CHM5250 - Assignment #6

(1) $$A + B \underset{k_{uni}}{\overset{k_D}{\rightleftharpoons}} AB \xrightarrow{k_2} P$$ show $$-\frac{d[B]}{dt} = \frac{k_2 k_D [A][B]}{k_{uni} + k_2}$$

$$\frac{d[B]}{dt} = -k_D[A][B] + k_{uni}[AB]$$

$$\frac{d[AB]}{dt} = 0 = k_D[A][B] - k_{uni}[AB] - k_2[AB]$$

Solve for [AB] and plug into $\frac{d[B]}{dt}$

$$k_D[A][B] = k_{uni}[AB] + k_2[AB]$$

$$[AB] = \frac{k_D[A][B]}{k_{uni} + k_2}$$

$$\frac{d[B]}{dt} = -k_D[A][B] + \frac{k_{uni} k_D [A][B]}{k_{uni} + k_2} = k_D[A][B]\left(\frac{k_{uni}}{k_{uni} + k_2} - 1\right)$$

$$-\frac{d[B]}{dt} = k_D[A][B]\left(1 - \frac{k_{uni}}{k_{uni} + k_2}\right)$$

$$\frac{k_{uni} + k_2 - k_{uni}}{k_{uni} + k_2} = \frac{k_2}{k_{uni} + k_2}$$

$$\boxed{-\frac{d[B]}{dt} = k_D[A][B]\left(\frac{k_2}{k_{uni} + k_2}\right) = \frac{k_2 k_D [A][B]}{k_{uni} + k_2}}$$

54.4 (2) $k = \dfrac{4\pi(D_A + D_B)\beta}{1 + [4\pi(D_A+D_B)\beta / k_R \exp(-V(R)/k_BT)]}$

a. units of $D = \frac{m^2}{s}$ $\beta = m$ $rate_{AB} = k_R[A][B]$ if conc. in molecules/m^3

$k_R = \dfrac{rate}{[A][B]} = \dfrac{molec./m^3 \cdot s}{\frac{molec.}{m^3} \cdot \frac{molec.}{m^3}}$

$k = \dfrac{m^2/s \cdot m}{[m^2/s \cdot m / m^3/molec \cdot s]}$ $k_R = \dfrac{m^3}{molec. \cdot s}$

$k = \dfrac{m^3/s}{[(m^3/s)/(m^3/molec. \cdot s)]} = \dfrac{m^3 s^{-1}}{m^3 s^{-1} \, molec. \, s \, m^{-3}}$

$\boxed{k = \dfrac{m^3}{molec. \cdot s}}$ ← or more generally, $\boxed{concentration^{-1} s^{-1}}$

b. If diffusion limited, k_R very large, so

$$\frac{4\pi(D_A + D_B)\beta}{k_R \exp\left(\frac{-V(R)}{k_BT}\right)} \longrightarrow 0$$

then $k = \dfrac{4\pi(D_A + D_B)\beta}{1 + 0} = \boxed{4\pi(D_A + D_B)\beta}$

c. $k_D = 4\pi(D_A + D_B)\beta = \frac{m^2}{s} \cdot m = \frac{m^3}{s}$ (actually $\frac{m^3}{molecule \cdot s}$)

$k = \dfrac{m^3}{molecule \cdot s}\left(\dfrac{1000\,L}{1\,m^3}\right)\left(\dfrac{6.022 \times 10^{23}\,molecules}{1\,mole}\right) = \boxed{\left(\dfrac{m^3}{molec. \cdot s}\right)\left(6.022 \times 10^{26}\right)}$

S4.4 (cont.)

d. $$k = \frac{4\pi(D_A + D_B)\beta}{1 + \left[4\pi(D_A+D_B)\beta / k_R \exp\left(-V(R)/k_BT\right)\right]}$$

k_R will be small if slow → can't particularly simplify this expression

OR $$A + B \underset{k_{uni}}{\overset{k_D}{\rightleftharpoons}} AB \xrightarrow{k_2} \text{products}$$

If slow, $k_2 << k_{uni}$

so $k_D[A][B] = k_{uni}[AB]$ $\qquad K_{eq} = \frac{k_D}{k_{uni}} = \frac{[AB]}{[A][B]}$

$$[AB] = \frac{k_D[A][B]}{k_{uni}} \qquad [AB] = \frac{k_D[A][B]}{k_{uni}} = K_{eq}[A][B]$$

Rate = $d[AB]/dt$ since only change in [AB] is from k_2 rxn. (1st rxn. e = lib.)

$$\frac{d[AB]}{dt} = -k_2[AB] - k_{uni}[AB] + k_D[A][B]$$

$$\frac{d[AB]}{dt} = -K_{eq}k_2[A][B] - K_{eq}k_{uni}[A][B] + k_D[A][B]$$

$$\frac{d[AB]}{dt} = [A][B]\left(-K_{eq}k_2 - K_{eq}k_{uni} + k_D\right) = [A][B]\left(-K_{eq}k_2\right)$$

(k_D ↑ $K_{eq}k_{uni}$)

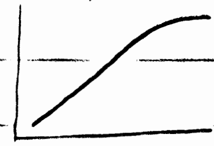
$$\frac{d[AB]}{dt} = -K_{eq}k_2[A][B] = -k[A][B]$$

so, $$\boxed{k_{slow} = K_{eq}k_2}$$

S4.1 ③ This is an integrated rate law question. See which plot is linear:

[A] vs. t — 0^{th} order
ln [A] vs. t — 1^{st} order
1/[A] vs. t — 2^{nd} order

None of the plots is linear, but 2^{nd} order looks like:



Try dropping highest three points in all three plots: now 2^{nd} order plot is clearly best

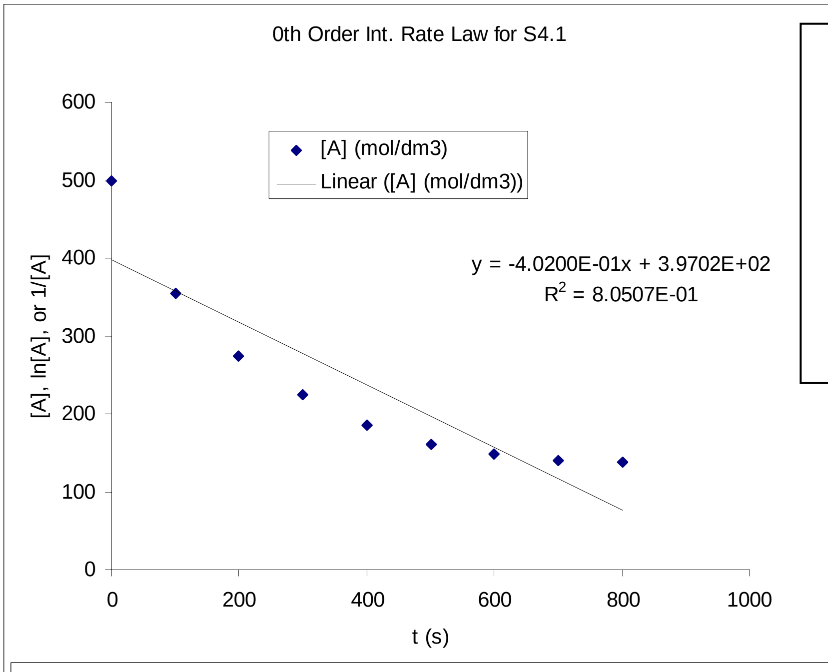
$$k = \text{slope} = \boxed{8.52 \times 10^{-6} \ \frac{dm^3}{mol \cdot s}}$$

$$\text{units} = \frac{1/(mol\ dm^{-3})}{s} = \frac{dm^3}{mol \cdot s}$$

OR to be absolutely proper: $\frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt$ ← since $2A \rightarrow P$

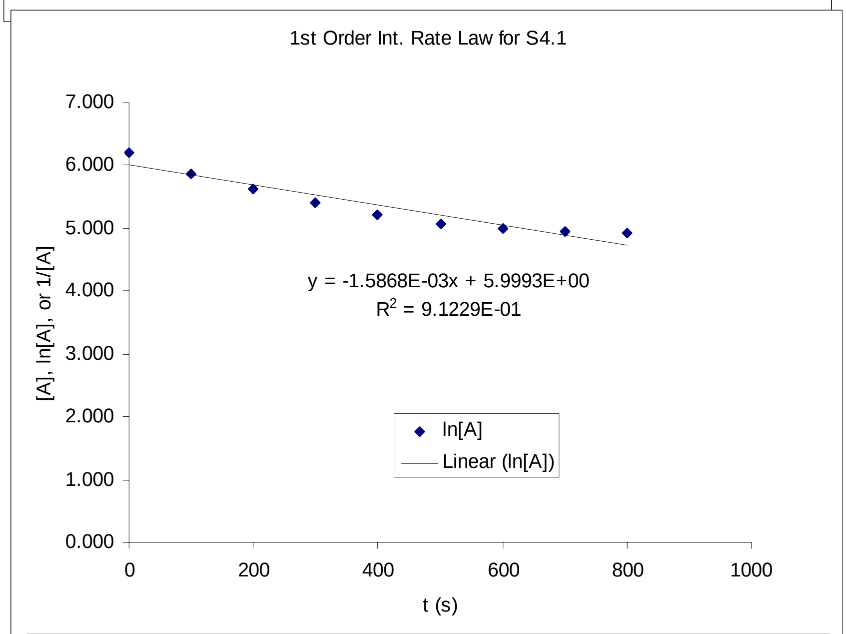
so slope = $2k$ & $k = 4.26 \times 10^{-6} \ \frac{dm^3}{mol \cdot s}$

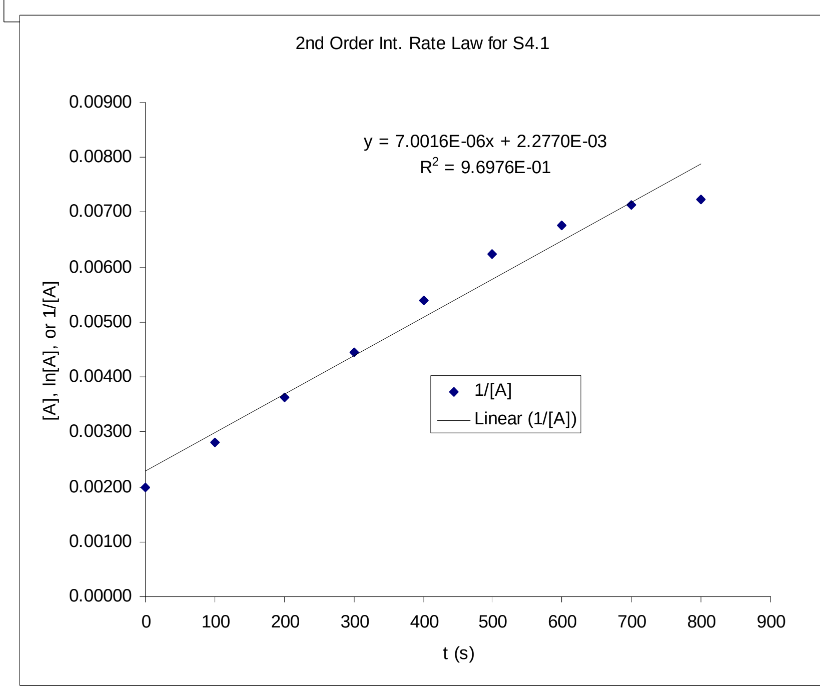
Plots are attached.



t (s)	[A]/10-2	[A] (mol/dm3)	ln[A]	1/[A]
0	5.00	500	6.215	0.00200
100	3.55	355	5.872	0.00282
200	2.75	275	5.617	0.00364
300	2.25	225	5.416	0.00444
400	1.85	185	5.220	0.00541
500	1.60	160	5.075	0.00625
600	1.48	148	4.997	0.00676
700	1.40	140	4.942	0.00714
800	1.38	138	4.927	0.00725

Plots this page use all data points





Plots this page drop the last three data points