Directions: You have two hours to complete this exam. This exam is closed book and no electronic devices are allowed EXCEPT a calculator. Make sure to clearly label your answers. You can tear off the first sheet of this exam with the periodic table and equations. Make sure to put your name on the second page of this exam!

R = 0.08206 L-atm/mol-K

T (Kelvin) = °C + 273.15

Volts (V) = 1 J/C

F = 96,485 C/mol

$G^\circ = -nFE^\circ$

$G = G^\circ + RT\ln Q$

$G^\circ = -RT\ln K$

$\Delta G^\circ = H^\circ - T S^\circ$

$\Delta H^\circ_{rxn} = \Sigma n\Delta H^\circ_f \text{ products} - \Sigma n\Delta H^\circ_f \text{ reactants}$

$\Delta S^\circ_{rxn} = \Sigma n\Delta S^\circ \text{ products} - \Sigma n\Delta S^\circ \text{ reactants}$

$\Delta G^\circ_{rxn} = \Sigma\Delta G^\circ_f \text{ products} - \Sigma n\Delta G^\circ_f \text{ reactants}$

R = 8.314 J/mol-K

pH = -log([H3O+])

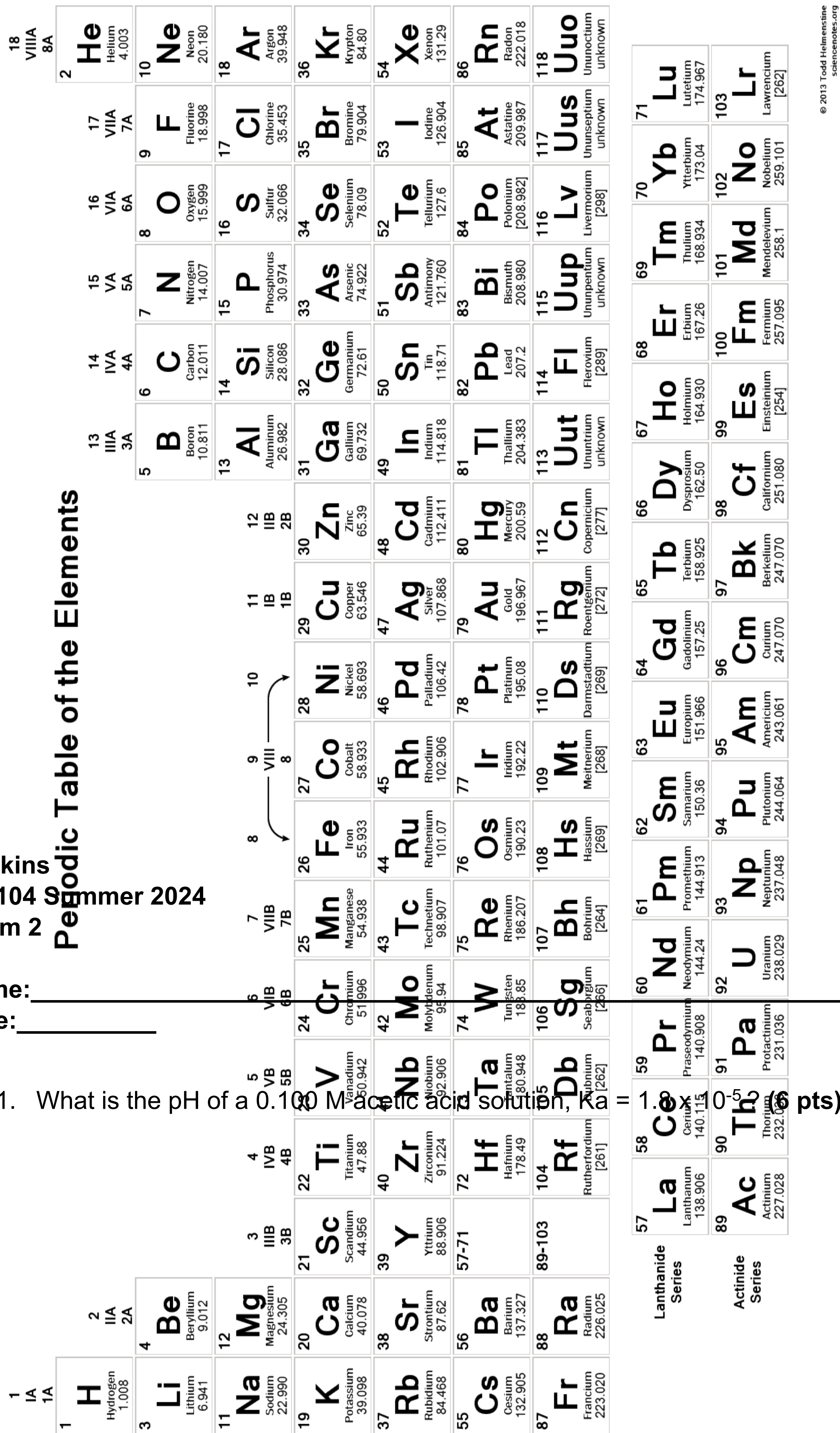
$$pH = pK_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

Kw at 25°C = 1.00×10^{-14}

Kw = Ka x Kb

Watkins
Ch 104 Summer 2024
Exam 2

Name:____
Date:___________



1. What is the pH of a 0.100 M acetic acid solution, $K_a = 1.8 \times 10^{-5}$? **(6 pts)**

#1

$x = \sqrt{0.100 \times 1.8 \times 10^{-5}}$ $x = 1.3 \times 10^{-3}$

$pH = 2.87$

$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$

I	0.100 M	0	0
C	$-x$	$+x$	$+x$
E	0.100	x	x

2. A 20.0 mL sample of a 0.100 M ammonia solution is titrated with 0.200 M HCl. Answer the following questions. **Kb for ammonia is 1.8 x 10^{-5} (14 pts)**

a. What is the pH BEFORE any titrant is added?

$x = \sqrt{0.100 \times 1.8 \times 10^{-5}}$ $x = [OH^-] = 1.3 \times 10^{-3}$

$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

I	0.100M	0	0
C	$-x$	$+x$	$+x$
E	0.100	x	x

$pOH = 2.87$

$pH = 11.13$

$K_a NH_4^+ =$ $pK_a =$

5.6×10^{-10} $0.0084\text{L} \times \frac{0.200\text{mol}}{\text{L}} = 0.00016$ mol

b. What is the pH after 8.00 mL of HCl have been added

	NH_3	+ H_3O^+	→ H_2O +	NH_4^+
start	0.0020mol	0.0016	∅	+0.0016 mol
	−0.0016	−0.0016		
	4×10^{-4} mol	∅		

use HH eq.

$pH = 9.25 + \log\left(\frac{4 \times 10^{-4}}{0.0016}\right)$

$pH = 8.64$

c. What is the volume of titrant at the equivalence point?

$V_{titrant} = 10.0\text{mL}$

@ eq pt mol acid = mol base

$0.00020\text{mol} \times \frac{1\text{L}}{0.200\text{mol}} = 0.001\text{L}$

$\frac{0.0020\text{mol}}{0.0300} = NH_4^+$

$V_{total} = 30.0\text{mL}$

d. What is the pH at the equivalence point?

	$NH_4^+_{(aq)}$	+ $H_2O_{(l)}$ ⇌	NH_3 (gas)	+ H_3O^+ (aq)
I	0.067M		∅	∅
C	−x		+x	+x
E	0.067		x	x

2.continued

e. What is the pH after 30.0 mL of HCl have been added?

$V_{total} = 50.0\text{mL}$

20.0mL excess HCl

$x = \sqrt{5.6 \times 10^{-10} \cdot 0.067}$

$x = [H_3O^+] = 6.1 \times 10^{-6}\text{ M}$

$pH = -\log(6.1 \times 10^{-6})$

d) 5.21

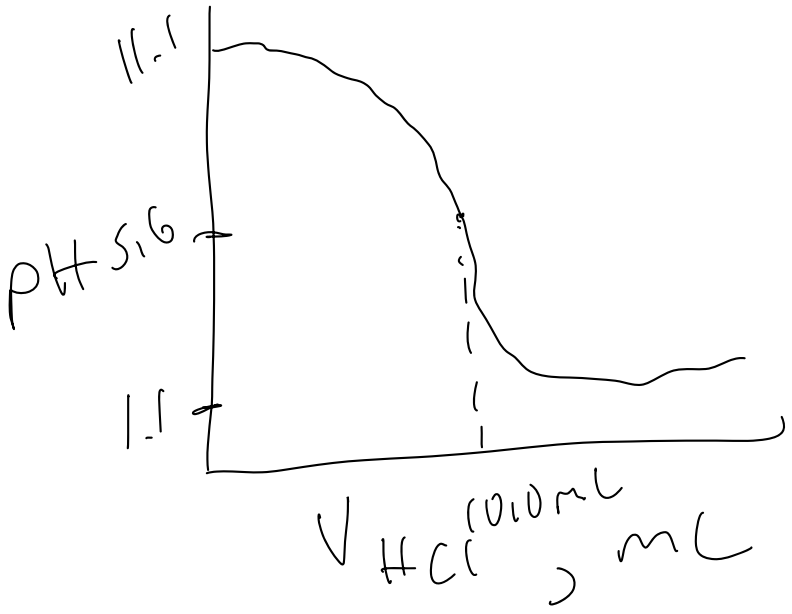
$0.0200\text{L} \times \frac{0.200\text{mol}}{\text{L}} =$

0.00400mol

$0.050\text{L} = 0.080\text{M}$

$pH = -\log([0.08]) = 1.1$

f. Sketch the titration curve making sure to label the axes



3. Your research advisor wants you to prepare 1.00 L of a 0.100 M buffer solution with a pH of 9.6. You have available 1.00 M ammonium chloride and 1.00 M ammonia in the lab. What volumes of each should you use to prepare the buffer? (the remaining volume is distilled water) **The Kb for ammonia 1.8 x 10^{-5} (10 pts)**

$K_a = 5.6 \times 10^{-10}$ $\quad pK_a = 9.25$

x is acid
y is base

$x + y = 0.100\ mol$

$9.6 = 9.25 + \log\left(\frac{y}{x}\right)$

$$\frac{y}{x} = 2.24$$

$$\frac{0.100 - x}{x} = 2.24$$

$$2.24x = 0.100 - x$$

$$\frac{3.24x}{3.24} = \frac{0.100}{3.24}$$

$x = 0.031\ L$ acid

$y = 0.069\ L$ base

4. Classify each of the following salt solutions as acidic, basic or neutral. Write a chemical equation to explain your answer. (**6 pts)**

a. Ammonium chloride acidic

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + NH_{3(aq)}$$

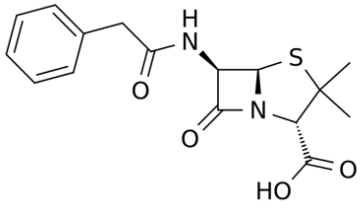
b. Sodium sulfate basic

$$SO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + OH^-(aq)$$

c. Potassium acetate basic

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

5. One of the most common antibiotics is penicillin G (benzylpenicillinic acid), which has the following structure: **(10 pts)**



It is a weak monoprotic acid, reacting with water : HPen+ H_2O ⍰ Pen- + H_3O+ where HPen denotes the parent acid and Pen- the conjugate base. Penicillin G is produced by growing molds in fermentation tanks at 25oC and a pH range of 4.5 to 5.0. The crude form of this antibiotic is obtained by extracting the fermentation broth with an organic solvent in which the acid is soluble. pKa for HPen is 2.74.

Penicillin G is not suitable for oral administration, but the sodium salt (NaPen) is because it is soluble. Calculate the pH of the 0.12 *M* NaPen solution that is formed when a tablet containing the salt is dissolved in a glass of water.

pKb for Pen^- is $14 - 2.74 = 11.26$

$K_b = 10^{-11.26}$ $K_b = 5.5 \times 10^{-12}$

$$Pen^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HPen_{(aq)} + OH^-_{(aq)}$$

	Pen^-		$HPen$	OH^-
I	0.12 M		$\emptyset$	$\emptyset$
C	$-x$		$+x$	$+x$
E	0.12		x	x

$x = \sqrt{5.5 \times 10^{-12} \cdot 0.12} = [OH^-]$

$= 7.4 \times 10^{-7} M$

$pOH = 6.13$

$pH = 7.87$

6. Answer the following questions regarding lead (II) fluoride, **Ksp = 2.7 x 10 $^{-8}$ (10 pts)**

a. What is the concentration of lead (II) ion and fluoride ion at equilibrium in water?

$$PbF_{2(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2F^-_{(aq)}$$

		Pb^{2+}	F^-
I		$\emptyset$	$\emptyset$
C		x	$2x$
E		x	$2x$

$K_{sp} = x(2x)^2$ $2.7 \times 10^{-8} = 4x^3$

$x = 0.0020\ M = [Pb^{2+}]$

$0.0040\ M = [F^-]$

b. What is the concentration of lead (II) Ion and fluoride ion at equilibrium in 0.100 M sodium fluoride

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$

I	0	0.100
C	+x	+2x
E	x	0.100

$K_{sp} = x(0.100)^2 \quad x = 2.7 \times 10^{-6}\ M$

$= [Pb^{2+}]$

$[F^-] = 0.100\ M$

c. If you mix 10.0 mL of 0.100 M potassium fluoride in the lab and 20.0 mL of 0.0100 M lead (II) nitrate, will a precipitate form?

$[F^-] = \frac{0.0100L \times 0.100 mol/L}{0.030L} = 0.033M$

$[Pb^{2+}] = \frac{0.0200L \times 0.0100 mol/L}{0.030L} = 0.0067M$

$Q = [Pb^{2+}][F^-]^2$

7. The entropy change for a reaction is found to be 47.50 J/K. The enthalpy change for the reaction is 21.25 kJ at 25.0°C. **(8 pts)**

a. What is the ΔG°? Is the reaction spontaneous at 25.0°C?

$Q = (0.0067)(0.033)^2$

$Q = 7 \times 10^{-6}$

$Q < K_{sp}$

yes ppt forms

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = 21.25\ kJ - (298\ K \times 0.04750\ \frac{kJ}{K})$

$\Delta G^\circ = -7.095\ kJ$

b. If not at what temperature does the reaction become spontaneous (you will need to assume that ΔH and ΔS do not change significantly with temperature).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

set $\Delta G^\circ = 0$ to solve for T

$$0 = \Delta H - T\Delta S$$

$$\frac{T\Delta S}{\Delta S} = \frac{\Delta H}{\Delta S} \qquad T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{21.28\ \text{kJ}}{0.04750\ \frac{\text{kJ}}{\text{K}}} = 447\ \text{K}$$

8. Circle the salt that would be more soluble in an acidic solution. Briefly explain your answer. **(4 pts)**

a. Magnesium carbonate
b. Sodium chloride
c. Ammonium nitrate
d. Potassium iodide

Explanation: H_3O^+ reacts with CO_3^{2-} thus ↓ $[CO_3^{2-}]$ reaction will shift towards products to re-establish equilibrium

9. ΔG° is −32.7 kJ/ at 25.0 °C for the synthesis of ammonia **(10 pts)**

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

a. What is the equilibrium constant at 25.0 °C? Is this equilibrium reactant or product favored?

$$\Delta G^\circ = -RT\ln K$$

$$K = e^{-\Delta G^\circ/RT}$$

$$K = e^{-(-32,700/8.314 \cdot 298)}$$

$K = 5.4 \times 10^{5}$

QLK

b. Calculate the non-standard Gibb's Free Energy, ΔG, for the same reaction under the following conditions, the initial concentration of nitrogen gas is 2.0 M, concentration of hydrogen gas is 6.0 M and ammonia gas is 0.10 M.

$\Delta G = \Delta G^{\circ} + RT \ln Q$

$\Delta G = -32{,}700\ \frac{J}{} + (8.314\ J/mol \cdot K)(298K) \ln (2.3 \times 10^{-5})$

$\Delta G = -59\ kJ$

$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$ $Q = \frac{(0.100)^2}{(2.0)(6.0)^3}$ 2.3×10^{-5}

c. Based on your answer from part b, which direction will the reaction proceed to establish equilibrium?

towards products

10. Answer the following questions regarding the redox reaction below (**6 pts)**

$MnO_4^- + H_2O_2 \text{ ---> } Mn^{2+} + O_2$

a. Balance the equation in acidic solution

$[5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

$[H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5$

b. What is the oxidation number of Mn in the MnO_4^-?

+7

$6H^+$

a) cont

$10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O$

$+ 5H_2O_2 \rightarrow 5O_2 + 10H^+ + 10e^-$

$6H^+ + 2MnO_4^- + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$

c. What is the oxidation number of oxygen gas?

0

11. A voltaic cell is constructed for the redox reaction:

$3Ag^+ (aq) + Fe (s) \rightleftharpoons Fe^{3+} (aq) + 3Ag (s)$

Answer the following questions. The standard reduction potentials are given below. (**12 pts)**

cathode: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

anode: $Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^-$

$Ag^+ (aq) + e^- \rightleftharpoons Ag (s)$ $E_{red} = 0.800$ V

$Fe^{3+} (aq) + 3e^- \rightleftharpoons Fe (s)$ $E_{red}° = -0.04$ V

a. In the voltaic cell the standard cell potential is (positive or negative?) circle one.

b. A voltaic cell has a (spontaneous or non-spontaneous) redox reaction? Circle one.

c. And the standard Gibbs free energy for this redox reaction is (positive or negative?) circle one.

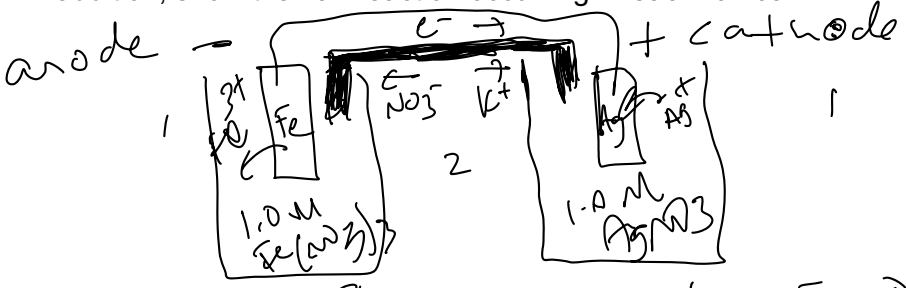
d. What is the standard cell potential for the described voltaic cell if all concentrations of ions are 1.0 M and the reaction is at 25.0 °C

$E°_{cell} = E°_{cathode} - E°_{anode}$

$E^\circ_{cell} = 0.800\,V - (-0.04\,V) =$

0.84V

e. Draw a diagram of the voltaic cell being sure to include all key components. In addition, show the half-reaction occurring in each half-cell.

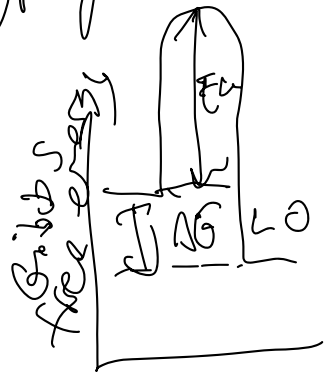


$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^-$ 1

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$ 1

12. The conversion of diamond to graphite is a spontaneous process. Explain how a "diamond is forever" and we do not observe diamond jewelry turning into graphite under normal lab conditions. **(4 pts)**

A spon process has a $\Delta G < 0$ however diamond → graphite the activation energy is so large that the reaction rate is very, very slow in lab. We would need to add a catalyst or have very high temp. So a piece of diamond



Bonus (2 pts)

would convert to carbon.

Pay it forward, One tip you would give next summer's post bacs for general chemistry such as a study strategy.