GRADE 11 CHEMISTRY
UNIT 4
CHEMICAL KINETICS

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Introduction

- Every chemical reaction proceeds at a different rate or speed.
- Some reactions proceed very slowly and may take a number of days to complete; while others are very rapid, requiring only a few seconds.
- For example, rusting of iron could start quickly, while ripening of fruits may be completed in a few days. On the other hand, weathering of stone may take more than a decade and the breakdown of plastics in the environment takes more than hundred years.
- However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds.

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- To be useful reactions must occur at a reasonable rate.
- The area of chemistry that is concerned with reaction rates is called **chemical kinetics.**
- The word **“kinetic”** suggests movement or change.
- **Chemical kinetics** refers to the rate of reaction, which is the change over times in the concentration of a reactant or a product.

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The Rate of reaction

- The rate of a chemical reaction measures the change in concentration of a reactant or a product per unit time.
- This means that the rate of a reaction determines how fast the concentration of a reactant or product changes with time.

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- For example, for a general reaction:

$$\text{Reactants} \rightarrow \text{Products}$$

- This equation tells us that, during the course of a reaction, reactant molecules are consumed while product molecules are formed.
- As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

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- **It is more convenient to express the rate in terms of change in concentration with time.**

$$\text{Rate of reaction} = \frac{\text{Change in concentration of substance}}{\text{change in time}} = \frac{\Delta c}{\Delta t}$$

Note that Δ denotes the difference between the final and initial state.

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- **Consider the progress of a simple reaction in which A molecules are converted to B molecules:**

A →B

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{A}]}{\Delta t} \quad \text{or rate} = \frac{\Delta[\text{B}]}{\Delta t}$$

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- in which, Δ[A] and Δ[B] are the changes in concentration ($molL^{-1}$) over a period Δt.
- Because the concentration of A decreases during the time interval, Δ[A] is a negative quantity.
- The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive.
- On the other hand, the rate of product formation does not require a minus sign because Δ[B] is a positive quantity (the concentration of B increases with time).

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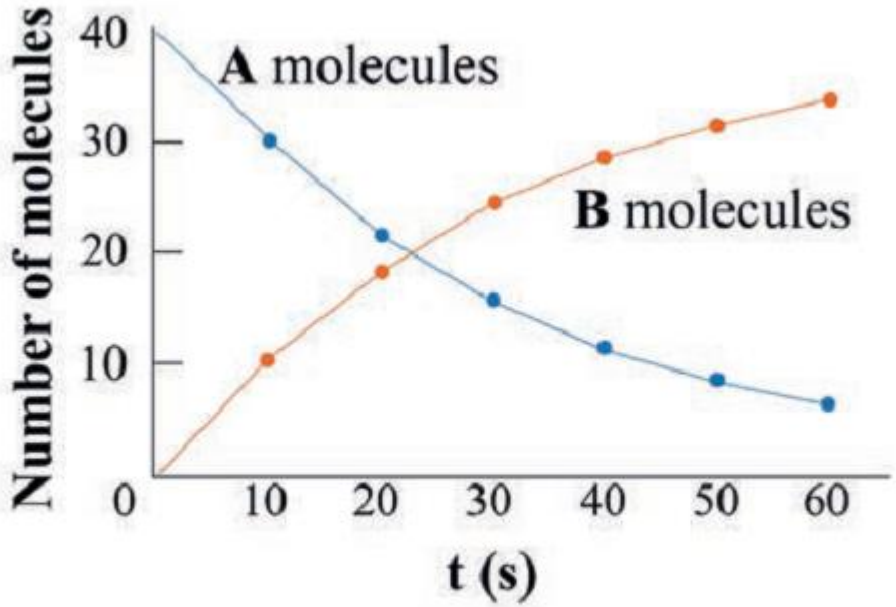


Figure 4.1: The rate of reaction A → B, represented as the decrease of A molecules with time and the increase of B molecules with time

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- For more complex reactions, we must be careful in writing the rate expression.
- Consider, for example, the reaction:

$$2A \rightarrow B$$

- Two moles of A disappear for each mole of B that forms, that is, the rate at which B forms is one half the rate at which A disappears.
- We write the rate as either:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \quad \text{or rate} = \frac{\Delta[B]}{\Delta t}$$

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Similarly, for the reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow \mathbf{c}\mathrm{C} + d\mathrm{D}$$

the rate is given by $\text{Rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$

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Example 4.1

1. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

   a. $I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

   b. $3O_2(g) \rightarrow 2O_3(g)$

   c. $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

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Exercise 4.1

3. Consider the reaction of:

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.037 mol $L^{-1}s^{-1}$.

a. At what rate is N_2O_5 being formed?

b. At what rate is NO_2 reacting?

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Exercise 4.1

4. Consider the reaction of:

$$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$$

Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078 mol $L^{-1}s^{-1}$.

a. At what rate is P_4 being formed?

b. At what rate is PH_3 reacting?

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Determination of Rate of Reaction

- Reaction rate is change in an observable property over time.
- This could be a colour change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).
- The observable (measurable) properties can be used to determine the change in concentration over time.

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- Consider, for example, the thermal decomposition of gaseous dinitrogen pentoxide, N_2O_5, to give the brown gas nitrogen dioxide:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

Colorless Brown Colorless

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

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Table 4.1: Concentrations (mol $L^{-1}s^{-1}$) as a function of time at 55 °C for the thermal decomposition of gaseous dinitrogen pentoxide (N_2O_5)

Time (s)	N_2O_5	NO_2	O_2
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

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The average rate of formation of O_2?

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The average rate of formation of NO_2?

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- The average rate of formation of NO_2 during the time period 300-400s is 3.7×10^{-5} $molL^{-1}s^{-1}$, which is four times the rate of formation of O_2,

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The average rate of formation of N_2O_5?

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- In general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds

What could be the possible reason for this decrease in the rate of reaction with time?

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600	0.0072	0.0256	0.0064
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Example 4.2

Using the data in **Table 4.1,** if $[N_2O_5] = 1.20 \times 10^{-2}$ mol L^{-1} at 300 s, calculate $[NO_2]$ and $[O_2]$ at t = 300 s.

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Example 4.2

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- Often, chemists want to know the rate of a reaction at a specific time t rather than the rate averaged over a time interval Δt.
- For example, what is the rate of formation of NO_2 at time t= 350s? Such instantaneous rate is calculated from the slope of a tangent drawn at any points on the graph of concentrations versus time
- The slope of tangent taken at the initial point of the graph is assumed to be equal to its initial rate.
- In the initial rate the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts.

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Example 4.3

Consider the gas-phase reaction that occurs when we mix 1.000 moles of hydrogen and 2.000 moles of iodine chloride at 230 °C in a closed 1.000-liter container.

$$H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g)$$

From the experimental data given in the table below, determine the instantaneous rate of reaction at time, $t = 2$ s.

Time (s)	0	1	2	3	4	5	6	7	8
[ICl] (mol L^{-1})	2.000	1.348	1.052	0.872	0.748	0.656	0.586	0.530	0.484
[H_2] (mol L^{-1})	1.000	0.674	0.526	0.436	0.374	0.328	0.293	0.265	0.242

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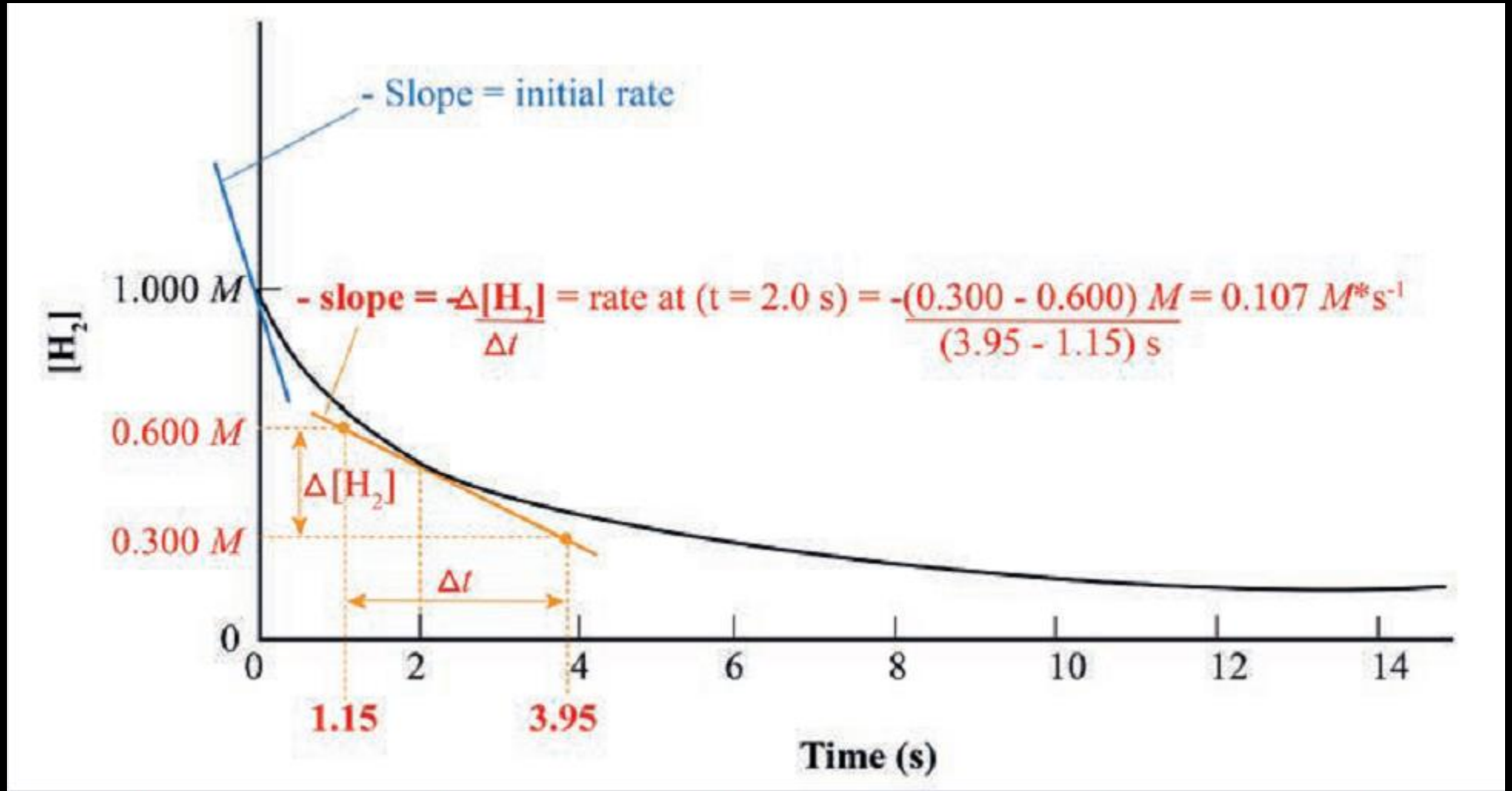


Figure 4.3: A plot of the hydrogen concentration versus time, using data of the above table

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Exercise 4.2

1. Using the initial concentrations and the fact that $[O_2] = 0.64 \times 10^{-2}$ mol. L^{-1} at $t = 600$ s in **Table 4.1,** calculate $[N_2O_5]$ and $[NO_2]$ at $t = 600$ s.

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2. Consider the reaction:

$2C_2H_4(g) \rightarrow C_4H_8(g)$

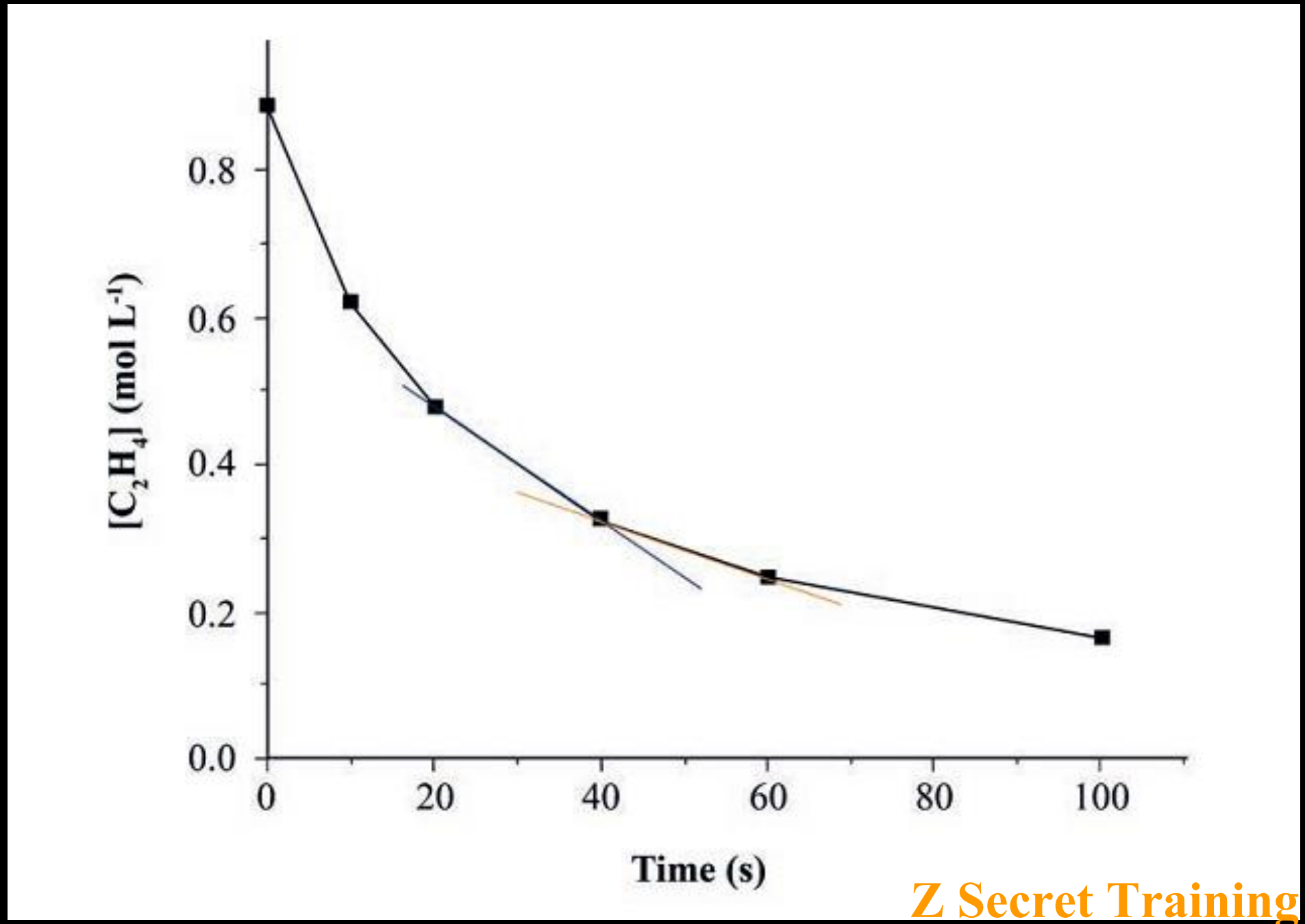
From the experimental data given in the table below, plot a graph for the consumption of ethylene, C_2H_4, versus time.

a. Calculate the rate of reaction between the time intervals 10 s to 30 s.

b. Calculate the rate of reaction at 45 s.

Time (s)	0	10	20	40	60	100
$[C_2H_4]$ (mol L^{-1})	0.884	0.621	0.479	0.328	0.250	0.169

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Conditions needed for a chemical reaction

- Chemical reactions are usually explained by the collision theory.
- The assumption of the collision theory is that chemical reactions take place due to collisions between molecules.
- **Conditions needed for a chemical reaction**

  Collisions between reactants

  Proper Orientation

  Activation energy

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1.Collisions between reactants

- The collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact).
- The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate } \alpha \ \frac{\text{number of collisions}}{\text{second}}$$

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2. Proper Orientation

- According to collision theory, the more collisions there are the faster the rate of reaction would be.
- However, not all collisions between reacting species result in a reaction.
- This is because collisions between reactants can be either effective or ineffective.
- **Effective collisions** are collisions that result in a reaction to form the desired products.
- **Ineffective collisions** are collisions that do not result in a reaction to form the desired products.
- Thus, the collision between molecules should have the proper orientation

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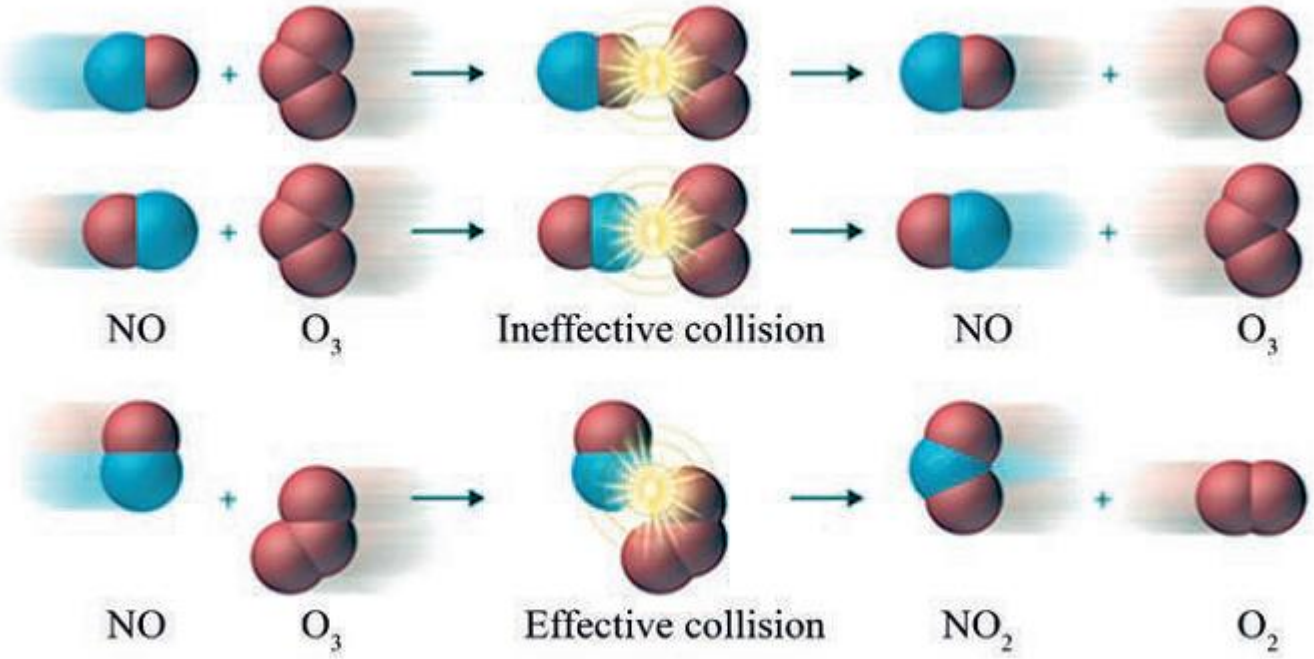


Figure 4.5: The effect of molecular orientation on the reaction of NO and O_3

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3. Activation energy

- If the collisions between the reactant molecules do not have sufficient energy, then no reaction will occur.
- Therefore, for the reaction to take place collision must always occur with sufficient energy to break the bonds in the reactants and form new bonds in the product.
- Thus, minimum amount of energy needed for the reaction is known as activation energy, Ea.

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- According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature.
- As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably.
- This causes the particles of the reactants to collide more frequently and with greater energy. This results in increase in reaction rate.

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factors that affecting the rate of a chemical reaction

- The rates at which reactants are consumed and products are formed during chemical reactions vary greatly.
- Even a chemical reaction involving the same reactants may have different rates under different conditions.
- factors that affecting the rate of a chemical reaction

Change in temperature,

Concentration,

Nature of reactant,

Surface area

Presence of a catalyst

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i. Nature of the reactants

- The rate of a reaction depends on the chemical nature of the substances in the reaction.
- Even similar reactions may have different rates under the same conditions.
- For example, if small pieces of the metal iron and sodium are left in air, the sodium reacts completely overnight, whereas the iron is barely affected

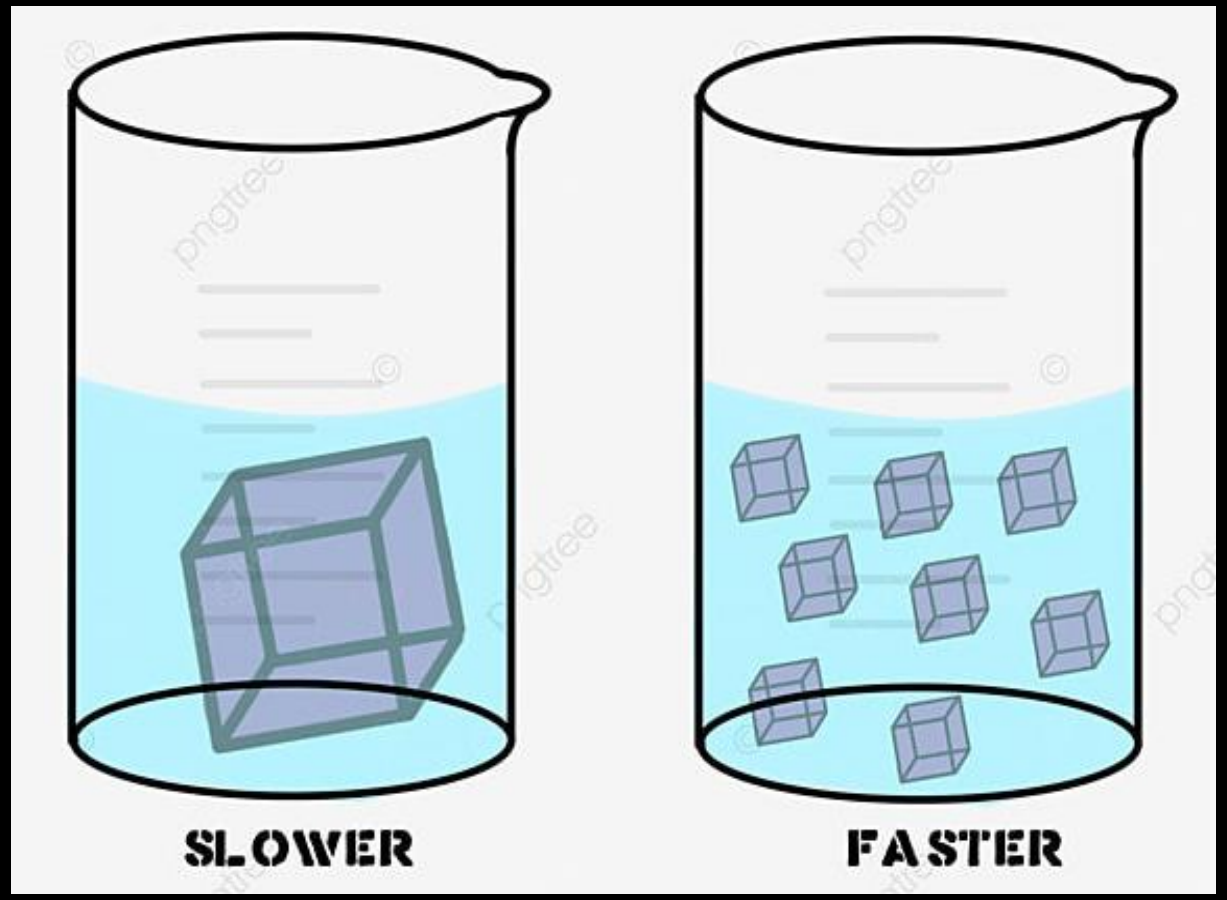
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ii. Surface Area of Reactants

- Reactions can be classified as homogeneous (same phase) and heterogeneous (different phases).
- the rate of reaction between two phases depends to a great extent on the surface area of contact between them.
- Finely divided solids, react more rapidly than the same amount of the substance in a large body because of the greater surface area available.

$$NO\ (g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g)$$

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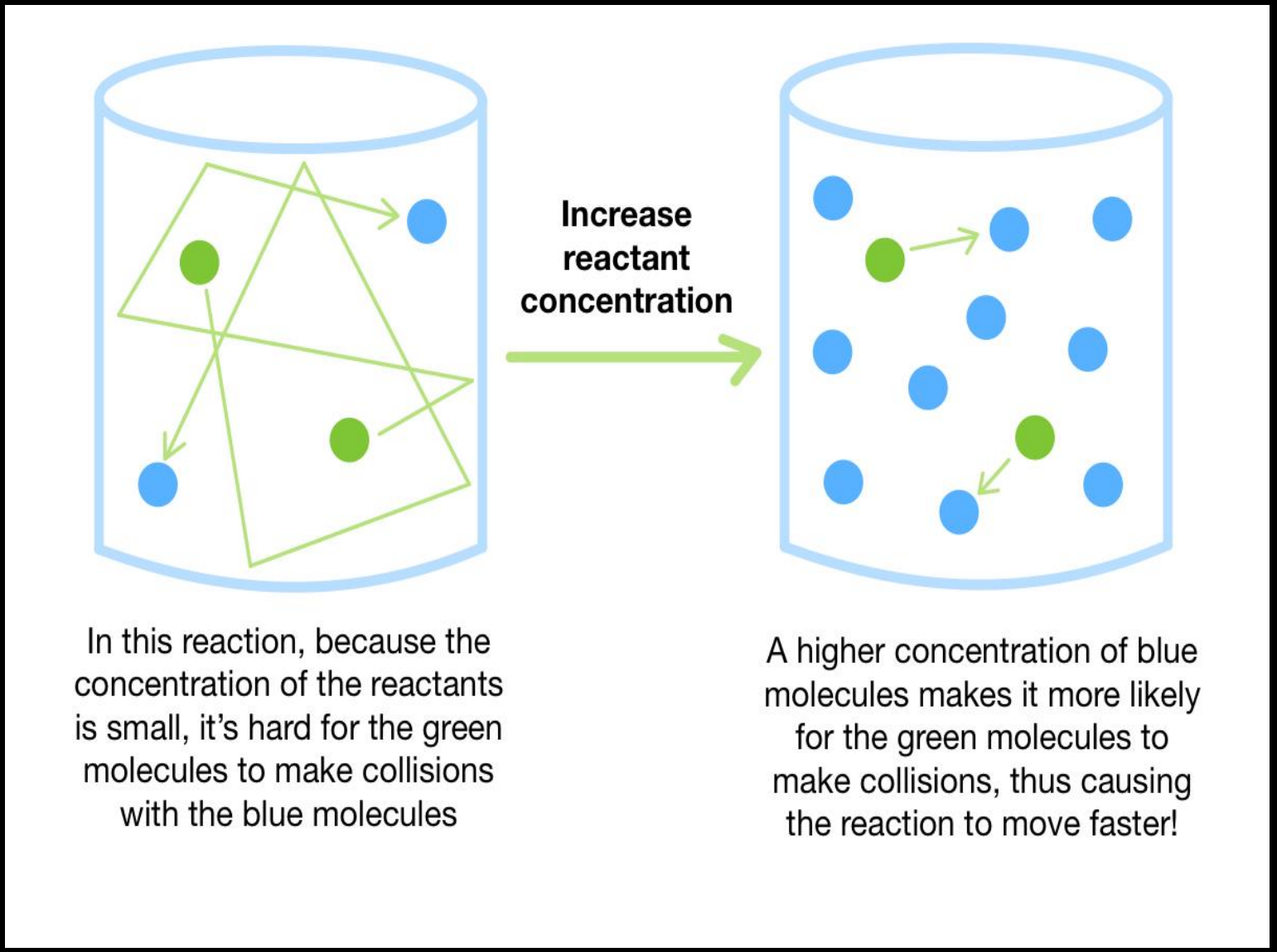


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iii. Concentration of Reactants

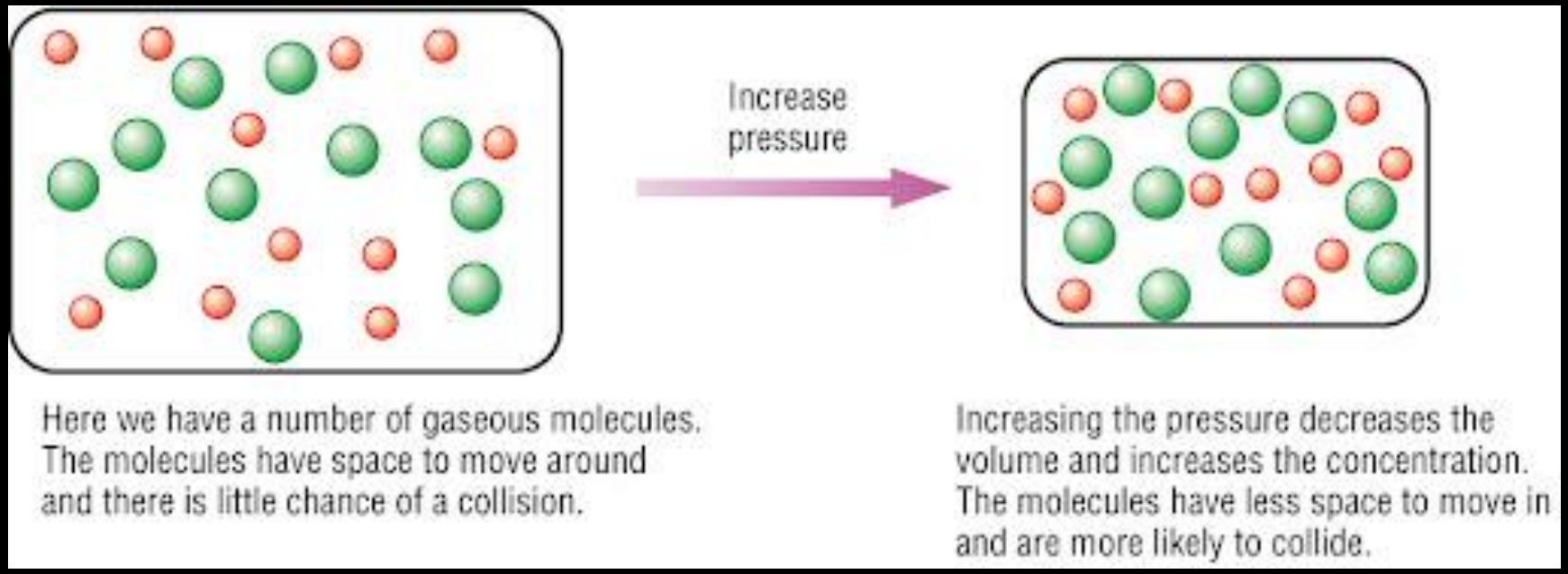
- At a fixed temperature, the rate of a given reaction depends on the concentration of the reactants.
- Reaction rates often increases when the concentration of one or more of the reactants increases.
- This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction.

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- In the case of reactions that involve gaseous reactants, an increase in pressure can increase the concentration of the gases which may lead to an increase in the rate of reaction.
- However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.



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iv. Temperature of Reactants

- Temperature usually has a major effect on the rate of reaction.
- Molecules at higher temperatures have more thermal energy.
- Generally, an increase in the temperature of a reaction mixture increases the rate of chemical reactions.
- This is because, as the temperature of the reaction mixture raises, the average kinetic energy of the reacting particles increases.
- So, they collide more frequently and with greater energy.

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- The effect of temperature on rate of reaction can be experienced in our daily life.
- For example, foods cook faster at higher temperature than at lower ones.
- In many cases, the rate of a reaction in a homogeneous system is approximately doubled by an increase in temperature of only 10 °C.

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v. Presence of a Catalyst

- A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with a lower activation energy, Ea.
- An activation energy is the minimum energy required to start a chemical reaction.
- Catalysts are not used up by the reactions, rather they are recovered at the end of the reaction.
- Although a catalyst speeds up the reaction, it does not alter the position of equilibrium.

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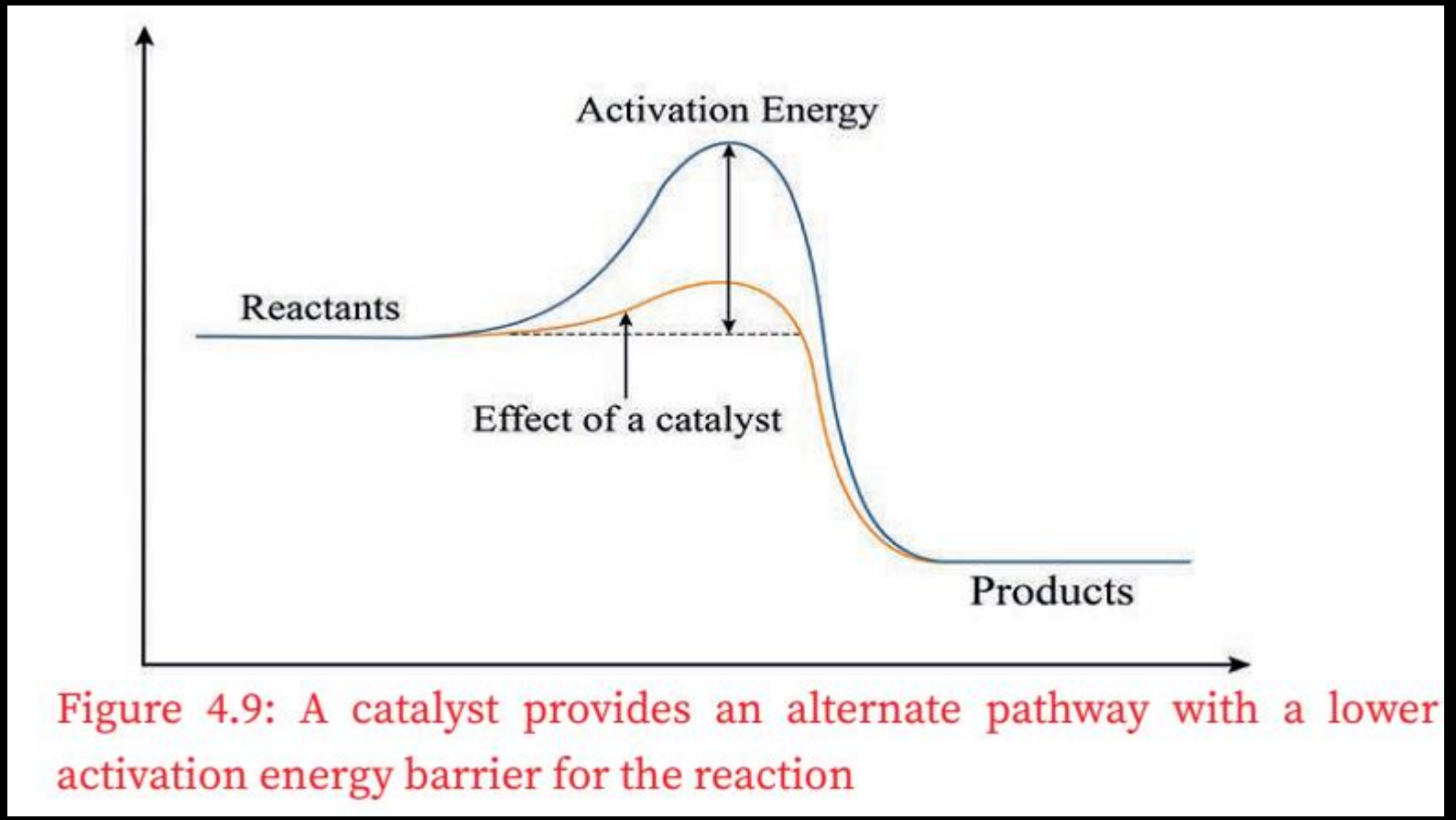


Figure 4.9: A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction

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Chemical catalysts can be either positive or negative.

- **Positive catalysts** increase the rate of reaction by lowering the Ea.

Example 4.4

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$; $V_2O_5(s)$ as catalyst.

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- **Negative catalysts or inhibitors** decrease the rate of reaction by increasing the value of Ea.

Example 4.5

$OCl^-(aq) + I^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$; $OH^-(aq)$ as inhibitor.

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- Example 4.4 represents **heterogeneous catalysts** as state of reactants and catalyst is different,
- while Example 4.5 represents **homogeneous catalyst** as both reactants and catalyst are in same state.
- A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar.
- The chemical reactions in living things are controlled by biochemical catalysts called **enzymes.**

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THE END

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