Self Practice Paper (SPP)

1. In the formation of sulphur trioxide by the contact process $2SO_2(g) + O_2(g)\ 2SO_3(g)$ The rate of reaction is expressed as $-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4}$ mol L^{-1} sec^{-1}. The rate of disappearance of (SO_2) will be –

(1) 5×10^{-4} mol L^{-1} S^{-1} (2) -2.25×10^{-4} mol L^{-1} S^{-1}
(3) 3.75×10^{-4} mol L^{-1} S^{-1} (4) 50.0×10^{-4} mol L^{-1} S^{-1}

2. The specific rate constant of a first order reaction depends on the :

(1) Conc. of the reactant (2) Conc. of the product
(3) Time (4) Temperature

3. If the rate of the reaction is equal to the rate constant, the order of the reaction is :

(1) 0 (2) 1 (3) 2 (4) 3

4. In a first order reaction the reacting substance has half-life period of ten minutes. What fraction of the substance will be left after an hour the reaction has occurred ? :

(1) 1/6 of initial concentration (2) 1/64 of initial concentration
(3) 1/12 of initial concentration (4) 1/32 of initial concentration

5. For a certain reaction, a plot of $\{[C_0 - C] / [C]\}$ against the time t, yields a straight line. C_0 = initial conc. of the reactant and C is the reactant concentration after time t. What is the order of the reaction :

(1) 3 (2) zero (3) 1 (4) 2

6. The rate constant of a first order reaction is 4×10^{-3} sec. At a reactant concentration of 0.02 M. the rate of reaction would be :

(1) 8×10^{-5} M sec^{-1} (2) 4×10^{-3} M sec^{-1} (3) 2×10^{-1} M sec^{-1} (4) 4×10^{-1} M sec^{-1}

7. In a first order reaction the a/(a–x) was found to be 8 after 10 minute. The rate constant is

(1) $(2.303 \times 3\log2)/10$ (2) $(2.303 \times 2\log3)/10$ (3) $10 \times 2.303 \times 2\log3$ (4) $10 \times 2.303 \times 3\log2$

8. A first order reaction has a half life period of 69.3 sec. At 0.10 mol lit^{-1} reactant concentration rate will be :

(1) 10^{-4} M sec^{-1} (2) 10^{-3} M sec^{-1} (3) 10^{-1} M sec^{-1} (4) 6.93×10^{-1} M sec^{-1}

9. Select the rate law that corresponding to the data shown for the following reaction A + B C

Exp.	**[A]**	**[B]**	**Initial rate**
1.	0.012	0.035	0.10
2.	0.024	0.070	1.6
3.	0.024	0.035	0.20
4.	0.012	0.070	0.80

(1) Rate = $K[B]^3$ (2) Rate = $K[B]^4$ (3) rate = $K[A][B]^3$ (4) Rate = $K[A]^2[B]^2$

10. How much faster would a reaction proceeds at 25°C than at 0°C if the activation energy is 65 kJ ?

(1) 2 times (2) 5 times (3) 11 times (4) 16 times

11. The energy of activation of a forward reaction is 50 Kcal. The energy of activation of its backward reaction is (If reaction is exothermic)

(1) Equal to 50 Kcal.
(2) Greater than 50 Kcal.
(3) Less than 50 Kcal.
(4) Either greater or less than 50 Kcal.

12. An exothermic reaction $X \rightleftharpoons Y$ has an activation energy 30 KJ mol^{-1}. If energy change (ΔE) during the reaction is –20 KJ, then the activation energy for the reverse reaction is :

(1) 10 KJ
(2) 20 KJ
(3) 50 KJ
(4) –30 KJ

13. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$ the experimental rate expression is $-\frac{dc}{dt} = k[NO_2]^2$ the number of molecules of CO involves in the slowest step will be :

(1) 0
(2) 1
(3) 2
(4) 3

14. The reaction, $X + 2Y + Z \rightarrow N$ occurs by the following mechanism

(i) $X + Y \rightleftharpoons M$ very rapid equilibrium
(ii) $M + Z \rightarrow O$ slow
(iii) $O + Y \rightarrow 1\ N$ very fast

What is the rate law for this reaction

(1) Rate = k[Z]
(2) Rate = $k[X][Y]^2[Z]$
(3) Rate = [N]
(4) Rate = k[X] [Y] [Z]

15. Following mechanism are given for the reaction

$2A + B \rightleftharpoons D + E$

step -1 $A + B \rightleftharpoons C + D$ – (slow)
step-2 $A + C \rightleftharpoons E$ – (fast)

the rate constant experience for the reaction is ५

(1) $r = K[A]^2[B]$
(2) r = K [A] [B]
(3) $r = K[A]^2$
(4) r = K[A][C]

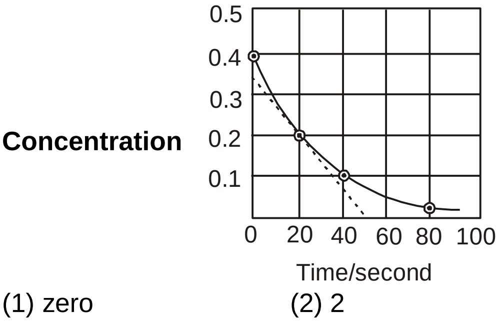
16. According to the mechanism a reaction proceeds via a single transtion state. Choose the correct options.

(1) It is unimolecular reaction.
(2) It is bimolecular reaction.
(3) It is an elementry reaction.
(4) It is a complex reaction.

17. Rate of formation of SO_3 in the following reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is 100 g min^{-1}. Hence rate of disappearance of O_2 is :

(1) 50 g min^{-1}
(2) 40 g min^{-1}
(3) 200 g min^{-1}
(4) 20 g min^{-1}

18. A reaction follows the given concentration (M)–time graph. Perdict the order of the reaction



(1) zero
(2) 2
(3) –1
(4) 1

19. For rate constant is numerically the same for three reactions of first, second and third order respectively. Which of the following is correct :

(1) if [A] = 1 then $r_1 = r_2 = r_3$
(2) if [A] < 1 then $r_1 > r_2 > r_3$
(3) if [A] > 1 then $r_3 > r_2 > r_1$
(4) All

20. For a reaction of the type A + B $\rightarrow$ products, It is observed that doubling the concentration of A cause the reaction rate to be four times increased, but doubling the amount of B does not effect the rate. The equation is

(1) Rate = K [A] [B] (2) Rate = K $[A]^2$ (3) Rate = K $[A]^2[B]$ (4) Rate = K $[A]^2[B]^2$

21. The rate for the reaction

RCl + NaOH (aq) $\rightarrow$ ROH + NaCl

is given by rate = K_1[RCl] The rate of the reaction is –

(1) Doubled on doubling the concentration of NaOH

(2) Halved on reducing the concentration of RCl to half

(3) Decreased on increasing the temperature of reaction

(4) Unaffected by increasing the temperature of the reaction

22. For the reaction 4A + B $\rightarrow$ 2C + 2D

The incorrect statement is :

(1) The rate of disappearance of B is one fourth the rate of disappearance of A

(2) The rate of appearance of C is half the rate of disappearance of B

(3) The rate of formation of D is half the rate of consumption of A

(4) The rates of formation of C and D are equal

23. In presence of HCl, sucrose gets hydrolysed into glucose and fructose. The concentration of sucrose was found to reduce from 0.4 M to 0.2 M in 1 hour and to 0.1 M in 2 hours. The order of the reaction is :

(1) zero (2) one (3) two (4) None of these

24. Two substances A ($t_{1/2}$ = 5 min) and B ($t_{1/2}$ = 15 min) are taken in such a way that initially [A] = 4[B]. The time after which both the concentration will be equal is : (Assume that reaction is first order)

(1) 5 min (2) 15 min

(3) 20 min (4) concentration can never be equal

25. For the reaction 2A + 3B $\longrightarrow$ products, when A is in excess and on changing the concentration of B from 0.1 M to 0.4 M, rate becomes doubled, Thus, order with respect to B would be :

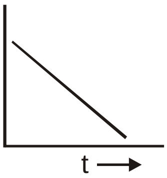
(1) 1 (2) 2 (3) –1 (4) 0.5

26. From different sets of data of $t_{1/2}$ at different initial concentration say 'a' for a given reaction, the product [$t_{1/2} \times a$] is found to be constant. The order of reaction is :

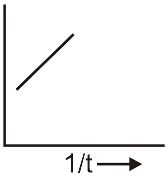
(1) 2 (2) 1 (3) Zero (4) 3

27. Which of the following curves represent a I^{st} order reaction :

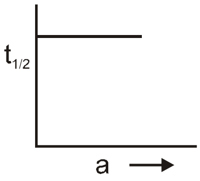
(1) log (a–x)



(2) log (a – x)



(3) $t_{1/2}$



(4) 1 & 3 both

28. The time elapsed of a certain reaction between 33% and 67% completion of a first order reaction is 30 minutes. What is the approximate time needed for 25% completion?

(1) 150.5 minutes (2) 12.5 minutes (3) 180.5 minutes (4) 165.5 minutes

29. A reaction $2A + B \xrightarrow{k} C + D$ is first order with respect to A and 2nd order with respect to B. Initial conc. (t = 0) of A is C_0 while B is $2C_0$. If at t = 30 minutes the conc. of C is $C_0/4$ then rate expression at t = 30 minutes is :

(1) $R = 7\ C_0^3\ k/16$ (2) $R = 27\ C_0^3\ k / 32$ (3) $R = 247\ C_0^3\ k / 64$ (4) $R = 49\ k\ C_0^3 / 32$

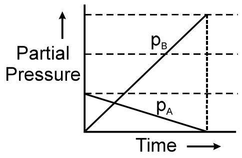
30. In a certain gaseous reaction between X and Y, $X + 3Y \rightleftharpoons XY_3$ The initial rates are reported as follows –

[X]	[Y]	Rate
0.1 M	0.1 M	0.002 Ms^{-1}
0.2 M	0.1 M	0.002 Ms^{-1}
0.3 M	0.2 M	0.008 Ms^{-1}
0.4 M	0.3 M	0.018 Ms^{-1}

The rate law is

(1) $r = K\,[X]\,[Y]^3$ (2) $r = K[X]^0[Y]^2$ (3) $r = K\,[X]\,[Y]$ (4) $r = [X]^0[Y]^3$

31. If for a reaction in which A(g) converts to B(g) the reaction carried out at const. V & T results into the following graph.



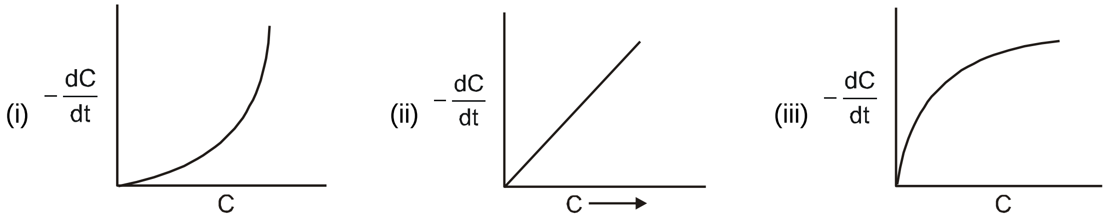
(1) then the reaction must be A(g) → 3B(g) and is a first order reaction.

(2) then the reaction must be A(g) → 3B(g) and is a second order reaction.

(3) then the reaction must be A(g) → 3B(g) and is a zero order reaction.

(4) then the reaction must be A(g) ↔ 3B(g) and is a first order reaction.

32. In three different reactions, involving a single reactant in each case, a plot of rate of the reaction on the y–axis, versus concentration of the reactant on the x–axis, yields three different curves shown below.



What are the possible orders of the reactions (i), (ii), (iii) ?

(1) 1, 2, 3 (2) 2, 1, 1/2 (3) 0, 1, 2 (4) 0, 1, 1/2

33. Starting with equal concentration of reactants what will be the comparison of the initial rate of first order and second order reactions.

(1) first order has higher initial rate. (2) both will have equal inital rate

(3) second order has higher initial rate. (4) nothing can be said.

34. The decomposition of N_2O into N_2 & O_2 in presence of gaseous argon follow second order kinetics with $k = (5.0 \times 10^{11}\ L\ mol^{-1}\ s^{-1})\ e^{-\frac{41570\ K}{T}}$ (K stands for Kelvin units). The energy of activation of the reaction is

(1) 5.0×10^{11} J (2) 41570 J (3) 5000 J (4) 345446.70 J

35. The reaction of NO_2 (g) and O_3 (g) is first-order in NO_2 (g) and O_3 (g)

$$2\ NO_2\ (g) + O_3\ (g) \longrightarrow N_2O_5\ (g) + O_2\ (g)$$

The reaction can take place by mechanism :

I : $NO_2 + O_3 \xrightarrow{slow} NO_3 + O_2$

$NO_3 + NO_2 \xrightarrow{fast} N_2O_5$

II : $O_3 \underset{k_b}{\overset{k_a\ fast}{\rightleftharpoons}} O_2 + [O]$

$NO_2 + O \xrightarrow{slow} NO_3$

$NO_3 + NO_2 \xrightarrow{fast} N_2O_5$

Select correct mechanism.

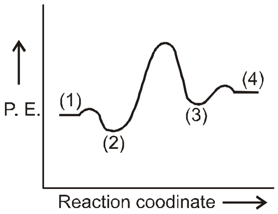
(1) I only (2) II only (3) both I and II (4) None of I and II

36. A simple mechanism for enzyme-catalyzed reaction is given by the following set of equations

E (enzyme) + S (reactant) $\rightleftharpoons$ ES (intermediate-1)

ES (intermediate-1) $\rightleftharpoons$ EP (intermediate-2)

EP (intermediate-2) $\rightleftharpoons$ E (enzyme) + P (product)



This is known as the Michaelis–Menten mechanism. The potential energy diagram is shown in the fig. Which of the following sets of identifications is correct ? (Assume that the temperature and pressure are constant).

	(1)	(2)	(3)	(4)
(1)	E + P.	EP	ES	E + S
(2)	ES	Activated complex	EP	Activated complex
(3)	EP	Activated complex	ES	Activated complex
(4)	E + S	ES	EP	E + P

37. 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 mole h^{-1}. What will be the rate of consumption of H_2 ?

(1) 0.001 mole h^{-1} (2) 0.0015 mole h^{-1} (3) 0.0066 mole h^{-1} (4) 0.002mole h^{-1}

38. What is the order of hydrolysis of ethyl acetate in medium

(1) 2 (2) 0 (3) 1 (4) –1

39. If half life $t_{1/2} = \frac{1}{ka}$; then what will be order ?

(1) 2 (2) 2 (3) 0 (4) –2

40. Half life period of a first order reaction is given By

(1) $\frac{a}{2K}$ (2) $\frac{1}{aK}$ (3) $\frac{\log 2}{K}$ (4) $\frac{\ln 2}{K}$

41. Summation of molecularity and order of Reaction may be :

(1) a whole number (2) a positive number (3) a negative number (4) All of these

42. All radioactive decompostion reactions are :

(1) 2nd order (2) 1st order (3) 0 order (4) 3 order

43. The reaction of hydrogen and iodine monochloride is given as

$$H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$$

The reaction is of first order with respect to $H_2(g)$ and $ICl(g)$, following mechanisms were proposed

Mechanism A

$H_2(g) + 2ICl(g)\ \ 2HCl\ (g) + I_2\ (g)$

Mechanism B

$H_2(g) + ICl(g) \longrightarrow 2HCl\ (g) + HI(g)$; slow

$HI(g) + ICl(g) \longrightarrow HCl\ (g) + I_2\ (g)$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction ?

(1) B only (2) A and B both (3) Neither A nor B (4) A only

44. The bromination of acetone that occurs in acid solution is represented by this equation

$CH_3COCH_3(aq) + Br_2(aq)\ \ CH_3COCH_2Br\ (aq) + H^+(aq) + Br^-(aq)$

These kinetic data were obtained for given reaction concentrations.

Initial concentrations, M

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of Br_2 , $M\ s^{-1}$?

5.7×10^{-5}

5.7×10^{-5}

1.2×10^{-4}

3.1×10^{-4}

Based on these data, the rate equation is

(1) Rate = $k\ [CH_3COCH_3]\ [H^+]$ (2) Rate = $k\ [CH{=}COCH_3][Br_2]$

(3) Rate = $k\ [CH_3COCH_3]\ [Br_2]\ [H^+]^2$ (4) Rate = $k\ [CH_3COCH_3]\ [Br_2]\ [H^+]$

45. The reaction

$$N_2O_5 \text{ in } CCl_4 \text{ (solution)} \longrightarrow 2NO_2 \text{ (solution)} + 1/2\ O_2(g)$$

is of first order in N_2O_5 with rate constant $6.2 \times 10^{-4}\ s^{-1}$. What is the value of rate of reaction when $[N_2O_5] = 1.25$ mole L^{-1} ?

(1) 5.15×10^{-5} mole $L^{-1}\ s^{-1}$ (2) 6.35×10^{-3} mole $L^{-1}\ s^{-1}$

(3) 7.75×10^{-4} mole $L^{-1}\ s^{-1}$ (4) 3.85×10^{-4} mole $L^{-1} s^{-1}$

SPP Answers

1.	(1)	**2.**	(4)	**3.**	(1)	**4.**	(2)	**5.**	(4)	**6.**	(1)	**7.**	(1)
8.	(2)	**9.**	(3)	**10.**	(3)	**11.**	(2)	**12.**	(3)	**13.**	(1)	**14.**	(4)
15.	(2)	**16.**	(3)	**17.**	(4)	**18.**	(4)	**19.**	(4)	**20.**	(2)	**21.**	(2)
22.	(2)	**23.**	(2)	**24.**	(2)	**25.**	(4)	**26.**	(1)	**27.**	(4)	**28.**	(2)
29.	(4)	**30.**	(2)	**31.**	(3)	**32.**	(2)	**33.**	(4)	**34.**	(4)	**35.**	(3)
36.	(4)	**37.**	(2)	**38.**	(3)	**39.**	(2)	**40.**	(4)	**41.**	(4)	**42.**	(2)
43.	(1)	**44.**	(1)	**45.**	(3)								

SPP Solutions

1. $\frac{-d[O_2]}{dt} - \frac{1}{2}\frac{d[O_2]}{dt} + \frac{1}{2}\frac{d[SO_3]}{dt} = 2.5 \times 10^{-4}\ Ms^{-1}$

$\frac{d[SO_2]}{dt} = 5 \times 10^{-4}\ MSe^{-1}$, so $R = \frac{2.5 \times 10^{-4}}{2} = 1.25 \times 10^{-4}\ MSe^{-1}$

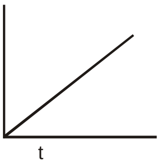
$\frac{d[NH_2]}{dt} = 3 \times 1.25 \times 10^{-4} = 3.75 \times 10^{-4}\ MSe^{-1}$

3. $R = k\,[A]^m$ if $M = 0 \Rightarrow R = K$

4. $t_{1/2} = 10$No. of Half life $= \frac{60}{10} = 6$ half life $C_t = \frac{C_O}{(2)^n} = \frac{C_O}{(2)^6} = \left(\frac{C_O}{64}\right)$

5. $\left[\frac{C_O - C}{C}\right]$ For second order reaction $\frac{1}{C} = \frac{1}{C_O} + kt$

$\frac{1}{C} - \frac{1}{C_O} = kt$ $\left(\frac{C_O - C}{C}\right)$



$\left[\frac{C_O - C}{C}\right] = (KC_O)t$ So reaction is second order

6. $R = K\,[A]$
$R = 4 \times 10^{-3} \times 0.02$
$= 8 \times 10^{-5}\ MSt^{-1}s$

7. $K = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{10}\log 8 = \frac{2.303}{10} \times \log 2^3 = \frac{2.303 \times 3\log 2}{10}\ min^{-1}$

8. $t_{1/2} = \frac{0.693}{k}$; $k = \frac{0.693}{69.3} = 10^{-2}$ sec
$R = k[A]$
$R = 10^{-2} \times 0.1\ Msec^{-1} = 10^{-3}\ Msec^{-1}$

9. $A + B \rightarrow C$

$R = K\,[A]^m\,[B]^n$

compere exp. (1) (3)

$$\frac{0.2}{0.1} = [2]^m \quad m = 1$$

compere exp. (2) & (3)

$$\frac{1.6}{0.2} = \left(\frac{0.07}{0.035}\right)^n \quad n = 3$$

$R = k\,A]\,[B]^3$

10. $$\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\,\frac{(T_2 - T_1)}{T_1T_2} = \frac{65\times10^3\times(298-273)}{2.303\times8.3\times298\times273}$$

calculation we find $\frac{K_2}{K_1} = 11$

11. $\Delta H = Eaf - Eab < 0$ (for exothermic)

$50 - Eab < 0$ So $Eab > 50$

12. $-20 = 30 - Eab$

$Eab = 50.$

14. Rate = $k_1\,[M]\,[Z]$ .....(1)

from equation (1) $K_{eq} = \frac{[M]}{[x][y]}$. $M = k_{eq}\,[x]\,[y]$ .....(2)

put the value of M from (2) to (1)

Rate = k_1 keq $[x]\,[y]\,[z]$ Rate = $k\,[x]\,[y]\,[z]$

17. $\frac{d}{dt}[SO_3] = 100$ gram / min $= \frac{100}{80}$ mole / min = 1.25 mole/min

$$\frac{-1}{2}\frac{d}{dt}[SO_2] = \frac{-d}{dt}[O_2] = \frac{1}{2}\frac{d}{dt}[SO_3]$$

$$\frac{-d}{dt}[O_2] = \frac{1.25}{2}\text{ mole/min} = \frac{1.25}{2}\times 32\text{ gram/min} = 20\text{ gram/min}$$

18. Half life of the reaction is constant. Hence first order.

19. Rate law for

Ist order	IInd order	IIIrd order
Rate = $K[A]^1$	$R_2 = K[A]^2$	$R_3 = K[A]^3$

than we can say $[A] = 1$ $r_1 = r_2 = r_3$ $[A] < 1$ then $r_1 > r_2 > r_3$

y $[A] > 1$ then $r_3 > r_2 > r_1$

20. Rate wrt A is 2 and wrt B is zero.

21. Rate wrt RCl is 1.

22. $4A + B \;\; 2C + 2D$

$$-\frac{1}{4}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{1}{2} = \frac{1}{2}\frac{d[D]}{dt}$$

23. $0.4 \longrightarrow 0.2 \longrightarrow 0.1$

$t_{1/2}$ = 1hr. 1hr.

$t_{1/2}$ is censtant, so Ist asder.

24. A : $a \xrightarrow{5min} 2a \xrightarrow{5min} a \xrightarrow{5min} a/2$

$\underline{B\qquad}$: a $\xrightarrow{5min}$ a/2
So time is 15 mintes.

25. A is in excess, so Rate will be independent of change in concentration.
$R = k\,[B]^n$

$R = R\,4^n\,[B]^n \qquad n = \frac{1}{2}$.

26. For zero order $t_{1/2} = \frac{a_0}{2k}$, so $\underline{t_{1/2} \times a_0} = \frac{a^2}{2k}$ is not a constant.
For 1st order $t_{1/2}$ is constant so $\underline{t_{1/2} \times a_0}$ is not constant.

For 2nd order $t_{1/2} = \frac{1}{a_0 k}$ so $\underline{t_{1/2} \times c_0 = k}$ is constant.

28. $t_1 = \frac{2.303}{k} \log\left(\frac{100}{67}\right) \Rightarrow t_2 = \frac{2.303}{k} \log\left(\frac{100}{33}\right)$

$(t_2 - t_1) = \frac{2.303}{k}\left[\log\frac{100}{33} \times \frac{67}{100}\right] \Rightarrow (t_2 - t_1)\ \frac{2.303}{k} \times 0.30 = 30$

$k = \frac{2.303}{30} \times \frac{30}{100} = 2.303 \times 10^2 \Rightarrow t = \frac{2.303}{2.303 \times 10^{-2}} \log\left(\frac{100}{75}\right)$

t = 100 [log 4 – log 3] = 100 [.6020 × 0.4771] = 12.49 = 12.5 minute

29. $2A + B \xrightarrow{k} C + D$
$r = K\,[A]^1\,[B]^2 \qquad r_o = K\,(C_O)^1\,(2C_O)^2 = 4K\,(C_O)^3$ ......(1)

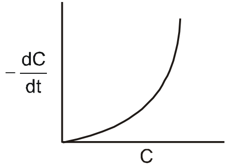
$\quad 2A \quad + \quad B \qquad C \quad + \quad D$
$t = 0 \quad C_0 \qquad 2C_0 \qquad 0 \qquad 0$
$\quad (C_0 - 2x) \quad (2C_0 - x) \qquad x \qquad x$

$x = \left(\frac{C_O}{4}\right) \qquad [A] = C_O - \frac{C_O}{2} = \frac{C_O}{2} \qquad [B] = 2C_O - \frac{C_O}{4} = \frac{7C_O}{4}$

$r = K\left(\frac{C_O}{2}\right)\left(\frac{7C_O}{7}\right)^2 = \frac{49K(C_O)^3}{32}$

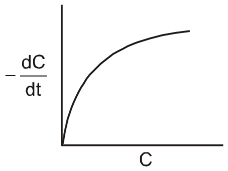
31. From the given graph it is clear that the concentration decrease linearly with time then zero order Reaction and A → 3B type.

32. it is a parabolic graph of $y = x^2$



So This is the graph of second order

$y^2 = x \qquad y = (x)\ \frac{1}{2}$



$\frac{-dc}{dt} = K\,\frac{-dc}{dt}$ So reaction is $\left(\frac{1}{2}\right)$ order.

33. For first order : rate = $k_I\,[C]^1$
For second order : rate = $k_{II}\,[C]^2$

Compression depends on the value of k_I and k_{II}.

34. $E_a = 41570 \times R = 41570 \times 8.31 = 345446.70$ J

35. For Rxn rate determining step is slowest step

Then in 1st mechanism

$$\text{Rate} = k\,[NO_2]\,[O_3] \qquad .....(i)$$

But in 2nd mechanism

$$O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O] \qquad ....(1)$$

$$NO_2 + O \xrightarrow{\text{slow}} NO_3 \qquad ....(2)$$

$$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5 \qquad ....(3)$$

Then for Rxn (1)

$$\frac{k_a}{k_b} = \frac{[O_2]\ \ [O]}{[O_3]} = k_{eq} \qquad ....(4)$$

by Rxn (2)

$$\text{Rate} = k\,\frac{k_{eq}\ \ [O_3]}{[O_2]}\ \ [NO_2]\,[O] \qquad ....(ii) \quad \text{put value of [O] from (4) to (ii)}$$

$$\text{Rate} = k\ \ \times [NO_2]$$

$$\text{Rate} = \frac{k_1\ \ [NO_2]\ \ [O_3]}{[O_2]}$$

37. $N_2(g) + 3H_2\,(g) \rightarrow 2NH_3(g)$

$$\frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt} \quad \Rightarrow \quad \frac{-d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2} \times 0.001 = 0.0015 \text{ mole h}^{-1}$$

39. $t_{1/2} \propto a^{1-n}$

here $t_{1/2} \propto a^{-1}$

$-1 = 1-n \Rightarrow n = 2$

43. rate of reaction always depends on slow step.

$H_2(g) + ICl(g) \longrightarrow HCl(g) + I_2(g)$ is first order reaction with respect to H_2 and I_2. Thus the mechanism B will be more consistent with the given information.

44. Let the order of reaction wrt CH_3COCH_3. Br_2 and H^+ are x,y and z respectively. Thus,

Rate (r) = $[CH_3COCH_3]^x[Br_2]^y[H^+]^z$

$5.7 \times 10^{-5} = (0.30)^x\,(0.05)^y\,(0.05)^z$ .... (i)

$5.7 \times 10^{-5} = (0.30)^x\,(0.10)^y\,(0.05)^z$ .... (ii)

$1.2 \times 10^{-4} = (0.30)^x\,(0.10)^y\,(0.10)^z$ .... (iii)

$3.1 \times 10^{-4} = (0.40)^x\,(0.05)^y\,(0.20)^z$ .... (iv)

From Eqs. (i) and (ii) $y = 0$

From Eqs. (ii) and (iii) $z \approx 1$

From Eqs.(i) and (iv) $x \approx 1$

Thus, rate law $\propto [CH_3COCH_3]^1[Br_2]^0[H^+]^1 = k = [CH_3COCH_3][H^+]$