The UNIVERSITY OF BRITISH COLUMBIA

Department of CHEMICAL and BIOLOGICAL ENGINEERING

CHBE 241: MATERIAL and ENERGY BALANCES

FINAL – EXAMINATION

Instructions:

- Hand calculators are allowed
- The only allowed material is the formula sheet provided to you.
- Solve individually all 3 problems.
- If any of these rules are not respected, it will be dealt with according to University Policy on student ethics during examination.

*** *use a maximum of two significant figures after the decimal point* ****

The 3 problems are given on the next 2 pages (double-sided)

Formula sheet is on the LAST PAGE

Problem 1:

Pure $CaCl_2$ solid powder is fed at a rate of 1.2 kg/min into a mixer that initially holds 100 kg of water. The exit $CaCl_2 - H_2O$ solution leaves at a rate of: $2t$ kg/min, where t – time in minutes. The mixing is fast and uniform therefore you can assume continuous stirred tank (CSTR) operation. The molar mass of $CaCl_2$ is: 111 g/mol. The pressure is constant 1 atm(abs).

Calculate the following:

a) The total mass in the mixer after 10 minutes.
b) Weight fraction of $CaCl_2$ in the *exit* solution after 10 minutes.
c) The exit solution mass flow rate is: *2t* in [kg/min]. What is the unit for the factor 2 and how do you interpret it?
d) Now consider a steady-state continuous mixer where both water and $CaCl_2$ powder (1.2 kg/min) are flowing into the mixer and the homogeneous $CaCl_2$-H_2O solution is flowing out with a mass flow rate of 20 kg/min. The streams going in the mixer are both at 15 ^{0}C and is desirable to obtain an exit $CaCl_2$-H_2O solution at 25 ^{0}C. The specific enthalpy change associated with the dissolution (or solvation) of $CaCl_{2,(s)}$ in water for the composition in the mixer is equal to: -80 kJ/mol_$CaCl_2$ at 25 ^{0}C. The mixer exerts 1 kW of constant shaft power.
   Construct a conceptual process enthalpy scheme in order to calculate the heat flow expressed in *kJ/s* [= kW] that needs to be transferred to or from the continuous mixer to operate at 25 ^{0}C. The heat capacity of solid $CaCl_2$ is 72.9 J/(mol K) and the water heat capacity is 4.18 J/(g K).
   Assume: a) heat capacities are constant over the temperature interval of 15 to 25 ^{0}C, b) as reference, consider the specific enthalpies at 273 K are zero for all pure species.

Marking scheme: a) 10%; b) 10%, c) 5%, d) 10%

Problem 2:

Propane (C_3H_8) and n-butane (C_4H_{10}) are separated by flash (equilibrium) distillation. The normal (i.e., at 1 atm) boiling point of *propane* is 230.9 K whereas the normal boiling point of *n-butane* is 272.5 K. The Antoine equation coefficients for both hydrocarbons are given in the Table.

Table I: Antoine equation coefficients for propane and n-butane, respectively. *Reference:* Yaw's Handbook of Antoine coefficients.

Compound	A	B	C
Propane	7.01887	889.864	257.084
n-Butane	7.00961	1002.48	248.145

The Antoine equation is: $log P^{sat} = A - \frac{B}{T+C}$,

where P^{sat} – saturation vapor [mmHg]; T – temperature [^{0}C].

Note: 1 atm = 760 mmHg

Calculate / perform the following:

a) The mole fraction of propane in a *liquid* mixture that has a normal bubble (or boiling) point equal to 241.8 K.
b) The mole fraction of propane *vapor* in equilibrium with the liquid at 241.8 K.
c) Sketch the ***T*** **–*x,y*** diagram using the propane mole fractions. Label on your diagram the bubble point and dew point curves, and the phases present in the distinct regions of the diagram. **Note:** this mixture does not form azeotrope and sketching means conceptually correct diagram but not on an exact scale.
d) A flash distillation column is fed with 1000 mol/s liquid mixture composed of propane – n-butane with a propane mole fraction of 0.65. This mixture is heated to 241.8 K and the mixture fast separates (flashes) in a vapor and a liquid phase that are in equilibrium. Calculate the vapor and the liquid phase molar flow rates, respectively. **Hint:** use your diagram from question *c)* to visualize the separation.
e) Calculate the *fractional recovery of propane in the vapor phase.*

Marking scheme:

a) 10%; b) 5%, c) 5%, d) 10%, e) 5%

Problem 3:

Sulfur dioxide (SO_2) is converted to SO_3 by reaction with air using two reactors connected in series (so called two stage conversion). The product SO_3 has many uses including the production of H_2SO_4. A *gas feed stream* (denoted by *F*) is fed to the first reactor at a molar flow rate of 100 mol/s having the following molar composition: SO_2 10 %, O_2 9%, N_2 81 %. The fractional SO_2 conversion in the *first reactor* is 0.75 and the fractional SO_2 conversion in the *second reactor* is 0.65.

To boost the *overall* SO_2 fractional conversion of the plant to 0.95, some of the exit gas mixture from reactor 2 is recycled back to the inlet of reactor 2 using a splitter. The recycle stream is denoted by *R*. The other stream from the splitter is the *product gas stream* (denoted by *P*).

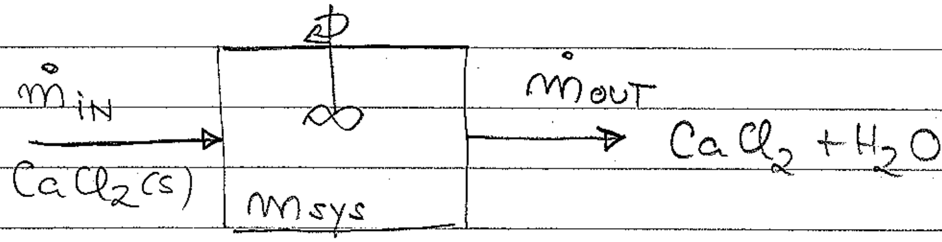
Calculate / perform the following:

a) Draw a complete block flow diagram for the two-stage SO_3 production plant and write down the reaction.
b) Calculate the *ratio* of the recycle per product gas mixture molar flow rates ($\dot{R}/\dot{P}$) from the splitter, to assure the goal of 0.95 overall SO_2 fractional conversion. *(As a senior engineer you can instruct your subordinate operator technologist to input this ratio value in the software that is controlling the splitter. Your subordinate, having never taken CHBE 241, will be amazed how you came up with this number).*
c) Calculate the overall O_2 fractional conversion.

d) BONUS (extra 3% - after all the other questions were attempted): why use 2 reactors in series with different SO_2 fractional conversions, instead of one reactor with 0.95 SO_2 fractional conversion? Explain briefly.

Marking scheme:

a) 5%; b) 20%, c) 5%



a) The total mass in the mixture after 10 min...

→ mass balance non-steady state on $CaCl_2$:
differential form:

$$\frac{d\, m_{sys,CaCl_2}}{dt} = \dot m_{CaCl_2,IN} - \dot m_{CaCl_2,OUT} \quad ; \quad (1)$$

→ total mass balance ($CaCl_2$ + H_2O) non-steady state
differential form:

$$\frac{d m_{sys}}{dt} = \dot m_{IN} - \dot m_{OUT} = \underbrace{1{,}2}_{= \dot m_{CaCl_2,IN}} - 2 \cdot t \quad ; \quad (2)$$

integrate eq. (2)

$$\int_{100 = m_{sys,0}}^{m_{sys,f}} d m_{sys} = \int_{0}^{t_f = 10\,min} (1{,}2 - 2\cdot t)\, dt$$

$$m_{sys,f} - 100 = 1{,}2 \cdot t \Big|_0^{10} - t^2 \Big|_0^{10}$$

$$m_{sys,f} - 100 = 12 - 10^2 \Rightarrow \underline{\underline{m_{sys,f} = 12\ kg}}$$

b) weight fraction of $CaCl_2$ in the exit solution after 10 minutes:

w - $CaCl_2$ weight fraction

→ From eq. (1) for 10 minute = Δt time interval we can write the integral mass balance on $CaCl_2$ as:

$$\underbrace{\Delta m_{sys, CaCl_2}}_{\text{accumulated in the mixer in } \Delta t} = \dot{m}_{CaCl_2, IN} \Delta t - \dot{m}_{CaCl_2, OUT} \Delta t \quad ; \quad (3)$$

→ due to perfect mixing, CSTR operation, the weight fraction of $CaCl_2$ in the mixer and in the exit solution are the same: w: $CaCl_2$ weight fraction

$$w \, m_{sys, f} = \dot{m}_{CaCl_2, IN} \Delta t - w \cdot \dot{m}_{OUT} \Delta t \quad ; \quad (4)$$

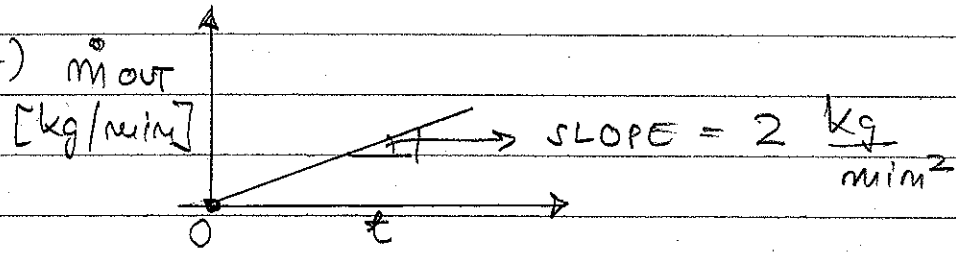
$$12 w = 1.2 \times 10 - w \underbrace{(2t)}_{= 20 \text{ kg/min at } t = 10 \text{ min}} \times 10$$

$$12 w + 200 w = 12 \Rightarrow w = 0.057 \text{ (i.e. } 5.7 \% \text{ wt)}$$

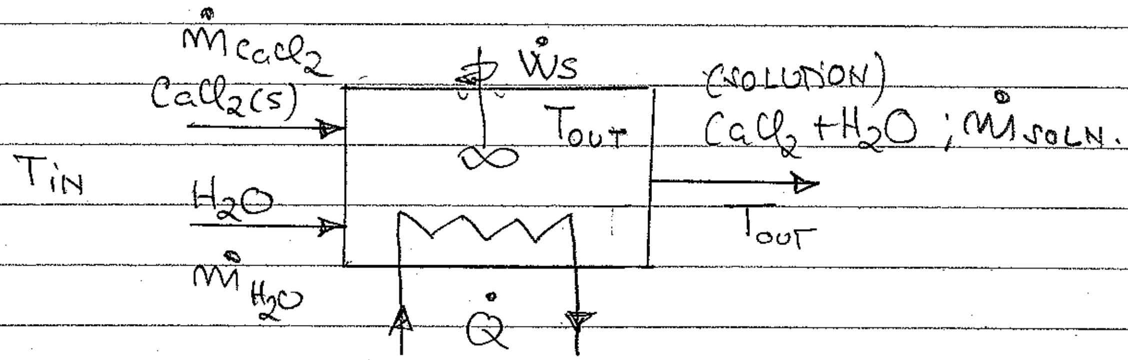
c) $\dot{m}_{OUT} = 2t \left[\frac{kg}{min}\right] \Rightarrow [t] = min$

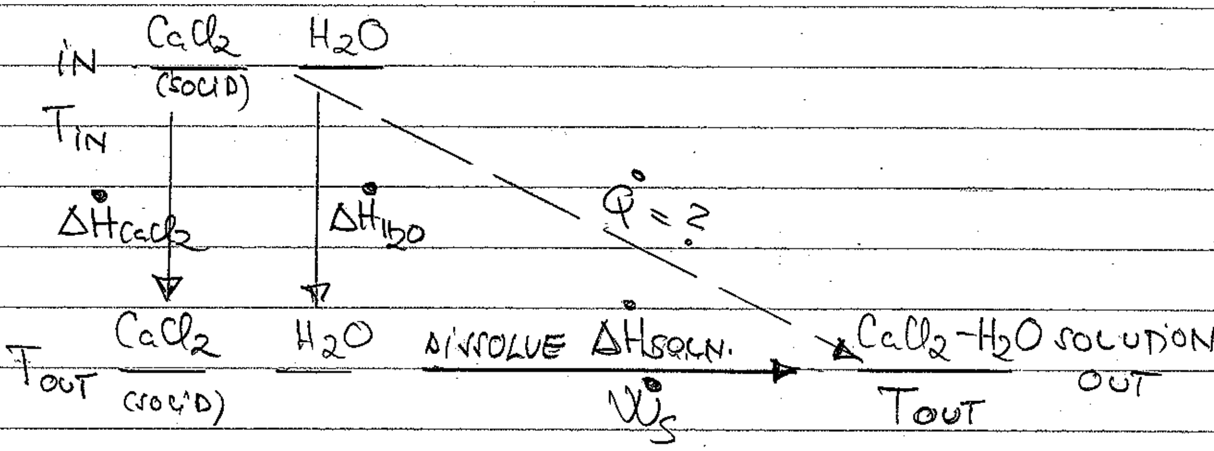
$$[2] = \frac{kg}{min^2}$$

⇒ slope of the exit mass flow rate vs. time curve c)



d)





$$\dot{Q} = \underbrace{\Delta\dot{H}_{CaCl_2(s)} + \Delta\dot{H}_{H_2O}}_{\substack{\text{sensible heats} \\ T_{IN} \rightarrow T_{OUT}}} + \underbrace{\Delta\dot{H}_{SOLN.}}_{\substack{\text{enthalpy flow} \\ \text{of dissolution}}} + \underbrace{\dot{W}_S}_{\substack{\text{mixer} \\ \text{shaft} \\ \text{power}}}$$

$$\dot{Q} = \dot{m}_{CaCl_2}\, \bar{C}_{P_{CaCl_2}} (T_{OUT} - T_{IN}) + \dot{m}_{H_2O}\, \bar{C}_{P_{H_2O}} (T_{OUT} - T_{IN})$$

$$+\ \dot{m}_{CaCl_2}\, \Delta\hat{H}_{SOLN, CaCl_2} + 1 ;$$

$$\hat{\Delta H}_{soln,CaCl_2} = -80 \frac{kJ}{mol_{CaCl_2}} = -\frac{80}{111} \frac{kJ}{g_{CaCl_2}}$$

$$\hat{\Delta H}_{soln.CaCl_2} = -0.72 \frac{kJ}{g} = -720 \frac{kJ}{kg_{CaCl_2}}$$

$$\bar{C}_{P\,CaCl_2} = 72.9 \frac{J}{mol \cdot k} = \frac{72.9}{111} \frac{kJ}{kg_{CaCl_2}\,k} = 0.66 \frac{kJ}{kg_{CaCl_2}}$$

$$\dot{m}_{CaCl_2(s)} = 1.2\ kg/min = 0.02\ kg/s$$

$$\dot{m}_{H_2O} = \dot{m}_{soln} - \dot{m}_{CaCl_2(s)} = 20-1.2 = 18.8 \frac{kg}{min}$$

$$= 0.31\ kg/s$$

Substitute numerical values: kJ/(kg.k)

$$\dot{Q} = 0.02 \times 0.66 \times (25-15) + 0.31 \times 4.18 \times (25-15) + 0.02 \times (-720) + 1$$

$$\underline{\underline{\dot{Q} = -0.31\ kJ/s}}$$ (exothermic, heat must be removed from the continuous mixer)

at 1 atm

PROPANE : index 1 $\qquad T_{bp,1} = 230.9\ K$
BUTANE : index 2 $\qquad T_{bp,2} = 272.5\ K$

a) Mole fraction of propane (1) in a liquid mixture that boils at : 241.8 K (1 atm)

$$\begin{cases} P_1 = X_1 P_1^{sat}(T) & T = 241.8\,K \\ P_2 = X_2 P_2^{sat}(T) \\ P_1 + P_2 = 1\,atm & \text{(normal boiling point of the mixture)} \end{cases}$$

$$\Rightarrow \quad X_1 P_1^{sat}(T) + X_2 P_2^{sat}(T) = 1$$

Also $\quad X_1 + X_2 = 1$

$$\Rightarrow \quad X_1 P_1^{sat}(T) + (1 - X_1) P_2^{sat}(T) = 1$$

$$X_1 = \frac{1 - P_2^{sat}(T)}{P_1^{sat}(T) - P_2^{sat}(T)} \qquad (1)$$

ANTOINE:
EQ. $\quad \underset{[mmHg]}{\log P_1^{sat}(T)} = 7.01887 - \dfrac{889.864}{T(°C) + 257.084}$

$$T = 241.8\,K = -31.2\,°C$$

$$\log P_1^{sat}(T) = 7.01887 - \frac{889.864}{-31.2 + 257.084}$$

$$P_1^{sat}(T) = 1200.6 \text{ mmHg} = 1.58 \text{ atm}$$

$$\log P_2^{sat}(T) = 7.00961 - \frac{1002.48}{-31.2 + 248.145}$$

$$P_2^{sat}(T) = 244.7 \text{ mmHg} = 0.32 \text{ atm}$$

Substitute in eq. (1):

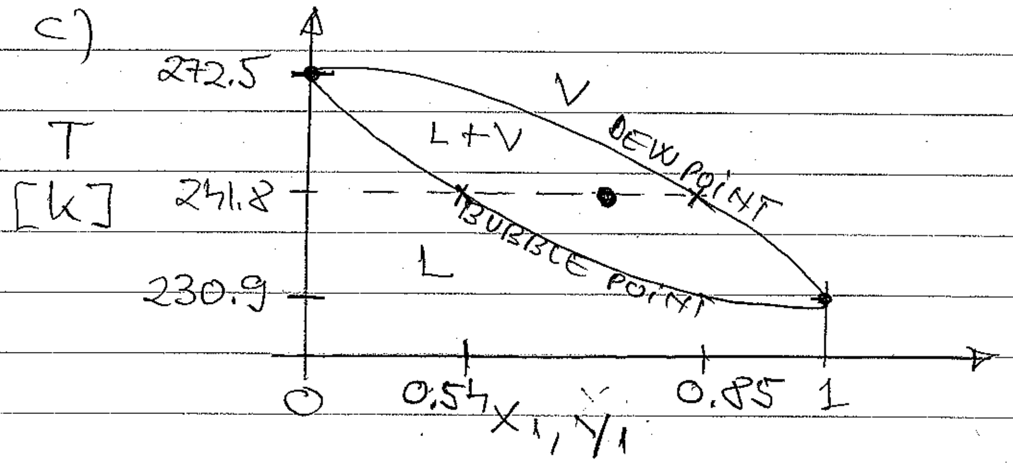
$$x_1 = \frac{1 - 0.32}{1.58 - 0.32} = \underline{\underline{0.54}}$$

b) mole fraction of propane vapor in equilibrium with liquid at 241.8 K

$$P_1 = 0.54 \cdot 1.58 = 0.85 \text{ atm}$$

$$y_1 = \frac{P_1}{P_1 + P_2} = \frac{0.85}{1} = \underline{\underline{0.85}}$$

c)



(3)

d) feed $z_F = 0.65$ (propane) heated to 241.8K

⇒ from diagram, is in 2phase zone, mixture splits into a liquid phase (with $x_1 = 0.54$) and a vapor phase (with $y_1 = 0.85$).

Inverse lever rule:

$$\frac{\dot{m}_V}{\dot{m}_L} = \frac{z_F - x_1}{y_1 - z_F} = \frac{0.65-0.54}{0.85-0.65} = 0.55$$

$$\dot{m}_V + \dot{m}_L = 1000 = \dot{m}_F$$

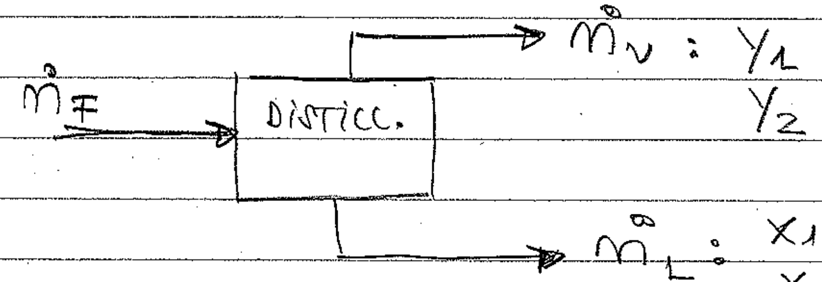
$$0.55\dot{m}_L + \dot{m}_L = 1000$$

$$\underline{\underline{\dot{m}_L = 645.2 \text{ mol/s}}}$$

$$\underline{\underline{\dot{m}_V = 354.8 \text{ mol/s}}}$$

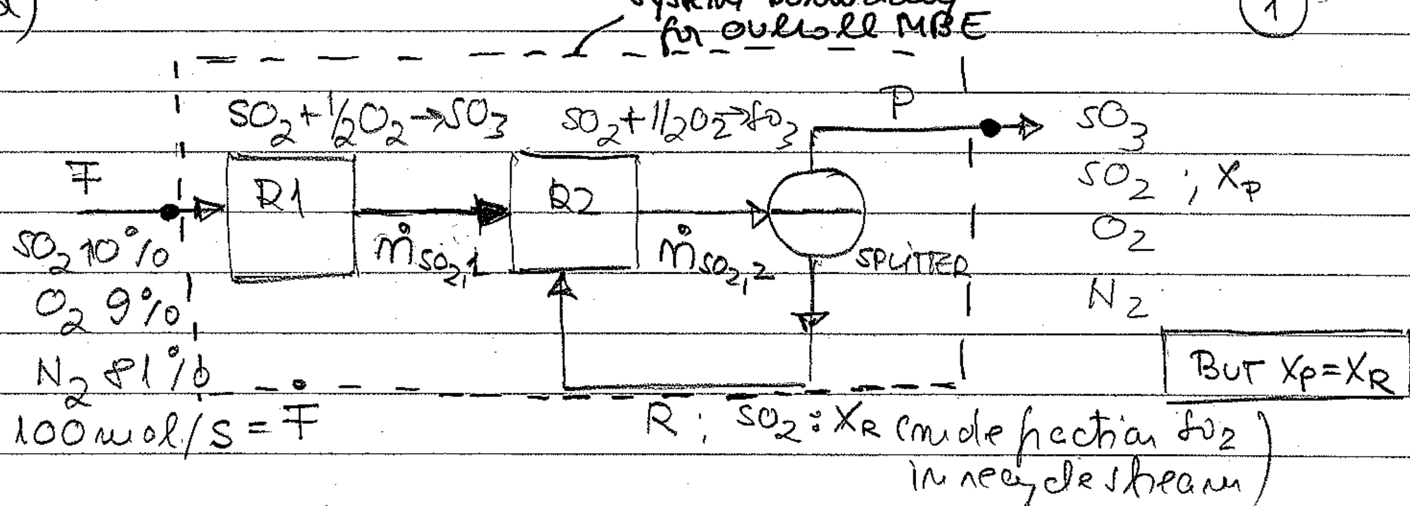
e) propane fractional recovery in vapor phase

$$f_{R,1,V} = \frac{y_1 \dot{m}_V}{z_F \dot{m}_F} = \frac{0.85 \times 354.8}{0.65 \times 1000} = \underline{\underline{0.46 \ (46\%)}}$$



equilibrium between vapor and liquid

a)



b) SO_2 MBE:

1. overall conversion and MBE

$$\text{OVERALL} \Rightarrow f_{c,SO_2} = \frac{-\sum_{k=1}^{2} \nu_{SO_2,k}\,\xi_k}{x_{SO_2,F}\,\dot{F}} = \frac{-(-\xi_1 - \xi_2)}{x_{SO_2,F}\,\dot{F}}$$

ξ_1 and ξ_2 extent of reaction in reactor 1 and 2, respectively

$$f_{c,SO_2} = \frac{\xi_1 + \xi_2}{x_{SO_2,F}\,\dot{F}} \stackrel{!}{=} 0.95 \qquad (1)$$

Also,

$$\underset{\text{(OUT)}}{x_{SO_2,P}\,\dot{P}} = \underset{\text{(FEED)}}{x_{SO_2,F}\,\dot{F}} - \underset{\text{(OVERALL CONSUMED)}}{f_{c,SO_2}\,(x_{SO_2,F}\,\dot{F})}$$

$$x_{SO_2,P}\,\dot{P} = (1 - f_c)\,x_{SO_2,F}\,\dot{F} \qquad (2)$$

2. conversion of SO_2 per reactor R1

$$f_{c,SO_2,1} = \frac{(-\nu_{SO_2}\,\xi_1)}{x_{SO_2,F}\,\dot{F}} = \frac{\xi_1}{x_{SO_2,F}\,\dot{F}} = 0.75 \; ; \quad (3)$$

$$\xi_1 = 0.75 \times 0.1 \times 100 = 7.5 \text{ mol/s}$$

conversion of SO_2 per reactor R_2

$$0.65 = f_{c,SO_2,2} = \frac{(-\gamma_{SO_2}\xi_2)}{\dot{n}_{SO_2,1} + X_{SO_2,R}\dot{R}} = \frac{\xi_2}{\dot{n}_{SO_2,1} + X_{SO_2,R}\dot{R}} \quad ; \quad (4)$$

– Substitute the value for ξ_1 into eq. (1)

GOAL

$$0.95\, X_{SO_2,F}\dot{F} = \xi_1 + \xi_2$$

$$0.95 \times 0.1 \times 100 = 7.5 + \xi_2 \Rightarrow \xi_2 = 2 \text{ mol/s}$$

– Use Eq. (4)

$$0.65\left(\dot{n}_{SO_2,1} + X_{SO_2,R}\dot{R}\right) = 2 \quad ; \quad (5)$$

In order to obtain $\dot{R}$, we need $X_{SO_2,1}$ and $X_{SO_2,R}$

Note: since stream R comes out of a splitter, the compositions of streams R and P are identical. Thus, $X_{SO_2,P} = X_{SO_2,R}$.

From eq. (2): $X_{SO_2,R}\dot{P} = (1-f_c)X_{SO_2,F}\dot{F}$; (6)

$\Rightarrow$ Now we have
$$\begin{cases} 0.65\left(\dot{n}_{SO_2,1} + X_{SO_2,R}\dot{R}\right) = 2 \\ X_{SO_2,R}\dot{P} = (1-0.95)\times 0.1 \times 100 \\ \qquad\quad = 0.5 \end{cases}$$

To determine $\dot{n}_{SO_2,1}$ $\rightarrow$ MBE on REACTOR 1

$$\dot{m}_{SO_2,1} = X_{SO_2,F}\,\dot{F} - \xi_1$$

$$\dot{m}_{SO_2,1} = 0.1 \times 100 - 7.5 = 2.5 \text{ mol/s}$$

$\Rightarrow$ Now from the previous system of eqns:

$$\begin{cases} X_{SO_2,R}\,\dot{R} = \dfrac{2}{0.65} - 2.5 = 0.58 \\ X_{SO_2,R}\,\dot{P} = 0.5 \end{cases} \quad (7)$$

$$\Rightarrow \begin{cases} X_{SO_2,R} = \dfrac{0.58}{\dot{R}} \\ X_{SO_2,R}\,\dot{P} = 0.5 \end{cases} \Rightarrow 0.58\left(\dfrac{\dot{P}}{\dot{R}}\right) = 0.5$$

$$\Rightarrow \boxed{\dfrac{\dot{R}}{\dot{P}} = 1.16}$$

c) OVERALL FRACTIONAL CONVERSION OF O_2

$$f_{c,O_2} = \frac{-\sum_{k=1}^{2} \nu_{O_2,k}\,\xi_k}{X_{O_2,F}\,\dot{F}} = \frac{-\left(\left(-\frac{1}{2}\right)\xi_1 - \left(\frac{1}{2}\right)\xi_2\right)}{X_{O_2,F}\,\dot{F}}$$

$\xi_1 = 7.5$ mol/s; $\xi_2 = 2$ mol/s (from previous)

$$f_{c,O_2} = \frac{7.5 + 2}{2\,(0.09 \times 100)} = \underline{\underline{0.53}}$$

d) Two SO_2 conversion reactors in series operating each at lower conversion could be better than having one reactor operated at a high fractional conversion of 0.95 because:

To achieve a very high fractional conversion in a single reactor it requires longer time in the reactor (so-called residence time). Considering these are flow reactors, this implies for one reactor larger size to assure the same production flow rate (this means greater capital cost and possibly higher operating cost with more extensive heat transfer requirements).