Practice Problem P6

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

a) \((P_0, V_0, T_0) \rightarrow (P_1, V_1, T_0)\) (isothermal) Assume \(C_p\) is constant

\[
dS = \frac{C_p}{T} dT - \frac{R}{P} dP
\]

for ideal gas or in extensive form: \(dS^i = n \frac{C_p}{T} dT - n \frac{R}{P} dP\)

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

\[
\Delta S^i = N \int_{T_0}^{T_1} \frac{C_p}{T} dT - N \int_{P_0}^{P_1} \frac{R}{P} dP
\]

So for our case, we can write

\[
\Delta S^i = 0 - N \int_{P_0}^{P_1} \frac{R}{P} dP
\]

d\(T\) term goes away because isothermal

\[
\Delta S^i = -NR\ln\left(\frac{P_1}{P_0}\right)
\]

(ans)

b) Two steps: \((P_0, V_0, T_0) \rightarrow (P_0, V_1, T_1) \rightarrow (P_1, V_1, T_0)\) \(C_p\) is a constant

First step: \(\Delta S^i_1 = N \int_{T_0}^{T_1} \frac{C_p}{T} dT - N \int_{P_0}^{P_1} \frac{R}{P} dP = N \int_{T_0}^{T_1} \frac{C_p}{T} dT\)

Second step: \(\Delta S^i_2 = N \int_{T_1}^{T_0} \frac{C_p}{T} dT - N \int_{P_0}^{P_1} \frac{R}{P} dP\)

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

\[
\Delta S^i = \Delta S^i_1 + \Delta S^i_2 = N \int_{T_0}^{T_1} \frac{C_p}{T} dT + N \int_{T_1}^{T_0} \frac{C_p}{T} dT - N \int_{P_0}^{P_1} \frac{R}{P} dP = -N \int_{P_0}^{P_1} \frac{R}{P} dP = -NR\ln\left(\frac{P_1}{P_0}\right)
\]

(ans)

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

c) What if \(C_p\) is not a constant: \(C_p/R = A + BT + CT^2?\)

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 \(C_p\). \(\Delta S^i_1\) and \(\Delta S^i_2\) will have to be evaluated differently, but the overall \(\Delta S^i\) is the same.

Note: This does not mean that in every process it doesn’t matter whether the \(C_p\) is assumed to be constant. It’s just that in our case, the change in entropy doesn’t depend on that assumption.
Practical Problem PT1

We’re adding $1.055 \times 10^6$ kJ to a 18.14 kg mol mixture of 50 mol% ethylene and 50 mol% ethane, initially 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:

$$Q = n \int_{T_i}^{T_f} C_p dT$$

(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:

$$Q = n_{\text{ethylene}} \int_{T_i}^{T_f} C_p_{\text{ethylene}} dT + n_{\text{ethane}} \int_{T_i}^{T_f} C_p_{\text{ethane}} dT$$

where $n_{\text{ethylene}} = n_{\text{ethane}} = 50\% \times 18.14$ kgmol

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

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

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

From table C.1:

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<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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<tbody>
<tr>
<td>ethylene</td>
<td>1.424</td>
<td>$14.394 \times 10^{-3}$</td>
<td>$-4.392 \times 10^{-6}$</td>
<td>0</td>
</tr>
<tr>
<td>ethane</td>
<td>1.131</td>
<td>$19.225 \times 10^{-3}$</td>
<td>$-5.561 \times 10^{-6}$</td>
<td>0</td>
</tr>
</tbody>
</table>

$$1.055 \times 10^6 \int_{T_{i,0}}^{T_f} \left( 1.424 + 14.394 \times 10^{-3} T - 4.392 \times 10^{-6} T^2 \right) dT$$

$$+ 0.5 \times 18.14 \int_{T_{i,0}}^{T_f} \left( 1.131 + 19.225 \times 10^{-3} T - 5.561 \times 10^{-6} T^2 \right) dT$$

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

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

Solving this gives us $T_f = 1132 \text{ K}$. 

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

HCN: \[ \text{In} + \text{Gen.} = \text{Out} + \text{Acum.} \] 
\[ 0 + G_{HCN} = 10 \text{ mol/hr}. \]

Reaction: 
\[ \frac{G_{HCN}}{2} = \frac{G_{C_2H_2}}{-1} \Rightarrow G_{C_2H_2} = -5 \text{ mol/hr} \]

\[ G_{N_2} = -5 \text{ mol/hr} \]

\[ C_2H_2 + N_2 \rightarrow 2 \text{ HCN} \]
\[ \text{Out} = \text{In} + \text{Gen} = 10 \text{ mol/hr} - 5 \text{ mol/hr} = 5 \text{ mol/hr} \]

Note that this means 5 \text{ 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 
\[ n \Delta H = \Delta H^e + Q + W_s \]

\[ \Delta H = \Delta H_{\text{sensible}} + \Delta H_{\text{latent}} + \Delta H_{\text{rxn}} \]

\[ \text{no change in T or P} \quad \text{no phase change} \]

\[ Q = n \Delta H_{\text{rxn, 673 K}} \]

To find \( \Delta H_{\text{rxn, 673 K}} \), First find \( \Delta H_{\text{rxn, 298 K}} \) [12 pts.]

\[ \Delta H_{\text{rxn, 298 K}} = \sum_i v_i \Delta H_f^i \]

\[ = H_{C_2H_2}^f - \frac{1}{2} H_{C_2H_2}^f - \frac{1}{2} H_{N_2}^f \]

\[ = (135,100 \text{ J/mol}) - \frac{1}{2} (227,480 \text{ J/mol}) - \frac{1}{2} (0) \]

\[ = 21,360 \text{ J/mol HCN} \quad [\text{from Appendix C Table C.4}] \quad \Delta H_{\text{rxn, 673 K}} = 213,600 \text{ J/hr} \]
Now find $\Delta H_{\text{rxn}}$ @ 673 K. You can approach this 2 ways:

1) Path Process

$\frac{1}{2} C_2 H_2 + \frac{1}{2} N_2 \quad \xrightarrow{673 \text{ K}} \quad HCN \quad \xrightarrow{673 \text{ K}} \quad \Delta H_{\text{rxn, 673}}$

$\frac{1}{2} C_2 H_2 + \frac{1}{2} N_2 \quad \xrightarrow{298 \text{ K}} \quad \Delta H_3$

$\Delta H_{\text{rxn, 673}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_3 = \Delta H_{\text{rxn, 298}}$

$\Delta H_1 = \frac{1}{2} \int_{673}^{298} C_p C_2 H_2 \, dT + \frac{1}{2} \int_{673}^{298} C_p N_2 \, dT$

$\Delta H_3 = \int_{298}^{673} C_p \text{HCN} \, dT$

where $\frac{C_p}{R} = A + BT + CT^2 + DT^2$

with constants from Table C.1

$\Delta H_1 = -1978.7193 \text{ K} \cdot R = -15619.672 \text{ J/mol HCN}$

$\Delta H_3 = 1897.8609 \text{ K} \cdot R = 15695.675 \text{ J/mol HCN}$

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

$\Delta H_{\text{rxn, 673}} = 21436 \text{ J/mol HCN}$

2) Aggregate $C_p$

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

Find the aggregate $C_p = \sum C_p = A_{\text{eff}} + B_{\text{eff}} T + C_{\text{eff}} T^2 + D_{\text{eff}} T^2$

where $A_{\text{eff}} = \sum \nu_i A_i$, etc.

then $\Delta H_{\text{rxn, 673}} = \sum \int_{298}^{673} C_p \text{eff} \, dT + \Delta H_{\text{rxn, 298}}$
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<tbody>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-1/2</td>
<td>6.192</td>
<td>1.952 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>-1.299 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
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<tr>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-1/2</td>
<td>3.280</td>
<td>0.593 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>-0.040 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>HCN</td>
<td>1</td>
<td>4.736</td>
<td>1.359 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>-0.725 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>effective</td>
<td></td>
<td></td>
<td>0.030</td>
<td>0.0865 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
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\[
\int_{298}^{673} c_{P, eff} \, dT = R \int_{298}^{673} \left[A_{eff} + B_{eff} T + C_{eff} T^{-2}\right] \, dT \\
= R \left[A_{eff} (673 - 298) + B_{eff} \frac{(673^2 - 298^2)}{2} - C_{eff} \left(\frac{1}{673} - \frac{1}{298}\right)\right] \\
= R \left[11.250 \text{ K} + 15.748 \text{ K} + -17.857 \text{ K}\right] \\
= R \left[9.141 \text{ K}\right] = \left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(9.141 \text{ K}) \\
= 75.998 \frac{\text{J}}{\text{mol}} \text{ HCN} \\
\left[\Delta H^d_{298 \rightarrow 673} = 760 \frac{\text{J}}{\text{hr}}\right]
\]

\[
\Delta H_{\text{run, 673}} = \int_{298}^{673} c_{P, eff} \, dT + \Delta H_{\text{run, 298}} \\
= 76 \frac{\text{J}}{\text{mol}} \text{ HCN} + 21,360 \frac{\text{J}}{\text{mol}} \text{ HCN} \\
= 21,436 \frac{\text{J}}{\text{mol}} \text{ HCN} \left[= 42,872 \frac{\text{J}}{\text{mol}} \text{ C}_2\text{H}_2\right]
\]

\[Q = n \Delta H_{\text{run, 673}} = (10 \frac{\text{mol}}{\text{hr}} \text{ HCN})(21,436 \frac{\text{J}}{\text{mol}} \text{ HCN}) \]
\[= 214,360 \frac{\text{J}}{\text{hr}} \]
\[= 59.5 \text{ W}\]
Feed = F

1.0 F = butene

Basis: F = 1 mol

Balance on butene:

1.0 F + (-1) E = 0.8 P

in generation
out

Balance on ethene:

0 + (2) E = 0.2 P

in generation
out

\[ 2 \left( 1 \text{ mol} - 0.8 \text{ P} \right) = 0.2 \text{ P} \]

\[ P = 1.11 \text{ mol} \]

\[ \text{mol ethene/mol feed} = 0.2 \left( 1.11 \right) = 0.222 \text{ mol} \]

System boundary = entire system

Balance on butene:

1.0 F + (-1) E = 0

in generation
out

\[ E = F \]
Balance on ethene:

\[ O + 2E = P \text{, since } E = F \]
\[ \therefore 2F = P \]

\[ \implies \text{system boundary = distillation column} \]

Balance on butene:

\[ .8C = R \text{ (no generation)} \]

Balance on ethene:

\[ .2C = \bullet P \text{ (no generation)} \]

\[ \therefore \quad \frac{R}{P} = \frac{4}{1} = \frac{R}{2F} \quad \therefore \quad \frac{R}{F} = \frac{8}{1} \]

\[ F : R : P = 1 : 8 : 2 \]