Answers

Rate of a reaction

1	b	2	a	3	d	4	b	5	b
6	c	7	c	8	c	9	a	10	b
11	b	12	b	13	c	14	d	15	b
16	b	17	c	18	b	19	d	20	a
21	b	22	a	23	d	24	c	25	a
26	a	27	a	28	b	29	b	30	b
31	a	32	c	33	b	34	a	35	c
36	d	37	a	38	b	39	a	40	c
41	a	42	b						

Rate law and Rate constant

1	d	2	c	3	a	4	b	5	a
6	a	7	a	8	c	9	b	10	b
11	b	12	d	13	a	14	c	15	d
16	d	17	c	18	a	19	c	20	c
21	b	22	a	23	a	24	d	25	b
26	a	27	a	28	c	29	c	30	d
31	d	32	c	33	c	34	d	35	b
36	c	37	c	38	a	39	c	40	b
41	a	42	d	43	a	44	c	45	c
46	a	47	b	48	b	49	c	50	b
51	b	52	a	53	a	54	d	55	d
56	c	57	d	58	b	59	b	60	b
61	c	62	d	63	c	64	b	65	c
66	d	67	b	68	c	69	c	70	b
71	d	72	d	73	b	74	b	75	d
76	b	77	b	78	c	79	c	80	c
81	b	82	b	83	c	84	a	85	a
86	c	87	c	88	a	89	c	90	c
91	b	92	b	93	c	94	b	95	b
96	d	97	b	98	c	99	a	100	c
101	b	102	d	103	c	104	c	105	a
106	d	107	a	108	b	109	c	110	b
111	c	112	d	113	b	114	b	115	d
116	d	117	b	118	d	119	a	120	b
121	d	122	b	123	d	124	c	125	d
126	b	127	d	128	d	129	b	130	a
131	ac	132	c	133	d	134	c	135	a
136	a	137	c	138	c	139	d	140	c
141	c	142	c	143	c	144	a	145	c
146	c	147	c	148	b	149	b	150	a
151	d	152	a	153	d	154	c	155	c
156	b	157	a	158	b	159	d	160	c
161	b	162	b	163	b	164	abd	165	ad
166	b	167	d	168	b	169	d	170	b
171	c	172	c	173	c	174	a		

Collision theory, Energy of activation and Arrhenius equation

1	b	2	b	3	b	4	c	5	a
6	d	7	d	8	b	9	c	10	b
11	d	12	d	13	a	14	d	15	a
16	b	17	d	18	b	19	b	20	a
21	c	22	a	23	d	24	b	25	a
26	ab	27	c	28	b	29	b	30	c
31	b	32	d	33	c	34	c	35	a
36	a								

Photochemical reaction

1	a	2	a	3	c	4	b		

Critical Thinking Questions

1	a	2	c	3	a	4	d	5	c
6	c	7	c	8	b	9	a	10	d
11	c	12	a	13	d	14	d	15	b
16	d	17	a	18	b	19	c	20	e

Assertion & Reason

1	b	2	b	3	b	4	b	5	a
6	a	7	d	8	e	9	a	10	d
11	a								

Answers and Solutions

Rate of a reaction

1. (b) Rate of reaction continuously decreases with time.

2. (a) The rate of reaction depends upon conc. of reactant, surface area of reactant, temperature, presence of light and catalyst.

3. (d) According to law of mass action.

4. (b) $R = K[RCl]$, if $[RCl]$ =1/2, then rate = R/2.

5. (b) $2^2 = 4, 3^2 = 9$

6. (c) The rate of chemical reaction $\propto$ The product of the molar conc. of the reactants (at constant T)

7. (c) Rate of reaction = $\frac{dx}{dt} = \left[\frac{0.2-0.1}{10}\right] = \frac{0.1}{10}$

$= 0.01\, mol\, dm^{-3}\, min^{-1}$

8. (c) As reaction progressing the concentration of the reactants decreases and the concentration of the product increases.

9. (a) $\frac{-d(N_2)}{dt} = -\frac{1}{3}\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt} = \frac{3}{2} \times 40 \times 10^{-3}$

$= 60 \times 10^{-3}$.

10. (b) Greater are the concentrations of the reactants, faster is the reaction. Conversely, as the concentrations of the reactants decreases, the rate of reaction also decreases.

11. (b) Ionic reactions are very fast reactions i.e. take place instantaneously.

12. (b) Rate = $K(A)^2(B)^1$ on doubling the active mass of A the rate of reaction increase 4 times.

13. (c) 'A' will disappear at twice the rate at which 'B' will decrease.

14. (d) When volume is reduced to $\frac{1}{4}$, concentrations become four times.

16. (b) $\frac{-dN_2}{dt} = \frac{-1}{3}\frac{dH_2}{dt} = \frac{1}{2}\frac{dNH_3}{dt}$

$\frac{dH_2}{dt} = \frac{3}{2} \times 0.001 = 0.0015 kg\, hr^{-1}$.

18. (b) $-\frac{dc}{dt}$ refers as decrease in concentration of the reactant with time.

19. (d) The rate of a reaction depends upon concentration of reactant.

20. (a) $-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d(D)}{dt}$.

21. (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\frac{-\Delta[N_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

$\therefore \frac{\Delta[H_2]}{\Delta t} = \frac{3}{2} \times \frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2} \times 2 \times 10^{-4}$

$= 3 \times 10^{-4}\, mol\, litre^{-1} sec^{-1}$

22. (a) Increase in concentration of $B = 5 \times 10^{-3} mol\, l^{-1}$

$Time = 10$ sec

Rate of appearance of $\text{B} = \frac{\text{Increase of conc. B}}{\text{Time taken}}$

$= \frac{5 \times 10^{-3} mol\, l^{-1}}{10\text{ sec}} = 5 \times 10^{-4} mol\, l^{-1}\, Sec^{-1}$

24. (c) The rate of formation of SO_3 is $1.28 \times 10^{-3}\, g/sec$.

26. (a) $\frac{K_t + 10}{K_t} = \frac{r_t + 10}{r_t} = 2$; For an increase of temperature to 50^oC, *i.e.* 5 times, the rate increases by 2^5 times, *i.e.* 32 times.

28. (b) $\frac{K_t + 10}{K_t} = \frac{r_t + 10}{r_t} = 2$.

For an increase of temperature to $20°C$ *i.e.* 2 times, the rate increase by 2^2 times, *i.e.* 4 times.

29. (b) $\frac{k_t + 10}{K_t} = \frac{r_t + 10}{r_t} = 2$

For an increase of temperature to 90^oC *i.e.* 9 times, the rate increases by 2^9 times *i.e.* 512.

30. (b) Catalyst increases the rate by decreasing the activation energy.

31. (a) For 10K rise in temperature, the rate of reaction nearly doubles.

32. (c) Temperature coefficient $\frac{K_{35^oC}}{K_{25^oC}} = \frac{K_{308k}}{K_{298k}} = 2$ and 3 for most reactions.

33. (b) Catalyst decrease energy of activation.

34. (a) Thus both rate and rate constant K increase with temperature, $r = k(\text{reactant})^{\text{n}}$ and $k = Ae^{-E_a/RT}$

35. (c) Enzymes does not always increase activation energy.

36. (d) Catalyst reduce the activation energy for reaction and thus increase the rate of reaction.

37. (a) Catalyst affect only activation energy. It brings down the activation energy of reaction.

38. (b) As we know that the velocity constant become double by increasing the temperature by 10°C so if at 290 K, velocity constant $= 3.2 \times 10^{-3}$ then at 300 K, velocity constant $= 2(K_{290}) = 2 \times 3.2 \times 10^{-3} = 6.4 \times 10^{-3}$.

39. (a) Higher the value of rate constant so, faster the reaction rate.

40. (c) Rate of reaction may increase or decrease with increase in temperature. If reaction is exothermic, rate decreases with increasing temperature while that of endothermic reactions increase with increasing temperature.

41. (a) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

Rate of reaction with respect to NO_2

$= \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{4} \times \frac{5.2 \times 10^{-3}}{100} = 1.3 \times 10^{-5} ms^{-1}$

42. (b) In first phase, $K = \frac{2.303}{20}\log\frac{90}{100}$ .....(i)

In second phase $K = \frac{2.303}{t}\log\frac{81}{100}$ .....(ii)

From eq. (i) $\frac{2.303}{20}\log\frac{90}{100} = \frac{2.303}{t}\log\frac{81}{100}$

$$t = \frac{20(\log 81 - \log 100)}{(\log 90 - \log 100)}$$

$$= \frac{20(1.908-2)}{(1.954-2)} = \frac{20\times(-0.092)}{(-0.046)} = 40 \text{ minutes}$$

Rate law and Rate constant

1. (d) Molecularity of the reaction does not influence the rate of reaction.

2. (c) The rate law for an reaction can be given by; rate $= K(A)(B)^2$, *i.e.* the powers are raised which are given as coefficient of reactant.

3. (a) $p_0 = 500\, atm$

$$K = \frac{2.303}{t}\log_{10}\frac{p_0}{p_t}$$

$$3.38\times10^{-5} = \frac{2.303}{10\times60}\log\frac{500}{p_t}$$

or $0.00880 = \log\frac{500}{p_t} \Rightarrow \frac{500}{1.02} = 490\, atm$

4. (b) It is a pseudo-unimolecular reaction.

5. (a) $A + 2B \rightarrow C + D$

$$\frac{-d[A]}{dt} = 5\times10^{-4}$$

$$-\frac{1}{2}\frac{d[B]}{dt} = \frac{5\times10^{-4}}{2} = 2.5\times10^{-4} mol^{-1}\sec^{-1}$$

8. (c) For following reaction, $2NO_{(g)} + O_2(g) \rightarrow 2NO_2(g)$

When the volume of vessel change into $\frac{1}{3}$ then concentration of reactant become three times.

The rate of reaction for first order reaction $\propto$ concentration. So rate of reaction will increases three times.

9. (b) $2A + B \rightarrow$ Products

According to question : Rate of reaction of 'A' $\propto$ [B] as increase in rate is double when [B] is doubled.

Rate of reaction $\propto$ [A] [B] as increase in rate is 8 times when concentration of both reactant is doubled. It means that order of reaction is 3 and overall rate reaction should be $r = K[A]^2[B]$

10. (b) Let the rate of reaction depends on *x* power of [*A*]. Then

$r_1 = k[A]^x$ and $r_2 = k[2A]^x$

$$\therefore \frac{r_1}{r_2} = \frac{[A]^x}{[2A]^x} = \frac{1}{4} = \left(\frac{1}{2}\right)^2 \quad (\because r_2 = 4r_1)$$

$\therefore x = 2$. As the reaction rate does not depend upon the concentration of B. Hence, the correct rate law will be rate $= K[A]^2[B]^o$ or $= K[A]^2$

11. (b) Velocity constant '*K*' is characteristic constant of a reaction and depends only on temperature and catalyst.

12. (d) Unit of *K* for 1st order reaction is $Time^{-1}$.

13. (a) $K = Ae^{-E_a/RT}$ by this equation it is clear that rate constant of a reaction depends on temperature

14. (c) $k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$; $t = 2\times10^2,\ a = 800,\ a-x = 50$

$$k = \frac{2.303}{2\times10^2}\log_{10}\frac{800}{50} = \frac{2.303}{2\times10^2}\log_{10}16$$

$$= \frac{2.303}{2\times10^2}\log_{10}2^4 = \frac{2.303}{2\times10^4}\times4\times0.301$$

$$= 1.38\times10^{-2}\ s^{-1}$$

15. (d) Rate of reaction is quadrupled on doubling the concentration. Thus $r \propto [A]^2$.

16. (d) *K* is not constant for all the reaction.

19. (c) Rate determining step is a slow step by which rate of reaction can be determined.

20. (c) It is a second order reaction and the unit of *k* for second order reaction is *litre* $mol^{-1}\ sec^{-1}$.

21. (b) For reversible reaction rate constant is also reverse.

22. (a) Rate $= K(N_2O_5) = 6.2\times10^{-1}\times1.25$

$$= 7.75\times10^{-1}\ mol\ l^{-1}\ s^{-1}$$

23. (a) We know that for first order kinetics

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$(a-x) = 0.05\ mol\ l^{-1}, 6 = \frac{2.303}{t}\log\frac{0.5}{0.05}$$

or $t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6} = 0.384\min$

24. (d) Rate $= K(N_2O_5)$ hence $2.4\times10^{-5} = 3.0\times10^{-5}(N_2O_5)$

or $(N_2O_5) = 0.8\ mol\ l^{-1}$

25. (b) $R = K[A],\ 1.02\times10^{-4} = 3.4\times10^{-5}, [N_2O_5]$

or $(N_2O_5) = \frac{1.02\times10^{-4}}{3.4\times10^{-5}}, K = 3$

26. (a) Rate law for the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

is $r = k[N_2O_5]$ first order reaction.

28. (c) Rate constant depends on temperature only.

29. (c) According to Arhenius concept

Rate constant $K = A_e^{-E_a/RT}$, Hence rate constant depends only upon temperature of the system.

30. (d) For $2A + B \rightarrow C$

Rate $= K[A][B]$

Value of rate constant $K = Ae^{-Ea/RT}$ here *K* is independent of the initial concentration of *A* and *B*.

31. (d) The specific rate constant of a first order reaction depends upon the temperature of reaction.

32. (c) Unit of *K* for first order reaction $= sec^{-1}$

35. (b) The rate of zero order reaction is not depend on the concentration of the reactants.

36. (c) The unit of *K* for zero order reaction $= mole\ litre^{-1} sec^{-1}$.

37. (c) Order of reaction is sum of the power raised on concentration terms to express rate expression.

38. (a) The concentration of reactant does not change with time for zero order reaction (unit of *K* suggests zero order) since reactant is in excess.

39. (c) $r = K[A]^m$ also $2r = K[4A]^m$, $\frac{1}{2} = \left(\frac{1}{4}\right)^m$

$\therefore m = \frac{1}{2}$

40. (b) $K = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$ gives constant value of *K*. With the given date. Hence it is 1^{st} order.

42. (d) $r = K[A]^n$, $100r = K[10A]^n$

Thus $\frac{1}{100} = \left(\frac{1}{10}\right)^n$ or $n = 2$

43. (a) It is a standard example of first order because in that reaction rate of reaction affected by only one concentration term.

44. (c) Inversion of cane sugar is a Pseudo unimolecular reaction.

45. (c) For 1^{st} order reaction

$$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

46. (a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2\times10^{-4}} = 1117.7$ *sec.*

47. (b) $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$\frac{0.693}{T} = \frac{2.303}{t}\log\frac{100}{100-30}$$

$\therefore T = 58.2$ *min.*

48. (b) Order of reaction = $\frac{3}{2}+\frac{3}{2} = \frac{3+3}{2} = \frac{6}{2} = 3$

49. (c) Two molecules are taking part in elementary step.

50. (b) Because two molecules are taking part in elementary step.

51. (b) The overall order of a reaction is sum of powers T raised on concentration terms in order to write rate expression.

52. (a) It is a first order reaction as is clear from rate law expression, $r = k(H_2O_2)$

53. (a) For 1^{st} order reaction half life is independent of concentration.

54. (d) $K = \frac{1}{t}\log e\left(\frac{a}{a-x}\right) = \frac{1}{15}\log e\left(\frac{35}{35-9}\right) = \frac{1}{15}\log e\left(\frac{35}{26}\right)$

56. (c) $k = \frac{0.693}{30} = 0.0231$; $t = \frac{2.303}{k}\log\left(\frac{100}{100-75}\right)$

$$t = \frac{2.303}{0.0231}\log 4 = 60 \text{ minutes}$$

57. (d) $Rate = K(sugar)(H_2O)^o$

58. (b) Derive $t_{1/2}$ from $K_t = 2.303\log\frac{a}{a-x}$, putting $t = \frac{1}{2}$ and $x = \frac{a}{2}$. Therefore it is $\frac{0.693}{K}$.

59. (b) $r \propto [X]^2$ or $r = k[X]^2$

60. (b) $t_{1/2} = \frac{0.693}{k}, \frac{0.693}{1.1\times10^{-9}} = 6.3\times10^8$ *sec.*

61. (c) $t_{1/2} \propto \frac{1}{(a)}$ for II order reaction.

62. (d) Order of reaction is an experimental value, while molecularity is a theoretical value.

63. (c) *K* for 1^{st} order reaction = per unit time *i.e.* $Time^{-1}$.

64. (b) $R = K[A][B]^0$ so molecularity is two and order is two.

65. (c) Rate of zero order reaction is independent of the concentration of the reactant and remains constant throughout the reaction.

66. (d) $t_{1/2} \propto \frac{1}{(a)^{n-1}}$

67. (b) $t_{1/2} \propto \frac{1}{(C_o)^{n-1}}$ $\therefore$ reaction is of first order.

68. (c) For 1^{st} order reaction half life is independent of concentration.

69. (c) $K = \frac{0.693}{t_{1/2}}, K = \frac{0.693}{138.6 \text{ min}} = 0.005 \text{ min}^{-1}$

70. (b) $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$

It is a pseudo-unimolecular reaction.

71. (d) $t_{1/2} \propto \frac{1}{K}$ and $K \propto t$

73. (b) For zero order reactions $\frac{dx}{dt} = K(A)^o$

74. (b) It is an bimolecular and second order reaction.

75. (d) $\frac{dx}{dt} = (HI)^2$, then order of reaction = 2

76. (b) Rate = $K(\text{Sucrose})(H_2O)^o$

77. (b) Because in this reaction one molecule of N_2O_5 is used.

78. (c) Integrated velocity equation for first order reaction is: $k = \frac{2.303}{t}\log\frac{(A)_o}{(A)}$

80. (c) $t_{1/2} = \frac{2.303\log 2}{K} = \frac{0.693}{K}$

81. (b) Inversion of sugar is a pseudo-unimolecular reaction.

82. (b) For 1^{st} order reaction

$$\log(a-x) = \log a - \frac{kt}{2.303}$$

$$y = c + mx$$

83. (c) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3.46\times10^{-3}} = 200\,min$

84. (a) $\frac{1}{Time}\times(conc.) = \frac{moles\ l^{-1}}{Time} = moles\ l^{-1}time^{-1}$ for zero order reaction.

85. (a) The order of reaction is $\frac{3}{2}$ and molecularity is 2.

87. (c) Molecularity can never be fractional.

88. (a) As doubling the initial conc. doubles the rate of reaction, order = 1.

89. (c) When *B* is in excess, it becomes a pseudo-unimolecular reaction.

90. (c) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.35} = 9.99\times10^{-3} = 0.01 s^{-1}$

91. (b) $k = \frac{0.693}{24}hr^{-1} = \frac{2.303}{96}\log\frac{10}{a-x}$

or $\log\frac{10}{a-x} = 1.2036$ or $1 - \log(a-x) = 1.2036$

or $\log(a-x) = -0.2036 = \bar{1}.7964$

or $(a-x) = \text{antilog}\,\bar{1}.7964 = 0.6258\,gm$

92. (b) $0.08\ mol\ l^{-1}$ to $0.01\ mol\ l^{-1}$ involves 3 half-life. So the t is 30 minutes

93. (c) $t_{1/2}$ of II order reaction is inversely proportional to initial concentration of reactants.

94. (b) As $r = k(H_2O_2)$, it is a reaction of 1st order.

97. (b) $r = k(C_A)^{3/2}(C_B)^{-1/2}$

Order = $\frac{3}{2} + \left(-\frac{1}{2}\right) = \frac{2}{2} = 1$

98. (c) If rate $= K(A)^m(B)^n$, then order of reaction $= m + n$.

99. (a) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100\ \text{sec}} = 6.93 \times 10^{-3} sec^{-1}$

100. (c) $t_{1/2} = \frac{0.693}{k}$

101. (b) $t_{1/2} = \frac{0.693}{k}$, $k = \frac{0.693}{480} = 1.44 \times 10^{-3}\ \text{sec}^{-1}$.

102. (d) $r = k(A)^2$, when concentration is doubled

$r = k(2A)^2 = k\,4(A)^2$ the rate becomes 4 times.

103 (c) $r = K[FeCl_3]^2[SnCl_2]^1$. Order $= 2 + 1 = 3$

105. (a) $t_{1/2}$ for I order reaction independent of initial concentration.

107. (a) The rate will be given by slowest step. Thus $r = K[A][B_2].\ K_c = \frac{[A][A]}{[A_2]}$ or $[A] = [K_c]^{1/2}[A_2]^{1/2}$

$r = K \times [K_c]^{1/2}[A_2]^{1/2}[B_2] = K[A_2]^{1/2}[B]$. Thus order is $0.5 + 1 = 1.5$

108. (b) For 1st order reaction half life is independent of concentration.

110. (b) Rate = $K[A]^{1/2}[B]^{3/2}$

$\therefore O.R. = \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$

112. (d) The rate of this photochemical reaction is independent of the concentration, therefore, it is zero order reaction.

113. (b) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.6932\ hr^{-1}} = 1\ hr$.

114. (b) The unit of rate constant shows that reaction is of first order. For first order reaction, half life is independent of initial conc. of the reactant. Thus,

$t_{1/2} = \frac{0.693}{0.69 \times 10^{-1}} = \frac{0.693 \times 60}{0.69 \times 10^{-1}} = 600\ \text{sec}$

115. (d) *Given* : Rate constant of the first order reaction $(K) = 3 \times 10^{-6}$ per sec and initial concentration $[A] = 0.10M$. We know that initial rate constant

$K[A] = 3 \times 10^{-6} \times 0.10 = 3 \times 10^{-7} ms^{-1}$.

116. (d) It is the characteristic of pseudo-unimolecular reactions.

117. (b) It is a second order reaction.

118. (d) $r = K\,[\text{reactant}]$

$\therefore K = \frac{1.0 \times 10^{-2}}{0.2} = 0.05$

$t_{1/2} = \frac{0.693}{0.05} = 13.86\,s$

119. (a) For first order reactions rate is depend on the concentration of one reactant.

120. (b) Molecularity of a reaction never become zero or fraction.

121. (d) $t = \frac{2.303}{k}\log\frac{a}{a-x}$

$t = \frac{2.303}{1.155 \times 10^{-3}}\log\frac{100}{100-50} = 600\ \text{sec}$

122. (b) Rate = $K[A]^{3/2}[B]^{-1}$

$\therefore O.R. = \frac{3}{2} + (-1) = \frac{1}{2}$

123. (d) $t_{1/2} \propto (CO)^o$ *i.e.* half life for 1st order is independent of initial concentration.

124. (c) $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$

Rate = $K[NO]^2[Cl_2]^1$, $\therefore O.R. = 2 + 1 = 3$

125. (d) $8 \times 10^{-5} = \frac{1}{t}\left[\frac{1}{0.5} - \frac{1}{1}\right]$; $8 \times 10^{-5} = \frac{1}{t}[2-1]$

$t = \frac{1}{8 \times 10^{-5}} = 0.125 \times 10^5 = 1.25 \times 10^4 min.$

126. (b) $r = k[\text{reactant}]^{-1}$ $\therefore k = \frac{0.693 \times 10^{-2}}{1}$ also

$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.693 \times 10^{-2}} = 100\ \text{min}$.

127. (d) $t_{1/2} = \frac{1}{Ka}$ for second order reactions.

128. (d) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$; $k = \frac{2.303}{30}\log\left(\frac{100}{100-75}\right)$

$k = \frac{2.303}{t}\log\left(\frac{100}{100-93.75}\right)$ Put the value of K from above equation we get the value of t therefore $\therefore\ t = 60\ \text{min}$.

129. (b) $k = \frac{0.693}{45}\ \text{min}^{-1} = \frac{2.303}{t_{99.9\%}}\log\frac{a}{a - 0.999a}$ or

$t_{99.9\%} = \frac{2.303 \times 45}{0.693}\log 10^3 = 448\ \text{min} \approx 7.5\ hrs$

130. (a) Given A(a) = 2.00 *m*, t = 200 *min* and a(a-x) = 0.15 *m* we know

$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{200}\log\frac{2.00}{0.15}$

$= \frac{2.303}{200} \times (0.301 + 0.824) = 1.29 \times 10^{-2}\ \text{min}^{-1}$

131. (a,c) The unit for zero order reaction is $mol\ litre^{-1} time^{-1}$

132. (c) It is a third order reaction because

$\text{Rate} = \text{K}[\text{NO}]^2[O_2]^1 \quad \therefore O.R. = 2 + 1 = 3$

133. (d) Order of a reaction is decided by relative concentration of reactants.

134. (c) Unit of rate constant for second order reaction is $mol^{-1} litre\ time^{-1}$

135. (a) $R = K[A]^2[B]$ order of reaction $= 2 + 1 = 3$

136. (a) Units of 1st rate constant order reaction are sec^{-1} and for zero order reaction, these are $mol\ litre^{-1}\ sec^{-1}$ *i.e.* $M\ sec^{-1}$.

137. (c) This reaction is bimolecular and first order of reaction.

138. (c) $t_{1/2} = \frac{0.693}{k}$ Given $t_{1/2} = 693\ \text{sec}$

$$693 = \frac{0.693}{k},\ k = \frac{693\times10^{-3}}{693};\ k = 10^{-3} = 0.001\ \text{sec}^{-1}.$$

139. (d) $2A + B \to C + B$

Rate = $k[A]^2[B]^1$

$\therefore O.R. = 2 + 1 = 3$ and molecularity is $3[2A + B]$.

140. (c) In photochemical reactions the rate of reaction is independent of the concentration of reacting species.

141. (c) We know that $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$10^{-3} = \frac{2.303}{t}\log\frac{a}{(a-\frac{2a}{3})},\ 10^{-3} = \frac{2.303}{t}\log 3$$

$$10^{-3} = \frac{2.303}{t}\times 0.4771,\ t = \frac{2.303\times0.4771}{10^{-3}} = 3300\ \text{sec}$$

142. (c) $R = K(A)^2,\ R' = K(2A)^2,\ \therefore \frac{R'}{R} = 4$

$R = K(A)^2,\ R' = K(3A)^2,\ \frac{R'}{R} = 9$

144. (a) $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

$k = \frac{2.303}{32}\log\left(\frac{100}{100-75}\right)$ .... (i)

$k = \frac{2.303}{t}\log\left(\frac{100}{100-50}\right)$ ....(ii)

from the two equation (i) and (ii), $t = 16$ minutes.

146. (c) The relation between half – life period and initial concentration (c) for a n^{th} order reaction is given by $t_{1/2} \propto \frac{1}{C^{n-1}}$ for first order reaction $(n = 1)$. $t_{1/2} \propto \frac{1}{C^{1-1}}$ or $t_{1/2} \propto C^0$.

147. (c) $R = k[NO]^2[O_2],\ R' = k[2NO]^2[2O_2]$

$R' = k\times4[NO]^2[O_2] = k\times8[NO]^2[O_2]$

$$\frac{R'}{R} = \frac{k\times8[NO]^2[O_2]}{k[NO]^2[O_2]} = 8$$

148. (b) For zero order reaction $r = k$.

149. (b) $k = \frac{2.303}{t}\log\frac{0.8}{0.6} = 2.303\log\frac{4}{3}$

$t = \frac{2.303}{k}\log\frac{0.9}{0.675} = \frac{2.303}{k}\log\frac{4}{3}$; $t = 1$ *hour.*

150. (a) For zero order reaction

Velocity constant $= \frac{dx}{dt} = \frac{\text{Concentration}}{\text{Time}}$

Unit = concentration × time^{-1}.

151. (d) $H_2 + Br_2 \rightleftharpoons 2HBr$ is a 1.5 order reaction

i.e., $K = [H_2][Br_2]^{1/2}$.

152. (a) When in any chemical reaction, one of the reactant is present in large excess, then the second order reaction becomes first order reaction and is known as pseudo unimolecular reaction *e.g.,*

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

in this reaction molecularity is 2 but order of reaction is found to be first order experimentally, so it is an example of pseudo unimolecular reaction.

153. (d) $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\,\text{years}}$

If initial concentration $a = 10\ gm$ and final concentration

$x = \frac{a}{2} = 5\ gm$

then, $t = \frac{2.303}{K}\log\frac{a}{a-x} = \frac{2.303}{.693}\times10\times\log\frac{10}{5}$

$$= \frac{2.303\times10\times\log 2}{.693} = \frac{2.303\times10\times0.301}{0.693} = 10\ \text{years}.$$

154. (c)The concentration of the reactants decrease from 0.8 to 0.4 in 15 *min* i.e., $T_{1/2} = 15$ *min*, concentration from 0.1*m* to 0.025 will fall in 2 half lives so total time taken $= 2\times T_{1/2} = 2\times15 = 30$ *min.*

155. (c) $K = \frac{2.303}{1\,hr}\log\frac{100}{25} = \frac{2.303}{t}\log\frac{100}{50}$

$\therefore\ \log 4 = \frac{1}{t}\log 2$

$\therefore\ 2\log 2 = \frac{1}{t}\log 2$; $t = \frac{1}{2}hr$.

156. (b) $x_{(g)} \to y_{(g)} + z_{(g)}$

The reaction is a first order reaction hence,

$$K = \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{0.693}{10\ \text{min}}$$

$$= \frac{2.303}{t}\log\frac{a}{a/10} = \frac{0.693}{10} = \frac{2.303}{t}\log 10$$

$$\therefore\ t = \frac{2.303\times10}{.693} = 33\,\text{min}.$$

157. (a) For the first order reaction $t = \frac{2.303}{K}\log\frac{a}{a-x}$

Given: $a = 0.5\ mol/litre$; $a - x = 0.05\ ,mol/litre$

$K = 6\ \text{sec}^{-1}$.

$$t = \frac{2.303}{6}\log\frac{0.5}{0.05} = \frac{2.303}{6}\log 10 = \frac{2.303}{6} = 0.384\ \text{sec}.$$

158. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

159. (d) Rate $\left(\frac{dx}{dt}\right) = K.c$; $1.5\times10^{-2} = K\times0.5$

For first order $K = \frac{1.5\times10^{-2}}{0.5} = 3\times10^{-2}\ \text{min}ute^{-1}$

$t_{1/2} = \frac{.693}{K} = \frac{.693}{3\times10^{-2}} = 23.1\ \text{min}ute$.

160. (c) For first order reaction $K = \frac{2.303}{t}\log\frac{a}{a-x}$

Given: $a = \frac{1}{10} = .1m$; $a - x = \frac{1}{100} = .01m$; $t = 500$ *sec*

$$\therefore\ K = \frac{2.303}{500}\log\frac{.10}{.01} = \frac{2.303}{500}\log 10$$

$$= \frac{2.303}{500} = 0.004606 = 4.6\times10^{-3}\ \text{sec}^{-1}.$$

161. (b) For zero order reaction, rate of reaction is independent of concentration $R = K[\text{Reactant}]^0$

162. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

163. (b) $t_{1/2} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow \frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$\Rightarrow \frac{1}{4^1} = \frac{1}{4^{n-1}} \quad \therefore n-1=1 \,;\, n=2$.

164. (abd) By Vant's Hoff equation, $\frac{d\ln k}{dt} = \frac{\Delta H^o}{RT^2}$

or $\ln k_p = -\frac{\Delta H^o}{RT} + I$. Hence (a) is correct (b) is also correct as plot of log (X) vs time is linear. (c) is wrong because $p \propto T$ at constant volume. (d) is correct by Boyle's law.

165. (ad) (a) is correct because degree of dissociation $= 1 - e^{-kt}$ at any time *t*.

(b) is wrong because plot of log [A] vs *t* is a straight line

(c) is wrong because time taken for 75% reaction is two half life.

(d) is correct because in $k = Ae^{-E_a/RT}$, $E_{a/RT}$ is dimensionless hence *A* has the unit of *K*.

166. (b) $aA \rightarrow xP$

Rate of reaction = $[A]^a$

Order of reaction = *a*

$[A]_1 = 2.2\ mM,\ r_1 = 2.4\ m\ M\ s^{-1}$ ...(i)

$[A]_2 = 2.2/2\ mM,\ r_1 = 0.6\ m\ M\ s^{-1}$ or, $\frac{2.4}{4}$ ...(ii)

On reducing the concentration of *A* to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$

Order of reaction = 2.

167. (d) Order of a reaction can be fractional.

168. (b) $t_{1/4} = \frac{2.303}{K}\log\frac{1}{1-\frac{1}{4}} = \frac{0.29}{K}$.

169. (d) $R = K[A]$

$2 \times 10^{-5} = K \times 10^{-2}$

$K = 2 \times 10^{-3}\ \sec^{-1}$

$t_{1/2} = \frac{.693}{K} = \frac{.693}{2 \times 10^{-3}} = \frac{693}{2} = 347\sec$

170. (b) $R = k[B]^n\,;\ \frac{1}{4}R = k[2B]^n\,; 4 = \left(\frac{1}{2}\right)^n\,;\ 4 = 2^{-n}\,;\ n = -2$.

171. (c) $T = t_{1/2} \times n$ *i.e.* $12 = 3 \times n \Rightarrow n = 4$

$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

172. (c) $K = 1.7 \times 10^{-5}\,s^{-1}$

$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.7} \times 10^5 = 11.32h$

173. (c) $A + B \rightarrow C$

On doubling the concentration of A rate of reaction increases by four times. Rate $\propto [A]^2$

However on doubling the concentration of B, rate of reaction increases two times. Rate $\propto [B]$

Thus, overall order of reaction = 2 + 1= 3.

174. (a) In case of zero order reaction, the concentration of reactant decreases linearly with time, as its rate is independent of the concentration of the reactants.

Collision theory, Energy of activation and Arrhenius equation

1. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

2. (b) All collisions are not effective and does not result in the formation of the products

3. (b) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

4. (c) The increase in collision frequency brings in an increase in effective collisions and thus rate of reaction increases.

5. (a) Slower reaction rate indicates higher energy of activation.

6. (d) Energy of activation decreases, rate of reaction will increases.

7. (d) Number of collision depend upon pressure, concentration and temperature.

9. (c) The definition of activation energy.

10. (b) Activation energy is the energy needed by reactant molecules to gain threshold energy level.

11. (d) All other are different forms of Arrhenius equation.

12. (d) Increase in the rate of reaction is determined by the increase in the number of effective collisions.

13. (a) Energy of activation reduced by increasing temperature.

14. (d) The definition of threshold energy.

15. (a) The definition of activation energy.

16. (b) When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

17. (d) In exothermic and endothermic reactions will be more and less than E_a respectively.

19. (b) The value of activation energy for a chemical reaction primarily dependent on the nature of reacting species.

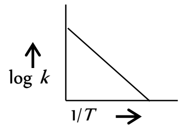
20. (a) Arrhenius equation is $\log k = \log A - \frac{E_a}{RT}$

22. (a) A graph plotted between $\log k$ vs $\frac{1}{T}$ for calculating activation energy.

24. (b) When $E_a = 0$ rate constant is independent of temperature.

25. (a) It is modified form of Arrhenius equation.

28. (b) A graph plotted between $\log k$ Vs $\frac{1}{T}$ for calculating activation energy is shown as from Arrhenius equation



$\log k = \log A - \frac{E_A}{2.303\ RT}$

30. (c) It is Arrhenius equation.

31. (b) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

If $\frac{K_2}{K_1} = 2$

$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$

$$E_a = .3010 \times 2.303 \times 8.314 \left(\frac{300 \times 310}{10} \right)$$

$$= 53598.59 \ Jmol^{-1} \ = 54 \ kJ \ .$$

32. (d) When $E_a = 0$, the rate of reaction becomes independent of temperature.

(E_a = Energy of activation).

33. (c) When k increases, rate of reaction also increases, $k = \frac{pz}{e^{E/RT}}$

for k to increase *p*, *z*, *T* should increase and *E* should decrease. ($e \approx 2.7$).

34. (c) Endothermic reactions are those which involve absorption of heat. High activation energy means potential energy of product must be much greater than reactants.

35. (a) For endothermic reaction $\Delta H = +ve$

Then from equation $\Delta H = E_{a_{F.R.}} - E_{a_{B.R.}}; E_{B.R.} < E_{F.R.}$

36. (a) Arrhenius suggested an equation which describes rate constant (K) as a function of temperature.

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - e^{E_a/RT}$$

Photochemical reactions

2. (a) $H_2O \xrightarrow{\text{Photolysis}} OH^- + H^+$

3. (c) Stark - Einstein was given the law of photochemical equivalence.

4. (b) In photochemical reaction the rate of formation of product is directly proportional to the intensity of absorbed light.

Critical Thinking Questions

1. (a) For the given reaction :

$$-\frac{\Delta[I_2]}{\Delta t} = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

2. (c) $-\frac{1}{3}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} \quad \therefore \frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

3. (a) Concentration of reactants decreases while concentration of product increases.

4. (d) $R = K(A)^n(B)^m$

$$R' = K(2A)^n\left(\frac{B}{2}\right)^m \ = K(A)^n 2^n (B)^m 2^{-m}$$

$$= K(A)^n (B)^m 2^{n-m}, \ \frac{R'}{R} = \frac{K(A)^n (B)^m 2^{n-m}}{K(A)^n (B)^m} = 2^{n-m}$$

5. (c) $\ln K = \ln \ - \frac{E_a}{RT}$ is Arrhenius equation. Thus plots of ln *K* vs 1/T will give slope $= -E_a/RT$ or $-E_a/2.303R$.

6. (c) For a reaction E_a for forward reaction $= E_a$ for backward reaction + ΔH.

7. (c) As $K^{'} > K^{''}, E_a^{'} < E_a^{''}$ (Greater the rate constant, less is the activation energy).

8. (b) $T_2 = T(say), T = 25^o C = 298K,$

$$E_a = 104.4 \text{ kJ } mol^{-1} = 104.4 \times 10^3 \text{ J } mol^{-1}$$

$$K_1 = 3 \times 10^{-4}, \ K_2 = ?,$$

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{J } mol^{-1}}{2.303 \times (8.314 \text{ J } k^{-1} \ mol^{-1})}$$

$$\left[\frac{1}{298K} - \frac{1}{T}\right] \text{As T} \rightarrow \infty, \frac{1}{\text{T}} \rightarrow 0$$

$$\therefore \log \frac{K_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3 \text{ J } mol^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log \frac{K_2}{3 \times 10^{-4}} = 18.297, \ \frac{K_2}{3 \times 10^{-4}} = 1.98 \times 10^{18} \text{ or}$$

$$K_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14} s^{-1}$$

9. (a) Because reaction is exothermic

10. (d) $k = Ae^{-E^0/RT} \ \underset{y}{\log K} = \underset{c}{\log A} - \underset{mx}{E^o/RT} \ \therefore \log K \ Vs \ \frac{1}{T}$.

11. (c) $\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

12. (a) $2.303 \log \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

$$\log \frac{K_2}{K_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{K_2}{K_1} = 1.63; \ K_2 = 1.63 \, K_1; \frac{1.63K_1 - K_1}{K_1} \times 100 = 63.0\%$$

13. (d) Combustion is an exothermic process, which is expected to be favoured by low temperature, but it is not true. Combustion include burning of particles which takes place at higher temperature. Thus at high temperature due to combustion of more particles, the reaction proceeds at higher rate.

14. (d) Rate constant $= 2.3 \times 10^{-2} \sec^{-1}$

It means it is a first order reaction (because unit of rate constant is sec^{-1})

For first order reaction $K = \frac{1}{t}\ln\frac{a}{a-x}$

$$Kt = \ln\frac{a}{a-x} = \ln\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

15. (b) Because as reaction progresses the amount of acetic acid increases.

16. (d) Half life of a reaction is found to be inversely proportional to the cube of initial concentration. The order of reaction is 4.

17. (a) It is similar to $y = mx + c$

18. (b) $r = K[A]^n, \ 100r = K[10A]^n$

Thus $\frac{1}{100} = \left(\frac{1}{10}\right)^n$ or $n = 2$

19. (c) Concentration will fall from 0.1 *M* concentration to 0.025 *M* concentration within 2 half lives.

$$2 \times T_{1/2} = 40 \ min$$

$$\therefore \ T_{1/2} = 20 \ min$$

Rate of reaction = K . c $= \frac{0.693}{T_{1/2}}.c$

$$= \frac{0.693}{20} \times 10^{-2} M/\text{min} \quad = 3.47 \times 10^{-4} M/\text{min}^{-1}.$$

20. (e) % distribution of $B = \frac{K_1}{K_1 + K_2} \times 100$

$$= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$$B\% = 76.83\%$$

$$\%\text{Distribution of } C = \frac{K_2}{K_1 + K_2} \times 100$$

$$= \frac{3.8 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-4}} \times 100$$

$$C\% = 23.17\%$$

Assertion and Reason

1. (b) Instantaneous rate of a reaction is equal to small change in concentration (dx) during a small interval of time (dt) at that particular instent of time divided by the time interval.

2. (b) Molecularity of a reaction can be defined only for an elementary reaction because complex reaction does not take place in one single step and it is almost impossible for all the total molecules of the reactants to be in a state of encounter simultaneously.

3. (b) For a zero order reaction, $t_{1/2} = [A_0]/2K$.

4. (b) According to Arrhenius equation, $K = Ae^{-E_a/RT}$ when $E_a = 0, K = A$.

6. (a) For a first order reaction, $K = \frac{2.303}{t} \log \frac{a}{a - x}$, where *a* is initial concentration, and *x* is the amount reacted in time *t*. For half-life $x = a/2$, $t = t_{1/2}$

$$K = \frac{2.303}{K} \log \frac{a}{a - a/2}$$

$$t_{1/2} = \frac{2.303}{K} \log 2 = \frac{0.693}{K}.$$

7. (d) $H_2 + Cl_2 \rightarrow 2HCl$ has much higher quantum efficiency than $H_2 + Br_2 \rightarrow 2HBr$. The first step of secondary process of $H_2 + Cl_2 \rightarrow 2HCl$ is exothermic while the same for $H_2 + Br_2 \rightarrow 2HBr$ is endothermic.

8. (e) Vision is a fast photochemical reaction in which the compound, retinal, present in the eye undergoes isomerisation by absorbing a photon of light.

9. (a) The emission of cold light during a chemical reaction is called chemiluminescence.

10. (d) The rate reaction is never negative. Minus sign used in expressing the rate only shows that the concentration of the reactant is decreasing.

11. (a) Rate expression $\frac{dx}{dt} = K[A]^m[B]^n$

Shows that the total order of reactions is $m + n + O = m + n$ as the rate of reaction is independent of concentration of *C*, *i.e.* the order with respect to *C* is zero. This is the reason that *C* does not figure in the rate expression.