Rate Laws

The effect of concentration on the rate of reaction is described using a **rate law**. A rate law is an equation that can be used to calculate the reaction rate for any given concentration of reactants.

For a reaction with a single reactant ($A \rightarrow B$), the rate law can be expressed as

$$rate = k\left[A\right]^x$$

where k is the **specific rate constant**, which has a unique value for every reaction, and [*A*] is the concentration of the reactant *A*.

The exponent x in the rate law above is called the **reaction order**. The reaction order for a reactant defines how the rate is affected by the concentration of that reactant. For example, the rate law for the decomposition of H_2O_2 is

$$rate = k\left[H_2O_2\right]$$

Because $x = 1$ in this equation, the decomposition of H_2O_2 is said to be first order in H_2O_2. Because the reaction is first order in H_2O_2, the reaction rate changes in the same proportion that the concentration of H_2O_2 changes. In other words, doubling the concentration of H_2O_2 will double the reaction rate. Similarly, if the concentration of H_2O_2 is reduced to one-half, the reaction rate is halved as well.

Other Reaction Orders

The overall order of a chemical reaction is the sum of the orders for the individual reactants in the rate law. Many chemical reactions, especially those having more than one reactant, are not first order. Consider a reaction with two reactants.

$$A + B \rightarrow products$$

The rate law for such a reaction is

$$rate = k\left[A\right]^x\left[B\right]^y$$

where x and y are the reaction orders for *A* and *B*, respectively. An example of such a reaction is shown below.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The rate law for this reaction is

$$rate = k[NO]^2[H_2]$$

This rate law was determined experimentally. The data tells us that the rate depends on the concentration of the reactants as follows:

- If $[NO]$ doubles, the rate quadruples.
- If $[H_2]$ doubles, the rate doubles.

The reaction is described as second order in NO, first order in H_2, and third order overall.

Determining Reaction Order

Reaction order is determined experimentally using the **method of initial rates**. This method determines reaction order by comparing the initial rates of a reaction carried out with varying reactant concentrations. To understand this method, consider the general reaction

$$A + B \rightarrow products$$

Suppose this reaction is carried out with varying concentrations of *A* and *B* and yields the initial rates shown below.

Trial	**Initial [*A*] (M)**	**Initial [*B*] (M)**	**Initial Rate (M/s)**
1	0.100	0.100	0.002
2	0.200	0.100	0.004
3	0.200	0.200	0.016

Recall that the general rate law for this type of reaction is

$$rate = k[A]^x[B]^y$$

To determine x, the concentrations and reaction rates in Trials 1 and 2 are compared. As you can see, while [*B*] remains constant, [*A*] doubles. Also, the rate in Trial 2 is double the rate in Trial 1. Because doubling the concentration of *A* doubles the rate, the reaction must be first order in *A*.

To determine y, the concentrations and reaction rates in Trials 2 and 3 are compared. You can see that while [*A*] remains constant, [*B*] doubles. Also, the rate in Trial 3 is quadruple the rate in Trial 2. Because $2^y = 4$, y must equal 2. Thus, the reaction is second order in *B*.

The information above can be combined to write the overall rate law for this reaction.

$$rate = k[A][B]^2$$

The overall reaction is third order.

Note: If changing the concentration of a reactant has no effect on the reaction rate, then the reaction order of that reactant is zero, and that reactant will not appear in the rate law (since $[A]^0 = 1$).

Determining the Specific Rate Constant

Once the rate law for a reaction is known, the specific rate constant can be determined by substituting experimentally determined concentration and rate data into the rate law.

For the example above, if we substitute the data for Trial 1 into the rate law, we get

$$\begin{aligned} rate &= k[A][B]^2 \\ 0.002 &= k(0.100)(0.100)^2 \\ 0.002 &= k(0.001) \\ k &= \frac{0.002}{0.001} \\ k &= 2 \end{aligned}$$

Thus, the overall rate law for this example would be

$$rate = 2[A][B]^2$$

The units of *k* depend on the units of the rate and concentrations used in the calculation.

Example

For the reaction $NO_2(g)+CO(g)\rightarrow NO(g)+CO_2(g)$, the following data was obtained.

Trial	**Initial [NO_2] (M)**	**Initial [CO] (M)**	**Initial Rate (M/s)**
1	0.100	0.100	0.005
2	0.100	0.200	0.005
3	0.400	0.200	0.080

Determine the rate law and rate constant for this reaction.

Worksheet

Determine the rate law and rate constant for each of the following.

1. $H_2O_2(g) + 2HI(g) \rightarrow 2H_2O(g) + I_2(g)$

Trial	$[H_2O_2]$ (M)	[HI] (M)	Rate (M/s)
1	0.10 M	0.10 M	0.0076
2	0.10 M	0.20 M	0.0152
3	0.20 M	0.10 M	0.0152

2. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

Trial	$[H_2]$ (M)	$[I_2]$ (M)	Rate (M/s)
1	1.0	1.0	0.20
2	1.0	2.0	0.40
3	2.0	2.0	0.80

3. $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

Trial	$[NO_2]$ (M)	$[F_2]$ (M)	Rate (M/min)
1	1.0	1.0	1.0×10^{-4}
2	2.0	1.0	2.0×10^{-4}
3	1.0	2.0	2.0×10^{-4}

4. $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

Trial	[NO] (M)	$[Br_2]$ (M)	Rate (M/h)
1	1.0	1.0	1.30×10^{-3}
2	2.0	1.0	5.20×10^{-3}
3	1.0	2.0	4.16×10^{-2}

5. $ClO^{3-}(aq) + 9I^-(aq) + 6H^+(aq) \rightarrow 3I^{3-}(aq) + Cl^-(aq) + 2H_2O(l)$

Trial	$[ClO^{3-}]$ (M)	$[I^-]$ (M)	$[H^+]$ (M)	Rate (M/s)
1	0.10	0.10	0.10	X
2	0.10	0.20	0.10	2X
3	0.20	0.20	0.10	4X
4	0.20	0.20	0.20	16X

Given the rate law provided, predict the effect on the initial rate of the following changes in the conditions (temperature, concentration, volume).

6. Nitrogen monoxide gas and hydrogen gas react according to the rate law:

$$rate = k[NO]^2[H_2]$$

How does the rate change if:

a) the concentration of hydrogen is doubled.
b) the concentration of nitrogen monoxide is doubled.
c) the concentration of hydrogen is cut in half.
d) the volume of the container is cut in half.
e) the volume of the container is doubled.
f) the temperature is increased.
g) the concentration of nitrogen monoxide is doubled while the concentration of hydrogen is cut in half.
h) the concentration of hydrogen is doubled while the concentration of nitrogen monoxide is cut in half.

7. The rate law of a particular reaction between gases X, Y and Z is found to be

$$rate = k[Y]^2[Z]$$

How does the initial rate change if:

a) the concentration of X is doubled.
b) the concentration of Y is tripled.
c) the concentration of Z is quadrupled.
d) the volume of the container is cut in half.
e) the volume of the container is doubled.
f) the temperature is increased.
g) the concentration of X is quadrupled while the concentration of Y and Z are doubled.
h) the concentration of Z is cut in half while the concentration of Y is doubled.
i) the concentration of Y and Z are tripled while the concentration of X is cut in thirds.