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# BSK1133 PHYSICAL CHEMISTRY

# CHAPTER 4
# REACTION MECHANISM
# (PART B)

## PREPARED BY:

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## Aims

➢ To understand the deviation of Arrhenius equation using theory of kinetic.

➢ To understand the mechanism of a chemical reaction.

# Description

**Expected Outcomes**

❖ Able to understand the deviation of Arrhenius equation using theory of kinetic

❖ Able to understand the mechanism and important parameters in a chemical reaction

**References**

✓ Atkins, P & Julio, D. P. (2006).Physical Chemistry (8th ed.). New York: Oxford.

✓ Chang, R. (2005).Chemistry (8th ed.). New York: McGraw Hill.

✓ Atkins, P & Julio, D. P. (2012). Elements of Physical Chemistry (sixth ed.). Freeman, Oxford.

✓ Silbey, R. J., Alberty, A. A., & Bawendi, M. G. (2005). Physical Chemistry. New York: John Wiley & Sons.

✓ Mortimer R. G. (2008) Physical Chemistry, Third Edition , Elsevier Academic press, USA.

# 4.4 Integrated Rate Law

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❖ 4.6 Reaction Rate and Temperature

❖ 4.7 Collision Theory

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# 4.6   Reaction Rates and Temperature

Reaction rate is directly proportional to temperature.

*Increasing the temperature will affected to increases the rate of chemical reactions.*

In general, reaction rates approximately double if you increase the temperature by 10 °C.

# 4.7 Collision theory

Assuming a reaction of :

$$A + CD \rightarrow AC + D$$

In a single reaction step, at a certain reaction time, the C-D bond starts to break, and A-C bond starts to form.

$$A + C\text{-}\text{-}\text{-}D \rightarrow A\text{-}\text{-}\text{-}C + D$$

At this specific point, all three nuclei (A---C---D) are weakly linked together.

# Collision theory

In a molecular collision theory:

- When molecules get close to each other, they tend to repel.

- Thus, in order to allow chemical reaction and collision happen, energy need to be inserted to force the molecules to get close.

- This inserted energy is the **kinetic energy**.

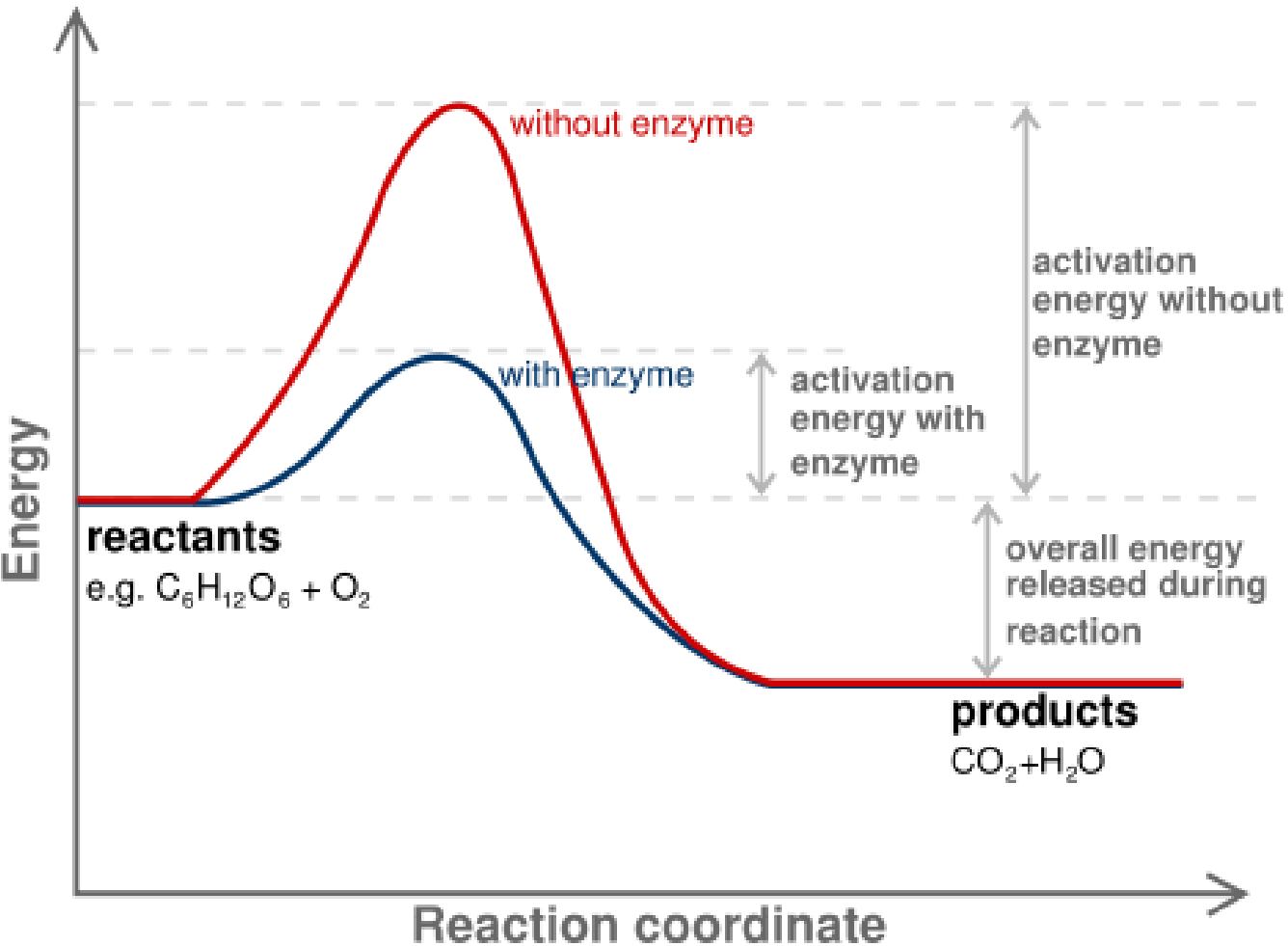- When the molecule get closer, the energy change to **potential energy**.

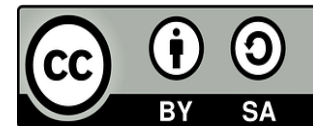# Collision theory

**A---C---D$^{\ddagger}$**

- This state is the called as **transition state activated complex**

- At this stage, the molecules has higher potential energy as compared to its initial state

# Collision theory



Energy vs Reaction coordinate diagram. The red curve labeled "without enzyme" rises to a higher peak; the blue curve labeled "with enzyme" rises to a lower peak. Labels: "activation energy without enzyme", "activation energy with enzyme", "overall energy released during reaction", "reactants e.g. $C_6H_{12}O_6 + O_2$", "products $CO_2 + H_2O$".

# Collision theory

Based on the illustrated graph, few important parameters can be seen:

1. The energy difference between **products** and **reactants** is called enthalpy different of the reaction ($\Delta H$)

2. The energy difference between the **reactants** and **transition state** is activation energy ($\mathbf{E_{a\ foward}}$)

3. Activation energy can be reversible depend on the reaction process:

   between the **products** and **transition state** is activation energy ($\mathbf{E_{a\ reverse}}$)

# Activation energy

- Is the minimum energy need to allow a transition state to occur / reaction happen

- The value of **activation energy ($E_a$)** is always **be positive.**

- Since higher temperature give higher reaction rate, it affected to lowering the activation energy at higher temperature.

- This is because, high temperature, higher collision frequency, thus greater collision energy produce

# Collisions

An individual molecule collides with other molecules about once every billionth of a second (one billion collisions per second).

If every collision was successful in creating products, then every reaction would be almost instantaneous. This is impossible.

The facts is that, **Not every collision will breaks the activation energy barrier!**

# Collisions

The fraction of collisions that have enough energy to break the activation barrier is given by

$$f = e^{-E_a/RT}$$

$E_a$ = activation energy

$T$ = temperature (Kelvin)

$R$ = gas constant ($8.314 \ J \cdot K^{-1} \cdot mol^{-1}$)

- In an effective collision, molecules need to collide at a correct orientation to form a reaction.

- If the molecules does not collide in a correct orientation:

  - no reaction occur

  - not give specific product

  - higher activation energy as the molecule will just bounce off

# Steric factor

Steric factor (p) defined as the ratio between the experimental value and the one predicted by collision theory of the rate constant

In NO + Cl$_2$;

**Steric factor** in this case would be **p ~ 0.5** since half the collisions lead to the **wrong transition state.**

# reaction : A + CD → AC + D

## Collision rate = Z [A] [CD]

Z = constant (that relates to the **collision frequency)**.

Recall:

1. Only a **fraction (f)** of the collisions have an equal or greater energy than the activation energy.

2. Only at a proper molecule orientation allow reaction to occur. Thus, certain **stearic factor (p)** will allow correct orientation.

# reaction : A + CD → AC + D

**Reaction rate** = p x f x Collision rate
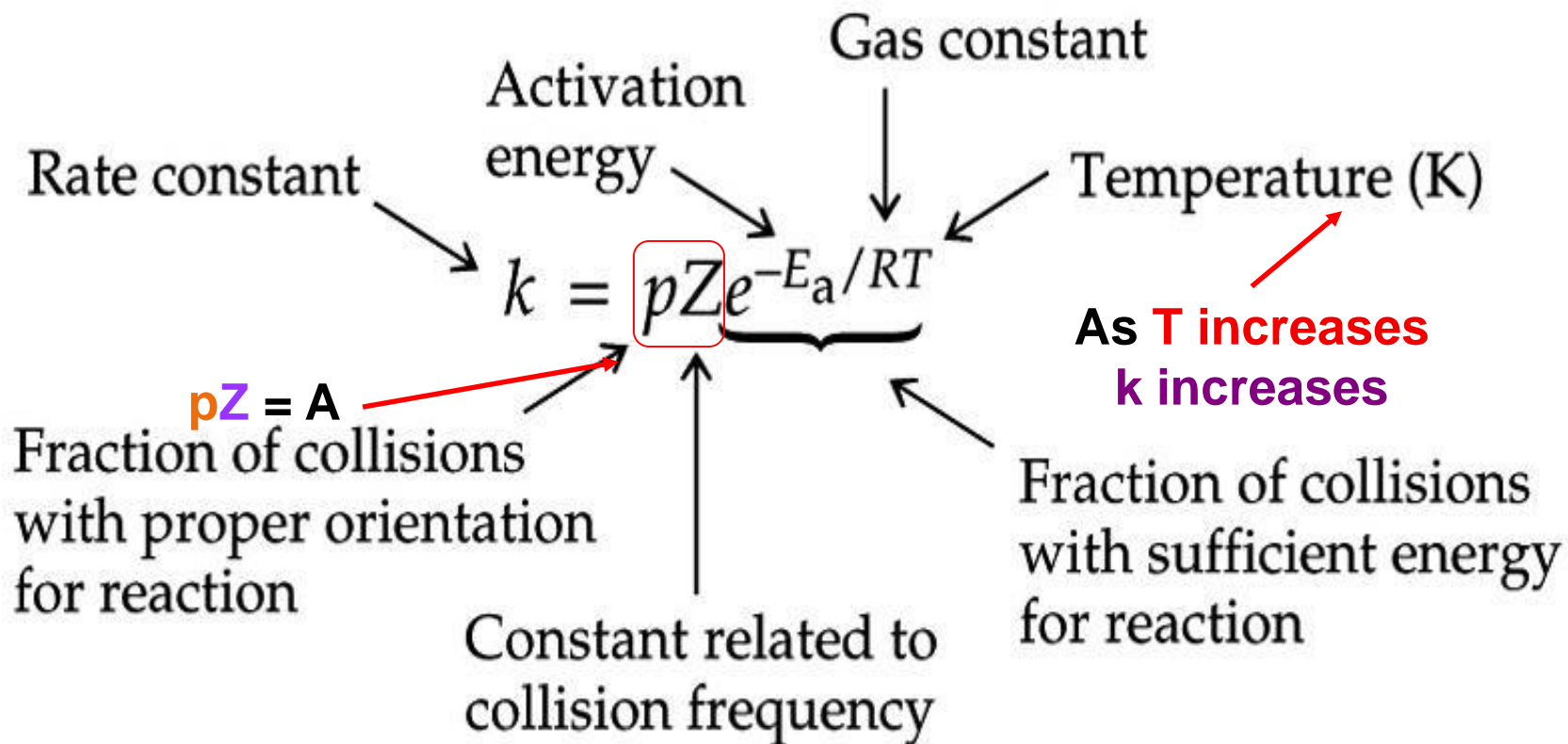
**Reaction rate** = pfZ [A] [CD]

General equation of rection rate:

Reaction rate = **k [A] [CD]**

$$k = pfZ = pZ \, e^{-E_a/RT} = A \, e^{-E_a/RT}$$

(**A** is a frequency factor= pZ)

# 4.8   Arrhenius Equation



Gas constant

Activation energy

Rate constant

Temperature (K)

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

As **T increases**
**k increases**

**pZ** = **A**

Fraction of collisions with proper orientation for reaction

Constant related to collision frequency

Fraction of collisions with sufficient energy for reaction

# Using the Arrhenius Equation

Arrhenius equation can be use to calculate the activation energy, Ea at two different temperature with known value of rate constant, k.

Using the equation below:

$$k = A\, e^{-E_a/RT}$$

$$\ln k = \ln (A\, e^{-E_a/RT})$$

$$\ln k = \ln (A) + \ln (e^{-E_a/RT})$$

$$\ln k = \ln (A) - (E_a/RT)$$

Graphical method can be use to calculate the value of activation energy, Ea

$$\underset{y}{\ln k} = \underset{m}{\left(\frac{-E_a}{R}\right)}\underset{x}{\left(\frac{1}{T}\right)} + \underset{b}{\ln A}$$

**Ea = - slope x R**

$$\ln k_2 - \ln k_1 = (-E_a/R)\,(1/T_2 - 1/T_1)$$

$$OR$$

$$\Delta\,(\ln k) = (-E_a/R)\,\Delta(1/T)$$

Changes! Final minus initial

**Be Careful!!**

Your textbook says

$$\ln (k_2/k_1) = (E_a/R) (1/T_1 - 1/T_2)$$

This is absolutely correct as well!
Use whichever form of the relation that you feel more comfortable with mathematically.

# 4.9  Reaction Mechanisms

A **reaction mechanism** is the **sequence of molecular events** that defines the **pathway** of the overall reaction.

- The molecular events or known as the elementary reactions describe the behaviour of the **individual molecules.**
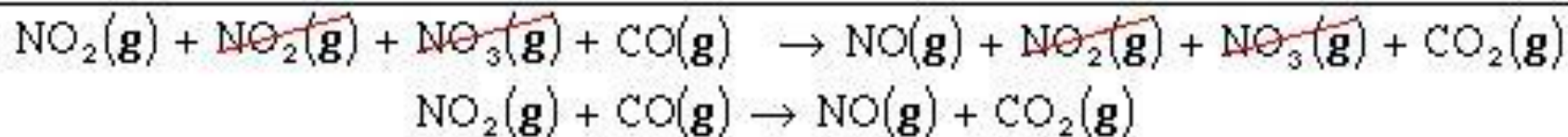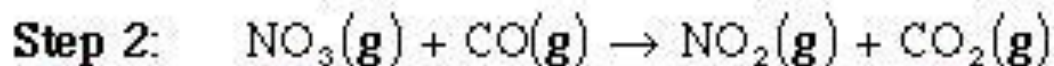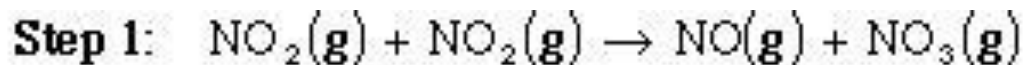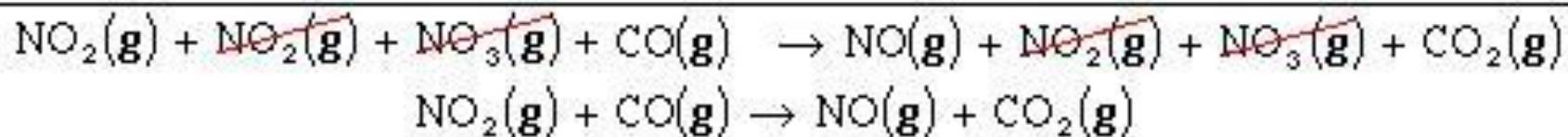- While the overall reaction tells us **stoichiometry.**

# $NO_2 (g) + CO (g) \rightarrow NO (g) + CO_2 (g)$

**Two elementary reactions have take place to form the above complete reaction:**

① $2 NO_2 \rightarrow NO$ and $NO_3$

② $NO_3 + CO \rightarrow NO_2$ and $CO_2$

# $NO_2$ (g) + CO (g) → NO (g) + $CO_2$ (g)
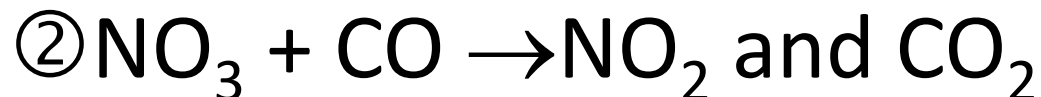
## Adding all the elementary reactions will form the final overall reaction!

$$\text{Step 1:} \quad NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$$
$$\text{Step 2:} \quad NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

$$NO_2(g) + \cancel{NO_2(g)} + \cancel{NO_3(g)} + CO(g) \rightarrow NO(g) + \cancel{NO_2(g)} + \cancel{NO_3(g)} + CO_2(g)$$
$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

# $NO_2$ (g) + CO (g) → NO (g) + $CO_2$ (g)

Step 1:   $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

Step 2:   $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

$NO_2(g) + \cancel{NO_2(g)} + \cancel{NO_3(g)} + CO(g) \rightarrow NO(g) + \cancel{NO_2(g)} + \cancel{NO_3(g)} + CO_2(g)$

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$
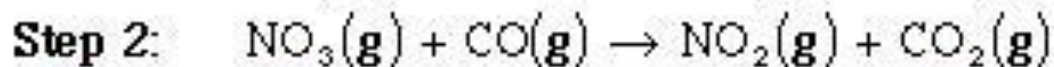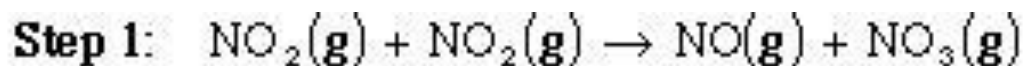
The chemical that is **formed** in one elementary step and **consumed** later in another elementary step can be "crossed-out"

*Summation of the elementary reactions will form the overall reaction*

# Reaction intermediate

A **reaction intermediate** is a chemical/species that is **formed** in an elementary step reaction and been **consumed** later in another elementary step reaction.

The reaction intermediate will be crossed out and it **never** being seen in the overall reaction equation!

# 4.10 Molecularity

The **molecularity** of an **elementary reaction:**

is the **number of reactant molecules** of the elementary step reaction.

A **one molecule** : **unimolecular**.
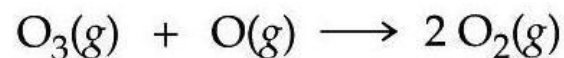
A **two molecule** : **bimolecular**.

A **three molecule :** **termolecular**

# Molecularity

**Unimolecular**

$$O_3{}^*(g) \longrightarrow O_2(g) + O(g)$$

**Bimolecular**

$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$

**Termolecular**

$$O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$$
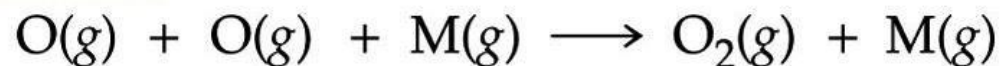
# Chances for molecularity

- The chances of a **unimolecular reaction** are **good**
  - it only depend on one molecule.

- The chances of a **bimolecular reaction isn't difficult** and happens quite often
  - requires two molecules to collide with each other

- The chances of a **termolecular reaction** are **not very good**
  - requires that three molecules collide with each other <u>at the same time</u>.

- The **chances** of **four or more** molecules colliding <u>at the same time</u> are **almost impossible**.

# 4.11 Rate Laws and Reaction Mechanisms

Unlike an overall reaction, the rate law for an elementary reaction follows *DIRECTLY* from the molecularity of the step reaction
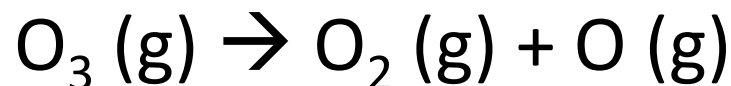
Example:

$$aA + bB \rightarrow \text{products}$$

$$\text{rate} = k\,[A]^a\,[B]^b$$

**Unimolecular** elementary reaction

- example:

$$O_3 \, (g) \rightarrow O_2 \, (g) + O \, (g)$$

$$\text{rate} = k \, [O_3]$$

**Bimolecular** elementary reaction

- example:

$$A + B \rightarrow \text{products}$$

$$\text{rate} = k \, [A] \, [B]$$

# Elementary reaction rate laws

## Rate Laws for Elementary Reactions

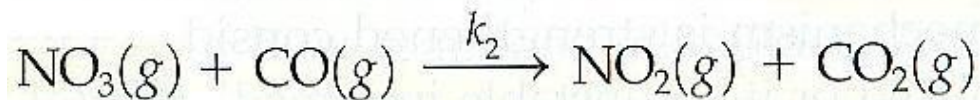| Elementary Reaction | Molecularity | Rate Law |
|---|---|---|
| A $\longrightarrow$ Products | Unimolecular | Rate $= k[A]$ |
| A + A $\longrightarrow$ Products | Bimolecular | Rate $= k[A]^2$ |
| A + B $\longrightarrow$ Products | Bimolecular | Rate $= k[A][B]$ |
| A + A + B $\longrightarrow$ Products | Termolecular | Rate $= k[A]^2[B]$ |
| A + B + C $\longrightarrow$ Products | Termolecular | Rate $= k[A][B][C]$ |

# Mechanisms and overall rate law

As discussed, the overall rate law and the mechanism of overall reaction is determine from the elementary reaction.

- **For a single elementary reaction**, the overall rate law is the **same** with the rate law of the elementary reaction.

- **For a two or more elementary reaction step**, the overall rate of reaction is the **same** with the slowest rate of the elementary reaction.

# $NO_2$ (g) + $CO$(g) $\rightarrow$ $NO$ (g) + $CO_2$ (g)
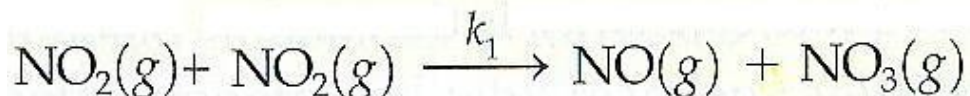
$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g) \qquad \text{Slower, rate-determining}$$

$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \qquad \text{Faster}$$

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad \text{Overall reaction}$$

The second step has to wait for the first step to create the $NO_3$, which is then used rapidly for the second step reaction.

# Conclusion

❖ Temperature gives a significant effect to the reaction rate.

❖ Arrhenius equation is derived from the molecular collisions theory.

❖ A chemical reaction rate is depending on its elementary reaction.

❖ Order of a reaction can only be determined graphically.

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