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SKMM 4453 **Chemical Kinetics Assignment** **SEM 2016/17-I**

1. The reaction rate of methane in a four-step, quasi-global mechanism of propane oxidation is shown in equation (1) where $a, b, and\ c$ are 0.9, 1.18, and - 0.37 respectively. $[X]$ is molar concentration of species X.

$$\frac{d[C_2H_4]}{dt} = -10^x \exp(-E_A/R_u T)[C_2H_4]^a[O_2]^b[C_nH_{2n+2}]^c, \qquad (1)$$

i) Explain about the self-inhibating phenomenon of the reaction in (1).
ii) What is the total order of the C_2H_4 consumption?
iii) What are the orders of reaction with respect to each species shown in equation (1)

2. Given the following three-step mechanism where B, B*, M, and k are stable species, intermediate species, third body, and reaction rate constant respectively.

$$B + M \overset{k_f,k_b}{\longleftrightarrow} B^* + M$$
$$B^* \overset{k_{f'}}{\longrightarrow} \text{products}$$

i) Using steady state approximation, find the differential equation to express the rate of production of products as a function of stable species and third body concentrations. State all your assumptions.
ii) Explain the low and high pressure effects on the total order of reaction found in (i)

Problems from textbook (Turn's) as attached

1. Problem 4-6
2. Problem 4-7
3. Problem 4-16

QUESTIONS AND PROBLEMS

4.1 Make a list of all of the bold-faced words in Chapter 4 and discuss their meanings.

4.2 Several species and their structural forms are given below. Using sketches of colliding molecules, show that the reaction $2H_2 + O_2 \rightarrow 2H_2O$ is highly improbable based on simple collisions and the given structures.

H_2 : H—H
O_2 : O=O
H_2O : H—O—H

4.3 Consider the reaction $H_2 + O_2 \rightarrow HO_2 + H$. Show that this is likely to be an elementary reaction. Use a sketch, as in problem 4.2. The structure of the hydroperoxy radical is H–O–O.

4.4 Consider the reaction $CH_4 + O_2 \rightarrow CH_3 + HO_2$. Although a CH_4 molecule may collide with an O_2 molecule, a chemical reaction may not necessarily occur. List two factors important in determining whether or not a reaction occurs during a collision.

4.5 Consider the overall oxidation reaction of propane:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O.$$

The following global mechanism has been proposed for this reaction:

$$\text{Reaction rate} = 8.6 \cdot 10^{11} \exp(-30/R_u T)[C_3H_8]^{0.1}[O_2]^{1.65},$$

where CGS units (cm, s, gmol, kcal, K) are employed.

A. Identify the order of the reaction with respect to propane.
B. Identify the order of the reaction with respect to O_2.
C. What is the overall order of the global reaction?
D. Identify the activation energy for the reaction.

4.6 In a global, single-step mechanism for butane combustion, the reaction order with respect to butane is 0.15 and with respect to oxygen is 1.6. The rate coefficient can be expressed in Arrhenius form: the pre-exponential factor is $4.16 \cdot 10^9$ $[(\text{kmol/m}^3)^{-0.75}/\text{s}]$ and the activation energy is 125,000 kJ/kmol. Write out an expression for the rate of butane destruction, $d[C_4H_{10}]/dt$.

4.7 Using the results of problem 4.6, determine the volumetric mass oxidation rate of butane, in kg/s-m^3, for a fuel–air mixture with an equivalence ratio of 0.9, temperature of 1200 K, a pressure of 1 atm.

4.8 Classify the following reactions as being either global or elementary. For those identified as elementary, further classify them as unimolecular, bimolecular, or termolecular. Give reasons for your classification.

B. Write out a complete expression for the Br-atom reaction rate, d[Br]/dt.

C. Write out an expression that can be used to determine the steady-state concentration of the hydrogen atom, [H].

4.16 Consider the following chain-reaction mechanism for the high-temperature formation of nitric oxide, i.e., the Zeldovich mechanism:

$$O + N_2 \overset{k_{1f}}{\rightarrow} NO + N \qquad \text{Reaction 1}$$

$$N + O_2 \overset{k_{2f}}{\rightarrow} NO + O \qquad \text{Reaction 2}$$

A. Write out expressions for d[NO]/dt and d[N]/dt.

B. Assuming N atoms exist in steady state and that the concentrations of O, O_2, and N_2 are at their equilibrium values for a specified temperature and composition, simplify your expression obtained above for d[NO]/dt for the case of negligible reverse reactions. (*Answer*: $d[NO]/dt = 2k_{1f}[O]_{eq}[N_2]_{eq}$.)

C. Write out the expression for the steady-state N-atom concentration used in part B.

D. For the conditions given below and using the assumptions of part B, how long does it take to form 50 ppm (mole fraction $\cdot 10^6$) of NO?

$$T = 2100\,K,$$
$$\rho = 0.167\,kg/m^3,$$
$$MW = 28.778,$$
$$\chi_{O,eq} = 7.6 \cdot 10^{-5} \text{ (mole fraction)},$$
$$\chi_{O_2,eq} = 3.025 \cdot 10^{-3} \text{ (mole fraction)},$$
$$\chi_{N_2,eq} = 0.726 \text{ (mole fraction)},$$
$$k_{1f} = 1.82 \cdot 10^{14} \exp[-38,370/T(K)] \text{ with units of cm}^3\text{/gmol-s}.$$

E. Calculate the value of the reverse reaction rate coefficient for the first reaction, i.e., $O + N_2 \leftarrow NO + N$, for a temperature of 2100 K.

F. For your computations in part D, how good is the assumption that reverse reactions are negligible? Be quantitative.

G. For the conditions of part D, determine numerical values for [N] and χ_N. (*Note*: $k_{2f} = 1.8 \cdot 10^{10}\, T \exp(-4680/T)$ with units of cm^3/gmol-s.)

4.17 When the following reaction is added to the two reactions in problem 4.16, the NO formation mechanism is called the extended Zeldovich mechanism:

$$N + OH \overset{k_{3f}}{\rightarrow} NO + H.$$

With the assumption of equilibrium concentrations of O, O_2, N_2, H, and OH applied to this three-step mechanism, find expressions for: