

Exercise 17.2b(H)

Reaction Mechanisms

Name: _____

Date: _____ Per: _____

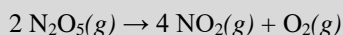
For a chemical reaction its rate, or rate of reaction, is expressed in terms of how fast the concentration of a substance changes in the course of a chemical reaction.

$$\text{Rate of reaction} = \text{time } \Delta[\text{product}] \quad \text{or} \quad \text{Rate of reaction} = - \text{time } \Delta[\text{reactant}]$$

One symbol you should become familiar with is the []. Brackets from here on out will mean "the concentration of in molarity"

Relative Rates: Notice the rates above only differ in a '-' sign. This is there because rates must be positive, and the change of your reactants is negative, so you must have a negative sign.

Consider the following reaction:



The rate can be expressed the following ways:

$$\text{rate} = \frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = 2 \frac{\Delta[\text{O}_2]}{\Delta t}$$

DIRECTIONS: Answer the following in the space provided.

1. Consider the reaction: $4\text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$:

If, in a certain experiment, over a specific time period, 0.0048 mole of PH_3 is consumed in a 2.0 L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

P_4 : _____ H_2 : _____

2. In the Haber process for the production of ammonia, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$:

What is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

3. Consider the general reaction, $a\text{A} + b\text{B} \rightarrow c\text{C}$, and the following average rate data over some time period Δt :

Determine a set of possible coefficients to balance this general reaction.

$$\begin{aligned} -\frac{\Delta A}{\Delta t} &= 0.0080 \text{ mol/L} \cdot \text{s} \\ \frac{\Delta B}{\Delta t} &= 0.0120 \text{ mol/L} \cdot \text{s} \\ \frac{\Delta C}{\Delta t} &= 0.0160 \text{ mol/L} \cdot \text{s} \end{aligned}$$

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

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 (or rate-limiting) step**.

When the rate-determining step occurs **first** in a reaction mechanism, the rate law of the overall reaction will be the same as the rate law of that step.

DIRECTIONS: Answer the following in the space provided.

4. Given the mechanism:

step 1:	$2\text{NO} \rightarrow \text{N}_2\text{O}_2$	
step 2:	$\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	(slow)
step 3:	$\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$	

- 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]. _____

- d. What is the overall order of the reaction? _____

- e. What is the molecularity of the rate determining step? _____

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

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

- a. Deduce the rate law.

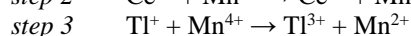
- b. The following 3 mechanisms have been proposed. The species M and N are called *intermediates*, they are formed in early steps and consumed in later steps. Complete the table for each mechanism by providing the molecularity of each step, the overall reaction for the mechanism, and the rate law of the mechanism.

Mechanism I				Mechanism II			Mechanism III		
Step	Elementary Steps	Speed	Molecularity	Elementary Steps	Speed	Molecularity	Elementary Steps	Speed	Molecularity
1	$X + Y \rightarrow M$	(slow)		$Y \rightarrow M$	(slow)		$Y \rightarrow M$	(slow)	
2	$X + M \rightarrow Z$	(fast)		$X + M \rightarrow Z$	(fast)		$M + X \rightarrow N$	(fast)	
3							$N + X \rightarrow Z$	(fast)	
Overall Reaction									
Rate Law									

- c. Which mechanism is consistent with the rate law from part a.? _____

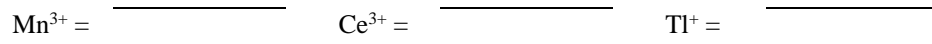
Another common component of reaction mechanisms is a **catalyst**. These are compounds that change the reaction mechanism and provide a pathway with a lower activation energy, and correspondingly faster reaction rate. They are a **reactant** in an early step in the mechanism and a **product** in a later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

6. A reaction occurs by the following mechanism.



- a. Write the overall reaction: _____

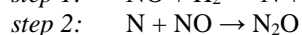
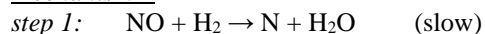
- b. Identify each of the components as a reactant, product, intermediate or catalyst:



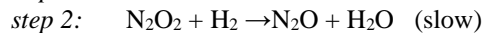
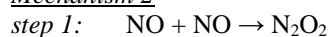
- c. Assuming that the catalyst is involved in the rate determining step, what is the rate law for this reaction? _____

7. The rate of the reaction shown below was studied: $2NO + H_2 \rightarrow N_2O + H_2O$. It was found that the rate doubled when the $[H_2]$ 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?

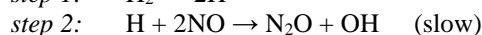
Mechanism 1



Mechanism 2



Mechanism 3



Mechanism 4

