CH302H – Principles of Chemistry II: Honors
Spring 2014, Unique 51880

Exam 3
3 April 2014

Name: Key

You may use any material you wish provided it does not have a heartbeat nor does it connect to a wireless or cellular network.

Honor Code:

"The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community."

I certify that the work on this exam is entirely my own.

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Signature Date

1. The pK_a values for phosphoric acid (H_3PO_4) are 2.15, 7.20, and 12.35. Coca Cola® has a pH of 2.52 and contain phosphates.

a) What are the two dominant forms of phosphate in Coca Cola®? ***(10 pts)***

H_3PO_4 , $H_2PO_4^-$

b) Which form of phosphate in the Coca Cola® is in the highest concentration? ***(8pts)***

$H_2PO_4^-$

2. 25 mL of 0.0030 F chloroacetic acid ($ClCH_2COOH$) (K_a=1.36x10^{-3}) is titrated with 0.010 F NaOH.

a) What volume of base is needed to reach the equivalence point? ***(10 pts)***

$$V_B = \frac{V_A M_A}{M_B} = \frac{(25)(0.003)}{0.01} = \boxed{7.5\text{ ml of NaOH}}$$

b) What is the solution pH after 3.0 mL of titrant has been added? ***(10 pts)***

$$C_A = \frac{(25)(0.003) - (3)(0.01)}{25+3} = 1.6 \times 10^{-3}\ M$$

$$C_B = \frac{(3)(0.01)}{28} = 1.07 \times 10^{-3}\ M = [ClCH_2COO^-]$$

$$pH = pka + \log \frac{[ClCH_2COO^-]}{[ClCH_2COOH]}$$

$$= 2.866 + \log \frac{(1.07 \times 10^{-3})}{(1.6 \times 10^{-3})} = \boxed{2.69}$$

c) What is the pH at the equivalence point? ***(10 pts)***

At equivalence point, all of $ClCH_2COOH$ converts to conjugate base

$$ClCH_2COO^- + H_2O \rightleftharpoons ClCH_2COOH + OH^-$$

I $\quad \frac{(25)(0.003)}{32.5} \quad 0 \quad 0$

C $\quad -x \quad +x \quad +x$

E $\quad 2.3\times10^{-3} - x \quad +x \quad +x$

$$\therefore K_b = \frac{k_w}{K_a} = \frac{10^{-14}}{1.36\times10^{-3}} = 7.35\times10^{-12} = \frac{[OH][ClCH_2COOH]}{[ClCH_2COO^-]}$$

$$7.35\times10^{-12} = \frac{x^2}{(2.3\times10^{-3}-x)}$$; Assume $x \ll 2.3\times10^{-3}$

$\therefore x = 1.3\times10^{-7}$ (assumption good)

$\therefore [OH] = 1.3\times10^{-7}$; $pOH = 6.88$; $pH = 14 - p[OH] = \boxed{7.11}$

3. Given the following electrochemical cell:

Pt | Fe^{2+}(0.001 M); Fe^{3+} (0.002 M) || Cu^{2+} (0.003 M) | Cu

a) Which electrode is the anode? ***(5 pts)*** ☒ Pt ☐ Cu

b) Write the balanced chemical reaction implied by this cell. ***(5 pts)***

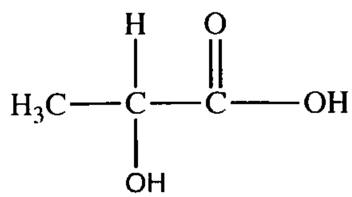
$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad]\times 2$$
$$Cu^{2+} + 2e^- \longrightarrow Cu$$
$$2Fe^{2+} + Cu^{2+} \longrightarrow 2Fe^{3+} + Cu$$

c) Using your answer in b), the oxidizing agent is Cu^{2+}.. ***(5 pts)***

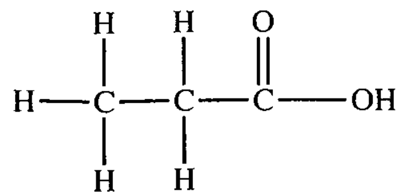
d) If this reaction proceeded in the reverse direction when the Cu electrode was connected to the Pt electrode, then this is a(an) ☐ electrolytic cell ☒ galvanic (or voltaic) cell. ***(5 pts)*** (both)

4. Shown below are the structures for Lactic and Propanoic acid. Which acid has the <u>smallest</u> pK_a, i.e., is the

most acidic? *(~~10~~ 5 pts)* ☒ lactic acid ☐ propanoic acid



Lactic Acid



Propanoic Acid

5. You wish to prepare a <u>phosphate buffer</u> to maintain a pH at 7.00. (for phosphoric acid: pK_{a1}=2.15; pK_{a2} = 7.20; pK_{a3} = 12.35)

a) Which acid and conjugate base would you use for this buffer? ***(10 pts)***

$H_2PO_4^-$ & HPO_4^{2-}

b) In what ratio would you find them in the buffered solution? (Be sure you are clearly show which species you are ratioing, e.g., $[H_nX]/[H_{n-1}X] = 1.34 \times 10^3$) ***(10 pts)***

$$pH = pKa + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$7.0 = 7.2 + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.631 \quad \text{or,}$$

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.58$$

6. a) What is the molar solubility of $PbCl_2$? ($K_{sp} = 1.7\text{x}10^{-5}$) ***(10 pts)***

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$$

$$S \qquad 2S$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$1.7 \times 10^{-5} = S(2S)^2$$

$$S = 0.016\ M$$

BONUS b) Pb^{2+} also forms a weak, soluble complex with chloride ($PbCl_4^{2-}$; $K_f = 25$). We prepare a liter of solution to which we add several grams of $PbCl_{2(s)}$ as well as 1 mole of NaCl. What is the total amount of soluble Pb ($[Pb^{2+}]$ and $[PbCl_4^{2-}]$) in the solution? ***(8 pts)***

① $PbCl_2 \rightarrow Pb^{2+} + 2Cl^- \qquad ksp = 1.7 \times 10^{-5}$

② $Pb^{2+} + 4Cl^- \rightleftharpoons PbCl_4^- \qquad kf = 5$

③ $C^\circ_{Cl} = [Cl^-] + 4[\cancel{PbCl_4^-}]$ ☆

④ $C^\circ_{Pb} = [\cancel{Pb^{2+}}] + [PbCl_4^{2-}]$ ☆ ok

ok.

⑤ $C^\circ_{Cl} = (C^\circ_{\cancel{Pb}})2 + 1.0$

This is small

ok.

$\therefore [Cl^-] = 1M$

$ksp = [Pb^{2+}][Cl^-]^2$

$[Pb^{2+}] = \frac{1.7 \times 10^{-5}}{1} = 1.7 \times 10^{-5} M$

$Kf = \frac{[PbCl_4^-]}{[Pb^{2+}][Cl^-]^4}$

$[PbCl_4^-] = K_f \times [Pb^{2+}] \times [Cl^-]^4$

$= 4.25 \times 10^{-4} M$

$\therefore$ total $Pb = [Pb^{2+}] + [PbCl_4^-] = \boxed{4.42 \times 10^{-4} M}$

Scratch paper