

3. CHEMICAL KINETICS

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Concept of reaction rate

1. What is meant by the term rate of a reaction? How is it expressed? 2
What is meant by the rate of a chemical reaction? $\frac{1}{2}$
2. Write the rate expression of each component in the following reaction: 2
 $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$
3. Write the rate expression for the following reaction 2
 $\text{I}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
If the rate of formation of I_2 is $9.1 \times 10^{-6} \text{ mol L}^{-1}\text{S}^{-1}$, what will be the rate of disappearance of HI ? 2
4. In a reaction, $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$; the rate of disappearance of I_2 is found to be 10^{-6} mole per litre per second. What would be the corresponding rate of appearance of HI ? 2
5. For a reaction, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$, the rate of disappearance N_2O_5 is $4 \times 10^{-6} \text{ mol L}^{-1}\text{S}^{-1}$, what will be the rate of formation of NO_2 ? 2
6. For a reaction $2 \text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g})$. The rate of decomposition of ozone is $1.2 \times 10^{-4} \text{ mol L}^{-1}\text{sec}^{-1}$. What will be the rate of formation of oxygen? 2
7. Decomposition of N_2O_5 is expressed by the equation, 2
 $\text{N}_2\text{O}_5 \rightarrow 2 \text{NO}_2 + \frac{1}{2} \text{O}_2$
If during a certain time interval, the rate of decomposition of N_2O_5 is $1.8 \times 10^{-3} \text{ mol lit}^{-1} \text{ min}^{-1}$, what will be the rate of formation of O_2 during the same interval? 2
8. Write down the rate expressions for the given reaction. 2
 $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
If 2.24 liters of O_2 at NTP are produced in 30 minutes. What is the rate of disappearance of $\text{N}_2\text{O}_5(\text{g})$?
($1.1 \times 10^{-4} \text{ mol sec}^{-1}$)
9. In the following given reaction: 2
 $\text{SO}_3 + 3 \text{H}_2\text{S} \rightarrow 3 \text{H}_2\text{O} + 4 \text{S}$
 - a. Express the rate of the above reaction in terms of reactant and product. 2
 - b. The concentration of H_2S decreased by 0.06 mol L^{-1} in 2 seconds.
 - i. Calculate the rate of formation of Sulphur. 1
 - ii. Why is the rate of formation of water not equal to the rate of disappearance of SO_3 ? 1
 - iii. Calculate the rate of disappearance of SO_3 ? 1
10. What is meant by the instantaneous rate of reaction? 1

Collision theory

11. Write short notes on the collision theory of reaction rate. 4
Define effective collision. 1
Define proper orientation. 1
12. Define proper orientation showing a hypothetical sketch during molecular collision. 2
What is meant by the effective collision of reacting species? Mention any one condition for a collision. 2
What are the essential conditions for the effective collision of reacting species? 2

Factors affecting reaction rate

Nature of reactants

Surface area of the reactants

13. Why does a bundle of sticks burn faster than a big single log? 1
14. Mention an example to show the effect of the surface area of the reactant on the rate of reaction. 1

Concentration

15. How do concentration and surface area of the reactant affect the rate of chemical reaction? 2

Pressure

Temperature

16. Why does the temperature increase the rate of reaction? 2

Catalyst

17. Give the factors that influence the rate of a reaction. 2
18. Describe factors affecting reaction rate. 5
19. How do concentration, temperature, catalyst, and surface area of reactants affect the rate of reaction? 4
20. Write a short note on the effect of temperature and catalyst on the rate of reaction. 5
21. How does a catalyst increase the rate of reaction? 2
 Draw an energy profile diagram to show the influence of the catalyst on the rate of chemical reaction. 2
 Draw an energy profile diagram for catalyzed and uncatalyzed reactions. 2
22. Various physical and chemical factors affect the rate of reaction, such as concentration of reactants, temperature, catalysts, surface area of reactants, etc.
 i) Give an example to show that the surface area of reactants affects the rate of reaction.
 ii) Why does temperature increase the rate of reaction? 1+1

Catalysis

Rate law equation, rate constant, and its units

23. Define the term rate law. 1
24. Define the term rate law equation. 1
25. Write short notes on the rate of chemical reaction and rate law. 4
26. A reaction is first order w.r to A and second order w.r. to B.
 i. Write the rate law equation.
 ii. How many times will the rate increase when the concentration of B is tripled? 2
27. What is the rate law expression for the following reaction:
 $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ 2
28. The following hypothetical reaction is second order, $\text{A} + \text{B} \rightarrow \text{Z}$ Write a possible rate law expression. 2
29. The reaction $\text{X} + \text{Y} \rightarrow \text{products}$; is a second order reaction. Write three different rate law expressions that may be true for the above reaction. 2
30. Give the rate law for a reaction which is second order in A and zero order in B. 2
31. Write the possible rate law equations of the following second-order reaction:
 $\text{P} + \text{Q} \rightarrow \text{Products}$ 2
 For a reaction, $\text{P} + \text{Q} \rightarrow \text{products}$, is a third-order reaction.
 Write the possible rate law expressions. 2
32. Write down the differences between the rate of a reaction and the rate constant. 1
33. Why is the rate law an experimental parameter? 1

Zero-order reaction

34. Define a zero-order reaction and find the unit of its rate constant. 2

First-order reaction

35. Define a first-order reaction. 1
36. Define a first-order reaction and write the unit of rate constant for a first-order reaction. 2
37. Write the rate law for a first-order reaction. What is the unit of the reaction? 2
38. Give a chemical reaction to show the reaction of first order. 2

Pseudo-order reaction

39. What is meant by pseudo-first-order reaction? Write an example of it. 3
Define the term pseudo-order reaction. 1
40. Distinguish between pseudo-first order and first order reaction, giving an example of each. 2

Second-order reaction

41. What is meant by a second-order reaction? Write its unit. 2
42. Identify the reaction orders if the units of rate constant are: a) min^{-1} b) $\text{mol l}^{-1} \text{min}^{-1}$ 2
Identify the order of a reaction if the unit of its rate constant is $\text{lit mol}^{-1} \text{s}^{-1}$.
43. What is the order of reaction whose rate constant has the same unit as the rate of reaction? 2
44. For a hypothetical reaction $\text{A} + \text{B} \rightarrow \text{Z}$. The rate of the above reaction doubles when the concentration of A is doubled, but there is no effect of a change in the concentration of B. 2
i) Write down the rate law.
ii) What is the unit of rate constant? 2
45. For the following hypothetical reaction $\text{M} + \text{N} \rightarrow \text{Q}$
When the concentration M is doubled, the rate becomes double. If the concentration of both N and M is doubled, the rate becomes 16 times.
i) Write down the rate equations.
ii) Find out the overall order of reaction. 2+2
46. For a reaction $\text{X} + \text{Y} \rightarrow \text{Z}$, the rate of reaction doubled when the concentration of X was doubled. However, the rate of reaction increased by 8 times when the concentrations of both X and Y were doubled.
i) Determine the rate of reaction. 2
ii) Write down the rate law equation. 1
47. For a reaction $\text{X} + \text{Y} \rightarrow \text{Z}$, the rate of reaction increases four times when the concentration of X is doubled. The rate of reaction increases sixteen times when the concentration of both X and Y is doubled.
i) Find the overall order of reaction. 2
ii) Write down the rate law equation. 1
iii) What is the value of the rate constant when concentrations of X and Y are 0.2 mol L^{-1} and 0.4 mol L^{-1} , respectively, since the rate of reaction is $2 \times 10^{-2} \text{ mol L}^{-1} \text{s}^{-1}$. 2
48. For a hypothetical reaction, $2\text{A} + 3\text{B} \rightarrow \text{M} + \text{N}$, concentration of M increases by 0.02 mol L^{-1} in 10 sec.
i) Write down the rate law expression for the above reaction.
ii) Calculate the rate of formation of M.
iii) What is the rate of disappearance of B?
iv) Define rate of reaction. 1+1+1+1
49. State Hess's law of constant heat summation. Enthalpy of formation of water $\text{H}_2\text{O(l)}$, carbon dioxide $\text{CO}_2(\text{g})$, and benzene $\text{C}_6\text{H}_6(\text{l})$ are -286 kJ , -395 kJ , and $+52 \text{ kJ}$, respectively. [1]
a) Give the correct chemical equation for the standard enthalpy of combustion of benzene. [1]
b) Calculate the standard enthalpy of combustion of benzene from the above data. [3]
50. a) Write any two differences between order and molecularity of a reaction. [2]
b) Draw a graph showing the relationship between concentration of reactant and time for a zero-order reaction. [1]
c) The experimental data for a hypothetical reaction $\text{X} + \text{Y} \rightarrow \text{Z}$ is:

Expt. no	[X] mol L^{-1}	[Y] mol L^{-1}	Initial rate ($\text{mol L}^{-1} \text{s}^{-1}$)
I	0.5	0.5	1.6×10^{-4}
II	0.5	1.0	3.2×10^{-4}
III	1.0	1.0	3.2×10^{-4}

Determine the rate constant and write down the rate law equation from the above data. [3+1]

- d) What is the order of reaction with respect to X? [1]

1. a) i) What is meant by rate of reaction? [1]

For a reaction $\text{X} + \text{Y} \rightarrow \text{Z}$, the rate of reaction doubled when the concentration of X was doubled. However, the

rate of reaction increased eight times when the concentrations of both X and Y were doubled.

ii) Determine the order of the reaction. [2]

iii) Write down the rate law equation. [1]

b) The following data were obtained for the reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g})$:

Expt. No.	$[\text{NO}_2]$ (mol L ⁻¹)	$[\text{F}_2]$ (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
1	0.20	0.05	6×10^{-3}
2	0.40	0.05	1.2×10^{-2}
3	0.80	0.10	4.8×10^{-2}

Find out the rate of the above reaction when the concentrations of $[\text{NO}_2]$ and $[\text{F}_2]$ are 0.50 and 0.60 mol L⁻¹ respectively. [4]

51. For the reaction $2\text{A} + \text{B} \rightarrow \text{product}$, following data were obtained

Experiment	$[\text{A}]$, moleLitre ⁻¹	$[\text{B}]$, moleLitre ⁻¹	Initial rate, moleLitre ⁻¹ s ⁻¹
1	0.50	0.50	1.6×10^{-4}
2	0.50	1.00	3.2×10^{-4}
3	1.00	1.00	3.2×10^{-4}

Find,

i) order with respect to A and B.

1

ii) the value of the rate constant of reaction

1

iii) the rate of reaction when the concentration of A and B is 0.5M and 0.4 M, respectively.

1

52. For a hypothetical chemical reaction $m\text{P} + n\text{Q} \rightarrow \text{Z}$; the rate law is $\text{rate} = K [\text{P}]^m [\text{Q}]^n$. Where K is the rate constant of the reaction (m+n) is the overall order.

i) Define rate law.

ii) Why is the rate law an experimental parameter?

iii) What is meant by rate constant?

iv) Mention a difference between order and molecularity of reaction.

v) For the above reaction, the orders of reaction with respect to P and Q are first order and zero order, respectively. Experimental data obtained from the reaction are as follows.

Expt.	$[\text{P}]$, M	$[\text{Q}]$, M	Initial rate, M/sec
I	0.1	0.1	2×10^{-2}
II	A	0.2	4×10^{-2}
III	0.4	0.4	C
IV	B	0.2	2×10^{-2}

b. Identify the value of A, B, and C.

a. Calculate the rate constant (k).

1+3

53. The following data are given for the reaction: $2\text{X} + \text{Y} \rightarrow \text{product}(\text{Z})$

Expt. No.	$[\text{X}]$, mol L ⁻¹	$[\text{Y}]$, mol L ⁻¹	Rate of formation of (Z) mol L ⁻¹ s ⁻¹
1	0.1	0.1	7.0×10^{-3}
2	0.3	0.2	8.4×10^{-2}
3	0.3	0.4	3.36×10^{-1}
4	0.4	0.1	2.8×10^{-2}

i. Calculate the order of reaction with respect to Y and X.

ii. Half-life of reaction with respect to X.

iii. The rate of formation of Z when $[\text{X}] = 0.6 \text{ mol L}^{-1}$ & $[\text{Y}] = 0.3 \text{ mol L}^{-1}$. 4

54. For the reaction, $\text{Cl}_2 + 2 \text{NO} \rightarrow 2 \text{NOCl}$, the data obtained are;

Expt no.	Initial concentration of Cl_2 in mol L^{-1}	Initial concentration of NO in mol L^{-1}	Initial rate of rx ⁿ ($\text{mol L}^{-1} \text{s}^{-1}$)
1	0.020	0.010	2.40×10^{-4}
2	0.020	0.030	2.16×10^{-3}
3	0.040	0.030	4.32×10^{-3}

Determine

- Order of reaction with respect to Cl_2 and NO , and the overall rate of reaction
- If the concentration of Cl_2 is 0.50 mol L^{-1} and NO is 0.40 mol L^{-1} , what is the rate?

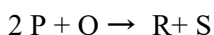
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55. The following data are given for the reaction: $2 \text{X} + \text{Y} \rightarrow \text{product}(\text{Z})$

Expt No.	[X], mol L^{-1}	[Y], mol L^{-1}	Rate of formation of (Z) $\text{mol L}^{-1} \text{s}^{-1}$
1	0.1	0.1	7.0×10^{-3}
2	0.3	0.2	8.4×10^{-2}
3	0.3	0.4	3.36×10^{-1}
4	0.4	0.1	2.8×10^{-2}

- Calculate the order of reaction with respect to Y and X.
- Half-life of reaction with respect to X.
- The rate of formation of Z when $[\text{X}] = 0.6 \text{ mol L}^{-1}$ & $[\text{Y}] = 0.3 \text{ mol L}^{-1}$. 4

56. The following data were obtained at 300K for the reaction



Expt.No	[P] (mol L^{-1})	[Q] (mol L^{-1})	Rate of formation of S (mol L^{-1})
1	0.10	0.10	0.0075
2	0.30	0.20	0.0900
3	0.30	0.40	0.3600
4	0.40	0.10	0.0300

Calculate:

- Order of reaction with respect to P and Q
- Overall order of reaction
- Rate law equation
- Value of the Rate constant
- Rate of formation of S when $[\text{P}] = 0.800 \text{ mol L}^{-1}$ and $[\text{Q}] = 0.500 \text{ mol L}^{-1}$.

57. Consider the following reaction and experimental data.

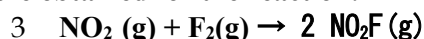
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Experiment	Initial Concentration (mole/L)		Initial Reaction Rate (mole/L/s)
	NH_4^+	NO_2^-	
1	0.2500	0.2500	1.25×10^{-3}
2	0.5000	0.2500	2.50×10^{-3}
3	0.2500	0.1250	6.25×10^{-4}

- What is the rate law of the reaction?
- What is the order with respect to reactants and the overall order?

58. The following data were obtained for the reaction:



Experiment number	Initial concentrations (mol L^{-1})		Initial rate ($\text{mol L}^{-1} \text{s}^{-1}$)
	$[\text{NO}_2]$	$[\text{F}_2]$	
1	0.2	0.05	6×10^{-3}
2	0.4	0.05	1.2×10^{-2}
3	0.8	0.10	4.8×10^{-2}

Find the above rate of reaction when the initial concentrations of NO_2 and F_2 are 0.5 and 0.6 mol L^{-1} , respectively.

4

59. The experimental data for the reaction $2 \text{A} + \text{B}_2 \rightarrow 2 \text{AB}$ are as below.

Expt.	[A], (molL ⁻¹)	[B ₂], (molL ⁻¹)	Rate, (molL ⁻¹ s ⁻¹)
1	0.50	0.50	1.6x10 ⁻⁴
2	0.50	1.00	3.2x10 ⁻⁴
3	1.00	1.00	3.2x10 ⁻⁴

Calculate the rate of formation of AB when the initial concentration of A = 1.00 mol L⁻¹ and B₂ = 2.00 mol L⁻¹. 4

60. The reaction between X and Y is of first order w r to X and zero order w r to Y. Fill in the blanks in the following table.

Exp no.	[X]	[Y]	Initial rate
1.	0.1	0.1	2x 10 ⁻²
2.	-	0.2	4 x 10 ⁻²
3.	0.4	0.4	-
4.	-	0.2	2 x 10 ⁻²

61. Order of reaction can be experimentally determined by comparing the rate of reaction with the change in concentration of a particular reactant.
- Define order of reaction.
 - Write down the unit of rate constant of a zero-order reaction.
 - Give any two points of difference between order and molecularity of a reaction. 1+1+2

Order and molecularity of reaction

62. Give four points of difference between order and molecularity of reaction. 2
63. Give one example of a reaction whose order and molecularity are equal. 1
64. Define the term order of a reaction. 1
65. Why is the order of a reaction an experimental parameter? 1
66. Define the term molecularity of reaction. 1
- Write short notes on order and molecularity of reaction. 4
67. Molecularity of a reaction will never be zero. Give a reason. 1
68. How is the order of reaction determined? 1

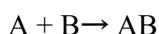
Integrated rate law for a first-order reaction

69. Derive the relation $k = \frac{2.303}{t} \log \frac{a}{a-x}$. Show that for the first-order reaction, the time required for the half change (half-life period) is independent of initial concentrations. 2+1
70. A first-order reaction is 50% completed in 1.26 x 10¹⁴ s. How much time would it take for 90% completion? 2
71. A first-order reaction is 90% complete in 30 minutes. How long will it take to be 99% complete? (Answers = 3600 s, 3598.43 s, 3612.55 s, 60 min, 59.97 min, 60.43 min, 60.4 min, 1 hr, 1/24 day) 3
72. A first-order reaction will take 100 minutes to complete 60% of the reactant into product. What time will it take to complete 90% of the reactant to product? (ans = 251.41 minutes; 250 min;) 3
73. A first-order reaction will take 100 minutes to complete 60% of the reactant into the product. What time will it take to complete 75% of the reactant to the product? (ans = 151.37 min) 2
74. In a first-order reaction, 40% of the reactant gets converted into product in 30 minutes. What time would it take to convert 75% into a product? (ans = 81.56 min) 3
75. 99% of a first-order reaction is completed in 32 minutes. What time will it take to complete 99.9% of the reaction? 4
76. What will be the initial rate of reaction if its rate constant is 1 x 10⁻³ min⁻¹ and the concentration of the reactant is 0.2 mol l⁻¹? How much of the reactant will be converted into the product in 500 minutes? 2

Half-life reaction

77. Define the half-life of a reaction. 2
78. Show that the half-life for a reaction is independent of the initial concentration of reactant. 2

79. Deduce the relation that the half-life for a reaction is directly proportional to the initial concentration of the reactant. 2
80. Why is the half-life period of a first-order reaction independent of the initial concentration? 2
81. Mention the major application of the half-life period in biological scientific research. 1
82. Define the half-life period of a reaction. The half-life periods of two reactions, A and B, are 3.21×10^2 minutes and 569 minutes, respectively. Which of these is a faster reaction? 2
83. Calculate the half-life period of a first-order reaction when the rate constant is 5 year^{-1} . 2
84. The rate of a first-order reaction is $1.5 \times 10^2 \text{ mol l}^{-1} \text{ min}^{-1}$ at 0.5M concentration of the reactant. What is the half-life of the reaction? 2
85. The rate of first order reaction is $6.932 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$ and initial concentration of reactants is 0.1 mol. Find its half-life period. 2
86. For a first-order reaction, the concentration of the reactant is reduced to 25% in 1 hour.
- Calculate the half-life period of the reaction. 2
 - How much concentration of the reactant is converted into products in 2 hours? 2
87. A and B react together to give product AB.



When the concentrations of A and B are both $0.0100 \text{ mol dm}^{-3}$, the rate of formation of AB is $7.62 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. When the concentrations of A and B are both $0.0200 \text{ mol dm}^{-3}$, the rate of formation of AB is $3.05 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

- Write the three possible rate equations that are consistent with these data. [2]
- Choose one of the rate equations you have written in (i), and calculate the value of the rate constant, k. Include the units of k. 2
- Explain why it is not possible to calculate a value for the half-life, $t_{1/2}$, of this reaction using the value of the rate constant k calculated in (ii) and the equation $k = 0.693 / t_{1/2}$.

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