CBE 40445 Fall 2020 Final Exam 11/16/20

1. **CSTR vs. Batch reactor** *A***—>** *M***, exothermic reaction** (55 points)

Consider a simple first order reaction of *A*—>*M*. A batch reactor will be compared to a CSTR with the required conversion, $f_A = .95$ (that is, the exit C_A concentration/molar flow will be 5% of the feed, C_{A0} .)

Consider first the batch reactor. Suppose that its volume of *V* = 100 l is filled with reactant *A* that has a concentration, $C_{A0} = 1$ mole/l. The heat capacity of the *A* and *M* are the same: $C_{DA} =$ C_{pM} = 100 J/(mole K). The initial temperature is T_{feed} = 300 K. The reaction rate constant is $k =$ 1015 Exp[-10000/*T*] (1/s) and the heat of reaction is Δ*H*r = - 5,000 J/mol.

- a. What batch time will be needed for the requisite conversation of 95% of the *A* into *M* if the temperature is kept at 300K?
- b. What quantity of heat must be removed to keep the reactor at 300K?
- c. If the reactor were operated adiabatically, what would the final temperature be?
- d. For an adiabatic reactor, the maximum reaction **rate** does not always occur at $f_A = 0$. Explain why this is so.
- e. Sketch the reactor temperature as a function of time for the adiabatic case.
- f. Under what conditions could the reactor temperature rise and then decrease during the course of a reaction?

Now, independently consider a CSRT with a feed stream of 1 I/s at 300K, where $C_{A0} = 1$ mol/l. The heat capacity of the *A* and *M* are the same: $C_{pA} = C_{pM} = 100$ J/(mole K). The reaction rate constant is $k = 10^{15}$ Exp[-10000/*T*] (1/s) and the heat of reaction is $\Delta H_r = -5,000$ J/mol.

- g. What reactor volume is needed to accomplish the requisite conversion of 95% of the *A* into *M* if the temperature is kept at 300K?
- h. If the reactor is operating at 300K, what is the heat removal rate?
- i. If an adiabatic CSTR is used to convert 95% of the 1 l/s A feed, what is the steady state temperature?
- j. For this case, what is the necessary residence time?

One additional question:

k. If the batch reactor has a feed of 50% *A* and 50% inert (that both have the same heat capacity), so that only 50 moles of *A* are in the feed, what is the final temperature if the 95% conversion is accomplished adiabatically?

2. Production of methanol from CO₂ (20 points)

Mechanistic Understanding of Alloy Effect and Water Promotion for Pd-Cu Bimetallic Catalysts in CO₂ Hydrogenation to Methanol Xiaowa Nie, \hbar^* Xiao Jiang \hbar^* Haozhi Wang \hbar^* Wenjia Luo, Michael J. Janik, \hbar Yonggang Chen, \hbar Xinwen Guo,^{**</sub>†®} and Chunshan Song*

While we all like batteries, it is hard to find a system/process that has higher volumetric and mass energy densities for storage than organic liquids. Aliphatic hydrocarbons may be best but methanol is a more accessible chemical synthesis pathway. As will many of these "green" processes, the desire is to use CO2 as the carbon source (which was presumably scrubbed from some combustion process.)

In the publication above, the reaction

$CO_2 + 3 H_2 \neq CH_3 OH + H_2 O$

is studied using a novel catalyst that is a specific formulation of palladium (.3) and copper (.7).

The accompanying news article states a conversion of 24% is achieved at between 356 and 482 F. The pressure is not given in the news article but the publication shows a plot that could have been the source of the claims where the pressure is 5 MPa and the temperature is 523K.

- a. Find the standard conditions equilibrium constant for the above reaction.
- b. Find the equilibrium constant at 523K.
- c. At 523K and 5 MPa, what is the equilibrium product mix if the gas phase were assumed to be ideal.
- d. If this is not close to 24%, what could be going wrong? (Or should we believe press releases?)
- e. What would the equilibrium conversion be if the reaction were conducted at 1 ATM and 298 K?

extra credit:

- f. The press release neglects to specify that CO is actually produced in greater amounts than methanol. What equilibrium constant describes this reaction and what would the CO, CO₂ and H_2 mix be at 523K and 5 MPa?
- g. For the conditions of this reaction explain how to deal with non-idealities for the gas fugacity.

3. Power expenditure by a flying insect. (20 points)

The typical power consumption for a flying insect of the size of a "Yellowjacket" is about 1W/g, almost all of which is used for flying. These creatures weigh about 0.1g.

On October 10, during some serious halloween decorating, a wayward Yellowjacket managed to sting Professor McCready on the ear. (Fortunately only part of a possible venom dose.)

The temperature was 74F. Most likely the offending insect flew approximately 2 meters from the nest in the ground to the ear.

Such an event could almost certainly not have occurred the previous week when the temperature was 58 F. Explain quantitatively.

4. Analysis of a sequential reaction (30 points)

Consider a reaction scheme we have seen before for A-> M using a catalyst on a surface.

$$
A + * \underset{k_{des}}{\overset{k_{ads}}{\longleftrightarrow}} A * \overset{k_2}{\rightarrow} M + *
$$

It is not too hard to show that the rate of this reaction sequence is

$$
r = \frac{k_2 K_{ads} [A] [*]_{0}}{1 + \frac{k_2}{k_{des}} + K_{ads} [A]},
$$

where

$$
K_{ads} \equiv \frac{k_{ads}}{k_{des}}
$$

- A. For which values of which parameters could the initial adsorption step be close to equilibrium?
- B. If this is not the case, could the A^* concentration be approximated as being at a steady state concentration? Explain.
- C. Adsorption experiments have provided a value of 10 I/mol for K_{ads}, also k_{des} =0.1/s. Use these rate data to "estimate" k_2 and $[^*]_0$.

D. Suppose that an inert, *B*, is present that can also reversibly adsorb on the surface as

$$
B + * \underset{k_{Bdes}}{\xleftarrow{k_{Bads}}} B * \qquad K_{Bads} = \frac{k_{Bads}}{k_{Bdes}}
$$

Explain why this inert will affect the observed reaction rate of A->M.

E. What you would have to know to quantify this effect?

5. Designing a packed bed reactor. (60 points)

For all of the reasons, it has been a grueling semester, so let's make this last problem as straight forward as possible.

You wish to design a tubular reactor that is packed with spherical catalyst pellets. Even though the reaction mechanism is complex, the high catalyst loading and excess (let's say H_2) allows the A->M (obviously a hydrogenation) to be modeled as being first order.

The heat capacity of the A and M are the same: $C_{pA} = C_{pM} = 100$ J/(mole K). The initial temperature is $T_{\text{feed}} = 300$ K. The reaction rate constant is $k = 10^{15}$ Exp[-15000/T] (1/s) and the heat of reaction is Δ*H*r = - 125,000 J/mol.

The reactor must convert 90% of the A to M.

- A. If this reaction were operated in an adiabatic reactor, what would the exit temperature be?
- B. Why is adiabatic operation not a reasonable strategy?

If the reactor is processing many kilomoles/hour, presumably, it would not be possible to use just one large tube filled with catalyst. So a bank of tubes will be needed.

The thermal conductivity for the *A* and *M* is about 0.06 W/(K-m) (and is not a significant function of pressure). The conductivity of the packing is about 1 W/(K-m). The heat capacity of the packing is 700 J/K-kg and its density is 300 kg/ $m³$. For a flow in a packed bed the convective effects are strong giving an effective dispersion coefficient of $0.001 \text{ m}^2/\text{s}$.

C. Provide an estimate of the maximum tube size.

D. If sufficient cooling exists, to keep the temperature to 400K, what is the maximum catalyst radius $(= 3 L_p)$ that allows the effectiveness to be at least 0.76 (= Tanh[1.]). Note that the effective diffusivity $(D_{TA}e)$ inside the pellet is .001 cm²/s.

As always, the void fraction, ε =0.37, the density of the gases are 10 kg/m³ and the viscosity of the gas mixture is 4X10-5 kg/(m-s).

E. If you pick as an initial value of the superficial velocity, "*U*", 1 m/s, is the pressure drop an *acceptable* value?

F. What tradeoffs could you make to get reasonable fluid mechanics while effectively using the catalyst and processing the requisite amount of material.

G. Estimate the necessary length of this reactor.

Correlation for mass transfer in a packed bed :

$$
Sh = \frac{k d_{\text{particle}}}{D_{\text{fluid}}} = \frac{.25}{\epsilon} \text{ Re}^{.425} \left(\frac{\mu}{\rho D_{\text{fluid}}} \right)^{.333}
$$

Biot number:

$$
B\dot{\mathbf{1}}_m = \frac{k_c \ d_{particle}}{D_{TA}^e}
$$

Test 3 additions

Exit time distribution:

Energy balance a batch reactor;

$$
\int_0^t U A_H (T^* - T) d\bar{t} = \frac{-\Delta H_r|_{T^0}}{v_{\ell}} n_{\ell}^0 f_{\ell} + \sum_i \left(n_i \int_{T_{\text{initial}}}^{T_{\text{final}}} C_{p_i} dT \right) \tag{9.3.8}
$$

or in differential form:

$$
UA_H(T^*-T) = \frac{-\Delta H_r|_{T^0}}{v_\ell} n_\ell^0 \frac{df_\ell}{dt} + \sum_i (n_i C_{p_i}) \frac{dT}{dt}
$$
(9.3.9)

Notice that [see Equations (1.2.10) and (1.3.2)]:

$$
\frac{n_e^0}{-v_\ell} \frac{df_\ell}{dt} = \frac{d\Phi}{dt} = rV
$$
 (9.3.10)

Energy balance for a plug flow reactor:

 r_1 V = $\frac{F_1^0 d f_1}{r_1}$ $-\mathbf{v}_1$

Energy balance for a CSTR:

$$
r_1 V = \frac{F_1^0 \, f_1^f}{-v_1} \, , \quad f_1^0 = 0
$$

out the reaction isothermally at the inlet temperature and then evaluating
reat effects at reactor outlet conditions, that is leat effects at reactor outlet conditions, that is,

$$
\dot{Q} = \frac{F_{\ell}^{0} (\Delta H_{r}|_{T^{0}}) (f_{\ell}^{f} - f_{\ell}^{0})}{(-v_{\ell})} + \sum \left(F_{i}^{f} \int_{T^{0}}^{T^{f}} C_{p_{i}} dT \right)
$$
(9.5.1)

 ϵ superscript f denotes the final or outlet conditions. For adiabatic opera- $0.$

Test 2 additions to the formula sheet

$$
N_{Ax} = -D_{AB} \frac{dC_A}{dx}
$$

\n
$$
S_h = \frac{\bar{k}_c (2R_p)}{D_{AB}}
$$

\n
$$
-\frac{dN_A}{dx} = \frac{2k_s}{R_{pore}} C_A
$$

\n
$$
N_A = -D_{TA} \frac{dC_A}{dx}
$$

\n
$$
\frac{d^2C_A}{dx^2} - \frac{2k_s}{D_{TA}R_{pore}} C_A = 0
$$

\n
$$
\frac{d^2C_A}{dx^2} - \phi^2 C_A = 0
$$

$$
r_{\rm obs} = 4\pi (R_p)^2 D_{TA}^e \frac{dC_A}{d\bar{r}}\bigg|_{\bar{r} = R_r}
$$

$$
\eta = \frac{\mathbf{r}_{\text{obs}}}{\mathbf{r}_{\text{max}}} = \frac{4\pi (R_p)^2 D_{TA}^e \frac{dC_A}{d\bar{r}} \bigg|_{\bar{r} = R_p}}{\frac{4}{3} \pi (R_p)^3 k C_{AS}} = \frac{3}{R_p} \frac{D_{TA}^e}{k} \frac{\frac{dC_A}{d\bar{r}} \bigg|_{\bar{r} = R_p}}{C_{AS}}
$$

$$
L_p = \frac{V_p}{S_p}
$$

$$
\eta = \frac{\tanh(\phi_0)}{\phi_0}
$$

Figure 6.3.9 |

Effectiveness factor $[\eta = \tanh(\phi_0)/\phi_0]$ for a first-order
reaction in a catalyst as a function of the Thiele modulus with generalized length parameter.

Table 6.3.2 | Characteristic length
parameters of common pellet shapes.

$$
\phi_0 = \frac{V_p}{S_p} \sqrt{\frac{k}{D_{TA}^e}} = \left[\frac{R_p}{\frac{R_p}{x_p} + 2}\right] \sqrt{\frac{k}{D_{TA}^e}}
$$

$$
\phi_0 = \frac{V_p}{S_p} \sqrt{\frac{n+1}{2} \frac{k C_{AS}^{n-1}}{D_{TA}^e}} \qquad n > -1
$$

$$
\mathbf{r}_{\text{obs}} = \eta k C_{AS}^n
$$

$$
\Delta G - \Delta G^0 = R_g T \sum_{i=1}^{NCOMP} v_i \ln a_i = R_g T \ln \left(\prod_i a_i^{v_i} \right) \qquad \Delta G^0 = -R_g T \ln \left[\frac{a_W^{\overline{w}} a_S^{\overline{s}} \cdots}{a_A^{\overline{a}} a_B^{\overline{b}} \cdots} \right] = -R_g T \ln K_a
$$

cquinomum constant.

$$
\left[\frac{\partial(\ln K_a)}{\partial T}\right]_P = \frac{\Delta H^0}{R_g T^2} \qquad K_a = \exp\left[-\Delta G^0/(R_g T)\right]
$$

$$
a = \bar{f}_i/\bar{f}_i^0 \qquad \bar{f}_i = X_i \bar{\phi}_i P \qquad K_a = \left[\frac{X_w^{\overline{w}} X_s^{\overline{s}} \cdots}{X_A^{\overline{a}} X_B^{\overline{b}} \cdots}\right] \left[\frac{\overline{\phi}_w^{\overline{w}} \overline{\phi}_s^{\overline{s}} \cdots}{\overline{\phi}_A^{\overline{a}} \overline{\phi}_B^{\overline{b}} \cdots}\right] P^{\overline{w} + \overline{s} + \cdots - \overline{a} - \overline{b} \cdots}
$$

The fractional conversion is defined as:

$$
f(t) = \frac{\Phi(t)}{\Phi_{\text{max}}}
$$
 (1.2.9)

and can be calculated from Equations $(1.2.3)$ and $(1.2.8)$:

$$
f_{\ell} = (-v_{\ell}) \frac{\Phi}{n_{\ell}^{0}} = 1 - \frac{n_{\ell}}{n_{\ell}^{0}}
$$
 (1.2.10)

Equation $(1.2.10)$ can be rearranged to give:

$$
n_{\ell} = n_{\ell}^{0} (1 - f_{\ell}) \tag{1.2.11}
$$

where $0 \le f_{\ell} \le 1$. When the thermodynamics of the system limit Φ such that it cannot reach Φ_{max} (where $n_{\ell} = 0$), Φ will approach its equilibrium value Φ^{eq} ($n_{\ell} \neq 0$ value of n_{ℓ} determined by the equilibrium constant). When a reaction is limited by

THIS EXPRESSION IS EITHER MOSITIAE OF Educit to vero it the system has reaction eduilibrium. The reaction rate, like Φ , is an extensive property of the system. A specific rate called the *volumic rate* is obtained by dividing the reaction rate by the volume of the system, V :

$$
r = \frac{1}{V} \frac{d\Phi}{dt} \quad \left(\frac{\text{mol}}{\text{time-volume}}\right) \tag{1.3.2}
$$

Differentiation of Equation (1.2.3) gives:

$$
dn_i = v_i d\Phi \tag{1.3.3}
$$

Substitution of Equation $(1.3.3)$ into Equation $(1.3.2)$ yields:

$$
r = \frac{1}{v_i V} \frac{dn_i}{dt} \tag{1.3.4}
$$

tion (1.2.1), then the number of moles of component A_i , at any time t will be given by the equation:

$$
n_i(t) = n_i^0 + \mathbf{v}_i \Phi(t) \tag{1.2.3}
$$

that is an expression of the *Law of Definitive Proportions* (or more simply, a mole balance) and defines the parameter, Φ , called the *extent of reaction*. The extent of reaction is a function of time and is a natural reaction variable.

concentrations, C_i , is desired. Since $C_i = n_i/V$, Equation (1.3.4) can be written as:

$$
r = \frac{1}{v_i V} \frac{d}{dt} (C_i V) = \frac{1}{v_i} \frac{dC_i}{dt} + \frac{C_i}{v_i V} \frac{dV}{dt}
$$
(1.3.6)

Note that only when the volume of the system is constant that the volumic rate can be written as:

$$
r = \frac{1}{v_i} \frac{dC_i}{dt}, \text{ constant } V \tag{1.3.7}
$$

Without the to must monocitate the country of oriental terms are a convertion. Come the monocitant theory

Rule II

 $\sqrt{1 + \epsilon}$

The rate of an irreversible (one-way) reaction can generally be written in the form:

$$
r = k(T)F(C_i, T) \tag{1.4.1}
$$

where $\overline{F}(C_i, T)$ is a function that depends on the composition of the system as expressed by the concentrations C_i .

Rule III

The rate constant generally depends on the absolute temperature, T, following the law first proposed by Arrhenius in 1889:

$$
k = \overline{A} \exp\left[\frac{-E}{RT}\right] \tag{1.4.2}
$$

Rule IV

Frequently, the function $\overline{F}(C_i)$ in the expression $r = k\overline{F}(C_i)$ can approximately be written as:

$$
\overline{F}(C_i) = \prod C_i^{\alpha_i}
$$

Awiipiyy yi fiyayiiyii fiatyy

Consider the unimolecular reaction:

$$
A \rightarrow \text{products} \tag{1.5.1}
$$

Using the Guldberg-Waage form of the reaction rate to describe this reaction gives:

$$
r = kC_A \tag{1.5.2}
$$

From Equations $(1.3.4)$ and $(1.5.2)$:

$$
r = \frac{1}{v_i V} \frac{dn_i}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = kC_A
$$

$$
\frac{dn_A}{dt} = -kn_A \qquad \text{(variable } V\text{)}
$$
\n(1.5.3)\n
$$
\frac{df_A}{dt} = k(1 - f_A) \qquad \text{[using Equation (1.2.11)]} \tag{1.5.4}
$$

Consider the bimolecular reaction:

$$
A + B \rightarrow \text{products} \tag{1.5.7}
$$

Using the Guldberg-Waage form of the reaction rate to describe this reaction gives:

$$
r = kC_A C_B \tag{1.5.8}
$$

 $\bar{\mathbf{r}}$

$$
r = \frac{1}{v_i V} \frac{dn_i}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = kC_A C_B
$$

$$
r = \left(\frac{\overline{k}T}{h}\right) \exp\left[\frac{\Delta S_0^+}{R_g}\right] \exp\left[\frac{-\Delta H_0^+}{R_g T}\right] C_A C_B
$$

$$
\frac{dn_i}{dt} = 0 - 0 + (v_i V)
$$

accumulation input output amount

roaucea by reaction The material balance can also be written in terms of the fractional conversion and it is:

$$
n_i^0 \frac{df_i}{dt} = -(v_i \, \mathbf{r}) V^0 (1 + \varepsilon_i f_i) \quad \text{with } f_i = 0 \, \text{Qt} = 0 \tag{3.2.2}
$$

where $|\varepsilon_i| > 0$ for nonconstant volume.

Since the reactor is at steady-state, the difference in F_i^0 (input) and F_i (output) must be due to the reaction. (In this text, the superscript 0 on flow rates denotes the input to the reactor.) The material balance on a CSTR is written as:

where A_C is the cross-sectional area of the tube. Also, $A_C dL = dV_R$, so Equation $(3.4.1)$ can be written as:

$$
\frac{dF_i}{dV_R} = v_i \tag{3.4.2}
$$

or

$$
F_i^0 \frac{df_i}{dV_R} = -v_i \mathbf{r}
$$
 (3.4.3)

Integration of Equation (3.4.3) gives:

$$
\frac{V_R}{F_i^0} = \int_{f_i^0}^{f_i^{\text{outlet}}} \frac{df_i}{(v_i r)} \quad \text{or} \quad \tau = \frac{V_R}{v} = C_i^0 \int_{f_i^0}^{f_i^{\text{outlet}}} \frac{df_i}{(v_i r)} \tag{3.4.4}
$$

If changes in volume due to reaction are negligible, then $[F_i = C_i v;$ moles of i /time = (moles of i /volume) (volume/time)]:

$$
\frac{dC_i}{d\tau} = \frac{dC_i}{d(V_R/v)} = v_i r \tag{3.4.5}
$$

$$
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
$$

$$
-\int_{C_{A0}}^{C_A} \frac{1}{\xi^2} d\xi = \frac{1}{C_A} - \frac{1}{C_{A0}}
$$

$$
\int_{x_0}^x \frac{1}{(\xi - \alpha)} d\xi = \ln\left(\frac{x - \alpha}{x_0 - \alpha}\right)
$$

$$
\int_{x_0}^x \frac{1}{\xi} d\xi = \ln\left(\frac{x}{x_0}\right)
$$

Periodic table of the elements

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC). © Encyclopædia Britannica, Inc.

UNITS

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^{1.} The International Steam Table (IT) BTU.
2. The thermochemical calorie.