1. How is the rate of a chemical reaction measured?
   By monitoring concentration of a reactant or product over time.

2. Write out a generic rate law for the reaction $2A + B_2 \rightarrow 4C$.
   
   \[ \text{Rate} = k[A]^x[B_2]^y \]

3. What does the order tell you?
   How the rate will vary with concentration changes.

4. How does temperature affect rates?
   Temperature changes will change the rate constant $k$.

5. What is activation energy?
   Look up in glossary.
6. \[ A (g) + 3B (g) \rightarrow 2C (g) \]

Use the tabulated data to answer the questions about this reaction, which is carried out in a 1.0 L container at 25°C.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>M ([\text{A}]_0)</th>
<th>M ([\text{B}]_0)</th>
<th>Initial rate of formation of C, (\frac{M}{\text{min}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.20</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.20</td>
<td>2.0</td>
</tr>
</tbody>
</table>

a. For experiment 1, give the initial rate of disappearance of
i. A

0.25 M/min

ii. B

0.25 M/min

b. Determine the orders of A and B.

Use experiments 2 and 3 to determine the order of A by ratio the rate laws for those two runs.

\[
\frac{2.0 \, \text{M/min}}{2.0 \, \text{M/min}} = \frac{k[0.20]^x[0.20]^3}{k[0.10]^x[0.20]^3}
\]

\[
1.0 = (2.0)^x
\]

\[
x = \frac{\log(1.0)}{\log(2.0)} = 0
\]

Use experiments 2 and 3 to determine the order of A by ratio the rate laws for those two runs. Y = 3.

c. Calculate the value of the rate constant and give its units.

Use any of the experiments and plug in the values for rate, concentration and order and solve for \(k\).

\[
\text{Rate} = k[\text{A}]^x[\text{B}]^y
\]

\[
2.0 \, \text{M/min} = k[0.10]^0[0.20]^3
\]

\[
k = \frac{2.0 \, \text{M/min}}{[0.10]^0[0.20]^3} = 250 \, \text{min}^{-1}
\]

d. Write out the rate law for the reaction.

\[
\text{Rate} = 250\, \text{min}^{-1}[\text{B}]^3
\]

The \([\text{A}]^0\) term does not show up since changing the concentration of A will not affect the rate.
7. The nitrogen dioxide (NO₂) produced during driving is a health hazard. Chemists attempting to remove it have investigated the effect of heating it to high temperatures. At 300 °C the concentration of NO₂ drops with time as in the table below. Find the order of reaction and the rate constant.

<table>
<thead>
<tr>
<th>t(sec)</th>
<th>[NO₂] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.40E+00</td>
</tr>
<tr>
<td>5</td>
<td>2.60E-01</td>
</tr>
<tr>
<td>10</td>
<td>1.28E-01</td>
</tr>
<tr>
<td>20</td>
<td>7.58E-02</td>
</tr>
<tr>
<td>30</td>
<td>5.38E-02</td>
</tr>
<tr>
<td>40</td>
<td>4.17E-02</td>
</tr>
<tr>
<td>50</td>
<td>3.40E-02</td>
</tr>
<tr>
<td>60</td>
<td>2.87E-02</td>
</tr>
</tbody>
</table>

Solution:

1) Test which rate equation produces a straight-line plot.
2) Find the rate constant from the slope of the line.

1<sup>st</sup>-order: $\ln[\text{NO}_2]_t = -kt + \ln[\text{NO}_2]_0$

2<sup>nd</sup>-order: $\frac{1}{[\text{NO}_2]_t} = kt + \frac{1}{[\text{NO}_2]_0}$

To test these, you first need to first calculate values of $\ln[\text{NO}_2]$ and $1/[\text{NO}_2]$.

<table>
<thead>
<tr>
<th>t(sec)</th>
<th>[NO₂] (M)</th>
<th>$\ln[\text{NO}_2]$</th>
<th>$1/[\text{NO}_2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.40E+00</td>
<td>0.875469</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>2.60E-01</td>
<td>-1.34707</td>
<td>3.85</td>
</tr>
<tr>
<td>10</td>
<td>1.28E-01</td>
<td>-2.05412</td>
<td>7.80</td>
</tr>
<tr>
<td>20</td>
<td>7.58E-02</td>
<td>-2.58022</td>
<td>13.20</td>
</tr>
<tr>
<td>30</td>
<td>5.38E-02</td>
<td>-2.92316</td>
<td>18.60</td>
</tr>
<tr>
<td>40</td>
<td>4.17E-02</td>
<td>-3.17805</td>
<td>24.00</td>
</tr>
<tr>
<td>50</td>
<td>3.40E-02</td>
<td>-3.38099</td>
<td>29.40</td>
</tr>
<tr>
<td>60</td>
<td>2.87E-02</td>
<td>-3.54962</td>
<td>34.80</td>
</tr>
</tbody>
</table>

Then plot these values:
The 1\textsuperscript{st}-order plot is curved, but the 2\textsuperscript{nd}-order plot is a good straight line. Hence, the reaction is 2\textsuperscript{nd}-order with a rate law $r = k [\text{NO}_2]^2$.

In this case the rate constant $k$ is equal to the slope of the 2\textsuperscript{nd}-order plot. Pick two locations on the line to define the slope.

$k = \text{Slope} = 16.2 \text{ M}^{-1}/30.0 \text{ s} = 0.540 \text{ M}^{-1} \text{s}^{-1}$

8. In automobile exhausts, the following reaction can occur between nitrogen dioxide and carbon monoxide.

$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$

To design better emission control systems, chemists need to know as much as possible about the kinetics of this reaction. The experimental rate law is $r = k[\text{NO}_2]^2$. Explain which of the two mechanisms below better represents this reaction.

\textit{Mechanism A} \\
$\text{NO}_2 \xrightarrow{k_1 \text{ (slow)}} \text{NO} + \text{O}$ \hspace{1cm} $\text{CO} + \text{O} \xrightarrow{k_2 \text{ (fast)}} \text{CO}_2$

\textit{Mechanism B} \\
$\text{2NO}_2 \xrightarrow{k_1 \text{ (slow)}} \text{NO}_3 + \text{NO}$ \hspace{1cm} $\text{CO} + \text{NO}_3 \xrightarrow{k_2 \text{ (fast)}} \text{NO}_2 + \text{CO}_2$

\textbf{Solution}

Both mechanisms correctly reproduce the reaction stoichiometry. In A, the intermediate is an O atom; in B, it is an NO$_3$ molecule.

\textit{Mechanism A} \\
$\text{NO}_2 \xrightarrow{k_1} \text{NO} + \text{O}$ \hspace{1cm} $\text{CO} + \text{O} \rightarrow \text{CO}_2$

\textit{Mechanism B} \\
$\text{2NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ \hspace{1cm} $\text{CO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{CO}_2$

Both mechanisms have a slow initial step which will therefore be rate-determining. The rate law in each case will be that of the initial step.

\begin{center}
\begin{tabular}{l|l}
\textbf{Mechanism} & \textbf{Rate Law} \\
A & $r = k_1 [\text{NO}_2]$ \\
B & $r = k_1 [\text{NO}_2]^2$ \\
Expt. law & $r = k [\text{NO}_2]^2$
\end{tabular}
\end{center}

Only mechanism B has a \textit{bimolecular} elementary initial step that correctly reproduces the experimental rate law with $k = k_1$. 
9. Cows digesting grass emit large quantities of global-warming methane gas into the atmosphere. As an atmospheric chemist, you are interested in knowing what role that methane plays in the cycling of chlorine in the atmosphere via the reaction:

$$\text{Cl}(g) + \text{CH}_4(g) \rightarrow \text{CH}_3\text{Cl}(g) + \text{H}(g)$$

The rate constant at 25.0 °C is $6.02 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. At 65,000 ft in the stratosphere, where the temperature is -60 °C, the rate constant is $1.08 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. What is the activation energy for this reaction?

Solution

$$T_1 = 25.0 \degree C = 298 \text{ K}$$

$$T_2 = -60 \degree C = 213 \text{ K}.$$ 

Putting in the $k$ values given:

$$\ln \left( \frac{1.08 \times 10^7 \text{ M}^{-1} \text{s}^{-1}}{6.02 \times 10^7 \text{ M}^{-1} \text{s}^{-1}} \right) = \frac{E_a}{8.314 \text{ J mol}^{-1} \text{K}^{-1}} \left( \frac{1}{298 \text{ K}} - \frac{1}{213 \text{ K}} \right)$$

and so

$$E_a = \frac{\ln(0.179) \times 8.314}{(0.00336 - 0.00470)} = 1.06 \times 10^3 \text{ J/mol}$$

Or, $E_a = 10.6 \text{ kJ/mol}$

10. Given the following mechanism, write the overall reaction and the rate law for the overall reaction:

$$\text{A} + \text{B} \rightarrow 2\text{C} \quad \text{SLOW}$$

$$\text{C} + \text{A} \rightarrow \text{D} \quad \text{FAST}$$

Solution:

To determine the overall reaction, you must add together all of the mechanism steps.

$$2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$$

The slow step controls the overall reaction rate. Since it is an elementary step, the rate law can be written directly from the balanced equation.

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

Challenge Question: The specific rate constant for the first-order decomposition of $\text{N}_2\text{O}_5$ (g) to $\text{NO}_2$ (g) and $\text{O}_2$ (g) is $7.48 \times 10^{-3} \text{ s}^{-1}$ at a given temperature. Find the length of time required for the total pressure in the system containing $\text{N}_2\text{O}_5$ at an initial pressure of 0.100 atm to rise to 0.155 atm.

Solution: For the challenge question, you must change the pressures to concentration in order to write a first order rate law. Also, use the integral form of the rate law. Remember, the ideal gas law can be used.

$$\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 (g) + 1/2 \text{O}_2 (g)$$
Initially, all of the pressure is due to the N$_2$O$_5$. As the reaction progresses, we have a mixture of all three gases and must apply Dalton’s Law. All of the gases are at the same temperature and volume.

At time =0, N$_2$O$_5$ concentration will be $P_i/RT = n_i/V$; 0.100atm/RT=n$_i$/V
At time =t, N$_2$O$_5$ concentration will be $P_f = P_{N_2O_5}+P_{NO_2}+P_{O_2}$. From Dalton’s Law, we know $n_f=n_{N_2O_5}+n_{NO_2}+n_{O_2}$ From the balanced chemical equation, we can determine by how much the moles change.

Let us assume that T is 200K and V is 2.0L (any T and V will work. Why? we are creating a ratio.)

$n_i=0.100\text{atm}*2.0L/0.08206\text{(L*mol/atm*K)}*200K = 0.01218 \text{ moles}$

$n_f=P_f*V/RT=0.155\text{atm}*2.0L/0.08206\text{(L*mol/atm*K)}*200K = 0.01889$

$n_f=X + 2X +1/2X=0.01889$  $X$ is the amount of moles of N$_2$O$_5$ that will decompose by time t.

$X= 5.397 \times 10^{-3}$

The moles of N$_2$O$_5$ at time t is $0.01218 - 5.397 \times 10^{-3} = 6.782 \times 10^{-3}$

Now we can use the integral rate law for a first order reaction.

$$\ln \left[6.782 \times 10^{-3}\text{mol/2.0L}\right]=-7.48\times 10^{-3} \text{sec}^{-1} * t + \ln[0.01218\text{mol/2.0L}]$$

$t=97 \text{ sec}$