«Chemical balance. Chemical kinetics»

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* Lecture plan

1) State of equilibrium
2) Le Chatelier's principle
3) Basic concepts
4) The rate of a chemical reaction
5) Effect of Reagent Concentration on Reaction Rate
6) The effect of temperature on the reaction rate
7) The phenomenon of catalysis

1. State of equilibrium

Chemical Reactions :

- **practically irreversible**

$$H_2 + ½\, O_2 = H_2O$$

- **completely irreversible**

$Pb(N_3)_2 \rightarrow Pb + 3N_2$ (decomposition of explosives)

- **reversible**

$$H_2 + I_2 \rightarrow 2HI$$

1. State of equilibrium

Reversible chemical reactions are reactions that proceed simultaneously in two directions.

1. State of equilibrium

Chemical equilibrium is a time-invariant (P, V, T = const) state of a system containing substances capable of interacting.

True (stable, thermodynamic) equilibrium (3 signs)

Apparent (metastable, retarded) equilibrium - only 1 sign is satisfied - this is invariance in time.

1. State of equilibrium

In 1864 (K. Guldberg and P. Waage) formulated

The Law of Mass Action (LMA):

“**The equilibrium constant** is the ratio of the product of equilibrium concentrations of reaction products in powers equal to stoichiometric coefficients to the product of equilibrium concentrations of reactants in powers equal to stoichiometric coefficients at constant pressure and temperature

1. State of equilibrium

aA + bB ↔ cC + dD

$$K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \qquad K_p = \frac{P_C{}^c \cdot P_D{}^d}{P_A{}^a \cdot P_B{}^b}$$

where [A], [B] are equilibrium concentrations of substances (mol/L);

P_A, P_B are partial pressures of gases.

1. State of equilibrium

$$K_p = K_c (RT)^{\Delta n}$$

where Δn – change in the number of moles of gases as a result of the reaction.

The law of Acting Masses includes only concentrations of solutions, gases (gas pressures). Condensed substances in their own phase ($H_2O_{(l)}$, $KCl_{(s)}$, etc.) are not included in the formula.

$$Fe_2O_{3\ (s)} + 3H_{2\ (g)} = 2Fe_{\ (s)} + 3H_2O_{\ (l)}$$

$$K_C = \frac{1}{[H_2]^3}$$

1. State of equilibrium

The relation that relates the Gibbs energy to the equilibrium constant is the **van't Hoff equation**.

$$K = e^{-\frac{\Delta G_T^\circ}{RT}}$$

$$\ln K = -\frac{\Delta G_T^\circ}{RT}$$

$$\Delta G_T^\circ = -RT \ln K$$

2. Le Chatelier's principle

«If an external stress is applied to an equilibrium system, such a reaction will occur in the system, which will partially weaken this impact, and the system will try to restore the balance»

2. Le Chatelier's principle

Influence of temperature: with an increase in temperature (↑ T), the equilibrium of a chemical reaction shifts towards **an endothermic reaction.**

Influence of pressure (for gas-phase reactions): at an increase in pressure (↑ P), the equilibrium of a chemical reaction shifts towards **a decrease in volume**.

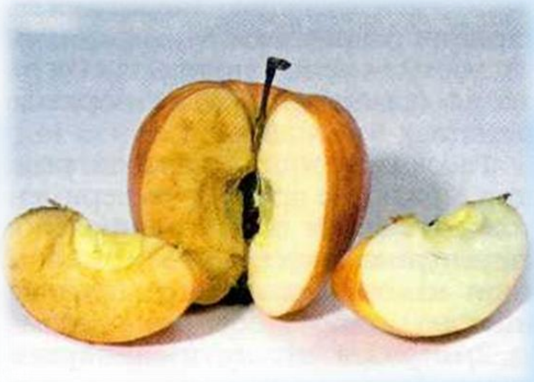
Influence of concentration: with an increase in the concentration of reagents ↑ [reagents], the equilibrium of a chemical reaction shifts towards the **formation of products** and vice versa.

The purpose of studying chemical kinetics

Answer two questions :

1. What is the rate of a chemical reaction?
2. What is the mechanism of a chemical reaction?

We can predict the patterns of reactions and manage processes.



3. Basic concepts

Chemical kinetics is branch of chemistry that studies the rate and mechanisms of chemical reactions

Phase composition processes can be divided :

Homogeneous is flowing throughout the volume of the reacting substances.

Heterogeneous is flowing at the interface.

Topochemical is flowing with a change in the structure of the reacting solids.

3. Basic concepts

A reaction mechanism is a sequence of elementary stage.

An elementary stage is a single act of formation or breaking of a chemical bond.

Chemical reactions are divided according to the mechanism

Simple reactions are reactions that take place in one elementary step.

Complex reactions are reactions that take place in several steps.

3. Basic concepts

Complex reactions are divided according to the mechanism :

- Sequential:

$$Na_2S_2O_3+H_2SO_4=Na_2SO_4+SO_2+S+H_2O$$

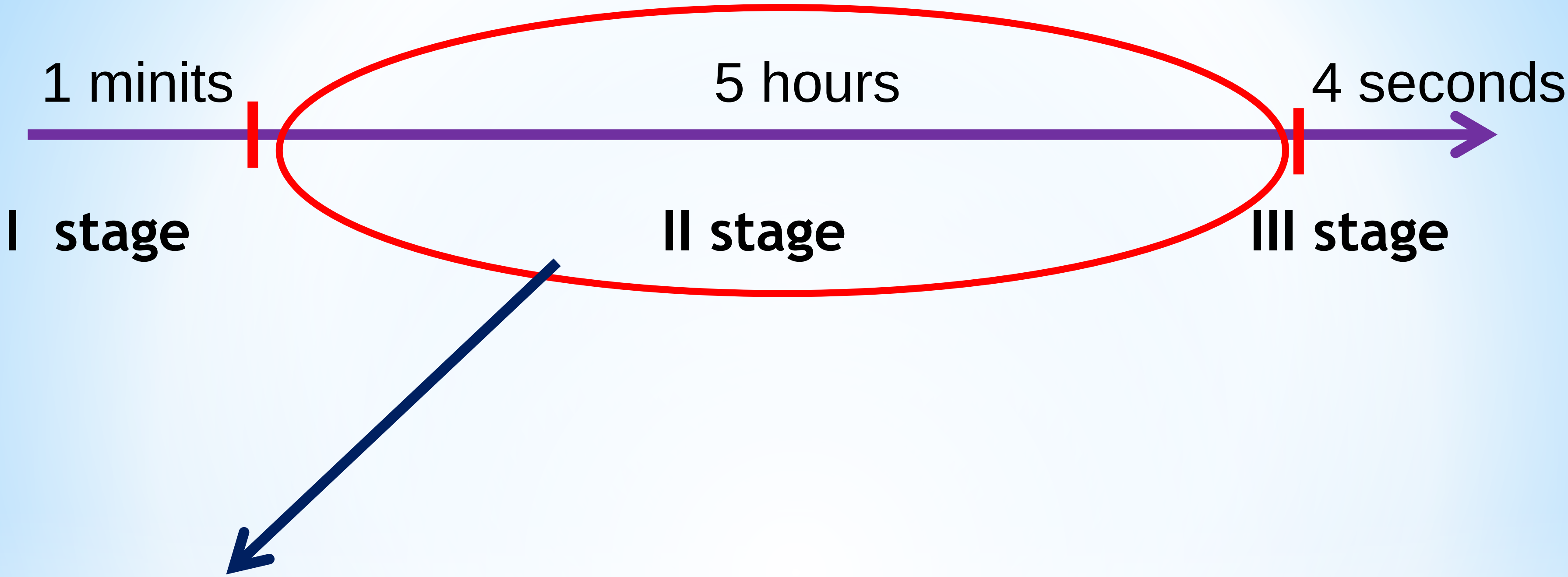
1. $Na_2S_2O_3+H_2SO_4=H_2S_2O_3$
2. $H_2S_2O_3=H_2SO_4+S$
3. $H_2SO_4=+SO_2+S+H_2O$

- Parallel:

$$4KClO_3 \rightarrow 3KClO_4+KCl$$

$$4KClO_3 \rightarrow 4KCl+6O_2$$

3. Basic concepts



The limiting stage is the slowest stage determining the speed of the whole process.

4. The rate of a chemical reaction

The rate of a chemical reaction ($V_{c.r.}$) is the number of elementary acts of interaction occurring per unit time per unit volume for homogeneous reactions or per unit interface for heterogeneous reactions.

$$V_{гом} = \frac{\Delta n}{V\Delta t} = \pm\frac{\Delta C}{\Delta t} \quad и \quad V_{гет} = \frac{\Delta n}{S\Delta t}$$

4. The rate of a chemical reaction

$$aA + bB = cC + dD$$

$$V_t = -\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{C}\frac{dC_C}{dt} = \frac{1}{d}\frac{dC_D}{dt}$$

4. The rate of a chemical reaction

Factors affecting the rate of a chemical reaction :

1. the nature of the reagents;
2. concentration of reagents;
3. temperature;
4. pressure (for gas-phase reactions);
5. reaction surface area (for heterogeneous reactions);
6. catalysts or inhibitors.

4. The rate of a chemical reaction

1867 г. Гульдберг и Вааге

Закон действующих масс

СХР прямо пропорциональна произведению конц. реагентов в степенях = стехиом-ким коэфф. (для простых р-ций) и некоторым числам – для сложных р-ций.

5. Effect of Reagent Concentration on the Rate of a Chemical Reaction

For a **simple** reaction :

aA + bB = cC +dD

Mathematical expression of the law (kinetic equation):

$$V = k \cdot C_A^a \cdot C_B^b$$

V is rate of chemical reaction,
к is rate constant,
C_A and C_B is molar concentrations of reagents,
a and b is kinetic order of the reaction with respect to substance A and B

5. Effect of Reagent Concentration on the Rate of a Chemical Reaction

For a **complex** reaction :

aA + bB = cC +dD

Mathematical expression of the law (kinetic equation):

$$V = k \cdot C_A^{\alpha} \cdot C_B^{\beta}$$

α and β are private orders that are determined empirically

5. Effect of Reagent Concentration on the Rate of a Chemical Reaction

Rate constant (k)

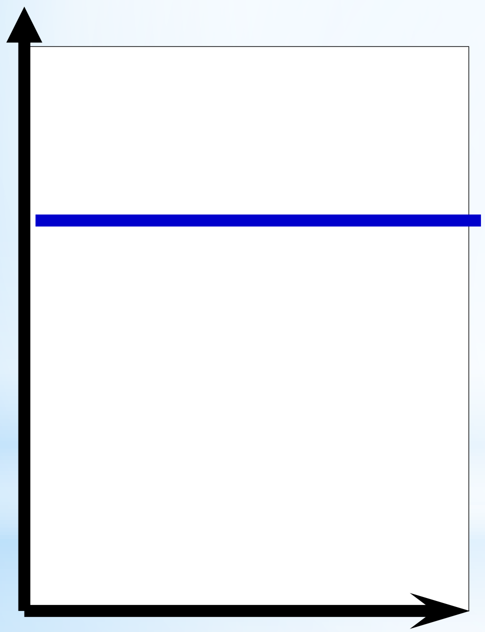
The physical meaning of k is the reaction rate at concentrations of reactants of 1 mol/L.

The rate constant (k) does not depend on the concentrations of the reagents, but **depends** on the nature of the reagents, temperature and the catalyst.

5. Effect of Reagent Concentration on the Rate of a Chemical Reaction

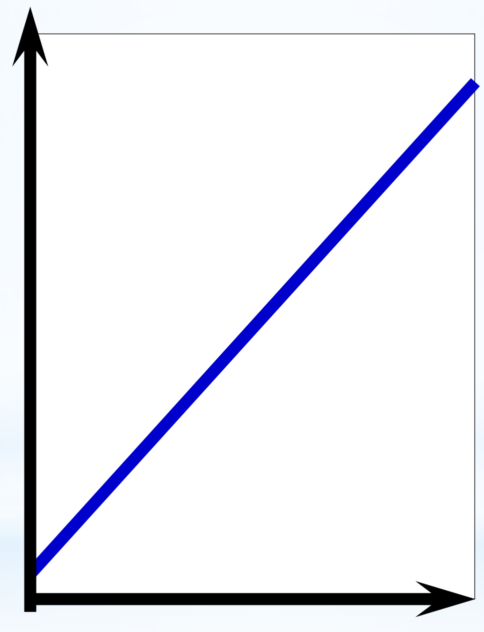
Graphic definition n

1) n=0



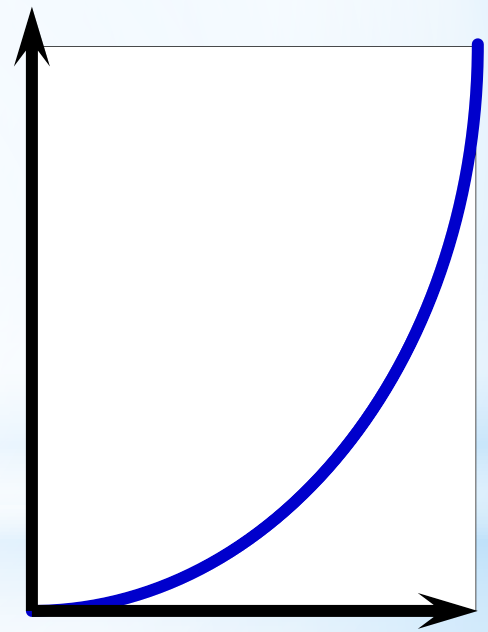
$V=k \cdot C^0$

2) n=1



$V=k \cdot C^1$

3) n>1



$V=k \cdot C^2$

5. Effect of Reagent Concentration on the Rate of a Chemical Reaction

$$CaO(к) + CO_2\ (г) = CaCO_3\ (к)$$

$$V = kC_{CO_2}^{\alpha}$$

If **solid or liquid substances** (not solutions) participate in the reaction, then their concentration in the kinetic equation is **not taken into account**

6. The effect of temperature on the reaction rate

Van't Hoff's rule: the rate of a simple reaction increases by 2-4 times with an increase in temperature by 10 degrees.

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

γ is **van't Hoff** temperature coefficient.

6. The effect of temperature on the reaction rate

Arrhenius activation theory

This is necessary for the reaction to proceed:

1) collision of molecules
2) molecules have enough energy
3) favorable orientation of molecules

6. The effect of temperature on the reaction rate

Arrhenius equation

$$k = k_0 \cdot e^{-\frac{E_a}{RT}}$$

where κ_0 is a pre-exponential factor that does not depend on T and takes into account the number of collisions of molecules.

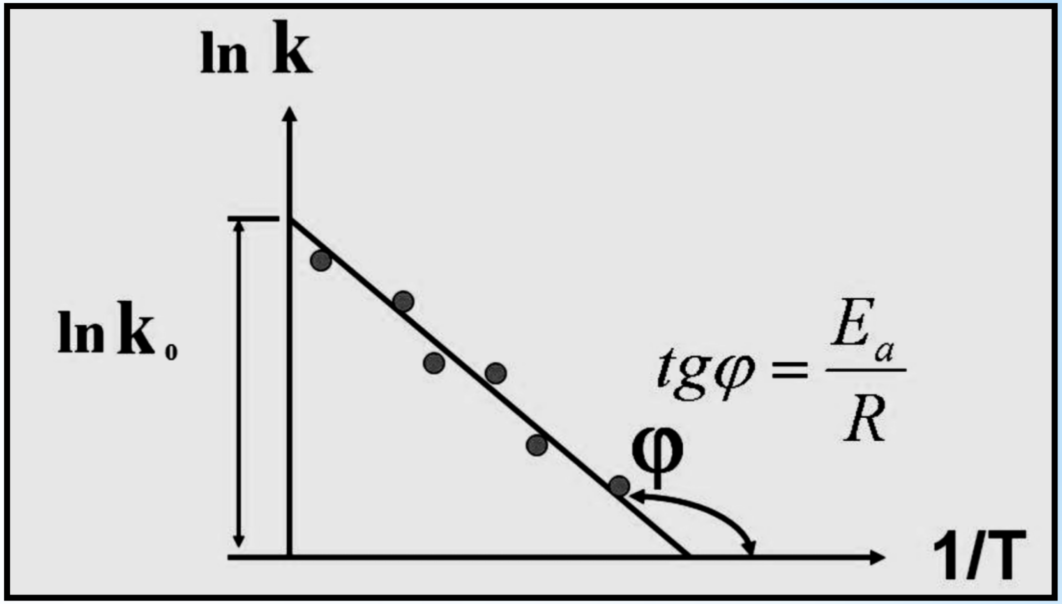
The activation energy (E_a) is the excess energy that molecules must have in order for an interaction to occur between them. **[kJ/mol]**

6. The effect of temperature on the reaction rate

1. $k_1 = k_0 \cdot e^{-\frac{E_a}{RT_1}}$

2. $\ln k_1 = \ln k_o - \frac{E_a}{RT_1}$

3. $\ln \frac{k_2}{k_1} = \frac{E_a \cdot (T_2 - T_1)}{R \cdot T_1 \cdot T_2}$



7. The phenomenon of catalysis

Catalysis is the phenomenon of changing the rate of a chemical reaction with the participation of a catalyst.

Catalysts are substances that repeatedly participate in the intermediate stages of the reaction, but leave it chemically unchanged.

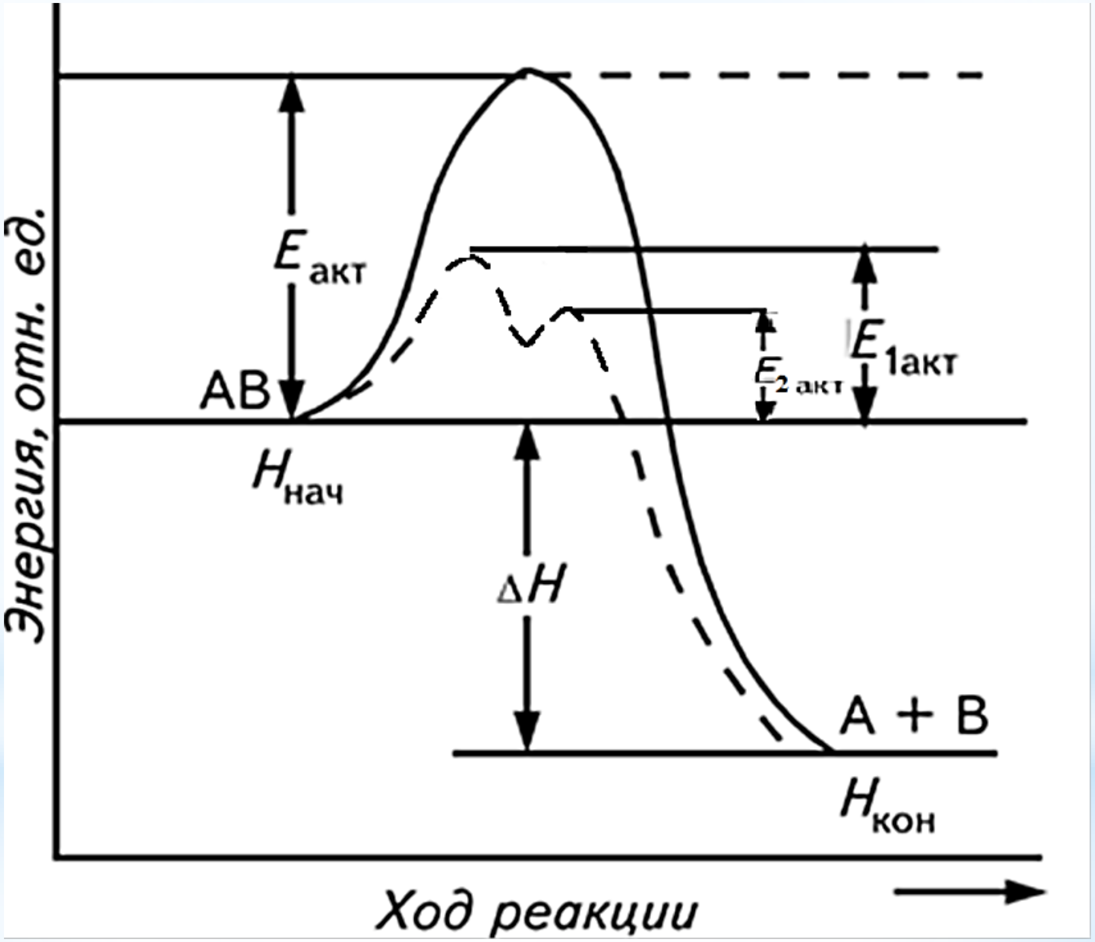
7. The phenomenon of catalysis

Homogeneous catalysis is a process in which the catalyst and reagents are in the same phase.

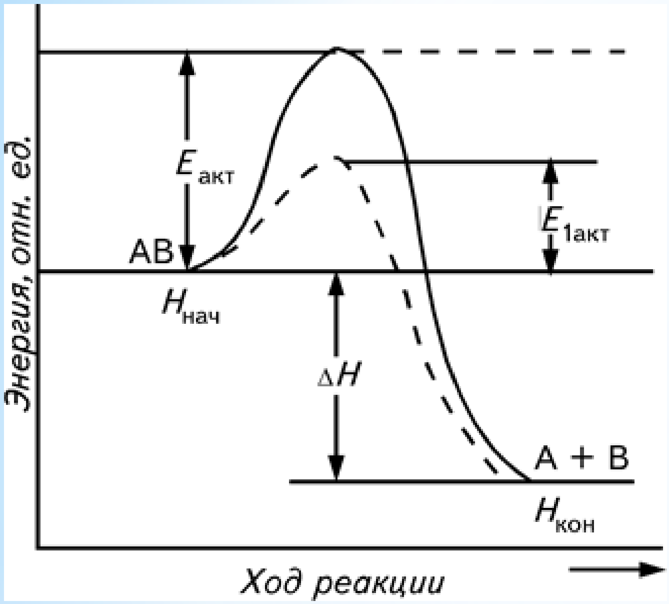
Heterogeneous catalysis is a process in which the catalyst and reactants are in different phases.

7. The phenomenon of catalysis

$$AB = A + B$$



7. The phenomenon of catalysis



$$\ln\frac{k_2}{k_1} = \frac{E_a - E_a^1}{R \cdot T}$$

E_a – энергия активации (без катализатора),

E_a^1 – энергия активации (с катализатором).

$$\frac{V_к}{V} \approx e^{\Delta E_к / RT}$$

Conclusion

1. We can predict the rate of a process by looking at the kinetics.

2. We can influence the rate of the process by determining the value of the activation energy

Home task № 1.

1. In which system the increasing of pressure will cause of the shifting equilibrium to the right?

$$2HI_{(g)} \leftrightarrow H_{2(g)} + I_{2(g)}$$

$$C_{(s)} + S_{2(g)} \leftrightarrow CS_{2(g)}$$

$$C_3H_{6(g)} + H_{2(g)} \leftrightarrow C_3H8_{(g)}$$

$$H_{2(g)} + F_{2(g)} \leftrightarrow 2HF_{(g)}$$

2. Predict the effect of increasing the temperature on the reaction:

$$H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}\ \Delta Hr = +\ 41.2\ kJ/mol$$

<u>Home task № 2.</u>

1. For the reaction $2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$ how will the rate of the reaction change if the pressure in the system is increased three times?

2. For the reaction $2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$ how will the rate of the reaction change if the concentration of the NO is increased three times?