Physical chemistry

Tutorial 4 (*22-10-2013*)

1. The proposed mechanism for the reaction for the decomposition of N_2O_5 is as given below. Experimentally, the rate was found out as rate= k $[N_2O_5]$. Account for the rate law.

   $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$, $\upsilon = k [N_2O_5]$

   (1) $N_2O_5 \rightleftharpoons NO_2 + NO_3$ k_1, k'_1
   (2) $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ k_2
   (3) $NO + N_2O_5 \rightarrow NO_2 + NO_2 + NO_2$ k_3

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 23, page 863, Problem No: 23.1b)

2. Consider the following chain mechanism:

   (1) $A_2 \longrightarrow A^{\bullet} + A^{\bullet}$

   (2) $A^{\bullet} \longrightarrow B + C$

   (3) $A^{\bullet} + P \longrightarrow B^{\bullet}$

   (4) $A^{\bullet} + B^{\bullet} \longrightarrow P$

   Use the steady state approximation to deduce that the rate law for the consumption of A_2.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 23, page 864, Problem No: 23.5b)

3. Calculate the collision frequency, z, and the collision density, Z, in carbon monoxide, R = 180 pm at 25^0C and 100 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume?

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 904, Problem No: 24.1b)

4. Calculate the magnitude of the diffusion-controlled rate constant at 298 K for a species in (a) decylbenzene, (b) concentrated sulfuric acid. The viscosities are 3.36 cP and 27 cP, respectively.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 905, Problem No: 24.6b)

5. A rate constant is found to fit the expression $k_2 = (6.45 \times 10^{13}) \exp[-(5375\ K)/T]\ dm^3mol^{-1}s^{-1}$ near 25^0C. Calculate $\Delta^{\ddagger}G$ for the reaction at 25^0C.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 24, page 905, Problem No: 24.11b)

6. Calculate the frequency of molecular collisions per square centimeter of surface in a vessel containing a)Nitrogen b) methane at 25^0C when the pressure is (i) 10 Pa (ii) 0.150 μ Torr.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.1b)

7. The adsorption of a gas is described by the Langmuir isotherm with K = 0.777 kPa-1 at 25^0C. Calculate the pressure at which the fractional surface coverage is (a) 0.20, (b) 0.75.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.8 b)

8. A certain solid sample adsorbs 0.63 mg of CO when the pressure of the gas is 36 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 4.0 kPa and the temperature is 300 K is 0.21 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.

   (Physical Chemistry, ***Atkins, P.W.; Paula, J. D.***, 8th ed.; Oxford: New York, 2006; Chapter 25, page 953, Problem No: 25.9 b)