LECTURE №3

CHEMICAL KINETICS

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Our goal: is to understand chemical reactions at the molecular level.

Chemical reactions require varying lengths of time for completion, depending on the characteristics of the reactants and products and the conditions under which the reaction is run.

Many reactions are over in a fraction of a second, whereas others can take much longer.

Chemical kinetics is the study of reaction rates, how reaction rates change under varying conditions, and what molecular events occur during the overall reaction.

Chemical kinetics is the study of the speed with which a chemical reaction occurs and the factors that affect this speed. *This information is especially useful for determining how a reaction occurs.*

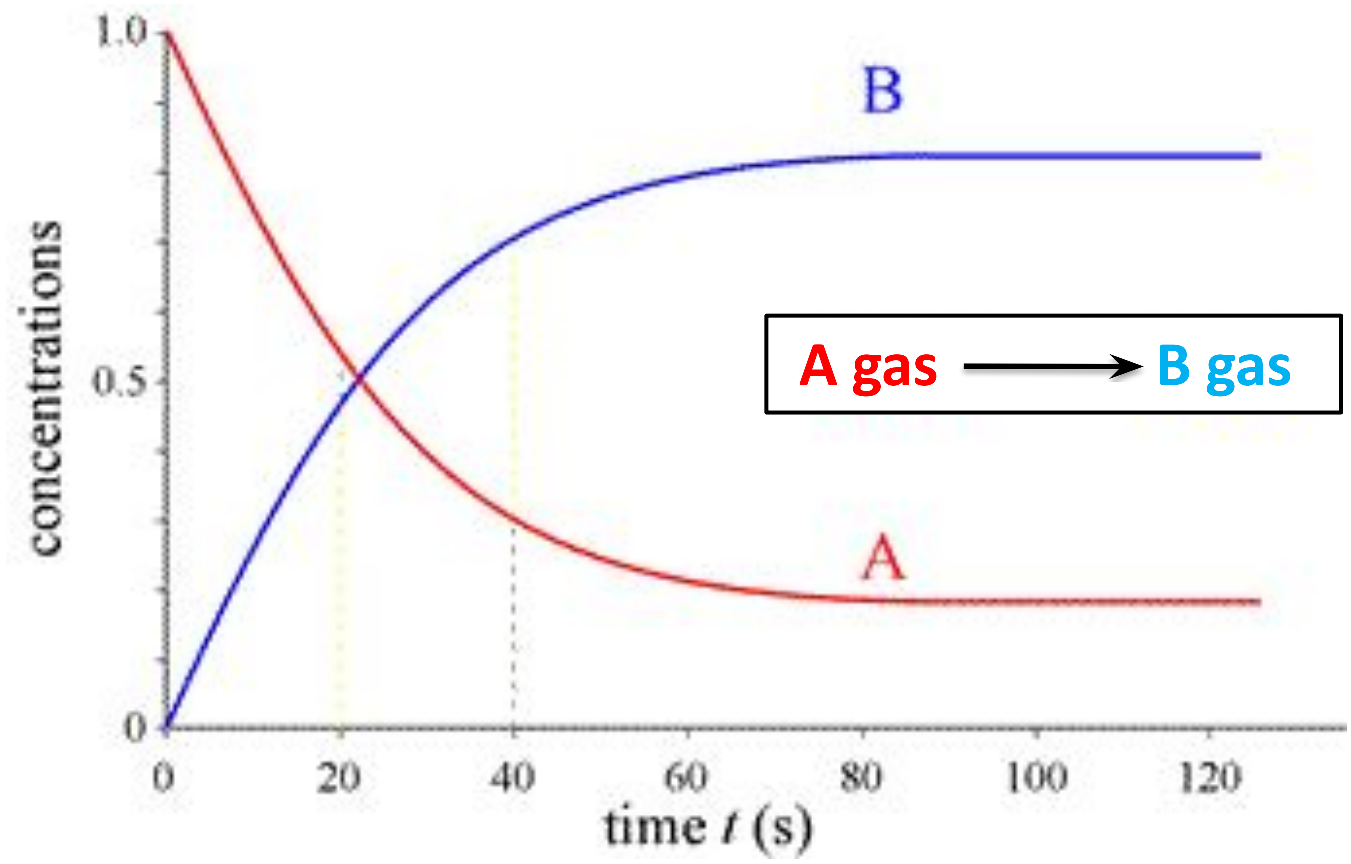
The rate of a reaction is the amount of product formed or the amount of reactant used up per unit of time.

Therefore, **the reaction rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of reactant per unit time. The usual unit of reaction rate is moles per liter per second, *mol/l*s*.**

$$\upsilon = \frac{C^2 - C^1}{\tau_2 - \tau_1} = \pm \frac{\Delta C}{\Delta \tau}$$

During chemical reaction, reactants are consumed, products are formed.

Amount of reactants decreases↓, amount of product increases↑



THE RATE OF CHEMICAL REACTION

HOMOGENEUOS REACTION RATE
is the change moles of reactants in volume (*l*) of solution per unit time

HETEROGENEUOS REACTION RATE
is the change moles reactants on 1m^2 surface per unit time

$$\upsilon = \pm \frac{n(X)}{\Delta V \cdot \Delta t}$$

$$\upsilon = \pm \frac{n(X)}{\Delta S \cdot \Delta t}$$

$mol/м^3 \cdot s \quad mol/м^2 \cdot s \quad mol/l \cdot s$

FACTORS AFFECTING THE REACTION RATE:

- Nature of the reactant (gas, liquid or solid)
- Surface area
- Concentration
- Temperature
- Catalyst
- Pressure (gases)

Nature of the reactant and products

In organic reaction a large number of bonds are broken and a large number of bonds are formed. Such reactions proceed at a slower rate: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

sugar **glucose** **fructose**

In ionic reactions the reactants are in ionic form and no bonds have to be broken up. Such reactions proceed at a faster rate:

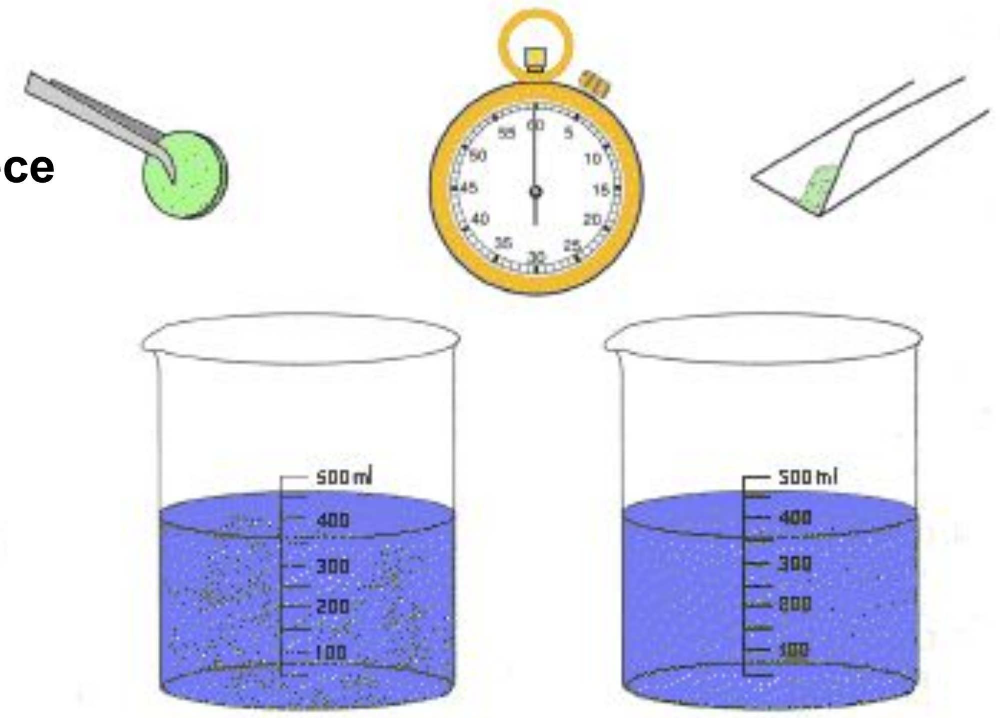
$$Ag^{+} + NO_3^{-} + Na^{+} + Cl^{-} \rightarrow AgCl\downarrow + Na^{+} + NO_3^{-}$$

cation **anion**

HOW SURFACE AREA AFFECTS THE RATE OF REACTION?

$$CaCO_{3(s)} + 2HCl_{(\ell)} \longrightarrow CaCl_{2(s)} + H_2O_{(\ell)} + CO_{2(g)}$$

marble piece



marble powder

HCl dilute

LAW OF MASS ACTION

At constant temperature, the rate of a chemical reaction is directly proportional to the product of the molar concentrations of reacting species, with each concentration term raised to the power equal to the numerical coefficient of the species in the chemical equilibrium:

$$aA + bB \rightarrow cC + dD$$

$$\upsilon = k \cdot [A]^a \cdot [B]^b$$

here ***k*** is the reaction rate constant that depends on temperature:

- It has a fixed value at a particular temperature.
- Value of K varies with temperature.
- Value of K remains unaltered with the change in concentration of reactants.

FOR EXAMPLE:

Homogeneous reactions which occur in one phase only. It may be a gaseous phase or a liquid phase:

$$2SO_{2(g)} + O_{2(g)} = 2SO_{3(g)}$$

Rate of forward reaction: $\upsilon_1 = k_1 \cdot [SO_2]^2 \cdot [O_2]$

Rate of backward reaction: $\upsilon_2 = k_2 \cdot [SO_3]^2$

Heterogeneous reactions which take place in two or more phases (e.g., gaseous reactions taking place on the surface of a solid catalyst or on the walls of the container):

$$4Al_{(s)} + 3O_{2(g)} = 2Al_2O_{3(s)}$$

$$\upsilon_1 = k_1 \cdot [1]^4 \cdot [O_2]^3 = \mathbf{k_1 \cdot [O_2]^3}$$

$$\upsilon_2 = k_2 \cdot [1]^2 = k_2$$

THE EFFECT OF TEMPERATURE ON REACTION RATE

described by principle of Vant Hoff "***In the temperature range from 0°C to 100°C, at a temperature increase of 10°C degrees the rate of chemical reaction increases by 2 – 4 times***"

γ **- temperature coefficient is a number indicating how many times will increase the reaction rate with increasing temperature at 10°C**

$$V_{t_2} = V_{t_1} \cdot \gamma^{\frac{t_2 - t_1}{10}}$$

$$\frac{V_{t_2}}{V_{t_1}} = \gamma^{\frac{t_2 - t_1}{10}}$$

An example: how to change the speed of the reaction at a temperature increase of 40°C, if the temperature coefficient is equal to 3:

$$\Delta V = \gamma^{\frac{\Delta t}{10}} = 3^{\frac{40}{10}} = 3^4 = 81$$

The reaction rate increases 81-fold

Why does increased temperature increase the rate of reaction?

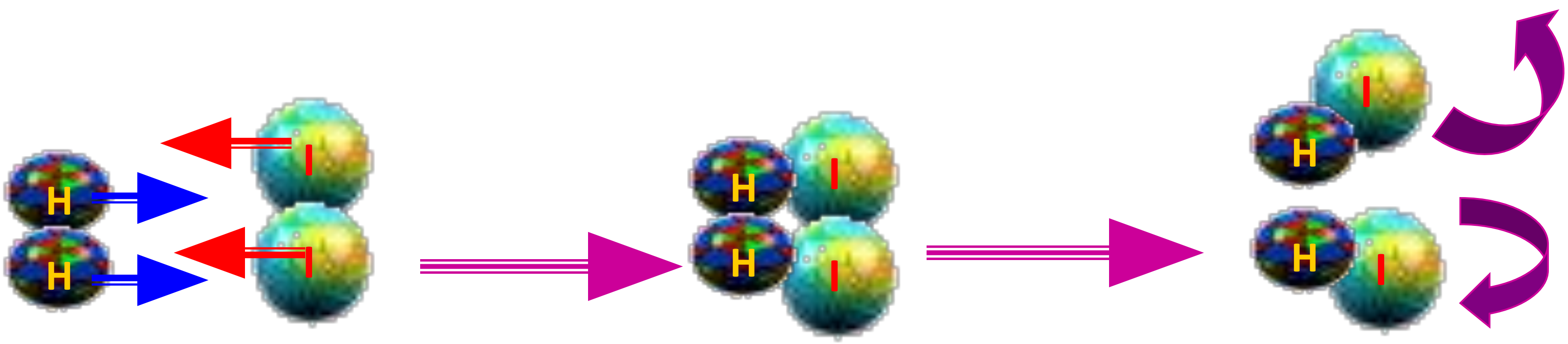
At a higher temperature, particles have more energy. This means they move faster and are more likely to collide with other particles. When the particles collide, they do so with more energy, and so the number of successful collisions increases.

Collision theory states that before any chemical reactions can occur, particles of the reactants have to collide with each other .

Effective collision – collision that produces chemical reactions by achieving the minimum energy and correct collision orientation .

Activation energy is the minimum energy needed by the reactant particles to react and it is different for each reation.

Colliding particles must have equal or be more than the activation energy.



Correct collision orientation

Effective collision

Reaction happens

The rate of a reaction depends on the temperature at which it is run. As the temperature increases, the molecules move faster and therefore collide more frequently. The molecules also carry more kinetic energy. Thus, the proportion of collisions that can overcome the activation energy for the reaction increases with temperature.

The only way to explain the relationship between temperature and the rate of a reaction is to assume that the rate constant depends on the temperature at which the reaction is run. ***In 1889, Svante Arrhenius showed that the relationship between temperature and the rate constant for a reaction obeyed the following equation:***

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

A **is the proportionality constant called the frequency factor or pre exponential factor.**

DETERMINE THE ACTIVATION ENERGY

$$k = A \cdot \exp\left(-\frac{E_a}{RT}\right)$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$E_a = \frac{R \cdot T_1 \cdot T_2}{T_1 - T_2} \cdot \ln \frac{k_1}{k_2} = \frac{2{,}3 \cdot R \cdot T_1 \cdot T_2}{T_2 - T_1} \cdot \lg \frac{k_2}{k_1}$$

- **$E_a > 100$ kJ – big value, the reaction proceeds very slowly**
- **$E_a < 50$ kJ – small value, the reaction proceeds very quickly**

CHEMICAL EQUILIBRIUM

The irreversible reaction moves in one direction only from reactant to product:

$$2KClO_3 \xrightarrow{t^{\circ}} 2KCl + 3O_2$$

The reversible reactions can move in both directions. The stage of reversible reaction when the rate of forward reaction becomes equal to rate of back reaction is known as *equilibrium* and can be represented in terms of equilibrium constant.

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

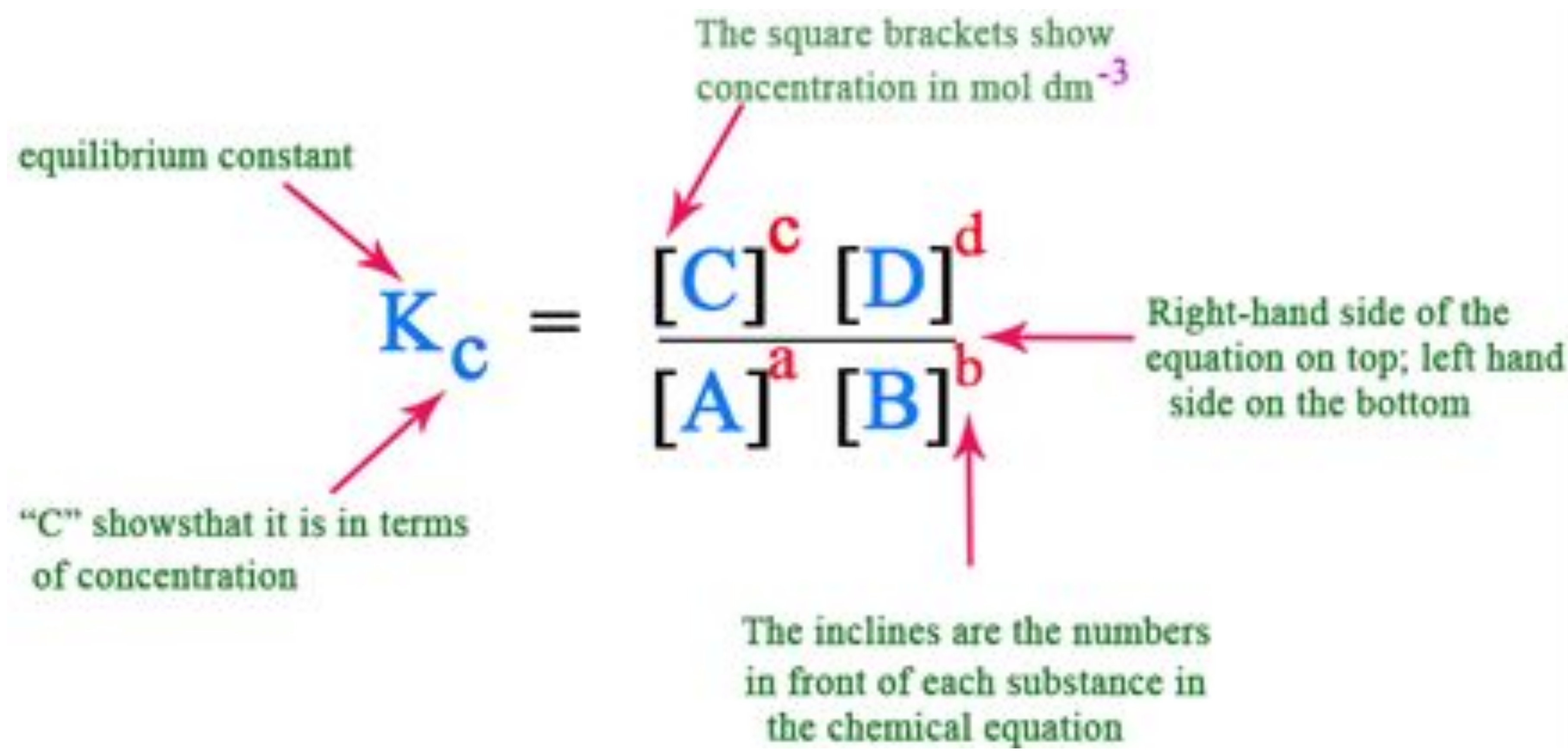
$$aA + bB \rightarrow cC + dD$$

Forward reaction: $$\upsilon_1 = k_1 \cdot [A]^a \cdot [B]^b$$

Back reaction: $$\upsilon_2 = k_2 \cdot [C]^c \cdot [D]^d$$

Equilibrium constant: $$K_P = \frac{\vec{k}_1}{\overleftarrow{k}_2} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

"At a given temperature, the product of concentrations of the reaction product each raised to the respective stoichiometric coefficients in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value"



Value of chemical equilibrium constant

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$$

$$\upsilon_1 = k_1 \cdot [N_2] \cdot [H_2]^3$$

$$\upsilon_2 = k_2 \cdot [NH_3]^2$$

$$\upsilon_1 = \upsilon_2$$

$$K_P = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3}$$

HOMOGENEOUS REACTION

HETEROGENEOUS REACTION

$$2Na_{(S)} + 2H_2O_{(aq)} \rightarrow 2NaOH_{(aq)} + H_{2\ (g)}$$

$$\upsilon_1 = k_1 \cdot [H_2O]^2$$

$$\upsilon_2 = k_2 \cdot [NaOH]^2 \cdot [H_2]$$

$$\upsilon_1 = \upsilon_2$$

$$K_P = \frac{[NaOH]^2 \cdot [H_2]}{[H_2O]^2}$$

The most important condition for the equilibrium is that ΔG of the reaction should be 0.

ΔG = 0 The reaction is at equilibrium

This means when ΔG is zero both the forward reaction and reverse reaction takes place simultaneously.

$$\Delta G^0 = - RT \ln K_P$$

Анри-Луи Ле-Шателье
(1850–1936)

CONDITIONS THAT AFFECT THE EQUILIBRIUM

The conditions that affect the equilibrium are described according to Le Chatelier's principle:

***If a system at equilibrium is disturbed by changing the variables such as pressure, temperature or concentration, then the system will tend to adjust itself so as to minimize the effect of that change as far as possible*.**

This principle of Le Chatelier's highlights the behavior of a system at equilibrium, if it is subjected to changes in parameters like pressure, temperature, or concentration.

FACTORS AFFECTING EQUILIBRIUM

Some of the factors which affect the equilibrium constant value are:

1. ***Concentration***. If the concentration of one ingredient is changed, the equilibrium shifts toward the formation of products, i.e. in the direction of the reaction which occurs with the greatest speed and reduces the concentration of the reactants.
2. ***Temperature***. Change in temperature shifts the equilibrium to the favorable side, i.e. towards the endothermic reaction, and vice versa.

3. ***Pressure***. The pressure change affects only on those systems where in at least one of the substances in the gaseous state. As the pressure increases, the equilibrium shifts in the direction of decreasing the amount of gaseous substances, i.e. towards of fewer moles of gaseous substances, and vice versa.

4. ***Catalyst does not affect to Equilibrium,*** it may increases both the forward as well as reverse reaction speeds.

CATALYST

- **A catalyst will change the rate of reaction.**
- **A catalyst only changes the rate of reaction but not the quantity of products.**
- **A catalyst does not undergo any chemical change at the end of the reaction.**

PRESSURE

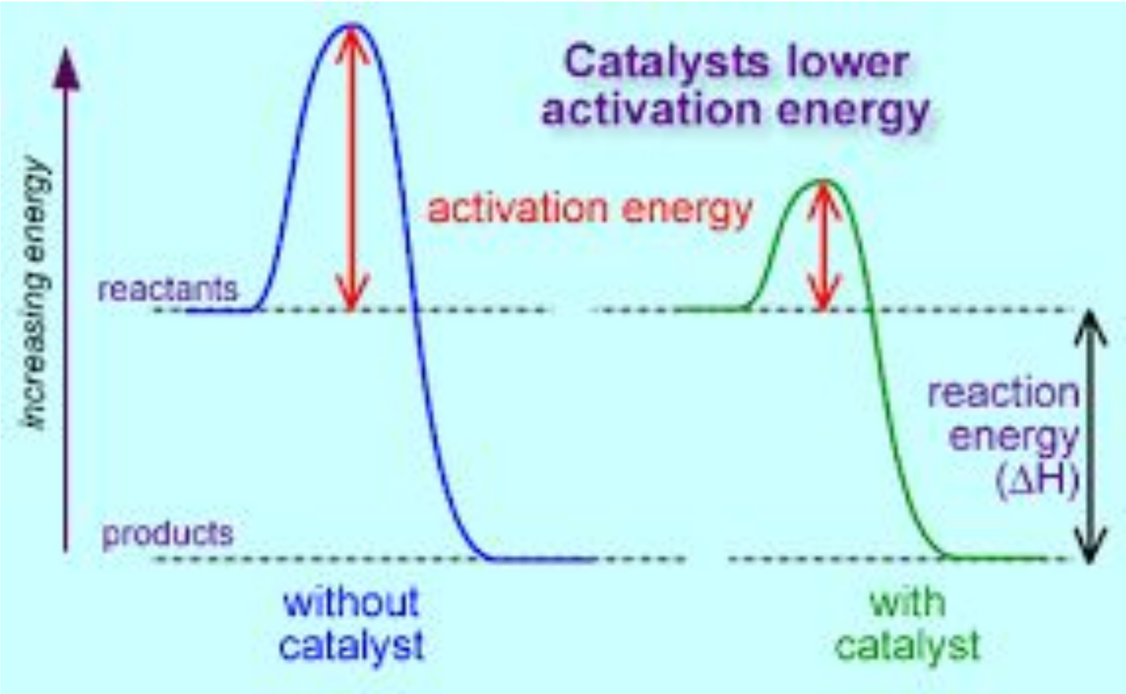
- **Pressure can affect the rate of reaction only if it involves gases.**
- **A higher pressure can increase the rate of reaction.**
- **The increase of pressure will compress the gas.**
- **The particles of a gas will collide more frequently when in a compressed state (smaller volume).**

Catalysts are substances that change the rate of a reaction without itself being consumed.

Catalysts never produce more product – they just produce the same amount more quickly.

Catalysts increase the rate of a reaction by decreasing the activation energy of the reaction.

Catalysts change the mechanism by which the process occurs.



$$rate_{catalyzed} > rate_{uncatalyzed}$$

QUIZ ME

1 What is the discipline that studies chemical reactions with respect to *reaction rates, effect of various variables, rearrangement of atoms, formation of intermediates etc*.?

- **Electrochemistry**
- **Chemical thermodynamics**
- **Physical thermodynamics**
- **Chemical kinetics**

NEXT

QUIZ ME

2 What drives chemical reactions?

- Energy
- Activation Energy
- Electrons
- Physical conditions

NEXT

QUIZ ME

3 Which one of the following reactions reacts the most rapidly at room temperature??

- $2\ H_2 + O_2 \rightarrow 2\ H_2O$
- $C_{12}H_{22}O_{11}$ (sugar) $\rightarrow 12\ C + 11\ H_2O$
- $H^+ + OH^- \rightarrow H_2O$ (neutralization)
- $^*H + OH \rightarrow H_2O$ (radical reaction)

NEXT