Kinetics
5.4 Elementary Reactions
5.7 Introduction to Reaction Mechanisms
5.8 Reaction Mechanism and Rate Law
Worksheet Key

1) A two step mechanism is outlined below.

$F_2 + NO_2 \rightarrow NO_2F + F$ (slow step)

$NO_2 + F \rightarrow NO_2F$ (fast step)

a. What is the overall reaction?

$F_2 + 2\ NO_2 \rightarrow 2\ NO_2F$

b. Identify the intermediate in this reaction mechanism. Justify your answer.

F is an intermediate, as it is produced and consumed in the reaction.

c. What is the rate law for each of the elementary steps?

Step 1. Rate = $k_1[F_2][NO_2]$

Step 2. Rate = $k_2[F][NO_2]$

d. What is the rate law for the overall reaction?

Rate = $k[F_2][NO_2]$

2) A two step mechanism is outlined below.

$NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$ (slow step)

$NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$ (fast step)

a. What is the overall reaction?

$2\ NO_2Cl(g) \rightarrow 2\ NO_2(g) + Cl_2(g)$

b. Identify the intermediate in this reaction mechanism. Justify your answer.

$Cl(g)$ is an intermediate, as it is produced and consumed in the reaction.

c. What is the rate law for each of the elementary steps?

Step 1. Rate = $k_1[NO_2Cl]$

Step 2. Rate = $k_2[NO_2Cl][Cl]$

d. What is the rate law for the overall reaction?

Rate = $k_1[NO_2Cl]$

3) The rate law for the overall reaction outlined below is: Rate = $k[NO][Cl_2]$.

$$NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$$
$$\underline{NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g)}$$
$$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$$

a. Identify the intermediate in this reaction mechanism. Justify your answer.

$NOCl_2$ is an intermediate, as it is produced and consumed in the reaction.

b. Which step occurs the fastest? Justify your answer.

Step 2. $NOCl_2(g) + NO(g) \rightarrow 2\ NOCl(g)$ is the fast step, because it does not determine the rate of the overall reaction. The rate law for the overall reaction is the same as the rate law for the first step, which means that the first step is the slow, rate determining, step.

c. Which step determines the overall rate of the reaction? Explain.

Step 1. $NO(g) + Cl_2(g) \rightarrow NOCl_2(g)$ determines the rate of the overall reaction. We know this because the rate law of the overall reaction is: Rate = $k[NO][Cl_2]$. This is also the rate law for this step. Step 1 is the slow step, which determines the rate of the overall reaction.

4) A two step reaction is outlined below.

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq) \qquad \text{(slow step)}$$
$$H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq) \qquad \text{(fast step)}$$

a. What is the overall reaction?

$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

b. Identify the intermediate in this reaction mechanism. Justify your answer.

$IO^-(aq)$ is an intermediate, as it is produced and consumed in the reaction.

c. What is the rate law for each of the elementary steps?

Step 1. Rate = $k_1[H_2O_2][I^-]$
Step 2. Rate = $k_2[H_2O_2][IO^-]$

d. What is the rate law for the overall reaction?

Rate = $k[H_2O_2][I^-]$

5) The reaction below was found to be second order for A and zero order for B.

$$A(aq) + B(aq) \rightarrow C(aq) + D(aq)$$

The following mechanism was proposed for this reaction.

Step 1) 2 A → C + E (slow step)

Step 2) B + E → A + D (fast step)

a. What is the rate law for this reaction?

Rate = $k[A]^2$

b. Give two reasons why the above mechanism is possible.

1. When the two reactions are added together, we get A + B → C + D, which is the same as the overall reaction.
2. The slow step is consistent with the rate law, as B is zero order and thus is not included in the rate law; and A is second order and raised to the power of 2 in the rate law, which means that two A particles collide in the rate determining step.

6) A two step mechanism is outlined below.

$2\,NO(g) \rightleftharpoons N_2O_2(g)$ (fast equilibrium)

$N_2O_2(g) + Br_2(g) \rightarrow 2\,NOBr(g)$ (slow)

a. What is the overall reaction?

$$2\,NO(g) + Br_2(g) \rightarrow 2\,NOBr(g)$$

b. Identify the intermediate in this reaction mechanism. Justify your answer.

$N_2O_2(g)$ is an intermediate, as it is produced and consumed in the reaction.

c. What is the rate law for the overall reaction?

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

$$\text{Rate} = k_2[N_2O_2][Br_2]$$

$$\text{Rate} = k_2\left(\frac{k_1}{k_{-1}}[NO]^2\right)[Br_2]$$

$$\text{Rate} = k_3[NO]^2[Br_2]$$

d. What is the order of the reaction with respect to NO according to the above mechanism? Justify your answer.

The reaction is second order with respect to NO, as the [NO] is raised to the power of 2 in the rate law.

7) Elementary steps that involve three or more reacting species are very rare. Explain why this is.

All *ter*molecular elementary steps are very rare, as they require the simultaneous collision of three particles with correct orientations and enough energy. Elementary steps that require the simultaneous collision of more than three reactant particles are very rare for the same reason.