

### Worksheet – Reaction Mechanisms

The sequence of **elementary steps** that leads to the formation of products is called the **reaction mechanism**. There are three types of elementary steps:

- unimolecular**      $A \rightarrow \text{product}$      rate =  $k[A]$
- bimolecular**      $A+A$  or  $A+B \rightarrow \text{product}$      rate =  $k[A]^2$  or  $k[A][B]$
- termolecular**      $A+A+A$  or  $A+A+B \rightarrow \text{product}$      rate =  $k[A]^3$  or  $k[A]^2[B]$  etc.

These describe literally what is happening at the atomic scale.

The **sum** of the elementary steps must give the **overall balanced equation**.

They must also explain the experimentally determined **rate law**. The **slowest step** in the reaction mechanism will determine the overall rate of the reaction and is called the **rate determining step**.

1. The kinetics of the reaction:  $2X + Y \rightarrow Z$  was studied and the results are:

Expt	$[X]_0$ (M)	$[Y]_0$ (M)	Initial rate (M/s)
1	0.20	0.10	$7.0 \times 10^{-4}$
2	0.20	0.20	$1.4 \times 10^{-3}$
3	0.40	0.20	$1.4 \times 10^{-3}$
4	0.60	0.60	$4.2 \times 10^{-3}$

a. Deduce the rate law including the value of  $k$  with units

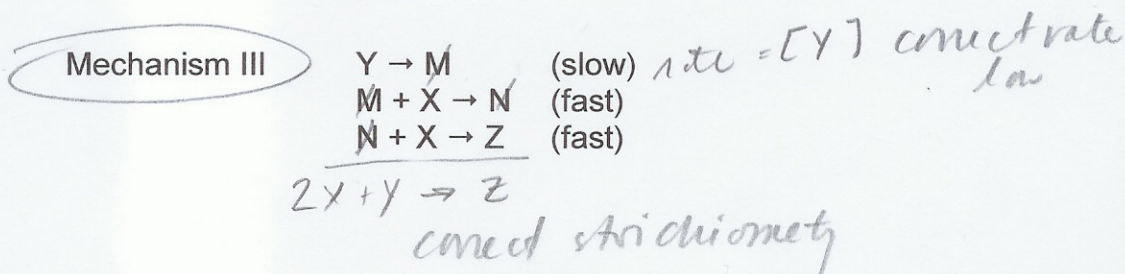
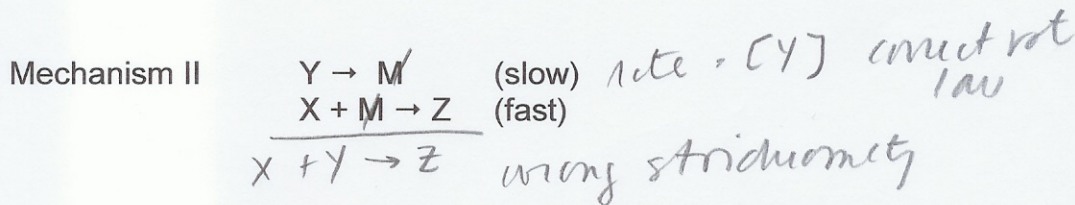
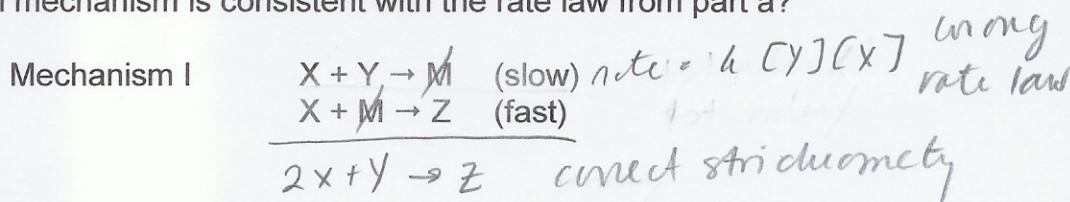
$$\frac{1.4 \times 10^{-3}}{7 \times 10^{-4}} = \frac{(2.0)^a}{(1.0)^a} \cdot 2 = 2^a \quad a = 1 \quad [Y]^1$$

$$\frac{1.4 \times 10^{-3}}{1.4 \times 10^{-3}} = \frac{[.4]^b}{[.2]^b} \quad 1 = 2^b \quad b = 0 \quad [X]^0$$

Note =  $k[Y]$   
 $7.0 \times 10^{-4} \text{ M s}^{-1} = k [1.0 \text{ M}]$   
 $k = 7 \times 10^{-3} \text{ s}^{-1}$

b. The following 3 mechanism have been proposed. The species M and N are called *intermediates*, they are formed in early steps and consumed in later steps. What is the overall reaction for each mechanism?

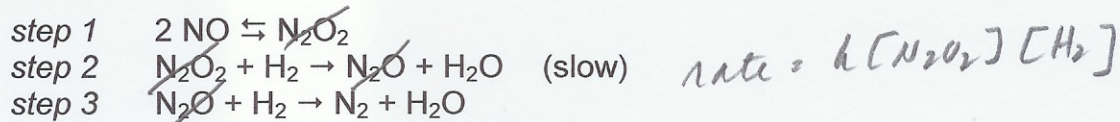
What is the molecularity of each step? What is the rate law derived from each? Which mechanism is consistent with the rate law from part a?



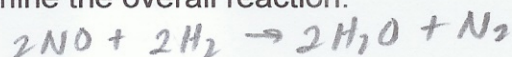
There are often **equilibrium steps** in mechanisms. We will usually assume that they are not rate limiting. The concentration of the species involved can be determined by setting up the equilibrium expression:

$$K = [\text{product}]^p / [\text{reactant}]^r \text{ so that, for example, } [\text{reactant}]^r = K [\text{product}]^p$$

2. Given the following mechanism:



a. Determine the overall reaction.



b. Are there any intermediates in this reaction mechanism?



c. Determine the rate law. Intermediates **may not** appear in rate laws. Use the equilibrium expression to write the rate law only in terms of [reactants].

$$K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad [\text{N}_2\text{O}_2] = K [\text{NO}]^2$$

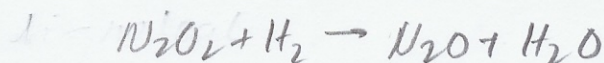
$$\text{rate} = k [\text{N}_2\text{O}_2] [\text{H}_2]$$

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

d. What is the overall order of the reactions?

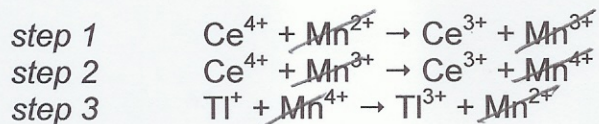
3rd order

e. What is the molecularity of the rate determining step? *bi-molecular*

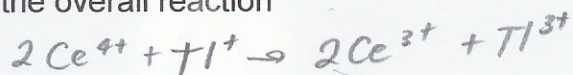


Another common component of reaction mechanisms is a **catalyst**. These are compounds that change the reaction mechanism and provide a pathway with a lower activation energy, and correspondingly faster reaction rate. They are a **reactant** in an early step in the mechanism and a **product** in a later step. They do not appear in the overall reaction, but do appear in the rate law.

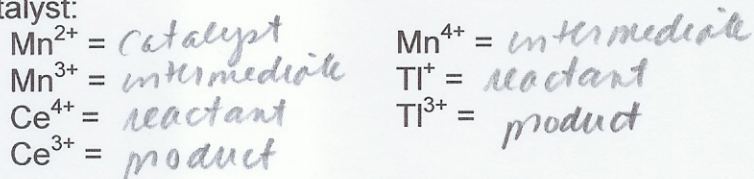
3. A reaction occurs by the following mechanism.



- a. Write the overall reaction



- b. Identify each of the components as a reactant, product, intermediate or catalyst:

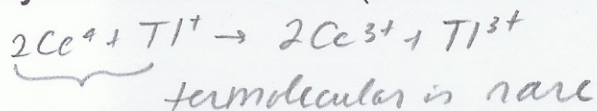


- c. Assuming that the catalyst is involved in the rate determining step, what is the rate law for this reaction?

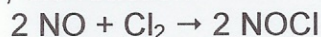
$$\text{rate} = k [\text{Ce}^{4+}] [\text{Mn}^{2+}]$$

*Mn<sup>2+</sup> is catalyst ∴ step 1 is rate determining*

- d. Why is the **uncatalyzed** reaction so slow? (Hint: look at the molecularity)

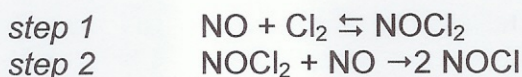


4. Under certain conditions, the reaction:



is found to be second order in NO and first order in Cl<sub>2</sub>.

Given the following mechanism,

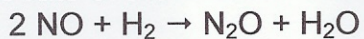


what are the relative rates of the two elementary steps under these conditions?

*if step 1 is rate determining rate = k<sub>1</sub> [NO] [Cl<sub>2</sub>] 1st order in NO*  
*if step 2 is rate determining rate = k<sub>2</sub> [NO] [NOCl<sub>2</sub>] [Cl<sub>2</sub>] 1st order in Cl<sub>2</sub>*  
 $= k_2 [\text{NO}]_2 [\text{Cl}_2]$   
*2nd order in NO 1st order Cl<sub>2</sub>*

$$k_2 \ll k_1$$

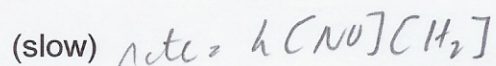
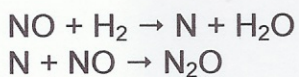
5. The rate of the reaction shown below was studied:



It was found that the rate doubled when the  $[\text{H}_2]$  was doubled. It was also found that the rate increased by a factor of four when the NO concentration was doubled. Which of the following mechanisms is/are consistent with these data?

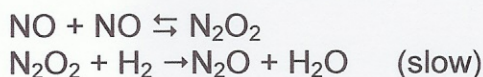
$$\text{rate} = k [\text{H}_2] [\text{NO}]^2$$

step 1  
step 2



consistent

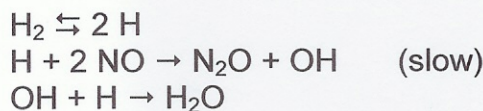
step 1  
step 2



$$K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad [\text{N}_2\text{O}_2] = K[\text{NO}]^2$$

$$\text{rate} = k [\text{N}_2\text{O}_2] [\text{H}_2] = kK [\text{NO}]^2 [\text{H}_2]$$

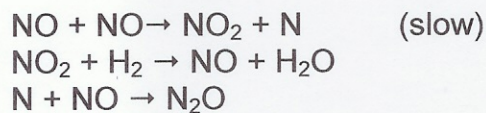
step 1  
step 2  
step 3



$$K = \frac{[\text{H}]^2}{[\text{H}_2]} \quad [\text{H}] = K^{1/2} [\text{H}_2]^{1/2}$$

$$\text{rate} = k [\text{H}] [\text{NO}]^2 = kK^{1/2} [\text{H}_2]^{1/2} [\text{NO}]^2$$

step 1  
step 2  
step 3



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