

CHM5250 - Homework #1 (Due 8/29/07)

① S1.3b.

rxn. of order n: $-\frac{1}{n} \frac{d[A]}{dt} = k[A]^n$ $nA \rightarrow P$

Rearrange: $\frac{1}{[A]^n} d[A] = -nk dt$

$$\int_{[A]_0}^{[A]_+} \frac{1}{[A]^n} d[A] = -nk \int_0^+ dt$$

$$\left(\int x^n dx = \frac{1}{n+1} x^{n+1} \quad \text{and} \quad \frac{1}{[A]^n} = [A]^{-n} \right)$$

$$\left(\frac{1}{-n+1} \right) [A]^{-n+1} \Big|_{[A]_0}^{[A]_+} = -nk t \Big|_0^+$$

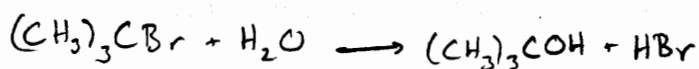
$\underbrace{\hspace{10em}}_{= -nk(t-0) = -nkt}$

$$\left(\frac{1}{n-1} \right) \left(\frac{1}{[A]_+^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = +nkt$$

$$\frac{1}{[A]_+^{n-1}} = ktn(n-1) + \frac{1}{[A]_0^{n-1}}$$

② S1.8

90% $\text{CH}_3\text{CO}_2\text{H}$, 10% H_2O



plot $\ln[(\text{CH}_3)_3\text{CBr}]$ vs. t (1st order) and $\frac{1}{[(\text{CH}_3)_3\text{CBr}]}$ vs. t (2nd order)

whichever plot is linear gives order of the rxn.

Plot of $\ln[]$ vs. t is linear: $\ln[(\text{CH}_3)_3\text{CBr}]_t = -kt + \ln[(\text{CH}_3)_3\text{CBr}]_0$
(see attached graphs)

$$y = -0.0129x - 2.2343$$

$$\text{slope} = -k$$

$$-0.0129 = -k$$

$$k = \boxed{0.0129 \text{ min}^{-1}} \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = \boxed{0.000215 \text{ s}^{-1}}$$

$$\text{For 1}^{\text{st}} \text{ order, } t_{1/2} = \frac{\ln 2}{k} = \frac{0.69315}{0.000215 \text{ s}^{-1}} = 3224 \text{ s} = \boxed{3.22 \times 10^3 \text{ s}}$$

$$\text{or } t_{1/2} = \frac{0.69315}{0.0129 \text{ min}^{-1}} = \boxed{53.7 \text{ min}}$$

③ S1.106

$$\text{rate} = k[\text{A}]^{1/2}[\text{B}]^{2/3}$$

$$\left(\frac{\text{molecules}}{\text{cm}^3 \text{ s}} \right) = k \left(\frac{\text{molec.}^{1/2}}{\text{cm}^{3/2}} \right) \left(\frac{\text{molec.}^{2/3}}{\text{cm}^{2/3}} \right) \rightarrow 12/6$$

$$\left(\frac{\text{molec.}}{\text{cm}^3 \text{ s}} \right) = k \left(\frac{\text{molec.}^{7/6}}{\text{cm}^{21/6}} \right)$$

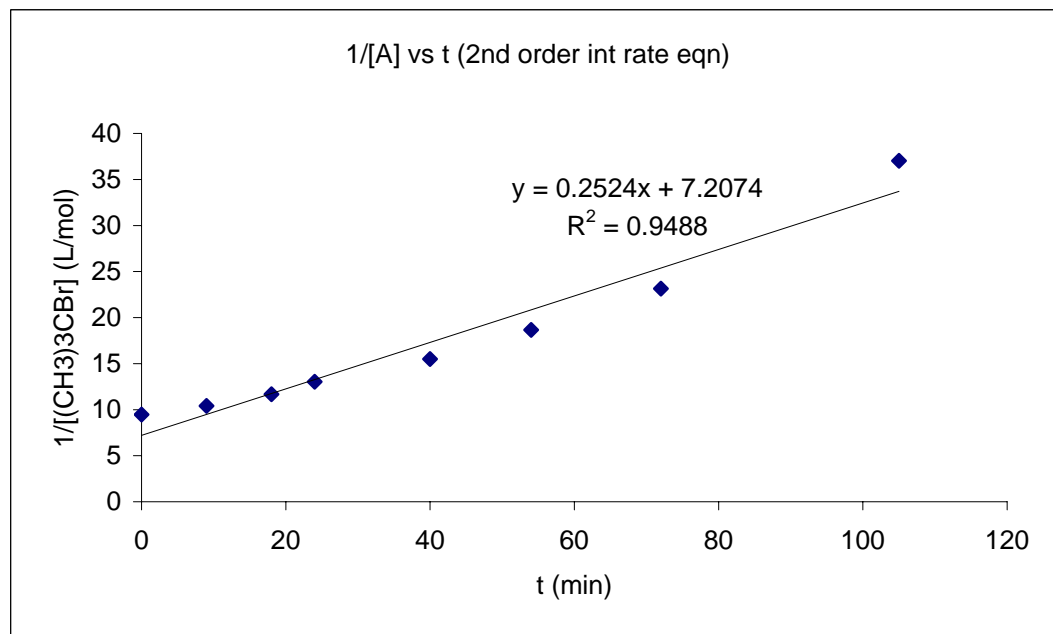
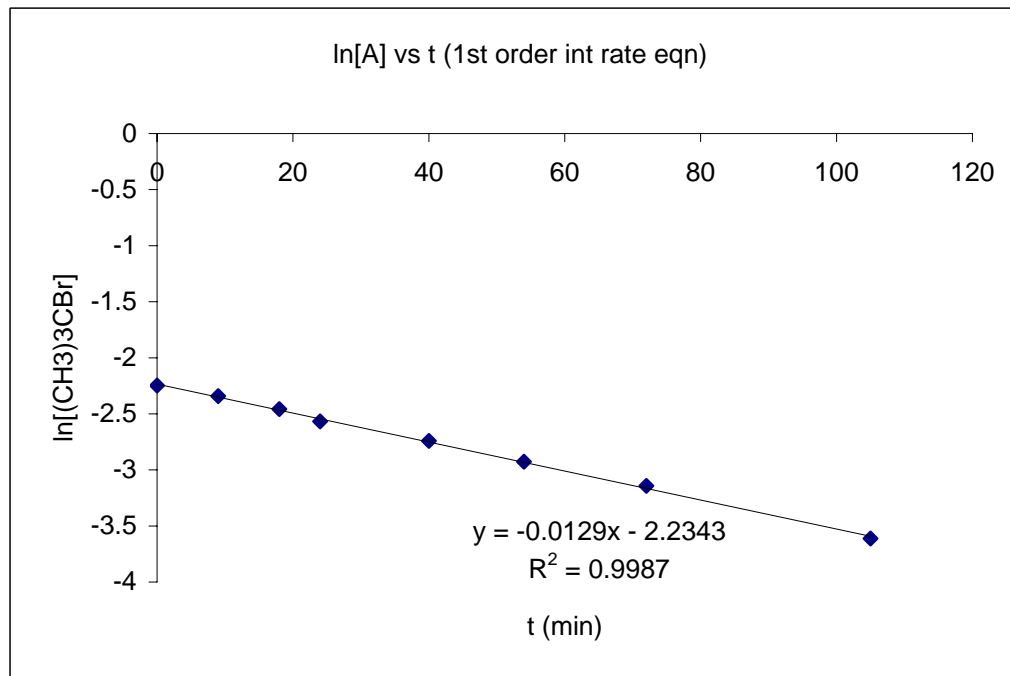
$$k = \left(\frac{\text{molec. cm}^{21/6}}{\text{cm}^3 \text{ s molec.}^{7/6}} \right) = \boxed{\left(\frac{\text{cm}^{1/2}}{\text{molec.}^{1/6} \text{ s}} \right)}$$

$$\frac{21}{6} - \frac{18}{6} = \frac{3}{6} = \frac{1}{2}$$

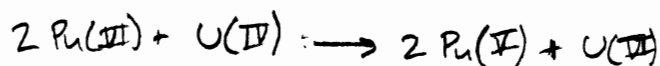
$$\frac{6}{6} - \frac{7}{6} = -\frac{1}{6}$$

t(min)	(CH ₃) ₃ CBBr(mol L ⁻¹)	1/[] (L mol ⁻¹)	ln[]
0	0.1056	9.46969697	-2.248097
9	0.0961	10.40582726	-2.342366
18	0.0856	11.68224299	-2.45807
24	0.0767	13.03780965	-2.567854
40	0.0645	15.50387597	-2.74109
54	0.0536	18.65671642	-2.926206
72	0.0432	23.14814815	-3.141915
105	0.027	37.03703704	-3.611918

t_{1/2} 53.73233958 min



④ E 1.1



$$-\frac{d\text{Pu(VI)}}{dt} = k_a [\text{Pu(VI)}][\text{U(IV)}] \quad [\text{H}^+] = \text{const.} \quad k_a = 2.2 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

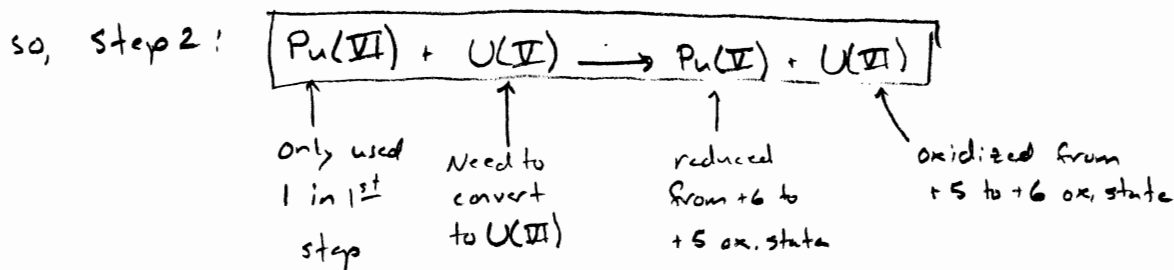
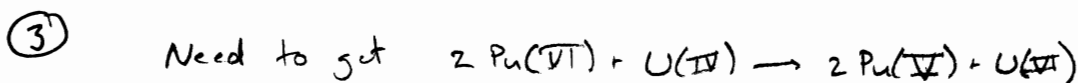
③ a. If $-\frac{d\text{U(IV)}}{dt} = k_b [\text{Pu(VI)}][\text{U(IV)}]$, what's k_b ?

from eqn: $-\frac{1}{2} \frac{d\text{Pu(VI)}}{dt} = -\frac{1}{1} \frac{d\text{U(IV)}}{dt}$

$$\frac{d\text{Pu(VI)}}{dt} = 2 \frac{d\text{U(IV)}}{dt}$$

$$k_a = 2 k_b$$

$$k_b = \frac{2.2 \text{ L/mol}\cdot\text{s}}{2} = \boxed{1.1 \frac{\text{L}}{\text{mol}\cdot\text{s}}}$$



② c. $k_1 \approx k_{\text{rds}}$ Overall rate law is $-\frac{d\text{U(IV)}}{dt} = k_b [\text{Pu(VI)}][\text{U(IV)}]$

which is consistent w/ given RDS, so $k_b = k_{\text{rds}}$ and

then $\boxed{k_1 = k_b = 1.1 \frac{\text{L}}{\text{mol}\cdot\text{s}}}$

③ d. Must be 1st order in U(IV) and Pu(VI):

