Reaction Mechanism

We come now to one of the more important reasons to study the rates of reactions: to understand the **reaction mechanism,** the sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products.

For a reaction to occur, particles must collide. As a result of these collisions, there may be rearrangements of particles and chemical bonds. Let us look at the following reaction:

$$5\,Fe^{+2}_{(aq)} + MnO_4^{-1}{}_{(aq)} + 8\,H^{+1}_{(aq)} \longrightarrow 5\,Fe^{+3}_{(aq)} + Mn^{+2}_{(aq)} + 4\,H_2O_{(l)}$$

What is the likelihood of this reaction happening in one step?

What must happen?

It is unrealistic to look at equations such as the one above, and think that the reaction would take place in one stage, i.e. when five Fe^{+2} ions , one MnO_4^{-1} ion and eight H^{+1} ions come together and collide at the same instant in time !!

Most reactions occur in a sequence of steps - each step involving only one or two particles. Such a sequence of steps is known as the **reaction mechanism** Each step in a mechanism is called an **elementary step** or elementary reaction. These steps can involve one molecule - ***unimolecular***, or involve collisions of two molecules, (same of different molecules) - ***bimolecular***, and in rare cases three molecules - ***termolecular***. Each elementary step has its own activation energy and the steps must add up to give the balanced equation for the overall reaction. Together the overall reaction is the sum of the elementary steps.

For most reactions, the individual steps cannot be seen or detected. A mechanism is just a theory of what might be taking place. Determining a mechanism can be a difficult task. Generally, the mechanism is a theory reflecting the step-by-step production of reaction products.

In any sequence of steps, some elementary steps are faster than others. The differences may be very large. It often happens that one step is much slower than all the others. This is called the **rate determining step** of the reaction. The overall rate of the reaction will be determined by the rate determining step of the reaction, compare to the slowest worker determining the rate of production on a production line. When studying the kinetics of a reaction we are studying the kinetics of the rate determining step.

The rate equation or the rate law for the reaction identifies the species involved in the rate determining step.

Example 1: Let us look at a chemical reaction, the decomposition of ozone, O_3:

$$2\,O_3 \longrightarrow 3\,O_2$$

A study of this reaction indicates that if the concentration of O_3 is doubled, then the rate of reaction doubles. To explain this, the following mechanism is proposed :

	O_3	$\longrightarrow O_2 + O$	**Slow**
	$O + O_3$	$\longrightarrow 2\,O_2$	Fast
Overall reaction:	$2\,O_3$	$\longrightarrow 3\,O_2$	

Note that each step requires one or two molecules to collide. The first step being slow is the rate determining step and only altering its concentration has any effect on the rate of the reaction
The oxygen atom produced in the first step is used up in the second step and does not appear as the final product - it is termed the ***intermediate***.

Def. Intermediate: species that are produced in one step and are consumed in another.

For the above reaction: Rate $\propto$ [reactant], Rate $= k\,[O_3]^1$ **First Order Reaction**
k = Rate Constant

Most chemical reactions proceed by a sequence of steps, each involving only one or two particle collisions. The mechanism of a chemical reaction cannot be deduced from the net equation for the reaction.

If we know the stoichiometry for an elementary process, we can predict its **rate law or rate equation.**

The coefficients of the reactants in the rate determining step are equal to the exponents in the rate law.

Similarly, if we know the rate law, we can deduce the elementary process - the rate determining step of the reaction.
By knowing the rate law for the overall equation you thus, know the form of the rate determining step.

The rate equation for a reaction *cannot* be predicted from its overall stoichiometry. In contrast, *the rate equation of an elementary step is given by the product of the rate constant and the concentrations of the reactants in that step.*

In general, consider a reaction between A and B:

$$A + B \longrightarrow \text{Products}$$

The rate of reaction depends on the concentrations of A and B, but one can not simply say that the rate of the reaction is proportional to the concentration of a and proportional to the concentration of B. The relationship is:

$$\text{Reaction rate} \propto [A]^m [B]^n = k\,[A]^m [B]^n$$

This equation is the rate equation, the powers 'm' and 'n' are usually integers , 0,1, or 2 and are characteristic of the reaction. The reaction is of **order** 'm' with respect to A and of order 'n' with respect to B. The overall order of reaction is (m + n). The proportionality constant 'k' is called the **rate constant** for the reaction.

Example 2 $2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$ $\Delta H = -112.8$ kJ

Step I	$2\,NO_{(g)} \longrightarrow N_2O_{2(g)}$	**slow**	$\Delta H = +34.0$ kJ
Step II	$N_2O_{2\,(g)} + O_{2\,(g)} \longrightarrow 2\,NO_{(g)}$	fast	$\Delta H = -146.8$ kJ

Determine: a) rate determining step (b) overall equation (c) write the rate law
(d) state the intermediate, (e) the order of the reaction? (f) draw a potential energy diagram.

Example 3 $4\,HBr_{(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(g)} + 2\,Br_{2(g)}$

A study of this reaction indicates that increasing the concentration of either the HBr or the O_2 will increase the rate in a similar fashion. Hence the rate determining step involves ...
Mechanism

$HBr + O_2 \longrightarrow HOOBr$	**slow**
$HOOBr + HBr \longrightarrow 2\,HOBr$	fast
$2\,HOBr + 2\,HBr \longrightarrow 2\,H_2O + 2\,Br_2$	fast

Example 4

The hypochlorite ion undergoes self oxidation-reduction to give the chlorate, ClO_3^{-1} , and chloride ions:

$$3\ ClO^{-1}_{(aq)} \longrightarrow ClO_3^{-1}{}_{(aq)} + 2\ Cl^{-1}_{(aq)}$$

It is thought that the reaction occurs in two steps:

$$ClO^{-1}_{(aq)} + ClO^{-1}_{(aq)} \longrightarrow ClO_2^{-1}{}_{(aq)} + Cl^{-1}_{(aq)} \quad \text{fast}$$
$$ClO_2^{-1}{}_{(aq)} + ClO^{-1}_{(aq)} \longrightarrow ClO_3^{-1}{}_{(aq)} + Cl^{-1}_{(aq)} \quad \textbf{slow}$$

What is the molecularity of each step? Write the rate law for the reaction. Show that the sum of these reactions gives the equation for the net reaction. What is the order with respect to each reactant? What is the overall order?

The rate constant for a reaction relates the rate to the concentrations of the reactants.

Example: A solution of P, of concentration 0.20 mol dm^{-3} undergoes a first order reaction at an initial rate of 3.0×10^{-4} mol dm^{-3} s^{-1}. Calculate the rate constant.

Solution: Since, for a first-order reaction:

Rate $= k\,[P]^1$

3.0×10^{-4} mol dm^{-3} s^{-1} = k 0.20 moldm^{-3}

The rate constant, $k = 1.5 \times 10^{-3}\ s^{-1}$

The unit of a first-order rate constant is $time^{-1}$, a second-order rate constant has the unit $concentration^{-1}\ time^{-1}$

An Easy Way to Determine the Order of a Reaction from Initial Rate

Consider the initial rates of reaction (mol / L•s) at 800ºC for:

$$\mathbf{2\ H_{2(g)} + 2NO_{(g)} \longrightarrow N_{2(g)} + 2\ H_2O_{(g)}}$$

	Series 1			**Series 2**		
	Conc. H_2 (mol/L)	**Conc. NO (mol/L)**	**Rate (mol/Ls)**	**Conc. H_2 (mol/L)**	**Conc. NO (mol/L)**	**Rate (mol/Ls)**
Expt. 1	0.10	0.10	0.10	0.10	0.10	0.10
Expt. 2	0.20	0.10	0.20	0.10	0.20	0.40
Expt. 3	0.30	0.10	0.30	0.10	0.30	0.90
Expt. 4	0.40	0.10	0.40	0.10	0.40	1.60

One way to determine the order of a reaction is to obtain the initial rate (i.e., the rate at t = 0) as a function of concentration of reactant. The reasoning involved is indicated in the following example.

EXAMPLE: The initial rate of decomposition of ethanal, (acetaldehyde), CH_3CHO:

$$CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$$

was measured at a series of different concentrations with the following results:

Conc. CH_3CHO (mol/L)	0.10	0.20	0.30	0.40
Rate (mol/L•s)	0.085	0.34	0.76	1.4

Using these data, determine the order of the reaction; that is, determine the value of m in the equation

rate = $k\,[CH_3CHO]^m$

Solution Let us write down the rate expression at two different concentrations:

$$\text{rate}_2 = k[\text{conc.}_2]^m$$
$$\text{rate}_1 = k[\text{conc.}_1]^m$$

Dividing the first equation by the second,

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{[\text{conc.}_2]^m}{[\text{conc.}_1]^m}$$

Now let us substitute data, taking $\text{conc.}_2 = 0.20$ M, $\text{conc.}_1 = 0.10$ M;

$$\frac{0.34}{0.085} = \frac{[0.20]^m}{[0.10]^m}$$

Simplifying,

$$4 = 2^m$$

Clearly, m = 2; that is, the reaction is second order.

EXERCISE Repeat the calculation, using the data at 0.40 and 0.30 M.
Answer : $1.4/0.76 = (0.40/0.30)^m$. Solving, m = 2 (approximately).
Thus, rate law is given by the expression: Rate = $k\,[CH_3CHO]^2$

Now determine the rate law of the reaction above, (H_2 + NO —>) with the data provided.