

Rate law and Rate constant

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

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

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

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

146. (c) The relation between half – life period and initial concentration (c) for a n^{th} 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) $k = \frac{2.303}{t} \log \frac{0.8}{0.6} = 2.303 \log \frac{4}{3}$

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

150. (a) For zero order reaction

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

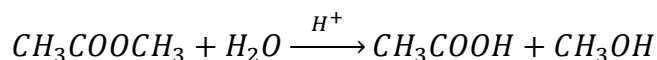
$$\text{Unit} = \text{concentration} \times \text{time}^{-1}.$$

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.,



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

$$\begin{aligned} \text{then, } t &= \frac{2.303}{K} \log \frac{a}{a-x} = \frac{2.303}{.693} \times 10 \times \log \frac{10}{5} \\ &= \frac{2.303 \times 10 \times \log 2}{.693} = \frac{2.303 \times 10 \times 0.301}{0.693} = 10 \text{ years.} \end{aligned}$$

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

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

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

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

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



The reaction is a first order reaction hence,

$$K = \frac{0.693}{t_1} = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{0.693}{10 \text{ min}}$$

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

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

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

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

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

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

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

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

$t_1 = \frac{.693}{K} = \frac{.693}{3 \times 10^{-2}} = 23.1 \text{ minute.}$

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

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

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

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.

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

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

164. (abd) By Vant's Hoff equation, $\frac{d \ln k}{dt} = \frac{\Delta H^0}{RT^2}$

or $\ln k_p = -\frac{\Delta H^0}{RT} + I$. 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 $k = Ae^{-\frac{E_a}{RT}}$, $\frac{E_a}{RT}$ is dimensionless hence A has the unit of K .

166. (b) $aA \rightarrow xP$

Rate of reaction $= [A]^a$

Order of reaction $= a$

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

$[A]_2 = 2.2/2 \text{ mM}, r_2 = 0.6 \text{ mM s}^{-1}$ or, $\frac{2.4}{4} \dots(ii)$

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) $R = K[A]$

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

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

$$t_{\frac{1}{2}} = \frac{.693}{K} = \frac{.693}{2 \times 10^{-3}} = \frac{693}{2} = 347 \text{ sec}$$

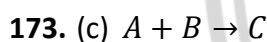
170. (b) $R = k[B]^n$; $\frac{1}{4}R = k[2B]^n$; $4 = \left(\frac{1}{2}\right)^n$; $4 = 2^{-n}$; $n = -2$.

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) $K = 1.7 \times 10^{-5} \text{ s}^{-1}$

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



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

However on doubling the concentration of B , rate of reaction increases two times.

$$\text{Rate} \propto [B]$$

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) $R = K[A]$

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

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

$$t_{\frac{1}{2}} = \frac{.693}{K} = \frac{.693}{2 \times 10^{-3}} = \frac{693}{2} = 347 \text{ sec}$$

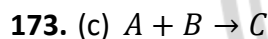
170. (b) $R = k[B]^n$; $\frac{1}{4}R = k[2B]^n$; $4 = \left(\frac{1}{2}\right)^n$; $4 = 2^{-n}$; $n = -2$.

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) $K = 1.7 \times 10^{-5} \text{ s}^{-1}$

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



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

However on doubling the concentration of B , rate of reaction increases two times.

$$\text{Rate} \propto [B]$$

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.

