CH103 General Chemistry II

2019 Fall semester Quiz 1 (Ch. 18)

Date: Sep 23 (Mon)   *Time: 19:00~19:45*

Professor Name	Class	Student I.D. Number	Name

*Write down the units for your answers. **Every answer <u>without</u> the proper unit gets 0.5 point deduction.**

1. The decomposition of benzene diazonium chloride $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$ follows first order kinetics. The rate constant is $4.3 \times 10^{-5} \, s^{-1}$. Write the integrated rate law and calculate its partial pressure after 10.0 hours given that initial partial pressure of $C_6H_5N_2Cl$ is 0.0088 atm. (total 8 pts)

$$P_{C_6H_5N_2Cl} = \left(P_{C_6H_5N_2Cl}\right)_0 e^{-kt} = \left(P_{C_6H_5N_2Cl}\right)_0 \exp(-kt) \ldots + 4 \, pts$$

***Simply writing the rate law (NOT the *integrated* rate law)

$$rate = k \times P_{C_6H_5N_2Cl} = k[C_6H_5N_2Cl]$$

cannot get any points.

Convert the elapsed time (10.0 h) to seconds (36000 s) and substitute it, together with the initial partial pressure and the rate constant, into the preceding equation

$$P_{C_6H_5N_2Cl} = (0.0088 \, atm) \times \exp\left((-4.3 \times 10^{-5} \, s^{-1})(36000 \, s)\right) = 0.0019 \, atm \ \ldots + 4 \, pts$$

2. The decomposition of hydroxylamine (NH_2OH) in the presence of oxygen follows the rate law:

$$-\frac{d[NH_2OH]}{dt} = k_{obs}[NH_2OH][O_2]$$

$k_{obs} = 0.237 \times 10^{-4}$ L mol^{-1} s^{-1} at 0°C and $k_{obs} = 2.64 \times 10^{-4}$ L mol^{-1} s^{-1} at 25°C.

R = 8.315 J K^{-1} mol^{-1}

Calculate E_a and the factor A for this reaction (total 8 pts)

Solution

Let us write the Arrhenius equation at two different temperatures T_1 and T_2:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad \text{and} \quad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

If the first equation is subtracted from the second, the term ln A cancels out, leaving

$$\ln k_2 - \ln k_1 = \ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \cdots +2pts$$

which can be solved for E_a. In the present case, $T_1 = 273$ K and $T_2 = 298$ K; therefore,

$$\ln \frac{2.64 \times 10^{-4}}{0.237 \times 10^{-4}} = \frac{-E_a}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{273 \text{ K}}\right)$$

$$2.410 = \frac{E_a}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}} (3.07 \times 10^{-4} \text{ K}^{-1})$$

$$E_a = 6.52 \times 10^4 \text{ J mol}^{-1} = 65.2 \text{ kJ mol}^{-1} \quad \cdots +3pts$$

Now that E_a is known, the constant A can be calculated by using data at either temperature. At 273 K,
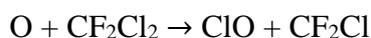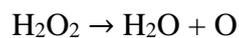
$$\ln A = \ln k_1 + \frac{E_a}{RT}$$

$$= \ln(0.237 \times 10^{-4}) + \frac{6.52 \times 10^4 \text{ J mol}^{-1}}{(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(273 \text{ K})}$$

$$= -10.65 + 28.73 = 18.08$$

$$A = e^{18.08} = 7.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^- \quad \cdots + 3pts$$

3. Consider the following reaction mechanism: (9 pts)

$$H_2O_2 \rightarrow H_2O + O$$

$$O + CF_2Cl_2 \rightarrow ClO + CF_2Cl$$

$$ClO + O_3 \rightarrow Cl + 2\ O_2$$

$$Cl + CF_2Cl \rightarrow CF_2Cl_2$$

a) What is the molecularity of each elementary step? (2 pts: no partial points)

First: unimolecular

Second: bimolecular

Third: bimolecular

Fourth: bimolecular

You must use the correct terms; simply writing the numbers or abbreviations cannot get any points.

One incorrect answer deducts all 2 points; all answers should be correct.

b) Write the overall equation for the reaction. (3 pt: no partial points – you do not need to show balancing process)
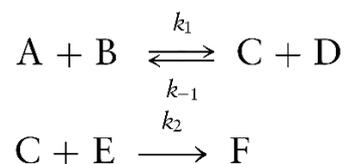
$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2 \quad \ldots\ldots +3\ pts$$
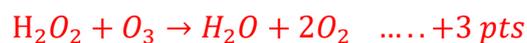
c) Identify the reaction intermediate(s). (4 pts)

O, ClO, CF$_2$Cl, and Cl

+1 pt for each reaction intermediate

4. (7 pts) Consider the following reaction mechanism:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$C + E \overset{k_2}{\longrightarrow} F$$

By making a steady-state approximation for the concentration of C, express the rate of production of the product F in terms of the concentration of A, B, D, and E.

If the concentration of intermediate C is constant (the steady state approximation), the rate of disappearance of C must equal its rate of appearance

$$k_1[A][B] = k_{-1}[C][D] + k_2[C][E] \ldots + 2 \text{ pts}$$

The rate of the reaction can be expressed in terms of the rate of appearance of a product, for example,
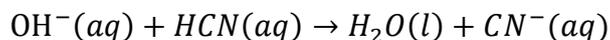
$$\text{rate} = \frac{d[F]}{dt} = k_2[E][C] \ldots + 2 \text{ pts}$$

Solve the steady-state equation for [C] and substitute the answer in the preceding equation:

$$\text{rate} = \frac{k_1 k_2[A][B][E]}{k_2[E] + k_{-1}[D]} \ldots + 3 \, pts$$

If the final rate equation is correct, all 7 points are given. If not, partial points can be given according to the criteria above.

5. (Total 8 pts) The rate for the reaction

$$OH^-(aq) + HCN(aq) \rightarrow H_2O(l) + CN^-(aq)$$

is first order in both OH⁻ and HCN concentrations, and the rate constant k at 25 °C is 3.7 x 10⁹ mol⁻¹ s⁻¹.

(a) Let C_0 = initial concentration of OH⁻, C = concentration of OH⁻ at time t, and k = rate constant. Derive an equation that shows relationship between C_0 and C. Assume that initial concentration of HCN is also C_0. (5 pts)

$$\text{rate} = \frac{-d[OH^-]}{dt} = k[OH^-][HCN]$$

Throughout the reaction $[OH^-] = [HCN] = C$. Therefore,

$$\frac{-dC}{dt} = kC^2 \dots + 2\text{ pts}$$

Integrating this equation and inserting C_0 yields the following equation:

$$\frac{1}{C} = \frac{1}{C_0} + kt \dots + 3\text{ pts}$$

OH-와 HCN의 초기 농도가 같다는 전제 조건이 빠진 관계로 전원 정답 처리

All students get the full five points. There should have been a condition: initial concentration of OH- and HCN is equivalent.

(b) Suppose 0.500 L of a 0.0020 M NaOH solution is rapidly mixed with the same volume of a 0.0020 M HCN solution. Calculate the time (in seconds) required for the OH⁻ concentration to decrease to a value of 1.0 x 10⁻⁴ M. (3 pts)

Substitute the given values in the problem:

$$\frac{1}{C} = \frac{1}{C_0} + kt \rightarrow \frac{1}{0.00010\ M} - \frac{1}{0.0010\ M} = (3.7 \times 10^9 L\ mol^{-1}\ s^{-1}) \times t$$

$$\therefore t = 2.4 \times 10^{-6}\ s \dots + 3\text{ pts}$$