# UNIT - 1B | PAPER - 1

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VERSION : 2.00

LAST UPDATED : 01-03-2025

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# UNIT 1B - PAPER 1

# CHEMICAL KINETICS AND ELECTRO CHEMISTRY

1. Conservation Of Energy
2. Enthalpy & Free Energy
3. Catalysts
4. Collision
5. Transition State Theory
6. Enzyme Catalyst
7. Standard Electrode Potentials
8. EMF
9. Electrochemical Series.

ANIKET BHARDWAJ CHEMISTRY
FOR IIT JAM - NET - JRF - UPSC

# UNIT - 1B-2 | PAPER - 1

# THE CONCEPT OF ENTHALPY AND ENTROPY

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# INTRODUCTION

- In physics, thermodynamics is the study of the effects of heat, energy and work on the system.
- The term enthalpy was introduced by a Dutch scientist, Hieke kamerlingh Onnes in 1909
- The word enthalpy means total heat content .
- Enthalpy tells us how much heat is added or removed from the system.
- The term entropy was introduced by the scientist Rudolf Clausius in 1859
- This idea comes from the concept that heat always flows from hot to cold regions.
- Entropy is the measure of disorderness of the system.

# ENTHALPY

- It is defined as the sum of internal energy of a system and the product of its pressure and volume .
- It is denoted by the symbol H .
- Units used to express – calorie and joulesl
- It deals with the heat contained in any system. Thereby ,it changes when heat enters or leaves the system.

$$H=U+PV$$

- H- enthalpy, U - internal energy, P - pressure, V – volume.
- Change in enthalpy

$$. \Delta H=\Delta U+P\Delta V$$

# ENTHALPY

- When enthalpy change more than zero ,energy enters into the system and the reaction is endothermic.
- When the energy is lost from a system the enthalpy change is less than zero and the reaction is exothermic.
- The sign of $\Delta$ H is negative or positive depends upon the heat is evolved or absorbed,
- When the heat is evolved $\Delta H$ -ve
- Heat is absorbed $\Delta H$ +ve
- Change in enthalpy measured calorimetrically.
- As q represents the heat absorbed from the surroundings medium or heat given upto the medium
- $\Delta H = q$

# STANDARD ENTHALPY CHANGE

- It is the measure of energy released/consumed when one mole of substance is created under standardized conditions from its pure elements.
- symbol $\Delta H^{\circ}f$

# CHARACTERISTICS OF ENTHALPY

- Enthalpy is an extensive property (depends upon the amount of substance)
- It is a state function (depends upon the state variables)
- It is a useful and important thermodynamic function
- When a system undergoes physical and chemical change ,it's enthalpy also changes
- $\Delta H = H$ final - $H$ initial

# HESS'S LAW

- Because the enthalpy is a state function the enthalpy change is depends upon the identity of the products and reactants.
- It is independent of whether the reaction takes place in a series of steps / all at once.

# REACTION ENTHALPY

- It is very useful information to know how much heat a reaction will give off/absorb. This quantity is called reaction enthalpy.

# IMPORTANCE OF ENTHALPY

- Measuring the change in enthalpy allows us to determine whether the reaction exothermic/endothermic.
- Enthalpy change occurs during a change in the State of matter .
- Change in enthalpy is used to measure heat flow in calorimetrically.

# RELATIONSHIP BETWEEN ΔH AND ΔU

- ΔH and ΔU related by the equation

$$\Delta H=\Delta U+P\Delta V$$

- For reactions between solids and liquids ,ΔV is very small

$$\Delta H=\Delta U$$

- For the reactions involving gases

$$\Delta H=\Delta U+P\Delta V$$

$$\Delta H=\Delta U+P(V2-V1)$$

$$\Delta H=\Delta U+PV2-PV1$$

# ENTROPY

- It is a quantity introduced to denote the orderliness of a system
- It is a measure of the degree of disorder any system
- It is designated by the symbol S.
- The SI unit for entropy is joules /kelvin
- In the ice crystals –entropy minimum
- In a liquid state – entropy increases.

# CHANGE IN ENTROPY

- Calculated only for a reversible process.
- It is defined as the ratio of the amount of heat taken up to the absolute temperature at which the heat absorbed.
- Entropy change $(\Delta S) = \dfrac{\text{Heat absorbed in a reversible process}}{\text{Temperature in kelvin}}$

# TOTAL ENTROPY OF AN ISOLATED SYSTEM

- Can never decrease
- Must increase – irreversible process
- Remain constant – reversible process.
- All physical process occur with an increase in entropy when changes in both the system and it's surroundings are considered.

**Entropy changes in a closed system**

- In a closed system the exchange of energy is possible but not matter, with the surroundings.
- So, far a closed system as the process moves towards equilibrium, the entropy of the system Plus the surroundings increases.

**Free energy**

- As the system moves towards equilibrium in a spontaneous process it loses energy and that can be used to perform work.

# ENTROPY AT MOLECULAR LEVEL

- For a given substance ,the entropy of the liquid state is greater than the entropy of the solid.
- Entropy increases when a substance broken up into multiple parts.
- Entropy increases when a temperature increases.
- Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules.

# DIFFERENCE BETWEEN ENTHALPY AND ENTROPY

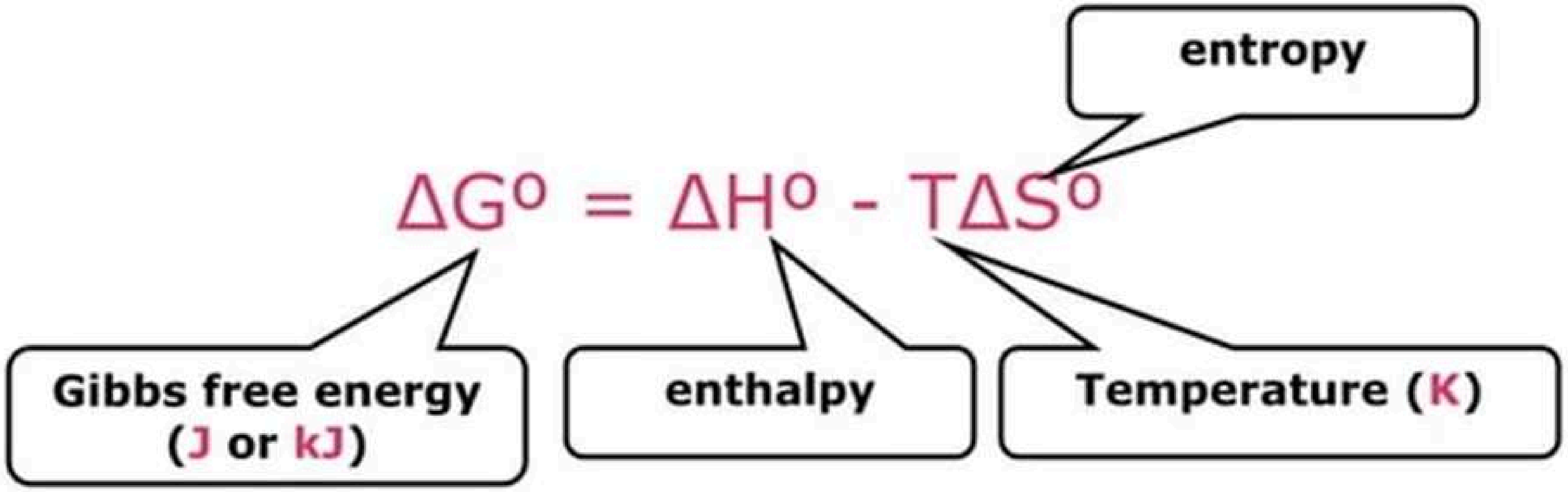
| **Enthalpy** | **Entropy** |
|---|---|
| The term was given by Hieke Kamerlingh Onnes | The term was given by Rudolf Clausius |
| It is a kind of energy | It is the property of the matter |
| It is the sum total of the internal energy and energy flow. | It is the measure of the randomness of molecules. |
| The natural system always favours the minimum enthalpy. | The natural system favors maximum entropy. |
| Its symbol is H | Its symbol is S. |
| Its unit is joules per mol. | It unit is joules per kelvin. |
| Enthalpy is positive for endothermic reactions | Entropy is positive for spontaneous process |
| Enthalpy is negative  for exothermic reactions | Entropy is negative  for non spontaneous process. |

# DIFFERENCE BETWEEN ENTHALPY AND ENTROPY

| Enthalpy | Entropy |
|---|---|
| It is the sum of internal energy and the product of P&V | It is the amount of heat transferred reversible in and out of the system at a given temperature. |
| $H=U+P\ V$ | $dS=dq\ rev/T$ |
| According to the first law of thermodynamics, the energy of the universe is constant. | According to the second law of thermodynamics the entropy of the universe is always increasing. |

# FREE ENERGY

- Gibbs realized that for a reaction, a certain amount of energy goes to an increase in entropy of a system and a certain amount goes to a heat exchange for a reaction.
- Gibbs Free Energy (G) is a state variable, measured in KJ/mol.



entropy

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

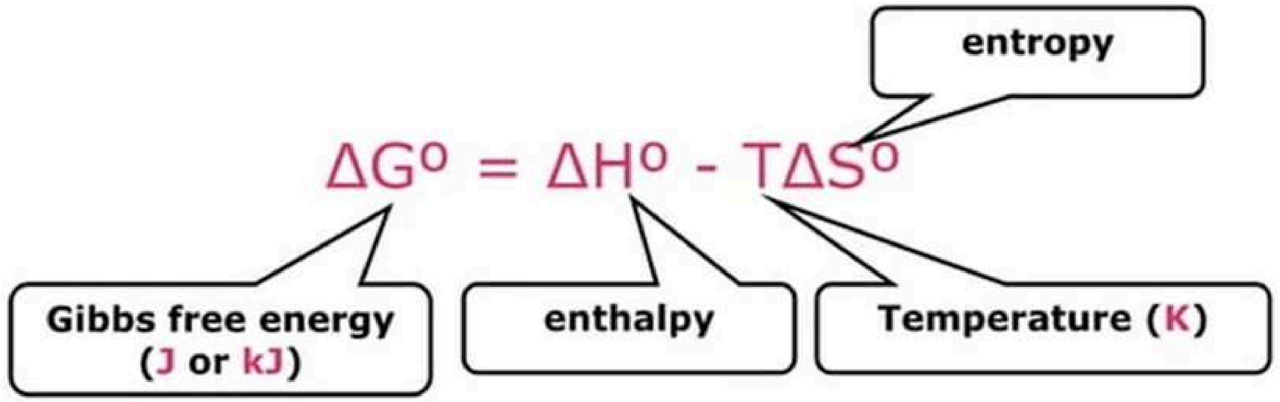
Gibbs free energy (J or kJ)

enthalpy

Temperature (K)

# FREE ENERGY

- When ΔG is negative → forward reaction has excess energy and will occur spontaneously.
- When ΔG is positive → energy is to be put to the system to make reaction go.
- exergonic reaction: A chemical reaction where the change in the Gibbs free energy is negative, indicating a spontaneous reaction.
- endergonic reaction: A chemical reaction in which the standard change in free energy is positive, and energy is absorbed.
- Gibbs free energy specifically refers to the energy associated with a chemical reaction that is available after accounting for entropy.



entropy

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Gibbs free energy (J or kJ)

enthalpy

Temperature (K)

- In other words, Gibbs free energy is usable energy or energy that is available to do work.
- For all spontaneous reaction ΔG is always negative.

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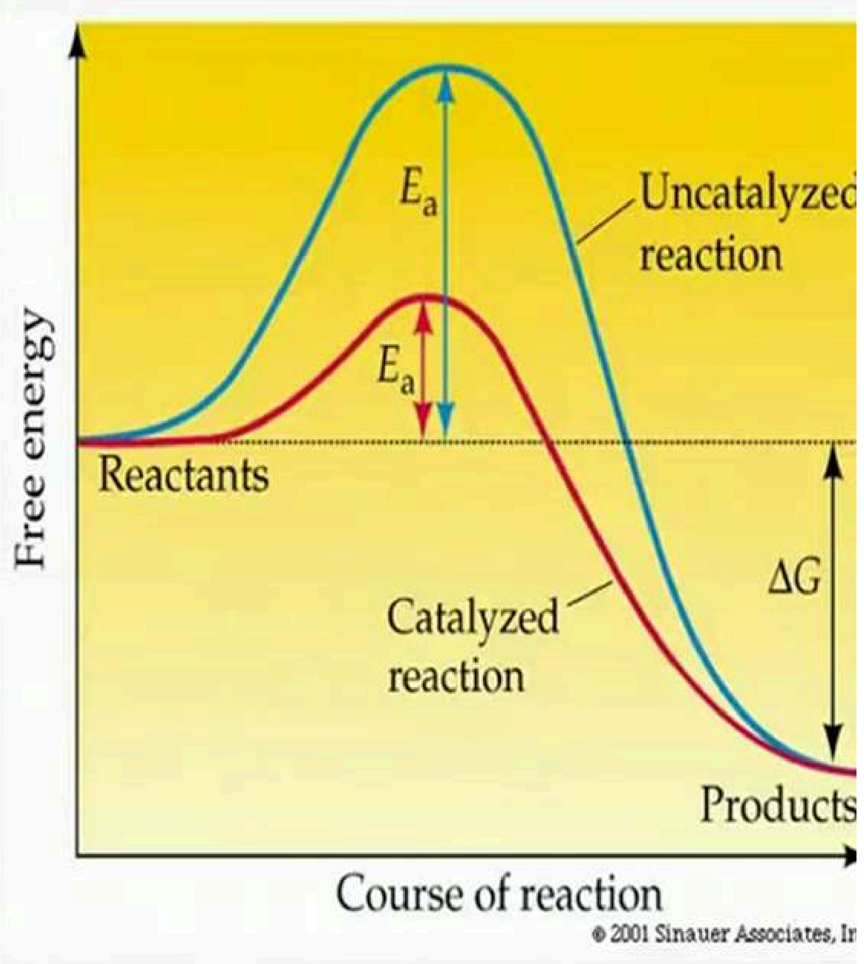
# CATALYSTS

- Catalyst = A substance that speeds up the rate of reaction by lowering the activation energy.
- Offers an alternate pathway of reaction
- is not consumed (used up) by the reaction



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# COLLISION THEORY

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# INTRODUCTION

Collision theory is a theory proposed independently by Max Trautz (German) in 1916 and **William Lewis**(British) in 1918, that qualitatively explains how **chemical reactions** occur and why **reaction rates** differ for different reactions.

William Lewis

Max Trautz

- **Collison -**When 2 or more objects collide, or run into each other.

- **Collison Theory -** The theory that only soe Collison between particles cause chemical changes. Effective collisions must have enough energy to break preexisting bonds and to form new bonds.

# REACTION RATE

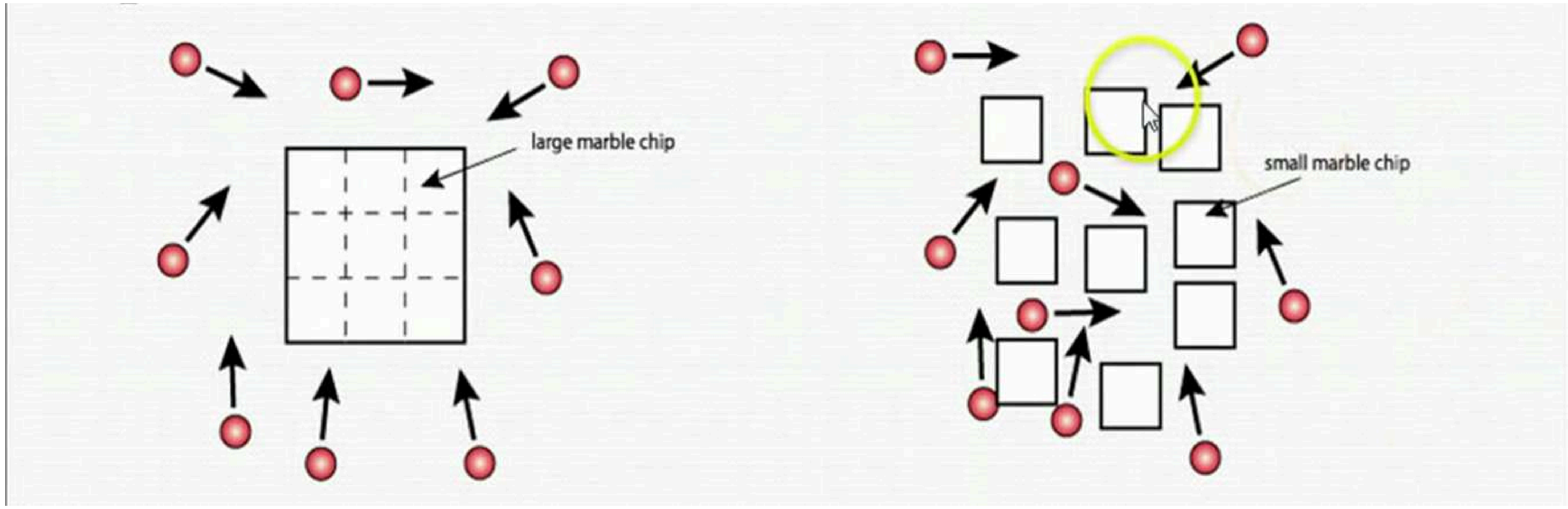
- The reaction rate ( rate of reactions ) or speed of reaction is defined as how fast or slow a reaction takes place.
- Reaction rate has to do with the speed of a substance particles.

1. Fast reaction rate = fast moving particles
2. Slow reaction rate = slow moving particles

# FACTORS AFFECTING REACTION RATE

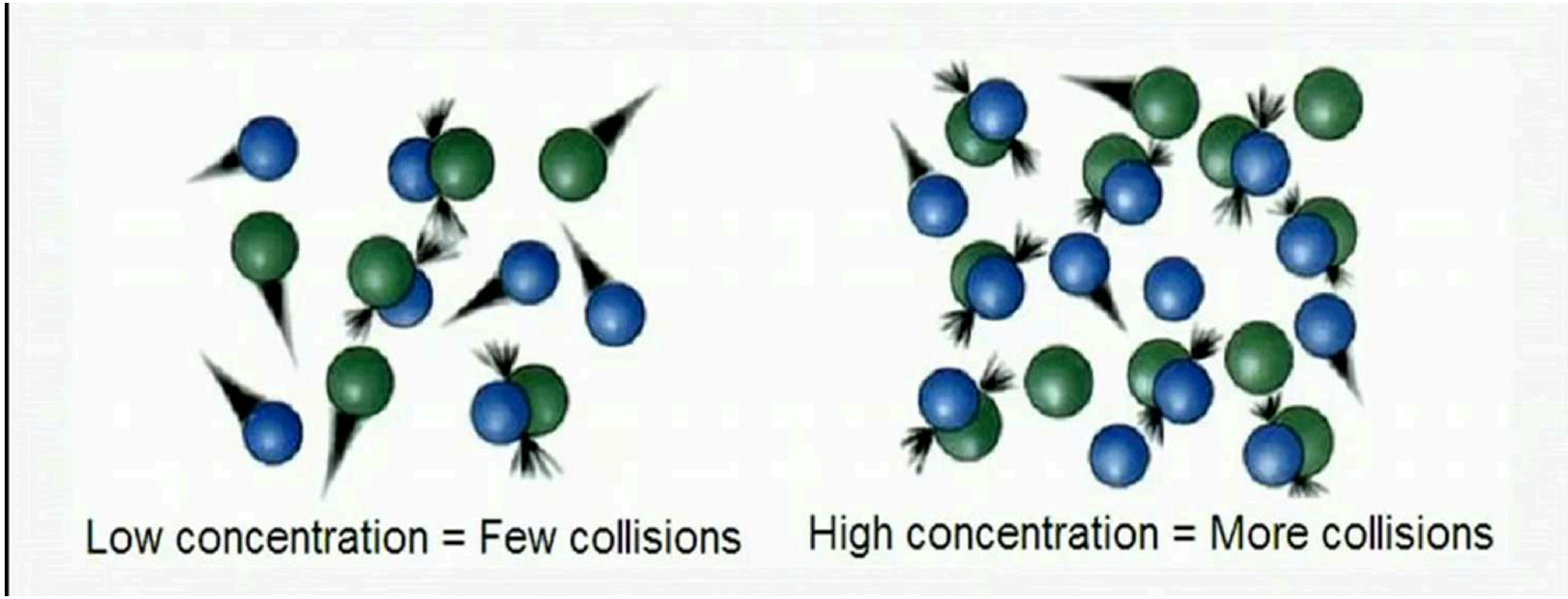
Many factors affect collisions and hence,

1. Surface area of a solid reactant = how big the particles of the reactant are



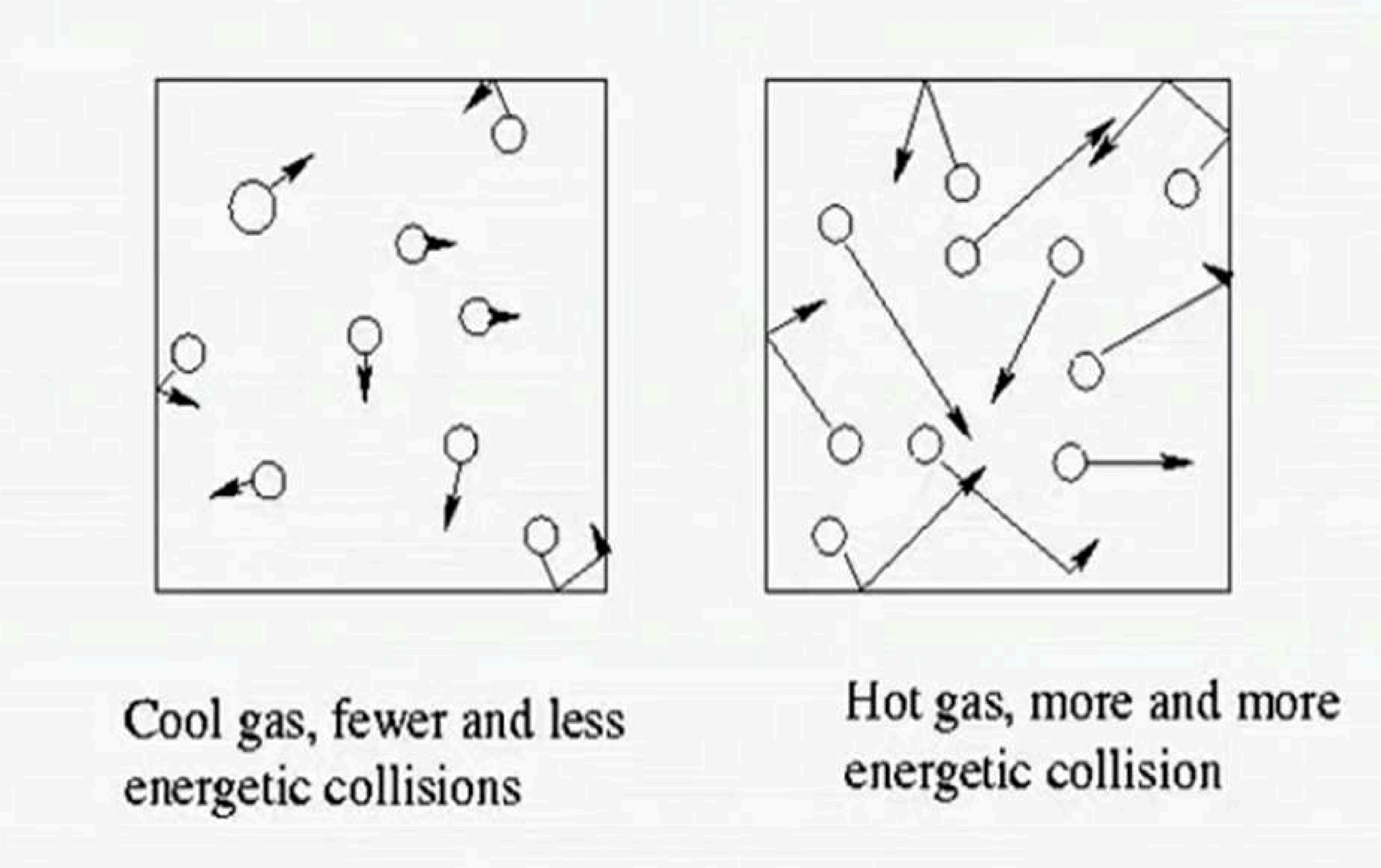
# FACTORS THAT AFFECT IT

2. concentration of reactant = amount of reactant



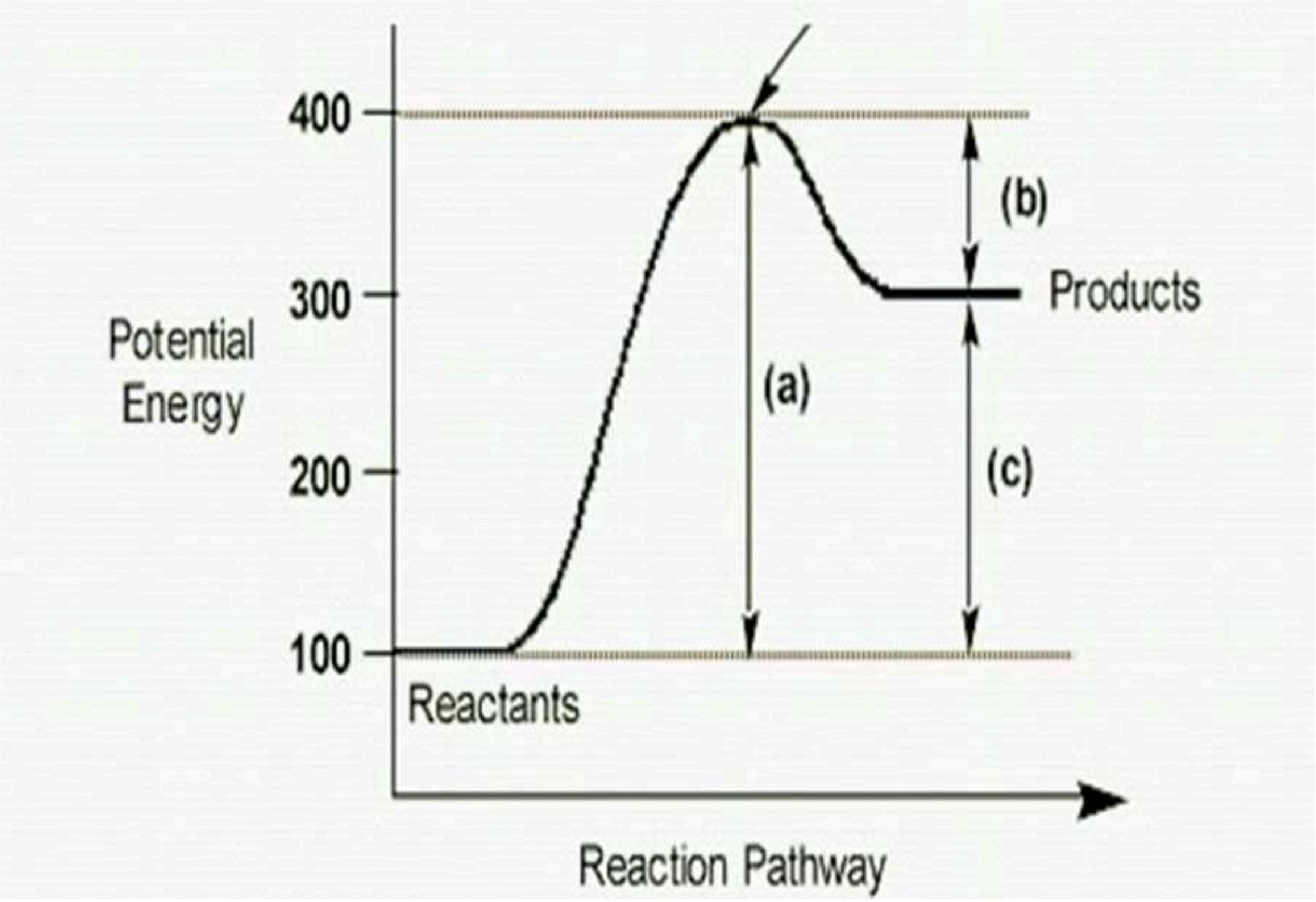
# REACTION RATE

3. Temperature = average kinetic energy ; how "hot" an object is



# ACTIVATION ENERGY

activation energy = the minimum amount of energy needed to initiate or start a chemical reaction. $(E_a)$



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# TRANSITION STATE THEORY

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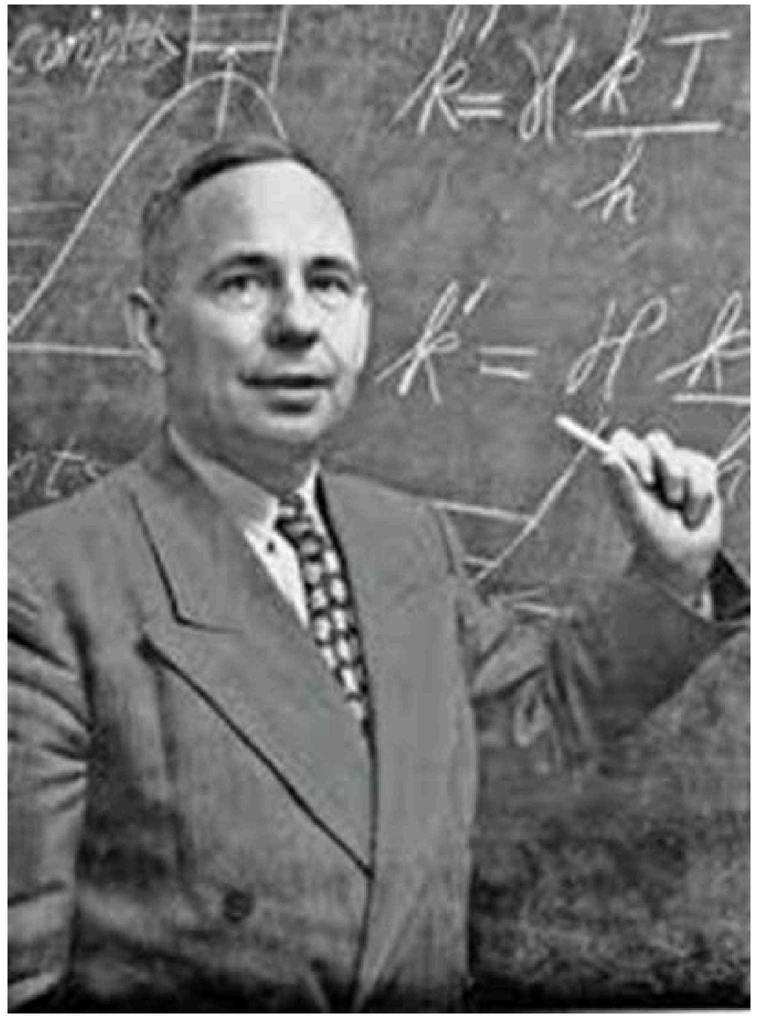
# INTRODUCTION

This theory was developed simultaneously in 1935 by Henry Eyring, then at Princeton University



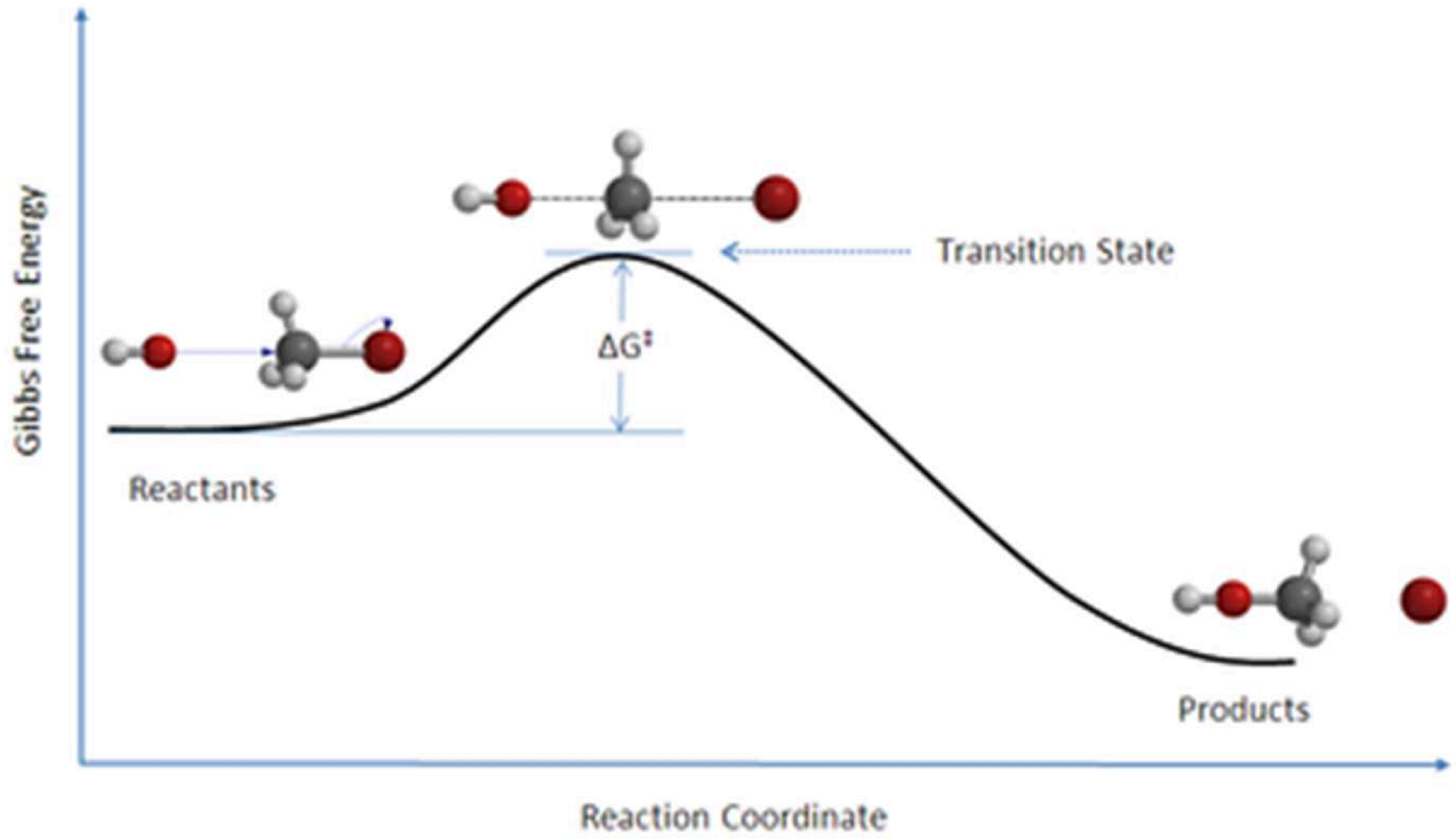
Henry Eyring

According to Transition State Theory

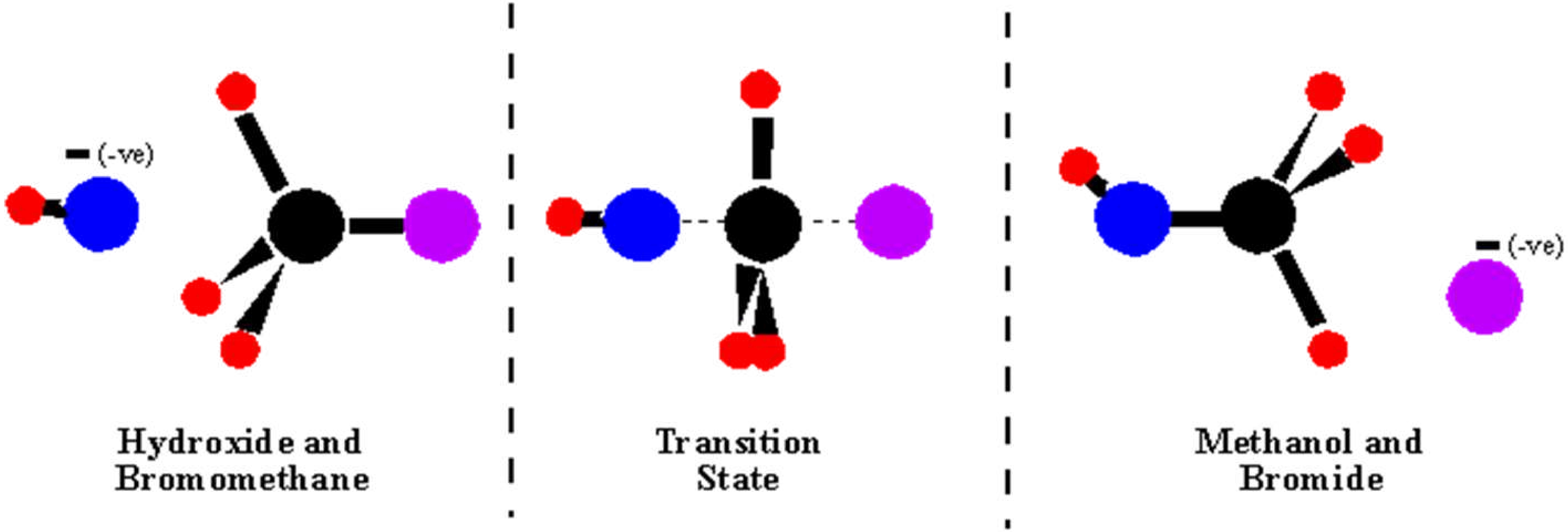
between the state where molecules are reactants and the state where molecules are products, there is a state known as the transition state. In the transition state, the reactants are combined in a species called the activated complex.

The theory suggests that there are three major factors that determine whether a reaction will occur:

- The concentration of the activated complex
- The rate at which the activated complex breaks apart
- whether it breaks apart to reform the reactants or whether it breaks a part to form a new complex, the products.



Reaction: $HO^- + CH_3Br \rightarrow [HO\text{---}CH_3\text{---}Br]^\ddagger \rightarrow CH_3OH + Br^-$


- (-ve)
Hydroxide and Bromomethane
Transition State
Methanol and Bromide
- (-ve)

- The example reaction shown above involves the reactants, hydroxide and bromomethane, forming the products, methanol and bromide.
- The first part of the image shows the reactants. The second part of the image shows the transition state, in which the activated complex is formed, with rearranged molecules and different bonds.
- The activated complex is clearly different than the reactants or the products.
- A successful collision and reaction have clearly occurred because in the third part of the image products (methanol and bromide) are formed that are different than the reactants (hydroxide and bromomethane).

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