ChE 467
Sample Exam Questions

1) 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) Which of the reactions need collision partners? If a reaction needs a collision partner, explain what the collision partner will do. If the reaction does not need a collision partner, explain why not.
c) How do energy transfer barriers to reaction affect each of the reactions above?
d) How do momentum transfer barriers to reaction affect each of the reactions above?
e) 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
f) What other products would you expect if you ran the reaction?
g) Estimate the heat of reaction of the first four steps in your mechanism
h) Estimate the activation barrier for those four steps
i) Estimate the preexponential for each of those four steps
j) Based on your results in i) guess what temperature you would need to operate at to get a rate of 1/min
k) What type of homogeneous catalyst would you use to catalyze the reaction?
l) How would the homogeneous catalyst work?
m) What type of heterogeneous catalyst would you use to catalyze the reaction?
n) How would the heterogeneous catalyst work?

2) Compare and contrast: Collision theory, transition state theory, and the RRKM model. What are the key assumptions in each model? What are the key predictions of each model? Where do the models fail? How is transition state theory different from Tolman's model? How is collision theory different than Tolman's equation?

3) Use transition state theory and collision theory and the data in table P7.17 to estimate the rate of the reaction

$$\mathrm{H} + \mathrm{HBr} \rightarrow \mathrm{H}_2 + \mathrm{Br} \qquad (7.17.1)$$

at 400 K.

Table P7.17 Data for the transition state of reaction 7.17.1

	Linear transition state	Reactants	
		H	HBr
r_{HH}	1.5Å		1.414 Å
r_{HBr}	1.42Å		
υH-Br	2340 cm^{-1}		2650 cm^{-1}
υHHBr (bend)	460 cm^{-1}		
υHHBr (bend)	460 cm^{-1}		
Curvature	320 cm^{-1}		
I	10.4 AMO - Å^2		1.99 AMO Å^2
$E^{\ddagger}$	1.21 kcal/mole		
g_e	4	1	4

4) One of the key steps in the reproduction cycle of the HIV-1 virus is for the virus to produce an enzyme protease which catalyzes the hydrolysis of a protein in your blood cells. The enzyme produces fragments which act as the building block for the production of more viruses. One class of AIDs drugs work by mimicking the transition state for the reaction and binding to the active site on the enzyme. *Erickson and Wlodawer, Annu. Rev. Biochem. 62:543-585, 1993* describe the findings. Explain how the transition state analogs block the transition state.

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

6) 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, what you would measure, and how you would analyze your data.

7) Explain in your own words the factors that cause saddle point energies to differ from activation energies.

8) Why do activation barriers arise during chemical reactions? What are the key factors in determining whether a reaction is activated? Why are activation energies reduced for fairly exothermic reactions? What happens with very exothermic reactions? Why?

9) Compare and contrast the Marcus equation, the Polanyi relationship and the Blowers-Masel approximation. Be sure to consider the key features of the derivation and the predictions. Why does the Marcus equation predict parabolic behavior for very exothermic and endothermic reactions while the Blowers-Masel approximation predicts linear behavior. What are the key different assumptions of the two models.

10) What are the key physical forces that are represented by the intrinsic barrier?
a) According to the Marcus equation, what variables affect the intrinsic barrier
b) According to the Blowers-Masel equation, what variables affect the intrinsic barrier
c) How would charge transfer prior to reaction affect the intrinsic barrier?
d) How would steric repulsions affect the intrinsic barrier?
e) What other factors affect the intrinsic barrier (Hint look in chapter 12).

11) How do catalysts change rates of reactions? List the key ways that catalysts change reactions and give an example of each of the effects. What makes some catalysts better than others? List equations where appropriate.

12) How do solvents change rates of reactions? List the key ways that solvents change reactions and give an example of each of the effects. What makes some solvents better than others? Which solvents are best for different classes of reactions/

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				

Table 6.2 Simplified expressions for the average velocity and the translational, rotational, vibrational partition function. Derivations are given in example 6.B and 6.C.

Type of Mode	**Partition Function**	**Partition function after substituting in values of k_B, h_p**
Average velocity of a molecule	$\bar{v} = \left(\frac{8\, k_B\, T}{p m_g}\right)^{1/2}$	$\bar{v} = 2.52\times10^{13}\ \frac{\text{Å}}{\text{sec}}\left(\frac{T}{300K}\right)^{1/2}\left(\frac{1AMU}{m_g}\right.$
Translation of a molecule in three dimensions, (partition function per unit volume)	$q_t^3 = \frac{\left(2\pi m_g k_B T\right)^{3/2}}{\left(h_p\right)^3}$	$q_t^3 = \frac{1.16}{\text{Å}^3}\left(\frac{T}{300K}\right)^{3/2}\left(\frac{m_g}{1AMU}\right)^{3/2}$
Rotation of a linear molecule	$q_r^2 = \frac{8\pi I k_B T}{S_n\left(h_p\right)^2}$	$q_r^2 = \left(\frac{12.4}{S_n}\right)\left(\frac{T}{300K}\right)\left(\frac{I}{1\text{Å-AMU}}\right)$
Rotation of a nonlinear molecule	$q_r^2 = \frac{\left(8\pi k_B T\right)^{\frac{3}{2}}\left(I_a I_b I_c\right)^{\frac{1}{2}}}{S_n\left(h_p\right)^3}$	$q_r^3 = \left(\frac{43.7}{S_n}\right)\left(\frac{T}{300K}\right)^{\frac{3}{2}}\left(\frac{I_a I_b I_c}{1\text{Å}^3\text{-AMU}^3}\right)^{\frac{3}{2}}$
Vibration of a harmonic oscillator	$q_V = \frac{1}{1-\exp(-h_p\upsilon / k_B T)}$	$q_V = \frac{1}{1-\exp\left(-\left(\frac{\upsilon}{209.2\text{cm}^{-1}}\right)\left(\frac{300K}{T}\right)\right)}$