CHEMICAL ENGINEERING 200 Mid-Term Solutions

Test: Oct. 23, 2013.
80 minutes (18:05-19:25)

SPECIAL INSTRUCTIONS: *This is a closed book test. You are permitted only the equation sheet (Appendix 1 attached) provided to you with the test, plus the compressibility charts and Appendix B from Felder and Rousseau. You may use the least-squares feature on your calculator to aid you in answering any linear fitting equations if not specified otherwise. Please answer in the given booklet neatly. Sloppy, disorganized work may not be graded. Justify clearly any assumptions you make and provide the source of any data you use which is not supplied. Final answers should be provided with the correct number of significant digits.* ***This test consists of four questions on two pages and 35 points.*** *Please bring any discrepancy to the attention of the invigilator – you are responsible for ensuring your test is complete.*

Problem 1 (5 points): Many enzyme-substrate complexes encountered in biological systems are modeled with the so-called Michaelis-Menten kinetic model. Here, the reactant that is catalyzed by the enzyme (E) is termed the substrate, S. Overall, the reaction to produce the product P is given by:

$S + E \rightarrow P + E$.

The kinetic model assumes that the enzyme binds to substrate to form an enzyme-substrate complex ES in a reversible equilibrium reaction. The product is then released from the complex and the enzyme is regenerated. The rate of product generation is given by the following.

$\frac{d[P]}{dt} = \frac{k_b[E]_0[S]}{\frac{k_{a'}+k_b}{k_a}+[S]} = \frac{k_b[E]_0[S]}{K_M+[S]}$ where K_M is defined as the Michaelis constant.

Take the rate of product formation $\frac{d[P]}{dt} = V$ and the maximum rate of product formation to occur at high [S] such that $\left.\frac{d[P]}{dt}\right|_{high[S]} = k_b[E]_0 = V_{\max}$.

a) Re-arrange the equation above in terms of V and $V_{\max}$ and show how you can extract K_M and k_b from an appropriate plot.

$\frac{d[P]}{dt} = V = \frac{V_{\max}[S]}{K_M+[S]}$ **(1 point)**

$$\frac{1}{V} = \frac{1}{V_{\max}} + \frac{K_M}{V_{\max}}\frac{1}{[S]}$$

Thus, a plot of 1/V versus 1/[S] should be linear with a slope of $K_M/V_{\max}$, which would provide the ratio of k_b/K_M and an intercept of $1/V_{\max}$, which would provide k_b. **(1 point)**

b) Given the following data and the relationship derived in a), determine K_M and k_b.

The regression can be done after suitable transformation of the variables. The equation is:

$\frac{1}{V} = 2.0\frac{1}{S} + 46$ **(1 point)**

From the intercept, k_b can be determined.

$$\frac{1}{V_{\max}} = 46\frac{L \cdot s}{mol}$$

$$\therefore k_b = \frac{V_{\max}}{E_0} = \frac{1}{46}\frac{mol}{L \cdot s}\frac{1}{1.25x10^{-3}}\frac{L}{mol} = 17s^{-1}$$ **(1 point)**

The slope can be used to determine K_M.

$$slope = 2.0\ s = \frac{K_M}{V_{\max}}$$

(1 point)

$$\therefore K_M = 2.0\ s \cdot V_{\max} = 2.0\ s \cdot \frac{1}{46}\frac{mol}{L \cdot s} = 0.044\ \frac{mol}{L}$$

$\frac{dP}{dt}$ **(mol L^{-1} s^{-1})**	**[S] (mol L^{-1})**
0.0040	0.010
0.0080	0.025
0.0125	0.050
0.0160	0.20

(initial enzyme concentration = $[E]_0 = 1.25 \times 10^{-3}$ mol L^{-1})

Problem 2 (15 points): Formaldehyde is used in many industrial products. For example, it is used as a monomer with phenol to produce phenol formaldehyde resins used in circuit boards, credit cards, insulating materials etc. Formaldehyde (CH_2O) is produced by the catalytic oxidation of methanol (CH_3OH). A side reaction however consumes some of the formaldehyde to produce formic acid (CH_2O_2).

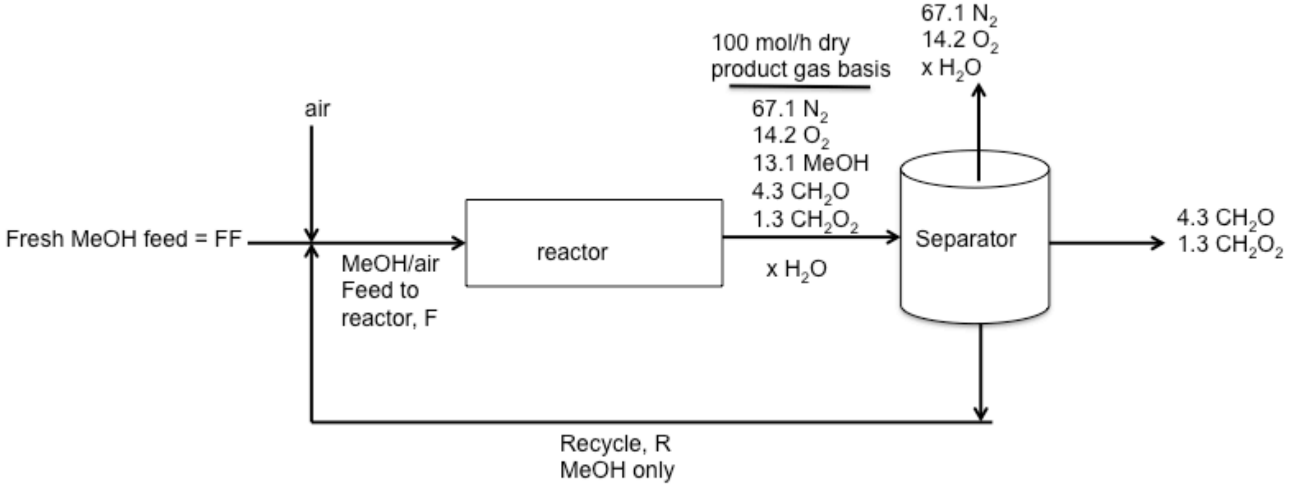
$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O$$

$$CH_2O + \frac{1}{2}O_2 \rightarrow CH_2O_2$$

Methanol and air are fed to a reactor. The product stream exiting the reactor consists of the following on a dry molar basis: 67.1% N_2, 14.2% O_2, 13.1% CH_3OH, 4.3% CH_2O and 1.3% CH_2O_2. The reactor effluent is then fed to a separator unit where the formaldehyde and formic acid are removed in one stream, while water, N_2 and O_2 are removed in another stream. The entire methanol from the separatory unit is recycled with fresh methanol feed to the reactor.

Determine the following:

- Draw a process diagram based on the description above **(2 points)**



- The composition of the feed stream to the reactor (i.e. air to methanol ratio)

Basis: 100 mol/h of dry product gas exiting reactor.

N_2 balance: N_2 flow in = 67.1 mol/h so O_2 flow in = (21/79)67.1 mol/h = 17.6 mol/h
Air fed = 84.7 mol/h. **(1 point)**
Use the extents of reaction around the reactor.

$$n_{CH_3OH} = n_{CH_3OH,0} - \zeta_1$$

$$n_{O_2} = n_{O_2,0} - \frac{1}{2}\zeta_1 - \frac{1}{2}\zeta_2$$

$$n_{CH_2O} = \zeta_1 - \zeta_2 \qquad \textbf{(2.5 points)}$$

$$n_{H_2O} = \zeta_1$$

$$n_{CH_2O_2} = \zeta_2$$

Thus, $n_{CH2O2} = \zeta_2$ = 1.3 mol/h. The first extent can be determined from the expression for the moles for the formaldehyde.

$$n_{CH_2O} = 4.3 = \zeta_1 - \zeta_2$$

$$\zeta_1 = 5.6\ mol/h$$

(2 points for extents)

Then, the rest of the concentrations in the product stream can be determined.

$$n_{CH_3OH} = n_{CH_3OH,0} - \zeta_1$$

$$\therefore n_{CH_3OH,0} = 13.1 + 5.6 = 18.7 mol/h$$

(1 point for MeOH, 1 point for O_2)

$$n_{O_2} = n_{O_2,0} - \frac{1}{2}\zeta_1 - \frac{1}{2}\zeta_2$$

$$n_{O_2,0} = 14.2 + 0.5[1.3 + 5.6] = 17.6\ mol/h$$

We thus have the composition of the feed stream to the reactor: 67.1 mol/h N_2, 17.6 mol/h O_2 (84.7 mol/h air) and 18.7 mol/h MeOH. (air:MeOH = 4.5:1). **(1 point)**

- The recycle ratio (i.e. ratio of total recycle to fresh feed).

We know how much MeOH was remaining from the dry gas product assay (13.1 mol/h). All of this was recycled. The MeOH feed to the reactor was 18.7 mol/h. Thus, the fresh feed of MeOH is 5.6 mol/h.
Recycle ratio = 13.1/5.6 = 2.2. **(1 point)**

- The single pass and overall conversion of methanol **(1 point)**

$$f_{MeOH,\text{single pass}} = \frac{5.6 mol.h \text{ MeOH reacted}}{18.7 mol \text{ MeOH fed to reactor}} = 0.30$$

$$f_{MeOH,\text{overall}} = \frac{5.6 mol.h \text{ MeOH reacted}}{5.6 mol \text{ MeOH fresh feed to process}} = 100\%$$

- The single pass and overall yield of formaldehyde **(1 point)**

$$yield_{\text{single pass}} = \frac{4.3 mol\ \text{CH}_2\text{O}}{18.7 mol\ \text{MeOH (if all MeOH reacts to form CH}_2\text{O)}} = 0.18$$

(1 point)

$$yield_{\text{overall}} = \frac{4.3 mol\ \text{CH}_2\text{O}}{5.6 mol\ \text{MeOH (if all MeOH reacts to form CH}_2\text{O)}} = 0.80$$

- The selectivity of formaldehyde relative to formic acid

$$selectivity = \frac{mol\, CH_2O}{mol\, CH_2O_2} = \frac{4.3}{1.3} = 3.3 \;\textbf{(0.5 points)}$$

Problem 3 (10 points): Liquid ammonia (NH_3) is used as a fertilizer and is spread across a field from a tank as shown in *Figure 1* below. After spreading, there is some ammonia left in the tank (tank volume of 150 ft^3) but it is now in gaseous form. The weight remaining of ammonia, based on weighing the tank before and after discharge, is 155 lb at 305.3 psig. The tank is sitting outdoors and the contents in the tank are at a temperature of 125 ^oF. You are told by your supervisor that the specific volume of NH_3 gas is 1.15 ft^3/lb, and thus there should be only 130 lb of NH_3 remaining in the tank. Is this latter statement correct? Show your calculations. (additional information: note that using ^oR is akin in imperial units to using K for SI units).

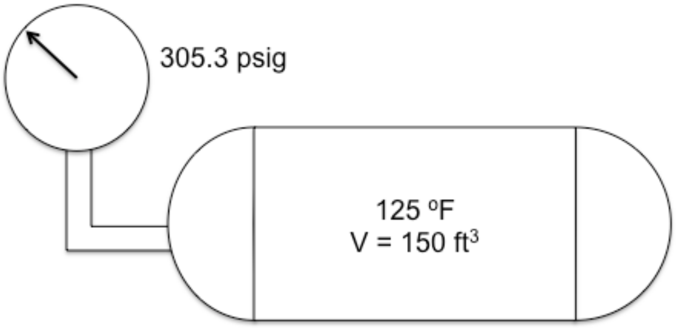


Figure 1: Tank that is used to store ammonia.

$P_{absolute}$ = 305.3 psig + 14.7 psi (atmospheric) = 320 psia **(1 point)**

T(^oR) = 125 ^oF + 460 ^oR = 585 ^oR **(1 point)**

Gas constant: $R = 10.732 \frac{psi\, ft^3}{lb\,mol \cdot {}^oR}$ **(1 point)**

Taking a 1 lb mass basis and assuming that the gas behaves ideally, the specific volume can be determined.

$$V = \frac{nRT}{P} = \frac{\dfrac{lb_m}{17\dfrac{lb_m}{lbmol}} \cdot 10.732 \dfrac{psi\, ft^3}{lb\,mol \cdot {}^oR} \cdot 585 {}^oR}{320\, psi} = 1.15 \frac{ft^3}{lb_m} \;\textbf{(1 point)}$$

Mass of contents inside = 150 ft^3/1.15 ft^3/lb_m = 130 lb_m. **(1 point)**

Therefore, the supervisor assumed that the gas was behaving as an ideal gas.

Now, let's lift that assumption and assume that the gas is non-ideal.

$$P_r = \frac{P}{P_c} = \frac{320}{1636} = 0.2 \;\textbf{(1 point)}$$

$$T_r = \frac{T}{T_c} = \frac{585}{729.9} = 0.8 \;\textbf{(1 point)}$$

From the compressibility charts, we find that z ≈ 0.84. **(1 point)**

We can compare the ideal to non-ideal specific volumes:

$$\frac{pV_{ideal}}{pV_{real}} = \frac{RT}{zRT}$$

$$V_{real} = zV_{ideal} = 0.97 \frac{ft^3}{lb_m}$$

(1 point)

Thus, the mass inside the tank is 150 lb_m/0.97 ft^3/lb_m = 155 ft^3, which is what was actually measured. Thus the gas was non-ideal and this accounted for the difference in the mass. **(1 point)**

Problem 4 (5 points): Humid air with 25 mol% water vapour is cooled isobarically at 1 atm from 200ºC to 15ºC.

a) Determine the dew point and the degrees of superheat of the feed air.
b) How much water condenses per cubic meter of feed gas?

a) Using Antoine's equation or Table B.3 for vapour pressure of water. At the dew point,

$$p_{H_2O} = p^*_{H_2O}(T_{dp})$$

$$p_{H_2O} = 0.25 \cdot 760 mm\ Hg = 190 mm\ Hg$$

By interpolation from vapour pressure tables, $T_{dp} = 65.3^o C$.

(0.5 points for partial pressure and 0.5 points for $\mathbf{T_{dp}}$)

Thus, the degree of superheat of feed air = 200 ºC - 65.3 ºC = 134.7 ºC ≈ 135 ºC. **(1 point)**

b) How much water condenses?

At 15 ºC, the composition of water in the air is:

$$y_{H_2O} = \frac{p_{H_2O}}{P} = \frac{p^*_{H_2O}(15^o C)}{P} = \frac{12.788 mm\ Hg}{1 atm \cdot 760 mm\ Hg} = 0.017 \frac{mol\ H_2O}{mol}$$ **(1 point)**

The product from the vessel is air (with some water vapour) with amount Q_1 (moles) and condensed water with amount Q_2 (moles). A dry air balance gives the following (taking 100 mol of inlet air):

$$75 mol\ air = Q_1(1 - y_{H_2O})$$

$$Q_1 = \frac{75\ mol\ air}{1 - 0.017} = 77 mol$$ **(1 point)**

$$\therefore Q_2 = 23 mol\ H_2O\ condensed.$$

$$V = \frac{nRT}{P} = \frac{100 mol}{1 atm} \cdot \frac{0.08206 L \cdot atm}{mol \cdot K} \cdot 473 K \cdot \frac{m^3}{10^3 L} = 3.9 m^3 feed\ gas$$ **(0.5 points)**

$$\therefore \frac{23 mol\ H_2O}{3.9 m^3 feed\ gas} \cdot 18 \frac{g}{mol} = 0.11 \frac{kg\ water}{m^3 feed\ gas}$$ **(0.5 points)**