Given: The feed to an ammonia synthesis reactor contains a stoichiometric ratio of N_2 and H_2. The equilibrium relationship for this process is:

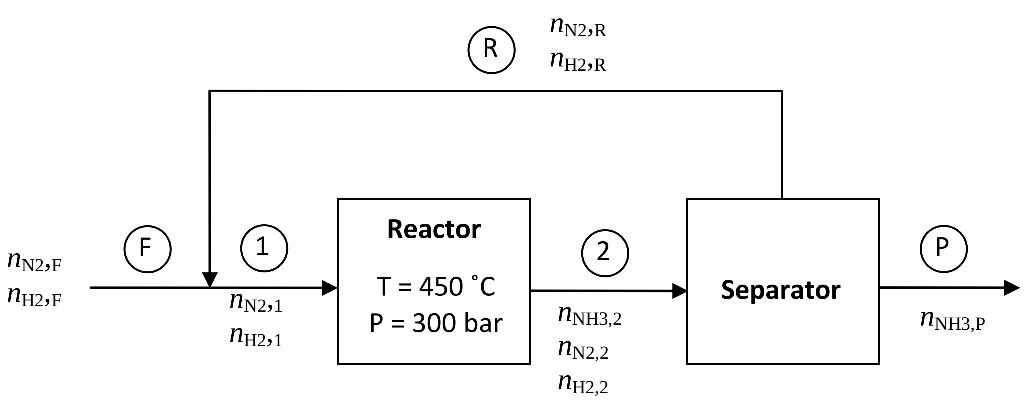
$$K_{eq}=\frac{x_{NH_3}^{\ 2}}{x_{N_2}x_{H_2}^{\ 3}}=0.35 \text{ (at 450 °C and 300 bar)}$$

The single-pass conversion through the reactor is 0.25, and unused N_2 and H_2 from the reactor will be separated from the ammonia and recycled. The product stream is pure ammonia.

Predict: The overall conversion of the process and the recycle stream molar flow rates and composition if we assume the same productivity as the process without recycle.

Strategy: Mass balances with equilibrium relationships

Step 1: Draw PFD; *label all intermediate streams*



Step 2: Here, one can draw multiple control volumes – around reactor, separator, mixing point (where the input stream is mixed with the recycle stream), and the overall process. Mass balances can be performed around each control volume. In addition, if we use the same reactor as above, stream 2 will be at equilibrium, and its yield relative to stream 1 will be the same as in the problem without recycle (i.e. 0.25)

Step 3: Choose same basis: $n_{NH3,P}$ = 100 mol/h NH_3 since we are assuming the same productivity as the non-recycle process.

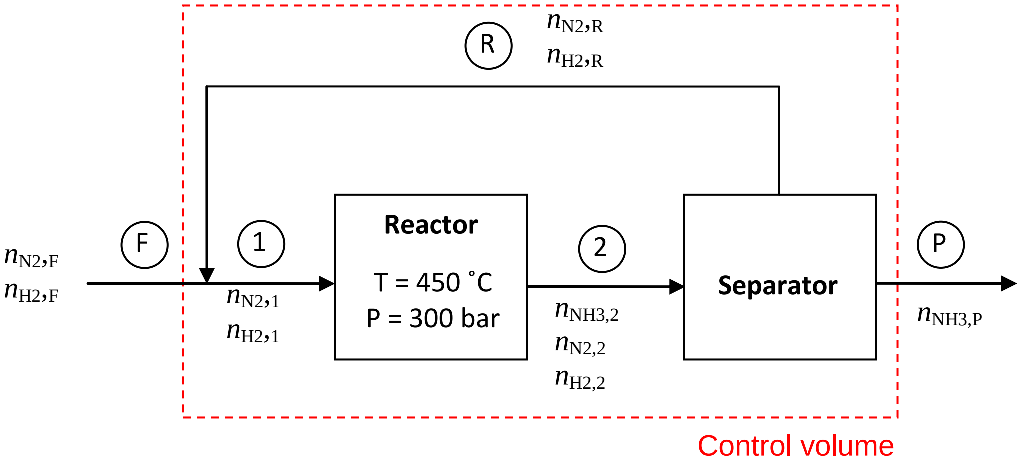
Step 4: In order to determine the overall conversion, we need to know (1) the moles of N_2 that were reacted in the overall process and (2) the moles of N_2 that were fed to the overall process. (We could also calculate the overall conversion using H_2. Since we have a stoichiometric feed, the overall conversion of N_2 will be the same as the overall conversion of H_2.)

(1) 100 mol/h of NH3 are produced so calculated moles of N_2 that must have been reacted to produce that NH_3:

$$\frac{100\ mol\ NH_3}{h}\cdot\frac{1 mol\ N_2}{2\ mol\ NH_3}=\frac{50\ mol\ NH_3}{h}$$

(2) Need to know $n_{N2,F}$. We have many possible choices for a control volume on which to perform a mass balance. Careful consideration of the different possibilities shows that the simplest route to finding $n_{N2,F}$ is to perform a mass balance on the overall process. (Try going through different possible control volumes to prove this to yourself.)

Mass balance around overall process:



N_2 balance: ACCN=IN-OUT+GEN-CONS

$$0=n_{N2,F}-0+0-\frac{n_{NH3,P}}{2}$$

$$0=n_{N2,F}-0+0-\frac{100\text{ mol/h}}{2}$$

i.e. $n_{N2,F}$ = **50 mol/h**

Note that for every mole of NH_3 produced, 0.5 moles of N_2 are consumed.

We can also easily determine nH2,F:

H_2 balance: ACCN=IN-OUT+GEN-CONS

$$0=n_{H2,F}-0+0-1.5n_{NH3,P}$$

$$0=n_{H2,F}-0+0-1.5(100\text{mol/h})$$

$n_{H2,F}$ = **150 mol/h**

Note that for every mole of NH_3 produced, 1.5 moles of H_2 are consumed.

We can now calculate the overall conversion:

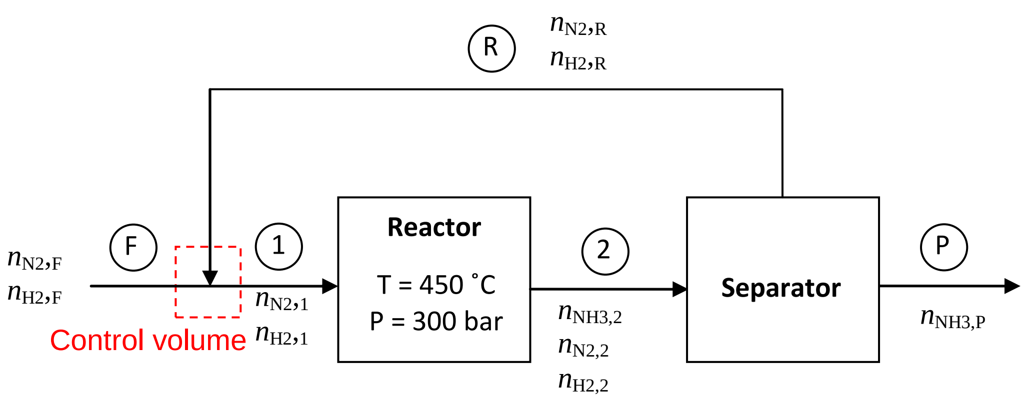
$$\text{Overall conversion of } N_2 = \frac{\text{moles } N_2 \textbf{ reacted in process}}{\text{moles } N_2 \textbf{ fed to process}} = \frac{50\frac{\text{mol}}{\text{h}}}{50\frac{\text{mol}}{\text{h}}} = 1$$

Step 5: We are also asked to find the molar flow rates and composition of the recycle stream.

From the earlier equilibrium calculation for the process without recycle, the streams 1 and 2 are related as follows [via the fact that 25% of the reactants (i.e. N_2 and H_2) get converted into NH_3]:
$n_{N2,2} = 0.75n_{N2,1}$, $n_{H2,2} = 0.75n_{H2,1}$,

Using the fact that 2 moles of NH_3 is produced from every 1 mole of N_2, we can also conclude that:
$n_{NH3,2} = 2(n_{N2,1} - n_{N2,2}) = 2(n_{N2,1} - 0.75n_{N2,1})=0.5n_{N2,1}$

Mass balance around mixing point of the fresh feed stream and stream 1:



N_2 balance: ACCN=IN-OUT+GEN-CONS

$$0=n_{N2,F}+n_{N2,R}-n_{N2,1}+0-0$$

$$0=50\frac{\text{mol}}{\text{hr}}+n_{N2,R}-n_{N2,1}$$

$$\text{i.e. } n_{N2,1}=50\frac{\text{mol}}{\text{hr}}+n_{N2,R}$$

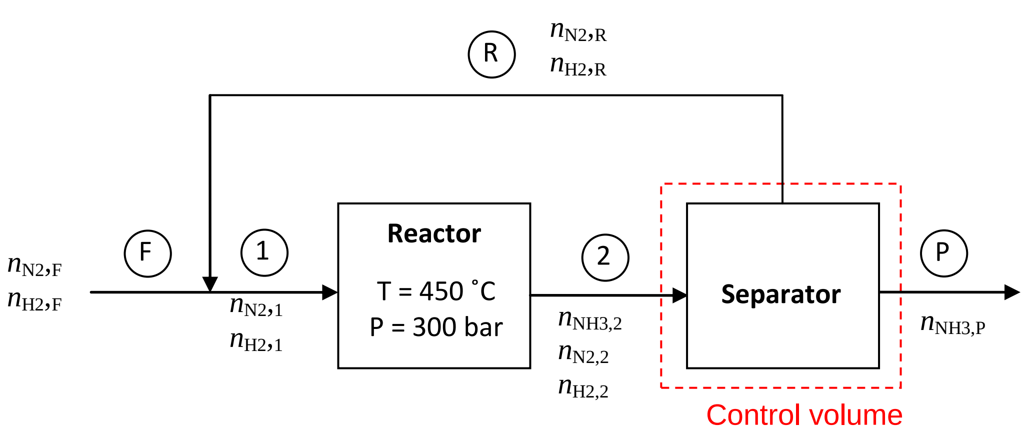
H_2 balance: ACCN=IN-OUT+GEN-CONS

$$0=n_{H2,F}+n_{H2,R}-n_{H2,1}+0-0$$

$$0=150\frac{\text{mol}}{\text{hr}}+n_{H2,R}-n_{H2,1}$$

$$\text{i.e. } n_{H2,1}=150\frac{\text{mol}}{\text{hr}}+n_{H2,R}$$

Mass balance around separator:



N_2 balance: ACCN=IN-OUT+GEN-CONS

$$0=n_{N2,2}-n_{N2,R}+0-0$$

Remembering that $n_{N2,1} = n_{N2,R} + 50$ mol/hr and that $n_{N2,2} = 0.75n_{N2,1}$:

$$0=0.75n_{N2,1}-n_{N2,R}$$

$$0=0.75(n_{N2,R}+50)-n_{N2,R}$$

$37.5 = 0.25 n_{N2,R}$

$n_{N2,R} = \frac{\boldsymbol{150 mol}}{\boldsymbol{hr}}$

H_2 balance: ACCN=IN-OUT+GEN-CONS

$0 = n_{H2,2} - n_{H2,R} + 0 - 0$

Remembering that $n_{H2,1} = n_{H2,R} + 150$ mol/hr and that $n_{H2,2} = 0.75 n_{H2,1}$:

$0 = 0.75 n_{H2,1} - n_{H2,R}$

$0 = 0.75(n_{H2,R} + 150) - n_{H2,R}$

$112.5 = 0.25 n_{H2,R}$

$n_{H2,R} = \frac{\boldsymbol{450 mol}}{\boldsymbol{hr}}$

Thus, by having a steady state recycle stream consisting of 150 mol/hr N_2 and 450 mol/hr H_2, we can achieve the ***same productivity*** (our basis of 100 mol/hour) as before, and also get ***complete conversion*** of a stoichiometric feed into 100 mol/h NH_3.