2012 FALL Semester Midterm Examination
For General Chemistry II (CH103)

Date: October 25 (Thu),   Time Limit: 14:30 ~ 16:30

Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Professor Name	Class	Student I.D. Number	Name

Problem	points	Problem	points	TOTAL pts
1	/16	**7**	/10	
2	/6	**8**	/6	
3	/5	**9**	/6	
4	/6	**10**	/14	**/100**
5	/8	**11**	/16	
6	/7			

** This paper consists of 11 sheets with 11 problems (page 9: claim form, page 10: periodic table, page 11: fundamental constants). Please check all page numbers before taking the exam. Write down your work and answers in the sheet.

 Please write down the unit of your answer when applicable. You will get 30% deduction for a missing unit.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.
(채점답안지 분배 및 이의신청 일정)

 1. Period, Location, and Procedure

   1)   Return and Claim Period: *October 29 (Mon, 7: 00 ~ 8:00 p.m.)*

   2)   *Location: Room for quiz session*

   3)   Procedure:

   Rule 1: Students cannot bring their own writing tools into the room. (Use a pen only provided by TA)

   Rule 2: With or without claim, you must submit the paper back to TA. (Do not go out of the room with it)

If you have any claims on it, you can submit the claim paper with your opinion. After writing your opinions on the claim form, attach it to your mid-term paper with a stapler. Give them to TA.

(The claim is permitted only on the period. Keep that in mind! A solution file with answers for the examination will be uploaded on 10/29 on the web.)

 2. Final Confirmation

   1) Period: November 1 (Thu) – 2 (Fri)

   2) Procedure: During this period, you can check the final score of the examination *on the website*.

   ** *For further information, please visit General Chemistry website at www.gencheminkaist.pe.kr.*

<The Answers>

Problem	points	Problem	points	TOTAL pts
1	3+3+5+5/16	**7**	5+5/10	
2	2+2+2/6	**8**	3+3/6	
3	/5	**9**	3+3/6	
4	3+3/6	**10**	3+3+2+2+4/14	**/100**
5	2+3+3/8	**11**	4+4+5+3/16	
6	2+5/7			

1.

(a) A 1.00% aqueous solution of NaCl will contain 1.00 g of NaCl for 99.0 g of water. To use the freezing point depression equation, we need the molality of the solution:

$$\text{molality} = \frac{\left(\dfrac{1.00 \text{ g}}{58.44 \text{ g} \cdot \text{mol}^{-1}}\right)}{0.0990 \text{ kg}} = 0.173 \text{ mol} \cdot \text{kg}^{-1}$$

$$\Delta T_f = i k_f m$$
$$\Delta T_f = i\,(1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1})(0.173 \text{ mol} \cdot \text{kg}^{-1}) = 0.593 \text{ K}$$
$$i = 1.84$$

(b) molality of all solute species (undissociated NaCl(aq) plus Na^+ (aq) + Cl^-(aq)) $= 1.84 \times 0.173 \text{ mol} \cdot \text{kg}^{-1} = 0.318 \text{ mol} \cdot \text{kg}^{-1}$

(c) If all the NaCl had dissociated, the total molality in solution would have been $0.346 \text{ mol} \cdot \text{kg}^{-1}$, giving an i value equal to 2. If no dissociation had taken place, the molality in solution would have equaled 0.173 $\text{mol} \cdot \text{kg}^{-1}$.

$$\text{NaCl(aq)} \rightleftharpoons \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$
$$\left(0.173 \text{ mol} \cdot \text{kg}^{-1} - x\right) \quad x \quad x$$

$$0.173 \text{ mol} \cdot \text{kg}^{-1} - x + x + x = 0.318 \text{ mol} \cdot \text{kg}^{-1}$$

$$0.173 \text{ mol} \cdot \text{kg}^{-1} + x = 0.318 \text{ mol} \cdot \text{kg}^{-1}$$

$$x = 0.145 \text{ mol} \cdot \text{kg}^{-1}$$

$$\% \text{ dissociation } = \left(\frac{0.145 \text{ mol} \cdot \text{kg}^{-1}}{0.173 \text{ mol} \cdot \text{kg}^{-1}} \right)(100) = 83.8\%$$

d)

$$m = \frac{\triangle T_b}{K_b} = \frac{0.029°C}{0.51°C\,m^{-1}} = 0.057m = 0.057\,mol\,kg^{-}$$

in 100 g solvent 0.0057 mol solute

$$M = \frac{1.0g}{0.0057mol} = 1.8 \times 10^2 \,g\,mol^{-}$$

molecular formula is $C_6H_{12}O_6$ (sugar glucose)

2.

(a) For methanol and ethanol, we expect the types of intermolecular attractions in the mixture to be similar to those in the component liquids, so that an ideal solution is predicted.

(b) For HF and H_2O, the possibility of intermolecular hydrogen bonding between water and HF would suggest that negative deviation would be observed, which is the case.
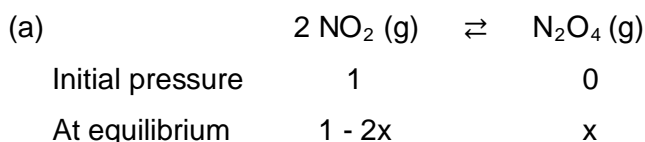
(c) Because hexane is nonpolar and water is polar with hydrogen bonding, we would expect a mixture of these two to exhibit positive deviation (the interactions between the different molecules would be weaker than the intermolecular forces between like molecules).

3. $K = (K_1)^2 = (3.1 \times 10^4)^2$

$\Delta n = 4 - (4 + 2) = -2$, $T = 400 + 273.15 \text{ K} = 673 \text{ K}$

$K_c = (RT)^{-\Delta n} K = (0.083145 \text{ K}^{-1} \times 673 \text{ K})^2 \times (3.1 \times 10^4)^2 = 2.9 \times 10^{12}$

4.

(a)

	2 NO_2 (g)	$\rightleftarrows$	N_2O_4 (g)
Initial pressure	1		0
At equilibrium	1 - 2x		x

$K = x / (1 - 2x)^2 = 6.97$ $x = 0.383$
$P_{NO2} = 0.234$ atm, $P_{N2O4} = 0.383$ atm

(b) $P_{NO2} + P_{N2O4} = 1$ atm, $K = P_{N2O4} / P_{NO2}{}^2 = x / (1 - x)^2 = 6.97$
   $x = 0.686$
   $P_{NO2} = 0.314$ atm, $P_{N2O4} = 0.686$ atm

5. (a) Lewis acid: CO_2, Lewis base: H_2O

   (b) The $-CCl_3$ group that is bonded to the carboxyl group, -COOH, in trichloroacetic acid, is more electron withdrawing than the CH_3 group in acetic acid. Thus, trichloroacetic acid is the stronger acid.

   (c) The $-CH_3$ group in acetic acid has electron-donating properties, which means that it is less electron withdrawing than the $-H$ attached to the carboxyl group in formic acid, HCOOH. Thus, formic acid is a slightly stronger acid than acetic acid.

6. (a) pH = $-\log(6.55 \times 10^{-7}) = 6.184$

(b)

We can use the relationship derived in the text,

$[H_3O^+]^2 - [HA]_{initial}[H_3O^+] - K_w = 0$, in which HA is any strong acid.

$[H_3O^+]^2 - (6.55 \times 10^{-7})[H_3O^+] - (1.00 \times 10^{-14}) = 0$

Solving using the quadratic equation gives

$[H_3O^+] = 6.70 \times 10^{-7}$, pH = 6.174.

7.

(a) This value is calculated as described in Example 11.12. First, we calculate the molarity of the starting phosphorous acid solution:

$\dfrac{0.122 \text{ g}}{81.99 \text{ g} \cdot \text{mol}^{-1}} \Big/ 0.0500 \text{ L} = 0.0298 \text{ mol} \cdot \text{L}^{-1}$. We then use the first acid

dissociation of phosphorous acid as the dominant equilibrium. The

K_{a1} is 1.0×10^{-2}. Let H_2P represent the fully-protonated phosphorus acid.

Concentration $(\text{mol} \cdot \text{L}^{-1})$	$H_2P(aq)$	+ $H_2O(l)$	$\rightleftharpoons$	$HP^-(aq)$	+ $H_3O^+(aq)$
initial	0.0298	—		0	0
change	$-x$	—		$+x$	$+x$
final	$0.0298 - x$	—		$+x$	$+x$

$K_a = \dfrac{[H_3O^+][HP^-]}{[H_2P]} = 1.0 \times 10^{-2}$

$1.0 \times 10^{-2} = \dfrac{x \cdot x}{0.0298 - x} = \dfrac{x^2}{0.0298 - x}$

If we assume $x \ll 0.0298$, then the equation becomes

$x^2 = (1.0 \times 10^{-2})(0.0298) = 2.98 \times 10^{-4}$

$x = 1.73 \times 10^{-2}$.

Because this value is more than 10% of 0.0300, the full quadratic solution should be undertaken. The equation is

$x^2 = (1.0 \times 10^{-2})(0.0298 - x)$ or

$x^2 + (1.0 \times 10^{-2}x) - (2.98 \times 10^{-4}) = 0$.

Using the quadratic formula, we obtain $x = 0.013$.

$pH = 1.89$

The calculation is performed as in part (a):

$$1.0 \times 10^{-2} = \frac{(0.0159 + x)x}{0.0112 - x}$$

$$x = 3.75 \times 10^{-3}$$

$$pH = 2.42$$

8. At pH = 12, the effective charge of lysine is -1, and that of tyrosine is -2.

9.

(a) $K_{sp} = [Ca^{2+}][OH^-]^2$

$5.5 \times 10^{-5} = (x)(2x)$

$X = 2.4 \times 10^{-2}$ mol/L

2.4×10^{-2} mol/L x 74 g/mol x 0.5L = 0.89g

(b) $[OH^-]^2 = 2 \times 2.4 \times 10^{-2}$ M

pOH = 1.32

pH = 14 -1.32 = 12.68

10. (a) $\Delta G° = -nFE°_{cell} = -2.303RT \log K$

   $-2 \times 9.65 \times 10^4$ C/mol x 1.10V

   $= -2.303 \times 8.31$ J/(mol·K) x 298K x log K

   log K = 37.2

   $K = 1.6 \times 10^{37}$

(b)

$$E_{cell} = E^0_{cell} - \frac{0.0592}{n} \log Q$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{0.001}{10.0} = 1.00 \times 10^-$$

$$n = 2$$

$$E_{cell} = 1.10 - \frac{0.0592}{2} \log (1.0 \times 10^{-4})$$

$$= 1.10 - (-0.12)$$
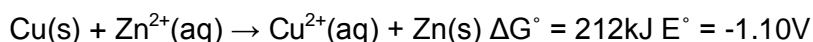
$$= 1.22 \ V$$

(c) A spontaneous redox reaction occurs, driven forward by a fall in free energy.

Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s) ΔG° = -212kJ E° = 1.10V

(d) Nothing.

Cu(s) + Zn^{2+}(aq) → Cu^{2+}(aq) + Zn(s) ΔG° = 212kJ E° = -1.10V
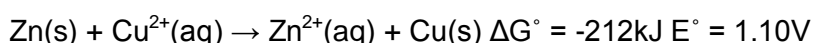
is not spontaneous. Zn^{2+} does not oxidize copper.

(e)

$$1 \, mol \ Cu = 2 \, mol \ e^-$$

$$0.404g \ Cu \times \frac{1 \, mol \ Cu}{63.6g \ Cu} \times \frac{2 \, mol \ e^-}{1 \, mol \ Cu} \times \frac{9.65 \times 10^4 C}{1 \, mole^-}$$

$$= 1.23 \times 10^3 C$$

$$Current = \frac{charge}{time} = \frac{1.23 \times 10^3 C}{5hr \times 3600s/hr} = \frac{1.23 \times 10^3 C}{1.80 \times 10^4 s} = 6.83 \times 10^{-2}$$

11. (a)

$$Anode: \quad Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e-$$

$$Cathode: \ PbO_2 + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$
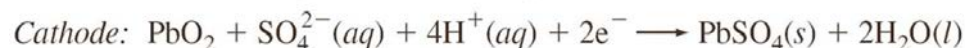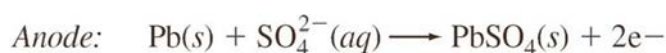
Copyright © 2006 Pearson Education, Inc., Publishing as Benjamin Cummings

(b) (Volume of the acid solution = 724 ml

Initial mass of H_2SO_4 = 724 x 1.29 x 0.38 = 355g

Initial conc of $[H_2SO_4]$ = (355 / 98.09) / 0.724 = 5.0 M

$[SO_4^{2-}]$= 5 M, $[H_3O^+]$ = 10 M

$E°_{cell}$= $E°_{cathode}$ - $E°_{anode}$ = 1.46 – (-0.36) = 1.82 v

$$E_{cell} = E_{cell}° - \frac{RT}{nF} \ln Q$$

.

$Q = 1/ ([SO_4^{2-}]^2 [H^+]^4) = 1/ (5^2 \times 10^4) = 4 \times 10^{-6}$

$E = E° - RT/nF \ln Q = E° - RT/2F \ln Q$

$= 1.82 - (0.05917 / 2) \log 4 \times 10^{-6}$

$= 1.82 - 0.02959 \log 4 \times 10^{-6} = 1.98$ v

(c)

The overall reaction is: $Pb + PbO_2 + H_2SO_4 \rightarrow 2 PbSO_4 + 2 H_2O$

Initial mass of H_2SO_4:   724 mL x 1.29 g / 1 mL x 0.380 = 355 g

Final mass of H_2SO_4:   724 mL x 1.19 g / 1 mL x 0.260 = 224 g

Mass of H_2SO_4 reacted ☐ 355 g – 224 g = 131 g

$$\text{Moles of } H_2SO_4 \text{ reacted } = 131 \text{ g} \times \frac{1 \text{ mol}}{98.09 \text{ g}} = 1.34 \text{ mol}$$

$$Q = 1.34 \text{ mol } H_2SO_4 \times \frac{2 \text{ mol } e^-}{2 \text{ mol } H_2SO_4} \times \frac{96500 \text{ C}}{1 \text{ mol } e^-} = \mathbf{1.29 \times 10^5 \text{ C}}$$

(d) $t = \dfrac{Q}{I} = \dfrac{1.29 \times 10^5 \text{ C}}{22.4 \text{ A}} = 5.76 \times 10^3 \text{ s} = \mathbf{1.60 \text{ hr}}$

1. (Total 16 pts) A 1.00 wt % NaCl(aq) solution has a freezing point of -0.593 $^{\circ}$C. k_f of water is 1.86 K·kg·mol^{-1}.

(a) (3 pts) Estimate the van't Hoff i factor from the data.

(Answer)

(b) (3 pts) Determine the total molality of all solute species. The molality calculated from the freezing point depression is the sum of the molalities of the undissociated NaCl(aq), Na$^+$(aq), and Cl$^-$(aq).

(Answer)

(c) (5 pts) Calculate the percentage dissociation of NaCl in this solution.

(Answer)

(d) (5 pts) A 1.0 g sample of an unknown molecular compound $C_nH_{2n}O_n$, dissolved in 100 g of water, produces a boiling point elevation of 0.029 $^{\circ}$C (k_b = 0.51 K·kg·mol^{-1}). Compute the molar mass and molecular formula.

(Answer)

2. (total 6 pts) Which of the following mixtures would you expect to show a positive deviation, negative deviation, or no deviation (that is, form an ideal solution) from Raoult's law? Explain your conclusion.

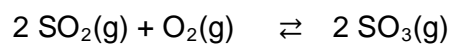(a) (2 pts) methanol, CH_3OH, and ethanol, CH_3CH_2OH

(Answer)

(b) (2 pts) HF and H_2O
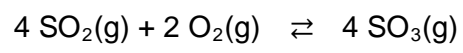
(Answer)

(c) (2 pts) hexane, C_6H_{14}, and H_2O

(Answer)

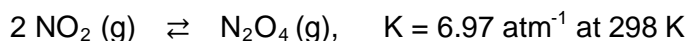3. (total 5 pts) At 400 $^{\circ}$C, the equilibrium constant of the following reaction,

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$$

is 3.1×10^4. What is the value of K_c (equilibrium constant in terms of concentration) for the following

reaction at 400 $^{\circ}$C?

$$4 \text{ SO}_2(g) + 2 \text{ O}_2(g) \quad \rightleftarrows \quad 4 \text{ SO}_3(g)$$

(Answer)

4. (total 6 pts) Nitrogen dioxide gas (NO_2) undergoes dimerization reaction to $N_2O_4(g)$ at 298 K.

$$2 \, NO_2 \, (g) \; \rightleftarrows \; N_2O_4 \, (g), \quad K = 6.97 \, atm^{-1} \text{ at 298 K}$$

(a) (3 pts) Calculate the partial pressure of NO_2 and N_2O_4 at equilibrium when the initial pressure of NO_2 was 1 atm, and there was no N_2O_4 at the beginning.

(Answer)

(b) (3 pts) What are the partial pressures of NO_2 and N_2O_4, if the total pressure at the equilibrium is 1 atm?

(Answer)

5. (total 8 pts) (a) (2 pts) The hydration of carbon dioxide produces carbonic acid as shown in the following chemical equation. Identify the acid and the base of this reaction based on Lewis definition of acids and bases.

$$CO_2(g) + H_2O(l) \; \rightleftarrows \; H_2CO_3(aq)$$
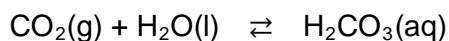
(Answer)

(b) (3 pts) Suggest an explanation for the different strength of acetic acid and trichloroacetic acid.

(Answer)

(c) (3 pts) Suggest an explanation for the different strength of acetic acid and formic acid.

(Answer)

6. (total 7 pts) (a) (2 pts) Calculate the pH of 6.55×10^{-7} M $HClO_4$(aq), ignoring the effect of the autoprotolysis of water.

(Answer)

(b) (5 pts) Repeat the calculations, taking into account the autoprotolysis of water.

(Answer)

7. (total 10 pts) Suppose that 0.122 g of phosphorus acid, H_3PO_3, is dissolved in water and that the total volume of the solution is 50.0 mL. K_{a1} is 1.0×10^{-2}.

(a) (5 pts) Estimate the pH of this solution.

(Answer)

(b) (5 pts) Estimate the pH of the solution that results when 5.00 mL of 0.175 M NaOH(aq) is added to the phosphorus acid solution.

(Answer)

8. (Total 6 pts) Two of amino acids are shown with pKa's for all acid(base) sites and their expected form at pH=7.0. In this case, the effective charge of lysine is +1 and that of tyrosine 0. What will be the effective charges of these two amino acids at pH = 12?
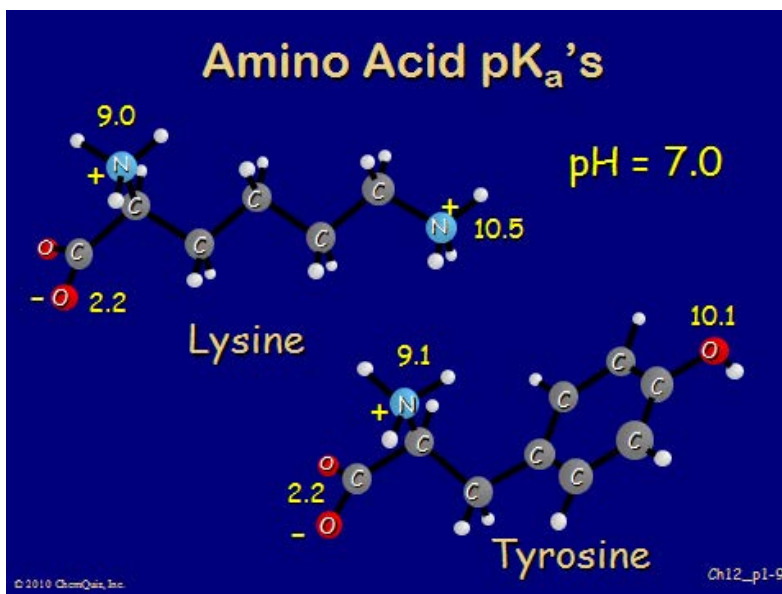
(Answer)

9. (total 6 pts) Calcium hydroxide is a slightly soluble base ($K_{sp} = 5.5 \times 10^{-5}$). A 1.0 g sample of solid $Ca(OH)_2$ is shaken with 0.5 L of water.
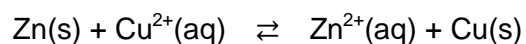
(a) (3 pts) Calculate the mass (grams) of $Ca(OH)_2$ that dissolves.

(Answer)

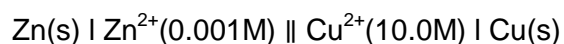(b) (3 pts) What is the pH of the saturated $Ca(OH)_2$ solution formed in this process?

(Answer)

10. (total 14 pts) (a) (3 pts) Calculate the equilibrium constant at 25 °C for the reaction.

$$Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$$

The corresponding standard cell potential is 1.10V.

(Answer)

(b) (3 pts) Which is the potential at 25 °C of the following cell?

$$Zn(s) \mid Zn^{2+}(0.001M) \parallel Cu^{2+}(10.0M) \mid Cu(s)$$

(Answer)

(c) (2 pts) What happens when we dip a strip of zinc into a solution of $CuSO_4$?
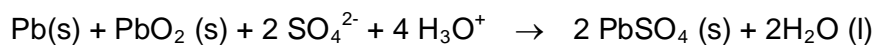
(Answer)

(d) (2 pts) What happens when we dip a strip of copper into a solution of $ZnSO_4$?
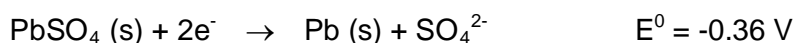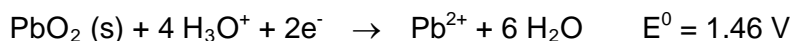
(Answer)

(e) (4 pts) When an aqueous solution of copper(II) sulfate, $CuSO_4$, is electrolyzed, copper metal is deposited. If a constant current was passed for 5 h and 404 mg of copper metal were deposited, what must have been the current?

(Answer)

11. (total 16 pts) The concentration of sulfuric acid in the lead storage battery of an automobile over a period of time has decreased from 38.0% by mass (density =1.29 gmL^{-1}) to 26 % (density = 1.19 gmL^{-1}) at 25 °C. Assume the volume of the acid remains constant at 724 mL and all the sulfuric acid is dissociated to SO_4^{2-} and H_3O^+. The overall reaction is as follows.

$$Pb(s) + PbO_2 \text{ (s)} + 2\ SO_4^{2-} + 4\ H_3O^+ \rightarrow 2\ PbSO_4 \text{ (s)} + 2H_2O \text{ (l)}$$

Standard reduction potential

$$PbO_2 \text{ (s)} + 4\ H_3O^+ + 2e^- \rightarrow Pb^{2+} + 6\ H_2O \qquad E^0 = 1.46 \text{ V}$$

$$PbSO_4 \text{ (s)} + 2e^- \rightarrow Pb \text{ (s)} + SO_4^{2-} \qquad\qquad E^0 = -0.36 \text{ V}$$

(a) (4 pts) Write the half cell reactions at anode and cathode.

(Answer)

(b) (4 pts) What is the initial cell potential?

(Answer)

(c) (5 pts) Calculate the total charge in coulombs supplied by the battery.

(Answer)

(d) (3 pts) How long (in hours) will it take to recharge the battery back to the original sulfuric acid concentration using a current of 22.4 A?

(Answer)