

Surname : _____ Given name : _____

Student number: _____

Chemistry 1311D
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 $M^{-3/2} s^{-1}$

$$R = k []^x$$
$$\frac{M}{s} = k \left(\frac{M}{s} \right)^{3/2} []^x \quad x = \frac{5}{2} = 2.5$$

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

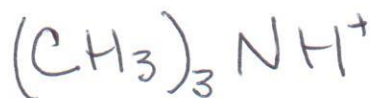
products \rightarrow more gas molecules

INCREASE volume

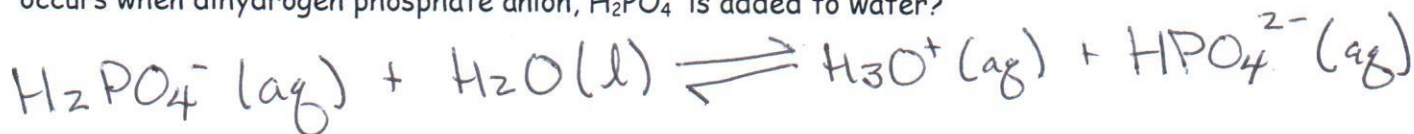
c) (1 point) Write the equilibrium constant, K , for
 $Zn(s) + 2H^+(aq) \rightleftharpoons H_2(g) + Zn^{2+}(aq)$

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

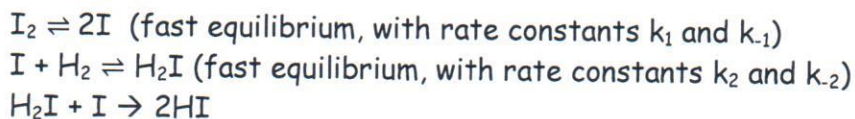
d) (1 point) What is the conjugate acid of trimethyl amine, $(CH_3)_3N$?



e) (1 point) Potassium 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 3rd step $R = k_3 [\text{H}_2\text{I}][\text{I}]$

H_2I & 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 1st 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°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	1.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	1.67×10^{-7}
②	2.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	3.33×10^{-7}
③	1.0×10^{-4}	1.0×10^{-2}	2.0×10^{-2}	0.42×10^{-7}
④	1.0×10^{-4}	2.0×10^{-2}	4.0×10^{-2}	13.3×10^{-7}

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

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

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

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

$$\frac{R_1}{R_4} = \frac{1.67}{13.3} = \frac{[\text{I}^-]_1^z}{[\text{I}^-]_2^z} = \left(\frac{2.0}{4.0}\right)^z \quad \begin{aligned} 0.125 &= (0.5)^z \\ \log(0.125) &= z \log(0.5) \\ -0.90 &= z(-0.30) \end{aligned} \quad z = 3$$

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

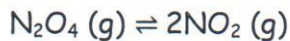
b) (2 points) Determine the rate constant for this reaction (include units).

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, N₂O₄. Equilibrium is established



and the resulting concentrations of N₂O₄ and NO₂ are 9.6 × 10⁻³ M and 3.9 × 10⁻² 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. FONT

$$K(298) = 0.157$$

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

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



$$0.119$$

$$0.483$$

$$x$$

$$-2x$$

$$0.119 + x$$

$$0.483 - 2x$$

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

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

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

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

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

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

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

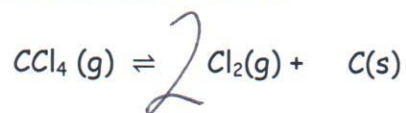
$$= 0.119 + 0.483 - 0.145$$

$$= 0.457$$

$$= 0.46 \text{ bar}$$

5. At 700 K, carbon tetrachloride, $\text{CCl}_4(\text{g})$, decomposes to $\text{Cl}_2(\text{g})$ and graphite, $\text{C}(\text{s})$. The equilibrium constant for this reaction is $K = 0.76$.

a) (1 point) Balance the chemical reaction:



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

$$K = \frac{P_{\text{Cl}_2}^2}{P_{\text{CCl}_4}}$$

c) (4 points) A sample of $\text{CCl}_4(\text{g})$ is placed in a reaction vessel and decomposes. What is the starting pressure of the $\text{CCl}_4(\text{g})$ that will produce a final total equilibrium pressure of all gases of 1.0 bar.

Hint: Set up an ICE table with "y" as the initial pressure of $\text{CCl}_4(\text{g})$



i	y	—	—
c	-x	+2x	—
e	y-x	2x	—

$$P_T = 1.0 = y - x + 2x$$

$$y = 1 - x$$

$$(y - x) = 1 - 2x$$

$$K = \frac{P_{\text{Cl}_2}^2}{P_{\text{CCl}_4}} = \frac{(2x)^2}{(y-x)} = \frac{(2x)^2}{1-2x} = 0.76$$

$$0.76 - 1.52x = 4x^2$$

$$4x^2 + 1.52x - 0.76 = 0$$

$$x = \frac{-1.52 \pm \sqrt{(1.52)^2 - 4(4)(-0.76)}}{8}$$

$$= 0.28$$

$$P_{\text{CCl}_4} = y = 1 - x = 1 - 0.28 = 0.72 \text{ bar}$$

d) (2 points) What is the volume of the reactor that initially contained 1 mole of $\text{CCl}_4(\text{g})$

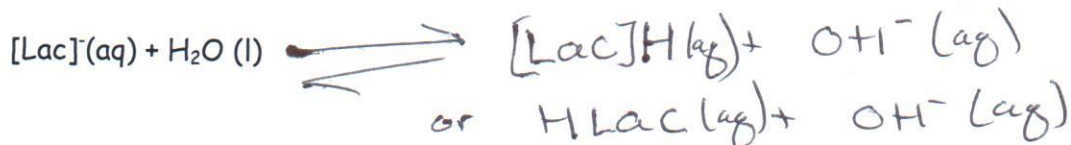
$$V = \frac{nRT}{P} = \frac{(1)(0.08314)(700\text{K})}{0.72 \text{ bar}}$$

$$= 80.8 \text{ L}$$

$$= 81 \text{ L}$$

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 Ca^{2+} and $[\text{Lac}]^-$ in aqueous solution. Complete the hydrolysis reaction for the lactate anion in aqueous solution:



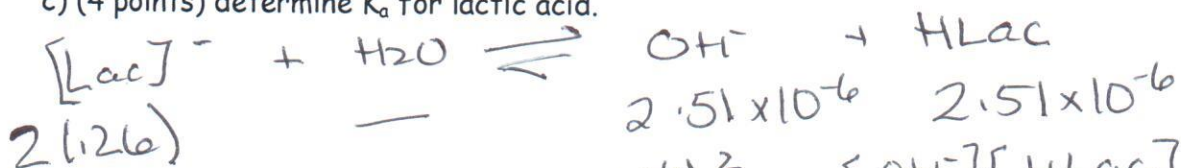
b) (1 point) The pH of a solution of 0.26 M $\text{Ca}(\text{Lac})_2$ is found to be 8.4, determine the $[\text{OH}^-]$ of the solution.

$$\text{pH} = 8.4$$

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

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

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
Total	/42

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

Surname : _____ Given name : _____

Student number: _____

Chemistry 1311D

Test 2 V2, November 19, 2015

80 minutes

You may remove the last 2 pages

Professor: Wendy Pell

1. a) (1 point) ^{of} The half life a reaction doubles when the concentration of the reactant is halved. What is the order of the reaction?

$$t_{1/2} = \frac{\ln 2}{k} \text{ 1st}$$

$$t_{1/2} = \frac{A_0}{2k} \text{ 0th}$$

$$t_{1/2} = \frac{1}{k[A_0]} \text{ 2nd}$$

$$t_{1/2} = \frac{A_0}{4k} = t_{1/2}/2$$

$$= \frac{2}{kA_0} = 2(+1/2)$$

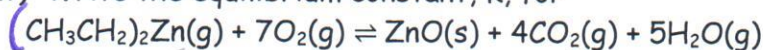
Pressure

2nd order

b) (1 point) How would you adjust the ~~volume~~ ^{of} a reaction vessel to favour production of products in the following reaction: $2 \text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}(g)$

products = more gas
= low pressure

c) (1 point) Write the equilibrium constant, K, for

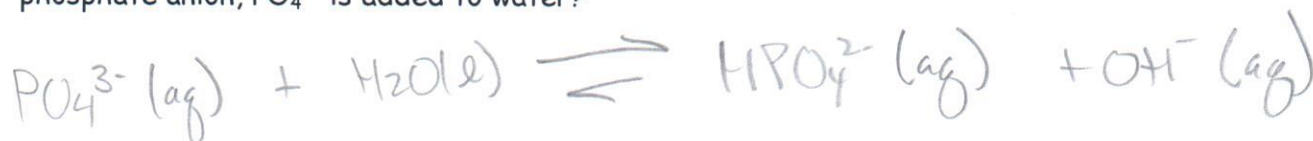


$$K = \frac{[\text{CO}_2]^4 P_{\text{H}_2\text{O}}^5}{P_{(\text{CH}_3\text{CH}_2)_2\text{Zn}}}$$

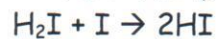
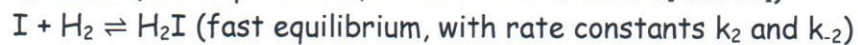
d) (1 point) What is the conjugate acid of pyridine, $\text{C}_5\text{H}_5\text{N}$?



e) (1 point) Potassium phosphate, K_3PO_4 , is an alkaline salt. What hydrolysis reaction occurs when phosphate anion, PO_4^{3-} 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

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.

$$21.0 \text{ M}^{-1} \text{ s}^{-1}$$

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

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°C and the following initial rate data were obtained:

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

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

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

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

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