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5.111 Principles of Chemical Science
Fall 2008

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Third Hour Exam**5.111**

Write your name below. This is a closed book exam. Solve all 6 problems. Read all problems thoroughly and read all parts of a problem. Many of the latter parts of a problem can be solved without having solved earlier parts. Show all work to receive full credit. Physical constants, formulas, standard reduction potentials, and a periodic table are given on the last two pages of the exam. You may detach the last 2 pages after the exam has started.

1. THERMODYNAMICS (12 points)_____

2. CHEMICAL EQUILIBRIUM (12 points)_____

3. ACID-BASE EQUILIBRIUM (12 points)_____

4. ACID-BASE TITRATION (22 points)_____

5. OXIDATION/REDUCTION (30 points)_____

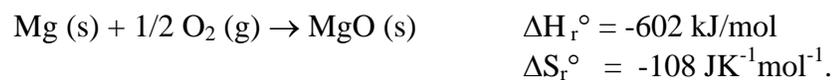
6. OXIDATION/REDUCTION (12 points)_____

Total (100 points)_____

Name_____

1. THERMODYNAMICS (12 points total)

Consider the formation of MgO (s).



(Assume that ΔH_r° and ΔS_r° are independent of temperature.)

(a) (6 points) Calculate ΔG_r° for the formation of MgO (s) at 0 °C (273 K). Is the reaction spontaneous or non-spontaneous at 0 °C?

(b) (6 points) Is there a temperature at which the formation of MgO switches from spontaneous to non-spontaneous or vice versa? If no, explain briefly why not. If yes, calculate the temperature (T^*) at which the spontaneity of the reaction switches.

2. CHEMICAL EQUILIBRIUM (12 points total)

Explain the effect of each of the following stresses on the position of the following equilibrium:



The reaction as written is exothermic.

(a) (4 points) The equilibrium mixture is cooled. Explain your answer.

(b) (4 points) The volume of the equilibrium mixture is reduced at constant temperature. Explain your answer.

(c) (4 points) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant. Explain your answer.

3. ACID-BASE EQUILIBRIUM (12 points total)

(a) (6 points) Calculate the pH in a solution prepared by dissolving 0.050 mol of acetic acid (CH_3COOH) and 0.20 mol of sodium acetate (NaCH_3COO) in water and adjusting the volume to 500. mL. The pK_a for acetic acid (CH_3COOH) is 4.75.

(b) (6 points) Suppose 0.010 mol of NaOH is added to the buffer from part (a). Calculate the pH of the solution that results.

4. ACID-BASE TITRATION (22 points total)

A 10.0 mL sample of 0.20 M HNO_2 (aq) solution is titrated with 0.10 M NaOH (aq). (K_a of HNO_2 is 4.3×10^{-4}).

(a) (5 points) Calculate the volume of NaOH needed to reach the equivalence point.

(b) (12 points) Calculate the pH at the equivalence point. Check assumptions for full credit.

(c) (5 points) Calculate the pH with 2.00 mL of NaOH added past the equivalence point.

5. OXIDATION/REDUCTION REACTIONS (30 points total)

For a cell constructed with a Cu (s) | Cu²⁺ (aq) anode and Ag⁺ (aq) | Ag (s) cathode at 25.00 °C.

(a) (5 points) Write the overall balanced equation under acidic conditions.

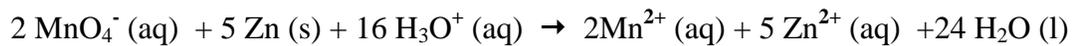
(b) (13 points) Calculate the cell potential at 25.0°C under non-standard conditions:
[Cu²⁺] = 0.300 M and [Ag⁺] = 0.0500 M

(c) (6 points) Is the above cell a galvanic or electrolytic cell under standard conditions? Explain your choice of answer.

(d) (6 points) Of the following, list all of the atoms or ions that will oxidize Ag (s):
Au⁺ (aq), Pb²⁺ (aq), Zn (s), Cr³⁺ (aq), Ni (s), Au (s).

6. OXIDATION-REDUCTION (12 points total)

The following reaction has an $\Delta E^\circ(\text{cell})$ of 2.27 V and a $K = 10^{383}$ at 25°C:



(a) (4 points) What is the oxidation number for Mn in MnO_4^- ?

(b) (4 points) How many electrons are transferred in this reaction (in other words, what is “n”)?

(c) (4 points) Would you expect a large quantity of MnO_4^- ions at equilibrium at 25°C? Why or why not?

Equations and constants for Exam 3

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\mathfrak{F} \text{ (Faraday's constant)} = 96,485 \text{ C mol}^{-1}$$

$$1\text{V} = 1 \text{ J/C}$$

$$1\text{A} = 1\text{C/s}$$

$$K_w = 1.00 \times 10^{-14} \quad \text{at } 25^\circ\text{C}$$

$$14.00 = \text{pH} + \text{pOH} \quad \text{at } 25^\circ\text{C}$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\ln \left(\frac{K_2}{K_1} \right) = - \left(\frac{\Delta H^\circ}{R} \right) \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_w = K_a K_b$$

$$\text{p}K_a = -\log [K_a]$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} \cong \text{p}K_a - \log \left(\frac{[\text{HA}]}{[\text{A}^-]} \right)$$

$$\Delta E^\circ(\text{cell}) = E^\circ(\text{cathode}) - E^\circ(\text{anode})$$

$$RT/\mathfrak{F} = 0.025693 \text{ V at } 25.00^\circ\text{C}$$

$$\mathfrak{F}/RT = 38.921 \text{ V}^{-1} \text{ at } 25.00^\circ\text{C}$$

$$\Delta E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/\mathfrak{F} n) \ln Q$$

$$\ln K = (n\mathfrak{F}/RT) \Delta E^\circ$$

$$E_3^\circ = [n_1 E_1^\circ(\text{reduction}) - n_2 E_2^\circ(\text{oxidation})]/n_3$$

$$\Delta G^\circ_{\text{cell}} = -(n)(\mathfrak{F}) \Delta E^\circ_{\text{cell}}$$

$$Q = It$$

Standard Reduction Potentials at 25°C

Half-Reactions	E° (volts)
$\text{Au}^+ (\text{aq}) + \text{e}^- \Rightarrow \text{Au} (\text{s})$	1.69
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$	1.51
$\text{Ag}^+ (\text{aq}) + 1\text{e}^- \rightarrow \text{Ag} (\text{s})$	0.80
$\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Cu} (\text{s})$	0.34
$\text{AgCl} (\text{s}) + 1\text{e}^- \rightarrow \text{Ag} (\text{s}) + \text{Cl}^- (\text{aq})$	0.22
$\text{Sn}^{4+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+} (\text{aq})$	0.15
$2\text{H}^+ (\text{aq}) + 2\text{e}^- \Rightarrow \text{H}_2$	0
$\text{Pb}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Pb} (\text{s})$	-0.13
$\text{Sn}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Sn} (\text{s})$	-0.14
$\text{Ni}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Ni} (\text{s})$	-0.23
$\text{Fe}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Fe} (\text{s})$	-0.44
$\text{Cr}^{3+} (\text{aq}) + 3\text{e}^- \Rightarrow \text{Cr} (\text{s})$	-0.74
$\text{Zn}^{2+} (\text{aq}) + 2\text{e}^- \Rightarrow \text{Zn} (\text{s})$	-0.76

