UNIT 2

Part 2

CHEMICAL KINETICS

Reaction Mechanism

Reaction Mechanism

Rate law

↕

Reaction mechanism

Definitions

- ***Reaction Mechanism***: The series of steps (*elementary processes*) *by which a reaction proceeds.*
- ***Molecularity***: The *number of bodies* which come together, or *collide*, in an elementary process. (*I.e., uni-, bi-, ter*molecular.)
- ***Order of an elementary process***: The order of an elementary process can be predicted. It is numerically equal to its molecularity.

- ***Intermediate***: An *intermediate species* is one which is formed and consumed in the course of a reaction (It is neither a reactant nor a product.)
- ***Rate determining step***: The *slowest step* in a reaction.

TABLE 14.3 Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Requirements which a *valid reaction mechanism* must satisfy:

a) Sum elementary steps = Overall balanced chemical equation for the reaction

b) The mechanism must agree with the experimentally determined rate law.

Exercise 4

What rate law is predicted from the following mechanism for the decomposition of ozone:

(1) $O_3 \rightarrow O_2 + O$ (slow)

(2) $O + O_3 \rightarrow 2O_2$ (fast)

Exercise 5

For the reaction $2NO + O_2 \rightarrow 2NO_2$ the experimental rate law is

$$R = k[NO][O_2].$$

Suggest a simple, valid mechanism consistent with the above rate law for this reaction.

Exercise 6

$$NO_2 + CO \rightarrow CO_2 + NO$$

It is known from experiment that at T > 500 K

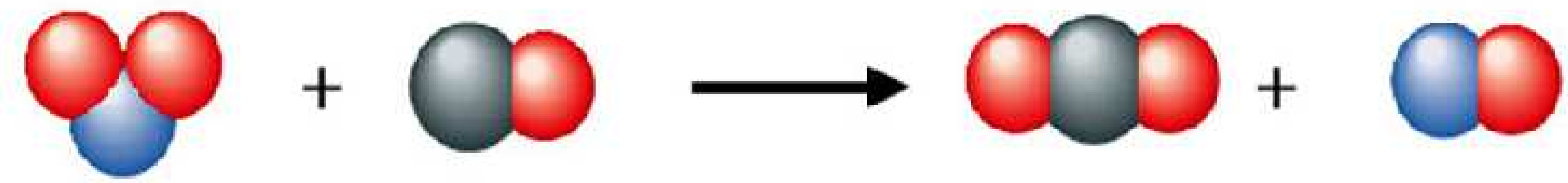
$$\frac{d[CO_2]}{dt} = k[NO_2][CO]$$

while at T < 500 K

$$\frac{d[CO_2]}{dt} = k'[NO_2]^2$$

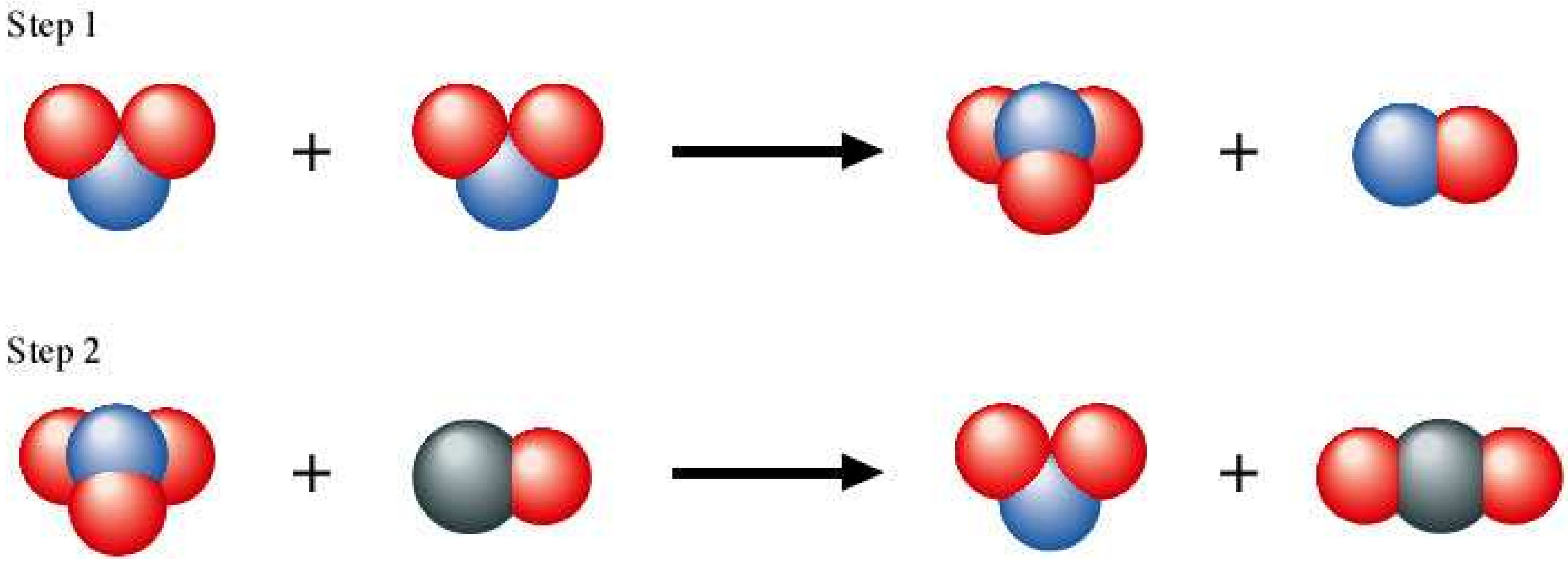
Propose valid mechanisms for the above.

A Molecular Representation of the Elementary Steps in the Reaction of NO_2 and CO



$T > 500$ K $\qquad R = k\,[NO_2][CO]$

A Molecular Representation of the Elementary Steps in the Reaction of NO_2 and CO



$T < 500$ K $\qquad R = k' [NO_2]^2$

Reaction Kinetics Models

- Collision Theory
- Transition State Theory

Collision Theory

Collision Theory

EXPERIMENTAL OBSERVATIONS

Reactions can be *slow* or *fast;* the *rate of reaction* depends on*:*

(a) the *concentration* of the reactants*:*

$$R = k[L]^m[M]^n$$

(b) on the *temperature* at which the reaction takes place.

$k = f(T)$ ("doubles with every 10 K rise")

The Rate Constant

<u>Svante Arrhenius (1889)</u>

ACTIVATION ENERGY

$$k = Ae^{-E_a/RT}$$

FREQUENCY FACTOR

ARRHENIUS, Svante August
Nobel Laureate CHEMISTRY 1903

Svante August Arrhenius

1859 -1927

Collision Model

For reaction to take place between two molecules these must come into contact with each other, in other words, they must *collide*.

$$Rate \propto \#\ collisions\ dm^{-3}\ s^{-1} \propto\ concentration$$

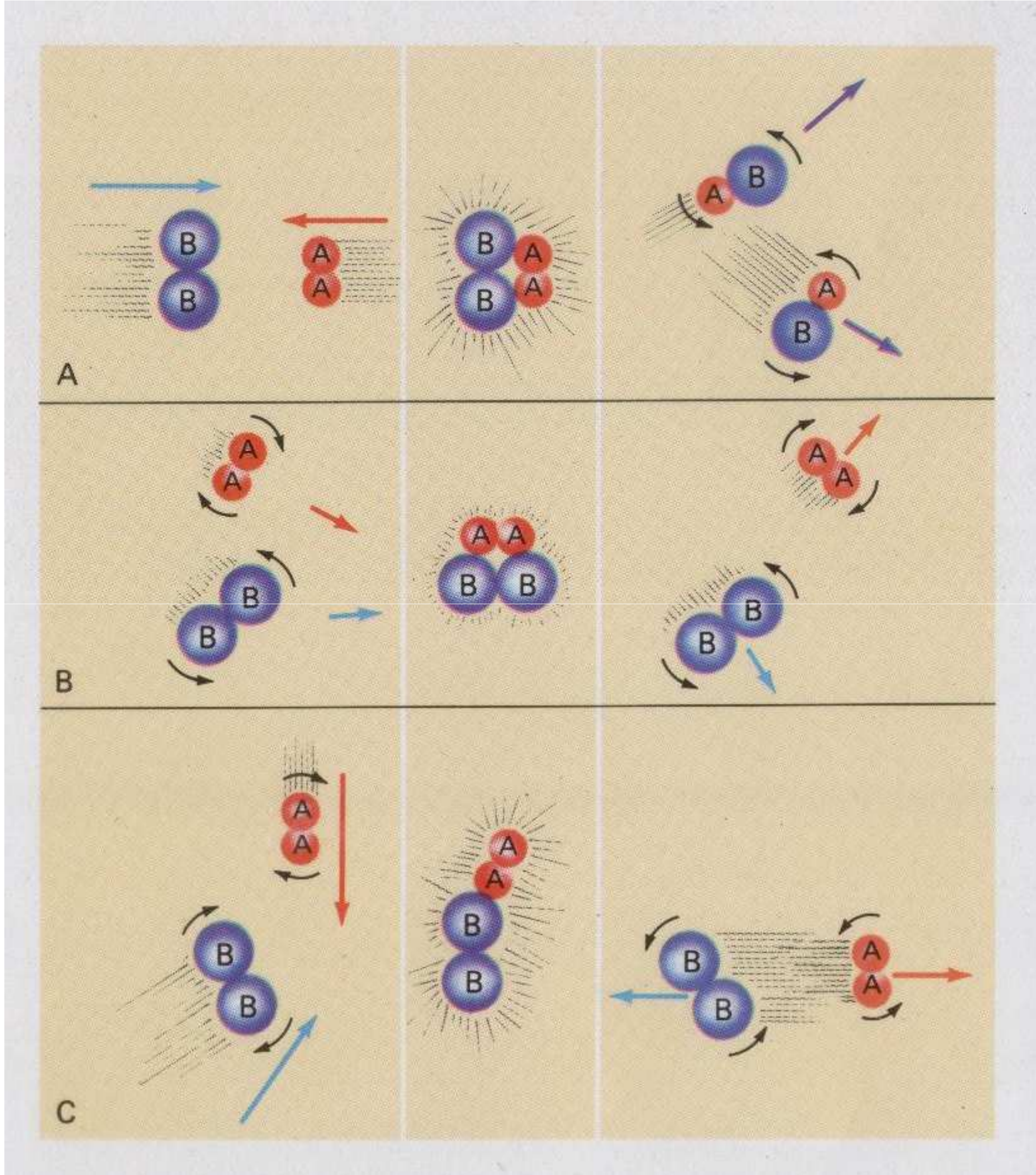
COLLISION FREQUENCY, ***Z***

At STP, one dm^3 contains $\approx 3 \times 10^{22}$ gas particles and the total number of collisions is $\approx 1 \times 10^{32}\ s^{-1}$. If every collision lead to reaction all the particles in this volume would react in $\approx 3 \times 10^{-10}$ s.

Few reactions are so fast

Postulates

- *Reactive collisions* result only when the particles $\boldsymbol{E_{kin} \geq E_a}$.
- The orientation of the reacting particles is also important. The ***steric factor, p,*** is introduced to allow for this additional requirement.



A
B
C

Letting, N/N_0 = fraction of particles with $E_{kin} \geq E_a$, we can write

$$R \propto p \cdot Z \cdot N/N_0$$

Assuming a Maxwell-Boltzmann distribution of energies

$$\frac{N}{N_0} = e^{-E_a/RT}$$

and substituting for $Z = \beta\,[L]^m[M]^n$,
we obtain

$$
\begin{aligned}
R &= p\beta[\mathrm{L}]^{\mathrm{m}}[\mathrm{M}]^{\mathrm{n}}\, e^{-Ea/RT} \\
&= p\beta e^{-Ea/RT}[\mathrm{L}]^{\mathrm{m}}[\mathrm{M}]^{\mathrm{n}} \\
&= k[\mathrm{L}]^{\mathrm{m}}[\mathrm{M}]^{\mathrm{n}}
\end{aligned}
$$

and

$$
\boldsymbol{k = p\beta\, e^{-E_a/RT}}
$$

which is identical in form to the experimental Arrhenius equation.

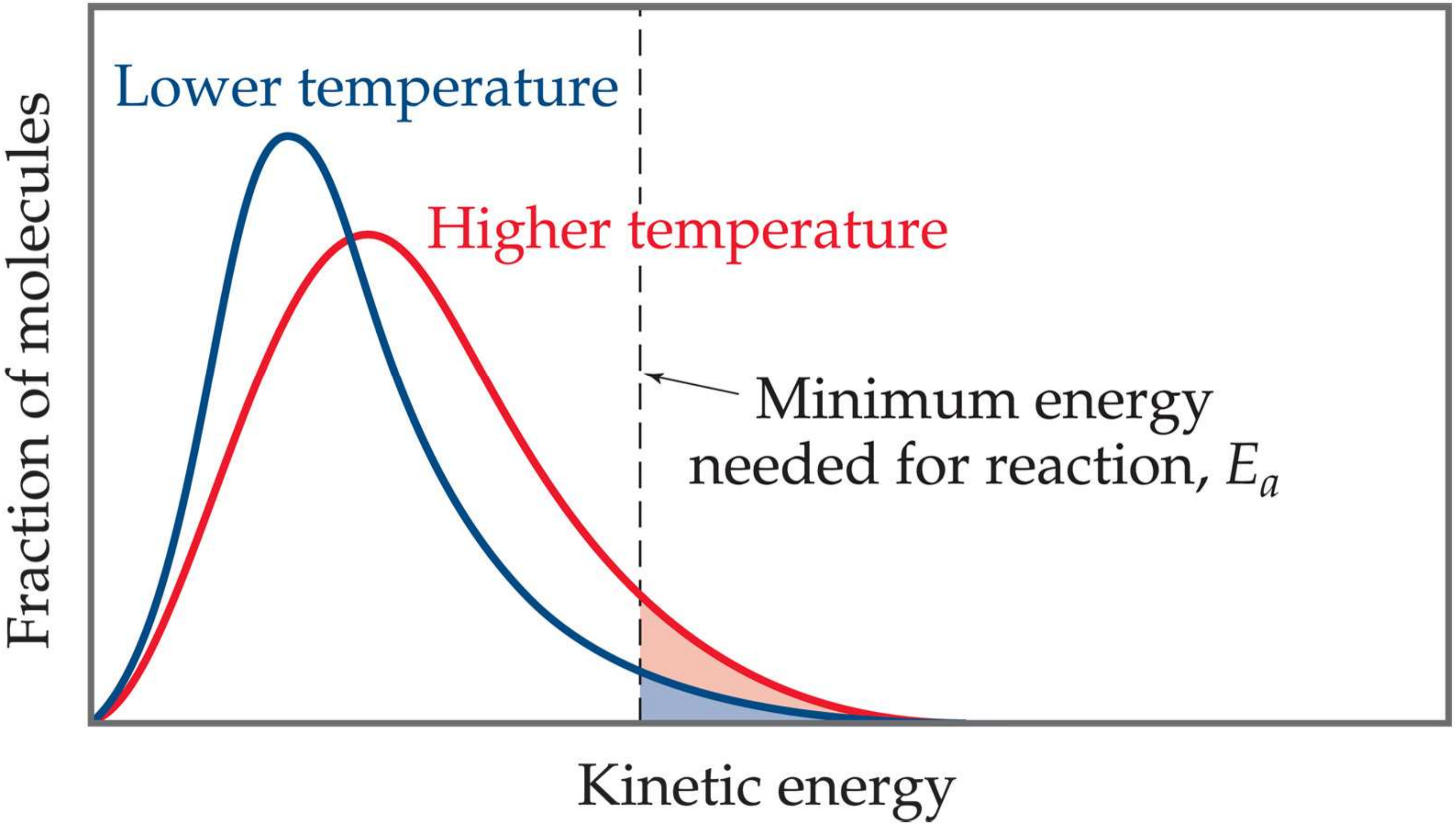
The Rate Constant

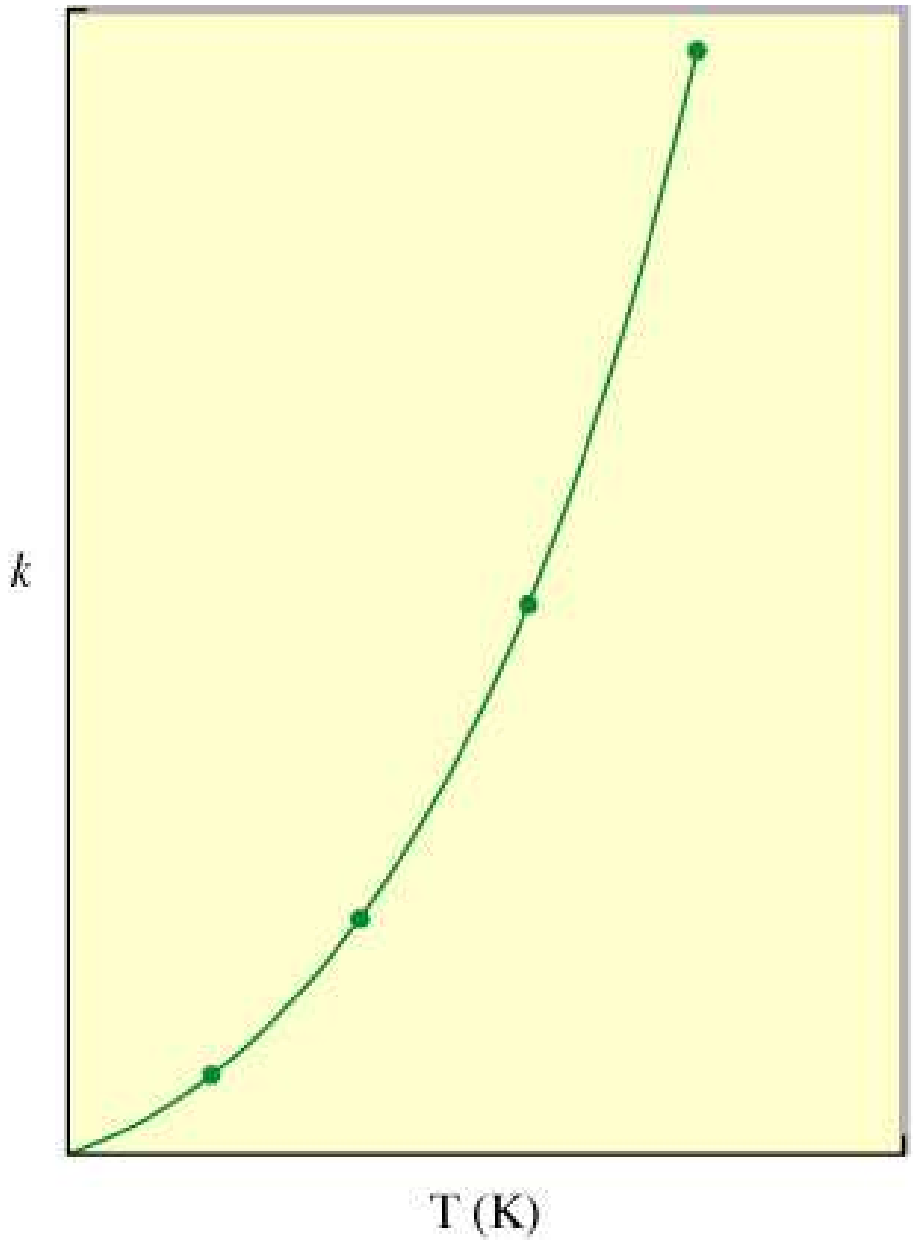
Svante Arrhenius (1889)

ACTIVATION ENERGY

$$k = Ae^{-E_a/RT}$$

FREQUENCY FACTOR


Lower temperature
Higher temperature
Minimum energy
needed for reaction, E_a
Fraction of molecules
Kinetic energy


k
T (K)

Activation Energy

The logarithmic form of the Arrhenius equation is very useful in the evaluation of the activation energy of a reaction.

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

Exercise 7

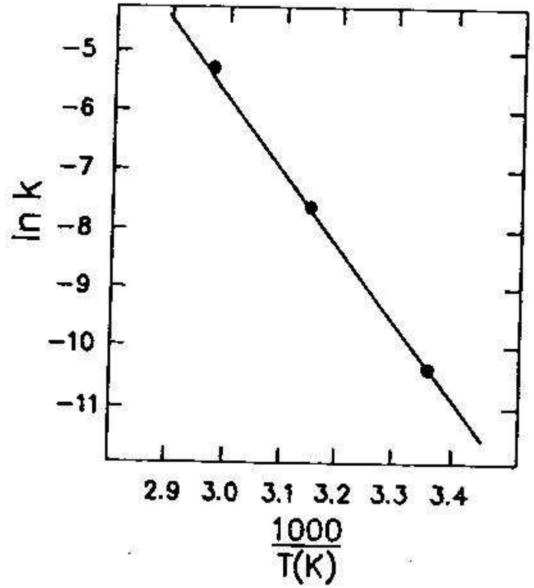
The rate constant for the gas phase decomposition of N_2O_5 has the following temperature dependence:

T/K	*k/s*$^{-1}$
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

Calculate the activation energy for the reaction.

Again we graph ln k vs. 1/T

T (K)	1/T	k (s^{-1})	ln k
338	2.96×10^{-3}	4.9×10^{-3}	-5.32
318	3.14×10^{-3}	5.0×10^{-4}	-7.60
298	3.36×10^{-3}	3.5×10^{-5}	-10.26



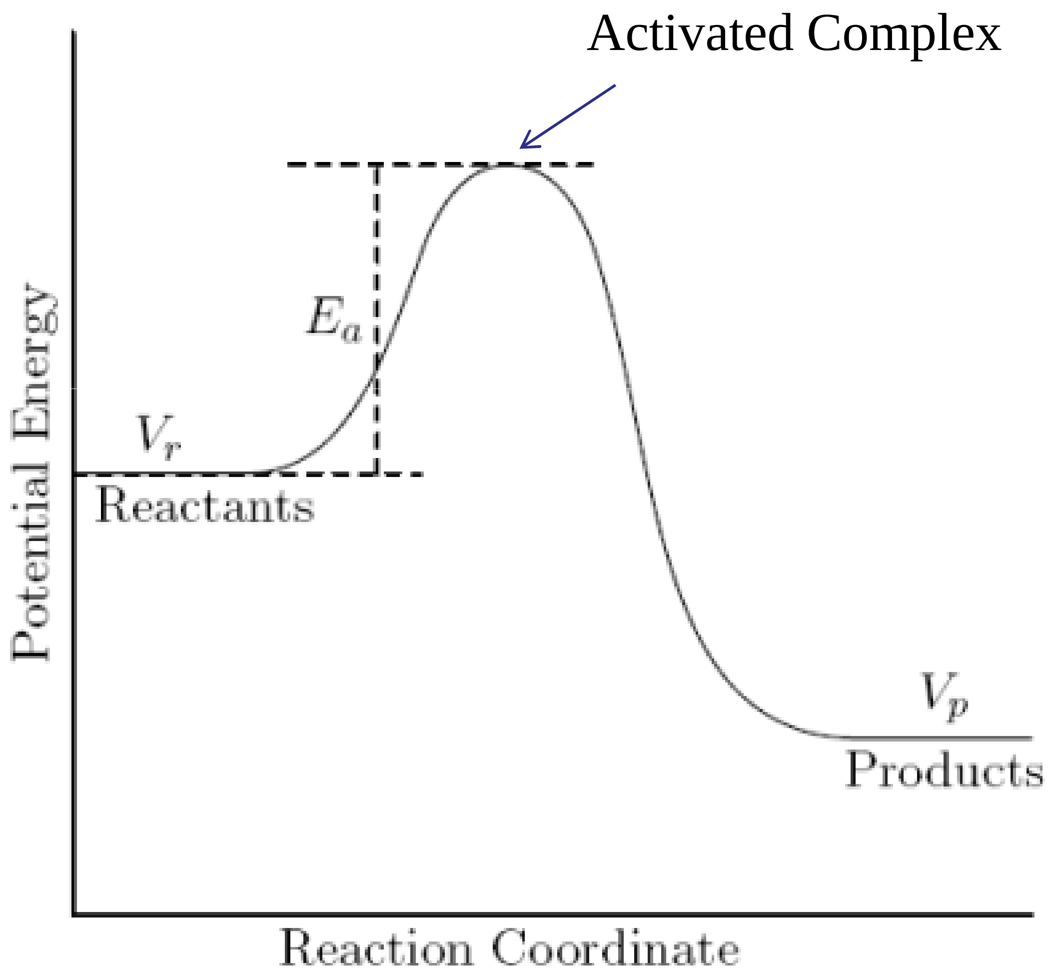
$$\text{Slope} = \frac{-10.76 - (-5.85)}{3.40 \times 10^{-3} - 3.00 \times 10^{-3}} = -1.2 \times 10^{4}\ \text{K}$$

$$\text{Slope} = \frac{-E_a}{R}$$

$$E_a = -\text{Slope} \times R = 1.2 \times 10^{4}\ \text{K} \times \frac{8.3145\ \text{J}}{\text{K mol}} = 1.0 \times 10^{5}\ \text{J/mol or } 1.0 \times 10^{2}\ \text{kJ/mol}$$

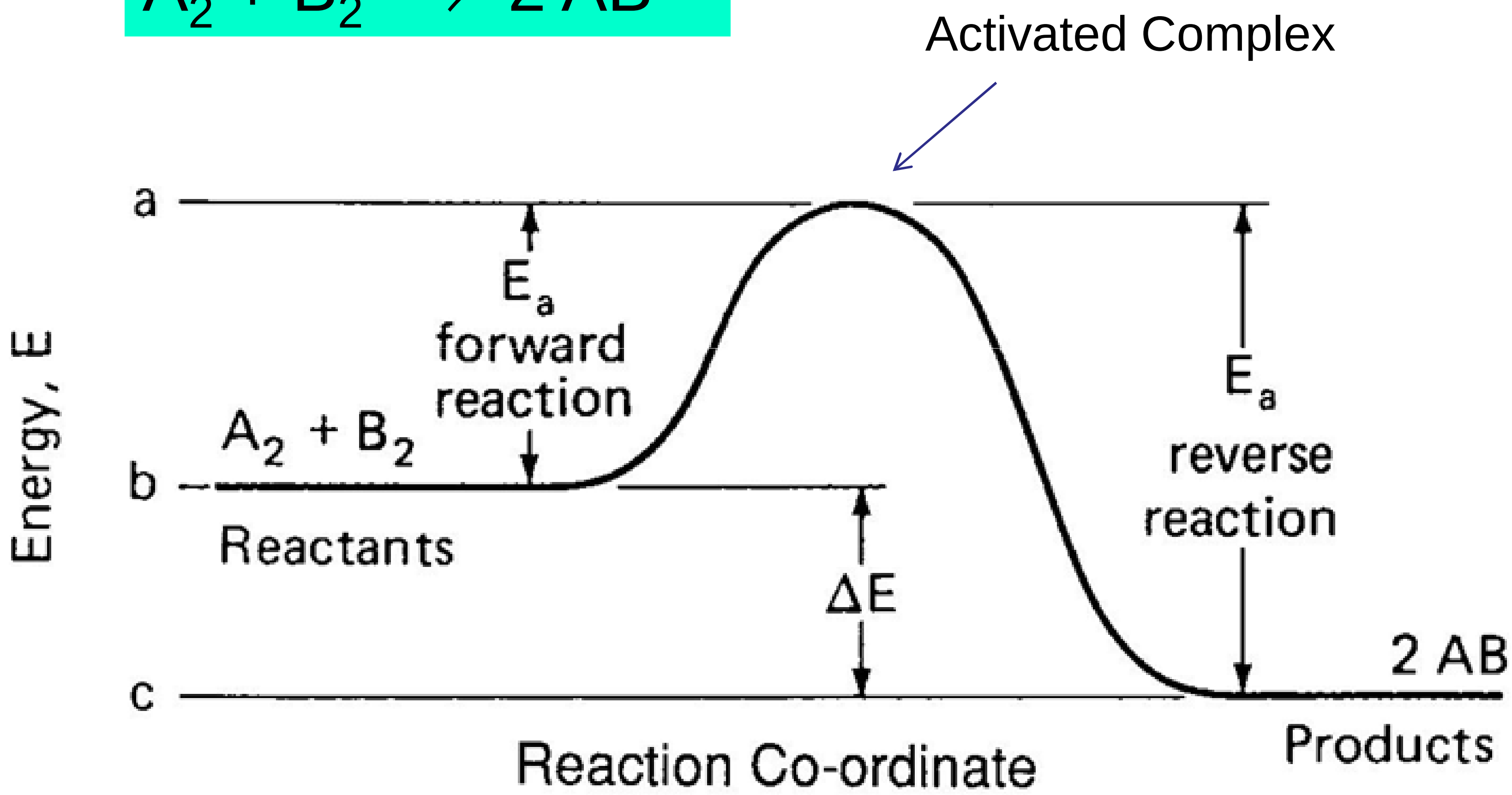
Energy Changes During a Reaction

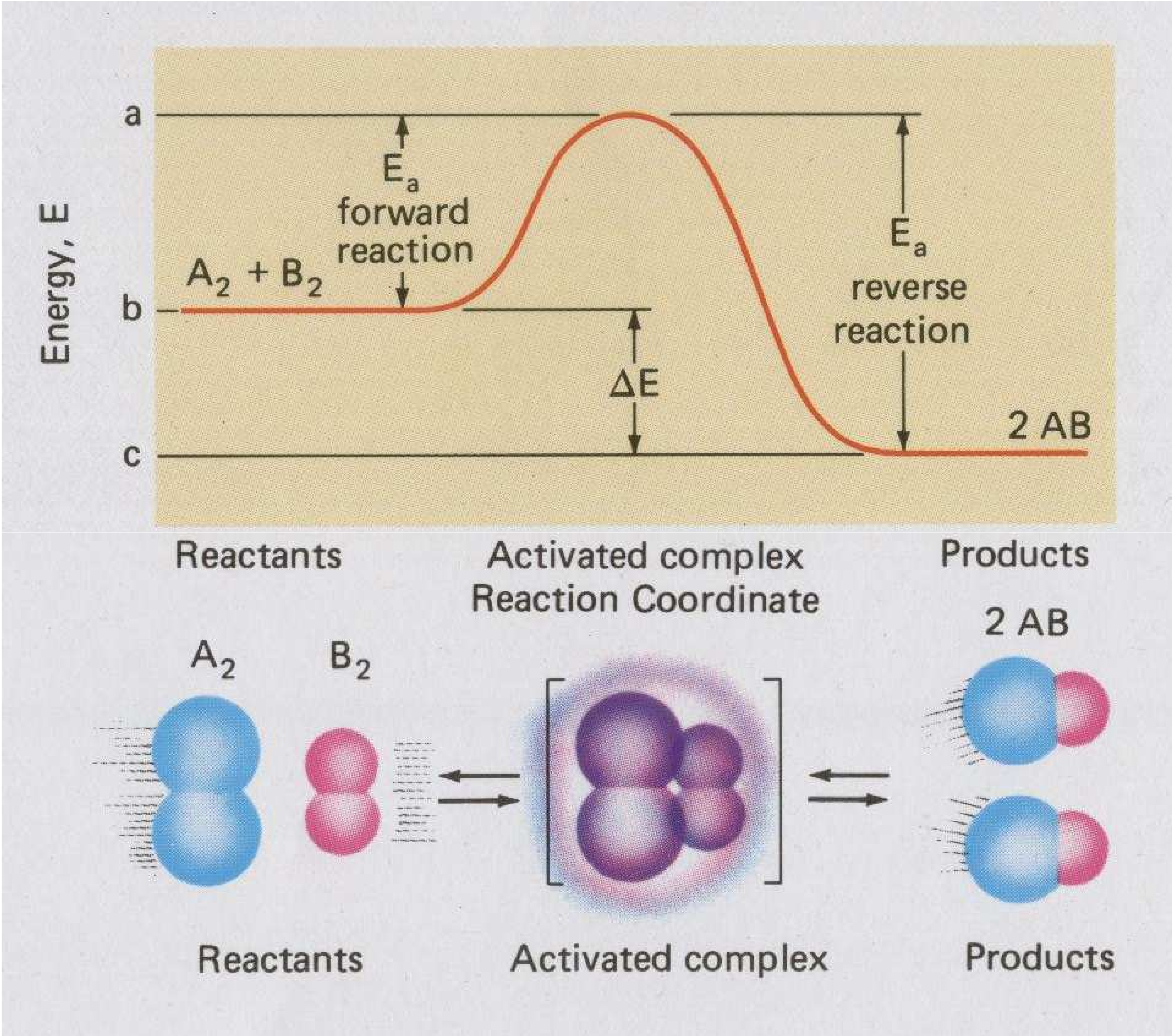
Potential Energy Profiles



Potential Energy Profiles

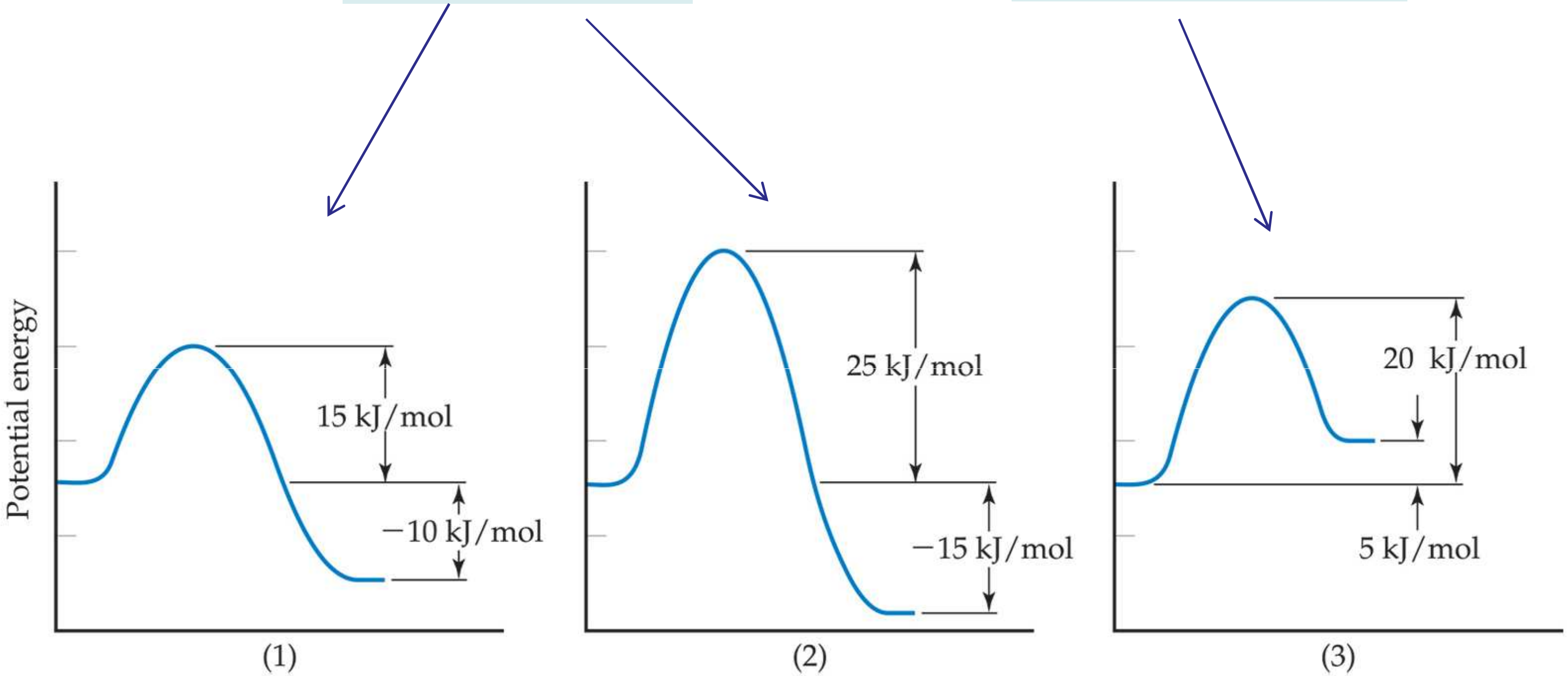
$A_2 + B_2 \rightarrow 2\,AB$




a
b
c
Energy, E
E_a
forward
reaction
$A_2 + B_2$
E_a
reverse
reaction
ΔE
2 AB
Reactants
Activated complex
Reaction Coordinate
Products
2 AB
A_2
B_2
Reactants
Activated complex
Products

EXOTHERMIC

ENDOTHERMIC



Exercise 8

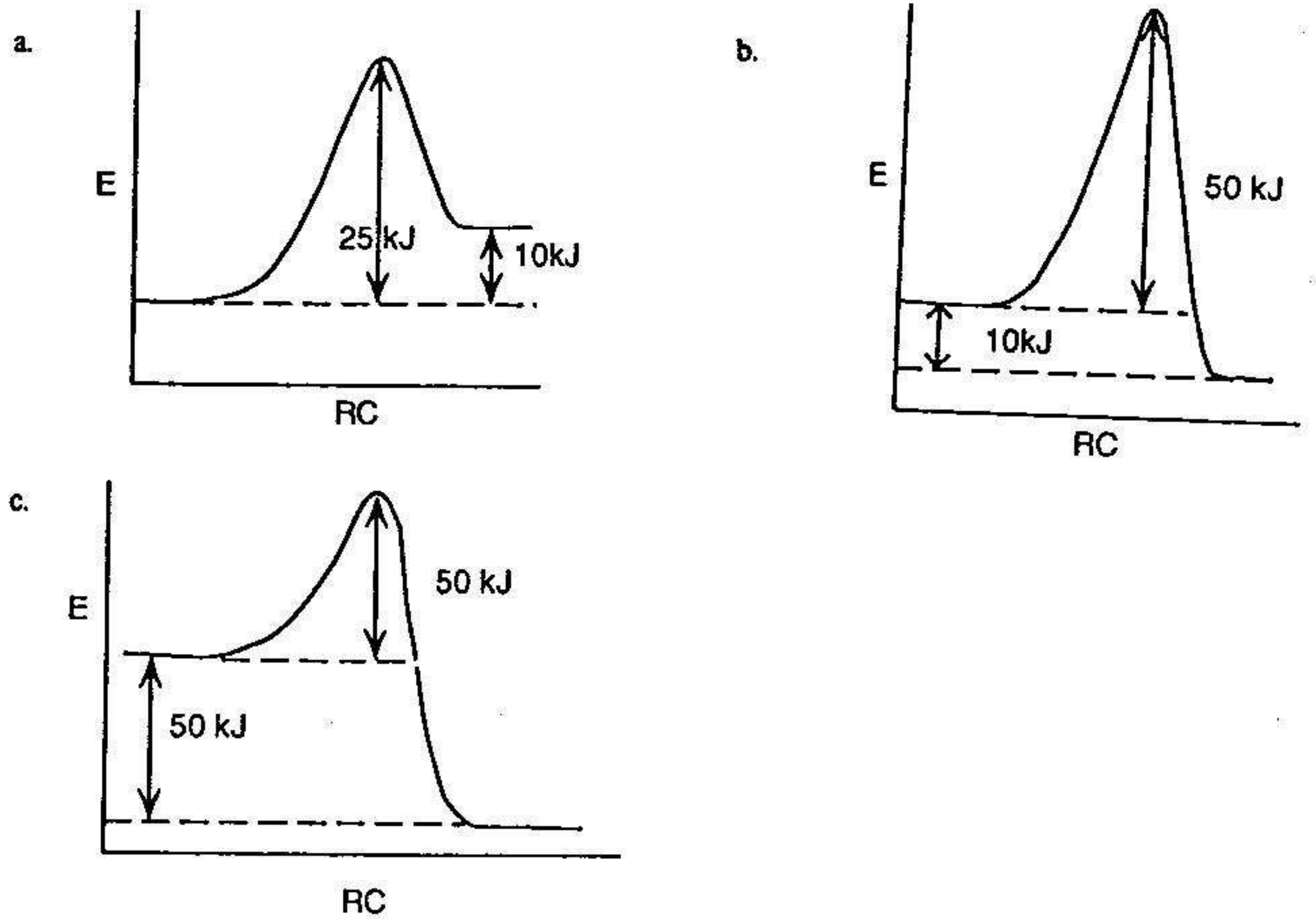
Draw a rough sketch of the energy profile for each of following cases:

(a) ΔE = +10 kJ/mol E_a = 25 kJ/mol

(b) ΔE = -10 kJ/mol E_a = 50 kJ/mol

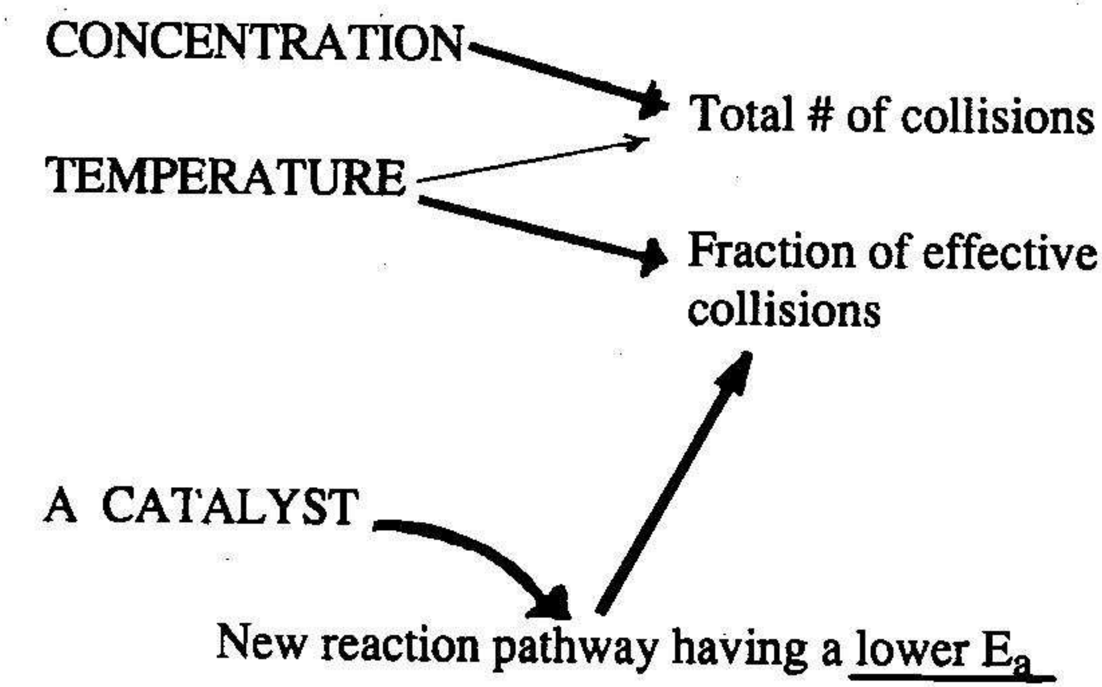
(c) ΔE = -50 kJ/mol E_a = 50 kJ/mol

Which of these three reactions will have the highest rate at 298 K, assuming the same *A* value for all three?



The reaction in (a) will have the greater rate since it has the lowest activation energy.

CONDITIONS THAT AFFECT REACTION RATES?

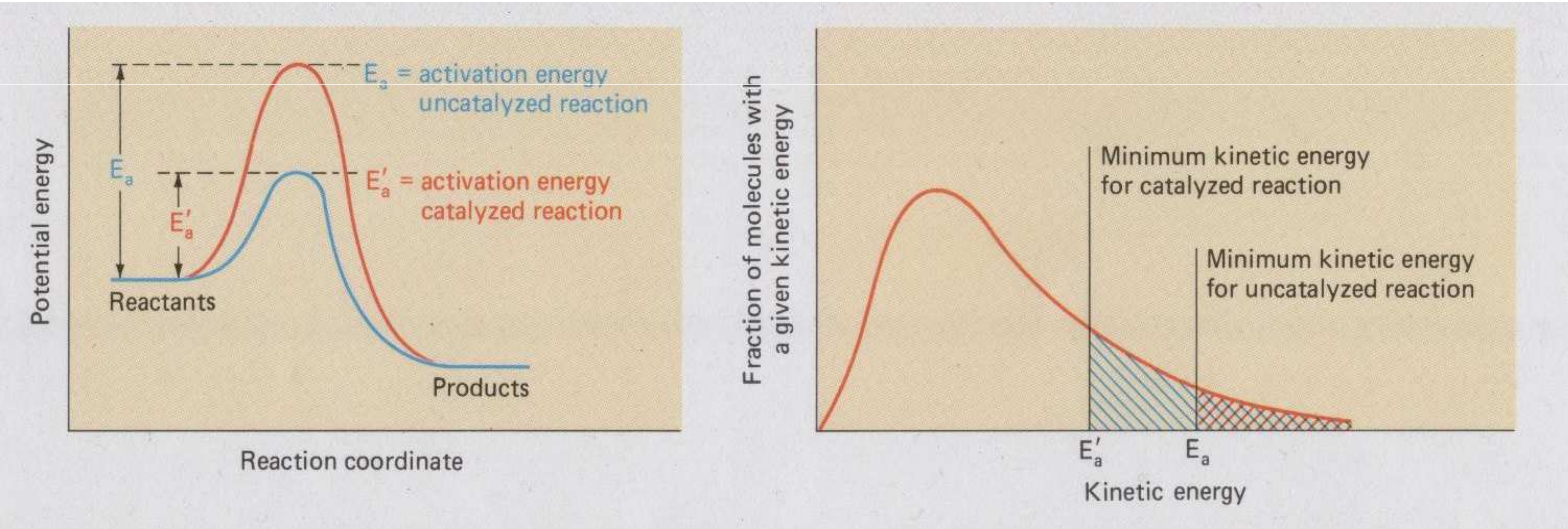


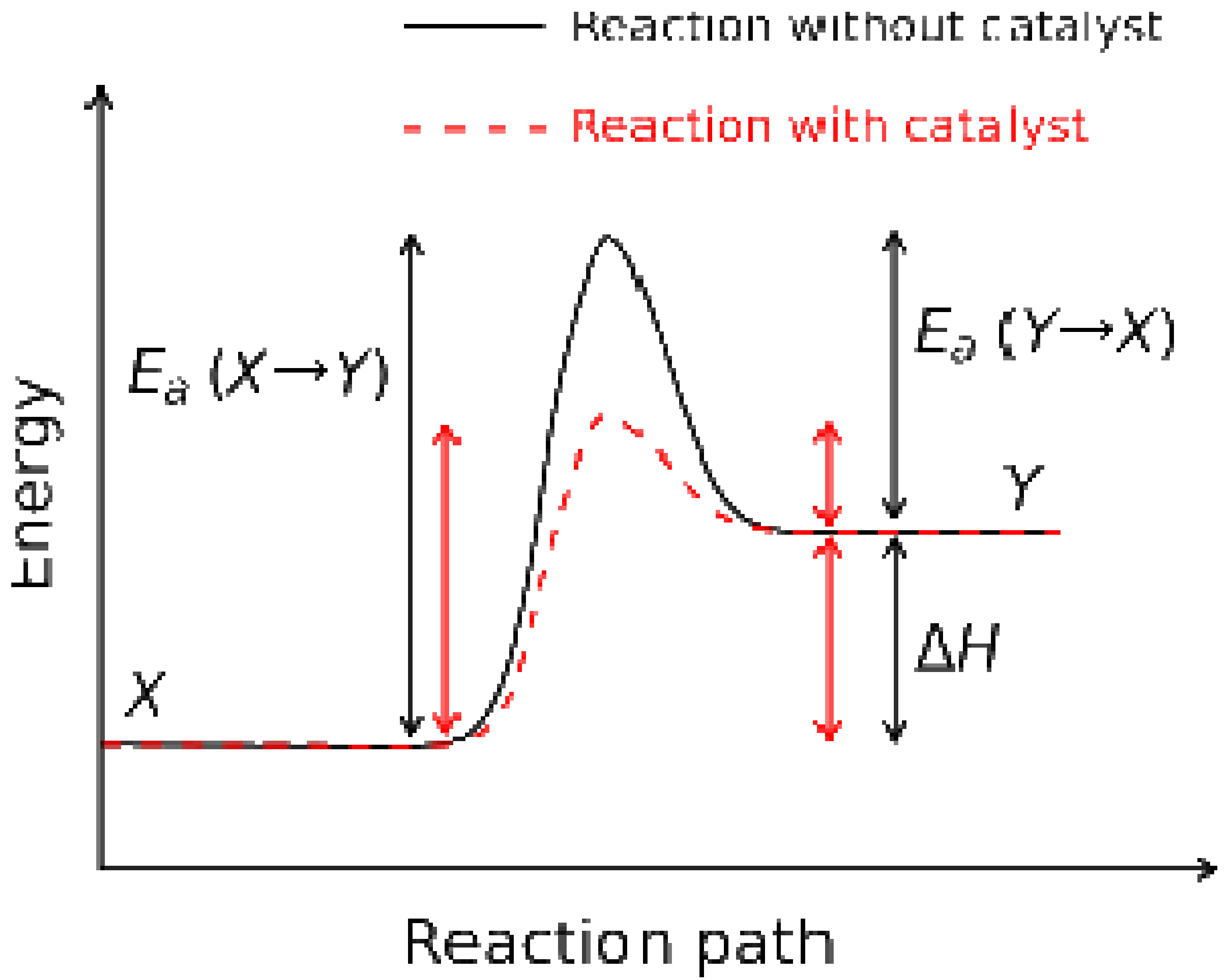
Catalysis

Catalysis

"The term ***catalysis*** is applied generally to cases where the *rate* of a chemical reaction is *accelerated* by the presence of a *substance* which is itself *unchanged chemically* in the process. The substance causing the acceleration is called a ***catalyst***."

A catalyst accelerates a process essentially by *lowering its energy of activation, E_a*, so that at a fixed temperature a relatively larger fraction of molecules possess the energy necessary for reactive collision.





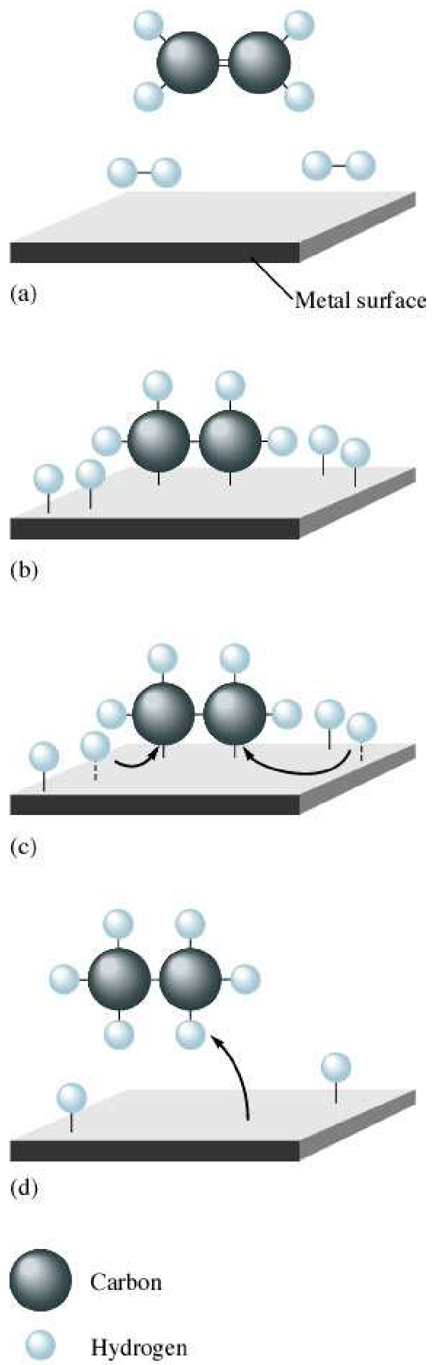
Reaction without catalyst
Reaction with catalyst
Energy
E_a (X→Y)
E_a (Y→X)
X
Y
ΔH
Reaction path

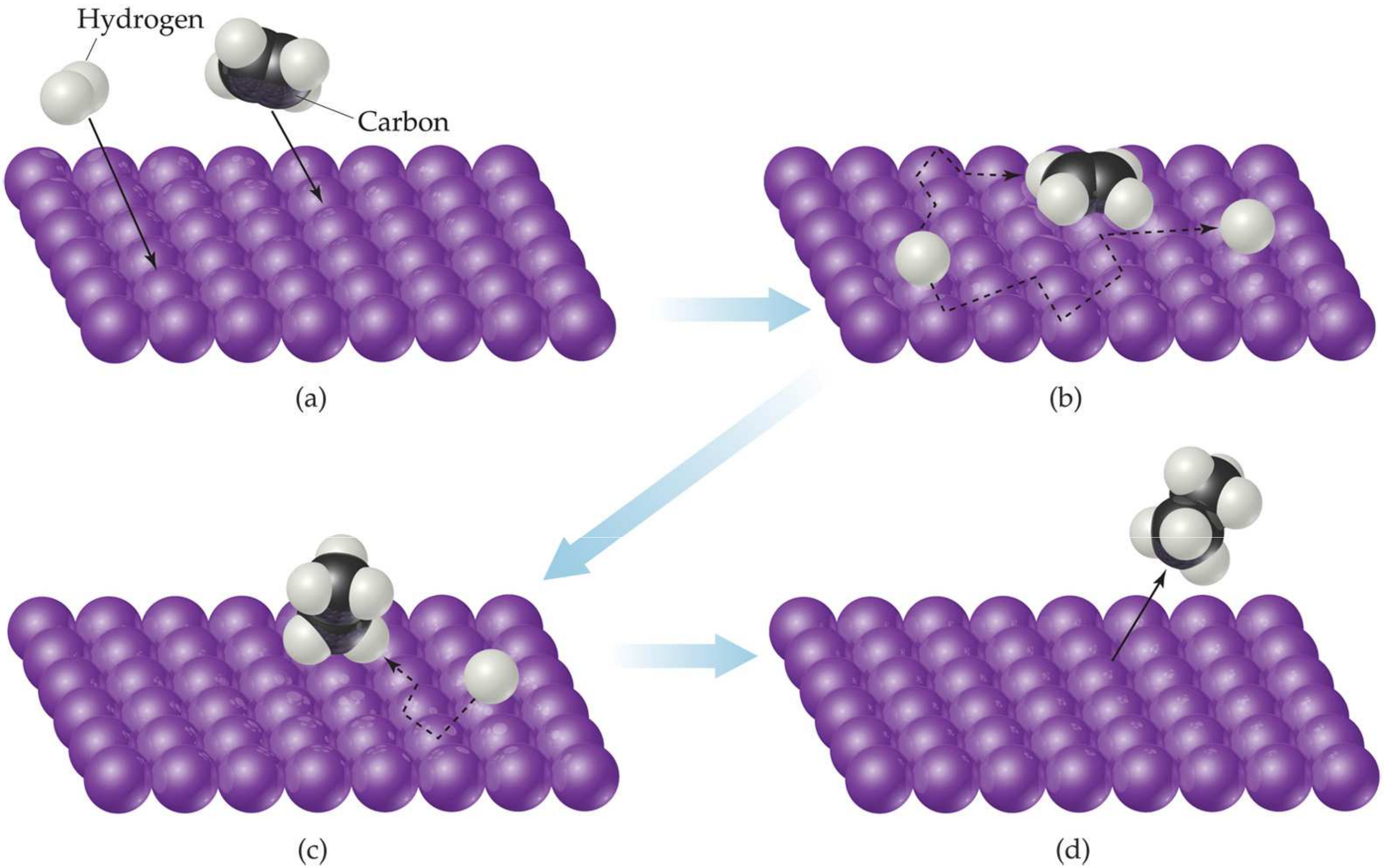
Types of Catalysis

There are two broad categories of catalysis:

- ***Homogeneous catalysis*** **-** a catalytic process where the catalyst is part of the *same phase* as the reactants
- ***Heterogeneous catalysis*** **-** the catalyst forms a *separate phase*.

Heterogeneous Catalysis of the Hydrogenation of Ethylene.

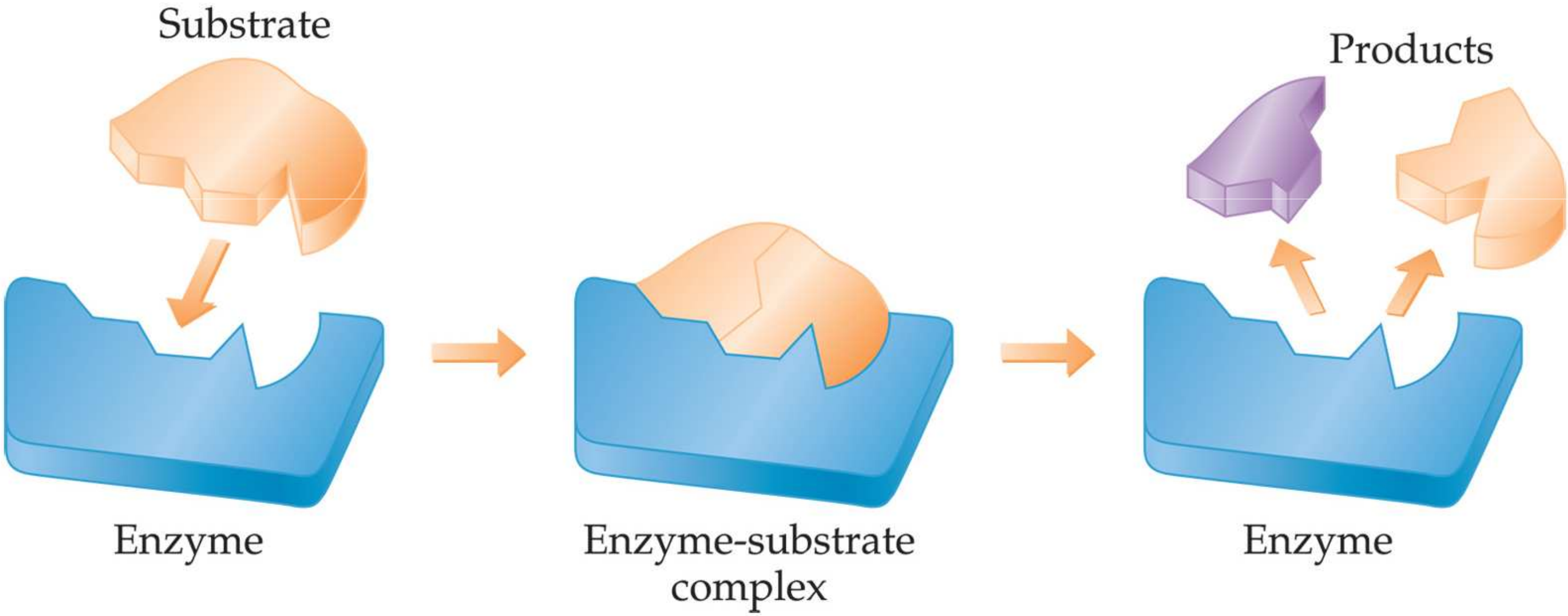




The Catalytic Hydrogenation of Ethylene

Enzyme Catalysis

Lock-and-key model



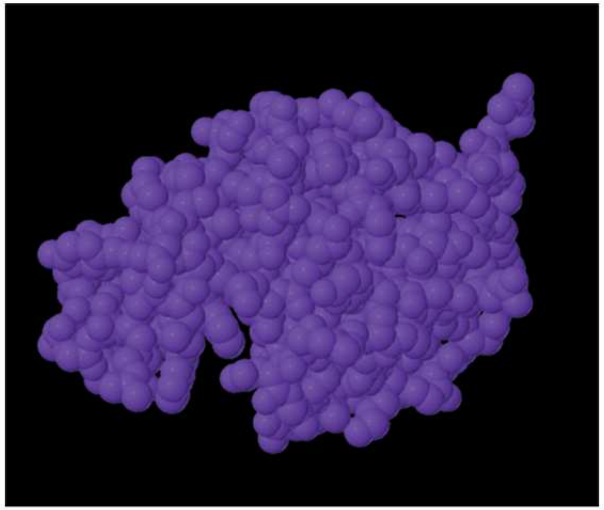
Terminology

Active site -The active site of an enzyme is the region of the enzyme where the catalysis occurs.

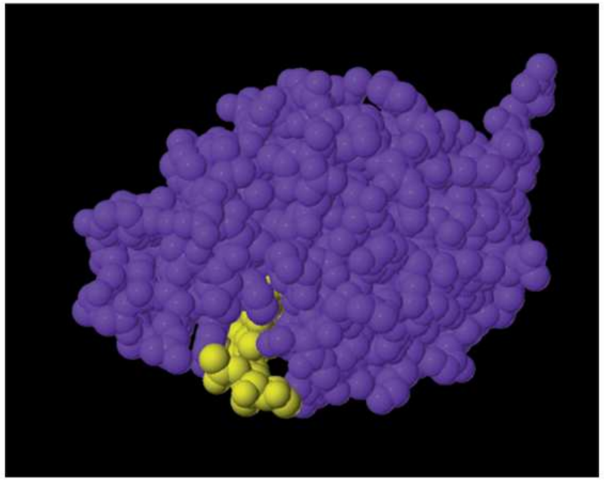
Substrate - The substrate is the substance that is converted to product. In order for catalysis to occur, the substrate must bind at the active site of the enzyme. It is not unusual for an active site to change its shape as substrate binds.

a) A molecular model of the enzyme ***lysozyme***. Note the characteristic cleft, which is the location of the active site.

b) Lysozyme with a bound substrate molecule.



(a)



(b)

End of Unit 2