

CH 302 Worksheet 16 More Kinetics: Answer Key

[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 $3.7(1.4 \times 10^{-4} \text{ M/s}) = 5.2 \times 10^{-4}$ 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: $\text{rate} = k[\text{A}][\text{B}]^3/[\text{C}]^2$
5. Calculate the rate constant k.
 $k = (\text{rate})[\text{C}]/[\text{A}][\text{B}]^3 = (1.4 \times 10^{-4} \text{ M/s})(0.1 \text{ M})^2/((0.1 \text{ M})(0.1 \text{ M})^3)$
 $= \mathbf{0.014 \text{ M}^{-1}\text{s}^{-1}}$
6. If $A = 10^8 \text{ M}^{-1}\text{s}^{-1}$ and $T = 298 \text{ K}$, what is E_a for this reaction?
 $k = A \exp(-E_a/RT) \Rightarrow \ln k = \ln A - E_a/RT \Rightarrow$
 $E_a = RT \ln(A/k) = (8.3144 \text{ J/mol K})(298 \text{ K}) \ln(10^8/0.014) = \mathbf{56.2 \text{ kJ/mol}}$

You start out with 1.0 M A. Assume the rate of the reaction $2\text{A} \rightarrow \text{A}_2$ depends only on [A]. Assume that $A = 3.4 \times 10^8$ (units depend on the order), $E_a = 65 \text{ kJ/mol}$, and $T = 298 \text{ K}$. 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)
 $[\text{A}] = [\text{A}]_0 - akt = 1.0 \text{ M} - 2(1.37 \times 10^{-3} \text{ M s}^{-1})(300 \text{ s}) = \mathbf{0.175 \text{ M}}$
 $t_{1/2} = 0.5[\text{A}]_0/ak = 0.5(1.0 \text{ M})/(2 \times 1.37 \times 10^{-3}) = \mathbf{182 \text{ s}}$
8. First order
Answer: $\ln[\text{A}] = \ln[\text{A}]_0 - akt$
 $[\text{A}] = [\text{A}]_0 \exp(-akt) = (1.0 \text{ M}) \exp(-2(1.37 \times 10^{-3})(300 \text{ s})) = \mathbf{0.438 \text{ M}}$
 $t_{1/2} = 0.693/ak = 0.693/(2 \times 1.37 \times 10^{-3}) = \mathbf{253 \text{ s}}$

9. Second Order

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

$[A] = ([A]_0^{-1} + akt)^{-1} = ((1.0 \text{ M})^{-1} + 2(1.37 \times 10^{-3})(300 \text{ s}))^{-1} = \mathbf{0.548 \text{ M}}$

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

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 $3.7 \times 10^{-6} \text{ M}^{-2}\text{s}^{-1}$ at 298 K and $6.80 \times 10^{-2} \text{ M}^{-2}\text{s}^{-1}$ at 600 K. Calculate the activation energy E_a for this reaction.

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

$E_a = R \ln(k_2/k_1)(1/T_1 - 1/T_2)^{-1} = (8.3144) \ln(6.80 \times 10^{-2} / 3.7 \times 10^{-6})(1/298 - 1/600)^{-1}$
 $= \mathbf{48.3 \text{ kJ/mol}}$

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

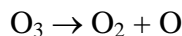
Answer: $k = A \exp(-E_a/RT)$

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

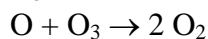
13. What would be k for the reaction in #11 at 0°C?

Answer: $k = (1097) \exp(-48334 / (8.3144 \times 273)) = \mathbf{6.20 \times 10^{-7} \text{ M}^{-2}\text{s}^{-1}}$

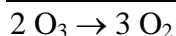
14. Write the rate expression for the following multi-step reaction.



fast



slow

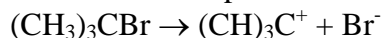


overall

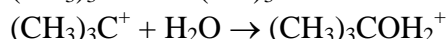
Answer: Notice that the O cancels out, leaving an overall rate law of

rate = $k[\text{O}_3]^2/[\text{O}_2]$

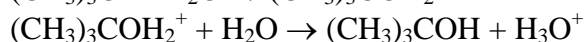
15. Write the rate expression for the following multi-step reaction.



slow



fast



fast

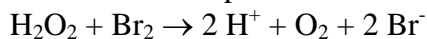


overall

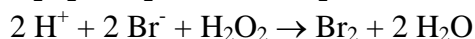
Answer: Only the first reaction matters. So the overall law is

rate = $k[(\text{CH}_3)_3\text{CBr}]$

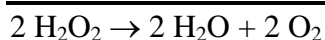
16. Write the rate expression for the following multi-step reaction.



slow



fast

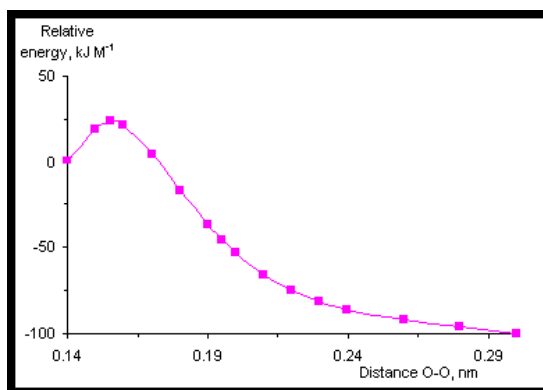


overall

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

rate = $k[\text{H}_2\text{O}_2][\text{Br}_2]$

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 as a general “reaction coordinate”). Assume this is in 1 L of solution, so $1 \text{ kJ M}^{-1} = 1 \text{ kJ mol}^{-1}$. Approximately what is ΔG for this reaction? What is E_a ?
Answer: $\Delta G = -100 \text{ kJ/mol}$, $E_a = 25 \text{ kJ/mol}$
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 $[A] = 0.235 \text{ M}$ is found to be $1.4 \times 10^{-3} \text{ M/s}$. What is k for this reaction?
Answer: $\text{rate} = k[A]$
 $k = \text{rate}/[A] = (1.4 \times 10^{-3} \text{ M/s})/(0.235 \text{ M}) = 5.96 \times 10^{-3} \text{ s}^{-1}$
20. What is the preexponential factor A for the above reaction?
Answer: $k = A \exp(-E_a/RT)$
 $A = k \exp(E_a/RT) = (5.96 \times 10^{-3} \text{ s}^{-1}) \exp(25000/(8.3144 \times 298)) = 144 \text{ s}^{-1}$