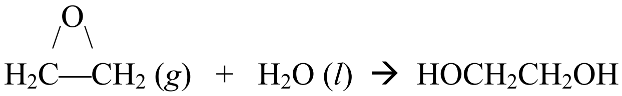
10.213 Chemical Engineering Thermodynamics
Spring 2002

Test 1 Solution

Problem 1 (50 points; 25 points for each part)

Ethylene glycol [$HOCH_2CH_2OH$], also known as 1,2-ethanediol, is prepared by the hydrolysis of ethlene oxide [cyclic-CH_2CH_2O] in the reaction shown below:



$$H_2C{-}CH_2\,(g) + H_2O\,(l) \rightarrow HOCH_2CH_2OH$$

Consider a single-pass process where ethylene oxide is combined with water to generate ethylene glycol. In the process, the molar water to ethylene ratio entering the reactor is 5 and the reaction proceeds with 90% conversion of the entering ethylene oxide. The reactants (gaseous ethylene oxide and liquid water) enter the reactor at 80 ºC. The products from the reactor are separated by distillation in a second processing unit yielding a top stream that is water-rich (and also contains some ethylene oxide but no ethylene glycol) and a bottom stream (the product) that is ethylene glycol-rich. An analysis of the bottom stream shows that it has an ethylene glycol to water molar ratio of 10 and contains no ethylene oxide. For convenience, use the labels E for ethylene oxide, W for water, and G for ethylene glycol as your subscripts on flows.

a) If the reactants are stored at 25 ºC and must be heated to 80 ºC before entering the reactor,
   i) determine the amount of heat that must be provided to the process per mole of ethylene oxide in the feed stream and
   ii) determine the amount of heat that must be provided to the process *per mole of ethylene glycol produced in the final product stream*.

Solution

i) Select as basis 1 mole of ethylene oxide (E). Thus the total flow into heater includes the 1 mol of E (vapor) and 5 mol of water (W) (liquid) as the molar ratio entering the reactor is 1:5.

Need heat required to raise this stream from 25 ºC to 80 ºC.

From Table C.1, C_p^{ig}/R for E = $-0.385 + (23.463 \times 10^{-3})*T - (9.296 \times 10^{-6})*T^2$

From Table C.2, C_p/R for liquid W = $8.712 + (1.25 \times 10^{-3})*T - (0.18 \times 10^{-6})*T^2$

For the mixture, the aggregate C_p = 1*(C_p for E) + 5*(C_p for W) given their feed ratio

Thus, for the mixture, $C_p/R = (-0.385 + 5*8.712) + (23.463+5*1.25)\times10^{-3}*T - (9.296+5*0.18)\times10^{-6}*T^2$

or C_p/R of the mixture = $43.175 + (29.713 \times 10^{-3})*T - (10.196 \times 10^{-6})*T^2$

Integration of $(C_p/R)dT$ over the limits of temperature (298 K to 353 K) gives

$\Delta H/R = 43.175*(353 - 298) + (14.856 \times 10^{-3})*(353^2 - 298^2) - (3.399 \times 10^{-6})*(353^3 - 298^3)$

or $Q = \Delta H = (2374.6 + 531.9 - 59.6\text{ K})R = (2847\text{ K})*R$ = **23.7 kJ heat added per mole E in feed**

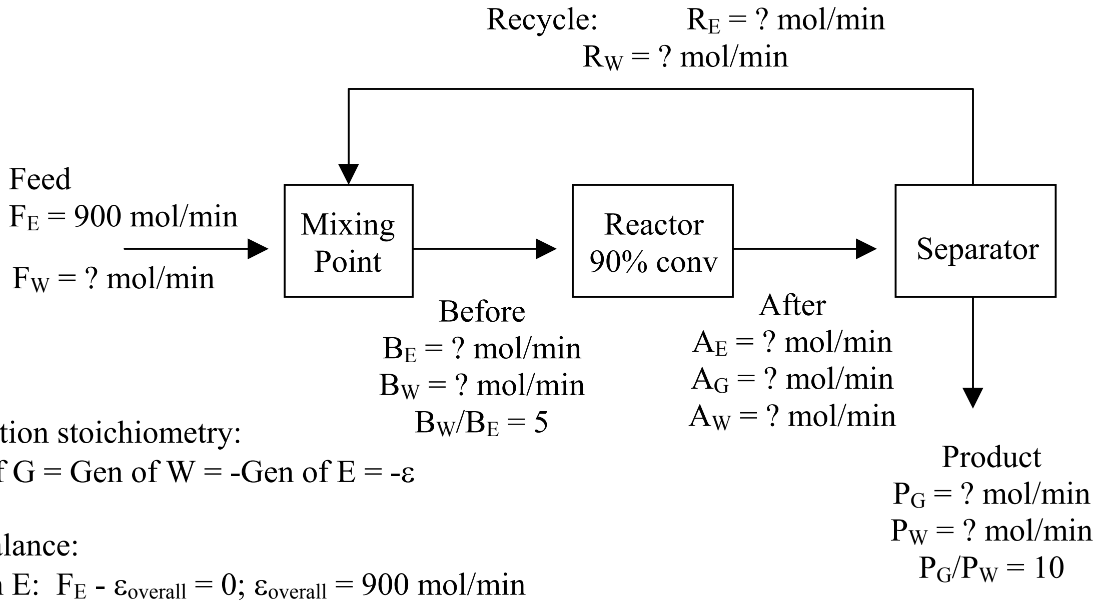
ii) At 100% conversion, 1 mole of E generates 1 mole of G by reaction stoichiometry. Here, the reaction proceeds with a single pass conversion of 90%. Thus, for every 1 mole of E feed to the process/reactor, 0.9 mole of G exit the reactor. As all G exits in bottom stream, a process with a 1 mole basis of E as feed produces 0.9 mole of G in the product stream.

The heat requirement will be (2.66 kJ/mole E in feed)*(1 mol E in feed)/(0.9 mol G in product) or (23.7/0.9) kJ/mol G in product or **26.3 kJ/mol G in product**.

b) The generation of ethylene glycol by the process examined in a) generates an environmentally unfriendly aqueous waste stream that contains ethylene oxide, a carcinogen. To remedy this situation, a modified process has been developed where the water-rich stream containing ethylene oxide that exits the separation unit is instead recycled back to mix with the input streams to the reactor. As in a), the molar ratio of water to ethylene oxide that enters the reactor is 5, the reaction proceeds with 90% conversion of the entering ethylene oxide through a single-pass through the reactor, and an analysis of the ethylene glycol product shows that it has an ethylene glycol to water molar ratio of 10 and contains no ethylene oxide. If the flow rate of ethylene oxide into the process is 900 mole/min, determine:

i) the flow rate of water entering the process,
ii) the flow rate and composition of the product stream, and
iii) the flow rate and composition of the stream exiting the reactor.

Solution: Begin by drawing a flow sheet and include known/given information



From reaction stoichiometry:

Gen of G = Gen of W = -Gen of E = $-\varepsilon$

Overall balance:

On E: $F_E - \varepsilon_{overall} = 0$; $\varepsilon_{overall} = 900$ mol/min

On G: $0 + \varepsilon_{overall} = P_G$; $\mathbf{P_G} = 900$ mol/min **ans to ii)**

As $P_G/P_W = 10$, then $\mathbf{P_W} = 0.1P_G = 90$ mol/min **ans to ii)**

On W: $F_W - \varepsilon_{overall} = PW$; thus $\mathbf{F_W} = (\varepsilon_{overall} = 900) + (P_W = 90) = 990$ mol/min **ans to i)**

Around Separator

On G: $\mathbf{A_G} = P_G = 900$ mol/min **ans to iii)**

Around Reactor (generation term = ε_R; could be different than $\varepsilon_{overall}$)

On G: $0 + \varepsilon_R = A_G = 900$ mol/min (from above); thus $\varepsilon_R = 900$ mol/min

On E: $B_E - \varepsilon_R = A_E = (1-0.9)B_E$ (as 90% of B_E is converted in the reactor); $\varepsilon_R = 0.9B_E$

As $\varepsilon_R = 0.9B_E$ and $\varepsilon_R = 900$ mol/min, then $B_E = 1000$ mol/min

As $B_W = 5\ B_E$ (given in problem statement); $B_W = 5000$ mol/min

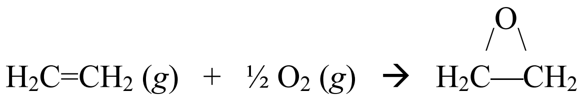
As $A_E = B_E - \varepsilon_R$, then $\mathbf{A_E} = (1000 - 900)$ mol/min = 100 mol/min **ans to iii)**

On W: $B_W - \varepsilon_R = A_W$; $(5000 - 900)$ mol/min = A_W or $\mathbf{A_W} = 4100$ mol/min **ans to iii)**

(For completeness (not necessary), $R_E = A_E = 100$ mol/min and $R_W = 4010$ mol/min.)

Problem 2 (25 points)

Ethylene oxide is produced by the partial oxidation of ethylene:

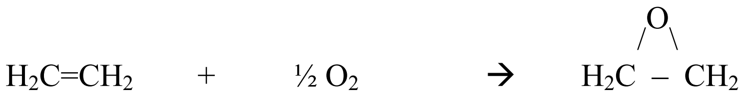


$$H_2C{=}CH_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_2C\overset{O}{-}CH_2$$

Both ethylene and oxygen are supplied to a reactor at 25 ºC and 100 bar. Determine the relative *volumetric* flow rates for the two compressed gases (i.e., cm^3 per second of ethylene / cm^3 per second of oxygen) into the reactor required to supply a stoichiometric feed. At the given conditions, ethylene and oxygen do NOT behave as ideal gases. To receive full credit, your solution should yield a final numerical answer rather than leaving equations; however, answers assuming ideal gas behavior will receive no credit.

Solution:

Reaction:



$$H_2C{=}CH_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2C\overset{O}{-}CH_2$$

Stoichiometric feed → molar ratio of ethylene to oxygen is 2:1.

T = 298.15 K and P =100 bar (same for both streams)

Since ideal gas is not a good representation of the system, we use generalized correlation.

	Ethylene	**Oxygen**	
$\mathbf{P_c}$	50.4 bar	50.43 bar	
$\mathbf{T_c}$	282.3 K	154.6 K	from Appendix B
ω	0.087	0.022	
$\mathbf{P_r = P / P_c}$	(100 bar / 50.4 bar) = 1.984	(100 bar / 50.43 bar) = 1.983	
$\mathbf{T_r = T / T_c}$	(298.15 K / 282.3 K) = 1.056	(298.15 K / 154.6 K) = 1.929	
$\mathbf{Z^0}$	0.35	0.95	from tables E.3 and E.4 or charts
$\mathbf{Z^1}$	-0.026	0.15	
$\mathbf{Z = Z^0 + \omega Z^1}$	0.35 + 0.087 (-0.026) = 0.348	0.95 + 0.022 (0.15) = 0.953	

$Z_{eth} = 0.348$ and $Z_{O2} = 0.953$

$$Z = \frac{PV}{RT} = \frac{PV^t}{nRT} \rightarrow V^t = \frac{nRTZ}{P}$$

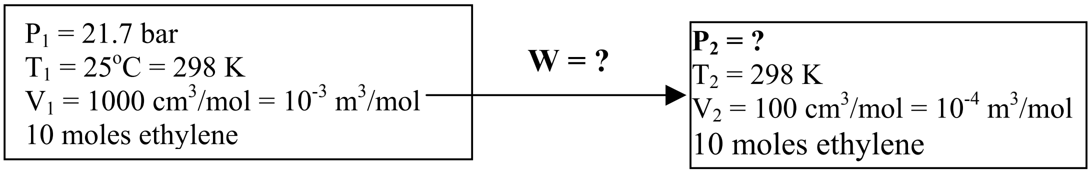
$$\frac{V^t_{eth}}{V^t_{O2}} = \frac{\dfrac{n_{eth}RTZ_{eth}}{P}}{\dfrac{n_{O2}RTZ_{O2}}{P}} = \frac{n_{eth}Z_{eth}}{n_{O2}Z_{O2}} = \frac{2}{1}\cdot\frac{0.348}{0.953} = \mathbf{0.73} \quad \text{(ans)}$$

The relative volumetric flow rate of ethylene to oxygen = 0.73 (cm^3/s ethylene per cm^3/s oxygen).

Problem 3 (25 points)
Ten moles of ethylene are to be compressed isothermally from their initial state (P = 21.7 bar, T = 25 ºC, and V = 1000 cm^3/mol) to 100 cm^3/mol. Under these conditions, the behavior of the gas is well described by the van der Waals equation of state.

i) Estimate the pressure at the final state.
ii) Determine the work required to perform this compression.

Solution:



$P_1 = 21.7$ bar
$T_1 = 25^oC = 298$ K
$V_1 = 1000$ cm^3/mol $= 10^{-3}$ m^3/mol
10 moles ethylene

W = ?

P_2 = ?
$T_2 = 298$ K
$V_2 = 100$ cm^3/mol $= 10^{-4}$ m^3/mol
10 moles ethylene

van der Waals
EOS applies

i) Estimate P_2.

$$\text{van der Waals: } P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

To calculate a and b, from Appendix B: $P_c = 50.4$ bar, $T_c = 282.3$ K for ethylene

$$a = 0.4218750\frac{R^2T_c^2}{P_c} = 0.4218750\frac{(8.314\ \text{J/mol K})^2(282.3\ \text{K})^2}{50.4\ \text{bar}\cdot(10^5\ \text{Pa}/1\ \text{bar})} = 0.461\,(\text{m}^3/\text{mol})^2\ \text{Pa}$$

$$b = 0.125\frac{RT_c}{P_c} = 0.125\frac{(8.314\ \text{J/mol K})(282.3\ \text{K})}{50.4\ \text{bar}\cdot(10^5\ \text{Pa}/1\ \text{bar})} = 5.821\cdot10^{-5}\ \text{m}^3/\text{mol}$$

Then,
$$P_2 = \frac{RT_2}{(V_2-b)} - \frac{a}{V_2^{\,2}} = \frac{(8.314\ \text{J/mol K})(298\ \text{K})}{(10^{-4}-5.821\cdot10^{-5})\ \text{m}^3/\text{mol}} - \frac{0.461\,(\text{m}^3/\text{mol})^2\ \text{Pa}}{(10^{-4}\ \text{m}^3/\text{mol})^2}$$

$$P_2 = 1.318\cdot10^7\ \text{Pa} = \mathbf{131.8\ bar}\quad \text{(ans)}$$

ii) Determine work required for the compression.

$$W = -\int_{V_1}^{V_2} nPdV = --n\int_{V_1}^{V_2}\frac{RT}{(V-b)} - \frac{a}{V^2}dV \qquad \text{(substituting van der Waals expression for P)}$$

$$W = -n\left[RT\cdot\ln(V-b) + a\left(\frac{1}{V}\right)\right]_{V_1}^{V_2} = -n\left[RT\cdot\ln\left(\frac{V_2-b}{V_1-b}\right) + a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)\right]$$

$$W = -10\ \text{mol}\left[(8.314\ \text{J/mol K})(298\ \text{K})\cdot\ln\left(\frac{(10^{-4}-5.821\cdot10^{-5})\ \text{m}^3/\text{mol}}{(10^{-3}-5.821\cdot10^{-5})\ \text{m}^3/\text{mol}}\right)\right.$$
$$\left. + 0.461\,(\text{m}^3/\text{mol})^2\ \text{Pa}\left(\frac{1}{10^{-4}\ \text{m}^3/\text{mol}} - \frac{1}{10^{-3}\ \text{m}^3/\text{mol}}\right)\right]$$

$$W = 35680\ \text{J} = \mathbf{35.68\ kJ}\quad \text{(ans)}$$

The sign of the work makes sense: for compression, work is being done *on* the system.