Doon Public School, Bhuj

Holiday Homework

Dear Students,

“The hardest part of remote learning is that we aren’t together. We want our students to know that even though we aren’t together, you are still very much cared and everything we do is for you.” It is now the time to take this task on as a lesson in space management, time management, and self-management. It is also time to embrace technology, make judicious use of it to plan and prepare for your academics.

This is your Holiday Homework which must be written in fair chemistry notebook. Make this time absolutely useful for you.

Class-XII **Subject-Chemistry**

Chapter-4 Chemical Kinetics

1. For a first order reaction A → B the rate constant is x min^{-1} . If the initial concentration of A is 0.01M , the concentration of A after one hour is given by the expression.

a) $0.01\ e^{-x}$

b) $1\ \times 10^{-2}\ (1-e^{-60x})$

(c) $(1\times 10^{-2})\ e^{-60x}$

d) none of these

Solution

option (c)

$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$k=\left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$$e^{kt}=\left(\frac{[A_0]}{[A]}\right)$$

$$[A]=[A_0]e^{-kt}$$

In this case

$k = x\ \text{min}^{-1}$ and $[A_0] = 0.01\text{M} = 1 \times 10^{-2}\text{M}$

t = 1 hour = 60 min

$[A]= 1 \times 10^{-2}\ (\ e^{-60x})$

2. A zero order reaction X →Product , with an initial concentration 0.02M has a half life of 10 min. if one starts with concentration 0.04M, then the half life is

a) 10 s
b) 5 min
c) 20 min
d) cannot be predicted using the given information

Solution

option (c)

for $n \neq 1$ $\quad t_{1/2} = \dfrac{2^{n-1}-1}{(n-1)\,k\,[A_0]^{n-1}}$

for $n = 0$ $\quad t_{1/2} = \dfrac{1}{2\,k\,[A_0]^{-1}}$

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

$$t_{1/2} \; \alpha \; [A_0] \text{———} (1)$$

given

$[A_0] = 0.02M$; $t_{1/2} = 10\,min$

$[A_0] = 0.04M$; $t_{1/2} = ?$

substitute in (1)

$10\ min\ \alpha\ 0.02M$ ——— (2)

$t_{1/2}\ \alpha\ 0.04M$ ——— (3)

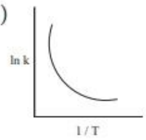
$(3)/(2)$

$$\Rightarrow \frac{t_{1/2}}{10\,min} = \frac{0.04\ M}{0.02\ M}$$

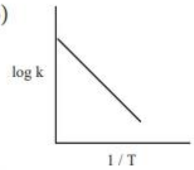
$$t_{1/2} = 2 \times 10\,min = 20\,min$$

3. Among the following graphs showing variation of rate constant with temperature (T) for a reaction, the one that exhibits Arrhenius behavior over the entire temperature range is

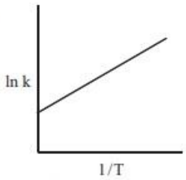
a)



b)



c)



d) both (b) and (c)

d) both (b) and (c)

Ans: (b)

Solution

$k = A\, e^{-(Ea/RT)}$

$\ln k = \ln A - (E_a/R)\ (1/T)$

this equation is in the form of a straight line equatoion

$y = c + m\,x$

a plot of lnk vs 1/T is a straight line with negative slope

4. For a first order reaction A → product with initial concentration x mol L^{-1} , has a half life period of 2.5 hours . For the same reaction with initial concentration (x/2) mol L^{-1} the half life is

a) (2.5 × 2) hours

b) (2.5 / 2) hours

c) 2.5 hours

d) Without knowing the rate constant, $t_{1/2}$ cannot be determined from the given data

Solution

For a first order reaction

$t_{1/2} = 0.693/k$

$t_{1/2}$ does not depend on the initial concentration and it remains constant (whatever may be the initial concentration)

$t_{1/2}$ = 2.5 hrs

5. For the reaction, $2NH_3 \rightarrow N_2 + 3H_2$

, if $\frac{-d[NH_3]}{dt} = k_1[NH_3]$,

$\frac{d[N_2]}{dt} = k_2[NH_3]$, $\frac{d[H_2]}{dt} = k_3[NH_3]$

then the relation between k_1, k_2 and k_3 is

a) $k_1 = k_2 = k_3$

b) $k_1 = 3k_2 = 2k_3$

c) 1.5 $k_1 = 3\ k_2 = k_3$

d) 2 $k_1 = k_2 = 3\ k_3$

Solution

$$Rate = \left(\frac{-1}{2}\right)\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \left(\frac{1}{3}\right)\frac{d[H_2]}{dt}$$

$$\left(\frac{1}{2}\right)k_1[NH_3] = k_2[NH_3] = \left(\frac{1}{3}\right)k_3[NH_3]$$

$$\left(\frac{3}{2}\right)k_1 = 3k_2 = k_3$$

$(3/2)k_1 = 3k_2 = k_3$

$1.5\ k_1 = 3k_2 = k_3$

6. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the

a) rate is proportional to the surface coverage

b) rate is inversely proportional to the surface coverage

c) rate is independent of the surface coverage

d) rate of decomposition is slow

Solution

At low pressure the reaction follows first order, therefore

Rate α $[reactant]^1$

Rate α (surface area)

At high pressure due to the complete coverage of surface area, the reaction follows zero order.

Rate α$[reactant]^0$

Therefore the rate is independent of surface area.

7. For a reaction Rate = k$[acetone]^{3/2}$ acetone then unit of rate constant and rate of reaction respectively is

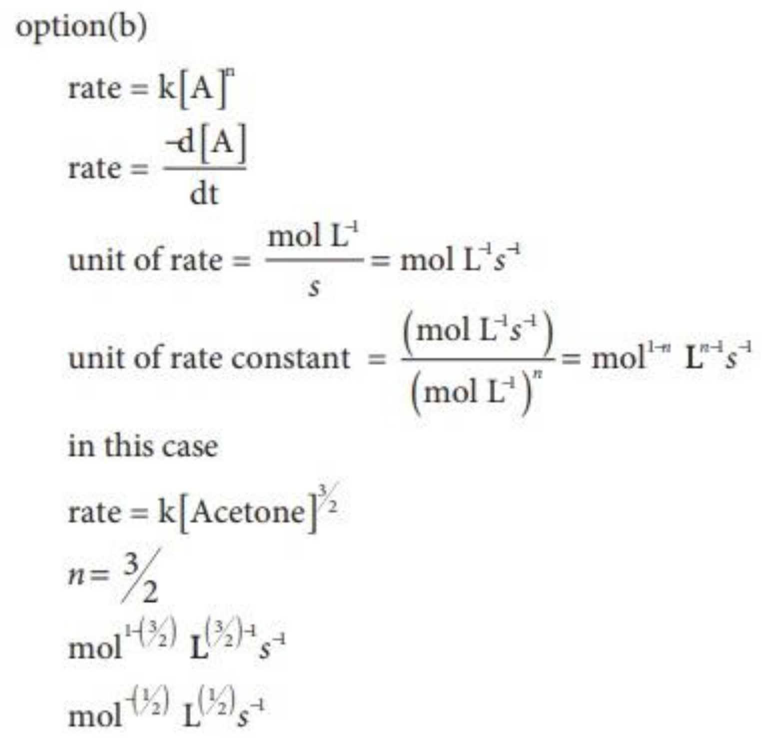
a) (mol $L^{-1}s^{-1}$), ($mol^{-1/2}\ L^{1/2}\ s^{-1}$)

b) ($mol^{-1/2}\ L^{1/2}s^{-1}$), (mol $L^{-1}\ s^{-1}$)

c) ($mol^{1/2}\ L^{1/2}s^{-1}$), (mol $L^{-1}\ s^{-1}$)

d) (mol Ls^{-1}), ($mol^{1/2}$ $L^{1/2}$ s^{-1})

Solution



option(b)

$$\text{rate} = k[A]^n$$

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

$$\text{unit of rate} = \frac{\text{mol } L^{-1}}{s} = \text{mol } L^{-1}s^{-1}$$

$$\text{unit of rate constant} = \frac{(\text{mol } L^{-1}s^{-1})}{(\text{mol } L^{-1})^n} = \text{mol}^{1-n}\ L^{n-1}s^{-1}$$

in this case

$$\text{rate} = k[\text{Acetone}]^{3/2}$$

$$n = 3/2$$

$$\text{mol}^{1-(3/2)}\ L^{(3/2)-1}s^{-1}$$

$$\text{mol}^{-(1/2)}\ L^{(1/2)}s^{-1}$$

8. The addition of a catalyst during a chemical reaction alters which of the following quantities?

a) Enthalpy

b) Activation energy

c) Entropy

d) Internal energy

Solution

A catalyst provides a new path to the reaction with low activation energy. i.e., it lowers the activation energy.

9. Consider the following statements :

(i) increase in concentration of the reactant increases the rate of a zero order reaction.

(ii) rate constant k is equal to collision frequency A if $E_a = 0$

(iii) rate constant k is equal to collision frequency A if E_a = °

(iv) a plot of ln(k) vs T is a straight line

(v) a plot of ln (k) vs 1/T is a straight line with a positive slope.

Correct statements are

a) (ii) only

b) (ii) and (iv)

c) (ii) and (v)

d) (i), (ii) and (v)

Solution

In zero order reactions, increase in the concentration of reactant does not alter the rate. So statement (i) is wrong.

$k = A\ e^{-(Ea/RT)}$

if Ea = 0 so, statement (ii) is correct, and statement (iii) is wrong

$k = A\ e^{0}$

$k = A$

$\ln k = \ln A - (E_a / R)\ (1/\ T)$

this equation is in the form of a straight line equatoion

$y = c + m\ x$

a plot of lnk vs 1/T is a straight line with negative slope

so statements (iv) and (v) are wrong.

10. In a reversible reaction, the enthalpy change and the activation energy in the forward direction are respectively $-x$ kJ mol^{-1} and y kJ mol^{-1} . Therefore , the energy of activation in the backward direction is

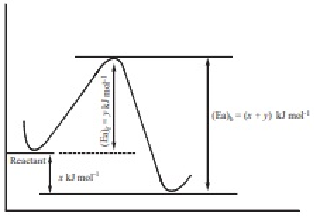
a) ($y - x$) kJ mol^{-1}

b) ($x + y$)J mol^{-1}

c) ($x - y$) kJ mol^{-1}

d) ($x + y$) × 10^3 J mol^{-1}

Solution



(x+y) kJmol^{-1}

(x+y) 10^3 $Jmol^{-1}$

11. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 200K to 400K? (R = 8.314 $JK^{-1}mol^{-1}$)

a) 234.65 kJ $mol^{-1}K^{-1}$

b) 434.65 kJ $mol^{-1}K^{-1}$

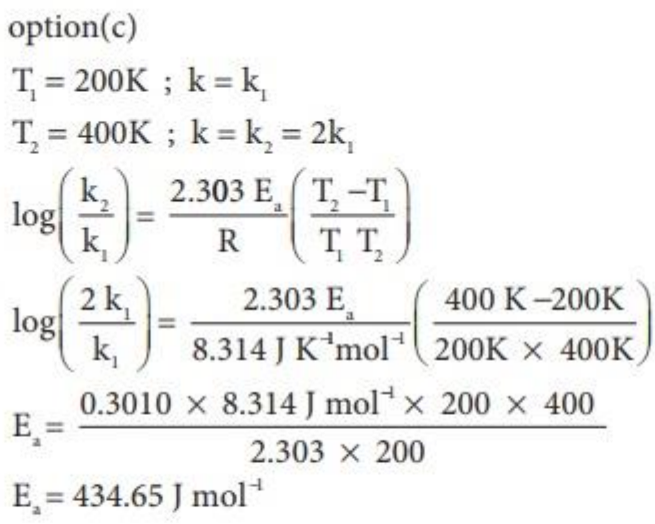
c) 434.65 J $mol^{-1}K^{-1}$

d) 334.65 J $mol^{-1}K^{-1}$

Solution

T_1 = 200K ; k = k_1

T_2 = 400K ; k = k_2 = $2k_1$



option(c)

$T_1 = 200K \;;\; k = k_1$

$T_2 = 400K \;;\; k = k_2 = 2k_1$

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

$$\log\left(\frac{2\,k_1}{k_1}\right) = \frac{2.303\, E_a}{8.314\ J\ K^{-1} mol^{-1}}\left(\frac{400\ K - 200K}{200K \times 400K}\right)$$

$$E_a = \frac{0.3010 \times 8.314\ J\ mol^{-1} \times 200 \times 400}{2.303 \times 200}$$

$E_a = 434.65\ J\ mol^{-1}$

12.  ; This reaction follows first order kinetics. The rate constant at particular temperature is 2.303×10^{-2} $hour^{-1}$. The initial concentration of cyclopropane is 0.25M. What will be the concentration of cyclopropane after 1806 minutes? (log 2 = 0.3010)

a) 0.125M

b) 0.215M

c) 0.25 × 2.303M

d) 0.05M

Solution

option(b)

$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$2.303\times10^{-2}\ \text{hour}^{-1}=\left(\frac{2.303}{1806\ \text{min}}\right)\log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{2.303\times10^{-2}\ \text{hour}^{-1}\times1806\ \text{min}}{2.303}\right)=\log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{1806\ \times10^{-2}}{60}\right)=\log\left(\frac{0.25}{[A]}\right)$$

$$0.301=\log\left(\frac{0.25}{[A]}\right)$$

$$\log 2=\log\left(\frac{0.25}{[A]}\right)$$

$$2=\left(\frac{0.25}{[A]}\right)$$

$$[A]=\left(\frac{0.25}{2}\right)=0.125\text{M}$$

13. For a first order reaction, the rate constant is 6.909 min^{-1}.the time taken for 75% conversion in minutes is

a) $\left(\frac{3}{2}\right)\log 2$ b) $\left(\frac{2}{3}\right)\log 2$

c) $\left(\frac{3}{2}\right)\log\left(\frac{3}{4}\right)$ d) $\left(\frac{2}{3}\right)\log\left(\frac{4}{3}\right)$

Ans: (b)

Solution

option(b)

$$k=\left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$[A_0]=100\ ;\ [A]=25$$

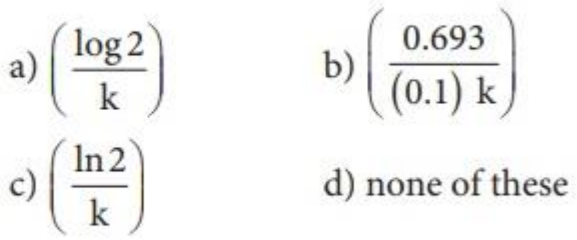
$$6.909=\left(\frac{2.303}{t}\right)\log\left(\frac{100}{25}\right)$$

$$t=\left(\frac{2.303}{6.909}\right)\log(4)$$

$$t=\left(\frac{1}{3}\right)\log 2^2$$

$$t=\left(\frac{2}{3}\right)\log 2$$

14. In a first order reaction $x \rightarrow y$; if k is the rate constant and the initial concentration of the reactant x is 0.1M, then, the half life is



a) $\left(\frac{\log 2}{k}\right)$

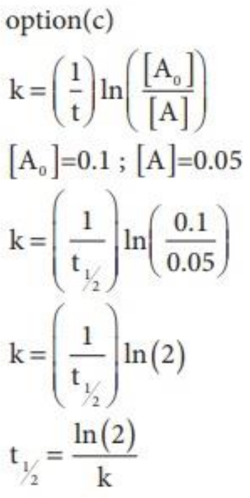
b) $\left(\frac{0.693}{(0.1)\,k}\right)$

c) $\left(\frac{\ln 2}{k}\right)$

d) none of these

Ans: (c)

Solution



option(c)

$$k = \left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$[A_0]=0.1$; $[A]=0.05$

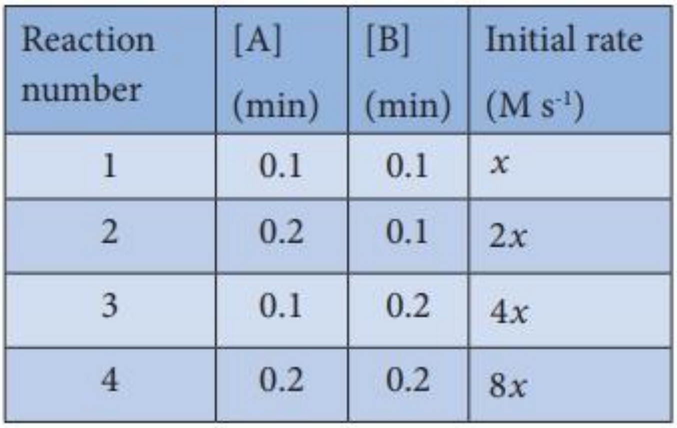
$$k = \left(\frac{1}{t_{1/2}}\right)\ln\left(\frac{0.1}{0.05}\right)$$

$$k = \left(\frac{1}{t_{1/2}}\right)\ln(2)$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

15. Predict the rate law of the following reaction based on the data given below

$2A + B \rightarrow C + 3D$



Reaction number	[A] (min)	[B] (min)	Initial rate (M s^{-1})
1	0.1	0.1	x
2	0.2	0.1	$2x$
3	0.1	0.2	$4x$
4	0.2	0.2	$8x$

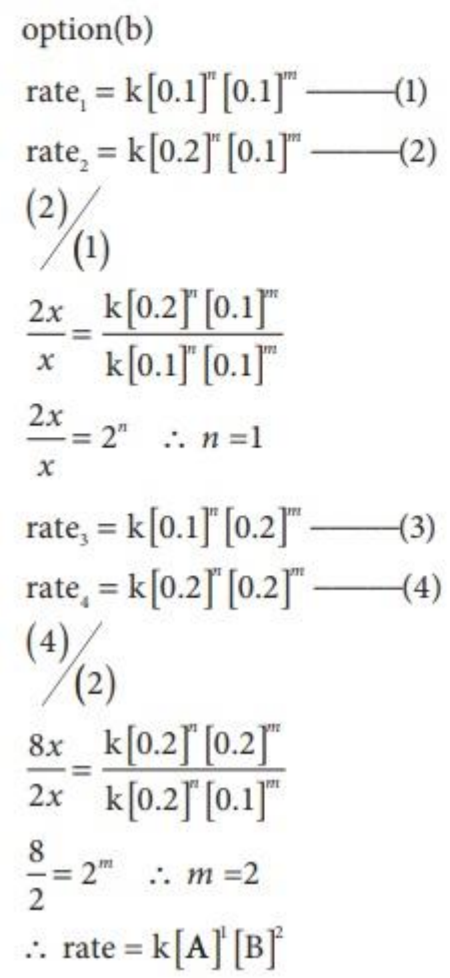
a) rate = k [A]^2 [B]

b) rate = k [A][B]^2

c) rate = k [A][B]

d) rate = k [A]$^{1/2}$ [B]$^{3/2}$

Solution



option(b)

$$\text{rate}_1 = k[0.1]^n[0.1]^m \text{———}(1)$$

$$\text{rate}_2 = k[0.2]^n[0.1]^m \text{———}(2)$$

$$(2)/(1)$$

$$\frac{2x}{x} = \frac{k[0.2]^n[0.1]^m}{k[0.1]^n[0.1]^m}$$

$$\frac{2x}{x} = 2^n \quad \therefore\ n = 1$$

$$\text{rate}_3 = k[0.1]^n[0.2]^m \text{———}(3)$$

$$\text{rate}_4 = k[0.2]^n[0.2]^m \text{———}(4)$$

$$(4)/(2)$$

$$\frac{8x}{2x} = \frac{k[0.2]^n[0.2]^m}{k[0.2]^n[0.1]^m}$$

$$\frac{8}{2} = 2^m \quad \therefore\ m = 2$$

$$\therefore\ \text{rate} = k[A]^1[B]^2$$

16. Assertion: rate of reaction doubles when the concentration of the reactant is doubles if it is a first order reaction.

Reason: rate constant also doubles

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false.

Solution

For a first reaction, If the concentration of reactant is doubled, then the rate of reaction also doubled.

Rate constant is independent of concentration and is a constant at a constant temperature,

17. The rate constant of a reaction is 5.8 × 10^{-2} s^{-1} . The order of the reaction is

a) First order

b) zero order

c) Second order

d) Third order

Solution

The unit of rate constant is s-1 and it indicates that the reaction is first order.

18. For the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.5×10^{-2} mol L^{-1} s^{-1}. The rate of formation of NO_2 and O_2 is given respectively as

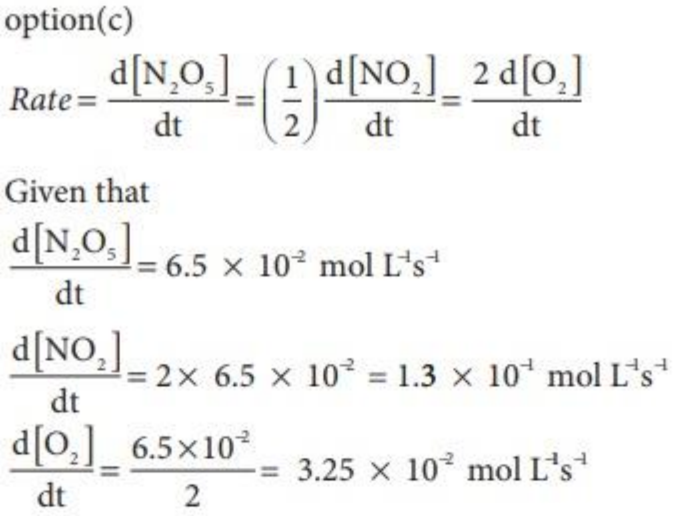
a) (3.25×10^{-2} mol $L^{-1}s^{-1}$) and (1.3×10^{-2} mol $L^{-1}s^{-1}$)

b) (1.3×10^{-2} mol $L^{-1}s^{-1}$) and (3.25×10^{-2} mol $L^{-1}s^{-1}$)

c) (1.3×10^{-1} mol $L^{-1}s^{-1}$) and (3.25×10^{-2} mol $L^{-1}s^{-1}$)

d) None of these

Solution



option(c)

$$Rate = \frac{d[N_2O_5]}{dt} = \left(\frac{1}{2}\right)\frac{d[NO_2]}{dt} = \frac{2\,d[O_2]}{dt}$$

Given that

$$\frac{d[N_2O_5]}{dt} = 6.5 \times 10^{-2} \text{ mol } L^{-1}s^{-1}$$

$$\frac{d[NO_2]}{dt} = 2 \times 6.5 \times 10^{-2} = 1.3 \times 10^{-1} \text{ mol } L^{-1}s^{-1}$$

$$\frac{d[O_2]}{dt} = \frac{6.5 \times 10^{-2}}{2} = 3.25 \times 10^{-2} \text{ mol } L^{-1}s^{-1}$$

19. During the decomposition of H_2O_2 to give dioxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is

a) 0.75 mol min^{-1}

b) 1.5 mol min^{-1}

c) 2.25 mol min^{-1}

d) 3.0 mol min^{-1}

Solution

option(d)

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

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

no of moles of oxygen = (48/32) = 1.5 mol

∴ rate of formation of oxygen = 2 ×1.5 = 3 mol min^{-1}

20. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

a) Zero

b) one

c) Fraction

d) none

Solution

For a first order reaction $t_{1/2}$ is independent of initial concentration .i.e., ∴ $n \neq 1$; for such cases

$$t_{1/2} \;\alpha\; \frac{1}{[A_0]^{n-1}} \quad \text{-------} \; (1)$$

If $[A_0] = 2[A_0]$; then $t_{1/2} = 2t_{1/2}$

$$2\,t_{1/2} \;\alpha\; \frac{1}{[2\,A_0]^{n-1}} \quad \text{------} \; (2)$$

$$\frac{(2)}{(1)} \Rightarrow$$

$$2 = \frac{1}{[2A_0]^{n-1}} \times \frac{[A_0]^{n-1}}{1}$$

$$2 = \frac{[A_0]^{n-1}}{[2A_0]^{n-1}}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$2 = \left(2^{-1}\right)^{n-1}$$

$$2^1 = \left(2^{-n+1}\right)$$

$$n = 0$$

21. In a homogeneous reaction A →B + C + D , the initial pressure was P_0 and after time t it was P. expression for rate constant in terms of P_0, P and t will be

a) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0 - P}\right)$

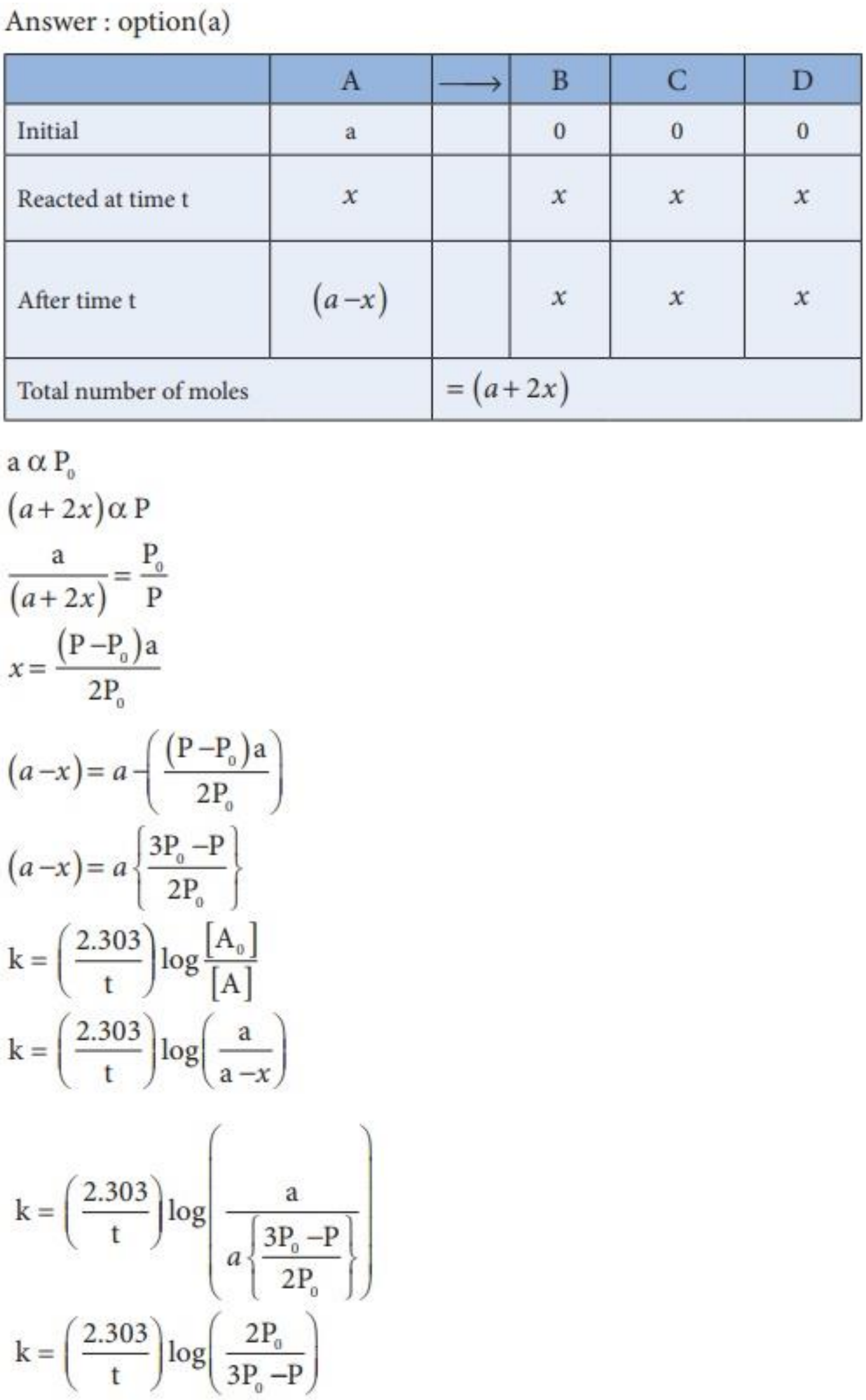
b) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{P_0 - P}\right)$

c) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{3P_0 - P}{2P_0}\right)$

d) $k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0 - 2P}\right)$

Ans: (a)

Solution



Answer : option(a)

	A	$\longrightarrow$	B	C	D
Initial	a		0	0	0
Reacted at time t	x		x	x	x
After time t	$(a-x)$		x	x	x
Total number of moles		$=(a+2x)$			

$$a \propto P_0$$

$$(a+2x) \propto P$$

$$\frac{a}{(a+2x)} = \frac{P_0}{P}$$

$$x = \frac{(P-P_0)a}{2P_0}$$

$$(a-x) = a - \left(\frac{(P-P_0)a}{2P_0}\right)$$

$$(a-x) = a\left\{\frac{3P_0-P}{2P_0}\right\}$$

$$k = \left(\frac{2.303}{t}\right)\log\frac{[A_0]}{[A]}$$

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

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{a}{a\left\{\frac{3P_0-P}{2P_0}\right\}}\right)$$

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0-P}\right)$$

22. If 75% of a first order reaction was completed in 60 minutes , 50% of the same reaction under the same conditions would be completed in

a) 20 minutes

b) 30 minutes

c) 35 minutes

d) 75 minutes

Solution

$t_{75\%} = 2t_{50\%}$

$t_{50\%} = (t_{75\%} / 2) = (60/2) = 30$ min

23. The half life period of a radioactive element is 140 days. After 560 days , 1 g of element will be reduced to

a) (1/2)g

b) (1/4)g

c) (1/8)g

d) (1/16)g

Solution

In 140 days ⟹ initial concentration reduced to (1/2)g

In 280 days ⟹ initial concentration reduced to (1/4)g

In 420 days ⟹ initial concentration reduced to (1/8)g

In 560 days ⟹ initial concentration reduced to (1/16)g

24. The correct difference between first and second order reactions is that

a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.

b) The half life of a first order reaction does not depend on $[A_0]$; the half life of a second order reaction does depend on $[A_0]$.

c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.

d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.

Solution

For a first order reaction

$t_{1/2} = 0.6932/k$

For a second order reaction

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)\,k\,[A_0]^{n-1}}$$

$$n = 2$$

$$t_{1/2} = \frac{2^{2-1}-1}{(2-1)\,k\,[A_0]^{2-1}}$$

$$t_{1/2} = \frac{1}{k\,[A_0]}$$

25. After 2 hours, a radioactive substance becomes $(1/16)^{th}$ of original amount. Then the half life (in min) is

a) 60 minutes

b) 120 minutes

c) 30 minutes

d) 15 minutes

Solution

Answer : option(c)

$$1 \xrightarrow{t_{1/2}} \left(\frac{1}{2}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{4}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{8}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{16}\right)$$

$4t_{1/2}$ = 2 hours

$t_{1/2}$ = 30 min

Very Short Type Questions(1 Mark)

1. Express the rate of the following reaction in terms of the formation of ammonia.

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Solution . $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$$\frac{d[N_2]}{dt} = \frac{d[H_2]^3}{dt} = \frac{d[NH_3]^2}{dt}$$

2. Define elementary step in a reaction.

Solutions: Elementary step : Each step of a complex reaction is called an elementary step.

3. Why does the rate of a reaction not remain constant throughout the reaction process?

Solution:The rate of a reaction does not remain constant throughout the reaction process because the rate of the reaction depends upon concentration of reactants which keeps on decreasing.

4. Define the half-life period of reaction (t½).

Solution: The time taken for half of the reaction to complete, i.e., the time in which the concentration of a reactant is reduced to half of its original value Is called half-life period of the reaction.

When $t = t_{1/2}$ $[R] = [R_0]/2$

5. If half-life period of a first order reaction is x and 3/4th life period of the same reaction is y, how are x and y related to each other?

Solution: For a First order reaction, $k = \frac{0.693}{t1/2} = \frac{0.693}{x}$

For ¾ th life of a period $a = a$

$$a - x = a - \frac{3}{4a} = \frac{1}{4a}$$

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

$$\frac{0.693}{x} = \frac{2.303}{y}\log\frac{a}{\frac{a}{4}}$$

$$\frac{0.693}{x} = \frac{2.303}{y}2log2$$

$$\frac{0.693}{x} = \frac{0.693\ \times 2}{y}$$

$$y = 2x$$

6. Define the following term : Pseudo first order reaction (1/2, Delhi 2014)

Solution: A reaction of second order which obeys the first order rate law is known as pseudo first order

reaction.

e.g., Inversion of cane sugar :

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Rate=$k[C_{12}H_{22}O_{11}]^1 [H_2O]^0$

7. Define rate law and rate constant.

Solution: Rate Law is the mathematical expression based on the experimental fact , which describes the reactions rate in terms of concentrations of reacting species. It can not be written in form of a balanced chemical equation.

Rate constant is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

8. The rate of formation of a dimer in a second order reaction is 7.5×10^{-3} mol $L^{-1}s^{-1}$ at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant.

Solution

Let us consider the dimerisation of a monomer M

$2M \rightarrow (M)_2$

Rate= $k [M]^n$

Given that n=2 and $[M] = 0.05$ mol L^{-1}

Rate = 7.5×10^{-3} mol $L^{-1}s^{-1}$

$k = Rate/[M]^n$

$k = 7.5x10^{-3}/(0.05)^2 = 3mol^{-1}Ls^{-1}$

9. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s^{-1}.

Solution

$$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

$$k = \frac{2.303}{1 \min} \log \frac{[0.08]}{[0.04]}$$

$$k = 2.303 \log 2$$

$$k = 2.303 \times 0.3010$$

$$k = 0.6932 \min^{-1}$$

$$k = \left(\frac{0.6932}{60} \right) s^{-1}$$

$$k = 1.153 \times 10^{-2} \ s^{-1}$$

10. A gas phase reaction has energy of activation 200 kJ mol^{-1}. If the frequency factor of the reaction is 1.6×10^{13} s^{-1} Calculate the rate constant at 600 K. ($e^{-40.09} = 3.8 \times 10^{-18}$)

Solution

$$k = A\, e^{-\left(\frac{E_a}{RT}\right)}$$

$$k = 1.6 \ \times 10^{13} s^{-1} e^{-\left(\frac{200 \times 103 \text{ J mol}^{-1}}{8.314 \text{JK}^{-1} \text{mol}^{-1} \times 600 \text{K}}\right)}$$

$$k = 1.6 \ \times 10^{13} s^{-1} \ e^{-(40.1)}$$

$$k = 1.6 \ \times 10^{13} s^{-1} \times 3.8 \times 10^{-18}$$

$$k = 6.21 \times 10^{-5} s^{-1}$$

11. Is rate of reaction always constant?

Ans. No. rate of a reaction is not always constant. It depends on many factors such as

concentration, temperature etc.

12. Can order of reaction be zero? Give example.

Ans. Yes, decomposition of ammonia on a hot platinum surface is a zero order of reaction at high pressure.

13. What do you understand by rate law expression?

Ans. The rate law is the expression in which rate is given in terms of molar concentration of reactants with each term raised to some power ,which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

14. Is it possible to determine or predict the rate law theoretically by merely looking at the equation?

Ans. No, the rate law can not be predicted by merely looking at the balanced chemical equation but must be determined experimentally.

15. Define the term chemical kinetics?

Ans. The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical Kinetics.

16. Define – Rate of reaction and the factors affecting the rate of reaction.

Ans. Rate of reaction can be defined as the change in concentration of a reactant or product per unit time. Factors affecting the rate of reaction are temperature, concentration of

17. What is average rate of a reaction? How is it determined?

Ans. Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration of reactant or product by the time interval

For the reaction: A B av = $Rav = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

18. What are the units of rate of a reaction?

Ans. The units of rate of a reaction are Mol $L^{-1}s^{-1}$. In gaseous reaction the unit of rate of reaction is atom s^{-1}.

19. Identify the reaction order for from each of the following rate constant –

a) k= $2.3 \times 10^{-5} Lmol^{-1}s^{-1}$

b)k= 3.1×10^{-4} s^{-1}

Ans. a) Since the units of rate constant are $Lmol^{-1}s^{-1}$ The reactions is of second order.

b) Since the units of rate constant is s^{-1}The reaction is of first order.

20. Consider the equation The rate law for $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

this equation is first order with respect to and second order with respect to NO. write the rate law for this reaction.

Solution: the rate law for this equation will be $R=K[NO]^2\,[H_2]$

Short Type I (2 Mark)

1. Define the terms – i) Order of a reaction ii) Molecularity of a reaction.

Ans. i) Order of a reaction.

The sum of powers of the concentration of the reactants in the rate law expression is called order of that reaction.

ii) Molecularity of a reaction.

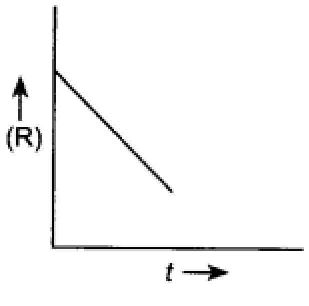
The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

2. What are elementary and complex reactions?

Ans. The reactions taking place in one step are called elementary reactions whereas when a sequence of elementary reactions, called mechanism , gives us the product , it is called

complex reaction.

3. For a chemical reaction R —> P, the variation in the concentration (R) vs.



(i) Predict the order of the reaction.

(ii) What is the slope of the curve?

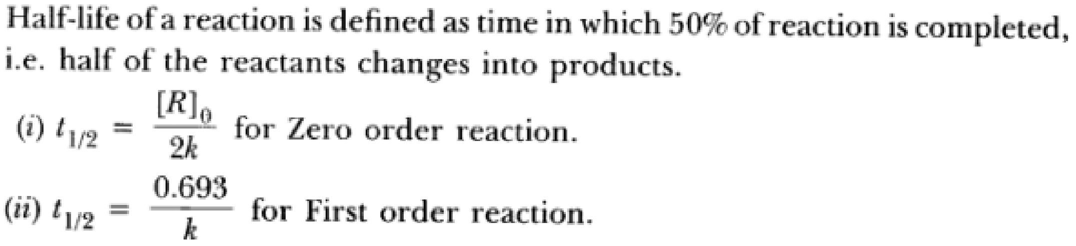
Answer :

(a)Zero order reaction

(b) slope = -k

4. Define half-life of a reaction. Write the expression of half-life for
(i) zero order reaction and (ii) first order reaction

Answer :



Half-life of a reaction is defined as time in which 50% of reaction is completed, i.e. half of the reactants changes into products.

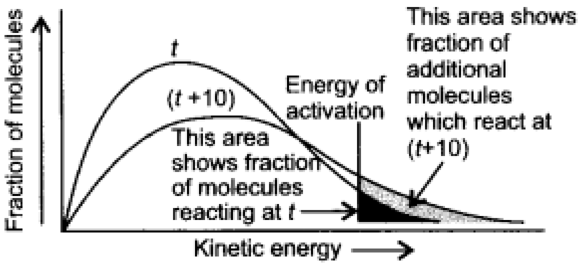
(i) $t_{1/2} = \frac{[R]_0}{2k}$ for Zero order reaction.

(ii) $t_{1/2} = \frac{0.693}{k}$ for First order reaction.

5. How does change in temperature affect the rate of reaction? How can this effect the rate constant of the reaction represented quantitatively

Answer :

Rate of reaction increases with increase in temperature. The rate of reaction nearly doubles with 10° rise in temperature as shown in following diagram



Distribution curve showing temperature dependence of a rate of reaction.

Short Type II (3 Marks)

1. The following data were obtained during the first order thermal decomposition of S02Cl2 at a constant volume: Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010)

Solution

$$\begin{aligned} k &= \frac{2.303}{t}\log\frac{[R]_0}{[R]} \\ &= \frac{2.303}{t}\log\frac{p_i}{p_i - x} \\ &= \frac{2.303}{t}\log\frac{p_i}{p_i - p_t + p_i} \\ &= \frac{2.303}{t}\log\frac{p_i}{2p_i - p_t} \\ &= \frac{2.303}{100}\log\frac{0.4}{2\times 0.4 - 0.7} \end{aligned}$$

$$\boxed{\begin{array}{l} \begin{array}{cccc} SO_2Cl_2(g) & \longrightarrow SO_2(g) & + & Cl_2(g) \\ p_i & 0 & & 0 \\ p_i - x & x & & x \end{array} \\ p_t = p_i - x + x + x = p_i + x \\ \boxed{x = p_t - p_i} \\ \text{where } p_i = \text{initial pressure} \\ \quad p_i - x = \text{final pressure} \\ \quad p_t = \text{total pressure} \end{array}}$$

$$\Rightarrow \quad k = \frac{2.303}{100}\log\frac{0.4}{0.8 - 0.7} = \frac{2.303}{100}\log 4$$

$$\Rightarrow \quad k = \frac{2.303 \times 0.6021}{100} = \frac{1.386}{100\,\text{s}}$$

$$\Rightarrow \quad k = 1.386 \times 10^{-2}\ \text{s}^{-1}$$

2. (a) For a reaction A + B —> P, the rate law is given by $r = k[A]^{1/2}\ [A]^2$

What is the order of this reaction?

(b) A first order reaction is found to have a rate constant k = 5.5 X 10-14 s-1. Find the half life of the reaction.

Answer :

(*a*) Order of reaction $= \frac{1}{2} + 2 = 2\frac{1}{2}$ or 2.5

(*b*) For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}\,\text{s}^{-1}} = 0.126 \times 10^{14}\ \text{s} = 1.26 \times 10^{13}\ \text{s}$$

3. For a reaction $x + y + z \rightarrow$products the rate law is given by rate = k $[x]^{3/2}\,[y]^{1/2}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.

Solution

$$\text{rate} = k[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$$

$$\text{overall order} = \left(\frac{3}{2} + \frac{1}{2}\right) = 2$$

i.e., second order reaction.

Since the rate expression does not contain the concentration of z , the reaction is zero order with respect to z.

4. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?

Solution

We know that, $k = 0.693/ t_{1/2}$

$k = 0.693/ 8.0$ minutes= 0.087 minutes^{-1}

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.087\ \text{min}^{-1}} \log\left(\frac{100}{1}\right)$$

$$t = 52.93\,\text{min}$$

5. The activation energy of a reaction is 225 k Cal mol^{-1} and the value of rate constant at 40°C is $1.8 \times 10^{-5}\ s^{-1}$. Calculate the frequency factor, A.

Solution

Here, we are given that

$E_a = 22.5$ kcal mol^{-1} = 22500 cal mol^{-1}

T = 40°C = 40 + 273 = 313 K

$k = 1.8 \times 10^{-5}\ \text{sec}^{-1}$

Substituting the values in the equation

$$\log A = \log k + \left(\frac{E_a}{2.303RT}\right)$$

$$\log A = \log\left(1.8 \times 10^{-5}\right) + \left(\frac{22500}{2.303 \times 1.987 \times 313}\right)$$

log A = log (1.8) −5 + (15.7089)

log A = 10.9642

A = antilog (10.9642)

$A = 9.208 \times 10^{10}$ collisions s^{-1}

<u>Long Type (5 Marks)</u>

1. The rate law for a reaction of A, B and C has been found to be rate = $k\,[A]^2\,[B][L]^{3/2}$.How would the rate of reaction change when

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

(i) Concentration of [L] is quadrupled

Solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

$$(i) \text{ when } [L] = [4L]$$

$$\text{Rate} = k[A]^2[B][4L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(2)}$$

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) Concentration of both [A] and [B] are doubled

Solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

$$(ii) \text{ when } [A] = [2A] \, and \, [B] = [2B]$$

$$\text{Rate} = k[2A]^2[2B][L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(3)}$$

Comparing (1) and (3) ; rate is increased by 8 times.

(iii) Concentration of [A] is halved

Solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

$$(iii) \text{ when } [A] = \left[\frac{A}{2}\right]$$

$$\text{Rate} = k\left[\frac{A}{2}\right]^2[B][L]^{3/2}$$

$$\text{Rate} = \left(\frac{1}{4}\right)\left(k[A]^2[B][L]^{3/2}\right)\text{-----(4)}$$

(iv) Concentration of [A] is reduced to(1/3) and concentration of [L] is quadrupled.

Solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

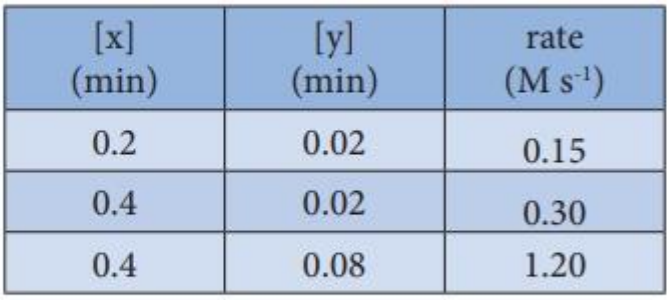
$$(iv) \text{ when } [A] = \left[\frac{A}{3}\right] \text{and} [L] = [4L]$$

$$\text{Rate} = k\left[\frac{A}{3}\right]^2[B][4L]^{3/2}$$

$$\text{Rate} = \left(\frac{8}{9}\right)\left(k[A]^2[B][L]^{3/2}\right) \text{-----(5)}$$

Comparing (1) and (5) ; rate is reduced to 8/9 times.

2. **(a) For the reaction 2*x* + *y* → L find the rate law from the following data.**



[x] (min)	[y] (min)	rate (M s^{-1})
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

Solution

$$\text{rate} = k[x]^n[y]^m$$
$$0.15 = k[0.2]^n[0.02]^m \text{ ——— (1)}$$
$$0.30 = k[0.4]^n[0.02]^m \text{ ——— (2)}$$
$$1.20 = k[0.4]^n[0.08]^m \text{ ——— (3)}$$
$$(3)/(2)$$
$$\frac{1.2}{0.3} = \frac{k[0.4]^n[0.08]^m}{k[0.4]^n[0.02]^m}$$
$$4 = \left(\frac{[0.08]}{[0.02]}\right)^m$$
$$4 = (4)^m$$
$$\therefore\ m = 1$$
$$(2)/(1)$$
$$\frac{0.30}{0.15} = \frac{k[0.4]^n[0.02]^m}{k[0.2]^n[0.02]^m}$$
$$2 = \left(\frac{[0.4]}{[0.2]}\right)^n$$
$$2 = (2)^n$$
$$\therefore\ n = 1$$
$$\text{Rate } = k\,[x]^1[y]^1$$
$$0.15 = k\,[0.2]^1[0.02]^1$$
$$\frac{0.15}{[0.2]^1[0.02]^1} = k$$
$$k = 37.5\ \text{mol}^{-1}\text{L}\ s^{-1}$$

(b) The rate constant for a first order reaction is 1.54×10^{-3} s^{-1}. Calculate its half life time.

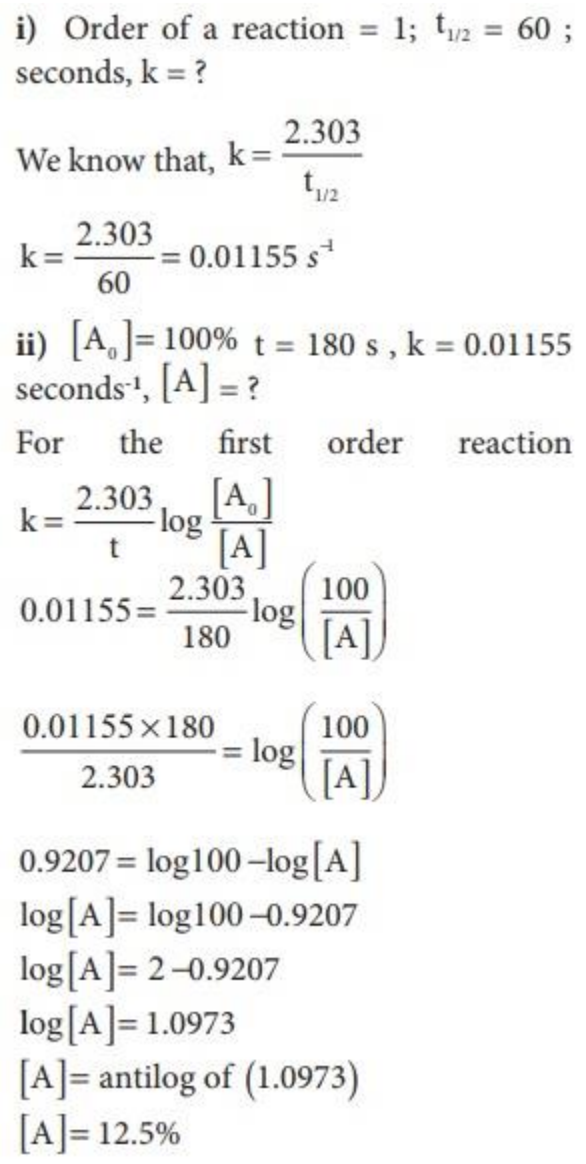
Solution

We know that, $t_{1/2} = 0.693/ k$

$t_{1/2} = 0.693/1.54 \times 10^{-3}\ s^{-1} = 450$ s

3**. (a) The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?**

Solution



i) Order of a reaction = 1; $t_{1/2} = 60$; seconds, k = ?

We know that, $k = \frac{2.303}{t_{1/2}}$

$$k = \frac{2.303}{60} = 0.01155\ s^{-1}$$

ii) $[A_0] = 100\%$ t = 180 s , k = 0.01155 seconds^{-1}, $[A] = ?$

For the first order reaction

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$0.01155 = \frac{2.303}{180}\log\left(\frac{100}{[A]}\right)$$

$$\frac{0.01155 \times 180}{2.303} = \log\left(\frac{100}{[A]}\right)$$

$$0.9207 = \log 100 - \log[A]$$

$$\log[A] = \log 100 - 0.9207$$

$$\log[A] = 2 - 0.9207$$

$$\log[A] = 1.0973$$

$$[A] = \text{antilog of } (1.0973)$$

$$[A] = 12.5\%$$

(b) A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

Solution

i) Let A = 100M, $[A_0]$–$[A]$ = 20M,

For the zero order reaction

$k=([A_0]-[A] / t)$

$k=(20M / 20min) = 1\ Mmin^{-1}$

Rate constant for a reaction = $1Mmin^{-1}$

ii) To calculate the time for 80% of completion

$k = 1Mmin^{-1}$, $[A_0]$ = 100M, $[A_0]-[A]$ = 80M, t = ?

Therefore

$t=([A_0]-[A] / k) = (80M / 1Mmin^{-1}) = 80min$