1. Problem 27–9 in McQuarrie & Simon:

   Consider the reaction mechanism:

   $$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \tag{1}$$

   $$\mathrm{C} \xrightarrow{k_2} \mathrm{P} \tag{2}$$

   Write the expression for $d[\mathrm{P}]/dt$, the rate of product formation. Assume equilibrium is established in the first reaction before any appreciable amount of product is formed, and thereby show that

   $$\frac{d[\mathrm{P}]}{dt} = k_2 K_c [\mathrm{A}][\mathrm{B}]$$

   where K_c is the equilibrium constant for step (1) of the reaction mechanism. This assumption is called the *fast-equilibrium approximation*.

2. Problem 27–11 in McQuarrie & Simon:

   Consider the decomposition reaction of $N_2O_5(g)$

   $$2\,\mathrm{N_2O_5(g)} \xrightarrow{k_{\mathrm{obs}}} 4\,\mathrm{NO_2(g)} + \mathrm{O_2(g)}$$

   A proposed mechanism for this reaction is

   $$\mathrm{N_2O_5(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2(g)} + \mathrm{NO_3(g)}$$
   $$\mathrm{NO_2(g)} + \mathrm{NO_3(g)} \xrightarrow{k_2} \mathrm{NO(g)} + \mathrm{NO_2(g)} + \mathrm{O_2(g)}$$
   $$\mathrm{NO_3(g)} + \mathrm{NO(g)} \xrightarrow{k_3} 2\,\mathrm{NO_2(g)}$$

   Assume that the steady-state approximation applies to both the NO(g) and $NO_3(g)$ reaction intermediates to show that this mechanism is consistent with the experimentally observed rate law

   $$\frac{d[\mathrm{O_2}]}{dt} = k_{\mathrm{obs}}[\mathrm{N_2O_5}]$$

   Express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

3. What is the ratio of the probability of finding a molecule moving with the average speed to the probability of finding a molecule moving with three times the average speed?

4. The following table gives the frequency of firefly flashing as a function of temperature. Find the activation energy for the process.

Frequency (min^{-1})	T (K)
15.9	302
14.8	301
12.5	300
12.0	299
11.5	297
10.0	296
8.0	292

5. A rule-of-thumb used to be that chemical reaction rates would roughly double for a ten-degree increase in temperatures, say from $T_1 = 300K$ to $T_2 = 310K$. For what activation energy E_a would this be exactly correct?

6. For this problem, you'll need to consult the paper [A Radzicka and R Wolfenden, *Science* **267**, 90-93 (1995) available to us at http://www.jstor.org]. In particular, we'll be looking at Figure 2, specifically the curve for 1-Methylorotate decarboxylation. This figure shows an Arrhenius plot for the uncatalyzed reaction of 1-methylrotic acid (OMP).

   (a) Estimate $\Delta H^\dagger$ from the figure.

   (b) Estimate $\Delta S^\dagger$ at T=300K.

   (c) At 25 °C, the enzyme OMP decarboxylase accelerates this reaction 1.4×10^{17}-fold. How fast is the catalyzed reaction at 25 °C?

   (d) What is the binding constant of the enzyme to the transition state of the reaction at T=300K? (Here you'll need to find other sources than your textbook or our notes...)

   This is a real research problem.

7. 10 point extra credit problem:

   A Physical Chemistry student is caught without an umbrella in the rain and wishes to get to her dorm, 1 km away, in the driest possible condition. Should she walk or run? In order to answer this question, calculate the ratio of the rain drop collisions with the student's body under the two conditions. Assume that the cross section is independent of direction (i.e. that the student is spherical), that the student runs at 8 m/s, that she walks at 3 m/s, and that the rainfall is constant with a velocity of 15 m/s.

   (Hint: Let N be the density of raindrops; let Z = number of collisions/unit time between the student and the raindrops; let v_s be the student's velocity (either $v_s = v_{\text{walk}}$ or $v_s = v_{\text{run}}$); let D be the distance to the dorm (=1 km); and note then that the number of collisions is given by Z, the number of collisions per unit time, times the time it takes to walk or run to the dorm, D/v_s: wetness $\propto ZD/v_s$.)