CHEM 1002 A, V Midterm Test #2
March 8, 2013

Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

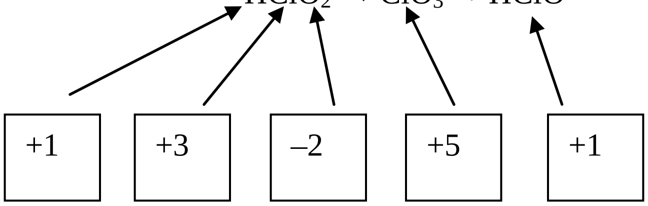
1. Explain why mixing 1 L of 1 M $NH_{3(aq)}$ with 1 L of 0.5 M $HCl_{(aq)}$ makes a buffered solution.

   The HCl reacts with half of the $NH_{3(aq)}$, creating $NH_4{}^{+}{}_{(aq)}$ by the reaction:
   $NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$. The solution then contains equal concentrations of a weak base ($NH_{3(aq)}$) and its conjugate acid ($NH_4{}^{+}{}_{(aq)}$), which makes it a buffered solution.

2. $CdCO_{3(s)}$ is only slightly soluble in water. Will it be more or less soluble in a basic solution than in a pH neutral solution? Show the relevant reactions and explain. K_a for $HCO_3{}^{-}{}_{(aq)}$ is 4.7×10^{-11}
   $CdCO_{3(s)}$ dissolves according to:
   $CdCO_{3(s)} \rightleftharpoons Cd^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)}$
   But $CO_3{}^{2-}{}_{(aq)}$ is basic because its conjugate acid $HCO_3{}^{-}{}_{(aq)}$ is weakly acidic. Thus:
   $CO_3{}^{2-} + H_2O_{(l)} \rightleftharpoons HCO_3{}^{-}{}_{(aq)} + OH^{-}{}_{(aq)}$
   In a basic solution, $[OH^{-}{}_{(aq)}]$ is high. This pushes the second equilibrium to the left, increasing $[CO_3{}^{2-}{}_{(aq)}]$. This pushes the first equilibrium to the left, causing $CdCO_{3(s)}$ to precipitate out of solution. Its solubility is therefore lower in a basic solution.

3. Write the oxidation numbers of each of the indicated atoms in the reaction:

$$HClO_2 \rightarrow ClO_3{}^{-} + HClO$$



4. Referring to the table of standard reduction potentials at the end of this test, predict what is formed at the anode and at the cathode when an aqueous solution of $Na_2SO_{4(aq)}$ is electrolyzed.

   The only species initially in solution are $H_2O_{(l)}$, $Na^{+}{}_{(aq)}$ and $SO_4{}^{2-}{}_{(aq)}$. From the reduction potentials, we see that water will oxidize to $O_{2(g)}$ at a more positive potential than $SO_4{}^{2-}{}_{(aq)}$ oxidizes to $S_2O_8{}^{2-}{}_{(aq)}$. $O_{2(g)}$ and $H_3O^{+}{}_{(aq)}$ are therefore produced at the anode.
   Furthermore, water will be reduced at a more positive potential than $Na^{+}{}_{(aq)}$. $H_{2(g)}$ and $OH^{-}{}_{(aq)}$ are therefore produced at the cathode.

5. Write the shorthand notation of the electrochemical cell which has the reaction:

$$3\ Fe^{2+}{}_{(aq)} + 2\ Cr^{3+}{}_{(aq)} + 24\ H_2O_{(l)} \rightarrow 3\ Fe_{(s)} + 2\ CrO_4{}^{2-}{}_{(aq)} + 16\ H_3O^{+}{}_{(aq)}$$

$$Pt_{(s)}\ |\ CrO_4{}^{-}{}_{(aq)}, Cr^{3+}{}_{(aq)}, H_3O^{+}{}_{(aq)}\ \|\ Fe^{2+}{}_{(aq)}\ |\ Fe_{(s)}$$

6. Explain in detail why fluoroacetic acid is a stronger acid that chloroacetic acid.

Fluorine is more electronegative than chlorine. The F atom therefore pulls electrons towards itself very strongly. In fluoroacetic acid, electrons are therefore drawn towards the F atom and away from the O–H bond. This weakens the O–H bond, making this a stronger acid.

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Part B. Answer any three of the following four questions (B1, B2, B3, B4). If you answer all four, the best three answers will count. (20 marks each)

B1. (a) Calculate the pH of a 1.5 M solution of sodium nitrite, $NaNO_{2(aq)}$. K_a for $HNO_{2(aq)}$ is 5.6×10^{-4}.

$NaNO_{2(aq)} \rightarrow Na^{+}_{(aq)} + NO_2^{-}{}_{(aq)}$

$NO_2^{-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HNO_{2(aq)} + OH^{-}_{(aq)}$ $\qquad K_b = \dfrac{K_w}{K_{a,HNO_2}} = \dfrac{1.0\times10^{-14}}{5.6\times10^{-4}} = 1.79\times10^{-11}$

$$\frac{x(x)}{1.5-x} = 1.79\times10^{-11}$$

K_b is so small that $x \ll 1.5$, thus $\dfrac{x(x)}{1.5} = 1.79\times10^{-11}$. Solving, $x = [OH^{-}_{(aq)}] = 5.18 \times 10^{-6}$ M

$pH = 14 - pOH = 14 - (-\log_{10}(5.18 \times 10^{-6})) = 14.00 - 5.29 = 8.71$

(b) Calculate solubility of $CdCO_{3(s)}$ (in g L^{-1}) in pure water. K_{sp} for $CdCO_{3(s)}$ is 1.0×10^{-12}.

$CdCO_{3(s)} \rightleftharpoons Cd^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$ $\qquad K_{sp} = 1.0 \times 10^{-12}$

In pure water, $[Cd^{2+}_{(aq)}][CO_3^{2-}{}_{(aq)}] = 1.0 \times 10^{-12}$. Thus $[Cd^{2+}_{(aq)}] = [CO_3^{2-}{}_{(aq)}] = 1.0 \times 10^{-6}$.
The solubility of $CdCO_{3(s)}$ is therefore 1.0×10^{-6} mol L^{-1} (172.4 g mol^{-1}) = 1.72×10^{-4} g L^{-1}.

(c) Calculate the solubility of $CdCO_{3(s)}$ (in g L^{-1}) in 1.0 M $Na_2CO_{3(aq)}$.

$$[Cd^{2+}_{(aq)}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{1.0\times10^{-12}}{1.0}$$
$$= 1.0\times10^{-12}\,mol^{-1}$$
$$\text{Solubility} = [Cd^{2+}{}_{(aq)}] = 1.0\times10^{-12}\,mol\ L^{-1}(172.4\ g\ mol^{-1})$$
$$= 1.72\times10^{-10}\,g\ L^{-1}$$

B2. Calculate the concentrations of all species present (in M) and the pH in a 0.50 M solution of telluric acid, $H_6TeO_{6(aq)}$. For this acid, $K_{a1} = 2.0 \text{ x } 10^{-8}$, $K_{a2} = 1.0 \text{ x } 10^{-11}$ and $K_{a3} = 3.0 \text{ x } 10^{-15}$. Use the back of this page to finish your calculations if necessary. **Please put your answers in the boxes at the bottom of this page.**

$$H_6TeO_{6(aq)} + H_2O_{(l)} \rightleftharpoons H_5TeO_6{}^{-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

$$\frac{[H_5TeO_6{}^{-}{}_{(aq)}][H_3O^{+}{}_{(aq)}]}{[H_6TeO_{6(aq)}]} = K_{a_1}$$

$$\frac{x(x)}{0.5 - x} = 2.0\times10^{-8}$$

Solving, using the quadratic equation, x = 0.0001 or -0.0001. Since x is a concentration, we must use the positive root, thus x = 0.0001.

Thus, $[H_6TeO_{6(aq)}] = 0.5 – x = 0.50$ M
$[H_5TeO_6{}^{-}{}_{(aq)}] = x = 0.0001$ M
$[H_3O^{+}{}_{(aq)}] = x = 0.0001$ M
$pH = -\log_{10}[H_3O^{+}{}_{(aq)}] = -\log_{10}(0.0001) = 4.00$

$$H_5TeO_6{}^{-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_4TeO_6{}^{2-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

$$\frac{[H_4TeO_6{}^{2-}{}_{(aq)}][H_3O^{+}{}_{(aq)}]}{[H_5TeO_6{}^{-}{}_{(aq)}]} = K_{a_2}$$

$$\text{thus, } [H_4TeO_6{}^{2-}{}_{(aq)}] = \frac{K_{a_2}[H_5TeO_6{}^{-}{}_{(aq)}]}{[H_3O^{+}{}_{(aq)}]} = \frac{K_{a_2}(0.0001)}{(0.0001)} = K_{a_2} = 1.0\times10^{-11}\text{M}$$

$$H_4TeO_6{}^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3TeO_6{}^{3-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$$

$$\frac{[H_3TeO_6{}^{3-}{}_{(aq)}][H_3O^{+}{}_{(aq)}]}{[H_4TeO_6{}^{2-}{}_{(aq)}]} = K_{a_3}$$

$$\text{thus, } [H_3TeO_6{}^{3-}{}_{(aq)}] = \frac{K_{a_3}[H_4TeO_6{}^{2-}{}_{(aq)}]}{[H_3O^{+}{}_{(aq)}]} = \frac{3.0\times10^{-15}(1.0\times10^{-11})}{(0.0001)} = 3.0\times10^{-22}\text{M}$$

$$[OH^{-}{}_{(aq)}] = \frac{K_w}{[H_3O^{+}{}_{(aq)}]} = \frac{1.0\times10^{-14}}{0.0001} = 1.00\times10^{-10}\text{M}$$

$[H_6TeO_{6(aq)}]$	$[H_5TeO_6{}^{-}{}_{(aq)}]$	$[H_4TeO_6{}^{2-}{}_{(aq)}]$	$[H_3TeO_6{}^{3-}{}_{(aq)}]$	$[H_3O^{+}{}_{(aq)}]$	$[OH^{-}{}_{(aq)}]$	pH
0.50 M	0.0001 M	$1.0 \text{ x } 10^{-11}$ M	$3.0 \text{ x } 10^{-22}$M	0.0001 M	$1.00 \text{ x } 10^{-10}$M	4.00

B3. Balance the following reaction in a basic solution: $Cl_2 \rightarrow Cl^- + ClO_4^-$

Oxidation:

$Cl_2 \rightarrow ClO_4^-$
$Cl_2 \rightarrow 2\ ClO_4^-$
$Cl_2 + 8\ H_2O \rightarrow 2\ ClO_4^-$
$Cl_2 + 8\ H_2O \rightarrow 2\ ClO_4^- + 16\ H^+$
$Cl_2 + 8\ H_2O \rightarrow 2\ ClO_4^- + 16\ H^+ + 14\ e^-$

Reduction:

$Cl_2 \rightarrow Cl^-$
$Cl_2 + 2\ e^- \rightarrow Cl^-$

Cross Multiply and Add:

$Cl_2 + 8\ H_2O \rightarrow 2\ ClO_4^- + 16\ H^+ + 14\ e^-$
$7\ Cl_2 + 14\ e^- \rightarrow 14\ Cl^-$

$8\ Cl_2 + 8\ H_2O \rightarrow 2\ ClO_4^- + 14\ Cl^- + 16\ H^+$

Convert to Basic Solution:

$8\ Cl_2 + 8\ H_2O + 16\ OH^- \rightarrow 2\ ClO_4^- + 14\ Cl^- + 16\ H^+ + 16\ OH^-$
$8\ Cl_2 + 8\ H_2O + 16\ OH^- \rightarrow 2\ ClO_4^- + 14\ Cl^- + 16\ H_2O$

$8\ Cl_2 + 16\ OH^- \rightarrow 2\ ClO_4^- + 14\ Cl^- + 8\ H_2O$

or

$4\ Cl_2 + 8\ OH^- \rightarrow ClO_4^- + 7\ Cl^- + 4\ H_2O$

B4. (a) It takes 74.6 seconds to produce 0.1086 g of a solid metal (“M”) using a current of 2.50 A from a solution of $MCl_{2(aq)}$. Identify the metal.

$it = nF$

$$n = \frac{it}{F} = \frac{2.50\text{ C s}^{-1}(74.6\text{ s})}{96487\text{ C mol}^{-1}} = 0.001933\text{ mol e}^{-}$$

Because the metal is divalent, $n_M = \dfrac{0.001933\text{ mol}}{2} = 0.0009665\text{ mol}$

And so its atomic weight is $M_M = \dfrac{0.1086\text{ g}}{0.0009665\text{ mol}} = 112.4\text{ g mol}^{-1}$

Referring to the periodic table, only <u>Cd</u> has this atomic weight.

(b) Calculate the equilibrium constant at 30°C for the reaction:

$$5\,Pb^{4+}_{(aq)} + 2\,Mn^{2+}_{(aq)} + 24\,H_2O_{(l)} \rightarrow 5\,Pb^{2+}_{(aq)} + 2\,MnO_4{}^{-}_{(aq)} + 16\,H_3O^{+}_{(aq)}$$

$E^o_{cell} = 1.69\text{ V} – 1.51\text{ V} = 0.18\text{ V}$

$\Delta G^o = –nFE^o$

$$K = e^{\frac{-\Delta G^o}{RT}} = e^{\frac{nFE^o}{RT}}$$
$$= e^{\frac{10(96487\text{ C mol}^{-1})(0.18\text{ J C}^{-1})}{8.314\text{ J K}^{-1}\text{mol}^{-1}(30+273.15)\text{K}}}$$
$$= e^{68.9}$$
$$= 8.4\times10^{29}$$