Chemistry 413
Sample Exam 3 Questions

Statistical Mechanics: Chapters 12-15

Topics:

- configurations, weights, probabilities
- calculate partition function q for simple systems
- behavior of q as $T \to \infty$ and as $T \to 0$
- calculating U
- calculating p_n's (especially for vibrational levels)
- q_T, q_R, q_v
- θ_T, θ_R, θ_v + when high T expression is o.k.
- C_v and equipartion theory

Suggested Problems:

- Chapters 12 and 13: P13.9, P13.10, P13.11, P13.18, P13.20, P13.23
- Chapter 14: Q14.4, Q14.8, P14.4, P14.20 (just a few, not all ten), P14.22, P14.26, P14.37
- Chapter 15: Q15.4, Q15.8, P15.2, P15.8, P15.15

Kinetics, Chapters 16,17,18,19

Some important concepts:

- collision theory
- maxwell distribution of speeds, speed and relationships to temperature, mass
- collision frequency
- diffusion
- elementary kinetics, differential and integrated rate laws
- half-lives
- flooding/isolation method and initial rates method
- mechanisms, writing rate laws for and/or consistency of mechanism with rate law
- Arrhenius and temperature dependence of rate constants
- fast pre-equilibrium approximation
- steady-state approximation
- radical chain reactions
- photochemical reactions
- activation vs. diffusion controlled reactions
- activated complex theory/transition state theory
- Langmuir-Hinshelwood and Eley Rideal Mechanisms
- kinetic isotope effect (if time allows)

Suggested problems:

- Chapter 16: Q16.3, P16.23, P16.32
- Chapter 17: Q17.3
- Chapter 18: P18.2, P18.7, P18.13, P18.20, P18.30
- Chapter 19: P19.1, P19.6, P19.8, P19.20, P19.32

These are a selection of problems I have used on past exams, rather than one actual complete exam. Most of these are kinetics problems. Please make sure to try the book problems for more statistical mechanics concepts. There are many good representative statistical mechanics problems in suggested book problems, so they are underrepresented in the problems below.

1. Suppose a system of 4 molecules has a total energy of $E_{tot} = 4(\epsilon+\epsilon_o)$ where the energy of each molecule can be in the range $\epsilon_o, \epsilon_o + \epsilon, \epsilon_o + 2\epsilon, \epsilon_o + 3\epsilon, \epsilon_o + 4\epsilon$. Find all possible configurations, calculate the weight of each, identify most probable configuration, and calculate the probability of observing the ϵ_o state.

2. Is the high temperature limit for q_R, the rotational partition function, valid for the molecule N_2 at 15K? (B = 1.998 cm^{-1})

3. What is the partition function for a system with a triply degenerate level at O cm^{-1}, and a doubly degenerate level at 300 cm^{-1} at 3000 K?

4. The vibrational absorption band of $^{12}C^{16}O$ occurs at $\nu_o = 2143\ cm^{-1}$. What is the probability of finding CO molecules in the first excited vibrational state at 2000 K?

5. Pre-exponential factors (A) calculated from collision theory are typically higher than experimental values. What accounts for the deviation? How can we change our model to incorporate these ideas and make A(theory) closer to A(experimental)?

6. For the series reaction mechanism:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where $k_2 >> k_1$.

   (a) Draw a graph which illustrates the concentrations of all the species involved as a function of time. Assume there is only A initially.

   (b) For the above system, which one of the following plots would result in a straight line?

      i. [A] vs t
      ii. [A] vs $\frac{1}{t}$
      iii. ln [A] vs t
      iv. $\frac{1}{[A]}$ vs t

7. In a kinetic study of the decomposition of A, Eunice collected the following data:

time (min)	[A] (M^{-1} sM^{-1})
0.0	0.0200
20.0	0.0027
40.0	0.0004

Based on these data, what is the order of the reaction? What is k?

8. An absorbing substance was exposed to 450 nm light from a 75 W light source for 30 minutes. The intensity of the transmitted light was 60% of the intensity of the incident light. As a result of the irradiation 0.152 moles of the absorbing substance decomposed. Determine the quantum efficiency.

9. The stoichiometric equation for a reaction is:

$$A + B + C \rightarrow D$$

The initial rate of formation of D is measured with the following results:

Initial [A] (M)	Initial [B] (M)	Initial [C] (M)	Initial Rate (M s^{-1})
1.0	1.0	1.0	1.3×10^{-2}
2.0	1.0	1.0	2.6×10^{-2}
2.0	1.0	2.0	5.2×10^{-2}
2.0	2.0	2.0	5.2×10^{-2}

   (a) What is the rate law?

   (b) What is the rate constant, k (be careful with units)?

10. True or False and Multiple Choice Please Write out TRUE or FALSE, not just T or F

(a) TRUE or FALSE: The half life of a first order reaction is independent of t he concentration of the species involved

(b) Consider the concurrent elementary reactions below:

$$\begin{array}{ccc} A & \xrightarrow{k_1} & B \\ \Big\downarrow k_2 & & \\ C & & \end{array}$$

If $k_1 = 2k_2$ and only A was present initially the ratio [B]:[C] will be:
(a) 1:2 (b) 2:1 (c) 1:4 (d) 4:1

11. The rate of bacterial hydrolysis of fish muscle is twice as great at 2.2°C as it is at -1.1°C. Estimate an activation energy for this reaction. Comment on what implications this has for the storage of fish for food.

12. Consider the following chain mechanism:

$$A_2 \xrightarrow{k_1} 2A\bullet$$

$$A\bullet \xrightarrow{k_2} B\bullet + C$$

$$A\bullet + P \xrightarrow{k_3} B\bullet$$

$$A\bullet + B\bullet \xrightarrow{k_4} P$$

(a) Identify each step as initiation, propagation, retardation, branching or termination.

(b) What is the overall rate law? Begin by writing expressions for $\frac{d[A\bullet]}{dt}$ and $\frac{d[B\bullet]}{dt}$.

13. Distinguish between a diffusion-controlled reaction and an activation-controlled reaction. Describe the features of each and how are they different, then answer the following:

(a) The following reactions are largely diffusion controlled:

- The combination of iodine atoms in water.
- The combination of methyl radicals in toluene.

(b) The viscosities of water and toluene are $1.002 \times 10^{-3}\ kg\ m^{-1}\ s^{-1}$ and $5.90 \times 10^{-4}\ kg\ m^{-1}\ s^{-1}$. Estimate the ratio of the rate constants of the two reactions.

14. Describe the flooding/isolation method. Under what conditions may it be used?