

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 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?

$$\begin{aligned} \Delta G &= \Delta H - T\Delta S \\ \Delta G &= -602 \text{ kJ/mol} - 273(-0.108 \text{ kJmol}^{-1}\text{K}^{-1}) \\ &\quad \underbrace{\hspace{10em}}_{+ 29.48} \end{aligned}$$

$$\Delta G = -572.52$$

- 573 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.

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

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

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

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

$$\mathbf{T^* = 5570 \text{ K}}$$

2. CHEMICAL EQUILIBRIUM (12 points total)

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



The reaction as written is exothermic.

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

—————→ 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.

—————→ 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.

←————— 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 mol g ← 2 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 (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.

buffer problem

$$\text{pH} \cong \text{pK}_a - \log \left[\frac{[\text{HA}]}{[\text{A}^-]} \right]$$

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

$$\text{pH} \cong 4.75 - \underbrace{\log 0.25}_{+ 0.602}$$

$$\text{pH} = 4.75 + 0.602$$

$$\text{pH} \cong \mathbf{5.35}$$

(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.

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

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

$$\text{pH} \cong \text{pK}_a - \log \left[\frac{[\text{HA}]}{[\text{A}^-]} \right]$$

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

$$\text{pH} = 4.75 - \underbrace{\log 0.19}_{+ 0.721}$$

$$\text{pH} = 4.75 + 0.721$$

$$\text{pH} = \mathbf{5.47}$$

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). (K_a of HNO₂ is 4.3 x 10⁻⁴).

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

$$0.0100 \text{ L} \times \frac{0.20 \text{ mol}}{\text{L}} = 0.0020 \text{ mol of NaOH needed}$$

$$0.0020 \text{ mol NaOH} \times \frac{\text{L}}{0.10 \text{ mol}} = 0.020 \text{ L or } \mathbf{20. \text{ mL}}$$

(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⁻.

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

	NO ₂ ⁻	+	H ₂ O	⇌	HNO ₂	+	OH ⁻
I	0.0667				0		0
C	-x				+x		+x
E	0.0667 - x				+x		+x

$$K_w = K_a K_b \quad K_b = \frac{1.00 \times 10^{-14}}{4.3 \times 10^{-4}} = 0.233 \times 10^{-10} \text{ or } 2.33 \times 10^{-11}$$

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

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

$$\text{pOH} = -\log(1.247 \times 10^{-6})$$

$$\text{pOH} = 5.90$$

$$\mathbf{pH} = 14.00 - 5.90 = \mathbf{8.10} \text{ (accept 8.08, 8.09, or 8.10)}$$

Check assumption:

$$\frac{1.247 \times 10^{-6}}{0.0667} \times 100 \%$$

$$= 0.00186\%$$

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

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

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

$$\text{new volume} = 0.032 \text{ L}$$

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

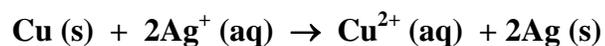
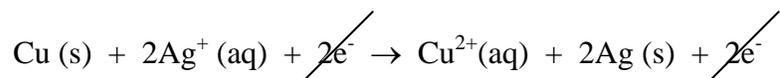
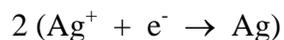
$$= 2.204$$

$$\text{pH} = 14.00 - 2.204 = \mathbf{11.80}$$

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 25.0°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:
 $[\text{Cu}^{2+}] = 0.300 \text{ M}$ and $[\text{Ag}^+] = 0.0500 \text{ M}$

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

$$E^\circ_{\text{cell}} = 0.80 - 0.34 = 0.46 \text{ V}$$

$$n = 2$$

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (1/n)(RT/\mathfrak{F})\ln Q$$

$$= E^\circ_{\text{cell}} - \frac{0.025693 \text{ V}}{2} \ln 120$$

$$= 0.46 \text{ V} - 0.06150 \text{ V}$$

$$= \mathbf{0.40 \text{ V}}$$

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

galvanic

ΔE° is positive, so ΔG° is negative

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

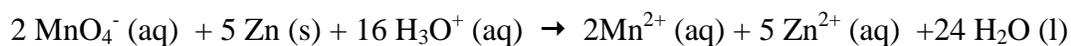
Au^+ (aq), Pb^{2+} (aq), Zn (s), Cr^{3+} (aq), Ni (s), Au (s).

Au⁺ only

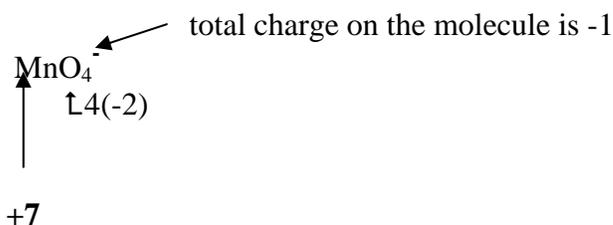
higher redox potential than Ag^+

6. OXIDATION-REDUCTION (12 points total)

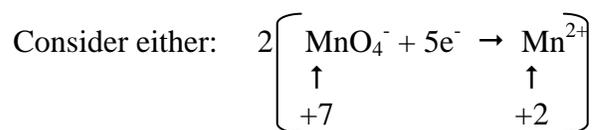
The following reaction has an $\Delta E^\circ(\text{cell})$ of 2.27 V and a $K = 10^{383}$ at 25°C:



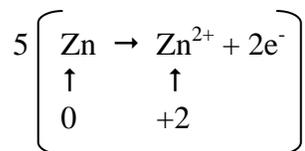
(a) (4 points) What is the oxidation number for Mn in MnO_4^- ?



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



or



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

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

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

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

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

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

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

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

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

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

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

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

$$K_w = K_a K_b$$

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

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

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

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

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

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

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

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

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

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

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

$$Q = It$$

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

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<td>51.996</td> <td>54.938</td> <td>55.847</td> <td>58.933</td> <td>58.69</td> <td>63.546</td> <td>65.38</td> <td>69.72</td> <td>72.59</td> <td>74.922</td> <td>78.96</td> <td>79.904</td> <td>83.80</td> <td>88.906</td> <td>91.224</td> <td>92.906</td> <td>95.94</td> <td>101.07</td> <td>102.906</td> <td>106.42</td> <td>107.868</td> <td>112.41</td> </tr> <tr> <td>37</td> <td>Rb</td> <td>38</td> <td>Sr</td> <td>39</td> <td>Y</td> <td>40</td> <td>Zr</td> <td>41</td> <td>Nb</td> <td>42</td> <td>Mo</td> <td>43</td> <td>Tc</td> <td>44</td> <td>Ru</td> <td>45</td> <td>Rh</td> <td>46</td> <td>Pd</td> <td>47</td> <td>Ag</td> <td>48</td> <td>Cd</td> </tr> <tr> <td>85.468</td> <td>87.62</td> <td>88.906</td> <td>87.62</td> <td>88.906</td> <td>91.224</td> <td>92.906</td> <td>95.94</td> <td>101.07</td> <td>102.906</td> <td>106.42</td> <td>107.868</td> <td>112.41</td> <td>114.82</td> <td>118.69</td> <td>121.75</td> <td>127.60</td> <td>126.904</td> <td>131.29</td> <td>132.905</td> <td>137.33</td> 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Elements																		19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	39.098	40.08	44.956	47.88	49.942	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.38	69.72	72.59	74.922	78.96	79.904	83.80	88.906	91.224	92.906	95.94	101.07	102.906	106.42	107.868	112.41	37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	85.468	87.62	88.906	87.62	88.906	91.224	92.906	95.94	101.07	102.906	106.42	107.868	112.41	114.82	118.69	121.75	127.60	126.904	131.29	132.905	137.33	138.905	140.908	144.24	145.909	150.36	157.25	158.925	162.50	164.930	167.26	168.934	173.04	174.967	55	Cs	56	Ba	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	132.905	137.33	138.905	178.49	178.49	180.948	183.85	186.21	190.2	192.22	195.08	196.966	200.59	204.38	207.2	208.98	209	210	210	210	210	210	210	210	87	Fr	88	Ra	89	Ac	† 104	Unq	† 105	Unp	† 106	Unh	(263)	(262)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(223)		226.025	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	227.028	<table border="1"> <thead> <tr> <th colspan="18">Inner Transition Metals</th> </tr> </thead> <tbody> <tr> <td>58</td> <td>Ce</td> <td>59</td> <td>Pr</td> <td>60</td> <td>Nd</td> <td>61</td> <td>Pm</td> <td>62</td> <td>Sm</td> <td>63</td> <td>Eu</td> <td>64</td> <td>Gd</td> <td>65</td> <td>Tb</td> <td>66</td> <td>Dy</td> <td>67</td> <td>Ho</td> <td>68</td> <td>Er</td> <td>69</td> <td>Tm</td> <td>70</td> <td>Yb</td> <td>71</td> <td>Lu</td> </tr> <tr> <td>140.12</td> <td>140.908</td> <td>140.908</td> <td>144.24</td> <td>144.24</td> <td>144.24</td> <td>145</td> <td>150.36</td> <td>150.36</td> <td>151.96</td> <td>151.96</td> <td>157.25</td> <td>157.25</td> <td>158.925</td> <td>158.925</td> <td>162.50</td> <td>162.50</td> 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Metals																		58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu	140.12	140.908	140.908	144.24	144.24	144.24	145	150.36	150.36	151.96	151.96	157.25	157.25	158.925	158.925	162.50	162.50	164.930	164.930	167.26	167.26	168.934	168.934	173.04	173.04	174.967	174.967	174.967	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr	232.038	231.036	231.036	238.029	238.029	238.029	237.048	237.048	244	244	243	243	247	247	247	247	251	251	252	252	257	257	258	258	259	259	260	260
The Active Metals		The Nonmetals		Noble Gases																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
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87	Fr	88	Ra	89	Ac	† 104	Unq	† 105	Unp	† 106	Unh	(263)	(262)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)	(261)																																																																																																																																																																																																																																																																																																																																																																																																																																																																		
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<table border="1"> <thead> <tr> <th colspan="18">Inner Transition Metals</th> </tr> </thead> <tbody> <tr> <td>58</td> <td>Ce</td> <td>59</td> <td>Pr</td> <td>60</td> <td>Nd</td> <td>61</td> <td>Pm</td> <td>62</td> <td>Sm</td> <td>63</td> <td>Eu</td> <td>64</td> <td>Gd</td> <td>65</td> <td>Tb</td> <td>66</td> <td>Dy</td> <td>67</td> <td>Ho</td> <td>68</td> <td>Er</td> <td>69</td> <td>Tm</td> <td>70</td> <td>Yb</td> <td>71</td> <td>Lu</td> </tr> <tr> <td>140.12</td> <td>140.908</td> <td>140.908</td> <td>144.24</td> <td>144.24</td> <td>144.24</td> <td>145</td> <td>150.36</td> <td>150.36</td> <td>151.96</td> <td>151.96</td> <td>157.25</td> <td>157.25</td> <td>158.925</td> <td>158.925</td> <td>162.50</td> <td>162.50</td> <td>164.930</td> <td>164.930</td> <td>167.26</td> <td>167.26</td> <td>168.934</td> <td>168.934</td> <td>173.04</td> <td>173.04</td> <td>174.967</td> <td>174.967</td> <td>174.967</td> </tr> <tr> <td>90</td> <td>Th</td> <td>91</td> <td>Pa</td> <td>92</td> <td>U</td> <td>93</td> <td>Np</td> <td>94</td> <td>Pu</td> <td>95</td> <td>Am</td> <td>96</td> <td>Cm</td> <td>97</td> <td>Bk</td> <td>98</td> <td>Cf</td> <td>99</td> <td>Es</td> <td>100</td> <td>Fm</td> <td>101</td> <td>Md</td> <td>102</td> <td>No</td> <td>103</td> <td>Lr</td> </tr> <tr> <td>232.038</td> <td>231.036</td> <td>231.036</td> <td>238.029</td> <td>238.029</td> <td>238.029</td> <td>237.048</td> <td>237.048</td> <td>244</td> <td>244</td> <td>243</td> <td>243</td> <td>247</td> <td>247</td> <td>247</td> <td>247</td> <td>251</td> <td>251</td> <td>252</td> <td>252</td> <td>257</td> <td>257</td> <td>258</td> <td>258</td> <td>259</td> <td>259</td> <td>260</td> <td>260</td> </tr> </tbody> </table>																		Inner Transition Metals																		58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu	140.12	140.908	140.908	144.24	144.24	144.24	145	150.36	150.36	151.96	151.96	157.25	157.25	158.925	158.925	162.50	162.50	164.930	164.930	167.26	167.26	168.934	168.934	173.04	173.04	174.967	174.967	174.967	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr	232.038	231.036	231.036	238.029	238.029	238.029	237.048	237.048	244	244	243	243	247	247	247	247	251	251	252	252	257	257	258	258	259	259	260	260																																																																																																																																																																																																																																																																																																																																						
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