Chemistry 132 NT

More can be accomplished with the phrase "I must do something" than with the phrase "something should be done".

Anon

The burning of steel wool

Rates of Reaction

Module 2

Changes of Concentration with Time

- **Concentration-Time Equations**
- **Half-Life**
- **Graphing Kinetic Data**

Review

- The effect of **concentration** on reaction rate.
- Determination of the Rate Law for a given reaction by the **method of initial rates**.

Change of Concentration with Time

- A **rate law** simply tells you how the rate of reaction changes as reactant concentrations change.
  - A more useful mathematical relationship would show <u>how a reactant concentration changes over a period of time</u>.

Change of Concentration with Time

- A **rate law** simply tells you how the rate of reaction changes as reactant concentrations change.
  - Using calculus we can transform a rate law into a mathematical relationship between concentration and time.
  - This provides a **graphical method** for determining rate laws.

Concentration-Time Equations

- **Zero-Order Rate Law**
  - Suppose we look at a simple generic zero order reaction of the reactant “A” to form products.

$$\text{A ® products}$$

  - Remember that the rate of this reaction is unaffected by the concentration of “A”.
  - It’s Rate Law would be:

$$\text{Rate} = k[A]^o = k$$

Concentration-Time Equations

- **Zero-Order Rate Law**
  - You could write the rate law in the form;

$$\text{Rate} = -\frac{D[A]}{Dt} = k[A]^o = k$$

  - Using calculus, we can derive the following relationship between [A] and time,”t”.

$$[A]_t = -kt + [A]_o$$

Concentration-Time Equations

- **Zero-Order Rate Law**
  - You could write the rate law in the form;

$$\text{Rate} = -\frac{D[A]}{Dt} = k[A]^o = k$$

  - Here **$[A]_t$** is the concentration of reactant A at time t, and **$[A]_o$** is the initial concentration.

$$[A]_t = \enclose{circle}{-}kt + [A]_o$$

A Problem To Consider

- Suppose that the decomposition of a hypothetical compound “A” is zero order with a rate constant of 1.8 x 10^{-4} (mol/L·s). If the initial concentration of “A” is 1.00 mol/L, **what is the concentration of “A” after 600 seconds**?
- The zero-order concentration-time equation for this reaction would be:

$$[A]_t = -kt + [A]_o$$

A Problem To Consider

- Suppose that the decomposition of a hypothetical compound “A” is zero order with a rate constant of 1.8 x 10^{-4} (mol/L·s). If the initial concentration of “A” is 1.00 mol/L, **what is the concentration of “A” after 600 seconds**?
- Substituting the given information we obtain:

$$[A]_t = [-(1.8 \times 10^{-4})(600) + (1.00)]\ \text{mol/L}$$

$$[A]_t = [-(0.108) + (1.00)]\ \text{mol/L}$$

$$\boxed{[A]_t = 0.892\ \text{mol/L}}$$

Concentration-Time Equations

- First-Order Rate Law
  - Suppose we look at a simple generic first order reaction of the reactant “A” to form products.

$$A \rightarrow \text{products}$$

  - In a first-order reaction, the rate is directly proportional to the concentration of “A”.
  - Its Rate Law would be:

$$\text{Rate} = k[A]$$

Concentration-Time Equations

- First-Order Rate Law
  - You could write the rate law in the form;

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

Concentration-Time Equations

- First-Order Rate Law
  - Using calculus, you get the following equation.

$$\ln\frac{[A]_t}{[A]_o} = -kt$$

  - Here **$[A]_t$** is the concentration of reactant A at time t, and **$[A]_o$** is the initial concentration.
  - The ratio **$[A]_t/[A]_o$** is the fraction of A remaining at time **t**.

A Problem To Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s^{-1}. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, **what is the concentration of N_2O_5 after 825 seconds**?
- The first-order time-concentration equation for this reaction would be:

$$\ln\frac{\overset{?}{[N_2O_5]_t}}{[N_2O_5]_o} = -kt$$

A Problem To Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s^{-1}. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, **what is the concentration of N_2O_5 after 825 seconds**?
- Substituting the given information we obtain:

$$\ln\frac{[N_2O_5]_t}{1.65\times 10^{-2}\,\mathrm{mol/L}} = -(4.80\times 10^{-4}\,\mathrm{s}^{-1})\times(825\,\mathrm{s})$$

A Problem To Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s^{-1}. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, **what is the concentration of N_2O_5 after 825 seconds**?
- Substituting the given information we obtain:

$$\ln\frac{[N_2O_5]_t}{1.65\times 10^{-2}\,\mathrm{mol/L}} = -0.396$$

A Problem To Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of 4.8 x 10^{-4} s^{-1}. If the initial concentration of N_2O_5 is 1.65 x 10^{-2} mol/L, **what is the concentration of N_2O_5 after 825 seconds**?
- Taking the inverse natural log of both sides we obtain:

$$\frac{[N_2O_5]_t}{1.65\times 10^{-2}\,\mathrm{mol/L}} = e^{-0.396} = 0.673$$

A Problem To Consider

- The decomposition of N_2O_5 to NO_2 and O_2 is first order with a rate constant of $4.8 \times 10^{-4}\ s^{-1}$. If the initial concentration of N_2O_5 is 1.65×10^{-2} mol/L, **what is the concentration of N_2O_5 after 825 seconds**?
- Solving for $[N_2O_5]$ at 825 s we obtain:

$$[N_2O_5] = (1.65 \times 10^{-2}\,\text{mol/L}) \times (0.673) = \boxed{0.0111\,\text{mol/L}}$$

A Problem To Consider

- In the presence of excess thiocyanate ion, SCN^-, the following reaction is first order in iron(III) ion, Fe^{3+}; the rate constant, k, is 1.27 h^{-1}.

$$Fe^{3+}(aq) + SCN(aq) \rightarrow Fe(SCN)^{2+}(aq)$$

How many **hours** are required for this reaction to **reach 90% completion**?

- First, we must note that a 90% completion implies that only 10% of the reactants are left. This implies

$$\frac{[Fe^{3+}]_t}{[Fe^{3+}]_o} = 0.10$$

A Problem To Consider

- In the presence of excess thiocyanate ion, SCN^-, the following reaction is first order in iron(III) ion, Fe^{3+}; the rate constant, k, is 1.27 h^{-1}.

$$Fe^{3+}(aq) + SCN(aq) \rightarrow Fe(SCN)^{2+}(aq)$$

How many **hours** are required for this reaction to **reach 90% completion**?

- Going to our first-order concentration-time equation, we obtain:

$$\ln\frac{[Fe^{3+}]_t}{[Fe^{3+}]_o} = -kt$$

A Problem To Consider

- In the presence of excess thiocyanate ion, SCN^-, the following reaction is first order in iron(III) ion, Fe^{3+}; the rate constant, k, is 1.27 h^{-1}.

  $$\mathbf{Fe^{3+}(aq) + SCN(aq) \text{ ® } Fe(SCN)^{2+}(aq)}$$

  How many **hours** are required for this reaction to **reach 90% completion**?
- Substituting values for k and the ratio $[Fe^{3+}]_t/[Fe^{3+}]_o$

$$\mathbf{\ln(0.10) = -(1.27\ h^{-1})t}$$

A Problem To Consider

- In the presence of excess thiocyanate ion, SCN^-, the following reaction is first order in iron(III) ion, Fe^{3+}; the rate constant, k, is 1.27 h^{-1}.

  $$\mathbf{Fe^{3+}(aq) + SCN(aq) \text{ ® } Fe(SCN)^{2+}(aq)}$$

  How many **hours** are required for this reaction to **reach 90% completion**?
- Solving for t we get:

$$t = \frac{\mathbf{\ln(0.10)}}{\mathbf{-1.27\ h^{-1}}} = \boxed{\mathbf{1.81\ hours}}$$

Concentration-Time Equations

- Second-Order Rate Law
  - You could write the rate law in the form

$$\mathbf{Rate} = -\frac{\mathrm{D}\mathbf{[A]}}{\mathrm{D}\mathbf{t}} = \mathbf{k[A]^2}$$

Concentration-Time Equations

- Second-Order Rate Law
  - Using calculus, you get the following equation.

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

  - Here $[A]_t$ is the concentration of reactant A at time **t**, and $[A]_o$ is the initial concentration.

Concentration-Time Equations

- Rate Law Summary
  - The following table summarizes the Rate Laws and concentration-time equations we have just outlined.

	Rate Law	Concentration-time equation
Zero-order	Rate=k$[A]^0$	$[A]_t = -kt + [A]_o$
First-order	Rate = k$[A]^1$	$\ln\frac{[A]_t}{[A]_o} = -kt$
Second-order	Rate = k$[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$

Half-life

- The **half-life** of a reaction is the time required for the reactant concentration to decrease to one-half of its initial value.
  - For a first-order reaction, the half-life is independent of the initial concentration of reactant.
  - In one half-life the amount of reactant decreases by one-half. Substituting into the first-order concentration-time equation, we get:

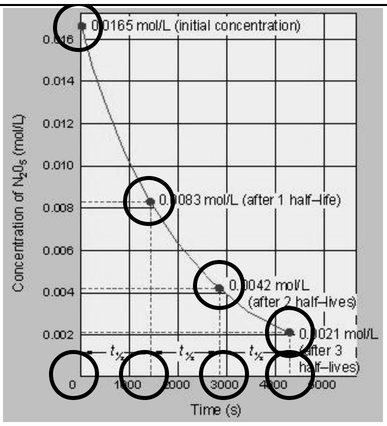
$$\ln(\tfrac{1}{2}) = -kt_{\frac{1}{2}}$$

Half-life

- The **half-life** of a reaction is the time required for the reactant concentration to decrease to one-half of its initial value.
  - Solving for $\mathbf{t_{1/2}}$ we obtain:

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

  - The next slide illustrates the half-life of a first-order reaction.



Half-life

- Sulfuryl chloride, SO_2Cl_2, decomposes in a first-order reaction to SO_2 and Cl_2.

$$SO_2Cl_2(g) \text{ ® } SO_2(g) + Cl_2(g)$$

- At 320 °C, the rate constant is 2.2×10^{-5} s^{-1}. What is the half-life of SO_2Cl_2 vapor at this temperature?
- Substitute the value of k into the relationship between k and $t_{1/2}$.

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

Half-life

- Sulfuryl chloride, SO_2Cl_2, decomposes in a first-order reaction to SO_2 and Cl_2.

$$SO_2Cl_2(g) ® SO_2(g) + Cl_2(g)$$

- At 320 °C, the rate constant is $2.2 \text{ x } 10^{-5} \text{ s}^{-1}$. What is the half-life of SO_2Cl_2 vapor at this temperature?
- Substitute the value of k into the relationship between k and $t_{1/2}$.

$$t_{\frac{1}{2}} = \frac{0.693}{2.20 ´ 10^{-5} \text{ s}^{-1}}$$

Half-life

- Sulfuryl chloride, SO_2Cl_2, decomposes in a first-order reaction to SO_2 and Cl_2.

$$SO_2Cl_2(g) ® SO_2(g) + Cl_2(g)$$

- At 320 °C, the rate constant is $2.2 \text{ x } 10^{-5} \text{ s}^{-1}$. What is the half-life of SO_2Cl_2 vapor at this temperature?
- Substitute the value of k into the relationship between k and $t_{1/2}$.

$$t_{\frac{1}{2}} = 3.15 ´ 10^4 \text{s}$$

Half-life

- For a **second-order reaction** half-life depends on the initial concentration and becomes larger as time goes on.
  - Again, assuming that $[A]_t = ½[A]_o$ after one half-life, it can be shown:

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

  - Each succeeding half-life is twice the length of its predecessor.

Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - Note that the zero-order concentration-time equation can be identified as the equation of a straight line.

$$\underset{\overset{\uparrow}{y}}{[A]_t} = \underset{\overset{\uparrow}{m}}{-k}\,\underset{\overset{\uparrow}{x}}{t} + \underset{\overset{\uparrow}{b}}{[A]_o}$$

Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - Note that the zero-order concentration-time equation can be identified as the equation of a straight line.
  - This means if you **plot [A] vs. time** you will get a **straight line for a zero-order reaction**.

Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the first-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

$$\ln\frac{[A]_t}{[A]_o} = -kt$$

Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the first-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

$$\ln[A]_t - \ln[A]_o = -kt$$

Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the first-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

$$\underset{\substack{\uparrow\\ y}}{\ln[A]_t} \underset{\substack{\\ =}}{=} \underset{\substack{\uparrow\\ m}}{-k}\underset{\substack{\uparrow\\ x}}{t} \underset{\substack{\\ +}}{+} \underset{\substack{\uparrow\\ b}}{\ln[A]_o}$$

Graphing Kinetic Data

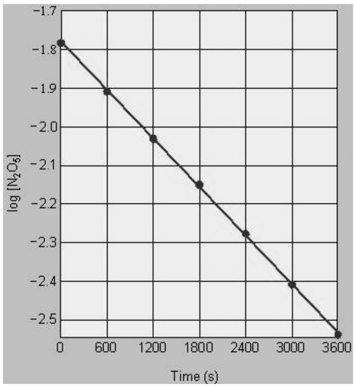
- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the first-order concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.
  - This means if you **plot ln[A] vs. time** you will get a **straight line for a first-order reaction**.

Plot of log [N_2O_5] versus time.

Time (s)	[N_2O_5]	log[N_2O_5]
0	0.0165	1.783
600	0.0124	-1.907
1200	0.0093	-2.032
1800	0.0071	-2.149
2400	0.0053	-2.276
3000	0.0039	-2.409
3600	0.0029	-2.538

$2N_2O_5(g)$ ® $4NO_2(g) + O_2(g)$

The figure displayed shows a plot of log [N_2O_5] at various times during the decomposition reaction. The fact that the points lie on a straight line is confirmation that the rate law is first order.



Graphing Kinetic Data

- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the **second-order** concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.

$$\frac{1}{[A]_t} = \underset{\uparrow}{kt} + \underset{\uparrow}{\frac{1}{[A]_o}}$$

y = mx + b

Graphing Kinetic Data

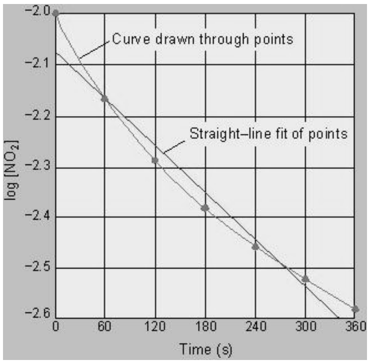
- In addition to the method of initial rates, discussed earlier, rate laws can be deduced by **graphical methods**.
  - If we rewrite the **second-order** concentration-time equation in a slightly different form, it can be identified as the equation of a straight line.
  - This means if you **plot 1/[A] vs. time** you will get a **straight line for a second-order reaction**.
  - The next slide illustrates the graphical method of deducing the order of a reaction.

Plotting the data for the decomposition of nitrogen dioxide at 330°C.

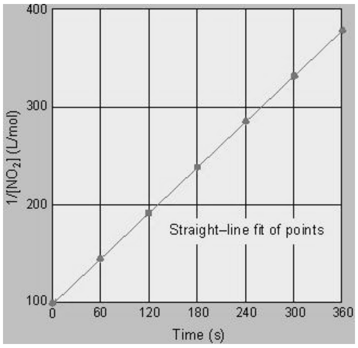
Time (s)	(A) log$[NO_2]$	(B) 1/$[NO_2]$
0	-2.000	100
60	-2.166	146
120	-2.286	193
180	-2.379	239
240	-2.456	286
300	-2.521	332
360	-2.578	379

$2NO_2(g)$ ® $2NO(g) + O_2(g)$

Plot of log $[NO_2]$ against time. Note that a straight line does not fit the points well.



Plot of $1/[NO_2]$ against time. Note how closely the points follow the straight line, indicating that the decomposition is second order.



Operational Skills

- Using the concentration-time equation for first-order reactions
- Relating the half-life of a reaction to the rate constant

Time for a few review questions.