Chem 104
Solution to Extra Problems for Chapter 14

Chapter 14, Extra Problem 1. The radioactive isotope ^{54}V decays by beta emission with a half-life of 55 s. (a) What fraction of a sample of ^{54}V will remain after 220 s? (b) What fraction will remain after 75 s?

Solution.

(a) First determine how many half-lives have elapsed:

$$h = 220\text{ s}/55\text{ s} = 4$$

From $[A] = [A]_o(1/2)^h$, the fraction $[A]/[A]_o = (1/2)^4 = 1/16 = 0.062_5 = 0.063$

(You should be able to do this kind of problem, in which a whole number of half-lives have elapsed, without a calculator.)

(b) Use the same approach for this, but use your calculator to find $(1/2)^h$.

$$h = 75\text{ s}/\ 55\text{ s} = 1.3_{64}$$

$$[A]/[A]_o = (1/2)^{1.364} = 0.38_{86} = 0.39$$

Chapter 14, Extra Problem 2. Consider the hypothetical reaction $A_2(g) + 2B(g) + 2C_2(g) \rightarrow 2AC(g) + 2BC(g)$ for which the following kinetic data have been collected.

Exp.	$[A_2]$, mol/L	[B], mol/L	$[C_2]$, mol/L	Rate, mol/L·s
1	0.120	0.240	0.120	3.62×10^{-4}
2	0.480	0.240	0.120	7.24×10^{-4}
3	0.480	0.240	0.360	7.24×10^{-4}
4	0.480	0.120	0.240	3.62×10^{-4}

(a) Determine the rate law expression for the reaction. (b) Calculate the value of the rate constant, k, with the proper units.

Solution.

(a) From experiments 1 and 2, multiplying $[A_2]$ by 4 while keeping the other reactant concentrations the same causes the rate to increase by a factor of 2. Therefore, the order with respect to $[A_2]$ is 1/2, because $(4)^{1/2} = 2$. From experiments 2 and 3, multiplying [C] by three while keeping the other reactant concentrations the same causes no change in rate. Therefore, the order with respect to [C] is 0; i.e., rate does not depend on [C]. Because the rate is zero order in [C], we can use either experiments 3 and 4 or 2 and 4 to see the effect of changing [B] on rate while $[A_2]$ is held constant. By either comparison, diminishing [B] by half causes the rate to go to half. Therefore, the reaction is first order in [B]. The overall differential rate law for the reaction is $Rate = k[A_2]^{1/2}[B]$, which is 3/2 order overall.

(b) Use data from any experiment and solve $Rate = k[A_2]^{1/2}[B]$ for k.

$$k = 4.35 \times 10^{-3}\ (\text{mol/L})^{-1/2}\cdot\text{s}^{-1}$$

Chapter 14, Extra Problem 3: Consider the hypothetical reaction $A_2(g) + 2B(g) + 2C_2(g) \rightarrow 2AC(g) + 2BC(g)$ for which the experimentally determined rate law has been found to be $Rate = k[A_2]^{½}[B]$. The following two mechanisms have been proposed for this reaction.

Mechanism I:

$A_2 \rightleftharpoons 2A$	fast equilibrium
$A + B \rightleftharpoons AB$	fast equilibrium
$AB + C_2 \rightarrow AC + BC$	slow

Mechanism II:

$A_2 \rightleftharpoons 2A$	fast equilibrium
$A + B \rightarrow AB$	slow
$AB + C_2 \rightarrow AC + BC$	fast

(a) Show that both proposed mechanisms are consistent with the overall stoichiometry of the reaction, $A_2(g) + 2B(g) + 2C_2(g) \rightarrow 2AC(g) + 2BC(g)$.

(b) What species are reaction intermediates in each mechanism?

(c) Derive the rate law expression for each mechanism in terms of observable reactant species (A_2, B, and C_2). On the basis of your rate law expressions, which mechanism is more plausible?

Solution:

(a) The equations are actually the same in both cases. In either, the second step equation and the third step equation need to be multiplied by 2 in order for all steps to add to the overall stoichiometry.

$$A_2 \rightarrow \cancel{2A}$$
$$\cancel{2A} + 2B \rightarrow \cancel{2AB}$$
$$\cancel{2AB} + 2C_2 \rightarrow 2AC + 2BC$$

$$A_2 + 2B + 2C_2 \rightarrow 2AC + 2BC$$

(b) A and AB are reaction intermediates. Neither is present initially as a reactant or finally as a product. Both are produced and consumed in the course of the mechanism.

(c) Mechanism I:

From the slow rate-determining step (step 3), the overall rate is $Rate = rate_3 = k_3[AB][C_2]$. But AB is a reaction intermediate, so we need to derive an expression in terms of observable reactants for [AB]. From the step 2 equilibrium, we can write $rate_2 = rate_{-2}$; i.e., the forward and reverse rates are equal. From the molecularity of the processes, we can then write

$$k_2[A][B] = k_{-2}[AB] \;\Rightarrow\; [AB] = (k_2/k_{-2})[A][B] = K_2[A][B]$$

But this expression for [AB] still involves an unobservable reaction intermediate, A. From the step 1 equilibrium, we can write $rate_1 = rate_{-1}$, and from the molecularity of the forward and reverse processes we can write

$$k_1[A_2] = k_{-1}[A]^2 \Rightarrow [A]^2 = k_1/k_{-1}[A_2] = K_1[A_2] \Rightarrow [A] = K_1^{½}\,[A_2]^{½}$$

Substituting this expression for [A] into the previous expression for [AB] gives

$$[AB] = K_2\{K_1^{½}\,[A_2]^{½}\}[B] = K_2K_1^{½}\,[A_2]^{½}\,[B]$$

Substituting this expression for [AB] into $Rate = rate_3 = k_3[AB][C_2]$ gives

$$Rate = k_3\{K_2K_1^{½}\,[A_2]^{½}\,[B]\}[C_2] = k\,[A_2]^{½}\,[B]\,[C_2]$$

This does not match the experimentally observed $Rate = k[A_2]^{½}\,[B]$, so it is not plausible.

Mechanism II:

From the slow rate-determining step (step 2), the overall rate is $Rate = k_2[A][B]$. But A is a reaction intermediate, so we need to derive an expression in terms of observable reactants for

[A]. From the step 1 equilibrium, we can write $rate_1 = rate_{-1}$, and from the molecularity of the forward and reverse processes we can write

$$k_1[A_2] = k_{-1}[A]^2 \Rightarrow [A]^2 = k_1/k_{-1}[A_2] = K_1[A_2] \Rightarrow [A] = K_1^{1/2}\,[A_2]^{1/2}$$

Substituting this into $Rate = k_2[A][B]$ gives

$$Rate = k_2\{K_1^{1/2}\,[A_2]^{1/2}\}[B] = k[A_2]^{1/2}\,[B]$$

This matches the observed rate law, so Mechanism II is more plausible.