Solution

CHEMICAL KINETICS

Class 12 - Chemistry

1. Elementary reactions have the same value of order and molecularity because the elementary reaction proceeds in a single step.
2. The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
3. i. Rate of growth of population, if there is no change of birth and death rates.
   ii. Radioactive decay in which the number of nuclei disintegrating is proportional to the number of nuclei present.
4. For first order reaction, $t_{1/2} = 0.693/k$
   it is provided that $t_{1/2}$ = 60 min
   then, k = 0.693/60 = 0.01386 min-1
5. The rate law is experimentally determined. It cannot be predicted by merely looking at the balanced chemical equation.
6.

Order of Reaction	**Unit of k**
1. Zero order reaction	$mol\, L^{-1} s^{-1}$
2. First order reaction	s^{-1}
3. Second order	$mol^{-1}\, Ls^{-1}$
4. n^{th} order reaction	$(mol/\,L)^{1-n} s^{-1}$

7. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$
   So, $t_{1/2} = \frac{0.693}{5.5\times10^{-14}\text{sec}^{-1}} = 1.26 \times 10^{13}$s
8. The properties of products formed are entirely different from that of the reactants, therefore, chemical reactions are irreversible.
9. a. Rate = k $[A]^x$ $[B]^y$
   order of a reaction = x + y
   So order = $\frac{1}{2} + \frac{3}{2}$ = 2, i.e., second order
   b. order = $\frac{3}{2}$ + (-1) = $\frac{1}{2}$, i.e., half order.
10. 2 H_2(g) + O_2(g) $\rightarrow$ 2 H_2O(l)
    This reaction does not take place at the room temperature because the activation energy of the reaction is very high.
11. It is given that a reaction is first order in A and second order in B.
    a. The differential rate equation will be
    $-\frac{d[R]}{dt} = k[A][B]^2$
    b. If the concentration of B is increased three times, then
    $-\frac{d[R]}{dt} = k[A][3B]^2 = 9.k[A][B]^2$
    Therefore, the rate of reaction will increase 9 times.
    c. When the concentrations of both A and B are doubled,
    $-\frac{d[R]}{dt} = k[A][B]^2 = k[2A][2B]^2 = 8.k[A][B]^2$
    Therefore, the rate of reaction will increase 8 times.
12. For the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$
    Assume rate law expression as
    Rate = $k[N_2O_5]^x$
    According to question
    $34 \times 10^{-5} = k[1.13 \times 10^{-2}]^x$ ... (i)
    $25 \times 10^{-5} = k[0.84 \times 10^{-2}]^x$ ...(ii)
    $18 \times 10^{-5} = k[0.62 \times 10^{-2}]^x$ ...(iii)
    From eq.(i) and eq.(ii)
    $\frac{34\times10^{-5}}{25\times10^{-5}} = \frac{k[1.13\times10^{-2}]^x}{k[0.84\times10^{-2}]^x}$
    $[1.36] = [1.36]^x$
    x = 1

i. Order of reaction=1

ii. Rate law expression

Rate = $k[N_2O_5]$

iii. Rate constant

$k = \frac{[Rate]}{[N_2O_5]} = \frac{34\times10^{-5}}{1.13\times10^{-2}}$

$k = 30.09 \times 10^{-3}$

$k = 3.0 \times 10^{-2}\text{min}^{-1}$

13. Here $T_1 = 300K$

$T_2 = 310K$

$k_1 = 6.0 \times 10^{-4} s^{-1}$

$E_a = 3.05 \times 10^5 J\,mol^{-1}$

and $k_2 = ?$

We know that

$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[\frac{T_2-T_1}{T_1T_2}\right]$

$\log k_2 - \log 6.0 \times 10^{-4} = \frac{3.05\times10^5}{2.303\times8.314} \left(\frac{310-300}{310\times300}\right)$

$\log k_2 - (-4 + 0.7782) = \frac{3.05\times10^5}{19.147} \times \frac{10}{93000}$

$\log k_2 - (-3.2218) = \frac{3.05\times1000}{19.147\times93}$

$\log k_2 + 3.2218 = 1.7128$

log k_2 = 1.7128 - 3.2218

$\log k_2 = -1.5090$

k_2 = antilog (-1.5090)

$k_2 = 3.097 \times 10^{-2} s^{-1}$

14. Here $T_1 = 600K$

$T_2 = 700K$

$E_a = 209KJ/mol$

$= 209000Jmol^{-1}$

$k_1 = 1.60 \times 10^{-5} s^{-1}$

$k_2 = ?$

Using the formula

$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{700-600}{600\times700}\right]$

$\log k_2 - \log 1.60 \times 10^{-5} = \frac{209000}{2.303\times8.314} \left[\frac{100}{600\times700}\right]$

$\log k_2 = \log 1.60 \times 10^{-5} + 2.599$

$\log k_2 = -4.796 + 2.599$

= - 2.197

k_2= anti log (-2.197)

$= 6.36 \times 10^{-3} s^{-1}$

15. T_1= 273 + 50 = 323 K

T_2= 273 + 100 = 373 K

K_1= K

K_2 = 3K

Using the formula,

$log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$\log \frac{3K}{K} = \frac{E_a}{2.303\times8.314}\left[\frac{373-323}{373\times323}\right]$

$\log 3 = \frac{E_a\times50}{2.303\times8.314\times373\times323}$

$E_a = 22011.76\, J\,mol^{-1}$

16. The thermal decomposition of SO_2Cl_2 at a constant volume can be represented by the following equation:

$$\begin{matrix} & SO_2Cl_{2(g)} & \rightarrow & SO_{2(g)} & + & Cl_{2(g)} \\ At\ t=0 & P_0 & & 0 & & 0 \\ At\ t=t & P_0-p & & p & & p \end{matrix}$$

After time, t, total pressure, $P_t = (P_0 - p) + p + p$

$P_t = P_0 + p; p = P_t - P_0$

Therefore,

$P_0 - p = P_0 - (P_t - P_0) = 2P_0 - P_t$

For a first order reaction,

$k = \frac{2.303}{t}\log\frac{P_0}{P_0-p}$

$= \frac{2.303}{t}\log\frac{P_0}{2P_0-P_t}$

When t= 100 s, $k = \frac{2.303}{100\ s}\log\frac{0.5}{(2\times0.5)-0.6} = 2.231\times10^{-3}s^{-1}$

When$P_t = 0.65atm$

$P_0 + p = 0.65$

$p = 0.65 - P_0$

= 0.65 - 0.5

= 0.15 atm

Therefore, when the total pressure is 0.65 atm, pressure of $SOCL_2$ is

$P_{SOCl_2} = P_0 - p$

= 0.5 - 0.15

= 0.35 atm

Hence, the rate of equation, when total pressure is 0.65 atm, is given by,

$Rate = k(P_{SOCl_2})$

$= \left(2.23\times10^{-3}s^{-1}\right)(0.35\,atm)$

$= 7.8\times10^{-4}atm\,s^{-1}$

17. a. Given half life $t_{1/2}$ for decomposition of nitramide=2.1 h

i. $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1h}$

$= 0.33\ h^{-1}$

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

$= \frac{2.303}{K}\log\frac{100}{100-99}$

$= \frac{2.303}{k}(\log 100 - log1) = \frac{2.303}{k}\log 100 = \frac{2.303}{k}\times 2$

$= \frac{4.606}{0.33h^{-1}} = 13.96\,h$

ii. Amount decomposed = 99% of 6.2 g

$= \frac{6.2\times99}{100}$ = 6.138 g

1 mole of NH_2NO_2 (62 g) produces 22.4 L at STP

6.138 g will produce= $\frac{22.4}{61}\times 6.138$

= 2.217 L at STP

b. $X \rightarrow Y$

Rate $= k[\mathrm{X}]^2$

$Rate' = k[3\mathrm{X}]^2$ when concentration of X is increased to 3 times the original concentration

$= 9k[X]^2 = 9\times Rate$

The rate of formation of 'Y' will increase to 9 times the original rate because reaction is second order and concentration is increased 3 times.

18. a. Negative sign means that rate of reaction is expressed in term of reactant and concentration of reactant decreases with time.

b. i. For first order reaction

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

$k = \frac{2.303}{15}\log\frac{100}{100-80}$

= 0.015 min^{-1}

ii. $k = \frac{2.303}{k}\log\frac{100}{10}$

$= \frac{2.303}{0.015}\log 10$

= 153.53 min

iii. $k = \frac{2.303}{t}\log\frac{0.8}{0.8-2\times0.8}$

$= \frac{2.303}{0.015}\log\frac{0.80}{0.64}$

$= \frac{2.303}{0.015}\log\frac{10}{8}$

= 15 min

19. From Arrhenius equation, we obtain $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

Also, $k_1 = 4.5\times10^3 s^{-1}$

T_1 =273 + 10 = 283 K

$k_2 = 1.5\times10^4 s^{-1}$

$E_a = 60\,kJ\,mol^{-1} = 6.0\times10^4\,J\,mol^{-1}$

Then, $\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{6.0\times10^4\ Jmol^{-1}}{2.303\times8.314\ JK^{-1}mol^{-1}}\left(\frac{T_2-283}{283T_2}\right)$

$0.5229 = 3133.6279\left(\frac{T_2-283}{283T_2}\right)$

$\frac{0.5229\times283T_2}{3133.627} = T_2 - 283$

0.0472 T_2 = T_2 - 283, 0.9528 T_2 = 283

T_2 = 297.019 K (approximately)

= 297 K = 24 ^{0}C

Hence, k would be $1.5\times10^4 s^{-1} at\ 24^0C$.