**Rate Law**

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



The rate of consumption of A is directly proportional to its concentration. That is, the faster A is consumed, the lower its concentration.

This is represented by the equation:

**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

The constant k, is known as the **specific rate constant** for the reaction. The rate constant and the order can only be determined experimentally.

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.

Changing temperature would change the speed of the reactant particles and hence change the rate constant. Temperature is the only factor which affects the rate constant.

**Order of Reaction**

Rate law is represented by the equation:

**Rate = k[A]x,**

where x represents the order of the reaction.

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

For example, in our reaction where A → products,

If the order of the reaction was a **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.

If the reaction were a **second order** reaction, x = 2, doubling the concentration would increase the rate by a factor of 2x = 22 = 4. That is, the rate would increase four times. Tripling the concentration of A would cause the rate to increase nine times (3x = 32 = 9).

If the rate of the reaction did not depend on the concentration of A, it would be a zero order reaction, x = 0. This means a change in the concentration of A does NOT change the rate of the reaction.

For a reaction with more than one reactant, such as

A + B → products

The rate law would be:

**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. Even though the rate of formation of the products and the rate of consumption of reactants is related to their reaction stoichiometry, the rate law cannot usually be determined from the molar coefficients.

There several ways to determine the rate law of a reaction:

* the differential rate law, which uses calculus
* integrated rate law, whuch uses concentration vs time graphs
* initial rates method

The goal of each of these methods is to determine the order of each reactant.

We will be using the initial rates method in this course. The initial rates method uses the effect of changes in concentration of one reactant on the initial reaction rate, while keeping the other reactant concentrations constant.

**Rate Law Using Initial Rates**

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

H2O2 + 2 HI → 2 H2O + I2

|  |  |  |  |
| --- | --- | --- | --- |
| Trial | [H2O2] (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 |

**Solution.**

According to reaction stoichiometry, you would expect the rate law to be:

rate = k[H2O2][HI]2

But, by comparing trials 1 and 2 it can be seen that keeping [H2O2] constant while doubling [HI] doubles the rate. Using ratios makes the relationships easier to see:



This indicates that the reaction is first order in HI, NOT second order as the stoichiometry suggests.

Next we choose two trials where [H2O2] is changed but [HI] does not change. We can use trials 1 and 3: doubling [H2O2] doubles the rate as well.

Using ratios,



The reaction is then first order in [H2O2].

The rate law for this reaction is

rate = k[H2O2][HI]

The total order of this reaction is the sum of the orders or exponents. Total order = 1 + 1 = 2.

**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:

Rate = k[A]x[B]y

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

Using Trials 1 & 2, [B] remains constant



Reactant A is second order

There is no trial where [A] remains constant, so we must use both Δ[A] and Δ[B] to determine the order for [B]

If we use Trials 1&3,

From the rate law, (Δ[A])2× Δ[B]order= Δrate



The order is first for [B]

Therefore, the rate law is **Rate = k[A]2[B]**

**Determining the Specific Rate Constant**

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

**Solution.**

The data for example 2 is

|  |  |  |  |
| --- | --- | --- | --- |
| 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 |

The rate law was determined to be

rate = k[A]2[B]

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.

Let’s use the data from trial 1:



For this course, the value of k has no units.

Try calculating the value of k for each trial.

Within experimental error, the values of k for each trial should be equal because the reaction was performed under the same conditions.

**Example 4.** For the reaction

3 A(g) + B(g) + 2 C(g) → 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.

**Solution.**

a. Comparing trials 1 and 2, [B] and [C] remain constant and doubling [A] increases rate 2x.



Therefore the reaction is first order in A.

Comparing Trials 2 and 3, [A] and [C] remain constant and doubling [B] increases rate 4x.



Therefore the reaction is second order in B.

Comparing Trials 2 and 4, [A] and [B] remain constant and doubling [C] results in no change in the rate.



Therefore the reaction is zero order in C.

The rate law for the reaction is:

**rate = k[A][B]2**

b. To find the value of k, we use that data from any one trial. We can use data from trial #1:

by rearranging the rate law, then substituting the values for [A] and [B] in Trial 1, we can solve for k.



c. If we know the value of the rate constant, we can just substitute values into our rate law:

rate = k[A][B]2
rate = (200)(0.50 mol/L)(0.40 mol/L)2
rate = 16.0 mol/Ls

d. In order to determine the concentration of A, we can substitute known values into the rate law, then solve for [A].

Rearrange the rate law equation substitute values answer contains correct units



**Rate Law and Stoichiometry**

We have learned, for most reactions, the rate law, the specific rate constant, *k*, and the mechanism of a reaction can only be determined experimentally, not from the reaction stoichiometry.

However, for reactions that occur in a single step (elementary reactions) the order of each reactant in the rate law is equal to the coefficient in the reaction's balanced equation.

For the elementary reaction:

*a*A + *b*B → *c*C + *d*D

the rate law is

rate = k[A]*a*[B]*b*,

where a and b are the molar coefficients for the elementary reaction.

**Example 5.** One of the reactions that results in smog is the reaction of ozone, O3(g) and nitrogen monoxide, NO(g). This reaction is thought to occur in a single elementary step according to the equation:

O3(g) + NO(g) → NO2(g) + O2(g)

Determine the rate law for this reaction.

**Solution.**

Since this is an elementary reaction, the molar coefficients become the order for each reactant. Therefore, the reaction is first order in ozone and first order in nitrogen monoxide.

The rate law should be: **rate = k[O3][NO]**

**Rate Law and Reaction Mechanisms**

We have seen that rate law for reactions which occur in more than one step do NOT correspond to the coefficients in its balanced net equation.

The rate law for these equations corresponds to the stoichiometry of the rate determining step. Those reactants which are zero order, do not appear in the RDS and, hence do not affect reaction rate significantly.

**Example 6.** The mechanism for the reaction

3 M + N → P + 2 Q

is below:



a) What is the rate law for this reaction?
b) What would be the effect of tripling the [M]?
c) What would be the effect of doubling the [N]?

**Solution.**

a) Since the only reactant present in the RDS is M, and its coefficient is 2, the order of the reaction will be 2.

The rate law is: **Rate = k[M]2**

b) 3 x [M] causes the rate to increase by

3order = 32 = 9.

The rate increases by 9 times.

c) N is not present in the RDS. The reaction is then zero order in N. There is, therefore, no effect on the rate by changing the concentration of N.

Chemists will deduce the mechanism of a reaction by first determining the rate law experimentally, then proposing a mechanism.

For the reaction

2 NO2(g) + Cl2(g) → 2 NO2Cl(g),

the rate law was determined to be

Rate = k[NO2][Cl2]

A suggested mechanism would have the molar coefficients of NO2 and Cl2, in the RDS, equal to one. The product of this step would have to reflect this, likely resulting in a reaction intermediate.

The remaining steps would be acceptable if the sum of all steps resulted in the net equation.

A possible RDS could be NO2 + Cl2 → NO2Cl + Cl

Cl would be a reaction intermediate.

A step to follow might be NO2 + Cl → NO2Cl

To check if the mechanism is acceptable, we determine if the sum of the steps is equal to the net equation.



Remember, chemists cannot determine a mechanism definitively, just suggest a possible mechanism which reflects experimental data.