CHEMISTRY

```
11. Rate = 2 \times 10^{-4} mol dm<sup>-3</sup> min<sup>-1</sup>; x = 18.12%
                                                                                12. % decomposition = 67.21\%
13. (a) order wrt NO = 2, Cl_{1} = 1
                                                                                (b) r = k[Cl_{2}]^{1}[NO_{2}]^{2}
      (c) k = 8 lit^2 mol^{-2} sec^{-1}
                                                                                (d) r = 0.256 \text{ mol lit}^{-1} \text{sec}^{-1}
14. (a) Rate = 1 \times 10^{-2} mol lit<sup>-1</sup> sec<sup>-1</sup> (b) rate after 1 min = 5.49 \times 10^{-3} mol lit<sup>-1</sup> sec<sup>-1</sup>
                                                                                16. (i) t_{99\%} = 13.95 hour (ii) 2.217 litre
15. total pressure = 0.75 atm
                                                         (iii) initial rate of conversion of A = 0.1 mol lit<sup>-1</sup> hour<sup>-1</sup>
17. (i) n = 2 (ii) K = 1.2 \text{ mol lit}^{-1}
                                                         (ii) K = 2.66 \times 10^8 \text{ lit}^2 \text{ mol}^{-2} \text{sec}^{-1}
 18. (i) order w.r.t A = 2; B = 1
                                                         (iv) A = 1.140 \times 10^{18}
   (iii) E_a = 55.44 \text{ kJ/mol}
 19. t = 20.39 \min
                                                        (b) k = 4 \times 10^{-2} \text{ lit mol}^{-1} \text{ sec}^{-1}
20. (a) order with r.t. A = 2, B = 0
   (c) rate = 16 \times 10^{-4} mol lit<sup>-1</sup> sec<sup>-1</sup>
21. DE = 18.33 K cal mol<sup>-1</sup>; k = 9.22 \times 10^{-4} sec<sup>-1</sup>
22. (a) E_a = 24.83 kcal mol<sup>-1</sup> (b) K = 2.35 \times 10^{-5} \text{ sec}^{-1} (c) T = 513 K
23. E_a = 2.2 \times 10^4 \text{ J mol}^{-1}; A = 5.42 \times 10^{10}
24. K = 3.4354 \times 10^{-3}
                                                                               25. E_{a} = 100 \text{ kJ mol}^{-1}
26. (a) (i) O.R. = I order (ii) K = 0.069 hr<sup>-1</sup> (b) t_{1/2} = 24.06 min
27. order = 1 k = 2.30 \times 10^{-2} \text{ sec}^{-1}
29. (a) r = k[A][B]° (b) k = 5 \times 10^{-1} \text{ sec}^{-1}
                                                                                28. 1.005 \times 10^{-4} \text{ min}^{-1}
30. (i) 1, (ii) 6.93 \times 10^{-3} \text{ min}^{-1}, (iii) 200 min, (iv) 950 mm Hg
31. 0 order
```

000

	80.	geon	netrical is	omerisa	ation	81.	$\ln \frac{k_2}{k_1}$	<u>!</u>					
True/	False.												
	82.	Т	83.	F	84.	F	85.	Т	86.	F	87.	F	
	88.	Т	89.	F	90.	F	91.	Т	92.	Т	93.	F	
	94.	Т	95.	F	96.	Т							
[
						Exerci	ise–12						
	1.	В	2.	С	3.	D	4.	С	5.	Α	6.	А	
	7.	Α	8.	D	9.	А	10.	С	11.	Α	12.	В	
	13.	С	14.	С	15.	D	16.	в	17.	С	18.	D	
	19.	D											

Exercise-13												
01.	A	02.	D	03.	D	04.	D	05.	A	06.	D	
07.	С	08.	D	09.	С	10.	Α	11.	D	12.	С	
13.	D	14.	Α	15.	С	16.	Α	17.	Α	18.	D	
19.	С											

Exercise– 14					
1.B	2. T	3. F			
4. concentration of reactants	5. acidic, I	6. D	7. D		
8. Mn ⁺² ions	9. B	10. F	11. D		
12. C	13. B	14. A	15. A		
16. B	17. C	18. C	19. A		
20. A, D	21. A	22. D	23. B		
24. A	25. C	26. C	27. D		
28. D	29. A	30. D	31. A		
32. ABD					

Eve	rcis	e_	15
LAU	1 013	<u> </u>	1.0

1. (a) Rate = $k[A]^{1}[B]^{2}$ (b) $k = 0.1 \text{ lit}^{2} \text{ mol}^{-2} \text{min}^{-1}$	
2. 5.25% , 128.33 hr	3. 398.78 min

- 4. (a) $K_1 = 2.31 \times 10^{-2} \text{ min}^{-1}$, $k_2 = 6.93 \ 10^{-2} \text{ min}^{-1}$
 - **(b)** $E_a = 43.85 \text{ kJ mol}^{-1}$ **(c)** $93.85 \text{ kJ mol}^{-1}$
- **5.** (a) $K = 6.23 \times 10^{-3} \text{ sec}^{-1}$ (b) P = 0.033 atm **6.** T = 311.35 K
- 7. (a) = I order (b) k = $1.308 \times 10^{-2} \text{ min}^{-1}$ (c) 73%

8.
$$k = 5.206 \times 10^{-3} \text{ min}^{-1}$$
 9. $-\frac{dx}{dt} = k [B_2]^{-1}$ **10.** K_u at 300 K = 0.0327 min^{-1}

Exercise - 05

1. $A = 115.98 \text{ sec}^{-1}$ 2. total pressure = 379.73 mm Hg3. $K = 7.512 \times 10^{-3} \text{ min}^{-1}$ 4. 1.188×10^{17} 5. $A = 2p^0 -$ 6. 36.2%7. 1 : 2.4498. (a) 90 mm(b) 47 mm(c) 10.677 min

Exercise - 06									
1. ABC	2. ABCD	3. ABCD	4. ABCD	5. AB	6. AC				
7. ABC	8. AC	9. ABC	10. BC	11. ABCD	12. BCD				
13. D	14. C	15. CD	16. C	17. CD	18. B				
19. B	20. BC								

					Exerc	ise - 07					
01. A	A-r; B-j	o, C-t, d	-q			02. A	A-r, B-s	s, C-q, D)-p,r		
03. C		04. E)	05. B		06. A	L	07. A		08. E)
					Exerc	ise - 08					
01.	В	02.	А	03.	С	04.	D	05.	в	06.	А
07.	в	08.	С	09.	D	10.	А	11.	Α	12.	Α
13.	D	14.	в	15.	D	16.	В	17.	С	18.	С
	٨	20	C	21	С	22	Δ				

 01.
 D
 02.
 B
 03.
 C
 04.
 A
 05.
 D
 06.
 B

 07.
 B
 08.
 C
 09.
 D
 10.
 B

Exercise-10												
1.	3	2.	2	3.	3	4.	2	5.	2	6.	3	
7.	2	8.	6	9.	0	10.	3					

			Exercise-11		
Fill in the bl	anks				
62.	pseudo, first	63.	faster	64.	photochemical
65.	slowest	66.	order	67.	0.693/k
68.	0.5	69.	may or may not	70.	visible radiations
71.	atm sec ^{-1}	72.	k_{308}/k_{298}	73.	k
74.	cannot	75.	three	76.	$-\Delta[B]/\Delta t$
77.	At $T \longrightarrow \infty$	78.	dark	79.	1/2

ANSWER SHEET

Exercise - 01

1. H 5. S 12. S 16. H 18. 2	$_2 + Cl_2 \rightarrow 2HCl$ econd order Second order Tirst order 20.35×10^{12} sec.	 9.30 × 10⁻⁵ mol L⁻¹ sec⁻¹ 8.548 min 13. Zero order 17. 103.27 × log 5 = 72.19 ± 	 4. First order 11. 0.384 min 14. 111.838 kJ mol⁻¹ min.
19. 8	$8.52 \times 10^{-4} \mathrm{s}^{-1}$	20. $k_2 = 30.98 \times 10^{-3} \text{ sec}^{-1}$	21. 53.599 kJ
28. t	= 62.13 minutes	29. 51.86 kJ mol ⁻¹	33. First order
34. 3	3.8%	35. 146.68 min	
36. (i) 1.49 × 10 ⁻² min ⁻¹ (ii)	154.56 (iii) 29.94 min	37. 22.01 kJ mol ⁻¹
39	No relation	40. a/k	$41 \qquad -\frac{dx}{dt} = \mathbf{k}$
43	0.038 s (a) [(i) Nature of react (iii) Catalyst, (iv) T	44. (b) $1.25 \times 10^{-4} \text{ mol}^{-1}$ ant, (ii) concentration of reactan remperature,]	L s ⁻¹ , 3.75×10^{-4} mol ⁻¹ L s ⁻¹ OR t (b) [1847.37]

	Exercise - 02								
1. B	2. B	3. D	4. C	5. A	6. A				
7. B	8. B	9. B	10. B	11. A	12. C				
13. B	14. D	15. A	16. D	17. A					

Exercise - 03

1. T = 310.96 K 4. $r_2/r_1 = 2.34 \times 10^{13}$	2. = $8.88 \times$ 5. (i) t = 53.	10 ³² .4 sec (ii	3. $A = 5.04 \times 10^5 \text{ s}^{-1}$ i) total pressure = 0.201 atm
6. $1.09 \times 10^{-5} \text{ mol lit}^{-1} \text{sec}^{-1}$	7. tin	$he = 6 \times 10^{-1}$	⁹ sec
8. (a) $\Delta H = -10 k J/mol$		(b) $E_{f} = 3$	$60 \text{ kJ/mol}; \text{E}_{b} = 40 \text{kJ/mol}$
(c) $E_f = 10 \text{ kJ/mol}$; $E_b = 2$	20 kJ/mol	(d) NO	$9. K = \frac{2.303}{t} log \frac{2P_0}{3P_0 - P}$
	Б.	0.4	

Exercise - 04						
1. B	2. B	3. B	4. A	5. B	6. B	
7. B	8. B	9. C	10. B	11. B	12. C	
13. B	14. D	15. C	16. A	17. C	18. D	
19. D	20. C	21. B	22. B			

Q.28 The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of A is mixed with 12 moles of B. However, as soon as B is added, A starts polymerising into a completely insoluble solid. The polymerisation follows first order kinetics. After 100 minutes, 0.525 mole of a solute is dissolved which arrest the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation, and ideal behaviour for the final solution.

2004

Q.29 For the given reaction , $A + B \longrightarrow$ Products

T 11				
Follo	wino	data	were	orven
1 0110		uuuu		Siten

	Initial conc.	Initial conc.	Initial rate
	(m/L)	(m/L)	$[ml^{-1}s^{-1}]$
	[A]	[B]	
	0.1	0.1	0.05
	0.2	0.1	0.1
	0.1	0.2	0.05
(a)	write the rate equations.	(b)	calculate the rate constant.

2005

Q.30 At constant temperature and volume, X decomposes as

 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$; Px is the partial pressure of X.

Observation No.	Time (in minute)	P_x (in mm of Hg)
1	0	800
2	100	400
3	200	200

- (i) What is the order of reacion with respect to X?
- (ii) Find the rate constant.
- (iii) Find the time for 75% completion of the reaction
- (iv) Find the total pressure when pressure of X is 700 mm of Hg.

2010

31. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained.

[R] (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

the order of the reaction is

Q.20 The following data are for the reaction $A + B \longrightarrow$ products :

Conc. of A (M)	conc. of B (M)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0 ×10-4
0.2	0.2	1.6 ×10-3
0.5	0.1	1.0 ×10 ⁻²
0.5	0.5	1.0 ×10 ⁻²

- (a) What is the order with respect to A and B for the reaction?
- (b) Calculate the rate constant.
- (c) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M respectively.

1997

- **Q.21** The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is 3.56×10^9 s⁻¹, calculate its rate constant at 318 K and also the energy of activation.
- Q.22 The rate constant for the first order decomposition of a certain reaction is given by the equation,

$$ln \text{ K}(\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

Calculate :

(i)

- (a) the energy of activation.
- (b) the rate constant at 500 K.
- (c) At what temperature will its half life period be 256 minute?

1998

Q.23 The rate constant of a reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C. Evaluate the Arrhenius parameters. A and E_a.

1999

Q.24 The rate constant for an isomerisation reaction, $A \longrightarrow B$ is 4.5×10^{-3} min⁻¹. If the initial concentration of A is 1M, calculate the rate of the reaction after 1 hr.

2000

Q.25 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation energy barrier by 20 kJ mol⁻¹.

2001

Q.26 (a) In a reaction with initially 0.12 M, the concentration of reactant is reduced to 0.06 M in 10 hour and to 0.03 M in 20 hour.

What is order of reaction? (ii) What is rate constant?

- (b) The rate of a first order reaction is $0.04 \text{ mol litre}^{-1}\text{s}^{-1}$ at 10 minute and $0.03 \text{ mol litre}^{-1}\text{sec}^{-1}$ at 20 minute after initiation. Find the half life of the reaction.
- **Q.27** Some $PH_3(g)$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant.

Time (sec)	0	60	120	∞
P(mm Hg)	262.40	272.90	275.51	276.40

Q.13 The data given below are for the reaction of NO and Cl, to form NOCl at 295 K.

[Cl ₂]	[NO]	Initial rate (mol litre ⁻¹ sec ⁻¹)
0.05	0.05	1 × 10-3
0.15	0.05	3 × 10-3
0.05	0.15	9 × 10 ⁻³

What is the order w.r.t NO and Cl₂ in the reaction ? **(a)**

(b) Write the rate expression.

- Calculate the rate constant. (c)
 - (d) Determine the reaction rate when conc. of Cl, and NO are 0.2 M and 0.4 M respectively.
- Q.14 A substance reacts according to I order kinetics and rate constant for the reaction is 1×10^{-2} sec⁻¹. If its initial concentration is 1 M,

What is initial rate? (a)

- **(b)** What is rate after 1 minute?
- Q.15 The gas phase decomposition of dimethyl ether follows first order kinetics, CH OCH (~) $CH(\alpha) + H(\alpha) + CO(\alpha)$

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minute? Assume ideal gas behaviour.

1994

Q.16 The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

 $NH_2NO_2(aq.) \longrightarrow N_2O(g) + H_2O(l)$

If 6.2 g of NH₂NO₂ is allowed to decompose, calculate

- (i) time taken for NH₂NO₂ to decompose 99%.
- (ii) volume of dry N₂O produced at this point measured at STP.
- **Q.17** The progress of reaction $A \rightarrow nB$ with time is

presented in the figure. Determine :

- (i) the value of n
- (ii) the equilibrium constant, K and
- the initial rate of conversion of A. (iii)



[A]	[B]	Initial rate mol litre ⁻¹ sec ⁻¹	
mol litre ⁻¹	mol litre ⁻¹	300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	$2.0 imes 10^{-3}$
$5.0 imes 10^{-4}$	$6.0 imes 10^{-5}$	4.0×10^{-3}	-
1.0×10^{-3}	$6.0 imes 10^{-5}$	1.6×10^{-2}	-

Calculate :

- the order of reaction with respect to A and with respect to B. (i)
- the rate constant at 300 K. (ii)
- (iii) the energy of activation.
- the pre-exponential factor. (iv)

1995

Q.19 At 380 °C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol⁻¹. Calculate the time required for 75 % decomposition at 450°C.



- Q.4 A Ist order reaction is 50 % complete in 30 minute at 27°C and in 10 minute at 47°C. Calculate the :
 - (a) Rate constant for reaction at 27° C and 47° C.
 - (b) Energy of activation for the reaction.
 - (c) Energy of activation for the reverse reaction if heat of reaction is -50 kJ mol^{-1} .
- 1989
- **Q.5** The decomposition of Cl₂O₇ at 400 K in the gas phase to Cl₂ and O₂ is of I order . After 55 sec at 400 K, the pressure of Cl₂O₇ falls from 0.062 to 0.044 atm. Calculate :
 - (a) the rate constant. (b) pressure of Cl_2O_7 after 100 sec.
- 1990
- **Q.6** In the Arrehenius equation for a certain reaction, the values of A and E_a (energy of activation) are 4×10^{13} sec⁻¹ and 98.6 kJ mol⁻¹ respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute ?
- **Q.7** Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50 % in 53 minute and 73 % in 100 minute.
 - (a) What is the order of reaction?
 - (b) Calculate velocity constant.
 - (c) How much will it decompose in 100 minute at the same temperature but at an initial pressure of 600 mm?

- **Q.8** The decomposition of N_2O_3 according to equation $2N_2O_3(g) \longrightarrow 4NO_2(g) + O_2(g)$ is a first order reaction. After 30 minute from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of reaction.
- Q.9 The experimental data for the reaction, $2A + B_2 \longrightarrow 2AB$ are as follows. Write probable rate expression.

[A]	[B ₂]	Rate
mol litre ⁻¹	mol litre-1	mol litre ⁻¹ sec ⁻¹
0.50	0.50	1.6×10^{-4}
0.50	1.0	3.2 ×10 ⁻⁴
1.00	1.0	3.2 ×10-4

1992

- Q.10 Two reaction (I) A → Products (II) B → Products follows first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minute. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (II) is half that of reaction (I). Calculate the rate constant of reaction (II) at 300 K.
- **Q.11** What will be the initial rate of a reaction if its rate constant is 10⁻³ min⁻¹ and the concentration of reactant is 0.2 mol dm⁻³? How much of reactant will be converted into products in 200 minute?
- 1993
- **Q.12** A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol⁻¹. When a 20% solution of A was kept at 25°C for 20 minute, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature ?

2010

31. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is



2011

32. For the first order reaction

 $2N_2O_2(g) \rightarrow 4NO_2(g) + O_2(g)$

(A) The concentration of the reactant decreases exponentially with time.

(B) the half-life of the reaction decreases with increasing temperature.

(C) the half-life of the reaction depends on the initial concentration of the reactant.

(D) the reaction proceeds to 99.6% completion in eight half-life duration.

EXERCISE - 15 IIT FLASH BACK - SUBJECTIVE TYPE QUESTIONS

1987

- Q.1 For the reaction, $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1×10^{-4} mol lit⁻¹ min⁻¹. In the second experiment when the initial concentration of A and B are 0.1 M and 0.3 M, the initial rate is 9.0×10^{-4} mol litre⁻¹ minute⁻¹. In the third experiment when the initial conc. of both A & B are 0.3 M, initial rate is 2.7×10^{-3} mol litre⁻¹ minute⁻¹.
 - (a) Write rate law for this reaction.
 - (b) Calculate the value of specific rate constant for this reaction.
- Q.2 A first order gaseous reactions has $K = 1.5 \times 10^{-6} \text{ sec}^{-1}$ at 200 °C. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction ?
- 1988
- **Q.3** Thermal decomposition of a compound is of first order. If 50 % sample of the compound is decomposed in 120 minute, how long will it take for 90 % of the compound to decompose ?

2001

Q.23 If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process $AB + hv \rightarrow AB^*$, rate of formation of AB^* is directly proportional to (A) C (B) I (C) I² (D) C.I.

2002

Q.24 Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions –

(A)	$\operatorname{Rate} = -\frac{d[\mathcal{N}_2]}{dt} = -\frac{1}{3}\frac{d[\mathcal{H}_2]}{dt} = \frac{1}{2}\frac{d[\mathcal{N}\mathcal{H}_3]}{dt}$
(B)	Rate = $-\frac{d[\mathcal{N}_2]}{dt} = -3\frac{d[\mathcal{H}_2]}{dt} = 2\frac{d[\mathcal{N}\mathcal{H}_3]}{dt}$
(C)	Rate $= \frac{d[\mathcal{N}_2]}{dt} = \frac{1}{3} \frac{d[\mathcal{H}_2]}{dt} = \frac{1}{2} \frac{d[\mathcal{N}\mathcal{H}_3]}{dt}$
(D)	$\text{Rate} = -\frac{d[\mathcal{N}_2]}{dt} = -\frac{d[\mathcal{H}_2]}{dt} = \frac{d[\mathcal{N}\mathcal{H}_3]}{dt}$

2003

Q.25 In a first order reaction the conc. of reactant decreases from 800 mol/dm³ to 50 mol/dm³ in 2 $\times 10^4$ sec. The rate constant of reaction in sec⁻¹ is –

(A) 2×10^4	(B) 3.45×10^{-5}	(C) 1.386 × 10 ⁻⁴	(D) 2×10^{-4}
---------------------	---------------------------	------------------------------	------------------------

2004

Q.26 The reaction X \longrightarrow Product follow first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M.(A) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.47 \times 10^{-5} \text{ M min}^{-1}$ (C) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (D) $1.73 \times 10^{-5} \text{ M min}^{-1}$

2005

- Q.27 Which one of the following statement for order of reaction is not correct?
 - (A) Order can be determined experimently
 - (B) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
 - (C) It is not affected with the stoichiometric coefficient of the reactants
 - (D) Order cannot be fractional.

2007

Q.28 Consider a reaction $aG + bH \rightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

A) 0 (B) 1 (C) 2 (I	D)	1		
---------------------	----	---	--	--

2008

29. Under the same reaction conditions, initial concentration of 1.386 mol dm⁻³ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio of the rate constants for first order (k_1) and zero order (k_0) of the reactions is

(A) 0.5 mo	$I^{-1} dm^3$ (B)	1.0 mol dm ⁻³ (C	1.5 mol dm^{-3} (D) 2.0 mol ⁻¹ dm ³
------------	-------------------	-----------------------------	-----------------------------	------------------------------------------

Q.12 The reaction $L \longrightarrow M$ is started with 10 g of L. After 30 and 90 minutes, 5 g and 1.25 g of L are left respectively. The order of reaction is :

(D) 3

(A) 0 (B) 2 (C) 1
----------------	-----

1994

Q.13 The first order reaction has a half life period of 69.3 s. At 0.10 mol ℓ^{-1} reactant concentration, the reaction rate will be :

A) $1.0 \times 10^{-4} \text{ mol } \ell^{-1} \text{s}^{-1}$	(B) $1.0 \times 10^{-3} \mod \ell^{-1} s^{-1}$
C) $1.0 \times 10^{-1} \text{ mol } \ell^{-1} \text{s}^{-1}$	(D) $6.39 \times 10^{-4} \text{ mol } \ell^{-1} \text{s}^{-1}$

Q.14 For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h⁻¹. The rate of conversion of H_2 under the same condition is ______ kg h⁻¹. (A) 0.0017 kg h⁻¹ (B) 0.002 kg h⁻¹ (C) 0.003 kg h⁻¹ (D) 0.005 kg h⁻¹

1995

Q.15 The rate constant of a first order reaction is $4 \times 10^{-3} \text{ s}^{-1}$. At a reactant concentration of 0.02 mol ℓ^{-1} , the rate of reaction would be :

(A) $8 \times 10^{-5} \text{ mol } \ell^{-1} \text{s}^{-1}$	(B) $4 \times 10^{-3} \mod \ell^{-1} s^{-1}$
(C) $2 \times 10^{-1} \text{ mol } \ell^{-1} \text{s}^{-1}$	(D) $4 \times 10^{-1} \text{ mol } \ell^{-1} \text{s}^{-1}$

1996

Q.16 The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25 °C are 3.0×10^{-4} s⁻¹, 104.4 kJ mol⁻¹ and 6.0×10^{14} s⁻¹ respectively. The value of the rate constant as T $\longrightarrow \infty$ is : (A) 2.0 × 10¹⁸ s⁻¹ (B) 6.0 × 10¹⁴ s⁻¹ (C) infinity (D) 3.6 × 10³⁰ s⁻¹

(A) $2.0 \times 10^{18} \text{ s}^{-1}$	(B) 6. $0 \times 10^{14} \text{ s}^{-1}$	(C) infinity	(D) $3.6 \times 10^{30} \text{ s}^{-1}$
-----------------------------------------	------------------------------------------	--------------	-----------------------------------------

Q.17 The rate constant (k) for the reaction $2A + B \longrightarrow$ Products, was found to be $2.58 \times 10^{-5} \ell$ mol⁻¹ s⁻¹ after 15 sec, $2.60 \times 10^{-5} \ell$ mol⁻¹ s⁻¹ after 30 sec and $2.55 \times 10^{-5} \ell$ mol⁻¹ s⁻¹ after 50 sec. Hence the order of the reaction is : (A) 0 (B) 1 (C) 2 (D) 3

1997

- **Q.18** In the Arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as the rate constant at : (A) T = 0 (B) T = 298 K (C) T $\rightarrow \infty$ (D) none
- Q.19 The rate constant of a first order reaction, $A \rightarrow Products$, is $60 \times 10^{-4} s^{-1}$ its rate at [A] =0.01 ml ℓ^{-1} would be : (A) 60×10^{-6} mol ℓ^{-1} min⁻¹ (B) 36×10^{-4} mol ℓ^{-1} min⁻¹

(A) $60 \times 10^{-6} \text{ mol } \ell^{-1} \text{ min}^{-1}$	(B) $30 \times 10^{-4} \text{ mol } \ell^{-1} \text{ min}^{-1}$
(C) $60 \times 10^{-2} \text{ mol } \ell^{-1} \text{ min}^{-1}$	(D) $36 \times 10^{-1} \text{ mol } \ell^{-1} \text{ min}^{-1}$

1998

- **Q.20** For a first order reaction :
 - (A) the degree of dissociation is equal to $(1-e^{-kt})$
 - (B) a plot of reciprocal concentration of the reactant vs time gives a straight line
 - (C) the time taken for the completion of 75% reaction is thrice the t_{12} of the reaction
 - (D) the pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}

1999

Q.21 For a first order reaction $A \longrightarrow$ Product, the rate of reaction at $[A] = 0.2 \mod \ell^{-1}$ is $1.0 \times 10^{-2} \mod \ell^{-1} \min^{-1}$. The half life period for the reaction is :

(A) 052 S (B) 440 S (C) 410 S (D) 140 S (D)	14 s
-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	------

	(I) $Cl_{a} + H_{a}S \rightarrow H$	$I^{+} + Cl^{-} + Cl^{+} + HS^{-}$	(slow)	
	$Cl^{+} + HS^{-} \rightarrow l$	$I^{+} + Cl^{-} + S$	(fast)	
	(II) $H_s S \Longrightarrow H^+$	$+ HS^{-}$	(fast equili	brium)
	$Cl_{*}^{2} + HS^{-} \rightarrow 2$	$Cl^{-} + H^{+} + S$	(slow)	,
	(A) I only		(B) II only	7
	(C) Both I and II		(D) Neith	er I nor II
18.	The time for half li of the reactant A is 0.50 to 0.25 mol L	fe period of a certain rea 2.0 mol L ⁻¹ . How mucl ⁻¹ if it is a zero order rea	action A \rightarrow Products is 1 a time does it take for its action?	h when the initial concentration concentration to come from (2010)
	(A) l h	(B)4h	(C) 0.5 h	(D) 0.25 h
19.	The rate of a chem raised by 50°C, the	ical reaction doubles fo rate of the reaction inc	r every 10°C rise of tem rease by about:	perature. If the temperature is (2011)
	(A) 10 times	(B) 24 times	(C) 32 times	(D) 64 times
	EX	ERCISE - 14 II'	r flash back	- MCQ
1987				
0.1	The rate of reaction	n between A and B inc	reases by a factor of 10	0, when the concentration of A
C.	is increased 10 fo	lds. The order of react	ion with respect to A is	: (D) 20
0.2	For a first order	reaction, the rate of the	reaction doubles as th	e concentration of the reactants
×	double.			[True/False]
Q.3	Catalyst makes a	reaction more exother	mic.	[True/False]
Q.4	The rate of chemi	cal change is directly p	proportional to	
Q.5	The hydrolysis of	ethyl ethanoate in	medium is a	order reaction.
1988				
Q.6	The rate law for t	he reaction, RCl+N	$aOH(aq) \longrightarrow ROH +$	NaCl
	is given by, Rate =	= K[RCI]. The rate of re	eaction will be –	
	(R) doubled o	n doubling the concent	ration of NaOH	
	(C) halved on	reducing the concentr	ation of NaOH to one h	alf
	(D) halved on	reducing the concentra	tion of RCl to one half	
Q.7	In the first order r	eaction, the concentra	tion of reactant decrea	ses from 1.0 M to 0.25 M in 20
	minutes. The valu	e of specific rate is –		
	(A) 69.32	(B) 6.932	(C) 0.6932	(D) 0.06932
1989				
Q.8 1990	The decolorization	n of KMnO ₄ by oxalic	e acid is catalysed by	
Q.9	The half life of a f	rst order reaction is 10	minutes. The time requ	ired for the concentration of the
	reactant to chang	e from 0.08 M to 0.01	M is :	
	(A) 20 minutes	(B) 30 minutes	(C) 40 minutes	(D) 50 minutes
Q.10 1992	The rate of an exo	thermic reaction increa	ases with increase in te	mperature. [T/F]
Q.11	The rate of a gased	ous reaction is given by	the expression k. [A].[B]. If the volume of the reaction
	vessel is suddenly	reduced to one fourth o	or the initial volume, the	reaction rate relative to original
	(A)	(B)	(C) 8	(D) 16
	(**)			

09.	Consider an endoth	ermic reaction X	\rightarrow Y with the activat	ion energies E _b and E	for the backward	
	and forward reaction	ons, respectively. I	n general		(2005)	
	$(\mathbf{A}) \mathbf{E}_{\mathbf{b}} = \mathbf{E}_{\mathbf{f}}$		(B) no definite rel	ation between E_b and	E _f	
	$(C) E_{b} < E_{f}$		(D) $E_{b} > E_{f}$			
10.	The following mech	nanism has been p	roposed for the reacti	on of NO with Br, to	formNOBr: (2006)	
	$NO(g) + Br_2(g) =$	\rightarrow NOBr,(g)	NOBr ₂ (g)	+ NO(g) = 2	NOBr(g)	
	If the second step is	s the rate determin	ning step, the order of	f the reaction with rea	pect to NO(g) is	
	(A) 2	(B) 1	(C) 0	(D) 3		
11. A reaction was found to be second ordr with respect to the concentration of carb the concentration of carbon monoxide is doubled, with everything else kept the s reaction will		bon monoxide. If same, the rate of				
	(A) double		(B) remain unchar	nged	(2006)	
	(C) triple		(D) increase by a	factor of 4		
12.	Rate of a reaction c	an be expressed l	by Arrhenius equation	on as : $k = A e^{-E/RT}$	(2006)	
	In this equation, E i	s represents				
	(A) the fraction of r	nolecules with en	ergy greater than the a	ectivation energy of the	e reaction	
	(B) the energy abov		biliding molecules wi	ireact		
	(C) the energy below	w which colliding	molecules will not re	act		
	(D) the total energy	of the reacting m	olecules at a tempera	ture, I		
13.	The energies of act mol ⁻¹ and 200 kJ m (forward and rever 2AB) in the present	ivation for forwa ol ⁻¹ , respectively. se) reactions by 1 ce of catalyst will	and reverse reacting $The presence of a cat 00 kJ mol-1. The entry be$	ons for $A_2 + B_2$ alyst lowers the active halpy change of the r		
	(A) 300 kJ mol^{-1}		(B) 120 k	J mol ⁻¹		
	(C) 280 kJ mol ^{-1}		(D) 20 kJ	mol ⁻¹		
14.	Consider the reacti	on, $2A + B \rightarrow Pro$	oducts			
	When concentration of B alone was doubled, the half-life did not change. When the concentration of					
	(A) I mol-l a-l	(P) no unit	(C) mol $I = 1$ c^{-1}	(D) = 1	(2007)	
	(A) L IIIOI S	(B) no unit	(C) IIIOI L S	(D) \$	(2007)	
15.	For a reaction ½ A by the expression	\rightarrow 2B, the rate of	f disappearance of A	is related to the rate	of apperance of B (2008)	
	$(\mathbf{A}) - \mathbf{d}[\mathbf{A}] / \mathbf{dt} = 4$	d [B] / dt	(B)-d[A]/dt = (1/2) d[B] / dt		
	(C) - d[A]/dt = (1/4)	4) d[B]/dt	(D)-d[A]/dt = d[B]/dt		
16.	The half-life of a fir of 99% of the react	rst order chemical ion will be (Giver	reaction is 6.93 minu n: $\log 2 = 0.301$)	tes. The time required	for the completion (2009)	
	(A) 46.06 min.		(B)460.6	min.		
	(C) 230.3 min.		(D) 23.03	min.		
17.	Consider the reacti	$\log \operatorname{Cl}_2(\operatorname{aq}) + \operatorname{H}_2 S$	$(aq) \rightarrow S(s) + 2H^{+}(a)$	$q) + 2Cl^{-}(aq)$	(2010)	
	The rate equation f	or the reaction is i	$rate = k[Cl_2][H_2S]$			
	Which of the follow	ving mechanisms i	s/are consistent with t	his rate equation?		

19. Consider the reaction, $2A + B \rightarrow$ Products

 $\begin{array}{c|c} When \ concentration \ of \ B \ along \ was \ doubled, \ the \ half-life \ die \ not \ change. \ When \ the \ concentration \ of \ A \ alone \ was \ doubled, \ the \ rate \ increased \ by \ two \ times. \ The \ unit \ of \ rate \ constant \ for \ this \ reaction \ is \ (A) \ L \ mol^{-1}s^{-1} \qquad (B) \ no \ unit \qquad (C) \ mol \ L^{-1}s^{-1} \qquad (D) \ s^{-1} \ \end{array}$

EXERCISE - 13 AIEEE FLASH BACK

01.	. The rate law for a reaction between the substances A and B is given by rate = $k [A]^n [B]^m$ (20)				B] ^m (2003)	
	On doubling the con rate to the earlier rate	centration of A and reduce of the reaction will be a	cing the concentration o	fB to half, the rat	io of the new	
	$(A) 2^{(n-m)}$	(B) $1/2^{(m+n)}$	(C)(m+n)	(D)(n-m)		
02.	For the reaction syste increasing the press respect to NO, the ra	$\operatorname{cm} 2\operatorname{NO}(g) + \operatorname{O}_2(g) \to 21$ ure on it. If the reaction is the of reaction will	$NO_2(g)$ volume is sudde s first order with respec	nly reduced to hat et to O_2 and secor	lf its value by nd order with (2003)	
	(A) increase to four t	imes of its initial value	(B) diminish to one -	fourth of its initial	value	
	(C) diminish to one-e	eight of its initial value	(D) increase to eight	times of its initial	value	
03. In respect of the equation $k = A \exp(-E_a/RT)$ in chemical kinetics, which one of the statements is correct?				nich one of the fol	lowing (2003)	
	(A) R is Rydberg's c	onstant	(B) k is equilibrium c	onstant		
	(C) A is adsorption f	actor	(D) E_a is the energy of	ofactivation		
04.	The rate equation for statement in relation	or the reaction $2A + B$ to this reaction is that the	\rightarrow C is found to be:	rate = $k [A] [B]$.	The correct (2004)	
	(A) unit of k must be	$e s^{-1}$				
	(B) $t_{1/2}$ is a constant					
	(C) rate of formation	n of C is twice the rate of	disappearance of A			
	(D) value of k is inde	pendent of the initial con	centrations of A and B			
05.	In a first order reaction The time taken for the	on, the concentration of the concentration to change	he reactant decreases from 0.1 M to 0.025	om 0.8 to 0.4 M in M is	n 15 minutes. (2004)	
	(A) 30 minutes		(B) 15 minutes			
	(C) 7.5 minutes		(D) 60 minutes			
06.	Identify the correct s	tatement regarding enzyr	nes.		(2004)	
	(A) Enzymes are s (T \sim 100 K).	pecific biological catal	ysts that normally fu	nctions at high t	emperatures	
	(B) Enzymes are nor	(B) Enzymes are normally heterogeneous catalysts that are very specific in action.				
	(C) Enzymes are spe	cific biological catalysts	that cannot be poisoned	l.		
	(D) Enzymes are spe	cific biological catalysts	that posses well-defined	l active sites		
07.	A reaction involving	two different reactions c	an never be a		(2005)	
	(A) second order rea	iction	(B) bimolecular react	tion		
	(C) unimolecular rea	ction	(D) first order reaction	on		
08.	$t_{1/2}$ can be taken as the the rate constant for	ne time taken for the con- a first order reaction is k	centration of a reactant t , the $t_{1/4}$ can be written	to drop to 3/4 of as	its value. If (2005)	
	(A) 0.69/k	(B) 0.75/k	(C) 0.10/k	(D) 0.29/k		

9.	In a first order reaction minutes. The time taken (A) 30 min	, the concentration of for the concentration t (B) 60 min	the reactant, decrease to change fro 0.1 M to 0 (C) 7.5 min	from 0.8 M to 0.4 M in 15 025 M is (D) 15 min
10.	For the reaction A + B – times and doubling the c reaction.	→ C, it is found that do concentration of B doub	ubling the concentration bles the reaction rate. WI	n of A increase the rate by 4 nat is the overall order of the
11.	(A) 4 For the reaction; $2N_2O$ 10^{-3} M in 100 seconds t (A) 1.3×10^{-5} Ms ⁻¹	(B) $3/2$ $_{5}(g) \rightarrow 4NO_{2}(g) + O_{2}(g)$ hen the rate of the reac (B) $5 \times 10^{-4} \text{ Ms}^{-1}$	(C) 3 g) if the concentration tion is (C) 7.6×10^{-4} Ms ⁻¹	(D) 1 of NO ₂ increases by 5.2 × (D) 2×10^{-3} Ms ⁻¹
12.	A first order reaction is 1 (A) 30 min	10% complete in 20 mi (B) 40 min	n. The time taken for 19 (C) 50 min	% completion is (D) 38 min
13.	For the reaction 2A + B Which of the following	$B \rightarrow 3C + D$ does not express the rea	action rate?	
	$(A) - \frac{d[A]}{2dt}$	$(B) - \frac{d[B]}{dt}$	$(C) - \frac{d[C]}{3dt}$	(D) $\frac{d[D]}{dt}$
14.	Consider the reaction	$N_2(g) + 3H_2(g) \rightarrow 2NG$	G ₃ (g)	
	The equality relationship	p between $\frac{d[NH_3]}{dt}$ an	$d - \frac{d[H_2]}{dt}$ is	
	(A) $\frac{d[NH_3]}{dt} = \frac{d[H_2]}{dt}$		(B) $\frac{d[\mathrm{NH}_3]}{dt} = -\frac{1}{3}$	$\frac{d[H_2]}{dt}$
	(C) $\frac{d[\mathrm{NH}_3]}{dt} = -\frac{2}{3} \frac{dl}{dt}$	$\frac{[H_2]}{dt}$	(D) $\frac{d[\mathrm{NH}_3]}{dt} = -\frac{3}{2}\frac{d}{dt}$	$\frac{[H_2]}{dt}$
15.	The following mechanis $NO(g) + Br_2(g)$ $NOBr_2(g) + NGBr_2(g)$	sm has been proposed f $\rightarrow \text{NOBr}_2(g)$ $O(g) \rightarrow 2\text{NOBr}(g)$	for the reaction of NO w	ith Br_2 to form NOBr:
	If the second step is the (A) 1	rate determining step, (B) 0	the order of the reaction (C) 3	with respect to NO (g) is (D) 2
16.	The reaction of hydrogen	n and iodine monochlor	ride is given as:	
	$H_{2}(g) + 2ICI(g)$ This reaction is of first on Mechanism A : H_{2}(g) 2I Mechanism B : H_{2}(g) + H(\alpha) +	$\rightarrow 2\text{HCl}(g) + l_2(g)$ rder with respect to $H_2(g)$ $CI(g) \rightarrow 2\text{HCl}(g) + l_2(g)$ $-ICI(g) \rightarrow \text{HCl}(g) + \text{HI}(g)$ $ICI(g) \rightarrow \text{HCl}(g) + 120$	g) and (CI(g), following 1 g) [(g) ; slow a) : fast	nechanisms were proposed:
	Which of the above mec (A) A only	hanism (s) can be consi (B) B only	istent with the given info $(C)(1)$ and (2) both	rmation about the reaction (D) neither (1) nor (2)
17.	If 60% of a first order re completed in approxima (A) 40 minutes	eaction was completed ately : (log 4 = 0.60, log (B) 50 minutes	in 60 minutes, 50% of $g_5 = 0.69$) (C) 45 minutes	the same reaction would be (D) 60 minutes
18.	The energies of activation mol^{-1} and 200 kJ mol^{-1} n (forward and reverse) re 2AB) in the presence of (A) 300	on for forward and reve respectively. The prese eactions by 100 kJ mol f catalyst will be (in kJ r (B) 120	erse reactions for $A_2 + B$ nce of catalyst lowers th r^{-1} . The enthalpy change mol ⁻¹) (C) 280	2 \rightarrow 2AB are 180 kJ the activation energy of both to of the reaction (A ₂ +B ₂ → (D)-20
	· · · /	N 2	· · /	Construction of the second

- **89.** With the increase in temperature, the value of k for endothermic reactions decreases with the rise in temperature.
- 90. Order of a reaction increases with the rise in temperature.
- 91. For a second order reaction, the slope of graph between rate and $(\text{conc.})^2$ is equal to k.
- 92. The dimensions of pre exponential factor A in the Arrhenius equation for second order reaction are $L \text{ mol}^{-1} \text{ s}^{-1}$.
- **93.** The increase in the rate of reaction by increasing the temperature by 10° is due to the increase in the total number of collisions between the reacting particles.
- 94. Molecularity of the reaction is always a whole number greater than zero.
- 95. The combustion reaction s are highly exothermic, and therefore, their activation energy is zero.
- 96. The rates of photochemical reactions, generally depends upon the intensity of radiation.

EXERCISE - 12 QUESTION FROM OTHER EXAM

1.	In the first order reactions:	on, 75% of the reactant c	lisappeared in 1.38 h, the rate co	nstant of the reaction	
	(A) $3.6 \times 10^{-3} \mathrm{s}^{-1}$	(B) $2.8 \times 10^{-4} \mathrm{s}^{-1}$	(C) $17.2 \times 10^{-3} \text{ s}^{-1}$	(D) $1.8 \times 10^{-5} \text{ s}^{-1}$	
2.	In a reversible reactio	$n 2NO_2 \xrightarrow{k_1} N_2O_4$, the rate of disappearance of N	O_2 is equal to	
	(A) $\frac{2k_1[NO_2]^2}{k_2}$		(B) $2k_1[NO_2]^2 - 2K_2[N_2O_4]$		
	(C) $k1[NO_2]^2 - k_2[N_2]^2$	O ₄]	(D) $(2k_1 - k_2) [NO_2]$		
3.	For a chemical reaction of A is increased four	$n, A \rightarrow B$, it is found that times. The order of the r	at the rate of reaction doubles wh eaction with respect to A is	en the concentration	
	(A) 2	(B) 1	(C) zero	(D) 1/2	
4.	The rate constant is given the reaction to proceed	ven by the equation, K = d more rapidly?	PZe ^{-E/RT} . Which factor should re	egister a decrease for	
	(A) T	(B) Z	(C) E	(D) P	
5.	The first order rate c decomposition is	onstant for the decomp	position of N_2O_5 is 6.2×10^{-4} s	sec ⁻¹ . The $t_{1/2}$ of the	
	(A) 1117.7 sec	(B) 111.7 sec	(C) 228.4 sec	(D) 168.9 sec	
6.	The activation energy of a chemical reaction can be determined by (A) evaluating rate constants at two different temperatures (B) changing concentrations of reactants (C) evaluating rate constant at standard temperature (D) evaluating velocities of reaction at two different temperatures.				
7.	The reaction $A \rightarrow B$ f moles of B is 1 hour. W of B?	ollows first order kinet What is the time taken for	ics. The time taken for 0.8 mole conversion of 0.9 mole of A to pr	of A to produce 0.6 roduces 0.675 moles	
	(A) 1 hour	(B) 0.5 hour	(C) 0.25 hours	(D) 2 hours	
8.	The rate law of reaction the concentration of A reaction will be	n between the substance A and halving the conc.	es A and B is given by rate = $k[A]$ of B, the ratio of the new rate t] ⁿ [B] ^m . On doubling o the earlier state of	
	(A) $\frac{l}{2^{m+n}}$	(b) m + n	(C) n - m	(D) $2^{(n-m)}$	

EXERCISE - 11 FILL IN THE BLANKS

- 62. Hydrolysis of ethyl acetate in an acidic solution is an example of order.
- 63. If the activation energy of the reaction is low, it proceeds at rate.
- 64. The reaction taking place under the influence of visible light is called. reaction.
- 65. In a multi-step reaction, the step determines the rate of the reaction
- 66. The sum of powers to which the concentration terms are raised in the rate law is called of the reaction
- 67. For a first order reaction, the half life period is equal to
- 68. The order of reaction with respect to B, whose rate law is, rate = $k[A]^{3/2}[B]^{1/2}$ is.....
- 69. The order and molecularity of a complex reaction be same.
- 70. In photochemical reactions, the necessary activation energy is provided by
- 71. The unit of rate of gaseous reaction are.....
- 72. Temperature coefficient =
- 73. For a zero order reaction $A \longrightarrow$ products, the plot of [A] vs time has a slope =
- 74. Rate law..... be written from the balanced equation of the reaction.
- **75.** $t_{1/2}$ of certain reaction is inversely proportional to the square of concentration of the reactant. The order of the reaction is.....
- 76. For the reaction $x_A + y_B \longrightarrow lL = mM$, the average rate of disappearance of $B = \dots$
- 77. In the arrhenius equation, $k = A \exp(-E/RT)$, A may be termed as rate constant at
- 78. Photochemical reactions cannot take place in
- 79. The $t_{0.5}$ of a first order reaction is the $t_{0.75}$ of the first order reaction.
- 80. When retinal absorbs a photon of light, it undergoes......
- 81. $\frac{E_a}{R} = \frac{T_1 T_2}{T_2 T_1} X....$

TRUE AND FALSE

- 82. When Δ t is infinitesimally small, the average rate equals to instantaneous rate?
- 83. The reaction rate constant, k for a given reaction varies directly as the rate varies.
- 84. The sped of any chemical reaction is directly proportional to the molar concentrations.
- **85.** In a rate equation, the powers to which the concentrations are raised cannot be determined by inspection of the balanced equation.
- 86. A chain reaction, once started, cannot be stopped till it is complete.
- 87. The value of ΔG for spontaneous photochemical reaction should be < 0.
- **88.** The rate constant of a first order reaction whose $t_{1/2}$ is 6.93 s will be 10 s⁻¹.

3. The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is

 $2 HgCl_2 + K_2C_2O_4 \rightarrow 2 KCl + 2 CO_2 + Hg_2Cl_2$

The weight of Hg,Cl, are precipitated from different solutions in given time are as:

8			8
Time	HgCl ₂	$K_2C_2O_4$	Hg ₂ Cl ₂ formed
	(mol litre ⁻¹)	(mol litre ⁻¹)	(mol litre ⁻¹)
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031
Find the o	rder of reaction will be.		

- 4. The product $(t_{1/2} \times a)$ is found to be constant for different sets of data of $t_{1/2}$ at different initial concentration say 'a' for a given reaction. The order of the reaction is/are.
- 5. The following graph shows how $t_{1/2}$ of a reactant 'R' changes with the initial reactant concentration a_0 . The order of the reaction will be.



- 6. For a chemical reaction $A \rightarrow B$, the rate of the reaction is 2×10^{-3} mol dm⁻³S⁻¹, when the initial concentration is 0.05 mol dm⁻³. The rate of the same reaction is 1.6×10^{-2} mol dm⁻³S⁻¹ when the initial conc. is 0.1 mol dm⁻³. The order of the reaction is.
- 7. A drop of a solution (Volume = 0.05 mL) contains 6×10^{-7} mole of H⁺. If the rate of disappearance of H⁺ is 6×10^{5} mol L⁻¹S⁻¹, long will it take for the H⁺ in the drop to disappear is found to 'x' × 10⁻⁸ sec. Find the value of 'x' is/are.
- 8. For a certain first order reaction, the time required for half of an initial amount to dicomposes is 3 min. If the initial concentration of A is 1 molar, the time required to reduced the concentration of A to 0.25 M ia/re. $[\ln 2 = 0.693, \ln 4 = 1.39]$
- 9. The rate of a reaction depends on concentration according to the reaction as follows:

$$\frac{-dc}{dt} = \frac{k_1 C}{1 + k_2 C}$$

The order of the reaction when concentration is very high is.

10. For the given reaction, $A \rightarrow$ Product



EXERCISE - 9 REASONING TYPE

This section contains FIVE questions. Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (A), (B), (C) and (D) out of which ONLY ONE is correct.

- (A) Statement 1 is True, Statement 2 is True, Statement 2 is a correct explanation for Statement - 1
- (B) Statement 1 is True, Statement 2 is True; Statement 2 is NOT a correct explanation for Statement 1
- (C) Statement -1 is True, Statement -2 is False
- (D) Statement 1 is False, Statement 2 is True
- 01. Statement-1: Half-life period is always independent of initial concentration. Statement-2: Half-life period in inversely proportional to rate constant.
- **02.** Statement-1: ΔG for photochemical spontaneous reaction may or may not be -ve Statement-2: Half-life period in inversely proportional to rate constant.
- **03.** Statement-1: The rate of reaction can also increase with its product if one of the product act as catalyst.
 - Statement-2: A catalyst lowers the activation energy of reactions.
- 04. Statement-1: In zero order reaction, the conc. us. time graph is a straight time Statement-2: The rate of change of conc. per unit time in zero order reaction remains constant.
- 05. Statement-1: The order of a reaction is always positive Statement-2: Half-life period in inversely proportional to rate constant.
- 06. Statement-1: Order of a reaction cannot be written from the balanced equation. Statement-2: Rate law can provide some clue about the reaction mechanism.
- 07. Statement-1: The rate of a reaction changes with the change in time Statement-2: The concentration of reactants decrease with the passage of time.
- **08.** Statement-1: The reaction rate of most of the reactions doubles when temperature is increased from 298 K to 308 K.
 - Statement-2: The activation energy of reaction decreases with increase in temperature.
- **59.** Statement-1: The order of a reaction is related to molecularity of a reaction. Statement-2: Molecularity of the reaction cannut be fractional.
- **10.** Statement-1: The slowest step in reaction is the rate determining step. Statement-2: Order of a reaction is given by rate law expression

EXERCISE - 10 INTEGER TYPE

Starting with one mole of a compound A, it is found that the reaction is 3/4 completed in 1 hour, if reaction is second order. Find the value of rate constant is/are.

2. The half life period and initial concentration for a reaction are as follows.

Initial conc:	350	540	158
t _{1/2} :	425	275	941
E: 14 1 C	1 6	• /	

Find the value of order of reaction is/are.

PARAGRAPH-V

A chemical reaction is proceeding as

$$A + A \xrightarrow{K_2} A^* + A$$

 $A^* \xrightarrow{k_1} \Pr{oducts}$

To study the kinetics, steady state approximation is used.

17. The rate of disappearance of A is

(A)
$$K_{2}[A]^{2} - K_{-2}[A]^{2}$$
 (B) $K_{-2}[A]^{2} - K_{2}[A]^{2}$
(C) $K_{2}[A]^{2} - K_{-2}[A][A^{*}]$ (C) $K_{-2}[A][A^{*}] - K_{2}[A^{2}]$

18. The conditions under which this reaction is a Pseudo-first-order reaction

(A)
$$\frac{K_2}{K_1}[A] >> 1$$
 (B) $\frac{K_2}{K_1}[A] << 1$ (C) $\frac{K_{-2}}{K_1}[A] >> 1$ D($\frac{K_{-2}}{K_1}[A] << 1$

19. The conditions under which the reaction is Pseudo-Second order reaction

(A)
$$\frac{K_{-2}}{K_1} [A] << 1$$
 (B) $\frac{K_{-2}}{K_1} [A] >> 1$ (C) $\frac{K_2}{K_1} [A] << 1$ (D) $\frac{K_2}{K_1} [A] >> 1$

PARAGRAPH-VI

In first order reaction, the rate is determined by the change of one concentration term only. The unit of rate constant is $time^{-1}$. The half-life period is independent of concentration. Acid hydrolysis of disaccharides, all radioactive decays are few examples of first order reactions.

- 20. Inversion of sugar follows first order rate equation which ca be followed by noting the change in rotation of the plane of polarized light is the polarimeter. If r_{∞} , r_t and r_0 are the rotations at $t = \infty$, t = t and t = 0, then first order reaction can be written as
 - (A) $K = \frac{1}{t} \log e \frac{r_{\infty} r_t}{r_0 r_{\infty}}$ (B) $K = \frac{1}{t} / n \frac{r_t r_{\infty}}{r_0 r_{\infty}}$

(C)
$$K = \frac{1}{t} / n \frac{r_{\infty} - r_0}{r_{\infty} - r_t}$$
 (D) $K = \frac{1}{t} / n \frac{r_{\infty} - r_t}{r_{\infty} - r_0}$

21. For a first order reaction, the graph between $\log\left(\frac{a}{a-x}\right)$ versus time is a straight line. The

slope of the line equals to

(A)
$$-\frac{k}{2.303}$$
 (B) $-k \times 2.303$ (C) $+\frac{k}{2.303}$ (D) $2.303 k$

22. The half-time of first order decomposition of nitramide is 2.1 hour at $15^{\circ}C$. If 6.2 g of NH_2NO_2 is allowed to decompose, the time taken to decompose 99% would be : (A) 13.957 h (B) 6.978 h (C) 4.606 h (D)) 27.914 h **12.** The energy of activation and specific rate for a first order reaction at 27°C

are 23 kcal/mole and 4.81×10^{-5} sec⁻¹ respectively. Determine the temperature at which the half life of the reaction is 2 hours (log2=0.3010) (A) 305.5 K (B) 350 K (C) 325 K (D) 310 K

13. Two reaction proceed at 25° at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of the second is 2.5. Find the ratio of the rates of these reactions at 95°C. (A) 5.362 (B) 3.184 (C) 1.324 (D) 4.768

PARAGRAPH-IV

Order of reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. The kinetic equation of nth order reaction is:

$$k \times t = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

Half life of nth order reaction depends on initial concentration according to the following relation:

$$t_{1/2}\alpha \frac{1}{a^{n-1}}$$

Unit of the rate constant varies with the order but general relation for unit of nth order reaction is:

Unit of
$$k = \left[\frac{1}{conc.}\right]^{n-1} \times time^{-1}$$

The differential rate law for nth order reaction may be given as:

$$\frac{dx}{dt} = k \left[A \right]^n$$

Where, A denotes the reactant. Answer the following questions:

14. The rate constant for zero order reaction is (where $C_0 \& C_t$ are concentrations of reactants at respective time):

(A)
$$k = \frac{C_0}{2t}$$
 (B) $k = \frac{C_0 - C_t}{t}$ (C) $k = \ln \frac{C_0 - C_t}{2t}$ (D) $k = \frac{C_0}{C_t}$

15. The half life for a zero order reaction equals to:

(A)
$$\frac{1}{2}\frac{k}{a^2}$$
 (B) $\frac{a^2}{2k}$ (C) $\frac{2k}{a}$ (D) $\frac{a}{2k}$

16. For a reaction: $I^- + OCl^- \rightarrow IO^- + Cl^$ in an aqueous medium, the rate of the reaction is given by

$$\frac{d\left[IO^{-}\right]}{dt} = k \frac{\left[I^{-}\right]\left[OCI^{-}\right]}{\left[OH^{-}\right]}$$

The overall order of the reaction is:

05. Which of the following plot is correct four the above reaction.



PARAGRAPH-II

The rate of a reaction depends upon the temperature and quantitatively expressed in the form of Arrhenius equation, $k = A.e^{E_a/RT}$. The exponential term represents the fraction of molecules having energy to reach the transition state or cross the energy barrier. Pre exponential factor gives the number of collisions per unit time the data of two reaction is given below:

- (i) For the first reaction it is observed that $3.6 \times 10^{-16\%}$ reactant molecules exist in the activated state of a reaction at 300 K.
- (ii) At 25°C, the E_a of the second reaction, NO(g) + Cl₂(g) \rightarrow NOCl(g) + Cl(g) is 8.5 × 10⁴ J mol⁻¹. The fraction of collisions with sufficient is 1.2×10^{-15} .

06.	The activation energy o	f the first reaction is		
	(A) 100 kJ	(B) 150 kJ	(C) 200 kJ	(D) 250 kJ
07.	If a graph is plotted bet	ween k against 1/T, the i	ntercept obtained is	
	(A) log k	(B) log A	(C)-Ea/2.303 R	(D) log 1/T
08.	The dimensions of A wi	ll be:		
	$(A) \operatorname{J} \operatorname{mol}^{-1}$	(B) mol/time	(C) time ⁻¹	(D) dimension less

When the temperature of reaction (2) is raised to 35°C, the fraction of molecular collisions will become.
(A) 1.2 × 10⁻¹⁴
(B) 2.4 × 10⁻¹⁵
(C) 1.82 × 10⁻¹⁵
(D) 2.65 × 10⁻¹⁵

(A)
$$1.2 \times 10^{-14}$$
 (B) 2.4×10^{-15} (C) 1.82×10^{-15} (D) 3.65×10^{-15}

10. If at under different conditions E_{a_1} and E_{a_2} are the activate energy of reaction second reaction. If $E_{a_1} = 40 \text{ J mol}^{-1}$ and $E_{a_2} = 80 \text{ J mol}^{-1}$ the, (A) $k_1 > k_2$ (B) $k_1 < k_2$ (C) $k_1 = k_2$ (D) $k_1 + k_2 = 0$

PARAGRAPH-III

A chemical reaction occurs when the existing bonds of the reactants are broken down and new bonds come into existence in the molecules of products The basic requirement for a reaction to occur is that there should be physical contact between reacting species, i.e., they must collide with one another. Effective collisions which bring chemical change are few inspite of large number of actual collisions. For a collision to be effective, the following two conditions must be satisfied: (i) Reacting species must possess adequate energy to over come the energy barrier. (ii) Reacting molecules must be properly oriented at the time of collision.

The minimum amount of energy which the colliding particles must possess as to make the chemical reaction to occur is called threshold energy. The excess energy (over and above the average energy of the reacting species) required by the reacting species to undergo chemical reaction is called activation energy (E_a)

The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction (R = 2 cal K⁻¹ mol⁻¹) (log3 = 0.48)
 (A) 6.97 kcal/mole
 (B) 3.21 kcal/mole
 (C) 8.14 kcal/mole
 (D) 7.25 kcal/mole

07. Match the following

Column I		Colu	Column II		Column III	
Orde	r	Valu	e of t _{0.5}		Unit	of K
(i)	Zero	(a)	t _{0.5} =	(A)	1.mole ⁻¹ t	ime-1
(ii)	One	(b)	t _{0.5} =	(B)	time-1	
(iii)	Two	(c)	$t_{0.5} =$	(C)	l ² .mole ² ti	me ⁻¹
(iv)	Three	(d)	$t_{0.5} =$	(D)	mol l ⁻¹ tin	ne ⁻¹
(A) i-b,D, ii-a,B, iii-d,A iv-c-C			0.5	(B) i-a,A, ii-c,B, iii-b,C iv-d-D		
(C) i-	c,C, ii-b,A, iii-a,B iv	-d-D) (A) i-d,B, ii-c,C, iii-b,D iv-a-A		-a-A	
Match the following						
	column I		Colur	nn II		Column II
(i)	$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}$	Ο,	(a)	Order = 3,	(A)	molecularit

(i)	$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$	(a)	Order = 3,	(A)	molecularity $= 2$
(ii)	$N_2O_2 \rightarrow N_2O + \frac{1}{2}O_2$	(b)	Order = 2,	(B)	molecularity $= 3$
(iii)	$2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$	(c)	Order = 1,	(C)	molecularity = 1
(iv)	$2NO + O_2 \rightarrow 2NO_2$	(d)	Order = 1,	(D)	molecularity=1
(A) i-	a,C, ii-b,D, iii-c,A, iv-d,B		(B) i-d,A, ii-c,B, iii-b	,C, iv-a	a,D
(C) i-	c,C, ii-d,D, iii-a,B, iv-b,A		(D) i-d,C, ii-c,D, iii-l	,A, iv-	a,B

EXERCISE - 8 LINKED COMPREHENSION TYPE

PARAGRAPH-I

08.

In a parallel reaction, the reactant A (radioactive metal) decays by two parallel pathways to form product B and C.

A
$$k_1$$
 B; conc. at time t = x
C : conc. at time t = y

The ratio of concentration of [B] : [C] are 2 : 98 to and the $t_{1/2}$ of the reaction is 22 years.

- The decay constant for B is: 01. (B) $63 \times 10^{-5} \text{ y}^{-1}$ (A) $31.5 \times 10-5 \text{ y}^{-1}$ (C) $126 \times 10^{-5} \text{ y}^{-1}$ (D) $189 \times 10^{-5} \text{ y}^{-1}$.
- The decay constant for c is correctly given as 02. (A) 0.03 y^{-1} (B) 0.06 y^{-1} (C) 0.09 y⁻¹ (D) 1.5 y⁻¹.
- 03. Starting with 2.0 kg of A the amount of C that shall be obtained of the 44 years will be: (A) 0.5 kg (B) $4.9 \times 10 - 3$ kg (C) 1.47 kg (D) 1.5 kg
- If the concentration of B and C of the time t is x and y moles respectively than and r_{B} and r_{C} is the rate 04. of formation of B and C then which of the following is correct?

(A)	$-\frac{d[A]}{dt} = k_1[A] + k_2[B]$	(B) $-\frac{d[A]}{dt} = k_1[B] + k_2[C]$
(C)	$t_{0.5} = \frac{0.693}{(k_1 - k_2)}$	(D) $\frac{r_{\rm B}}{r_{\rm C}} = \frac{x}{y}$

02.		Column-I					Column-II
	(A)	Half-life of a z	ero order reaction		(p)	$H_2 + C$	l ₂ 2HCl
	(B)	Average rate o	f a reaction		(q)	Active	mass
	(C)	Molar concent	ration		(r)	a/2k	
	(D)	Zero order read	ction		(s)	$\Delta x/\Delta t$	
03.	Match	the following					
		Column A				Colum	ın B
	(i)	Half life of firs	st order reaction		(a)	Active	mass
	(ii)	Arrhenius equa	ation		(b)	k =	
	(iii)	Molar concent	tration		(c)	$t_{1/2} =$	
	(iv)	Half life perio	d of zero order reaction	ı	(d)	1/2	
	(A) i-ł	o, ii-a, iii-d, iv-c	;	(B) i-a,	ii-c, ii	i-b, iv-d	
	(C) i-c	, ii-b, iii-a, iv-d	l	(D) i-c	, ii-b, ii	i-d, iv-a	L
04.	Match	the following					
		Column A				Colum	ın B
	(i)	Rate of reaction	on		(a)	Mol L	⁻¹ time ⁻¹
	(ii)				(b)		
	(iii)	Unit of rate of	reacton		(c)	Averag	ge rate of reaction
	(A) i-0	e, ii-a, iii-b	(B) i-a, ii-b, iii-c	(C) i-a,	, ii-c, ii	i-b	(D) i-b, ii-c, iii-a
05.	Match	the following					
		Column A				Colum	ın B
	(i)	Zero order rea	action		(a)		
	(ii)	First order rea	tion		(b)		
	(iii)	Second order	reaction		(c)	- = k[A] ² [B]
	(iv)	Instantaneous	rate		(d)	$H_{2} + C$	l ₂ 2HCl
	(v)	Temperature c	oefficient		(e)	CH ₃ CO	$OOCH_3 + NaOH \rightarrow$
						CH ₃ CO	OONa + CH₃OH
	(vi)	Rate equation	for third order reaction	l I	(f)	$2H_2O_2$	\rightarrow H ₂ O + O ₂
	(vii)	Acidic hydrol	ysis of ester		(g)	Pseudo	o-unimolecular reaction
	(A) i-e	e, ii-f, iii-g, iv-c	, v-a, vi-d, vii-b	(B) i-d	, ii-f, ii	i-e, iv-b	, v-a, vi-c, vii-g
	(C) i-e	e, ii-g, iii-f, iv-d	, v-a, vi-c, vii-b	(D) i-b	, ii-c, ii	i-a, iv-d	l, v-f, vi-g, vii-e
06.	Match	the following					
		Column I			Co	lumn I	I
		order			Rate	reaction	1
	(i)	Zero			(a)	$\mathbf{k}_2 =$	
	(ii)	One			(b)	$\mathbf{k}_0 =$	
	(iii)	Two			(c)	$k_{3} =$	
	(iv)	Three			(d)	$k_1 = lo$	g
	(A) i-ł	o, ii-d, iii-a, iv-	-c	(B) i-d	, ii-b, i	ii-c, iv-	·a
	(C) i-c	, ii-a, iii-b, iv-	-d	(D) i-a	ı, ii-b,	iii-c, iv	-d

15.
$$H \xrightarrow{Et} CI + OH^{-} \longrightarrow H \xrightarrow{Et} OH, HO \xrightarrow{Et} H$$

Me Me Me II

Which of the following statements are correct?

- (A) it is unimolecular nucleophilic substitution reaction S_{N^1} if I or II is formed.
- (B) it is bimolecular nucleophilic substituton reaction S_{N^2} if I or II is formed.
- (C) it is S_{N^1} if I and its enantiomer are formed so that mixture is racemic.
- (D) it is S_{N^2} if II is formed.
- 16. The reaction, $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ Initial pressure of A and B are respectively $p_A = 0.60$ atm, $p_B = 0.80$ atm. When $p_C = 0.20$ atm, the rate of the reaction relative to the initial rate, is

(A) $\frac{1}{49}$	(B) $\frac{1}{24}$	(C) $\frac{1}{6}$	(D) $\frac{1}{4}$
48	24	6	× 4

17. Rate constant k varies with temperature by eqn:

$$log k (min^{-1}) = 5 - \frac{2000 \text{ K}}{\text{T}}. We can conclude}$$
(A) pre-expontial factor A is 5
(B) E_a is 2000 kcal
(C) pre-exponential factor A is 10⁵
(D) E_a is 9.212 kcal.

18. The rate law for the dimerisation of NO₂ is

$$\frac{-d[NO_2]}{dt} = k [NO_2]^2$$

Which of the following changes will change the value of the specific rate constant, K;(A) Doubling the total pressure on the system(B) doubling the temperature(C) both(D) none

19. For a reaction for which the activation energies of the forward and reverse directions are equal in value:

(A) the stoichiometry is the mechanism	(B) $\Delta H = 0$
(C) $\Delta S = 0$	(D) the order is zero.

- **20.** A reaction is catalysed by H⁺ ion. In presence of H_A, rate constant is 2×10^{-3} min⁻¹ and in presence of H_B rate constant is 1×10^{-3} min⁻¹ HA and HB both being stronge acids, we may conclude.
 - (A) Equilibrium constant is 2
 - (B) H_A is stronger than HB
 - (C) relative strength of HA and HB is 2
 - (D) HA is weaker than HB and relative strength is 0.5

EXERCISE - 7 MATRIX MATCHING

01. Column-I

Column-II

- (A) First order reaction (p)
 (B) Number of reacting particles which collide (q) simultaneously to bring about chemical change
- Generally high for thermal reactions
- (r) May have $\Delta G > 0$ or < 0.

≠ 1.

(C) Molar Concentration(D) Zero order reaction

- (s) Sum of the exponents of
 - concentration term in rate law

- 8. In which of the following ways does an activated complex differ from an ordinary molecule ?
 - (A) It is quite unstable and has no independent existence.
 - (B) ΔH_{f}° is probably positive
 - (C) The system has a greater vibrational character.
 - (D) The system has no vibrational character.
- 9. The basic theory behind Arrhenius's equation is that
 - (A) the number of effective collisions is proportional to the number of molecules above a certain threshold energy
 - (B) as the temperature increases, so does the number of molecules with energies exceeding the threshold energy.
 - (C) the rate constant is function of temperature.
 - (D) the activation energy and pre-exponential factor are always temperature-independent
- 10. In arrhenius's equation, $k = A \exp\left(-\frac{E_a}{RT}\right)$. A may be termed as the rate constant at
 - (A) very low temperature(C) zero activation energy
- (B) very high temperature(D) the boiling temperature of the reaction mixture
- 11. Which of the following statements are correct about half-life period.
 - (A) It is proportional to initial concentration for zeroth order.
 - (B) average life= 1.44 half-life for first order reaction
 - (C) time of 75% reaction is thrice of half-life period in second order reaction
 - (D) 99.9% reaction takes place in 100 minutes for the case when rate constant is 0.0693 min⁻¹
- 12. $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Half-life period is independent of concentration of zinc at constant pH. For the constant concentration of Zn, rate becomes 100 times when pH is decreased from 3 to 2. Hence

(A)
$$\frac{dx}{dt} = k[Zn]^0[H^+]2$$
 (B) $\left(\frac{dx}{dt}\right) = k[Zn][H^+]^2$

- (C) rate is not affected if concentration of zinc is made four times and that of H⁺ ions is halved.
- (D) rate becomes four times if concentration of H^+ ion is doubled at constant Zn concentration,.
- **13.** In which of the following case, E_a of the backward reaction is greater than that of the forward reaction?

(A)
$$A + 10 \text{ kcal} \longrightarrow B$$
, $E_a = 50 \text{ kcal}$ (B) $A + 20 \text{ kcal} \longrightarrow B$, $E_a = 40 \text{ kcal}$
(C) $A + 40 \text{ kcal} \longrightarrow B$, $E_a = 10 \text{ kcal}$ (D) $A - 40 \text{ kcal} \longrightarrow B$, $E_a = 20 \text{ kcal}$

14. $A \longrightarrow B + C$ (g) (g) (g)

$$\frac{-d[A]}{dt} = k[A]$$

At the starting pressure is 100 mm and after 10 min, pressure is 120 mm. hence rate constant (min⁻¹) is:

(A)
$$\frac{2.303}{10}\log\frac{120}{100}$$
 (B) $\frac{2.303}{10}\log\frac{100}{20}$ (C) $\frac{2.303}{10}\log\frac{100}{80}$ (D) $\frac{2.303}{10}\log\frac{100}{120}$

EXERCISE - 6 MCQ WITH MORE CORRECT ANSWER

- 1. Which of the following statement are correct?
 - (A) The order of a reaction is the sum of the components of all the concentration terms in the rate equation.
 - (B) The order of a reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentration all other reactants constant
 - (C) Orders of reactions can be whole numbers of fractional numbers.
 - (D) The order of a reaction can only be determined from the stoichiometric equation for the reaction.
- 2. Which of the following statements are correct?
 - (A) The rate of the reaction involving the conversion of ortho-hydrogen to parahydrogen is $d[H_2]$

$$\frac{1}{dt} = k[H_2]^{3/2}$$

- (B) The rate of the reaction involving the thermal decomposition of acetaldehyde is $k[CH,CHO]^{3/2}$
- (C) In the formation of phosgene gas from CO and Cl_2 , the rate of the reaction is $k[CO][Cl_1]^{1/2}$
- (D) In the decomposition of H_2O_2 , the rate of the reaction is $k[H_2O_2]$.
- 3.Which of the following isomerization reactions is of the first order ?(A) cyclopropane \rightarrow propane(B) cis-but-2-ene \rightarrow trans-but-2-ene(C) vinyl allyl ether \rightarrow pent-4-enal(D) CH₃NC \rightarrow CH₃CN
- 4. Which of the following reactions is of the first order ?
 - (A) The decomposition of ammonium nitrate in an aqueous solution
 - (B) The inversion of cane-sugar in the presence of an acid
 - (C) The acidic hydrolysis of ethyl acetate
 - (D) All radioactive decays.
- 5. Which of the following are examples of unimolecular reactions?

(A)
$$O_3 \rightarrow O_2 + O$$

(B) $CH_2 - CH_2 \longrightarrow CH_3 CH = CH_2$
(C) $NO + O_3 \rightarrow NO_2 + O_2$
(D) $O + NO + N_2 \rightarrow + NO_2 + N_2$

- 6. The calculation of the pre-exponential factor is based on the
 - (A) idea that, for a reaction to take place, the reactant species must come together
 - (B) Calculation of the molecularity of the reaction
 - (C) idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products
 - (D) calculation of the order of the reaction
- 7. Which of the following are examples of pseudo-unimolecular reactions?

(A)
$$CH_3CO_2C_2H_5 + H_2O \xrightarrow{H^+} CH_3CO_2H + C_2H_5OH$$

- (B) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12} + C_6H_{12}O_6$ (glucose) (fructose)
- (C) $CH_3COCl + H2O \longrightarrow CH_3CO_2H + HCl$
- (D) $CH_3CO_2C_2H_5 + H_2O \xrightarrow{OH^-} CH_3CO_2H + C_2H_5OH$

Q.22 The decomposition of a gaseous substance A to yield gaseous products,

A (g) \longrightarrow 2 B (g) + C (g) follows first order kinetics . If the total pressure at the start of an experiment & 9 minutes after the start are 169 mm and 221 mm, what is the rate constant ? (A) 0.6804 min⁻¹ (B) 0.3024 min⁻¹ (C) 0.4536 min⁻¹ (D) 0.3780 min⁻¹

EXERCISE - 5 BRAIN STORMING SUBJECTIVE QUESTION

Q.1 The rate constant for the forward reaction , $A \longrightarrow$ Products is given by

$$\log k (\sec^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{\text{T}}$$

and the rate constant for the reverse reaction is $1.2 \times 10^{-4} \text{ sec}^{-1}$ at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given Enthalpy of the reaction = -478 kJ/mol

Q.2 The decomposition of a compound A, at temp. T according to the equation $2P(g) \longrightarrow 4Q(g) + R(g) + S(l)$

is a first order reaction. After 30 min. from the start of the decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 min. Given Vapour pressure of S(l) at temp. T = 32.5 mm Hg.

- **Q.3** The time required for 10% completion of a first order reaction at 377°C is 55.2 min and the fraction of molecules at 450°C have sufficient energy to react is 1.92×10^{-16} . Calculate its rate constant at 400°C. Assuming the energy of activation to be constant within this temperature range.
- Q.4 The complexion of Fe²⁺ with the chelating agent dipyridyl (abbreviated dipy) has been studied kinetically in both the forward and reverse directions. For the complex reaction,
 - $Fe^{2+} + 3 \text{ dipy} \longrightarrow [Fe(\text{dipy})_3]^{2+}$ the rate of the formation of the complex at 25°C is given by Rate = $(1.45 \times 10^{13} \text{ L}^3 \text{ mol}^{-3}\text{s}^{-1}) [Fe^{2+}] [\text{dipy}]^3$
 - and for the reverse of the above equation, the rate of disappearance of the complex is : $Rate = (1.22 \times 10^{-4} \text{ s}^{-1}) [Fe(dipy)_3^{2+}]$

What is stability constant of the complex ?

- Q.5 For a homogeneous gaseous phase reaction : $2A \longrightarrow 3B + C$, the initial pressure of reactant was P° while pressure at time 't' was P. Find the pressure after time 2t. Assume I order reaction.
- Q.6 The decomposition of compound A in solution is a first order process with an activation energy of 52.3 kJ mol⁻¹. 10 percent solution of A is decomposed in 10 min at 10°C. How much decomposition would be observed with a 20 percent solution after 20 min at 20°C.
- Q.7 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g).$

The rate constant of decomposition is 4.78×10^{-3} min⁻¹. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hour of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

- **Q.8** At 100°C the gaseoactivation for forwardus reaction $A \rightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm. Hg. From these data find :
 - (a) initial pressure of A(b) the pressure of A at the end of 10 minutes(c) the half life period of the reaction.

- Q.14 For a certain reaction of order n, the time for half change, $t_{1/2}$, is given by $t_{1/2} = \frac{[2-\sqrt{2}]}{k} \times C_0^{1/2}$ where k is the rate constant and C_0 is the initial concentration what is n : (A) 1 (B) 2 (C) 0 (D) 0.5
- **Q.15** In the Lindemann theory of unimolecular reactions, it is shown that the apparent rate constant for such a reaction is $k_{app} = \frac{k_1C}{1+aC}$ where C is the concentration of the reactant, k_1 and α are constants. Calculate the value of C for which k_{app} has 90% of its limiting value at C tending to infinitely large values, given $\alpha = 9 \times 10^5$. (A) 10⁻⁶ mol/litre (B) 10⁻⁴ mol/litre (C) 10⁻⁵ mol/litre (D) 5 × 10⁻⁵ mol/litre
- Q.16 Given that for a reaction of order n the integrated form of the rate equation is

 $k = \frac{1}{t(n-1)} \left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}} \right]$ where C₀ and C are the values of the reactant concentration at the

start and after time t . What is the relationship between $t_{3/4}$ and $t_{3/4}$ where $t_{3/4}$ is the time required for C to become $\frac{1}{4} C_0$:

(A) $t_{3/4} = t_{1/2} [2^{n-1} + 1]$	(B) $t_{3/4} = t_{1/2} [2^{n-1} - 1]$
(C) $\mathbf{t}_{3/4} = \mathbf{t}_{\frac{1}{2}} [2^{n+1} - 1]$	(D) $t_{3/4} = t_{1/2} [2^{n+1} + 1]$

Q.17 Rate constant of a reaction is 0.0693 min⁻¹. Starting with 10 mol, rate of the reaction after 10 min is :

A) $0.693 \text{ mol min}^{-1}$	(B) $0.0693 \times 2 \text{ mol min}^{-1}$
C) $0.0693 \times 5 \text{ mol min}^{-1}$	(D) $0.0693 \times (5)^2 \text{ mol min}^{-1}$

Q.18 The instantaneous rate of disappearance of the MnO_4^- ion in the following reaction is $4.56 \times 10^{-3} Ms^{-1}$

 $2 \text{ MnO}_{4}^{-} + 10 \text{ I}^{-} + 16 \text{ H}^{+} \longrightarrow 2 \text{ Mn}^{2+} + 5 \text{ I}_{2} + 8 \text{ H}_{2}\text{O}$ The rate of appearance of I₂ is : (A) $1.14 \times 10^{-3} \text{ Ms}^{-1}$ (B) $5.7 \times 10^{-3} \text{ Ms}^{-1}$

$A_{j} = 1.14 \times 10^{-1} \text{ MIS}$	$(D) 5.7 \times 10^{-1} \text{Ms}$
C) $4.56 \times 10^{-4} \mathrm{Ms^{-1}}$	(D) $1.14 \times 10^{-2} \text{ Ms}^{-1}$
	-

- Q.19 Which of the following statements is not correct?
 - (A) Law of mass action and rate law expressions are same for single step reactions
 - (B) Molecularity of the slowest elementary step of a complex reaction gives molecularity of reaction
 - (C) Both order and molecularity have normally a maximum value of 3
 - (D) Molecularity of a complex reaction $A + 2B \longrightarrow C$ is 3.
- Q.20 Which of the following are correct?
 - (A) total collision rate ∞ mean speed ∞ absolute temperature

(B) total collision rate
$$\propto \frac{1}{\text{mean speed}} \propto \frac{1}{\text{absolute temperature}}$$

- (C) total collision rate ∞ mean speed ∞ (absolute temperature)^{1/2}
- (D) total collision rate ∞ (mean speed)² \propto (absolute temperature)³
- Q.21 The rate equation for an autocatalytic reaction,

$$A + R \xrightarrow{k} R + R$$
 is $-r_A = -\frac{dC_A}{dt} = kC_A C_R$

The rate of disappearance of reactant A is maximum where :

(A)
$$C_A = 2 C_R$$
 (B) $C_A = C_R$ (C) $C_A = C_R/2$ (D) $C_A = (C_R)^{1/2}$

Q.6 For a gas reaction at T(K) the rate is given by $-\frac{dp_A}{dt} = k'p_A^2 atm/hr$. If the rate equation is

expressed as
$$:-r_{A} = -\frac{1}{V} \frac{dN_{A}}{dt} = kC_{A}^{2}$$
, mol/(litre-hr), the rate constant k is given by –
(A) k = k' (B) k = k' RT (C) k = k'/RT (D) k = k'(RT)^{2} where R = ideal gas law constant, cal/g mol K.

The activation energies of two reactions are E_{a1} and E_{a2} with $E_{a1} > E_{a2}$. If the temperature of the Q.7 reacting system is increased from T₁ to T₂ predict which of the following alternative is correct

(A)
$$\frac{K'_1}{K_1} = \frac{K'_2}{K_2}$$
 (B) $\frac{K'_1}{K_1} > \frac{K'_2}{K_2}$ (C) $\frac{K'_1}{K_1} < \frac{K'_2}{K_2}$ (D) $\frac{K'_1}{K_1} < 2\frac{K'_2}{K_2}$

The reaction $v_1A + v_2B \rightarrow$ products is first order with respect to A and zero-order with respect Q.8 to B. If the reaction is started with $[A_0]$ and $[B_0]$, the integrated rate expression of this reaction would be-

(A)
$$\ell n \frac{[A]_0}{[A]_0 - x} = k_1 t$$

(B) $\ell n \frac{[A]_0}{[A]_0 - v_1 x} = v_1 k_1 t$
(C) $\ell n \frac{[A]_0}{[A]_0 - v_1 x} = k_1 t$
(D) $\ell n \frac{[A]_0}{[A]_0 - v_1 x} = -v_1 k_1 t$

Q.9 When the mechanism of reaction is not known, one often attempts to fit the data with an nth order rate equation of the form

$$-r_{A} = -\frac{dC_{A}}{dt} = kC_{A}^{n}$$

for $n \neq 1$, the integration of this equation yields –

Q.10 For the chemical reaction $A \rightarrow$ products, the rate of disappearance of A is given by :

$$-r_{A} = -\frac{dC_{A}}{dt} = k_{1}C_{A}/(1+k_{2}C_{A})$$

At low C_A the reaction is of the first-order with rate constant : (A) k/k, (B) k, (C) k, k, (D) k/(k, +k,)

$$(B) k_1 (C) k_1 k_2 (D) k_1 (k_1 + k_2)$$

Q.11 In an old rock, the mass ratio of $\frac{238}{92}$ U to $\frac{206}{82}$ Pb is found to be 595 : 103. The age of the rock is (Mean life of $^{238}_{92}$ U is T₀) 698

(A)
$$T_0 \ln 1.2$$
 (B) $T_0 \ln \frac{698}{595}$ (C) $T_0 \frac{\ln 1.2}{\ln 2}$ (D) $T_0 \frac{\ln \frac{598}{595}}{\ln 2}$

Q.12 For the consecutive unimolecular-type first order reaction A $\xrightarrow{k_1}$ R $\xrightarrow{k_2}$ S, the concentration of component A, C_A at any time t is given by -

(A)
$$C_A = C_{A_0} e^{(k_1 + k_2)t}$$
 (B) $C_A = C_{A_0} e^{-(k_1 + k_2)t}$ (C) $C_A = C_{A_0} e^{-k_1 t}$ (D) $C_A = C_{A_0} e^{k_1 t}$

Q.13 The energy of activation for a reaction is 100 kJ/mol. Presence of a catalyst lowers the energy of activation by 75%. The ratio of k_{cat}/k_{uncat} (T = 298 K) – (A) 23.4 × 10¹⁵ (B) 2.34 × 10¹³ (C) 1.324 × 10⁵ (D) 3.25 × 10⁶

- (a) Calculate ΔH of the reaction.
- (b) Calculate the energy of activation for forward and backward reaction.
- (c) The dotted line curve is the path in the presence of a catalyst. What is the energy of activation for the forward and backward reaction in the presence of the catalyst?What is the lowering in activation energy in the presence of the catalyst?
- (d) Will the catalyst change the extent of the reaction ?
- Q.9 For a homogeneous gaseous reaction, $A \longrightarrow B + C + D$ the initial pressure was p_0 while pressure after time 't' was p. Derive an expression for the rate constants 'k' in terms of p_0 , p and t. Assume the reaction to be first order.

EXERCISE - 4 BRAIN STORMING MCQ WITH SINGLE CORRECT ANSWER

- Q.1 The rate of reaction becomes 2 times for every 10°C rise in temperature. How the rate of reaction will increase when temperature is increased from 30°C to 80°C :
 (A) 16 (B) 32 (C) 64 (D) 128
- Q.2 For the consecutive unimolecular-type first order reaction A $\xrightarrow{k_1}$ R $\xrightarrow{k_2}$ S, the concentration of component R, C_p at any time t is given by :

$$C_{R} = C_{AO} K_{1} \left[\frac{e^{-k_{1}t}}{(k_{2} - k_{1})} + \frac{e^{-k_{2}t}}{(k_{1} - k_{2})} \right]$$

if $C_A = C_{AO}$, $C_R = C_{RO} = 0$ at t = 0

the time at which the maximum concentration of R occurs is :

(A)
$$t_{max} = \frac{k_2 - k_1}{\ln(k_2 / k_1)}$$
 (B) $t_{max} = \frac{\ln(k_2 / k_1)}{k_2 - k_1}$ (C) $t_{max} = \frac{e^{k_2 / k_1}}{k_2 - k_1}$ (D) $t_{max} = \frac{e^{k_2 - k_1}}{k_2 - k_1}$

- Q.3 A consecutive reaction A $__{k_1}$ B $__{k_2}$ C is characterised by (A) maxima in the concentration of A (C) maxima in the concentration of C (D) high exothermicity
- Q.4 For the chemical reaction $A + B + C \xrightarrow{k} D$, it was found that the rate of the reaction doubled when the concentration of B was doubled, that the rate of reaction doubled when the concentration of both A and B were doubled, and quadrupled when the concentration of both B and C were doubled. The order of the reaction is : (A) 2 (B) 3 (C) 4 (D) 6
- Q.5 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

A
$$k_1 = 1.26 \times 10^{-4} \text{s}^{-1}$$
 and $k_2 = 3.8 \times 10^{-5} \text{s}^{-1}$
The percentage distributions of B and C are :

 (A) 80% B and 20% C
 (B) 76.83% B and 23.17 % C

 (C) 90% B and 10% C
 (D) 60% B and 40% C

- Q.14 A \longrightarrow B, $\Delta H = -10 \text{ kJ mol}^{-1}$, $E_a = 50 \text{ kj mol}^{-1}$, then E_a of B \longrightarrow A will be: (A) 40 kj mol^{-1} (B) 50 kj mol⁻¹ (C) -50 kj mol^{-1} (D) 60 kj mol⁻¹
- **0.15** If for any reaction, the rate constant is equal to the rate of the reaction at all concentration. The order is :

(A) 0	(B) 2	(C) 1	(D) 3
-------	-------	-------	-------

- **Q.16** For a given reaction the concentration of the reactant plotted against time gave a straight line with negative slope. The order of the reaction is : (A) 3 (B) 2 (D)0 (C) 1
- Q.17 What is the order of a chemical reaction A + 2B C. If the rate of formation of C increases by a factor of 2.82 on doubling the concentration of A and increases by a factor of 9 on tripling the concentration of B.

(A) 7/2 (B) 7/4 (C) 5/2 (D) 5/4

EXERCISE - 3 CONCEPTUAL SUBJECTIVE QUESTIONS

- 0.1 In Arrhenius equation for a certain reaction, the value of A and E (activation energy) are 4 \times 10¹³ sec⁻¹ and 98.6 kJ mol⁻¹ respectively. At what temperature, the reaction will have specific rate constant 1.1×10^{-3} sec⁻¹?
- 0.2 The rate constant is given by Arrhenius equation, $k = Ae^{-Ea/RT}$ calculate the ratio of the catalysed and uncatalysed rate constants at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.
- **Q.3** At 407 K, the rate constant of a chemical reaction is 9.5×10^{-5} s⁻¹ and at 420 K, the rate constant is 1.9×10^{-4} s⁻¹. Calculate the frequency factor of the reaction.
- Q.4 The energy of activation for a reaction is 100 kJ mol⁻¹. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C, other things being equal.
- Q.5 The gas phase decomposition, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ follows the first order rate law. At a given temperature the rate constant of the reaction is 7.5 $\times 10^{-3}$ s⁻¹. The initial pressure of N₂O₆ is 0.1 atm.
 - (i) Calculate time of decomposition of N₂O₅ so that the total pressure becomes 0.15 atm.
 - (ii) What will be the total pressure after 150 seconds?
- Q.6 In hydrogenation reaction at 25°C, it is observed that hydrogen gas pressure falls from 2 atm to 1.2 atm in 50 min. Calculate the rate of reaction in molarity per sec. R = 0.0821 litre atm degree⁻¹mol⁻¹.
- **Q.7** A drop of solution (volume 0.05 ml) contains 3×10^{-6} mol H⁺ ions. If the rate of disappearance of the H⁺ ions is 1×10^7 mol litre⁻¹ sec⁻¹, how long would it take for H⁺ ions in the drop to disappear?
- **Q.8** Consider Fig. for a reaction, $A_2 + B_2 \implies 2AB$



Progress of the reaction ---

EXERCISE - 2 CONCEPTUAL MCQ WITH SINGLE CORRECT ANSWER

Q.1	The rate of the simple is doubled-	rate of the simple reaction $2NO + O_2 \longrightarrow 2NO_2$, when the volume of the reaction vessel ubled-		
	(A) will grow eight times of its initial rate(B) rate reduce to one-eights of its initial rate(C) will grow four times of its initial rate(D) reduce to one-fourth of its initial rate			e-eights of its initial rate arth of its initial rate
Q.2	The rate expression f the initial concentrati (A) $C_A \times 2$; $C_B \times 2$	For the reaction $A(g) +$ on of A and B will cause (B) $C_A \times 2$; $C_B \times 4$	B(g) → C(g) is rate = 1 se the rate of reaction in (C) $C_A \times 1$; $C_B \times 4$	$KC_{A}^{2}C_{B}^{4}$. What changes in necesse by a factor of eight (D) $C_{A} \times 4$; $C_{B} \times 1$
Q.3	Given that k is the rate constant for some order of any reaction at temperature T, then the value of $T \propto \log k$, (where A is the Arrhenius constant) is – (A) A/2.303 (B) A (C) 2.303 (D) log A			
Q.4	According to the Arrh the rate constant of a (A) T	enius equation a straigl chemical reaction (log (B) log T	nt line is to be obtained k) against – (C) 1/T	by plotting the logarithm of (D) log 1/T
Q.5	Select the rate law that $A + B \longrightarrow C$	at corresponds to the da	ata shown for the follow	wing reaction :
	(A) rate = $k[B]^3$	(B) rate = $k[B]^4$	(C) rate = $k[A][B]^3$	(D) rate = $k[A]^{2}[B]^{2}$
Q.6	If in the fermentation sugar is reduced to 0 (A) 1	of sugar in an enzymat .06 M in 10h to 0.03 M (B) 2	ic solution that is 0.12 I in 20 h, what is the or (C) 3	M, the concentration of the rder of the reaction : (D) 0
Q.7	Which of the following (A) (B) (C)	ng curves represents a l (D)	Ist order reaction :	
Q.8	Rate constant of a rea 75% to activate is :	action with a virus is 3.	$3 \times 10^{-4} \mathrm{s}^{-1}$. Time require	red for the virus to become
Q.9	(A) 35 min Inversion of a sugar for in rotation of the plan at $t \rightarrow \infty$, $t = t$ and (A) $k =$ (B) k	(B) 70 min bllows first order rate eq e of polarization of light t = 0, then first order n = (C) k =	(C) 105 min uation which can be fol nt in the polarimeter. Of reaction can be writter (D) k =	(D) 175 min lowed by noting the change fr_{x} , r_{t} and r_{0} are the rotation 1 as –
Q.10	The half life period o is 10 minutes. In wha concentration :	f a first order reaction , t period of time is the co	$A \longrightarrow Product$ oncentration of A is red	uced to 10% of the original
Q.11	(A) 26 min For the reaction B + (A) 2k $C_B C_D^2$	(B) 33 min $2D \rightarrow 3T$, $-=kC_BC_BC_BC_BC_BC_BC_B^2$ (C) 44	(C) 71 min $_{D}^{2}$. The expression for $_{C} C_{B} C_{D}^{2}$ (D) k	(D) 90 min , - will be : $C_B C_D^2$
Q.12	 2 For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be : (A) more than 20 minutes (B) less than 20 minutes (C) equal to 20 minutes (D) infinity 			
Q.13	 .13 Time required to decompose half of the substance for nth order reaction is inversely proportional to: (A) aⁿ⁺¹ (B) aⁿ⁻¹ (C) aⁿ⁻² (D) aⁿ 			ion is inversely proportional (D) a ⁿ

18.	A subs $L^{-1}S^{-1}$.	nstant 'k' mol 005, 2001]	
19.	The re	[2005]	
20.	Prove require	wice the time [2006]	
21.	The ra	the constant for a first order reaction is 60 s ⁻¹ . How much time will it take that the normalized of the reactant to $1/10^{th}$ of its initial value?	to reduce the [2007]
22.	(a) De (b ra (a) Lis (b w	[2008] would be the OR act containing of the artefact.	
23.	Define	the following	[2009]
24.	A first	(i) Elementary step in a reaction (ii) Rate of a reaction order reaction has a rate constant of 0.0051 min ⁻¹ . If we begin with 0.10 M cor	ncentration of
	the rea	ctant, what concentration of the reactant will be left after 3 hours?	[2009]
25.	(a)	Explain the following terms	[2010]
	(b)	The decomposition of phosphine, PH ₃ , proceeds according to the following ed $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$ It is found that the reaction follows the following rate euation: Rate = k[PH ₃]. The half-life of PH ₃ is 37.9 s at 120°C. (i) How much time is required for 3/4 th of PH ₃ to dcompose? (ii) what fraction of the original sample of PH ₃ remains behind after 1 m OR	ninute?
	(a)	Explain the following terms:	
	(b)	(i) Order of reaction (ii) Molecularity of reaction The rate of a reaction increases four times when the temperature changes from K. Calculate the energy of activation of the reaction, assuming that it does not temperature. $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$	a 300K to 320 t change with
26.	Define	e order of a reaction	[2011]
27.	What reaction (i) L ⁻¹	do you understand by the rate law and rate constant of a reaction? Identify to n if the units of its rate constant are: mol s^{-1} (ii) L mol ⁻¹ s^{-1}	the order of a [2011]
28.	The t	constant of urth of initial [2011]	

EX	ERCISE - 1 CBSE FLASH BACK
1.	Give one example of photochemical reaction. [2000]
2.	For the reaction $3H_2(g) + N_2(g) 2NH_3(g)$, how are the rate of reaction and interrelated ? [2000]
3.	The rate of reaction is given by: Rate = k $[N_2O_5]$. In this equation what does k stand for ? [2000]
4.	Why is the instantaneous rate of a reaction does not change when a part of the reacting solution is taken out? [2000]
5.	Under what conditions does the rate of a reaction equal its rate constant? [2000]
6.	A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction. [2000]
7.	In general it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction? ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
8.	Show that the time required for the completion of $3/4^{th}$ reaction of first order is twice the time required for completion of $1/2$ of the reaction. [2000]
9.	What is the effect of catalyst on activation energy ? Explain.ORWhat aspect of the reaction is influenced by the presence of catalyst which increases the rate or possibility of the reaction ?[2001]
10.	A reactant with initial concentration 'a' mol lit ⁻¹ follows zero order kinetic with a rate constant k mol lit ⁻¹ sec ⁻¹ . In how much time will the reaction go to completion ? [2001]
11.	A reaction is 50% completed in 2 hour and 75% complete in 4 hours what is the order of the reaction.? [1996, 2001]
12.	The reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ is a first order reaction with $k = 2.2 \times 10^{-5} s^{-1}$ at 320°C. Calculate the percentage of SO_2Cl_2 that is decomposed on heating this gas for 30 min. [2001]
13.	Calculate the time required for the completion of 90% of a reaction of first order kinetics.
14.	 [t_{1/2} reaction = 44.1 minutes] [2001] The decomposition of compound is found to follow a first order rate law. If it takes 15 minutes for 20 per cent of original material to react. calculate : (i) the specific rate constant (ii) the time at which 10 per cent of the original material remains unreacted (iii) the time it takes for the next 20 per cent of the reactant left to react after the first
15.	The rate constant of reaction is 1.5×10^7 sec ⁻¹ at 50 °C and 4.5×10^7 sec ⁻¹ at 100 °C. Calculate the value of activation energy E for the reaction $[P = 8, 314 \text{ IK}^{-1} \text{ mol}^{-1}]$ [2003]
16.	What are photochemical reactions? Explain the mechanism of the photochemical reaction between hydrogen and chlorine gas. [2003]
17.	How does the value of rate constant vary with reactant concentration? [2004, 2005]

10. k = A, but it is not reasonable since E_a can not be zero

11.	2033.8	12.	86.1°C	13.	124.46 mol ⁻¹
14.	2.1645×10^4	15 . 34	9.04 K	16.	311 K
17.	8.88×10 ³²	18. 5.	$.04 \times 10^5 \mathrm{s}^{-1}$	19.	2.34×10 ¹³

Daily Practice Problems - 13

01.	1, 0, 1.386	02. 6.2364×10^{-3} , 0.0332 atm
03.	doubled, unaffected	04. $\frac{dx}{dt} = k[A]^{1}[B]^{2}[C]^{0}$, rate becomes doubled
05.	$8.12 \times 10^{-6} (n/V)/sec$	06. 0.3584 hr ⁻¹ , 0.658
07.	525 sec	08. rate = $k [P_{NO}]^2 [P_{H_2}]^1$, 2.22 atm ⁻² min ⁻¹
09. D	10. B 11. B 12. A	13. A 14. B 15. D 16. A 17. B 18. D
I9. B	20. A	

000

7.	$K = \frac{2.303}{t} \log_{10} \frac{2P_0}{3P_0 - P} $ 8. 26 sec 9. 85.64 10. 1.58 × 10 ⁻² , 233 atm
11.	130.41 12. $P'_{(CH_3)_2N_2} = 127.55 \text{ mm}$, $P'_{C_2H_6} = 72.45 \text{ mm}$
13.	(i) 6.93×10^{-2} M/min.(ii) 3.465×10^{-2} M/min(iii) 1.7325×10^{-2} M/min.(iv) 8.67×10^{-3}
14.	7.8×10 ⁻⁴ atm s ⁻¹ 15. $2P^{\circ} - \frac{(2P^{\circ} - P)^{2}}{P^{0}}$ 16. 0.033 atm
	Daily Practice Problems - 09

1.	$k = 2.0 \times 10^{-2} \text{ min}^{-1}$	3.	I, $3.2 \times 10^{-2} \text{ min}^{-1}$ 5.	108.23 ml
8.	m = 1, n = 1	9.	$k = 3.12 \times 10^{-3} \text{ min}^{-1}$	
10.	$r = k [sugar]^{1} [H^{+}]$	11.	$6.2 \times 10^{-4} \mathrm{sec^{-1}}$	

Daily Practice Problems - 10

4.

6.

- 2. $K_b = 1.7 \times 10^{-5} \text{ sec}^{-1} \text{ } K_c = 1.35 \times 10^{-4} \text{ (order = 1 for each path)}$
- 3.methyl cyclopentene =23%, cyclohexane = 77%4.1990 sec.5.76.8, 23.26.6 = 4 times7.4,83 mins6.6 = 4 times156156
- 9. (b) $t_{1/2} = 36 \min$ 10. 156

Daily Practice Problems - 11

- **1.** 7.5937 **2.** 1.88 **3.** $E_A = 209.6 \text{ kJ}$
 - Large value of E 5. $k = 3.19 \times 10^{-2} \text{ L mol}^{-1} \text{s}^{-1}$
- **6.** 63.18 kJ/mol **7.** 6.4×10^9 **8.** 0.002
- **9.** 24.7 kJ/mol **10.** 4.768

Daily Practice Problems - 12

- 1. $k = 5.10 \times 10^{-5} \text{ s}^{-1}$; E = 92.011 kJ/mol; $A = 6.73 \times 10^{11} \text{ s}^{-1}$
- **2.** $k = 10^{-2} \text{ s}^{-1}$; E = 87.297 kJ/mol; $A = 2.2 \times 10^{14} \text{ s}^{-1}$
- 3. $k = 5 \times 10^{-4} \, s^{-1}$; $E = 94.78 \, kJ/mol$; $A = 10^{15} \, s^{-1}$
- 4. $t = 19 \text{ sec}, E_a = 67.6 \text{ kJ mol}^{-1}$ 5. $E_a^{f} = 50.80 \text{ kJ/mol}; E_a^{b} = 27.61 \text{ kJ/mol}$
 - T = 310K 7. 311.2
- **8.** $\approx 12 \text{ kcal}$ **9.** 65 kJ/mole

Daily Practice Problems - 05

1. 2.	(a) Rate = k[NH ₄ ⁺] [NO ₂ ⁻] (b) 3.0×10^{-4} M/s (c) 6.1×10^{-6} M/s (i) $r = k[A]^{-1}[B]^{1/2}$ (ii) wrt : A = -1, B = 1/2, C = 0 ,overall order = -1/2			
	(iii) $k = \frac{63}{\sqrt{3}} \times 10^{-9}$ (iv) rate of reaction increas	es by $2\sqrt{2}$ times		
3.	(i) $k[A_2]^3[B_2]$ (ii) order wrt $A_2 = 3$; O. wr	$t B_2 = 1$, overall order = 4		
	(iii) $k = 7.5 \times 10^3 \text{ (mol/lit)}^{-3/\text{sec}}$ (iv)	rate of reaction decrease to $\frac{1}{16}$		
4 .	(a) 2 and 1 (b) $r = K[Cl_2]^1[NO]_2$ (c) 8 litre ² mo	$1^{-2} \sec^{-1}$ (d) 0.256 mol litre ⁻¹ sec ⁻¹		
5. 6.	$60 \text{ mol}^{-1} \text{ L sec}^{-1}$ (a) K[A] ¹ [B] ² (b) 1	$0^{-1} = 0.1 L^2 mol^{-2} min^{-1}$		
7.	(a) Rate = $K[A]^2[B]^0$ (b) K	$L = 4 \times 10^{-2} \text{ L mol}^{-1} \text{ sec}^{-1}$		
	(c) Rate = 16×10^{-4} mol L ⁻¹ sec ⁻¹ 8.	3		
9.	(a) 0.8 liter mol ⁻¹ time ⁻¹ (b) 1.28×10^{-3} 10.	$4.88 \times 10^{-8} \text{mol}^{-2} \text{L}^{2} \text{min}^{-1}$		
	Daily Practice Problem	s - 06		
1.	(i) $a = R_0 K$, $b = \frac{-R_0 K^2}{2}$, $c = \frac{R_0 K^3}{C}$			
2.	(i) $t_{1/2} = 66.66 \text{ min}, \text{ k} = 0.01039 \text{ min}^{-1}$ (ii) k	$x = 0.06386 \text{ min}^{-1}$; t = 36.06 min		
	(iii) 0.03465 min^{-1} (iv)	(i) 0.740 s (ii) 2.005 s		
4.	0.09 5. (a	(b) No change		
6. o	$K = 2.5 \times 10^{-4} \text{ sec}^{-1} \qquad 7. \text{ (a}$) 46.2 minute (b) 107.3 minute $12.5.9\%$ (iii) $6.25.9\%$ (iii) $1.5.6\%$		
o. 10	$\begin{array}{c} \textbf{(a)} 2.232 \times 10^{-2} \text{ mm}^{-2} \textbf{(b)} 62.12 \text{ minute} \textbf{9. (i)} \\ 15.86\% \qquad \qquad 11 2.4 \text{ hrs} 12 12 12 12 12 12 12 1$	12.5%, (II) $0.25%$, (III) $1.50%3.95 hrs 2.217 lit$		
13.	41 months, 79.4 months 14. 72.18 m	in.		
	Daily Practice Problem	s - 07		
1.	Time at this point is $t_{1/2}$ because [A] = [B]: Also $\frac{d}{d}$	$\frac{[A]}{dt} + \frac{d[B]}{dt} = 0$		
2.	5.25 %, 128.33 hr 3. 400	4. 211 torr, 13.57 min		
5.	Zero order 6. 200 minute	7. 3.59×10^2 , 1.1×10^3 sec		
8. 10	0.023 mol/L 9. (i) 250 secon (i) 2070 sec (ii) 2772 sec (iii) 1386 sec (iv)	ads (ii) $0.01386 \text{ M sec}^{-1}$		
10.	(i) 2077 see (ii) 2772 see, (iii) 1560 see. (iv)	5-05 sec.		
	Daily Practice Problem	s - 08		
1.	$k = \frac{1}{t} ln \frac{P_3}{2(P_3 - P_2)}$ 2. $k = \frac{1}{t} ln \frac{P_3}{(P_3 - P_2)}$	3. $k = \frac{1}{t} ln \frac{V_1}{(2V_1 - V_2)}$		
	$1 4V_3 1 r_{\infty}$			

4. $k = \frac{1}{t} ln \frac{4V_3}{5(V_3 - V_2)}$ 5. $k = \frac{1}{t} ln \frac{r_{\infty}}{(r_{\infty} - r_t)}$ 6. $8.6 \times 10^{-4} \sec; 13.43 \text{ minute}$

ANSWER SHEET Daily Practice Problems - 01 3. (B) (D) **2.** (C) 4. (B) 5. (A) 1. $\frac{\Delta[\text{NO}]}{\text{dt}} = 3.5 \times 10^{-2} \text{ mol } \text{dm}^{-3} \text{ s}^{-1} \frac{\Delta[\text{H}_2\text{O}]}{\text{dt}} = 5.3 \times 10^{-2} \text{ mol } \text{dm}^{-3} \text{ s}^{-1}$ 6. $6.0 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$ 7. 8. (a) 1.6×10^{-4} M/s; (b) 3.2×10^{-4} M/s **10.** $0.005 \text{ mol } L^{-1} \text{ minute}^{-1}$ 9. (a) NH_3 (b) H_2 , $4. \times 10^{-10} \text{ mol } L^{-1} \text{ sec}^{-1}$ 12. 0.005 mol lit⁻¹ min⁻¹ 11. $3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$ $3.5 \times 10^{-5} s^{-1}$, $4.2 \times 10^{-5} mol L^{-1} s^{-1}$ 13. 14. 0.9×10^{-3} mol litre⁻¹ min⁻¹ $0.7 \text{ mol } L^{-1} \text{ or } 0.7 \text{ M}$ **Daily Practice Problems - 02** 3. (B) 4. (B) 1. (C) 2. (D) 5. (D) 6. (D) 7. (a) Rate = $k[CH_3Br][OH^-]$ (b) rate will decrease by factor of 5 (c) rate will increase by factor of 4 (a) $k[Br^{-}][BrO_{3}^{-}][H^{+}]^{2}$ 8. (c) rate will increase by the factor of 9 **(b)** 4 (d) rate will decrease by factor of 1/4order w.r.t. [NO] = 2; order w.r.t. $[Cl_2] = 1$ 9. (ii) $atm^{-1/2} time^{-1}$ 10. (i) 3/2 (iii) increased by 64 times **Daily Practice Problems - 03** $\frac{-d[A]}{dt} = K[A][B] \qquad 3.$ Rate = $K[A]^2$. [B] 2. O(g)1. $r = k [NO_2] [F_2]$ 6. 4. 3 5. $r = k [NO]^2 [Br_2]$ $\frac{\mathrm{d}\,\mathrm{x}}{\mathrm{d}\,\mathrm{t}} = \mathrm{K}\,[\mathrm{A}]^0$ 7. 8. 1 **9.** r = K [A] [B]**10.** 1 **Daily Practice Problems - 04** (i) $7.5 \times 10^{-7} \,\mathrm{M \ min^{-1}}$ (ii) rate increased by 64 times 1. 2. $8 \times 10^{-9} \text{ M}^{-2} \text{ s}^{-1}$ 3. (i) $7.5 \times 10^{-4} \text{ Ms}^{-1}$ (ii) zero order] 4. $[r = K[O_3]^2 [O_2]^{-1}]$ 5. (a) $2 N_2 O(g) \longrightarrow 2 N_2(g) + O_2(g)$ (b) oxygen atom (c) (i) unimolecular (ii) bimolecular (d) not defined 6. 3/2 $H_2 + HCl \rightarrow HCl + HI$ slow $\mathbf{r} \propto [\mathbf{H}_2][\mathbf{ICl}]$ $HI + ICl \rightarrow HCl + I_{2}$ fast 7. $r = k[H_2][IC1]$ $\overline{H_2 + 2HCl} \rightarrow 2HCl + I_2$ 8. $k_{eq} = 1$, rate = $k_2(C) (A_2)^{1/2}$ **9.** $r = K [NO]^{2}[H_{2}]$, where $K = k_{2} \times K_{1}$

]	12.	Two substances A and B are present such that $[A_0] = 4[B_0]$ and half-life of A is 5 minuteand that of B is 15 minute. If they start decaying at the same time following first orderkinetics how much time later will the concentration of both of them would be same.(A) 15 minute(B) 10 minute(C) 5 minute(D) 12 minute				
	13.	The rate of a reaction If the rate of reaction 4×10^{-4} , the rate com (A) 2×10^{-4} mole ^{1/2} (C) 2×10^{-4} mole ^{-1/2}	increases 4-fold when is 4×10^{-6} mole L ⁻¹ S ⁻¹ stant of the reaction w L ^{-1/2} S ⁻¹ ² , L ^{1/2} S ⁻¹	a concentration of react L^{-1} mole L^{-1} when conce ill be (B) 1×10^{-2} S ⁻¹ (D) 25 mole ⁻¹ L min	tant is increased 16 times. entration of the reactant is 1^{-1}	
	14.	A catalyst lowers 10 kJ mole^{-1} . The ten that of the catalysed (A) -123° C	the activation energy mperature at which the at 27°C is (B) 327°C	ergy of a reaction euncatalysed reaction (C) 327°C	from 20 kJ mole ⁻¹ to will have the same rate as $(D) + 23^{\circ}C$	
	15. The reaction , $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A and B are $P_A = 0.60$ and $P_B = 0.80$ atm. When $P_C = 0.2$ atm the rate of reaction relative to the initial rate is				rocess. In an experiment, m. When $P_C = 0.2$ atm the	
	16.	Thermal decompositi is decomposed in 12 decompose ? (A) 399 min	(D) 1724 ion of a compound is of 20 minutes , show how (B) 410 min	first order . If 50 % of a long will it take for 9 (C) 250 min	a sample of the compound 00 % of the compound to (D) 120 min	
	17.	If concentration are m a 3 rd order reaction a (A) mol lit ⁻¹ min ⁻¹	neasured in mole/litre ar are (B) lit ² mol ⁻² min ⁻¹	nd time in minutes, the u (C) lit mol ⁻¹ min ⁻¹	(D) min ⁻¹	
	18.	What is the activation	n energy for the decom	position of N ₂ O ₅ as		
		$N_2O_5 \rightleftharpoons 2$	$NO_2 + \frac{1}{2}O_2$			
		If the values of the rat (A) $102 \times 10^2 \text{ kJ}$	te constants are 3.45×1 (B) 488.5 kJ	10 ⁻⁵ and 6.9 × 10 ⁻³ at 27 (C) 112 kJ	°C and 67°C respectively. (D) 112.5 kJ	
	19.	Half life period for a the concentration of (A) 20 minutes	first order reaction is 2 the reactants from 0.03 (B) 60 minutes	0 minutes. How much 8 M to 0.01M (C) 40 minutes	time is required to change (D) 50 minutes	
	20. The kinetic datas for the reaction: $2A + B_2 \longrightarrow 2AB$ are as given below: [A] [B ₂] Rate mol L ⁻¹ mol L ⁻¹ mol L ⁻¹ min ⁻¹ 0.5 1.0 2.5 × 10 ⁻³ 1.0 1.0 5.0 × 10 ⁻³ 0.5 2.0 1 × 10 ⁻²					
1		(A) 1 and 2	(B) 2 and 1	(C) 1 and 1	(D) 2 and 2	

2.	The decomposition of Cl_2O_7 at 440K in the gas phase to Cl_2 and O_2 is a first order reaction									
	(i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm calculate that rate constant									
	(ii) Calculate the pressure of Cl_2O_7 after 100 sec. of decomposition at this temperature.									
3.	Rate law for the following reaction is									
	Ester + H ⁺ \longrightarrow Acid + Alcohol; is $\frac{dx}{dt} = K [ester]^1 [H^+]^0$									
	What would be the effect on the rate if									
	 (i) Concentration of ester is doubled ? (ii) Concentration of H⁺ ion is doubled ? 									
4.	The reaction $2A + B + C \rightarrow D + 2E$; is found to be first order in A; second order in B and zero order in C									
	 (i) Give the rate law for the above reaction in the form of a differential equation. (ii) What is the effect on the rate of increasing the concentration of A, B and C two times? 									
5.	At 27°C it was observed, during a reaction of hydrogenation that the pressure of H ₂ gas decreases from 2 atm to 1.1 atm in 75 min. Calculate the rate of reaction (molarity/sec). Given ($R = 0.082$ /litre atom K ⁻¹ mole ⁻¹)									
6.	In presence of an acid N-chloro acetanilide changes slowly into p-chloro acetanilide. Former substance liberated iodine from KI and not the later and hence progress of reaction can be measured by titrating iodine liberated with $Na_2S_2O_3$ solution, the results obtained were as follows:									
	Time (hours) 0 1 2 4 6 8									
	(a–x)i.e., hypo 45 32 22.5 11.3 3.7 2.9 show that reaction is uniomlecular and find out the fraction of N-chloroacetanilide decomposed after three hours.									
7.	For the decomposition of dimethyl ether, A in the Arrhenius equation $K = Ae^{-E/RT}$ has a value of 1.26 $\times 10^{13}$ and E_a value of 58.5 kcal. Calculate half life period for first order decomposition at 527°C.									
8.	For the reaction,									
	$2NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$ at 900 K, the following data are obtained : Initial pressure Initial pressure									
	of NO (atm) of $H_2(atm)$ (atm min ⁻¹)									
	0.150 0.400 0.020									
	0.075 0.400 0.005 0.150 0.200 0.010									
	Find the rate law and the value of rate constant.									
9.	$ \begin{array}{c} \mbox{If a reaction } A+B \longrightarrow C \mbox{ is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy 70 kJ/mol, the activation energy for the reverse reaction is (A) 30 kJ/mol (B) 40 kJ/mol (C) 70 kJ/mol (D) 100 kJ/mol \\ \end{array} $									
10.	The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, 104.4 kJ mol ⁻¹ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively the value of the rate constant as $T \longrightarrow \infty$ is :									
	(A) $2.0 \times 10^{18} \text{s}^{-1}$ (B) $6.0 \times 10^{14} \text{s}^{-1}$ (C) ∞ (D) $3.6 \times 10^{30} \text{s}^{-1}$									
11.	The inversion of cane sugar proceeds with half–life of 500 minute at pH 5 for any concentration of sugar. However if $pH = 6$, the half–life changes to 50 minute. The rate law expression for									
	the sugar inversion can be written as (A) $r = K [cucar]^2 [H]^6$ (B) $r = K [cucar]^1 [H]^6$									
	(C) $r = K[sugar]^{0}[H^{+}]^{6}$ (D) $r = K[sugar]^{0}[H^{+}]^{1}$									

(b)
$$CO + 3H_2 \xrightarrow{Ni} CH_4 + H_2O$$
, $CO + 2H_2 \xrightarrow{ZnO} CH_3OH$
 $CO + H_2 \xrightarrow{Cu} HCHO$

It may therefore be concluded that in some cases nature of products formed depends upon the presence and nature of catalyst used.

- (vi) A catalyst does not make reaction more exothermic
- (vii) Catalyst's activity is more or less specific : A catalyst for one reaction is not necessary to catalyse the another reaction.

10. Types of Catalysis :

- 1. **Homogeneous catalysis :** The reaction in which catalyst and the reactants have same phase. It includes two types.
 - (a) Gaseous phase catalysis: When reactants and catalyst are in gaseous phase e.g. chamber process for H₂SO₄.

$$2SO_2(g) + O_2(g) \xrightarrow{NO} 2SO_3(g)$$

(b) **Solution phase catalysis :** The reactions in which catalyst and reactants are in solution phase or liquid phase of miscible nature.

 $\text{RCOOR}'_{(l)} + \text{H}_2\text{O}_{(l)} \xrightarrow{H^+} \text{RCOOH} + \text{R'OH}$

- 2. Heterogeneous catalysis : The reactions in which catalyst and reactants form phase ≥ 2 .
 - (a) Solid-liquid catalysis : Reactant : Liquid Catalyst : Solid

$$2H_2O_{2(l)} \xrightarrow{MnO_{2(s)}} 2H_2O + O_2$$

Liquid-Liquid catalysis ::

$$2H_2O_{2(l)} \xrightarrow{Hg(l)} 2H_2O + O_2$$

atalysis : Reactant : gases Catalyst : solid

Two aspects of solid catalyst are more significant, one is activity and the other is selectivity. Activity is the ability of catalyst to accelerate chemical reactions; the degree of acceleration can be as high as 10¹⁰ times in certain reactions. Selectivity is the ability of catalyst to direct reaction to yield particular reaction (excluding others). For example, n-heptane selectivity gives toluene in presence of Pt catalyst. Similarly,

 $CH_3 - CH = CH_2 + O_2$ give $CH_2 = CHCHO$ selectivity over Bismuth molybdate catalyst.

Daily Practice Problems - 13

1.	. Rate of a reaction $A + B \rightarrow$ Products; is given below as a function of different initial						
	[A] mol/litre	[B] mol litre ⁻¹	Initial rate mol litre ⁻¹ time ⁻¹				
	0.01	0.01	0.005				
	0.02	0.01	0.010				
	0.01 0.02		0.005				
Determine the order of the reaction with respect to A and with respect to B. What is the							
	of A in the reaction	on?					

(b)

- For the reaction A → products, the time for half change is 5000 second at 300K and 1000 second at 310 K. If the reaction obeys first order kinetic, calculate energy of activation.
- 14. Two reactions of same order have equal exponential factors but their activation energy differ by 24.9 kJ mol⁻¹. Calculate the ratio between the rate constant of these reactions at 27° C. [R = 8.314 JK⁻¹ mol⁻¹]
- 15. The energy of activation of a I order reaction is 104.5 kJ mol⁻¹ and pre-exponential factor A in Arrhenius equation is 5×10^{13} sec⁻¹. At what temperature will the reaction have half life of 1 minute?
- 16. In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol₋₁ respectively. At what temperature, the reaction will have specific rate constant $1.1 \times 10^{-3} \text{ sec}^{-1}$?
- 17. The rate constant is given by Arrhenius equation $k = Ae^{-E_a/RT}$ Calculate the ratio of the catalysed and uncatalysed rate constant at 25°C if the nergy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.
- 18. At 407 K the rate constant of a chemical reaction is $9.5 \times 10^{-5} s^{-1}$ and at 420 K, the rate constant is $1.9 \times 10^{-4} s^{-1}$. Calculate the frequency factor of the reaction.
- **19.** The energy of activation for a reaction is 100 kJ mol⁻¹. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C?

9. Catalysis :

Catalyst is a substance which alters the rate of reaction with or without involvement into the reaction. It alters rate of reaction by providing a new path for the conversion of reactants to products by changing the energy of activation. A positive catalyst decreases and a negative catalyst inceases the energy of activation.



Characteristics Of Catalyst

- (i) A catalyst remains unchanged chemically at the end of reaction, however its physical state may change. e.g. MnO_2 used as catalyst in granular form for the decomposition of $KCIO_3$, is left in powder form at the end of reaction.
- (ii) A catalyst never initiate a chemical reaction. It simply influences the rate of reaction. Exception : combination of H₂ and Cl₂ takes place only when moisture (catalyst) is present.
- (iii) A small quantity of catalyst is sufficient to influence the rate of reaction e.g. 1 g atom of Platinum is sufficient to catalyse 108 litre of H₂O₂ decomposition.
- (iv) A catalyst does not influence the equilibrium constant of reaction. It simply helps in attaining equilibrium earlier. It alters the rate of forward & backward reactions equally.
- (v) A catalyst normally does not alter the nature of products in a reaction. However some exceptions are found to this characteristic.
 - (a) HCOOH $\xrightarrow{\text{AlCl}_3}$ H O + CO, HCOOH $\xrightarrow{\text{Cu}}$ H + CO

	Daily Practice Problems - 12
•	For the displacement reaction $\begin{bmatrix} Co(NH_3)_5CI]^{2+} + H_2O \longrightarrow \begin{bmatrix} Co(NH_3)_5(H_2O) \end{bmatrix}^{3+} + CI^{-}$
	the rate constant is given by , $ln [k/(min^{-1})] = -\frac{11067}{T} + 31.33.$
	Evaluate k, E and A for the chemical reaction at $25 {}^{\circ}\mathrm{C}$.
2.	For the reaction, $2 N_2 O_5 \longrightarrow 4 NO_2 + O_2$
	the rate constant is given by , $ln [k(sec^{-1})] = -\frac{10500}{T} + 33$.
	Evaluate \mathbf{k} , \mathbf{E} and \mathbf{A} for the chemical reaction at 27 °C.
5.	For a first order reaction, the rate constant is given by , $ln[k(sec^{-1})] = -\frac{11400}{T} + 34.7$
	Evaluate k, E and A for the chemical reaction at 27 °C.
.	The time required for 20 % completion of a first order reaction at 27 °C is 1.5 times that required for its 30 % completion at 37 °C. If the pre exponential factor for the reaction is $3 \times 10^9 \text{ sec}^{-1}$, calculate the time required for 40 % completion at 47 °C and also the energy of activation.
5.	The rate constant of a reaction increases by 7 % when its temperature is raised from 300 K to 301 K while its equilibrium constant increases by 3 %. Calculate the activation energy of the forward and reverse reactions.
).	The energy of activation and specific rate constant for a first-order reaction at 25°C $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$ (in CCl ₄) (in CCl ₄) are 100 kJ/mole and 3.46×10^{-5} s ⁻¹ respectively. Determine the temperature at which the half-life of the reaction is 2 hours.
' .	In Arrhenius' equation for a certain reaction, the value of A and E (activation energy) are $4 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol ⁻¹ respectively. If the reaction is of first order, at what temperature will its half-life period be ten minutes?
8.	What is the energy of activation of a reaction if its rate doubles when the temperature is raised from 290 K to 300 K ?
	For the reaction $A + B \longrightarrow C + D$; $\Delta H = +20$ kJ/mole, the activation energy of the forward reaction is 85 kJ/mole. Calculate the activation energy of the reverse reaction.
0.	What is the value of the rate constant, predicted by the Arrhenius's equation if $T \longrightarrow \infty$? Is this value physically reasonable?
1.	The activation energy of a certain uncatalysed reaction at 300 K is 76 kJ mol ⁻¹ . The activation energy is lowered by 19 kJ mol ⁻¹ by the use of catalyst. By what factor, the rate of catalysed reaction is increased ?
2.	Given that K (sec ⁻¹) = $5 \times 10^{14} e^{-124080/RT}$ where activation energy is expressed in joule. Calculate the temperature at which reaction has $t_{1/2}$ equal to 25 minute. Assume I order reaction.

k = Total number of collisions per unit volume per unit time \times number of effective collisions

$$\Rightarrow \quad k = Ae^{-1}$$

$$\Rightarrow \quad \ln k = \ln A - \frac{E_a}{RT} \Rightarrow \quad \log k = \log A - \frac{E_a}{2.303 \text{ RT}} \quad \log_k k$$

$$\Rightarrow \quad \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Rightarrow \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303 \text{ R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \text{ Where } k_1 \text{ and } k_2 \text{ are rate constants at temperatures } T_1 \& T_2$$

respectively. Thus, knowing these values E_a can be calculated. When the value of E_a is known, the value of A can be calculated by substituting its value in equation $k = Ae^{-E_a/RT}$. In equation (2), the value of R has to be inserted in the same unit in which E_a is desired.

Temperature Coefficient : μ "Temperature coefficient of a chemical reaction is defined as the ratio of rate constants of a reaction at two temperatures differing by 10°".

$$\mu = \text{Temperature coefficient} = \frac{k_{T+10}}{k_T} \approx 2 \text{ to } 3$$

Daily Practice Problems - 11

- 1. Two first order reactions proceed at 25 °C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75 °C.
- 2. The half life of a substance in a first-order reaction is 100 minutes at 323.2 and 15 min at 353.2 K. Calculate the temperature coefficient of the rate constant of this reaction .
- 3. The activation energy for the reaction, $O_3(g) + NO(g) \longrightarrow NO_2(g) + O_2(g)$ is 9.6 kJ/mole. Prepare an activation energy plot if ΔH^o for this reaction is – 200 kJ/mole. What is the energy of activation for the reverse reaction ?
- 4. Which reaction will have the greater temperature dependence for the rate constant-one with a small value of energy of activation (E) or one with a large value of E?
- 5. For a chemical reaction the energy of activation is $85 \text{ J} \text{ mol}^{-1}$. If the frequency factor is, $4.0 \times 10^9 \text{ L} \text{ mol}^{-1} \text{s}^{-1}$, what is the rate constant at 400 K?
- 6. A bottle of milk stored at 300 K sours in 36 hours. When stored in a refrigerator at 275 K it sours in 360 hrs. Calculate the energy of activation of the reaction involved in the souring process.
- 7. Calculate the ratio of the catalysed and uncatalysed rate constant at 20 °C if the energy of activation of a catalysed reaction is 20 kJ mol⁻¹ and for the uncatalysed reaction is 75 kJ mol^{-1} .
- **8.** Two reactions of same order have equal pre-exponential factors but their activation energies differs by 41.9 J/mole. Calculate the ratios between rate constants of these reactions at 600 K.
- 9. Rate constant of a reaction changes by 2 % by 0.1 °C rise in temperature at 25 °C. The standard heat of reaction is $121.6 \text{ kJ} \text{ mol}^{-1}$. Calculate E_a of reverse reaction.
- 10. Two reactions proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of the second is 2.5. Find the ratio of the rates of these reactions at 95 °C.

		∠ ^B					
9.	(a)	The reaction A proceeds in parallel channels $A \searrow_C$ Although the $A \rightarrow C$ branch is					
10.		themodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so					
	(b)	In the above problem, suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value?					
	A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant 1.7×10^{-2} sec ⁻¹						
	Meanwhile the multiplication of bacteria (1 bacterium \rightarrow 2 bacteria) which also follows first						
	order	kinetics with rate constant 1.5×10^{-3} sec ⁻¹ also continued. Calculate the number of					
	bacte	rial left after 2 minutes if the initial number of bacteria is 10^3 .					

8. Arrhenius Theory :

In 1889 Arrhenius recognised the temperature dependence of rates or rate constant. He has given an emperical relation which can be written as

 $\mathbf{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E}_{a}/\mathbf{R}\mathbf{T}} \qquad \dots \dots (1)$

k is the rate constant (of any order other than zero order), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature. Activation energy (E_a) is the minimum energy required by a reactant at a certain temperature to undergo transformation into product. Arrhenius clearly assumed that reactions occur because of collisions between atoms and molecules of the reactant.

He assumed the activation energy to be the least value of energy which the colliding molecules must possess for the collision to yield a product. If we plot graph between activation energy and progress of a reaction (expressed as reaction co-ordinate), we get a graph as shown in figure.



Reaction Co-ordinate

The difference between the energies of the reactant and the transition state (TS) is called $(E_a)_f$. $\Delta H = (E_a)_f - (E_a)_b$

A, the pre-exponential factor or the frequency factor or the Arrhenius constant is the number of effective collisions occurring per unit time. Effective collision is the number of collisions occurring per unit time in which orientation of the colliding molecules is proper. $e^{-E_a/RT}$ gives the fraction of the effective collision that have the sufficient activation energy. Therefore the product of A and $e^{-E_a/RT}$ gives the number of collisions per unit time that forms the product and is called its number of productive collisions which is the rate constant, k. For all practical calculations, we shall assume that E_a and A are temperature independent. Both A and E_a are characteristics of the reaction.

Rate constant (k) is a measure of rate of reaction which depends upon a) total number of collisions per unit volume per unit time (Frequency factor A) b) total number of effective collisions (Boltzmann Factor = $e^{-E_a/RT}$)

Daily Practice Problems - 10

1. An organic compound A decomposes following two parallel first order mechanisms :

 $K_1 = \frac{1}{5}$ $K_1 = \frac{1}{9}$ and $k_1 = 1.3 \times 10^{-5} \text{ sec}^{-1}$

Calculate the concentration ratio of C to A, if an experiment is allowed to start with only A for one hour .

- 2. Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate const. at certain temp., measured in terms of disappearance of 'A' was 1.52 × 10⁻⁴ sec⁻¹. Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane. (B) and the other to cis-1,2-dideuterocyclopropane (C). (B) was found to constitute 11.2 % of the reaction product, independently of extent of reaction. What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products ?
- 3. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K , the first order rate constant for the formation of cyclohexane was measured as 1.26×10^{-4} s⁻¹, and for the formation of methyl cyclopentene the rate constant was 3.8×10^{-5} s⁻¹. What is the percentage distribution of the rearrangement products ?
- 4. For the reaction,

 $[\operatorname{Cr}(\operatorname{H}_{2}\operatorname{O})_{4}\operatorname{Cl}_{2}]^{+}(\operatorname{aq}) \xrightarrow{K_{1}} [\operatorname{Cr}(\operatorname{H}_{2}\operatorname{O})_{5}\operatorname{Cl}]^{2+}(\operatorname{aq}) \xrightarrow{K_{2}} [\operatorname{Cr}(\operatorname{H}_{2}\operatorname{O})_{6}]^{3+}(\operatorname{aq})$

 $k_1 = 1.78 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 5.8 \times 10^{-5} \text{ s}^{-1}$ for the initial concentration of $[Cr(H_2O)_4Cl_2]^+$ is 0.0174 mol/litre at 0 °C. Calculate the value of t at which the conc. of $[Cr(H_2O)_5Cl]^{2+}$ is maximum.

5. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as A $k_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$ and $k_2 = 3.6 \times 10^{-5} \text{ sec}^{-1}$. Calcualte

the % distribution of B and C.

- 6. For the reaction $A \longrightarrow B \longrightarrow Ct_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.
- 7. The reaction

paths by

cis-Cr(en)₂(OH)⁺₂
$$\overbrace{k_2}^{k_1}$$
 tran-Cr(en)₂(OH)⁺₂

is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is 3.3×10^{-4} s⁻¹. In an experiment starting with the pure cis form, how long would it take for half the equilibrium amount of the trans isomer to be formed?

8. For the two parallel reactions A $\underline{k_1}$, B and $\underline{k_2}$, C, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by $E' = \frac{k_1 E_1 + k_2 E_2}{k_1 E_1 + k_2 E_2}$

$$E' = \frac{k_1 E_1 + k_2 I}{k_1 + k_2}$$



In general concentration of A decreases exponentially, the concentration of B initially increases upto a maximum and then decreases thereafter, and the concentration of C increases steadily until it reaches its final value $[A]_0$, when all A has changed into C.

Maximum Concentration of B: Equation (6) is

$$[B] = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{e^{-k_1 t} - e^{-k_1' t}\} \qquad \dots \dots \dots (6)$$

At the maximum concentration of B, we have

$$\frac{d[B]}{dt} = 0$$

Hence, differentiating equation (6) with respect to t, we get

 $\frac{k_1}{k_1'} \!=\! e^{(k_1-k_1')t_{max}}$

$$\frac{d[B]}{dt} = [A]_0 \left(\frac{k_1}{k_1' - k_1}\right) \{-k_1 e^{-k_1 t} + k_1' e^{-k_1' t}\} \qquad \dots \dots (8)$$

Equating equation (8) to zero, we get

$$-k_1 e^{-k_1 t_{max}} + k_1' e^{-k_1' t_{max}} = 0$$

or

or
$$\ln\left(\frac{k_1}{k_1'}\right) = (k_1 - k_1')t_{max}$$

or

substituting equation (9) in equation (6), we get

 $t_{max} = \frac{1}{k_1 - k_1'} \ln\left(\frac{k_1}{k_1'}\right)$

$A \xrightarrow{k_1} B \xrightarrow{k'_1} C$

Let the initial concentration of A be $[A]_0$ and let after time t, the concentrations of A, B and C be [A], [B] and [C], respectively. It is obvious that

$$[A]_0 = [A] + [B] + [C]$$
(1)

Differential Rate Law : The differential rate expressions are

$$-\frac{d[A]}{dt} = k_1[A] \qquad(2)$$
$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] \qquad(3)$$

$$\frac{d[C]}{dt} = k_1'[B] \qquad \dots \dots (4)$$

On integrating equation (2), we get

Substituting [A] from equation (5) into equation (3), we get

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k'_1[B]$$
$$\frac{d[B]}{dt} + k'_1[B] = k_1[A]_0 e^{-k_1 t}$$

Integrated Rate Law : Multiplying the above expression throughout by exp $(k'_1 t)$, we get

$$\frac{d[B]}{dt} + k_1'[B]e^{k_1't} = k_1[A]_0 e^{-(k_1 - k_1')t}$$

The left side of the above expression is equal to $d([B]e^{k'_1})/dt$. Hence, the above expression

can written as , $d\{[B]e^{k_1^t}\} = k_1[A]_0 e^{-(k_1-k_1^t)t} dt$ Integrating the above expression with [B] = 0 at t = 0, we get

$$[B]e^{k't} = k_1[A]_0 \left[\frac{e^{-(k_1-k'_1)t}}{-(k_1 - k'_1)} + \frac{1}{k_1 - k'_1} \right]$$

$$[B] = k_1[A]_0 \left[\frac{e^{-k_1t}}{-(k'_1 - k_1)} + \frac{e^{-k'_1t}}{k_1 - k'_1} \right]$$

$$[B] = k_1[A]_0 \left(\frac{k_1}{k'_1 - k_1} \right) \{e^{-k_1t} - e^{-k'_1t}\} \qquad \dots\dots(6)$$

Substituting equations (5) and (6) in equation (1), we get

or

$$[A]_{0} = [A]_{0}e^{-k_{1}t} + [A]_{0}\left(\frac{k_{1}}{k_{1}'-k_{1}}\right)(e^{-k_{1}t}-e^{-k_{1}'t}) + [C]$$
$$[C] = [A]_{0}\left[1 - \frac{1}{k_{1}'-k_{1}}(k_{1}'e^{-k_{1}t}-k_{1}e^{-k_{1}'t})\right] \qquad \dots \dots (7)$$

Figure Illustrates the general appearance of the variations of concentrations of A, B and C during the progress of the reaction.

(ii) $CH_3CH_2Br + KOH - CH_3CH_3OH + KBr - CH_2 = CH_2 + KBr + H_2O$

Reactions involving opposing or reversible reactions :

Such reactions results in equilibrium. In other words the reactant changes to product and vice versa.

Say we have an opposing reaction in which both forward and backward reactions are first order, viz.,

 $(k_1 \text{ and } k_2 \text{ are rate constant of forward and backward reaction})$

Say initial conc. of A and B are a and b mol L⁻¹ respectively.

If after time t, x moles/L of A change into B, then conc. of A and B will be (a - x) and (b + x) respectively.

The net rate of the reaction would be given as :

Rate = $k_1 (a - x) - k_2 (b + x) \dots (i)$ [: both processes occur simultaneously]

When equilibrium is reached, the net rate is zero

Thus, $k_1(a-x_e) = k_2(b+x_e) (e = equilibrium)$

Hence, (

$$(b + x_e) = \frac{k_1}{k_2} (a - x_e)$$
 or $b = \frac{k_1}{k_2} (a - x_e) - x_e$

Substituting value of b in eqn. (i)

Rate of reaction,
$$\frac{dx}{dt} = k_1(a-x) - k_2 \left[\frac{k_1}{k_2}(a-x_e) - x_e + x \right]$$

on solving, we get

Rate = $(k_1 + k_2) (x_e - x)$

After rearranging and integrating the equation, we get an equation similar to first order reaction as shown below.



or
$$(k_1 + k_2) = \frac{1}{t} \log \frac{x_e - x_0}{x_e - x}$$

The equation is similar to first order reaction except that the measured rate constant is now the sum of the forward and the reverse rate constants.

7. Consecutive or Sequential Reactions :

In many cases, the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. One of the examples of consecutive reactions involves the following steps.

11. A solution of N_2O_5 in CCl₄ at 45 °C produces 5.02 mL of O_2 in 1198 sec and 9.58 mL O_2 after a long time. Calculate rate constant assuming I order for the reaction.

 $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$

6. Reactions involving Two First Order Parallel Reactions Or Concurrent Reactions :

These are reactions in which a reacting substance do not follow a particular path to give a particular set of products. It follows one or more paths to give different products. For example,



The reactant A follows two different paths to form B and C. (The change in concentration of A, B and C is given in figure below)





Let initial conc. of $A = a \mod L^{-1}$ and say the amount transformed in time $t = x \mod L^{-1}$. If y and z be amounts of B and C formed at time t, then

$$\frac{dx_{A}}{dt} = \frac{dy_{B}}{dt} + \frac{dz_{C}}{dt}$$

Now if the reaction is unimolecular and k_1 and k_2 are rate constants for formation of B and C from A then

rate of formation of y,
$$\frac{dy_B}{dt} = k_1(a - x);$$

and rate of formation of z, $\frac{dz_C}{dt} = k_2(a - x)$

Thus,
$$\frac{dx_A}{dt} = k_1(a-x) + k_2(a-x) = (k_1 + k_2)(a-x)$$

If
$$k_1 + k_2 = k$$
, Then $\frac{dx_A}{dt} = k(a - x)$ (Here $r_f B \neq r_f C$)

or the rate of reaction will be k(a-x)

Some examples of side reactions

(i)
$$C_6H_5N = NCl + CH_3CH_2OH - C_6H_6 + N_2 + HCl + CH_3CHO C_6H_6 + OC_2H_5 + N_2HCl$$

	Daily Practice Problems - 09										
1.	The following data represe	ent for tl	ne deco	omposi	tion of	fNH ₄ NO	$_2$ in $\frac{1}{2}$	aqueou	ıs soluti	on	
	Time in minute	10		15		20		25		x	
	Volume of N ₂ (in mL)	6.25		9.0		11.40		13.65	5	33.0	5
	(a) Show that reaction	n is of	I orde	r.	(b)	Calcu	late	velocit	v const	ant.	
2.	Derive the O. R. for deco	mposit	ion of	H,O, f	rom tł	ne follow	ing	data			
	Time in minute		10	15	;	20	2	25	x		
	Vol. of O ₂ given by	H ₂ O ₂	6.30	8.	95	11.40	1	3.5	35.75		
3	Decomposition of diazobe	nzene o	hlorid	e was	follow	ved at co	nsta	nt tem	nerature	• hvn	neasuring
0.	volume of N_2 evolved at o	definite	interv	als of	time.	Calculat	e O.	R. and	l rate co	onstar	nt
	Time in minute	0		2.0	5	5.5	7.0)	×		
	Volume of N ₂ in ml	L 0		10	2	25	35		163		
4.	The decomposition of N	√20, ir	n chlor	roforn	ı was	followe	d by	/ meas	uringt	the vo	olume of
	O_2 gas evolved; $2N_2O_5$ -	$\rightarrow 2N$	$I_2O_4 +$	$O_2(g).$	The r	naximui	n vo	olume	of O ₂ g	as ot	otainable
	was 100cm ³ . In 500 mi	nutes,	90cm	3 of O ₂	₂ were	e evolve	d. C	alcula	te the fi	rst o	rder rate
	constant of the reaction	1.									
5.	The specific rate constant	t of the	e decoi	mposit	ion of	N_2O_5 is	0.0	08 min	¹ . The	volu	me of O_2
	reaction. NO ₂ formed is c	lissolve	ed in C	CL.	volu	ine that v	vou		onecte	uatu	lie ella ol
6	Derive order of reaction	for the	decor	nnositi	on of	H O fro	um tl	ne foll	wing	lata	
0.	Time in minute		uccor		011 01	10	1 20		20		
	Volume of KMnO ₄ nee	eded fo	r H2O	2 25		16	10).5	7.09		
7	The lain etime of hereine land	.	<u></u>				- 110	21 - 4 24			1
/.	withdrawing 2 mL of the	reaction	n mixti	ure at i	nterva	ls of(t)	аddi	ng 50 i	nL wat	er and	d titrating
	with baryta water. Detern	nine the	veloc	ity con	stant o	of hydrol	ysis				
	t (in minute)	0	75	5	11	9	259)	∞		٦
	Titre value (in mL)	19.24	24	4.20	26	.60	32.	23	42.0	3	
8.	The acid catalysed hydro	lysis of	an org	ganic c	ompo	und A at	30°0	C has h	alflife	of 10	0 minute
	when carried out in a buffer solution of $pH = 5$ and 10 minute when carried out at $pH = 4$					t pH = 4.					
	Both the times the half li	fe are i $-\frac{1}{2}$	ndepe	ndent	of the	initial c	onc	entrati	on of A	. If tl	ne rate of
0	Le de circumient of company	:-к[А	J [U], wii			1		11. 		1:
9.	obtained	ugar in	presei	nce of a	an acio	a, the 101	IOW	ingpo	larimete	er rea	dings are
	Time in minute 0)	30		90		230)	∞		
	Rotation in degree +	-46.75	+4	1.0	+30).75	+12	2.75	-18	.75	

Calculate rate constant.

10. The inversion of cane sugar proceeds with constant half life of 500 minutes at pH = 5 for any concentration of sugar. However, if pH = 6, the half life changes to 50 minutes. Derive the rate law for inversion of cane sugar.

5.	$S \longrightarrow G + F$	
	Time t	∞
	rotation r _t	r_{∞}
_		
6.	In the decomposition of oxalic acid following o	data were obtained:
	Pressure in mm 22.0 17.0	13.4
	Determine the rate constant K and half life per	riod, if reaction obeys I order kinetics.
7.	For a homogeneous gaseous reaction , A —— pressure after time t was P. Derive an expressi t. assume I order reaction.	$B + C + D$, the initial pressure was P_0 while on for rate constant K in terms of P_0 , P and
8.	Acetone on heating gives CO and other hydro kinetics w.r.t. acetone concentration. The half li acetone taken in a container at 600 °C reduce	carbons at 600°C. The reaction obeys I order fe period is 81 sec. Calculate the time in which s its pressure from 0.5 atm to 0.4 atm.
9.	Dimethyl ether gaseous phase decomposition i $CH_3OCH_3 \longrightarrow CH_4 + H_2 + CO \text{ at } 750 \text{ K have}$ the time in which initial pressure of 400 mm in	s : ing rate constant 6.72×10^{-3} min ⁻¹ . Calculate closed container becomes 750 mm.
10.	 The decomposition of Cl₂O₇ at 400 K in gased After 55 sec at 400 K, the pressure of reacting Calculate the rate constant of reaction. Also ca 100 second. 	bus phase to Cl_2 and O_2 is of I order reaction. on mixture increase from 0.62 to 1.88 atm. alculate the pressure of reaction mixture after
11.	. In the vapour phase decomposition of ethyler the initial pressure and the pressure after 5 mir respectively. If the reaction follows I order kinet	te oxide, $C_2H_4O \longrightarrow CH_4 + CO$ at 414.5°C, nute were 116.51 mm and 122.56 mm of Hg ics, what must be the pressure after 12 minutes?
12.	2. Calculate the partial pressures of reactants an an initial pressure of 200 mm for 30 minute rete constant is $2.5 \times 10^{-4} \text{ sec}^{-1}$.	d products, when azomethane decomposes at according to $(CH_3)_2 N_2 \longrightarrow C_2H_6 + N_2$. The
13.	B. Rate constant of a first order reaction $A \longrightarrow B$	3 is 6.93×10^{-2} minute. If initial concentration
	of reactant is 1 M. Then calculate :	
	(i) Initial rate	(ii) Rate after 600 seconds
14.	(III) Kate after / 5% of the reaction is completed for	the first order thermal decomposition of
	$SO_2Cl_{2(g)}$ at a constant volume.	
	$\mathrm{SO}_2\mathrm{Cl}_{2(\mathrm{g})} \to \mathrm{SO}_{2(\mathrm{g})}^+$	$Cl_{2(g)}$
	Exp. Time (sec ^{-1}) Total pr	essure (atm)
	1. 0 0	J.S) 6
15	2 100	in 0.65 atmagnhana
15.	For a homogeneous gaseous phase reaction: 2 was P° while pressure at time 't' was P. Find the	$A^{3/4} \rightarrow 3B + C$, the initial pressure of reactant pressure after time 2t. Assume I order reaction
16.	 6. The decomposition of Cl₂O₇ at 400 K in the sec at 400 K, the pressure of Cl₂O₇ falls from (a) The rate constant. 	gas phase to Cl_2 and O_2 is of I order. After 550.062 to 0.044 atm. Calculate :(b)Pressure of Cl_2O_7 after 100 sec.

3.	Thermal decomposition of a compound is of first order. If 50 % sample of the compound is decomposed in 120 minute, how long will it take for 90 % of the compound to decompose ?						
4.	The decomposition of NH_3 on tungsten surface follows zero order kinetics. The half life is 5 minutes for an initial pressure of 70 torr of NH_3 . If the initial pressure had been 0.25 atm, what would the total pressure after 3 minutes ? What is the half life ?						
5.	In a reaction, the decrease in reactant's concentration is 20 % in 20 minute and 40 % in 40 minute. Calculate order of reaction and rate constant.						
6.	A substa time in w	nce is reduced to one third of its orig hich it will be reduced to one ninth	inal cor of its or	ncentration in 100 minute. Calculate the iginal value. Assume I order .			
7.	For the decomposition of N_2O_5 , the rate constant is $6.2 \times 10^{-4} \text{ sec}^{-1}$ at 45°C. It begins with one mole of N_2O_5 in a litre flask, how long would it take for 20% N_2O_5 to decompose and how long for 50 % ?						
8.	Decomposition of $N_2O_5(g)$ into $NO_2(g)$ and $O_2(g)$ is a first order reaction. If the initial concentration of $N_2O_5(g)$, i.e., $[N_2O_5]_0$ is 0.030 mol litre ⁻¹ , what will be its concentration after 30 minute? Bate constant of reaction is $1.35 \times 10^{-4} \text{ sec}^{-1}$.						
9.	In a first order reaction concentration of reactant decreases from 10 M to 2.5 M in 500 seconds. Calcualte : (i) $t_{1/2}$ of the reaction (ii) rate of reaction when concentration is 5 M.						
10.	Rate constant of a first order reaction is 10^{-3} sec. Calculate time in seconds when concentration is changing from :						
	(i) 2	M to 0.25 M	(ii)	16 M to 1 M			
	(iii) 6	.4 M to 1.6 M	(iv)	4 M to 0.125 M			

	Daily Pra	actice Pr	oblems - 08	
1.	In ths case we have $A \longrightarrow B + C$			
	Time	t	∞	
	Total pressure of $A + B + C$ Find k.	P ₂	P ₃	
2.	$A \longrightarrow B + C$			
	Time	t	00	
	Total pressure of (B + C) Find k.	P ₂	P ₃	
3	$A \longrightarrow B + C$			
	Time	0	t	
	Volume of reagent	Ŭ,	V ₂	
	The reagent reacts with A, B and	l C. Find k.	2	
4.	$A \longrightarrow 2B + 3C$			
	Time	t	∞	
	Volume of reagent	V_2	V ₃	
	Reagent reacts with A, B and C.	Find k.	-	

5.	 The change, A→B shows I order: (a) How will the rate of reaction change when the concentration of A is tripled? (b) What will be the change in half life period in doing so? 								
6.	The virus prepared in a chemical bath shows inactivation process obeying I order. Calculate the rate constant for the viral inactivation if in the beginning 1.5% of the virus is inactivated per minute. Also calculate the time required for its, (a) 50% inactivation (b) 80% inactivation.								
7.	Show that for I order reaction, the time required for 99.9% decomposition of the reaction is ten folds to the time required for half of the reaction.								
8.	The time required for 20 % completion for a reaction is 10 minute for I order reaction.Calculate :(a) specific reaction rate.(b) Time required for 75 % completion								
9.	The half life for a I order reaction $A \longrightarrow$ Product, is 10 minute. What % of A remains after (i) 1/2 hour (ii) 2/3 hour (iii) 1 hour								
10.	The reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ obeys I order kinetics with rate const. $3.2 \times 10^{-5} \text{ sec}^{-1}$ at 320 °C. What % of SO_2Cl_2 will be decomposed on heating gas for 90 minute?								
11.	It was found that can sugar solution in water was hydrolysed to the extent of 25 per cent in one hour. Calculate the time that will be taken for the sugar to be hydrolysed to the extent of 50 $\%$, assuming that the reaction is of the first order.								
12.	The half time of first order decomposition of nitramide is 2.1 hour at 15°C.								
	If 6.2 g of NH-NO ₂ is allowed to decompose, calculate								
	(a) time taken for NH_2NO_2 to decompose 99% and								
	(b) volume of dry N_2O produced at this point measured at STP.								
13.	A drug becomes ineffective after 30% decomposition. The original concentration of a sample was								

- 5mg/mL which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?
- 14. A first order reaction is 20% completed in 10 minutes. Calculate the time taken for the reaction to go to 80% completion.

Daily Practice Problems - 07

1. For the first order reaction, A→ B, shown in the figure, what is the significance of the point at which the two curves cross each other. How is the slopes of the two curves be related at this point ?



2. A first order gaseous reactions has $K = 1.5 \times 10^{-6} \text{ sec}^{-1}$ at 200 °C. If the reaction is allowed to run for 10 hour, what percentage of initial concentration would have changed into products. What is the half life period of reaction ?

$$k = \frac{1}{t} \ln \frac{a}{a - x} \implies k = \frac{2.303}{t} \log \frac{a}{a - x} \implies k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$
$$\frac{[A]_0}{[A]} = e^{kt} \implies \frac{[A]}{[A]_0} = e^{-kt} \implies [A] = [A]_0 e^{-kt}$$

	Reaction	Expression for rate constant
(a)	$N_2O_5 \rightarrow 2NO_2 + 1/2 O_2$	$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$
		Here V_t = volume of O_2 after time t and V_{∞} = volume of O_2 after infinite time.
(b)	$NH_4NO_2(aq) \rightarrow 2H_2O + N_2$	Same as above, here V_t and V_{∞} are volume of N_2 at time t and at infinite time respectively.
(c)	$H_2O_2 \rightarrow H_2O + 1/2O_2$	$k = \frac{2.303}{t} \log \frac{V_o}{V_t}$
		Here V_o and V_t are the volume of KMnO ₄ solution used for titration of same volume of reaction mixture at zero (initially) and after time t.
(d)	$CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_{o}}{V_{\infty} - V_{t}}$
		Here V_o , V_t and V_{∞} are the volumes of NaOH solution used for titration of same volume of reaction mixture after time 0, t and infinite time respectively.
(e)	$ \begin{array}{c} C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 \\ \text{d-Structure} & \text{d-Glu cos e} \ell \text{-Fructose} \end{array} $	$k = \frac{2.303}{t} \log \frac{r_o - r_\infty}{r_t - r_\infty}$

Daily Practice Problems - 06

- 1. Show that for a first order reaction, $R \longrightarrow P$ the concentration of product can be represented as a function of time by, $[P] = at + bt^2 + ct^3 + \dots$ and express a, b and c in terms of $[R]_0$ and K.
- 2. (i) Substance A decomposes by the first order reaction. Starting initially with [A] = 2.00 M, after 200 minutes [A] = 0.25 M. For this reaction what is $t_{1/2}$ and k?
 - (ii) A first order reaction is 40 % complete after 8 min. How long will it take before it is 90 % complete ? What is the value of the rate constant ?
 - (iii) For a certain reaction it takes 20 minutes for the initial concentrations of 34.8 mol L^{-1} to become 17.4 mol L^{-1} and another 20 minutes to become 8.7 mol L^{-1} . Calculate the rate constant of the reaction.
 - (iv) For a first order reaction in which $k = 5.48 \times 10^{-1} \text{ sec}^{-1}$. Find : (a) $t_{1/3}$ (b) $t_{2/3}$
- 3. Show that for a first order reaction

(i)	$t_{25\%} = 0.415t_{1/2}$	(ii)	$t_{87.5\%} = 3t_{1/2}$	(iii)	$t_{90\%} = 3.33 t_{1/2}$
(iv)	$t_{99\%} = 6.66t_{1/2}$	(v)	$t_{99.9\%} = 10t_{1/2}$	(vi)	$t_{99\%} = 2t_{90\%}$
(vii)	$t_{99.9\%} = 3t_{90\%}$				

4. The solution of H_2O_2 of normality 0.73 is catalytically decomposed. What will be the concentration at the end of 45 minute, assuming the decomposition to follow first order rate law if half life is 15 minute?

7.	The fo	llowing data a	re for the reaction A	or the reaction $A + B \rightarrow$ products:					
	conc.	ofA(M)	conc. of B(M)	-	initial rate (mol L ⁻¹ s ⁻¹)				
		0.1	0.1		4.0×10^{-4}				
		0.2	0.2		1.6×10^{-3}				
		0.5	0.1		1.0×10^{-2}				
		0.5	0.5		1.0×10^{-2}				
	(a) wh	at is the order	w.r.t. A and B for the	reaction					
	(b) Ca	lculate the rate	constant.						
	(c) De	termine the rea	acion rate when the	concentrati	ions of A and B are 0.2	M and 0.35 M			
	respect	tively.							
8.	The ch	emical reactio	n between K ₂ C ₂ O ₄ ai	nd HgCl ₂ , is	s				
		$2 Hg Cl_2 + K_2$	$C_2O_4 \longrightarrow 2KCl + 2$	$CO_2 + Hg_2$	2Cl ₂				
	The we	eights of Hg ₂ C	l2 are precipitated from	m different	solutions in given time a	are as:			
	Time	HgC	K_2C_2	O_4	HgCl ₂ formed				
		(mol l	itre ⁻¹) (mol lit	re ⁻¹)	(mol litre ⁻¹)				
	60	0.418	0.40)4	0.0032				
	65	0.836	0.40)4	0.0068				
	120	0.836	0.20)2	0.0031				
	Calcul	ate order of rea	action.						
9.	For a g	gaseous reaction	$n 2A + B_2 \longrightarrow 2AE$	B, the follow	wing rate data were obta	ained.			
	Rate o	f disappearanc	$e of B_2$	mol litre ⁻¹					
				[A]	$[B_2]$				
	1.8×1	10-3		0.015	0.15				
	$1.08 \times$	10-2		0.090	0.15				
	5.4 × 1	10-3		0.015	0.45				
	Calcul	ate: (a) the rate	e constant, (b) rate of	formation	of AB when $[A] = 0.2$ a	and $[B_2] = 0.04$			
10.	Forar	eaction at 800	$^{\circ}C, 2 \text{ NO} + 2H_2$ —	\rightarrow N ₂ + 2H ₂	O, the following data v	vere obtained.			
					1				
		$[NO] \times 10^{-4}$	$[H_2] \times 10^{-3}$		$-\frac{1}{2} d[NO] l dt \times 10^{-4}$				
		mol/litre	mol/litre		2 mol / litre/sec				
	(i)	1.5	4.0						
	(i) (ii)	0.5	2.0						
	(iii)	0.5	2.0		0.24				
	What i	is the order of t	his reaction wrt N(Dand H.? 4	u.27 Also calculate rate const	tant			
	(iii) What i	0.5 is the order of t	2.0 his reaction w.r.t. NO	O and H_2 ? A	0.24 Also calculate rate const	tant.			

5. Reactions of the First Order :

A reaction is said to be of the first order if the rate of the reaction depends upon only on concentration term only. Thus we may have For the reaction : $A \longrightarrow$ Products at t = 0 a 0 at t = t (a-x) x Then according to Law of Mass Action. Rate of reaction ∞ [A]. Rate of reaction ∞ (a-x)

i.e.,
$$\frac{dx}{dt} \propto (a-x) \implies \frac{dx}{dt} = k(a-x)$$

where k is called the rate constant or the specific reaction rate for the reaction of the first order.

- (a) What is the rate law?
- (b) What is the value of the rate constant?
- (c) What is the reaction rate when the concentrations are $[NH_4^+] = 0.39$ M and $[NO_2^-] = 0.052$ M?

2. Find :

- (i) rate law expression
- (ii) order of reaction with respect to each reactant and overall order of reaction
- (iii) value and unit of rate constant
- (iv) effect on rate of reaction on changing the volume to $1/8^{\text{th}}$ of the original.

For the reaction , $A + B + C \longrightarrow product$ given :

Experiment No.	[A] ₀ 10 ⁻⁴ (m/l)	[B] ₀ 10 ⁻² (m/l)	[C] ₀ 10 ⁻¹ (m/l)	Initial rate × 10 ⁻⁶ (m/l/s)
1	7	3	5	9
2	7	6	5	12.7
3	7	6	2	12.7
4	14	3	5	4.51

3. Initial rate data at 25°C are listed in the table for reaction, $A_2 + B_2 \longrightarrow 2AB$

Experiment No.	$[A_2]_0 (m/l)$	$[B_2]_0 (m/l)$	Initial rate (m/l/s)
1	1.5×10^{-3}	3.2×10^{-4}	$8.1 imes 10^{-8}$
2	4.5×10^{-3}	9.6×10^{-4}	$6.56 imes 10^{-6}$
3	3×10^{-3}	1.6×10^{-4}	3.24×10^{-7}

using that, determine

(i) rate law

(ii) order of reaction with respect to A_2 and B_2 and overall order of reaction

(iii) value and unit of rate constant

- (iv) effect on rate of reaction on doubling the volume of container.
- 4. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

initial rate (mornitre sec)
1×10^{-3}
3×10^{-3}
9×10^{-3}

(a) What is the order w.r.t. NO and Cl_2 in the reaction

(b) Write the rate expression (c) Calculate the rate constant

(d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively.

- 5. The rate of a reaction starting with initial concentration of 2×10^{-3} M and 1×10^{-3} M are equal to 2.40×10^{-4} Ms⁻¹ and 0.60×10^{-4} M sec⁻¹ respectively. Calculate the order of reaction w.r.t. reactant and also the rate constant.
- 6. For the reactoin $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1×10^{-4} mol litre⁻¹ minute⁻¹. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.3 M, the initial rate is 9.0×10^{-4} mol litre minute⁻¹. In the third experiment when the initial concentrations of both A and B are 0.3 M, the initial rate is 2.7×10^{-3} mol litre⁻¹ minute⁻¹.

(a) write rate law for this reaction

(b) Calculate the value of specific rate constant for this reaction.

Graphical method :

In this method, graph of concetration and time is used to find the order of reaction.





(b) Plots of conc., [A] vs. time, t for different order reactions on the basis of integrated rate laws



Half-life method :

For a given reaction,
$$t_{1/2} \propto \frac{1}{a^{n-1}} \implies \frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{a_1}{a_2}\right)^{n-1}$$

Order of reaction =
$$n = 1 + \frac{\log(t_{1/2})_2 - \log(t_{1/2})_1}{\log[A]_1 - \log[A]_2}$$

Plots of $t_{1/2}$ vs. initial concentration, a for different order reactions $[t_{1/2} a^{1-n}]$



Ostwald Isolation Method :

In this method order of each reactant is determined by taking all the other reactants in excess. Over all order of reaction will be the sum of individual.

		Daily Prac	tice Problem	ıs - 05
1. Initial rate data at 25°C are listed in the table for the reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$				on
	Experiment	Initial [NH4 ⁺]	Initial [NO ₂ ⁻]	Initial rate of consumption
	No.			of NH ₄ (M/s)
	1.	0.24	0.10	7.2×10^{-6}
	2.	0.12	0.10	$3.6 imes 10^{-6}$
	3.	0.12	0.15	$5.4 imes 10^{-6}$

The following two step mechanism has been proposed for the gas-phase decomposition of 5. nitrous oxide (N_2O) : Step I : $N_2O(g) \longrightarrow N_2(g) + O(g)$ $N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g)$ Step II : Write the chemical equation for overall reaction. (a) **(b)** Identify any reaction intermediates. (c) What is the molecularity of each of the elementary reactions? (d) What is the molecularity of the overall reaction? 6. What is the order of reaction, $A_2 + B_2 \longrightarrow 2 AB$; having following mechanism $A_2 \longrightarrow A + A$ (fast) $A + B_2 \longrightarrow AB + B$ (slow) $A + B \longrightarrow AB$ (fast) The following reaction has a second-order rate law : 7. $H_2(g) + 2ICl(g) \longrightarrow I_2(g) + 2HCl(g) Rate = k[H_2] [ICl]$ Derive a possible reaction mechanism. Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine 8. the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial concentration of reactants. $A_2 + C \rightarrow A + AC$ $\begin{array}{ccc} A_2 & & & k_1 = 10^{10} \mathrm{s}^{-1} \mbox{ (forward)} \\ & & k_{-1} = 10^{10} \, \mathrm{M}^{-1} \mathrm{s}^{-1} \mbox{ (reverse)} \\ A + C \longrightarrow \mathrm{AC} & & k_2 = 10^{-4} \, \mathrm{M}^{-1} \mathrm{s}^{-1} \mbox{ (slow)} \end{array}$ 9. For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested: $2NO \implies N_2O_2$ equilibrium constant K_1 (fast) $N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$ (slow) $N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$ (fast) Establish the rate law for given reaction.

4. Methods of determining order of reaction :

Initial rate method:

In this method order of reaction is estimated by comparing different initial rates of a reaction by changing the concentration of one of the reactants and keeping others concentration to be a constant.

 $r = k[A]^{x}[B]^{y}[C]^{z}$, if molar concentration of B and C is kept constant then $r = k[A]^{x}$

since rate of reaction is proportional to the concentration of reactants at that time,

$$\frac{\mathbf{r}_{1}}{\mathbf{r}_{2}} = \left(\frac{\left[\mathbf{A}\right]_{1}}{\left[\mathbf{A}\right]_{2}}\right)^{x} \Rightarrow \text{ order with respect to } \mathbf{A} = \mathbf{x} = \frac{\log \mathbf{r}_{1} - \log \mathbf{r}_{2}}{\log \left[\mathbf{A}\right]_{1} - \log \left[\mathbf{A}\right]_{2}}$$

Integrated rate law method:

In this method different rate constant equations are used as hit and try method for given set of values and checked where it is applicable to result almost same values of k.

For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, following mechanism has been provided : 5. $NO_2 + F_2 \xrightarrow{slow} NO_2F + F$ $NO_2 + F \xrightarrow{fast} NO_2F$ What would be the rate expression of the above reaction. The reaction $2NO + Br_2 \longrightarrow 2NOBr$, Obey's the following mechanism: 6. $NO + Br_2 \xrightarrow{\text{fast}} NOBr_2$; $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$ Find the rate expression of the above reaction. The reaction $2A \longrightarrow B + C$ follows zero order kinetics. Find the differential rate equation 7. for the reaction. For the elementary step, $(CH_3)_3$. $CBr(aq) \longrightarrow (CH_3)_3 C^+(aq) + Br^-(aq)$ find the molecularity. 8. Following mechanism has been proposed for a reaction, 9. $2 A + B \longrightarrow D + E$ $A + B \longrightarrow C + D$ (slow) $A + C \longrightarrow E$ (fast) Find the rate law expression. 10. A reaction, $A_2 + B_2 \longrightarrow 2AB$ occurs by the following mechanism; $\begin{array}{ccc} A_2 \xrightarrow{} & A + A & & \dots \dots (slow) \\ A + B_2 \longrightarrow & AB + B & & \dots \dots (fast) \end{array}$ $A + B \longrightarrow AB$ (fast) Find its order

Daily Practice Problems - 04

- For the reaction : $2A + B_2 + C \longrightarrow A_2B + BC$, the rate law expression has been 1. determined experimentally to be $R = k [A]^2 [C]$ with , $k = 3.0 \times 10^{-4} M^{-2} min^{-1}$.
 - (i) Determine the initial rate of the reaction, started with concentration $[A] = 0.1 M, [B_2] = 0.35 M \& [C] = 0.25 M$
 - (ii) What is the effect on rate of reaction and rate constant on changing the volume to 1/4th of initial value.
- For the reaction, $2A + B + C \longrightarrow A_2B + C$ 2. the rate = k[A] [B]² with k = 2.0×10^{-6} M⁻² s⁻¹. Calculate the initial rate of the reaction when [A] = 0.1 M, [B] = 0.2 M and [C] = 0.8 M. Also calculate the rate when [A] = 0.06 M.
- 3. The decomposition of ammonia on platinum surface follow the change. $2NH_3 \longrightarrow N_2 + 3H_2$
 - If the decomposition is zero order then what are the rate of production of N_2 and H_2 , (i) if K = 2.5×10^{-4} Ms⁻¹?
 - If the rate obeys $-\frac{d[NH_3]}{dt} = \frac{K_1[NH_3]}{1+K_2[NH_3]}$, what will be the order for decomposition (ii)
 - of NH₃, if (i) [NH₃] is very less and (ii) [NH₃] is very very high? K₁ and K₂ are constants.
- 4. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows :

$$O_3 \Longrightarrow O_2 + O \qquad \dots \qquad (fast)$$

 $O + O_3 \longrightarrow 2O_2$ (slow) Find the rate law expression

	(C)	The order of reaction increases with increasing temperature.		
	(D)	The order of reaction can only be determined by experiment		
6.	The ra	e rate of the reaction $A + B + C \longrightarrow P$ is given by :		
		$r = \frac{d[A]}{dt} = k [A]^{1/2} [B]^{1/2} [C]^{1/4}.$ The order of the reaction is:		
	The re	action is :		
	(A) 1	(B) 2 (C) $1/2$ (D) $5/4$		
7.	Brome	omethane is converted to methanol in an alkaline solution :		
		$CH_{3}Br(aq) + OH^{-}(aq) \longrightarrow CH_{3}OH(aq) + Br^{-}(aq)$		
	The re	action is first order in each reactant.		
	(a)	Write the rate law.		
	(b)	How does reaction rate change if the OH ⁻ concentration is decreased by factor of 5?		
	(c)	what is the change in rate if the concentrations of both reactants are doubled ?		
8.	The or	in acidic solution is described by the equation Br^{-} by BrO_{3}^{-} in acidic solution is described by the equation		
	The re	$3Br_{(aq)} + BrU_{3}^{-}(aq) + 0H^{+}(aq) \longrightarrow 3Br_{2}(aq) + 3H_{2}U(l)$ e reaction is first order in Br_{-}^{-} first order in BrO_{-}^{-} and second order in H^{+}		
	(a)	Write the rate law		
	(b)	What is the overall reaction order?		
	(c)	How does the reaction rate change if the H ⁺ concentration is tripled ?		
	(d)	What is the change in rate if the concentrations of both Br^- and BrO_3^- are halved ?		
9.	For th	e reaction $2NO + Cl_2 \longrightarrow 2 NOCl$, it is found that doubling the concentration of		
	both r alone,	eactants increases the rate by the factor of 8, but doubling the Cl_2 concentration only doubles the rate What is the order of the reaction with respect to NO and Cl_2 ?		
10.	If the	pressure of gaseous reactant is changed by 3 times the rate of reaction changes by		
	5.2 tin	nes. Determine		
	(i)	order of reaction (ii) unit of rate constant		
	(iii)	effect on rate of reaction if volume of container is reduced to $\frac{1}{16}$ th of the original		

3. Rate Law and Mechanism :

In case of reactions for which order and molecularity is not same, a mechanism is proposed, it involves a large number of elementary steps. Rate lass is applied to RDS and if intermediates are present in RDS, they are eleminated using a fast step to write the over all rate law and order is determined.

Daily Practice Problems - 03

- 1. Find the rate law for the single-step reaction , $2A + B \longrightarrow 2C$
- 2. Find the correct expression the rate of reaction of elementary reaction , $A + B \longrightarrow C$.
- **3.** Find the intermediate in the following reaction mechanism :

 $O_3(g) \Longrightarrow O_2(g) + O(g), O_3 + O \longrightarrow 2O_2$

4. The elementary step of the reaction, 2Na + Cl₂ → 2NaCl is found to follow III order kinetics, find its molecularity

2. Molecularity and Order :

Molecularity of a chemical reaction is a theoretical quantity and accounts the number of molecules in the reaction represented by an overall reaction. However it may be 1, 2 or 3. It should nichter be zero nor fractional.

Order of a chemical reaction is an experimental quantity and accounts only those reactant molecules which do invelove in a chemical reaction and experiences a measurable change in their concentration during the course of reaction. It is expressend in terms of individual reactant or product and with respect to overall reaction. Order of a reaction may be zero. positive, fractional or even negative.

 $aA + bB \longrightarrow products$ molecularity = a + b

A complicated reaction has no molecularity of its own but molecularity of each of the steps involved in its mechanism.

For example :

The reaction : $2NO + 2H_2 \implies N_2 + 2H_2O$, takes place in the sequence of following

three steps . I. NO + NO \implies N₂O₂ (fast and reversible)

II. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$ (slow)

III. $N_2O + H_2 \longrightarrow N_2 + H_2O$ (fast)

Slowest elementary step is RDS. Rate law as proposed by Law of Mass Action is applicable to only slow step and hence **Order of reaction is defined as the sum of the powers of the concentration terms appearing in experimentally observed rate law.**

Rate constant (k):

In general, let a reaction represented by the chemical equation

 $aA + bB \longrightarrow Products$

obeys the following rate law, Rate α [A]^m [B]ⁿ, or Rate = k[A]^m [B]ⁿ, then order of reaction is (m + n). Where k = rate constant of reaction, a constant at constant temp and is actually the rate of reaction when conc. of each reactant is equal to unity k is also called **velocity constant** or **specific reaction** rate.

Unit of rate constant: $\mathbf{k} = [\text{conc.}]^{1-n} \sec^{-1}$, $[\text{mole/litre}]^{1-n} \sec^{-1}$

Daily Practice Problems - 02

1.	In a reaction, the (A) 1	rate expression is, rate = (B) 2	K[A] [B] ^{2/3} [C] ⁰ , the o (C) 5/3	rder of reaciton is : (D) Zero
2.	For the reaction, H is true about this r	$I_2(g + Br_2(g) = 2HBr(g), t)$ eaction :	the reaction rate = K $[H_2]$	$[[Br_2]^{1/2}$. Which statement
	(A) The reaction	s of second order	(B) Molecularity of	the reaction is $3/2$
	(C) The unit of K	is sec ⁻¹	(D) Molecularity of	the reacion is 2
3.	J.The dimensions of the rate constant of a second order reaction involves :(A) Neither time nor concentration(B) Time and concentration(C) Time and square of concentration(D) Only time		olves : ntration	
4.	The rate constant (A) First order	for a reaction is 10.8 × 1 (B) Zero order	0 ⁻⁵ mol litre ⁻¹ sec ⁻¹ . Th (C) Second order	e rection obeys : (D) Half order
5.	Which statement (A) The order (B) A second	about the order of reacti of reaction must be a po order reaction is also bin	on is correct ? sitive integer polecular	

	$(A) - \frac{dC}{dt} = -\frac{1}{V} \frac{dn}{dt} = -\frac{1}{RT} \frac{dP}{dt} \qquad (B) \frac{dC}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$		
	(C) $\frac{dC}{dt} = \frac{RT}{V} \frac{dn}{dt} = -\frac{dP}{dt}$ (D)All		
6.	When ammonia is treated with O_2 at elevated temperatures, the rate of disappearance of ammonia is found to be 3.5×10^{-2} mol dm ⁻³ s ⁻¹ during a measured time interval. Calculate the rate of appearance of nitric oxide and water.		
7.	The following reaction was carried out at 44°C N-Q- \longrightarrow 2NQ+ $\frac{1}{2}$ Q-		
	The concentration of NO ₂ is 6.0×10^{-3} M after 10 minutes of the start of the reaction. Calculate the rate of production of NO ₂ over the first ten minutes of the reaction.		
8.	The oxidation of iodide ion by arsenic acid, H ₃ AsO ₄ , is described by the balance equation : $3I^{-}(aq) + H_3AsO_4(aq) + 2H^{+}(aq) \longrightarrow I_3^{-}(aq) + H_3AsO_3(aq) + H_2O(l)$ (a) If $-\Delta[I^{-}] / \Delta t = 4.8 \times 10^{-4}$ M/s, what is the value of $\Delta[I_3^{-}] / \Delta t$ during the same time interval ?		
	(b) What is the average rate of consumption of H ⁺ during that time interval ?		
9.	The decomposition of ammonia on platinum surface follow the change. $2NH_3 \longrightarrow N_2 + 3H_2$		
	(a) What does $\frac{-d[NH_3]}{dt}$ denote? (b) What does $\frac{d[N_2]}{dt}$ and $\frac{d[H_2]}{dt}$ denote?		
10.	In a reaction, $2A \rightarrow$ Products, the concentration of A decreases from 0.5 mol litre ⁻¹ to 0.4 mol litre ⁻¹ in 10 minute. Calculate average rate during this interval		
11.	The rate constant for the reaction:		
	$CO_2 + OH^- \longrightarrow HCO_3^-$		
	in the aqueous solution is 4×10^{-3} litre mol ⁻¹ sec ⁻¹ . Calculate the number of mole of CO ₂ and OUT we does not solve a solution of the solution of		
	the mole of HCO_2^- formed per second.		
12.	In a reaction the concentration of a reactant (A) changes from 0.200 mol litre ⁻¹ to 0.150 mol		
	litre ⁻¹ in 10 minutes. What is the average rate of reaction during this interval?		
13.	Decomposition of N_2O_5 is expressed by the equation $N_1O_2 \rightarrow 2NO_2 + 14O_2$		
	$N_2U_5 \rightarrow 2NU_2 + \frac{1}{2}U_2$ If in a certaion time interval rate of decomposition of N ₂ O ₂ is 1.8×10 ⁻³ mol litre ⁻¹ min ⁻¹ what		
	will be the rates of formation of NO_2 and O_2 during the same interval?		
14.	If the decomposition of nitrogen penta oxide		
	$2N_2O_5 \rightarrow 4NO_2 + O_2$, follows a first order kinetics.		
	(i) Calculate the fate constant for a 0.04 M solution, if the instantaneous fate is 1.4×10^{-6} mol L s ⁻¹		
	(ii) Also calculate the rate of reaction when the concentration of N_2O_2 is 1.20 M		
	(iii) What concentration of N_2O_5 would give a rate of 2.45 ' 10^{-5} mol $L^{-1}s^{-1}$?		

Factors Affecting the Reaction Rate :

The rate of any particular reaction depends upon the following factors: (i) Concentration of the reactants (iv) Presence of a cata

- Concentration of the reactants (iv) Pre Pressure of gaseous reactants (v) Sur
- (iv) Presence of a catalyst
 (v) Surface area of the reactants

(iii) Temperature

(ii)

(vi) Presence of light

For example, from the (figure) in the present case, at time t = 10 minutes, $\Delta x = 0.04$ mole and $\Delta t = 20$ minutes = $20 \times 60 = 1200$ seconds, therefore, rate of reaction at the end of 10 minutes will be $0.04/1200 = 3.33 \times 10^{-5}$ mol L⁻¹ s⁻¹.

Average rate of reaction = $\frac{dx}{dt} = \frac{x_2 - x_1}{t_2 - t_1}$, from the (figure) between the time interval 5

to 15 minutes, Average rate $=\frac{0.03-0.012}{15-5}=\frac{0.018}{10}=0.0018 \text{ mol } L^{-1} \text{ min}^{-1}$

Units of the Rate of Reaction :

For solution phase reactions concentration of the reactants and for gas phase reaction partial pressure is used to define rate of reaction, therefore the unit of the rate of reaction is moles litre⁻¹ sec⁻¹ (mol $L^{-1} s^{-1}$) or atm sec⁻¹.

Average rate of reaction = $\frac{\Delta c}{\Delta t} = \frac{\Delta p}{\Delta t}$, PV = nRT , P = CRT,

Average rate of reaction = $\frac{\Delta p}{\Delta t} = \frac{\Delta c}{\Delta t (RT)}$

Differential rate equation:

Consider a chemical reaction $aA+bB \rightarrow cC+dD$, differential rate equation may be given

as $\frac{\mathrm{dx}}{\mathrm{dt}} = -\frac{1}{\mathrm{a}} \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{dt}} = -\frac{1}{\mathrm{b}} \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{dt}} = +\frac{1}{\mathrm{c}} \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{dt}} = +\frac{1}{\mathrm{d}} \frac{\mathrm{d}[\mathrm{D}]}{\mathrm{dt}}.$

Daily Practice Problems - 01

1.	In the reaction; $A + 2B \longrightarrow 3C + D$ which of the following expressions does not describe changes in the concentration of various species as a function of time:
	(A) $\frac{d[C]}{dt} = \frac{-3d[A]}{dt}$ (B) $\frac{3d[D]}{dt} = \frac{d[C]}{dt}$ (C) $\frac{3d[B]}{dt} = \frac{-2d[C]}{dt}$ (D) $\frac{2d[B]}{dt} = \frac{d[A]}{dt}$
2.	 Which of the following statement is correct for a reaction X + 2Y → prodcuts : (A) The rate of disappearance of X = twice the rate of disappearance of Y (B) The rate of disappearance of X = 1/2 rate of appearance of products (C) The rate of appearance of products = 1/2 the rate of disappearance of Y (D) The rat of appearance of products = 1/2 the rate of disappearance of X
3.	For the reaction, $4A + B \longrightarrow 2C + 2D$, The statement not correct is :(A)The rate of disppearance of B is one fourth the rate of disappearance of A(B)The rate of appearance of C is half the rate of disappearance of B(C)The rate of formation of D is half the rate of consumption of A(D)The rates of formation of C and D are equal
4.	For the reaction $2A + B \longrightarrow C + D$, $-\frac{d[A]}{dt} = k[A]^2[B]$. The expression for $\frac{-d[B]}{dt}$ will be: (A) K[A]^2[B] (B) 1/2K[A]^2[B] (C) K[A]^2[2B] (D) K[2A]^2[B]
5.	Which is correct relation in between $\frac{dC}{dt}$, $\frac{dn}{dt}$ and $\frac{dP}{dt}$ where C, n, P, represents concentration, mole and pressure terms for gaseous phase reactant A(g) \longrightarrow product.

CHEMICAL KINETICS

Introduction :

Chemical Kinetics is the brach of Physical Chemistry which deals with speed of chemical reaction, factors affecting rate of reaction and meachanism of reactions.

1. Rate of Reaction :

Rate of a chemical reaction is the change in the concentration of any one of the reactants or products per unit time i.e., decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Hence the rate of a reaction may be given as follows:

 $Rate of reaction = \frac{Decrease in the concentration of a reactant}{Time interval}$ $or = \frac{Increase in the concentration of a product}{Time interval}$ In general, for any reaction of the type $A + B \longrightarrow C + D$

Rate of reaction =
$$-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[C]}{\Delta t}$$

It may be emphasized that the rate of reaction is always POSITIVE. The minus sign along with the first term is used simply to show that the concentration of the reactants A and

B is decreasing while plus sign along with the other two terms is used to show that the concentration of the products C and D is increasing.

Average Rate and Instantaneous Rate of Reaction :

A difficulty arises in stating the rate of reaction as above. This is because according to the Law of Mass Action, the rate of reaction depends upon the molar concentrations of reactants which keep on decreasing with the passage of time (while those of the products keep on increasing). Therefore, the rate of reaction does not remain constant throughout. Thus the rate of reaction as defined above is the 'average rate of reaction' during the time interval chosen.

