Name KEY

CH302H **EXAM 4** Spring 2013

True or False Write "T" for true, or "F" for false (2 pts each)

T **1.** Oxygen has an oxidation number of -2 except when it is bonded to itself or to fluorine.

F **2.** Elements to the left and bottom of the periodic table tend to be good oxidizing agents, while elements at the top and right tend to be good reducing agents.

T **3.** Element B will reduce the cation of element A (A^+), but will not reduce the cation of element C (C^+). Element C can reduce the cation of element A.

T **4.** The anode has a negative sign where anions migrate toward and the cathode has a positive sign where cations migrate toward.

T **5.** When a voltmeter measures $E°$, it also indirectly measures $\Delta G°$.

T **6.** The standard hydrogen electrode (S.H.E.) is an arbitrary standard half-cell used as a reference point with an arbitrary potential.

F **7.** Electrical potential is an extensive property, that depends on the amount of substance.

T **8.** The Nernst equation relates the concentrations of any chemical species to cell potential.

F **9.** The more negative the standard cell potential, the larger the value of the equilibrium constant, and the farther the equilibrium lies to the right.

T **10.** A fuel cell differs from an ordinary battery in that the reactants are not contained within the cell but instead are continuously supplied from an external reservoir.

F **11.** A sacrificial anode is an easily reduced metal that corrodes instead of a less reactive metal to which it is connected.

T **12.** An electrolytic cell converts electrical energy to chemical energy when an electric current drives a reaction with a negative value of E in a direction away from equilibrium.

F **13.** The main factor to limit or ban the use of NiCd batteries is that they are notorious for cell inefficiency and waste valuable energy.

T **14.** In a voltaic cell the surface area of the electrodes is a major factor in determining the maximum current that the cell can deliver.

F **15.** Aluminum is oxidized more readily than iron. Therefore, the corrosion of aluminum products such as automobile parts, window frames and cooking utensils is more prominent than iron products.

Free Response

16. Assign oxidation numbers to each element in the following ions: (2 pt each)

(a) ClO_3^- O-2, Cl+5 (b) SO_3^{2-} O-2, S+4 (c) $C_2O_4^{2-}$ O-2, C+3

(d) C_2H_6 C-3, H+1 (e) $Na_2B_4O_7$ Na+1, B+3, O-2 (f) Mg_2Si_2O Mg+2, Si-1, O-2

17. (a) Use the following reactions to arrange the elements A, B, C, and D in order of their decreasing ability as reducing agents: (2 pts) Any element higher in the activity series will react w/ the ion of any element lower in the series.

$C + B^+ \rightarrow C^+ + B$ C is higher than B

$D + B^+ \rightarrow D^+ + B$ D is higher than B

$A + C^+$ no reaction C is higher than A

$A^+ + D$ no reaction A is higher than D

C > A > D > B

(b) Which of the following reactions would you expect to occur according to the activity series you established in part (a)? Circle your choice. (2 pts)

(1) $A^+ + C \rightarrow A + C^+$ B/C C is above A in the activity series (2) $A^+ + B \rightarrow A + B^+$ will NOT occur B/C B is below A in the activity series

18. For parts (a) and (b) write balanced net ionic equations for the following reactions in acidic solution, then for parts (c) and (d) write balanced net ionic equations in basic solution: (2 pts each)

(a) $MnO_4^-(aq) + IO_3^-(aq) \rightarrow MnO_2(s) + IO_4^-(aq)$

$2\,H^+(aq) + 2\,MnO_4^-(aq) + 3\,IO_3^-(aq) \rightarrow 2\,MnO_2(s) + 3\,IO_4^-(aq) + H_2O(l)$

(b) $H_2O_2(aq) + ClO_4^-(aq) \rightarrow ClO_2^-(aq) + O_2(g)$

$ClO_4^-(aq) + 2\,H_2O_2(aq) \rightarrow ClO_2^-(aq) + 2\,H_2O(l) + 2\,O_2(g)$

(c) $Fe(OH)_2(s) + CrO_4^{2-}(aq) \rightarrow Fe(OH)_3(s) + Cr(OH)_4^-(aq)$

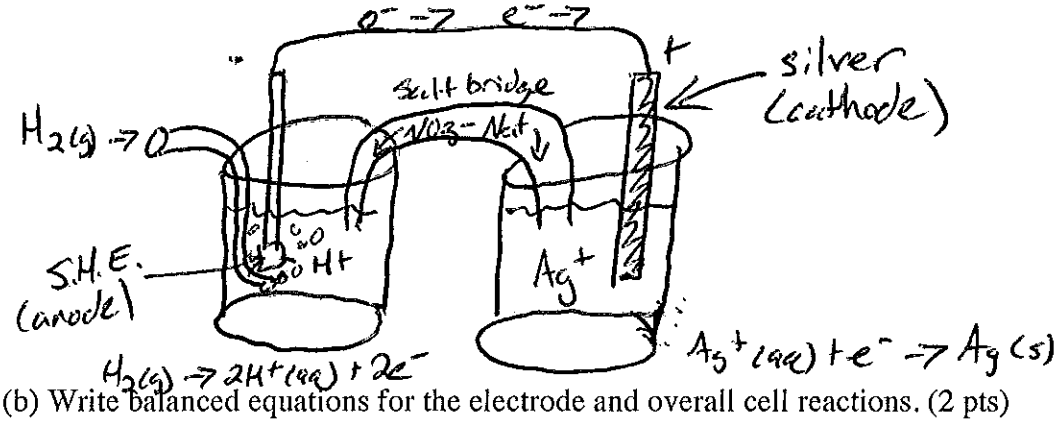
$3\,Fe(OH)_2(s) + 4\,H_2O(l) + CrO_4^{2-}(aq) \rightarrow 3\,Fe(OH)_3(s) + Cr(OH)_4^-(aq) + OH^-(aq)$

(d) $Cu(OH)_2(s) + N_2H_4(aq) \rightarrow Cu(s) + N_2(g)$

$2\,Cu(OH)_2(s) + N_2H_4(aq) \rightarrow 2\,Cu(s) + 4\,H_2O(l) + N_2(g)$

19. An H_2/H^+ half-cell(anode) and an Ag^+/Ag half-cell(cathode) are connected by a wire and a salt bridge.

(a) Sketch the cell, indicating the direction of spontaneous electron and ion flow. (2 pts)



(b) Write balanced equations for the electrode and overall cell reactions. (2 pts)

anode rxn: $H_2(g) \rightarrow 2\,H^+(aq) + 2e^-$

cathode rxn: $2\,Ag^+(aq) + 2e^- \rightarrow 2\,Ag(s)$

overall rxn: $H_2(g) + 2\,Ag^+(aq) \rightarrow 2\,H^+(aq) + 2\,Ag(s)$

(c) Give the shorthand notation for the cell. (1 pt)

$Pt(s) \mid H_2(g) \mid H^+(aq) \,\|\, Ag^+(aq) \mid Ag(s)$

20. Consider a voltaic cell that uses the following half reactions:

$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \;\; Mn^{2+}(aq) + 4\,H_2O(l)$

$Sn^{4+}(aq) + 2\,e^- \;\; Sn^{2+}(aq)$

(a) Write a balanced equation for the overall cell reaction. (2 pts)

$2\,MnO_4^-(aq) + 16\,H^+(aq) + 5\,Sn^{2+}(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Sn^{4+}(aq) + 8\,H_2O(l)$

(b) What is the oxidizing agent, and what is the reducing agent? (2 pts)

MnO_4^- is the oxidizing agent, Sn^{2+} is the reducing agent

(c) Calculate the standard cell potential. (2 pts)

$E^\circ = 1.51\,V + (-0.14\,V) = 1.37\,V$

21. Consider a voltaic cell that uses the following half-reactions:

$2\ H^+(aq) + 2\ e^-$ $H_2(g)$

$Al^{3+}(aq) + 3\ e^-$ $Al(s)$

(a) Calculate the cell potential at 25°C if the ion concentrations are 0.10 M and the partial pressure of H_2 is 10.0 atm. (4 pts) $2\,Al(s) + 6H^+(aq) \rightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)$

$E^\circ = E^\circ_{ox} + E^\circ_{red} = 1.66\,V + 0.00\,V = 1.66\,V$

$$E = E^\circ - \frac{0.0592\,V}{n}\log\frac{[Al^{3+}]^2(P_{H_2})^3}{[H^+]^6} = 1.66\,V - \frac{(0.0592\,V)}{6}\log\frac{(0.10)^2(10.0)^3}{(0.10)^6} = 1.59\,V$$

(b) Calculate ΔG° (in kilojoules) and K for the cell reaction at 25°C. (4 pts)

$$\Delta G^\circ = -nFE^\circ = -(6\,mole^-)\left(\frac{96{,}500\,C}{1\,mole^-}\right)(1.66\,V)\left(\frac{1\,J}{1\,C\cdot V}\right) = -961\,kJ$$

$\Delta G^\circ = -RT\ln K \Rightarrow K = e^{-\Delta G^\circ/RT}$ SOLVE USING LOGARITHMS!

(c) Calculate the mass change (in grams) of the aluminum electrode after the cell has supplied a constant current of 10.0 A for 25.0 min. (2 pts)

$$\text{mass Al} = 10.0\,\frac{C}{s} \times 25\,min \times \frac{60\,s}{1\,min} \times \frac{1\,mole^-}{96{,}500\,C} \times \frac{1\,mol\,Al}{3\,mole^-} \times \frac{26.98\,g\,Al}{1\,mol\,Al} = 1.40\,g$$

22. A Daniell cell delivers a constant current of 0.100 A for 200.0 h. How many grams of zinc are oxidized at the anode? (3 pts) $Zn \rightarrow Zn^{2+} + 2e^-$

$$\frac{It}{nF} = \frac{(0.100\,A)(720{,}000\,s)}{2(96{,}500\,C)} = 0.373\,mol\,Zn \times \frac{65.38\,g\,Zn}{1\,mol\,Zn}$$

$24.39\,g\,Zn$

23. Consider the following substances: $Fe(s)$, $PbO_2(s)$, $H^+(aq)$, $Al(s)$, $Ag(s)$, and $Cr_2O_7^{2-}(aq)$.

(a) Which is the strongest oxidizing agent? (b) Which is the strongest reducing agent? (2 pts)

PbO_2 is the strongest oxidizing agent

Al is the strongest reducing agent

(c) Which substance(s) can be oxidized by $Cu^{2+}(aq)$? (d) Which can be reduced by $Ce^{3+}(aq)$? (3 pts)

Fe and Al

PbO_2

24. When suspected drunk drivers are tested with a Breathalyzer, the alcohol (ethanol) in the exhaled breath is oxidized to acetic acid with an acidic solution of potassium dichromate:

$3\ CH_3CH_2OH(aq) + 2\ Cr_2O_7^{2-}(aq) + 16\ H^+(aq) \rightarrow 3\ CH_3CO_2H(aq) + 4\ Cr^{3+}(aq) + 11\ H_2O(l)$

The color of the solution changes because some of the orange $Cr_2O_7^{2-}$ is converted to the green Cr^{3+}. The Breathalyzer measures the color change and produces a meter reading calibrated in terms of blood alcohol content.

(a) What is $E°$ for the reaction if the standard half-cell potential for the reduction of acetic acid to ethanol is 0.058 V? (4 pts)

oxidation: $3CH_3CH_2OH(aq) + 3H_2O(l) \rightarrow 3\ CH_3CO_2H(aq) + 12H^+(aq) + 12e^-$ $E° = -0.058V$

reduction: $2Cr_2O_7^{2-}(aq) + 28\ H^+(aq) + 12e^- \rightarrow 4\ Cr^{3+}(aq) + 14H_2O(l)$ $E° = 1.33\ V$

overall $E° = 1.27\ V$

(b) What is the value of E for the reaction when the concentrations of ethanol, acetic acid, $Cr_2O_7^{2-}$, and Cr^{3+} are 1.0 M and the pH is 4.00? (4 pts)

$$E = E° - \frac{(0.0592\ V)}{n} \log \frac{[CH_3CO_2H]^8[Cr^{3+}]^4}{[CH_3CH_2OH]^3[Cr_2O_7^{2-}]^2[H^+]^{16}}$$

$$E = 1.27\ V - \frac{(0.0592\ V)}{12} \log\left(\frac{(1.0)^3(1.0)^4}{(1.0)^3(1.0)^2(0.00010)^{16}}\right) = 0.95\ V$$

25. Calculate K_{sp} for $FeCO_3$ at 25°C. (3 pts)

$FeCO_3(s) + 2e^- \rightarrow Fe(s) + CO_3^{2-}$ $E° = -0.756\ V$

$Fe(s) \rightarrow Fe^{2+} + 2e^-$ $E° = -0.414\ V$

overall $E° = -0.316\ V$

$-nFE° = -RT\ln K$

$E° = \frac{RT}{nF}\ln K \Rightarrow K = e^{\frac{nFE°}{RT}} \Rightarrow K = K_{sp} = 2.07 \times 10^{-11}$

26. At one time on Earth, iron was present mostly as iron(II). Later, once plants had produced a significant quantity of oxygen in the atmosphere, the iron became oxidized to iron(III). Show that $Fe^{2+}(aq)$ can be spontaneously oxidized to $Fe^{3+}(aq)$ by $O_2(g)$ at 25°C assuming the following reasonable environmental conditions: $[Fe^{2+}] = [Fe^{3+}] = 1.0 \times 10^{-7}$ M, pH = 7.0, and P_{O2} = 160 mm Hg. (6 pts)

$4\ Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4\ Fe^{3+}(aq) + 2H_2O(l)$

oxidation $4\ Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + 4e^-$ $E° = -0.77\ V$

reduction $O_2(g) + 4\ H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $E° = 1.23\ V$

overall $E° = 0.46\ V$

$P_{O_2} = 160\ mm\ Hg \times \frac{1.00\ atm}{760\ mm\ Hg} = 0.211\ atm$

$$E = E° - \frac{(0.0592\ V)}{n} \log [Fe^{3+}]^4 / [Fe^{2+}]^4[H^+]^4(P_{O_2})$$

$$E = 0.46\ V - \frac{(0.0592\ V)}{4} \log (1\times10^{-7})^4 / (1\times10^{-7})^4(1\times10^{-7})^4(0.211)$$

$E = 0.46\ V - 0.42\ V = 0.04\ V$ B/C E is positive, the rxn is spontaneous