물리화학2 숙제 2 - 10월 7일

(2008년 10월 14일 수업 전 제출)

1. (1) Distinguish between a pre-equilibrium approximation and a steady-state approximation.

(2) A first-order decomposition reaction is observed to have the following rate constants at the indicated temperatures. Estimate the activation energy.

$k/(10^{-3})s^{-1}$	2.46	45.1	576
θ/℃	0	20.0	40.0

(3) Distinguish between a primary and a second kinetic isotope effect.

2. A reacts to form either B or C according to,

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

(1) Derive equations for the concentrations of [B] and [C] as functions of time. (at t=0, $[A]=[A]_0$, $[B]=[B]_0=0$, $[C]=[C]_0=0$)

(2) Express the half life of A, $t_{1/2}$ for the reaction terms of k_1 and k_2 ?

(3) Show that E_a the observed activation energy for the disappearance of A, is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Where E_1 is the activation energy for the first reaction and E_2 is the activation energy for the second reaction.

3. There is a reaction of 1st order in forward and 2nd order in reverse.

$$A \underset{k_b}{\overset{k_a}{\rightleftharpoons}} B + C$$

Derive a relaxation time constant (τ) to be $\dfrac{1}{k_a + 2k_b[B]_{eq}}$

4. The reaction mechanism

$$A_2 \rightleftharpoons A + A \text{ (fast)}$$

$$A + B \longrightarrow P \text{ (slow)}$$

involves an intermediate A. Deduce the rate law for the reaction.

5. 논문 (Orkin et al., J. Phys. Chem., 1997, 101:174)에서 다음과 같은 hydroxyl 라디칼과 chlorobromomethane 사이의 반응에 대한 반응 속도 상수가 결정되었다.

$$OH\cdot + CH_2BrCl \rightarrow \text{생성물}$$

이 반응에 대하여 얻어진 자료는 다음 표와 같다.

T(K)	k [cm^3/(molecule·second)]
298	1.11×10^{-13}
313	1.34×10^{-13}
330	1.58×10^{-13}

(1) 그래프를 작성하여 Arrhenius 식이 성립함을 확인하고, A와 E_A를 결정하시오.
(2) 앞의 결과에서 얻은 정보를 이용하여 370K 에서의 속도 상수를 계산하시오. 이것을 실험적으로 얻어진 값 2.10×10^{-13} cm^3/(molecule·second) 과 비교하시오.