Rates of reaction components

In General: $$a \, A + b \, B \rightarrow c \, C + d \, D$$

$$\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Sample problem: The rate of formation of NH$_3$ in the reaction N$_2$(g) + 3 H$_2$ $\rightarrow$ 2 NH$_3$(g) was reported as 1.2 mmol L$^{-1}$ s$^{-1}$ under a certain set of conditions. What is the rate of consumption of H$_2$?

The rate of a reaction may depend upon:

* Concentration of reactants
* Concentration of products
* Mechanism of the reaction
* Time
An Empirical Rate Law:
An experimentally determined, macroscopic rate law

Expression relating rate to concentrations and time

Many different functional forms are in principle possible!

Reaction rate becomes catastrophically fast: heat or moles of gas produced faster than the surroundings can respond. Supersonic!
Example: Decomposition of $\text{N}_2\text{O}_5$

$$\text{N}_2\text{O}_5 \rightarrow 2 \text{NO}_2 + \frac{1}{2} \text{O}_2$$

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = f([\text{N}_2\text{O}_5],[\text{N}_2\text{O}],[\text{O}_2],...,t)?$$

The rate law depends on the overall microscopic mechanism and cannot in general be inferred from the net reaction!

For example, the following two mechanisms will give very different rate laws for the decomposition of $\text{N}_2\text{O}_5$:

Bimolecular collision results in the formation of 4 $\text{NO}_2$ and one $\text{O}_2$

Collision with the wall results in the formation of 2 $\text{NO}_2$ and one $\text{O}$
How do we find the rate law?

A Zero Order Rate Law

\[ [N_2O_5](t) = -kt + [N_2O_5]_o \]

A First Order Rate Law

\[ [N_2O_5](t) = [N_2O_5]_o e^{-kt} \]

\[ \frac{d[N_2O_5]}{dt} = -k \]

\[ \frac{d[N_2O_5]}{dt} = -k [N_2O_5]^0 \]

Rate Constant
Empirical rate laws

\[ \text{A} \rightarrow \text{B} \]

\[ \frac{-d[A]}{dt} = k [A]^0 \quad \text{0}^{\text{th}} \text{ Order} \]

\[ \frac{-d[A]}{dt} = k [A]^1 \quad \text{1}^{\text{st}} \text{ Order} \]

\[ \frac{-d[A]}{dt} = k [A]^2 \quad \text{2}^{\text{nd}} \text{ Order} \]

\[ \vdots \]

\[ \text{A} + \text{B} \rightarrow \text{C} \]

\[ \frac{-d[A]}{dt} = k [A][B] \]

Overall 2\text{nd} Order
1\text{st} order in A
1\text{st} order in B

\[ \frac{-d[A]}{dt} = k [A]^2[B] \]

Overall 3\text{rd} Order
2\text{nd} order in A
1\text{st} order in B

\[ \vdots \]
Sample Problem:

The reaction \[ 2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl} \] was studied at -10\(^\circ\)C. The following data were obtained for the rate of loss of Cl\(_2\).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>[NO](_o)</th>
<th>[Cl(_2)](_o)</th>
<th>(\frac{d[\text{Cl}_2]}{dt})(_o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 M</td>
<td>0.10 M</td>
<td>-0.18 M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.10 M</td>
<td>0.20 M</td>
<td>-0.35 M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.20 M</td>
<td>0.20 M</td>
<td>-1.45 M/s</td>
</tr>
</tbody>
</table>

(a) What is the rate law?
(b) What is the rate constant?