

CE 329, Fall 2015
Assignment 16, Practice 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

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

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

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

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

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

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

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

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

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

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

Other Relationships

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

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

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

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

Short Answer Questions (5 points each)

1. Which of the following is the Arrhenius expression?

- $K_j = \exp \left\{ \frac{-\Delta G_j}{RT} \right\}$
- $k_j = \exp \left\{ \frac{\Delta S_j}{R} \right\} \exp \left\{ \frac{-\Delta H_j}{RT} \right\}$
- $K_j = K_{0,j} \exp \left\{ \frac{-\Delta H_j}{RT} \right\}$
- $k_j = k_{0,j} \exp \left(\frac{-E_j}{RT} \right)$
- $k_j = k_{0,j} T^a \exp \left(\frac{-E_j}{RT} \right)$

2. True or False? Every mechanism has a rate determining step.

3. A Lineweaver-Burke plot is (choose all that are true)

- a plot of a linearized form of a Michaelis-Menten kinetic expression
- used to determine whether the kinetics of an enzyme-catalyzed reaction obey Michaelis-Menten kinetics
- used to determine the values of the parameters appearing in a Michaelis-Menten kinetic expression

- d. parabolic in shape with the concave side facing up
 - e. parabolic in shape with the concave side facing down
4. The age function is measured by applying a stimulus and measuring a response.
- a. The stimulus is applied at the inlet to the reactor and the response is measured at the inlet to the reactor.
 - b. The stimulus is applied at the outlet from the reactor and the response is measured at the outlet from the reactor.
 - c. The stimulus is applied at the outlet from the reactor and the response is measured at the inlet to the reactor.
 - d. The stimulus is applied at the inlet to the reactor and the response is measured at the outlet from the reactor.
 - e. The stimulus can be applied at either the inlet or the outlet of the reactor, and the response is measured at the other location.
5. The limiting values of the age function are
- a. $F(0) = 1$ and $F(1) = \infty$
 - b. $F(1) = 0$ and $F(\infty) = \infty$
 - c. $F(0) = 1$ and $F(1) = \infty$
 - d. $F(0) = 0$ and $F(\infty) = 1$
 - e. $F(0) = -\infty$ and $F(1) = \infty$

Problems (25 Points Each)

1. During the chlorination of toluene, the catalyst exists as an Al_2Cl_6 dimer. The activation of the catalyst requires a small amount of HCl to be initially present (or to form via the uncatalyzed reaction). The activation process may then proceed as indicated in equations (1) and (2). These steps can be thought of as initiation steps.



Reactions (3) through (5) can then be postulated as propagation steps.



Assume a system initially contains Cl_2 , C_7H_8 , and a very small amount of HCl, and that the fluid's volume is V . To start the reaction suppose that N moles of Al_2Cl_6 is added to the fluid. Assume reaction (1) to be at quasi-equilibrium, reactions (2) and (5) to be reversible, and reactions (3) and (4) to be irreversible. Do **not** assume any one step to be rate-determining. You may make the steady-state approximation for reactive intermediates. Letting C^0 denote N/V , derive and simplify a rate expression for the chlorination of toluene.

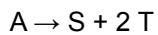
2. The kinetics of the gas-phase reaction shown in equation (1) were studied in an isothermal, 3.27 L batch reactor maintained at 500 K.



In one experimental run the starting mixture was at a pressure of 340 mm Hg and consisted of a 2:1 (propylene:cyclohexadiene) mixture of the reactants. The total pressure was measured as a function of time and data below were recorded. Using the integral method, test a rate expression that is first order in both propylene and cyclohexadiene, and second order overall, $r_{\text{C}_9\text{H}_{14}} = kP_{\text{C}_3\text{H}_6}P_{\text{C}_6\text{H}_8}$.

time (h)	P (mm Hg)
0	340
1	336.08
2	325.27
3	323.58
4	320.16
5	312.17
6	307.14
7	304.77
8	298.69
9	297.32
10	291.54
11	292.47
12	286.36

3. The gas phase decomposition of di-t-butylperoxide (A) was studied in a 276 cc CSTR at 505 K. Carbon dioxide was added to the reactant as an inert diluent (I). Test a first order rate expression for this reaction using the data given.



Pressure (mm Hg)	Inlet molar flow of A (mol/s)	Inlet molar flow of I (mol/s)	Outlet molar flow of S (mol/s)
7.0	5.29E-06	1.69E-04	4.87E-07
11.3	4.59E-06	1.27E-04	7.55E-07
19.5	8.10E-06	1.68E-04	1.74E-06
19.3	8.14E-06	1.67E-04	1.79E-06
11.0	5.22E-06	8.56E-05	1.25E-06