# **Chemical Kinetics**

- Units of rate constant of first and zero order reactions in terms of molarity M unit are respectively
  - (a)  $\sec^{-1}$ ,  $M\sec^{-1}$  (b)  $\sec^{-1}$ , M
  - (c)  $Msec^{-1}$ ,  $sec^{-1}$  (d) M,  $sec^{-1}$ .
- For the reaction  $A + 2B \rightarrow C$ , rate is given by  $R = [A][B]^2$  then the order of the reaction is

- (a) 3
- (b) 6
- (c) 5
- (d) 7.
- The differential rate law for the reaction 3.

 $H_2 + I_2 \rightarrow 2HI$  is [2002]

- (a)  $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$
- (b)  $\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt}$
- (c)  $\frac{1}{2} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$
- (d)  $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$
- If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is [2002]
  - (a) 16 grams
- (b) 2 grams
- (c) 32 grams
- (d) 8 grams.
- The integrated rate equation is [2002]  $Rt = \log C_0 - \log C_t$

The straight line graph is obtained by plotting

- (a) time vs  $\log C_t$  (b)  $\frac{1}{\text{time}}$  vs  $C_t$
- (c) time vs  $C_t$  (d)  $\frac{1}{\text{time}}$  vs  $\frac{1}{C_t}$

- 6. The half-life of a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be
  - (a)  $8.0\,\mathrm{g}$
- (b) 12.0 g
- (c)  $16.0 \,\mathrm{g}$
- (d) 4.0 g
- In respect of the equation  $k = Ae^{-E_a/RT}$  in chemical kinetics, which one of the following statements is correct? [2003]
  - (a) A is adsorption factor
  - (b) E<sub>a</sub> is energy of activation
  - (c) R is Rydberg's constant
  - (d) k is equilibrium constant
- For the reaction system: 8.

[2003]

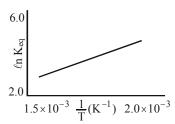
- $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O<sub>2</sub> and second order with respect to NO, the rate of reaction will
- diminish to one-eighth of its initial value
- increase to eight times of its initial value
- increase to four times of its initial value
- diminish to one-fourth of its initial value
- In a first order reaction, the concentration of the 9. reactant, decreases from 0.8 M to 0.4 M is 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is [2004]
  - (a) 7.5 minutes
- (b) 15 minutes
- (c) 30 minutes
- (d) 60 minutes
- The rate equation for the reaction  $2A + B \rightarrow C$  is found to be: rate = k[A][B]. The correct statement in relation to this reaction is that the [2004]
  - rate of formation of C is twice the rate of disappearance of A
  - (b)  $t_{1/2}$  is a constant
  - (c) unit of k must be  $s^{-1}$
  - value of k is independent of the initial concentrations of A and B

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16. A reaction was found to be second order wit

- 11. The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is [2004]
  - (a) 3.125 g
- (b) 2.084 g
- (c) 1.042 g
- (d) 4.167 g
- 12. A reaction involving two different reactants can never be [2005]
  - (a) bimolecular reaction
  - (b) second order reaction
  - (c) first order reaction
  - (d) unimolecular reaction
- 13. A schematic plot of  $\ln K_{eq}$  versus inverse of temperature for a reaction is shown below [2005]



The reaction must be

- (a) highly spontaneous at ordinary temperature
- (b) one with negligible enthalpy change
- (c) endothermic
- (d) exothermic
- 14.  $t_{\frac{1}{4}}$  can be taken as the time taken for the

concentration of a reactant to drop to  $\frac{3}{4}$  of its initial value. If the rate constant for a first order

reaction is K, the  $\frac{t_1}{4}$  can be written as

- (a) 0.75/K
- (b) 0.69/K [2005]
- (c) 0.29/K
- (d) 0.10/K
- 15. Consider an endothermic reaction  $X \to Y$  with the activation energies  $E_b$  and  $E_f$  for the backward and forward reactions, respectively. In general [2005]
  - (a) there is no definite relation between  $E_b$  and  $E_f$
  - (b)  $E_b = E_f$
  - (c)  $E_b > E_f$
  - (d)  $E_b < E_f$

16. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will [2006]

- (a) increase by a factor of 4
- (b) double
- (c) remain unchanged
- (d) triple
- 17. Rate of a reaction can be expressed by Arrhenius equation as: [2006]

$$k = A e^{-E/RT}$$

In this equation, E represents

- (a) the total energy of the reacting molecules at a temperature, T
- (b) the fraction of molecules with energy greater than the activation energy of the reaction
- (c) the energy above which all the colliding molecules will react
- (d) the energy below which all the colliding molecules will react
- **18.** The following mechanism has been proposed for the reaction of NO with Br<sub>2</sub> to form NOBr:

$$NO(g) + Br_2(g) \longrightarrow NOBr_2(g)$$

$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is [2006]

- (a) 3
- (b) 2
- (c) 1
- (d) 0
- 19. The energies of activation for forward and reverse reactions for  $A_2 + B_2 \rightleftharpoons 2AB$  are  $180 \text{ kJ mol}^{-1}$  and  $200 \text{ kJ mol}^{-1}$  respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by  $100 \text{ kJ mol}^{-1}$ . The enthalpy change of the reaction  $(A_2 + B_2 \rightarrow 2AB)$  in the presence of a catalyst will be (in kJ mol<sup>-1</sup>) [2007]
  - (a) 20
- (b) 300 (d) 280
- (c) 120 **20.** Consider the 1
- 20. Consider the reaction, 2A + B → products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate

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increased by two times. The unit of rate constant for this reaction is

(a)  $s^{-1}$ 

(b)  $L \text{ mol}^{-1} \text{ s}^{-1}$ 

(c) no unit

- (d)  $\text{mol } L^{-1} s^{-1}$ .
- A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the [2007] room?
  - (a) 100 days
- (b) 1000 days
- (c) 300 days
- (d) 10 days.
- 22. For a reaction  $\frac{1}{2}A \rightarrow 2B$ , rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression

(a) 
$$-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$$
 (b)  $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$ 

(c) 
$$-\frac{d[A]}{dt} = \frac{d[B]}{dt}$$
 (d)  $-\frac{d[A]}{dt} = 4\frac{d[B]}{dt}$ 

- The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be  $(\log 2 = 0.301)$ [2009]
  - (a) 23.03 minutes
- (b) 46.06 minutes
- (c) 460.6 minutes
- (d) 230.03 minutes
- The time for half life period of a certain reaction  $A \longrightarrow Products$  is 1 hour. When the initial concentration of the reactant 'A', is  $2.0 \text{ mol } L^{-1}$ . how much time does it take for its concentration to come from 0.50 to 0.25 mol L<sup>-1</sup> if it is a zero order reaction? [2010]
  - (a) 4 h
- (b)  $0.5 \, h$
- (c)  $0.25 \,\mathrm{h}$
- (d) 1 h
- **25.** Consider the reaction :

$$Cl_2(aq) + H_2S(aq) \rightarrow$$

$$S(s) + 2H^{+}(aq) + 2Cl^{-}(aq)$$

The rate equation for this reaction is

rate =  $k[Cl_2][H_2S]$ 

Which of these mechanisms is/are consistent with this rate equation?

A. 
$$Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$$
 (slow)

$$Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$$
 (fast)

B. 
$$H_2S \rightleftharpoons H^+ + HS^-$$
 (fast equilibrium)

$$Cl_2 + HS^- \rightarrow 2Cl^- + H^+ + S \text{ (Slow)}$$

- (b) Both A and B
- (c) Neither A nor B (d) A only

A reactant (A) from two products: [2011RS]

 $A \xrightarrow{k_1} B$ , Activation Energy  $Ea_1$ 

A  $\xrightarrow{k_2}$  C, Activation Energy  $Ea_2$ If  $Ea_2 = 2 Ea_1$ , then  $k_1$  and  $k_2$  are related as:

(a) 
$$k_2 = k_1 e^{Ea_1/RT}$$
 (b)  $k_2 = k_1 e^{Ea_2/RT}$ 

(c) 
$$k_1 = Ak_2e^{Ea_1/RT}$$
 (d)  $k_1 = 2k_2e^{Ea_2/RT}$ 

- For a first order reaction  $(A) \rightarrow \text{products the}$ concentration of A changes from 0.1 M to 0.025 M in 40 minutes.

The rate of reaction when the concentration of A is 0.01 M is:

- (a)  $1.73 \times 10^{-5}$  M/min (b)  $3.47 \times 10^{-4}$  M/min
- (c)  $3.47 \times 10^{-5}$  M/min (d)  $1.73 \times 10^{-4}$  M/min
- The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be: (R  $= 8.314 \,\mathrm{JK^{-1}} \,\mathrm{mol^{-1}} \,\mathrm{and} \,\mathrm{log} \,2 = 0.301)$  [2013]

  - (a)  $53.6 \text{ kJ mol}^{-1}$  (b)  $48.6 \text{ kJ mol}^{-1}$
  - (c)  $58.5 \text{ kJ mol}^{-1}$
- (d)  $60.5 \text{ kJ mol}^{-1}$
- For the non stoichiometric reaction  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of <i>C</i> (mol L <sup>-1</sup> s <sup>-1</sup> )		
0.1 M	0.1 M	$1.2 \times 10^{-3}$		
0.1 M	0.2 M	$1.2 \times 10^{-3}$		
0.2 M	0.1 M	$2.4 \times 10^{-3}$		

The rate law for the formation of C is: [2014]

(a) 
$$\frac{dc}{dt} = k[A][B]$$

(a) 
$$\frac{dc}{dt} = k[A][B]$$
 (b)  $\frac{dc}{dt} = k[A]^2[B]$ 

(c) 
$$\frac{dc}{dt} = k[A][B]^2$$
 (d)  $\frac{dc}{dt} = k[A]$ 

(d) 
$$\frac{dc}{dt} = k[A]$$

Higher order (>3) reactions are rare due to:

#### [JEE M 2015]

- shifting of equilibrium towards reactants due to elastic collisions
- loss of active species on collision
- (c) low probability of simultaneous collision of all the reacting species
- (d) increase in entropy and activation energy as more molecules are involved

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- 31. Decomposition of H<sub>2</sub>O<sub>2</sub> follows a first order reaction. In fifty minutes the concentration of H<sub>2</sub>O<sub>2</sub> decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H<sub>2</sub>O<sub>2</sub> reaches 0.05 M, the rate of formation of O<sub>2</sub> will be: [JEE M 2016]
  - (a)  $2.66 \, \text{L min}^{-1} \, \text{at STP}$
  - (b)  $1.34 \times 10^{-2} \text{ mol min}^{-1}$
  - (c)  $6.96 \times 10^{-2} \,\mathrm{mol \, min^{-1}}$
  - (d)  $6.93 \times 10^{-4} \, \text{mol min}^{-1}$

- **32.** Two reactions  $R_1$  and  $R_2$  have identical preexponential factors. Activation energy of  $R_1$ exceeds that of  $R_2$  by 10 kJ mol<sup>-1</sup>. If  $k_1$  and  $k_2$ are rate constants for reactions  $R_1$  and  $R_2$ respectively at 300 K, then  $ln(k_2/k_1)$  is equal to:
  - $(R = 8.314 \text{ J mol}^{-1}\text{K}^{-1})$

[JEE M 2017]

- (a) 8
- (b) 12
- (c) 6
- (d) 4

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

#### SOLUTIONS

- 1. (a) For a zero order reaction. rate  $=k[A]^{\circ}$  i.e. rate =khence unit of  $k = M.\sec^{-1}$ For a first order reaction. rate = k[A] $k = M.\sec^{-1}/M = \sec^{-1}$
- 2. (a) NOTE Order is the sum of the power of the concentrations terms in rate law expression.

Hence the order of reaction is = 1 + 2 = 3

3. (d) rate of appearance of HI =  $\frac{1}{2} \frac{d[HI]}{dt}$ 

rate of formation of  $H_2 = \frac{-d[H_2]}{dt}$ 

rate of formation of  $I_2 = \frac{-d[I_2]}{dt}$ 

hence  $\frac{-d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt}$ 

or 
$$-\frac{2d[H_2]}{dt} = -\frac{2d[I_2]}{dt} = \frac{d[HI]}{dt}$$

4. (d)  $t_{1/2} = 5$  years, T = 15 years hence total number of half life periods  $= \frac{15}{5} = 3$ .

$$\therefore \text{ Amount left} = \frac{64}{(2)^3} = 8g$$

- 5. (a) Rt =  $\log C_o \log C_t$ It is clear from the equation that if we plot a graph between  $\log C_t$  and time, a straight line with a slope equal to  $-\frac{k}{2.303}$  and intercept equal to  $\log [A_o]$  will be obtained.
- 6. **(d)**  $t_{1/2} = 3 \text{ hrs. } T = 18 \text{ hours}$  $\therefore T = n \times t_{1/2}$

$$\therefore n = \frac{18}{3} = 6$$

Initial mass  $(C_0) = 256 g$ 

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$$\therefore C_n = \frac{C_0}{2^n} = \frac{256}{(2)^6} = \frac{256}{64} = 4g.$$

- 7. **(b)** In equation  $k = Ae^{-E_a/RT}$ ; A = Frequency factor <math>k = velocity constant, R = gas constant and  $E_a = energy of activation$
- 8. **(b)** r = k [O<sub>2</sub>][NO]<sup>2</sup>. When the volume is reduced to 1/2, the conc. will double
  ∴ Newrate=k [2O<sub>2</sub>][2 NO]<sup>2</sup>=8 k [O<sup>2</sup>][NO]<sup>2</sup>
  The new rate increases to eight times of its initial.
- 9. (c) As the concentration of reactant decreases from 0.8 to 0.4 in 15 minutes hence the  $t_{1/2}$  is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.
- **10. (d)** The velocity constant depends on temperature only. It is independent of concentration of reactants.
- 11. (a)  $N_t = N_0 \left(\frac{1}{2}\right)^n$  where n is number of half life periods.

$$n = \frac{\text{Total time}}{\text{half life}} = \frac{24}{4} = 6$$

$$N_t = 200 \left(\frac{1}{2}\right)^6 = 3.125 \text{ g}.$$

**12. (d)** The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

**NOTE** The reaction involving two different reactant can never be unimolecular.

13. (d) The graph show that reaction is exothermic.

$$\log k = \frac{-\Delta H}{RT} + 1$$

For exothermic reaction  $\Delta H < 0$ 

 $\therefore$  log k Vs  $\frac{1}{T}$  would be negative straight line with positive slope.

**14.** (c) 
$$t_{1/4} = \frac{2.303}{K} \log \frac{1}{3/4} = \frac{2.303}{K} \log \frac{4}{3}$$

$$= \frac{2.303}{K} (\log 4 - \log 3)$$

$$= \frac{2.303}{K} (2 \log 2 - \log 3)$$

$$= \frac{2.303}{K} (2 \times 0.301 - 0.4771) = \frac{0.29}{K}$$

- 15. (d) Enthalpy of reaction  $(\Delta H) = E_{a_{(f)}} E_{a_{(b)}}$  for an endothermic reaction  $\Delta H = +Ve$  hence for  $\Delta H$  to be negative  $E_{a_{(b)}} < E_{a_{(f)}}$
- 16. (a) Since the reaction is 2nd order w.r.t CO. Thus, rate law is given as.  $r = k [CO]^2$ Let initial concentration of CO is a i.e. [CO] = a  $\therefore r_1 = k (a)^2 = ka^2$ when concentration becomes doubled, i.e. [CO] = 2a  $\therefore r_2 = k (2a)^2 = 4ka^2$   $\therefore r_2 = 4r_1$
- So, the rate of reaction becomes 4 times.

  17. (c) In Arrhenius equation k = A e<sup>-E/RT</sup>, E is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.
- 18. (b) (i)  $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$ (ii)  $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$ Rate law equation =  $k[NOBr_2][NO]$ But  $NOBr_2$  is intermediate and must not appear in the rate law equation

from Ist step 
$$K_C = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

 $\therefore [NOBr_2] = K_C[NO][Br_2]$ 

 $\therefore$  Rate law equation =  $k \cdot K_C [NO]^2 [Br_2]$ hence order of reaction is 2 w.r.t. NO.

19. (a)  $\Delta H_R = E_f - E_b = 180 - 200 = -20 \, kJ/mol$ The nearest correct answer given in choices may be obtained by neglecting sign.

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**20. (b)** For a first order reaction  $t_{1/2} = \frac{0.693}{K}$  i.e.

for a first order reaction  $t_{1/2}$  does not depend up on the concentration. From the given data, we can say that order of reaction with respect to B=1 because change in concentration of B does not change half life.

Order of reaction with respect to A=1 because rate of reaction doubles when concentration of B is doubled keeping concentration of A constant.

 $\therefore$  Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol<sup>-1</sup> sec<sup>-1</sup>.

21. (a) Suppose activity of safe working = A Given  $A_0 = 10A$ 

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda} log \frac{A_0}{A} = \frac{2.303}{0.693/30} log \frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

22. (b) The rates of reactions for the reaction

$$\frac{1}{2}A \longrightarrow 2B$$

can be written either as

$$-2\frac{d}{dt}[A]$$
 with respect to 'A'

or 
$$\frac{1}{2} \frac{d}{dt} [B]$$
 with respect to 'B'

From the above, we have

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

or 
$$-\frac{d}{dt}[A] = \frac{1}{4}\frac{d}{dt}[B]$$

i.e., correct answer is (b)

23. (b) For first order reaction,

$$k = \frac{2.303}{t} \log \frac{100}{100 - 99}$$

$$\frac{0.693}{6.93} = \frac{2.303}{t} \log \frac{100}{1}$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

 $t = 46.06 \, \text{min}$ 

24. (c) For the reaction  $A \rightarrow Product$  given  $t_{1/2} = 1$  hour

for a zero order reaction

$$t_{\text{completion}} = \frac{A_0}{k} = \frac{\text{initial conc.}}{\text{rate constant}}$$

$$\therefore t_{1/2} = \frac{\left[A_0\right]}{2k}$$

or 
$$k = \frac{A_0}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \text{ mol lit}^{-1} \text{ hr}^{-1}$$

Further for a zero order reaction

$$k = \frac{dx}{dt} = \frac{\text{change in concentration}}{\text{time}}$$

$$1 = \frac{0.50 - 0.25}{\text{time}}$$

 $\therefore$  time = 0.25 hr.

25. (d) Since the slow step is the rate determining step hence if we consider option (1) we find

Rate = 
$$k[Cl_2][H_2S]$$

Now if we consider option (2) we find

Rate = 
$$k[\operatorname{Cl}_2][\operatorname{HS}^-]$$
 ...(1)

From equation (i)

$$k = \frac{\left[H^{+}\right]\left[HS^{-}\right]}{H_{2}S}$$

or 
$$\left[ HS^{-} \right] = \frac{k \left[ H_{2}S \right]}{H^{+}}$$

Substituting this value in equation (1) we find

Rate = 
$$k \left[ \text{Cl}_2 \right] K \frac{\left[ \text{H}_2 \text{S} \right]}{\text{H}^+} = k' \frac{\left[ \text{Cl}_2 \right] \left[ \text{H}_2 \text{S} \right]}{\left[ \text{H}^+ \right]}$$

hence only, mechanism (1) is consistent with the given rate equation.

**26.** (c) 
$$k_1 = A_1 e^{-Ea_1/RT}$$
 .....(i)

$$k_2 = A_2 e^{-Ea_2/RT}$$
 .....(ii)

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On dividing eqn (i) from eqn. (ii)

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} (E_{a_1} - E_{a_1}) / RT$$
(iii)

Given  $Ea_2 = 2Ea_1$ 

On substituting this value in eqn. (iii)

$$k_1 = k_2 A \times e^{Ea_1/RT}$$

27. (b) For a first order reaction

$$k = \frac{2.0303}{t} \log \frac{a}{a - x} = \frac{2.303}{40} \log \frac{0.1}{0.025}$$
$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6020}{40}$$
$$= 3.47 \times 10^{-2}$$

= 
$$3.47 \times 10$$
  
R =  $k(A)^1 = 3.47 \times 10^{-2} \times 0.01$   
=  $3.47 \times 10^{-4}$ 

**28.** (a) Activation energy can be calculated from the equation

$$\frac{\log k_2}{\log k_1} = \frac{-E_a}{2.303R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Given 
$$\frac{k_2}{k_1} = 2$$
;  $T_2 = 310 \text{ K}$ ;  $T_1 = 300 \text{ K}$ 

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

$$E_a = 53598.6 \text{ J/mol} = 53.6 \text{ kJ/mol}.$$

**29.** (d) Let rate of reaction =  $\frac{d[C]}{t} = k[A]^x [B]^y$ 

Now from the given data

$$1.2 \times 10^{-3} = k [0.1]^{x} [0.1]^{y}$$
 .....(i)

$$1.2 \times 10^{-3} = k [0.1]^{x} [0.2]^{y}$$
 ....(ii)

$$2.4 \times 10^{-3} = k [0.2]^{x} [0.1]^{y}$$
 .....(iii)

Dividing equation (i) by (ii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x [0.1]^y}{k[0.1]^x [0.2]^y}$$

We find, v = 0

Now dividing equation (i) by (iii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k[0.1]^x [0.1]^y}{k[0.2]^x [0.1]^y}$$

We find, x = 1

Hence 
$$\frac{d[C]}{dt} = k[A]^1[B]^0$$

**30. (c)** Reactions of higher order (>3) are very rare due to very less chances of many molecules to undergo effective collisions.

**31. (d)** 
$$H_2O_2(aq) \rightarrow H_2O(aq) + \frac{1}{2}O_2(g)$$

For a first order reaction

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

Given a = 0.5, (a - x) = 0.125, t = 50 min

$$k = \frac{2.303}{50} \log \frac{0.5}{0.125}$$

$$= 2.78 \times 10^{-2} \text{ min}^{-1}$$

$$r = k[H_2O_2] = 2.78 \times 10^{-2} \times 0.05$$

$$= 1.386 \times 10^{-3} \text{ mol min}^{-1}$$

Now

$$-\frac{d\big[H_2O_2\big]}{dt} = \frac{d\big[H_2O\big]}{dt} = \frac{2d\big[O_2\big]}{dt}$$

$$\therefore \frac{2d[O_2]}{dt} = -\frac{d[H_2O_2]}{dt}$$

$$\therefore \frac{d[O_2]}{dt} = \frac{1}{2} \times \frac{d[H_2O_2]}{dt}$$

$$= \frac{1.386 \times 10^{-3}}{2} = 6.93 \times 10^{-4} \,\text{mol min}^{-1}$$

**32.** (d) From arrhenius equation,

$$k = A.e^{\frac{-Ea}{RT}}$$

so, 
$$k_1 = A.e^{-E_{a_1}/RT}$$
 ....(1)

$$k_2 = A.e^{-E_{a_2}/RT}$$
 .....(2)

On dividing equation (2) (1)

$$\Rightarrow \frac{k_2}{k_1} = e^{\frac{(E_{a_1} - E_{a_2})}{RT}}$$

$$ln\left(\frac{k_2}{k_1}\right) = \frac{E_{a_1} - E_{a_2}}{RT} = \frac{10,000}{8.314 \times 300} = 4$$

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