CHEM 1423
Chapters 16
Homework Solutions

TEXTBOOK HOMEWORK

16.15 2 D + 3 E 2 G + H

$$Rate = -\frac{1}{2}\frac{\Delta[D]}{\Delta t} = -\frac{1}{3}\frac{\Delta[E]}{\Delta t} = -\frac{\Delta[F]}{\Delta t} = +\frac{1}{2}\frac{\Delta[G]}{\Delta t} = \frac{\Delta[H]}{\Delta t}$$

$$\frac{\Delta[H]}{\Delta t} = 0.1 Ms^{-1} \cdot \frac{1\, mol\, H}{2\, mol\, D} = 0.05\, Ms^{-1}$$

16.27 $R_o = k[A]_o^x [B]_o^y [C]_o^z$

(a) Compare Expt. 1 and 2

$$\frac{R_{o,2}}{R_{o,1}} = \left(\frac{[A]_{o,2}}{[A]_{o,1}}\right)^x \rightarrow \frac{1.25x10^{-2}}{6.25x10^{-3}} = \left(\frac{0.10}{0.05}\right)^x$$

$$2.0 = 2.0^x \rightarrow x = 1$$

Compare Expt. 2 and 3

$$\frac{R_{o,2}}{R_{o,2}} = \left(\frac{[B]_{o,3}}{[B]_{o,2}}\right)^y \rightarrow \frac{5.00x10^{-2}}{1.25x10^{-2}} = \left(\frac{0.10}{0.05}\right)^y$$

$$4.0 = 2.0^y \rightarrow y = \frac{\ln(4.0)}{\ln(2.0)} = \frac{1.386}{0.693} = 2$$

Compare Expt. 1 and 4

$$\frac{R_{o,4}}{R_{o,1}} = \left(\frac{[C]_{o,4}}{[C]_{o,1}}\right)^z \rightarrow \frac{6.25x10^{-3}}{6.25x10^{-3}} = \left(\frac{0.02}{0.01}\right)^z$$

$$1.0 = 2.0^z \rightarrow z = \frac{\ln(1.0)}{\ln(2.0)} = \frac{0}{0.693} = 0$$

$$R_o = k[A]_o^x [B]_o^y [C]_o^z = k[A]_o^1 [B]_o^2 [C]_o^0 = k[A]_o [B]_o^2$$

(b)

$$k = \frac{R_o}{[A]_o [B]_o^2} = \frac{6.25x10^{-3}\, Ms^{-1}}{(0.05M)(0.05M)^2} = 50.\, M^{-2}s^{-1}$$

Note: Above result obtained using Expt. 1. You get the same answer for k using any of the other experiments

16.31 $k = 0.2\ M^{-1}s^{-1}$, $[AB]_o = 1.50$ M , $[AB] = (1/3)(1.50\ M) = 0.50$ M , t = ?

$$\frac{1}{[AB]} = kt + \frac{1}{[AB]_o}$$

$$t = \frac{1}{k}\left\{\frac{1}{[AB]} - \frac{1}{[AB]_o}\right\} = \frac{1}{0.2\,M^{-1}s^{-1}}\left\{\frac{1}{0.50\,M} - \frac{1}{1.50\,M}\right\} = 6.67\,s$$

16.32 $k = 0.2\ M^{-1}s^{-1}$, $[AB]_o = 1.50$ M , t = 10 s , [AB] = ?

$$\frac{1}{[AB]} = kt + \frac{1}{[AB]_o} = (0.2\,M^{-1}s^{-1})(10\,s) + \frac{1}{1.50\,M} = 2.67\,M^{-1}$$

$$[AB] = \frac{1}{2.67\,M^{-1}} = 0.375\,M \approx 0.38\,M$$

16.47 $E_a = 33.6$ kJ/mol $= 3.36x10^4$ J/mol
$k_1 = 4.7x10^{-3}\ s^{-1}$, $T_1 = 25\ ^oC = 298$ K , $T_2 = 75\ ^oC = 348$ K , k_2 = ?

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

$$\ln\left(\frac{k_2}{4.7x10^{-3}\,s^{-1}}\right) = -\frac{3.36x10^4\ J/mol}{8.31\,J/mol\cdot K}\left(\frac{1}{348\,K} - \frac{1}{298\,K}\right) = 1.949$$

$$\frac{k_2}{4.7x10^{-3}\,s^{-1}} = e^{1.949} = 7.025$$

$$k_2 = 7.025\left(4.7x10^{-3}\,s^{-1}\right) = 0.033\,s^{-1}$$

16.48 $k_1 = 4.50x10^{-5}\ M^{-1}s^{-1}$, $T_1 = 195\ ^oC = 468$ K , $k_2 = 3.20x10^{-3}\ M^{-1}s^{-1}$, $T_2 = 258\ ^oC = 531$ K
E_a = ? , A = ?

Calculation of E_a

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

$$E_a = \frac{-\left(8.31\,{}^{J}\!/\!{}_{mol\cdot K}\right)\ln\left(\frac{3.20x10^{-3}}{4.50x10^{-5}}\right)}{\left(\frac{1}{531K} - \frac{1}{468\,K}\right)} = 1.398x10^5\ J/mol = 139.8\,kJ/mol \approx 140.\ kJ/mol$$

Calculation of A

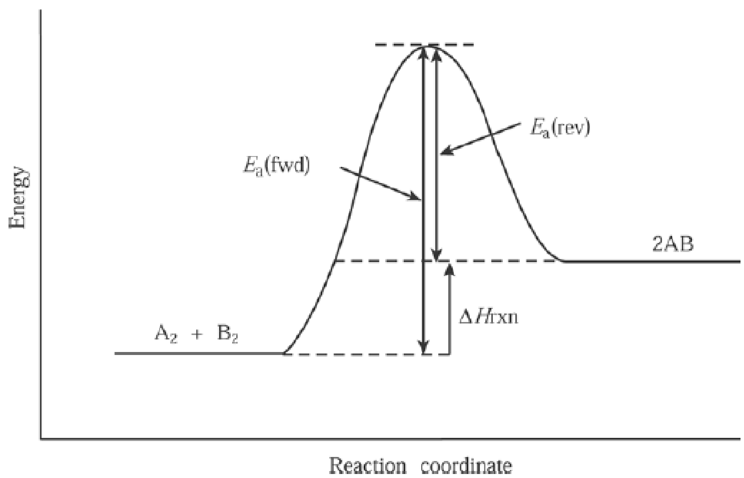
$$\ln(k_1) = \ln(A) - \frac{E_a}{R}\frac{1}{T_1} \rightarrow \ln(A) = \ln(k_1) + \frac{E_a}{R}\frac{1}{T_1}$$

$$\ln(A) = \ln\left(4.50x10^{-5}\right) + \frac{1.398x10^5\ J/mol}{8.31\,J/mol\cdot K}\frac{1}{468\,K} = 25.94$$

$$A = e^{25.94} = 1.84x10^{11}$$

Note: You get the same result using k_2 and T_2

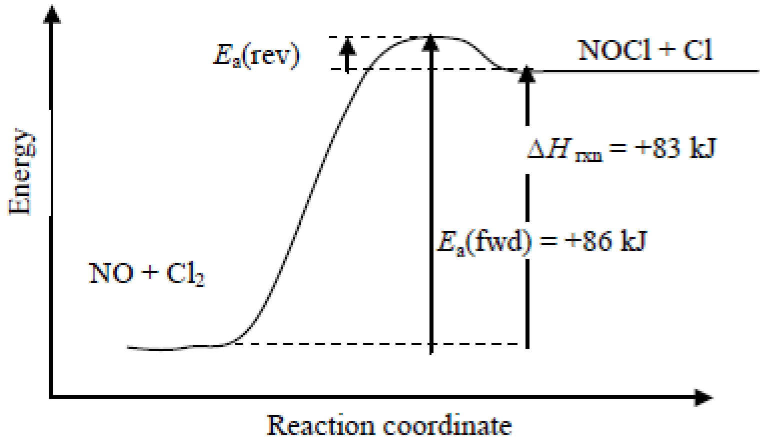
16.50 (a)



(b) E_a(fwd) = 125 kJ/mol , E_a(rev) = 85 kJ/mol

$$E_a(rev) = E_a(fwd) - \Delta H_{rxn}$$
$$\Delta H_{rxn} = E_a(\text{fwd}) - \text{E}_a(rev) = 125 - 85 = +40\,kJ/mol$$

16.52 (a)



(b) E_a(fwd) = 86 kJ/mol , □H_{rxn} = +83 kJ/mol

$$E_a(rev) = E_a(fwd) - \Delta H_{rxn} = 86 - 83 = +3 kJ/mol$$

16.60

(1) $Cl_2 + NO_2 \rightarrow Cl + NO_2Cl$

(2) $Cl + NO_2 \rightarrow NO_2Cl$

(a) Add the two steps and simplify

$Cl_2 + NO_2 + Cl + NO_2 \rightarrow Cl + NO_2Cl + NO_2Cl$

Simplifies to

$Cl_2 + 2\,NO_2 \rightarrow 2\,NO_2Cl$

(b) Cl is a reaction intermediate because it is created in one step and used up in another step. It does not appear in the overall reaction equaton.

(c) (1) Bimolecular $R_1 = k_1[Cl_2][NO_2]$ Slow

(2) Bimolecular $R_2 = k_2[Cl][NO_2]$ Fast

(d) Yes, the mechanism is consistent with the rate law. The slow step in the mechanism is the first step, with the rate law, $R_1 = k_1[Cl_2][NO_2]$. This is the same as the observed rate law.

16.72 $R_o = k[H^+]_o[Suc]_o$ $[H^+]_o$ - 0.01 M , $[Suc]_o$ = 1.0 M

(a) $[Suc]_a$ = 2.5 M $\frac{R_a}{R_o} = \frac{[Suc]_a}{[Suc]_o} = \frac{2.5\,M}{1.0\,M} = 2.5$ Rate increases by factor of 2.5

(b) $[Suc]_a$ = 0.5 M $\frac{R_b}{R_o} = \frac{[Suc]_b}{[Suc]_o} = \frac{0.5\,M}{1.0\,M} = 0.5$ Rate decreases by factor of 2

(c) $[H^+]_c$ = 0.001 M $\frac{R_c}{R_o} = \frac{[H^+]_c}{[H^+]_o} = \frac{0.0001M}{0.01M} = 0.01$ Rate decreases by factor of 100

(d) $[Suc]_d$ = 0.10 M $\frac{R_d}{R_o} = \frac{[Suc]_d}{[Suc]_o}\frac{[H^+]_d}{[H^+]_o} = \frac{0.10\,M}{1.0\,M}\frac{0.10\,M}{0.010\,M} = 1.00$ Rate unchanged

$[H^+]_d$ = 0.10 M

16.75 $[DDT]_o$ = 275 ppbm , $[DDT]_t$ = 10 ppbm

First Calculate k

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.\,yr} = 0.0578\,yr^{-1}$$

Solve for time

$$\ln[DDT] = -kt + \ln[DDT]_o$$

$$t = -\frac{1}{k}\left\{\ln[DDT] - \ln[DDT]_o\right\} = -\frac{1}{k}\ln\left(\frac{[DDT]}{[DDT]_o}\right)$$

$$t = -\frac{1}{0.0578\,yr}\ln\left(\frac{10}{275}\right) = 57.3\,yr \approx 57.\,yr$$