Exercise 12.5
Reaction Mechanisms

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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.

Rate of reaction = *time* Δ[*product*] or Rate of reaction = – *time* Δ[*reac*tant]

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:

$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g) + O_2(g)$$

The rate can be expressed the following ways:

$$\text{rate} = \frac{-\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = 2\frac{\Delta[O_2]}{\Delta t}$$

DIRECTIONS: Answer the following in the space provided.

1. Consider the reaction: $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$:

   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?

2. In the Haber process for the production of ammonia, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$:

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

   _____

   _____

3. Consider the general reaction, aA + bB → cC , and the following average rate data over some time period Δt:

$$-\frac{\Delta A}{\Delta t} = 0.0080\ mol/L \cdot s$$

$$-\frac{\Delta B}{\Delta t} = 0.0120\ mol/L \cdot s$$

$$\frac{\Delta C}{\Delta t} = 0.0160\ mol/L \cdot s$$

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

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 → product	rate = k[A]
bimolecular	A+A → product	rate = k[A]^2
or	A+B → product	rate = k[A][B]
termolecular	A+A+A → product	rate = k[A]^3
or	A+A+B→ product	rate = k[A]^2[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.

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DIRECTIONS: Answer the following in the space provided.

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

Expt	$[X]_0$ (M)	$[Y]_0$ (M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-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 including the value of k with units.

   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		Elementary Step	Speed	Molecularity
	Step 1	$X + Y \rightarrow M$	(slow)	
	Step 2	$X + M \rightarrow Z$	(fast)	
	Overall Reaction			
	Rate Law			

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

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

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

5. Write the rate laws for the following elementary reactions.

   a. $CH_3NC(g) \rightarrow CH_3CN(g)$

   b. $O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

   c. $O_3(g) \rightarrow O_2(g) + O(g)$

   d. $O_3(g) + O(g) \rightarrow 2O_2(g)$

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6. A proposed mechanism for a reaction is:

$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ slow

$C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ fast

$C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ fast

a. Write the rate law expected for this mechanism.

b. What is the overall balanced equation for the reaction?

c. What are the intermediates in the proposed mechanism?

What happens when the first step in a multi-step reaction is not the rate-limiting step? When the rate-determining step is not the first step in a reaction mechanism, the steps preceding the rate-determining step are considered to be part of a system at equilibrium. By equating the rates of the forward and reverse reactions, the contribution to the rate law may be determined for these steps.

Step	Equation	Rate	Rate Law	
1	$2A \leftrightharpoons B$	(fast step)	$Rate_{forward} = k_{forward}[A]^2$	$Rate_{reverse} = k_{reverse}[B]$
2	$B + C \rightarrow 2D$	(slow step)	$Rate = k_2[B][C]$	

For Step 1, $Rate_{forward} = Rate_{reverse}$	$k_{forward}[A]^2 = k_{reverse}[B]$
solving for [B]	$[B] = (k_{forward}/k_{reverse})[A]^2$
substituting [B] into $Rate_2$	$Rate = k_2(k_{forward}/k_{reverse})[A]^2[C]$
replacing $k_2(k_{forward}/k_{reverse})$ *with k'*	$Rate = k'[A]^2[C]$

generally, $[reactant]^r = k[product]^p$

7. Given the mechanism:

step 1:	$2NO \rightarrow N_2O_2$	
step 2:	$N_2O_2 + H_2 \rightarrow N_2O + H_2O$	(slow)
step 3:	$N_2O + H_2 \rightarrow N_2 + H_2O$	

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?

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

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.

8. A reaction occurs by the following mechanism.

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$
step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$
step 3 $Tl^{+} + Mn^{4+} \rightarrow Tl^{3+} + Mn^{2+}$

a. Write the overall reaction

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

Mn^{2+} = _____ Ce^{4+} = _____ Mn^{4+} = _____ Tl^{3+} = _____
Mn^{3+} = _____ Ce^{3+} = _____ Tl^{+} = _____

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

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

9. Under certain conditions, the reaction: $2NO + Cl_2 \rightarrow 2NOCl$, is found to be second order in NO and first order in Cl_2. Given the following mechanism,

step 1: $NO + Cl_2 \rightarrow NOCl_2$
step 2: $NOCl_2 + NO \rightarrow 2NOCl$

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

10. 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
step 1: $NO + H_2 \rightarrow N + H_2O$ (slow)
step 2: $N + NO \rightarrow N_2O$

Mechanism 2
step 1: $NO + NO \rightarrow N_2O_2$
step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

Mechanism 3
step 1: $H_2 \rightarrow 2H$
step 2: $H + 2NO \rightarrow N_2O + OH$ (slow)
step 3: $OH + H \rightarrow H_2O$

Mechanism 4
step 1: $NO + NO \rightarrow NO_2 + N$ (slow)
step 2: $NO_2 + H_2 \rightarrow NO + H_2O$
step 3: $N + NO \rightarrow N_2O$