Rate law and Rate constant

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

$k = \frac{2.303}{32} log\left(\frac{100}{100-75}\right)$ .... (i)

$k = \frac{2.303}{t} log\left(\frac{100}{100-50}\right)$ ....(ii)

from the two equation (i) and (ii), $t = 16$minutes.

146. (c) The relation between half – life period and initial concentration (c) for a nth order reaction is given by $t_{\frac{1}{2}} \propto \frac{1}{C^{n-1}}$ for first order reaction $(n = 1)$. $t_{\frac{1}{2}} \propto \frac{1}{C^{1-1}}$ or $t_{\frac{1}{2}} \propto C^0$.

147. (c) $R = k[NO]^2[O_2]$, $R' = k[2NO]^2[2O_2]$

$R' = k \times 4[NO]^2[O_2] = k \times 8[NO]^2[O_2]$

$\frac{R'}{R} = \frac{k\times 8[NO]^2[O_2]}{k[NO]^2[O_2]} = 8$

148. (b) For zero order reaction $r = k$.

149. (b) $k = \frac{2.303}{t} log\frac{0.8}{0.6} = 2.303\, log\frac{4}{3}$

$t = \frac{2.303}{k} log\frac{0.9}{0.675} = \frac{2.303}{k} log\frac{4}{3}$; $t = 1 hour$.

150. (a) For zero order reaction

Velocity constant $= \frac{dx}{dt} = \frac{\text{Concentration}}{\text{Time}}$

Unit= concentration $\times$ time^{-1}.

151. (d) $H_2 + Br_2 \rightleftharpoons 2HBr$ is a 1.5 order reaction i.e., $K = [H_2][Br_2]^{\frac{1}{2}}$.

152. (a) When in any chemical reaction, one of the reactant is present in large excess, then the second order reaction becomes first order reaction and is known as pseudo unimolecular reaction *e.g.,*

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

in this reaction molecularity is 2 but order of reaction is found to be first order experimentally, so it is an example of pseudo unimolecular reaction.

153. (d) $K = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{10\text{years}}$

If initial concentration $a = 10\ gm$ and final concentration $x = \frac{a}{2} = 5\ gm$

then, $t = \frac{2.303}{K} log \frac{a}{a-x} = \frac{2.303}{.693} \times 10 \times log \frac{10}{5}$

$= \frac{2.303 \times 10 \times log\ 2}{.693} = \frac{2.303 \times 10 \times 0.301}{0.693} = 10$ years.

154. (c) The concentration of the reactants decrease from 0.8 to 0.4 in 15 *min* i.e., $T_{\frac{1}{2}} = 15 min$, concentration from $0.1m$ to 0.025 will fall in 2 half lives so total time taken $= 2 \times T_{\frac{1}{2}} = 2 \times 15 = 30 min$.

155. (c) $K = \frac{2.303}{1\ hr} log \frac{100}{25} = \frac{2.303}{t} log \frac{100}{50}$

$\therefore$ $\boldsymbol{log\ 4 = \frac{1}{t} log\ 2}$

$\therefore$ $\boldsymbol{2\ log\ 2 = \frac{1}{t} log\ 2; t = \frac{1}{2} hr}$.

156. (b) $x_{(g)} \rightarrow y_{(g)} + z_{(g)}$

The reaction is a first order reaction hence,

$$K = \frac{0.693}{t_{\frac{1}{2}}} = \frac{2.303}{t} log \frac{a}{a-x} = \frac{0.693}{10\ min}$$

$$= \frac{2.303}{t} log \frac{a}{\frac{a}{10}} = \frac{0.693}{10} = \frac{2.303}{t} log\, 10$$

$$\therefore \quad t = \frac{2.303 \times 10}{.693} = 33 min.$$

157. (a) For the first order reaction $t = \frac{2.303}{K} log \frac{a}{a-x}$

Given: $a = 0.5\ \frac{mol}{litre}$; $a - x = 0.05\ , \frac{mol}{litre}$

$K = 6\, sec^{-1}$.

$$t = \frac{2.303}{6} log \frac{0.5}{0.05} = \frac{2.303}{6} log\, 10 = \frac{2.303}{6} = 0.384 \text{ sec} .$$

158. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

159. (d) Rate $\left(\frac{dx}{dt}\right) = K\ .\ c;\ 1.5 \times 10^{-2} = K \times 0.5$

For first order $K = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}\, minute^{-1}$

$$t_{\frac{1}{2}} = \frac{.693}{K} = \frac{.693}{3 \times 10^{-2}} = 23.1\ minute.$$

160. (c) For first order reaction $K = \frac{2.303}{t} log \frac{a}{a-x}$

Given: $a = \frac{1}{10} = .1m;\ a - x = \frac{1}{100} = .01m;\ t = 500\ sec$

$$\therefore \quad K = \frac{2.303}{500} log \frac{.10}{.01} = \frac{2.303}{500} log\, 10 = \frac{2.303}{500} = 0.004606 = 4.6 \times 10^{-3}\, sec^{-1} \quad .$$

161. (b) For zero order reaction, rate of reaction is independent of concentration $R = K[\text{Reactant}]^0$

162. (b) The radioactive disintegration reactions are of first order because in this rate of disintegration depends on the concentration term of radioactive material only.

163. (b) $t_{\frac{1}{2}} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow \frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$\Rightarrow \frac{1}{4^1} = \frac{1}{4^{n-1}} \therefore \quad n-1=1; n=2.$

164. (abd) By Vant's Hoff equation, $\frac{d\,ln\,k}{dt} = \frac{\Delta H^o}{RT^2}$

or $ln\,k_p = -\frac{\Delta H^o}{RT} + I$. Hence (a) is correct (b) is also correct as plot of log (X) vs time is linear. (c) is wrong because $p \propto T$ at constant volume. (d) is correct by Boyle's law.

165. (ad)(a) is correct because degree of dissociation $= 1 - e^{-kt}$ at any time *t*.

(b) is wrong because plot of log [A] vs *t* is a straight line

(c) is wrong because time taken for 75% reaction is two half life.

(d) is correct because in $k = Ae^{-\frac{E_a}{RT}}, E_{\frac{a}{RT}}$ is dimensionless hence *A* has the unit of *K*.

166. (b) $aA \rightarrow xP$

Rate of reaction = $[A]^a$

Order of reaction = *a*

$[A]_1 = 2.2\ mM$, $r_1 = 2.4\ m\ M\ s^{-1}$ ...(i)

$[A]_2 = 2.2/2\ mM$, $r_1 = 0.6\ m\ M\ s^{-1}$ or, $\frac{2.4}{4}$ ...(ii)

On reducing the concentration of *A* to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$

Order of reaction = 2.

167. (d) Order of a reaction can be fractional.

168. (b) $t_{\frac{1}{4}} = \frac{2.303}{K} log \frac{1}{1-\frac{1}{4}} = \frac{0.29}{K}$.

169. (d) $\boldsymbol{R = K[A]}$

$\boldsymbol{2 \times 10^{-5} = K \times 10^{-2}}$

$K = 2 \times 10^{-3}\, sec^{-1}$

$t_{\frac{1}{2}} = \frac{.693}{K} = \frac{.693}{2\times10^{-3}} = \frac{693}{2} = 347 sec$

170. (b) $R = k[B]^n; \frac{1}{4}R = k[2B]^n; 4 = \left(\frac{1}{2}\right)^n; 4 = 2^{-n}; n = -2.$

171. (c) $T = t_{\frac{1}{2}} \times n$ *i.e.* $12 = 3 \times n \Rightarrow n = 4$

$N = N_0\left(\frac{1}{2}\right)^n \Rightarrow \frac{N}{N_0} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$

172. (c) $K = 1.7 \times 10^{-5} s^{-1}$

$\boldsymbol{t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{1.7} \times 10^5 = 11.32h}$

173. (c) $A + B \rightarrow C$

On doubling the concentration of A rate of reaction increases by four times. Rate $\propto [A]^2$

However on doubling the concentration of B, rate of reaction increases two times. Rate $\propto [B]$

Thus, overall order of reaction = 2 + 1= 3.

174. (a) In case of zero order reaction, the concentration of reactant decreases linearly with time, as its rate is independent of the concentration of the reactants.

Order of reaction = 2.

167. (d) Order of a reaction can be fractional.

168. (b) $t_{\frac{1}{4}} = \frac{2.303}{K} log \frac{1}{1-\frac{1}{4}} = \frac{0.29}{K}.$

169. (d) $\boldsymbol{R = K[A]}$

$\boldsymbol{2 \times 10^{-5} = K \times 10^{-2}}$

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172. (c) $K = 1.7 \times 10^{-5} s^{-1}$

$\boldsymbol{t_{\frac{1}{2}} = \frac{0.693}{K} = \frac{0.693}{1.7} \times 10^5 = 11.32h}$

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174. (a) In case of zero order reaction, the concentration of reactant decreases linearly with time, as its rate is independent of the concentration of the reactants.