

CHEM 2141 Survey of Physical Chemistry Homework #6
due Thursday March 30th 5:00 PM. (UPDATED AS OF 3:40 PM SATURDAY 3/25/06)

The homework problems are:
Ch: 10 - 1,2,6,9,13,16,18,19,26
Ch. 11 - 9, 10

For problems **10.6** and **10.18** I will accept both rate constants, either k or $k_{\text{empirical}}$
 i.e. $3A \rightarrow P$, If this overall rxn is first order in A: $-1/3 d[A]/dt = k[A]$

$$-d[A]/dt = 3k[A] = k_{\text{emp}}[A] \text{ where } k_{\text{emp}} = 3k$$

where k_{emp} is the empirical (apparent) rate constant.

For **Problem 10.6** Note that the pressures are proportional to the moles. So you might want to treat this the way you would an "equilibrium" problem by noting the decrease in $2x$ mole of N_2O_5 leads to $4x$ moles of NO_2 and x moles of O_2 . Thus at time t the total no. of moles is: initial moles of $N_2O_5 - 2x + 4x + x =$ initial moles of $N_2O_5 + 3x$. So if you treat this as pressure: total pressure = initial pressure of $N_2O_5 + 3x$. Where the change in the pressure of N_2O_5 is $-2x$.

(This development should be similar to your study of chemical equilibrium from general chemistry).

	$2 N_2O_5(g)$	\rightarrow	$4NO_2(g)$	$O_2(g)$
Initial moles (pressure since vol. Same)	$P_0 = 500\text{Torr}$		0	0
Change in moles (change pressure in Torr units)	$-2x$		$+4x$	$+x$
Final pressure (at time t)	$P_{N_2O_5} = P_0 - 2x$		$4x$	x

Note the first order decay of $N_2O_5(g)$ is given as:

$$\ln \frac{P_{N_2O_5}}{P_0} = -kt \quad \text{or} \quad P_{N_2O_5} = P_0 \exp(-kt) = P_0 - 2x$$

Thus at a time t , you may determine x (pressure), which will allow you to determine the total pressure

10.13 – You might just want to determine this by deduction. Determine successive half-lives, i.e. two half lives would lead to $1/4$ of the initial concentration, 3 half lives would lead to $1/8^{\text{th}}$ etc.

10.16 – Treat this initially as an equilibrium problem where you can determine the final number of moles and hence the concentration for $CH_3COOC_2H_5$ in terms of product concentration $[P]$. Note concentration is proportional to moles. Next use the appropriate expression for $A+B \rightarrow P$ from Table 10.4 *This is a long tedious problem.*

$[P]$ = concentration of product : either $[CH_3CO_2^-]$ or $[CH_3CH_2OH]$
 let $[A]$ = the ester $= [CH_3COOC_2H_5]$
 let $[B]$ = $[OH^-]$

	$\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq})$	$\text{OH}(\text{aq}) \rightarrow$	$\text{CH}_3\text{CO}_2^-(\text{aq})$	$\text{CH}_3\text{CH}_2\text{OH}(\text{aq})$
Initial moles (concentration since vol. Same)	$[\text{CH}_3\text{COOC}_2\text{H}_5]_0 = 0.150$	$[\text{OH}]_0 = 0.055$	0	0
Change in moles (change concentration)	-x	-x	x	x
Final concentration (at time t)	$[\text{CH}_3\text{COOC}_2\text{H}_5]_0 - x = [\text{CH}_3\text{COOC}_2\text{H}_5]$	$[\text{OH}]_0 - x = [\text{B}]$	$x = [\text{P}]$	$x = [\text{P}]$

$[\text{CH}_3\text{COOC}_2\text{H}_5]_0 - [\text{P}] = [\text{CH}_3\text{COOC}_2\text{H}_5] = [\text{A}]$
 Now use expression at bottom of Table 10.4

10.18 – Use your calculator to test $\ln[\text{A}]$ vs t (1st order) and $1/[\text{A}]$ vs t (2nd order) plots for linearity – by determining the correlation coefficient. You can also look at slopes of adjacent x,y pair, but this is less clear due to error.

You need entries for [A]

To determine entries for [A], we may convert entries of [B]

	2A	\rightarrow	B
Initial moles (concentration since vol. Same)	$[\text{A}]_0 = ?$		$[\text{B}]_0 = 0$
Change in moles (change concentration)	-2x		x
Final concentration (at time t)	$[\text{A}]_0 - 2x = [\text{A}]$		$x = [\text{B}]$

At $t = \infty$: $[\text{A}]_\infty = [\text{A}]_0 - 2x = 0$ and $[\text{B}]_\infty = x = 0.312$ Thus you may find $[\text{A}]_0$

Thus at any time the concentration of $[\text{A}] = [\text{A}]_0 - 2x$ and the concentration of $[\text{B}] = x$, using this information you may find values of [A] since you are given values of [B]

10.19 – The book's answer of $3.66 \times 10^{11} \text{ mol L}^{-1} \text{ s}^{-1}$ is incorrect in both units and magnitude. The correct answer is $3.74 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ is

10.26

First order half life is given by

$t = \frac{\ln 2}{k}$ and $k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right)$ so using these two equations you can write a single equation that

relates the half-life to the temperature. If you write 2 such equations for the lifetime at 550 C. Of course this will require that you solve for E_{act} prior to solving for the lifetime. You need not know the value of A. This is essentially a system of 2 equations and 2 unknowns.