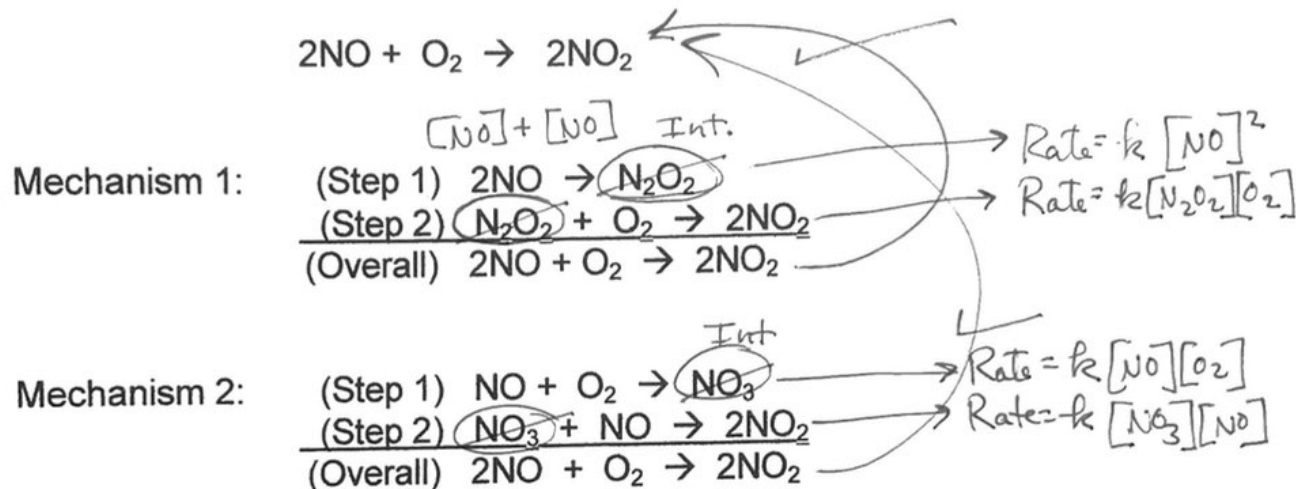


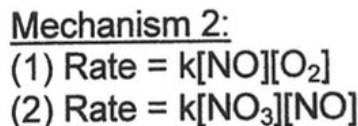
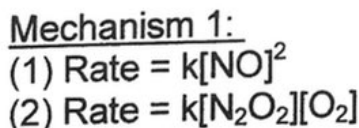
The Steady-State Assumption

Sometimes a reaction may have two possible mechanisms as in the case of the reaction below. When this is the case, how do you determine which mechanism is the most probable?



Both reactions pass the first test – they “add up” to the overall reaction.

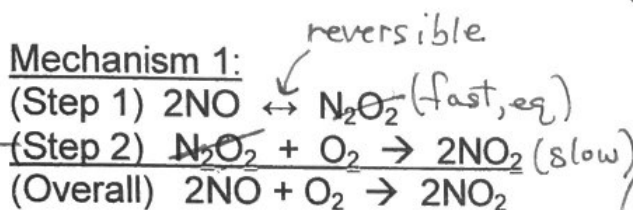
Next, determine the rate law for each elementary step. Remember, the rate law is related to the molecularity of the step.



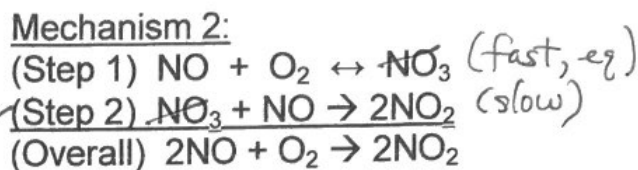
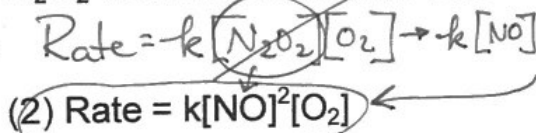
*If Step 1 is the rate-determining step, the decision is clear cut because the mechanisms give different rate laws. Remember, the overall rate law and the rate law for the rate-determining step are the same.*

If Step 2 is the rate-determining step, then we must use the steady-state assumption to rewrite these rate laws in terms of measurable reactants. (The second step in each mechanism contains an intermediate product and you cannot use a rate law that contains intermediates.) *If Step 2 is the rate-determining step, then we assume that Step 1 is fast and reversible.*

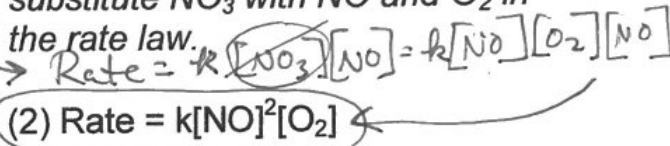
Rewriting Step 1 for each mechanism gives:



In mechanism 1, it "looks like"  $2\text{NO}$  is combining directly with  $\text{O}_2$ . Therefore, we can substitute  $\text{N}_2\text{O}_2$  with  $2\text{NO}$  in the rate law.



In mechanism 2, it "looks like"  $\text{NO}$  and  $\text{O}_2$  are combining directly with  $\text{NO}$ . Therefore, we can substitute  $\text{NO}_3$  with  $\text{NO}$  and  $\text{O}_2$  in the rate law.



If Step 2 is the rate-determining step, both mechanisms yield the same rate law. To determine which mechanism is correct, additional experiments must be designed to identify the intermediate,  $\text{NO}_3$  or  $\text{N}_2\text{O}_2$ , that is formed during the reaction.

### Collision Theory and Reaction Profile

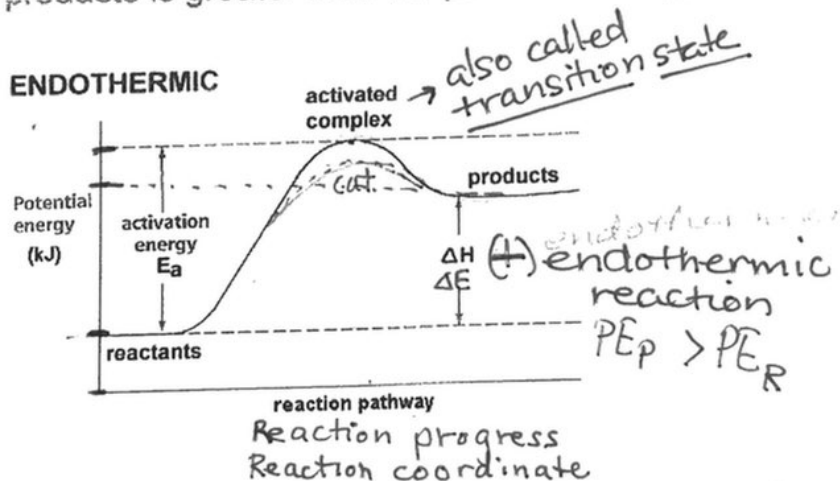
- Collision theory states that the frequency of effective collisions between reactants determines the rate of the reaction.
- For a collision to be effective, the molecules must collide with
  - \* (1) sufficient energy and (2) the proper orientation so that products can form.
- As molecules approach on a collision course, they do not act like billiard balls simply bouncing off each other. Instead, as the molecules get closer, their orbitals interact and distort each other. This distortion weakens bonds within the molecules so that at the moment of collision some bonds are so weak that they break and new bonds may form.
- Activated complex is the term given to the molecules at the moment of collision. You can think of the activated complex as no longer reactants, but not yet product – bonds are partially broken and partially formed. This is a very high energy state. \*

Transition state

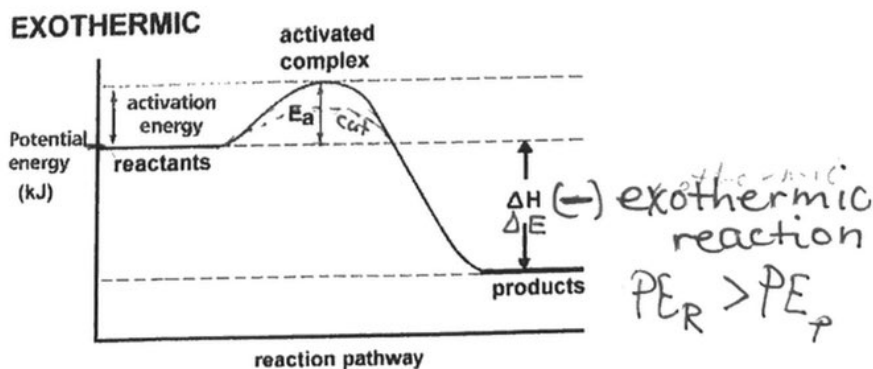
- A reaction profile plots the increase in potential energy of the reactants as they approach, reaching a maximum at the moment of collision, and then the decrease in potential energy as the products recoil.
- In a reaction profile, the minimum amount of kinetic energy that must be converted into potential energy in order to form products is called the activation energy,  $E_a$ .
- Reaction profiles can be used to determine whether a reaction is endothermic or exothermic. This is possible because the potential energy difference between the products and the reactants is equal to the enthalpy of the reaction,  $\Delta H$ :

$$\Delta H = PE_{\text{products}} - PE_{\text{reactants}}$$

- When heat is absorbed from the surroundings, the reaction is endothermic and  $\Delta H$  is positive. For endothermic reactions the potential energy of the products is greater than the potential energy of the reactants.

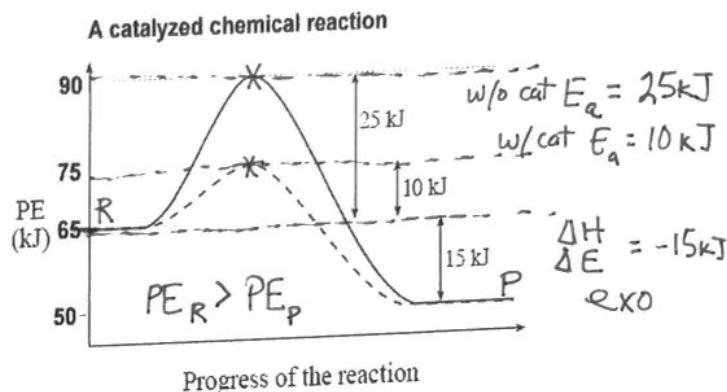


- When heat is released to the surroundings, the reaction is exothermic and  $\Delta H$  is negative. For exothermic reactions the potential energy of the reactants is greater than the potential energy of the products.



- Reaction profiles also allow us to explain the action of **catalysts**. A catalyst is a substance that increases the rate of a reaction without itself being reacted. It speeds up a reaction by providing an alternative reaction pathway that has a lower energy of activation.

In the potential energy diagram shown here, the regular, uncatalyzed pathway is shown as a solid line, and the catalyzed pathway is shown as the dotted line.  $\Delta H$  for both the catalyzed and uncatalyzed reaction is  $-15 \text{ kJ}$ . Since  $\Delta H$  is independent of the pathway, it is not changed by the presence of a catalyst.



- In a reaction profile, the rate constant, and therefore the rate of a chemical reaction, are inversely related to the energy of activation. When the activation energy is low, a large proportion of the collisions will have sufficient energy for a reaction to occur. Conversely, a high activation energy indicates that few collisions will have enough activation energy to convert reactants into products.

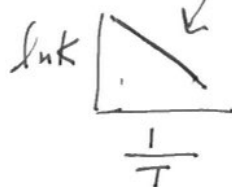
- The **Arrhenius equation** relates the energy of activation ( $E_a$ ) to the rate constant ( $k$ ).

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T_{\text{temp}}} + \ln(A) \quad (R=8.31 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$y = (m)(x) + b$$

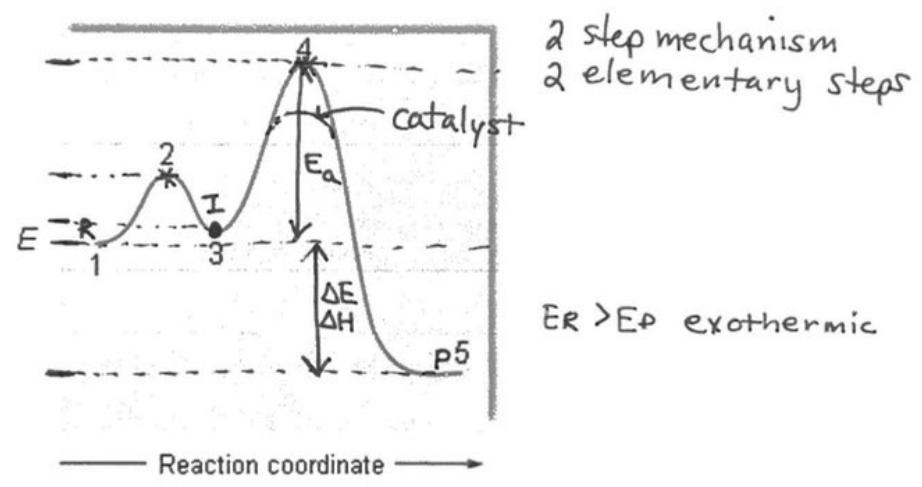
If the rate constant,  $k$ , obeys the Arrhenius equation then a plot of  $\ln k$  versus  $1/T$  gives a straight line. The slope and intercept of the line can be used to find the values of  $E_a$  and  $A$  for that reaction. Most reactions do not obey the Arrhenius equation.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

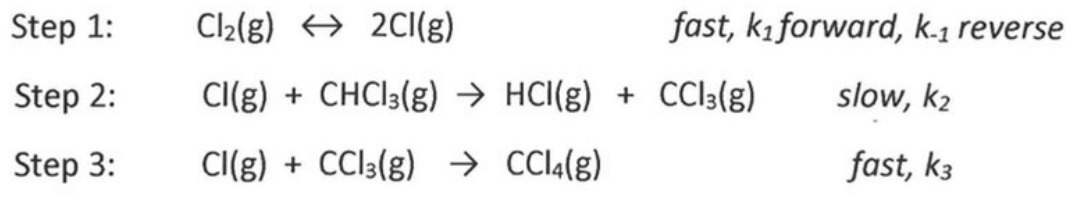


### Reaction Mechanisms and Reaction Profiles Practice

1. A. How many elementary steps are in the reaction mechanism shown below?
- B. On the energy profile below, indicate
  - a. the position of the reactants and products
  - b. the activation energy for the overall reaction
  - c.  $\Delta E$  for the reaction
  - d. the point on the plot that represents the energy of the intermediate 3
  - e. the transition state (activated complex) 2 + 4
  - f. the rate-determining step step 2
  - g. how a catalyst would affect the reaction  $\downarrow E_a$  of step 2
- C. Is the overall reaction endothermic or exothermic?



2. Consider the following 3-step mechanism for an exothermic reaction.



A. What is the overall reaction?

B. What are the reaction intermediates?

\* C. Write the rate law that is consistent with this mechanism, showing how you derive it.