3. MECHANISMS OF CHEMICAL REACTIONS

Problem 3-01 Reaction mechanisms

The decomposition **$NO_2Cl = NO_2 + 1/2\ Cl_2$** is a first-order reaction for which the following mechanism was proposed:

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl$$
$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

Assume that atomic chlorine is so reactive that it cannot be proved in the reaction mixture. Show that the proposed mechanism corresponds to experimental reaction order.

$$\left[-\frac{\mathrm{d}c_{NO2Cl}}{\mathrm{d}\tau} = 2\,k_1 \cdot c_{NO2Cl}\right]$$

Problem 3-02 Reaction mechanism

Mechanism of ozone decomposition in the presence of ozone can be described by the following reaction steps:

$$Cl_2 + O_3 \xrightarrow{k_1} ClO^{\bullet} + ClO_2^{\bullet}$$
$$ClO_2^{\bullet} + O_3 \xrightarrow{k_2} ClO_3^{\bullet} + \ O_2$$
$$ClO_3^{\bullet} + O_3 \xrightarrow{k_3} ClO_2^{\bullet} + 2\,O_2$$
$$ClO_3^{\bullet} + ClO_3^{\bullet} \xrightarrow{k_4} Cl_2 + 3\,O_2$$

Radical $ClO^{\bullet}$ decomposes to elements without causing a chain reaction. The rate of the first initiation step is negligibly small in comparison with the rest. Write the equation describing the time decrease of ozone concentration.

$$\left[-\frac{\mathrm{d}[O_3]}{\mathrm{d}\tau} = 2\,k_3 \cdot \left(\frac{k_1}{k_4}\right)^{1/2} \cdot [Cl_2]^{1/2} \cdot [O_3]^{3/2}\right]$$

Problem 3-03 Reaction mechanism

The decomposition of nitric oxide, $N_2O_5 = 2\ NO_2 + ½\ O_2$, proceeds probably according to the following scheme

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$
$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$
$$NO_2 + NO_3 \xrightarrow{k_3} NO_2 + NO + O_2$$
$$NO + N_2O_5 \xrightarrow{k_4} 3\ NO_2$$

NO and NO_3 are unstable intermediates. Write the rate equation of the decomposition.

$$\left[-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau} = \frac{2\,k_1 \cdot k_3}{(k_2 + k_3)} \cdot [N_2O_5]\right]$$

Problem 3-04 Reaction mechanism

The following mechanism was proposed for the reaction **N_2O_5 (g) + NO (g) = 3 NO_2** (g):

$$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$$
$$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$$
$$NO + NO_3 \xrightarrow{k_3} 2\,NO_2$$

Experiments revealed that the rate of N_2O_5 extinction is independent of NO concentration. Under which circumstances will the proposed mechanism correspond to experimentally found fact that the reaction follows the first-order kinetics?

$$\left[-\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau}=\frac{k_3\cdot k_1\cdot c_{N_2O_5}\cdot c_{NO}}{k_2\cdot c_{NO_2}+k_3\cdot c_{NO}},\ \text{for}\ k_2\cdot c_{NO_2} << k_3\cdot c_{NO}:\ -\frac{\mathrm{d}c_{N_2O_5}}{\mathrm{d}\tau}=k_1\cdot c_{N_2O_5}\right]$$

Problem 3-05 Reaction mechanisms, apparent activation energy

Certain reaction proceeds as the sequence of the following elementary steps:

$$A + B \xrightarrow{k_1} C + B$$
$$C + B \xrightarrow{k_2} A + B$$
$$C \xrightarrow{k_3} D$$

(a) Assuming that C is an unstable intermediate, which cannot be detected in the reaction mixture, write the rate law expressing the rate of product D formation.

(b) What change in this rate law will occur in case that the second elementary step is much faster than the third one? Calculate the apparent activation energy under these conditions, if you know the values activation energies: E_1^* = 15 kJ mol^{-1}, E_2^* = 40 kJ mol^{-1}, and E_3^* = 10 kJ mol^{-1}.

$$\left[\text{(a)}\ \frac{\mathrm{d}c_D}{\mathrm{d}\tau}=\frac{k_1\cdot k_3\cdot c_A\cdot c_B}{k_3+k_2\cdot c_B}\ ;\text{(b)}\ \frac{\mathrm{d}c_D}{\mathrm{d}\tau}=\frac{k_1\cdot k_3}{k_2}\cdot c_A\ \ (k_2\cdot c_B >> k_3),\ E^*=-15\ \text{kJ mol}^{-1}\right]$$

Problem 3-06 Photosynthesis

Standard reaction Gibbs energy of photosynthesis,

$$\mathbf{CO_2 + H_2O = {}^1\!/_6\, C_6H_{12}O_6 + O_2,}$$

is $\Delta_r G^{\ominus}$ = 528 kJ mol^{-1}. If you can assume that all the incident energy is used for photosynthesis, estimate the number of photons of red light (λ = 680 nm), absorbed by chlorophyll, needed to bind one molecule of carbon dioxide.

[$N_\varepsilon = 3$]

Problem 3-07 Quantum yield of a photochemical reaction

The study of the photolysis of gaseous hydrogen iodide,

$$\mathbf{2\,HI(g) = H_2(g) + I_2(g),}$$

induced by light of wavelength of 253.7 nm, revealed that absorption of energy of 307 J brought about the decomposition of $1.3\cdot10^{-3}$ mol HI. Calculate the quantum yield of this photoreaction.

[$\phi = 2$]

Problem 3-08 Quantum yield of a photochemical reaction

Quantum yield of the ethylene formation from dipropyl ketone due to the light of wavelength of 313.5 nm was found to be $\phi = 0.21$. What is number of molecules and what is number of moles of ethylene per second will arise during irradiation by a lamp which has a power of 50 W in the spectral region of interest? Assume that the sample absorbs all incident light.

[$N_{ethylene} = 1.656 \cdot 10^{19}$ molecules s^{-1} , $n_{ethylene} = 2.75 \cdot 10^{-5}$ mol s^{-1}]

Problem 3-09 Quantum yield of a photochemical reaction

The apparatus for quantum yield determination was calibrated by the measurement of the decomposition of pure uranyl oxalate. The quantum yield of the photochemical decomposition uranyl oxalate at the wavelength of incident light λ = 300 nm is known to be $\phi_{oxalate}$ = 0.57. To decompose $6.2 \cdot 10^{-3}$ mol of oxalate took 2 hours. The apparatus was then used to determine of the quantum yield of acetone decomposition. The cell was filled with pure acetone and after 4 hours of radiation (again λ = 300 nm) the amount of the decomposed acetone was $3.7 \cdot 10^{-3}$ mol. What is the quantum yield of acetone decomposition?

[$\phi_A = 0.17$]