## Practice Problem P6

N moles of an ideal gas initially at ($P_0$, $V_0$, $T_0$).

a) ($P_0$, $V_0$, $T_0$) → ($P_1$, $V_1$, $T_0$) (isothermal) Assume Cp is constant

$$dS = \frac{Cp}{T}dT - \frac{R}{P}dP \qquad \text{for ideal gas} \qquad \text{or in extensive form: } dS^t = n\frac{Cp}{T}dT - n\frac{R}{P}dP$$

In this case, n = N. Integrating, we get:

$$\Delta S^t = N\int_{T_0}^{T_0}\frac{Cp}{T}dT - N\int_{P_0}^{P_1}\frac{R}{P}dP \qquad \text{So for our case, we can write}$$

$$\Delta S^t = 0 - N\int_{P_0}^{P_1}\frac{R}{P}dP \qquad \text{dT term goes away because isothermal}$$

$$\Delta S^t = -NR\ln(\frac{P_1}{P_0}) \qquad \text{(ans)}$$

b) Two steps: ($P_0$, $V_0$, $T_0$) → ($P_0$, $V_1$, $T_1$) → ($P_1$, $V_1$, $T_0$) Cp is a constant

First step: $$\Delta S_1{}^t = N\int_{T_0}^{T_1}\frac{Cp}{T}dT - N\int_{P_0}^{P_0}\frac{R}{P}dP = N\int_{T_0}^{T_1}\frac{Cp}{T}dT$$

Second step: $$\Delta S_2{}^t = N\int_{T_1}^{T_0}\frac{Cp}{T}dT - N\int_{P_0}^{P_1}\frac{R}{P}dP$$

Adding the two, we see that the dT terms cancel out.

$$\Delta S^t = \Delta S_1{}^t + \Delta S_2{}^t = N\int_{T_0}^{T_1}\frac{Cp}{T}dT + N\int_{T_1}^{T_0}\frac{Cp}{T}dT - N\int_{P_0}^{P_1}\frac{R}{P}dP = -N\int_{P_0}^{P_1}\frac{R}{P}dP = -NR\ln(\frac{P_1}{P_0}) \qquad \text{(ans)}$$

Same answer as part a), just as it should be, because S is a state function (path independent).

c) What if Cp is not a constant: $Cp/R = A + BT + CT^2$?
Well, normally this would make some difference somewhere. But in our case, we see that our answer (the $\Delta S$ for the overall process) does not depend on Cp. $\Delta S_1{}^t$ and $\Delta S_2{}^t$ will have to be evaluated differently, but the overall $\Delta S^t$ is the same.

Note: This does *not* mean that in every process it doesn't matter whether the Cp is assumed to be constant. It's just that in our case, the change in entropy doesn't depend on that assumption.

## Practice Problem PT1

We're adding 1.055 x $10^6$ kJ to a 18.14 kg mol mixture of 50 mol% ethylene and 50 mol% ethane, intiially at 260°C. Heat exchanger is operating at approximately atmospheric. What is the final temperature?

We know we're applying some Q at some constant pressure (approximately atmospheric) and we want to calculate T. We know that for constant pressure:

$Q = n\int CpdT = 1.055 \text{ x } 10^6$ kJ (Q is positive since we're adding to the system)

In fact, to be precise here, since we have a mixture, we'll write the terms for each species:

$$Q = n_{ethylene}\int_{T_o}^{T_f} Cp_{ethylene}dT + n_{ethane}\int_{T_o}^{T_f} Cp_{ethane}dT$$ where $n_{ethylene} = n_{ethane} = 50\% \text{ x } 18.14$ kgmol

We're not told that the Cp is constant. So we have to use Cp as a function of T from Appendix C. $Cp(T)/R = A + BT + CT^2 + DT^{-2}$. Putting that in our equation:

$$Q = n_{ethylene}\int_{T_{eth,0}}^{T_f} R(A_{ethylene} + B_{ethylene}T + C_{ethylene}T^2 + D_{ethylene}T^{-2})dT$$

$$+ n_{ethane}\int_{T_{eth,0}}^{T_f} R(A_{ethane} + B_{ethane}T + C_{ethane}T^2 + D_{ethane}T^{-2})dT$$

From table C.1:

| | A | B | C | D |
|---|---|---|---|---|
| **ethylene** | 1.424 | 14.394 x $10^{-3}$ | -4.392 x $10^{-6}$ | 0 |
| **ethane** | 1.131 | 19.225 x $10^{-3}$ | -5.561 x $10^{-6}$ | 0 |

$$1.055 \text{x} 10^9 \text{ J} = 0.5 \cdot 18.14 \text{ kgmol} R\int_{533\text{K}}^{T_f}(1.424 + 14.394 \cdot 10^{-3}T - 4.392 \cdot 10^{-6}T^2)dT$$

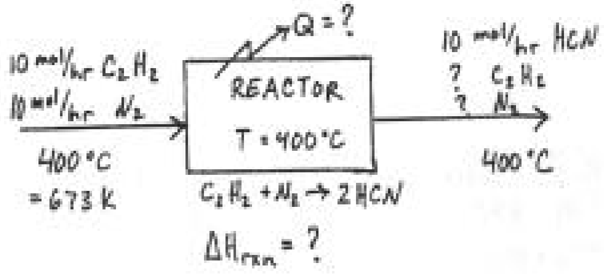
$$+ 0.5 \cdot 18.14 \text{ kgmol} R\int_{533\text{K}}^{T_f}(1.131 + 19.225 \cdot 10^{-3}T - 5.561 \cdot 10^{-6}T^2)dT$$

$$1.055 \text{x} 10^9 \text{ J} = 9.07 \text{ kg mol}\left[1.424(T_f - 533) + \frac{14.394 \cdot 10^{-3}}{2}(T_f^2 - 533^2) - \frac{4.392 \cdot 10^{-6}}{3}(T_f^3 - 533^3)\right] \ 8.314 \text{ J/mol K}$$

$$+ 9.07 \text{ kg mol}\left[1.131(T_f - 533) + \frac{19.225 \cdot 10^{-3}}{2}(T_f^2 - 533^2) - \frac{5.561 \cdot 10^{-6}}{3}(T_f^3 - 533^3)\right] \ 8.314 \text{ J/mol K}$$

Solving this gives us $T_f$ = **1132 K**.

PT2)



do a material balance to find the composition of the exit stream.

HCN: $\text{In} + \text{Gen.} = \text{Out} + \overset{0 \text{ steady state}}{\cancel{\text{Accum.}}}$

$$0 + G_{HCN} = 10 \text{ mol/hr.}$$

Reaction Stoichiom. $\frac{G_{HCN}}{2} = \frac{G_{C_2H_2}}{-1} = \frac{G_{N_2}}{-1} \Rightarrow \begin{matrix} G_{C_2H_2} = -5 \text{ mol/hr} \\ G_{N_2} = -5 \text{ mol/hr} \end{matrix}$

$C_2H_2$ & $N_2$: $\text{Out} = \text{In} + \text{Gen} = 10 \text{ mol/hr} - 5 \text{ mol/hr} = 5 \text{ mol/hr}$

Note that this means 5 mol/hr of $C_2H_2$ and $N_2$ pass directly through the reactor with no change in temperature, and they will not affect the heating / cooling requirements.

For the reactor to run isothermally, heat must be removed to satisfy the 1st Law:

1st Law for a Steady Flow process $\quad n\Delta H = \Delta H^t = Q + \underset{0 \text{ no shaft work in system}}{\cancel{W_s}}$

$$\Delta H = \underset{0 \text{ no change in T or P}}{\cancel{\Delta H_{sensible}}} + \underset{0 \text{ no phase change}}{\cancel{\Delta H_{latent}}} + \Delta H_{rxn}$$

$$\therefore \quad Q = n\,\Delta H_{rxn,673K}$$

To find $\Delta H_{rxn,673K}$, first find $\Delta H_{rxn,298}$ [12 pts.]

$$\Delta H_{rxn,298} = \sum_i \nu_i H^\circ_{f,298} \qquad \tfrac{1}{2} C_2H_2 + \tfrac{1}{2} N_2 \Rightarrow HCN$$

(+3 gen. eqn.)

$$= H^\circ_{f,HCN} - \tfrac{1}{2} H^\circ_{f,C_2H_2} - \tfrac{1}{2} H^\circ_{f,N_2}$$

$\downarrow$ from Appendix C Table C.4

(+4 specific eqn.)

$$= (135{,}100 \text{ J/mol}) - \tfrac{1}{2}(227{,}480 \text{ J/mol}) - \tfrac{1}{2}(0)$$

(+4 $H^\circ_f$ values)

$$= 21{,}360 \text{ J/mol HCN} \quad [= 42{,}720 \text{ J/mol } C_2H_2] \quad \overset{\Delta H^t_{298}}{[= 213{,}600 \text{ J/hr}]}$$

Now find $\Delta H_{rxn}$ @ 673 K. You can approach this 2 ways:

1) Path Process

$$\begin{tikzcd}
\frac{1}{2}C_2H_2 + \frac{1}{2}N_2 \text{ @ } 673\text{ K} \arrow[r, Rightarrow, "\Delta H_{rxn,673}"] \arrow[d, "\Delta H_1"] & HCN \text{ @ } 673\text{ K} \\
\frac{1}{2}C_2H_2 + \frac{1}{2}N_2 \text{ @ } 298\text{ K} \arrow[r, "\Delta H_2"'] & HCN \text{ @ } 298\text{ K} \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

$$\Delta H_{rxn,673} = \Delta H_1 + \underset{= \Delta H_{rxn,298}}{\underset{\downarrow}{\Delta H_2}} + \Delta H_3$$

$$\Delta H_1 = \frac{1}{2}\int_{673}^{298} C_{P\,C_2H_2}\,dT + \frac{1}{2}\int_{673}^{298} C_{P\,N_2}\,dT \quad =$$

$$\Delta H_3 = \int_{298}^{673} C_{P\,HCN}\,dT \qquad \text{where } \frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

with constants from Table C.1

$\Delta H_1 = -1878.7193 \text{ K} \cdot R = -15619.672$ J/mol HCN

$\Delta H_3 = 1887.8609 \text{ K} \cdot R = 15695.675$ J/mol HCN

$$\Delta H_{rxn,673} = (-15619.7 + 21360 + 15695.7) \text{ J/mol HCN}$$
$$= 21{,}436 \text{ J/mol HCN}$$

2) Aggregate $C_p$

$$\Delta H_{rxn,673} = \sum_i \int_{298}^{673} \nu_i C_{P_i}\,dT + \Delta H_{rxn,298}$$

Find the aggregate $C_p$: $\frac{C_p}{R} = A_{eff} + B_{eff}T + C_{eff}T^2 + D_{eff}T^{-2}$

where $A_{eff} = \sum_i \nu_i A_i$ etc.

then $\Delta H_{rxn,673} = \int_{298}^{673} C_{P,eff}\,dT + \Delta H_{rxn,298}$

|  | $\nu_i$ | A | B | C | D |
|---|---|---|---|---|---|
| $C_2H_2$ | $-\frac{1}{2}$ | 6.132 | $1.952 \times 10^{-3}$ | – | $-1.299 \times 10^{5}$ |
| $N_2$ | $-\frac{1}{2}$ | 3.280 | $0.593 \times 10^{-3}$ | – | $0.040 \times 10^{5}$ |
| HCN | 1 | 4.736 | $1.359 \times 10^{-3}$ | – | $-0.725 \times 10^{5}$ |
| effective |  | 0.030 | $0.0865 \times 10^{-3}$ |  | $-0.0955 \times 10^{5}$ |

$$\int_{298}^{673} c_{p,\mathrm{eff}}\, dT = R\int_{298}^{673} A_{\mathrm{eff}} + B_{\mathrm{eff}} T + D_{\mathrm{eff}} T^{-2}\, dT$$

$$= R\left[ A_{\mathrm{eff}}(673-298) + \frac{B_{\mathrm{eff}}}{2}(673^2-298^2) - D_{\mathrm{eff}}\left(\frac{1}{673}-\frac{1}{298}\right)\right]$$

$$= R[11.250\,\mathrm{K} + 15.748\,\mathrm{K} + -17.857\,\mathrm{K}]$$

$$= R[9.141\,\mathrm{K}] = (8.314\ \mathrm{J/mol\text{-}K})(9.141\,\mathrm{K})$$

$$= 75.998\ \mathrm{J/mol\ HCN} \qquad \left[\Delta H^{\circ}_{298\to 673} = 760\ \mathrm{J/hr}\right]$$

$$\Delta H_{rxn,673} = \int_{298}^{673} c_{p,\mathrm{eff}}\, dT + \Delta H_{rxn,298}$$

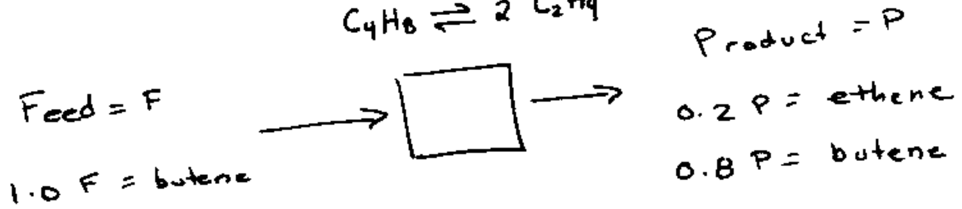
$$= 76\ \mathrm{J/mol\ HCN} + 21{,}360\ \mathrm{J/mol\ HCN}$$

$$= 21{,}436\ \mathrm{J/mol\ HCN} \qquad [= 42{,}872\ \mathrm{J/mol}\ C_2H_2]$$

$$\boxed{\begin{aligned} \therefore\quad Q = n\,\Delta H_{rxn,673} &= (10\ \mathrm{mol/hr\ HCN})(21{,}436\ \mathrm{J/mol\ HCN}) \\ &= 214{,}360\ \mathrm{J/hr} \\ &= 59.5\ \mathrm{W} \end{aligned}}$$

PT3)

$$\overset{\nu=-1}{C_4H_8} \rightleftharpoons \overset{\nu=+2}{2\,C_2H_4}$$



Basis : F = 1 mol

Balance on butene :

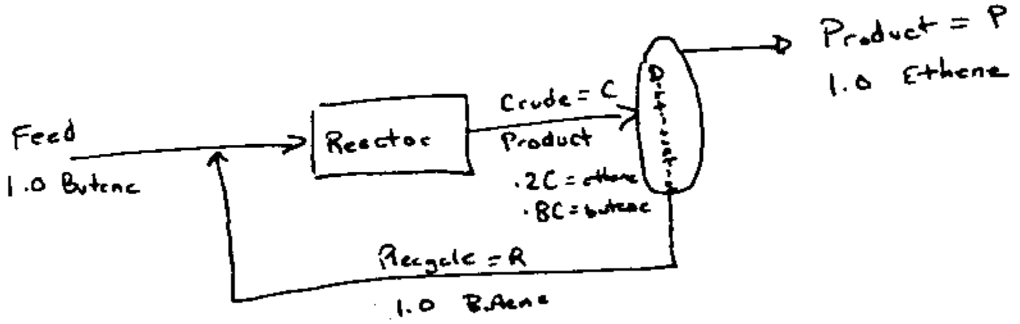
$$\underset{\text{in}}{1.0\ F} + \underset{\text{generation}}{(-1)\ \epsilon} = \underset{\text{out}}{0.8\ P} \qquad \therefore\ \epsilon = 1\text{ mol} - 0.8\ P$$

Balance on ethene :

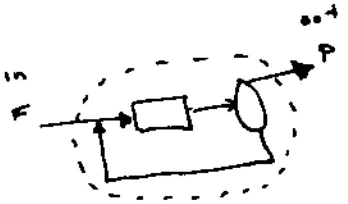
$$\underset{\text{in}}{0} + \underset{\text{generation}}{(2)\ \epsilon} = \underset{\text{out}}{0.2\ P}$$

$$\therefore\ 2\,(1\text{ mol} - 0.8\ P) = 0.2\ P \qquad \therefore\ P = 1.11\text{ mol}$$

$$\therefore\ \text{mol ethene / mol feed} = 0.2\,(1.11) = 0.222\text{ mol}$$



→ System boundary = entire system



Balance on butene :

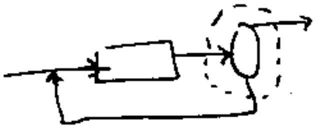
$$\underset{\text{in}}{1.0\ F} + \underset{\text{generation}}{(-1)\ \epsilon} = \underset{\text{out}}{0} \qquad \therefore\ \epsilon = F$$

Balance on ethene:

$$0 + 2\epsilon = P \text{ , since } \epsilon = F$$

$$\therefore \; 2F = P$$

→ System boundary = distillation column



Balance on butene:

$$.8C = R \qquad \text{(no generation)}$$

Balance on ethene:

$$.2C = P \qquad \text{(no generation)}$$

$$\therefore \; \frac{R}{P} = \frac{4}{1} = \frac{R}{2F} \qquad \therefore \; \frac{R}{F} = \frac{8}{1}$$

$$\boxed{F : R : P = 1 : 8 : 2}$$