CH 421 Homework 2

17 A: 2a) 3a) 5a) 7a) 9a)

2a) $\frac{d[NO]}{dt} = 0.24$ mmol $dm^{-3} s^{-1}$

for every 2 NO molecules generated, there is 1 Br_2 molecule generated.

Thus, $\frac{d[NO]}{dt} = 2\frac{d[Br_2]}{dt} \Rightarrow$ rate of formation of Br_2 $= 0.12$ mmol $dm^{-3} s^{-1}$

3a) $\frac{d[A]}{dt} = -2.7$ mol $dm^{-3} s^{-1}$

$\frac{d[B]}{dt} = -27.2$ mol $dm^{-3} s^{-1} = -5.4$ mol $dm^{-3} s^{-1}$

$\frac{d[C]}{dt} = 27.3$ mol $dm^{-3} s^{-1} = 8.1$ mol $dm^{-3} s^{-1}$

$\frac{d[D]}{dt} = 27$ mol $dm^{-3} s^{-1}$

5a) $k_r \rightarrow$ mol^{-1} dm^3 s^{-1}

$\frac{1}{3}\frac{d[C]}{dt} = k_r[A][B]$ $\quad -\frac{d[A]}{dt} = k_r[A][B]$

$\frac{d[C]}{dt} = 3k_r[A][B]$ $\quad \frac{d[A]}{dt} = -k_r[A][B]$

7a) (i) 2nd order: mol^{-1} dm^3 s^{-1} 3rd: mol^{-2} dm^6 s^{-1}

(ii) 2nd: kPa^{-1} s^{-1} 3rd: kPa^{-2} s^{-1}

9a) Assume 1.0M initial.

Not 0th order, rate changes.

$(\ln 0.9, \ln 0.71) \Rightarrow (-0.105, 2273)$

$(\ln 0.8, \ln 2.67) \Rightarrow (-0.223, 2.037)$

$\frac{2273 - 2.037}{-0.105 + 0.223} = \frac{0.236}{0.115} \approx 2$

2nd order reaction.

17B: 3a) 5a) 6a)

3) $t_{1/2} = \frac{\ln 2}{k_r} = \frac{\ln 2}{3.38\times10^{-5}\,s^{-1}} = 2.05\times10^{4}$ sec

$[A] = [A]_0 e^{-kt}$

$[A]_{2} = 500\, e^{-3.38\times10^{-5}\,s^{-1}\cdot 20s} = 499$ torr

$[A] = 500\, e^{-3.38\times10^{-5}\,s^{-1}\cdot 20\,min\cdot\frac{60s}{1\,min}} = 480.1$ torr

5a) $\frac{1}{[A]} - \frac{1}{[A]_0} = kt \Rightarrow \frac{1}{0.010} - \frac{1}{0.210} = 4.30\times10^{-4}\,t$

$t = 2.2\times10^{3}$ sec.

6a) $[A]_0 = 0.080\ mol\,dm^{-3}$ $[B]_0 = 0.060\ mol\,dm^{-3}$

$[B] = 0.030\ mol\,dm^{-3}$ $[A] = 0.080 - (0.060 - 0.030)$

$= 0.050\ mol\,dm^{-3}$

$\ln\left(\frac{\frac{[B]}{[B]_0}}{\frac{[A]}{[A]_0}}\right) = ([B]_0 - [A]_0)\,k_r\,t$

$\ln\left(\frac{\frac{0.030}{0.060}}{\frac{0.050}{0.080}}\right) = (0.060 - 0.080)\,k_r\,(t\cdot\frac{60min}{1hr}\cdot\frac{60sec}{1min})$

(1) $k_r = 3.1\times10^{-3}\ mol^{-1}\,dm^{3}\,s^{-1}$

(2) $t_{1/2} = \frac{1}{k_r[A]_0}$

$t_{1/2} = \frac{1}{3.1\times10^{-3}[0.080]} = 4032\,s$

$4.0\times10^{3}\,s$

$t_{1/2} = k_r[B]_0 = 5.4\times10^{3}\,s$

17D 1a) 2a) 3a)

(a) $k_r = Ae^{-E_a/RT}$

23×10^3 J/mol

$k_r = 8.1 \times 10^{-10}\ dm^3 mol^{-1} s^{-1}\ e^{\frac{-23\times10^3\ J/mol}{8.3145\ J/mol\cdot K \cdot 500K}}$

$k_r = 3.204 \times 10^{-12}\ dm^3 mol^{-1} s^{-1}$

2a) $3.80 \times 10^{-3}\ dm^3 mol^{-1} s^{-1} = Ae^{\frac{-E_a}{8.3145\ J/mol\cdot K \cdot 308K}}$

$2.67 \times 10^{-2}\ dm^3 mol^{-1} s^{-1} = Ae^{\frac{-E_a}{8.3145\ J/mol\cdot K \cdot 323K}}$

$\ln(3.80 \times 10^{-3}\ dm^3 mol^{-1} s^{-1}) = \ln A - \frac{E_a}{RT}$

$\ln(3.80 \times 10^{-3}) + \frac{E_a}{R(308K)} = \ln(2.67 \times 10^{-2}) + \frac{E_a}{R(323K)}$

$-1.9496 = \frac{E_a}{R(323)} - \frac{E_a}{R(308)}$

$-1.9496 \cdot R = \frac{308 E_a}{323 \cdot 308} - \frac{323 E_a}{308 \cdot 323}$

$-1617682 = -15 E_a$

$107.8\ kJ/mol = E_a$

$\frac{3.80 \times 10^{-3}}{e^{\frac{-107512}{8.3145 \cdot 308}}} = A = 6.49 \times 10^{15}\ dm^3 mol^{-1} s^{-1}$

3a) $\ln\left(\frac{k_{r2}}{k_{r1}}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln 3 = \frac{E_a}{R}\left(\frac{1}{299} - \frac{1}{322}\right)$

$\frac{R \cdot \ln 3}{\frac{1}{299} - \frac{1}{322}} = E_a = 34.9\ kJ/mol$

Extra Problems.

17A

2b) $-\frac{1}{2}\frac{d[CH_3]}{dt} = -\frac{d[CH_3CO_3]}{dt} \Rightarrow \frac{d[CH_3CO_3]}{dt} = \frac{1}{2}\left(1.2 \text{ mol dm}^{-3}\text{s}^{-1}\right)$

$= 0.6 \text{ mol dm}^{-3}\text{s}^{-1}$

3b) $\frac{d[S]}{dt} = -\frac{d[A]}{dt} = \frac{1}{3}\frac{-d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt}$

$\frac{d[A]}{dt} = -2.7 \text{ mol dm}^{-3}\text{s}^{-1}$ $\quad \frac{d[C]}{dt} = 2.7 \text{ mol dm}^{-3}\text{s}^{-1}$

$\frac{d[B]}{dt} = -8.1 \text{ mol dm}^{-3}\text{s}^{-1}$ $\quad \frac{d[D]}{dt} = 5.4 \text{ mol dm}^{-3}\text{s}^{-1}$

5b) $k_r \Rightarrow \text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

$\frac{d[C]}{dt} = v = k_r[A][B]^2$ $\quad \frac{d[A]}{dt} = -k_r[A][B]^2$

7b) (i) 2nd order: molecules^{-1} m^3, 3rd order: molecules^{-2} m^6

(ii) 2nd order: Pa^{-1}, 3rd order: Pa^{-2}

9b) $\log v = \log k + a\log[A]$ $\quad (-0.105, 2.303)$

$\log 11.01 = a\log 0.9 + \log k$ $\quad (-0.22, 2.186)$

$\log 8.90 = a\log 0.8 + \log k$

$\frac{2.303 - 2.186}{-0.105 - -0.22} = \frac{0.117}{0.115} = 1$

reaction is first order.

17 B

3b. $t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{3.56\times10^{-7}\,s^{-1}} = 1.95\times10^{6}\,s$

(i) $[A] = [A]_0 e^{-kt}$

$[A] = 33.0\times10^{3}\,Pa\; e^{-3.56\times10^{-7}\,s^{-1}(80\,min\times\frac{60\,s}{1\,min})} = 33\,kPa$

(ii) $[A] = 33.0\times10^{3}\,Pa\; e^{-3.56\times10^{-7}\,s^{-1}(\ldots)}$

$= 32.98\times10^{3}\,Pa$

$[A]_0 = 0.056\,mol\,dm^{-3}$ $[B]_0 = 0.030\,mol\,dm^{-3}$

$[A] = 0.040\,mol\,dm^{-3}$ $[B] = 0.030 - 2(0.016)$

$= 0.010\,mol\,dm^{-3}$

$\ln\left(\frac{[B]}{[B]_0}\right) = ([B]_0 - [A]_0)\,k_r\left(1.2\times10^{2}\,\frac{s}{1\,m}\times\frac{60\,s}{1\,min}\right)$

$-0.875 = (-0.020)\,t_r(3600)$

$1.2\times10^{-2}\,mol^{-1}\,dm^{3}\,s^{-1}$

$t_{1/2} = \frac{1}{k_r[A]_0} = 1.6\times10^{3}\,s$

$t_{1/e} = \frac{1}{k_r[B]_0} = 2.7\times10^{3}\,s$

(7D (B) 3b)

1b) $K_r = Ae^{-\frac{E_a}{RT}} \Rightarrow k_r = 4.00\times10^{15}\, e^{\frac{-261\times10^3}{8.314\cdot(20+273)}}$

$= 1.1839\times10^{-31}\ s^{-1}$

$t_{1/2} = \frac{\ln 2}{k_r} = 5.85\times10^{30}\ s$

$k_r = Ae^{-\frac{E_a}{RT}} \rightarrow k_r = 4.00\times10^{15}\ s^{-1} e^{\frac{-261\times10^3\ J/mol}{8.314\ J/mol\cdot K\cdot(50+273K)}}$

$= 9.24\times10^{-3}$

$t_{1/2} = \frac{\ln 2}{k_r} = 75\ s.$

3b. $\ln\left(\frac{k_{T2}}{k_{T1}}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln(2) = \frac{E_a}{R}\left(\frac{1}{25+273K} + \frac{1}{35+273K}\right)$

$\frac{R\cdot\ln 2}{\left(\frac{1}{298K} - \frac{1}{308K}\right)} = E_a = 52.8\ kJ/mol$