Chapter 10 Homework Solutions

10.1 The rate law is of the form: $\frac{\Delta \text{conc}}{\Delta time} = k \cdot conc^3$

1 mol/L = 1 M

Units of k are: $k = \frac{1}{conc^3}\frac{conc}{time} = \frac{1}{conc^2 \cdot time} = \frac{1}{M^2 s} = M^{-2}s^{-1}$

10.2 First order Reaction

$[A]_o$ = 220 mM/L = 0.220 M/L = 0.22 M

[A] = 56 mM/L = 0.056 M at t = $1.22x10^4$ s

$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt \;\rightarrow\; k = -\frac{1}{t}\ln\left(\frac{[A]}{[A]_o}\right) = -\frac{1}{1.22x10^4\ s}\ln\left(\frac{0.056}{0.220}\right) = 1.12x10^{-4}\ s^{-1}$$

10.3 Second order Reaction

$[A]_o$ = 220 mM/L = 0.220 M/L = 0.22 M

[A] = 56 mM/L = 0.056 M at t = $1.22x10^4$ s

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \;\rightarrow\; k = \frac{1}{t}\left(\frac{1}{[A]} - \frac{1}{[A]_o}\right) = \frac{1}{1.22x10^4\ s}\left(\frac{1}{0.056M} - \frac{1}{0.22M}\right) = 1.09x10^{-3}\ M^{-1}s^{-1}$$

10.4 k = 1.24 $cm^3mol^{-1}s^{-1}$ x 1 L / 1000 cm^3 = $1.24x10^{-3}$ L $mol^{-1}s^{-1}$ = $1.24x10^{-3}$ $M^{-1}s^{-1}$

$[A]_o$ = 0.260 M [A] = 0.026 M

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \;\rightarrow\; t = \frac{1}{k}\left(\frac{1}{[A]} - \frac{1}{[A]_o}\right) = \frac{1}{1.24x10^{-3}\ M^{-1}s^{-1}}\left(\frac{1}{0.026M} - \frac{1}{0.260M}\right) = 2.8x10^4\ s$$

10.5 E_a = 99.1 kJ/mol = $9.91x10^4$ J/mol k_2/k_1 = 1.10 T_1 = 25 °C = 298 K T_2 = ??

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

Therefore, $\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{E_a}\ln\left(\frac{k_2}{k_1}\right) = \frac{1}{298\,K} - \frac{8.314\,J/mol\cdot K}{9.91x10^4\;J/mol}\ln(1.10) = 3.348x10^{-3}\;K^{-1}$

$T_2 = 1/(3.348x10^{-3}\;K^{-1}) = 298.7\;K \approx 299\;K.$

Note: The reasons that T_2 is so close to T_1 are (1) The ratio is close to 1, (2) 99.1 kJ/mol is a very large E_a.

10.6 T_1 = 455 °C = 728 K T_2 = 550 °C = 823 K E_a = 251 kJ/mol = $2.51x10^5$ J/mol

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = -\frac{2.51x10^5\;J/mol}{8.314\,J/mol\cdot K}\left[\frac{1}{823\,K} - \frac{1}{728\,K}\right] = 4.79$$

$$\frac{k_2}{k_1} = e^{4.79} = 120 \rightarrow \frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{0.693/k_2}{0.693/k_1} = \frac{k_1}{k_2} = \frac{1}{120} = 8.31x10^{-3}$$

$(t_{1/2})_2 = 8.31x10^{-3}(t_{1/2})_1 = 8.31x10^{-3}(6.5x10^6\;s) = 5.40x10^4\;s$

10.7

[A_o]	**[B_o]**	**r_o**
0.10 M	2.0 M	8.50 Ms^{-1}
0.30	2.0	2.83
0.30	3.0	7.80

$r_o = k[A_o]^x[B_o]^y$

$$\frac{(r_o)_2}{(r_o)_1} = \left\{\frac{[A_o]_2}{[A_o]_1}\right\}^x\left\{\frac{[B_o]_2}{[B_o]_1}\right\}^y \rightarrow \frac{2.83}{8.50} = \left\{\frac{0.30}{0.10}\right\}^x\left\{\frac{2.0}{2.0}\right\}^y \rightarrow 0.333 = (3)^x$$

$$x = \frac{\ln(0.333)}{\ln(3.0)} = \frac{-1.10}{+1.10} = -1$$

$$\frac{(r_o)_3}{(r_o)_2} = \left\{\frac{[A_o]_3}{[A_o]_2}\right\}^x\left\{\frac{[B_o]_3}{[B_o]_2}\right\}^y \rightarrow \frac{7.80}{2.83} = \left\{\frac{0.30}{0.30}\right\}^x\left\{\frac{3.0}{2.0}\right\}^y \rightarrow 2.76 = (1.5)^y$$

$$y = \frac{\ln(2.76)}{\ln(1.5)} = \frac{1.02}{+0.405} = 2.5 = 5/2$$

$$r_o = k[A_o]^{-1}[B_o]^{5/2} = k\frac{[B_o]^{5/2}}{[A_o]} \rightarrow k = \frac{r_o[A_o]}{[B_o]^{5/2}}$$

Point #1: $k = \frac{(r_o)_1[A_o]_1}{[B_o]_1^{5/2}} = \frac{(8.50\,Ms^{-1})(0.10\,M)}{(2.0\,M)^{5/2}} = 0.15\,M^{-1/2}s^{-1}$

Points #2 and #3 give same value.

10.8 $[A]_o = 0.60$ M

(a) [A] = 0.30 M at t = 45 s

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \;\rightarrow\; k = \frac{1}{t}\left\{\frac{1}{[A]} - \frac{1}{[A]_o}\right\} = \frac{1}{45\,s}\left\{\frac{1}{0.30\,M} - \frac{1}{0.60\,M}\right\} = 3.70x10^{-2}\,M^{-1}s^{-1}$$

(b) [A] = ?? at t = 70 s

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt = \frac{1}{0.60\,M} + (3.70x10^{-2}\,M^{-1}s^{-1})(70\,s) = 4.26\,M^{-1}$$

Therefore, [A] = 1/(4.26 M^{-1}) = 0.23 M

(c) [A] = 0.15 M at t = ??

$$t = \frac{1}{k}\left\{\frac{1}{[A]} - \frac{1}{[A]_o}\right\} = \frac{1}{3.70x10^{-2}\,M^{-1}s^{-1}}\left\{\frac{1}{0.15\,M} - \frac{1}{0.60\,M}\right\} = 135\,s$$

10.9 $t_{1/2}$ = 5730 yr $\rightarrow$ $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\,yr} = 1.21x10^{-4}\,yr^{-1}$

$[^{14}C]_o = 1.1x10^{-12}$ $[^{14}C] = 7.2x10^{-13}$ t = ??

$$\ln\left\{\frac{[^{14}C]}{[^{14}C]_o}\right\} = -kt \;\rightarrow\; t = -\frac{1}{k}\ln\left\{\frac{[^{14}C]}{[^{14}C]_o}\right\} = -\frac{1}{1.21x10^{-4}\,yr^{-1}}\ln\left\{\frac{7.2x10^{-13}}{1.1x10^{-12}}\right\} = 3500\,yr$$

10.10 $^{40}K(s) \rightarrow {}^{40}Ar(g)$ $t_{1/2}$ = 1.25 billion years (1.25 by)

Prepare a table of the following type:

time	$[^{40}K]$	$[^{40}Ar]$	$[^{40}K]/[^{40}Ar]$	$[^{40}Ar]/[^{40}K]$
0	1 $[^{40}K]_0$	0 $[^{40}K]_0$	∞	0
1 $t_{1/2}$ = 1.25 by	0.50 $[^{40}K]_0$	0.50 $[^{40}K]_0$	1.00	1.00
2 $t_{1/2}$ = 2.50 by	0.25 $[^{40}K]_0$	0.75 $[^{40}K]_0$	0.33	3.00
3 $t_{1/2}$ = 3.75 by	0.125 $[^{40}K]_0$	0.875 $[^{40}K]_0$	0.14	7.00

(a) If a rock is 3.2 by old, then the ratio, $[^{40}Ar]/[^{40}K]$, must be between 3.00 and 7.00. Therefore, the correct answer is: (iii) 4.90

(b) If the ratio, $[^{40}K]/[^{40}Ar] = 0.75$, then the age must be between 1.25 by and 2.50 by Therefore, the correct answer is: (ii) 1.50 by

10.11 $[A]_o = 0.90$ M $\quad t_{1/2} = 150$ s $\quad [A]_o = 0.30$ M $\quad t_{1/2} = 260$ s

$$t_{1/2} \propto \frac{1}{[A]_o^{x-1}} \rightarrow \frac{(t_{1/2})_2}{(t_{1/2})_1} = \left\{\frac{([A]_o)_1}{([A]_o)_2}\right\}^{x-1}$$

$$\frac{260\,s}{150\,s} = \left\{\frac{0.90\,M}{0.30\,M}\right\}^{x-1} \rightarrow 1.73 = (3)^{x-1} \rightarrow x-1 = \frac{\ln(1.73)}{\ln(3)} = \frac{0.55}{1.10} = \frac{1}{2}$$

Therefore, x = 1/2 + 1 = 3/2

10.12 $k_1 = 1.5x10^{-3}\ s^{-1}$ at $T_1 = 40\ ^oC = 313$ K $\qquad k_2 = 8.6x10^{-2}\ s^{-1}$ at $T_2 = 80\ ^oC = 353$ K

(a) $$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \rightarrow E_a = -R\frac{\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2}-\frac{1}{T_1}} = -(8.314\,J/mol\cdot K)\frac{\ln\left(\frac{8.6x10^{-2}}{1.5x10^{-3}}\right)}{\frac{1}{353K}-\frac{1}{313K}}$$

$$= 9.30x10^4\ J/mol = 93.0\,kJ/mol$$

$$k_1 = Ae^{-\frac{E_a}{RT_1}} \rightarrow A = k_1 e^{+\frac{E_a}{RT_1}} = (1.5x10^{-3}\ s^{-1})e^{+\frac{9.30x10^4\ J/mol}{(8.314\,J/mol\cdot K)(313K)}} = 5.0x10^{12}\ s^{-1}$$

Using k_2 and T_2 gives the same value for A.

(b) k_3 = ??? at $T_3 = 130\ ^oC = 403$ K

$$k_3 = Ae^{-\frac{E_a}{RT_3}} = (5.0x10^{12}\ s^{-1})e^{-\frac{9.30x10^4\ J/mol\cdot K}{(8.314\,J/mol\cdot K)(403K)}} = (5.0x10^{12}\ s^{-1})e^{-27.76} = 4.4\,s^{-1}$$

(c) $(t_{1/2})_4 = 200$ s at T_4 = ?

$$k_4 = \frac{0.693}{(t_{1/2})_4} = \frac{0.693}{200\,s} = 3.47x10^{-3}\ s^{-1}$$

$$k = Ae^{-\frac{E_a}{RT}} \rightarrow \ln(k) = \ln(A) - \frac{E_a}{RT} \rightarrow \frac{E_a}{RT} = \ln\left(\frac{A}{k}\right) = \ln\left(\frac{5.0x10^{12}\ s^{-1}}{3.47x10^{-3}\ s^{-1}}\right) = 34.90$$

Therefore, $T = \frac{E_a}{34.90R} = \frac{9.30x10^4\ J/mol}{34.90(8.314\ J/mol \cdot K)} = 321K = 48\ ^oC$

10.13 Two points on Graph: (1) $\ln(k_1) = 6.0$ at $1000/T_1 = 2.60$ [$1/T_1 = 2.60x10^{-3}$]

(2) $\ln(k_2) = 0.0$ at $1000/T_2 = 3.80$ [$1/T_2 = 3.80x10^{-3}$]

$$k = Ae^{-\frac{E_a}{RT}} \rightarrow \ln(k) = \ln(A) - \frac{E_a}{R} \cdot \frac{1}{T} = Int + Slope \cdot \frac{1}{T}$$

$$Int = \ln(A) \quad and \quad Slope = -\frac{E_a}{R}$$

$$Slope = \frac{\ln(k_2) - \ln(k_1)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{0.0 - 6.0}{3.80x10^{-3}\ K^{-1} - 2.6x10^{-3}\ K^{-1}} = -5000\,K$$

$$Int = \ln(k_1) - slope \cdot \frac{1}{T_1} = 6.0 - (-5000\,K)(2.60x10^{-3}\ K^{-1}) = 19.0$$

$$E_a = -R \cdot slope = -(8.314\,J/mol \cdot K)(-5000\,K) = 41600\,J/mol = 41.6\,kJ/mol$$

$$A = e^{\text{int}} = e^{19.0} = 1.8x10^8\ \text{s}^{-1}$$