Rate Mechanism Worksheet
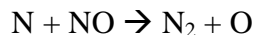
1. The rate law for the reaction: $2H_2 + 2NO \rightarrow N_2 + 2H_2O$ is rate $= k\,[H_2][NO]^2$
   Which of the following mechanisms can be ruled out on the basis of the observed rate expression?

   Mechanism 1:
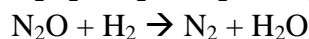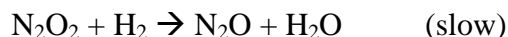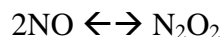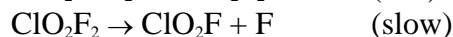 $H_2 + NO \rightarrow H_2O + N$ (slow)
   $N + NO \rightarrow N_2 + O$
   $O + H_2 \rightarrow H_2O$

   Mechanism 2:
   $H_2 + 2NO \rightarrow N_2O + H_2O$ (slow)
   $N_2O + H_2 \rightarrow N_2 + H_2O$

   Mechanism 3:
   $2NO \leftrightarrow N_2O_2$
   $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
   $N_2O + H_2 \rightarrow N_2 + H_2O$
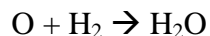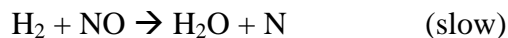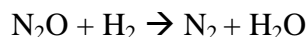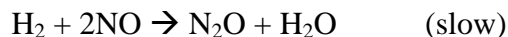
2. Which of the following reaction mechanisms is consistent with the rate law: rate $= k\,[ClO_2]^1[F_2]^1$. Justify your choice. (APQ from 1991 B)

   Mechanism I.
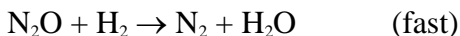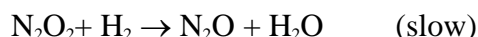 $ClO_2 + F_2 \leftrightarrow ClO_2F_2$ (fast)
   $ClO_2F_2 \rightarrow ClO_2F + F$ (slow)
   $ClO_2 + F \rightarrow ClO_2F$ (fast)

   Mechanism II
   $F_2 \rightarrow 2\,F$ (slow)
   $2\,(ClO_2 + F \rightarrow ClO_2F)$ (fast)

3. The reaction between NO and H_2 is believed to occur in the following three-step process. (APQ 1996D)

   $NO + NO \rightarrow N_2O_2$ (fast)
   $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
   $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)
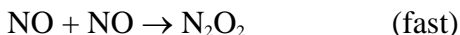
   a. Write a balanced equation for the overall reaction.
   b. Identify the intermediates in the reaction. Explain your reasoning.
   c. From the mechanism represented above, a student correctly deduces that the rate law for the reaction is rate $= k[NO]^2[H_2]$. The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an H_2 molecule. Are conclusions (1) and (2) correct? Explain.

4. Identify which of the reaction mechanisms represented below is consistent with the rate law: rate = k [A]^1[B]^1. Justify your choice. (APQ 1997B)

   Mechanism 1

   | A + B → C + M | *Fast* |
   | M + A → D | *Slow* |

   Mechanism 2

B ↔ M	*Fast equilibrium*
M + A → C + X	*Slow*
A + X → D	*Fast*

   Mechanism 3

A + B → M	*Fast equilibrium*
M + A → C + X	*Slow*
X → D	*Fast*
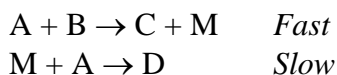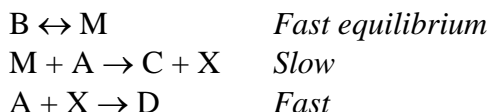
5. Use the information in the table below to answer the following questions. (APQ 200D)
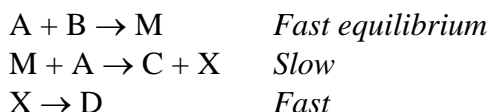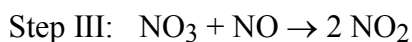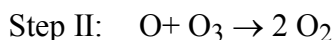
Experiment Number	Initial $[O_3]$ (mol L^{-1})	Initial $[NO]$ (mol L^{-1})	Initial Rate of Formation of $[NO_2]$ (mol L^{-1} s^{-1})
1	0.0010	0.0010	X
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4x

   a. Write the rate-law expression for the reaction.
   b. The following three-step mechanism is proposed for the reaction. Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (a). Explain.

   $$\text{Step I:} \quad O_3 + NO \rightarrow O + NO_3$$
   $$\text{Step II:} \quad O + O_3 \rightarrow 2\ O_2$$
   $$\text{Step III:} \quad NO_3 + NO \rightarrow 2\ NO_2$$

6. An environmental concern is the depletion of O_3 in Earth's upper atmosphere, where O_3 is normally in equilibrium with O_2 and O. A proposed mechanism for the depletion of O_3 in the upper atmosphere is shown below. (APQ 2002D)

   $$\text{Step I} \quad O_3 + Cl \rightarrow O_2 + ClO$$
   $$\text{Step II} \quad ClO + O \rightarrow Cl + O_2$$
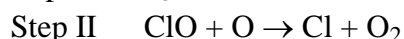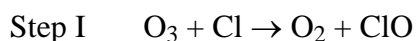
   a. Write a balanced equation for the overall reaction represented by Step I and Step II above.
   b. Clearly identify the catalyst in the mechanism above. Justify your answer.
   c. Clearly identify the intermediate in the mechanism above. Justify your answer.
   d. If the rate law for the overall reaction is found to be rate = $k[O_3]$ [Cl], determine the following.
      i. The overall order of the reaction
      ii. Appropriate units for the rate constant, k
      iii. The rate-determining step of the reaction, along with justification for your answer

7. The reaction between chloroform and chlorine gas proceeds in a series of three elementary steps.

$$\text{Step 1:} \quad Cl_{2(g)} \leftrightarrow 2Cl_{(g)} \qquad\qquad\qquad\qquad \text{Fast, reversible}$$
$$\text{Step 2:} \quad CHCl_{3(g)} + Cl_{(g)} \rightarrow CCl_{3(g)} + HCl_{(g)} \qquad \text{Slow}$$
$$\text{Step 3:} \quad CCl_{3(g)} + Cl_{(g)} \rightarrow CCl_{4(g)} \qquad\qquad\qquad \text{Fast}$$
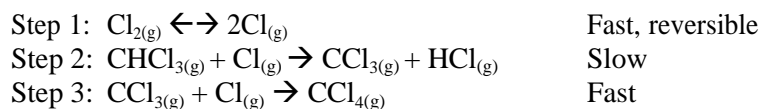
   a. Overall reaction?
   b. Which of the steps in the rate determining step?
   c. Write the rate expression for the rate determining step.
   d. What is the molecularity of each step?
   e. Identify any intermediates.
   f. Identify a catalyst

8. The rate equation for the reaction: $Cl_{2(aq)} + H_2S_{(aq)} \rightarrow S_{(s)} + 2HCl_{(aq)}$ was found to be rate $= k[Cl_2][H_2S]$. Which of the following mechanisms are consistent with this rate law?

(a) $Cl_2 \rightarrow 2Cl$ (slow)
     $Cl + H_2S \rightarrow HCl + HS$ (fast)
     $Cl + HS \rightarrow HCl + S$ (fast)
     Overall: $Cl_2 + H_2S \rightarrow S + 2HCl$

(b) $Cl_2 \rightarrow 2Cl$ (fast)
     $Cl + H_2S \rightarrow HCl + HS$ (fast)
     $Cl + HS \rightarrow HCl + S$ (slow)
     Overall: $Cl_2 + H_2S \rightarrow S + 2HCl$

(c) $Cl_2 + H_2S \rightarrow Cl + HS + HCl$ (slow)
     $Cl + HS \rightarrow HCl + S$ (fast)
     Overall: $Cl_2 + H_2S \rightarrow S + 2HCl$

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