The Rate Laws

We are interested to know how the rate of reaction depends on the concentrations of reactants. When chemical reaction takes place, the concentrations of reactants and products change continuously during the course of the life-span of the reaction. Hence, it becomes difficult to measure the change in concentration accurately. This further complicates if the reverse reaction occurs some point in time. Therefore, it is desirable to measure the initial reaction rate based on the initial (starting) concentrations. It happens that the rate is directly proportional to some power of initial concentrations of reactants. Based on this, we can write the rate law for a general type of reaction:

$$aA + bB \rightarrow cD + dD$$

The rate law for the above equation is

$$\text{rate } \alpha \ [A]^x[B]^y$$

The symbol α is the proportionality sign. This sign is not suitable for any kind of calculations and hence it must be removed. When we remove that we introduce a constant and the equation is written with an equal sign as follows.

$$\text{rate} = k\ [A]^x[B]^y \tag{1}$$

where k is known as **rate constant** is the proportionality constant between the reaction rate and reactant concentrations. The above equation is known as *rate law or rate equation*. If we know initial concentrations of A and B as well as k, x, and y, we can calculate the rate of reaction using the above equation. The values of k, x, and y are usually determined experimentally. The order of reaction is judged by the numerical values of x and y. Say for example, x =1 and y=2. Then we say the reaction is **first-order** with respect A, **second-order** with respect B, and overall it is **third-order** (3 = 1+2). If x=0 or y=0 or x=y=0, then we say the reaction is **zero-order** with respect A or zero-order with respect B or zero-order with respect to A and B. As you know anything to the power zero is one. That means the reaction rate is independent of the initial concentrations.

By knowing the x and y, we can better understand how the reaction rate depends on the initial concentrations. Suppose, for example, a particular reaction has yielded x = 2 and y =1. The rate law for the reaction according to Equation (1) is

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

Note that if either x =1 or y=1 or x = y= 1, the number one is omitted from the rate law expression because $[\ ]^1$ is the same as [ ]. This reaction is second-order with respect A, first-order with respect B, and overall it is third-order. This rate law tells us that if we double the concentration of A, the reaction rate will increase by a factor of 4 because of power 2 in the expression. Let us verify this statement assuming initially [A] = 1.0 M and [B] =1.0 and doubling [A] from 1.0 M to 2.0 M:

for [A] = 1.0 M   rate1 = k (1.0 M)^2 (1.0 M) = k (1.0 M^3)   (initial)

for [A] =2.0 M   rate2 = k (2.0 M)^2 (1.0 M) = 4 x k(1.0 M^3)   (doubling A)

Thus you can see

rate2 = 4 x rate1

Now if we double the concentration of B keeping the concentration of A constant, the reaction rate will double. Let test this statement setting [A]=1.0 M and [B] =1.0 M and doubling [B] from 1.0 M to 2.0 M:

for [B] = 1.0 M   rate3 = k (1.0 M)^2 (1.0 M) = k (1.0 M^3)   (initial)

for [B] = 2.0 M   rate4 = k (1.0 M)^2 (2.0 M) = 2 x k (1.0 M^3)   (doubling B)

Hence   rate4 = 2 x rate3

This simple analysis illustrates how the change in concentrations of reactants alters the reaction rate. In general,

- if the power of the reactant is 1, then the rate increases 2-fold times(doubles) when the concentration of the reactant is doubled (because 2^1)
- if the power of the reactant is 2, then the rate increases 4-fold times(quadruples) when the concentration of the reactant is doubled (because 2^2)
- if the power of the reactant is 3, then the rate increases 8-fold times when the concentration of the reactant is doubled (because 2^3)

Experimental Determination of Order of Reaction

To determine the rate law applicable to a particular chemical reaction, one needs to establish the exact values for x, y, and k that depends on whether one reactant or more than one reactant are involved.

One reactant: If a chemical reaction involves one reactant, it is a simple matter to determine the order of reaction by measuring the rate of reaction as a function of concentration of the reactant. If the rate doubles when the concentration of reactant is doubled, the reaction is the first-order. If the rate becomes 4-fold times (quadruples) when the concentration of the reactant is doubled, the reaction is the second-order and similarly, the third, the fourth, and the higher orders.

More than One reactant: If the reaction involves more than one component, we have to devise a "divide and conquer" method. We have to measure the rate law making it to depend on the concentration of one reactant at a time. How do we do that? It is simple. Fix the concentrations of all the reactants except the one in question and record the rate of reaction as a function of change in the concentration of the reactant in question. The same procedure is applied to all the remaining reactants. This is illustrated using the following example for two reactants.

Example

Consider the following reaction

$$2\ NO(g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

From the following data collected at 25^0 C, determine (a) the rate law (rate equation), (b) rate constant, and (c) rate of the reaction when [NO] = 5×10^{-3} M and [O_2] = 7×10^{-3} M.

Experiment	**[NO] (M)**	**[O_2] (M)**	**Initial Rate (M/s)**
1	2×10^{-3}	1×10^{-3}	1.25×10^{-4}
2	4×10^{-3}	1×10^{-3}	5.0×10^{-4}
3	4×10^{-3}	2×10^{-3}	10.0×10^{-4}

Solution

Notice that there are three experiments conducted. In experiment 1 and 2, the concentration of [NO] is doubled while keeping concentration of [O_2] constant. And in experiment 2 and 3, concentration of [O_2] is doubled while keeping the concentration of [NO] constant.

(a) The rate law

The rate equation for the above reaction is

$$\text{rate} = k\ [NO]^x\ [O_2]^y$$

Now, our task is to determine x and y based on the data given in the table that involved the following two steps:

- step 1. determine x
- step 2. determine y

Step 1. Determination of x

In determination of either x or y, you need to choose any two experiments where the concentration of one reactant is fixed and the other one varies. But the question is which two experiments to choose? Here lies the intelligent. When you want to determine x, choose two experiments where the concentration of base of y, i.e. $[O_2]$ is held constant. In this case experiment 1 and 2. Once you have decided which two experiments, then you write the rate equation for each experiment:

$\text{rate1} = k\,[2 \times 10^{-3}]^x\,[1 \times 10^{-3}]^y$ (experiment 1)

$\text{rate2} = k\,[4 \times 10^{-3}]^x\,[1 \times 10^{-3}]^y$ (experiment 2)

Now you take the ratio of these two rates and cancel similar terms in the numerator and denominator.

$$\frac{rate2}{rate1} = \frac{k\,[4x10^{-3}M]^x\,[1x10^{-3}M]^y}{k\,[2x10^{-3}M]^x\,[1x10^{-3}M]^y} = \frac{[5x10^{-4}M/s]}{[1.25x10^{-4}M/s]}$$

Therefore,

$$\frac{[4x10^{-3}M]^x}{[2x10^{-3}M]^x} = 4 \text{ or } 2^x = 4$$

Hence x = 2

Step 1. Determination of y

Now you chose experiments 2 and 3 because the concentration of base of x i.e. [NO] is constant. The rate equations for these two experiments are

$\text{rate2} = k\,[4 \times 10^{-3}]^x\,[1 \times 10^{-3}]^y$ (experiment 2)

$\text{rate3} = k\,[4 \times 10^{-3}]^x\,[2 \times 10^{-3}]^y$ (experiment 3)

Now you take the ratio of experiment 3 and 2, and cancel the similar terms in numerator and denominator.

$$\frac{rate3}{rate2} = \frac{k\,[4x10^{-3}M]^x\,[2x10^{-3}M]^y}{k\,[4x10^{-3}M]^x\,[1x10^{-3}M]^y} = \frac{[10x10^{-4}M/s]}{[5x10^{-4}M/s]}$$

Therefore,

$$\frac{[2x10^{-3}M]^y}{[1x10^{-3}M]^y} = 2 \text{ or } 2^y = 2$$

Hence y =1

The rate equation for this chemical equation is written as

$$\text{rate} = k\,[NO]^2\,[O_2]^1 = k\,[NO]^2\,[O_2]$$

which states that the reaction is second-order with respect to [NO], first-order with respect to $[O_2]$, and overall third-order.

(b) Rate constant

The rate constant k can be evaluated by rearranging the above rate equation as

$$k = \frac{rate}{[NO]^2[O_2]}$$

To calculate the k you can take the concentrations of [NO] and $[O_2]$ from **any one of the experiment.** It does not make any difference which data you take, all should yield the same result. Suppose, we take the data from the experiment 2, we get

$$k = \frac{5x10^{-4}}{[4 \text{ x } 10^{-3}]^2[1 \text{ x } 10^{-3}]} = 3.1 \text{ x } 10^4 \text{ / M}^2 \text{ .s}$$

Therefore, the rate law (equation) becomes

$$\text{rate} = 3.1 \text{ x } 10^4\,[NO]^2\,[O_2] \text{ / M}^2\text{.s}$$

(c) rate of the reaction when [NO] = 5 x 10^{-3} M and [O] = 7 x 10^{-3} M.

Now you substitute these values in the above equation to get the rate:

$$\begin{aligned}\text{rate} &= 3.1 \text{ x } 10^4\,[NO]^2\,[O_2] \text{ / M}^2\text{.s}\\ &= 3.1 \text{ x } 10^4\,(5 \text{ x } 10^{-3} \text{ M})^{2\,(}7 \text{ x } 10^{-3} \text{ M) / M}^2\text{.s}\\ &= 5.4 \text{ x } 10^{-3} \text{ M/s}\end{aligned}$$