CBE3223 – Kinetics and Reactor Design

Midterm Exam II

This examination is closed book, closed notes, open calculators, and you may use a one-page (front and back) equation/study sheet. Standard or graphing calculators are okay, but no smart phones, computers, or tablets are allowed except to email or chat with your instructor.

Please be sure to print your name, Net ID #, instructor, the subject "CBE-UY-3223", and the date on the first page of your examination solution. Please be sure to upload all of your solutions as a single electronic file (including any derivations, explanations, or calculated answers).

This is an untimed exam that must be submitted within 24 hours. Please note that you are expected to complete all solutions, from scratch to final draft, on your own and within the 24-hour window. You are expected to follow the NYU Tandon Student Code of Conduct and NYU's Policy on Academic Integrity for Students. You are not allowed to communicate the questions or any solutions to this examination with anyone until after the completion of the 24-hour window, i.e., not until after 12:30pm ET on April 13, 2021.

If you have a question for clarification while taking the examination, then you may either chat with the instructor in Zoom during the in-class 80 min examination period that begins at 12:30pm ET on April 12, 2021, in Zoom office hours, or you may email the instructor outside this class time but within the 24-hour window.

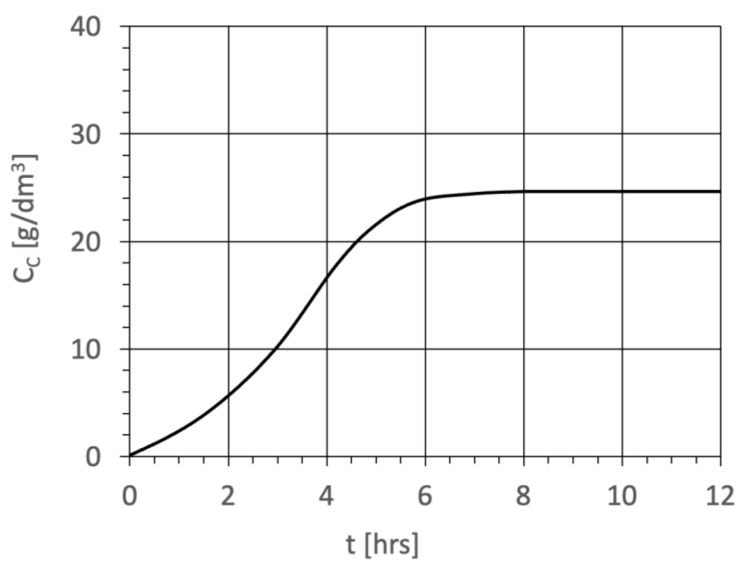
Problem	**%**
1	15
2	15
3	20
4	15
5	20
6	15
7	4
Total	**104**

1. New York City ranks among other top major U.S. cities for their number of tons of CO_2 equivalent generated each year from food waste [https://coolclimate.berkeley.edu/index]. You decide to startup a company that designs an anaerobic batch food digester that restaurants may use to reduce their carbon footprint. Microorganisms can break down pre-processed food waste and convert it into bio-oil useful for a number of applications that has a nominal resale value.

$$microorganisms + food\ waste \rightarrow more\ microorganisms + bio\text{-}oil$$

   a. **(5%)** Write all the equations that must be solved (i.e., mole balances, rate laws, and stoichiometry) to plot the concentration of microorganisms, food waste, and bio-oil product and the rates for growth, death, and maintenance as functions of time. Assume the microorganism growth rate follows the Monod equation.

   b. **(5%)** Shown below is the concentration of the microorganisms as a function of time when maintenance and death are neglected. Provided the initial concentration of food waste (C_{S0} = 400 g/dm^3) and the yield coefficient ($Y_{C/S}$ = 0.1 g/g), what should be the maximum concentration of food waste remaining in the digester within 24-hours if it takes 2 hours to clean the digester?



   c. **(5%)** Using the conditions in part (b), calculate the conversion of the food waste (X_S) and the total mass of food waste that can be converted in a 100 dm^3 digester in the 24-hour period.

2. You work for a biotechnology company that manufactures a portfolio of vaccines to treat terminal diseases caused by certain bacteria. In September 2020, your CEO calls an emergency company meeting to announce that effective immediately 15% of your operations will be diverted to manufacture a vaccine for the COVID-19 to help scale-up its production. After a debriefing with your engineering management team, you decide to use your existing chemostats for the initial step of the biosynthesis:

$$E.coli\ bacteria + S \rightarrow E.coli\ bacteria + [DNA\ Plasmids]_{E.coli\ bacteria} + byproducts$$

In this process, plasmid DNA templates (or rings of DNA) are mass produced within *E. coli bacteria* and later extracted by lysing the microorganisms.

a. **(10%)** If bacterial growth follows the Monod equation,

$$r_g = \frac{\mu_{max} C_S C_C}{K_S + C_S}$$

What is the dilution rate at which wash-out occurs? At what residence time should the reactor be operated? Assume steady-state operation and that cell death and maintenance can be neglected.

<u>*Additional information:*</u>
$\mu_{max} = 0.85\ h^{-1}$
$K_S = 2.5\ g/dm^3$
$C_{S0} = 15\ g/dm^3$

b. **(5%)** Let's now consider the case where the *E. coli* metabolism ceases once the concentration of the DNA product within the microorganisms reaches a critical concentration (C_P* with the empirical constant *n* = 0.5). If death of *E. coli bacteria* and maintenance cannot be neglected, then what other reactor scheme(s) and under what conditions could you consider and why? Please justify your answer with equations and/or derivations.

3. One month later, while enjoying your morning cup of tea, you read an email announcement from your CEO revealing your company's plans to divert additional operations for the second manufacturing step of the COVID-19 vaccine to produce 500 million doses of vaccine in 60 days. You just so happened to be the team leader of the enzymatic reactions division, and fortunately you were not leaning over your laptop when you read his message and instead spilled your hot tea on your scratch notepad. Or perhaps, unfortunately, because on your notepad you had already worked out all the derivations for the entire vaccine manufacturing process. Despite the running ink, you can make out part of your calculations but not all.

   The second manufacturing step involves an enzymatically-catalyzed transcription of mRNA on the DNA plasmids:

$$E + S + P_{mtr} \rightarrow E + P$$

Where mRNA polymerase (E) first binds to a sigma factor (S) and then transcription is initiated by the promoter (P_{mtr}) to form the mRNA product (P). On your notepad, you still can make out the first and the last elementary steps of the mechanism:

$$E + S \overset{K_S}{\leftrightarrow} E * S$$

$$E_m \xrightarrow{k_{cat}} P + E$$

You can also read the following equation, which describes the concentration of enzymes transcribing the mRNA product:

$$[E_m] = \frac{[E * S][P_{mtr}]}{K_{PS} + [E * S]}$$

Where K_{PS} is Michaelis-Menten constant for transcription. You continue to flip through the wet pages and realize the precious mRNA can also undergo degradation in the presence of enzyme R_{nase} according to the following mechanism:

$$R_{nase} + P \overset{K_R}{\leftrightarrow} R_{nase} * P$$

$$R_{nase} * P \overset{k_d}{\rightarrow} 0$$

Please complete the following – there is no time to waste!

a. **(15%)** If the three states of the mRNA polymerase (E) shown above are the only which participate in the full mechanism, then determine the maximum total R_{nase} concentration $[R_{nase,T}]_{max}$ that you can tolerate and still meet your production target on time. Assume continuous operation of four dedicated 500 dm^3 CSTRs for 12 days followed by 3 days of maintenance (i.e., 48 days of steady-state production).

Additional information:

1 mRNA vaccine dose ≈ 100 μg mRNA ≈ 0.0039 μmol mRNA
K_S = 2.6x10^{-4} μmol/dm^3
K_{PS} = 1.0x10^{-3} μmol/dm^3
K_R = 8.0 μmol/dm^3
k_{cat} = 3.9 min^{-1}
k_d = 7.2 min^{-1}
[S] = 3.0x10^{-2} μmol/dm^3
[E] = 0.13 μmol/dm^3
[P_{mtr}] = 3.0x10^{-2} μmol/dm^3
τ = 60 min

b. **(5%)** What could be done to minimize the impact of the enzymatic degradation on the amount of mRNA product wasted?

4. **(15%)** The gas-phase solid catalyzed reaction,

$$3H_2 + N_2 \leftrightarrow 2NH_3$$

is carried out over iron catalyst and proceeds by the following mechanism,

$$H_2 + 2S \leftrightarrow 2H\cdot S$$
$$N_2 + 2S \leftrightarrow 2N\cdot S$$
$$N\cdot S + H\cdot S \leftrightarrow HN\cdot S + S$$
$$NH\cdot S + H\cdot S \leftrightarrow H_2N\cdot S + S$$
$$H_2N\cdot S + H\cdot S \leftrightarrow NH_3\cdot S + S$$
$$NH_3\cdot S \leftrightarrow NH_3 + S$$

Derive a rate law assuming that the dissociative adsorption of N_2 is the rate limiting step. You may also assume that the dissociative adsorption of H_2 is very weak, since this exothermic reaction is carried out at elevated temperatures.

<u>**Solution:**</u> **What's wrong with this solution?** Justify your answer with derivations and be sure to show all your work.

$$-r'_{N2} = k_{N2}\left(P_{N2}C_v^2 - \frac{C_{N*S}}{K_{N2}}\right)$$

$$\frac{r_{AH2}}{k_{AH2}} \approx 0 \qquad C_{H*S} = \sqrt{K_{H2}P_{H2}}C_v$$

$$\frac{r_{S1}}{k_{S1}} \approx 0 \qquad C_{N*S} = \frac{C_v}{K_{P1}C_{H*S}}$$

$$\frac{r_D}{k_D} \approx 0 \qquad C_{NH3*S} = K_D P_{NH3} C_v$$

$$C_t = C_v + C_{H*S} + C_{N*S} + C_{NH3*S}$$

Substituting and solving gives,

$$-r'_{N2} = r'_{NH3} = \frac{k\left(KP_{N2} - \frac{P_{NH3}}{P_{H2}^3}\right)}{\left[1 + \sqrt{K_{H2}P_{H2}} + \frac{K_D P_{NH3}}{K_{P1}K_{P2}K_{P3}(K_{H2}P_{H2})^{3/2}}\right]^2}$$

$$rate = \frac{(kinetic\ factor)(driving - force\ group)}{(adsorption\ group)^n}$$

Where,

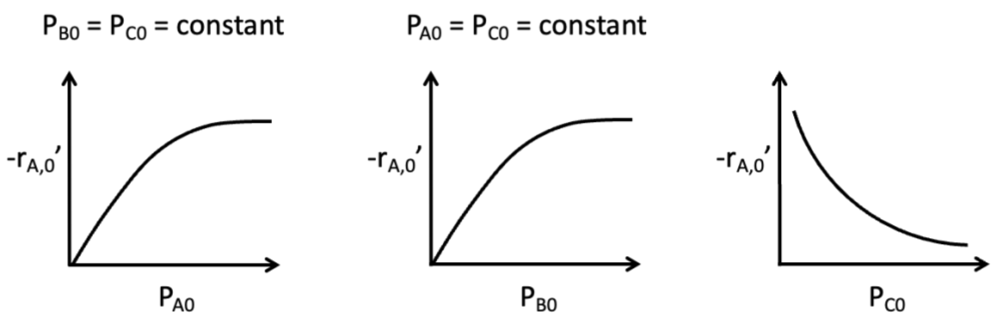
$$k = \left(\frac{k_{N2}C_t^2}{K_{H2}^3 K_{N2}}\right)\left(\frac{K_D}{K_{P1}K_{P2}K_{P3}}\right)^2$$

$$K = K_{H2}^3 K_{N2}\left(\frac{K_{P1}K_{P2}K_{P3}}{K_D}\right)^2$$

5. **(20%)** The following gas-phase reaction,

$$A + B \leftrightarrow C$$

is carried out over a solid catalyst that has two different types of surface sites S and S'. Experimental rate data is plotted in the figures below.



What can you say given the figures above? Be sure to propose a mechanism and use it to derive a rate law consistent with the data.

1. Species A could be adsorbed on the surface but only very weakly adsorbed.
2. Species A is not adsorbed on the surface.
3. Species B is adsorbed to one type of site on the surface.
4. Species A is adsorbed to one type of site on the surface.
5. Species C is adsorbed on the surface.

A. 1 and 2 are true.
B. 3 and 4 are false.
C. 1 and 4 are false.
D. 4 and 5 are true.
E. 2 and 5 are true.

6. **(15%)** Please indicate whether each of the following statements is true ("T") or false ("F"). Please write the correct answer in your bluebook.

T F Continuous-flow reactors can reduce the footprint requirements compared to batch reactors, and hence reduce the building space, energy requirements, and greenhouse gas emissions of pharmaceutical manufacturing.

T F Consider the elementary dehydrogenation $C_6H_{12} \leftrightarrow 3H_2 + C_6H_6$ carried out in an isothermal IMRCF reactor. Given the choice between two different membrane materials, one where the mass transfer coefficients $k_{C,H2} = 3k_{C,C6H6}$ and the other where $3k_{C,H2} = k_{C,C6H6}$, one should choose the second membrane to achieve a higher conversion for the same reactor temperature, feed conditions, and reactor volume.

T F Mixing in a single-phase, laminar flow (*Re* < 1) microreactor is accelerated by increasing the characteristic microchannel dimensions, and thus why microreactor technology can be used to measure kinetics where reactions occur within seconds-to-minutes.

T F Consider two elementary reactions in parallel where reactants A and B can form either desired (D) or undesired (U) product. Provided the following rates of reaction:

$$r_D = 10^9 exp(-10{,}000K/T)C_A^{2/3}C_B$$

$$r_U = 10^{13} exp(-15{,}000K/T)C_A C_B$$

The reactions should be carried out at the highest possible temperature in a semi-batch reactor where a small amount of A is added to B.

T F Membrane reactors can be used to increase conversion when the reaction is thermodynamically limited, as well as to increase the selectivity when multiple reactions are occurring. Replacement of conventional reactors by catalytic membrane reactors has an equivalent energy savings on the order of 10 trillion BTUs per year.

T F In an isothermal semi-batch reactor, the liquid volume is transient and if the reaction order is other than zero- or first-order, one must use numerical techniques to determine the concentrations and conversation as a function of time.

7. **(4%) Extra credit:** Recall the catalytic olefin polymerization that was discussed during lecture on complex reactions. In this example, artificial neural networks were used for:

   1. Temperature control of a microfluidic reactor and the reverse prediction of missing rate constants in the kinetics
   2. High-throughput screening of the activator and the monomer chemistry using microfluidics with robotics
   3. Prediction of the reaction space topology of a metallocene catalyst using microfluidics experiments
   4. Analyses of polymerization abstract word embeddings with natural language processing
   5. Prediction of the resultant polymer's properties based on the kinetics

   A. 2 and 5 are true.
   B. 1 and 4 are false.
   C. 4 and 5 are true.
   D. 1 and 2 are false.
   E. 1 and 3 are true.

Relationships:

$$C_C = Y_{C/S}(C_{S0} - C_S)$$

$$C_C = Y_{C/S}\left[C_{S0} - \frac{DK_S}{\mu_{max} - D}\right]$$

$$D_{maxprod} = \mu_{max}\left(1 - \sqrt{\frac{K_S}{K_S + C_{S0}}}\right)$$