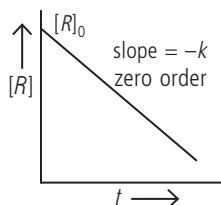




## TRY YOURSELF

## ANSWERS

- Rate of reaction =  $-\frac{1}{2} \frac{d[O_3]}{dt} = \frac{1}{3} \frac{d[O_2]}{dt}$
- (i) For zero order reaction, unit of  $k$  is  $\text{mol L}^{-1} \text{s}^{-1}$   
(ii) For second order reaction, unit of  $k$  is  $\text{L mol}^{-1} \text{s}^{-1}$
- The rate of a reaction increases by 4 times.
- $-\frac{d[A_2]}{dt} = k[A_2][B_2]^2$
- Order of a reaction =  $\frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$
- Rate =  $-\frac{d[x]}{dt} = k$
- A straight line with a negative slope is obtained.



8. Zero order reaction.

9. For the first order reaction,

$$\text{Rate constant, } k = \frac{2.303}{100} \log\left(\frac{a}{a-x}\right)$$

For 60% completion of the reaction, if  $a = 100$

$$a - x = 100 - 60 = 40$$

$$\text{Then, } k = \frac{2.303}{100} \log\left(\frac{100}{40}\right)$$

For 90% completion of the reaction,

$$a = 100$$

$$\text{and } a - x = 100 - 90 = 10$$

$$\text{Then, } k = \frac{2.303}{t} \log\left(\frac{100}{10}\right)$$

Substituting the value of  $k$  in eq. (ii),

$$\text{we have, } \frac{2.303}{100} \log\frac{100}{40} = \frac{2.303}{t} \quad [\because \log 10 = 1]$$

$$\text{or } \frac{1}{t} = \frac{1}{100} \log\frac{100}{40} \Rightarrow \frac{1}{t} = \frac{0.3979}{100} \Rightarrow t = \frac{100}{0.3979}$$

$$t = 251 \text{ min}$$

10. For first order reaction,  $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$

Let,  $a = 100$ , then  $x = 75$  and  $t = 90 \text{ min}$

$$k = \frac{2.303}{90} \log\frac{100}{25} = \frac{2.303}{90} \log 2^2$$

$$= \frac{2 \times 2.303}{90} \log 2 = \frac{2 \times 2.303 \times 0.30}{90}$$

For 60% completion,

$$t = \frac{2.303}{k} \log\frac{a}{a-x} = \frac{90 \times 2.303}{2 \times 2.303 \times 0.30} \log\frac{100}{100-60}$$

$$= \frac{90}{2 \times 0.30} \log 2.5 = \frac{90 \times 0.40}{2 \times 0.30} = 60 \text{ min}$$

$$11. t = \frac{2.303}{k} \log\frac{[R]_0}{[R]} = \frac{2.303}{231 \times 10^{-5}} \log\left(\frac{4}{2}\right)$$

$$= 996.9 \times 0.3010 = 300 \text{ s}$$

12. (i) The time required for the initial concentration of the reactant to be reduced to half of its value is known as half-life of a reaction.

(ii) The half-life of a first order reaction is independent of the initial concentration of the reactant.

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

13.  $t_{1/2} = 23 \text{ minutes}$

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} \Rightarrow k = \frac{0.693}{23} \text{ min}^{-1}$$

For 90% completion,

$$\dots(i) \quad t = \frac{2.303}{k} \log\left(\frac{a}{a-x}\right) \Rightarrow t = \frac{2.303 \times 23}{0.693} \log\left(\frac{100}{100-90}\right)$$

$$t = 76.4 \text{ minutes}$$

$$\dots(ii) \quad 14. t_{1/2} = \frac{0.693}{k} \Rightarrow \frac{0.693}{t_{1/2}} = k \Rightarrow \frac{0.693}{60} = k$$

$$k = 0.01155 \text{ min}^{-1} \Rightarrow k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$

Let the initial amount ( $a$ ) be 100.

$$0.01155 \text{ min}^{-1} = \frac{2.303}{240 \text{ min}} \log\left(\frac{100}{a-x}\right)$$

$$\frac{0.01155 \text{ min}^{-1} \times 240 \text{ min}}{2.303} = \log\left(\frac{100}{a-x}\right)$$

$$1.204 = \log 100 - \log(a-x)$$

$$\Rightarrow 1.204 = 2 - \log(a-x)$$

$$\log(a-x) = 2 - 1.204 = 0.796 \Rightarrow (a-x) = 6.25\%$$

$$15. \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

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

$$\text{Given: } \frac{k_2}{k_1} = 2, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_1 = 27^\circ\text{C} = 300 \text{ K},$$

$$T_2 = 37^\circ\text{C} = 310 \text{ K}$$

$$E_a = \frac{2.303 \times 8.314 \times 300 \times 310}{10} \log 2 = 53.6 \text{ kJ mol}^{-1}$$

$$16. \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{k_2}{2.35 \times 10^{-4}} = \frac{100 \times 10^3}{2.303 \times 8.314} \left[ \frac{303 - 293}{303 \times 293} \right] = 0.5882$$

$$\frac{k_2}{2.35 \times 10^{-4}} = \text{Antilog}(0.5882) = 3.875$$

$$k_2 = 2.35 \times 10^{-4} \times 3.875 = 9.106 \times 10^{-4} \text{ s}^{-1}$$

17. (a) A catalyst lowers the activation energy ( $E_a$ ) by providing an alternate pathway or reaction mechanism.

(b) Catalyst does not affect the Gibbs energy ( $\Delta G$ ) of a reaction.

$$18. T = 273 + 45^\circ\text{C} = 318 \text{ K}$$

$$k = A e^{-E_a/RT} \Rightarrow \log k = \log A - \frac{E_a}{2.303RT}$$

$$\log A = \log k + \frac{E_a}{2.303RT}$$

$$= \log(5 \times 10^{-4}) + \frac{102 \times 10^3}{2.303 \times 8.314 \times 318}$$

$$= -3.3010 + 16.7520 = 13.4510$$

$$A = \text{Antilog}(13.4510) = 2.8259 \times 10^{13} \text{ s}^{-1}$$

19. Fraction of molecules with energy equal to or greater than activation energy is  $x = e^{-E_a/RT}$

$$\log x = \frac{-E_a}{2.303RT} = \frac{-(262 \times 10^3)}{2.303 \times 8.314 \times 600} = -22.8058$$

$$x = \text{antilog}(-22.8058) = 1.5638 \times 10^{-23}$$

20. The equilibrium is attained faster in case of reaction in which catalyst is used as it lowers the activation energy.

