Kinetics & Mechanism

Physical Chemistry Tutorials

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Question 1

a) Define the following terms which relate to the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

i. the rate of reaction

ii. the rate expression or rate law

iii. the rate constant

b) A gas phase reaction of the type $2A \rightarrow B$ is monitored at 298 K by measuring the total pressure ($P_t = P_A + P_B$). Note that at t=0, the pressure is due to A only.

t / s	0	100	200	300	400
P_t / Torr	400	322	288	268	256

i. Derive an expression that gives the pressure of A, P_A, in terms of the total pressure P_t.

ii. Show that the data are consistent with a second order reaction.

iii. Show that the rate constant at 298 K is $k_2 = 8.06 \times 10^{-6}$ Torr^{-1}s^{-1}

iv. If the rate constant at 37°C is $k_2 = 1.73 \times 10^{-5}$ Torr^{-1}s^{-1}, show how to calculate the activation energy of the reaction.

Question 2

The kinetics of the thermal decomposition of ozone can be accounted for by the following mechanism:

(1)	$O_3 \rightarrow O_2 + O$	k_1
(2)	$O + O_3 \rightarrow O_2 + O_2$	k_2
(3)	$O + O_2 + M \rightarrow O_3 + M$	k_3

a) Show that the steady state concentration of oxygen atoms is given by

$$[O] = \frac{k_1[O_3]}{k_2[O_3] + k_3[O_2][M]}$$

b) Why is the species M included in both sides of reaction (3)?

c) Show that the rate of disappearance of ozone according to the above mechanism is

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_2[O_3] + k_3[O_2][M]}$$

d) Outline the assumptions upon which the use of the steady-state approximation is based. Are these assumptions justified?

Question 3

a) Explain what is meant by the half-life of a chemical reaction. The reaction $OH + C_2H_6 \rightarrow H_2O + C_2H_5$ was studied at 300K. For initial concentrations $[OH]_0 = [C_2H_6]_0$

= a_0, show that the half life of OH radicals is given by $(a_0k_1)^{-1}$, where k_1 is the bimolecular rate constant for the reaction.

b) For initial concentrations $[OH]_0$ = $[C_2H_6]_0$ = 1.5 x 10^{-10} mol dm^{-3}, the half life at 300 K was found to be 44 s. Determine the OH radical half life when $[OH]_0$ = 1.5 x 10^{-10} mol dm^{-3} and $[C_2H_6]_0$ = 1.5 x 10^{-7}mol dm^{-3} (i.e. in great excess over $[OH]_0$).

c) For $[OH]_0$ = $[C_2H_6]_0$ = 1.5 x 10^{-10} mol dm^{-3}, the half life $t_{1/2}$ of OH varies with temperature as shown in the table below. Deduce what you can from these data.

T / K	300	450	900
$t_{1/2}$ / s	44	12	1.85

d) For the recombination reaction represented by the stoichiometric equation O + O + M $\rightarrow$ O_2 + M the half life of oxygen atoms increases with increasing temperature. Account for this behaviour