

## 3.6: Day 23- Reaction Mechanisms

### D23.1 Multi-step Reactions and Rate-Determining Step

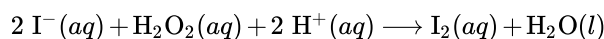
A valid mechanism for a multi-step reaction has these characteristics:

- The mechanism should consist of a series of unimolecular and/or bimolecular elementary reaction steps.
- The sum of the reaction steps should agree with the overall balanced reaction equation.
- The mechanism must agree with the experimentally observed rate law.

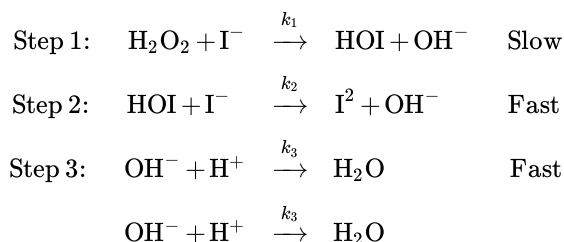
For elementary reactions, rate laws (and reaction order) can be derived directly from the stoichiometry of the chemical equations, but this is not true for a multi-step reaction where the balanced overall equation is not an elementary reaction. For some multi-step mechanisms, it is possible to derive the overall rate law from the known rate laws of the individual elementary steps. The overall rate law can also be determined from experimental data. If the experimental rate law agrees with the theoretical rate law (derived from the mechanism), the mechanism is a plausible theory for how the reaction occurs. Other experimental data can also support the plausibility of a mechanism. For example, if an intermediate proposed in the mechanism can be detected, that would support the mechanism.

Deriving rate law from a reaction mechanism can be a complex task. However, for many multi-step reactions, one elementary reaction step is *significantly slower* than the other steps, and this step limits the rate at which the overall reaction occurs. This *slowest step in a mechanism* is called the **rate-determining step** (or **rate-limiting step**), and it allows for some simplifying approximations.

As an example of a rate-determining step, consider the oxidation of iodide ions by hydrogen peroxide in aqueous solution:



The currently accepted mechanism for this reaction has three steps. The third step occurs twice each time the first and second steps take place, so it is written twice. For simplicity the states of matter have been omitted.

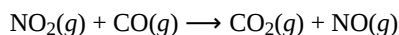


The first step is labeled slow, which means that the rate constant  $k_1$  is smaller than the other two rate constants. Steps 2 and 3 are labeled fast, because rate constants  $k_2$  and  $k_3$  are larger than  $k_1$ . Initially steps 2 and 3 cannot occur, because the concentration of one of their reactants is zero or very low. For example, the concentration of HOI is zero before the reaction begins because HOI is not a reactant in the overall reaction. Thus, step 2 cannot occur until there is some HOI available, which means that until step 1 produces some HOI and raises  $[\text{HOI}]$ , step 2 has zero rate. No matter how big the rate constant for step 2 might be, step 2 cannot go any faster than step 1. We say that the rate of step 2 is limited by the rate of step 1. Similarly, step 3 cannot occur until steps 1 and 2 produce some  $\text{OH}^{-}$ , so the rate of step 3 also limited by the rate of step 1. Thus, in this case, step 1 is the rate-limiting step.

#### Activity 1: Reaction Energy Diagram

### D23.2 First Step is Rate-Determining

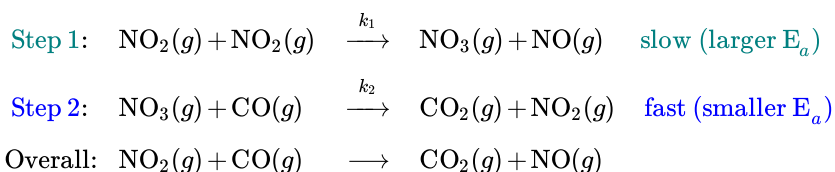
When the rate-determining step is the first step in a mechanism, the rate law for the overall reaction can be approximated as the rate law for the first step. The reaction of  $\text{NO}_2$  and  $\text{CO}$  provides an illustrative example:



At temperatures below 225 °C, the experimentally observed rate law is:

$$\text{rate} = k[\text{NO}_2]^2$$

This is consistent with a mechanism that involves these two elementary reaction steps:



Both steps in this mechanism are bimolecular elementary reactions, and the sum of the two steps agrees with the overall reaction (the  $\text{NO}_3$  that is formed in step 1 reacts away in step 2, and one of the  $\text{NO}_2$  molecules that reacts in step 1 is reformed in step 2, so only one  $\text{NO}_2$  molecule reacts overall).

Figure 1 shows the corresponding reaction energy diagram for this mechanism.  $E_{a,1}$  is the activation energy for step 1, and it reflects the energy difference between the reactants and the first transition state.  $E_{a,2}$  is the activation energy for step 2, and it reflects the energy difference between the intermediary minimum and the second transition state.

**Figure 1.** Reaction energy diagram for the  $\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}(g)$  reaction. Click on each “i” in the figure for additional information.

With  $E_{a,1}$  being much larger than  $E_{a,2}$ , step 1 has a smaller rate constant than step 2 ( $k_1 < k_2$ , assuming that the frequency factor ( $A$ ) for the two steps are similar). However, step 2 cannot occur until step 1 produces some amount of  $\text{NO}_3$  ( $\text{NO}_3$  is a reaction intermediate, and therefore its concentration is zero at the beginning of the reaction). Because  $k_2$  is larger, as soon as some  $\text{NO}_3$  molecules are formed, they readily react away (step 2 reaction). Hence, the concentration of  $\text{NO}_3$  is always very small, and the rate of step 2 cannot go faster than the rate of step 1.

Step 1 limits the rate of step 2, and is therefore the rate-determining step in this mechanism. Typically, the slowest reaction step is the one with the largest  $E_a$  and/or the highest energy transition state, as illustrated in Figure 1.

The stoichiometry of step 1, which is an elementary reaction, gives this rate law:

$$\text{rate}_1 = k_1[\text{NO}_2]^2$$

which can be approximated as the rate law for the overall reaction, and it is in agreement with the experimentally observed rate law.

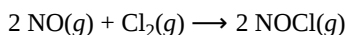
### D23.3 Equilibrium Approximation

When the rate-determining step is not the first step, the rate law can be approximated as the rate law for the rate-determining step. However, one or more of the reactants involved in the rate-determining step is a reaction intermediate formed from a previous step. Hence, the rate law for the rate-determining step includes the concentration of one or more reaction intermediates.

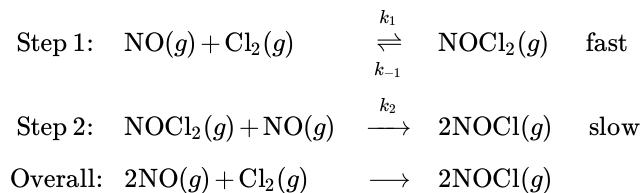
Experimentally, the concentration of a reaction intermediate is rarely measurable. (Even if it can be measured, the accuracy is usually low.) Therefore, experimentally determined rate laws are always expressed in terms of concentrations of reactants and/or products, for which accurate measurements are much easier to obtain.

In order to compare the theoretical rate law derived from the mechanism to the experimentally determined rate law, we must express the mechanism rate law only in terms of reactant and product concentrations, that is, we cannot simply use the rate law of the rate-determining step as is. If a preceding step that forms the reaction intermediate is at equilibrium, then we can make use of the **equilibrium approximation** to express the concentration of the intermediate in terms of concentrations of reactants.

For example, consider the following multi-step reaction:



The currently accepted mechanism for this reaction is:



**Figure 2.** Reaction energy diagram for the  $2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)$  reaction. Click on each “i” for more info.

Step 2 is the rate-determining step, and its rate law is:

$$\text{rate}_2 = k_2 [\text{NOCl}_2] [\text{NO}]$$

However, this rate law involves the concentration of an intermediate,  $[\text{NOCl}_2]$ , so it cannot be compared to experimental data. We need to express  $[\text{NOCl}_2]$  in terms of concentrations of reactants.

Step 1 in this mechanism is much faster than step 2 and it is a reversible reaction. Reversible means that not only can NO and  $\text{Cl}_2$  react to form  $\text{NOCl}_2$ , but  $\text{NOCl}_2$  rapidly reacts to form NO and  $\text{Cl}_2$ . That is, step 1 can go forward with rate constant  $k_1$  and backward with rate constant  $k_{-1}$ ; this is represented by the two arrows pointing in opposite directions.

Because step 2 is slow, reaction of  $\text{NOCl}_2$  with NO is much slower than reaction of  $\text{NOCl}_2$  to form NO and  $\text{Cl}_2$  (the reverse of step 1). Thus, when  $\text{NOCl}_2$  molecules are formed, they are more likely to decompose back to NO and  $\text{Cl}_2$  than to react in step 2. When enough  $\text{NOCl}_2$  has formed, we can approximate that the rate of its decomposition ( $\text{rate}_{-1}$ ) is equal to the rate at which it forms ( $\text{rate}_1$ ) and step 1 is at *equilibrium* ( $\text{rate}_1 = \text{rate}_{-1}$ ). This approximation allows us to express the rate laws of step 1 as:

$\text{rate}_1$	=	$\text{rate}_{-1}$
$k_1[\text{NO}][\text{Cl}_2]$	=	$k_{-1}[\text{NOCl}_2]$

This relationship can be rearranged to solve for the concentration of  $\text{NOCl}_2$ :

$$[\text{NOCl}_2] = \left( \frac{k_1}{k_{-1}} \right) [\text{NO}][\text{Cl}_2]$$

And substituting this into the rate law for step 2, we have:

$$\text{rate}_2 = k_2 [\text{NOCl}_2] [\text{NO}] = k_2 \left( \frac{k_1}{k_{-1}} \right) [\text{NO}][\text{Cl}_2][\text{NO}] = \left( \frac{k_1 k_2}{k_{-1}} \right) [\text{NO}]^2 [\text{Cl}_2]$$

If we make:

$$k' = \frac{k_1 k_2}{k_{-1}}$$

then the rate law for the overall reaction becomes:

$$\text{rate} = k' [\text{NO}]^2 [\text{Cl}_2]$$

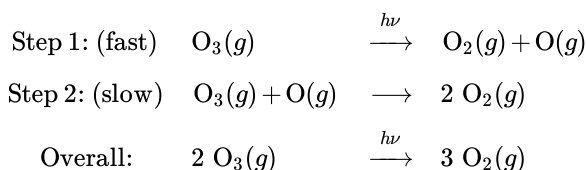
This rate law can be compared with experimental data to determine whether the proposed mechanism is a plausible one.

## Activity 2: Rate Law from Mechanism

### D23.4 Catalysts and Reaction Mechanisms

A **catalyst** *increases the rate of a reaction by altering the mechanism*, allowing the reaction to proceed via a pathway with lower activation energy than for the uncatalyzed reaction. A catalyzed mechanism must involve at least two steps, one where the catalyst interacts with a reactant to form an intermediate substance, and one where the intermediate then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. Hence, the catalyst is involved in the reaction mechanism but *is not consumed by the reaction*.

An extremely important example of catalysis involves the catalytic destruction of ozone in Earth's stratosphere, 10 to 40 km above the surface ([Section D22.1](#)). Stratospheric ozone intercepts ultraviolet radiation from the Sun that otherwise would reach Earth's surface, damaging many forms of life including humans. The reaction mechanism for this process is



In the first step, a photon of ultraviolet (UV) radiation with wavelength between 200 and 310 nm breaks a bond in the ozone molecule, forming  $\text{O}_2$  and an O atom; the UV radiation is indicated by  $h\nu$  above the reaction arrow. In the second step the O atom

from step 1 reacts with a second  $O_3$  molecule to form two oxygen molecules; this second step has higher activation energy and is the rate-limiting step.

Ozone is formed in the stratosphere by short-wavelength UV photons (wavelength below 240 nm) that break the double bonds in  $O_2$  molecules. The O atoms thus formed react with  $O_2$  molecules to form  $O_3$ . The concentration of  $O_3$  in the stratosphere is a small, constant value because the rate of formation of  $O_3$  equals the rate at which it reacts away according to the mechanism above. Anything that speeds up the  $2 O_3 \rightarrow 3 O_2$  reaction will reduce the concentration of ozone and allow more UV radiation to reach Earth's surface.

One catalyst for the ozone decomposition reaction is chlorine atoms, which can be generated in the stratosphere from chlorofluorocarbon molecules, which at one time were used in air conditioners and cans of aerosol sprays. An example chlorofluorocarbon is  $CF_2Cl_2$ . An ultraviolet photon can break a C–Cl bond in  $CF_2Cl_2$ , producing Cl atoms, which react with ozone via this simplified mechanism:

Step 1: (slow)	$Cl(g) + O_3(g)$	$\rightarrow$	$O_2(g) + ClO(g)$
Step 2: (fast)	$O_3(g) + ClO(g)$	$\rightarrow$	$2 O_2(g) + Cl(g)$
Overall:	$2 O_3(g)$	$\rightarrow$	$3 O_2(g)$

Notice that Cl is a reactant in the first step and a product in the second step, so Cl participates in the mechanism but is not consumed by the overall reaction; that is, Cl is a catalyst. Because Cl is not reacted away, a single Cl atom can destroy as many as 100,000  $O_3$  molecules before the Cl atom reacts with something else and is removed from the stratosphere. Discovery of the catalytic effect of Cl atoms led to an international agreement, the Montreal Protocol, halting production of chlorofluorocarbons and banning their use. The Montreal Protocol now has 197 signatory countries—an essentially unanimous international agreement that is reversing the trend to lower ozone concentrations in the stratosphere and greater UV radiation at Earth's surface.

Reactants or products can also be catalysts in a reaction. When a product catalyzes a reaction the reaction is called *autocatalytic*. An autocatalytic reaction can be dangerous because the reaction can “run away”; that is, it can speed up a lot as product is formed and produce products way too fast. An example of a reaction catalyzed by a reactant was in Day 23:

Step 1:	$NO_2(g) + NO_2(g)$	$\rightarrow$	$NO_3(g) + NO(g)$
Step 2:	$NO_3(g) + CO(g)$	$\rightarrow$	$CO_2(g) + NO_2(g)$
Overall:	$NO_2(g) + CO(g)$	$\rightarrow$	$CO_2(g) + NO(g)$

The second  $NO_2$  molecule in step 1 (highlighted in green) is a catalyst, because it is reformed as a product in step 2. This catalyzed reaction has the first step as the rate-determining step, which yields a reaction rate of:

$$\text{rate}_{\text{catalyzed}} = k_{\text{catalyzed}}[NO_2]^2$$

Without the catalytic action, this reaction ( $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$ ) would be a bimolecular elementary reaction (with only one transition state) with a rate law of:

$$\text{rate}_{\text{uncatalyzed}} = k_{\text{uncatalyzed}}[NO_2][CO]$$

Figure 3 shows the reaction energy diagrams of the catalyzed and uncatalyzed reactions. Because the reactants and products involved in both reactions are exactly the same, they are at the same energies (a catalyst has no effect on the relative energies of the reactants and products).

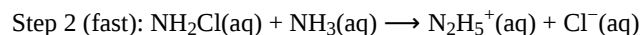
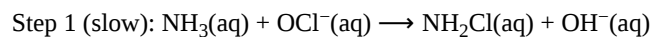
**Figure 3.** Reaction energy diagrams of catalyzed (green) and uncatalyzed (brown)  $NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$  reaction. Click on each “i” for more info.

The transition states, and therefore the activation energies, of the two pathway differ. The lower  $E_a$  in the catalyzed pathway results in  $k_{\text{catalyzed}} > k_{\text{uncatalyzed}}$ , and the reaction proceeds almost entirely via the faster pathway.

In this particular example, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states). Other catalyzed reactions might have more than two steps. Usually there are more mechanistic steps in a catalyzed reaction than in the uncatalyzed mechanism.

### Podia Question

The important industrial chemical hydrazine,  $\text{N}_2\text{H}_4$ , is produced by the Raschig process. Here is a proposed mechanism for the process:



1. Determine which is the rate-limiting step. Describe how this step limits the overall reaction rate.
2. Determine the overall reaction equation for the Raschig process.
3. Identify all reaction intermediates in the proposed mechanism.
4. Another student tells you that the reaction is second-order in ammonia and does not depend on any other concentration. The student says this is consistent with the mechanism written above. Explain why the student is, or is not, correct.

Two days before the next whole-class session, this Podia question will become live on [Podia](#), where you can submit your answer.

**Comments.** If you found any inconsistencies, errors, or other things you would like to report about this module, please use [this link](#) to report them. A similar link will be included in each day's material. We appreciate your comments.

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