CBE3223 – Kinetics and Reactor Design

Midterm Exam I

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).

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 March 9, 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 March 8, 2021, during Zoom office hours, or you may email the instructor outside this class time but within the 24-hour window.

1. **(15%)** The following elementary gas-phase reaction,

$$A \xrightarrow[cat]{} B$$
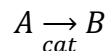
   is carried out in a fluidized CSTR followed by a packed-bed reactor (PBR) in series. Calculate the conversion exiting the CSTR if twice the weight of catalyst is used in the PBR downstream to achieve 90% conversion. Assume both reactors are operating isothermally at the same temperature and no pressure drop in either reactor.

2. The Haber-Bosh process is perhaps one of the most important industrial chemical reactions ever developed. Approximately 70-90% of ammonia synthesized by the reaction is used to make fertilizer, and ~50% of the world's food production relies on ammonia fertilizer. The remainder of the ammonia goes toward making pharmaceuticals, materials, and other chemicals. [Boerner, *C&EN*, 2019, 97(24), https://cen.acs.org/environment/green-chemistry/Industrial-ammonia-production-emits-CO2/97/i24] Chemists and engineers around the globe are trying to make ammonia synthesis more sustainable because the Haber-Bosch process,

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \Leftrightarrow NH_3$$
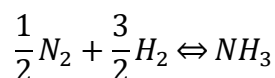
   accounts for ~1.4% global carbon dioxide emissions and consumes ~1% of the world's energy. This elementary gas-phase reversible reaction is carried out in an isothermal flow reactor. The molar feed is stoichiometric in N_2 and H_2, at a constant pressure of 15 atm and at a temperature of 227°C.

   a. **(15%)** Choosing H_2 as the basis for your calculation, find 90% of the equilibrium conversion, X_{ef}, given that $K_C = 10$ dm^3/mol.

   b. **(5%)** How would your answer to part (a) change if the reaction were instead carried out in a constant volume isothermal batch reactor?

3. **(15%)** Liquid-phase photochemical activation of Iridium (Ir^{III}) polypyridyl complexes, from their ground state to an excited catalytic state, are used in the pharmaceutical industry in photoredox catalysis:
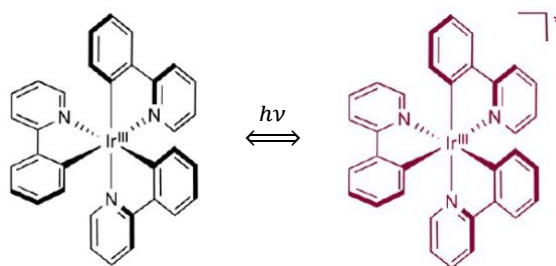

   The Ir^{III} complexes convert visible light into chemical energy to carry out useful carbon-carbon bond formations with organic substrates [Shaw *et al.*, *J. Org. Chem.*, 2016, 81, 6898-6926;

DOI: 10.1021/acs.joc.6b01449]. This green chemistry when performed in flow reactors can reduce the amount of chemical waste in pharmaceutical manufacturing compared to conventional batch reactor designs.

The photochemical activation shown above is carried out in an isothermal plug flow reactor (PFR) fitted with an LED source. What fraction of the intensity of light is necessary to achieve 95% conversion of the ground state Ir^{III} complex if the reaction is reversible, elementary, and the space time $\tau = 0.1$ min? Assume the specific reaction rate k_A is 70 min^{-1}, $K_C = 20$, and pure A is fed to the reactor.

4. Xylenes are used in solvents for a variety of commercial applications, as ingredients in aviation fuel and gasoline, and as precursors for polymers and fine chemicals. The solvent has also been used in upstream organic scale remediation where reservoir production increases impact about $1200 U.S. gross domestic product per barrel of crude oil equivalent. The gas-phase methylation of toluene with methanol to form xylenes,

$$C_6H_5CH_3 + CH_3OH \xrightarrow[cat]{} (CH_3)_2C_6H_4 + H_2O$$
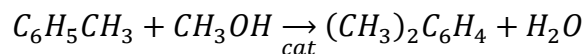
is carried out over a zeolite catalyst in an isothermal packed-bed reactor (PBR). The feed is equimolar in toluene and methanol, and the entering pressure is 10 atm.

Additional information:
$F_{A0} = 50$ mol/min
Specific reaction rate, $k_A = 0.5$ mol/(atm^2*kg-cat*min)
Pressure drop parameter, $\alpha = 0.037$ kg^{-1}

a. **(10%)** Choosing toluene as the basis of your calculation, what catalyst mass is needed to achieve 80% conversion if there is no pressure drop?

b. **(10%)** By how much would the conversion decrease if there is pressure drop in the PBR?

5. The Buchwald-Hartwig amination is a palladium-catalyzed C-N bond formation and perhaps the most widely used chemical reaction in medicinal chemistry [Dorel, *et al.*, *Angew. Chem. Int. Ed.*, 2019, 58(4), 17118-17129; DOI: 10.1002/anie.201904795]. You work for a major pharmaceutical company located in Indianapolis, IN, USA, and you want to continuously manufacture a biaryl amine that is a precursor for more than one of your blockbuster drugs. Until now, your company manufactured the compound in a batch reactor, but continuous manufacture with flow reactors could improve the yield, reduce the amount of chemical waste generated, and significantly decrease the footprint of your manufacturing facilities. According to the U.S. Department of Energy, the buildings sector accounts for about 76% of electricity use and 40% of all U.S. primary energy use and associated greenhouse gas (GHG) emissions. The non-elementary, liquid-phase Buchwald-Hartwig amination of an aryl amine with an aryl halide to form a biaryl amine is described by,

$$Ar''X + Ar'NH_2 \xrightarrow{cat} Ar'HNAr'' + NaX$$
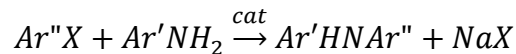
Oxidative addition of the aryl halide (Ar"X) to an organometallic complex in the mechanism controls the overall reaction rate, and thus the rate is first order in the aryl halide (Ar"X) and zero order in the aryl amine. The turnover number of the homogenous organometallic catalyst is sufficiently high such that its concentration remains constant, and thus $k' \approx k_A C_{cat0}$. The reaction generates an insoluble salt by-product (NaX), which makes it difficult to carry out the transformation in your company's 10 dm³ PFR without clogging the flow reactor. So, you decide instead to design a cascade of CSTRs in series to handle the solid-liquid slurry.

a. **(10%)** How many 2.0 dm³ CSTRs in series are needed to achieve the same conversion as the PFR if the volumetric flowrate is constant at 1.0 dm³/min and all reactors operate at an ambient indoor building temperature of 20°C? Choose the aryl halide (Ar"X) as the basis of your calculation. Assume the rate constant at this temperature $k' = 0.3$ min⁻¹ and the activation energy $E_A = 65$ kJ/mol.

b. **(5%)** After operating for 3-days in February you discover that the conversion exiting the last CSTR has dropped by 6% and your losing revenue fast. Further investigation during lunch, while the bowl of hot soup on your office desk goes cold, confirms that your intern last summer did purchased the CSTRs you requested. These reactors have an overflow as the exiting product stream to handle solid-liquid slurries, but they also ensure a fixed liquid level in each reactor. Your chemistry department designed the organometallic catalyst so well that you can operate the reactors without any heaters. What could have gone wrong that the conversion dropped? Please support your answer using calculations.

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   The reaction rate is related to the potential energy barrier height and to the conversion of translational energy into potential energy. The rate increases with the increasing fraction of collisions that have sufficient energy to cross over the barrier and form products.

> T   F   A reaction rate is independent of the temperature as the temperature goes to infinity.

> T   F   The rate constant for an irreversible, heterogeneously catalyzed, gas-phase, first-order reaction (A → products) is greater than its true value if measured in a PBR and significant pressure drop was neglected.

> T   F   The activation energy is the maximum increase in the potential energy of the products that must be provided to transform the reactants into products.

T   F   For two isothermal PFRs in series, of the same volume, in which there is no pressure drop, introducing a separator after the first reactor to remove the product would increase the overall conversion exiting the second reactor for a gas-phase reversible isomerization.

T   F   One can determine the fraction of molecular collision that have energies greater than the activation energy, E_A, by integration of the Maxwell-Boltzmann Distribution of Molecular Velocities from E_A to infinity.

7. **(4%) Extra credit:** Define the Damköhler number, both conceptually and mathematically, for a second order irreversible liquid-phase reaction. Use your answer to derive an expression for the Damköhler number in terms of the entrance conditions for a CSTR operating isothermally.

Relationships:

For a PFR: $\dfrac{F_A}{dV} = r_A$ and, $V = F_{A0} \int_{X_1}^{X_2} \dfrac{dX}{-r_A}$

For a PBR: $\dfrac{F_A}{dW} = r'_A$ and, $W = F_{A0} \int_{X_1}^{X_2} \dfrac{dX}{-r'_A}$

For a CSTR: $V = \dfrac{F_{A0} - F_A}{-r_A}$

$$\int_0^X \frac{dX}{1 - X} = \ln \frac{1}{1 - X}$$

$$\int_0^X \frac{dX}{(1 - X)^2} = \frac{X}{1 - X}$$

$$\int_0^W (1 - \alpha W)\, dW = W - \frac{1}{2}\alpha W^2$$

$$\frac{dp}{dW} = -\frac{\alpha}{2p}(1 + \varepsilon X)\frac{T}{T_0}$$

For $ax^2 + bx + c$,

$$p, q = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\int_0^X \frac{dX}{1 - yX} = -\frac{1}{y}\ln(1 - yX)$$

$$X_n = 1 - \frac{1}{(1 + \tau k_A)^n}$$

Gas constant, $R = 0.082 \dfrac{dm^3 * atm}{mol * K}$ and $R = 8.3145 \dfrac{J}{mol * K}$