Che 467
Fall 2000
Examples for Midterm

1. Define the following terms in three sentences or less

a) Mechanism
b) Rate Determining Step
c) Pseudo Steady State Approximation
d) Initiation-propagation mechanism
e)Van't Hoff's Method
f) Heterogeneous reaction
g) Homogeneous reaction
h) Statistican ensemble
i) Canonical ensemble
j) Grand Canonical ensemble
k) Partition function
l) Collision Theory
m) Transition State Theory
n) Rideal-Eley Mechanism
p) Monte Carlo Method

2. Compare and contrast a) Gas phase reactions and catalytic reactions. be sure to consider kinetics, mechanisms, relative rates, activation barriers

3. Compare integral methods and differential methods for the analysis of rate data. What are the advantages and disadvantages of each method?

4. Describe the various statistical methods that are used to see if rate data fits a kinetic model. What are the strengths and weaknesses of each method. Which method will you use if you what to impress someone about how well you did? What method would you use if you wanted to make sure your rate equation is the best one?

5. In our undergraduate labs we used to measure the rate of the reaction $CH_3CH_2OCOCH_3 + H_2O \Rightarrow CH_3CH_2OH + CH_3COOH$. The data in Table 1 were obtained.

a) Is this a direct or indirect measurement of the rate? (10 points)
b) Determine the order of the reaction. (40 points)
c) Determine the rate constant. (10 points)
d) How much would the rate change if you increased the temperature to 70 F? (10 points)

Table 1 Batch data for the hydrolysis of ethyl acetate at 60 F.

Time, mins	ethyl acetate concentration	Time, mins	ethyl acetate concentration
0	0.77	7	0.29
1	0.66	10	0.2
3	0.49	15	0.13
5	0.39	20	0.03

6. Assume you are working in the chemical industry and you have just had a major spill

of nitrophenol. You have been able to contain the spill but you have 100,000 ft^3 of contaminated soil, which needs to be treated. You go to the literature and learn that a bacteria called *pseudomonas* can digest the nitrophenol in soil. How would you measure the kinetics of the process so you could design a cleanup system? Be sure to consider what criterion you would use to decide whether to make direct or indirect measurements, qualitatively how you would make the measurements and how you will analyze your data. HINT: First decide what variables are important.

7. Assume that you are working in the semiconductor industry. IBM just announced that they have a new process to replace aluminum with copper in their chips. Your boss tells you, “We need a copper process too. Get me one.” You look in the literature, and find that you can deposit copper via the CVD reaction:

$$Cu(hfac)_2 + H_2 \Rightarrow Cu + H(hfac)$$

> where hfac is a hexafluoroacetylacetonate ligand. Your company already makes CVD reactors, so this seems like a good process for you to bring back to your boss. What would you do to measure the kinetics of the process so your company could sell a copper deposition process too? Be sure to say what you would do during the experiment, which variables are important, what you would measure, and how you would analyze your data.

8. Assume that you are working in the pharmaceutical industry. Your company just started selling Interluken-II and noticed that it degrades when it sits in a bottle for about four weeks. How would you measure the kinetics of the process? Be sure to consider which variables are important, what criterion would use to decide whether to make direct or indirect measurements, qualitatively how you would make the measurements and how you will analyze your data.

9. Pease, JACS 50(1928)1179 examined the reaction

$$C_2H_6 \Rightarrow C_2H_4 + H_2$$

a) Predict a mechanism for the reaction

b) Use your predicted mechanism to derive a rate equation for the reaction. Assume that ethylene, hydrogen and methane are the only products. Set up the equations but do not solve the algebra

c) What other products would you expect if you ran the reaction?

d) Estimate the heat of reaction of the first four steps in your mechanism

e) Estimate the activation barrier for those four steps

f) Based on your results in e) guess what temperature you would need to operate at to get a rate of 1/min

10. Numerically integrate the rate equation

$$\frac{dC}{dt} = -5C(1+t)$$

using a) eulers method b) inplict euler's method c) Second order runge-kutta method. In each case assume a time stem of 0.25 seconds, and integrate the rate equation for 4 time steps.

11. Calculate the partition function for HBr at 300 K (note Table 6.7 will be included with the exam)

Data forHBr	
υ	2650 cm^{-1}
bond length	1.414Å
m_H	1 AMU
m_{Br}	80AMU

Table.1 The contribution of various bonds to key thermodynamic properties. Data of Bensen[1971].

Bond	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole°K	Bond	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole°K
C—H	1.74	12.90	-3.83	C_D—C	2.6	-14.3	6.7
C—C	1.98	-16.40	2.63	C_D—H	2.6	13.8	3.2
C—F	3.34	16.9	-52.5	C_D—F	4.6	18.6	-3.9
C—O	2.7	-4.0	-12.0	C_D—C	—	—	7.5
O—H	2.7	24.0	-27.0	CO—H	4.2	26.8	-13.9
C—N	2.1	-12.8	9.3	CO—N	3.7	-0.6	-14.4
N—H	2.3	17.7	-2.6	C_B—H	3.0	11.7	3.25
C_B—C_B	—	—	10.0	C_B—C	4.5	-17.4	7.25

Table 2 The contribution of various functional to key thermodynamic properties. Data of Bensen[1971].

Ligand	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole°K	Ligand	C_p, cal/mole°K	S cal/mole°K	ΔH_f, kcal/mole°K
C—$(H)_3$C	6.19	30.41	-10.20	O—$(H)_2$	8.0	45.1	-57.8
C—$(H)_2(C)_2$	5.50	9.42	-4.93	O—(H)(C)	4.3	29.07	-37.9
C—(H)$(C)_3$	4.54	-12.07	-1.90	O—(H)(C_B)	4.3	29.1	-37.9
C—$(C)_4$	4.37	-35.10	0.50	O—(H)(C_D)	3.8	24.5	-58.1
C_D—$(H)_2$	5.10	27.61	6.26	O—$(C)_2$	-3.4	8.68	-23.2
C_D—(H)(C)	4.16	7.97	8.59	CO—$(H)_2$	8.5	52.3	26.0
C_D—$(C)_2$	4.10	-12.70	10.34	CO—(H)(C)	7.0	34.9	29.1
C_D—(C_D)(H)	4.46	6.38	6.78	CO—(H)(C_B)	7.0	—	29.1
C_D—(C_D)(C)	4.40	-14.6	8.88	CO—$(C)_2$	5.6	15.0	-31.4
C_D—(C_B)(H)	4.46	6.38	6.78	CO—(C)(O)	6.0	14.8	-35.1
C_D—(C_B)C	4.40	-14.6	8.64	C—$(H)_3$(O)	6.19	30.41	-10.8
C_D—(C_T)(H)	4.46	6.38	6.78	C—$(H)_2$(O)	4.99	9.8	.-8.1
C—(C_D)(C)$(H)_2$	5.2	9.80	-4.76	C—$(H)_3$(CO)	6.19	30.41	-10.08
C—(C_D)$(H)_2$	4.7	10.2	-4.29	C—$(H)_2$(CO)(C)	6.2	9.6	-5.2
C—(C_D)(C_B)$(H)_2$	4.7	10.2	-4.29	C_B—O	3.9	-10.2	-0.9
C—(C_T)(C)$(H)_2$	4.95	10.3	-4.73	C—(N)$(H)_3$	6.19	30.41	-10.08
C_T—(H)	5.27	24.7	26.93	C—(N)(C)$(H)_2$	5.25	9.8	-6.6
C_T—(C)	3.13	6.35	27.55	N—(C)$(H)_2$	5.72	29.71	4.8
C_T—(C_D)	2.57	6.43	29.20	N—$(C)_2$(H)	4.20	8.94	15.4
C_T—(C_B)	2.57	6.43	29.20	C—$(H)_3$(C)	12.7	42.5	-161
C_B—(H)	3.25	11.53	3.30	C—$(F)_2$(H)(C)	9.9	39.1	-102.3
C_B—C	2.07	-7.69	5.51	C—(F)$(H)_2$(C)	8.1	35.4	-51.5
C_B—C_D	3.59	-7.80	5.68	C—$(F)_2(C)_2$	9.9	17.4	-99

Table.3 The contribution of various functional to key thermodynamic properties of Radicals. Data of Bensen[1971].

Ligand	C_p, cal/mole°K	ΔS cal/mole°K	ΔH_f, kcal/mole°K	Ligand	C_p, cal/mole°K	ΔS cal/mole°K	ΔH_f, kcal/mole°K
•C—(C)(H)$_2$	5.99	30.7	35.82	C—(O•)(C)$_2$(H)	7.7	14.7	7.8
•C—(C)$_2$(H)	5.16	10.74	37.45	C—(O•)(C)$_3$	7.2	-7.5	8.6
•C—(C)$_3$	4.06	-10.77	38.00	•C—(H)$_2$(C$_D$)	5.39	27.65	23.2
C—(C•)(H)$_3$	6.19	30.41	-10.08	•C—(H)(C)(C$_D$)	4.58	7.02	25.2
C—(C•)(C)(H)$_2$	5.50	9.42	-4.95	•C—(C)$_2$(C$_D$)	4.00	-15.0	24.8
C—(C•)(C)$_2$(H)	4.54	-12.07	-1.90	•C—(C$_B$)(H)$_2$	4.10	26.85	23.0
C—(C•)(C)$_3$	4.37	-35.10	1.50	•C—(C$_B$)(C)(H)	5.30	6.38	24.7
C—(O•)(C)(H)$_2$	7.9	36.4	6.1	•C—(C$_B$)(C)$_2$	4.72	-15.46	25.5
H•	3		52.1	O•	3		59.5
CH3•			34.7				