Practice E4 Mechanisms

Name_______________________________Per_____

1. In a study of nitrosyl halides, a chemist proposes the following mechanism for the synthesis of nitrosyl bromide, NOBr, from nitrogen monoxide and bromine vapor.

   $20\ kJ + NO + Br_2 \rightleftharpoons NOBr_2$

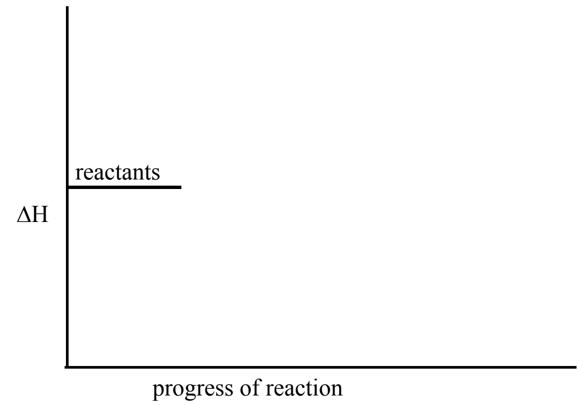
   $NOBr_2 + NO \rightleftharpoons 2NOBr + 60\ kJ$

   a. The rate law for this reaction is; rate = k $[NO]^2\ [Br_2]$. Which step is the slow step?

   b. Explain how this mechanism satisfies three criteria that makes the mechanism valid.

   c. Write the overall equation, and calculate the ΔH of the reaction.

   d. Sketch the potential energy diagram for this mechanism.
   Use arrows to indicate ΔH and label the energy values.



2. Consider the reaction: $2\ NO + O_2 \rightleftharpoons 2\ NO_2$ The experimentally determined rate law is: rate = k $[NO]^2\ [O_2]$.

I	$2NO \rightleftharpoons N_2 + O_2$	fast
	$N_2 + 2O_2 \rightarrow 2NO_2$	slow
II	$2NO \rightleftharpoons N_2O_2$	slow
	$N_2O_2 + O_2 \rightarrow 2NO_2$	fast
III	$NO + O_2 \rightleftharpoons NO_3$	fast
	$NO_3 + NO \rightarrow 2NO_2$	slow

   a. Which of these mechanisms is consistent with the rate law? If not, why not?

   b. Which of these mechanisms is most reasonable? Why?

3. A proposed mechanism for a reaction is shown below.

$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$	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 for the proposed mechanism?

P E.4 **Mechanisms** Name_______________________________Per_____

4. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

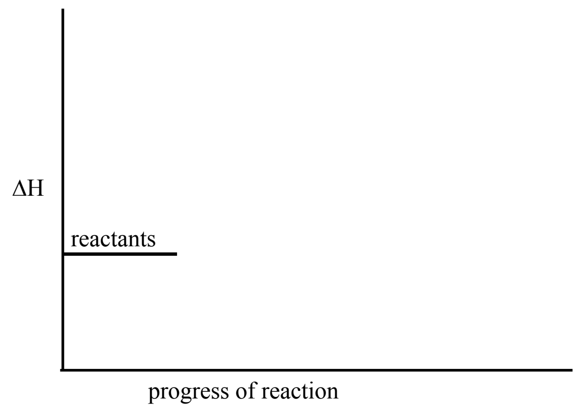
I.	$NO_2 + NO_2 \rightarrow NO_3 + NO$	slow
II.	$NO_3 + CO \rightarrow NO_2 + CO_2$	fast

   a. Write the rate law expected for this mechanism?

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

5. Consider the mechanism below.

$2AB + X \leftrightharpoons AB_2 + A$	$\Delta H = +250 kJ$	slow
$AB_2 + C \rightarrow X + BC + AB$	$\Delta H = -100 kJ$	fast



   a. Write the rate law expected for this mechanism?

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

   c. What are the intermediate(s) / catalyst(s) in this reaction?

   d. Sketch the energy diagram for this mechanism

6. Consider the mechanism below.

$2 AsO_2 \rightarrow AsO_3 + AsO$	fast
$AsO_3 + CO \rightarrow AsO_2 + CO_2$	slow

   a. Write the rate law expected for this mechanism?

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

7. Consider this three step mechanism for a reaction:

$F_2 \leftrightharpoons 2 F$	Fast
$F + CHF_3 \rightarrow HF + CF_3$	Slow
$F + CF_3 \rightarrow CF_4$	Fast

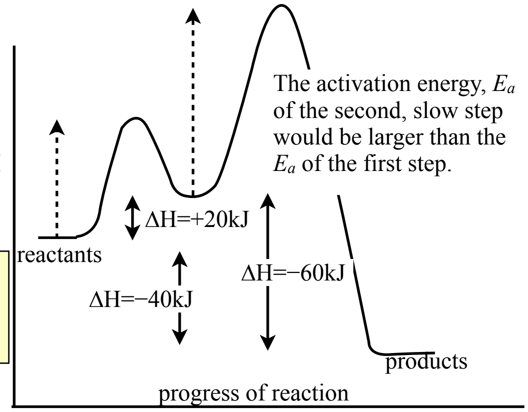
   a. What is the overall balanced equation for the reaction?
   b. Write the rate law expected for this mechanism.
   c. Identify the intermediates for the proposed mechanism?

Practice E4 Mechanisms *ANSWERS*

1. In a study of nitrosyl halides, a chemist proposes the following mechanism for the synthesis of nitrosyl bromide, NOBr, from nitrogen monoxide and bromine vapor.

$\cancel{20\text{ kJ}} + NO + Br_2 \rightleftharpoons \cancel{NOBr_2}$ FAST

$\cancel{NOBr_2} + NO \rightleftharpoons 2NOBr + 60\text{ kJ}$ **SLOW**



a. The rate law for this reaction is; rate = k $[NO]^2$ $[Br_2]$.
Which step is the slow step? The second step is the slow step.

b. Explain how this mechanism satisfies the three criteria for validity.

This mechanism is valid because (1) the reaction adds up to the overall reaction described in the text, (2) the reaction is reasonable because neither of the two steps has greater than bimolecularity, and (3) the observed rate law matches the rate law indicated by the mechanism.

c. Write the overall equation, and calculate the ΔH of the reaction.

$2NO + Br_2 \rightleftharpoons 2\ NOBr$ $\Delta H = -40\text{kJ}$

d. Sketch the potential energy diagram for this mechanism. Use arrows to indicate ΔH and label the energy values.

2. Consider the reaction: $2\ NO + O_2 \rightleftharpoons 2\ NO_2$ The experimentally determined rate law is: rate = k $[NO]^2$ $[O_2]$.

I $2NO \rightleftharpoons \cancel{N_2} + \cancel{O_2}$ fast
$\cancel{N_2} + \cancel{2}\ O_2 \rightarrow 2NO_2$ slow

Since the second step is the slow step, the rate law includes the circled items. Cross off one O_2 on each side, and the intermediate N_2 in the second reaction, the rate law for this mechanism would be rate = k $[NO]^2$ $[Br_2]$. While it **matches** the experimentally determined rate law, this mechanism is **less likely** because it involves termolecularity in the second step.

II $\boxed{2NO} \rightleftharpoons N_2O_2$ slow
$N_2O_2 + O_2 \rightarrow 2NO_2$ fast

Since the first step is the slow step, the rate law include only the reactants of the first step, give rate = k $[NO]^2$, which **does not match** the experimentally determined rate law.

III $NO + O_2 \rightleftharpoons \cancel{NO_3}$ fast
$\cancel{NO_3} + NO \rightarrow 2NO_2$ slow

After crossing off the intermediate NO_3 the rate law for this mechanism would be rate = k $[NO]^2$ $[Br_2]$, which **matches** the experimentally determined rate law. This mechanism is **more likely** than Mechanism I because it involves only bimolecular steps.

a. Which of these mechanisms is consistent with the rate law? If not, why not?
b. Which of these mechanisms is most reasonable? Why?

3. A proposed mechanism for a reaction is shown below.

$\boxed{C_4H_9Br} \rightarrow C_4H_9^+ + Br^-$ 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 for the proposed mechanism?

Since the slow step is the first step, the rate law would be:
rate = k $[C_4H_9Br]$

The overall reaction is:

$\mathbf{C_4H_9Br + 2\ H_2O \rightarrow Br^-\ \ C_4H_9OH + H_3O^+}$

An intermediate is a chemical that shows up as a product in one step, and disappears in a subsequent step.

There are two intermediates: **$C_4H_9^+$ and $C_4H_9OH_2^+$**

4. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

I. $\boxed{NO_2 + NO_2} \rightarrow NO_3 + NO$ slow
II. $NO_3 + CO \rightarrow NO_2 + CO_2$ fast

a. What is the overall balanced equation for the reaction?
b. Write the rate law expected for this mechanism?

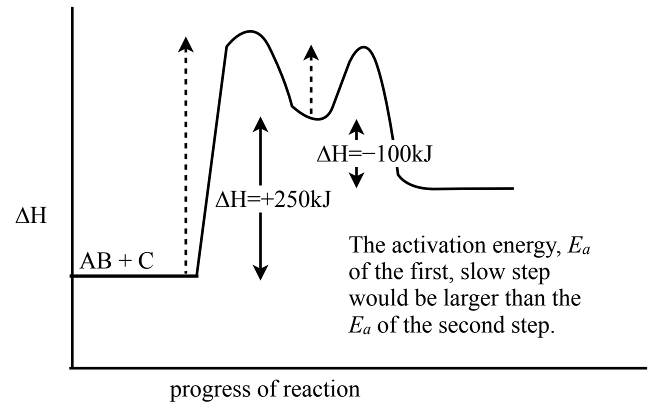
Since the slow step is the first step, and the stoichiometry of 2 NO_2 molecules, the rate law would be:
rate = k $[NO_2]^2$

The overall reaction is:

$\mathbf{NO_2 + CO \rightarrow NO + CO_2}$

5. Consider the mechanism below.

$$\boxed{2AB + X} \leftrightharpoons AB_2 + A \qquad \Delta H = +250\text{kJ} \qquad \text{slow}$$
$$AB_2 + C \rightarrow X + BC + AB \qquad \Delta H = -100\text{kJ} \qquad \text{fast}$$



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

The overall reaction is: **$AB + C \rightarrow A + BC$**

b. Write the rate law expected for this mechanism?

Since the slow step is the first step, and the stoichiometry of 2 AB molecules and one X molecule, the rate law would be: **rate = k $[AB]^2$ [X]**

c. What are the intermediate(s) / catalyst(s) in this reaction?

d. Sketch the energy diagram for this mechanism

An intermediate is a chemical that shows up as a product in one step, and disappears in a subsequent step.

A catalyst is a substance that is put in as a reactant, than comes out as a product in the same stoichiometric quantities, so that the catalyst drops out of the overall equation.

AB_2 is an intermediate, and **X is a catalyst**.

6. Consider the mechanism below.

$$2\,AsO_2 \rightarrow \cancel{AsO_3} + AsO \qquad \text{fast}$$
$$\cancel{AsO_3} + CO \rightarrow AsO_2 + CO_2 \qquad \text{slow}$$

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

The overall reaction is: **$AsO_2 + CO \rightarrow AsO + CO_2$**

b. Write the rate law expected for this mechanism?

Quickie Method: Cross off the intermediate, and catch all molecules up to and including the reactants of the slow step. The AsO on the product side will end up in the denominator. The build up of this product acts as an inhibitor.

$$rate_{overall} = k\frac{[AsO_2]^2[CO]}{[AsO]} \quad OR \quad rate_{overall} = k[AsO_2]^2[CO][AsO]^{-1}$$

The Real Method:

- Write a rate law for the foward first step.
- Since the first step is a fast step that occurs before a slow step, the reaction will start to go backwards as the products build and the first reaction step reach equilibrium. Thus write a rate law for the reverse step 1.
- Equilibrium is a state in which the forward and reverse reactions proceed at the same rate, thus we can set the forward rate step 1 equal to the reverse rate step 1
- Next write a rate law for the second, (slow) rate-determining step.
- However, we would like to eliminate the intermediate from this second step rate law. We can do this by solving the equilibrium equality from the first step for $[AsO_3]$ and substituting into the second step equation.
- Then cancel terms and squash all the k's together into $k_{combined}$.

$$rate_{1\,for} = k_f[AsO_2]^2 \quad and \quad rate_{1\,fwd} = k_{1\,rev}[AsO_3][AsO]$$

$$\text{thus} \quad k_{1\,for}[AsO_2]^2 = k_{1\,rev}[AsO_3][AsO]$$

$$rate = k_{2\,for}[AsO_3][CO]$$

$$k_{1\,for}[AsO_2]^2 = k_{1\,rev}[AsO_3][AsO] \qquad [AsO_3] = \frac{k_{1\,for}[AsO_2]^2}{k_{1\,rev}[AsO]}$$

$$rate_2 = k_{2\,for}[AsO_3][CO] \qquad rate_2 = k_{2\,for}\frac{k_{1\,for}[AsO_2]^2}{k_{1\,rev}[AsO]}[CO]$$

$$rate_{overall} = k_{combined}\frac{[AsO_2]^2[CO]}{[AsO]}$$

7. Consider this three step mechanism for a reaction:

$F_2 \leftrightharpoons 2\,F$	Fast
$F + CHF_3 \rightarrow HF + CF_3$	Slow
$F + CF_3 \rightarrow CF_4$	Fast

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

The overall reaction is: $\mathbf{F_2 + CHF_3 \rightarrow HF + CF_4}$

b. Write the rate law expected for this mechanism.

c. Identify the intermediates for the proposed mechanism?

$\mathbf{CF_3}$ is an **intermediate**

For this problem, the Quickie Method does not work.
Odds are in your favor that you will not see one like this on your AP exam, last time a fractional order showed up was in 2009.

The Real Method:

- Write a rate law for the foward first step.

$$rate_{1\,for} = k_{1\,for}[F_2]$$

- Since the first step is a fast step that occurs before a slow step, the reaction will start to go backwards as the products build and the first reaction step reach equilibrium. Thus write a rate law for the reverse step 1.

$$rate_{1rev} = k_{1rev}[F]^2$$

- Equilibrium is a state in which the forward and reverse reactions proceed at the same rate, thus we can set the forward rate step 1 equal to the reverse rate step 1

$$\text{thus}\quad k_{1\,for}[F_2] = k_{1rev}[F]^2$$

- Next write a rate law for the second, (slow) rate-determining step.

$$rate_{2\,for} = k_{2\,for}[F][CHF_3]$$

- However, we would like to eliminate the intermediate from this second step rate law. We can do this by solving the equilibrium equality from the first step for [F] and substituting into the second step equation.

$$\text{since}\quad k_{1\,for}[F_2] = k_{1rev}[F]^2$$

$$\text{Solve for}[F]\qquad [F] = \frac{k_{1\,for}\sqrt{[F_2]}}{k_{1rev}}$$

$$rate_{2\,for} = k_{2\,for}[F][CHF_3]$$

$$rate_{2\,for} = k_{2\,for}\frac{k_{1\,for}\sqrt{[F_2]}}{k_{1rev}}[CHF_3]$$

- Then cancel terms and squash all the k's together into $k_{combined}$.

$$rate_{overall} = k_{combined}[F_2]^{\frac{1}{2}}[CHF_3]$$