

SKMM 4453

Chemical Kinetics Assignment

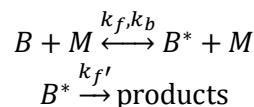
SEM 2016/17-I

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 .

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

- i) Explain about the self-inhibiting 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.



- 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)

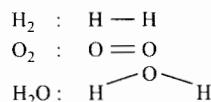
Problems from textbook (Turn's) as attached

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.

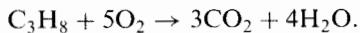
4.2 Several species and their structural forms are given below. Using sketches of colliding molecules, show that the reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ is highly improbable based on simple collisions and the given structures.



4.3 Consider the reaction $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{H}$. 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 $\text{H}-\text{O}-\text{O}$.

4.4 Consider the reaction $\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_3 + \text{HO}_2$. 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:



The following global mechanism has been proposed for this reaction:

$$\text{Reaction rate} = 8.6 \cdot 10^{11} \exp(-30/R_u T) [\text{C}_3\text{H}_8]^{0.1} [\text{O}_2]^{1.65},$$

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

- Identify the order of the reaction with respect to propane.
- Identify the order of the reaction with respect to O_2 .
- What is the overall order of the global reaction?
- Identify the activation energy for the reaction.

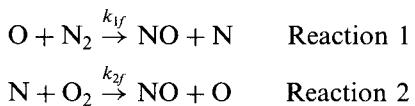
4.6 In a global, single-step mechanism for butane combustion, the reaction order with respect to butane is 0.15 and with respect to oxygen is 1.6. The rate coefficient can be expressed in Arrhenius form: the pre-exponential factor is $4.16 \cdot 10^9$ $[(\text{kmol}/\text{m}^3)^{0.75}/\text{s}]$ and the activation energy is 125,000 kJ/kmol. Write out an expression for the rate of butane destruction, $d[\text{C}_4\text{H}_{10}]/dt$.

4.7 Using the results of problem 4.6, determine the volumetric mass oxidation rate of butane, in $\text{kg}/\text{s}\cdot\text{m}^3$, 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, $d[\text{Br}]/dt$.
- C. Write out an expression that can be used to determine the steady-state concentration of the hydrogen atom, $[\text{H}]$.

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



- A. Write out expressions for $d[\text{NO}]/dt$ and $d[\text{N}]/dt$.
- 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 $d[\text{NO}]/dt$ for the case of negligible reverse reactions. (Answer: $d[\text{NO}]/dt = 2k_{1f} [\text{O}]_{eq} [\text{N}_2]_{eq}$)
- 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?

$$T = 2100 \text{ K},$$

$$\rho = 0.167 \text{ kg/m}^3,$$

$$MW = 28.778,$$

$$\chi_{\text{O},eq} = 7.6 \cdot 10^{-5} \text{ (mole fraction)},$$

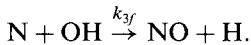
$$\chi_{\text{O}_2,eq} = 3.025 \cdot 10^{-3} \text{ (mole fraction)},$$

$$\chi_{\text{N}_2,eq} = 0.726 \text{ (mole fraction)},$$

$$k_{1f} = 1.82 \cdot 10^{14} \exp[-38,370/T(K)] \text{ with units of cm}^3/\text{gmol}\cdot\text{s}.$$

- E. Calculate the value of the reverse reaction rate coefficient for the first reaction, i.e., $\text{O} + \text{N}_2 \leftarrow \text{NO} + \text{N}$, 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 $[\text{N}]$ and χ_{N} . (Note: $k_{2f} = 1.8 \cdot 10^{10} T \exp(-4680/T)$ with units of $\text{cm}^3/\text{gmol}\cdot\text{s}$.)

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:



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