NAME _____ DATE _____

# Performance Task: Evaluate Reaction Mechanisms and Rate Data

## Goal of task

**Target Concept:** Reaction mechanisms must be consistent with the overall rate law of a chemical reaction and the stoichiometry of the reaction. The frequency and success of molecular collisions in elementary reactions is connected to the order and rate constant of the rate law.

For this task you will be evaluated on your ability to:

- Determine if a reaction mechanism is consistent with data determining the experimental rate law.

- Connect the rate law for an elementary reaction to the frequency and success of molecular collisions, including connecting the frequency and success to the order and the rate constant, respectively.

- Use representations (e.g., Boltzmann diagrams, energy profiles, and particulate diagrams) and relevant theories (e.g., collision theory and kinetic molecular theory) to justify predictions about the rate of a chemical reaction.

To be successful you must be able to:

- Make a claim as to the mechanism that matches experimental data, and justify this claim with evidence that relates to the rate law predicted by each of the proposed models. **[Building Block C]**

- Use particulate representations to understand how molecular interaction affects reaction rate. **[Building Block B]**

- Determine the rate law for a reaction through the analysis of initial rate data.

- Determine the rate law for a reaction using the reaction mechanism when the first step of not the rate determining step.

- Create and interpret graphical representations of rate law data. **[Building Block A]**

- Use the collision theory to understand factors that affect reaction rates. **[Building Block B]**

- Construct and interpret reaction energy profiles. **[Building Block B]**

- Understand that reactions can occur stepwise and can be represented by reaction mechanisms. **[Building Block C]**

- Evaluate proposed reaction mechanisms using the collision theory, intermediate analysis, and experimental detection of a reaction intermediate. **[Building Block C]**

- Use an energy profile to explain how catalysts influence reaction rates. **[Building Block D]**

- Use data collected by spectrophotometry to determine how concentration varies with time during the course of a reaction. **[Building Block A]**
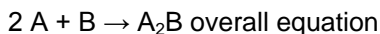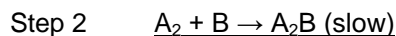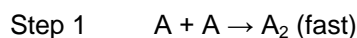
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## Task summary

You will work individually and with peers to develop an understanding regarding the relationship between rate law expressions and reaction mechanisms when the rate-determining step is not the first step. Additionally, the relationships among collision frequency, orientation, activation energy, order, rate constant, and rate law is studied.

## Task 1: Reaction Mechanisms, Rate Laws, and Order (individual or group)

Reaction mechanisms are a series of elementary steps that can be summed up to give the overall equation. The slow step in the rate mechanism is the rate-determining step and is used to determine the rate law for the overall equation. There are multiple proposed mechanisms that can fit the rate law and match the stoichiometry for a given chemical equation. Only experimental evidence can tell us if a proposed mechanism is consistent with the data. If the initial step in a reaction mechanism is also the slow step, then the rate law for that step is also the rate law for the overall equation. We're going to determine the rate law from the reaction mechanism when the first step is not the slow or rate-determining step.

Example: Determine the rate law for the following proposed reaction mechanism. What is the order of the rate law?

Step 1      $A + A \rightarrow A_2$ (fast)

Step 2      $\underline{A_2 + B \rightarrow A_2B \text{ (slow)}}$

         $2 A + B \rightarrow A_2B$ overall equation

Step 2 is the rate-determining step. Rate $step_2 = k_2 [A_2] [B]$, but we cannot have a reaction intermediate ($A_2$) in the rate law for the overall reaction. We need to replace $A_2$ in the rate law for the slow step.

Step 1 is fast and reaches equilibrium, where rate forward = rate reverse.
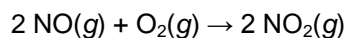
$k_1 [A]^2 = k_{-1} [A_2]$

$k_1/k_{-1} [A]^2 = [A_2]$

**Substituting**

Rate $step_2$ which is the $rate_{overall} = (k_1/k_{-1})\ k_2[A]^2[B] = k'\ [A]^2[B]$ ($k' = k_1/k_{-1} \cdot k_2$).

The rate law is overall third order; second order in A and first order in B.

**Practice**

1.  Consider the oxidation of nitrogen monoxide by oxygen. The reaction is:

    $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$

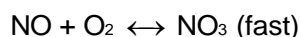    And the observed experimental rate law is: rate = $k[NO]^2[O_2]$.

    Termolecular collisions, collisions between three molecules at once, are very rare, which has led chemists to propose the following mechanism:

    NO + NO $\longleftrightarrow$ $N_2O_2$ (fast)
    $N_2O_2 + O_2$ $\rightarrow$ $2NO_2$ (slow)
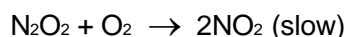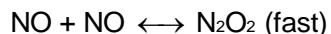
    Show the proposed mechanism is consistent with the experimental rate law.

2.  There is another mechanism that has been proposed for the oxidation of nitrogen monoxide by oxygen. The reaction is: $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$, and the observed experimental rate law is the same as in question 1: Rate = $k[NO]^2[O_2]$.

    NO + $O_2$ $\longleftrightarrow$ $NO_3$ (fast)
    $NO_3$ + NO $\rightarrow$ $2NO_2$ (slow)
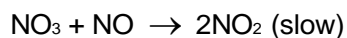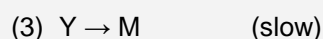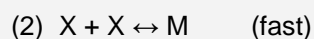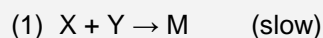
    a.  Demonstrate that this mechanism is consistent with the observed rate law.

    b.  Given that there are two acceptable mechanisms consistent with the observed rate law, is it possible to conclude that either of them is correct? What experimental evidence could the chemist use to eliminate one of them?

3.  Assume the reaction between $CH_4$ and $Cl_2$ is represented by the following mechanism:

    Step 1      $Cl_2(g) \leftrightarrow 2Cl(g)$ (fast)

    Step 2      $CH_4(g) + Cl(g) \rightarrow CH_3(g) + HCl(g)$ (slow)

    Step 3      $CH_3(g) + Cl \leftrightarrow CH_3Cl (g)$ (fast)

    a.  Write the overall equation for the reaction.

    b.  Identify any reaction intermediates.

    c.  Justify the rate law is first order in $CH_4$ and ½ order in $Cl_2$.

    d.  What are the units on the specific rate constant for this reaction?

**Stop.** Share results with partner or class and discuss any discrepancies among your answers.

## Check your understanding

☐ From the 1984 AP Chemistry Exam: For a hypothetical chemical reaction that has the stoichiometry
2 X + Y → Z, the rate law was determined to be: Rate = $k$ $[X]^0[Y]$.

Select from the following mechanisms the one most consistent with the observed data, and explain your choice. In these mechanisms, M and N are reaction intermediates.

(1) X + Y → M        (slow)

   X + M ↔ Z        (fast)

(2) X + X ↔ M        (fast)

   Y + M → Z        (slow)

(3) Y → M        (slow)

   M + X ↔ N        (fast)

   N + X ↔ Z        (fast)

☐ How does the chemist use the presence of reaction intermediates to determine if a proposed mechanism is inconsistent with rate law?

# Task 2: Connecting $k$ to the Rate Law, Frequency, Orientation, $E_a$, and $T$ (individual or group)

The rate of a chemical reaction is temperature dependent. Recall that the collision theory related the rate of a reaction to the energy and orientation of the colliding molecules and that a higher temperature resulted in more effective collisions. That was how the increase in rate was explained when the temperature rose. It did not indicate that an alternate mechanism or rate law was involved. The increase in rate is reflected in the fact that the rate constant, $k$, is temperature dependent.

The Arrhenius equation can be used to examine the relationship between temperature, orientation, collision frequency, and the rate constant. It can be expressed in several forms:

$k = Ae^{(-Ea/RT})$ or ln $k = -E_a/R$ (1/$T$) + ln A,

$k$ = the specific rate constant, A is the frequency factor, e $(^{-Ea/RT})$ is called the exponential factor and includes the activation energy, $E_a$, the universal gas constant ($R$= 8.31 J/mol.K) and temperature, $T$.

The frequency factor, A, depends on two different factors: (1) $p$ the orientation factor and (2) z the collision frequency. The collision frequency is typically on the order of $10^9$ collisions every second, but all of these collisions are not effective because the orientation of the molecules must be favorable and the energy must be sufficient for bonds to rearrange. Some orientations have a zero probability of being successful. Typically, collisions between two individual atoms have an orientation factor of 1. Some reactions have a collision factor of much less than one when molecules must collide with a very precise geometry and that means that A is very small and the rate constant is also small. The specific rate constant will increase when the orientation factor is high, meaning more of the collisions between molecules will have a favorable collision geometry.

1.  Which of the following reactions (if all other factors are the same except for the orientation factor) would be expected to have the higher specific rate constant, $k$? Explain your reasoning.

    (a)  $A(g) + B(g) \rightarrow AB(g)$

    (b)  $AB(g) + CD(g) \rightarrow AD(g) + CB(g)$

2.  Explain the direction of change in $k$ when a catalyst is added to a reaction.

3.  When comparing two reactions at the same temperature and of the same order and activation energy, what does it mean to say that the rate constant $k_1 > k_2$?

4.  Taking the natural log of the Arrhenius equation, $k = Ae^{(-Ea/RT)}$, gives us $\ln k = -E_a/R \, (1/T) + \ln A$, which is in the form of $y = mx + b$.

    How could the slope be used to calculate the activation energy for the reaction?

5.  What effect would a higher temperature have on the value of the rate constant, $k$? Explain the effect on $k$ in terms of the speed of the reacting molecules.

**Stop.** Share results with partner or class and discuss any discrepancies.

## Check your understanding

☐ Answer this question adapted from the 1992 AP Chemistry Exam.

$H_2(g) + I_2(g) \rightarrow 2\ HI(g)$
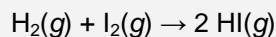
For the exothermic reaction represented above, carried out at 300 K, the rate law is as follows:

Rate = $k[H_2][I_2]$

Predict the effect of the following change on the initial rate of the reaction, and explain your prediction.

An increase in temperature to 500 K. In your explanation, include a diagram showing the number of molecules as a function of energy, and explain how that diagram relates to your answer.

☐ The rate law for $2NO(g) + O_2\ (g) \leftrightarrow 2\ NO_2(g)$ is rate = $k[NO]^2\ [O_2]$.

Each of these diagrams represents a mixture in which the number of each type of molecule represents its relative initial concentration. All diagrams represent the reactants at the same temperature and pressure.



(a)     (b)     (c)

● NO
○ $O_2$
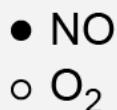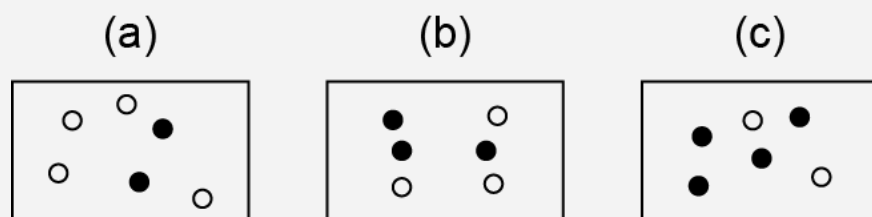
   i.   Which mixture has the fastest initial rate?

   ii.   Which mixture has the greatest rate constant, $k$?

   iii.   Which mixture has the greater ratio of product concentration to reactant concentration at equilibrium?
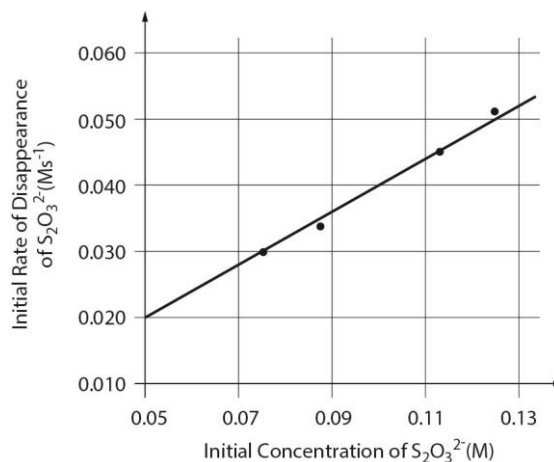
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# Task 3: Apply your understanding (in class or as homework)

1. Answer the following question from the 2009 AP Chemistry Exam, part A, question 2, form B.
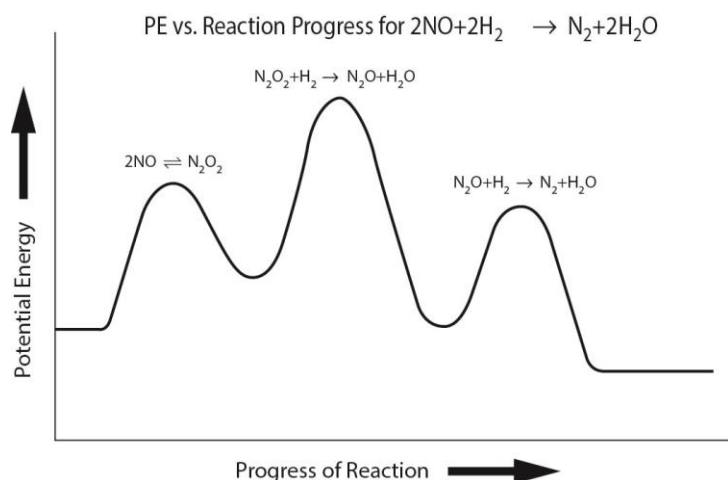
   $S_2O_3^{2-}(aq) + H^+ \rightarrow SO_3^{2-}(aq) + S(s)$
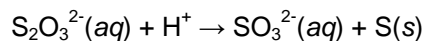
   A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial, the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given in the following table on the left and are plotted in the graph on the right.

| Trial | Initial Concentration of $S_2O_3^{2-}$ (aq) (M) | Initial Rate of Disappearance $S_2O_3^{2-}$ (aq) (M s$^{-1}$) |
|---|---|---|
| 1 | 0.050 | 0.020 |
| 2 | 0.075 | 0.030 |
| 3 | 0.088 | 0.034 |
| 4 | 0.112 | 0.045 |
| 5 | 0.125 | 0.051 |



   a. Identify the independent variable in the experiment.

   b. Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.

   c. Determine the value of the rate constant, $k$, for the reaction. Include units in your answer. Show how you arrived at your answer.

   d. In another trial, the student mixed 0.10 $M$ $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 $M$.

   e. On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

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2. The following graph was obtained for the progress of the reaction between NO and $H_2$ to produce $N_2$ and $H_2O$.

PE vs. Reaction Progress for $2NO+2H_2 \rightarrow N_2+2H_2O$

$N_2O_2+H_2 \rightarrow N_2O+H_2O$

$2NO \rightleftharpoons N_2O_2$

$N_2O+H_2 \rightarrow N_2+H_2O$

Potential Energy

Progress of Reaction

Based on the information presented in the graph:

a. Propose a mechanism for the reaction.

b. Propose a rate law consistent with the proposed mechanism.

c. Justify your answers.

3. The following is an exothermic elementary reaction with K > 1.

$$X(g)+Y(g) \rightleftharpoons XY(g)$$

a. Draw an energy profile (energy vs reaction progress) for the reaction and label the ΔH.

b. Compare the values of the rate constants, $k_{forward}$ and $k_{reverse}$. Justify your response by using rate laws and the relative concentrations of reactants and products at equilibrium.

c. Explain the relationship of both the activation energy and the temperature to the rate constant, using KMT.

4. The rate for a particular reaction is 0.040 M/s for a given set of concentrations. If the rate law for the reaction is:

$$\text{Rate} = \frac{k[W]^2[X]}{[Z]^2}$$

a. What is the overall order for the reaction?

b. If the concentrations of W and X remain the same but [Z] is doubled what is the new rate?

c. If the concentrations of both W and Z are doubled and the concentration of X is halved, what is the new rate?