

Name (in ink) ANSWER KEY

Student Number (in ink) \_\_\_\_\_

Winter 2016 SC/CHEM 1001 M - Quiz #1

January 28, 2016

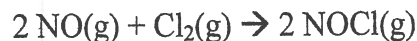
Calculators are permitted.

Answer all questions on this paper; **additional paper for rough work is not permitted.**  
**You may carry out your work in pencil if you wish, but please write your final answer in ink.**

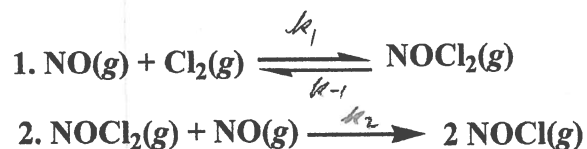
Time Allowed: 50 minutes

Total Marks = 30

1. (5 pts) Nitric oxide reacts with chlorine to give nitrosyl chloride, a useful laboratory reagent.  
 The overall chemical equation for this reaction is



A possible mechanism for this reaction is a fast pre-equilibrium followed by a slow reaction of the intermediate, as follows



Derive the rate law generated by this mechanism.

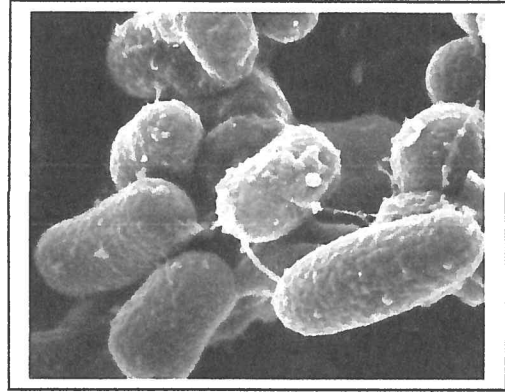
$$R = k_2 [\text{NOCl}_2] [\text{NO}]$$

$$K_1 = \frac{[\text{NOCl}_2]}{[\text{NO}][\text{Cl}_2]}$$

$$[\text{NOCl}_2] = K_1 [\text{NO}][\text{Cl}_2]$$

$$R = k_2 K_1 [\text{NO}]^2 [\text{Cl}_2] = k [\text{NO}]^2 [\text{Cl}_2]$$

2. (5 pts) The photo to the right is an electron microscope image of mycobacterium avium, a human pathogen responsible for respiratory infections that is sometimes found in hot tubs. This bacterium is killed by exposure to chlorine dioxide,  $\text{ClO}_2$ . The rate at which *M. avium* is killed increases by a factor of 12.9 when the temperature is raised from  $5.0^\circ\text{C}$  to  $30.0^\circ\text{C}$ . Calculate the activation energy for the destruction of *M. avium* by  $\text{ClO}_2$ .



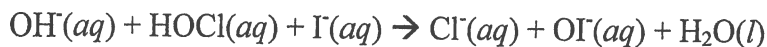
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln(12.9) = \frac{E_a}{8.314} \left(\frac{1}{278} - \frac{1}{303}\right) = 3.57 \times 10^{-5} E_a \quad (\text{J})$$

$$2.56 = 3.57 \times 10^{-5} E_a$$

$$E_a = 7.16 \times 10^4 \text{ J mol}^{-1} = 71.6 \text{ kJ mol}^{-1}$$

3. The following data has been measured for the kinetics of the reaction of iodide with hypochlorous acid in alkaline conditions, which has the chemical equation,



Experiment	Time(s)	[I <sup>-</sup> ]	[HOCl]	[OH <sup>-</sup> ]	Initial Rate (M s <sup>-1</sup> )
1	0	2.40 X 10 <sup>-4</sup>	1.60 X 10 <sup>-4</sup>	1.00	2.30 x 10 <sup>-6</sup>
	10.0	2.17 X 10 <sup>-4</sup>	1.37 X 10 <sup>-4</sup>	1.00	
2	0	1.20 X 10 <sup>-4</sup>	1.60 X 10 <sup>-4</sup>	1.00	1.20 x 10 <sup>-6</sup>
	10.0	1.08 X 10 <sup>-4</sup>	1.48 X 10 <sup>-4</sup>	1.00	
3	0	2.40 X 10 <sup>-4</sup>	4.00 X 10 <sup>-5</sup>	1.00	6.00 x 10 <sup>-7</sup>
	10.0	2.34 X 10 <sup>-4</sup>	3.40 X 10 <sup>-5</sup>	1.00	
4	0	1.20 X 10 <sup>-4</sup>	1.60 X 10 <sup>-4</sup>	2.00	6.00 x 10 <sup>-7</sup>
	10.0	1.14 X 10 <sup>-4</sup>	1.54 X 10 <sup>-4</sup>	2.00	

(a) (1/2 pt each) Determine the initial rate for each experiment, and write it in the column provided in the table

$$R = -\frac{\Delta[\text{I}^-]}{\Delta t} = -\frac{\Delta[\text{HOCl}]}{\Delta t}$$

(b) (1 pt each) Determine the order of the reaction in each of the three reagents.

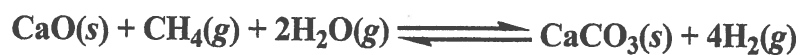
(i) OH<sup>-</sup> USE 2 AND 4  $[\text{OH}^-]_4/[\text{OH}^-]_2 = 2.00$ ,  $R_4/R_2 = 0.5 \Rightarrow \text{ORDER} = -1$

(ii) HOCl  $[\text{HOCl}]_3/[\text{HOCl}]_1 = 0.25$ ,  $R_3/R_1 = 0.25 \Rightarrow \text{ORDER} = 1$

(iii) I<sup>-</sup>  $[\text{I}^-]_2/[\text{I}^-]_1 = 0.5$ ,  $R_2/R_1 = 0.5 \Rightarrow \text{ORDER} = 1$

(c) (1 pt) What is the overall order of this reaction? |

4. (1 pt each) The following reaction, catalysed by iridium, is endothermic at 700 K.



For a reaction mixture at equilibrium at 700 K, how would each of the following changes affect the total quantity of  $\text{CaCO}_3$  in the reaction mixture once equilibrium is re-established?

- (a) increasing the temperature    *INCREASE*
- (b) adding calcium oxide (CaO)    *NO EFFECT*
- (c) removing methane ( $\text{CH}_4$ )    *DECREASE*
- (d) increasing the total volume    *INCREASE*
- (e) adding iridium    *NO EFFECT*
- (f) adding water    *INCREASE*

5. (3 pts) One late evening in your lab, you observe the following reaction at 25°C,



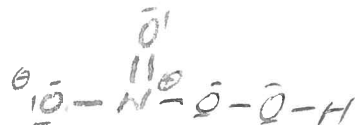
Excitedly, your colleague proposes the following 4-step mechanism,

1.  $\text{NH}_3 + \text{O}_3 \rightarrow \text{H}_2\text{O} + \text{HNO}_2$  fast
2.  $\text{HNO}_2 + \text{H}_2\text{O} + \text{O}_3 \rightarrow \text{H}_2\text{O}_2 + \text{HNO}_4$  fast
3.  $\text{HNO}_4 + \text{NH}_3 \rightarrow 2\text{H}_2\text{O} + \text{N}_2 + \text{O}_2$  slow
4.  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$  fast

There are several glaring issues wrong with this mechanism. Please identify any three of them.  
NOTE: you will get 1 pt for each correct answer (up to three), and -1 for each incorrect answer (down to zero).

1. STEP 2 - TRIMOLECULAR COLLISION (HIGHLY IMPROBABLE)
2.  $\text{HNO}_4$  - HIGHLY IMPROBABLE SPECIES
3.  $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$  DOESN'T HAPPEN AT 25°C OR WE WOULD HAVE NO  $\text{O}_2$  IN ATMOSPHERE

IF YOU SAY  $\text{HNO}_4$  IS PEROXYNITRIC ACID,



TITEN IT IS HIGHLY IMPROBABLE THAT STEP 3 WOULD BE SLOW STEP COMPARED TO STEP 2

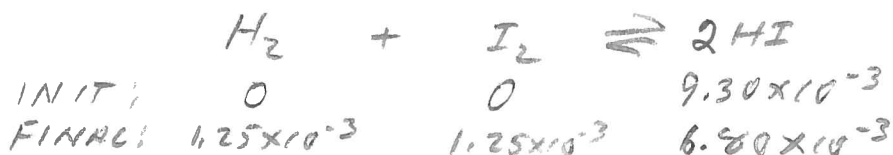
6. The following reaction takes place at 1000 K.



(a) (2 pts) write the  $K_p$  expression for the above reaction.

$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}}$$

(b) (3 pts)  $9.30 \times 10^{-3}$  mol of HI was placed in an evacuated 2.00 L flask at 1000 K. After equilibrium is reached, the number of mol of  $\text{I}_2$  was found to be  $1.25 \times 10^{-3}$  mol. Calculate the value of  $K_p$ .



$$P_x V = n_x RT$$

$$P_x = n_x \left( \frac{RT}{V} \right)$$

$$K_p = \frac{n_{\text{HI}}^2}{n_{\text{H}_2} n_{\text{I}_2}} \cdot \frac{(RT/V)^2}{(RT/V)^2} = \frac{(6.80 \times 10^{-3})^2}{(1.25 \times 10^{-3})^2} = 29.6$$