2011 FALL Semester Mid-term Examination For General Chemistry II (CHEM103)

* Both equations/procedures and answers should be correct to get the point; otherwise, no point is given. Double-check your calculations.

Date: October 26 (Wed), 2011, Time Limit: 7:00 ~ 9:00 p.m.

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.	Name

Problem	points	Problem	points	TOTAL pts
1	/8	8	/10	
2	/4	9	/5	
3	/10	10	/5	
4	/5	11	/10	(100
5	/10	12	/8	/100
6	/5	13	/5	
7	/10	14	/5	

****** This paper consists of 9 sheets with 14 problems. Please check all page numbers before taking the exam. Write down your work and answers in the (Answer) space below each question.

(And periodic table and A CLAIM FORM is attached on last page for claims on the marked exam paper later)

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 31 (Mon, 7:00 p.m. ~ 8:00 p.m.)
 - 2) Location: Room for quiz session
 - 3) Claim Procedure:

(During the period, you can take the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it.)

To get more information, visit the website at <u>www.gencheminkaist.pe.kr</u>.

2. Final Confirmation

1) Period: November 3(Thu)-4(Fri)

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

CHEM 103: General Chemistry II Mid-Term Examination (100 points): Answers

1. (a) F, (b) F, (c) T, (d) F

2. (a) Higher pressure and (b) lower temperature

3. (a) $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 12610 \text{ J mol}^{-1}$

$$K = \exp(-\Delta G^{\circ}/RT) = 0.02256$$

(b) $\Delta G = RTIn(Q/K), Q = P(N_2O_4)/P(NO_2)^2$

At equilibrium, Q=K. Since the volume is constant, partial pressure of gas molecules does not be altered. Therefore, Q=K and $\Delta G = 0$.

(c) Partial pressures of both reactant and product will be half the values at equilibrium. Then,

Q/K = (1/2)/(1/4) = 2

 $\Delta G = RTln2 = (8.31447 J K^{-1} mol^{-1}) x (400 K) X ln2 = 2305.26 J mol^{-1}$

4. (b)

The reaction (b) shows that the reaction decreases the number of gas particles.

5. Any one of them is fine.

(a) $\Delta V = 0$ (b) $\Delta P = 0$ (c) $\Delta E = q_v = C_v \Delta T$ (d) $\Delta E = q_p - P \Delta T$ (e) $\Delta H = \Delta E + P \Delta V = q_p = C_p \Delta T$

6. n=PV/RT

 $M_2/M_1 = n_2/n_1 = T_1/T_2 = 300$ K/600K $M_2 = M_1/2 =$ **5.0 kg**

7. (a)

$$\begin{split} & [CH_{3}COOH] = 0.1 \text{ M}, \ [CH_{3}COO^{-}] = 0.1 \text{ M} \\ & pH = pK_{a} + log_{10}1 = \textbf{4.75} \\ & (b) \ CH_{3}COOH + OH^{-} \rightarrow CH_{3}COO^{-} + H_{2}O: \text{ K} = K_{a}/K_{W} = 1.8 \text{ x } 10^{9} \\ & \text{Therefore, all the quantity of OH^{-} will be used to consume CH_{3}COOH and produce CH_{3}COO^{-} \\ & [CH_{3}COOH] = 0.1 - 0.05 = 0.05, \ [CH_{3}COO^{-}] = 0.1 + 0.05 = 0.15 \\ & pH = pK_{a} + log_{10}3 = \textbf{5.23} \end{split}$$

8.

 $\Delta S = C_p \ln \frac{T_2}{T_1},$

where $C_{\rm P} = n\overline{C}_{\rm P} = \frac{5}{2}nR$.

 $\Delta S = 5/2 * (nR) * lnT_2/T_1$

 $= 5/2^{*}(3.5 \text{ mol})(8.314 \text{ Jmol}^{-1}\text{K}^{-1})\ln(273+77)/(273+50)$

= 5.8 JK⁻¹

9. Mole of N₂: $n = \frac{PV}{RT} = \frac{2.45 \times 1}{0.0821 \times 298} = 0.10 \text{ mol}$ Final mole of O₂: 0.30 × $\frac{0.30}{0.40} = 0.225 \text{ mol}$ Final partial pressure of O₂: $p = \frac{nRT}{V} = \frac{0.225 \times 0.0821 \times 298}{1} = 5.5 \text{ atm}$ Answer: 5.5 atm (or 5.6 atm)

10. $P_{ideal} = 18.3 \text{ atm}$ $P_{real} = 16.0 \text{ atm}$ Deviation = 12.6%

11. (a) This is exothermic reaction, thus an exothermic reaction at equilibrium can oppose the stress of an increase in temperature by running backward, thereby consuming the heat energy that is added. The equilibrium position will then **shift to the left**, toward reagents.

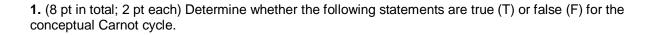
(b) using van't Hoff equation, $K_{100}{}^{0}{}_{C} = 6.72 \times 10^{-2}$

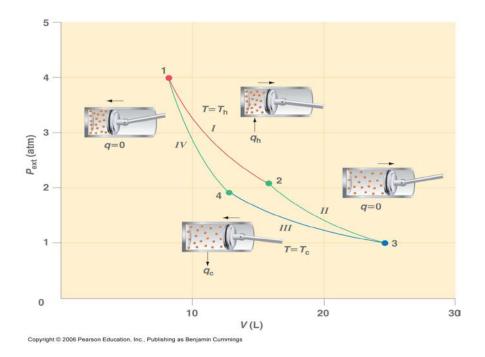
12. (a) CH_3NH_2 (aq) + $H_2O(I)$ (b) $[CH_3NH_3^+] = [OH^-] = x$, $K_b = \frac{x \times x}{0.20 - x}$, Assume x << 0.2, $x = \sqrt{0.20 \times 3.6 \times 10^{-4}} = 8.5 \times 10^{-3}$ $pOH = -log(8.5 \times 10^{-3}) = 2.07$ pH = 14 - pOH = 11.93

13.
$$\begin{array}{l} CH_{3}COOH + NH_{3} \Longrightarrow CH_{3}COO^{-} + NH_{4}^{+} \\ \\ K = \frac{K_{a}K_{b}}{K_{w}} \end{array}$$

14. D < C < B = A

Water vapor in air at 100%-humidity is in equilibrium with water. They have the same G. H₂O in the ethanol mixtures has a lower G than its pure state. Remember $\Delta G = \Delta G_0 + RT \ln V_0/V$





- (a) In stage II, $\Delta E = w$ with positive quantities. (Answer)
- (b) In stage III, $w = nRT_c \cdot \ell n(V_4/V_3)$ (Answer)
- (c) In stage IV, it is called an adiabatic compression. (Answer)
- (d) In stage I, q_h is lost from the gas to a hot reservoir. (Answer)

^{2.} (4 pt) Many gas molecules do not obey the equation of state, PV = nRT, and this nonideal behavior becomes more pronounced at (a) (lower, higher) pressure and (b) (lower, higher) temperature. Select the correct term for pressure and temperature.

3. (10 pt) Consider the following reaction, $2NO_2(g) \neq N_2O_4(g)$. The values of ΔH_0 and ΔS_0 are -58.03 KJ/mol and -176.6 J/K·mol, respectively. [R= 8.31447 J K⁻¹ mol⁻¹]

(a) (2 pt) Estimate the value of *K* (equilibrium constant) at 400 K. Assume that ΔH_o and ΔS_o are temperature independent.

(Answer)

(b) (4 pt) Estimate Gibbs free energy change at the same temperature (400 K) by injecting Ar gas into the system at equilibrium, while both volume and temperature are kept constant.(Answer)

(c) (4 pt) Estimate Gibbs free energy change at the same temperature (400 K) if the total volume becomes twice by the injected Ar gas, while both pressure and temperature remain constant. (Answer)

4. (5 pt) Which of the following chemical reactions has a negative change in entropy? (a) $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$ (b) $O(g) + O(g) \rightarrow O_2(g)$ (c) $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$ (d) $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(l)$ (Answer)

5. (10 pt in total; 2 pt each) Please fill the empty entries with correct equation or numbers.

Process Type	Conditions	Results
Isothermal	$\Delta T = 0$	$\Delta E = 0$
Isochoric	(a) ? = 0	(c) $\Delta E = ?$
Isobaric	(b) ? = 0	(d) $\Delta E = ?$; (e) $\Delta H = ?$

(Answer)

6. (5 pt) Sulfuric acid reacts with NaCl(s) to produce HCl(g): NaCl(s) + H₂SO₄(l) \rightarrow NaHSO₄(s) + HCl(g). A 10.0 kg of NaCl reacts completely with sulfuric acid to give a certain volume of HCl(g) at 300 K and P = 1.0 atm. If the same volume of HCl is collected at 600 K and P = 1.0 atm, what mass of NaCl has reacted? (Answer)

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7. (10 pt) Given the weak acid reaction, CH_3COOH \neq H^+(aq) + CH_3COO^-(aq),
(a) (5 pt) Calculate the pH value in a solution prepared by dissolving 0.1 mole of acetic acid and 0.1 mole of sodium acetate in water, and adjusting the volume to 1.0 L [pK_a(acetic acid) = 4.75]
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(Answer)

(b) (5 pt) Suppose 0.05 mol of NaOH is added to the solution in (a). Calculate the pH value of the resulting solution by assuming the constant volume. (Answer)

8. (10 pt) Calculate the value of ΔS (in J K⁻¹) in heating 3.5 moles of a monatomic ideal gas from 50 °C to 77 °C at constant pressure.

(Answer)

9. (5 pt) A 1.00-L flask contains nitrogen at a temperature of 25 °C and a pressure of 2.45 atm. The 0.30 mol of $O_2(g)$ is added to the flask and allowed to mix. Then a stopcock is opened to allow 0.10 mol of molecules to escape. What is the partial pressure of oxygen in the final mixture? (R = 0.0821 L atm K⁻¹ mol⁻¹)

10. (5 pt) Suppose 1.50 mol of NO₂ gas are compressed into a 2.00-L cylinder at 298 K. Calculate the pressure of this gas and deviation from ideal gas (van der Waals parameters of NO₂ gas: a = 5.294 atm L² mol⁻², b = 0.04435 L mol⁻¹).

(Answer)

11. (10 pt) You are trying to predict the shift in equilibrium for the $2NO_2(g) \neq N_2O_4(g)$ system, when it is heated to 100 °C. (a) (5 pt) Provide <u>a qualitative prediction of the shift</u> based on LeChatelier's principle. (b) (5 pt) Confirm your prediction with <u>a quantitative calculation of K</u> at 100 °C, given $\Delta H_0 = -13.67$ Kcal/mol, R = 1.9872 cal K⁻¹ mol⁻¹, and K = 6.97 at 25 °C.

12. (8 pt) Methylamine (CH₃NH₂; K_b : 3.6 × 10⁻⁴) is a weak base, and its conjugate acid is methylammonium. (a) (3 pt) Complete an equilibrium reaction of CH₃NH₂ in water. (b) (5 pt) Calculate pH of a 0.20 M aqueous solution of CH₃NH₂ (Neglect the autoionization of water). (Answer)

13. (5 pt) Derive the equilibrium constant for the reaction between acetic acid (CH₃COOH) and ammonia (NH₃), in terms of K_a of acetic acid, K_b of ammonia, and the autoionization constant K_w of water.

(Answer)

14. (5 pt) Pure water is in equilibrium with its vapor at a given temperature. List the following H₂O's in the increasing order of molar Gibbs free energy of H₂O (T = 298 K and P = 1 atm).

- A. Water vapor in air with 100% relative humidity.
- B. Pure water.
- C. Water in a mixture of 1:1 ethanol and water (molar ratio)
- D. Water in a mixture of 10:1 ethanol and water (molar ratio).

2011 FALL Semester Final Examination For General Chemistry II (CHEM103)

* **Both** equations/procedures and answers should be correct to get the point; otherwise, no point is given. Double-check your calculations.

Date: December 21 (Wed), 2011, Time Limit: 19:00 ~ 21:00 p.m.

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.	Name

Problem	points	Problem	points	TOTAL pts
1	/15	6	/15	
2	/11	7	/12	
3	/15	8	/3	/100
4	/5	9	/10	
5	/4	10	/10	

** This paper consists of 10 sheets with 10 problems. Please check all page numbers before taking the exam. Write down your work and answers in the (Answer) box below each question. (And periodic table and A CLAIM FORM is attached on last page for claims on the marked exam paper later)

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

1. Period, Location and Procedure

- 1) Return and Claim Period: December 26 (Mon, 11: 00 p.m. ~ 13: 00 p.m., 2 hours)
- 2) Location: Creative Learning Bldg.(E11)

Class	Room	Class	Room
Α	205	Ε	209
В	206	G	210
С	207	Н	211
D	208		

3) Claim Procedure:

(During the period, you can take the marked exam paper from your TA and should hand in the paper with a FORM for claims if you have any claims on it.)

To get more information, visit the website at www.gencheminkaist.pe.kr.

2. Final Confirmation

1) Period: December 26 (Mon, 21:00 p.m.) - 27(Tue, 13:00 p.m.)

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

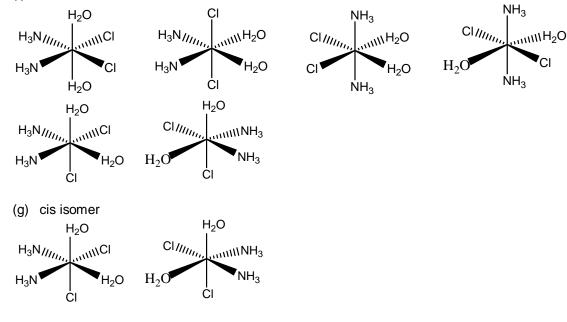
CHEM 103: General Chemistry II Final Examination (100 points): Answers

1.

- (a) Charge-charge interaction (s = 1) > charge-dipole interaction (s = 2) > dipole-dipole interaction (s = 3) > charge-induced dipole interaction (s = 4) > instantaneous dipole-induced dipole (dispersion) interaction (s = 6)
- (b) charge-induced dipole interaction and instantaneous dipole-induced dipole (dispersion) interaction
- (c) instantaneous dipole-induced dipole (dispersion) interaction and dipole-dipole interaction

2.

- (a) Coordination No = 6, oxidation state = +3
- (b) d^6 complex, 6 electrons in t_{2g}
- (c) CFSE = $-12/5\Delta_{o}$
- (d) Diamagnetic
- (e) 1 mol
- (f) 6 isomers



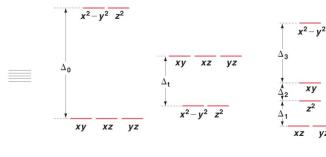
3.

(a) Octahedral

Spherical C



Square planar

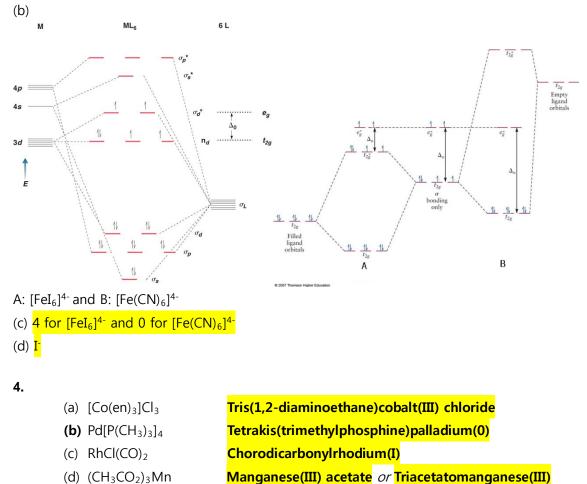


Tetrahedral

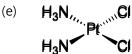


2

Fe²⁺ has 6 valence electrons in d-orbitals. If one fills up the electrons from the lowest energy level, there will be the largest energy gain for the octahedral structure, since all the 6 electrons occupy lower energy levels.

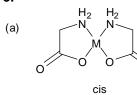


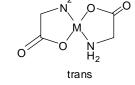
(d) (CH₃CO₂)₃Mn

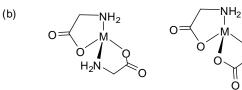


cis-Diamminedichoroplatinum(II)

5.







optical isomers

6.

step 1:
$$\operatorname{Br}_2 \xrightarrow{k_1} 2\operatorname{Br}$$
 (rapid equilibrium)
step 2: $\operatorname{Br} + \operatorname{H}_2 \xrightarrow{k_2} \operatorname{HBr} + \operatorname{H}$ (slow)
step 2: $\operatorname{H} + \operatorname{Br}_2 \xrightarrow{k_3} \operatorname{HBr} + \operatorname{Br}$ (fast)

We assume that the first step is in rapid equilibrium, $K = k_I/k_{-I} = [Br]^2 / [Br_2]$ Solving for [Br] gives $[Br] = (k_I/k_{-I})^{1/2} [Br_2]^{1/2}$

Substituting this expression for the intermediate concentration [Br] into the rate law for the ratedetermining step gives

rate = k_2 [Br] [H₂] = $k_2(k_1/k_1)^{1/2}$ [Br₂]^{1/2} [H₂] = k [H₂] [Br₂]^{1/2}

7.

(a) Integrated rate law is derived as [N₂O₄] = [N₂O₄]₀e^{-kt} Adding [N₂O₄] = 0.010 atm, [N₂O₄]₀ = 0.10 atm, and k = 5.1×10⁻⁶ s⁻¹, the t is calculated to be -kt = ln(0.01/0.1) = -2.303, t = 4.5×10⁵ s
(b) k = Aexp(-E_a/RT) k/k' = exp(-E_a/RT), add k = 5.1×10⁻⁶ s⁻¹, E_a = 54.9×1000 Jmol⁻¹. T = 303K, and T' = 573K, then k/k' = 3.47×10⁻⁵ k' = 0.147 thus, t = 16 s

8.

rate = *k*[H₂][NO]²

$$k_{f}[NO]^{2} = k_{r}[N_{2}O_{2}]$$
rate = $k_{2}[H_{2}][N_{2}O_{2}]$
rate = $\frac{k_{2}k_{f}}{k_{r}}[H_{2}][NO]^{2} = k[H_{2}][NO]^{2}$
9
(a)
Anode: $H_{2}(g) + 2OH(aq) \rightarrow 2H_{2}O(l) + 2e^{l}$
Cathode: $1/2O_{2}(g) + H_{2}O(l) + 2e^{l} \rightarrow 2OH(aq)$

(b) At standard condition, $w = |\Delta G^0| \times (\text{cell efficiency}) = |-nFE^0| \times 0.5$ Molar mass of H₂O = 18 g => 1g of water and 2e⁻ per each H₂O: n = 1/9 Therefore, w = 1/9 x 96485 x 1.229 x 0.5 J = 6588 J

10 (a) $Fe(s) + 2X^{+}(aq) \rightarrow Fe^{2+}(aq) + 2X(s)$ note: 2-point-deduction for missing (s) and (aq) (b) +0.80 V 1. (15 pts in total; 5 pt each) The potential energies of intermolecular forces have an inversepower dependence on the intermolecular distance R: $V(R) \propto 1/R^s$.

(a) List the 5 intermolecular forces in the order of magnitude (R > 1) and indicate the s value for each force.

(Answer)

(b) Which intermolecular forces are always attractive? (Answer)

(c) What kinds of interactions can occur for the covalently bonded compounds without any ionic groups?

- (11 pts in total) The octahedral complex, [Co(NH₃)₂(H₂O)₂Cl₂]Cl is a low spin complex [The atomic number of cobalt is 27].
 - (a) (1 pt) What are the coordination number of the complex and the oxidation state of the cobalt? (Answer)
 - (b) (1 pt) Determine the *d*-electron configuration of the cobalt. (Answer)
 - (c) (2 pt) Calculate the crystal field stabilization energy (CFSE) of this complex. (Answer)
 - (d) (1 pt) Does the complex have paramagnetic or diamagnetic property? (Answer)

(e) (1 pt) If 3 mol of $AgNO_3$ were added to the 1 mol of the above complex in aqueous solution, how many moles of AgCl are produced?

(Answer)

(f) (3 pts) How many isomers does this complex have? Draw all possible isomers of the complex.

(Answer)

(g) (2 pts) Which ones are optical isomers? (Answer)

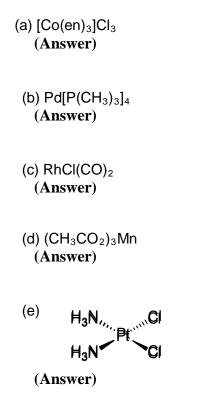
3. (15 pts in total) The ligands, I⁻ and CN⁻, stabilize Fe^{2+} by forming coordination complexes [Z for Fe = 26].

(a) (4 pts) Based on the crystal field theory, predict the reasonable structure of the complexes (among linear, square planar, tetrahedral, and octahedral ones), and justify your answer. (Answer)

(b) (6 pts in total; 3 pts each) Draw energy level diagram for each complex according to the ligand field theory.

- (c) (2 pts) How many unpaired electrons are present in each complex? (Answer)
- (d) (3 pts) Which ligand leads to the absorption of longer-wavelength light? (Answer)

4. (5 pts in total) Name the following coordination complexes.



 (4 pts in total; 2 pts each)The glycinate ion (NH₂-CH₂-COO⁻) can act as a bidentate ligand. Draw all possible isomers including optical isomers in (a) a square planar and (b) a tetrahedral complexes of M(glycinate)₂ (Do not simplify the ligand structures). (Answer) 6. (15 pts in total) Under certain conditions, the experimental rate law for the gas-phase reaction of molecular hydrogen with molecular bromine, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, is given by *rate* = $k[H_2][Br_2]^{1/2}$, and the atomic Br is found as an intermediate. Suggest a proper reaction mechanism consisting of 3 elementary reactions (5 pts), and show that your proposed mechanism is consistent with the observed rate law (10 pts).

(Answer)

7. (12 pts in total; 6 pts each) N_2O_4 decomposes spontaneously at room temperature in the gas phase, and the rate law governing the disappearance of N_2O_4 with time is $k[N_2O_4]$. At 30 °C, $k = 5.1 \times 10^{-6} \text{ s}^{-1}$, and the activation energy for the reaction is 54.9 kJmol⁻¹. Calculate the time (in seconds) required for the partial-pressure decrease of $N_2O_4(g)$ from 0.10 atm to 0.010 atm (a) at 30 °C and (b) at 300 °C [R = 8.31 JK⁻¹mol⁻¹]

8. (3 pts) The reaction mechanism of the reaction, $2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$, is as follows. Write the rate law.

- 9. (10 pts in total) The reaction for a fuel cell is given by $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$: $E^0 = 1.229 \text{ V}$.
 - (a) (5 pts) Complete the half-cell reactions at both anode and cathode at pH 14. (Answer)

(b) (5 pts) Calculate the electrical work generated per gram of water produced at the standard condition (1 atm and 25 °C) in the unit of Joule. Assume that the efficiency of the cell is 50% [Faraday constant F = 96485 Cmol⁻¹ and molar mass of H₂O = 18 g]. (Answer)

10. (10 pts in total) A student was given a standard $Fe(s)|Fe^{2+}(aq)$ half-cell and another half-cell containing an unknown metal X immersed in 1.00 M XNO₃(aq). When these two half-cells were connected at 25 °C, the complete cell functioned as a galvanic cell with $E_{cell} = +1.24$ V. $[E^{\circ}(Fe^{2+}/Fe) = -0.44$ V].

(a) (5 pts) The reaction was allowed to continue overnight and the two electrodes were weighed. The iron electrode was found to be lighter and the metal X electrode was heavier. Complete the balanced equation for the cell reaction.

(Answer)

(b) (5 pts) What is the reduction potential for the unknown X⁺/X couple? (Answer)