CHM1311 D - Assignment #4 **Student ID (first student only): _______________**

CHM1311 D: Principles of Chemistry

Prof. N. Goto
Assignment #4
Due Oct 31st, at the beginning of class

Assignments can be submitted individually, or by groups of up to 4 students.

1) Name: _________________ **Student ID:** ______________

2) Name: _________________ **Student ID:** ______________

3) Name: _________________ **Student ID:** ______________

4) Name: _________________ **Student ID:** ______________

Solutions must be written legibly, in the space provided. Adequate detail to the calculation (including units, appropriate sig figs) must be provided to make it possible for other students to understand how you arrived at the final solution. If more space is needed, use the back of the page. Do not add extra pages, as they will not be marked. Assignment pages must be stapled together.

NOTE: For each question a hint, or reference to an Office Hours video, Interactive LearningWare (ILW) problem or Chem FAQ module in WileyPLUS is given in brackets.

Question 1. (Video 13.19)

For the net reaction:

$$2AB + 2C \longrightarrow A_2 + 2BC$$

the following possible slow, first step has been proposed:

$$2\,AB \longrightarrow A_2 + 2\,B$$

a) What is the rate law predicted by this step? (1 mark)

$\text{Rate} = k[AB]^2$

b) What units are associated with the rate constant for this rate law? (1 mark)

$\text{Units of } k = \frac{\text{units of rate}}{M^2} = \frac{M\,min^{-1}}{M^2}$

$= M^{-1}min^{-1}\ (L \cdot mol^{-1} \cdot min^{-1})$

NOTE: Units of rate given in question was $mol\ L^{-1} min$. This was a typo, and so $M^{-1} min$ was also accepted as an answer.

c) Write additional steps that complete this mechanism. (1 mark)

$2\,AB \xrightarrow{k_1} A_2 + 2\,B$ slow

$2\,B + 2\,C \xrightarrow{k_2} 2\,BC$

$2\,AB + 2\,C \longrightarrow 2\,BC + A_2$

Question 2. (ILW 13.47)

The rate at which the heart of the terrapin turtle beats is 50 min^{-1} at 29.9 ^{o}C but only 19.9 min^{-1} at 21.0 ^{o}C. Calculate the "energy of activation" for the beating rate of the heart. (2 marks)

$$\ln\left(\frac{RATE_2}{RATE_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_a = \frac{-R\ln\left(\frac{RATE\ 2}{RATE\ 1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$= \frac{-8.314\ J\ K^{-1}mol^{-1}\ \ln\left(\frac{50.0\ min^{-1}}{19.9\ min^{-1}}\right)}{\left(\frac{1}{(273.15+29.9)K} - \frac{1}{(273.15+21.0)K}\right)}$$

$$= 76.7\ kJ\ mol^{-1}$$

Question 3. (See Example 13-8 in the textbook.)

The following rate information was collected at 25 ^{o}C for this aqueous reaction:

$$A + B \longrightarrow C + D$$

	$[A]_0$, M	$[B]_0$, M	Initial rate, M/s
1	0.185	0.133	3.35×10^{-4}
2	0.185	0.266	1.35×10^{-3}
3	0.370	0.133	6.75×10^{-4}
4	0.370	0.266	2.70×10^{-3}

a) Determine the rate law for this reaction. (3 marks)

$$\frac{RATE\ 1}{RATE\ 2} = \left(\frac{[B_0]_1}{[B_0]_2}\right)^x$$

$$\frac{3.35\times10^{-4}}{1.35\times10^{-3}} = \left(\frac{0.133}{0.266}\right)^x$$

$$0.25 = 0.5^x$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^x$$

$$x = 2$$

$$\frac{RATE\ 3}{RATE\ 1} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^y$$

$$\frac{6.75\times10^{-4}\ M/s}{3.35\times10^{-4}\ M/s} = \left(\frac{0.370}{0.185}\right)^y$$

$$2 = 2^y$$

$$\therefore y = 1$$

$$\therefore RATE = k[A][B]^2$$

b) What is the value of the rate constant? (1 mark)

$$k = \frac{RATE}{[A][B]^2}$$

FROM EXPERIMENT #1:

$$k = \frac{3.35\times10^{-4}\ M/s}{(0.185\ M)(0.133\ M)^2}$$

$$= 0.102\ M^{-2}s^{-1}$$

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Question 4. (ChemFAQ, 'Test a mechanism…')

For the following reaction in aqueous solution:

$$I^- + OCl^- \longrightarrow OI^- + Cl^-$$

Experimental evidence has been obtained suggesting that the mechanism is as follows:

$$OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + OH^- \text{ (fast)}$$

$$I^- + HOCl \xrightarrow{k_2} HOI + Cl^- \text{ (slow)}$$

$$HOI + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2O + OI^- \text{ (fast)}$$

a) Give a one-sentence explanation for why the concentration of water is not included in rate equations of aqueous phase reactions. (1 mark)

WATER IS PRESENT IN SUCH A LARGE AMOUNT RELATIVE TO THE CONCENTRATION OF REACTANTS ($[H_2O] = 55$ M) THAT ITS CONCENTRATION IS NOT CHANGED DURING THE REACTION - IT IS ≈ CONSTANT (WE CAN NOT VARY $[H_2O]$

b) What rate law does this mechanism predict? You will need to label each arrow with a rate constant (k_1, k_{-1}, k_2 etc…) (3 marks)

FROM THE SLOW STEP

$$RATE = k_2 [I^-][HOCl]$$

THE FIRST STEP IS IN RAPID EQUILIBRIUM:

$$\therefore k_1 [OCl^-] = k_{-1} [HOCl][OH^-]$$

$$\therefore [HOCl] = \frac{k_1}{k_{-1}} \frac{[OCl^-]}{[OH^-]}$$

SUB INTO RATE EQUATION

$$RATE = \frac{k_1 k_2}{k_{-1}} \times \frac{[OCl^-][I^-]}{[OH^-]}$$

Question 5. (See Example 13-12, and Figure 13-20 from textbook)

The reaction between ozone and nitrogen dioxide follows:

$$2NO_2(g) + O_3(g) \rightarrow N_2O_5(g) + O_2(g)$$

The reaction proceeds according to the experimental rate law rate = $k[NO_2][O_3]$, and NO_3 has been found to be an intermediate in the reaction.

a) Propose a two-step mechanism for the reaction that is consistent with the experimental data. (2 marks)

$$NO_2(g) + O_3(g) \longrightarrow NO_3(g) + O_2(g) \quad \text{SLOW}$$

$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

b) Consult the thermodynamic tables in the textbook to calculate ΔE_R^o for the overall reaction. (2 marks)

$\Delta H_R^\circ = \Sigma \nu \Delta H_{f,\text{products}}^\circ - \Sigma \nu \Delta H_{f,\text{reactants}}^\circ$

$= \Delta H_f^\circ(N_2O_5) - \Delta H_f^\circ(O_3) - 2\Delta H_f^\circ(NO_2)$

$= [13.3 - 142.7 - 2(33.2)]\ kJ\ mol^{-1}$

$= -195.8\ kJ\ mol^{-1}$

$\Delta n_g = n_{g,\text{products}} - n_{g,\text{reactants}}$

$= 2 - 3 = -1$

$\Delta E_R^\circ = \Delta H_R - RT\Delta n_g$

$= -195.8\ kJ\ mol^{-1} - (8.314\ J\ K^{-1} mol)(298.15 K)(-1)(10^{-3}\ kJ\ J^{-1})$

$= -193.3\ kJ\ mol^{-1}$

c) Calculate E_a for this reaction, given that the rate doubled when the temperature was raised from 25.00°C to 35.61°C. (2 marks)

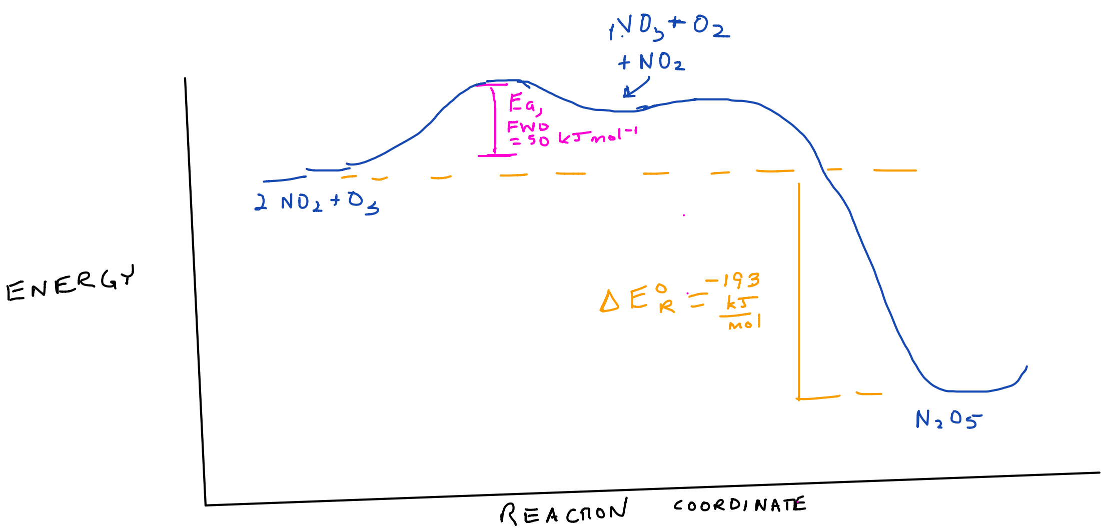
$\therefore \frac{\text{RATE 2}}{\text{RATE 1}} = 2$

$E_a = \frac{-R \ln 2}{\frac{1}{T_2} - \frac{1}{T_1}}$

$= \frac{(8.314\ J\ K^{-1} mol^{-1}) \ln 2}{\frac{1}{(273.15 + 35.61)K} - \frac{1}{298.15 K}}$

$= 50.00\ \frac{kJ}{mol}$

d) Sketch the activation energy diagram for the reaction and label it as completely as you can. (5 marks)



Question 6. (ILW 13.25)

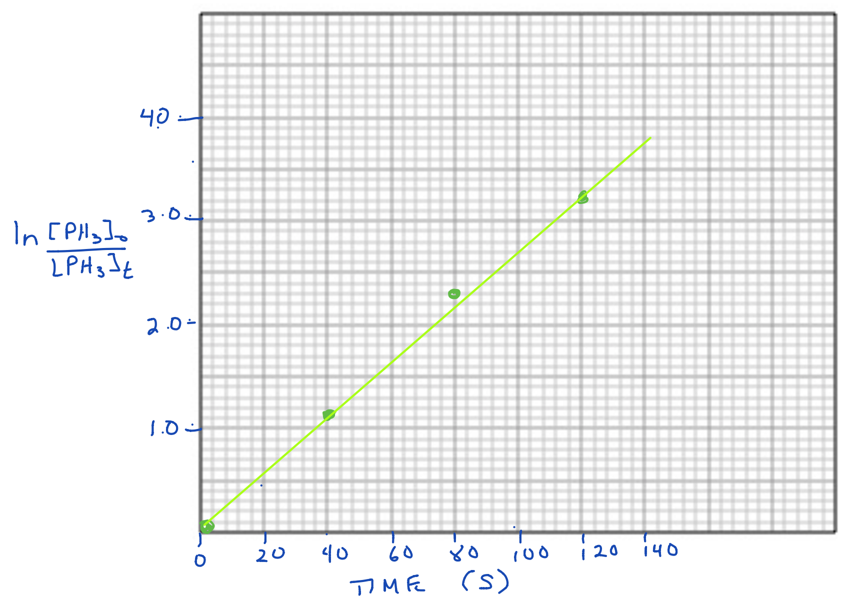
The rate of the reaction

$$4\ PH_3\ (g) \rightarrow P_4\ (g) + 6\ H_2\ (g)$$

was studied by injecting CO(g) into a reaction vessel and measuring the total pressure at constant volume.

Time (s)	0	40	80	120
$[PH_3]$ mM	5.38	1.79	0.57	0.22
$\ln \frac{[PH_3]_0}{[PH_3]_t}$	0	1.10	2.24	3.20

a) Use a graph to determine the order of the decomposition process. You may have to plot more than one graph to determine the order, but you only need to show the final graph used to prove the order. Be sure to label the axes of the graph. (3 marks)



$\text{SLOPE} = \frac{\Delta y}{\Delta x}$

$= \frac{2.2 - 1.1}{(80 - 40)s}$

$= 0.028\ s^{-1}$

$= 4k$

b) Determine the rate constant, including appropriate units. (1 mark) $4k = 0.028\ s^{-1}$

$k = 0.0072\ s^{-1}$

c) What concentration will remain after the reaction has been allowed to run for 3 minutes? (2 marks)

$\ln \frac{[PH_3]_t}{[PH_3]_0} = -4kt$

$[PH_3]_t = [PH_3]_0 e^{-4kt}$

$= (5.38\ mM)\ e^{-(0.028\ s^{-1})(3\ min)(60\ s/min)}$

$= 0.031\ mM$

Question 7. (See Example 13-7 and Figure 13-12 in textbook.)

For the reaction 2A + B → P, the following data was acquired:

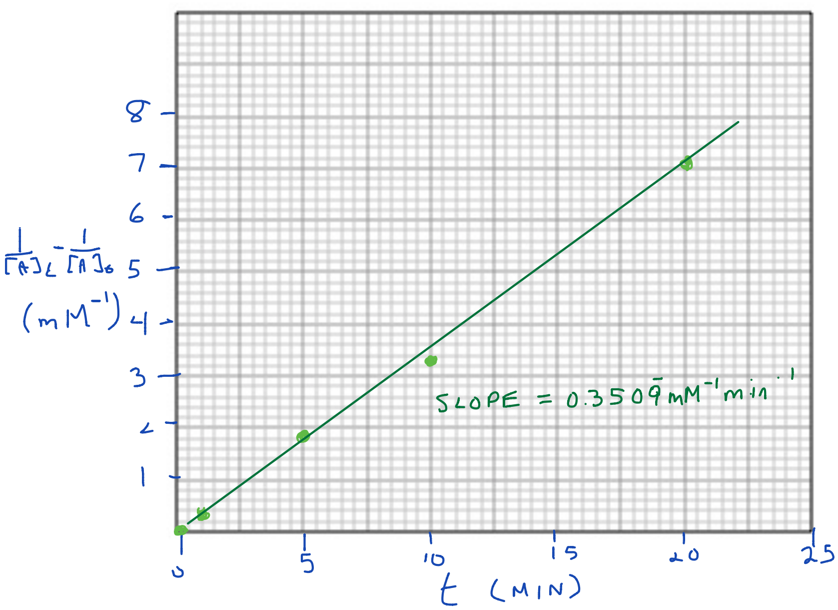
Experiment 1: $[B]_0$ = 1.35 M

***t* (min)**	0	1	5	10	20
[A] (mM)	1.000	0.745	0.355	0.231	0.124
$\frac{1}{[A]_t} - \frac{1}{[A]_0}$	0	0.3423	1.817	3.329	7.065

Experiment 2: $[B]_0$ = 0.75 M

***t* (min)**	0	1	5	10	20
[A] (mM)	1.000	0.850	0.551	0.371	0.206
$\frac{1}{[A]_t} - \frac{1}{[A]_0}$	0	0.1765	0.8149	1.695	3.854

Use graphs to determine the rate law for this reaction, and evaluate the rate constant. (6 marks)



PLOT OF $\frac{1}{[A]_t} - \frac{1}{[A]_0}$ vs t IS LINEAR ∴ 2nd ORDER IN [A]

SLOPE IS k_{obs}

$$\frac{k_{obs,1}}{k_{obs,2}} = \frac{k[B]_1^y}{k[B]_2^y}$$

$$\frac{0.3509\ mM^{-1}min^{-1}}{0.1919\ mM^{-1}min^{-1}} = \left(\frac{1.35\ M}{0.75\ M}\right)^y$$

$$1.829 = 1.8^y$$

∴ $y = 1$ 1st ORDER IN B

$$RATE = k[A]^2[B]$$

$$k_{obs} = k[B]$$

$$k = \frac{k_{obs}}{[B]}$$

FROM 1st EXPERIMENT:

$$k = \frac{(0.3509\ mM^{-1}MIN^{-1})(10^{-3}\ mM\ M^{-1})}{1.35\ M}$$

$$= 2.60 \times 10^{-4}\ M^{-2}\ MIN^{-1}$$