2024 SPRING Semester Final Examination For General Chemistry I

Date: June 12(Wed), Time Limit: 19:00 ~ 21:00

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	/10	6	/18	
2	/14	7	/14	
3	/5	8	/13	/100
4	/6	9	/10	
5	/10			

^{**} This paper consists of 17 sheets with 9 problems (*page 14 - 16*: Equation, constants & periodic table, *page 17*: claim form). Please check all page numbers before taking the exam. Write down your work and answers in the Answer 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. (채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

0 Return and Claim Period: June 14 (Friday, 12:00 ~ 14:00, 2 hrs)

The claim is permitted only on this period. Keep that in mind!

0 Location: Each designated room of Creative Learning Bldg. (E11)

Class	Room(E11)
A	207
В	208
С	Terman Hall
D	409

0 Procedure

Rule 1: Students cannot bring their writing tools into the rooms (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, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

WARNING!!

If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

2. Final Confirmation

- 1) Period: *June 15(Sat.)* ~ *16(Sun)*
- 2) Procedure: During this period, you can check final score of the examination *on the website* again. (No additional corrections. If no change in your score after reasoning, the claims were not accepted.)

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

1. (Total 10 points)

Indicate "O" for correct statements and "X" for incorrect statements.

- (1) The standard reduction potential is a ratio scale, like Kelvin. [Hint: Celsius and Fahrenheit are interval scales, but Kelvin is a ratio scale.] ()
- (2) Entropy could be considered to be measured on a ratio scale, in accordance with the third law of thermodynamics. ()
- (3) Given that E_{cell^o} for $A + B \rightarrow C + D$ is e, E_{cell^o} for $2A + 2B \rightarrow 2C + 2D$ is also e, because E_{cell^o} is an extensive property, like ΔG^o . (
- (4) The steady state in chemical kinetics is an equilibrium state. ()
- (5) The pH value is equal to pKa when [HA] is equal to [A-], especially for weak acids. ()
- (6) All spontaneous processes produce an increase in the entropy of the system. ()
- (7) During phase transitions, the change in enthalpy equals the product of the change in entropy and the absolute temperature. ()
- (8) The equilibrium is reached at the point, where the slope of the Gibbs free energy versus extent of reaction graph is zero. ()
- (9) Fractional distillation can be explained by Henry's law. ()
- (10) Aniline is more basic than cyclohexylamine due to the electron delocalization. ()

Each 1 point, no partial points

1	X	6	X
2	0	7	0
3	X	8	0
4	X	9	X
5	0	10	X

2. (Total 14 points)

Fill out the blanks

- 1. The relationship between the standard Gibbs energy change and the equilibrium constant for a reaction is (a). The constant K, is the value of the reaction quotient Q at equilibrium and is call the (b).
- 2. Osmotic flow can be stopped by applying a pressure, to the more (c) solution. In (d), the direction of flow is reversed by applying a pressure that exceeds the osmotic pressure to the more (c) solution. (e) are certain properties that depend only on the concentration of solution particles in a solution, and not on the identity of the solute.
- 3. A (f) is a step-by-step description of a chemical reaction consisting of a series of (g). Rate laws are written for the (g) and combined in to a rate law for the overall reaction.
- 4. The (h) describes an acid as a proton donor and a base as a proton acceptor. The combinations of HA/A- and B/HB+ (HA: an acid, B: a base) are known as (i).
- 5. Solutions that resist changes in pH upon the addition of small amounts of an acid or base are referred to as (j). Calculating the pH of (j) can be application of the (k) equation.
- 6. In the (1), E_{cell} for nonstandard conditions is related to E_{Cell}° and the reaction quotient Q. If $E_{cell} > 0$, the cell reaction is (m) in the forward direction for the stated conditions. A (n) consists of two half-cells with identical electrodes but different solution concentrations

Each 1 point, no partial points

a	$\Delta_{\mathbf{r}}G^{0} = -\mathbf{R}\mathbf{T}\mathbf{l}\mathbf{n}K$	j	buffer solutions
b	thermodynamic equilibrium	k	Henderson-Hasselbalch
	constant (그냥 equilibrium		
	constant도 정답 처리)		
c	Concentrated	1	Nernst equation
d	reverse osmosis	m	spontaneous
e	colligative properties	n	concentration cell
f	reaction mechanism		
g	elementary processes		
h	Brønsted-Lowry theory		
i	conjugate acid-base pairs		

3. (Total 5 points)

One proposed mechanism for the reaction between 2-chloroethnaol, CH₂ClCH₂OH, and hydroxide ions in aqueous solution, is as follows:

Use the steady-state approximation to determine the rate of formation for the product, (CH₂CH₂)O.

Using the steady-state approximation, while its concentration is not known during the reaction, the rate of change of its concentration is zero. Therefore,

$$\frac{d[CH_2ClCH_2O^{-}]}{dt} = k_1[CH_2ClCH_2OH][OH^{-}] - k_{-1}[CH_2ClCH_2O^{-}][H_2O] - k_2[CH_2ClCH_2O^{-}]$$
= 0
(2 points)

Rearranging the above expression to solve for [CH₂ClCH₂O⁻] gives the following expression

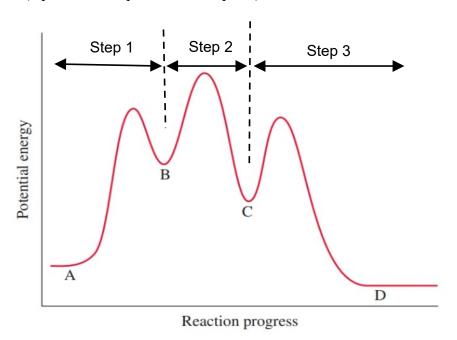
$$\left[\text{CH}_2\text{ClCH}_2\text{O}^{-}\right] = \frac{k_1\left[\text{CH}_2\text{ClCH}_2\text{OH}\right]\left[\text{OH}^{-}\right]}{k_1\left[\text{H}_2\text{O}\right] + k_2} \quad \text{(1point)}$$

The rate of formation of (CH₂CH₂)O is therefore

$$\frac{d[(CH_{2}CH_{2})O]}{dt} = k_{2}[CH_{2}CICH_{2}O^{-}] = \frac{k_{2}k_{1}[CH_{2}CICH_{2}OH][OH^{-}]}{k_{-1}[H_{2}O] + k_{2}}$$
 (2 points)

4. (Total 6 points)

By inspection of the reaction profile for the reaction A to D given below, answer the following questions. (6 points, each question is one point)



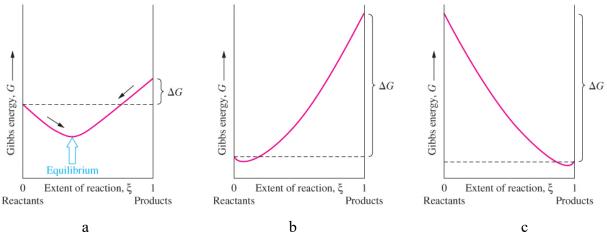
- (a) How many intermediates are there in the reaction?
- (b) How many transition states are there?
- (c) Which step has the largest rate constant?
- (d) Which step has the smallest rate constant?
- (e) Is the first step of the reaction exothermic or endothermic?
- (f) Is the overall reaction exothermic or endothermic?

Each 1 point

- (a) There are two intermediates (B and C).
- (b) There are three transition states (peaks/maxima) in the energy diagram.
- (c) The fastest step has the smallest Ea, hence, step 3 is the fastest step in the reaction.
- (d) Reactant A (step 1) has the highest Ea, and therefore the slowest smallest constant
- (e) Endothermic; energy is needed to go from A to B.
- (f) Exothermic; energy is released moving from A to D.

5. (Total 10 points)

The below contains Gibbs energy plotted against the extent of the reaction for a reaction $aA + bB \rightarrow cC + dD$. For $\xi = 1$ mol, the system contains stoichiometric amounts of products (c mol C and d mol D) at a total pressure P. $\Delta G = -1$ mol \times RT ln K + constant. Please answer the questions depending on estimated K values.



- (a) (3pts) Explain what the positive or negative slope of the red graph means. Which one has the highest and the lowest K value?
- (b) (4pts with 2pts each) For reaction $2Cl_2O(g) \rightarrow 2Cl_2(g) + O_2(g) \Delta_r H = -161 \text{ kJ/mol}$, is the entropy change positive or negative? Explain. (3pts \rightarrow 2pts) Is the reaction spontaneous at high or low temperatures? Explain. (3 pts \rightarrow 2pts)
- (c) (3pts) Which of the following graphs of Gibbs energy versus the extent of reaction represents an equilibrium constant close to 1?

Answer

- (a) (3 pts) The positive slope means ΔG is positive and the negative one means ΔG is negative. At c, K >> 1 (ΔG has a large negative value), at b, K << 1 (ΔG has a large positive value), at a, K \approx 1
- (b) Spontaneous in both cases due to the negative enthalpy and entropy: To answer this question, we must first determine whether the entropy change for the given reaction is positive or negative. The reaction produces three moles of gas from two moles; therefore, the entropy change for the reaction is positive. The Gibbs energy of a reaction is a function of enthalpy, entropy, and temperature ($\Delta_r G = \Delta_r H T \Delta_r S$). Since $\Delta_r H < 0$ and $\Delta_r S > 0$, this reaction will be spontaneous at any temperature.
- (c) Recall from (b) that, when K = 1. Therefore, we are looking for the graph with the smallest change in Gibbs energy between the products and the reactants. The correct answer is graph

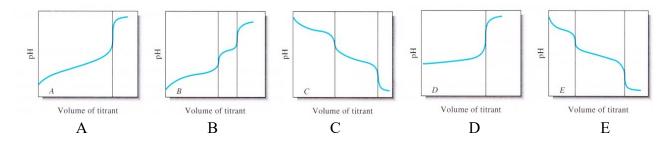
(a).

6. (Total 18 points)

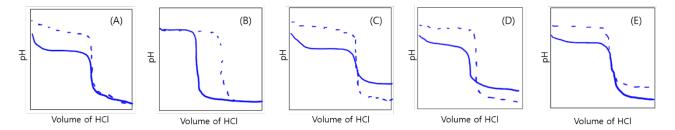
Use the table to answer the following questions.

Acid	Ka
HNO ₂	7.1×10^{-4}
CH ₃ COOH (HOAc)	1.75×10^{-5}
NH4 ⁺	5.70×10^{-10}
H ₃ PO ₄	7.11×10^{-3} ; 6.32×10^{-8} ; 4.5×10^{-13}
ethylene diammonia (*H ₃ NCH ₂ CH ₂ NH ₃ *)	1.42×10^{-7} ; 1.18×10^{-10}
salicylic acid (C ₆ H ₄ (OH)COOH)	1.06×10^{-3}
lactic acid	1.38×10^{-4}
Bromocresol green	2.19×10^{-5}
Bromothymol blue	7.94×10^{-8}
phenolphthalein	4.0×10^{-10}

- (a). (5 pts) Determine whether the aqueous solution of each of the following compounds is acidic, basic, or neutral.
- (1) NaNO₂
- (2) Na₂HPO₄
- (3) NaH₂PO₄
- (4) Na₃PO₄
- (5) NH₄OAc
- (b) (2 pts) Which titration curve would you expect when you titrate the aqueous solution of ethylene diammonia H₂NCH₂CH₂NH₂ (titrant) with an acid with known concentration (acid titrant)?



(c). (2 pts)Which figure describes curves for the titration of 0.10 M NH₃ (solid curve) and 0.10 M NaOH (dashed curve) with 0.10 M HCl correctly?



- (d). (3 pts) Which of the following titration will have the largest error (in the volume of titrant)?
- (1) Titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH using phenolphthalein
- (2) Titration of 50.00 mL of 0.000500 M HCl with 0.001000 M NaOH using bromothymol blue
- (3) Titration of 50.00 mL of 0.0100M H₂SO₄ with 0.0100M NaOH using bromocresol green
- (4) Titration of 50.00 mL of 0.0100M lactic acid with 0.0100M NaOH using bromothymol blue
- (5) Titration of 50.00 mL of 0.0100M NaH₂PO₄ with 0.0100M NaOH using bromocresol green
- (e). (3 pts) Which of the following is correct?
- (1) The pH of a buffer solution never changes regardless of addition of strong acid or base.
- (2) The pH of a buffer solution is constant regardless of the concentration of buffer components (HA and NaA).
- (3) Before equivalence points, a curve for the titration of acetic acid with NaOH is almost constant regardless of the concentration of acetic acid.
- (4) Buffer capacity is a function of pKa.
- (5) Strong base and its conjugate acid can form a buffer solution.
- (f). (3 pts) Which of the following is incorrect?
- (1) Indicators used for neutralization titration themselves are either acids or bases.
- (2) Species whose acid forms and conjugated base forms have distinctively different colors can be utilized as indicators.
- (3) Indicators' pH transition ranges depend on titrant's pKa's.
- (4) When a weak acid is titrated with a strong base, indicator with its pKa > 7 should be used.
- (5) When a strong acid is titrated with a strong base, the choice of indicator should depend on the concentration of analyte.

(a)

(1) $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$; thus, the solution will be basic.

(2)
$$\text{HPO}_4^{2-} + H_2 O \rightleftharpoons H_3 O^+ + \text{PO}_4^{3-} K_3 = 4.5 \times 10^{-13}$$

 $\text{HPO}_4^{2-} + H_2 O \rightleftharpoons \text{OH}^- + H_2 \text{PO}_4^- K_b = \frac{1.00 \times 10^{-14}}{6.32 \times 10^{-8}} = 1.58 \times 10^{-7}$

The second reaction is more dominant than the first one $(K_3 < K_b)$; thus, the solution will be basic.

(3)
$$H_2 PO_4^- + H_2 O \rightleftharpoons H_3 O^+ + HPO_4^- K_2 = 6.32 \times 10^{-8}$$

 $H_2 PO_4^- + H_2 O \rightleftharpoons OH^- + H_3 PO_4 K_b = \frac{1.00 \times 10^{-14}}{7.11 \times 10^{-3}} = 1.41 \times 10^{-12}$

Here K₂>K_b, so the first reaction is more dominant; thus, the solution will be acidic.

(4)
$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-K_b = \frac{1.00 \times 10^{-14}}{4.5 \times 10^{-13}} = 2.2 \times 10^{-2}$$
; thus, the solution will be basic.

(5)
$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_{NH4+} = 5.70 \times 10^{-10}$$

 $OAc^- + H_2O \rightleftharpoons HOAc + OH^- \qquad K_{OAc-} = K_w/K_{HOAc} = 5.71 \times 10^{-10}$

 $K_{NH4+} \sim K_{OAc-}$ Thus, the solution will be roughly neutral.

(b) The answer is C. Because of the following two reactions, the ethylene diammonia aquestion solution is basic and there are two equivalence points. Each reaction takes the same amount of titrant. Thus, D is incorrect.

$$H_2NCH_2CH_2NH_2 + H_2O \rightleftharpoons H_2NCH_2CH_2NH_3^+ + OH^-$$
 $K_{b1} = Kw/K_{a2} = 8.5 \times 10^{-5}$ $H_2NCH_2CH_2NH_3^+ + H_2O \rightleftharpoons {}^+H_3NCH_2CH_2NH_3^+ + OH^ K_{b2} = Kw/K_{a1} = 7.0 \times 10^{-8}$

(c) The answer is A.

Initial point before titration: pH of NaOH solution > pH of NH₃

Before equivalence point after beginning of the titration: There is NH₃ alone in the beginning and thus no buffer capacity will be observed. However, once the conjugated acid is formed, it becomes a buffer. Therefore, there will be a steep change in pH in the early phase while pH plateau will be observed afterwards.

At equivalence point: the same mole of HCl will be required to titrate either NaOH or NH₃, while the

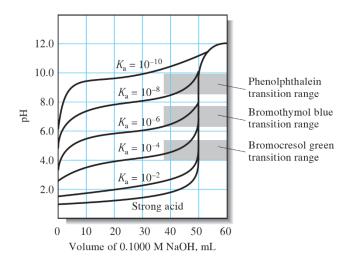
latter one will have a smaller change in pH near the equivalence point.

After the equivalence point: Adding more HCl is just like adding HCl into a neutral solution. Thus, the same change in pH for both solutions will be observed.

(d) The answer is 5.

The Ka's of indicators show that phenolphthalein, bromothymol blue, and bromocresol green are basic, neutral, and acidic indicators, respectively.

- 1 A strong acid and base reaction with a neutral equivalence point and large pH change => any indicator can be used.
- 2 A strong acid and base reaction with a neutral equivalence point but a small pH change due to dilute solutions => neutral indicator is ideal.
- 3 H₂SO₄ has an extremely large Ka₁ and thus both protons are dissociated at almost any pH. Only one neutral equivalence point (requiring double volume of basic solution compared to equivalent concentration HCl) with large pH change. => any indicator can be used.
- 4 Weak acid ($Ka\sim10^{-4}$) + strong base reaction; thus slightly basic equivalence point => neutral and basic indicators can be used (see below)
- 5 Very weak acid $H_2PO_4^-$ (Ka $\sim 10^{-8}$) + strong base reaction; basic equivalence point => acidic indicator cannot be used.



(e) The answer is 3.

(f) The answer is 3.

7. (Total 14 points)

Currently, CO₂ is being studied as a source of carbon atoms for synthesizing organic compounds. One possible reaction involves the conversion of CO₂ to methanol, CH₃OH.

$$CO_2(g) + 3H_2(g) \longrightarrow CH_3OH(g) + H_2O(g)$$

	$CO_{2(g)}$	H2(g)	CH ₃ OH(g)	H ₂ O(g)
$\Delta_{\rm r} H^{\rm o}$ (kJ/mol)	-393.5	0	-200.7	-241.8
$\Delta_{r}S^{o}$ (J/mol K)	213.7	130./	239.8	188.8

- (a) (6 pts) Using the data provided in the table, determine the reaction enthalpy, entropy, and Gibbs free energy at 298K.
- (b) (2 pt) At 298K, does this reaction proceed to any significant extent?
- (c) (3 pts) Explain how the production of methanol can be favored by either raising or lowering the temperature from 298K.
- (d) (3 pts) Calculate the equilibrium constant at 500K.
- (a) We determine the values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ from the data in Appendix D, and then the value of $\Delta_r G^\circ$ at 25 °C = 298 K.

$$\begin{split} & \Delta_{\rm r} H^{\circ} = \Delta_{\rm f} H^{\circ} \Big[{\rm CH_{3}OH}(g) \Big] + \Delta_{\rm f} H^{\circ} \Big[{\rm H_{2}O}(g) \Big] - \Delta_{\rm f} H^{\circ} \Big[{\rm CO_{2}}(g) \Big] - 3 \, \Delta_{\rm f} H^{\circ} \Big[{\rm H_{2}}(g) \Big] \\ & = -200.7 \, {\rm kJ/mol} + \big(-241.8 \, {\rm kJ/mol} \big) - \big(-393.5 \, {\rm kJ/mol} \big) - 3 \big(0.00 \, {\rm kJ/mol} \big) = -49.0 \, {\rm kJ/mol} \Big] \\ & \Delta_{\rm r} S^{\circ} = S^{\circ} \Big[{\rm CH_{3}OH}(g) \Big] + S^{\circ} \Big[{\rm H_{2}O}(g) \Big] - S^{\circ} \Big[{\rm CO_{2}}(g) \Big] - 3 \, S^{\circ} \Big[{\rm H_{2}}(g) \Big] \\ & = (239.8 + 188.8 - 213.7 - 3 \times 130.7) \, {\rm J} \, \, {\rm mol^{-1}K^{-1}} = -177.2 \, {\rm J} \, {\rm mol^{-1}K^{-1}} \\ & \Delta_{\rm r} G^{\circ} = \Delta_{\rm r} H^{\circ} - T \Delta_{\rm r} S^{\circ} = -49.0 \, {\rm kJ/mol} - 298 \, {\rm K} \left(-0.1772 \, {\rm kJ} \, \, {\rm mol^{-1}K^{-1}} \right) = +3.81 \, {\rm kJ/mol} \\ & 2 \, \, {\rm pts} \, \, {\rm each} \end{split}$$

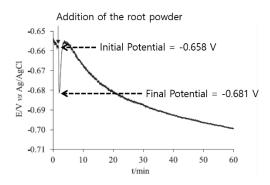
- (b) Because the value of $\Delta_r G^{\circ}$ is positive, this reaction does not proceed in the forward direction at 25°C.
- (c) Because the value of $\Delta_r H^\circ$ is negative and that of $\Delta_r S^\circ$ is negative, the reaction is *non-spontaneous* at high temperatures, if reactants and products are *in their standard states*. The reaction will proceed slightly in the forward direction, however, to produce an equilibrium mixture with small quantities of $CH_3OH(g)$ and $H_2O(g)$. Also, because the forward reaction is exothermic, this reaction is favored by lowering the temperature. That is, the value of K increases with decreasing temperature.

(d)
$$\Delta_{\rm r} G_{500{\rm K}}^{\rm o} = \Delta_{\rm r} H^{\circ} - T \Delta_{\rm r} S^{\circ} = -49.0 \,\text{kJ/mol} - 500.\text{K} \left(-0.1772 \,\text{kJ mol}^{-1} \,\text{K}^{-1} \right) = 39.6 \,\text{kJ/mol}$$
$$= 39.6 \times 10^{3} \,\text{J/mol} = -RT \,\text{ln} \, K_{p}$$
$$\ln K = \frac{-\Delta_{\rm r} G^{\circ}}{RT} = \frac{-39.6 \times 10^{3} \,\text{J/mol}}{8.3145 \,\text{J} \,\text{mol}^{-1} \,\text{K}^{-1} \times 500. \,\text{K}} = -9.53; \quad K = \mathrm{e}^{-9.53} = 7.3 \times 10^{-5}$$

8. (Total 13 points)

Industrial development has resulted in the release of toxic compounds such as heavy metals into the environment. One of novel removal strategies is biosorption, which refers to the adsorption of metal ions on dead biomass such as algae, crop residues, and fungi. This metal uptake by nonliving materials is an emerging low-cost, effective, and environmentally friendly technology.

The roots of *Eichhornia crassipes* were collected from a greenhouse, washed with deionized water, dried at oven and ground to a fine powder. To examine the biosorption capability of this material, Cd(NO₃)₂ in 0.100 M NaClO₄ solution was prepared and its open circuit potential was measured at -0.658 V with respect to an Ag|AgCl(NaCl 3 M) reference electrode. Upon addition of the root powder to the Cd²⁺ solution, the potential drops down to -0.681 V.



(a) (3 pts) Which of the following is a correct scheme for this potential measurement?

- 1. AgCl | Ag | NaCl (3M) || Cd(II) | Cd
- 2. AgCl | Ag | NaCl (3M)|| Cd | Cd (II)
- 3. Cd(II) | Cd || AgCl | NaCl (3M) | Ag
- 4. Cd | Cd (II) || AgCl | NaCl (3M) | Ag
- 5. Ag | AgCl | NaCl (3M) || Cd(II) | Cd

(b) (5 pts)With respect to SHE, $E_{Ag(I)/Ag^{+}}^{\circ}$ is + 0.799 V, and K_{sp} for AgCl(s) is $K_{sp} = [Ag^{+}][Cl^{-}] = 1.82 \times 10^{-10}$. Then, what is the electric potential E_{ref} of the Ag|AgCl (NaCl 3M) reference electrode with respect to SHE?

(c) (3 pts)The standard reduction potential of Cd²⁺ is -0.403 V with respect to SHE. What was the initial concentration of Cd(NO₃)₂?

(d). (2 pts) What percentage of Cd^{2+} was adsorbed by the root powder?

- (a) The answer is 5.
- (b) The answer is ± 0.194 V.

$$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$$
 $\Delta G_{1}^{0} = -zFE^{\circ} = -1 \cdot F \cdot (0.799 V)$
 $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$ $\Delta G_{2}^{0} = -RTln K = -RTln(1.82 \times 10^{-10})$

AgCl(s) +
$$e^- \to Ag(s) + Cl^-(aq)$$
 $\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$
= $-1 \cdot F \cdot (0.799 \text{ V}) - RT \ln(1.82 \times 10^{-10})$
 $\Delta G_3 = \Delta G_3^0 + RT \ln Q = -zFE_{ref}$
 $Q = [Cl^-(aq)] = 3 \text{ M}$

$$= -1 \cdot F \cdot (0.799 \, \text{V}) - RT ln(1.82 \times 10^{-10}) + RT ln([Cl^{-}(aq)]) = -1 \cdot F \cdot E_{ref}$$

Divide both sides by -F, and we get:

$$E_{ref} = (0.799 \text{ V}) + \left(\frac{RT}{F}\right) \ln(1.82 \times 10^{-10}) - \left(\frac{RT}{F}\right) \ln(3 \text{ M}) = 0.194 \text{ V}$$

(c) The answer is 8.7×10^{-3} M.

$$\begin{split} E_{cell} &= E^0(Cd(II)|Cd) + (0.0257/2)ln[Cd(II)] - E_{ref} \\ -0.658 \ V &= -0.403 \ V + (0.0257/2)ln[Cd(II)] - 0.194 \ V \\ &[Cd(II)]_{initial} = 8.7 \times 10^{-3} M \end{split}$$

(d) The answer is 83 %.

Using the above eqn, $[Cd(II)]_{final} = 1.5 \times 10^{-3} \text{ M}$

9. (Total 10 points)

For the voltaic cell,

$$Fe(s) | Fe^{2+}(aq) || Fe^{3+}(aq), Fe^{2+}(aq) | Pt(s)$$

- (a) (2 pts) Derive a balanced equation for the reaction occurring in the cell
- (b) (2 pts) If $E^{o}_{cell} = 1.21$ V, calculate $\Delta_{r}G^{o}$ and the equilibrium constant for the reaction.
- (c) (4 pts) Determine the potential for the cell:

$$Fe(s) \mid Fe^{2^{+}} \ (aq, \ 1.0 \times 10^{\text{-}3} \ M) \parallel Fe^{3^{+}} \ (aq, \ 1.0 \times 10^{\text{-}3} \ M), \ Fe^{2^{+}} \ (aq, \ 0.10 \ M) \mid Pt(s)$$

- (d) (2 pts) In light of (b) and (c), what is the likelihood of being able to observe the disproportionation of Fe²⁺ into Fe³⁺ and Fe under standard conditions?
- (a) We proceed by first deriving a balanced equation for the reaction occurring in the cell:

Oxidation:
$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$$

Reduction:
$$\{Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)\} \times 2$$

Net:
$$Fe(s) + 2 Fe^{3+}(aq) \rightarrow 3 Fe^{2+}(aq)$$

(b) $\Delta_r G^{\circ}$ and the equilibrium constant K can be calculated using

$$\Delta_{\rm r}G^{\circ} = -zFE^{\circ}_{\rm cell} = -RT \ln K$$
:

$$\Delta_{\rm r}G^{\circ} = -zFE^{\circ}_{\rm cell} = -2 \times 96485 \,\mathrm{C \ mol^{-1}} \times 1.21 \,\mathrm{V} = -233.5 \,\mathrm{kJ \ mol^{-1}}$$

$$\Delta_r G^{\circ} = -RT \ln K = -8.314 \text{ J K}^{-1} \text{mol}^{-1} \times 298.15 \text{ K} \times \ln K = -233.5 \times 1000 \text{ J mol}^{-1}$$

$$\ln K = 94.2 \Rightarrow K = e^{94.2} = 8.1 \times 10^{40}$$

(c) Before calculating voltage using the Nernst equation, we need to re-write the net reaction to take into account concentration gradient for Fe²⁺(aq):

Oxidation:
$$Fe(s) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3} \text{ M}) + 2 e^{-}$$

Reduction:
$$\{Fe^{3+}(aq, 1.0 \times 10^{-3} \text{ M}) + e^{-} \rightarrow Fe^{2+}(aq, 0.10 \text{ M})\} \times 2$$

Net:
$$Fe(s) + 2 Fe^{3+}(aq, 1.0 \times 10^{-3} M) \rightarrow Fe^{2+}(aq, 1.0 \times 10^{-3} M) + 2 Fe^{2+}(aq, 0.10 M)$$

Therefore.

$$Q = \frac{1.0 \times 10^{-3} \times (0.10)^2}{(1.0 \times 10^{-3})^2} = 10$$

Now, we can apply the Nerst equation to calculate the voltage:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{z} \ln Q = 1.21 \text{ V} - \frac{0.0257}{2} \ln 10 = 1.18 \text{ V}$$

(d) From parts (b) and (c) we can conclude that the reaction between Fe(s) and Fe³⁺(aq) is spontaneous. The reverse reaction (i.e. disproportionation of Fe²⁺(aq)) must therefore be nonspontaneous.

Physical Constants

Avogadro's number	$N_A = 6.02214179 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	$a_0 = 0.52917720859 \text{ Å} = 5.2917720859 \text{x} 10^{-11} \text{ m}$
Boltzmann's constant	$K_B = 1.3806504 \times 10^{-23} \text{ J K}^{-1}$
Electronic charge	$e = 1.602176487 \times 10^{-19} \text{ C}$
Faraday constant	$F = 96485.3399 \text{ C mol}^{-1}$
Masses of fundamental particles:	
Electron	$m_e = 9.10938215 \times 10^{-31} \text{ kg}$
Proton	$m_P = 1.672621637 \times 10^{-27} \text{ kg}$
Neutron	$m_n = 1.674927211 \times 10^{-27} \text{ kg}$
Permittivity of vacuum	$\epsilon_o = 8.854187817 \ x \ 10^{\text{-}12} \ C^{\text{-}2} \ J^{\text{-}1} \ m^{\text{-}1}$
Planck's constant	$h = 6.62606896 \times 10^{-34} \text{ J s}$
Ratio of proton mass to electron mass	$m_P / m_e = 1836.15267247$
Speed of light in a vacuum	$c = 2.99792458 \times 10^8 \text{ m s}^{-1} \text{ (exactly)}$
Standard acceleration of terrestrial gravity	$g = 9.80665 \text{ m s}^{-2} \text{ (exactly)}$
Universal and constant	$R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$
Universal gas constant	$= 0.0820574 \text{ L atm mol}^{-1} \text{ K}^{-1}$

Values are taken from the 2006 CODATA recommended values, as listed by the National Institute of Standards and Technology.

Conversion factors

Ångström	$1 \text{ Å} = 10^{-10} \text{ m}$
Atomic mass unit	$1 \text{ u} = 1.660538782 \text{ x } 10^{-27} \text{ kg}$
	$1 \text{ u} = 1.492417830 \text{ x } 10^{-10} \text{ J} = 931.494028 \text{ MeV}$ (energy equivalent form
	$E=mc^2)$
Calorie	1 cal = 4.184 J (exactly)
Electron volt	$1 \text{ eV} = 1.602177 \text{ x } 10^{-19} \text{ J} = 96.485335 \text{ kJ mol}^{-1}$
Foot	1 ft = $12 \text{ in} = 0.3048 \text{ m (exactly)}$
Gallon (U. S.)	1 gallon = 4 quarts = 3.785412 L (exactly)
Liter	$1 L = 10^{-3} \text{ m}^3 = 10^3 \text{ cm}^3 \text{ (exactly)}$

Liter-atmosphere 1 L atm = 101.325 J (exactly)

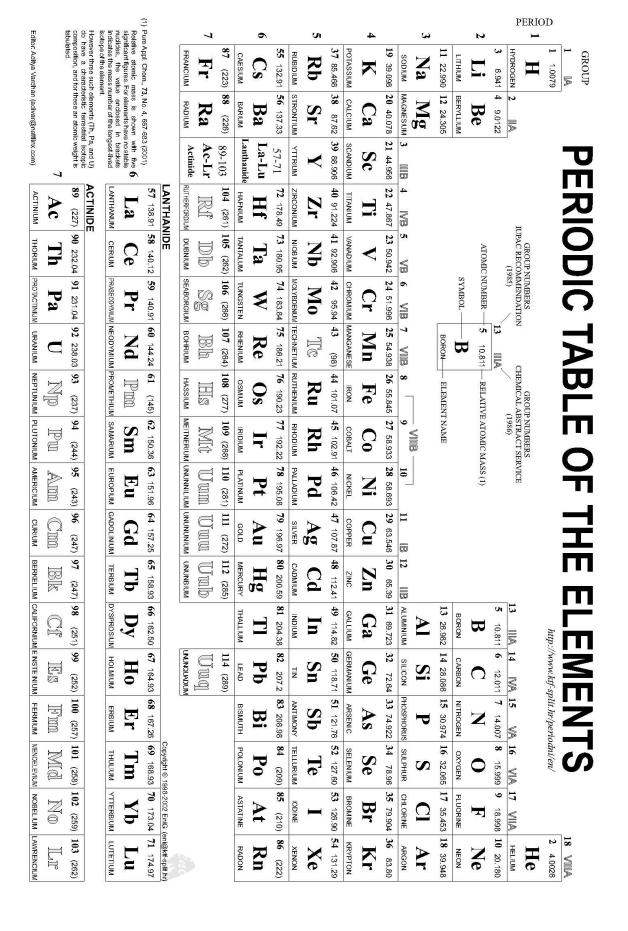
Metric ton 1 t = 1000 kg (exactly)

Pound 1 lb = 16 oz = 0.4539237 kg (exactly)

Rydberg 1 Ry = $2.17987197 \times 10^{-18} J = 1312.7136 \text{ kJ mol}^{-1} = 13.60569193 \text{ eV}$

Standard atmosphere $1 \text{ atm} = 1.01325 \text{ x } 10^5 \text{ Pa} = 1.01325 \text{ x } 10^5 \text{ kg m}^{-1} \text{ s}^{-2} \text{ (exactly)}$

Torr 1 torr = 133.3224 Pa



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