CHEMISTRY 204
Hour Exam III
April 25, 2019
Dr. D. DeCoste

Name ________**KEY**____________

Signature ______________________________

T.A. __________________________________

Section ________________________________

This exam contains 23 questions on 11 numbered pages. Check now to make sure you have a complete exam. You have two hours to complete the exam. Determine the **best** answer to the first 20 questions and enter these on the special answer sheet. Also, circle your responses in this exam booklet. **Show all of your work and provide complete answers to questions 21, 22 and 23.**

1-20	(60 pts.)	____________
21	(20 pts.)	____________
22	(30 pts)	____________
23	(10 pts.)	____________
Total	(120 pts)	____________

Useful Information:

- Unless otherwise noted, all solutions referred to on this exam are aqueous solutions at 25°C.
- 760 torr = 1.00 atm
- R = 0.08206 Latm/molK = 8.3145 J/Kmol
- K = °C + 273
- $N_A = 6.022 \times 10^{23}$

$P_{soln} = \chi_{solvent}P^{\circ}_{solvent}$ $\quad$ $P_{total} = P_A + P_B = \chi_A P^{\circ}_A + \chi_B P^{\circ}_B$

$\pi = iMRT$

$\Delta T = iK_f m_{solute}$ $\quad$ $\Delta T = iK_b m_{solute}$

K_f = 1.86 K/m for water $\quad$ K_b = 0.51 K/m for water

$\varepsilon = \varepsilon^{\circ} - \dfrac{0.0591}{n}\log(Q)$ $\quad$ F = 96,485 coulombs $\quad$ 1 Ampere = 1C/s

$\Delta G^{\circ} = -nF\varepsilon^{\circ}$

21. For the following questions, please provide complete, yet concise, explanations and show all work for any calculations.

a. You have climbed Mt. Everest in Tibet, which has an elevation of ~5.5 miles. The atmospheric pressure at the top of Mt. Everest is 239 torr.

i. The boiling temperature on Mt. Everest is lower than 100°C. **Why is this true?** Also, **explain** why a liquid boils **using the concept of vapor pressure**. **[5 points]**

- A liquid boils when its vapor pressure is equal to atmospheric pressure.
- Bubbles form in the liquid due to the random motion of the molecules and the pressure of these bubbles varies with temperature (an increase in temperature results in the increase in pressure in the bubble).
- Once the pressure in the bubble equals atmospheric pressure, it subsists and, being less dense than the liquid, rises to the surface.
- When the bubble reaches the surface, it "opens up" and the vapor in the bubble escapes.
- Thus, with a smaller atmospheric pressure, the temperature to boil is lower.

ii. You feel homesick for the boiling water in Champaign and want to get the water on Mt. Everest to boil at 100°C, so you add salt (NaCl). **Explain** why adding a non-volatile solute such as salt will increase the boiling temperature of water. **[3 points]**

- Adding a solute to a liquid lowers the vapor pressure – the solution has a lower vapor pressure than the pure liquid.
- This is because at the surface of an internal bubble, there are solute molecules. Since these are nonvolatile, they do not enter the bubble and therefore the pressure is reduced. At a liquid's normal boiling temperature, for example, the vapor pressure is less, thus the liquid does not boil.
- To increase the pressure to atmospheric pressure, we need to increase the temperature. Thus, a higher temperature is needed than for the pure liquid.

21. iii. You start with 4.00 liters of water at 25°C (at this temperature water has a density of 0.99713 g/mL). Assuming infinite solubility of NaCl, no ion pairing, and ideal behavior, **determine the mass of sodium chloride** you would need to add to your water to get the solution to boil at 100°C at the top of Mt. Everest. **Explain your thought process** and **show all work**. **[7 points]**

- The vapor pressure of water at 100°C is 760 torr.
- To get the water to boil at 100°C, we need the vapor pressure of the solution to be 239 torr.
- $P_{soln} = \chi_{water}P°_{water}$; 239 Torr = ($\chi_{solvent}$)(760 torr); χ_{water} = 0.314
- 4.00 L = 3988.52 g water = 221 moles water
- 0.314 = [moles water/(moles solute particles + moles water)] = [221/(x + 221)]; x = 482.8 moles
- 482.8 moles particles = 242.2 moles NaCl = **14.1 kg NaCl**

b. You are back in Champaign just in time for π day and to celebrate you decide to make a solution of methanol and water that has a vapor pressure of 31.4 torr at 25°C. You make the solution and seal it in a container, allowing the solution and its vapor to come to equilibrium. Given that at 25°C water has a vapor pressure of 23.8 torr and the vapor pressure of methanol is 97.7 torr, determine the composition (% by moles) of the solution and of the vapor. Assume ideal behavior. **Show all work. [5 points]**

- $P_{total} = P_A + P_B = \chi_A P°_A + \chi_B P°_B$; 31.4 torr = (1-X)(23.8) + (X)(97.7)
- X = 0.1028; solution is **10.3% methanol and 89.7% water by moles**.

P(methanol) = (0.1028)(97.7) = 10.04356 torr [10.04/31.4 = 32.0]
P(water) = (0.8972)(23.8) = 21.35356 torr [21.35/31.4 = 68.0]
Vapor is 68.0% water and 32.0% methanol.

22. These questions concern some of our electrochemistry lecture demonstrations. Please provide complete, yet concise, explanations and show all work for any calculations.

a. During the first electrochemistry lecture, I placed an excess of copper wire in 100.0 mL of a 0.100 *M* $AgNO_3$ solution. After a few minutes, silver metal was observed covering the wire and the solution began to turn blue from the Cu^{2+} ions in solution. Eventually, the system reached equilibrium.

i. Determine the **concentrations** (in molarity) **of Ag^+ and Cu^{2+}** and the **mass of silver metal** when the system reached equilibrium. **Show all work**. **[8 points]**

- Reaction is: $2Ag^+ + Cu \rightarrow Cu^{2+} + 2Ag$
- Standard potential ($\varepsilon°$)= 0.46V
  - $Ag^+ + e^- \rightarrow Ag$: 0.80V
  - $Cu \rightarrow Cu^{2+} + 2e^-$: –0.34V

$$\varepsilon = \varepsilon° - \frac{0.0591}{n}\log(Q);\ \varepsilon° = 0.46 = \frac{0.0591}{n}\log(K);\ n = 2$$

$K = 3.69 \times 10^{15}$ (very large; essentially to completion)

	$2Ag^+$ + Cu →	Cu^{2+} + 2Ag
BR	0.100*M*	0
AR	~0	~0.0500*M*

$[\sim 0.0500]/[Ag^+]^2 = 3.69 \times 10^{15}$

$[Ag^+] = 3.68 \times 10^{-9}$ *M*
$[Cu^{2+}] = 0.0500$*M*
Silver metal formed = 0.0100 mol = **1.08 g Ag**

22. ii. As we discussed, Cu^{+} is also produced but at a much lower concentration than Cu^{2+}. Solve for the **equilibrium concentration of Cu^{+}** (in molarity). **Show all work. [4 points]**

We have equilibrium concentrations of Ag^{+} and Cu^{2+} above, so we can use either to determine the equilibrium concentration of Cu^{+}. Note: $Cu^{+} + e^{-} \rightarrow Cu$: 0.52V.

Method One:

$Ag^{+} + Cu \rightarrow Cu^{+} + Ag$; $\varepsilon° = 0.28V$;n = 1; $K = 5.47 \times 10^{4}$.
$[Cu^{+}]/[3.68 \times 10^{-9}] = 5.47 \times 10^{4}$; $[Cu^{+}] =$ **2.01×10^{-4} *M***.

Method Two:

$Cu^{2+} + 2Cu \rightarrow 2Cu^{+} + Cu$; $\varepsilon° = -0.18V$;n = 2; $K = 8.10 \times 10^{-7}$.
$[Cu^{+}]^{2}/[0.0500] = 8.10 \times 10^{-7}$; $[Cu^{+}] =$ **2.01×10^{-4} *M***.

b. In lecture I also constructed a standard galvanic cell with Zn, Zn^{2+}, Cu, and Cu^{2+}.

The AA battery provides 1.5 V. Suppose we wanted to use the Zn/Cu cell that we made in lecture to power something requiring the AA battery. Keeping the ion of higher concentration (either Zn^{2+} or Cu^{2+}) at 1.00*M*, **determine and label** the concentration of the other ion. **Briefly explain** how you know which ion has the lower concentration and **show all work**. **[6 points]**

- Reaction is: $Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
- Standard potential ($\varepsilon°$)= 1.10V
  - $Zn^{2+} + 2e^{-} \rightarrow Zn$: –0.76V
  - $Cu^{2+} + 2e^{-} \rightarrow Cu$: 0.34V

$$\varepsilon = \varepsilon° - \frac{0.0591}{n}\log(Q)$$

$$1.50 = 1.10 - \frac{0.0591}{2}\log[\frac{[Zn^{2+}]}{[Cu^{2+}]}]$$

We need a larger voltage than standard, $[Cu^{2+}] > [Zn^{2+}]$; $[Cu^{2+}] = 1.00M$

Solving, we get **$[Zn^{2+}] = 2.91 \times 10^{-14}$ *M***

22. c. During the final electrochemistry lecture, I electroplated copper onto a spoon by placing a spoon (cathode) in an aqueous solution with 1.00*M* Cu^{2+} ions and a copper anode, and then providing current.

i. The reduction potential for Cu^{2+} to Cu is positive, so why doesn't copper form on the spoon without supplying electricity? **[3 points]**

- For copper to form from Cu^{2+}, we need to carry out the reaction $Cu^{2+} + 2e^- \rightarrow Cu$.
- Thus, we need electrons from somewhere. [We need something to be oxidized]
- The spoon is made of a metal (stainless steel) which does not oxidize readily to give electrons to the copper ions in the solution.

ii. Are there any metals we could place in an aqueous solution of Cu^{2+} that would work to get copper metal from the solution without providing electricity? If not, **explain why not**. If so, **provide an example** that would work. **In either case, defend your answer with words and numbers. [6 points]**

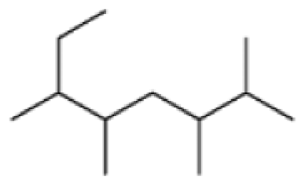
- Yes, some metals would do this.
- The standard reduction potential for the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ is +0.34 V.
- We then need to find a metal that will be oxidized (the reaction is $M \rightarrow M^{x+} + xe^-$) with a standard potential greater than –0.34V.
- Thus, the standard reduction potential of the metal ($M^{x+} + xe^- \rightarrow M$) must be less than +0.34V since we are going to have to switch the sign.
- So, Fe, Pb, Sn, Ni, Cd, Cr, and Zn would work.
- Example: with Fe (SRP = –0.44V), we get an overall potential of 0.78V
- [Actually Cr will not work since it forms a strong oxide coating, but we'll accept it here].

iii. One metal that would not work to plate out copper metal is sodium (so change your answer to part ii if you had that one). **Why wouldn't sodium work** in this case? **Defend your answer with words and numbers** and **write the equation for the reaction that will occur**. **[3 points]**

- Sodium will react with water since the overall potential is positive.
- $Na^+ + e^- \rightarrow Na$: –2.71V; $2H_2O + 2e^- \rightarrow H_2 + OH^-$: –0.83V
- Reaction will be: $2Na + 2H_2O \rightarrow H_2 + NaOH$; 1.88V

23. For each of the following, **neatly** draw the structures and name the compounds.

a. A friend at another university drops the name “2-ethyl-3-methyl-5-isopropylhexane” during a conversation. You chuckle and say, “Surely you mean __________.” What is the **correct name** of the molecule your friend incorrectly named? **Draw the structure** and **support** the name. **[4 points]**

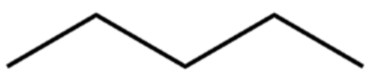


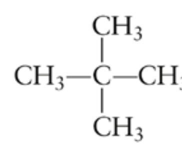
2,3,5,6-tetramethyloctane

b. You and a friend each have a compound with the formula C_5H_{12} and you each react your compound with chlorine gas. It turns out that you end up with three distinct monochlorination products and your friend ends up with only one.

Name both reactants (labeling which is yours and which is your friend’s) along with **all products**. Also, **draw all structures** (reactants and products). **[6 points]**

You had n-pentane (pentane), partner had 2,2-dimethylpropane (neopentane).

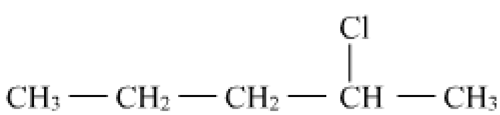


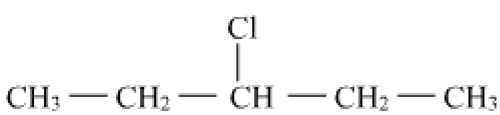


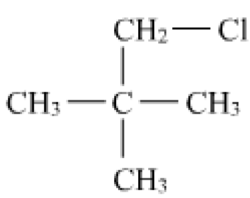
Neopentane

Isomers of chloropentane

1. $CH_3-CH_2-CH_2-CH_2-CH_2-Cl$ Chloropentane

2.  2-chloropentane

3.  3-chloropentane

4.  1-chloro-2, 2-dimethylpropane