DAILY PRACTICE PROBLEMS
CHEMISTRY SOLUTIONS
DPP/CC15

1. **(d)** Rate$_1$ = $k[A]^n\,[B]^m$

$$\text{Rate}_2 = k[2A]^n\left[\frac{1}{2}B\right]^m$$

$$\therefore\ \frac{\text{Rate}_2}{\text{Rate}_1}=\frac{k[2\text{A}]^n\left[\frac{1}{2}\text{B}\right]^m}{k[\text{A}]^n\,[\text{B}]^m}=(2)^n\left(\frac{1}{2}\right)^m$$

$$= 2^n\ .\ (2)^{-m} = 2^{n-m}$$

2. **(b)** According to Arrhenius equation

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

$$\log\frac{1.3\times10^{-3}}{1.3\times10^{-4}}=\frac{E_a}{2.303\times8.314}\left[\frac{1}{373}-\frac{1}{423}\right]$$

$$1=\frac{E_a}{2.303\times8.314}\left[\frac{1}{373}-\frac{1}{423}\right]$$

$E_a = 60$ kJ / mol

3. **(b)** $T_2 = T$(say), $T_1 = 25°\text{C} = 298\text{K}$,

$E_a = 104.4\ \text{kJ mol}^{-1} = 104.4\times10^3\ \text{J mol}^{-1}$

$k_1 = 3\times10^{-4}$, $k_2 = ?$,

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

$$\log\frac{k_2}{3\times10^{-4}}=\frac{104.4\times10^3\text{J mol}^{-1}}{2.303\times(8.314\text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{298}-\frac{1}{\text{T}}\right]$$

As $T\to\infty, \frac{1}{T}\to0$

$$\therefore\ \log\frac{k_2}{3\times10^{-4}}=\frac{104.4\times10^3\text{ J mol}^{-1}}{2.303\times8.314\times298}$$

$$\log\frac{k_2}{3\times10^{-4}}=18.297, \frac{k_2}{3\times10^{-4}}=1.98\times10^{18}$$

$$k_2=(1.98\times10^{18})\times(3\times10^{-4})=6\times10^{14}\text{s}^{-1}$$

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

Now from the given data

$1.2\times10^{-3} = \text{k}\,[0.1]^x[0.1]^y$ .....(i)

$1.2\times10^{-3} = \text{k}\,[0.1]^x[0.2]^y$ .....(ii)

$2.4\times10^{-3} = \text{k}\,[0.2]^x[0.1]^y$ .....(iii)

Dividing equation (i) by (ii)

$$\Rightarrow\ \frac{1.2\times10^{-3}}{1.2\times10^{-3}}=\frac{\text{k}[0.1]^x[0.1]^y}{\text{k}[0.1]^x[0.2]^y}$$

We find, $y = 0$

Now dividing equation (i) by (iii)

$$\Rightarrow\ \frac{1.2\times10^{-3}}{2.4\times10^{-3}}=\frac{\text{k}[0.1]^x[0.1]^y}{\text{k}[0.2]^x[0.1]^y}$$

We find, $x = 1$

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

5. **(d)** From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.

From 1st and 4th sets of data

Dividing eq. (4) by eq. (1)

$$\frac{1.25\times10^{-3}}{5.0\times10^{-3}}=\left[\frac{0.005}{0.010}\right]^x$$

or $0.25 = (0.5)^x$ or $(0.5)^2 = (0.5)^x$

$\therefore x = 2$

The order with respect to 'A' is 2 from the 1st and 3rd sets of data Dividing eq. (1) by eq. (3)

$$\frac{5.0\times10^{-3}}{1.0\times10^{-2}}=\left[\frac{0.005}{0.010}\right]^y$$

or $(0.5)^1 = (0.5)^y \Rightarrow y = 1$

The order with respect to 'B' is 1

So the order with respective the reactants A, B and C is 2, 1 and 0.

6. **(a,c)** In acid catalysed reaction, the rate constant is directly proportional to the extent of ionization of the acid and hence the strength of the acid.

Relative strength of (I)HX and (II)HY

$$=\frac{\alpha_{\text{I}}}{\alpha_{\text{II}}}=\frac{k_{\text{I}}}{k_{\text{II}}}=\frac{3\times10^{-3}}{5\times10^{-3}}=0.6$$

7. **(a,b,c)** Since $t_{1/2}$ is independent of initial concentration of sugar, the reaction is first order w.r.t. sugar. The rate increases ten fold on increasing H$^+$ ion concentration 10 times (decreasing pH by unity), the reaction is also first order in H$^+$ ion.

Since [H$^+$] in a particular run remains constant (H$^+$ ion being catalyst), the rate is independent of [H$^+$]. Hence, rate = k[sugar] (Pseudo first order reaction).

8. **(b,c,d)** On doubling the volume of the vessel, all the concentrations are halved at that moment.

$$\frac{(\text{Rate})_2}{(\text{Rate})_1}=\frac{k\left(\frac{[A]}{2}\right)^2\left(\frac{[B]}{2}\right)}{k\,[A]^2\,[B]}=\frac{1}{8}$$

9. **(b)** In more than one reactant system, the half-life time ($t_{1/2}$) is the time for half of the reactant present in small amount.

For set (1) and (2), B is in small amount and according to rate law, the reaction is of first order w.r.t B. So in these sets the half-life is independent of initial concentration and so the $t_{1/2}$ for set (2) will be same as that for set (1) i.e. 62.6 sec.

In set (3) and (4), A is present in small quantity and $t_{1/2}$ will depend on $[A]$. According to rate law expression the order w.r.t. A is 2.

$$\therefore\ t_{1/2}=\frac{1}{k.a}=\frac{1}{k[A]_0} \quad \text{or} \quad \frac{(t_{1/2})_3}{(t_{1/2})_4}=\frac{[A_0]_4}{[A_0]_3}$$

$$\text{or}\ \frac{625}{(t_{1/2})_4}=\frac{10}{5}\ \text{or}\ 2$$

$$\therefore\ (t_{1/2})_4=\frac{625}{2}=312.5\ \text{sec.}$$

i.e. $y = 312.5$ sec.

10. **(9)** $k=\frac{0.693}{15\ \text{hr}}=0.0462\ \text{hr}^{-1}$

$$k=\frac{2.3}{14\times 24\ \text{hr}}\log\frac{c_0}{c_t}$$

$$0.0462\ \text{hr}^{-1}=\frac{2.3}{14\times 24\ \text{hr}}\log\frac{1\text{Ci}}{c_t}$$

Solve for c_t:

$\therefore c_t = 1.82\times 10^{-7}\ \text{Ci} \approx 0.18\ \mu\text{Ci} = 0.02x\ \mu\text{Ci}$

$\therefore x = 9$

11. **(5)** $\frac{-d[\text{RX}]}{dt}=k_2[\text{RX}][\overset{\ominus}{\text{O}}\text{H}]$ (by S_N2 path way)

k_2 = rate constant of S_N2 reaction

$\frac{-d[\text{RX}]}{dt}=k_1[\text{RX}]$ (by S_N1 path way)

k_1 = rate constant of S_N1 reaction

$$\frac{-d[\text{RX}]}{dt}=k_2[\text{RX}][\overset{\ominus}{\text{O}}\text{H}]+k_1[\text{RX}]$$

$$-\frac{1}{[\text{RX}]}\frac{d[\text{RX}]}{dt}=k_2[\overset{\ominus}{\text{O}}\text{H}]+k_1$$

This is the equation of a straight line for $-\frac{1}{[\text{RX}]}\frac{d[\text{RX}]}{dt}$ vs $[\overset{\ominus}{\text{O}}\text{H}]$ plot with slope equal to k_2 and inercept equal to k_1.

From questions:

$k_2 = 2\times 10^3\ \text{mol}^{-1}\ \text{L hr}^{-1}$, $k_1 = 1\times 10^2\ \text{hr}^{-1}$

$[\text{RX}] = 1.0$ M and $[\overset{\ominus}{\text{O}}\text{H}] = 0.1$ M

Hence,

$$\frac{d[\text{RX}]}{dt}=2\times 10^3\times 1\times 0.1+1\times 10^2\times 1$$

$= 300\ \text{mol L}^{-1}\ \text{hr}^{-1}$

$= 5\ \text{mol L}^{-1}\ \text{min}^{-1}$

12. **(4)** $t_{1/2}=\frac{0.0693}{k_1}$

$$\text{Also, } t_{93.75}=\frac{2.303}{k_1}\log\frac{100}{100-93.75}$$

$$=\frac{2.303}{k_1}\log\frac{100}{6.25}$$

$$=\frac{2.303}{k_1}\log 2^4$$

$$=\frac{4\times 2.303\times\log 2}{k_1}=\frac{4\times 0.693}{k_1}=4t_{1/2}$$

13. **(5)** For second order reaction:

$[\text{R}]_{\text{initial}} = 0.08$, M; $[\text{R}]_{\text{final}} = 0.01$ M

$x = 0.08 - 0.01 = 0.07$ M

$\therefore (a-x) = 0.08 - 0.07 = 0.01$ M

$$k_2=\frac{1}{t}.\frac{x}{a(a-x)}$$

$$k_2=\frac{1}{70\ \text{min}}\times\frac{0.07\ \text{M}}{0.08\text{M}\times 0.01\text{M}} \quad \text{...(i)}$$

Now, time required to become concentration = 0.04 M. i.e., $x = 0.04$ M

$$k_2=\frac{1}{t}\times\frac{0.04\ \text{M}}{0.08\text{M}\times(0.08-0.04)\text{M}} \quad \text{...(ii)}$$

From Eqs. (i) and (ii)

$$\frac{0.07}{70\times 0.08\times 0.01}=\frac{0.04}{t\times 0.08\times 0.04}$$

$t = 10$ min $= 2x$ min

$\therefore x = 5$ min

14. **(1)** Rate $= k[a]^n$

$$\text{Case I: } r_1=k\left[\frac{a}{V}\right]^n \quad \text{... (i)}$$

$$\text{Case II: } \frac{r_1}{2}=k\left[\frac{a}{2V}\right]^n \quad \text{... (ii)}$$

By Eqs. (i) and (ii),

$(2)^1 = (2)^n$

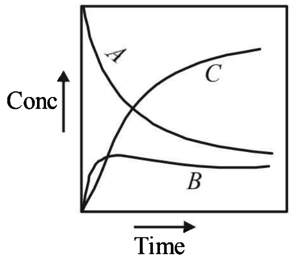
$\therefore n = 1$

15. **(c)** **16.** **(a)** **17.** **(c)**

18. **(c)** The concentration of A falls exponentially, whereas the amount of C will rise until it approaches that of A (not of B), thus (a) is incorrect.

The concentration of B will first increase and then it will decrease showing a maxima. (see figure below).

Thus (b) is incorrect and (c) is correct.



19. **(a)** We have

$C_0 = C_1 + C_2 + C_3$

The rate of disappearance of *A* is

$$-\frac{dC_1}{dt} = k_1 C_1 \quad ...(i)$$

Rearranging and integrating the above equation

$$C_1 = C_0 e^{-k_1 . t}$$

Since rate of formation of *B* is given by $k_1.C_1$ and the rate of decomposition of *B* into *C* is given by $k_2.C_2$, the rate at which *B* accumulates in the system is given by

$$\frac{dC_2}{dt} = k_1 C_1 - k_2 C_2$$

or $$\frac{dC_2}{dt} + k_2 C_1 = k_1 C_1$$

Putting the values of C_1 from equation (i)

$$\frac{dC_2}{dt} + k_2 C_2 = k_1 . C_0 . e^{-k_1 . t}$$

Multiplying both sides by $e^{k_2 t}$, we get

$$e^{k_2 . t} . \frac{dC_2}{dt} + e^{k_2 . t} . k_2 C_2 = k_1 . C_0 . e^{(k_2 - k_1)t}$$

On integration under the condition, $t = 0$ at $C_2 = 0$

$$C_2 = \frac{k_1 C_0}{k_2 - k_1}[e^{-k_1 . t} - e^{-k_2 . t}]$$

From this equation values of k_1 and k_2 can be determined.

20. **A - s; B - r; C - q; D - p**

(A) 2 moles of gaseous reactant gives 5 moles of gaseous products. Hence, pressure of the reaction system at constant volume and temperature will increase with the progress of the reaction.

(B) With the progress of the reaction, more and more CH_3COOH will be formed and total acid concentration would increase as the reaction proceeds. Hence, kinetics can be followed by titrimetric method.

(C) Volume of N_2 gas (at constant temperature and pressure) will increase with the progress of the reaction.

(D) Dextro rotatory sucrose on hydrolysis gives laevo rotatory equimolar mixture of glucose and fructose. Hence, measurement of optical rotation of the reaction mixture can be used to study the kinetics of the reaction. Optical rotation would decrease with time.