NAME: ____ANSWER KEY____ **UFID:**_____

Exam 5, CHM4411, April 21, 2009

Sign your initials and provide your UF ID at the top of each page.

Constants and Key Formulas

R = 8.314 J K^{-1} mol^{-1} = 8.314×10^{-2} L bar K^{-1} mol^{-1}; F = 96485 $C\ mol^{-1}$

$$\mu_j^{soln} = \mu_j^{\star}(l) + RT \ln \frac{P_j}{P_j^{\star}}$$

$$\kappa^2 = e^2 N_A m \left[\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0 \varepsilon_r kT}\right]$$

$$a_{\pm}^{\nu} \equiv a_+^{\nu_+} a_-^{\nu_-} = (\gamma_{\pm})^{\nu} \left(\frac{m_{\pm}}{m^{\circ}}\right)^{\nu} \qquad \mu_{\pm} = \mu_{\pm}^{\circ} + RT \ln a_{\pm}$$

$$I = \frac{1}{2}\sum_i \left(m_{i+} z_{i+}^2 + m_{i-} z_{i-}^2\right) \qquad \Pi = [B]RT$$

$$E = E^{\circ} - \frac{RT}{nF}\ln Q$$

NAME: ____ANSWER KEY____ **UFID:**_____

Section I. Multiple Choice [4pts each]

Choose the best answer to each question. Circle one answer only.

1. Consider a solution of two miscible liquids A and B exhibiting a high-boiling azeotrope. Which statement best describes the nature of the interactions between A and B?
   a. The A-B interactions are negligible.
   b. A-B interactions are about the same as the A-A and B-B interactions.
   c. A-B attractions are stronger than the A-A and B-B attractions
   d. A-B repulsions are increased relative to the A-A and B-B repulsions.
   e. The A-B attractions fall in-between the A-A and B-B attractions.

2. What happens to the chemical potential of the solvent when a solute is dissolved in it?
   a. It increases **b. It decreases** c. It stays the same.

3. For which of the following mixtures would the vapor pressure of both components most closely adhere to Raoult's Law at all compositions?

   a. acetone/benzene
   b. water/benzene
   c. NaCl/water
   d. ethanol/water
   e. octane/heptane

4. Complete the following statement: In an ***ideal-dilute*** solution,

   a. solvent and solute both obey Henry's Law for all x.
   b. solvent and solute both obey Raoult's Law for all x.
   c. solvent obeys Henry's Law, solute obeys Raoult's Law
   d. solvent obeys Raoult's Law, solute obeys Henry's Law
   e. solvent obeys Dalton's Law, solute obeys Raoult's Law

5. How does the thickness of the ionic atmosphere (i.e. the Debye-Huckel screening length) for a 1-1 electrolyte compare to that of a 2-1 electrolyte (all other factors being equal)?

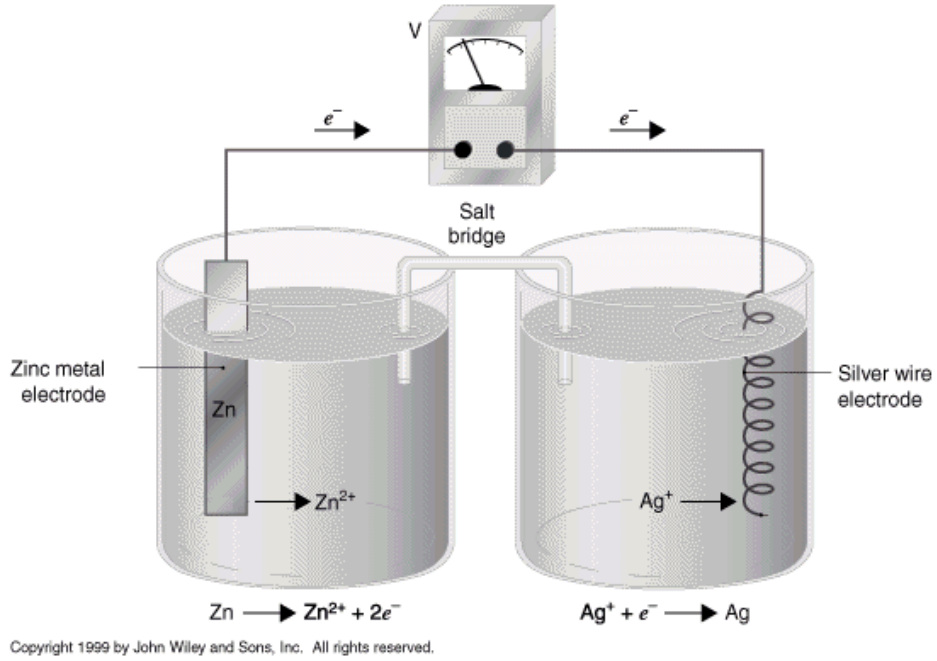
   a. $r_{11} / r_{21} = 2$ b. $r_{11} / r_{21} = 1 / 2$ c. $r_{11} / r_{21} = \sqrt{2}$
   d. $r_{11} / r_{21} = 1 / \sqrt{2}$ e. $\boxed{r_{11} / r_{21} = \sqrt{3}}$ f. $r_{11} / r_{21} = 1 / \sqrt{3}$

(see attached calculation)

6. Which of the following is not necessary for freezing point depression (a colligative effect) to be observed:

a. The chemical potential of the liquid is lowered.
b. The entropy of solution is increased.
c. Significant solvent-solute interactions.
d. A negative Gibbs energy of mixing.
e. Melting is an endothermic process.

Use the picture of the electrochemical cell below to answer the next two questions.



7. What would happen if the salt bridge was removed?

a. The voltage would drop to zero.
b. The current would drop to zero.
c. Both the current and voltage would drop to zero.
d. Nothing. The salt bridge serves no purpose.

8. Which electrode is the cathode?

a. Zn b. Zn^{2+} **c. Ag** d. Ag^{+} e. The voltmeter

9. Consider the half-cell reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$. By what factor are n, Q, E, and E° changed if all the stoichiometric coefficients are multiplied by the factor three?

a. 3, 3, 3, 3 b. 3, 9, 3, 3 c. 1, 9, 1, 1
d. 3, 9, 1, 1 **e. 3, 3, 1, 1**

NAME: ____ANSWER KEY____ **UFID:**_____

10. Pick the statement that does not apply to Debye-Huckel theory.

a. The solvent is treated as a dielectric medium.
b. Prediction of the "salting-in" effect.
c. A central ion is surrounded mostly by ions of opposite charge.
d. The screening length decreases with increasing ionic strength.
e. The activity coefficients of neutral molecules and ions can be estimated.

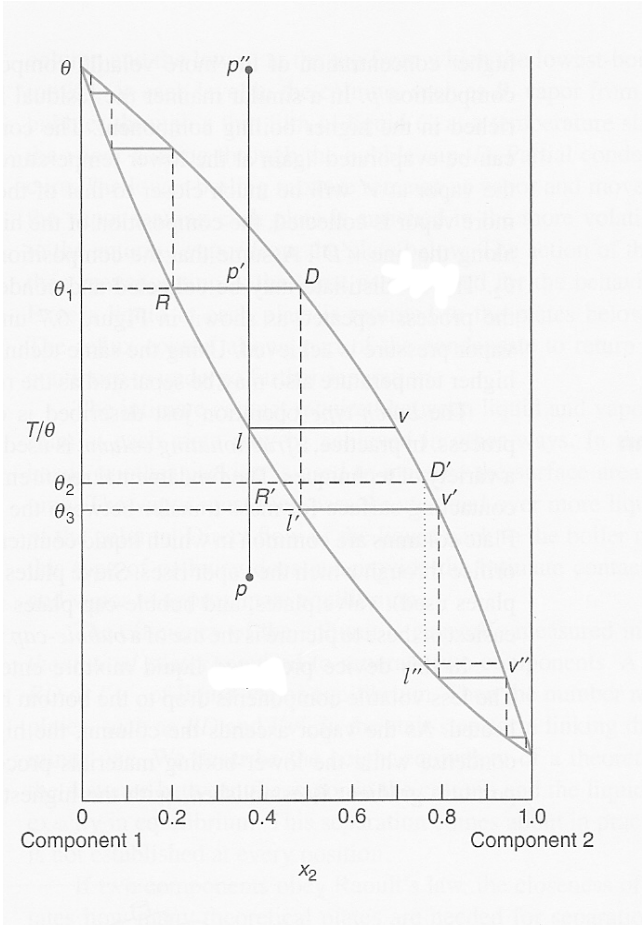
11. Bauxite (Al_2O_3) is the natural ore of Aluminum. Reduction of bauxite is a very endothermic process. Recently, an electrochemical method was introduced to efficiently separate the metal from the ore at the relatively mild temperature of 900 °C:

$$Al^{3+} + 3e^- \rightarrow Al \qquad E^\circ = -1.662\,V$$
$$2O_2^- \rightarrow O_2 + 4e^- \qquad E^\circ = 1.230\,V$$

The electrochemical cell used in this method is best classified as
a. electrolytic b. photovoltaic c. galvanic
d. a concentration cell e. a Daniell cell

Combining the standard potentials we see that the $E^\circ = -0.432\,V$. The reaction is not spontaneous and needs to be driven by an external potential. Therefore, it would be an electrolytic cell.

Refer to the temperature-composition phase diagram below to answer the next four True/False questions [3 points each].



12. At point p′, more vapor is present than liquid.
a. true b. false

13. Using a fractional distillation apparatus with 3 theoretical plates, a mixture initially at point R would yield a liquid with <90% purity in component 2.
a. true **b. false**

14. Component 1 is more volatile than component 2.
a. true **b. false**

15. If the mixture initially at point R′ is continuously boiled, the residue will reach point l′ and the boiling temperature will decrease from θ_2 to θ_3.
a. true **b. false**

Section II.

16. [10pts] A solution contains 1.50 g of solute in 30.0 g of benzene. The freezing point is 3.74 °C. The freezing point of pure benzene is 5.48 °C. The cryoscopic constant for benzene is k_F=4.9 K kg mol^{-1}. The melting point of benzene is 278.63 K. Calculate the molar mass of solute.

$$\Delta T_f = K_F m_B = K_F \frac{n_B}{0.03 kg} = \left(4.9 K\ kg\ mol^{-1}\right) \frac{\frac{1.50 g}{M_B}}{0.03 kg} = \frac{245 K\ g\ mol^{-1}.}{M_B}$$

$$M_B = \frac{245 K\ g\ mol^{-1}}{\Delta T_f} = \frac{245 K\ g\ mol^{-1}}{(5.48 - 3.74) K} = 140.8 g\ mol^{-1}$$

$\boxed{M_B = 140.8 g\ mol^{-1}}$

17. [15 pts] Consider the following Daniell cell at 298.15 K:

$$Ag(s)\,|\,AgCl(s)\,|\,Cl^-\left(aq,\ a_{Cl^-}=0.00500\right)\,\|\,Cd^{2+}\left(aq,\ a_{Cd^{2+}}=0.100\right)\,|\,Cd(s).$$

$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$ $\quad E^\circ = -0.2223$ V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $\quad E^\circ = -0.4030$ V

Overall reaction is

$Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq) \rightarrow Cd(s) + 2AgCl\ (s)$

a. What is the cell EMF?

$$\boxed{E^\circ_{cell} = -0.2223V - 0.4030V = -0.625V}$$

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$$Q = \frac{1}{\left(a_{Cd^{2+}}\right)\left(a_{Cl^-}\right)^2} = \frac{1}{(0.100)(0.005)^2} = 4.00\times10^5,\ \ln Q = 12.899$$

$$\boxed{E = E^\circ - \frac{RT}{nF}\ln Q = -0.6253V - \frac{8.314JK^{-1}mol^{-1}298.15K}{2\times96485Cmol^{-1}}12.899 = -0.791V}$$

b. Is the cell reaction spontaneous as written? Why or why not?

The cell reaction is not spontaneous because
$\Delta G = -nFE = -2\cdot96485\cdot(-0.791) = 152.6kJ > 0$

c. Calculate the equilibrium constant at 298.15K.

Equilibrium constant,

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

$$K = \exp\left(nFE^\circ / RT\right) = \exp\left(\frac{2\cdot96485\cdot(-0.625V)}{8.314\cdot298}\right)$$

$$\boxed{K = 7.06\times10^{-22}}$$

d. How much electrical work can this cell do? **+152. kJ.** Both (+) and (-) signs or **zero** are all acceptable responses.

e. What is the cell EMF at chemical equilibrium? **zero**

18. [10 pts] 1. Benzene and toluene form nearly ideal solutions. The boiling point of pure benzene is 80.1 °C.

a. Calculate the chemical potential of benzene relative to that of pure benzene when $x_{benzene} = 0.30$ at its boiling point. Assume $\gamma_{benz} = 0.93$.

$$\mu_{benz}^{soln} = \mu_{benz}^{*}(l) + RT \ln \frac{P_{benz}}{P_{benz}^{*}} = \mu_{benz}^{*}(l) + RT \ln a_{benz};$$

$$a_{benz} = \gamma_{benz} x_{benz} = (0.93)(0.30) = 0.279$$

$$\Delta\mu_{benz}^{soln} = \mu_{benz}^{soln} - \mu_{benz}^{*}(l) = \left(8.314 JK^{-1}mol^{-1}\right)(273.15 + 80.1)K \ln 0.279$$

$$\boxed{\Delta\mu_{benz}^{soln} = -3.75\ kJ\ /\ mol}$$

b. What is the vapor pressure of benzene in the solution at 80.1 °C?

Assuming the normal boiling, $p_{benz}^{*} = 1atm$

$$a_{benz} = \frac{p_{benz}}{p_{benz}^{*}}, \quad \boxed{p_{benz} = a_{benz} p_{benz}^{*} = (0.93)(0.30)(1bar) = 0.279bar}$$

19. [10 pts] The Henry's Law constant for N_2 in H_2O is 9.04×10^4 bar. The density of blood is 1.00kg/L. Air is 80% N_2 at sea level (1 bar). What volume of N_2 is released from the blood of a 60kg diver who breathed compressed air at a pressure of 40bar and is suddenly brought to sea level? The total volume of diver's blood is 4.50L.

Henry's Law: $P_{N_2} = x_{N_2} K_H \approx \frac{n_{N_2}}{n_{H_2O}} K_H$,

$$n_{N_2} = \frac{n_{H_2O}}{K_H} P_{N_2} \quad \text{where} \quad p_{N_2} = 0.8p$$

In 4.50L water, $n_{H_2O} = \frac{1000g}{L} \times 4.5L \times \frac{mol}{18.0g} = 250mol$

$$V_{N_2} = \frac{n_{N_2} RT}{P_{N_2}}, \quad V_{N_2} = \frac{n_{N_2} RT}{1bar} = \left(\frac{n_{H_2O}}{K_H} P_{N_2}\right)\frac{RT}{1bar}, \text{ where T =273.15K+37°C=310.15K}$$

$$\Delta V_{N_2} = \left(\frac{n_{H_2O}}{K_H}\right)\left(\frac{RT}{1bar}\right)\Delta p_{N_2}$$

$$= \frac{250mol}{9.04\times10^4 bar} \frac{0.08314 Lbar K^{-1}mol^{-1} 310.15K}{1bar}(0.8)(39bar)$$

$$\boxed{\Delta V_{N_2} = 2.22L}$$

Extra Credit [10 pts]

A polynomial fit to measurements of the total volume of a water/ethanol mixture at 25°C that contains 1.000 kg of water is:

$$v = 1002.93 + 54.6664x - 0.36394x^2 + 0.028256x^3$$

where $v = V / cm^3$, $x = n_E / mol$, and n_E is the number of moles of ethanol in the mixture.

What is the partial molar volume of water in a 50% by mass ethanol/water mixture?

$$\bar{V}_{EtOH} = \left(\frac{dV}{dn_{EtOH}}\right)_{n_{H_2O}} = \left(\frac{dv}{dx}\right)\frac{cm^3}{mol}$$

$$\frac{dv}{dx} = 54.6664 - 2 \cdot 0.36394x + 3 \cdot 0.028256x^2$$

For a 50% by mass ethanol/water mixture,

$$mass\ EtOH = mass\ H_2O = 1kg$$

$$n_{EtOH} = \frac{1000g}{46.038g\ mol^{-1}} = 21.72mol$$

$$n_{H_2O} = \frac{1000g}{18.01g\ mol^{-1}} = 55.55mol$$

$$\bar{V}_{EtOH} = 54.6664 - 2 \cdot 0.36394(21.72) + 3 \cdot 0.028256(21.72)^2$$
$$= 78.85cm^3 / mol$$

Total volume is:

$$v = 1002.93 + 54.6664(21.72) - 0.36394(21.72)^2 + 0.028256(21.72)^3$$
$$= 2,308.$$

Equating to $V = n_{EtOH}\bar{V}_{EtOH} + n_{H_2O}\bar{V}_{H_2O}$,

$$\bar{V}_{H_2O} = \frac{V - n_{EtOH}\bar{V}_{EtOH}}{n_{H_2O}} = \frac{2308. - (21.72)(78.85)}{55.55} = \boxed{10.7cm^3mol^{-1}}$$

Multiple Choice Answer Details

5. How does the thickness of the ionic atmosphere (i.e. the Debye-Huckel screening length) for a 1-1 electrolyte compare to that of a 2-1 electrolyte (all other factors being equal)?

The Debye-Huckel screening length is:

$r = 1 / \kappa$ where

$$\kappa^2 = e^2 N_A m \left[\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0 \varepsilon_r kT} \right]$$

Therefore,

$$1 / \kappa = \frac{c}{\left[\nu_+ z_+^2 + \nu_- z_-^2 \right]^{1/2}}$$ where c is a constant.

$$r_{11} / r_{21} = \frac{\left[2 + 4\right]^{1/2}}{\left[1 + 1\right]^{1/2}} = \sqrt{3}$$

e. $r_{11} / r_{21} = \sqrt{3}$

9. Consider the half-cell reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$. By what factor are n, Q, E, and E° changed if all the stoichiometric coefficients are multiplied by the factor three?

n→3n (3), Q is cubed (3), E→E (1), $E^\circ \rightarrow E^\circ$ (1)

e. 3, 3, 1, 1

Credit was also given for answer **d. 3, 9, 1, 1**.