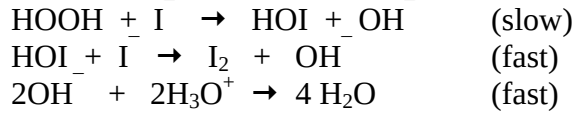
Chemistry 633 – Fall 2012 – Homework Problem Set 1 Name _____

Put answers on the blank lines where provided. Attach just enough work to show how you arrived at your answer and that you understand what you are doing. A few lines and/or calculations or spreadsheet may be sufficient. Where asked for, attach graphs and/or sections of a spread sheet. Attach work with a new problem starting on a new page using one side of the paper only. Present neat and organized work.

1. The mechanism of a reaction is shown below.



a) What is the overall or net reaction? _____

b) Which compounds are intermediates? _____

c) Predict the rate law (rate equation) based on this mechanism. _____

d) What is the overall order of the reaction? _____

a) Overall reaction: $HOOH + 2\,I^- + 2\,H_3O^+ \rightarrow I_2 + 4\,H_2O$

b) Intermediates: OH^- and HOI

c) Predicted mechanism: Rate = $k\,[HOOH][I^-]$

d) Overall order: 2nd order

2. For the reaction A + B → C, the rate constant at 215°C is 5.0×10^{-3} sec^{-1} and at 452° C it is $1.2 \times 10^{-1} sec^{-1}$.

a) What is the activation energy in kJ/mol? _____

b) What is the rate constant at 100 °C. _____

a) 39.4 kJ/mol $\mathbf{\ln(k_2/k_1) = -Eact \times R \times (1/T_2 - 1/T_1)}$

b) 2.50×10^{-4} s^{-1} (has to be smaller than that at 215C) use Eact and equation above to solve for k

3. The half-life of a radioisotope is found to be 4.55 minutes. Radioactive decay follows is a first order process. What percentage of isotope remains after 10 minutes and after 2.00 hours?

% remaining after 10 min _____

% remaining after 2 hours _____

$k = .693/4.55 = 0.152\ min^{-1}$ or $0.00253\ sec^{-1}$

after 10 min ln A%/100% = - k t ln[A/100] = -0.152 (10) A/100 = $e^{-1.52}$ = 0.2187 **A=22% remain after 10 min**
drops to 50% in 4.55 min to 25% in 9.1 min to 12.5% in 13.6 min so after 10 min it a bit less than 25% remains
after 2 hours ---- k = 0.152 min^{-1} **A_t = 1.15 x 10^{-6} %** (not much!!)

4. Given the following experimental data, find the rate law and the rate constant for the reaction:

$NO\ (g) + NO_2\ (g) + O_2\ (g) \rightarrow N_2O_5\ (g)$

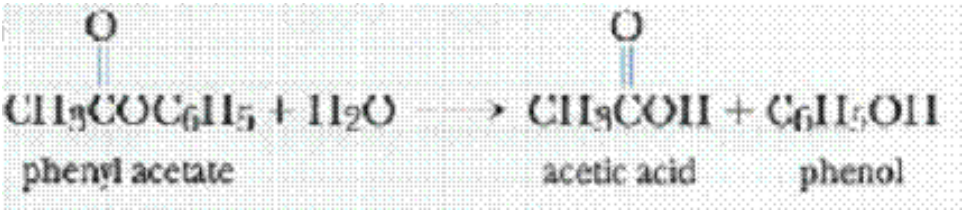
Run	$[NO]_o$, M	$[NO_2]_o$, M	$[O_2]_o$, M	Initial Rate, Ms^{-1}
1	0.10 M	0.10 M	0.10 M	2.1 x 10^{-2}
2	0.20 M	0.10 M	0.10 M	4.2 x 10^{-2}
3	0.20 M	0.30 M	0.20 M	1.26 x 10^{-1}
4	0.10 M	0.10 M	0.20 M	2.1 x 10^{-2}

Rate Equation _____

Rate Constant with units _____

Rate = $k[NO]\ [NO_2]$ k = 2.1 $M^{-1}s^{-1}$

5. Phenyl acetate is an ester that reacts with water (hydrolysis) forming acetic acid and phenol according to the reaction



The following concentration vs. time data was taken at 5°C.

Time (s)	[Phenyl acetate] (mol/L)
0.00	0.55
15.0	0.42
30.0	0.31
45.0	0.23
60.0	0.17
75.0	0.12
90.0	0.085

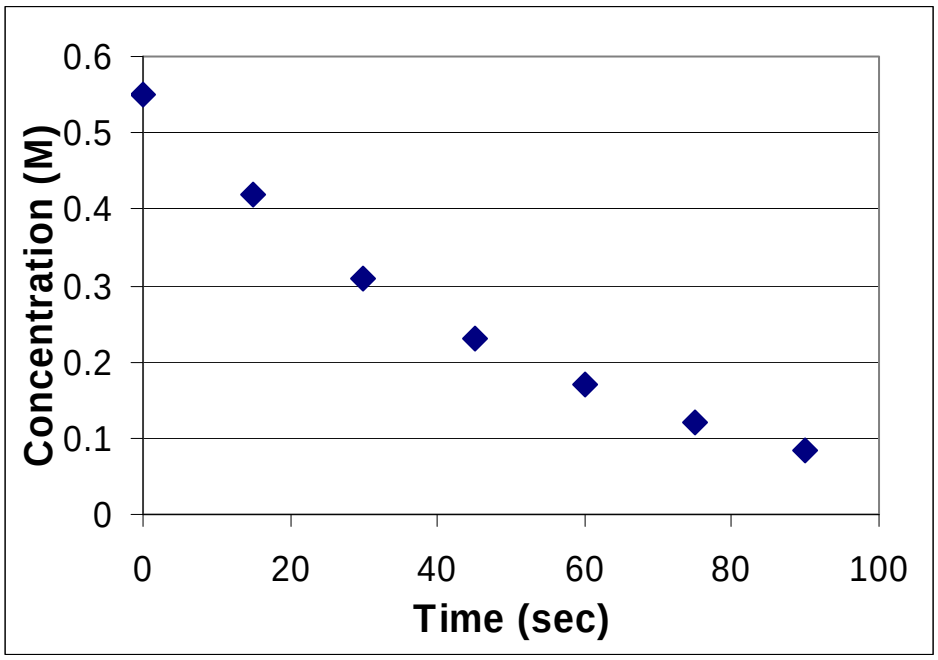
Using a spread sheet (Excel, etc.) generate the 4 graphs; (a) Conc. vs. Time, (b) 1/conc vs. time, (c) natural log of conc vs. time and natural log of rate on the y axis vs natural log of concentration on the x axis. Based on these graphs, what is the order and rate constant for this reaction? If it is 1st order or pseudo 1st order, what is the half-life in seconds?

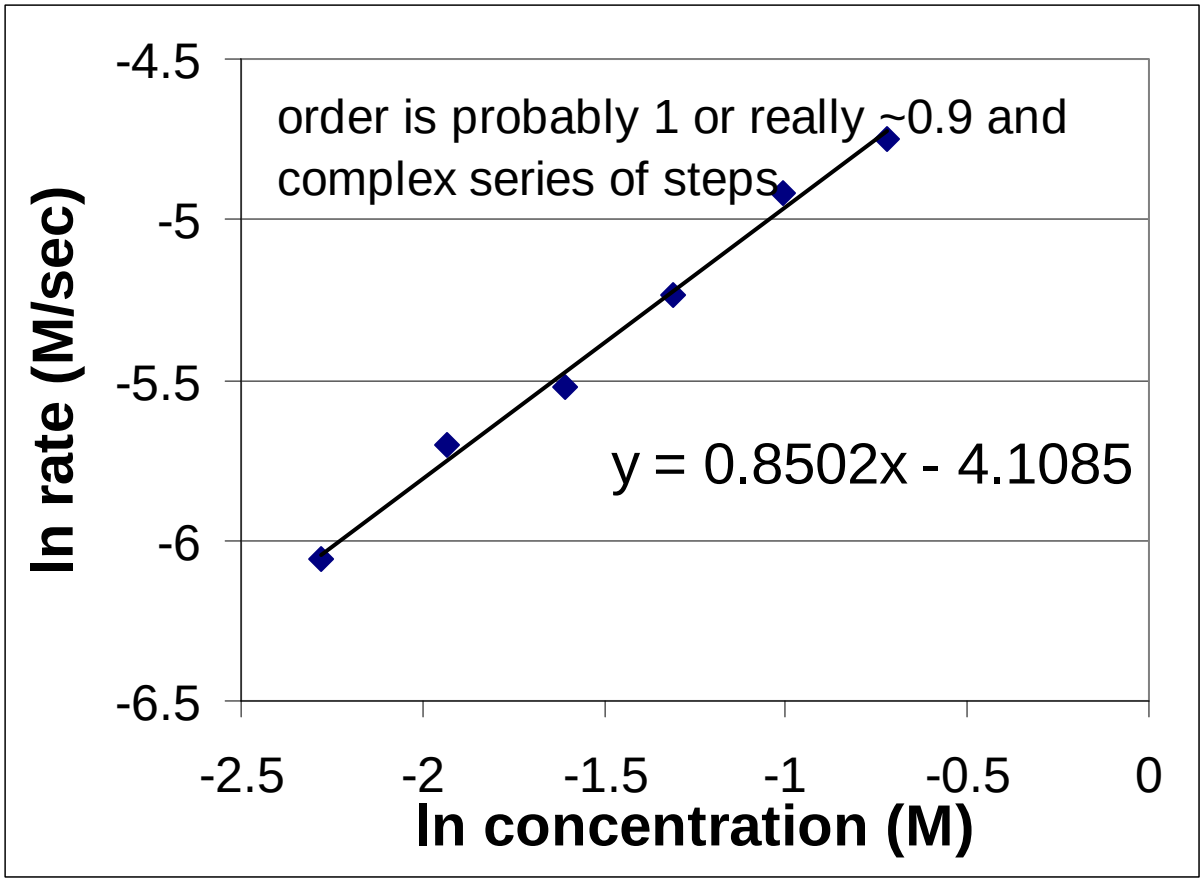
Reaction order = _____

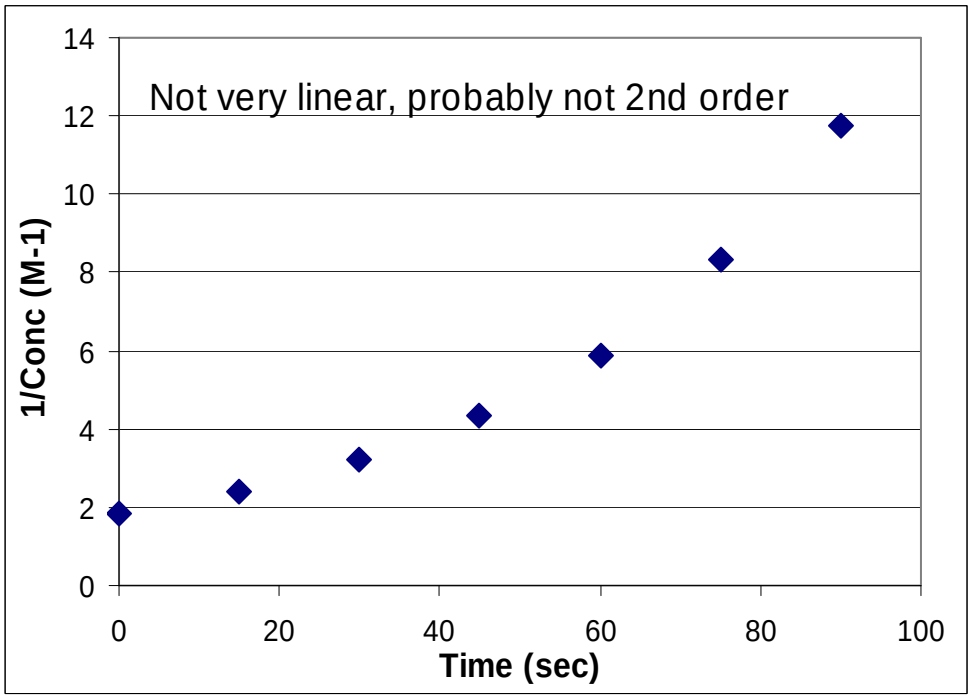
Rate constant (show units) = _____

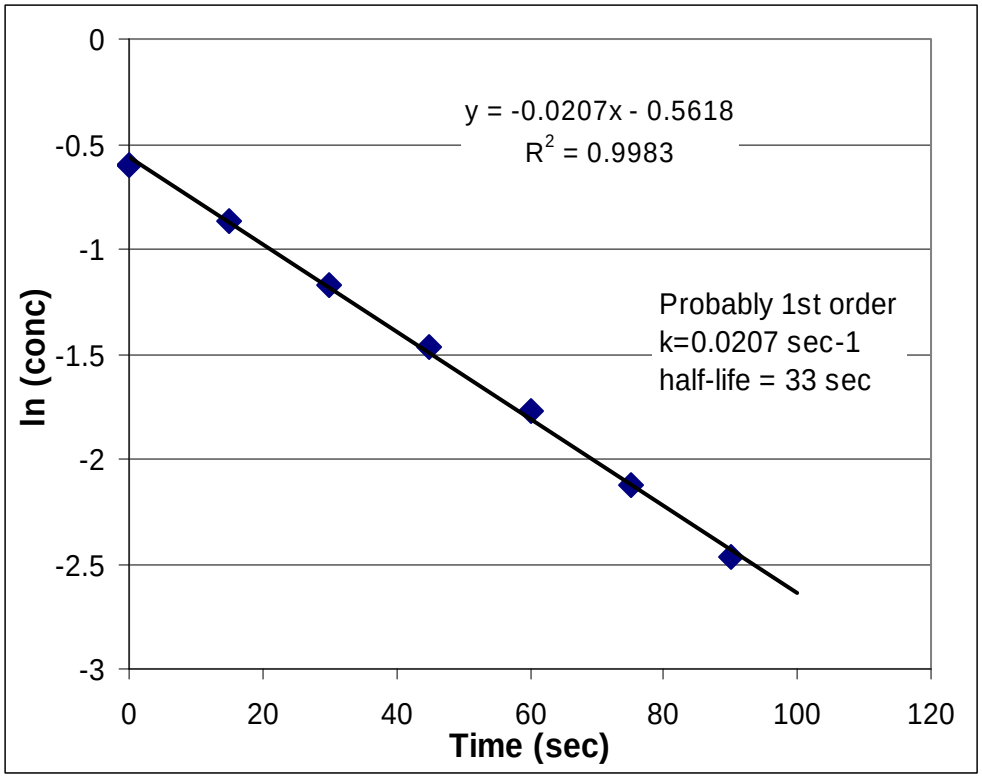
If 1^{st} or pseudo 1^{st} order half-life = _____

time sec	conc M	1/ conc	ln conc	dc/dt	at conc	ln rate	ln conc
0	0.55	1.818182	-0.59784				
15	0.42	2.380952	-0.8675	0.008667	0.485	-4.74827	-0.72361
30	0.31	3.225806	-1.17118	0.007333	0.365	-4.91533	-1.00786
45	0.23	4.347826	-1.46968	0.005333	0.27	-5.23378	-1.30933
60	0.17	5.882353	-1.77196	0.004	0.2	-5.52146	-1.60944
75	0.12	8.333333	-2.12026	0.003333	0.145	-5.70378	-1.93102
90	0.085	11.76471	-2.4651	0.002333	0.1025	-6.06046	-2.27789




order is probably 1 or really ~0.9 and complex series of steps
y = 0.8502x - 4.1085
ln rate (M/sec)
-4.5
-5
-5.5
-6
-6.5
-2.5
-2
-1.5
-1
-0.5
0
ln concentration (M)


Not very linear, probably not 2nd order
1/Conc (M-1)
14
12
10
8
6
4
2
0
0
20
40
60
80
100
Time (sec)



6. Data for the gas phase reaction $CO + NO_2 \rightarrow CO_2 + NO$ is shown in the table below.

	Reactant Concentration (mol/L)		Initial rate
	[CO]	[NO_2]	mol/L · h
1	5.0×10^{-4}	0.36×10^{-4}	3.4×10^{-8}
2	5.0×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
3	1.0×10^{-3}	0.36×10^{-4}	6.8×10^{-8}
4	1.5×10^{-3}	0.72×10^{-4}	?

What is the rate law or rate equation for this process? _____

What is the rate constant (show units) ? _____

Experiment #	Reactant Concentration (mol/Liter)		Initial Rate (mol/L-hr)
	CO	NO_2	
1	5×10^{-4}	0.36×10^{-4}	3.4×10^{-8}
2	5×10^{-4}	0.18×10^{-4}	1.7×10^{-8}
3	1.0×10^{-3}	0.36×10^{-4}	6.8×10^{-8}
4	1.5×10^{-3}	0.72×10^{-4}	?

with CO constant when NO_2 doubles in conc, rate doubles – so 1st in NO2
with NO_2 constatnt, when CO doubles in conc, rate doubles – so 1s in CO
When CO increases 3x and NO_2 increases 4x rate should go up 12x rate constant = 1.89 $M^{-1}sec^{-1}$
Initial rate for Experiment #4 = 20.4×10^{-8}