

## Reaction Mechanisms

- Based on the idea that reactions follow a path of multiple steps, you need to be able to derive a rate expression from a reaction mechanism.

### 3 Basic Rules

- The slow step is always rate determining.
- For any step in the reaction mechanism you can just use its stoichiometric coefficient as its rate-order.
- The final rate expression must include only species that are in the overall reaction. <-- use equilibrium expressions from fast steps to get rid of reaction intermediates.

### For example:

The overall reaction is  $2 \text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$

The rate law is found to be second order in  $\text{NO}_{(g)}$  and first order in  $\text{Cl}_{2(g)}$ . Derive this expression from the proposed reaction mechanism:

- $\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{NOCl}_{2(g)}$  fast
- $\text{NOCl}_{2(g)} + \text{NO}_{(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$  slow

- Slow step is rate determining:  $r = k[\text{NOCl}_2][\text{NO}]$
- $\text{NOCl}_2$  is a reaction intermediate so use an equilibrium constant expression to get rid of it.

$$K_c = \frac{[\text{NOCl}_2]}{[\text{NO}][\text{Cl}_2]} \quad [\text{NOCl}_2] = K_c[\text{NO}][\text{Cl}_2]$$

- Plug in:  $r = kK_c[\text{NO}][\text{Cl}_2][\text{NO}]$

$$r = kK_c[\text{NO}]^2[\text{Cl}_2]$$

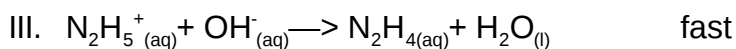
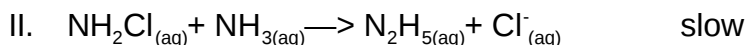
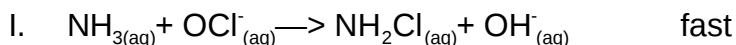
So your final rate law is:  $r = k'[\text{NO}]^2[\text{Cl}_2]$

## Student Packet: 4.5: Reaction Mechanisms: AssessMe questions

- 1) Which statement is true?
- A) A process is only observed to be first order when a unimolecular reaction is occurring.  
 B) A simple bimolecular process will produce a second order rate law.  
 C) A third order rate law indicates that a trimolecular process is involved in the reaction.  
 D) A rate law of order four or higher is almost never observed because this would require four or more molecules to simultaneously collide.  
 E) I'm clueless
- 2) The slowest step of a reaction is called the
- A) elementary process.                      B) order.  
 C) molecularity.                              D) rate-determining step.                      E) I'm clueless
- 3) For a certain reaction the rate law is,  $\text{rate} = k[\text{C}]^{3/2}$ . If the rate of the reaction is  $0.020 \text{ M}\cdot\text{s}^{-1}$  when  $[\text{C}] = 1.0 \text{ M}$ , what is the rate when  $[\text{C}] = 0.60 \text{ M}$ ?
- A)  $0.0093 \text{ M}\cdot\text{s}^{-1}$                       B)  $0.012 \text{ M}\cdot\text{s}^{-1}$   
 C)  $0.013 \text{ M}\cdot\text{s}^{-1}$                       D)  $0.010 \text{ M}\cdot\text{s}^{-1}$                       E) I'm clueless
- 4) The rate law of the reaction  $2\text{H}_2 + 2\text{NO} \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$  is second order in  $[\text{NO}]$  and first order in  $[\text{H}_2]$ . If  $[\text{NO}]$  is doubled and  $[\text{H}_2]$  is halved, the rate of the reaction will
- A) increase by a factor of 4.                      B) remain the same.  
 C) increase by a factor of 6.                      D) increase by a factor of 2.                      E) I'm clueless
- 5) Consider the reaction:  $a\text{A} + b\text{B} \longrightarrow c\text{C}$  which has a rate law:  $-\text{d}[\text{A}]/\text{dt} = k[\text{A}][\text{B}]$   
 For this reaction, which rate relationship is false?
- A)  $-\text{d}[\text{A}]/\text{dt} = (a/c)\text{d}[\text{C}]/\text{dt}$                       B)  $\text{d}[\text{A}]/\text{dt} = (a/b)\text{d}[\text{B}]/\text{dt}$   
 C)  $\text{d}[\text{A}]/\text{dt} = (a/c)\text{d}[\text{C}]/\text{dt}$                       D)  $-\text{d}[\text{B}]/\text{dt} = (b/c)\text{d}[\text{C}]/\text{dt}$                       E) I'm clueless
- 6) Consider the reaction:  $a\text{A} + b\text{B} \longrightarrow c\text{C}$   
 For this reaction, which of the following rate relationships cannot be true?
- A)  $-\text{d}[\text{A}]/\text{dt} = k[\text{A}][\text{B}]$                       B)  $-\text{d}[\text{A}]/\text{dt} = k[\text{A}]^2$   
 C)  $-\text{d}[\text{A}]/\text{dt} = k[\text{A}]^a[\text{B}]^b$                       D)  $-\text{d}[\text{A}]/\text{dt} = k[\text{A}][\text{C}]$                       E) I'm clueless

## Student Packet: 4.5: Reaction Mechanisms: ShowMe questions

1) What is the rate determining step in the following mechanism?

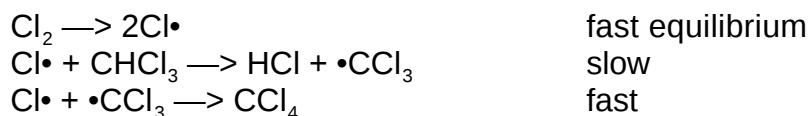


2) Given a reaction with stoichiometry of  $2\text{A} + \text{B} \longrightarrow \text{C}$  and the following experimental data:

| Experiment | [A] (M) | [B] (M) | Rate of formation of C (mol/L•min) |
|------------|---------|---------|------------------------------------|
| 1          | .1      | .2      | 2                                  |
| 2          | .05     | .1      | .5                                 |
| 3          | .05     | .2      | 1                                  |
| 4          | .1      | .05     | .5                                 |

Propose a reaction mechanism consistent with this data.

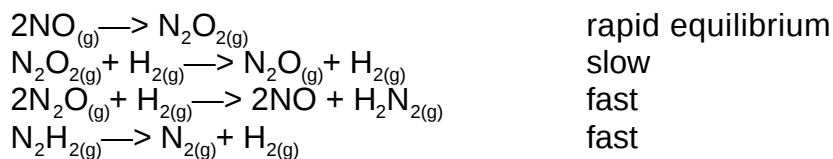
3) What is the rate law mechanism for the reaction with the mechanism:



in terms of the starting reagents?

4) It is known that the rate law for  $2\text{NO}_{(\text{g})} + \text{Br}_{2(\text{g})} \longrightarrow 2\text{NOBr}$  is  $r = k[\text{NOBr}_2][\text{NO}]$ .  
Based on this, propose a reaction mechanism that is consistent with this rate law.

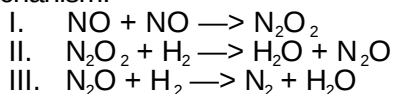
5) Is this mechanism:



valid for the reaction:  $2\text{NO}_{(\text{g})} + 2\text{H}_{2(\text{g})} \longrightarrow \text{N}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{g})}$ ?

## Student Packet: 4.5: Reaction Mechanisms: TestMe questions

- 1) Given the following data, what is the rate determining step for a reaction with the proposed mechanism:



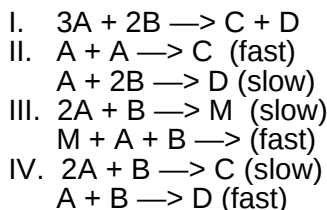
| Experiment | $[\text{NO}]_0 (\text{M})$ | $[\text{H}_2]_0 (\text{M})$ | Rate of $\text{N}_2 (\text{M/min})$ |
|------------|----------------------------|-----------------------------|-------------------------------------|
| 1          | .03                        | .03                         | .135                                |
| 2          | .03                        | .06                         | .27                                 |
| 3          | .06                        | .03                         | .54                                 |
| 4          | .06                        | .06                         | 1.08                                |

- A) I  
 B) II  
 C) III  
 D) No rate determining step: all steps are fast  
 E) Mechanism does not correlate with experimental data

- 2) For the reaction:  $3\text{A} + 2\text{B} \longrightarrow \text{C} + \text{D}$

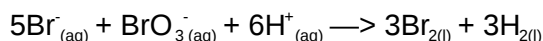
The rate law is observed to be  $r = [\text{A}]^2[\text{B}]$

Which of the following mechanisms are consistent with this rate law?

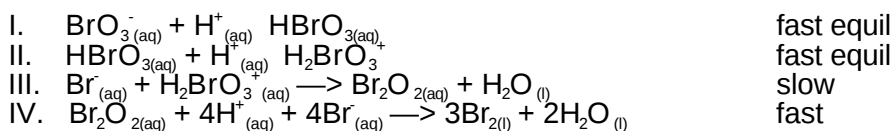


- A) I and II      B) II only      C) III only      D) III and IV      E) IV only

- 3) What is the rate determining step for the reaction:



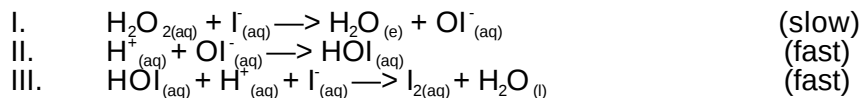
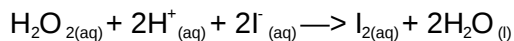
if the mechanism is:



- A) I  
 B) II  
 C) III  
 D) IV  
 E) None of the above mechanisms is inconsistent for this reaction

## Student Packet: 4.5: Reaction Mechanisms: TestMe questions

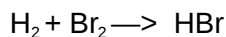
4) The following is a proposed mechanism for the reaction:



What is the rate equation for this mechanism?

- A)  $k [\text{H}_2\text{O}_2] [\text{I}^-]$
- B)  $k [\text{OI}^-] [\text{H}_2\text{O}]$
- C)  $k [\text{H}^+] [\text{OI}^-]$
- D)  $k [\text{HOI}] [\text{H}^+] [\text{I}^-]$
- E)  $k [\text{HOI}]$

5) What is the rate law for the reaction:



if it is known to proceed by the following mechanism:



- A)  $k [\text{H}_2] [\text{Br}_2]$
- B)  $k [\text{Br}_2]$
- C)  $k [\text{Br}_2]^{1/2} [\text{H}_2]$
- D)  $k [\text{H}_2]^{1/2} [\text{Br}_2]$
- E)  $k [\text{HBr}] [\text{H}_2]^{1/2}$