Ch 28

Hwk 11 Key

1. $-\frac{1}{4}\frac{d[NO_2]}{dt} = 5.2\times10^{-4}\ \frac{mol}{L\cdot s}$, $\frac{d[NO_2]}{dt} = -2.08\times10^{-3}\ \frac{mol}{L\cdot s}$

$-\frac{d[O_2]}{dt} = 5.2\times10^{-4}\ \frac{mol}{L\cdot s}$, $\frac{d[O_2]}{dt} = -5.2\times10^{-4}\ \frac{mol}{L\cdot s}$

$\frac{1}{2}\frac{d[N_2O_5]}{dt} = 5.2\times10^{-4}\ \frac{mol}{L\cdot s}$, $\frac{d[N_2O_5]}{dt} = 1.04\times10^{-3}\ \frac{mol}{L\cdot s}$

2. $\frac{v(rxn\ 2)}{v(rxn\ 3)} = \frac{k[A]^m[B]^n}{k[A]^m[B]^n}$ $\qquad \frac{4.20\times10^{-3}}{1.70\times10^{-2}} = \frac{k[4.60\times10^{-4}]^m[6.20\times10^{-5}]^n}{k[9.20\times10^{-4}]^m[6.20\times10^{-5}]^n}$

$0.247 = (0.5)^m$

$\ln 0.247 = m\ln(0.5)$, $m \cong 2$

$\frac{v(rxn\ 1)}{v(rxn\ 2)} = \frac{5.25\times10^{-4}}{4.20\times10^{-3}} = \frac{k[2.30\times10^{-4}]^2[3.10\times10^{-5}]^n}{k[4.60\times10^{-4}]^2[6.20\times10^{-5}]^n}$

$0.125 = 0.25(0.5)^n$

$0.5 = (0.5)^n$ $\qquad n = 1$

$v(t) = k[A]^2[B]$

$k = \frac{v(t)}{[A]^2[B]}$ $\qquad k_{rxn1} = \frac{5.25\times10^{-4}}{(2.30\times10^{-4})^2(3.10\times10^{-5})} = 3.20\times10^{8}\ \frac{1}{M^2 s}$

$k_{rxn2} = \frac{4.20\times10^{-3}}{(4.60\times10^{-4})^2(6.20\times10^{-5})} = 3.20\times10^{8}\ \frac{1}{M^2 s}$

$k_{rxn3} = \frac{1.70\times10^{-2}}{(9.20\times10^{-4})^2(6.20\times10^{-5})} = 3.24\times10^{8}\ \frac{1}{M^2 s}$

$k_{ave} = 3.21\times10^{8}\ \frac{1}{M^2 s}$

3. a) Because it is a base catalyzed reaction and the pH (i.e. concentration of H^+ + OH^-) will affect the rate.

$K_w = [H^+][OH^-] = 1\times10^{-14}$ $pH = -\log(H^+)$

OH^-	H^+	pH
0.52	1.92×10^{-14}	13.72
0.52	1.92×10^{-14}	13.72
0.84	1.19×10^{-14}	13.92
0.91	1.099×10^{-14}	13.96

} very basic

1.09890

b)

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{k[OCl^-]^m[I^-]^n[OH^-]^p}{k[OCl^-]^m[I^-]^n[OH^-]^p}$$

$$\frac{3.06\times10^{-4}}{5.44\times10^{-4}} = \frac{k(1.62\times10^{-3})^m(1.62\times10^{-3})^n(0.52)^p}{k(1.62\times10^{-3})^m(2.88\times10^{-3})^n(0.52)^p}$$

$0.5625 = (0.5625)^n$ $n=1$

$$\frac{\text{rate 2}}{\text{rate 4}} = \frac{k[1.62\times10^{-3})^m(2.88\times10^{-3})^n(0.52)^p}{k(1.62\times10^{-3})^m(2.88\times10^{-3})^n(0.91)^p} = \frac{5.44\times10^{-4}}{3.11\times10^{-4}}$$

$(0.57)^p = 1.75$

$p \ln 0.57 = \ln 1.75$

$p \cong -1$

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{k(2.71\times10^{-3})^m(1.62\times10^{-3})(0.84)^{-1}}{k(1.62\times10^{-3})^m(1.62\times10^{-3})(0.52)^{-1}} = \frac{3.16\times10^{-4}}{3.06\times10^{-4}}$$

$(1.67)^m(1.62)^{-1}$ $= 1.03$

$1.67^m = 1.66$

$m \approx 1$

$$v(t) = k\frac{[OCl^-][I^-]}{[OH^-]}$$ $$k = \frac{v(t)[OH^-]}{[OCl^-][I^-]}$$

$k_{ave} = 60.60\,\frac{1}{s}$

4. Yes $A = k e^{-E_a/RT}$

exponential term is unitless so k and A always have same units

5. $C_4H_8 \rightarrow 2 C_2H_4$

$v(t) = k [C_4H_8]$

$5.31 \times 10^{-5} \frac{M}{s} = k [0.214 M]$

$k = 2.48 \times 10^{-4} \frac{1}{s}$

$t_{1/2} = \frac{\ln 2}{k} = 2795 \text{ sec} \Rightarrow 46.6 \text{ min}$

6. see Excel sheet

a) $E_a = 791.2$ J/mol·K

$A = 4.88 \times 10^{-10}$ 1/M·s

b) $k(220\text{ K}) = 3.17 \times 10^{-10} \frac{1}{M \cdot s}$

c) $\Delta H^{\ddagger} = E_a - 2RT = -2867$ J/mol·K at 220 K

$K_c^{\ddagger} = \frac{kh}{k_B T}$ and $K_c^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$

$\frac{kh}{k_B T} = e^{-\Delta G^{\ddagger}/RT}$

$\ln \frac{kh}{k_B T} = -\Delta G^{\ddagger}/RT$, $\Delta G^{\ddagger} = -RT \ln\left(\frac{kh}{k_B T}\right)$
$= 9.33 \times 10^{4}$ J/mol

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

$S^{\ddagger} = \frac{\Delta G^{\ddagger} - \Delta H^{\ddagger}}{-T} = -437.3$ J/mol·K

Homework 11, Chapter 28, Problem 6

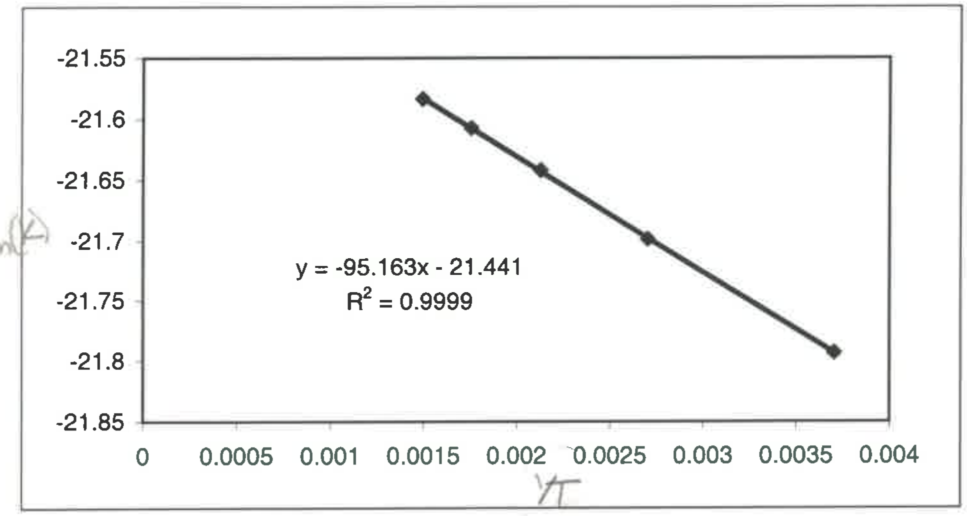
T	1/K	k	ln(k)
270	0.003703704	3.43E-10	-21.79329
370	0.002702703	3.77E-10	-21.69878
470	0.00212766	3.99E-10	-21.64206
570	0.001754386	4.13E-10	-21.60757
670	0.001492537	4.23E-10	-21.58365

$\ln k = \ln A - E_a/R \left(\frac{1}{T}\right)$

$y = b + mx$

$m = -E_a/R$

$b = \ln A$



-Ea/R	-95.163
ln(A)	-21.441

a)

So... Ea = 791.185182 J/mol*K

A = 4.87856E-10 $M^{-1}s^{-1}$

b) k=Ae^(-Ea/RT)

T= 220 K

R= 8.314 J/mol*K

k= 3.17E-10 $M^{-1}s^{-1}$

c)

$\Delta H^{\ddagger}$ = Ea-2RT= -2866.974818 J/mol

$\Delta G^{\ddagger}$ = 9.33E+04 J/mol

$\Delta S^{\ddagger} = (\Delta G^{\ddagger}-\Delta H^{\ddagger})/-T$ -437.2677279 J/mol*K

29-4

Overall $NO_2 + CO \rightarrow CO_2 + NO$

observed rate $\frac{d[CO_2]}{dt} = k_{obs}[NO_2]^2$

Proposed mechanism

① $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ rate determining step (rds)

② $NO_3 + CO \xrightarrow{k_2} CO_2 + NO_2$

Since ① is rds...

rate $\frac{d[CO_2]}{dt} = k_1[NO_2]^2$ $k_{obs} = k_1$

29-11

$2\,N_2O_5 \xrightarrow{k_{obs}} 4NO_2 + O_2$

proposed mechanism

$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

$NO_2 + NO_3 \xrightarrow{k_2} NO + NO_2 + O_2$

$NO_3 + NO \xrightarrow{k_3} 2NO_2$

2 intermediates $[NO_3]$ + $[NO]$ both w/ S.S.A.

$\frac{d[NO]}{dt} = \frac{k_2[NO_2][NO_3]}{[NO_3]} - \frac{k_3[NO_3][NO]}{[NO_3]} = 0/[NO_3]$

$k_2[NO_2] - k_3[NO] = 0$

$[NO] = \frac{k_2}{k_3}[NO_2]$

29-11 con't

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO_3][NO]$$

$$k_1[N_2O_5] = [NO_3](k_{-1}[NO_2] + k_2[NO_2] + k_3[NO])$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_3[NO]} \quad \leftarrow [NO] = \frac{k_2}{k_3}[NO_2]$$

$$= \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2] + k_2[NO_2]}$$

$$= \frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]}$$

$$\frac{d[O_2]}{dt} = k_2[NO_2][NO_3]$$

$$= k_2[NO_2]\left(\frac{k_1[N_2O_5]}{(k_{-1} + 2k_2)[NO_2]}\right)$$

$$= \underbrace{\frac{k_1 k_2}{k_{-1} + 2k_2}}_{k_{obs}}[N_2O_5]$$

29-13

$$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O + H_2O$$

$$\frac{d[N_2O]}{dt} = k_{obs}\frac{[O_2NNH_2]}{[H^+]}$$

mechanism

$$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+ \quad \text{fast eq}$$

$$O_2NNH^- \xrightarrow{k_2} N_2O + OH^- \quad \text{slow}$$

$$H^+ + OH^- \xrightarrow{k_3} H_2O \quad \text{fast}$$

$$K_c = \frac{k_1}{k_{-1}} = \frac{[O_2NNH^-][H^+]}{[O_2NNH_2]} \qquad [O_2NNH^-] = \frac{k_1}{k_{-1}} \frac{[O_2NNH_2]}{[H^+]}$$

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-] = \underbrace{\frac{k_2 k_1}{k_{-1}}}_{k_{obs}} \frac{[O_2NNH_2]}{[H^+]}$$

29-14

$$\frac{d[O_2NNH^-]}{dt} = k_1[O_2NNH_2] - k_{-1}[O_2NNH^-][H^+] - k_2[O_2NNH_2] = 0$$

$$[O_2NNH^-](k_{-1}[H^+] + k_2) = k_1[O_2NNH_2]$$

$$[O_2NNH^-] = \frac{k_1[O_2NNH_2]}{k_{-1}[H^+] + k_2}$$

$$\frac{d[N_2O]}{dt} = k_2[O_2NNH^-]$$

$$= \frac{k_2 k_1[O_2NNH_2]}{k_{-1}[H^+] + k_2}$$

Only if $k_2 \ll k_{-1}[H^+]$ does this rate match that from 29-13

29-24

Initiation: $CH_3CHO \xrightarrow{k_1} CH_3^{\cdot} + CHO^{\cdot}$

Propagation: $CH_3^{\cdot} + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO^{\cdot}$ intermediates

$CH_3CO^{\cdot} \xrightarrow{k_3} CH_3^{\cdot} + CO$

Termination: $2CH_3^{\cdot} \xrightarrow{k_4} C_2H_6$

Rxn: $CH_3CHO \rightarrow CH_4 + CO$

product $$\frac{d[CH_4]}{dt} = k_2[CH_3][CH_3CHO]$$

Steady state intermediates... CH_3 and CH_3CO

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - 2k_4[CH_3]^2 = 0$$

$$\frac{d[CH_3CO]}{dt} = k_2[CH_3][CH_3CHO] - k_3[CH_3CO] = 0$$

$$[CH_3CO] = \frac{k_2}{k_3}[CH_3][CH_3CHO]$$

$$k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3 \tfrac{k_2}{k_3}[CH_3][CH_3CHO] - 2k_4[CH_3]^2 = 0$$

$$k_1[CH_3CHO] = 2k_4[CH_3]^2$$

$$[CH_3] = \left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{1/2}$$

$$\frac{d[CH_4]}{dt} = k_2\left(\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{1/2}[CH_3CHO]\right)$$

$$= k_2\left(\frac{k_1}{2k_4}\right)^{1/2}[CH_3CHO]^{3/2}$$

40. $$2H_2O_{2(aq)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$$

$k_m = 25 \times 10^{-3}$ mol/dm^3

$k_2 = 4.0 \times 10^7$ 1/s

$[S]_0 = 4.32 \times 10^{-6}$ mol/dm^3

$[E]_0 = 0.016 \times 10^{-6}$ mol/dm^3

$$V = \frac{k_2[S]_0[E]_0}{k_m + [S]_0}$$

$$= \frac{(4.0\times10^7)(4.32\times10^{-6})(0.016\times10^{-6})}{(25\times10^{-3}) + (4.32\times10^{-6})}$$

$$= 1.11 \times 10^{-4}\ M/s$$

$$V_{max} = k_2 E_0 = 4.0\times10^7 \cdot 0.016\times10^{-6}$$

$$= 0.64\ M/s$$