Rate Law

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

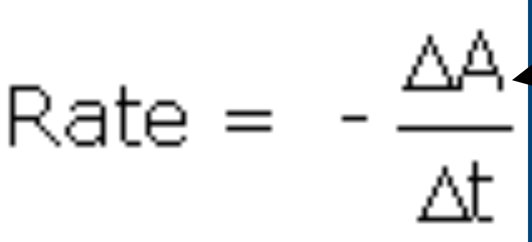
Rate Law

- **Rate Law** is an expression which relates the rate of a reaction to the concentration of the reactants

- Helps us calculate the rate of a reaction with given concentrations of reactants

- The rate law shows the quantitative effect of concentration on reaction rate

For the reaction: A → products



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

The rate of consumption of A is directly proportional to its concentration.

That is, the faster A is consumed (smaller), the lower its concentration (smaller numerator).

Rate Law

$$Rate = k[A]^x$$

Where

- k is the constant of proportionality
- [A] is the concentration of A
- x is the power, called the order of the reaction

k is the **specific rate constant**

Can only be determined experimentally (not from chemical reaction)

The rate constant is specific or unique for each reaction at a specific temperature, since its value depends upon the size, speed and types of molecules in the reaction.

Order of reaction

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

The **order** (x) of a reaction indicates how concentration of reactants affects the rate of a reaction.

For example, in our reaction where A → products,
First order reaction, x = 1, this would mean the reaction rate was directly proportional to changes in reactant concentration.
In a first order reaction, if the concentration of A were doubled, the rate would double. If the concentration were tripled, the rate would triple, etc.

Order of reaction

The **order** (x) of a reaction indicates how concentration of reactants affects the rate of a reaction.

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

Second order reaction, x = 2, doubling the concentration would increase the rate by a factor of $2^x = 2^2 = 4$. That is, the rate would increase four times. Tripling the concentration of A would cause the rate to increase nine times ($3^x = 3^2 = 9$).

Order of reaction

The **order** (x) of a reaction indicates how concentration of reactants affects the rate of a reaction.

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

Zero order reaction, x = 0, This means a change in the concentration of A does NOT change the rate of the reaction.

Order of reaction

For a reaction with more than one reactant,
such as A + B → products
The rate law would be:

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

The rate depends on both A and B concentrations. Each reactant can affect the rate differently.

The total order of the reaction is the sum of the order with respect to A and the order with respect to B, that is, $x + y$.

Determining the Rate Law of a Reaction

- The rate law can only be determined experimentally
- The rate law cannot usually be determined from the molar coefficients.

We will use the initial rates method to determine the order of each reactant which uses the effect of changes in concentration of one reactant while keeping the other constant.

Determining the Rate Law of a Reaction Using initial rates

Example 1. What is the rate law for the following reaction, given the experimental data below?

$H_2O_2 + 2\ HI \rightarrow 2\ H_2O + I_2$

Trial	$[H_2O_2]$ (mol/L)	[HI] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.10	0.0076
2	0.10	0.20	0.0152
3	0.20	0.10	0.0152

Determining the Rate Law of a Reaction Using initial rates

Example 1. What is the rate
the experim
H_2O_2 + 2

Trial	$[H_2O_2]$ (mol/L)	[
1	0.10	
2	0.10	
3	0.20	

Steps

1. To solve for H_2O_2, look at the table where the other reactant [HI] is constant while H_2O_2 is changing.

2. Use the equation:

3. Calculate the order

$$\frac{\text{rate trial 3}}{\text{rate trial 1}} = \left(\frac{[H_2O_2]_3}{[H_2O_2]_1}\right)^{\text{order}}$$

$$\frac{0.0152}{0.0076} = \left(\frac{0.20}{0.10}\right)^{\text{order}}$$

$$2 = 2^{\text{order}}$$

$$1 = \mathit{order}$$

4. Rate = $k[H_2O_2][HI]$

Determining the Rate Law of a Reaction Using initial rates

Example 2. For the reaction A + B → products, the following data was collected

Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0

Determine the rate law

Solution

The rate law will have the form:

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

Look for trial where one reactant remains constant and the other changes.

Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0

To find the order for [A] we can use these numbers

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[A]_2}{[A]_1}$$

$$\frac{18.0}{2.0} = \left(\frac{0.30}{0.10}\right)^{order}$$

$$9 = 3^{order}$$

$$2 = order$$

Solution

$$\text{Rate} = k[A]^2[B]^1$$

Determining the Specific Rate Constant

Example 3. Determine the value of the specific rate constant, k, for the reaction in example 2.

In order to determine the value of the rate constant we use the rate law and experimental data. We can use the data from any trial, substitute into the rate law and solve for k.

$$\text{rate} = k[A]^2[B]$$

$$k = \frac{\text{rate}}{[A]^2[B]}$$

$$k = \frac{2.0}{(0.10)^2(0.20)}$$

$$k = 1000$$

Trial	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.20	2.0
2	0.30	0.20	18.0
3	0.20	0.40	16.0

Example 4. For the reaction

$$3\,A(g) + B(g) + 2\,C(g) \rightarrow 2\,D(g) + 3\,E(g)$$

The following data was obtained:

Trial	[A] (mol/L)	[B] (mol/L)	[C] (mol/L)	Initial Rate (mol/Ls)
1	0.10	0.10	0.10	0.20
2	0.20	0.10	0.10	0.40
3	0.20	0.20	0.10	1.60
4	0.20	0.10	0.20	0.40
5	0.50	0.40	0.25	?
6	?	0.60	0.50	6.00

a. Write the rate law for this reaction.
b. Calculate the value of the rate constant.
c. Calculate the rate for Trial #5.
d. Calculate the concentration of A in Trial #6.