



Ex. 9

For an opposite reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$, given $k_1 = 0.006 \text{ min}^{-1}$, $k_{-1} = 0.002 \text{ min}^{-1}$. Only A existed at the beginning, $c_{A0} = 1 \text{ mol} \cdot \text{dm}^{-3}$, try to calculate

- (1) time needed when the concentrations of A and B are the same
- (2) the concentrations of A and B after 100 mins

$$(k_1 + k_{-1})t = \ln \frac{x_e}{x_e - x}$$

$$K_c = \frac{x_e}{c_{A0} - x_e} = \frac{k_1}{k_{-1}} = 3 \quad x_e = 0.75 \text{ mol} \cdot \text{L}^{-1}$$

(1) When $x = 0.5 \text{ mol} \cdot \text{L}^{-1}$, $t = 137 \text{ min}^{-1}$

(2) After 100 min, $c_B = x = 0.413 \text{ mol} \cdot \text{L}^{-1}$, $c_A = 0.587 \text{ mol} \cdot \text{L}^{-1}$



Ex. 11

A certain drug becomes ineffective when it decomposes by 30%. It has been measured that the drug decomposes 0.0069% and 0.35% per hour at 298.15K and 343.15K, and the decomposition rate of this drug is proportional to its concentration. At what temperature should the drug be stored to ensure its effectiveness within one year?



Ex. 12

For a first-order opposite reaction, $A \xrightleftharpoons[k_{-1}]{k_1} B$

The rate coefficient of the forward reaction and the equilibrium constant can be expressed as:

$$\lg(k_1/s^{-1}) = -\frac{2000}{T/K} + 4 \qquad \lg K = \frac{2000}{T/K} - 4$$

At the beginning of the reaction, $C_{A0}=0.5\text{mol/L}$, $C_{B0}=0.05\text{mol/L}$, try to calculate:

- (1) The activation energy of the backward reaction;
- (2) 400K, the concentration of A and B after 10s?
- (3) 400K, the equilibrium concentration of A and B?



TEST 1

The decomposition of a certain drug belongs to first order reactions. The relation between rate coefficient and temperature can be expressed as:

$$\ln(k/h^{-1}) = -\frac{8938}{T / K} + 20400$$

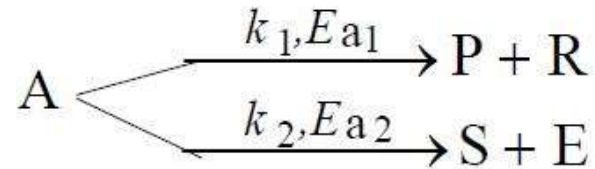
Try to calculate:

- (1) the rate coefficient at 303K?
- (2) Suppose that the drug becomes ineffective when it decomposes by 30%, how long can the drug be stored at 303K to ensure its effectiveness?
- (3) At what temperature should the drug be stored to ensure its effectiveness within 2 years?



Ex. 13

The following parallel reaction is performed in an isochoric vessel



- (1) At 323K, $c_p:c_s=2$; the conversion ratio of A was determined to be 50% after 10 mins; and the conversion ratio changed into 75% after further reacting for 10 mins. Try to calculate k_1 and k_2 ?
- (2) At 333K, $c_p:c_s=3$. try to calculate $E_{a,1}-E_{a,2}$



Ex. 14

The following gas reaction is performed in an isochoric vessel at 398K.



Only A was presented at the initial time. The total pressure of the system was measured to be 24.58kPa after 10mins and the corresponding molar fraction of A was 0.1085. Try to calculate:

- (1) Conversion ratio of A?
- (2) Rate coefficient?
- (3) Half-life?



Ex. 15

The reaction rate equation of reaction $A + 2B \rightarrow P$ can be expressed as

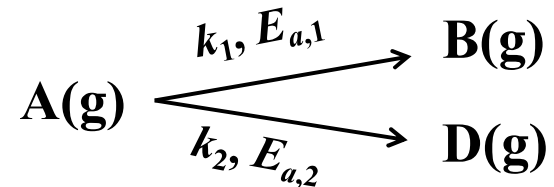
$$-\frac{dc_A}{dt} = k_A c_A^{0.5} c_B^{1.5}$$

- (1) when the initial concentrations of A and B are $0.10 \text{ mol} \cdot \text{dm}^{-3}$ and $0.20 \text{ mol} \cdot \text{dm}^{-3}$, the concentration of A is $c_A = 0.010 \text{ mol} \cdot \text{dm}^{-3}$ after reaction proceeding for 20s at 300K. calculate the concentration of A after further reacting for 20s
- (2) calculate the rate coefficients k_A and k_B at 300K
- (3) the initial concentrations of A and B are the same as those in condition (1). the concentration of A is $c_A = 3.90 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ after reaction proceeding for 20s at 400K. calculate the activation energy? (the activation energy is considered as a constant between 300-400K)



TEST 3

The following parallel reaction is performed at 1000K



given $k_1=0.0030\text{s}^{-1}$ and $k_2=0.0025\text{s}^{-1}$. (Suppose that only A was presented at the beginning)

Try to calculate:

- (1) time needed to consume 99% A
- (2) the ratio $c_B:c_D$ and the yield of B at 1000K
- (3) given $E_{a,1}=80\text{kJ/mol}$ and $E_{a,2}=90\text{kJ/mol}$, when $c_B:c_D = 3.6$, try to estimate the reaction temperature?
- (4) Calculate the apparent activation energy



Ex. 17

Compound A decomposed in solution to give N₂. the measured volume of N₂ at various reaction time was determined and listed as follows. Try to determine the rate coefficient of the reaction?

t / min	0	100	200	300	410	∞
V / cm^3	0	15.76	28.17	37.76	45.88	69.84

$$k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_A} = \frac{1}{t} \ln \frac{V_\infty - V_0}{V_\infty - V_t}$$

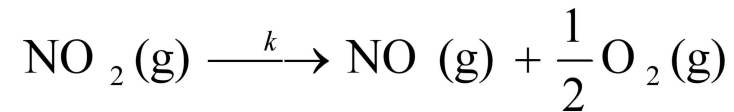
t / min	100	200	300	410
$k_A \times 10^3 / \text{min}^{-1}$	2.56	2.58	2.59	2.61

$$\bar{k}_A = 2.59 \times 10^{-3} \text{ min}^{-1}$$



Ex. 19

The rate equation of the following reaction is: $-\frac{dc_{\text{NO}_2}}{dt} = kc_{\text{NO}_2}^2$



The relation between the rate coefficient and temperature can be described as

$$\lg[k/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}] = -\frac{25.60 \times 10^3}{4.576(T/\text{K})} + 8.8$$

Try to calculate

(1) the activation energy and the rate coefficient at 400°C

(2) At 400, NO₂ with pressure of 26.7kPa was added to the reactor, estimate the time needed when the partial pressure of NO₂ declined to 16.1kPa



Ex. 20

The half time of the following reaction was in reverse proportion to the initial pressure of N_2O .



Two different experiments were performed at different temperatures. Results are listed as follows:

$T_1 = 967 \text{ K}$	$p_{0,1} = 38.7 \text{ kPa}$	$t_{1/2,1} = 1520 \text{ s}$
$T_2 = 1030 \text{ K}$	$p_{0,2} = 47.4 \text{ kPa}$	$t_{1/2,2} = 212 \text{ s}$

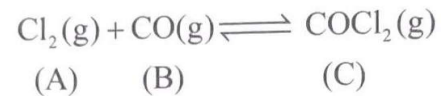
Try to calculate:

- (1) Rate coefficients at two temperatures
- (2) Apparent activation energy
- (3) At 1030K, $p_0=52.6\text{kPa}$, calculate the total pressure when $t=127\text{s}$
- (4) The molar fraction of N_2 at half time



Ex. 22

At 298K, the following reaction was taken place in a robust vessel .



The partial pressure of C was determined as a function of time at different initial pressures of reactants.

The data are listed as follows:

Experiment 1 $p_{\text{A}0}=53.3\text{kPa}$, $p_{\text{B}0}=0.530\text{kPa}$

t / min	0	34.5	69.0	138	∞
$p_{\text{C}} / \text{kPa}$	0	0.266	0.400	0.500	0.530

Experiment 2 $p_{\text{A}0}=213.3\text{kPa}$, $p_{\text{B}0}=0.530\text{kPa}$

t / min	0	34.5	69.0	∞
$p_{\text{C}} / \text{kPa}$	0	0.400	0.500	0.530

Suppose that the rate equation of the above reaction can be described as: $r = k p_{\text{A}}^x p_{\text{B}}^y$

Try to determine the value of x , and y



TEST

The rate equation of the reaction $A + B \xrightarrow{H^+} C + D$ can be presented as: $v = kc_A^\alpha [H^+]^\beta$

Three different experiments were performed and the results are listed in the following table

	A /mol L ⁻¹	[H ⁺] /molL ⁻¹	T /K	t _{1/2} /h	t _{3/4} /h
1	0.1	0.01	298	1.0	2.0
2	0.2	0.02	298	0.5	1.0
3	0.1	0.01	308	0.5	1.0

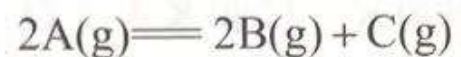
Try to calculate:

- (1) Partial orders α and β
- (2) Rate coefficients at 298K and 308K
- (3) Apparent activation energy



Ex. 25

The half time of the following gas reaction was in reverse proportion to the initial concentration of reactant.



Two different experiments were performed at different temperatures. Results are listed as follows:

No.	T / K	p_A^0 / kPa	$t_{1/2} / \text{s}$
1	900	39.20	1520
2	1000	48.00	212

Try to calculate:

(1) Rate coefficients at two temperatures

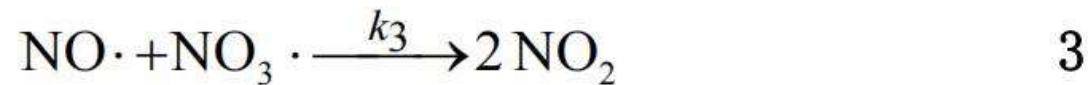
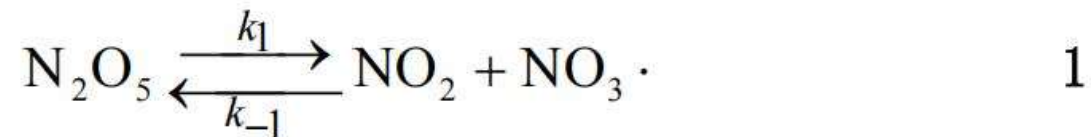
(2) At 1000K, $p_0=53.3\text{kPa}$, calculate the time consumed when the total pressure is $p=64\text{kPa}$

(3) When $p_0=53.3\text{kPa}$, the time needed when the total pressure reaches 64kPa is 100s , try to estimate the reaction temperature



Ex. 27

Mechanism of the decomposition reaction of N_2O_5 can be presented as



(1) If NO and NO_3 are active intermediates, try to give the production rate of O_2 by

Steady State Approximation

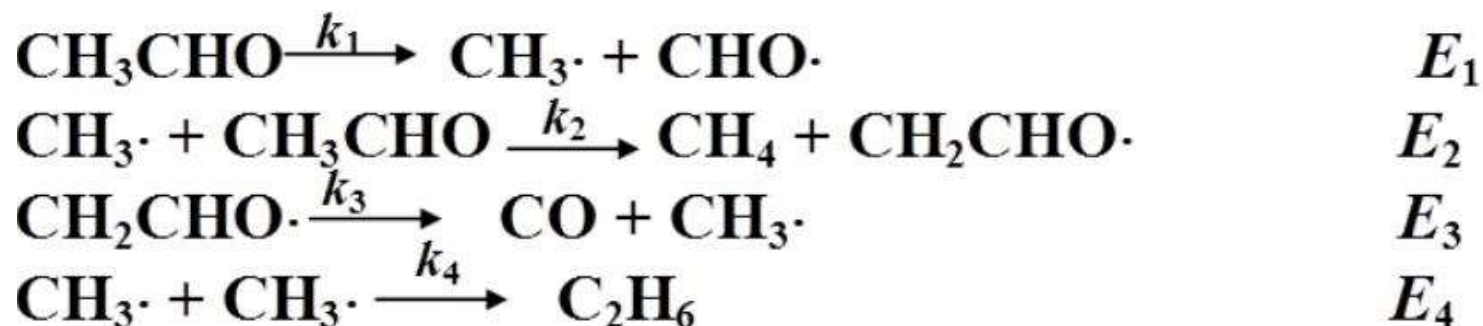
(2) Suppose the step 2 is the rate-controlled step, try to give the production rate of O_2

under the **Pre-Equilibrium Approximation**



Ex. 28

Mechanism of the reaction $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$ can be presented as



Try to give the express of $\frac{dc_{\text{CH}_4}}{dt}$ and the apparant activation energy of the reaction?