Chemistry 210

Exam 4

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number = 6.022×10^{23} units/mol $32.00^{\circ}F = 0.000^{\circ}C = 273.15K$ Density of Water = $1.000^{g}/_{mL}$ $R = 0.08206^{L \cdot atm}/_{mol \cdot K} = 8.314^{J}/_{mol \cdot K}$ PV=nRT $\Delta T_{fp/bp} = k_{fp/bp} \cdot m \cdot i$ For water: $k_{fp} = -1.86^{\circ C}/_{m}$ $k_{bp} = 0.512^{\circ C}/_{m}$ $P_{1} = X_{1}P_{1}^{\circ}$ $\Pi = MRTi$ $C_{1}V_{1} = C_{2}V_{2}$ Quadratic formula: $x = \frac{-b \pm \sqrt{b^{2} - 4ac}}{2}$

$$\begin{split} & \text{Integrated Rate Laws:} \\ & 0^{\text{th}} \text{ order} \qquad [A]_t = -kt + [A]_o \\ & 1^{\text{st}} \text{ order} \qquad \ln[A]_t = -kt + \ln[A]_o \\ & 2^{\text{nd}} \text{ order} \qquad 1/[A]_t = kt + 1/[A]_o \\ & k = Ae^{-Ea/RT} \\ & \ln(k) = \left(\frac{-E_a}{R}\right) \left(\frac{1}{T}\right) + \ln(A) \\ & \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ & pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right) \end{split}$$

| $E_{cell} = E^{o}_{cell} - {^{RT}}/_{nF} \ln Q$ |
|---|
| $E_{cell}^{o} = {RT \choose nF} ln K^{o}$ |
| $K^{o} = e^{(nF)}_{RT} E^{o}_{cell}$ |
| $F = 96485 \text{J}_{\text{V-mol of electrons}}$ |
| $\Delta G^{o} = \Delta H^{o}_{system} - T\Delta S^{o}_{system}$ |
| $\Delta G^{o} = -nFE^{o}_{cell} = -RTlnK^{o}$ |
| $\Delta G = \Delta G^{o} + RT lnQ$ |
| $F = 96485$ $^{\rm C}/_{\rm mol\ electrons}$ |
| 1A = 1 C / sec |

| | 1 | | | | | | | | | | | | | | | | |
|--------|--------|--------------|--------|--------------|--------------|--------|--------|--------|--------|------------------------|--------|--------|--------|--------|--------|--------------|--------|
| 1 | | | | | | | | | | | | | | | | | 2 |
| H | | | | | | | | | | | | | | | | | He |
| 1.0079 | | | | | | | | | | | | | | | | | 4.0026 |
| 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 |
| Li | Be | | | | | | | | | | | В | C | N | O | \mathbf{F} | Ne |
| 6.941 | 9.0122 | | | | | | | | | | | 10.811 | 12.011 | 14.007 | 15.999 | 18.998 | 20.180 |
| 11 | 12 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| 22.990 | 24.305 | | | | | | | | | | | 26.982 | 28.086 | 30.974 | 32.066 | 35.453 | 39.948 |
| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 |
| K | Ca | Sc | Ti | \mathbf{V} | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 39.098 | 40.078 | 44.956 | 47.88 | 50.942 | 51.996 | 54.938 | 55.847 | 58.933 | 58.69 | 63.546 | 65.39 | 69.723 | 72.61 | 74.922 | 78.96 | 79.904 | 83.80 |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 |
| Rb | Sr | \mathbf{Y} | Zr | Nb | Mo | Tc | Ru | Rh | Pd | $\mathbf{A}\mathbf{g}$ | Cd | In | Sn | Sb | Te | Ι | Xe |
| 85.468 | 87.62 | 88.906 | 91.224 | 92.906 | 95.94 | (98) | 101.07 | 102.91 | 106.42 | 107.87 | 112.41 | 114.82 | 118.71 | 121.76 | 127.60 | 126.90 | 131.29 |
| 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 |
| Cs | Ba | La | Hf | Ta | \mathbf{W} | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 132.91 | 137.33 | 138.91 | 178.49 | 180.95 | 183.84 | 186.21 | 190.23 | 192.22 | 195.08 | 196.97 | 200.59 | 204.38 | 207.2 | 208.98 | (209) | (210) | (222) |
| 87 | 88 | 89 | 104 | 105 | 106 | 107 | 108 | 109 | 110 | 111 | 112 | | 114 | | 116 | | |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | |
| (223) | 226.03 | 227.03 | (261) | (262) | (263) | (262) | (265) | (266) | (269) | (272) | (277) | | | | | | |

| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 |
|--------|--------|--------------|--------|--------|--------|--------|------------------------|--------|--------|--------|--------|--------|--------|
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| 140.12 | 140.91 | 144.24 | (145) | 150.36 | 151.97 | 157.25 | 158.93 | 162.50 | 164.93 | 167.26 | 168.94 | 173.04 | 174.97 |
| 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 |
| Th | Pa | \mathbf{U} | Np | Pu | Am | Cm | $\mathbf{B}\mathbf{k}$ | Cf | Es | Fm | Md | No | Lr |
| 232.04 | 231.04 | 238.03 | 237.05 | (244) | (243) | (247) | (247) | (251) | (252) | (258) | (258) | (259) | (260) |

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Multiple Choice (5pts each)

- 1. A large negative change in free energy means:
 - a. The reaction is very slow
 - b. The reaction is exothermic
 - c. The reaction is not spontaneous
 - d. The system is becoming more disordered
 - e. The reaction is spontaneous
- 2. For a reaction with a small negative ΔS :
 - a. Heat is liberated by the reaction
 - b. The system is becoming more ordered
 - c. The reaction is not spontaneous
 - d. The order of the system is increasing
 - e. The reaction proceeds very quicky
- 3. A reaction will be product-favored/spontaneous if:
 - a. $\Delta G^{o} < 0$
 - b. $K_{eq} < 1$
 - c. $\Delta H > 0$
 - d. $\Delta S^o < 0$
 - e. $E^{\circ}_{cell} < 0$
- 4. A reaction will be spontaneous at relatively high temperature if:
 - a. $\Delta H^{\circ}_{system} > 0$ and $\Delta S^{\circ}_{system} > 0$
 - b. $\Delta H^{o}_{system} < 0$ and $\Delta S^{o}_{system} > 0$
 - c. $\Delta H^{o}_{system} > 0$ and $\Delta S^{o}_{system} = 0$
 - d. $\Delta H_{\text{system}}^{\circ} > 0$ and $\Delta S_{\text{system}}^{\circ} < 0$
 - e. $\Delta H^o_{system} \le 0$ and $\Delta S^o_{system} \le 0$
- 5. In a spontaneous electrochemical voltaic cell, which of the following is *true*?
 - a. The cell potential is zero
 - b. Oxidation occurs at the cathode
 - c. Electrons flow from the cathode to the anode
 - d. Cations flow through the salt bridge from the cathode to the anode
 - e. The metal cathode gains mass as the cell reaction proceeds
- 6. For a spontaneous redox reaction, which of the following is *false*?
 - a. Oxidation is the process of losing electrons
 - b. Gaining electrons is reduction
 - c. Electrons appear on the left side of the oxidation half reaction
 - d. Water molecules are added to balance any extra oxygen atoms
 - e. ΔG is negative.

- 7. How are the change in Gibb's Free Energy and the equilibrium constant for a reaction related?
 - a. As K approaches zero, ΔG approaches zero
 - b. They're not.
 - c. The value of ΔG is equal to $(-\log K)$
 - d. As ΔG gets more positive, K approaches 1
 - e. As ΔG gets more negative, K gets very large

Problems:

8. For each of the following reactions, predict the sign of ΔS° and explain your answer (5pts each): $H_2SO_4(aq) + Mg(OH)_2(aq) \Leftrightarrow MgSO_4(s) + 2 H_2O(l)$

$$2 \text{ NO}_2(g) \Leftrightarrow 2 \text{ NO}(g) + \text{O}_2(g)$$

9. Give the oxidation number for each atom in the following formulas. (5pts each formula)

 Na_3PO_4 CH₃OH

10. Ammonia {NH₃(g)} can burn in oxygen to form nitrogen dioxide and water. How much energy can be liberated by burning 21.964g of ammonia in an unlimited supply of oxygen? (20pts)

11. You would like to plate 4.38g of chromium (atomic # = 24) using an electrolytic cell containing a solution of chromium(III) nitrate and operating at 2.37A. How long will you have to run the cell? (20pts)

- 12. You are studying the reaction of acetic acid $\{CH_3CO_2H(l)\}\$ with iso-propanol $\{C_3H_8O(l)\}\$ to produce isopropylacetate $\{C_5H_{10}O_2(1)\}$ and water. When you run the reaction at 22.67°C, you find that ΔG for this reaction is $-27.39^{kJ}/_{mol}$ and $\Delta S = +34.18^{J}/_{mol \cdot K}$ (20pts) a. Is the reaction endothermic or exothermic? (*Explain your answer with explicit calculations*.)

 - b. Over what temperature range is this reaction spontaneous?
- 13. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the reaction that occurs, identifying the oxidation and reduction half-reactions. (18pts each)

 $Au^{3+}(aq)|Au(s)$ and $Br_2(1)|Br^{-1}(aq)$

 $MnO_2(s)|Mn^{2+}(aq)$ and $Cr_2O_7^{-2}(aq)|Cr^{3+}(aq)$

Thermodynamic Values at 25°C:

| Substance | $\Delta H_{f}^{o}(^{kJ}/_{mol})$ | $S^{o}(^{J}/_{mol \cdot K})$ | $\Delta G_{f}^{o}(^{kJ}/_{mol})$ |
|-----------|----------------------------------|------------------------------|----------------------------------|
| $NH_3(g)$ | -46.11 | 192.45 | -16.45 |
| $O_2(g)$ | 0 | 205.138 | 0 |
| $NO_2(g)$ | 33.18 | 240.06 | 51.31 |
| $H_2O(g)$ | -241.8 | 188.8 | -228.6 |

Standard Reduction Potentials at 25°C:

| Half cell | E red (volts) | Half cell | E o (volts) |
|---|---------------|--------------------------------|-------------|
| $\operatorname{Cr}^{3+}(\operatorname{aq}) \operatorname{Cr}(\operatorname{s})$ | -0.74 | $MnO_2(s) Mn^{2+}(aq)$ | +1.21 |
| $Au^{3+}(aq) Au(s)$ | +1.50 | $Cr_2O_7^{-2}(aq) Cr^{3+}(aq)$ | +1.33 |
| $Br_2(1) Br^{-1}(aq)$ | +1.09 | | |