

## CH103 General Chemistry II

### 2019 Fall semester Quiz 2 (Ch. 18)

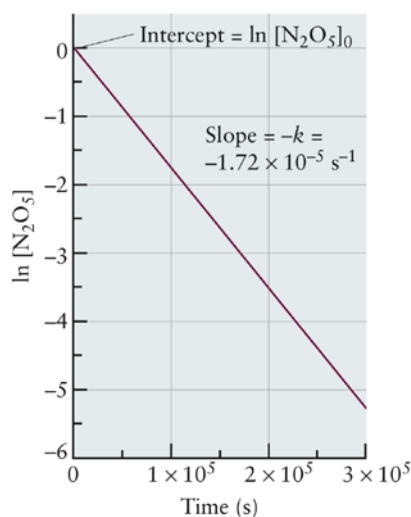
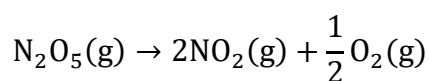
Date: Oct 7 (Mon)

Time: 19:00~19:45

Professor Name	Class	Student I.D. Number	Name

\*Write down the units for your answers. **Every answer without the proper unit gets 0.5 point deduction.**

1. (Total 9 pts) Consider the following graph, which demonstrates the decomposition of  $\text{N}_2\text{O}_5$  against time in a logarithmic scale.



(a) (3 pts) This reaction follows the \_\_\_\_\_ order kinetics. Fill in the blank.

First ...+3 pts

(b) (3 pts) Derive an integrated rate law for this reaction.

$$\frac{dc}{dt} = -kc \dots + 1 \text{ pt}$$

$$\frac{1}{c} dc = -k dt$$

$$\int_{c_0}^c \frac{1}{c} dc = -k \int_0^t dt$$

$$\ln \frac{c}{c_0} = -kt$$

$$c = c_0 e^{-kt} \dots + 2 \text{ pts}$$

(c) (3 pts) What is the half-life of  $N_2O_5$ ?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{1.72 \times 10^{-5} \text{ s}^{-1}} = 40300 \text{ s ... + 3 pts}$$

2. (Total 8 pts) In the reaction of pyridine ( $C_5H_5N$ ) and methyl iodide ( $CH_3I$ ) in benzene at  $25^\circ C$ , the following initial reaction rates were measured for different initial concentrations:

$[C_5H_5N]$ ( $\text{mol L}^{-1}$ )	$[CH_3I]$ ( $\text{mol L}^{-1}$ )	Rate ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
$1.00 \times 10^{-4}$	$1.00 \times 10^{-4}$	$7.50 \times 10^{-7}$
$2.00 \times 10^{-4}$	$2.00 \times 10^{-4}$	$3.00 \times 10^{-6}$
$2.00 \times 10^{-4}$	$4.00 \times 10^{-4}$	$6.00 \times 10^{-6}$

(a) (2 pts) Write the rate expression for this reaction.

$$\text{rate} = k[C_5H_5N][CH_3I] \dots + 2 \text{ pts}$$

(b) (3 pts) Calculate the rate constant  $k$  and give its units.

\* Students can use any of the three data points.

$$7.5 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(1.00 \times 10^{-4} \text{ mol L}^{-1})(1.00 \times 10^{-4} \text{ mol L}^{-1}) \text{ or}$$

$$3.00 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} = k(2.00 \times 10^{-4} \text{ mol L}^{-1})(2.00 \times 10^{-4} \text{ mol L}^{-1}) \text{ or}$$

$$6.00 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} = k(2.00 \times 10^{-4} \text{ mol L}^{-1})(4.00 \times 10^{-4} \text{ mol L}^{-1})$$

$$k = 75 \text{ L mol}^{-1} \text{ s}^{-1} \dots + 3 \text{ pts}$$

(c) (3 pts) Predict the initial reaction rate for a solution in which  $[C_5H_5N] = 8.00 \times 10^{-8} \text{ M}$  and  $[CH_3I] = 2.00 \times 10^{-4} \text{ M}$ .

$$\begin{aligned} \text{rate} &= (75 \text{ L mol}^{-1} \text{ s}^{-1})(8.0 \times 10^{-8} \text{ M})(2.0 \times 10^{-4} \text{ M}) \\ &= 1.2 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1} \dots + 3 \text{ pts} \end{aligned}$$

3. (Total 9 pts) The rate constant of the first-order reaction  $2\text{N}_2\text{O}(g) \rightarrow 2\text{N}_2(g) + \text{O}_2(g)$  is  $0.76 \text{ s}^{-1}$  at  $1000 \text{ K}$  and  $0.87 \text{ s}^{-1}$  at  $1030 \text{ K}$ .

(a) (3 pts) Calculate the activation energy ( $E_a$ ) of the reaction.

$$k = A \times \exp\left(-\frac{E_a}{RT}\right) \dots + 1 \text{ pt}$$

$$\ln k_1 - \ln k_2 = \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \times \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\begin{aligned} \therefore E_a &= \ln\left(\frac{k_1}{k_2}\right) \times R \times \frac{1}{\frac{1}{T_2} - \frac{1}{T_1}} = \ln\left(\frac{0.76}{0.87}\right) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \frac{1}{\frac{1}{1030\text{K}} - \frac{1}{1000\text{K}}} \\ &= 38.6 \text{ kJ mol}^{-1} \dots + 2 \text{ pts} \end{aligned}$$

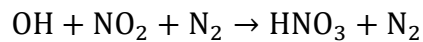
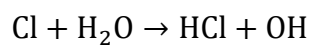
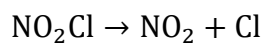
(b) (3 pts) Calculate the pre-exponential factor A of the reaction.

$$A = \frac{k}{\exp\left(-\frac{E_a}{RT}\right)} = \frac{0.76 \text{ s}^{-1}}{\exp\left(\frac{-38.6 \times 1000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1000 \text{ K}}\right)} = 78.9 \text{ s}^{-1} \dots + 3 \text{ pts}$$

(c) (3 pts) What would be the predicted rate constant at  $1100 \text{ K}$ ?

$$k \text{ at } 1100 \text{ K} = 78.9 \text{ s}^{-1} \times \exp\left(\frac{-38.6 \times 1000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1100 \text{ K}}\right) = 1.16 \text{ s}^{-1} \dots + 3 \text{ pts}$$

4. (Total 6 pts) Consider the following reaction mechanism:



a) Write the overall equation for the reaction. (3 pts: no partial points – you do not need to show balancing process)



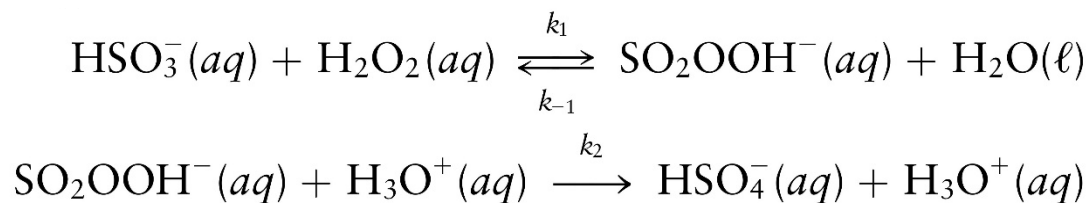
b) Identify the reaction intermediate(s). (3 pts)

$\text{NO}_2$ ,  $\text{Cl}$ ,  $\text{OH}$

Each missing species gets 1-point deduction.

Each species that is NOT a reaction intermediate gets 1-point deduction.

5. (8 pts) Consider the following reaction mechanism:



By making a steady-state approximation for the concentration of  $\text{SO}_2\text{OOH}^-$  (aq.), express the rate of production of  $\text{HSO}_4^-$  (aq.) in terms of the concentrations of  $\text{HSO}_3^-$  (aq.),  $\text{H}_2\text{O}_2$  (aq.), and  $\text{H}_3\text{O}^+$  (aq.).

According to the steady-state approximation,

$$\frac{d[\text{SO}_2\text{OOH}^-]}{dt} = \kappa_1 [\text{HSO}_3^-] [\text{H}_2\text{O}_2] - \kappa_{-1} [\text{SO}_2\text{OOH}^-] - \kappa_2 [\text{SO}_2\text{OOH}^-] [\text{H}_3\text{O}^+] = 0$$

... +3 pts

Solving for the concentration of  $\text{SO}_2\text{OOH}^-$  gives

$$[\text{SO}_2\text{OOH}^-] = \frac{\kappa_1 [\text{HSO}_3^-] [\text{H}_2\text{O}_2]}{\kappa_{-1} + \kappa_2 [\text{H}_3\text{O}^+]}$$

... +2 pts

so that the reaction rate is

$$\text{rate} = \kappa_2 [\text{SO}_2\text{OOH}^-] [\text{H}_3\text{O}^+] = \frac{\kappa_1 \kappa_2 [\text{HSO}_3^-] [\text{H}_2\text{O}_2] [\text{H}_3\text{O}^+]}{\kappa_{-1} + \kappa_2 [\text{H}_3\text{O}^+]}$$

... +3 pts