

Surname : \_\_\_\_\_ Given name : \_\_\_\_\_

Student number: \_\_\_\_\_

**Chemistry 1311F**  
**Test 2 V1, November 19, 2015**  
80 minutes  
You may remove the last 2 pages  
Professor: Wendy Pell

1. a) (1 point) Determine the order of a reaction if the rate constant has units  $M^{-5/2} s^{-1}$

3.5

$$R = k (M^{-5/2} s^{-1}) [ ]^x$$

$x = 7.5$

b) (1 point) How would you adjust the <sup>volume</sup> pressure of a reaction vessel to favour production of products in the following reaction:  $2 C(s) + O_2(g) \rightleftharpoons 2 CO(g)$   
*reactants*

- less moles  
- INCREASE pressure, decrease volume

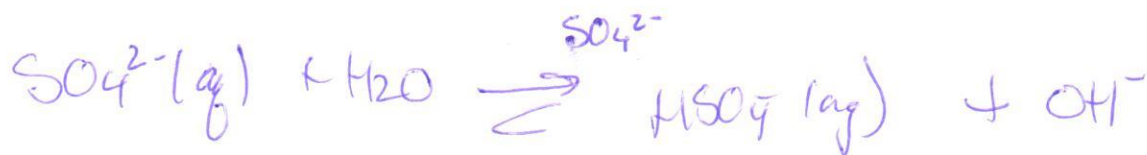
c) (1 point) Write the equilibrium constant, K, for  
 $Zn(s) + 2H^+(aq) \rightleftharpoons H_2(g) + Zn^{2+}(aq)$

$$K = \frac{[Zn^{2+}] P_{H_2}}{[H^+]^2}$$

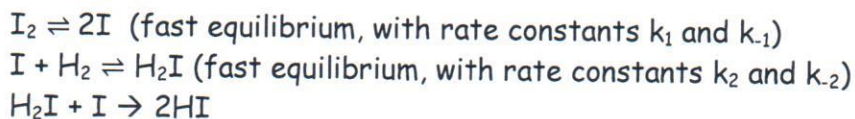
d) (1 point) What is the conjugate base of ~~trimethylamine~~,  $(CH_3)_3N$ ?  $\rightarrow$  trichloroacetic acid



e) (1 point) Potassium <sup>sulphate</sup> dihydrogen phosphate,  $KH_2PO_4$ , is an acidic salt. What hydrolysis reaction occurs when dihydrogen phosphate anion,  $H_2PO_4^-$  is added to water?



2. The following mechanism was proposed for the formation of hydroiodic acid, HI, from hydrogen and oxygen gases:



a) (4 points) Determine the overall rate law for this mechanism



RDS is 3<sup>rd</sup> step  $R = k_3 [\text{H}_2\text{I}][\text{I}]$

$\text{H}_2\text{I}$  &  $\text{I}$  are both intermediates, use fast equilibrium steps to get alternate expression for  $[\text{H}_2\text{I}]$  and  $[\text{I}]$

$$k_1 [\text{I}_2] = k_{-1} [\text{I}]^2; \quad [\text{I}] = \left(\frac{k_1}{k_{-1}} [\text{I}_2]\right)^{1/2}$$

$$k_2 [\text{I}][\text{H}_2] = k_{-2} [\text{H}_2\text{I}] \quad [\text{H}_2\text{I}] = \frac{k_2}{k_{-2}} [\text{H}_2][\text{I}] = \frac{k_2}{k_{-2}} [\text{H}_2] \left(\frac{k_1}{k_{-1}} [\text{I}_2]\right)^{1/2}$$

$$R = k_3 \frac{k_2}{k_{-2}} [\text{H}_2] \left(\frac{k_1}{k_{-1}} [\text{I}_2]\right)^{1/2} \times \left(\frac{k_1}{k_{-1}} [\text{I}_2]\right)^{1/2}$$

$$= \frac{k_3 k_2 k_1}{k_{-2} k_{-1}} [\text{H}_2][\text{I}_2] = k_T [\text{H}_2][\text{I}_2]$$

b) (1 point) If  $k_1 = 1.4 \times 10^{-3} \text{ s}^{-1}$ ;  $k_{-1} = 1.27 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ ;  $k_2 = 1.13 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$ ;  $k_{-2} = 1.48 \times 10^{-3} \text{ s}^{-1}$  and  $k_3 = 15 \text{ M}^{-1}\text{s}^{-1}$  determine the overall rate constant for the reaction.

$$\begin{aligned} R &= \frac{k_3 k_2 k_1}{k_{-2} k_{-1}} = \frac{15.0 \text{ M}^{-1}\text{s}^{-1} (1.13 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}) (1.40 \times 10^{-3} \text{ s}^{-1})}{(1.48 \times 10^{-3} \text{ s}^{-1}) (1.27 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1})} \\ &= 12.6 \text{ M}^{-1} \text{ s}^{-1} \end{aligned}$$

c) (1 points) How might you determine if your mechanism is correct?

1) do an experiment to see if Rxn is 1<sup>st</sup> order in  $[\text{H}_2]$  & first order in  $[\text{I}_2]$

2) detect intermediate

3) add a 'sink' for intermediates and see if rxn stops.

3. The reaction

$\text{H}_2\text{SeO}_3(\text{aq}) + 6\text{I}^-(\text{aq}) + 4\text{H}^+(\text{aq}) \rightarrow \text{Se}(\text{s}) + 2\text{I}_3^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$  was studied at  $0^\circ\text{C}$  and the following initial rate data were obtained:

	$[\text{H}_2\text{SeO}_3]_0$ (mol/L)	$[\text{H}^+]$ (mol/L)	$[\text{I}^-]$ (mol/L)	Initial Rate (mol / L s)
①	$1.0 \times 10^{-4}$	$2.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$1.67 \times 10^{-7}$
②	$2.0 \times 10^{-4}$	$2.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$3.33 \times 10^{-7}$
③	$1.0 \times 10^{-4}$	$1.0 \times 10^{-2}$	$2.0 \times 10^{-2}$	$0.42 \times 10^{-7}$
④	$1.0 \times 10^{-4}$	$2.0 \times 10^{-2}$	$4.0 \times 10^{-2}$	$13.3 \times 10^{-7}$

a) (5 points) What is the rate law for this reaction?

$$R = k [\text{H}_2\text{SeO}_3]^x [\text{H}^+]^y [\text{I}^-]^z$$

$$\frac{R_1}{R_2} = \frac{1.67}{3.33} = \frac{[\text{H}_2\text{SeO}_3]_1^x}{[\text{H}_2\text{SeO}_3]_2^x} = \left(\frac{1.0}{2.0}\right)^x ; 0.502 = (0.5)^x \quad x = 1$$

$$\frac{R_1}{R_3} = \frac{1.67}{0.42} = \frac{[\text{H}^+]_1^y}{[\text{H}^+]_2^y} = \left(\frac{2.0}{1.0}\right)^y ; 3.98 = (2)^y \quad y = 2$$

$$\frac{R_1}{R_4} = \frac{1.67}{13.3} = \frac{[\text{I}^-]_1^z}{[\text{I}^-]_2^z} = \left(\frac{2.0}{4.0}\right)^z$$

$$0.125 = (0.5)^z$$

$$\log(0.125) = z \log(0.5)$$

$$-0.90 = z(-0.30) \quad z = 3$$

$$R = k [\text{H}_2\text{SeO}_3] [\text{H}^+]^2 [\text{I}^-]^3$$

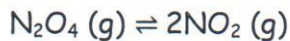
b) (2 points) Determine the rate constant for this reaction (include units).

Using rate law above and experimental data.

$$1.67 \times 10^{-7} = k [1.0 \times 10^{-4}] [2.0 \times 10^{-2}]^2 [2.0 \times 10^{-2}]^3$$

$$k = 5.25 \times 10^5 \text{ M}^{-5} \text{ s}^{-1}$$

4. A reaction vessel, at 77 °C, is filled with dinitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>. Equilibrium is established



and the resulting concentrations of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> are 9.6 × 10<sup>-3</sup> M and 3.9 × 10<sup>-2</sup> M, respectively.

a) (2 points) Determine the equilibrium constant for this reaction.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(3.9 \times 10^{-2})^2}{(9.6 \times 10^{-3})} = 0.158$$

$$K_p = K_c (RT)^{\Delta n} = 0.158 (0.08314 \times 350)^{2-1} = 4.61$$

b) (3 points) What is the equilibrium constant at 25 °C if the rxn is endothermic with  $\Delta_{\text{rxn}}H = 56.5 \text{ kJ}$

$$\ln \frac{K_1}{K_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left( \frac{K_2}{4.61} \right) = \frac{56.5 \times 10^3}{8.314} \left( \frac{1}{350} - \frac{1}{298} \right)$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{K_2}{4.61} = 0.0337$$

$$K_2 = 0.157$$

c) (5 points) The volume of the reaction vessel (in part a) doubles, and temperature is decreased to 25 °C. If the reaction is endothermic, with  $\Delta_{\text{rxn}}H = 56.5 \text{ kJ}$ , determine the total pressure once equilibrium is re-established.

$$K(298) = 0.157$$

$$P_{\text{N}_2\text{O}_4} = \left( \frac{n}{V} \right) (RT) = \left( \frac{9.6 \times 10^{-3}}{2} \right) (0.08314 \times 298) = 0.119 \text{ bar}$$

$$P_{\text{NO}_2} = \left( \frac{3.9 \times 10^{-2}}{2} \right) (0.08314 \times 298) = 0.483 \text{ bar}$$



$$0.119$$

$$0.483$$

$$x$$

$$-2x$$

$$0.119 + x$$

$$0.483 - 2x$$

$$K = 0.157 = \frac{(0.483 - 2x)^2}{(0.119 + x)}$$

$$0.01868 + 0.157x = 0.2334 - 1.932x + 4x^2$$

$$4x^2 - 2.089x + 0.2147 = 0$$

$$x = \frac{2.089 \pm \sqrt{(2.089)^2 - 4(4)(0.2147)}}{8}$$

$$= \frac{2.089 \pm 0.929}{8}$$

$$= 0.377 \text{ or } \underline{0.145} \text{ only real answer}$$

$$P_T = (0.119 + x) + (0.483 - 2x)$$

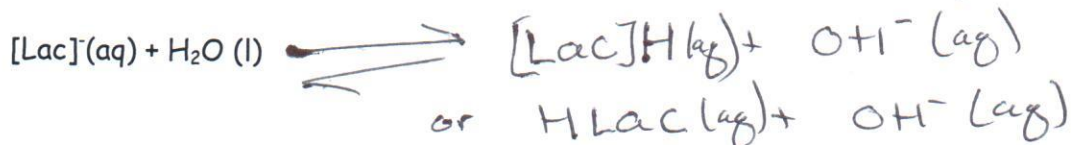
$$= 0.119 + 0.483 - 0.145$$

$$= 0.457$$

$$= 0.46 \text{ bar}$$

6. Lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , is a weak organic acid. Salts of this acid are called lactates and calcium lactate,  $\text{Ca}(\text{CH}_3\text{CH}(\text{OH})\text{COO})_2$ , can be used as a source of calcium. For simplicity represent calcium lactate as  $\text{Ca}(\text{Lac})_2$ .

a) (1 point) The alkaline salt  $\text{Ca}(\text{Lac})_2$  dissociates completely to form  $\text{Ca}^{2+}$  and  $[\text{Lac}]^-$  in aqueous solution. Complete the hydrolysis reaction for the lactate anion in aqueous solution:



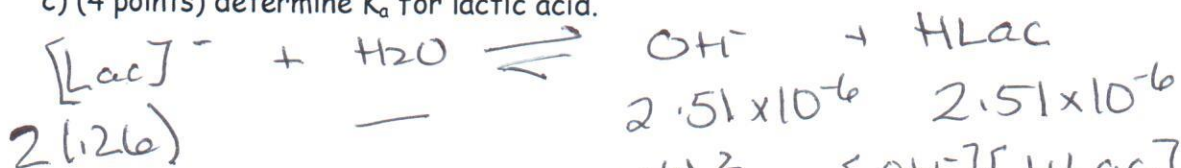
b) (1 point) The pH of a solution of 0.26 M  $\text{Ca}(\text{Lac})_2$  is found to be 8.4, determine the  $[\text{OH}^-]$  of the solution.

$$\text{pH} = 8.4$$

$$\text{pOH} = 14 - 8.4 = 5.6$$

$$[\text{OH}^-] = 10^{-5.6} = 2.51 \times 10^{-6} \text{ M}$$

c) (4 points) determine  $K_a$  for lactic acid.



$$K_b = \frac{(2.51 \times 10^{-6})^2}{2(0.26)} = \frac{[\text{OH}^-][\text{HLac}]}{[\text{Lac}]^-}$$

$$= 1.21 \times 10^{-11}$$

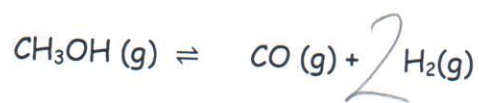
$$K_a = K_w / K_b = 10^{-14} / 1.21 \times 10^{-11} = 8.25 \times 10^{-4}$$

$$= 8.3 \times 10^{-4}$$

Question	
1	/5
2	/6
3	/7
4	/10
5	/8
6	/6
<b>Total</b>	<b>/42</b>

**BONUS:** What is a chemist's favourite thing to do with a pumpkin?

a) (1 point) Balance the chemical reaction:



b) (1 point) Write the expression for the equilibrium constant

$$K = \frac{P_{\text{H}_2}^2 P_{\text{CO}}}{P_{\text{CH}_3\text{OH}}}$$

c) (4 points) A 4.72 g sample of methanol is placed in an empty 1.00 L flask and heated to 250 °C. After the system has reached equilibrium, a tiny hole is drilled in the side of the flask allowing gaseous compounds to effuse out of the flask. Measurements of the effusing gas show that it contains 33.0 times as much  $\text{H}_2(\text{g})$  as  $\text{CH}_3\text{OH}(\text{g})$ . Determine the equilibrium constant,  $K$ , for this reaction.

$$\text{CH}_3\text{OH} \quad m = 32 \text{ g/mol} \quad 4.72 \text{ g} / 32 = 0.1475 \text{ moles}$$

$$T = 250^\circ\text{C} = 523 \text{ K}$$

$$P = \frac{n}{V} RT = 0.1475 (523) (0.08314) = 6.41 \text{ bar}$$



6.41					
-x	+x	2x		2x = 33(6.41 - x)	
6.41 - x	x	2x		211.53 - 33x	
				35x = 211.53	
				x = 6.04	

$$0.375 \quad 6.04 \quad 12.08$$

$$K = \frac{(6.04)(12.08)^2}{1.365} = 2.4 \times 10^3$$

d) (2 points) What the mole fraction and partial pressure of the methanol in the vessel at equilibrium?

$$P_T = 12.08 + 6.04 + 1.37 = 18.49$$

$$P_{\text{CH}_3\text{OH}} = 0.37$$

$$X_{\text{CH}_3\text{OH}} = \frac{P_{\text{CH}_3\text{OH}}}{P_T} = 0.02$$