During Class Invention

Integrated Rate Law Part II

1. The reaction:

 $B(g) \rightarrow products$

follows simple second order kinetics. When the initial concentration of B is 0.500 M the initial rate of the reaction is determined to be $8.40 \times 10^{-3} \text{ M s}^{-1}$. If the initial concentration of B is tripled, what would be the new initial rate of the reaction?

The rate law for the reaction that follows first order kinetics is Rate = $k[B]^2$

If the new [B] is equal to 3[B] then substitute into the rate law,

Rate = $k[3[B]]^2$

The initial rate will increase by a factor of 9.

Rate =
$$9 \cdot 8.40 \ge 10^{-3} \text{ M s}^{-1} = 7.56 \ge 10^{-2} \text{ M s}^{-1}$$

2. Write the integrated rate law for a reaction that follows simple first order kinetics.

$$\frac{1}{[\mathbf{A}]} - \frac{1}{[\mathbf{A}]_0} = \mathbf{k}\mathbf{t}$$

3a. The decomposition of NOCl(g)

$$2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g)$$

is a second order reaction with a rate constant of $0.0480 \text{ M}^{-1} \cdot \text{sec}^{-1}$ at 200 °C. In an experiment at 200 °C, the initial concentration of NOCl was 0.400 M. What is the concentration of NOCl after 15.0 min have elapsed?

$$\frac{1}{[\text{NOCI]}} - \frac{1}{[\text{NOCI]}_0} = \text{kt}$$

$$\frac{1}{[\text{NOCI]}} = \text{kt} + \frac{1}{[\text{NOCI]}_0}$$

$$\frac{1}{[\text{NOCI]}} = 0.0480 \text{ M}^{-1} \cdot \text{sec}^{-1} (15.0 \text{ min}) \left(\frac{60 \text{ sec}}{1 \text{ min}}\right) + \frac{1}{.400 \text{ M}}$$

$$\frac{1}{[\text{NOCI]}} = 45.7 \text{ M}^{-1}$$

$$[\text{NOCI]} = 0.0218 \text{ M}$$

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b. How many minutes will it take for the concentration of NOCl(g) to drop to 0.150 M?

$$\frac{1}{[\text{NOCI}]} - \frac{1}{[\text{NOCI}]_0} = \text{kt}$$

$$\frac{1}{0.150 \text{ M}} - \frac{1}{0.400 \text{ M}} = = 0.0480 \text{ M}^{-1} \cdot \text{sec}^{-1} \text{ (t)}$$
86.8 sec = t or 1.45 minutes

4. Derive a mathematical equation for the half-life for a reaction which follows simple second order kinetics.

We can also arrive at a half–life relationship for a second–order reaction of the type

$A(g) \rightarrow products$

At the half–life the $[A]_{t_{1/2}} = 0.5[A]_0$. Substituting

$$\frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$
$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$
$$\frac{1}{[A]_0} = kt_{1/2} \quad \text{so} \quad t_{1/2} = \frac{1}{k[A]_0}$$

5. The initial concentration of NOCl, described in 13b above, is 0.400 M. Calculate the half-life for the decomposition reaction.

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

$$t_{1/2} = \frac{1}{0.0480 \text{ M}^{-1} \cdot \text{sec}^{-1} \cdot (0.400 \text{ M})}$$

$$t_{1/2} = 52.1 \text{ sec}$$

6. Show how a plot of ln [concentration] versus time can provide the rate constant for a reaction which follows simple second order kinetics.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{[A]}$$
this equation fits the general equation for a line, $y = mx + b$, where
$$y = \frac{1}{[A]} : m = k : x = t$$
time

b. Using the following data establish that the decomposition NO₂ according to the reaction,

 $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

following second order kinetics. Determine the rate constant for the reaction.

Time (sec)	[NO ₂] (M)	$\frac{1}{[A]}$
0	0.0100	100
25	0.0088	114
50	0.0079	127
75	0.0071	141
100	0.0065	154
150	0.0055	182
175	0.0051	196
200	0.0048	208
250	0.0042	238
300	0.0038	263

