of 200 J/s .

- How long does it take to reach a state where only 300 cm^3 of liquid remain in the still pot?
- At this time, what is the average composition of the accumulated distillate, i.e., what is $x_{D,cum}$?

Pertinent data are as follows:

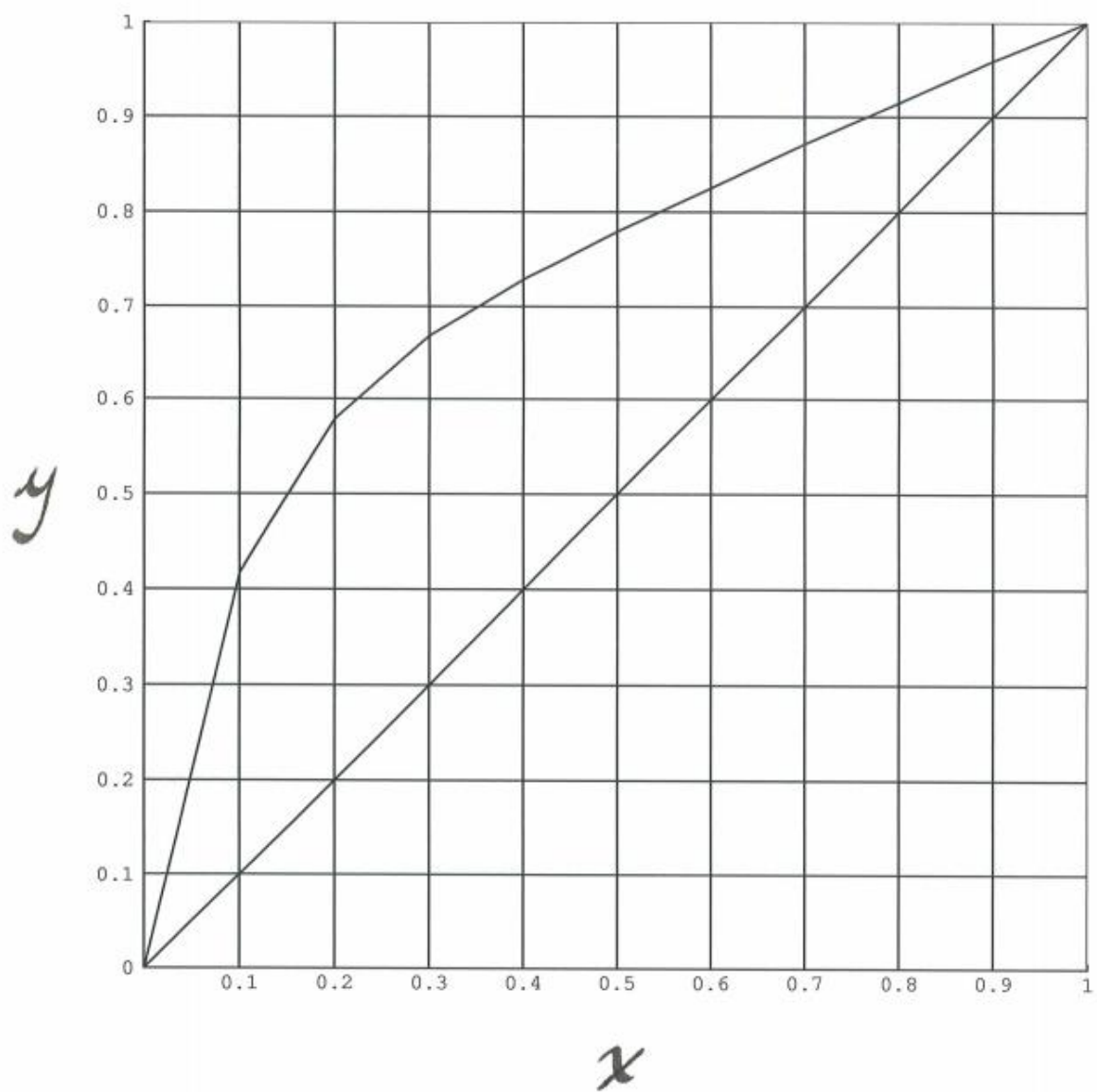
component	ΔH^{vap} at boiling point (J/mol)	$C_{P, \text{liq}}$ (J/mol K)	$C_{P, \text{vap}}$ (J/mol K)	normal boiling point (K)	Elroy's preference for liquid as a beverage
tetramethylbenzene (light)	41,600	370	264	471	very high
pentamethylbenzene (heavy)	43,400	400	290	505	moderately high

The molar volumes of tetramethylbenzene and pentamethylbenzene are given as functions of temperature by the empirical expressions

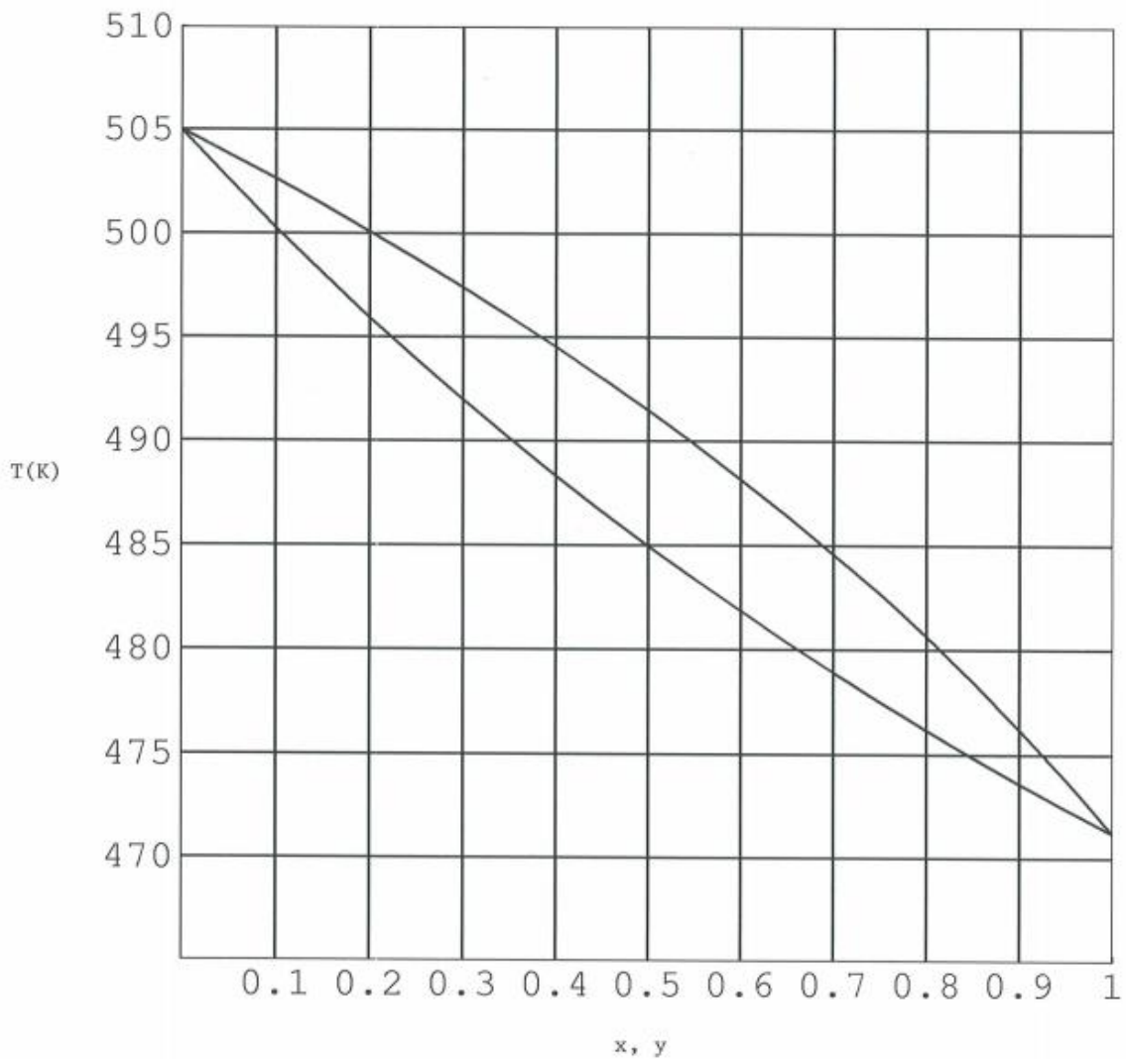
$$\begin{aligned}V_{\text{tetramethylbenzene}} &= (103 \text{ cm}^3/\text{mol}) + (0.20 \text{ cm}^3/\text{mol K}) T, \\V_{\text{pentamethylbenzene}} &= (116 \text{ cm}^3/\text{mol}) + (0.23 \text{ cm}^3/\text{mol K}) T.\end{aligned}$$

A Txy phase diagram at atmospheric pressure is supplied at no extra charge.

Methanol + water



TETRAMETHYLBENZENE + PENTAMETHYLBENZENE AT ATMOSPHERIC PRESSURE



Problem 1

1

(a) Constant reflux ratio $R = 2.0$

For any x_D , op. line for rectifying column is

$$y = \underbrace{\frac{R}{R+1}}_{\text{slope}} x + \frac{x_D}{R+1};$$

passes through (x_D, x_D) and has slope
 $= \frac{R}{R+1} = \frac{2}{3}$ (or intercept $\frac{x_D}{R+1} = \frac{x_D}{3}$).

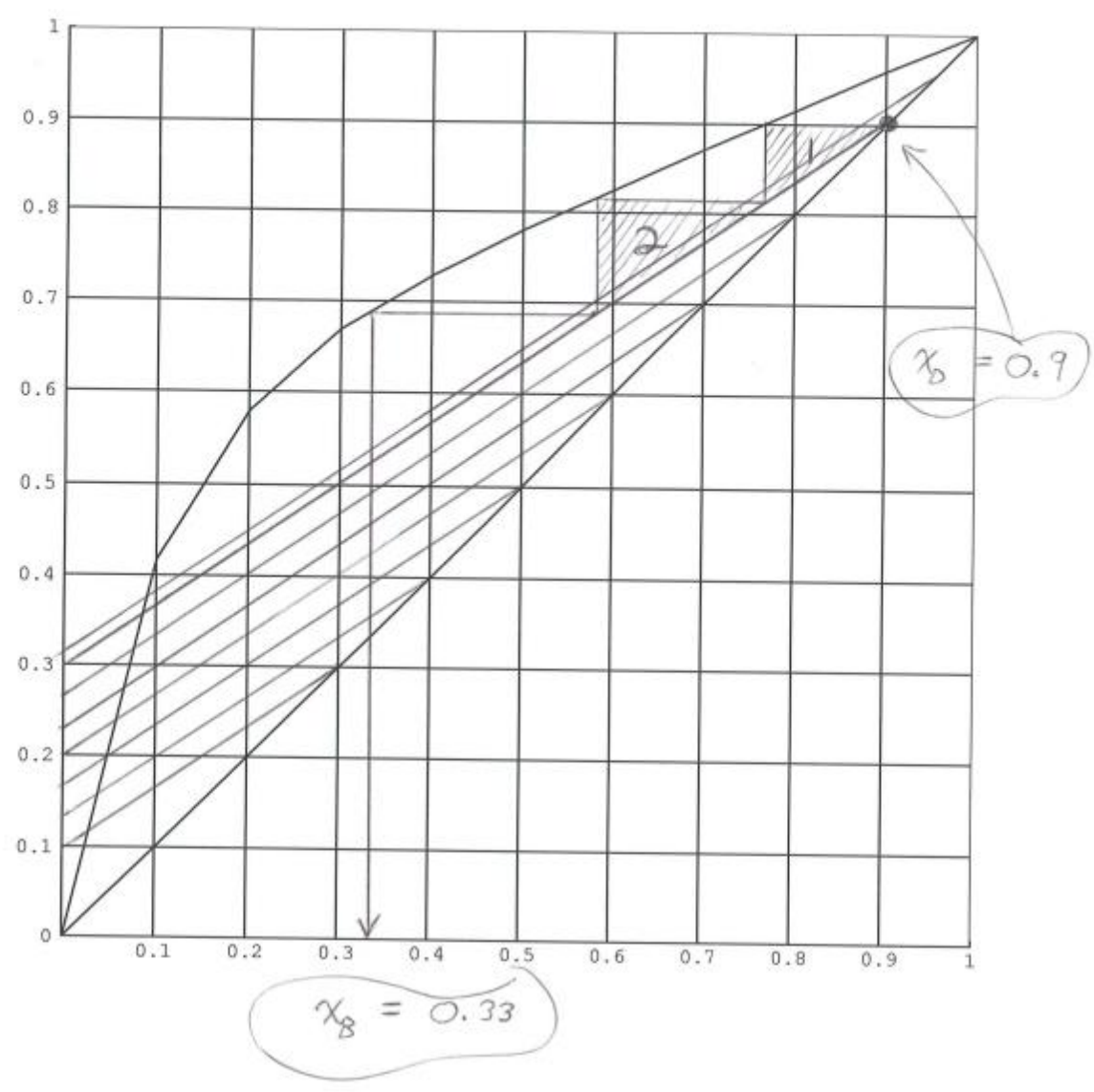
Pick a few values of x_D . For each draw op. line, make 2 steps for rectifying column + one more for VLE in still pot. Tabulate resulting values of x :

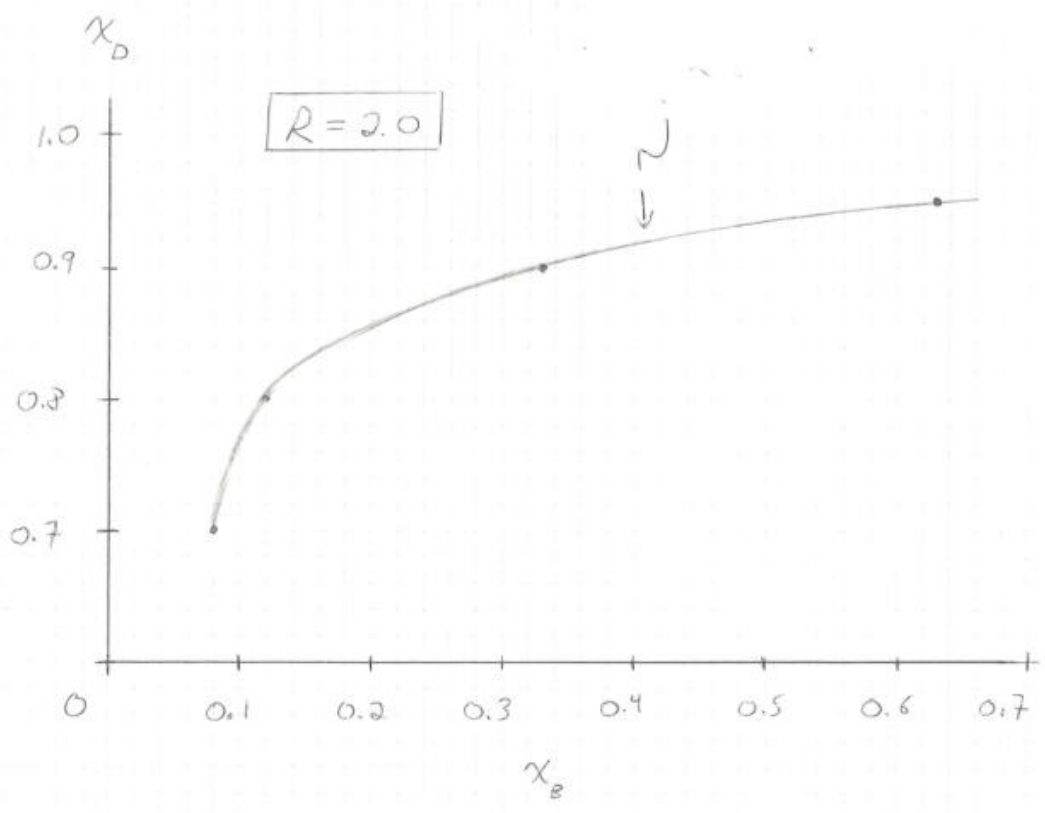
x_D	x_B
0.95	0.63
0.9	0.33
0.8	0.12
0.7	0.08

Graph shows steps only for $x_D = 0.9$ to avoid clutter. Then graph x_D as a function of x_B .

2

Constant reflux ratio $R = 2.0$





(b) Constant distillate composition $x_D = 0.90$.

For any R , draw op. line with $x_D = 0.9$. As R increases, op. line swivels down from point $(x_D, x_D) = (0.9, 0.9)$.

For each op. line make steps as before.

Table:

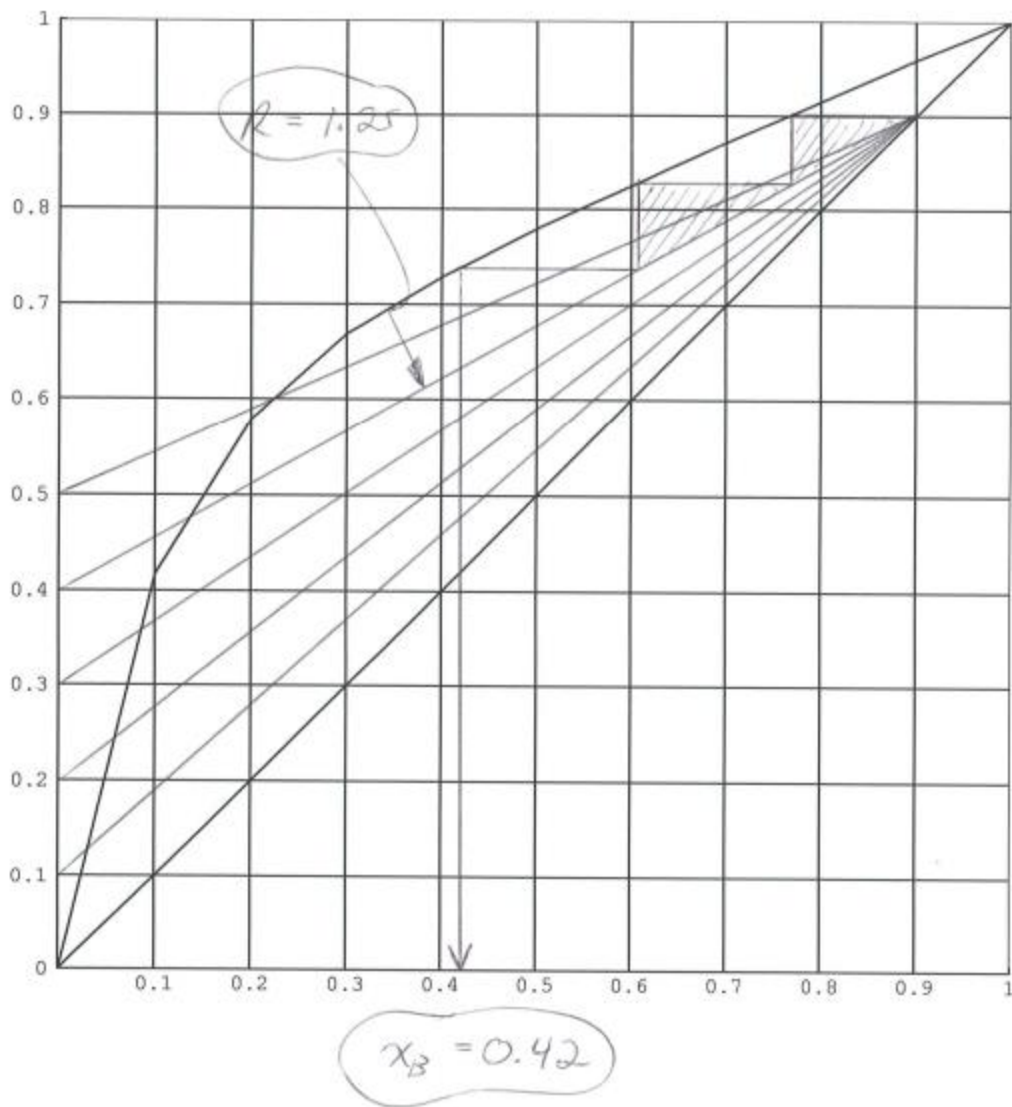
R	$x_D/(R+1)$	x_B
0.8	0.5	0.52
1.25	0.4	0.42
2	0.3	0.33
3.5	0.2	0.25
8	0.1	0.18
∞	0	0.14

extra column for y_i -intercept of op. line

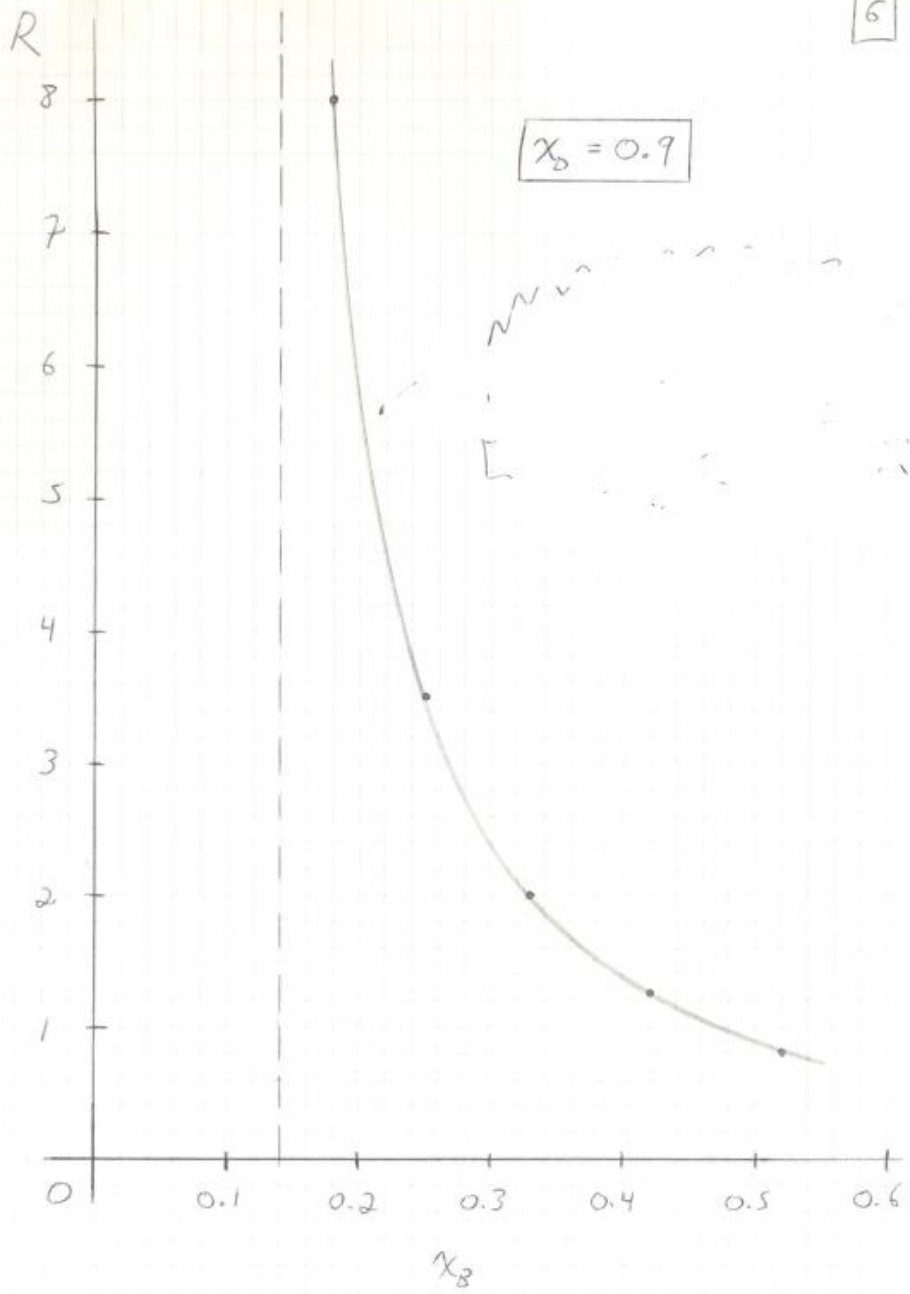
Graph shows steps only for $R = 1.25$ to avoid clutter. Then graph R as a function of x_B .

5

Constant distillate composition $x_D = 0.90$



6



Problem 2

1 = light = tetramethylbenzene
2 = heavy = pentamethylbenzene

(i) Preliminaries

What are the mole numbers? Assuming ideal liquid solution,

$$V = (0.5) V_1(298.15\text{K}) + 0.5 V_2(298.15\text{K})$$

initial temp
= 25°C = 298.15K

$$= \left\{ (0.5) \left[107 + (0.2)(298.15) \right] + (0.5) \left[115 + (0.2)(298.15) \right] \right\} \frac{\text{cm}^3}{\text{mol}}$$

$$= 173.60 \text{ cm}^3/\text{mol}$$

$$n_{B, \text{init}} = \frac{600 \text{ cm}^3}{173.60 \text{ cm}^3/\text{mol}} = 3.456 \text{ mol}$$

How long does it take to heat liquid to bubble point?

From phase diagram, $T_b = 485 \text{ K}$ since $x = 0.5$.

Enthalpy change of liquid is

$$\Delta H^L = n_{B, \text{init}} \left[\underbrace{(0.5)(370 \frac{\text{J}}{\text{mol K}}) + (0.5)(400 \frac{\text{J}}{\text{mol K}})}_{C_p \text{ of mixture}} \right] \underbrace{(485 - 298.15)}_{\text{temp. change}} \text{K}$$

$$= 2.486 \times 10^5 \text{ J}$$

$$\Delta t_{298.15\text{K} \rightarrow 485\text{K}} = \frac{\Delta H^L}{\dot{Q}} = \frac{2.486 \times 10^5 \text{ J}}{200 \text{ J/s}} = 1243 \text{ s}$$

(a little over 20 minutes).

[Note that an alternate way of calculating ΔH^L is to use formulas derived for mixture enthalpy. Just for fun, let's derive them

ONE MORE TIME! Arbitrarily select reference states
 s.l. $H=0$ for liquid ① at 471 K and
 s.l. $H=0$ for liquid ② at 471 K. Then

$$H_x = x [0 + 370(T - 471K)] + (1-x)[0 + 400(T - 471K)]$$

$$\boxed{H_x = (400 - 30x)(T - 471K)}$$

$$H_y = y [0 + 41,600 + 264(T - 471)] + (1-y) [0 + 400(505 - 471) + 43,400 + 290(T - 471 + 471 - 505)]$$

heat ② to normal bp. boil ② at normal bp.
 bring vapor ② to arbitrary temperature T

$$= y [41,600 + 264(T - 471)] + (1-y) [47,140 + 290(T - 471)]$$

$$\boxed{H_y = 47,140 - 5540y + (290 - 264y)(T - 471)}$$

Then $\Delta H^{\ominus} = n_{2, \text{mix}} [H(485K, 0.5) - H(298.15K, 0.5)]$

equimolar mixture @ 485K equimolar mixture @ 298.15K

$$= (3.456 \text{ mol}) \left\{ [400 - 30(0.5)](485 - 471) - [400 - 30(0.5)](298.15 - 471) \right\}$$

$$= 2426 \times 10^3 \text{ J (same)}$$

(ii) The actual batch distillation:

Values of n_B as a function of x_B . Use eq. (21.86) on p. 725
(with slight change in notation):

$$\ln\left(\frac{n_B}{n_{B,init}}\right) = \int_{x_{B,init}}^{x_B} \frac{dx}{x_D - x}$$

$y_{eqwt}(x)$
from phase diagram

Values for integration are as follows:

x	$x_D = y_{eqwt}(x)$	$\frac{1}{x_D - x}$
0.5	0.69	5.263
0.4	0.60	5.000
0.3	0.48	5.556
0.2	0.36	6.250

By trapezoid rule,

$$\int_{0.5}^{0.4} \frac{dx}{x_D - x} \approx \frac{1}{2}(-0.1)(5.263 + 5.000) = -0.5132$$

$$\int_{0.4}^{0.3} \frac{dx}{x_D - x} \approx \frac{1}{2}(-0.1)(5.000 + 5.556) = -0.5278$$

$$\int_{0.3}^{0.2} \frac{dx}{x_D - x} \approx \frac{1}{2}(-0.1)(5.556 + 6.250) = -0.5903$$

$$\begin{aligned} \text{Then when } x_B = 0.4, n_B &= n_{B,init} \exp\left[\int_{0.5}^{0.4} \frac{dx}{x_D - x}\right] \\ &= 3.456 \exp(-0.5132) \\ &= 2.069 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{when } x_B = 0.3, n_B &= n_{B,init} \exp\left[\int_{0.5}^{0.3} \frac{dx}{x_D - x}\right] \\ &= 3.456 \exp(-0.5132 - 0.5278) \\ &= 1.220 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{when } x_B = 0.2, \quad n_B &= n_{B, \text{init}} \exp\left[\int_{0.2}^{0.5} \frac{dx}{x_0 - x}\right] \\ &= 2.456 \exp(-0.5132 - 0.5278 - 0.5903) \\ &= 0.676 \text{ mol} \end{aligned}$$

(Average) mole fraction of ① in (well-mixed) accumulated distillate is given by

$$x_{D, \text{cum}} = \frac{n_{B, \text{init}} x_{D, \text{init}} - n_B x_B}{n_{B, \text{init}} - n_B}$$

3.456 mol
0.5

(Numerator = moles of ① not in still pot, ∴ accum. distillate;
denominator = total moles not in still pot, ∴ accum. distillate.)

Volume of liquid remaining in still pot is given by

$$V_B^L = n_B [x_B V_1(T) + (1-x_B) V_2(T)]$$

instantaneous temp of VLE between x_B and x_D

assuming ideal liquid solution

$$\Delta H^{\text{vap}} \text{ at any value of } x_B \text{ is just } H_g(T, y_{\text{equil}}(x_B)) - H_L(T, x_B),$$

literally the ^{x_B} difference between vapor & liquid enthalpies @ equil.

Boiling time for each interval in x_B : Calculate average ΔH^{vap} ; multiply by the number of moles of liquid evaporated and divide by the heating rate to determine the time increment:

$$\Delta t = \frac{(\Delta H^{vap})_{ave} (-\Delta n_B)}{\dot{Q}}$$

Master table, calculated by Elroy and checked by Elroy's pet Mushroom, is given below.

Summary table from columns marked with bold lines is as follows:

$t(s)^*$	$V_a^L (cm^3)$	$x_{D,cum}$
1243	739	0.69
→ 1533	449	0.649
1711	269	0.609
1886	152	0.573

By linear interpolation in table,

$$t = 1680 \text{ s} \text{ when } V_a^L = 300 \text{ cm}^3$$

and at this time

$$x_{D,cum} = 0.616$$

at start of distillation, $t = 1243 \text{ s}$.

x_B	$y = x_D = y_{\text{equil}}(x_B)$	n_B (mol)	$x_{D, \text{cum}}$	T (K)	V_1 (cm ³ /mol)	V_2 (cm ³ /mol)
0.5	0.69	3.456	0.69*	485	200.0	227.6
0.4	0.60	2.069	0.649	488	200.6	228.2
→ 0.3	0.48	1.220	0.609	492	201.4	229.2
0.2	0.36	0.676	0.573	496	202.2	230.1

3rd line

Sample calculation for 3rd line in table:

$$x_{D, \text{cum}} = \frac{(3.456)(0.5) - (1.220)(0.3)}{3.456 - 1.220} = 0.609$$

$$T = 492 \text{ K from phase diagram (sat. liq. w/ } x = 0.3)$$

$$V_1 = 103 + (0.2)(492) = 201.4 \text{ cm}^3/\text{mol}$$

$$V_2 = 116 + (0.23)(492) = 229.2 \text{ cm}^3/\text{mol}$$

$$V_3^{\text{L}} = (1.220 \text{ mol})[(0.3)(201.4) + (0.7)(229.2)] \frac{\text{cm}^3}{\text{mol}} = 269 \text{ cm}^3$$

$$H_x = [400 - 30(0.3)](492 - 471) = 8211 \text{ J/mol}$$

$$H_y = 47,140 - 5540(0.48) + [290 - 26(0.48)](492 - 471) = 50,301$$

* Ratio $\frac{n_{B, \text{init}} x_{D, \text{init}} - n_B x_B}{n_{B, \text{init}} - n_B} = \frac{0}{0}$ is indeterminate. However, first

bits of vapor are in equil. with liquid having composition $x_B = x_{D, \text{init}} = 0.5$

Thus $x_{D, \text{cum}} = y_{\text{equil.}}(0.5) = 0.69$.

V_B^t (cm ³)	H_x (J/mol)	H_y (J/mol)	ΔH^{vap} (J/mol)	t (s)
739	5,390	47,126	41,736	1243 †
449	6,596	48,481	41,885	1533
269	8,211	50,309	42,098	1711
152	9,850	52,162	42,312	1826

† $\Delta t = 290\text{ s}$
 $\Delta t = 178\text{ s}$
 $\Delta t = 115\text{ s}$

$$\Delta H^{vap} = 50,309 - 8,211 = 42,098 \text{ J/mol}$$

Average heat of vaporization from from $x_B = 0.4$ to $x_B = 0.3$
 is $\frac{1}{2}(41,885 + 42,098) = 41,992 \text{ J/mol}$. Elapsed time interval
 $\Delta t = \frac{(41,992 \text{ J/mol})(2.089 - 1.220) \text{ mol vaporized}}{200 \text{ J/s}} = 178 \text{ s}$

$$t = \underbrace{1533 \text{ s}}_{2^{\text{nd}} \text{ time for } x_B = 0.4} + \underbrace{178 \text{ s}}_{\text{time interval } \Delta t} = 1711 \text{ s}$$

† The actual batch distillation (i.e., evaporation) occurs after liquid changed to still pot reaches its bubble point of 485 K. This preliminary heating step took 1243 s.

x_B	$y = x_D = y_{\text{liquid}}(\%)$	n_B (mol)	$x_{D, \text{cum}}$	T (K)	V_1 (cm ³ /mol)	V_2 (cm ³ /mol)	V_B^{t} (cm ³)	H_x (J/mol)	H_y (J/mol)	ΔH^{vap} (J/mol)	t (s)
0.5	0.69	3.456	0.69*	485	200.0	227.6	739	5,390	47,126	41,736	1243 [†]
0.4	0.60	2.069	0.649	488	200.6	228.2	449	6,596	48,481	41,885	1533
0.3	0.48	1.220	0.609	492	201.4	229.2	269	8,211	50,309	42,098	1711
0.2	0.36	0.676	0.573	496	202.2	230.1	152	9,850	52,162	42,312	1826

$\Delta t = 290\text{ s}$
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Sample calculation for 3rd line in table:

$$x_{D, \text{cum}} = \frac{(3.456)(0.5) - (1.220)(0.3)}{3.456 - 1.220} = 0.609$$

$$T = 492\text{ K from phase diagram (sat. liq. w/ } x = 0.3)$$

$$V_1 = 103 + (0.2)(492) = 201.4\text{ cm}^3/\text{mol}$$

$$V_2 = 116 + (0.23)(492) = 229.2\text{ cm}^3/\text{mol}$$

$$V_B^{\text{t}} = (1.220\text{ mol})[(0.3)(201.4) + (0.7)(229.2)] \frac{\text{cm}^3}{\text{mol}} = 269\text{ cm}^3$$

$$H_x = [400 - 30(0.3)](492 - 471) = 8,211\text{ J/mol}$$

$$H_y = 47,140 - 5540(0.48) + [290 - 26(0.48)](492 - 471) = 50,309\text{ J/mol}$$

* Ratio $\frac{n_{B, \text{init}} x_{D, \text{init}} - n_B x_D}{n_{B, \text{init}} - n_B} = \frac{0}{0}$ is indeterminate. However, first

bit of vapor are in equilibrium with liquid having composition $x_B = x_{D, \text{init}} = 0.5$

$$\text{Then } x_{D, \text{cum}} = y_{\text{liquid}}(0.5) = 0.69.$$

$$\Delta H^{\text{vap}} = 50,309 - 8,211 = 42,098\text{ J/mol}$$

Average heat of vaporization from from $x_B = 0.4$ to $x_B = 0.3$

is $\frac{1}{2}(41,885 + 42,098) = 41,992\text{ J/mol}$. Elapsed time interval

$$\Delta t = \frac{(41,992\text{ J/mol})(0.089 - 1.220)\text{ mol vaporized}}{200\text{ J/s}} = 178\text{ s}$$

$$t = 1533\text{ s} + 178\text{ s} = 1711\text{ s}$$

2nd line for $x_B = 0.4$
 time interval Δt

† The actual batch distillation (i.e., evaporation) occurs after liquid changes to still pot reboiler its bubble point of 485 K. This preliminary heating step took 1243 s.