

**SOLUTIONS****EXERCISE #S-I**

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Rate of reaction

1. Rate of reaction = $\frac{2-1.1}{75} \text{ atm min}^{-1} = 0.012 \text{ atm min}^{-1}$

$$P = CRT \Rightarrow \Delta P = \Delta CRT \Rightarrow \frac{\Delta C}{\Delta t} = \frac{\Delta P}{\Delta t} \times \frac{1}{RT}$$

$$\frac{\Delta C}{\Delta t} = \frac{0.012}{0.08 \times 300} = 8.33 \times 10^{-6} \text{ M sec}^{-1}$$

2. (i) Rate of reaction = $\frac{1}{4} \frac{\Delta[\text{NO}]}{t} = \frac{1}{4} \times \frac{1.08 \times 10^{-2}}{3} = 9 \times 10^{-4} \text{ M sec}^{-1}$

(ii) $-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{t} = +\frac{1}{4} \frac{\Delta[\text{NO}]}{t}$

$$-\frac{\Delta[\text{NH}_3]}{t} = 3.6 \times 10^{-3} \text{ M sec}^{-1}$$

(iii) $\frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{t}$

$$\frac{\Delta[\text{H}_2\text{O}]}{t} = 5.4 \times 10^{-3} \text{ M sec}^{-1}$$

3. $-\frac{1}{3} \frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = +\frac{\Delta[\text{SO}_4^{2-}]}{\Delta t}$

(a) $-\frac{1}{3} \frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$

$$-\frac{\Delta[\text{I}^-]}{\Delta t} = -3 \times \frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = 3 \times 1.5 \times 10^{-3} \text{ M sec}^{-1}$$

(b) $-\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = +\frac{\Delta[\text{SO}_4^{2-}]}{\Delta t}$

$$+\frac{\Delta[\text{SO}_4^{2-}]}{\Delta t} = 1.5 \times 10^{-3} \text{ M sec}^{-1}$$



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4. $\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$

(a) $+ \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = +2 \times \frac{\Delta[\text{O}_2]}{\Delta t}$

$$+ \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = +2 \times \frac{\Delta[\text{O}_2]}{\Delta t} \Rightarrow + \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = +2 \times \frac{36}{32} \text{ M min}^{-1} \text{ M min}^{-1} = +2 \times \frac{36}{32} \times 18 \text{ gmin}^{-1}$$

(b) $+ \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = - \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$

$$- \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{36}{32} \text{ M min}^{-1} = \frac{36}{32} \times 34 \text{ gmin}^{-1}$$

Rate law and order of reaction

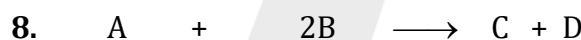
5. (i) Rate = $k [\text{A}]^1 [\text{B}]^2 [\text{C}]^0$

(ii) On doubling concentration rate will increases by a factor of 8 times.

6. Rate = $k [\text{A}]^2 [\text{B}_2]$

If volume is reduced to one third then concentration of A and B_2 each will increase by a factor of 3.

7. $\frac{k_{\text{BrO}^-}}{3} = \frac{k_{\text{BrO}_3^-}}{1} = \frac{k_{\text{Br}^-}}{2}$



P _i	0.6	0.8	0	0
P _f	0.6-0.2	0.8-0.4	0.2	

$$\text{rate}_{\text{initially}} = k \times 0.6 \times 0.8^2$$

$$\text{rate}_{\text{finally}} = k \times 0.4 \times 0.4^2$$

$$\frac{\text{rate}_{\text{final}}}{\text{rate}_{\text{initial}}} = \frac{0.4 \times 0.4^2}{0.6 \times 0.8^2}$$

Zero order reaction

9. For zero order reaction

$$[\text{A}]_t = [\text{A}]_0 - kt$$

$$\text{At } 10 \text{ min, } [\text{A}]_t = 10 - 1.2 \times 10^{-2} \times 600 = 10 - 7.2 = 2.8 \text{ M}$$



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$$t_{100\%} = \frac{[A]_0}{k} = \frac{10}{1.2 \times 10^{-2}} = 833.33 \text{ sec}$$

so at 20 min = 1200 sec $\Rightarrow [A]_t = 0$

$$10. \quad k = \frac{[A]_0 - [A]_t}{t} = \frac{0.1 - 0.09}{1} = 0.1 \text{ M min}^{-1}$$

$$11. \quad t_{100\%} = \frac{[A]_0}{k} = \frac{6 \times 10^{-6} / 0.1 \times 10^{-3}}{10^7} = 6 \times 10^{-9} \text{ sec.}$$

$$12. \quad k = \frac{[A]_0 - [A]_t}{t} = \frac{[A]_0 - 0.25[A]_0}{1} = 0.75[A]_0$$

$$t = \frac{[A]_0 - 0.1[A]_0}{k} = \frac{0.9[A]_0}{0.75[A]_0} = 1.2 \text{ hr.}$$

$$13. \quad [A]_t = [A]_0 - kt = 10 - 2 \times 10^{-6} \times 2 \times 24 \times 60 = 9.994 \text{ M}$$

First order reaction

$$14. \quad (i) \quad k = \frac{1}{72} \ln \left(\frac{a_o}{0.25a_o} \right)$$

$$k = \frac{2 \ln 2}{72} = \frac{\ln 2}{36}$$

$$t_{1/2} = 36 \text{ min.}$$

$$(ii) \quad t_{87.5\%} = 3 \times t_{50\%} = 3 \times 36 = 108 \text{ min.}$$

$$15. \quad (i) \quad k = \frac{1}{10} \ln \left(\frac{100}{80} \right) = 0.022 \text{ min}^{-1}$$

$$(ii) \quad k = \frac{1}{0.022} \ln \left(\frac{100}{25} \right) = 62.125 \text{ min}^{-1}$$

$$16. \quad t_{1/2} = \frac{0.693}{k}$$

$$t_{99.9\%} = \frac{1}{k} \ln \left(\frac{100}{0.1} \right) = 10 \times \frac{0.693}{k}$$



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17. (a) Rate = $k [A]$
 $= 5 \times 10^{-5} \times 1 = 5 \times 10^{-5} \text{ M sec}^{-1}$
- (b) $[A]_t = [A]_0 e^{-kt} = 1 \times e^{-5 \times 10^{-5} \times 60 \times 60} = 0.84 \text{ M}$
 Rate = $5 \times 10^{-5} \times 0.84 = 4.2 \times 10^{-5} \text{ M sec}^{-1}$

18. For 1st order reaction

$$k = \frac{1}{20} \ln\left(\frac{0.4}{0.2}\right) = \frac{0.7}{20} \text{ sec}^{-1}$$

$$\text{Rate} = k [A]$$

$$= \frac{0.7}{20} \times 0.2$$

$$= 7 \times 10^{-3} \text{ M sec}^{-1}$$

19. $k = \frac{1}{20} \ln\left(\frac{500}{250}\right) = \frac{\ln 2}{20}$

$$t_{1/2} = 40 \text{ month}$$

$$t = \frac{1}{k} \ln\left(\frac{100}{25}\right) = 40 \text{ month}$$

20. $k = \frac{1}{1} \ln\left(\frac{100}{98}\right)$

21. $\frac{[A]_t}{[A]_0} \times 100 = e^{-kt} \times 100 = e^{-3.8 \times 10^{-4} \times 90 \times 60} \times 100$

22. Let initial concentration of A and B are $3a_0$ & $2a_0$.

After three half life ($t = 15 \text{ sec}$)

$$\text{Concentration of A} = \frac{3a_0}{2^3} = \frac{3a_0}{8}$$

$$\text{Concentration of B} = \frac{2a_0}{2^2} = \frac{2a_0}{4}$$

$$\frac{C_A}{C_B} = \frac{3}{4}$$



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Experimental determination of order

23. $r = K [NO]^x [H_2]^y$

(i) \because when $[H_2]$ is halved rate of reaction is also halved so order w.r.t. $[H_2]$ is 1

\therefore when $[NO]$ is doubled rate of reaction become four time so order w.r.t. $[NO]$ is 2 so
total order of reaction = 2 + 1 = 3

(ii) $r = K[NO]^2 [H_2]$

(iii) $4.4 \times 10^{-4} = K = \times (1.5 \times 10^{-4})^2 \times 4 \times 10^{-3}$

$K = 0.488 \times 10^7 \text{ sec}^{-1} \text{ M}^{-2}$

rate = $0.488 \times 10^7 \times (1.1 \times 10^{-3})^2 \times 1.5 \times 10^{-3} = 0.88572 \times 10^{-2}$

24. Order of reaction = $1 + \frac{\ln((t_{1/2})_2 / (t_{1/2})_1)}{\ln(a_{o_1} / a_{o_2})}$

25. Order of reaction = $1 + \frac{\ln((t_{1/2})_2 / (t_{1/2})_1)}{\ln(a_{o_1} / a_{o_2})}$

26. $t_{1/2} \propto [A]_0^{1-n}$

$$\left(\frac{2}{1}\right)^{1-n} = \frac{50}{25}$$

$1 - n = 1 \Rightarrow n = 0$

27. Use Hit and Trial method.

28. Use Hit and Trial method.



$t = 0 \quad P_0 \quad 0 \quad 0$

$t = t \quad P_0 - x \quad x \quad x$

$t = \infty \quad 0 \quad P_0 \quad P_0$

$$2P_0 = P_3 \Rightarrow P_0 = \frac{P_3}{2}$$

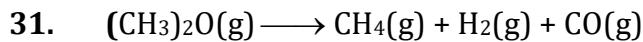
$$P_2 = P_0 + x \Rightarrow x = P_2 - P_0 = P_2 - \frac{P_3}{2} = \frac{2P_2 - P_3}{2}$$

$$K = \frac{1}{t} \ln \frac{P_0}{P_0 - x} = \frac{1}{t} \ln \frac{P_3/2}{P_3 - P_2}$$



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Experimental determination of First order rate constant



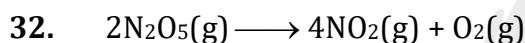
$$t = 0 \quad 312 \quad 0 \quad 0 \quad 0$$

$$t = t \quad 312 - x \quad x \quad x \quad x$$

$$P_t = 312 + 2x$$

$$\Delta P = 2x = 96 \Rightarrow x = 48$$

$$k = \frac{1}{390} \ln \frac{312}{312 - 48}$$



$$t = 0 \quad P_o \quad 0 \quad 0$$

$$t = t \quad P_o - x \quad 2x \quad \frac{x}{2}$$

$$t = \infty \quad 0 \quad 2P_o \quad \frac{P_o}{2}$$

$$\frac{5P_o}{2} = 584.5 \Rightarrow P_o = 233.8$$

$$P_t = P_o + \frac{3x}{2} = 284.5 \Rightarrow x = 33.8$$

$$k = \frac{1}{t} \frac{1}{30} \ln \frac{233.8}{233.8 - 33.8}$$



$$t = 0 \quad P_o \quad 0 \quad 0$$

$$t = t \quad 0.1 - x \quad 2x \quad \frac{x}{2}$$

$$0.1 + \frac{3x}{2} = 0.145 \Rightarrow x = 0.03$$

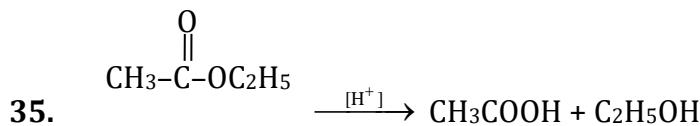
$$t = \frac{1}{7.48 \times 10^{-3}} \ln \frac{0.1}{0.1 - 0.03} = \frac{1000}{7.48} \ln \frac{0.1}{0.07} = 47.69 \text{ sec}$$



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34. $V_{\text{KMnO}_4} \propto [\text{H}_2\text{O}_2]$

$$K = \frac{1}{t} \ln \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t} = \frac{1}{t} \ln \frac{V_0}{V_t} = \frac{1}{600} \ln \frac{22.8}{13.8}$$

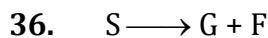


$t = 0$	a	0	0
$t = t$	$a-x$	x	x
$t = \infty$	0	a	a

$$a \propto 42.03 - 19.24$$

$$a - x \propto 24.02 - 19.25$$

$$k = \frac{1}{75} \ln \frac{42.03 - 19.24}{24.02 - 19.25} = \frac{1}{75} \ln \frac{22.79}{4.77}$$



$t = 0$	a	0	0
$t = t$	$a-x$	x	x
$t = \infty$	0	a	a

$$r_t \propto x \times r_G^\circ + x \times r_F^\circ \quad \dots \dots \text{(i)}$$

$$r_\infty \propto a \times r_G^\circ + a \times r_F^\circ \quad \dots \dots \text{(ii)}$$

$$r_\infty - r_t \propto (a-x)(r_G^\circ + r_F^\circ)$$

$$r_\infty - r_t \propto (a-x)(r_G^\circ + r_F^\circ)$$

$$K = \frac{1}{t} \ln \frac{r_\infty}{r_\infty - r_t}$$

37. $k = \frac{1}{t} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$

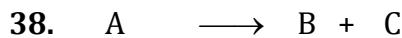
$$= \frac{1}{60} \ln \frac{-3.8 - 13.1}{-3.8 - 11.6} = \frac{1}{60} \ln \frac{16.9}{15.4}$$

$$t = \frac{1}{K} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$$

Put $r_t = 0$



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$$t = 0 \quad c \quad 0 \quad 0$$

$$t = t \quad c - x \quad x \quad x$$

$$t = \infty \quad 0 \quad c \quad c$$

$$\text{At } t = 6.93 \quad r_t = 2.5 = 20(c-x) + 30x - 40x$$

$$2.5 = 20c - 30x \quad \dots (1)$$

$$\text{At } t = \infty \quad r_\infty = -5 = 30c - 40c$$

$$-5 = -10c \Rightarrow c = \frac{1}{2} = 0.5$$

$$\therefore x = 0.25$$

$$k = \frac{1}{0.93} \ln\left(\frac{0.5}{0.5 - 0.25}\right)$$

$$k = 0.1 \text{ min}^{-1}$$

parallel first order reaction

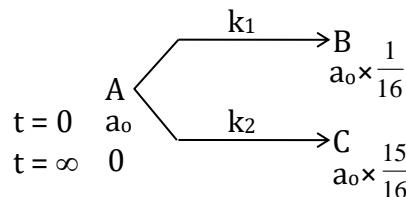


$$[A]_t = [A]_0 e^{-(x+10x) \times 1}$$

$$= [A]_0 e^{-11x}$$

$$[C]_t = \frac{x}{x+10x} [A]_0 (1 - e^{-11x}) = \frac{[A]_0}{11} (1 - e^{-11x})$$

40. $\frac{k_1}{k_2} = \frac{2 \times 10^{-3}}{3 \times 10^{-2}} = \frac{1}{15}$



$$\therefore [B]_\infty = \frac{a_0}{16} = 100$$

$$a_0 = 1600$$

$$\therefore t = \frac{1}{k_1 + k_2} \ln\left(\frac{a_0}{a_t}\right) = \frac{1}{(2 \times 10^{-3}) + (3 \times 10^{-2})} \ln\left(\frac{1600}{100}\right) = 86.625 \text{ min}$$



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41. $\frac{1}{(t_{1/2})_{\text{overall}}} = \frac{1}{60} + \frac{1}{90}$

$(t_{1/2})_{\text{overall}} = 36 \text{ min.}$

Reversible and sequential first order reaction

42. $\because k_1 \ggg k_2$

$$\therefore [C] = [A]_0 [1 - e^{-k_2 t}] = 20 (1 - e^{-0.0693 \times 10})$$

$= 10 \text{ M}$

43. $t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$

44. $\because K_{\text{eq}} = \frac{k_f}{k_b} = 0.16$

$$\frac{3.3 \times 10^{-4}}{k_b} = 0.16$$

$$\therefore k_b = \frac{3.3 \times 10^{-4}}{0.16} = 2.0625 \times 10^{-3}$$

$$\therefore t_{1/2} = \frac{0.693}{k_f + k_b} = \frac{0.693}{(3.3 \times 10^{-4} + 2.0625 \times 10^{-3})}$$

$= 389.96 \text{ sec}$

$= 4.83 \text{ min.}$

Effect of temperature on rate

45. $\Delta H = E_{a_f} - E_{a_b} \Rightarrow 72 = 77 - E_{a_b} \Rightarrow E_{a_b} = 5 \text{ kJ}$

46. $\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\ln (4) = \frac{E_a}{2} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$E_a = 13.44 \text{ kcal}$



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47. $k_{380^\circ\text{C}} = \frac{0.693}{360}$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

48. $\ln 1.75 = \frac{\varepsilon_a}{8.314} \left[\frac{1}{298} - \frac{1}{308} \right]$

49. Fraction of molecules = $e^{-E_a/RT}$

$$\Delta H = E_{a_f} - E_{a_b} \Rightarrow 0.12 = E_{a_f} - 0.02 \Rightarrow E_{a_b} = 0.14 \text{ kcal}$$

Effect of catalyst on rate

51. Increase in rate constant due to presence of catalyst = $e^{\frac{x}{RT}} = 1.718$

\therefore Decrease in E_a due to catalyst = $x = 2.25 \text{ kJ}$

E_a in the absence of catalyst = $6.05 + 2.25 = 8.3 \text{ kJ}$

$$\text{Slope} = -\frac{E_a}{R} = -\frac{8.3 \times 1000}{R} = -1000$$

Mechanism of Reaction

53. Rate = $k_1[N_2O_5]$

54. Rate = $k_2[NOBr_2][NO]$

$$\therefore K_{eq.} = \frac{[NOBr_2]}{[NO][Br_2]}$$

$$\therefore [NOBr_2] = K_{eq.} [NO] [Br_2]$$

$$\therefore \text{Rate} = k_2 K_{eq.} [NO]^2 [Br_2]$$

55. Rate = $k_2 [N_2O_2][H_2]$

$$\therefore K_{eq} = \frac{[N_2O_2]}{[NO]^2}$$

$$[N_2O_2] = K_{eq} [NO]^2$$

$$\therefore \text{Rate} = k_2 K_{eq.} [NO]^2 [H_2]$$