

CHEMICAL KINETICS

XII (CHEMISTRY)

CHAPTER - 4

1. Define rate of reaction.

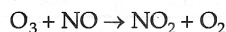
2. A reaction  $A \rightarrow B + C$  has a rate constant of  $4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$ .

(a) What is the order of the reaction?

(b) What is the molarity of A after one hour if the initial concentration of A is  $0.04 \text{ mol L}^{-1}$ ?

(c) What is the half-life of the reaction with  $[A]_0 = 0.04 \text{ mol L}^{-1}$ ?

3. The following table gives the concentration of NO as a function time in the reaction



Time (s)	0	0.011	0.027	0.052
[NO] ( $\text{mol L}^{-1}$ )	$2 \times 10^{-8}$	$1.8 \times 10^{-8}$	$1.6 \times 10^{-8}$	$1.4 \times 10^{-8}$

Calculate the average rate of reaction between 0.011 and 0.027 s. Also find the instantaneous rate at 0 and 0.027 s.

4. Write the rate law for the reaction  $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$  if the reaction is of the first order with respect to each reactant. The rate constant for the reaction is  $1.9 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  at 298 K. What is the rate of the reaction when  $[\text{NO}_2] = 1.8 \times 10^{-8} \text{ mol L}^{-1}$  and  $[\text{O}_3] = 1.4 \times 10^{-7} \text{ mol L}^{-1}$ ?

5. A substance decomposes at 500 K with a rate constant of  $3.46 \times 10^{-4} \text{ s}^{-1}$ . Calculate the half-life of the reaction. What fraction will remain undecomposed if the substance is heated for 1 hour at 500 K?

6. The following data were obtained for the reaction  $A + B \rightarrow C + D$ .

Experiment	[A]	[B]	Rate of formation of C ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
1.	0.01	0.02	$1 \times 10^{-5}$
2.	0.02	0.03	$3 \times 10^{-5}$
3.	0.03	0.03	$4.5 \times 10^{-5}$
4.	0.02	0.04	$4 \times 10^{-5}$

Calculate the rate of formation of C when  $[A] = 0.05 \text{ mol L}^{-1}$  and  $[B] = 0.05 \text{ mol L}^{-1}$ .

7. The following data were obtained at 300 K for the reaction  $2A + B \rightarrow C + D$ .

Experiment	[A]	[B]	Rate of formation of D ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
1.	0.1	0.1	$7.5 \times 10^{-3}$
2.	0.3	0.2	$9.0 \times 10^{-2}$
3.	0.3	0.4	$3.6 \times 10^{-1}$
4.	0.4	0.1	$3.6 \times 10^{-2}$

Calculate the rate of formation of D when  $[A] = 0.08 \text{ mol L}^{-1}$  and  $[B] = 0.5 \text{ mol L}^{-1}$ .

8. The following data were obtained for the initial rate method;

Experiment	Initial concentration of A	Initial concentration of B	Initial rate of formation of C ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
1.	0.02	0.05	0.0125
2.	0.03	0.05	0.0125
3.	0.04	0.05	0.0125
4.	0.05	0.05	0.0045
5.	0.05	0.02	0.0020
6.	0.05	0.01	0.0005

Find graphically the order of the reaction with respect to A and B. Find the rate constant of the reaction.

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9. The rate of formation of C in the reaction  $A + B \rightarrow C$  is dependent on the concentration of A as well as that of B. If the rate constant is  $1 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$ , the order with respect to A is 1 and the rate of formation of C is  $2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ . Find the order with respect to B if the initial concentrations of A and B are  $0.5 \text{ mol L}^{-1}$ .
10. NOCl decomposes as  $2\text{NOCl(g)} \rightarrow \text{NO(g)} + \text{Cl}_2\text{(g)}$

[NOCl] (mol L <sup>-1</sup> )	0.1	0.2	0.3	0.4
Rate (mol L <sup>-1</sup> s <sup>-1</sup> )	$1 \times 10^{-9}$	$4 \times 10^{-9}$	$9 \times 10^{-9}$	$1.6 \times 10^{-8}$

Find the rate constant and the overall order of the reaction.

11. For the reaction  $\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ , the following data were obtained.

[NO] (mol L <sup>-1</sup> )	0.2	0.4	0.6	0.6
[H <sub>2</sub> ] (mol L <sup>-1</sup> )	1	1	0.4	0.5
Rate (mol L <sup>-1</sup> s <sup>-1</sup> )	$3.6 \times 10^{-3}$	0.0144	0.0129	0.0162

Find the rate equation and rate constant with respect to each reactant.

12. For the reaction  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$  the following data were obtained.

[NO] (mol L <sup>-1</sup> )	0.3	0.4	0.4
[Cl <sub>2</sub> ] (mol L <sup>-1</sup> )	0.5	0.5	0.3
Rate (mol L <sup>-1</sup> min <sup>-1</sup> )	$6.75 \times 10^{-3}$	0.012	$7.2 \times 10^{-3}$

Find the rate equation and the rate constant.

13. The concentration of the reactant as a function of time for a first-order reaction was found to be as follows.

Time (min)	0	2	4	10	15
Concentration	1.0	1.12	1.27	1.82	2.46

Find the rate constant graphically.

14. The rate constant for a first-order reaction is  $5 \times 10^{-2} \text{ s}^{-1}$ . What is the half-life of the reaction? Find the time required for the concentration of the reactant to change from  $0.5 \text{ mol L}^{-1}$  to  $0.125 \text{ mol L}^{-1}$ .
15. A reaction of the first order was started with  $1 \text{ mol L}^{-1}$  of the reactant. It took 6.6 min for the concentration to become  $0.1 \text{ mol L}^{-1}$ . What is the half-life of the reaction?
16. A first-order reaction takes 100 minutes for completion of 60% of the reaction. Find the time required for 90% of the reaction to be completed.
17. For the reaction between bromine and formic acid the following data were obtained; the concentration of formic acid was virtually constant throughout the reaction.

Time (s)	0	60	120	180	240	600
[Br <sub>2</sub> ] (mol dm <sup>-3</sup> )	0.01	0.0081	0.0066	0.0053	0.0044	0.0013

What is the order of the reaction?

18. The concentration of the reactant for a reaction as a function of time is as follows.

Time (min)	0	2	4	6	10
Conc. (mol L <sup>-1</sup> )	0.5	0.35	0.28	0.22	0.17

Find the rate constant for the reaction.

19. A study of the rate of dimerisation of  $C_4H_6$  gave the following data.

Time (min)	0	10	50	100	150	200
$[C_4H_6]$ (mol $L^{-1}$ )	0.1	0.095	0.08	0.067	0.057	0.05

Find the rate constant.

20. For the reaction  $C_2H_6 \rightarrow 2CH_3$  the pressure was recorded as follows.

Time (min)	0	10	20	30	60
p (Torr)	0.1	0.072	0.0519	0.0374	0.014

Show that it is a first-order reaction and find the rate constant.

21. The rate constant of a first-order reaction becomes six times the original rate constant when the temperature is increased from 350 K to 410 K. Calculate the energy of activation for the reaction.
22. The slope of the line in the graph of  $\log k$  vs  $1/T$  for a reaction is  $-5400$  K. Calculate the energy of activation for this reaction.
23. The rate constants for a reaction as a function of temperature are given below.

Temperature (K)	200	300	400	500
Rate constant ( $s^{-1}$ )	$2.98 \times 10^{-5}$	$1.65 \times 10^{-6}$	$1.22 \times 10^{-8}$	$4.07 \times 10^{-8}$

Find the activation energy of the reaction graphically and rate constant at 600 K.

24. For the first-order hydrolysis of sucrose, the rate constant at 300 K is  $2.1 \times 10^{-11} s^{-1}$  and  $8.5 \times 10^{-11}$  at 310 K. Find the Arrhenius constant and the activation energy.
25. The rate constant for the decomposition of a substance is  $3890 L mol^{-1} s^{-1}$  at 300 K and  $2.62 \times 10^5 L mol^{-1} s^{-1}$  at 400 K. Find the Arrhenius constant and the activation energy.
26. The rate constants for the decomposition of acetaldehyde as a function of temperature are given below.

Temperature (K)	600	700	800	850	900	950
$k$ ( $L mol^{-1} s^{-1}$ )	$5.09 \times 10^{-5}$	0.01	0.515	2.62	11.1	40.6

Find the Arrhenius constant  $A$  and also the activation energy graphically.

27. If  $\Delta[NO_3]/\Delta t$  is  $-2.5 \times 10^{-2} mol L^{-1} s^{-1}$  in the following reaction, find the rate of appearance of  $NO_2$ .



28. Sucrose ( $C_{12}H_{22}O_{11}$ ) hydrolyses to glucose ( $C_6H_{12}O_6$ ) as  $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow C_6H_{12}O_6(aq)$ . The reaction is considered to be a pseudo-first-order reaction if a large excess of water is used. Determine the pseudo-first-order rate constant from the following data.

Time (s)	0	612	1600	3160
$[C_{12}H_{22}O_{11}]$ (mol $L^{-1}$ )	0.562	0.541	0.509	0.462

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