

Physical Chemistry (II) Examination Paper

1. Chemical Kinetics

I Choice (1 point for each, totally 30 points)

- For an elementary reaction $2A \xrightarrow{k} P$, what are the correct rate expressions of ν and ν_A
A: $\nu = kc_A^2$, $\nu_A = kc_A^2$; B: $\nu = kc_A^2$, $\nu_A = 2kc_A^2$; C: $\nu = 2kc_A^2$, $\nu_A = kc_A^2$
- The reaction rate equation of $A+2B \xrightarrow{k} pP$ is that $\nu = kc_A^{0.5}c_B^2c_P^{-0.5}$, what is the reaction order _____?
A: Zeroth; B: First; C: Second
- A unimolecular reaction _____ the elementary reaction.
A: can't be; B: must be; C: might be
- The experimental results showed that the rate equation of $2A+B \longrightarrow 2C + D$ is $\nu = k[A][B]$. If the initial concentrations of the reactants were $[A]_0 = 2[B]_0$, the rate equation changed into $\nu = k_a[A]^2$. What's the relationship between k_a and k _____.
A: $k_a = 0.5k$; B: $0.5k_a = k$; C: $k_a = k$
- The rate equation of the chemical reaction $A+2B \xrightarrow{k} pP$ is $\nu_A = k_A c_A^\alpha c_B^{2-\alpha}$. If the reaction rate ν_A is in direct proportional to c_A , then $\nu_A =$ _____.
A: $k_A c_A c_B$; B: $k_A c_A^2$; C: $k_A c_A^{0.5} c_B^{1.5}$
- The rate constant of the chemical reaction $2A+B \xrightarrow{k_A} C$ is $k_A = 0.095 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{min}^{-1}$. Which of the following is a linear plotting? _____.
A: $\ln\{c_A\} \sim t$; B: $c_A \sim t$; C: $1/c_A \sim t$
- For a zeroth reaction, $A \xrightarrow{k} B + C$, the half life of A is 25 min, the time for complete consumption of A is _____.
A: 50; B: 75; C: ∞
- For a $A \rightarrow Y$, if c_A shows a linear relationship with reaction time t , what is the reaction order _____?
A: Zeroth; B: First; C: Second
- During the reaction of $A \xrightarrow{k} B + C$, it is found that c_A shows a linear relationship with reaction time t , then the half life of A is _____ to its initial concentration $[A]_0$.
A: irrelevant; B: propotional; C: inversely proportional

10. The time needed for completing the reaction is c_0/k , then this is a _____ order reaction.
A: First; B: Second C: Zeroth;
11. For a zeroth reaction $A+2B \xrightarrow{k} P$, the initial consumption rate of A is v_{A0} at c_{A0} , when the initial concentration changes into $2c_{A0}$, the initial consumption rate of A is $v_{2,A0}$, then v_{A0} _____ $v_{2,A0}$
A: >; B: =; C: <
12. For an ideal gaseous reaction $2A(g) \rightarrow B(g)$, given that $-\frac{dc_A}{dt} = k_c c_A$ or $-\frac{dp_A}{dt} = k_p p_A$, then $k_c =$ _____.
A: k_p ; B: RTk_p ; C: k_p / RT
13. For a first order reaction $A+2B \xrightarrow{k} P$, the half life of A is 300 min. When the consumption rate of A is 1/4 of the initial one, the reaction time is _____.
A: 300 min; B: 600 min; C: 900 min
14. If the rate constant $k_A = 7.7 \times 10^{-4} \text{ s}^{-1}$, $c_{A0} = 0.1 \text{ mol} \cdot \text{dm}^{-3}$, then the half life of A is _____.
A: 600 s; B: 900 s; C: 1 800 s
15. The rate constant of $A+B \xrightarrow{k_A} 2C$ is $k_A = 5.18 \times 10^{-2} \text{ h}^{-1}$, which one of the following is correct?
A: $c_A \sim t$ is straight line; B: $\ln\{c_A\} \sim t$ is straight line; C: $1/c_A \sim t$ is straight line
16. In the reaction of $A \xrightarrow{k} B + C$, if only A existed at the beginning of the reaction, the time for the consumption 75% of A is 2 times of that for the consumption 50% of A, the time for the consumption $x\%$ of A is 3 times of that for the consumption 50% of A, then $x =$ _____.
A: 75.0; B: 87.5; C: 50
17. For a simple order reaction, $k_A = 0.1 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, $c_{A0} = 0.1 \text{ mol} \cdot \text{dm}^{-3}$, How much time does it take when the reaction rate decreases to the 1/4 of the initial rate?
A: 10 s; B: 100 s; C: 300 s
18. For a second order reaction $A \rightarrow B$, $t_{1/2}$ and $t_{3/4}$ are the reaction time for the consumption 50% and 75% of A, respectively. Then $t_{1/2}/t_{3/4} =$ _____.
A: 1/3; B: 1/2; C: 1/4
19. For an ideal gaseous reaction $2A(g) \rightarrow B(g)$, given that $-\frac{dc_A}{dt} = k_c c_A$ or $-\frac{dp_A}{dt} = k_p p_A$, then $k_c =$ _____.
A: k_p ; B: RTk_p ; C: k_p / RT

20. The apparent rate constant k of a complex reaction is $k = \frac{2k_2(2k_1/3k_3)^{2/3}}{E_a}$, in which k_i is the rate constant of each elementary reaction. Then the apparent $E_a =$ _____
- A: $E_a = E_2 + \frac{2}{3}(E_1 - E_3)$; B: $E_a = 2E_2 + \frac{2}{3}(2E_1 - 3E_3)$; C: $E_a = E_2 + (E_1 - 2E_3)^{2/3}$
21. At 300 K, for the first order opposite reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$ $K_c=2$. When $k_1 = 0.244s^{-1}$, then $k_{-1} =$ _____ s^{-1} .
- A: 0.122; B: 0.244; C: 0.488
22. For a first order parallel reaction $B \xleftarrow{k_1} A \xrightarrow{k_2} C$, given that $k_1 / k_2 = 0.5$. If only A exists at the beginning of the reaction, after a certain time, $c_B=0.0204 \text{ mol}\cdot\text{dm}^{-3}$, then $c_C=$ _____ $\text{mol}\cdot\text{dm}^{-3}$.
- A: 0.0204; B: 0.0408; C: 0.0816
23. The conversion of a reaction at equilibrium is 25%. With adding catalyst, the reaction rate is 20 times of the original one. Then the equilibrium conversion is _____.
- A: > 25%; B: < 25%; C: = 25%
24. For the reaction $2A \rightarrow 2B(g) + C(g)$, plotting the logarithms of rate constant against the reciprocal of temperature $\ln\{k\} \sim 1/(T / K)$, a straight line is obtained, the slope is -12.4×10^3 and the intercept is 31.36. The activation energy is _____ $\text{KJ}\cdot\text{mol}^{-1}$, assuming it is independent of temperature.
- A: 83.1; B: 93.1; C: 103.1
25. Increasing the reaction temperature, the reaction rate constant _____.
- A: must increase; B: must keep unchanged; C: not necessarily increase
26. At a certain temperature, when adding a specific catalyst into an opposite reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$, the rate constant k_1 increase 50%, then k_{-1} is _____.
- A: unchanged; B: increase 50%; C: decrease 50%
27. Arrhenius equation _____.
- A: can be applied to all types of chemical reactions;
B: can be applied to the reactions, of which the reaction rate increases exponentially with the temperature;
C: can be applied to explosion reactions
28. The effects of catalysts are to change _____.
- A: the reaction path; B: the equilibrium state; C: reaction enthalpy

29. The mechanism of reaction $A+2B \rightarrow P$ is as the following

$A+B \xrightarrow{k_1} C$; $C \xrightarrow{k_{-1}} A+B$; $C+B \xrightarrow{k_2} P$ where C is an active intermediate, then $dc_p / dt =$ _____.

A: $\frac{k_1 k_2 c_A c_B}{k_{-1} + k_2 c_B}$; B: $\frac{k_1 k_2 c_A c_B^2}{k_{-1} + k_2 c_B}$; C: $k_1 k_2 c_A c_B$

30. When the forward reaction of an opposite reaction is exothermic, for a specific conversion x , the most optimized temperature is T . then, the relation between the reaction rate v and the temperature $(dv/dT)_x =$ _____

A: > 0 ; B: $= 0$; C: < 0

II (5 points for each, totally 10 points)

- (1) The hydrolysis of Aspirin is a first-order reaction, with the rate constant of 7.92 d^{-1} and the activation energy of $56.43 \text{ kJ} \cdot \text{mol}^{-1}$ at 100°C . How long would it take for 30% of Aspirin to hydrolyze at 17°C ?
- (2) The dimerization of Butadiene (A), i.e. $2A(g) \rightarrow A_2(g)$, is a second-order reaction. Its reaction rate reduces by half when the temperature decreases from 326°C to 306°C . Estimate the activation energy.

III (10 points)

$\text{N}_2\text{O}_5(g)$ decomposes in a container with the volume V as $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$. At a certain temperature, the half life is $1.40 \times 10^3 \text{ s}$, and is irrelevant to the initial pressure of the reactant.

- (1) Calculate the rate constant of the reaction.
- (2) If the initial pressure of $\text{N}_2\text{O}_5(g)$ is $60.0 \times 10^3 \text{ Pa}$, calculate the total pressure of the reaction system at 10 s and 600 s, respectively.

IV (10 points)

For a first-order gaseous reaction $A(g) \rightarrow B(g)+D(g)$, if only $A(g)$ exists initially in the container with a pressure of 213 kPa at 450 K, after 100 s, the total pressure changes into 233 kPa. Calculate the rate constant of this reaction, the half life of A, and the conversion of A at 120 s. Given that the volume of the container is a constant.

V (10 points)

The decomposition of N_2O_5 in solvent CCl_4 is a first order reaction. At 313 K, the initial reaction rate is $v_0 = 1.00 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$, after 1 h it changes $v = 3.26 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$. Calculate

- (1) The rate constant. (2) The half life at 313 K, (3) The initial concentration c_0

VI (10 points)

For an opposite reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$, the rate constant k_{-1} and the equilibrium constant K

(dimension is 1) change with the temperature as:

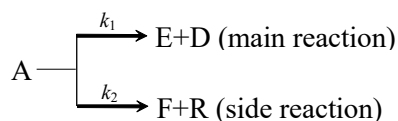
$$\lg(k_{-1} / \text{s}^{-1}) = -4000 / (T / \text{K}) + 8.0 ; \quad \lg K = 2000 / (T / \text{K}) - 4.0$$

(1) Calculate the order of the forward and reverse reactions respectively;

(2) At 400 K, if $c_{A,0} = 0.5 \text{ mol} \cdot \text{dm}^{-3}$, $c_{B,0} = 0$, calculate the concentrations of A and B after 10s

VII (10 points)

At a certain temperature, the first order gaseous parallel reaction undergoes in a closed container:



During the reaction process, the partial pressure of product F is always half of that of E. When we set the beginning of the reaction as $t=0$, then, the total pressure of the system change with the time as

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

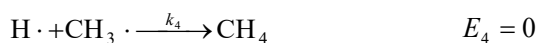
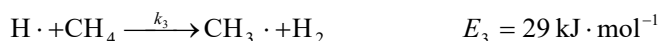
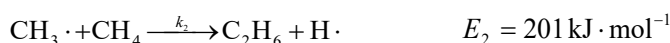
Assume the gases are the ideal gas, calculate:

(1) the rate constants of both main reaction and side reaction;

(2) the reaction time when the consumption of reactant A is 75%.

VIII (10 points)

The reaction mechanism of the complex reaction $2\text{CH}_4(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g})$ is composed of following elementary chain reactions, and their corresponding activation energy are as listed



(1) Derive the rate equation of the formation of $\text{C}_2\text{H}_6(\text{g})$ by the steady state approximation.

(2) Calculate the activation energy E_a of the complex reaction by those of elementary reactions.