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___ ANSWER KEY ____________________
1. THERMODYNAMICS (14 points total)
Consider the formation of MgO (s). Assume that $\Delta H^\circ_r$ and $\Delta S^\circ_r$ are independent of temperature.

$$\text{Mg (s) + 1/2 O}_2 (g) \rightarrow \text{MgO (s)}$$

$\Delta H^\circ_r = -602 \text{ kJ/mol}$
$\Delta S^\circ_r = -108 \text{ JK}^{-1}\text{mol}^{-1}$.

(a) (6 points) Calculate $\Delta G^\circ_r$ for the formation of MgO (s) at 0 ℃ (273 K). Is the reaction spontaneous or non-spontaneous at 0 ℃?

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

$$\Delta G = -602 \text{ kJ/mol} - 273(-0.108 \text{ kJmol}^{-1}\text{K}^{-1})$$

$$\Delta G = -572.52$$

- $573 \text{ kJ/mol}$ spontaneous

(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.

Yes.

$$0 = \Delta H - T^*\Delta S$$

$$T^* = \Delta H / \Delta S$$

$$T^* = \frac{-602 \text{ kJ/mol}}{-0.108 \text{ kJ/mol•K}}$$

$$T^* = 5574 \text{ K}$$

$T^* = 5570 \text{ K}$
2. CHEMICAL EQUILIBRIUM (12 points total)

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

\[ 3 \text{ NO (g)} \rightleftharpoons \text{N}_2\text{O (g)} + \text{NO}_2 (g) \]

The reaction as written is exothermic.

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

\[ \longrightarrow \text{ shift toward products} \]

Heat is produced in the forward direction. As heat is removed, the reaction will shift to produce more heat.

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

\[ \longrightarrow \text{ shift toward products} \]

If volume decreases, then the total pressure (and each partial pressure) increases. 3 mol of g to 2 mol of g reaction shifts to 2 mol of gas.

(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.

\[ \leftarrow \text{ shift toward reactants} \]

If total pressure is the same, volume must have increased. If volume increased, the partial pressure of each gas decreased, so shift to side with more mol of gas to compensate

\[ 3 \text{ mol g} \leftarrow 2 \text{ mol g} \]
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 (CH₃COOH) and 0.20 mol of sodium acetate (NaCH₃COO) in water and adjusting the volume to 500 mL. The pKa for acetic acid (CH₃COOH) is 4.75.

\[ \text{pH} \approx \text{pKa} - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right) \]

\[ \text{pH} \approx 4.75 - \log \left( \frac{0.050 \text{ mol}}{0.20 \text{ mol}} \right) \quad \text{ok to use mol b/c volume is the same} \]

\[ \text{pH} = 4.75 - \log 0.25 \]

\[ \text{pH} = 4.75 + 0.602 \]

\[ \text{pH} \approx 5.35 \]

(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.

\[ \text{mol of HA} = 0.050 \text{ mol} - 0.010 \text{ mol} = 0.040 \text{ mol} \]

\[ \text{mol of A}^- = 0.20 \text{ mol} + 0.010 \text{ mol} = 0.21 \text{ mol} \]

\[ \text{pH} \approx \text{pKa} - \log \left( \frac{[\text{HA}]}{[\text{A}^-]} \right) \]

\[ \text{pH} \approx 4.75 - \log \left( \frac{0.040 \text{ mol}}{0.21 \text{ mol}} \right) \quad \text{ok to use mol b/c volume is the same} \]

\[ \text{pH} = 4.75 - \log 0.19 \]

\[ \text{pH} = 4.75 + 0.721 \]

\[ \text{pH} = 5.47 \]
4. ACID-BASE TITRATION (22 points total)
A 10.0 mL sample of 0.20 M HNO₂ (aq) solution is titrated with 0.10 M NaOH (aq). (Kₐ of HNO₂ is 4.3 x 10⁻⁴).

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

\[
0.0100 \text{ L} \times 0.20 \text{ mol} = 0.0020 \text{ mol of NaOH needed}
\]

\[
0.0020 \text{ mol NaOH} \times \frac{\text{L}}{0.10 \text{ mol}} = 0.02 \text{ L or 20 mL}
\]

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

This is a weak base problem. All of the HNO₂ is converted to NO₂⁻.

\[
\text{initial mol of } \text{NO}_2^- = \frac{0.0020 \text{ mol}}{0.030 \text{ L}} = 0.0667 \text{ M}
\]

\[
\begin{array}{ccc}
& \text{NO}_2^- & + & \text{H}_2\text{O} & \rightleftharpoons & \text{HNO}_2 & + & \text{OH} \\
\text{I} & 0.0667 & & 0 & & 0 \\
\text{C} & -x & & +x & & +x \\
\text{E} & 0.0667 - x & & +x & & +x \\
\end{array}
\]

\[
K_w = K_aK_b \\
K_b = \frac{1.00 \times 10^{-14}}{4.3 \times 10^{-4}} = 2.33 \times 10^{-11} \text{ or } 2.33 \times 10^{-11}
\]

\[
K_b = \frac{x^2}{0.0667 - x} \approx \frac{x^2}{0.0667} = 2.33 \times 10^{-11}
\]

\[
x = 1.247 \times 10^{-6} = [\text{OH}]
\]

\[
p\text{OH} = -\log (1.247 \times 10^{-6})
\]

\[
p\text{OH} = 5.90
\]

\[
p\text{H} = 14.00 - 5.90 = 8.10 \text{ (accept 8.08, 8.09, or 8.10)}
\]

Check assumption:

\[
\frac{1.247 \times 10^{-6}}{0.0667} \times 100 \% = 0.00186%
\]
(e) (5 points) Calculate the pH with 2.00 mL of NaOH added past the equivalence point.

\[
0.0020 \text{ L} \times \frac{0.10 \text{ mol}}{\text{L}} = 0.00020 \text{ mol NaOH}
\]

\[
[\text{OH}^-] = \frac{0.00020 \text{ mol}}{10.0 \text{ mL} + 20. \text{ mL} + 2.00 \text{ mL}} = 0.00625 \text{ M}
\]

\[
\text{new volume} = 0.032 \text{ L}
\]

\[
\text{pOH} = -\log [\text{OH}^-] = -\log (0.00625)
\]

\[
= 2.204
\]

\[
\text{pH} = 14.00 - 2.204 = 11.80
\]

5. OXIDATION/REDUCTION REACTIONS (30 points total)
For a cell constructed with a Cu (s) | Cu\(^{2+}\) (aq) anode and Ag\(^+\) (aq) | Ag (s) cathode at 25.0°C.

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

\[
\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \\
2 (\text{Ag}^+ + e^- \rightarrow \text{Ag})
\]

\[
\text{Cu (s)} + 2\text{Ag}^+ (\text{aq}) + 2e^- \rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{Ag} (\text{s}) + 2e^-
\]

\[
\text{Cu (s)} + 2\text{Ag}^+ (\text{aq}) \rightarrow \text{Cu}^{2+} (\text{aq}) + 2\text{Ag} (\text{s})
\]
(b) (13 points) Calculate the cell potential at 25.0°C under non-standard conditions: [Cu²⁺] = 0.300 M and [Ag⁺] = 0.0500 M

\[ E_{\text{cell}}^\circ = E^\circ (\text{cathode}) - E^\circ (\text{anode}) \]

\[ E_{\text{cell}}^\circ = 0.80 - 0.34 = 0.46 \text{ V} \]

n = 2

\[ Q = \frac{(0.300)}{(0.0500)^2} \]

\[ E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{(1/n)(RT/\Delta F)}{\ln Q} \]

\[ = E_{\text{cell}}^\circ - \frac{0.025693 \text{ V}}{2} \frac{\ln 120}{4.787} \]

\[ = 0.46 \text{ V} - 0.06150 \text{ V} \]

\[ = 0.40 \text{ V} \]

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

**galvanic**

\( \Delta E^\circ \) is positive, so \( \Delta G^\circ \) is negative

(d) (6 points) Of the following, list all of the atoms or ions that will oxidize Ag (s):

\( \text{Au}^+ (aq), \text{Pb}^{2+} (aq), \text{Zn} (s), \text{Cr}^{3+} (aq), \text{Ni} (s), \text{Au} (s). \)

\( \text{Au}^+ \) only

Higher redox potential than Ag⁺
6. OXIDATION-REDUCTION (12 points total)
The following reaction has an $\Delta E^\circ$ (cell) of 2.27 V and a $K = 10^{383}$ at 25°C:

$$2 \text{ MnO}_4^- (aq) + 5 \text{ Zn} (s) + 16 \text{ H}_3\text{O}^+ (aq) \rightarrow 2\text{Mn}^{2+} (aq) + 5 \text{ Zn}^{2+} (aq) + 24 \text{ H}_2\text{O} (l)$$

(a) (4 points) What is the oxidation number for Mn in MnO$_4^-$?

The oxidation number for Mn is +7, as the total charge on the molecule is -1.

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

Consider either:

$$2 \left( \text{MnO}_4^- + 5e^- \rightarrow \text{Mn}^{2+} \right)$$

$$\uparrow \quad \text{+7} \quad \uparrow \text{+2}$$

or

$$5 \left( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \right)$$

$$\uparrow \quad \text{0} \quad \uparrow \text{+2}$$

10 electrons $n = 10$

(c) (4 points) Would you expect a large quantity of MnO$_4^-$ ions at equilibrium at 25°C? Why or why not?

No.

Expect a small quantity of MnO$_4^-$ ions because $K$ is huge.
Equations and constants for Exam 3

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

\[ pK_a = -\log [K_a] \]

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

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

\[ 1V = 1 \text{ J/C} \]

\[ 1A = 1\text{C/s} \]

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

\[ 14.00 = \text{pH} + \text{pOH} \text{ at } 25^\circ\text{C} \]

\[ RT/\mathcal{F} = 0.025693 \text{ V at } 25.00^\circ\text{C} \]

\[ \mathcal{F}/RT = 38.921 \text{ V}^{-1} \text{ at } 25.00^\circ\text{C} \]

\[ \Delta G^\circ = -RT \log K \]

\[ \Delta G = \Delta G^\circ + RT \log Q \]

\[ \Delta G = \Delta H^\circ - T\Delta S^\circ \]

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

\[ \Delta G^\circ_{\text{cell}} = -(n)(\mathcal{F}) \Delta E^\circ_{\text{cell}} \]

\[ K_w = K_a K_b \]

Standard Reduction Potentials at 25°C

<table>
<thead>
<tr>
<th>Half-Reactions</th>
<th>( E^\circ ) (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(^{3+}) (aq) + e(^-) (\rightarrow) Au (s)</td>
<td>1.69</td>
</tr>
<tr>
<td>( \text{MnO}_4^- ) (aq) + 8H(^+) (aq) + 5e(^-) (\rightarrow) Mn(^{2+}) (aq) + 4H(_2)O (l)</td>
<td>1.51</td>
</tr>
<tr>
<td>Ag(^+) (aq) + e(^-) (\rightarrow) Ag (s)</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu(^{2+}) (aq) + 2e(^-) (\rightarrow) Cu (s)</td>
<td>0.34</td>
</tr>
<tr>
<td>AgCl (s) + e(^-) (\rightarrow) Ag (s) + Cl(^-) (aq)</td>
<td>0.22</td>
</tr>
<tr>
<td>Sn(^{4+}) (aq) + 2e(^-) (\rightarrow) Sn(^{2+}) (aq)</td>
<td>0.15</td>
</tr>
<tr>
<td>2H(^+) (aq) + 2e(^-) (\rightarrow) H(_2)</td>
<td>0</td>
</tr>
<tr>
<td>Pb(^{2+}) (aq) + 2 e(^-) (\rightarrow) Pb (s)</td>
<td>-0.13</td>
</tr>
<tr>
<td>Sn(^{2+}) (aq) + 2 e(^-) (\rightarrow) Sn (s)</td>
<td>-0.14</td>
</tr>
<tr>
<td>Ni(^{2+}) (aq) + 2 e(^-) (\rightarrow) Ni (s)</td>
<td>-0.23</td>
</tr>
<tr>
<td>Fe(^{2+}) (aq) + 2 e(^-) (\rightarrow) Fe (s)</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cr(^{3+}) (aq) + 3 e(^-) (\rightarrow) Cr (s)</td>
<td>-0.74</td>
</tr>
<tr>
<td>Zn(^{2+}) (aq) + 2 e(^-) (\rightarrow) Zn (s)</td>
<td>-0.76</td>
</tr>
</tbody>
</table>
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