

KEY

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**ChBE 4300A – Kinetics and Reactor Design**  
**Exam #1 – February 13<sup>th</sup>, 2014 – 2 hours – Closed Book**

School of Chemical & Biomolecular Engineering

Georgia Institute of Technology

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Spring 2014

Problem #1		/10
Problem #2		/30
Problem #3		/30
Problem #4		/30
<b>Total</b>		<b>/100</b>

I have read the Georgia Institute of Technology Academic Honor code. I understand and accept my responsibility as a member of the Georgia Tech Community to uphold the Academic Honor Code at all times.

Signature: \_\_\_\_\_ Date: \_\_\_\_\_

***Remember:***

- No wireless devices are permitted at any time.
- Show all of your work.
- Explain your reasoning and state all assumptions.
- Additional worksheets are available if necessary.

Useful Constants:

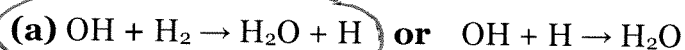
Avagadro's constant	$L$	$6.022 \times 10^{23}$ molecules/mol
Universal gas constant	$R$	$1.987 \text{ cal/mol-K} = 8.314 \text{ J/mol-K}$
Boltzmann's constant	$k_B$	$1.381 \times 10^{-23} \text{ J/K}$

**Problem 1. (10 points)**Name: KEY

Reaction rate constants are well known to follow the Arrhenius equation:

$$k = k_0 e^{-E_a/k_B T}$$

For each of the following sets of elementary reactions, circle the reaction with the largest activation energy ( $E_a$ ). Explain why for each.



↑ requires bond breaking

\*

a number of  
equally  
correct answers  
were also  
accepted

\*



↑  $\text{O}=\text{O}$  double bond is stronger

For each of the following sets of elementary reactions, circle the reaction with the largest pre-exponential factor ( $k_0$ ). Explain why for each.



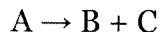
↑ less steric hindrance



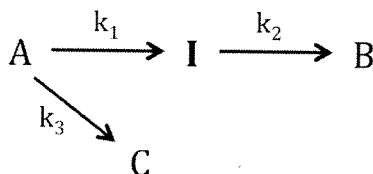
↑ orientation of H collision w/  $\text{Cl}_2$   
less constrained due to symmetry  
 $\text{H} \cdots \text{Cl}-\text{Cl} = \text{Cl}-\text{Cl} \cdots \text{H}$

**Problem 2. (30 points)**Name: KEY

Consider the overall reaction



which occurs via the following sequence of elementary steps:



(a) If the reactor only contains A with a concentration of  $C_{A0}$  at  $t = 0$ , what is the exact concentration of the intermediate I as a function of time?

Write system of ODEs:

$$\frac{dC_A}{dt} = -(k_1 + k_3)C_A$$

$$\frac{dC_B}{dt} = k_2 C_I$$

$$\frac{dC_I}{dt} = k_1 C_A - k_2 C_I$$

$$\frac{dC_C}{dt} = k_3 C_A$$

Integrate  $dC_A/dt$  w/  $C_A(t=0) = C_{A0}$ :

$$C_A(t) = C_{A0} e^{-(k_1 + k_3)t} \quad *$$

Substitute into  $dC_I/dt$ :

$$\frac{dC_I}{dt} + k_2 C_I = k_1 C_{A0} e^{-(k_1 + k_3)t}$$

Use an integrating factor:  $I = e^{k_2 t}$ 

$$C_I(t) = e^{-k_2 t} \left[ \int_0^t e^{k_2 t} k_1 C_{A0} e^{-(k_1 + k_3)t} dt + C \right]$$

Name: KEY

This page was intentionally left blank to provide you additional space for calculations.

$$C_I(t) = e^{-k_2 t} \left[ \frac{k_1 C_{A0}}{k_2 - k_1 - k_3} e^{(k_2 - k_1 - k_3)t} + C \right]$$

apply I.C.  $C_B(t=0) = 0$

3 
$$C = \frac{-k_1 C_{A0}}{k_2 - k_1 - k_3}$$

3 
$$C_I(t) = \frac{k_1 C_{A0}}{k_2 - k_1 - k_3} \left[ e^{-(k_1 + k_3)t} - e^{-k_2 t} \right]$$

(b) What is the concentration of I as a function of time if  $k_2 \gg k_1, k_3$ ? Explain the key differences between the exact and approximate solutions.

Method I: simplify full solution:

+6 
$$C_I(t) = \frac{k_1 C_{A0}}{k_2} e^{-(k_1 + k_3)t}$$

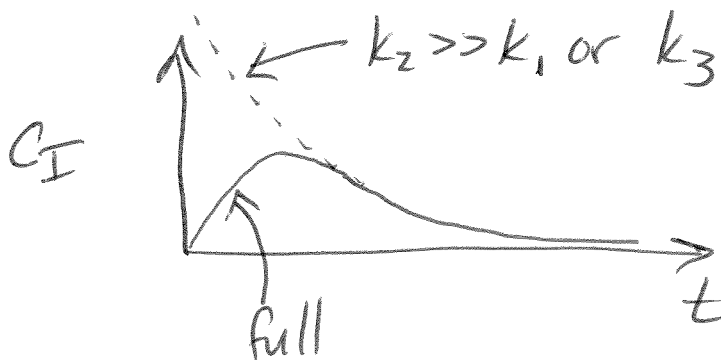
Method II: apply pseudo steady state approximation

+3 
$$\frac{dC_I}{dt} \approx 0 = k_1 C_A - k_2 C_I \Rightarrow C_I = \frac{k_1 C_A}{k_2}$$
  

$$\uparrow$$
  
 substitute \*

+3 
$$C_I(t) = \frac{k_1 C_{A0}}{k_2} e^{-(k_1 + k_3)t}$$

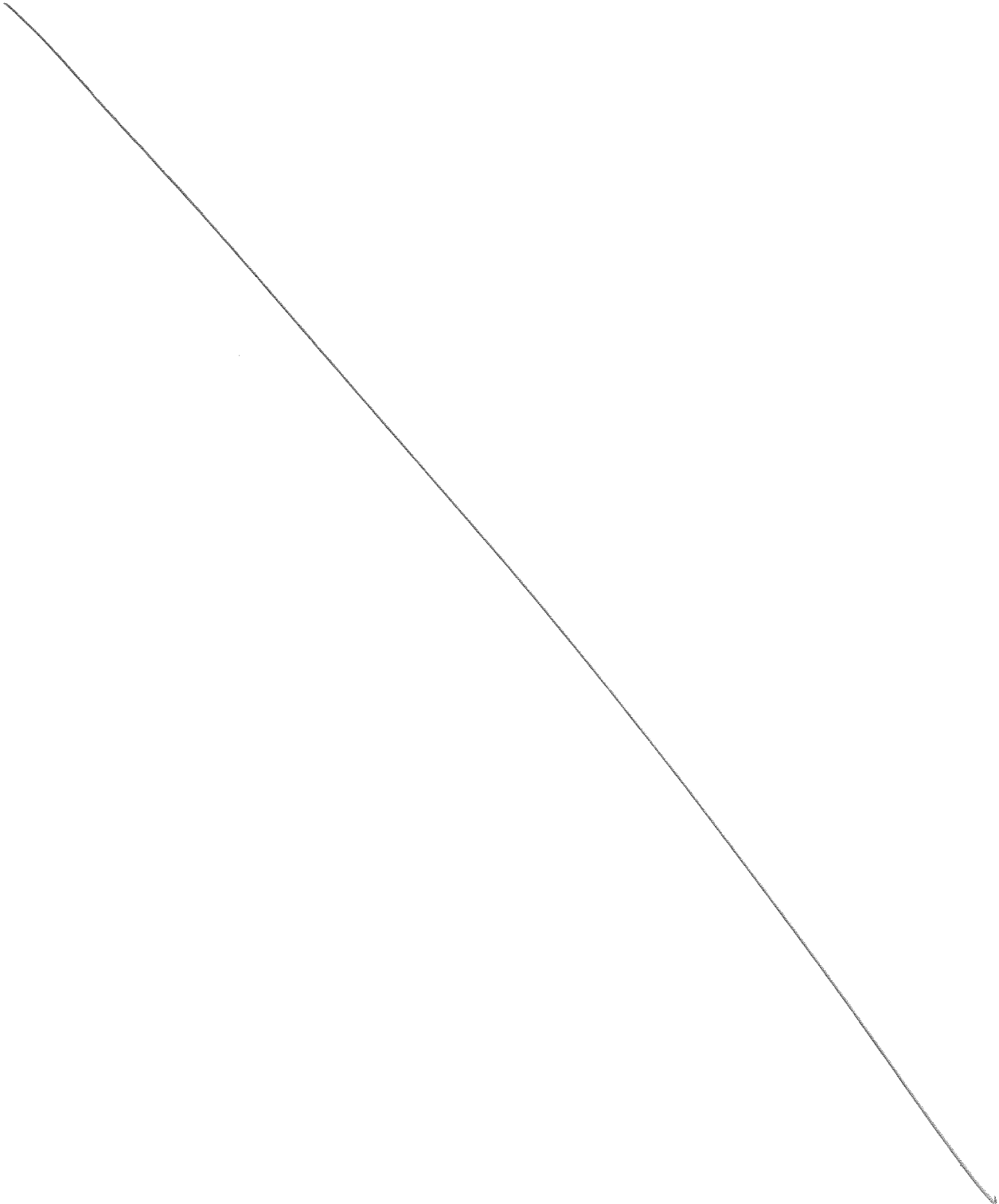
Similar to lecture:



– solutions similar at long times, but different at short times.

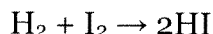
Name: KEY

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**Problem 3. (30 points)**Name: KEY

Consider the following reaction:



Two similar mechanisms have been proposed for this reaction. In both mechanisms, I and  $\text{H}_2\text{I}$  are intermediates.

Mechanism 1Mechanism 1'

(a) Write the complete set of ODEs describing these mechanisms.

System of ODEs is the same for both mechanisms!

$$\begin{aligned} \frac{dC_{\text{I}_2}}{dt} &= -k_1 C_{\text{I}_2} + k_{-1} C_{\text{I}}^2 \\ \frac{dC_{\text{H}_2}}{dt} &= -k_2 C_{\text{I}} C_{\text{H}_2} \\ \frac{dC_{\text{H}_2\text{I}}}{dt} &= k_2 C_{\text{I}} C_{\text{H}_2} - k_3 C_{\text{H}_2\text{I}} C_{\text{I}} \\ \frac{dC_{\text{I}}}{dt} &= 2k_1 C_{\text{I}_2} - 2k_{-1} C_{\text{I}}^2 - k_2 C_{\text{I}} C_{\text{H}_2} - k_3 C_{\text{H}_2\text{I}} C_{\text{I}} \\ \frac{dC_{\text{H}_2\text{I}}}{dt} &= k_2 C_{\text{I}} C_{\text{H}_2} - k_3 C_{\text{H}_2\text{I}} C_{\text{I}} \end{aligned}$$

long-lived reactants / products

Problem 3. – Continued

Name: KEY

(b) Considering the rates indicated for each elementary reaction (i.e., slow or fast), determine the most reduced (i.e., simplified) system of ODEs for each mechanism.

**\*\*DO NOT ATTEMPT TO SOLVE THESE SYSTEMS\*\***

Mechanism 1 : apply equilibrium approximation

$$2k_1 C_{I_2} - k_{-1} C_I^2 = 0$$

$$3 \quad 2K_1 C_{I_2} - C_I^2 = 0 \quad \text{where } K_1 = \frac{k_1}{k_{-1}}$$

take derivative w.r.t. time:

$$3 \quad 2K_1 \frac{dC_{I_2}}{dt} - 2C_I \frac{dC_I}{dt} = 0$$

$$3 \quad \frac{dC_I}{dt} = \frac{K_1}{C_I} \frac{dC_{I_2}}{dt} = \frac{K_1}{C_I} (-k_1 C_{I_2} + k_{-1} C_I^2)$$

↑

decoupled  $dC_I/dt$   
from equations for  $H_2$   
and  $H_2I$

→ all other ODEs remain the same.



Name: KEY

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Mechanism 1': apply pseudo steady state approximation

→ I and  $H_2I$  will both be short-lived

$$3 \quad \frac{dc_I}{dt} = 2k_1 C_{I_2} - 2k_{-1} C_I^2 - k_2 C_I C_{H_2} - k_3 C_{H_2I} C_I \approx 0$$

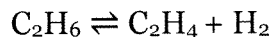
$$3 \quad \frac{dc_{H_2I}}{dt} = k_2 C_I C_{H_2} - k_3 C_{H_2I} C_I \approx 0$$

↑  
convert to algebraic  
equations

→ all other ODEs remain the same.

**Problem 4. (30 points)**Name: KEY

The thermal cracking of ethane



is typically performed in a steam diluent. Use the thermodynamic data provided to answer the following questions.

Component	Temperature (K)	$\Delta G$ (kcal/mol)
$\text{C}_2\text{H}_6$	900	21.00
	1000	26.13
$\text{C}_2\text{H}_4$	900	26.35
	1000	28.25
$\text{H}_2$	900	0.0
	1000	0.0
$\text{H}_2\text{O}$	900	-47.36
	1000	-46.04

(a) Is the reaction endothermic or exothermic?

$$\frac{\partial \ln K}{\partial T} = \frac{H}{RT^2} \Rightarrow \frac{\partial(\Delta G/T)}{\partial T} = -\frac{H}{T^2}$$

3  $\Delta G_{\text{rxn}}(900\text{K}) = 26.35 - 21.00 = 5.35 \text{ kcal/mol}$

3  $\Delta G_{\text{rxn}}(1000\text{K}) = 28.25 - 26.13 = 2.12 \text{ kcal/mol}$

3 as  $T \uparrow$ ,  $\Delta G \downarrow \Rightarrow \Delta H$  must be positive  
ENDOTHERMIC

Problem 4. - Continued

Name: KEY

(b) What is the equilibrium mixture (in partial pressure) at 1000 K, 1 atm total pressure for a mixture that is initially 1 mole of ethane and 5 moles of steam.

$$4 \quad K_a(1000 \text{ K}) = e^{-2120(1.987)(1000)} = 0.34$$

$$4 \quad K_a = K_y \overset{\approx 1}{K_p} = \frac{y_{\text{C}_2\text{H}_4} y_{\text{H}_2}}{y_{\text{C}_2\text{H}_6}} P$$

setup molar table:

component	initial	change	final
$\text{C}_2\text{H}_6$	1	$-x$	$1-x$
$\text{C}_2\text{H}_4$	0	$+x$	$x$
$\text{H}_2$	0	$+x$	$x$
$\text{H}_2\text{O}$	5	0	5
total			$6+x$

substituting into  $K_a$ :

$$K_a = \frac{x^2}{(6+x)(1-x)} P$$

$$4 \quad x = 0.75$$

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$$P_{C_2H_6} = \frac{1-x}{6+x} = 0.036 \text{ atm}$$

$$P_{C_2H_4} = \frac{x}{6+x} = 0.112 \text{ atm}$$

$$P_{H_2} = \frac{x}{6+x} = 0.112 \text{ atm}$$

$$P_{H_2O} = \frac{5}{6+x} = 0.740 \text{ atm}$$