These problems are intended to ***supplement*** the problems in the textbook, not ***replace*** them.

Questions

The following data were collected for a particular reaction:

Temperature (°C)	320	340	360	380	400
rate constant ($M^{-1}\cdot s^{-1}$)	2.88×10^{-4}	4.87×10^{-4}	7.96×10^{-4}	1.26×10^{-3}	1.94×10^{-3}

1. Graphically determine the activation energy.
2. Determine the activation energy using only the first and last sets of data.
3. Comment on how well the two activation energy values agree with each other, and propose a reason why.

Answer the following questions:

4. Calculate the activation energy for a reaction which has a rate constant of 2.61×10^{-5} s^{-1} at 190.0 °C and a rate constant of 3.02×10^{-3} s^{-1} at 250.0 °C.
5. Fireflies "flash" at a rate that depends on the temperature. At 29.0 °C, the average rate is 3.3 flashes every 10 seconds. At 23.0 °C, the average rate falls to 2.7 flashes every 10 seconds. Calculate the "energy of activation" for the flashing process.
6. At 35 °C, the rate constant for the hydrolysis of sucrose (where it splits into fructose and glucose) is 6.2×10^{-5} s^{-1}. The activation energy for this reaction is 108 kJ/mol. What is the rate constant at 45 °C?
7. The rates of many reactions approximately double for each 10 °C rise in temperature. Assuming a starting temperature of 25 °C, what would the activation energy be if the rate constant was twice as large at 35 °C?
8. The enzyme urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide. At 21 °C, the uncatalyzed reaction has an activation energy of 125 kJ/mol. The enzyme catalyzes a mechanism with an activation energy of 46 kJ/mol. By what factor does urease increase the rate of urea hydrolysis at 21 °C? In other words, is the catalyzed reaction 10 times faster, 25 times faster, etc. ? Assume the frequency factor is the same for both mechanisms. (Hint: use the Arrhenius equation to find the ratio of the two rate constants.)
9. A particular reaction has an activation energy of 418 kJ/mol and a rate constant of 7.62×10^{-6} s^{-1} at 25.0 °C. What is the rate constant at 75.0 °C?
10. Two first-order reactions have the same rate constant at 30 °C. Reaction A has an activation energy of 34.50 kJ/mol. Reaction B has an activation energy of 27.20 kJ/mol. Calculate the ratio of rate constants, k_A / k_B at 60 °C.

The reaction of nitrogen monoxide with oxygen to give nitrogen dioxide is an important process in the formation of brown smog:

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

Experiments show that this reaction is third order overall. The following mechanism has been proposed:

step 1 $NO + NO \rightarrow N_2O_2$
step 2 $N_2O_2 + O_2 \rightarrow NO_2 + NO_2$

11. If the first step is rate-determining, then what is the rate law for the overall reaction?
12. If the second step is rate-determining, then what is the rate law for the overall reaction?
13. Is either of these consistent with the experimental observations?

The following mechanism has been proposed for a different reaction that converts nitrogen monoxide to nitrogen dioxide during smog formation:

step 1	$CO + OH$	$\rightarrow$	$CO_2 + H$
step 2	$H + O_2$	$\rightarrow$	HOO
step 3	$HOO + NO$	$\rightarrow$	$OH + NO_2$

14. Write the overall reaction.
15. List any reaction intermediates.
16. List any catalysts.
17. If the first step is rate-determining, then what is the rate law for the overall reaction?
18. If the second step is rate-determining, then what is the rate law for the overall reaction?

A possible mechanism for a gas-phase reaction is:

step 1	$2\,NO$	$\rightleftarrows$	N_2O_2	(fast)
step 2	$N_2O_2 + H_2$	$\rightarrow$	$H_2O + N_2O$	(slow)
step 3	$N_2O + H_2$	$\rightarrow$	$N_2 + H_2O$	(fast)

19. Write the overall reaction.
20. List any reaction intermediates.
21. List any catalysts.
22. What is the rate law for the overall reaction?

The following mechanism has been proposed for a particular reaction:

step 1	$H_2O_2 + I^-$	$\rightarrow$	$H_2O + IO^-$	(slow)
step 2	$H_2O_2 + IO^-$	$\rightarrow$	$H_2O + O_2 + I^-$	(fast)

23. Write the overall reaction.
24. List any reaction intermediates.
25. List any catalysts.
26. What is the rate law for the overall reaction?

<u>Answers</u>

If you cannot figure out how to get the correct answer, go to your instructor, Science Tutoring Center, etc.

Note: Answers obtained graphically should be similar to those listed here, but probably will not be exactly equal.

1. 79.1 kJ/mol
2. 79 kJ/mol
3. Same since data fall very close to line.
4. 159 kJ/mol
5. 25 kJ/mol
6. $2\times10^{-4}\ s^{-1}$
7. 52 kJ/mol
8. 8×10^{13} times faster
9. $3\times10^{5}\ s^{-1}$
10. 1.3
11. rate = $k[NO]^2$
12. rate = $k[NO]^2[O_2]$
13. only the second one
14. $CO + O_2 + NO \rightarrow CO_2 + NO_2$
15. H and HOO
16. OH
17. rate = $k[CO][OH]$
18. rate = $k[CO][OH][O_2][CO_2]^{-1}$
19. $2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O$
20. N_2O and N_2O_2
21. none
22. rate = $k[NO]^2[H_2]$
23. $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$
24. IO^-
25. I^-
26. rate = $k[H_2O_2][I^-]$