Example 1

A 100 mol/h saturated liquid feed stream comprising 40 mole percent benzene and 60 mole percent toluene is to be separated by distillation at atmospheric pressure into a top product with benzene mole fraction 0.95 and a bottom product with toluene mole fraction 0.92.

(a) What is the minimum reflux ratio R_{min}, corresponding to an infinite number of stages $(N \to \infty)$?

(b) What is the minimum number of stages N_{min}, corresponding to total reflux $(R \to \infty)$?

(c) Assuming an operating reflux ratio of 2.0, calculate the rates of heat transfer required in the condenser and reboiler, q_c and q_r.

(d) Assuming an operating reflux ratio of 2.0, use the enthalpy-balance method to calculate exact values of y_{n+1} on the operating line at liquid-phase mole fractions $x_n = 0.8$, 0.6 and 0.4. (These exact values are not predicated on the assumption of constant molar flows.)
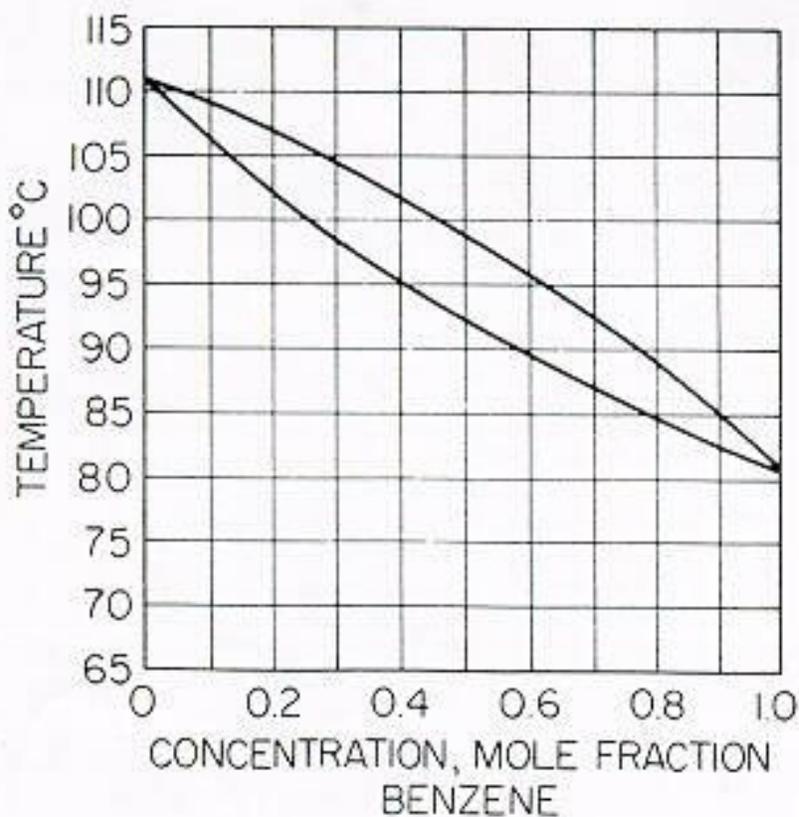
Benzene (1) – toluene (2) at atmospheric pressure
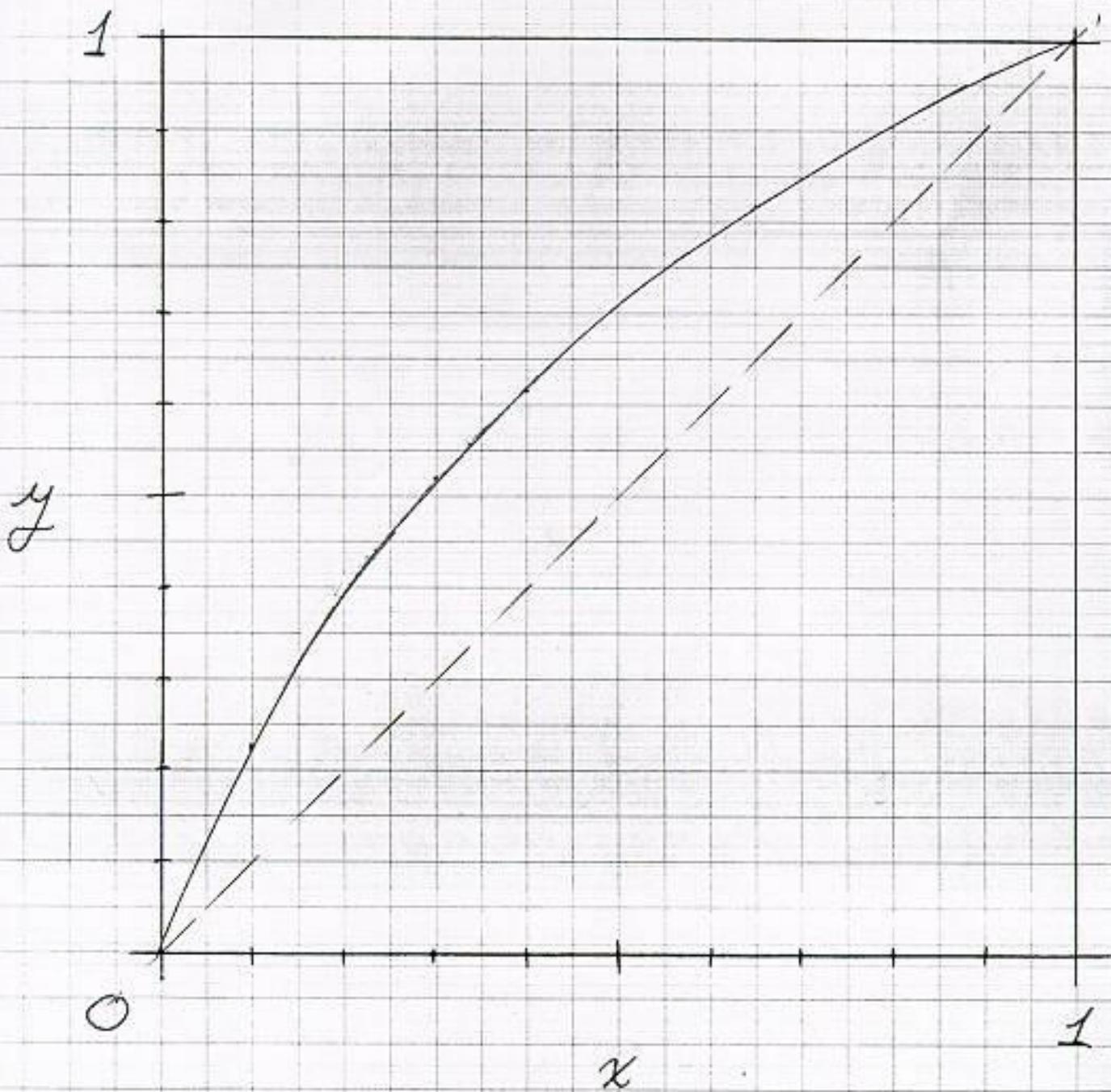
$\underline{100 \text{ mol basis}}$ $x_F = 0.40$ Total condenser !

$x_D = 0.95, \quad x_B = 0.08$

(a) $x_D/(R_{min}+1) = 0.38 \Rightarrow R_{min} = 1.5$

(b) $N_{min} = 5$ (excl. reboiler).

(c)
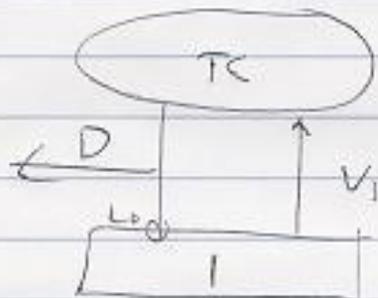
$D = F\left(\dfrac{x_F - x_B}{x_D - x_B}\right) = 36.8 \text{ mol}$

$B = F\left(\dfrac{x_D - x_F}{x_D - x_B}\right) = 63.2 \text{ mol}$

$R = L_0/D \Rightarrow L_0 = RD = 2D = 73.6 \text{ mol}$

$V_1 = L_0 + D = 110.4 \text{ mol}$

$L = L_0 = 73.6 \text{ mol}$

$V = V_1 = 110.4 \text{ mol}$

$\bar{L} = L + qF = 173.6 \text{ mol}$

$\bar{V} = V = 110.4 \text{ mol}$

36.8

$L/V = \dfrac{R}{R+1} = 0.6667$

73.6   110.4

$\bar{L}/\bar{V} = 1.5725$

173.6   110.4
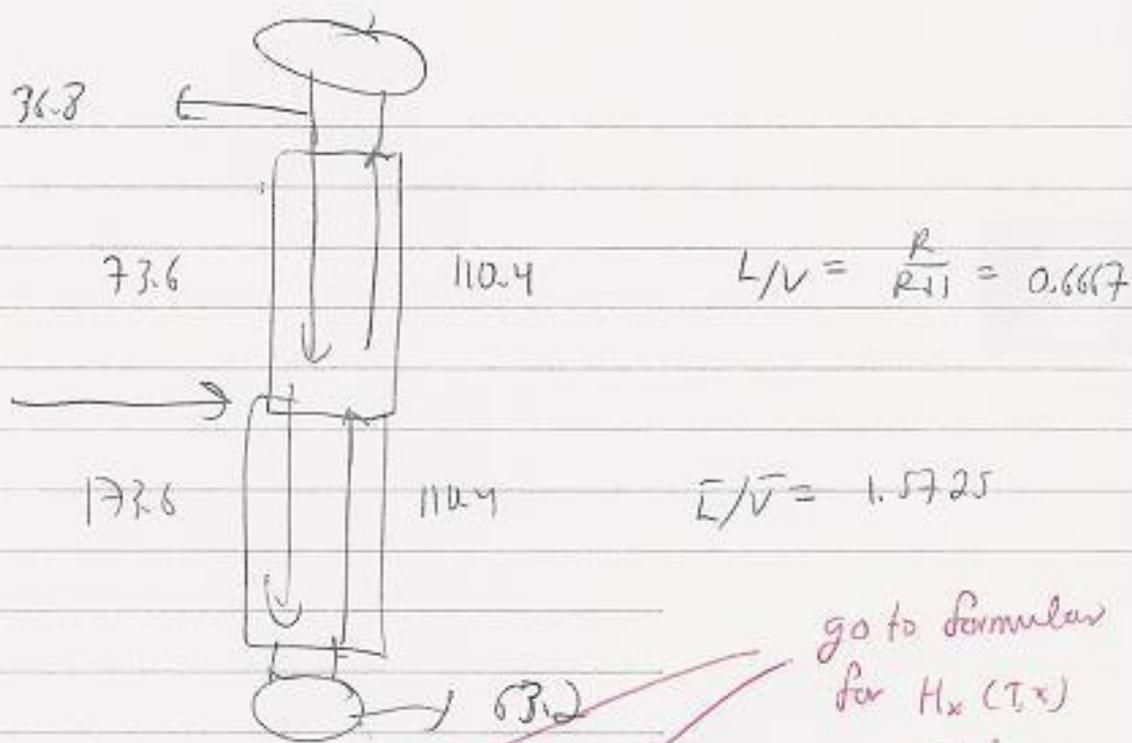
go to formulas for $H_x(T,x)$ and $H_y(T,y)$ below

(73.2)

$D\, H_D + L_o\, H_{x,o} - V_1\, H_{y,1} = -q_c$

$q_c = V_1\,(H_{y,1} - H_{x,o})$

    7471   67 cal/mol
    cal/mol

$= \left(110.4\ \dfrac{mol}{h}\right)(7471 - 67)\ \dfrac{cal}{mol} = \boxed{8.174 \times 10^{5}\ \dfrac{cal}{h}}$

$D H_D + B H_B - F H_F = q_r - q_c$

$q_r = D H_D + B H_B - F H_F + q_c$

$H_D : 67\ cal/mol \qquad liquid,\ 82°C,\ x = 0.75$

$H_F : 558\ cal/mol \qquad liquid,\ 91°C,\ x = 0.4$

$H_B : 1065\ cal/mol \qquad liquid,\ 107°C,\ x = 0.08$

$q_r = (36.8)(67) + (63.2)(1065) - (100)(558) + 8.174 \times 10^{5}$

$= \boxed{8.314 \times 10^{5}\ cal/h}$

(a)

Benzene (1) – toluene (2) at atmospheric pressure
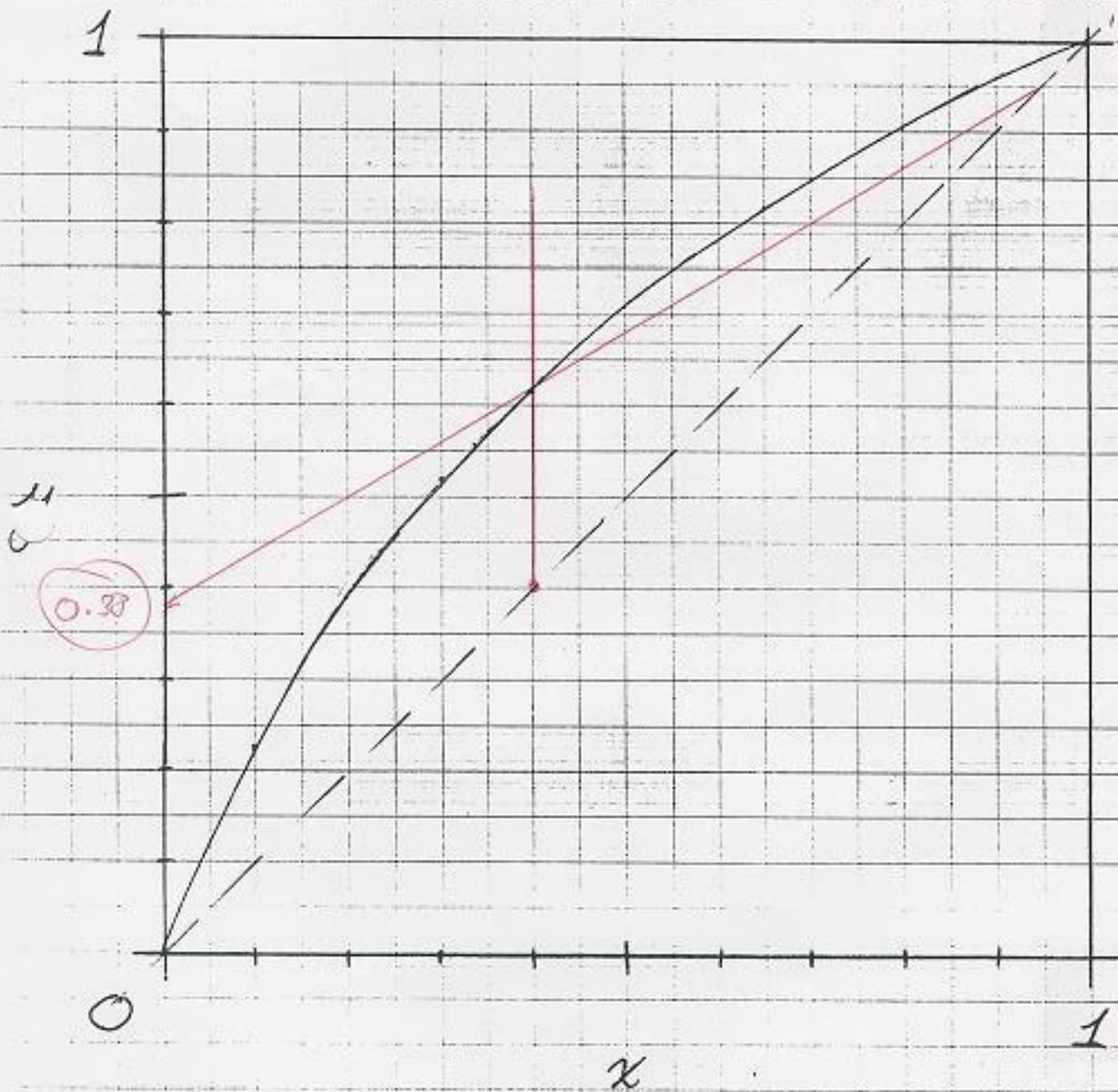
(2)

Benzene (1) – toluene (2) at
atmospheric pressure

1

y

RB

O

x

1
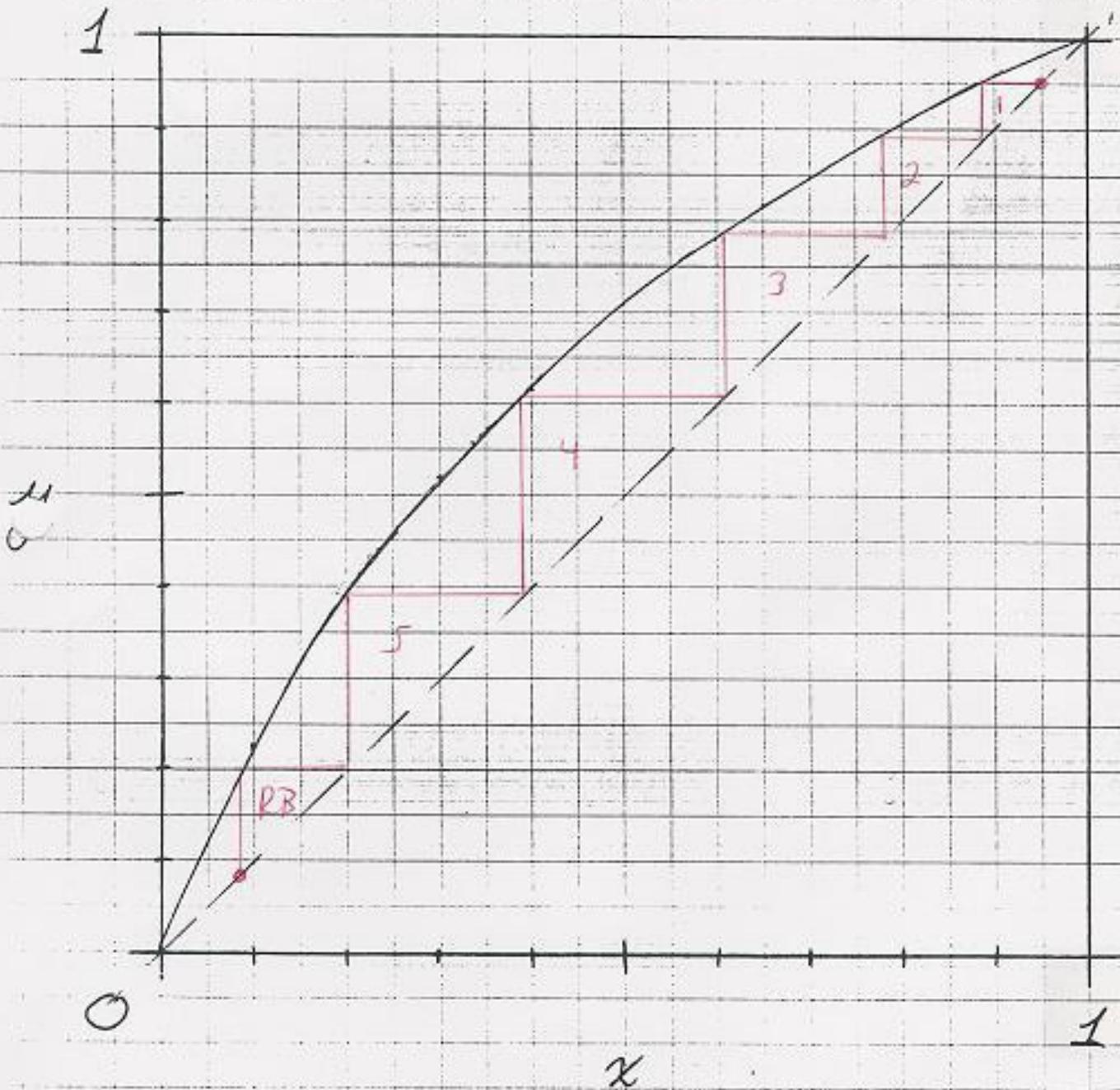
Benzene (1) – toluene (2) at atmospheric pressure
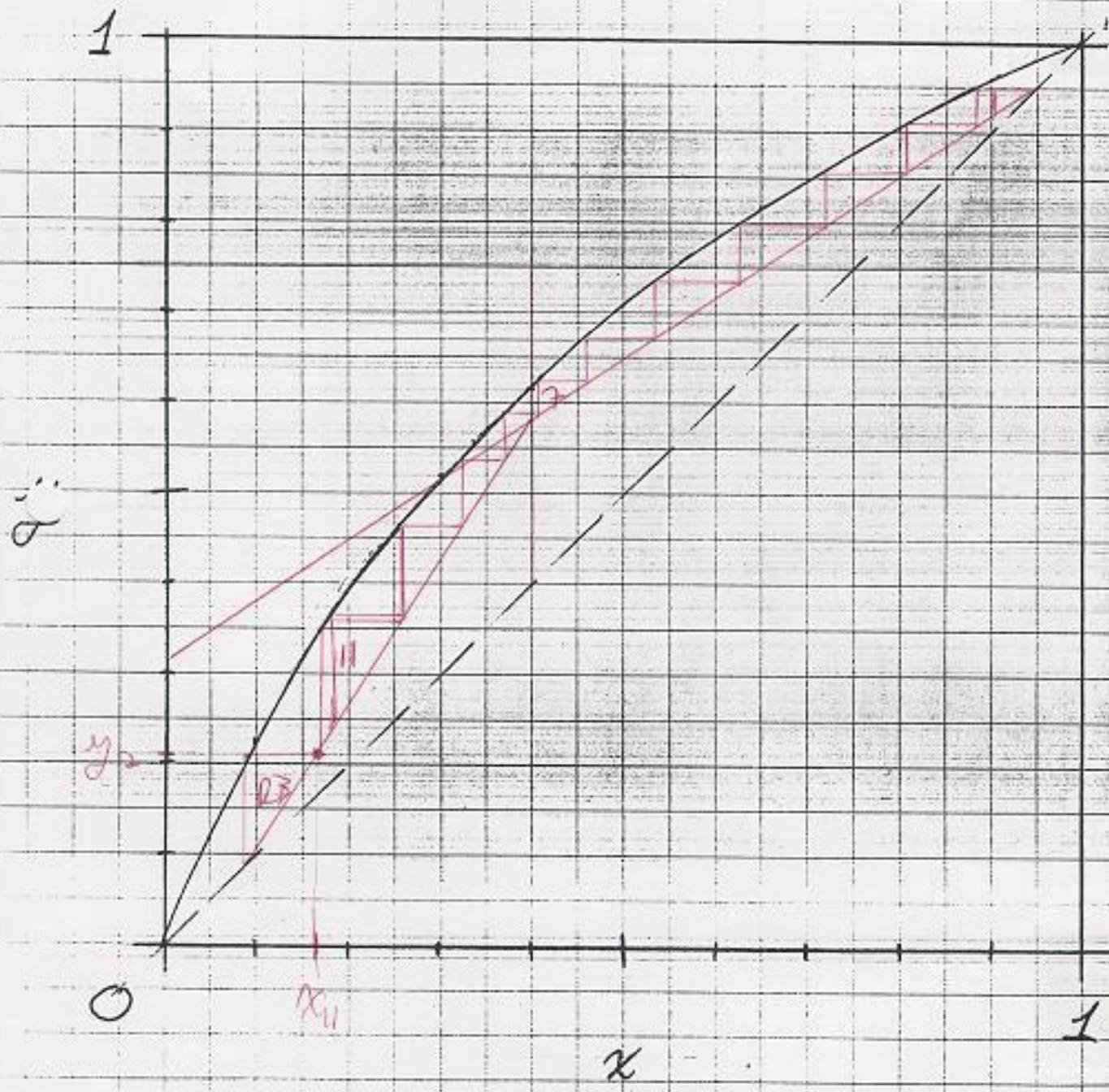
I Preliminaries

x, y denote mole fractions in liquid and vapor phases of more volatile component, benzene.

$$x_F = 0.40, \quad x_D = 0.95, \quad x_B = 1 - 0.92 = 0.08$$

<u>Basis:</u> $F = 100$ mol

Material balance equations (21.8) and (21.9) on p. 670:

$$D = F\left(\frac{x_F - x_B}{x_D - x_B}\right) = (100 \text{ mol})\left(\frac{0.40 - 0.08}{0.95 - 0.08}\right) = 36.8 \text{ mol}$$

$$B = F\left(\frac{x_D - x_F}{x_D - x_B}\right) = (100 \text{ mol})\left(\frac{0.95 - 0.40}{0.95 - 0.08}\right) = 63.2 \text{ mol}$$

Hey look! $D + B = 36.8 \text{ mol} + 63.2 \text{ mol} = 100 \text{ mol} = F$!

... serves as check of total material balance.

Reflux ratio
$$R = \frac{L_0}{D} = 2$$

so
$$L_0 = 2D = 73.6 \text{ mol}$$

Always $V_{n+1} = L_n + D$
   (distillate out = difference between vapor up and liquid down between any two trays (above feed tray))

$\therefore \; V_1 = L_0 + D = 73.6 \text{ mol}$
$\qquad\qquad\qquad + 36.8 \text{ mol}$
$\qquad\qquad = 110.4 \text{ mol}$

TOTAL CONDENSER:
$x_D = x_0 = y_1$!

total condenser

x_D

L_0, x_0

y_1, V_1

L_1, x_1 y_2, V_2

L_2, x_2 y_3, V_3

L_{n-1}, x_{n-1} y_n, V_n

L_n, x_n y_{n+1}, V_{n+1}
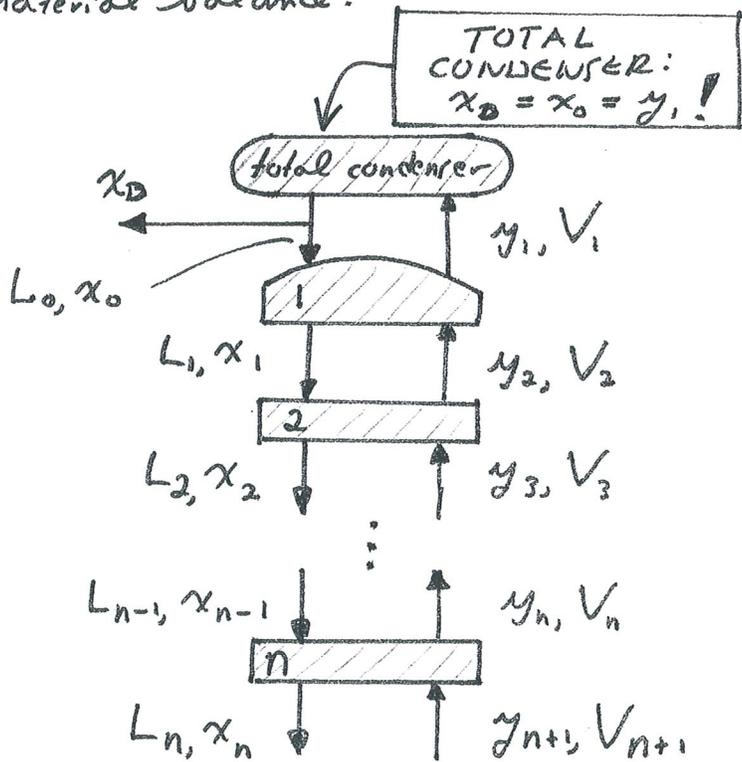
II Now a word about enthalpies...

As in Example 21.5, take enthalpy to be zero for liquid benzene and toluene at $80°C \cong$ boiling point of benzene. Then

$\qquad\qquad\qquad = 0$ by def.

pure liquids
$\begin{cases}
\text{(benzene) } H_x = H(80°C) + C_{p,\ell}(T - 80°C) \\
\qquad\qquad = 33(T - 80) \\
\text{(toluene) } H_x = H_x(80°C) + C_{p,\ell}(T - 80°C) \\
\qquad\qquad = 40(T - 80)
\end{cases}$

H_x in cal/mol
T in °C

$$\text{(benzene)} \quad H_y = \underbrace{H_x(80°C)}_{\substack{\text{liquid @} \\ \text{b.p.}}} + \underbrace{\Delta H_v(80°C)}_{\substack{\text{heat of} \\ \text{vaporization @ b.p.}}} + \underbrace{C_{p,v}(T-80°C)}_{\substack{\text{"sensible heat"} \\ \text{for vapor}}}$$

$$= 7360 + 23(T-80) \quad \longleftarrow \boxed{\text{given in book}}$$

$$\text{(toluene)} \quad H_y = \underbrace{H_x(80°C)}_{\text{liquid @ 80°C}} + \underbrace{C_{p,\ell}(110.6°C - 80°C)}_{\text{heat liquid to b.p.}} + \underbrace{\Delta H_v(110.6°}_{\substack{\text{heat of} \\ \text{vaporization} \\ \text{@ b.p.}}}$$

$$+ \underbrace{C_{p,v}(80°C - 110.6°C)}_{\substack{\text{cool vapor back} \\ \text{down to 80°C}}} + \underbrace{C_{p,v}(T-80°C)}_{\substack{\text{"sensible heat"} \\ \text{for temp. change} \\ \text{from 80°C.}}}$$

$$= 0 + 40(110.6-80) + 7960 + 33(80-110.6)$$
$$+ 33(T-80)$$

$$= 8174 + 33(T-80) \quad \longleftarrow \boxed{\text{given in book}}$$

left margin: pure vapors

Ideal solution: no heat of mixing, so

$$H_x = x(H_x)_{benzene} + (1-x)(H_x)_{toluene}$$

$$= x \cdot 33(T-80) + (1-x) \cdot 40(T-80)$$

$$\boxed{H_x = (40-7x)(T-80)} \quad \text{(liquid)} \quad \left\{ \begin{array}{l} H_x \text{ in } cal/mol \\ T \text{ in } °C \end{array} \right\}$$

Similarly for vapor

$$H_y = y(H_y)_{benzene} + (1-y)(H_y)_{toluene}$$

$$= y[7360 + 23(T-80)] + (1-y)[8174 + 33(T-80)]$$

$$\boxed{H_y = 8174 - 814y + (33-10y)(T-80)} \quad \text{(vapor)}$$
$$\left\{ \begin{array}{l} H_y \text{ in } cal/mol \\ T \text{ in } °C \end{array} \right\}$$

There are equations for liquid and vapor enthalpies as functions of temperature and composition — exactly what we need.

III. Enthalpies of streams entering and leaving condenser.

  liquid: saturated liquid with benzene mole fraction $= x_0 = x_D = 0.95$. From phase diagram (Fig. 21.2, p. 665), $T \cong 82°C$†

$$H_{x,0} = (40 - 7(0.95))(82-80) = 67 \text{ cal/mol}$$

  vapor: saturated vapor with benzene mole fraction $= y_1 = x_D = 0.95$. From phase diagram, $T \cong 83°C$‼

$$H_{y,1} = 8174 - 814(0.95) + (33-10(0.95))(83-80)$$
$$= 7471 \text{ cal/mol}$$

IV. Now all set for iterative calculation.

  Note: $x_F = 0.40$ and feed line is vertical (because feed enters as saturated (liquid). ∴ the points with $x_n = 0.4, 0.6, 0.8$ will have to lie on rectifying line.

  Proceed as outlined in book, pp. 695-696 (or in class) using equations

$$y_{n+1} = \frac{L_n x_n}{V_{n+1}} + \frac{D x_D}{V_{n+1}} \qquad (21.52)$$

$$V_{n+1} = L_n + D \qquad (21.53)$$

$$V_{n+1} H_{y,n+1} = L_n H_{x,n} + V_1 H_{y,1} - L_0 H_{x,0} \qquad (21.51) \text{ with slight notation changes}$$

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† Here is what is going on:
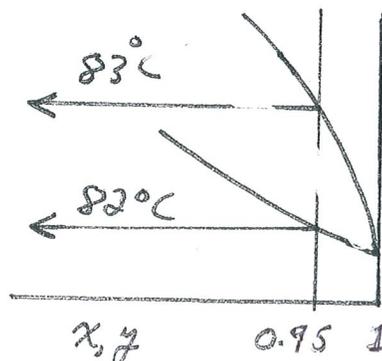
Step 1: Pick x_n (problem specifies values 0.4, 0.6, 0.8). This is saturated liquid; read of temperature from phase diagram and compute enthalpy $H_{x,n}$.

Step 2: <u>Estimate</u> y_{n+1} by making approximations $L_n \approx L_0$, $V_{n+1} \approx V_1$ in eq. (21.52). With this approx. value of y_{n+1}, corresponding to saturated vapor, read off temp. on phase diagram. Calculate $H_{y,n+1}$.

Step 3: Solve (21.53) for L_n (i.e., $L_n = V_{n+1} - D$) and substitute into (21.51). (21.51) now contains only one unknown quantity, namely V_{n+1}. Solve for V_{n+1}:

$$V_{n+1} = \frac{V_1 H_{y,1} - L_0 H_{x,0} - D H_{x,n}}{H_{y,n+1} - H_{x,n}}$$

Step 4: With new value for V_{n+1}, get corresponding improved value for L_n, from
$$L_n = V_{n+1} - D.$$

Step 5: Now get improved approximation for y_{n+1} from (21.52). Book stops here; to check convergence could repeat $(\cdot)$ calculation starting from this new value of y_{n+1}.

IV. Calculations organized in table on next page.

improved approx. using values of L_n and V_{n+1} in (21.52)

approx. using $L_n \approx L_0$, $V_{n+1} \approx V_1$ in (21.52)

x_n	T(sat. liq.) (°C)	$H_{x,n}$ (cal/mol)	y_{n+1}	T(sat. vap.) (°C)	$H_{y,n+1}$ (cal/mol)	V_{n+1} (mol)	L_n (mol)	y_{n+1}
0.8	85	172	0.850	87	7654	108.7	71.9	0.851
0.6	90	358	0.717	92	7900	107.0	70.2	0.720
0.4	95	558	0.583	96	8134	105.5	68.7	0.592

<u>Sample calcs for $x_n = 0.8$:</u>

$$H_{x,n} = (40 - 7(0.8))(85-80) = 172 \text{ cal/mol}$$

$$y_{n+1} \approx \frac{(73.6)(0.8)}{110.4} + \frac{(36.8)(0.95)}{110.4} = 0.850$$

$$H_{y,n+1} = 8194 - (814)(0.850) + (33 - 10(0.850))(87-80) = 7654$$

$$V_{n+1} = \frac{(110.4)(7471) - (73.6)(67) - (36.8)(172)}{7654 - 172} = 108.7$$

$$L_n = 108.7 - 36.8 = 71.9$$

$$y_{n+1} = \frac{(71.9)(0.8)}{108.7} + \frac{(36.8)(0.95)}{108.7} = 0.851$$

For $x_n = 0.4$ the change in y_{n+1} is the most.
One more iteration gives $y_{n+1} = 0.592$ again
to three digits, so this represents converged value

(NOT
REQUIRED)

Example 2

Joyous example, part (a). Based on the following tabulated data (compiled by yoo-no-hoo's pet mushroom), derive formulas for the enthalpies of liquid and vapor mixtures of n-hexane and n-octane. You may assume ideal gas and ideal liquid solution behavior.

substance	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)
n-hexane	28,853	218	172	342
n-octane	34,413	276	226	399

Joyous example, part (b). A 100 mol/h saturated vapor feed stream (60 mole percent n-hexane, 40 mole percent n-octane) is to be separated by continuous distillation at atmospheric pressure in a column fitted with a total condenser. There should be 95 percent recovery of the light and heavy keys in the distillate and bottom product. A reflux ratio equal to 1.15 times the minimum will be used. Calculate the rates of heat transfer in the condenser and reboiler, q_c and q_r. A Txy phase diagram at atmospheric pressure is attached.

n-hexane + n-octane at 1 atm
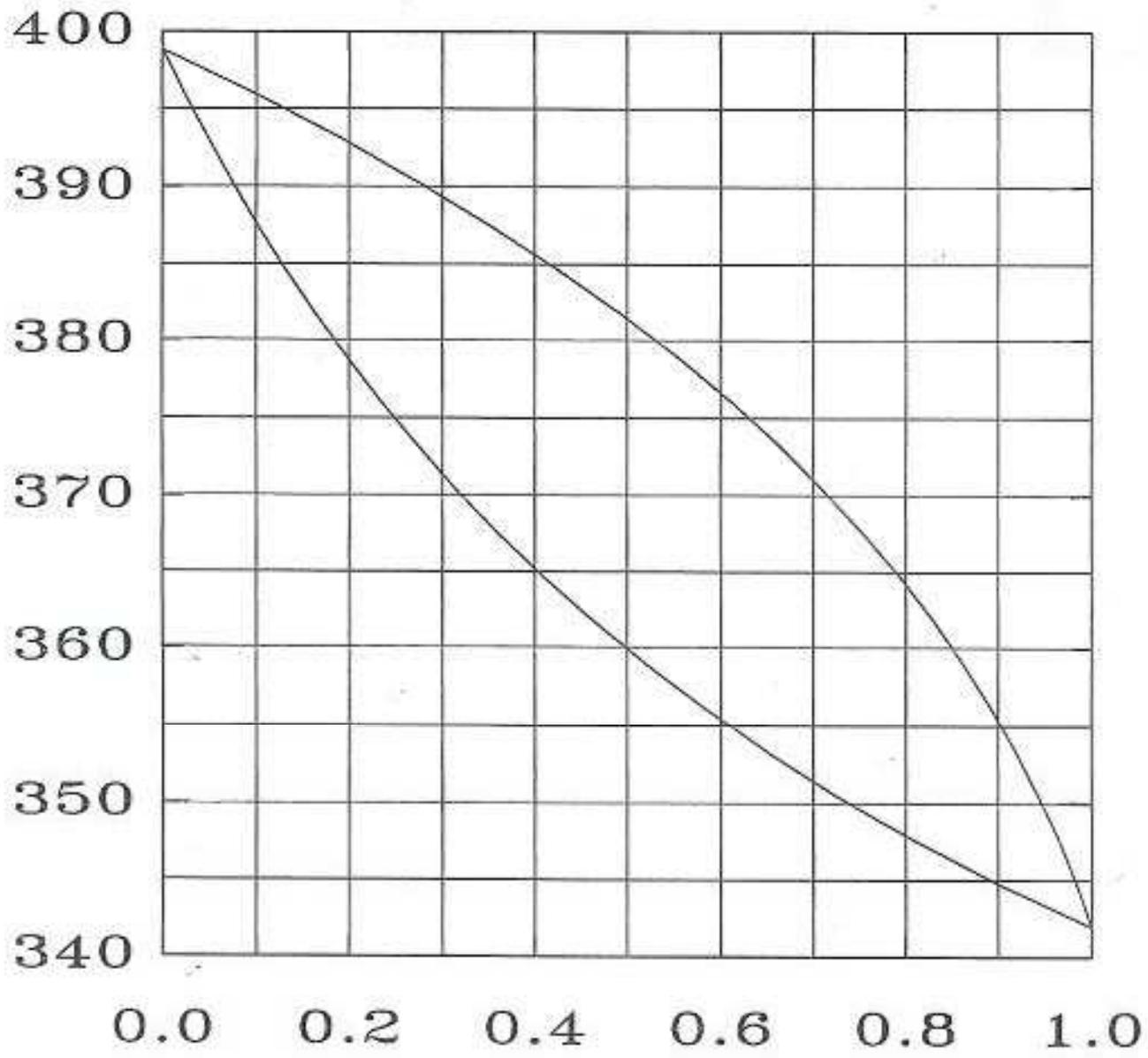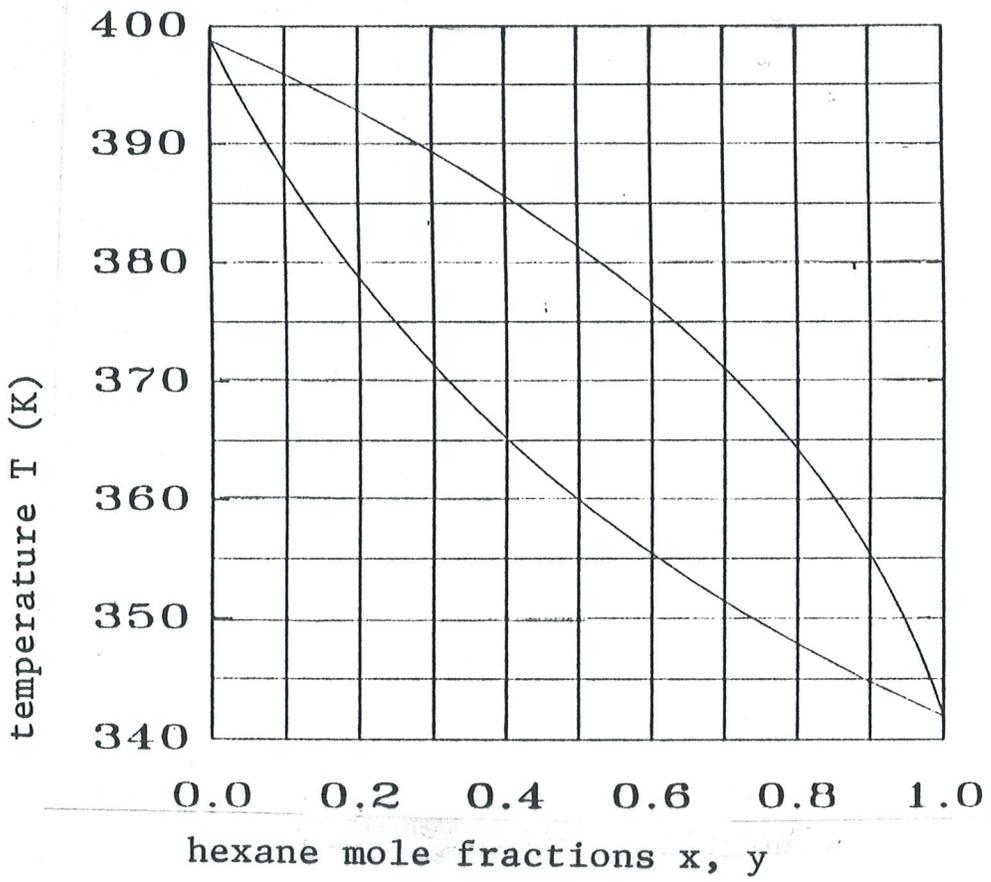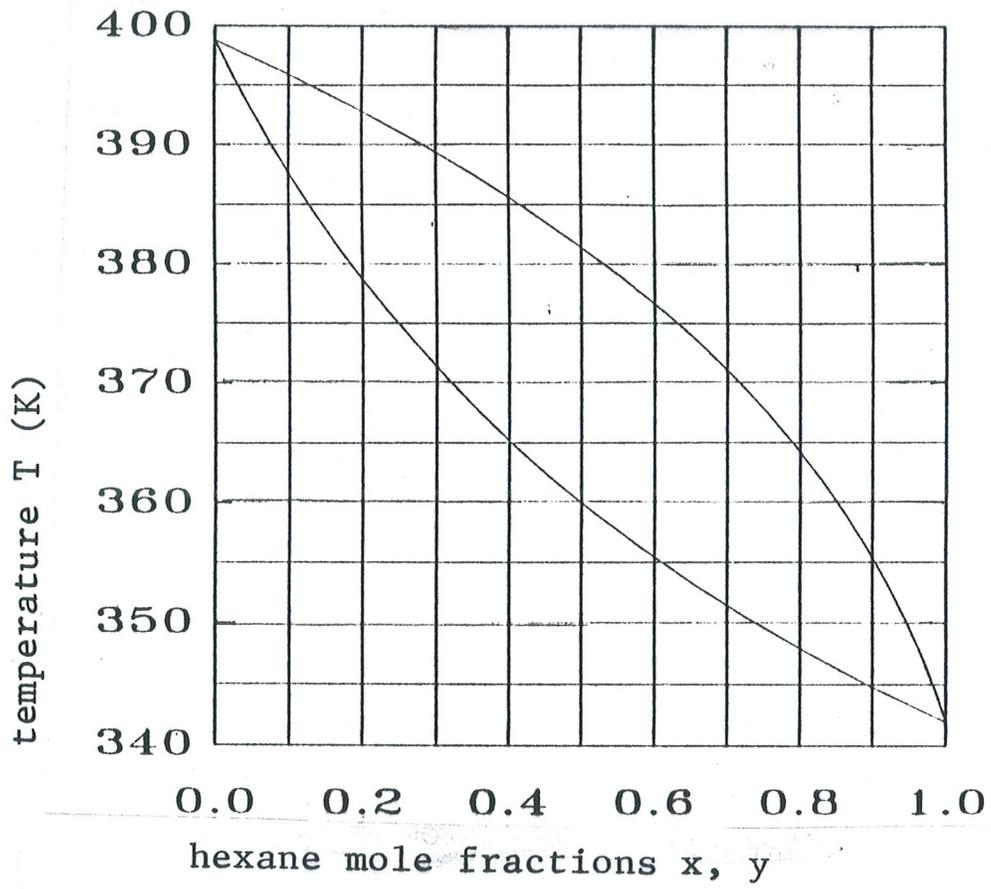
Part (a)

$$(H_x)_{hexane} = H_x(342K) + 218(T-342)$$
$$\phantom{(H_x)_{hexane} =} 0$$

$$(H_x)_{octane} = H_x(342K) + 276(T-342)$$
$$\phantom{(H_x)_{octane} =} 0$$

$$H_x = \underbrace{x \cdot 218(T-342)}_{hexane} + \underbrace{(1-x)\cdot 276(T-342)}_{octane}$$

$$\boxed{H_x = (276 - 58x)(T-342)} \quad (H_x \text{ in } J/mol, \ T \text{ in } K)$$

$$(H_y)_{hexane} = H_x(342K) + \underbrace{28,853}_{vaporization} + \underbrace{172(T-342)}_{change\ temp.\ of\ vapor}$$
$$\phantom{(H_y)_{hexane} =} 0$$

$$(H_y)_{octane} = H_x(342K) + \underbrace{276(399-342)}_{heat\ to\ boiling\ pt.} + \underbrace{34,413}_{vaporization}$$
$$\phantom{(H_y)_{octane} =} 0$$

$$+ \underbrace{226(T - 342 + 342 - 399)}_{\substack{change\ temp.\ of\ vapor\ from \\ 399K\ to\ arbitrary\ temp.\ T.}}$$

$$= 37263 + 226(T-342)$$

$$H_y = y\underbrace{\Big[28,853 + 172(T-342)\Big]}_{hexane} + (1-y)\underbrace{\Big(37,263 + 226(T-342)\Big)}_{octane}$$

$$\boxed{H_y = 37,263 - 8410y + (226 - 54y)(T-342)}$$
$$(H_y \text{ in } J/mol, \ T \text{ in } K)$$

Part (b)

(1 hour basis)

(i) Preliminaries

$F = 100$ mol $\begin{cases} 60 \text{ mol hex.} \\ 40 \text{ mol oct.} \end{cases}$

$(0.95)(60) = 57 \text{ mol hex.}$
$40 - 38 = 2 \text{ mol oct.}$

$D = 59 \text{ mol}$

$x_D = \dfrac{57}{59} = 0.966$

$(0.95)(40) = 38 \text{ mol oct.}$
$60 - 57 = 3 \text{ mol hex.}$

$B = 41 \text{ mol}$

$x_B = \dfrac{3}{41} = 0.073$
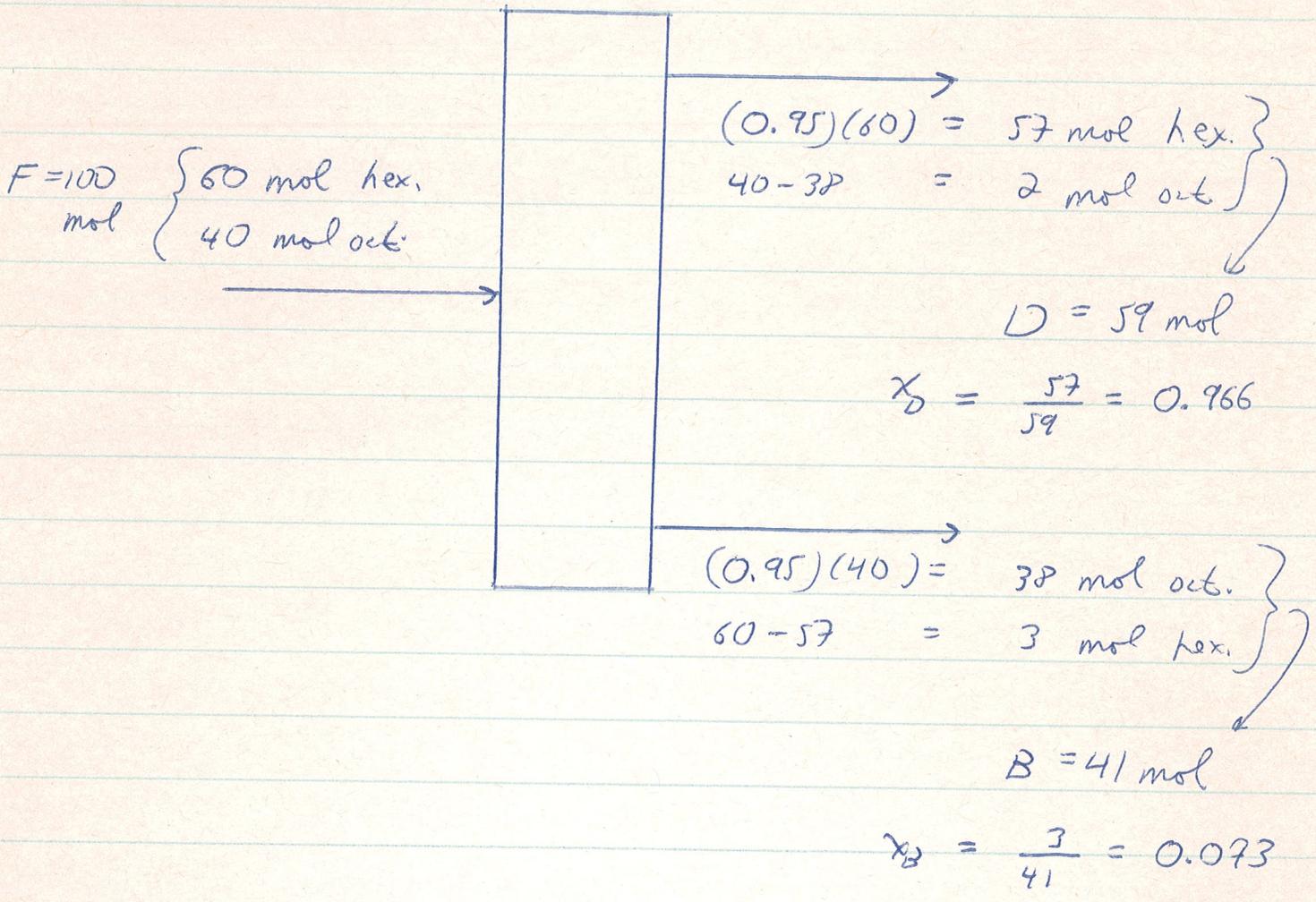
(ii) Equilibrium curve

Draw a few isotherms (horizontal lines)
and read off equil. x and y values. Make
table:

x	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
y	0	0.34	0.56	0.69	0.79	0.85	0.90	0.93	0.96	0.98	1.0

(iii) **Reflux ratio**

Intercept for minimum reflux is $\dfrac{x_D}{R_{min}+1} = 0.49$ ← 0.966

$\Rightarrow \quad R_{min} = 0.971$ (see graph p. 4)

Then $\quad R = (1.15)(0.971) = 1.12$

(iv) **Flow rates**

$R = \dfrac{L_0}{D}$ so $\quad L_0 = RD = (1.12)D$ ← 59 mol

$V_1 = L_0 + D = RD + D = (R+1)D = (2.12)D$

(v) **Enthalpies**

$H_{x,0}$:   Saturated liquid with $x = x_D = 0.966$.
From phase diagram, $T_{x,0} = 343\,K$.

(same as H_D, enthalpy of distillate)

$H_{x,0} = [276 - 58(0.966)](343 - 342) = 220\ J/mol$

$H_{y,1}$:   Saturated vapor with $x = x_D = 0.966$.
From phase diagram, $T_{y,1} = 347\,K$

$H_{y,1} = 37,263 - 8410(0.966)$
$\qquad\qquad + [226 - 54(0.966)](347 - 342)$
$\qquad = 30008\ J/mol$

H_F :   Saturated vapor with $y = 0.60$.
From phase diagram, $T_F = 377\,K$

$H_F = 37263 - 8410(0.60)$
$\qquad\qquad + [226 - 54(0.60)](377 - 342)$
$\qquad = 38993\ J/mol$

4

equil.

R-op. line for minimum reflux

$(x_D, y_D) = (0.966, 0.966)$

Feed line
(sat. vapor ⇒ horiz.)

$(x_F, x_F) = (0.60, 0.60)$

1.0

0.5

y

O 0.5   1.0

$x \rightarrow$
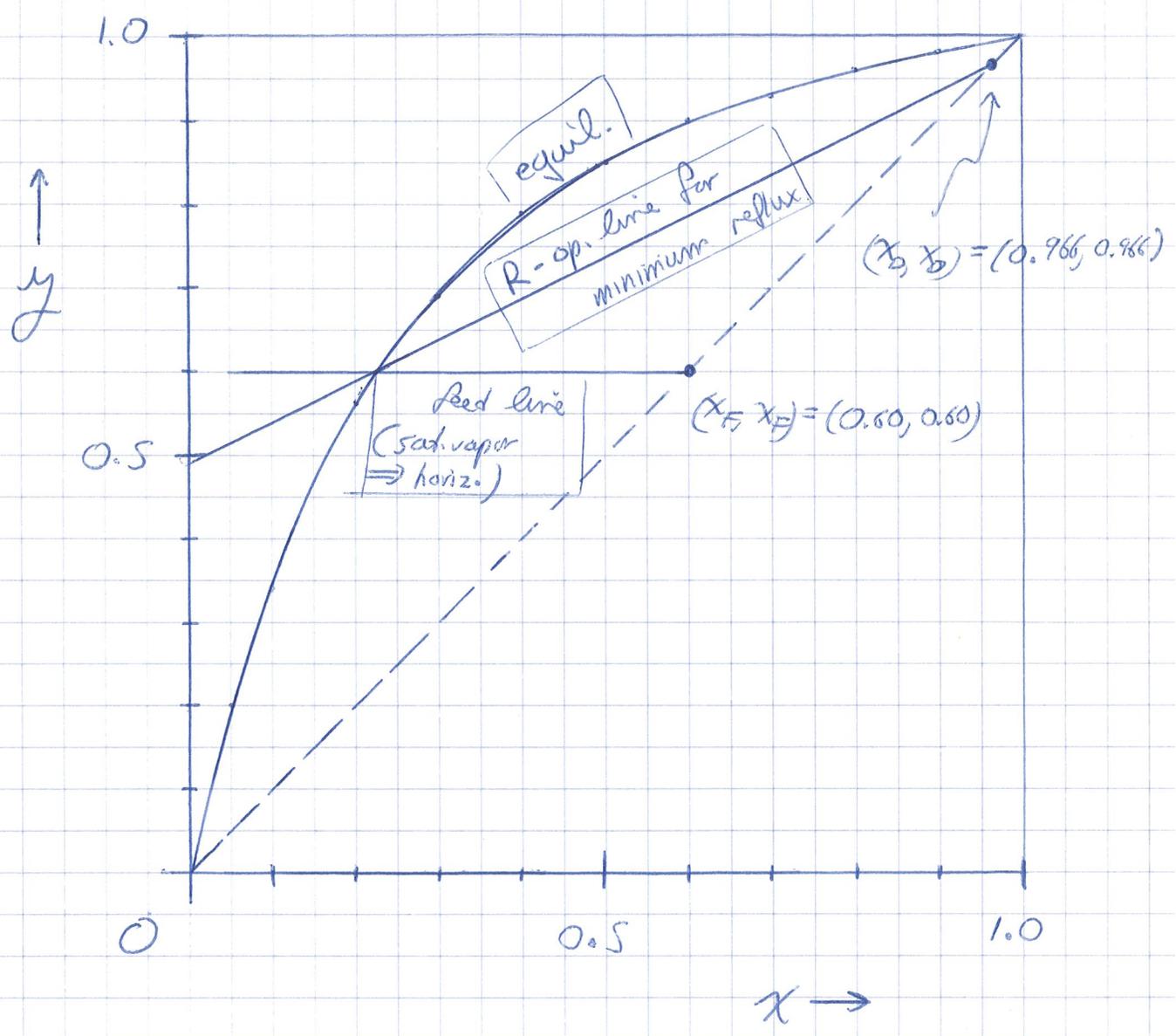
$\underline{H_B}$: Saturated liquid with $x = x_B = 0.073$

From phase diagram, $T_B = 390$ K.

$H_B = [276 - 58(0.073)](390 - 342) = 13045$ J/mol

(vi) <u>Enthalpy balance around condenser</u>

TC

D

the same

L_0

V_1
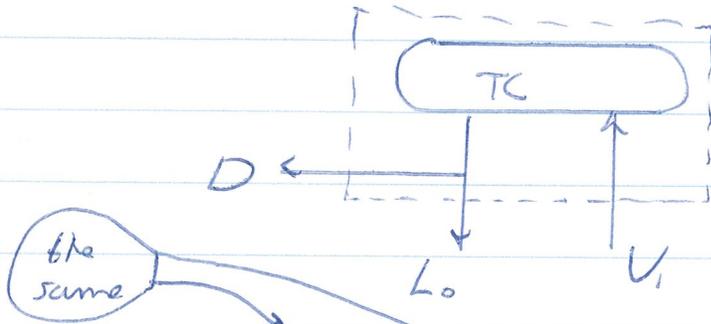
$D(H_D) + L_0(H_{x,0}) - V_1 H_{y_1} = -q_c$

$q_c = V_1 H_{y,1} - (L_0 + D) H_{x,0}$

$= V_1 (H_{y,1} - H_{x,0})$

$= (2.12)(59 \text{ mol})[30008 - 220]$ J/mol

$= 3.73 \times 10^6$ J in 1 hour

$q_c = 3.73 \times 10^6$ J/h $\times \dfrac{1 \text{ h}}{3600 \text{ s}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}}$

$\boxed{q_c = 1.04 \text{ kJ/s}}$

(vii) <u>Enthalpy balance around whole column</u>

$D H_D + B H_B - F H_F = q_r - q_c$

50

$q_r = (59 \text{ mol})(220 \text{ J/mol}) + (41 \text{ mol})(13045 \text{ J/mol})$

$- (100 \text{ mol})(38993 \text{ J/mol}) + q_c$

$= 0.38 \times 10^6$ J in 1h   or $\boxed{q_r = 0.11 \text{ kJ/s}}$