General Chemistry II

RR #4 Answer Key

Summer 2022

1. The decomposition of XY is second order in XY and has a rate constant of $7.02*10^{-3}$ M^{-1} s^{-1} at a certain temperature:
   a. How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.100 M?

Use the 2nd order integrated rate law and solve for t. The form of this equation below just subtracts the rightmost term from both sides to group the variables. Recognize the equation is $XY \rightarrow X + Y$.

$$\frac{1}{[XY]_t} - \frac{1}{[XY]_o} = kt$$

$$\frac{1}{0.0125\ M} - \frac{1}{0.100\ M} = (7.02 * 10^{-3}\ M^{-1}s^{-1})(t)$$

$$t = 9.97 * 10^3\ s$$

   b. How long will it take for the concentration of XY to decrease to 12.5% of its initial concentration when the initial concentration is 0.200 M?

Again, use 2nd order integrated rate law, notice $[XY]_0 = 0.200$ M.

Find 12.5% of initial concentration to find $[XY]_t$

$0.200\ M * .0125 = 0.025\ M = [XY]_t$

$$\frac{1}{[XY]_t} - \frac{1}{[XY]_o} = kt$$

$$\frac{1}{0.025\ M} - \frac{1}{0.200\ M} = (7.02 * 10^{-3}\ M^{-1}s^{-1})(t)$$

$$t = 4.99 * 10^3\ s$$

   c. If the initial concentration of XY is 0.052 M, what is the concentration of XY after 64 s?

This time, we have a known t=64s and we are solving for the unknown $[XY]64_{s.}$

$$\frac{1}{[XY]_t} - \frac{1}{[XY]_o} = kt$$

$$\frac{1}{[XY]_t} - \frac{1}{0.052\ M} = (7.02 * 10^{-3}\ M^{-1}s^{-1})(64\ s)$$

$$\frac{1}{[XY]_t} = 19.68005\ M^{-1}$$

$$[XY]_{64\ s} = \frac{1}{19.68005\ M^{-1}} = 0.051\ M$$

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2. Consider the equation for the decomposition of SO_2Cl_2: $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$. The concentration of SO_2Cl_2 was monitored at a fixed temperature as a function of time during the decomposition. The reaction was determined to be first order and has a rate constant of $2.90*10^{-4}\ s^{-1}$. If the reaction is carried out at the same temperature, and the initial concentration of SO_2Cl_2 is 0.0255 M, what will the SO_2Cl_2 concentration be after 865 seconds?

The rate law for this first order reaction can generally be written as:

$$Rate = 2.90 * 10^{-4} s^{-1} [SO_2Cl_2]^1$$

The 1st order integrated rate law can be used to find SO_2Cl_2 when t=865 s.

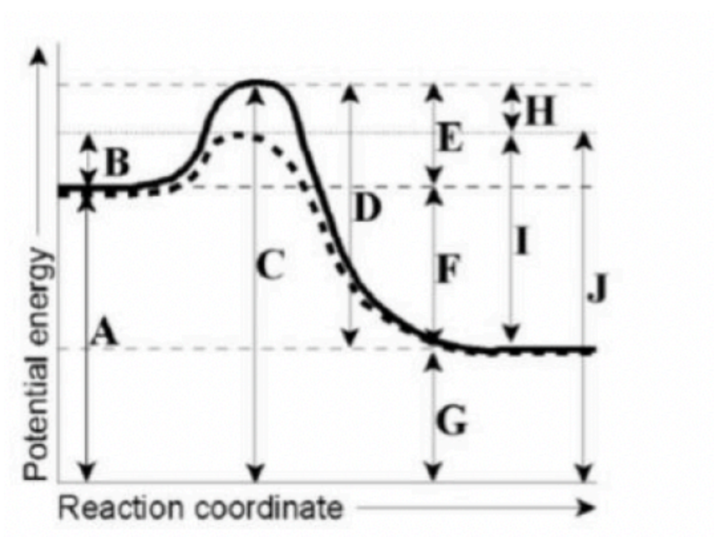
$$\ln[SO_2Cl_2]_{865s} = -kt + \ln[SO_2Cl_2]_0$$

$$\ln[SO_2Cl_2]_{865s} = (-2.90 * 10^{-4}) s^{-1} * 865 + \ln\,[0.0255]$$

$$\ln[SO_2Cl_2]_{865s} = -3.92$$

$$[SO_2Cl_2]_{865s} = e^{-3.92} = 0.0198\ M$$

3. Consider the following reaction coordinate diagram.



a. Is the reaction above exothermic or endothermic? Exothermic
b. Which letter represents the total energy of the reactants? A
c. Which letter represents the total energy of the products? G
d. Which letter represents ΔH for the catalyzed reaction? F
e. Which letter represents ΔH for the uncatalyzed reaction? F
f. Which letter represents the activation energy for the catalyzed reaction? B

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g. Which letter represents the activation energy for the uncatalyzed reaction? E
h. Which letter represents the total energy of the transition state for the catalyzed reaction? J
i. Which letter represents the total energy of the transition state for the uncatalyzed reaction? C

4. The half-life of a first-order reaction is 1.5 hours. How much time is needed for 94% of the reactant to change to product?

For first order, $k = \frac{0.693}{t_{1/2}}$ so k= 0.462 hr^{-1}.
If 94% changes to product, 6% remains.
Use integrated first order rate law and remember ln(1) = 0

$$\ln[0.06] = -(0.462hr^{-1})(t)$$
$$t = 6.09\ hr$$

5. The half-life for the radioactive decay of uranium-238 is 4.5 billion years and is independent of initial concentration. How long will it take for 21% of the U-238 atoms in a sample of U-238 to decay? If a sample of U-238 initially contained 1.5 x 10^{18} atoms when the universe was formed 13.8 billion years ago, how many U-238 atoms does it contain today?

As above, first order, $k = \frac{0.693}{t_{1/2}}$ so k= $1.54*10^{-10}$ yr^{-1}

If 21% decay, then 79% remain. Use integrated first order rate law.

$\ln(0.79) = -(1.54 * 10^{-10} yr^{-1})(t) + \ln(1)$
Remember ln (1) = 0. Solve for t, and t = 1.53 billion years (same as 1.53 x 10^9 years).

To find the number of atoms that remain, we can $\ln(\text{atoms})_t$. Remember, we can take the ln of any quantity, it doesn't have to be molarity.

$$\ln(\text{atoms})_{13.8\ bil} = -(1.54 * 10^{-10} yr^{-1})(13.8 * 10^9\ yr) + \ln(1.5 * 10^{18})$$

$$\ln(atoms)_{13.8\ bil} = 39.72$$

Raise both sides to the e power to isolate $(\text{atoms})_{13.8bil}$

$$e^{39.72} = 1.78 * 10^{17} atoms$$

6. The mechanism for the reaction of CH_3OH and HBr is believed to involve two steps. The overall reaction is exothermic.
Step 1: $CH_3OH + H^+ \leftrightarrow CH_3OH_2^+$ Fast

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Step 2: $CH_3OH_2^+ + Br^- \rightarrow CH_3Br + H_2O$ Slow

a. Write out the overall reaction.

$$CH_3OH + H^+ + Br^- \rightarrow CH_3Br + H_2O$$

b. Which step is the rate determining step?

Step 2 is rate determining

7. The data below were collected for this reaction at 500˚C: $CH_3CN(g) \rightarrow CH_3NC\ (g)$

Time (hr)	$[CH_3CN]$ (M)
0.0	1.000
5.0	0.794
15.0	0.501
20.0	0.393
25.0	0.316

a. What is the order of the reaction? Please explain your reasoning.

First order, if graphed we see that ln[CH3CN] is linear.

b. What is the value of the rate constant at this temperature?

Use first order integrated rate law.

$$\ln[A]_t = -kt + \ln[A]_0$$
$$k = \frac{\ln[A]_t - \ln[A]_0}{-t}$$

Plug in values from chart, I used 5.0 hr and 0.794 M. Note that ln(1)=0.

$k = \frac{\ln[0.794] - \ln[1]}{-5.0\ hr} = 0.046\ hr^{-1}$

c. What is the half life of this reaction (at the initial concentration)?

$k = \frac{0.693}{t}, t = 15.1\ hr$

d. How long will it take for 90% of the CH_3CN to convert to CH3NC?

If 90% converts, 10% remains and $[A]_t = 0.1$. Remember, ln(1) = 0.

Use integrated rate law.

$$\ln[A]_t = -kt + \ln[A]_0$$
$$\ln(0.1) = -0.046 hr^{-1} * t + \ln(1)$$

t = 50 hr

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8. The gas phase reaction $2N_2O_5$ (g) -> $4NO_2$ (g) + O_2 (g) has an activation energy of 103 kJ/ mol, and the rate constant is 0.0900 at 328.0 K. Find the rate constant at 308.9 K.

This solution uses two-point form of Arrhenius equation, but could be done in an alternate route.

$$ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$ln\frac{k_2}{0.0900} = -\frac{103\frac{kJ}{mol}}{8.31 * 10^{-3}\frac{kJ}{K * mol}}\left(\frac{1}{308.9\ K} - \frac{1}{328.0\ K}\right)$$

$$ln\frac{k_2}{0.0900} = -2.3366$$

$$\frac{k_2}{0.0900} = e^{-2.3366}$$

$$k_2 = 0.0087$$