CH 302 Spring 2007 Worksheet 13

[A]	[B]	[C]	rate
0.10 M	0.10 M	0.10 M	1.4×10^{-4} M/s
0.20 M	0.10 M	0.10 M	2.8×10^{-4} M/s
0.37 M	0.25 M	0.10 M	8.09×10^{-3} M/s
0.37 M	0.25 M	0.05 M	3.24×10^{-2} M/s

For the data given above, find the order of the reaction with respect to the indicated species.

1. A

   Answer: When you double the amount of A, the reaction rate doubles, so the reaction is **first-order in A**.

2. B

   Answer: We know the reaction is first-order in A. So multiplying A by 3.7 (from the first one) would yield a rate of $3.7(1.4 \times 10^{-4}$ M/s$) = 5.2 \times 10^{-4}$ if B and C were unchanged. Thus, multiplying B by 2.5 yielded a net change of $(8.09/0.52) = 15.6 = 2.5^3$. So the reaction is **third-order in B**.

3. C

   Answer: Halving C quadruples the reaction order. So the reaction is **of order -2 in C**.

4. Assume the reaction does not depend on any other species besides A, B, and C. Write the expression for the rate of the reaction in terms of the rate constant k.

   Answer: rate = $k[A][B]^3/[C]^2$

5. Calculate the rate constant k.

   $k = (\text{rate})[C]/[A][B]^3 = (1.4 \times 10^{-4}\ \text{M/s})(0.1\ \text{M})^2/((0.1\ \text{M})(0.1\ \text{M})^3)$
   $= \mathbf{0.014\ M^{-1}s^{-1}}$

6. If $A = 10^8\ \text{M}^{-1}\text{s}^{-1}$ and T = 298 K, what is E_a for this reaction?

   $k = A\exp(-E_a/RT) \Rightarrow \ln k = \ln A - E_a/RT \Rightarrow$
   $E_a = RT\ln(A/k) = (8.3144\ \text{J/mol K})(298\ \text{K}) \ln(10^8/0.014) =$ **56.2 kJ/mol**

You start out with 1.0 M A. Assume the rate of the reaction $2A \rightarrow A_2$ depends only one [A]. Assume that A = 3.4×10^8 (units depend on the order), E_a = 65 kJ/mol, and T = 298 K. If the reaction is the given order in A, calculate the amount of A left after five minutes and the half-life of A.

7. Zeroth order

   Answer: First, calculate k:

   $k = A \exp(-E_a/RT) = (3.4 \times 10^8) \exp(-65000/(8.3144 \times 298\ \text{K}))$
   $= 1.37 \times 10^{-3}$ (units depend on the order)

   $[A] = [A]_0 - akt = 1.0\ \text{M} - 2(1.37 \times 10^{-3}\ \text{M s}^{-1})(300\ \text{s}) =$ **0.175 M**
   $t_{1/2} = 0.5[A]_0/ak = 0.5(1.0\ \text{M})/(2 \times 1.37 \times 10^{-3}) =$ **182 s**

8. First order

   Answer: $\ln[A] = \ln[A]_0 - akt$
   $[A] = [A]_0 \exp(-akt) = (1.0\ \text{M})\exp(-2(1.37\times10^{-3})(300\ \text{s})) =$ **0.438 M**
   $t_{1/2} = 0.693/ak = 0.693/(2 \times 1.37 \times 10^{-3}) =$ **253 s**

9. Second Order

Answer: $1/[A] = 1/[A]_0 + akt$

$[A] = ([A]_0^{-1}+akt)^{-1} = ((1.0\ M)^{-1} + 2(1.37x10^{-3})(300\ s))^{-1} =$ **$0.548\ M$**

$t_{1/2} = 1/(ak[A]_0) = 1/(2\ x\ 1.37\ x\ 10^{-3}\ x\ 1.0\ M) =$ **$364\ s$**

10. For a (a) zeroth, (b) first, and (c) second order reaction, a plot of _______ vs. t is linear.

Answer: (a) [A] (b) ln[A] (c) 1/[A]

11. The reaction $3A + 5/2\ B \rightarrow 2\ C + 4\ D$ has a rate constant k of $3.7\ x\ 10^{-6}\ M^{-2}s^{-1}$ at 298 K and $6.80\ x\ 10^{-2}\ M^{-2}s^{-1}$ at 600 K. Calculate the activation energy E_a for this reaction.

Answer: $\ln(k_2/k_1) = (E_a/R)(1/T_1-1/T_2)$

$E_a = R\ln(k_2/k_2)(1/T_1-1/T_2)^{-1} = (8.3144)\ln(6.80x10^{-2}/3.7x10^{-6})(1/298-1/600)^{-1}$

= 48.3 kJ/mol

12. Calculate the pre-exponential factor A for the reaction in #11.

Answer: $k = A\ \exp(-E_a/RT)$

$A = k\ \exp(E_a/RT) = (3.7\ x\ 10^{-6})\exp(48334/(8.3144\ x\ 298)) =$ **$1097\ M^{-2}s^{-1}$**

13. What would be k for the reaction in #11 at 0°C?

Answer: $k = (1097)\ \exp(-48334/(8.4144\ x\ 273)) =$ **$6.20\ x\ 10^{-7}\ M^{-2}s^{-1}$**

14. Write the rate expression for the following multi-step reaction.

$O_3 \rightarrow O_2 + O$	fast
$O + O_3 \rightarrow 2\ O_2$	slow
$2\ O_3 \rightarrow 3\ O_2$	overall

Answer: Notice that the O cancels out, leaving an overall rate law of

rate = $k[O_3]^2/[O_2]$

15. Write the rate expression for the following multi-step reaction.

$(CH_3)_3CBr \rightarrow (CH)_3C^+ + Br^-$	slow
$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH_2^+$	fast
$(CH_3)_3COH_2^+ + H_2O \rightarrow (CH_3)_3COH + H_3O^+$	fast
$(CH_3)_3CBr + 2\ H_2O \rightarrow (CH_3)_3COH + Br^- + H_3O^+$	overall

Answer: Only the first reaction matters. So the overall law is

rate = $k[(CH_3)_3CBr]$

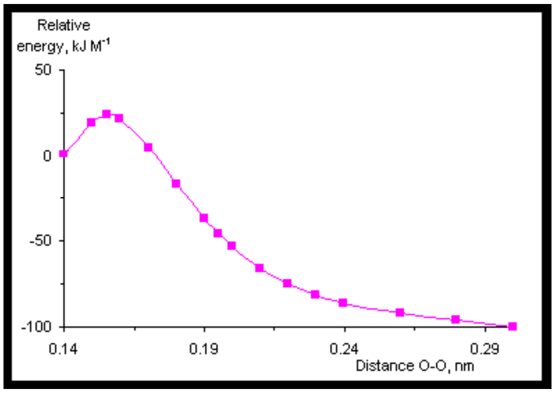
16. Write the rate expression for the following multi-step reaction.

$H_2O_2 + Br_2 \rightarrow 2\ H^+ + O_2 + 2\ Br^-$	slow
$2\ H^+ + 2\ Br^- + H_2O_2 \rightarrow Br_2 + 2\ H_2O$	fast
$2\ H_2O_2 \rightarrow 2\ H_2O + 2\ O_2$	overall

Answer: Only the first reaction matters. So the overall is

rate = $k[H_2O_2][Br_2]$

Note that Br_2 can speed up the reaction, but doesn't participate in the overall mechanism – it's a catalyst.



17. The above plot represents the energy profile of a reaction that involves breaking an O-O bond in terms of the O-O bond distance (treat this is a general "reaction coordinate"). Assume this is in 1 L of solution, so 1 kJ M^{-1} = 1 kJ mol^{-1}. Approximately what is ΔG for this reaction? What is E_a?
    Answer: ΔG = -100 kJ/mol, E_a = 25 kJ/mol
18. What is E_a for the reverse reaction?
    Answer: 125 kJ/mol
19. Assume the reaction described by the plot is a simple reaction of the form $A \rightarrow B + C$ and is first order overall and first order in A. The reaction rate when [A] = 0.235 M is found to be 1.4 x 10^{-3} M/s. What is k for this reaction?
    Answer: rate = k[A]
    k = rate/[A] = (1.4 x 10^{-3} M/s)/(0.235 M) = **5.96 x 10^{-3} s^{-1}**
20. What is the preexponential factor A for the above reaction?
    Answer: k = A exp(-E_a/RT)
    A = k exp(E_a/RT) = (5.96 x 10^{-3} s^{-1}) exp(25000/(8.3144 x 298)) = **144 s^{-1}**