

CE 329, Fall 2015
First Mid-Term Exam

You may only use pencils, pens and erasers while taking this exam. You may **NOT** use a calculator. You may not leave the room for any reason; if you do, you must first turn in your exam, and you will not be permitted to resume taking the exam.

This exam is printed on two-sided pages; there are 5 short answer questions, each worth 5 points and three problems worth 25 points each for a total of 100 points. Answer All questions, including the short answer questions, in the blue book that has been provided to you. When the exam ends, put these sheets inside your blue book and turn both in.

For the problems you only need to fully show what equations to use and to fully explain how to use them to obtain the requested answer. You do not need to perform any calculations, and you do not need to perform any algebra beyond that needed to obtain the equations to be solved. If you need to use numerical methods to answer a question, provide the information listed below

Numerical Methods

If you need to fit a linear model to data, you must state that it is necessary to fit a model to the data numerically and you must explicitly identify (a) the specific linear model being fit to the data, (b) the response and set variables in the model and (c) the parameters in the model. Then you must (d) show how to calculate the value of each response and set variable for an arbitrary data point. Once you have provided that information, you may assume that the correlation coefficient, the best value of each model parameter and its 95% confidence interval and either a model plot or a parity plot and residuals plots have been found using appropriate numerical software, and you may use those results as you need to complete the problem.

If the solution to a problem involves solving a set of non-linear algebraic equations, you must state that it is necessary solve a set of non-linear algebraic equations numerically and you must (a) explicitly identify the equations to be solved and an equal number of unknowns to be solved for by writing the equations in the form, $0 = f_i(\text{unknowns list}) = \text{expression}$. You then must (b) show how to calculate every quantity that appears in those functions, assuming you are given values for the unknowns. Once you have provided (a) and (b), you may assume that the values of the unknowns have been found numerically, and you may use those values as needed to complete the problem.

If the solution to a problem involves solving a set of initial value ordinary differential equations, you must state that it is necessary to solve a set of initial value ODEs numerically and you must (a) explicitly identify the equations to be solved, the independent variable and the dependent variables by writing the equations in the form, $(\text{derivative } i) = f_i(\text{independent variable, dependent variable list}) = \text{expression}$. Then you must list values or show how to calculate (b) initial values of the independent and dependent variables, (c) the final value of either the independent variable or one of the dependent variables and (d) every quantity that appears in those functions, assuming you are given values for the independent and dependent variables. Once you have provided (a), (b) and (c), you may assume that the

final values of the remaining independent and dependent variables have been found numerically, and you may use those values as needed to complete the problem.

If the solution to a problem involves solving a set of boundary value ordinary differential equations, you must state that it is necessary to solve a set of boundary value ODEs numerically and you must (a) explicitly identify the equations being solved, the independent and dependent variables in those equations and the boundaries of the range of the independent variable over which the equations are to be solved, (b) list values or show how to calculate boundary conditions for each dependent variable; the number of boundary conditions for a particular dependent variable must equal the highest order of derivative of that dependent variable appearing in the equations being solved and (c) list values or show how to calculate every quantity in the equations being solved other than the derivatives, assuming you are given values for the independent and dependent variables. Once you have provided (a), (b) and (c), you may assume that the value of each dependent variable and its first derivative with respect to the independent variable is known at any position between the boundaries, and you may use those values as needed to complete the problem.

Indefinite Integrals

$$\int a dx = ax; \int x^n dx = \frac{x^{n+1}}{n+1} \quad (n \neq -1); \int \frac{dx}{x} = \ln(x); \int \frac{dx}{(a+bx)} = \frac{1}{b} \ln(a+bx);$$

$$\int \frac{dx}{x^2(a+bx)} = -\frac{1}{ax} + \frac{b}{a^2} \ln\left(\frac{a+bx}{x}\right); \int \frac{dx}{x(a+bx)} = -\frac{1}{a} \ln\left(\frac{a+bx}{x}\right); \int \frac{dx}{(a+bx)^2} = -\frac{1}{b(a+bx)};$$

$$\int \frac{x^2 dx}{a+bx} = \frac{1}{b^3} \left[\frac{1}{2}(a+bx)^2 - 2a(a+bx) + a^2 \ln(a+bx) \right]; \int \frac{xdx}{(a+bx)^2} = \frac{1}{b^2} \left[\ln(a+bx) + \frac{a}{a+bx} \right];$$

$$\int \frac{x^2 dx}{(a+bx)^2} = \frac{1}{b^3} \left[a+bx - 2a \ln(a+bx) - \frac{a^2}{a+bx} \right]; \int \frac{xdx}{a+bx} = \frac{x}{b} - \frac{a}{b^2} \ln(a+bx);$$

Thermodynamic Relationships

$$\Delta H_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} \Delta H_{f,i}^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} (-\Delta H_{c,i}^0(298 \text{ K})); \quad K_j(T) = \prod_{\substack{i=\text{all} \\ \text{species}}} a_i^{y_{i,j}};$$

$$\Delta H_j^0(T) = \Delta H_j^0(298 \text{ K}) + \sum_{\substack{i=\text{all} \\ \text{species}}} \left(v_{i,j} \int_{298 \text{ K}}^T \hat{C}_{p,i} dT \right); \quad \Delta G_j^0(298 \text{ K}) = \sum_{\substack{i=\text{all} \\ \text{species}}} v_{i,j} \Delta G_{f,i}^0(298 \text{ K});$$

$$K_j(298 \text{ K}) = \exp\left\{ \frac{-\Delta G_j^0(298 \text{ K})}{R(298 \text{ K})} \right\}; \quad K_j(T) = K_j(298 \text{ K}) \exp\left\{ \int_{298 \text{ K}}^T \frac{\Delta H_j^0(T)}{RT^2} dT \right\}; \quad a_i = \frac{y_i P}{1 \text{ atm}};$$

$$a_i = \frac{y_i \phi_i P}{1 \text{ atm}}; \quad a_i = \gamma_i x_i; \quad a_i = x_i; \quad a_i = h_i x_i$$

Rate, Composition and Reaction Progress Relationships

$$\xi_j = \frac{(n_i - n_i^0)_j}{\nu_{i,j}}; \dot{\xi}_j = \frac{(\dot{n}_i - \dot{n}_i^0)_j}{\nu_{i,j}}; n_i = n_i^0 + \sum_{j=1}^{N_{ind}} \nu_{i,j} \xi_j; f_k = \frac{n_k^0 - n_k}{n_k^0}; r_j = \frac{r_{i,j}}{\nu_{i,j}} = \frac{1}{V} \frac{d\xi_j}{dt};$$

$$g_k = \frac{f_k}{(f_k)_{equil}} = \frac{n_k^0 - n_k}{n_k^0 - (n_k)_{equil}}; C_i = \frac{n_i}{V}; C_i = \frac{\dot{n}_i}{\dot{V}}; \dot{V} = \frac{\dot{n}_{total} RT}{P}; \dot{V} = \dot{V}^0 \left(\text{constant} \right); P = \frac{n_{total} RT}{V};$$

$$P = \frac{\dot{n}_{total} RT}{\dot{V}}; P_i = \frac{n_i RT}{V}; P_i = \frac{\dot{n}_i RT}{\dot{V}}; P_i = y_i P; \mu = \frac{r_g}{C_{cells}}$$

Elementary Reaction Relationships

$$r_{AB-forward} = N_{Av} \sigma_{AB} C_A C_B \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left(\frac{-E_j}{RT}\right); r_{AA-forward} = N_{Av} \sigma_{AA} C_A^2 \sqrt{\frac{2k_B T}{\pi \mu}} \exp\left(\frac{-E_j}{RT}\right);$$

$$r_{ABC-forward} = 8N_{Av} \sigma_{AB} \sigma_{BC} l C_A C_B C_C \sqrt{\frac{2k_B T}{\pi}} \left(\frac{1}{\mu_{AB}} + \frac{1}{\mu_{BC}}\right) \exp\left(\frac{-E_j}{RT}\right);$$

$$r_{j-forward} = \frac{q_{\ddagger}}{N q_{AB} q_C} \left\{ \frac{k_B T}{h} \right\} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) [AB][C];$$

$$r_j = k_{j,f} \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} - k_{j,r} \prod_{\substack{i=\text{all} \\ \text{products}}} [i]^{\nu_{i,j}} = k_{j,f} \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{\nu_{i,j}}}{K_{j,eq}} \right); r_{i,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{i,s} r_s; r_j = r_{s,d};$$

$$r_{RI,j} = \sum_{\substack{s=\text{all} \\ \text{steps}}} \nu_{RI,s} r_s = 0; C_{cat}^0 = C_{cat,free} + \sum_{\substack{i=\text{all} \\ \text{catalyst} \\ \text{complexing} \\ \text{species}}} \nu_{cat,i} C_{cat,i}; C_{i,surf} = C_{sites} \theta_i; \theta_{vacant} + \sum_{\substack{i=\text{all} \\ \text{adsorbed} \\ \text{species}}} \theta_i = 1$$

Age Function Relationships

$$F(\lambda) = \frac{w_t - w_0}{w_f - w_0}; F(\lambda) = 1 - \exp\left\{-\frac{\lambda}{\bar{t}}\right\}; F(\lambda) = \frac{\dot{M} \int_0^t [w_{out}(t) - w_0] dt}{m_{tot} t_0}; F(\lambda) = 0 \text{ for } t < \bar{t}; F(\lambda) = 1 \text{ for } t \geq \bar{t};$$

$$x_{total} = \sum_{x=0}^{x=\infty} x N(x); x_{total} = \int_{x=0}^{x=\infty} x dN(x); y_{total} = \sum_{x=0}^{x=\infty} y(x) N(x); y_{total} = \int_{x=0}^{x=\infty} y(x) dN(x);$$

$$N_{total} = \sum_{x=0}^{x=\infty} N(x); N_{total} = \int_{x=0}^{x=\infty} dN(x); y_{average} = \frac{\sum_{x=0}^{x=\infty} y(x) N(x)}{\sum_{x=0}^{x=\infty} N(x)}; y_{average} = \frac{\int_{x=0}^{x=\infty} y(x) dN(x)}{\int_{x=0}^{x=\infty} dN(x)}$$

Reactor Relationships

$$\tau = \frac{V}{\dot{V}^0}; \quad SV = \frac{1}{\tau}; \quad \frac{dn_i}{dt} = V \left(\sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j \right);$$

$$\dot{Q} - \dot{W} = \left(\sum_{\substack{i=\text{all} \\ \text{species}}} n_i \hat{C}_{p,i} \right) \frac{dT}{dt} + V \left(\sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) - V \frac{dP}{dt} - P \frac{dV}{dt}; \quad \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j = \dot{n}_i + \frac{d}{dt} \left(\frac{\dot{n}_i V}{\dot{V}} \right);$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \left(\dot{n}_i^0 \int_{T^0}^T \hat{C}_{p-i} dT \right) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j(T)) + V \left(\sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}} \right) \frac{dT}{dt} - P \frac{dV}{dt} - V \frac{dP}{dt};$$

$$\frac{\partial \dot{n}_i}{\partial z} = \frac{\pi D^2}{4} \left[\left(\sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j \right) - \frac{\partial}{\partial t} \left(\frac{\dot{n}_i}{\dot{V}} \right) \right]; \quad \frac{\partial P}{\partial z} = -\frac{G}{g_c} \left(\frac{4}{\pi D^2} \right) \frac{\partial \dot{V}}{\partial z} - \frac{2fG^2}{\rho D};$$

$$\frac{\partial P}{\partial z} = -\frac{1-\varepsilon}{\varepsilon^3} \frac{G^2}{\rho \Phi_s D_p g_c} \left[\frac{150(1-\varepsilon)\mu}{\Phi_s D_p G} + 1.75 \right];$$

$$\pi DU(T_e - T) = \frac{\partial T}{\partial z} \left(\sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i \hat{C}_{p-i} \right) + \frac{\pi D^2}{4} \left(\sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H_j \right) + \frac{\pi D^2}{4} \left[\frac{\partial T}{\partial t} \left(\sum_{\substack{i=\text{all} \\ \text{species}}} \frac{\dot{n}_i \hat{C}_{p-i}}{\dot{V}} \right) - \frac{\partial P}{\partial t} \right];$$

$$\frac{dn_i}{dt} = \dot{n}_i + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j;$$

$$\dot{Q} - \dot{W} = \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_i (\hat{h}_i - \hat{h}_{i,\text{stream}}) + \frac{dT}{dt} \sum_{\substack{i=\text{all} \\ \text{species}}} (n_i \hat{C}_{p,i}) + V \sum_{\substack{j=\text{all} \\ \text{reactions}}} (r_j \Delta H_j) - \frac{dP}{dt} V - P \frac{dV}{dt};$$

$$-D_{ax} \frac{d^2 C_i}{dz^2} + \frac{d}{dz} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j; \quad D_{er} \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r} \frac{\partial C_i}{\partial r} \right) - \frac{\partial}{\partial z} (u_s C_i) = \sum_{\substack{j=\text{all} \\ \text{reactions}}} \nu_{i,j} r_j;$$

$$\lambda_{er} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) - u_s \rho_{\text{fluid}} \tilde{C}_{p,\text{fluid}} \frac{\partial T}{\partial z} = \sum_{\substack{j=\text{all} \\ \text{reactions}}} r_j \Delta H$$

Other Relationships

$$\sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_{i,\text{hot}} \int_{T_{\text{hot},\text{in}}}^{T_{\text{hot},\text{out}}} \hat{C}_{p,i} dT + \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_{i,\text{cold}} \int_{T_{\text{cold},\text{in}}}^{T_{\text{cold},\text{out}}} \hat{C}_{p,i} dT = 0; \quad \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_{i,\text{hot}} \int_{T_{\text{hot},\text{in}}}^{T_{\text{hot},\text{out}}} \hat{C}_{p,i} dT + UA\Delta T = 0;$$

$$\Delta T_{AM} = \frac{T_{\text{cold},\text{out}} + T_{\text{hot},\text{out}}}{2} - \frac{T_{\text{cold},\text{in}} + T_{\text{hot},\text{in}}}{2}; \quad \Delta T_{LM} = \left(\frac{(T_{\text{hot},\text{out}} - T_{\text{cold},\text{in}}) - (T_{\text{hot},\text{in}} - T_{\text{cold},\text{out}})}{\ln \left\{ \frac{(T_{\text{hot},\text{out}} - T_{\text{cold},\text{in}})}{(T_{\text{hot},\text{in}} - T_{\text{cold},\text{out}})} \right\}} \right);$$

$$\Delta T_{\text{cold}} = T_{\text{hot},\text{out}} - T_{\text{cold},\text{in}}; \quad R_R = \frac{\text{recycle flow}}{\text{process exit flow}}; \quad \dot{n}_{i,\text{feed}} + \frac{R_R \dot{n}_{i,\text{reactor out}}}{1 + R_R} - \dot{n}_{i,\text{reactor in}} = 0;$$

$$\sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_{i,\text{feed}} \int_{T_{\text{feed}}}^{T_{\text{reactor in}}} \hat{C}_{p,i} dT + \sum_{\substack{i=\text{all} \\ \text{species}}} \dot{n}_{i,r} \int_{T_{\text{reactor out}} (=T_{\text{recycle}})}^{T_{\text{reactor in}}} \hat{C}_{p,i} dT = 0$$

Short Answer Questions (5 points each)

1. True or false: If you want to use a differential method of data analysis on batch reactor data, then the reactor must be operated differentially when the data are being collected.

2. True or false: In an ideal plug flow reactor, perfect radial mixing is assumed.

3. True or false: External transport limitations that affect the apparent rate of a heterogeneous catalytic reaction are the result of concentration and/or temperature gradients along the length of the catalyst pores.

4. The quantity, $1 - \exp\left\{\frac{-\lambda}{\bar{t}}\right\}$, represents

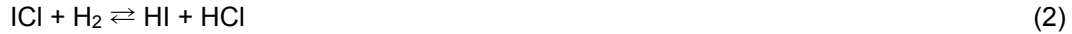
- The response of an ideal CSTR to a step change input.
- The age function for an ideal CSTR.
- The concentration gradient between the bulk fluid and the external surface of a heterogeneous catalyst.
- The Weisz-Prater criterion for the absence of internal mass transport limitations.
- An impulse stimulus for measuring the residence time distribution.

5. Write the Arrhenius expression.

Problems (25 Points Each)

6. The macroscopically observed reaction given in equation (1) takes place at the molecular level via the mechanism given in equations (2) and (3). Without making any additional assumptions beyond the Bodenstein steady state approximation, derive an expression for the rate of the overall reaction. Your answer should not include the concentration or partial pressure of any reactive intermediates.





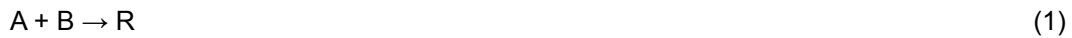
7. Gas phase reaction (1) below was studied in an isothermal, batch reactor. Initially the 1 L reactor contained pure reactant A at a temperature of 235 °C and a pressure of 1 atm. The reaction proceeded at 235 °C, with measurements of the total pressure being taken versus time. The resulting data are given in the table below. Use the data to test the validity of the rate expression given in equation (2) below using an integral analysis.



$$r_1 = k_1 P_A^2 \quad (2)$$

t (min)	P (atm)
1.07	1.09
2.40	1.25
4.11	1.35
6.40	1.42
14.39	1.65
38.37	1.86

8. The liquid phase reaction between A and B, equation (1), was studied in a 500 mL CSTR at 4 atm total initial pressure and 139 °C. The reactor was fed a solution containing A at a concentration of 0.8 M and B at a concentration of 1.0 M. The fractional conversion of A was measured as a function of space time; the data are given below. Determine whether the rate expression given in equation (2) adequately describes the data.



$$-r_A = k C_A C_B \quad (2)$$

space time (h)	f _A
0.00	0.000
1.00	0.142
2.00	0.209
3.00	0.244
4.00	0.286
5.00	0.297
6.00	0.325
7.00	0.303
8.00	0.316
9.00	0.330
10.00	0.315
11.00	0.334
12.00	0.333