Chapter 14 - Kinetics

Additional Practice Problems

1) A hypothetical reaction A ----> products is second order in A. The half-life of a reaction that was initially 1.66 M in A is 310 min. What is the value of the rate constant, *k*?

2) A reaction shows the same half-life regardless of the starting concentration of the reactant. Is it a zero-order, first-order or second-order reaction?

3) In three different experiments the following results were obtained for the reaction A ----> products: $[A]_0 = 1.00$ M, $t_{1/2} = 50$ min; $[A]_0 = 2.00$ M, $t_{1/2} = 25$ min; $[A]_0 = 0.50$ M, $t_{1/2} = 100$ min. Write the rate equation for this reaction and indicate the value of *k*.

4) Ammonia decomposes on the surface of a hot tungsten wire. Following are the half-lives that were obtained at 1100 °C for different initial concentrations of NH_3: $[NH_3]_0 = 0.0031$ M, $t_{1/2} = 7.6$ min; 0.0015 M, 3.7 min; 0.00068 M, 1.7 min. For this decomposition reaction, what is (a) the order of the reaction; (b) the rate constant *k*?

5) The gas-phase reaction of chlorine with carbon monoxide to form phosgene, $Cl_2\,(g) + CO\,(g)$ ----> $COCl_2\,(g)$, obeys the following rate law:

$$\text{Rate} = \frac{\Delta[COCl_2]}{\Delta t} = \boldsymbol{k}\,[Cl_2]^{3/2}\,[CO] \qquad \text{(exp. rate law)}$$

A mechanism involving the following series of steps is consistent with the rate law:

$$Cl_2 \rightleftharpoons 2C1$$
$$Cl + CO \rightleftharpoons COCl$$
$$COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$$

Assuming that this mechanism is correct, which of the steps above is the slow, or rate-determining, step? Explain.

Hint: try making each step the slowest step (rate-det. step) and see what rate law you get and if it agrees with the experimental rate law given.

Ch 14 - Additional Practice Problems - Solutions

14.26) $A \rightarrow$ products is 2nd order in A

$r = k[A]^2$ rate law for 2nd order rx.

The $\frac{1}{2}$-life for a 2nd order rx is,

$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$ $\quad t_{1/2} = 310\,min \quad [A]_0 = 1.66M$

$k = \frac{1}{t_{\frac{1}{2}}[A]_0}$

$k = \frac{1}{(310\,min)(1.66M)}$

$k = 1.943 \times 10^{-3}\,M^{-1}min^{-1}$

$= 1.94 \times 10^{-3}\,M^{-1}min^{-1}$

$t_{1/2} = 310\,min$ is the 1st half-life

& $[A]_{1,t_{1/2}} = \frac{1}{2}[A]_0 = \frac{1}{2}(1.66M) = 0.83M$

What is the 2nd half-life?

In this case $[A]_0 = [A]_{1,t_{1/2}} = \frac{1}{2}[A]_{start} = 0.83M$

$t_{2,\frac{1}{2}} = \frac{1}{k[A]_{1,t_{1/2}}} = \frac{1}{(1.943\times10^{-3}M^{-1}min^{-1})(0.83M)}$

$t_{2,\frac{1}{2}} = 620\,min$

The half-life for a 2nd order rx. increases (gets longer) as the reaction proceeds (as conc. of reactant decr.).

14.27) 1st order ½-life

$$t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$ is constant (independent of the initial conc.)

2nd order ½-life

$$t_{1/2} = \frac{1}{k[A]_0}$$

$t_{1/2}$ depends on the initial conc. (inc. as rx proceeds)

Since the problem states that the rx shows the same ½-life regardless of $[A]_0$, the rx must be first order

50)

	$[A]_0$ (M)	$t_{1/2}$ (min)
exp1	1.00	50
exp2	2.00	25
exp3	0.50	100

$t_{1/2}$ varies w. $[A]_0$ so can't be a 1st order rx. ($t_{1/2} = \frac{0.693}{k}$)

- could be zero order or 2nd order

$$t_{1/2} = \frac{[A]_0}{2k} \qquad t_{1/2} = \frac{1}{k[A]_0}$$

from these eqn's. can see that for a

1) zero order rx; $t_{1/2}$ dec. as rx. proceeds ($t_{1/2}\downarrow$, $[A]_0\downarrow$)

2) 1st order rx; $t_{1/2}$ constant

3) 2nd order rx; $t_{1/2}$ inc. as rx. proceeds ($t_{1/2}\uparrow$, $[A]_0\downarrow$)

from above data you can see as $[A]_0\downarrow$, $t_{1/2}\uparrow$ as per a 2nd order rx.

- as a matter of fact, as $[A]_0$ is cut in ½ the $t_{1/2}$ doubles

50) (cont.)

$\therefore r = k[A]^2 \qquad t_{1/2} = \frac{1}{k[A]_0}$

$k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{(50.\text{min})(1.00\text{M})} = 0.02\ \text{M}^{-1}\text{min}^{-1}$

– using exp 1 data

51) Similar to previous question.

	$[NH_3]_0$ (M)	$t_{1/2}$ (min)
exp 1	0.0031	7.6
exp 2	0.0015	3.7
exp 3	0.00068	1.7

a) order of rx

can see $t_{1/2}$ dec. as $[NH_3]_0$ dec. as for a zero order rx.

as a matter of fact as $[A]_0$ is cut in half, $t_{1/2}$ is cut in half

$[A]_{0,exp2} = \frac{1}{2}[A]_{0,exp1}$

$t_{1/2,exp1} = \frac{[A]_{0,exp1}}{k}$

$t_{1/2,exp2} = \frac{[A]_{0,exp2}}{k} = \frac{\frac{1}{2}[A]_{0,exp1}}{k} = \frac{1}{2}t_{1/2,exp1}$

Zero order rx., $r = k$

b) $t_{1/2} = \frac{[NH_3]_0}{2k}$

$k = \frac{[NH_3]_0}{2t_{1/2}} = \frac{0.0031\ \text{M}}{2 \cdot (7.6\text{min})} = 2.039\times10^{-4} = 2.0\times10^{-4}\ \text{M}\cdot\text{min}^{-1}$

14.64) For the rx:

$Cl_2(g) + CO(g) \longrightarrow COCl_2(g)$ $\quad r = k[Cl_2]^{3/2}[CO]$

(1) $Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl$ (fast) initiation step

(2) $Cl + CO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COCl$ (fast) } chain propagation steps

(3) $COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow) } chain propagation steps

just add these → $Cl_2 + CO \rightleftharpoons COCl_2$

This is a chain rx in which step (1) is an initiation step. Get Cl· radicals + only need a few of Cl· radicals from this step to get the rx. started. Once started Cl· is generated in step (3) from Cl_2. Steps (2) & (3) are the chain propagation steps and essentially happen an infinite number of times compared to step (1). This is often true of chain rx's. Thus, the overall rx results from adding steps (2) + (3).

Base rate on 3rd step (rate-determining) (if you assume step 2 is slow step you don't get proper rate law)

(4) $r = k_3[COCl][Cl_2]$

$[COCl]$ is intermediate - use (2) to obtain

$r_2 = r_{-2} \Rightarrow k_2[Cl][CO] = k_{-2}[COCl]$

$\therefore [COCl] = \frac{k_2}{k_{-2}}[Cl][CO]$ plug into (4)

(5) $r = k_3\left(\frac{k_2}{k_{-2}}\right)[Cl_2][CO][Cl]$ plug into (5)

$[Cl]$ is intermediate - use (1) to obtain

$k_1[Cl_2] = k_{-1}[Cl]^2 \Rightarrow [Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2}$

$r = k_3\left(\frac{k_2}{k_{-2}}\right)[Cl_2][CO]\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{1/2} = \frac{k_3 k_2}{k_{-2}}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[Cl_2]^{3/2}[CO]$