ACTIVATION ENERGY AND CATALYSIS

Introduction

- For a reaction to occur, molecules must collide. *The frequency of the **collisions** affects the rate of the reaction*. The frequency can be changed by
  a. *increasing or decreasing the **concentrations** of the reactants*
  b. *changing the **temperature** to change the velocities of the molecules.*

- When molecules collide, they do not all react. In order to react, the two *molecules must have the proper **orientation**.*

- Not all properly oriented collisions between molecules result in a reaction. The molecules must also have enough energy for the reaction to occur. *The minimum energy that is needed is called the **activation energy.***

- The activation energy is needed because existing bonds must be broken and new bonds must be formed. The point in the reaction at which this reconstruction is occurring is called the ***transition state*** or ***activated complex***.

- ***Catalysts** are substances that lower the activation energy and thereby increase the rate of reactions.* Catalysts are essential in the production of industrial chemicals. Biological catalysis, which are called *enzymes*, are essential for life and for the development of new pharmaceutical products.

Learning Objectives

- Understand the factors that limit the rate of a chemical reaction.
- Be able to determine the activation energy of a chemical reaction from reaction rate data.
- Recognize how catalysts can increase reaction rates.

Success Criteria

- Ability to produce a complete list of factors that affect the rate of a chemical reaction.
- Ability to identify three or more ways that the rate of a chemical reaction can be increased.
- Correct determination of activation energies from reaction rate data.
- Correct quantitative prediction of how large a rate increase will be produced by a given change in activation energy.

Prerequisites

- Rates of chemical reactions
- Reaction mechanisms

MODEL 1: **Energy vs Reaction Coordinate Diagram**

An energy vs reaction coordinate graph is used to show how the potential energy of the reactants changes as they are converted to products. The reaction coordinate is a measure of the progress of the reaction along the reaction pathway.

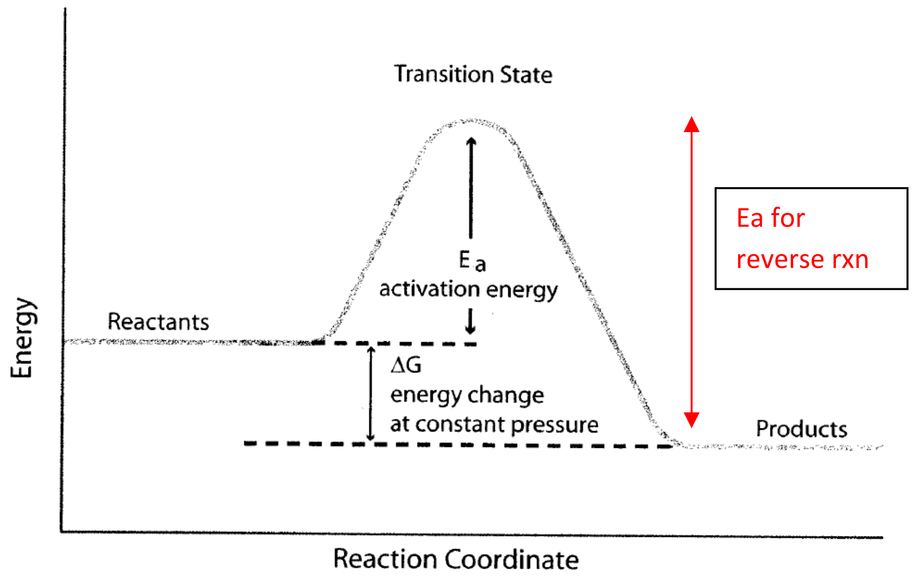


Fig. 1

EXERCISES

1a. Is the energy change in going from reactants to products in Fig. 1 positive or negative?

ΔG is negative

1b. According to Fig. 1, which has the higher energy, the reactants or the transition state?

Reactants

1c. As the temperature increases, does the fraction of molecules with high kinetic energy increase or decrease? Why do you think the rate of a chemical reaction increases with increasing temperature?

Increase; if a greater fraction of molecules have a kinetic energy large enough to get to the transition state (over the activation energy barrier), the rate of the reaction will be greater.

1d. Which molecules are most likely to reach the transition state and pass over to products when they collide

- those with high velocities and kinetic energies *or*

- those with low velocities and kinetic energies

1e. Give another reason why some collisions between molecules might not result in a chemical reaction.

The likelihood of a reaction occurring depends upon the orientation in which the reactant collide. The reactive parts of the molecules must come into contact for bonds to be broken and new bonds to be formed.

1f. Draw an arrow on the diagram in Fig. 1 to indicate the magnitude of the activation energy for the reverse reaction (products going back to reactants). Do you think the rate constant of the reverse reaction will be larger or smaller than that of the forward reaction?
(Explain your answer in terms of the fraction of molecules that have enough kinetic energy to reach the transition state)

The activation energy for the reverse reaction is the activation energy of the forward reaction plus ΔG. So, it is larger, which means the rate constant for the reverse reaction is smaller (see the Arhenius Eq). This is always the case for favorable reactions (exergonic, ΔG is negative). The opposite is true for unfavorable reactions (endergonic reactions, DG is positive). See problem 1i.

PROBLEMS

1g. Hydrogen and chlorine react to produce hydrochloric acid, but the reverse reaction also occurs at a slower rate. Consider the reaction

$$2HCl \rightarrow H_2 + Cl_2$$

Draw two diagrams, one showing an orientation of the two HCl molecules that is unfavorable for this reaction, and one showing an orientation that is favorable for this reaction.

Favorable			Unfavorable		
H		H	H		Cl
I	⟶⟵	I	I	⟶⟵	I
Cl		Cl	Cl		Cl

The Hs and Cls must line up so the transition state complex can form.

H------- H
I I
Cl-------Cl

1i. Draw an energy vs reaction coordinate diagram to illustrate a reaction in which the energy of the products is greater than the energy of the reactants. Label all quantities as per Fig. 1.

See diagram (3) in sample exercise 14.10 on pg 595 of Brown and LeMay, 11^{th} ed.

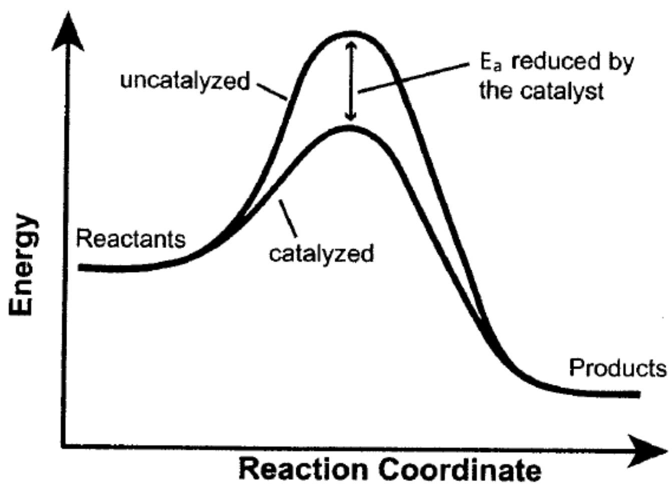
1j. Using your diagram from exercise 1i, identify which reaction (forward or reverse has the larger activation energy and which has the larger rate constant.

The forward reaction has the larger activation energy.

The reverse reaction has the larger rate constant.

MODEL 2: Lowering the Activation Energy - Catalysis

A catalyst changes the mechanism of a chemical reaction and lowers its activation energy. The catalyst participates in intermediate steps of the reaction, but it is neither produced nor consumed in the reaction so the balanced reaction equation remains the same.



EXERCISES

2a. What effect does a catalyst have on the activation energy of a reaction?

It lowers the activation energy, which increases the rate constant and speeds up the reaction

2b. What effect does a catalyst have on the change in free energy of a reaction?

A catalyst only effects the kinetics of the reaction not the thermodynamics of the reaction. The change in free energy (ΔG) remains the same.

2c. What effect does a catalyst have on the mechanism of a reaction?

It usually binds to the reactant(s) and orients the reactants optimally to speed up the reaction.

2d. What effect does a catalyst have on the stoichiometry of a reaction?

The overall stoichiometry does not change because the catalyst is not consumed or produced in the reaction.

2e. How does the rate of the rate limiting step in a reaction with a catalyst compare with the rate of the rate limiting step without the catalyst?

The catalyzed rate limiting step would occur faster because the catalyst lowers the activation energy which increases the rate constant.

2f. What are at least three ways that the rate of a chemical reaction can be increased?

Increase temperature; k is related to T (see Arhenius eq.)

Add catalyst; increases k

Increase concentrations of reactants; does not change k but does generally increase the reaction rate (for first and high orders reactions)

PROBLEMS (using the Arhenius Eq.; $k = Ae^{-Ea/RT}$)

2g. A catalyst reduces the activation energy for a reaction from 17 kJ mol^{-1} to 2 kJ mol^{-1}. By what factor is the rate accelerated?

(Assume that the frequency factor *A* does not change, and that the temperature is 200 K).

$K_2/k_1 = (e^{-Ea2/RT})/e^{-Ea1/RT})$

$= (e^{-2000/(8.314*200)}) / (e^{-17000/(8.314*200)}) = 8266.7$ or $8 \cdot 10^3$ with proper sig figs