

Solutions to Workbook-4 [Chemistry] | Chemical Kinetics

Daily Tutorial Sheet

Level - 0

- This is because the rate of reaction at any time depends upon the concentration of the reactants at that time which keep on decreasing with time
- $k = A e^{\frac{-E_a}{RT}}$ Arrhenius equation
- $H_2 + Br_2 \longrightarrow 2HBr$
 $Rate = k[H_2][Br_2]^{1/2}$
 $Order = 1\frac{1}{2}$
- $k = A e^{\frac{-E_a}{RT}}$
 $k = A e^0 \Rightarrow k = A$ (Collision frequency)
 Which means every collision results in product formation. Hence K is independent of T
- $Rate = k[A]^0 [B]^0$
- The minimum extra energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called activation energy.
- Units of Rate = $\text{mol L}^{-1} \text{sec}^{-1}$ Units of rate constant = $\frac{\text{mol L}^{-1} \text{sec}^{-1}}{\text{mol}^3 \text{L}^{-3}} = \text{mol}^{-2} \text{L}^2 \text{sec}^{-1}$
- The slowest elementary step written in the mechanism of a complex reaction is the rate determining step.
- (i) Rate of reaction is doubled (ii) no effect on reaction rate
- $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$
 Since $[H_2O]$ does not change largely
 $Rate = k[CH_3COOC_2H_5]^1$
- $r = Rate = k[A]^n \quad \dots (1)$
 $27r = k(3A)^n \quad \dots (2)$
 $27 = (3)^n \Rightarrow n = 3$
- $t_{1/2} = 2\text{Hrs}$
 After 75% completion, 2 half lives, $t_{1/2}$ is independent of initial concentration of reactant, reaction of 1st order.
- Does not depend upon concentration at constant temperature.
- $\frac{dx}{dt} = k \Rightarrow \int dx = k \int dt \Rightarrow \therefore x = kt + I$
 $t = 0, x = 0$
 $I = 0$
 Hence $x = kt \Rightarrow t = \frac{x}{k}$ for completion $x = a$; $t = a / k$
- $Rate = -\frac{d[x_2]}{dt} = -\frac{1}{3} \frac{d[y_2]}{dt} = \frac{1}{2} \frac{d[xy_3]}{dt}$
 $Rate \text{ of disappearance of } y_2 = \frac{-d[y_2]}{dt} = \frac{-3d[x_2]}{dt} = +\frac{3}{2} \frac{d[xy_3]}{dt}$

16. Rate = $k [\text{NO}]^2 [\text{O}_2]$

Let initially moles of NO = a

Moles of O_2 = b

Volume of vessel = 'V' L

Then $[\text{NO}] = \frac{a}{V} \text{ M}$

$[\text{O}_2] = \frac{b}{V} \text{ M}$

$(r_1) \text{ rate} = k \left[\frac{a}{V} \right]^2 \left[\frac{b}{V} \right] = \frac{ka^2b}{V^3}$

New volume = $V/3$

New concentration of $[\text{NO}] = \frac{a}{V/3} = \frac{3a}{V}$

New concentration of $\text{O}_2 = \frac{b}{V/3} = \frac{3b}{V}$

New rate $r_2 = k \left[\frac{3a}{V} \right]^2 \left[\frac{3b}{V} \right] = \frac{27ka^2b}{V^3}$

$\frac{r_2}{r_1} = 27$

There is no effect on order of reaction

17. $t_{1/2} = 69.3 \text{ min}$

$k = \frac{0.693}{69.3} = 0.01 \text{ min}^{-1}$

$$\begin{aligned} t_{80\%} &= \frac{2.303}{k} \log \frac{[R_0]}{[R]} \\ &= \frac{2.303}{0.01} \log \frac{R_0}{\frac{20}{100} R_0} = \frac{2.303}{0.01} \times \log 5 \\ &= \frac{2.303}{0.01} \times 0.6990 = 160.97 \text{ min} = 2.68 \text{ hrs.} \end{aligned}$$

18. Let $T_1 = 300 \text{ K}$ and $T_2 = 310 \text{ K}$; $E_a = 52000 \text{ Jmol}^{-1}$

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

Putting values we get : $k_2 = 2k_1$

Thus the rate of reaction doubles after every 10°C rise in temperature

19. $k = Ae^{-E_a/RT}$

If E_a is -ve, $e^{-E_a/RT} = e^x$ where $x = \frac{E_a}{RT}$

$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots x \ll 1 + x = 1 + \frac{E_a}{RT}$

$k = A \left(1 + \frac{E_a}{RT} \right)$

$k \gg A$

Which is impossible

Hence E_a is never negative.

$$\begin{aligned} 20. \quad \text{Rate} &= k[A][B]^2 = 2 \times 10^{-6} [0.1][0.2]^2 \\ &= 8 \times 10^{-9} \text{molL}^{-1} \text{sec}^{-1} \end{aligned}$$

$$[A]_{\text{Final}} = 0.06 \text{molL}^{-1}$$

Ratio of A to B is 2:1

$$[B]_{\text{Final}} = 0.2 - \left(\frac{0.04}{2}\right) = 0.18 \text{molL}^{-1}$$

$$\begin{aligned} \text{Rate} &= (2 \times 10^{-6})(0.06)(0.18)^2 \\ &= 3.89 \times 10^{-9} \text{molL}^{-1} \text{sec}^{-1} \end{aligned}$$

$$21. \quad r_1 = \text{rate} = k[R]^2$$

$$r_2 = k[2R]^2 \Rightarrow r_2 = 4r_1 \quad ; \quad r_3 = k\left[\frac{R}{2}\right]^2 \Rightarrow r_3 = \frac{1}{4}r_1$$

$$22. \quad \text{Fraction of molecules having energy equal to or greater than activation energy } x = e^{\frac{-E_a}{RT}}$$

$$\log x = \frac{-E_a}{2.303RT}$$

$$\log x = -\frac{209.5 \times 10^3}{2.303 \times 8.314 \times 581} = -18.8323$$

$$x = \text{antilog}(-18.8323) = \text{antilog}(19.1677) = 1.47 \times 10^{-19}$$

$$23. \quad \text{Rate} = k[A]^1[B]^0$$

$$\text{Exp. 1 : } 2 \times 10^{-2} = k(0.1)^1[0.1]^0$$

$$k = 0.2 \text{min}^{-1}$$

$$\text{Exp. 2 : } 4 \times 10^{-2} = 0.2[A][0.2]^0$$

$$[A] = 0.2 \text{molL}^{-1}$$

$$\text{Exp. 3 : } \text{Rate} = 0.2 \times 0.4 = 0.08 \text{molL}^{-1} \text{min}^{-1}$$

$$\text{Exp. 4 : } 2 \times 10^{-2} = 0.8[A] = 0.1 \text{molL}^{-1}$$

$$24. \quad t_{1/2} = \frac{0.693}{k} \Rightarrow \frac{0.693}{5730} (\text{yr})^{-1} = k$$

$$t = \frac{2.303}{k} \log \frac{R_0}{R}$$

$$\begin{aligned} t &= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80} = \frac{2.303 \times 5730}{0.693} \times 0.0969 \text{year} \\ &= 1845 \text{years.} \end{aligned}$$

$$25. \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} \text{yr}^{-1} = 2.466 \times 10^{-2} \text{yr}^{-1}$$

$$k = \frac{2.303}{t} \log \frac{R_0}{R}$$

$$2.466 \times 10^{-2} = \frac{2.303}{10} \times \log \frac{1}{R}$$

$$\log R = -0.1071$$

$$R = \text{antilog } 1.8929 = 0.7814^{1/4} \text{g.}$$