

Problem S-1

For a stoichiometrically-simple reaction, occurring in a continuous reactor at steady state

$$\frac{n_i - n_i^0}{\nu_i} = \frac{n_1 - n_1^0}{\nu_1} = \frac{n_2 - n_2^0}{\nu_2} = \dots$$

where n_i = moles of i in effluent per unit of time
 n_i^0 = moles i in feed per unit of time
 ν_i = stoichiometric coefficient of i

Thus, the given reaction is "single" if

$$\frac{n_T - n_T^0}{-1} = \frac{n_{H_2} - n_{H_2}^0}{-4} = \frac{n_{H_2S} - n_{H_2S}^0}{1} = \frac{n_{C_4} - n_{C_4}^0}{1}$$

$$\frac{n_T - n_T^0}{-1} = -(0.29 - 0.65) \text{ gr.moles/min.} = +0.36 \frac{\text{gr.moles}}{\text{min.}}$$

$$\frac{n_{H_2} - n_{H_2}^0}{-4} = -\frac{1}{4}(12.27 - 13.53) = +0.315 \frac{\text{gr.moles}}{\text{min.}}$$

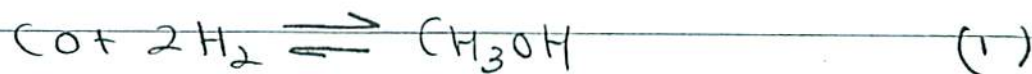
$$\frac{n_{H_2S} - n_{H_2S}^0}{1} = (0.56 - 0.59) = -0.03 \text{ gr.moles/min}$$

$$\frac{n_{C_4} - n_{C_4}^0}{1} = (0.38 - 0.20) = 0.18 \text{ gr.moles/min}$$

Above quantities are not equal. Therefore, reaction is not stoichiometrically-simple. If data are accurate, one or more additional reactions must be taking place.

Solution to Problem 5-3

(Problem 1-2)



Test whether system behaves as though one stoichiometrically - single reaction were taking place by applying the Law of Definite Proportions (LDP)

$$\sum (\text{extent of reaction}) = \frac{\Delta n_i}{\nu_i} = \frac{\Delta n_{\text{CO}}}{\nu_{\text{CO}}} = \frac{\Delta n_{\text{H}_2}}{\nu_{\text{H}_2}} = \frac{\Delta n_{\text{CH}_3\text{OH}}}{\nu_{\text{CH}_3\text{OH}}}$$

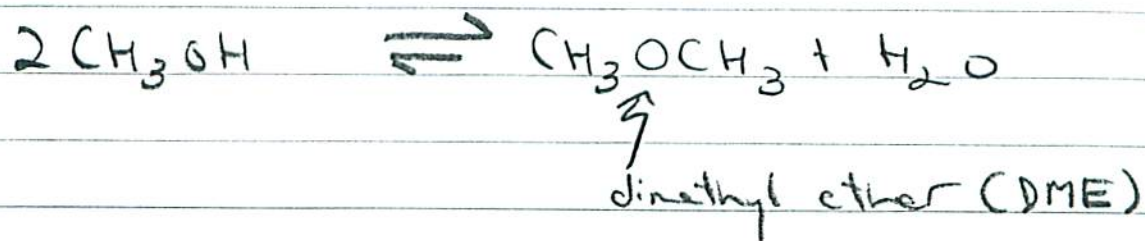
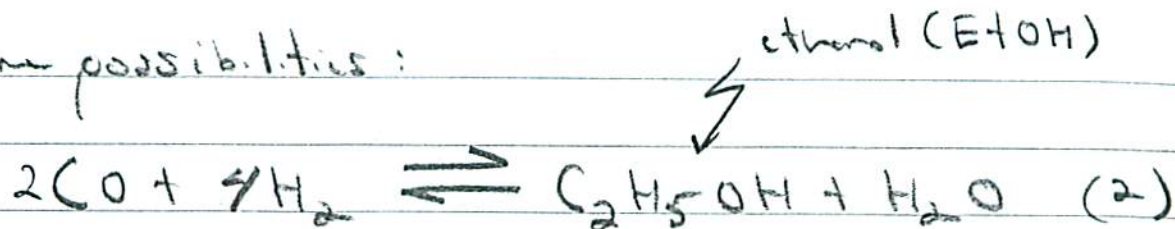
Species	$n(\text{in})$	$n(\text{out})$	Δn	ν_i	$\sum$
CO	100	83	-17	-1	17
H ₂	72	34	-38	-2	19
CO ₂	9	9	0	0	-
CH ₄	19	19	0	0	-
CH ₃ OH	2	13	11	+1	11

Since $\sum$ is not the same for all species, system does not obey the LDP. Does not behave as though one "single" reaction is taking place.

Clue - amount of methanol (CH₃OH) formed is less than predicted from amount of CO and H₂ reacted. However, CO and H₂ react in the proportion predicted by the above reaction.

Hypothesis - maybe another product is formed (not included in the product analysis) by the reaction of CO and H₂ in the ratio of 1:2

Some possibilities:



Note that both EtOH and DME have the formula $\text{C}_2\text{H}_6\text{O}$. The available data will not tell us which of these is formed

Suppose γ moles of $\text{C}_2\text{H}_6\text{O}$ and γ moles of H_2O are formed as the feed passes through the reactor. Then

Species	ΔN
CO	-17
H_2	-34
CO_2	-
CH_4	-
CH_3OH	+11
$\text{C}_2\text{H}_6\text{O}$	γ
H_2O	γ

Now, if 2 reactions are taking place, say (1) and (2), then the LDP is written as

$$\Delta N_i = \sum_j \alpha_{ij} \nu_{i,j}$$

Writing the LDP for each species

$$\Delta n_{CO} = \underline{X}_1(-1) + \underline{X}_2(-2) = -\underline{X}_1 - 2\underline{X}_2$$

$$\Delta n_{H_2} = \underline{X}_1(-2) + \underline{X}_2(-4) = -2\underline{X}_1 - 4\underline{X}_2$$

$$\Delta n_{MeOH} = \underline{X}_1(1) + \underline{X}_2(0) = \underline{X}_1 = 11$$

$$\Delta n_{EtOH} = \underline{X}_1(0) + \underline{X}_2(1) = \underline{X}_2 = \gamma$$

$$\Delta n_{H_2O} = \underline{X}_1(0) + \underline{X}_2(1) = \underline{X}_2 = \gamma$$

$$\Delta n_{CO} = -11 - 2(\gamma) = 17 \Rightarrow \gamma = 3$$

$$\Delta n_{H_2} = -2(11) - 4(\gamma) = -22 - 4(3) = -34$$

check

Hypothesis is consistent with data. (Note - data do not prove hypothesis)

To test - analyze feed and effluent for EtOH, DME, H₂O and other alcohols



(Problem 1-3)

Solution to Problem 5-4 (1-3)



Let: ϵ_k be the extent of Reaction k
- n_i^0 be the initial moles of Species i
- n_i be the moles of Species i after 10 hr.
- ν_{ki} be the stoichiometric coefficient of Species i in Reaction k

$$n_i - n_i^0 = \sum_k \nu_{ki} \epsilon_k$$

For quinoline ($\text{C}_9\text{H}_7\text{N}$), denoted "Q":

$$n_Q - n_Q^0 = -(1)\epsilon_1 + (0)\epsilon_2 + (0)\epsilon_3 = -\epsilon_1$$

$$40 - 100 = -\epsilon_1 \Rightarrow \boxed{\epsilon_1 = 60}$$

For decahydroquinoline ($\text{C}_9\text{H}_{17}\text{N}$), denoted "DHQ":

$$20 - 0 = (0)\epsilon_1 + (0)\epsilon_2 + (1)\epsilon_3 \Rightarrow \boxed{\epsilon_3 = 20}$$

For hydrogen, denoted "H":

$$290 - 500 = (-2)\epsilon_1 + (-1)\epsilon_2 + (-3)\epsilon_3$$

$$-210 = (-2)60 - \epsilon_2 - 3(20) = -180 - \epsilon_2$$

$$\boxed{\epsilon_2 = 30}$$

For tetrahydroquinoline ($C_9H_{11}N$), denoted "THQ":

$$n_{\text{THQ}} - n_{\text{THQ}}^{\circ} = (1)\epsilon_1 + (-1)\epsilon_2 + (-1)\epsilon_3$$

$$n_{\text{THQ}} = 60 - 30 - 20 = 10$$

$$\boxed{n_{\text{THQ}} = 10 \text{ mols}}$$

For butylbenzylamine ($C_9H_{13}N$), denoted "BBA":

$$n_{\text{BBA}} - n_{\text{BBA}}^{\circ} = (0)\epsilon_1 + (1)\epsilon_2 + (0)\epsilon_3 = \epsilon_2$$

$$\boxed{n_{\text{BBA}} = 30 \text{ mols}}$$

(Problem 1-4)

Solution to Problem 5-5

Species	Rate In	Rate Out	Δn	out - In	Rxn. 1 ξ
CO	308	41	-267	-1	267
H ₂	954	91	-863	-3	288
CH ₄	//	327	316	1	316
H ₂ O	2	269	267	1	267
CO ₂	92	92	0	0	-
N ₂	//	//	0	0	-

1) The system does not behave as though one, stoichiometrically-single reaction is taking place. The values of ξ , calculated with the stoichiometric coefficients for Rxn. 1, are not the same for all four species.

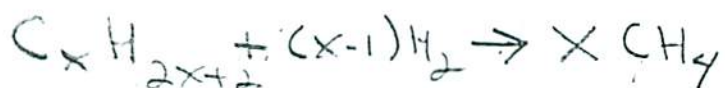
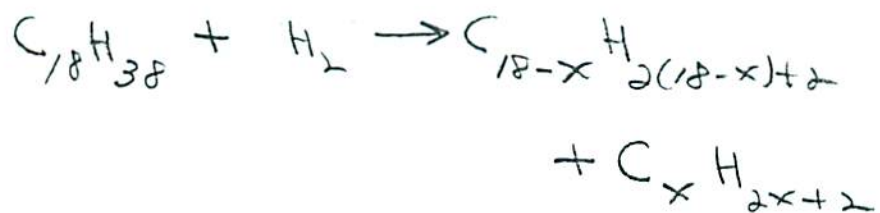
2) ξ has the same value for CO and H₂O. However, there is more CH₄ being produced and more H₂ being consumed than suggested by the ξ values for CO and H₂O.

"Extra" moles of CH₄ formed = $316 - 267 = 49$

Cover and above what we can account for from ξ value for CO and H₂O.

"Extra" moles of H₂ consumed = $863 - 3 \times 267$
= 62

This suggests that the hydrocarbon liquid is reacting with H₂.



The first reaction consumes H_2 without producing CH_4 . The second reaction produces roughly 1 mole of CH_4 / mole H_2 consumed. This is consistent with the data.

3) Suggestions:

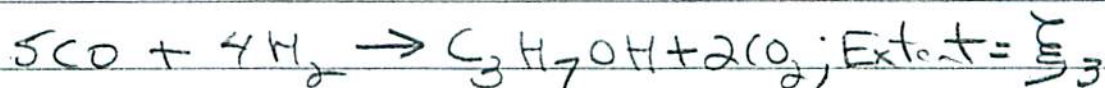
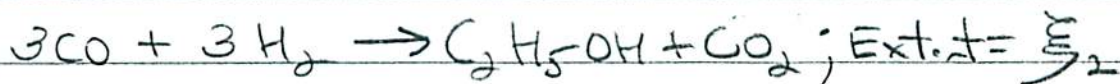
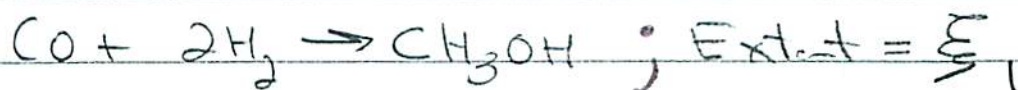
a) Check to see if the hydrocarbon liquid is being consumed (check level periodically, weigh at end of run, etc.)

b) analyze the exit gas for other hydrocarbons — C_2H_6 , C_3H_8 , etc.

Solution to S-6

Problem 1-5

Reactions:



Stoichiometric Table

<u>Species</u>	<u>In (mol/hr.)</u>	<u>Out (mol/hr.)</u>
CO	100	30
H ₂	100	30
CO ₂	0	F _{CO₂}
CH ₃ OH	0	F _{MeOH}
C ₂ H ₅ OH	0	5
C ₃ H ₇ OH	0	F _{PrOH}

Law of Definite Proportions:

$$\Delta N_i = N_{i,\text{out}} - N_{i,\text{in}} = \sum_{k=1}^3 \nu_{ki} \xi_k$$

or,

$$\Delta F_i = F_{i,\text{out}} - F_{i,\text{in}} = \sum_{k=1}^3 \nu_{ki} \xi_k$$

units of
mol/hr.

For C₂H₅OH:

$$5 - 0 = (0) \xi_1 + (1) \xi_2 + (0) \xi_3$$

$$\boxed{\xi_2 = 5}$$

For H_2 :

$$(30 - 100) = (-2)\xi_1 + (-3)\xi_2 + (-4)\xi_3$$

$$-70 = -2\xi_1 - 3 \times 5 - 4\xi_3$$

$$2\xi_1 + 4\xi_3 = 55 \quad (A)$$

For CO:

$$(30 - 100) = (-1)\xi_1 + (-3)\xi_2 + (-5)\xi_3$$

$$-70 = -\xi_1 - 3 \times 5 - 5\xi_3$$

$$\xi_1 + 5\xi_3 = 55 \quad (B)$$

Solving A & B simultaneously, $\boxed{\xi_1 = 9.17, \xi_3 = 9.17}$

For CO_2 :

$$F_{CO_2} - 0 = (1)\xi_2 + (2)\xi_3 = 23.33$$

$$\boxed{F_{CO_2} = 23.33}$$

For CH_3OH :

$$F_{MeOH} - 0 = (1)\xi_1; \quad \boxed{F_{MeOH} = 9.17}$$

For C_2H_5OH :

$$F_{PrOH} - 0 = (1)\xi_3; \quad \boxed{F_{PrOH} = 9.17}$$

Filling in the "Out" column of the Stoichiometric Table

<u>Species</u>	<u>Out (mol/hr)</u>	<u>y (mole fraction)</u>
CO	30	0.281
H ₂	30	0.281
CO ₂	23.33	0.219
CH ₃ OH	9.17	0.086
C ₂ H ₅ OH	5.0	0.047
C ₃ H ₇ OH	9.17	0.086
	<u>106.67</u>	<u>1.000</u>

Problem 5-7 (1-6)

Part 1

If the three given reactions are the only ones occurring, all of the data should be "explained" by the extents of these three reactions. We can calculate ξ_1 , ξ_2 , and ξ_3 from three data points and check to see if these values predict the fourth.



Species	Initial	3Hr.	
A	1	$1 - \xi_1$	$= 0.476$
CHA	0	$\xi_1 - \xi_2 - 2\xi_3$	$= 0.346$
CH	0	ξ_2	$= 0.080$
DCHA	0	ξ_3	$= 0.049$
H ₂	X	$X - 3\xi_1 - \xi_2$	
NH ₃	0	$\xi_2 + \xi_3$	

$$\left. \begin{aligned} \xi_1 &= 0.524 \\ \xi_2 &= 0.080 \\ \xi_3 &= 0.049 \end{aligned} \right\}$$

Use these values to check
CHA

$$0.524 - 0.080 - 2(0.049) \stackrel{?}{=} 0.346 \quad \text{OK}$$

Experimental data is consistent with assumption that three listed reactions are the only ones that occur

Part 2

$$\text{NH}_3 \text{ formed} = \xi_2 + \xi_3 = 0.080 + 0.049 = 0.129$$

moles NH_3 / mole A
charged

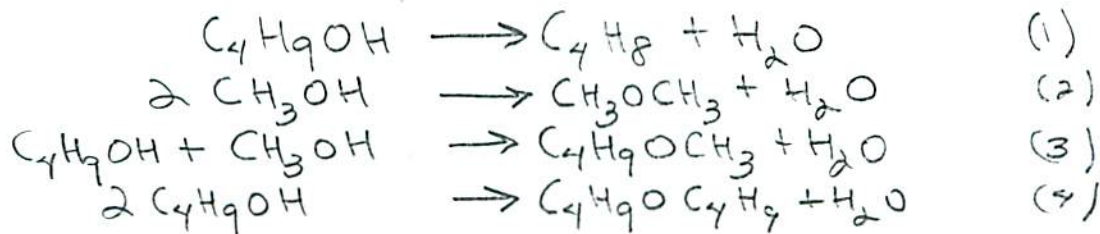
Part 3

$$\text{H}_2 \text{ consumed} = 3 \xi_1 + \xi_2 = 3(0.524) + 0.080$$

$$= 1.652 \frac{\text{moles H}_2}{\text{mole A charged}}$$

Problem S-8

(Problem 1-7)



Stoichiometric Table (Basis: 8,333 moles B/hr. inlet)

Species	Inlet (moles/h)	Effluent (moles/h)
$\text{C}_4\text{H}_9\text{OH}$	8,333	$8,333 - \xi_1 - \xi_3 - 2\xi_4$
CH_3OH	16,667	$16,667 - 2\xi_2 - \xi_3$
C_4H_8	—	ξ_1
H_2O	—	$\xi_1 + \xi_2 + \xi_3 + \xi_4$
CH_3OCH_3	—	ξ_2
$\text{C}_4\text{H}_9\text{OCH}_3$	—	ξ_3
$\text{C}_4\text{H}_9\text{OC}_4\text{H}_9$	—	ξ_4
N_2	10,000	10,000
Total	35,000	$35,000 + \xi_1$

Data:

$$\text{C}_4\text{H}_8(\text{out}) = 2923 \text{ moles/hr.} = \xi_1$$

$$\text{CH}_3\text{OCH}_3(\text{out}) = 3436 \text{ moles/h} = \xi_2$$

$$\text{C}_4\text{H}_9\text{OCH}_3(\text{out}) = 5038 \text{ moles/h} = \xi_3$$

$$\text{C}_4\text{H}_9\text{OC}_4\text{H}_9(\text{out}) = 22 \text{ moles/h} = \xi_4$$

$$\text{C}_4\text{H}_9\text{OH}(\text{out}) = 8,333 - 2,923 - 5,038 - 2(22) = 328 \text{ moles/h.}$$

$$X_{\text{isobutanol}} = \frac{8333 - 328}{8333} = 0.961$$

(2)

$$CH_3OH (out) = 16,667 - 2(3436) - 5038 = 4757 \text{ moles/h.}$$

$$X_{MeOH} = \frac{16,667 - 4,757}{16,667} = 0.715$$

$$Y_{H_2O} = \frac{\sum_1 + \sum_2 + \sum_3 + \sum_4}{35,000 + \sum_1} = \frac{2923 + 3436 + 5038 + 22}{35,000 + 2923}$$

$$Y_{H_2O} = 0.301$$

Problem 1-8



This type of reaction can be used to treat chlorinated organics prior to disposal. It is known generically as "hydrodechlorination". The HCl can be absorbed or adsorbed, and the C_2H_6 and unreacted H_2 can be burned.

$$\frac{r_{\text{C}_2\text{H}_3\text{Cl}_3}}{V_{\text{C}_2\text{H}_3\text{Cl}_3}} = \frac{r_{\text{H}_2}}{V_{\text{H}_2}} = \frac{r_{\text{C}_2\text{H}_6}}{V_{\text{C}_2\text{H}_6}} = \frac{r_{\text{HCl}}}{V_{\text{HCl}}}$$

a) $\frac{r_{\text{HCl}}}{V_{\text{HCl}}} = \frac{r_{\text{C}_2\text{H}_3\text{Cl}_3}}{V_{\text{C}_2\text{H}_3\text{Cl}_3}} \Rightarrow -r_{\text{C}_2\text{H}_3\text{Cl}_3} = \left(\frac{+1}{3}\right) r_{\text{HCl}}$

$\underbrace{V_{\text{HCl}}}_{(+3)} \quad \underbrace{V_{\text{C}_2\text{H}_3\text{Cl}_3}}_{(-1)}$

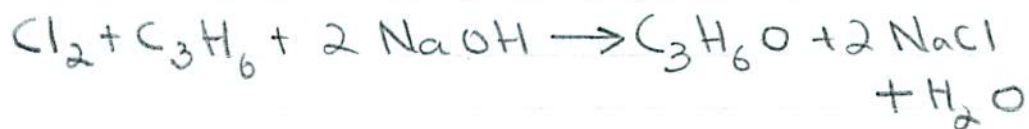
$25 \times 10^{-6} \frac{\text{moles}}{\text{g.cat.-min}}$

$$-r_{\text{C}_2\text{H}_3\text{Cl}_3} = 8.33 \times 10^{-6} \frac{\text{moles C}_2\text{H}_3\text{Cl}_3}{\text{g.cat.-min}}$$

b) $\frac{r_{\text{C}_2\text{H}_6}}{V_{\text{C}_2\text{H}_6}} = \frac{r_{\text{HCl}}}{V_{\text{HCl}}} \Rightarrow r_{\text{C}_2\text{H}_6} = 8.33 \times 10^{-6} \frac{\text{moles C}_2\text{H}_6}{\text{g.cat.-min}}$

$\underbrace{V_{\text{C}_2\text{H}_6}}_{(+1)} \quad \underbrace{V_{\text{HCl}}}_{(+3)}$

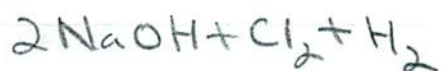
Problem 1-9



a) Poor example of "green chemistry"

- 7 atoms of by-products / 10 atoms product
- Cl_2 is hazardous
- neither Na nor Cl are in the final product
- Cl_2 manufacture is energy-intensive

b) Might be recycled back to Cl_2 :



Feasibility depends on:

- extent of organic contamination of NaCl
- proximity of $\text{C}_3\text{H}_6\text{O}$ plant to Cl_2 plant
- cost of power at $\text{C}_3\text{H}_6\text{O}$ plant

NaCl may have to be disposed of as waste.

c) Cl is for control of reaction rate / reaction selectivity

Problem 1-10



First, we will look up the standard free energies and enthalpies of formation at 25°C for N_2 , H_2 , and NH_3 *

Species	$\Delta G_{f,i}^\circ$ (kcal/mole)	$\Delta H_{f,i}^\circ$ (kcal/mole)
N_2	0.00	0.00
H_2	0.00	0.00
NH_3	-3.90	-10.96

$$\Delta G_R^\circ = \sum_i \nu_i \Delta G_{f,i}^\circ = (+2)(-3.90) = -7.80 \text{ kcal/mole}$$

$$\Delta H_R^\circ = \sum_i \nu_i \Delta H_{f,i}^\circ = (+2)(-10.96) = -21.92 \text{ kcal/mole}$$

However, we need to be careful about "per mole". For the reaction as written, these changes are per mole of N_2 . When 1 mole of N_2 disappears, the change in G° is -7.80 kcal and the change in H° is -21.92 kcal.

The values of ΔG_R° and ΔH_R° per mole of NH_3 are $1/2$ of those calculated above.

The values of ΔG_R° and ΔH_R° per mole of H_2 are $1/3$ of those calculated above.

*Perry, "Chemical Engineers Handbook" (6th ed.), Table 3-206 (p. 3-177-3-159)

Problem 1-11

Part 1:

Let ξ_A be the extent of Reaction A and ξ_B be the extent of Reaction B.

Stoichiometric Table:

Species:	Initial	Final	
Benzene	100	$100 - \xi_A$	$= 35$
Ethylene	100	$100 - \xi_A - \xi_B$	$= 2$
Ethyl Benzene	—	$\xi_A - \xi_B$	$= 39$
Diethyl Benzene	—	ξ_B	$= 19$

From the above table, we have 4 equations and 2 unknowns. Two equations will be used to calculate ξ_A and ξ_B . These values must then satisfy the

remaining 2 equations if the data are consistent with the hypothesis that Reactions A and B are the only reactions taking place.

From "Benzene",

$$100 - \xi_A = 35 \Rightarrow \xi_A = 65$$

From "Diethyl Benzene", $\xi_B = 19$

For "Ethylene",

$$100 - 65 - 19 \stackrel{?}{=} 2 \Rightarrow 16 \neq 2$$

For "Ethyl Benzene",

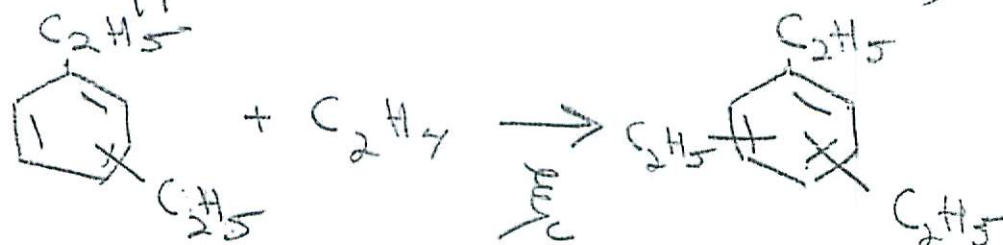
$$65 - 19 \stackrel{?}{=} 39 \Rightarrow 46 \neq 39$$

Part 2:

It seems logical that some triethyl benzene

(2)

might be formed, although there is no indication that an attempt was made to measure this species. Suppose there is a third reaction,



Then:

$$\text{Benzene: } 100 - \sum_A = 35 \Rightarrow \sum_A = 65$$

$$\text{Ethylene: } 100 - \sum_A - \sum_B - \sum_C = 2$$

$$\text{Ethyl benzene: } \sum_A - \sum_B = 39; \sum_B = \sum_A - 39 = 26$$

$$\text{Diethyl benzene: } \sum_B - \sum_C = 19; \sum_C = \sum_B - 19 = 7$$

Checking ethylene

$$100 - 65 - 26 - 7 \stackrel{?}{=} 2 \Rightarrow 2 = 2$$

Hypothesis is consistent with data.

Problem 1-12

Stoichiometric Table:

Species	I_n (moles/h)	O_{out} (moles/h) $\downarrow$
$C_2H_3Cl_3$	0.536	$0.536 - \xi_1 (= 0.074)$
H_2	5.357	$5.357 - \xi_1 - \xi_2 - \xi_3$
N_2	47.679	47.679
$C_2H_4Cl_2$	0	$\xi_1 - \xi_2 (= 0.111)$
C_2H_5Cl	0	$\xi_1 - \xi_3 (= 0.050)$
C_2H_6	0	$\xi_3 (= 0.301)$
HCl	0	$\xi_1 + \xi_2 + \xi_3$

ξ_i is extent of Reaction i

Part 1:

Approach - calculate ξ_1 from $C_2H_3Cl_3$ (out); calculate ξ_2 from $C_2H_4Cl_2$ (out); calculate ξ_3 from C_2H_5Cl (out). This value must check the value of calculated from C_2H_6 (out). This value is $\xi_3 = 0.301$

$$\begin{aligned}\xi_1 &= 0.536 - 0.074 = 0.462 \\ \xi_2 &= \xi_1 - 0.111 = 0.462 - 0.111 = 0.351 \\ \xi_3 &= \xi_2 - 0.050 = 0.351 - 0.050 = 0.301\end{aligned}$$

Checks C_2H_6 entry

Part 2: H_2 (out) = $5.357 - (\xi_1 + \xi_2 + \xi_3) = 4.293 \text{ mole/h}$

Part 3: HCl (out) = $\xi_1 + \xi_2 + \xi_3 = 1.117 \text{ mole/h}$