



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

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

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

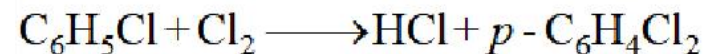
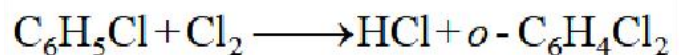
(1) When $x = 0.5 \text{ mol} \cdot \text{L}^{-1}$, $t = 137 \text{ min}^{-1}$

(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. 10

For the following parallel reaction in CS₂ solution (second order reaction):



The initial concentration of C₆H₅Cl and Cl₂ in the solution are both 0.5 mol · dm⁻³, after 30mins

15% C₆H₅Cl converted into o-C₆H₄Cl₂, and 25% C₆H₅Cl converted into p-C₆H₄Cl₂

Calculate the reaction rate coefficients k_1 and k_2 :

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = (k_1 + k_2)t \qquad \frac{1}{c_{A0}} \frac{\alpha}{1 - \alpha} = (k_1 + k_2)t$$

$$k_1 = 0.0166 (\text{mol} \cdot \text{L}^{-1} \text{min})^{-1}$$

$$k_2 = 0.0278 (\text{mol} \cdot \text{L}^{-1} \text{min})^{-1}$$



$$\frac{k_1}{k_2} = \frac{0.15}{0.25} = \frac{3}{5}$$

$$k_1 + k_2 = 0.0444 (\text{mol} \cdot \text{L}^{-1} \text{min})^{-1}$$



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. 11

$$\ln \frac{1}{1-0.3} = k \times 8760$$

$$k = 4.07 \times 10^{-5} \text{ hr}^{-1}$$

rate

298.15K $k_A = \frac{1}{1} \ln \frac{1}{1-0.000069} = 6.9 \times 10^{-5} \text{ hr}^{-1}$

343.15K $k_A = \frac{1}{1} \ln \frac{1}{1-0.0035} = 0.00351 \text{ hr}^{-1}$

activation energy

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad E_a = 74.2 \text{ kJ / mol}$$

$$\ln \frac{4.07 \times 10^{-5}}{6.9 \times 10^{-5}} = -\frac{74.2 \times 10^3}{8.314} \left(\frac{1}{T} - \frac{1}{298.15} \right)$$

temperature

$$T = 292.98 \text{ K}$$



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?



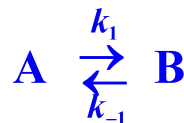
Ex. 12

$$\lg k_{-1} = \lg k_1 - \lg K = -\frac{4000}{T} + 8.0$$

$$\frac{1}{2.303} \ln k_{-1} = -\frac{4000}{T} + 8.0 \Rightarrow \ln k_{-1} = -\frac{9212}{T} + 18.424$$

$$E_a = RT^2 \frac{d(\ln k_{-1})}{dT} = 76.59 \text{ kJ} \cdot \text{mol}^{-1}$$

$$T = 400\text{K} \quad k_1 = 0.1\text{s}^{-1}, \quad k_{-1} = 0.01\text{s}^{-1}$$



$$t=0 \quad 0.5 \quad 0.05$$

$$t=t \quad 0.5-x \quad 0.05+x$$



Ex. 12

$$\frac{dx}{dt} = k_1(0.5 - x) - k_{-1}(0.05 + x) = 0.0495 - 0.11x$$

$$\ln \frac{0.0495}{0.0495 - 0.11x} = 0.11t$$

$$t=10\text{s} \quad x=0.3\text{mol} \cdot \text{L}^{-1}$$

$$c_A = 0.2\text{mol} \cdot \text{L}^{-1}, \quad c_B = 0.35\text{mol} \cdot \text{L}^{-1}$$

$$\frac{dx}{dt} = k_1(0.5 - x) - k_{-1}(0.05 + x) = 0.0495 - 0.11x = 0$$

$$x_e = 0.45\text{mol} \cdot \text{L}^{-1}$$

$$c_A = 0.05\text{mol} \cdot \text{L}^{-1}, \quad c_B = 0.5\text{mol} \cdot \text{L}^{-1}$$



TEST 1

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

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

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?



TEST 1

$$(1) \quad \ln(k / \text{h}^{-1}) = -\frac{8938}{303} + 20.400 = -9.098 \quad k(303 \text{ K}) = 1.119 \times 10^{-4} \text{ h}^{-1}$$

$$(2) \quad t = \frac{1}{k} \ln \frac{1}{1-y} = \frac{1}{1.119 \times 10^{-4} \text{ h}^{-1}} \ln \frac{1}{1-0.3} = 3187.5 \text{ h} = 132.8 \text{ d}$$

$$(3) \quad k(T) = \frac{1}{t} \ln \frac{1}{1-y} = \frac{1}{2 \times 365 \times 24 \text{ h}} \ln \frac{1}{1-0.3} = 2.036 \times 10^{-5} \text{ h}^{-1}$$

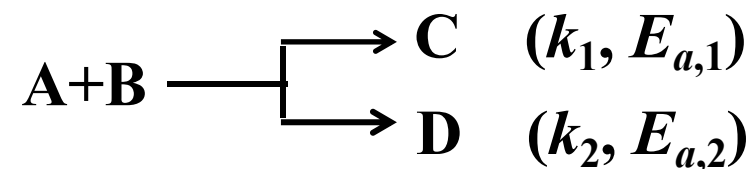
$$\ln(2.036 \times 10^{-5} \text{ h}^{-1}) = -\frac{8938}{T / \text{K}} + 20.400$$

$$T = 286.5 \text{ K}$$



TEST 2

For a second order parallel reaction, the initial concentration of A and B both are a mol/L, and there are no products presented at $t=0$.



- (1) try to give the integrated form of the rate equation?
- (2) at 500K, $a=0.5$, the concentration of C and D are 0.075 and 0.125mol/L respectively after 30mins, try to calculate k_1 and k_2 ?
- (3) at 500K, given $E_{a,1}=150\text{kJ/mol}$, try to calculate $E_{a,2}$ (two reactions have the same prefactors)



TEST 2

(1)

	[A]	[B]	[C]	[D]
$t = 0$	a	a	0	0
$t = t$	$a - x$	$a - x$	x_1	x_2

$$r = \frac{dx}{dt} = \frac{dx_1}{dt} + \frac{dx_2}{dt} = k_1(a-x)(a-x) + k_2(a-x)(a-x) = (k_1 + k_2)(a-x)^2$$

$$\int_0^x \frac{dx}{(a-x)^2} = (k_1 + k_2) \int_0^t dt$$

$$\frac{1}{a-x} - \frac{1}{a} = (k_1 + k_2)t$$

(2)

$$\frac{1}{0.30 \text{ mol} \cdot \text{dm}^{-3}} - \frac{1}{0.50 \text{ mol} \cdot \text{dm}^{-3}} = (k_1 + k_2) \times 30 \text{ min}$$

$$\frac{k_1}{k_2} = \frac{x_1}{x_2} = \frac{0.075}{0.125} = 0.60$$

$$k_1 = 0.0167 (\text{mol} \cdot \text{dm}^{-3})^{-1} \cdot \text{min}^{-1}$$

$$k_2 = 0.0278 (\text{mol} \cdot \text{dm}^{-3})^{-1} \cdot \text{min}^{-1}$$



TEST 2

(3)

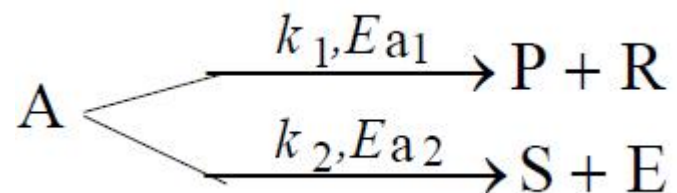
$$\frac{k_1}{k_2} = \frac{A_1 \exp\left(-\frac{E_{a,1}}{RT}\right)}{A_2 \exp\left(-\frac{E_{a,2}}{RT}\right)} = \exp\left(\frac{E_{a,2} - E_{a,1}}{RT}\right) \quad \ln \frac{k_1}{k_2} = \frac{E_{a,2} - E_{a,1}}{RT}$$

$$E_{a,2} = E_{a,1} + RT \ln \frac{k_1}{k_2} = 147.9 \text{ kJ} \cdot \text{mol}^{-1}$$



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. 13

(1) First order reaction $k_1 + k_2 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{10} = 0.0693 \text{ min}^{-1}$

$$\frac{k_1}{k_2} = 2, \quad \therefore k_1 = 0.0462 \text{ min}^{-1}, \quad k_2 = 0.0231 \text{ min}^{-1}.$$

(2) $\frac{k_1}{k_2} = \frac{A_1}{A_2} \cdot e^{-(E_{a1} - E_{a2})/RT}$, $\ln \frac{k_1}{k_2} = \ln \frac{A_1}{A_2} - (E_{a1} - E_{a2}) \cdot \frac{1}{RT}$ 。

$$\ln \frac{\left(\frac{k_1}{k_2}\right)_{T_2}}{\left(\frac{k_1}{k_2}\right)_{T_1}} = -(E_{a1} - E_{a2}) \frac{1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = -\frac{E_{a1} - E_{a2}}{R} \cdot \frac{T_1 - T_2}{T_2 \cdot T_1}$$

$$\ln \frac{3}{2} = -\frac{(E_{a1} - E_{a2})}{8.314} \times \frac{323 - 333}{333 \times 323}, \quad E_{a1} - E_{a2} = 36.3 \text{ kJ} \cdot \text{mol}^{-1}.$$



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. 14



$$\begin{array}{ccccccc} & t = t & 1 - \alpha & \alpha & \alpha & & \\ \frac{1 - \alpha}{1 + \alpha} = y_{\text{A}} & , & \alpha = \frac{1 - y_{\text{A}}}{1 + y_{\text{A}}} = \frac{1 - 0.1085}{1 + 0.1085} = 0.8042 \end{array}$$

$$(2) \quad p_{\text{A}} = p_{\text{A}0}(1 - \alpha), \quad \therefore p_{\text{A}0} = \frac{p_{\text{A}}}{1 - \alpha} = \frac{p y_{\text{A}}}{1 - \alpha} = \frac{24.58 \times 0.1085}{1 - 0.8042} = 13.62 \text{ kPa} \circ$$

$$c_{\text{A}0} = \frac{p_{\text{A}0}}{RT} = \frac{13.62 \times 10^3}{8.314 \times 373.15} = 4.39 \text{ mol} \cdot \text{m}^{-3} = 4.39 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3},$$

$$k_{\text{A}} = \frac{\alpha}{t c_{\text{A}0}(1 - \alpha)} = \frac{0.8042}{(10 \times 60) \times 4.39 \times 10^{-3} \times (1 - 0.8042)} = 1.559 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$$

$$(3) \quad t_{1/2} = \frac{1}{k_{\text{A}} c_{\text{A}0}} = \frac{1}{1.559 \times 4.39 \times 10^{-3}} = 146 \text{ s}$$



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)



Ex. 15

$$(1) \quad -\frac{dc_A}{dt} = kc_A^{0.5}c_B^{1.5} = kc_A^{0.5}(2c_A)^{1.5} = 2^{1.5}kc_A^2 = k'c_A^2$$

$$k'_{300K} = \frac{1}{t_{20s}} \left(\frac{1}{c_A} - \frac{1}{c_{A0}} \right) = \frac{1}{20} \left(\frac{1}{0.01} - \frac{1}{0.1} \right) = 4.5 \text{ mol}^{-1} \text{ L s}^{-1}$$

$$k'_{300K} = \frac{1}{t_{40s}} \left(\frac{1}{c'_A} - \frac{1}{c_{A0}} \right) = \frac{1}{40} \left(\frac{1}{c'_A} - \frac{1}{0.1} \right) = 4.5 \text{ mol}^{-1} \text{ L s}^{-1} \quad c'_A = 5.26 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$(2) \quad k'_{300K} = 2^{1.5} k_{A,300K}$$

$$k_{A,300K} = 1.59 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1} \quad k_{B,300K} = 2k_{A,300K} = 3.18 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$$



Ex. 15

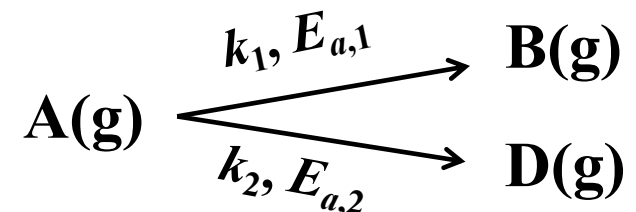
$$(3) \quad k'_{400K} = \frac{1}{t_{20s}} \left(\frac{1}{c_A} - \frac{1}{c_{A0}} \right) = \frac{1}{20} \left(\frac{1}{3.9 \times 10^{-3}} - \frac{1}{0.1} \right) = 12.3 \text{ mol}^{-1} \text{ L s}^{-1}$$

$$E_a = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{k'_{400K}}{k'_{300K}} = 10.0 \text{ kJ} \cdot \text{mol}^{-1}$$



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



TEST 3

$$(1) \quad t = \frac{1}{k_1 + k_2} \ln \frac{1}{1 - y_A} = \frac{1}{(0.0030 + 0.0025) \text{ s}^{-1}} \ln \frac{1}{1 - 0.99} = 837 \text{ s}$$

$$(2) \quad \frac{c_B}{c_D} = \frac{k_1}{k_2} = \frac{0.0030 \text{ s}^{-1}}{0.0025 \text{ s}^{-1}} = 1.2 \quad \frac{c_B}{c_B + c_D} = \frac{k_1}{k_1 + k_2} = \frac{0.0030 \text{ s}^{-1}}{(0.0030 + 0.0025) \text{ s}^{-1}} = 0.545$$

$$(3) \quad \frac{c_B}{c_D} = \frac{k_1}{k_2} = \frac{A_1 \exp(-E_{a,1} / RT)}{A_2 \exp(-E_{a,2} / RT)} = \exp \frac{E_{a,2} - E_{a,1}}{RT} = 3.6$$

$$\ln 3.6 = \frac{E_{a,2} - E_{a,1}}{RT} = \frac{(90 - 80) \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times T}$$

$$T = 939 \text{ K}$$



TEST 3

(4) $k = k_1 + k_2$

$$\begin{aligned} \frac{E_a}{RT^2} &= \frac{d \ln k}{dT} = \frac{d \ln(k_1 + k_2)}{dT} = \frac{1}{k_1 + k_2} \frac{d(k_1 + k_2)}{dT} = \frac{1}{k_1 + k_2} \frac{dk_1}{dT} + \frac{dk_2}{dT} \\ &= \frac{1}{k_1 + k_2} \left(k_1 \frac{d \ln k_1}{dT} + k_2 \frac{d \ln k_2}{dT} \right) \\ &= \frac{1}{k_1 + k_2} \left(\frac{k_1 E_1}{RT^2} + \frac{k_2 E_2}{RT^2} \right) \end{aligned}$$

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2} = \mathbf{84.54 \text{ kJ / mol}}$$



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

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

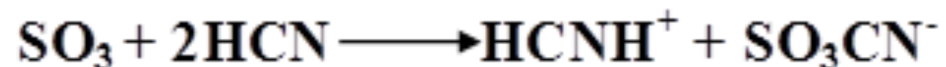
t / min	100	200	300	410
$k_A \times 10^3 / \text{min}^{-1}$	2.56	2.58	2.59	2.61

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



Ex. 18

At 298.15K, SO_3 is solubilized into excess HCN. These two substances reacted and gave the conductive ions. The reaction is as follows:



The measured conductivity as a function of time was listed in the following table

t/min	2	5	9	12	25	30	40
$\kappa \times 10^2 / \text{s} \cdot \text{m}^{-1}$	4.85	7.76	9.63	10.20	11.08	11.08	11.08

Suppose the rate equation of the reaction can be described as: $-\frac{dc_{\text{SO}_3}}{dt} = kc_{\text{SO}_3}$

Try to calculate the rate coefficient (Given that the conductivity is not zero at the beginning)



Ex. 18

$$Y_{\infty} = \kappa_{\infty} = 11.08 \times 10^{-2} \text{ s} \cdot \text{m}^{-1}$$

$$\ln \frac{\kappa_{\infty} - \kappa_0}{\kappa_{\infty} - \kappa_{t1}} = kt_1$$

$$\ln \frac{\kappa_{\infty} - \kappa_{t1}}{\kappa_{\infty} - \kappa_{t2}} = k(t_2 - t_1)$$

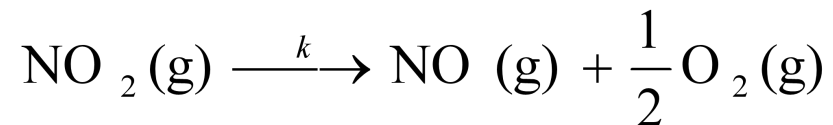
$$\ln \frac{\kappa_{\infty} - \kappa_0}{\kappa_{\infty} - \kappa_{t2}} = kt_2$$

$$\bar{k} = 0.198 \text{ min}^{-1}$$



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. 19

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

$$\ln[k/\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}] = -\frac{107.1 \times 10^3}{8.3145(T/\text{K})} + 20.3$$

$$E_a = 107.1 \text{ kJ} \cdot \text{mol}^{-1}, \quad k_{400^\circ\text{C}} = 3 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

$$\begin{aligned} t &= \frac{1}{k} \left(\frac{c_{\text{NO}_2,0} - c_{\text{NO}_2,t}}{c_{\text{NO}_2,0} c_{\text{NO}_2,t}} \right) = \frac{RT}{k} \left(\frac{p_{\text{NO}_2,0} - p_{\text{NO}_2,t}}{p_{\text{NO}_2,0} p_{\text{NO}_2,t}} \right) \\ &= \left[\frac{8.3145 \times 673.2}{3} \left(\frac{26.7 - 16.1}{26.7 \times 16.1} \right) \right] \text{s} = 46.0 \text{ s} \end{aligned}$$



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. 20

$$(1) \quad k_1(967 \text{ K}) = \frac{1}{t_{1/2,1} p_{0,1}} = \frac{1}{1520 \text{ s} \times 38.7 \text{ kPa}} = 1.70 \times 10^{-5} \text{ kPa}^{-1} \cdot \text{s}^{-1}$$

$$k_2(1030 \text{ K}) = \frac{1}{t_{1/2,2} p_{0,2}} = \frac{1}{212 \text{ s} \times 47.4 \text{ kPa}} = 9.95 \times 10^{-5} \text{ kPa}^{-1} \cdot \text{s}^{-1}$$

$$(2) \quad \ln \frac{k(T_2)}{k(T_1)} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{9.95 \times 10^{-5} \text{ kPa}^{-1} \cdot \text{s}^{-1}}{1.70 \times 10^{-5} \text{ kPa}^{-1} \cdot \text{s}^{-1}} = \frac{E_a}{R} \left(\frac{1}{967 \text{ K}} - \frac{1}{1030 \text{ K}} \right)$$

$$E_a = 232.3 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(4) \quad p = \frac{1}{2} p_0, \quad p_{\text{总}} = \frac{3}{2} p_0 - \frac{1}{2} p = \frac{5}{4} p_0$$

$$y(\text{N}_2) = \frac{p(\text{N}_2)}{p_{\text{总}}} = \frac{\frac{1}{2} p_0}{\frac{5}{4} p_0} = 0.4$$

(3)



$t = 0$

p_0

0

0

$t = t$

p

$p_0 - p$

$\frac{1}{2}(p_0 - p)$

$p_{\text{总}} = \frac{3}{2} p_0 - \frac{1}{2} p$

$$k_2 t = \frac{1}{a-x} - \frac{1}{a} \quad \frac{1}{p} = k_2 t + \frac{1}{p_0}$$

$$p = \left(k_2 t + \frac{1}{p_0} \right)^{-1} = \left(9.95 \times 10^{-5} \text{ kPa}^{-1} \cdot \text{s}^{-1} \times 127 \text{ s} + \frac{1}{52.6 \text{ kPa}} \right)^{-1} = 31.6 \text{ kPa}$$

$$p_{\text{总}} = \frac{3}{2} p_0 - \frac{1}{2} p = \left(\frac{3}{2} \times 52.6 - \frac{1}{2} \times 31.6 \right) \text{ kPa} = 63.1 \text{ kPa}$$



Ex. 21

Rate equation the following reaction of NO(g) A and H₂(g) B can be described as: $r = kp_A^x p_B^y$



The initial rates at different initial pressures are measured at 1000K and listed as follows:

No.	p_A^0 / kPa	p_B^0 / kPa	$r_0 / (\text{Pa} \cdot \text{min}^{-1})$
1	50.6	20.2	486
2	50.6	10.1	243
3	25.3	20.2	121.5

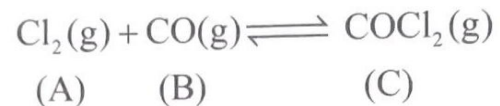
Try to calculate the partial order x, y, and rate coefficient k

$$k = \frac{r_0}{p_A^2 p_B} = \frac{486 \text{ Pa} \cdot \text{min}^{-1}}{(50.6 \text{ kPa})^2 \times 20.2 \text{ kPa}} = 9.4 \times 10^{-12} \text{ Pa}^{-2} \cdot \text{min}^{-1} = 9.4 \times 10^{-6} (\text{kPa})^{-2} \cdot \text{min}^{-1}$$



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



Ex. 22



$$t = 0 \quad p_{\text{A}}^0 \quad p_{\text{B}}^0 \quad 0$$

$$t = t \quad p_{\text{A}} = p_{\text{A}}^0 - p_{\text{C}} \quad p_{\text{B}} = p_{\text{B}}^0 - p_{\text{C}} \quad p_{\text{C}}$$

(1)

t / min	0	34.5	69.0	138	∞
$p_{\text{B}} / \text{kPa}$	0.530	0.264	0.130	0.030	0

$$y=1$$

(2)

t / min	0	34.5	69.0	∞
$p_{\text{B}} / \text{kPa}$	0.530	0.130	0.030	0

$$t_{1/2}(1) = 34.5 \text{ min} \quad t_{1/2}(2) = \frac{1}{2} \times 34.5 \text{ min} = 17.25 \text{ min}$$

$$\frac{k'(1)}{k'(2)} = \frac{\ln 2 / t_{1/2}(1)}{\ln 2 / t_{1/2}(2)} = \frac{1}{2}$$

$$\frac{k'(1)}{k'(2)} = \frac{kp_{\text{A}}^x(1)}{kp_{\text{A}}^x(2)} = \left(\frac{53.3}{213.3} \right)^x = \left(\frac{1}{4} \right)^x$$

$$x=0.5$$



TEST

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

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



TEST

$$v = k c_A^\alpha H^+{}^\beta = k' c_A^\alpha$$

$$k' = k H^+{}^\beta$$

$$t_{\frac{1}{2}} : t_{\frac{3}{4}} = 1:2$$

First order

$$\alpha=1$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{1}{0.5} = \frac{k'_2}{k'_1} = \frac{k H^+{}^\beta_2}{k H^+{}^\beta_1} = \frac{0.02^\beta}{0.01^\beta} \quad \beta = 1$$

$$k = \frac{\ln 2}{t_{1/2} H^+}$$

$$k_{298} = 69.31 \text{ mol}^{-1} \text{ L h}^{-1}$$

$$k_{308} = 138.63 \text{ mol}^{-1} \text{ L h}^{-1}$$

$$E_a = 52.89 \text{ kJ} \cdot \text{mol}^{-1}$$



Ex. 23

At 850K, NH_3 decomposed into N_2 and H_2 . The total pressure of the reaction system was determined as a function of time. The data are listed as follows:

t / s	200	400	600	800	1 000
$p_{\text{总}} / \text{kPa}$	30.40	33.38	36.40	39.40	42.40

Try to calculate the reaction order and rate coefficient k



$$t = 0 \quad p_{\text{A}}^0 \quad 0 \quad 0$$

$$t = t \quad p_{\text{A}} = p_{\text{A}}^0 - 2p \quad p \quad 3p$$

$$p_{\text{总}} = p_{\text{A}}^0 + 2p \quad 2p = p_{\text{总}} - p_{\text{A}}^0$$

$$p_{\text{A}} = p_{\text{A}}^0 - 2p = p_{\text{A}}^0 - (p_{\text{总}} - p_{\text{A}}^0) = 2p_{\text{A}}^0 - p_{\text{总}}$$

$$r = -\frac{1}{2} \frac{dp_{\text{A}}}{dt} = kp_{\text{A}}^n$$

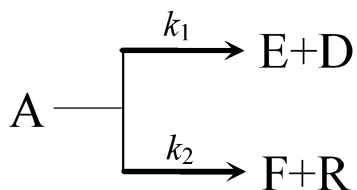
$$\frac{dp_{\text{A}}}{dt} = \frac{d(2p_{\text{A}}^0 - p_{\text{总}})}{dt} = -\frac{dp_{\text{总}}}{dt}$$

$$k = \frac{1}{2} \frac{dp_{\text{总}}}{dt} \approx \frac{1}{2} \frac{\Delta p_{\text{总}}}{\Delta t} = \frac{1}{2} \times \frac{3.0 \text{ kPa}}{200 \text{ s}} = 7.5 \text{ Pa} \cdot \text{s}^{-1}$$



Ex. 24

A gas parallel reaction is performed in an isochoric vessel.



The total pressure of the system varied with time and were listed as follows:

t/min	0	5	10	15	∞
p/kPa	1.67	2.11	2.40	2.60	3.00

Given that the partial pressure of E is twice of that for F and the reaction began before $t=0$

Try to calculate:

(1) Rate coefficients k_1 and k_2

(2) Time needed to consume 75% A



Ex. 24

$$-\frac{dc_A}{dt} = (k_1 + k_2)c_A = k_A c_A$$

$$(k_1 + k_2) = k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_A} = \frac{1}{t} \ln \frac{p_\infty - p_0}{p_\infty - p_t} \quad \overline{k_1 + k_2} = 0.080 \text{ min}^{-1}$$

$$k_1 + k_2 = 0.080 \text{ min}^{-1}$$

$$k_1 / k_2 = 2$$

$$k_1 = 0.054 \text{ min}^{-1} \quad k_2 = 0.027 \text{ min}^{-1}$$

$$t_{1/2} = \ln 2 / k_A = (\ln 2 / 0.080) \text{ min} = 8.7 \text{ min}$$

$$t = 2t_{1/2} = (8.7 \times 2) \text{ min} = 17.4 \text{ min}$$



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:

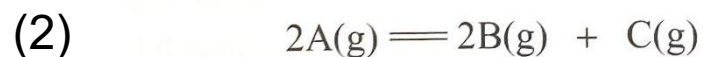
- (1) Rate coefficients at two temperatures
- (2) At 1000K, $p_0=53.3\text{kPa}$, calculate the time consumed when the total pressure is $p=64\text{kPa}$
- (3) When $p_0=53.3\text{kPa}$, the time needed when the total pressure reaches 64kPa is 100s, try to estimate the reaction temperature



Ex. 25

$$(1) \quad k_p(900 \text{ K}) = \frac{1}{p_A^0 t_{1/2}} = \frac{1}{39.20 \text{ kPa} \times 1520 \text{ s}} = 1.68 \times 10^{-5} (\text{kPa})^{-1} \cdot \text{s}^{-1}$$

$$k_p(1000 \text{ K}) = \frac{1}{48.00 \text{ kPa} \times 212 \text{ s}} = 9.83 \times 10^{-5} (\text{kPa})^{-1} \cdot \text{s}^{-1}$$



$$t=0 \quad p_A^0 \quad 0 \quad 0$$

$$t=t \quad p_A = p_A^0 - p \quad p \quad \frac{1}{2}p \quad p_t = p_A^0 + \frac{1}{2}p$$

$$p = 2(p_t - p_A^0) = 2 \times (64.00 - 53.33) \text{ kPa} = 21.34 \text{ kPa}$$

$$p_A = p_A^0 - p = (53.33 - 21.34) \text{ kPa} = 31.99 \text{ kPa}$$

$$t = \frac{1}{k_p} \left(\frac{1}{p_A} - \frac{1}{p_A^0} \right) = \frac{1}{9.83 \times 10^{-5} (\text{kPa})^{-1} \cdot \text{s}^{-1}} \times \left(\frac{1}{31.99 \text{ kPa}} - \frac{1}{53.33 \text{ kPa}} \right) = 127.25 \text{ s}$$

$$(3) \quad \ln \frac{k_p(1000 \text{ K})}{k_p(900 \text{ K})} = \frac{E_a}{R} \left(\frac{1}{900 \text{ K}} - \frac{1}{1000 \text{ K}} \right) = \ln \frac{9.83}{1.68}$$

$$E_a = 132.2 \text{ kJ} \cdot \text{mol}^{-1}$$

$$k_p(T) = \frac{1}{t} \left(\frac{1}{p_A} - \frac{1}{p_A^0} \right) = \frac{1}{100 \text{ s}} \times \left(\frac{1}{31.99 \text{ kPa}} - \frac{1}{53.33 \text{ kPa}} \right) = 1.25 \times 10^{-4} (\text{kPa})^{-1} \cdot \text{s}^{-1}$$

$$\ln \frac{k_p(T)}{k_p(900 \text{ K})} = \frac{E_a}{R} \left(\frac{1}{900 \text{ K}} - \frac{1}{T} \right)$$

$$T = 1015 \text{ K}$$

$$\ln \frac{1.25 \times 10^{-4} (\text{kPa})^{-1} \cdot \text{s}^{-1}}{1.68 \times 10^{-5} (\text{kPa})^{-1} \cdot \text{s}^{-1}} = \frac{132.2 \times 10^3}{8.314 \text{ K}^{-1}} \left(\frac{1}{900 \text{ K}} - \frac{1}{T} \right)$$