

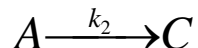
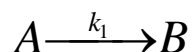
물리화학2 숙제 2 - 10월 7일
(2008년 10월 14일 수업 전 제출)

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.

$k/(10^{-3})\text{s}^{-1}$	2.46	45.1	576
$\theta/^{\circ}\text{C}$	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,

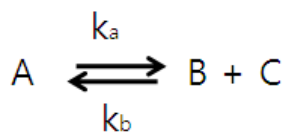


- (1) Derive equations for the concentrations of [B] and [C] as functions of time. (at $t=0$, $[A]=[A]_0$, $[B]=[B]_0=0$, $[C]=[C]_0=0$)
- (2) Express the half life of A, $t_{1/2}$ for the reaction terms of k_1 and k_2 ?
- (3) Show that E_a the observed activation energy for the disappearance of A, is given by

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

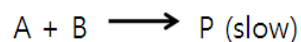
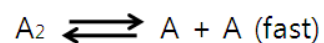
Where E_1 is the activation energy for the first reaction and E_2 is the activation energy for the second reaction.

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



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

4. The reaction mechanism



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.



이 반응에 대하여 얻어진 자료는 다음 표와 같다.

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

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