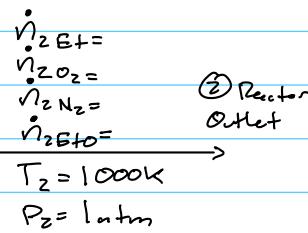
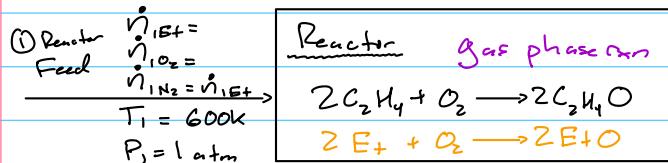


Ethylene Oxide Production

## 1. Problem Statement and Heat of Reaction Method

## a) PFD

Eq. molar Feed of  
 $N_2 \text{ & } E+$ :  
 $y_{1H_2} = y_{1E+}$  so  
 $\dot{n}_{1N_2} = \dot{n}_{1E+}$



Add. trans EGs

$$\textcircled{A} \quad \frac{\dot{n}_{1E+}}{\dot{n}_{1O_2}} = \frac{2}{1}$$

$$\textcircled{B} \quad \dot{f}_{E+} = \frac{\dot{n}_{1E+} - \dot{n}_{2E+}}{\dot{n}_{1E+}} = 0.3$$

We want to know:  $\dot{Q}_{\text{reactor}}$

## b) Reactor Dof

6 Vars Known ( $\dot{n}_{1E+}, \dot{n}_{1O_2}, \dot{n}_{2E+}, \dot{n}_{2O_2}, \dot{n}_{2N_2}, \dot{n}_{2E+O}$ )  
+ 1 Chemical Reaction (2)

- 4 Independent Material Balances (E+, O<sub>2</sub>, N<sub>2</sub>, E+O)

- 2 Additional Equations (A and B)

1 Dof

Not solvable unless we assume a basis. If we let  $\dot{n}_{1E+} = 100 \text{ mol/hr}$ , we can solve.

Assume a basis of

$\dot{n}_{1E+} = 100 \text{ mol/hr} \Rightarrow \text{molar}$

balances are solvable

c) 1<sup>st</sup> Law:  $\Delta E_p + \Delta E_k + \Delta H = \dot{Q} - \dot{W}_s$

no changes in height/ no moving parts  $\Rightarrow \Delta H = \dot{Q}_{\text{reactor}}$

Position or velocity or pump/turbines

$$\dot{Q}_{\text{reactor}} = \sum_i \dot{H}_i \dot{n}_i - \sum_i \dot{H}_i \dot{n}_i$$

$$= \sum_i \dot{H}_i^{\circ} + \left[ \dot{H}_{2E+} \dot{n}_{2E+} + \dot{H}_{2O_2} \dot{n}_{2O_2} + \dot{H}_{2N_2} \dot{n}_{2N_2} + \dot{H}_{2E+O} \dot{n}_{2E+O} \right] - \left[ \dot{H}_{1E+} \dot{n}_{1E+} + \dot{H}_{1O_2} \dot{n}_{1O_2} + \dot{H}_{1N_2} \dot{n}_{1N_2} \right]$$

## d) Determine Reference States

$\Delta H_f^\circ$  is standard heat of reaction so 298 K, 1 atm

Reference States:  $\begin{cases} E+(298K, 1 \text{ atm}, g) \\ E+O(298K, 1 \text{ atm}, g) \\ O_2(298K, 1 \text{ atm}, g) \end{cases}$

Gas phase rxn,  
and  $\Delta H_f^\circ$  is given  
in gas phase if



Ethylene Oxide Production (Continued)

g) How to Solve

(i) Write out and solve material balances to get all  $\dot{n}_i$  in streams 1 & 2, as well as extent of reaction  $\dot{\xi}$ (ii) Convert  $\dot{H}_i$  expression limits of integration to correct units for respective  $C_p$  values

$$\dot{H}_{1,Et} = \dot{H}_a = \int_{298K}^{600K} C_p \text{Et,g} dT \rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p \text{Et,g} dT$$

$$\dot{H}_{1,O_2} = \dot{H}_b = \int_{298K}^{600K} C_p O_2,g dT \rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p O_2,g dT$$

$$\dot{H}_{1,N_2} = \dot{A}_c = \int_{298K}^{600K} C_p N_2,g dT \rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p N_2,g dT$$

$$\dot{H}_{2,Et} = \dot{H}_d = \int_{298K}^{1000K} C_p \text{Et,g} dT \rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p \text{Et,g} dT$$

$$\dot{H}_{2,O_2} = \dot{H}_e = \int_{298K}^{1000K} C_p O_2,g dT \rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p O_2,g dT$$

$$\dot{H}_{2,N_2} = \dot{H}_f = \int_{298K}^{1000K} C_p N_2,g dT \rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p N_2,g dT$$

Table  
 B.1 needs T  
 in OC,  $C_p$  expression  
 for EtO remains  
 unchanged

(iii) Evaluate all  $\dot{H}_i$  expressions in streams 1 & 2 using integral expressions found in (f)(iv) Divide  $\dot{H}_{2,Et}$  by 1000 to get in units of  $\frac{kJ}{mol \cdot K}$ (v) Plug all  $\dot{n}_i$  and  $\dot{H}_i$  into energy balance, evaluate to get  $\dot{Q}_{react}$ Material Balances (not requested, just done for practice)Reactant Process:  $\dot{n}_{act} = \dot{n}_{in} + \text{gen/consump} \leftarrow \text{steady-state conditions}$ 

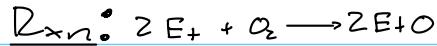
$$\text{Et: } \dot{n}_{2,Et} = \dot{n}_{1,Et} - 2\dot{\xi}_1$$

Add. term EGs

$$\text{O}_2: \dot{n}_{2,O_2} = \dot{n}_{1,O_2} - \dot{\xi}_1$$

$$\text{① } \frac{\dot{n}_{1,Et}}{\dot{n}_{1,O_2}} = \frac{2}{1} \quad \text{② } f_{Et} = \frac{\dot{n}_{1,Et} - \dot{n}_{2,Et}}{\dot{n}_{1,Et}} = 0.3$$

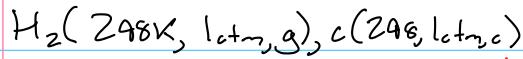
$$\text{H}_2: \dot{n}_{2,N_2} = \dot{n}_{1,N_2} + \dot{\xi}_1$$

How to Solve(i) Solve ~~①~~ expression for  $\dot{n}_{1,O_2}$ (ii) Solve ~~②~~ expression for  $\dot{n}_{2,Et}$ (iii) Solve Et Balance for  $\dot{\xi}_1$ (iv) Solve all other balances for all  $\dot{n}_i$

Ethylene Oxide Production (Continued)

2. Heat of Formation method on same system

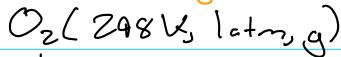
d) Reference States and Theoretical Paths

(Elements & Dinites  
at 298 K, 1 atm)Reference States: c (298 K, 1 atm, c) & O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> (298 K, 1 atm, g)

$$\downarrow \Delta H_{f, \text{Et}, g}^{\circ} = 52.28 \frac{\text{kJ}}{\text{mol}} \text{ Table B.1}$$



$$\downarrow \Delta T @ \text{constant } P_{\text{phase}}$$



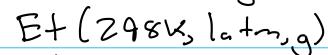
$$\downarrow \Delta T @ \text{constant } P_{\text{phase}}$$



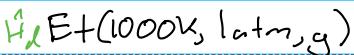
$$\downarrow \Delta T @ \text{constant } P_{\text{phase}}$$



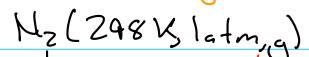
$$\downarrow \Delta H_{f, \text{Et}, g}^{\circ} = 52.28 \frac{\text{kJ}}{\text{mol}} \text{ Table B.1}$$



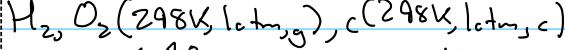
$$\downarrow \Delta T @ \text{constant } P_{\text{phase}}$$



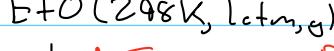
$$\downarrow \Delta T @ \overset{\text{constant}}{P_{\text{phase}}}$$



$$\downarrow \Delta T @ \overset{\text{constant}}{P_{\text{phase}}}$$



$$\downarrow \Delta H_{f, \text{ETO}, g}^{\circ} = -52.64 \frac{\text{kJ}}{\text{mol}} \text{ NIST}$$



$$\downarrow \Delta T @ \text{constant } P_{\text{phase}}$$



e) Molar enthalpy expressions

$$\hat{H}_{\text{Et}} = \Delta H_{f, \text{Et}, g}^{\circ} + \int_{298K}^{600K} C_p \text{Et}, g \, dT$$

$$\hat{H}_{\text{O}_2} = 0 + \int_{298K}^{600K} C_p \text{O}_2, g \, dT$$

$$\hat{H}_{\text{N}_2} = 0 + \int_{298K}^{600K} C_p \text{N}_2, g \, dT$$

$$\hat{H}_{\text{ETO}} = \Delta H_{f, \text{ETO}, g}^{\circ} + \int_{298K}^{1000K} C_p \text{ETO}, g \, dT$$

$$\hat{H}_{\text{O}_2} = 0 + \int_{298K}^{1000K} C_p \text{O}_2, g \, dT$$

$$\hat{H}_{\text{N}_2} = 0 + \int_{298K}^{1000K} C_p \text{N}_2, g \, dT$$

$$\hat{H}_{\text{ETO}} = \Delta H_{f, \text{ETO}, g}^{\circ} + \int_{298K}^{1000K} C_p \text{ETO}, g \, dT$$

f) All C<sub>p</sub> expressions previously defined in part f for question

1. These are independent of the solving method used, and all heat of formation values are defined in (2.d).

Ethylene Oxide Production (Continued)

g) How to Solve

(i) Write out and solve material balances to get all  $n_i$  in streams 1 & 2, as well as extent of reaction  $\dot{\xi}$ (ii) Convert  $\dot{H}_i$  expression limits of integration to correct units for respective  $C_p$  values

These exist  
one point of the  
actual  $\dot{H}_i$   
expressions,  
remember  $\Delta \dot{H}_i^0$

$$\begin{aligned} \int_{298K}^{600K} C_p \text{Et,g} dT &\rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p \text{Et,g} dT \\ \int_{298K}^{600K} C_p \text{O}_2\text{g} dT &\rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p \text{O}_2\text{g} dT \\ \int_{298K}^{600K} C_p \text{N}_2\text{g} dT &\rightarrow \int_{298K-273.15K}^{600K-273.15K} C_p \text{N}_2\text{g} dT \\ \int_{298K}^{1000K} C_p \text{Et,g} dT &\rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p \text{Et,g} dT \\ \int_{298K}^{1000K} C_p \text{O}_2\text{g} dT &\rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p \text{O}_2\text{g} dT \\ \int_{298K}^{1000K} C_p \text{N}_2\text{g} dT &\rightarrow \int_{298K-273.15K}^{1000K-273.15K} C_p \text{N}_2\text{g} dT \end{aligned}$$

Table  
B.1 needs T  
in °C,  $C_p$  expression  
for EtO remains  
unchanged

(iii) Divide integral expression for EtO by 1000 to get units of  $\frac{\text{kJ}}{\text{mol}\cdot\text{K}}$ (iv) Evaluate all  $\dot{H}_i$  expressions using modified/real  $C_p$  integral expressions in the respective  $\dot{H}_i$  expressions found in f, be sure to include  $\Delta \dot{H}_i^0$  values.(v) Plug all  $n_i$  and  $\dot{H}_i$  into energy balance, evaluate to get  $\dot{Q}_{\text{reac}}$

Ethylene Oxide Production (Continued)3. Qualitative Method Analysis

**(3 points)** Qualitatively describe how your solutions were different for each method

(*hint:* think about reference states, the time it took you to write the expressions, complexity of your equations, access to tabulated data).

For the Heat of Reaction method, I had to access some tables to be able to find the enthalpy of reaction for the system. This required going through Table B.1 and NIST chemical web book to find the enthalpies of formation for all species, and using a formula derived from Hess' law to find the enthalpy of reaction. This is the main difference between the two methods, requiring this extra step and few calculations in order to arrive at the same answer. Setting the reference states in this method requires setting them to the same used for the heat of formations found for the enthalpy of reaction. This is the same as the heat of formation method. Because of the nature of this problem, the reference state was very close to the reaction inlet and outlet conditions, so there was not as much time spent having to write out long expressions. For the Heat of Formation method, I still had to look for the heat of formation values from Table B.1 and NIST chemical web book. The nice thing about this method is that everything is consolidated into a few steps. I found this difference to be nice as the heat of formation is baked into every molar enthalpy calculation, and doesn't require finding a heat of reaction for the reaction beforehand. The reference states being the individual elements and diatomics at standard conditions wasn't an issue especially considering how close the process conditions were. The access to tabulated data and complexity of equations are ultimately about the same, so the real difference just comes from the continuity of the work. I can imagine the heat of reaction method taking much longer with multi-reaction systems, and would much prefer the heat of formation generally, but there was not much of a difference in this problem.

We are now finished learning new technical content for the course (yay!).

- a. Is there anything that you still find confusing about ENERGY balances?  
(including reactions, phase change, etc.)
- b. Is there anything that you still find confusing about MATERIAL balances  
(including reactions, phase change, etc.)

A. I don't find anything confusing about energy balances anymore. I was having some trouble seeing the theoretical paths and defining the enthalpies for each step, but now I feel I have a strong understanding of the steps that need to be taken. The only thing I'm wondering about is if in the heat of formation method, if the species formed is a solid, what different steps (if any) would need to be taken in order to solve the problem correctly. I am also curious how problems might look if we were unable to ignore kinetic and potential energies, or how the introduction of shaft work would change the problem's approach. Specifically, how would these systems impact the process of choosing and defining a reference state?

B. I don't find anything confusing about material balances. I believe I have a strong understanding of all material balance topics, including VLE, Equations of State, Phase changes, etc. The material balance part of questions, while redundant at this point, feel second nature to me. Going into future chemical engineering classes, I am curious to see how non-steady-state processes differ from what we've covered in this class, and how much of this courses material will carry over into those (and other) situations.