ELECTROCHEMISTRY (no calculator)

(All questions may be completed without the use of a calculator. All answers given were generated without the use of a calculator.)

1) Balance each skeleton reaction, calculate $\varepsilon°_{cell}$, and state whether or not the reaction is spontaneous.

   a) $Co(s) + H^+(aq) \longrightarrow Co^{+2}(aq) + H_2(g)$
   b) $Mn^{+2}(aq) + Br_2(l) \longrightarrow MnO_4^{-1}(aq) + Br^{-1}(aq)$ (in acidic solution)
   c) $Hg_2^{+2}(aq) \longrightarrow Hg^{+2}(aq) + Hg(l)$
   (Answers: (a) Yes, ε°= +0.28 V, (b) No, ε°= -0.44 V, (c) No, ε°= -0.07 V)

2) Use the following half-reactions to write three spontaneous reactions, calculate ε° for each reaction, and rank the strength of the oxidizing and reducing agents:

   $Al^{+3}(aq) + 3e^{-1} \longrightarrow Al(s)$ ε° = -1.66 V
   $N_2O_4(g) + 2e^{-1} \longrightarrow 2NO_2^{-1}(aq)$ ε° = 0.867 V
   $SO_4^{-2}(aq) + H_2O + 2e^{-1} \longrightarrow SO_3^{-2}(aq) + 2OH^{-1}(aq)$ ε° = 0.93 V

   (Answers: The three spontaneous reactions would be between:
   (1) $Al(s) + N_2O_4(g)$
   (2) $Al(s) + SO_4^{-2}(aq)$
   (3) $SO_4^{-2}(aq) + NO_2^{-1}(aq)$
   Strongest to weakest reducing agent: $Al(s) > NO_2^{-1}(aq) > SO_3^{-2}(aq)$
   Strongest to weakest oxidizing agent: $SO_4^{-2}(aq) > N_2O_4(g) > Al^{+3}(aq)$)

3) A voltaic cell consists of a metal A/A^+ electrode and a metal B/B^+ electrode, with the A/A^+ electrode negative. The initial $[A^+]/[B^+]$ is such that $\varepsilon_{cell} > \varepsilon°_{cell}$.

   a) How do $[A^+]$ and $[B^+]$ change as the cell operates?
   b) How does ε_{cell} change as the cell operates?
   c) What is $[A^+]/[B^+]$ when $\varepsilon_{cell} > \varepsilon°_{cell}$? Explain.
   d) Is it possible for $\varepsilon°_{cell}$ to be greater than ε_{cell}? Explain.
   (Answers: (a) $[A^+]$ increases and $[B^+]$ decreases.
   (b) ε_{cell} decreases.
   (c) $[A^+] < [B^+]$
   (d) Yes, if $[A^+] > [B^+]$)

4) A concentration cell consists of two Sn/Sn^{+2} half-cells. The electrolyte in compartment A is 0.10 M $Sn(NO_3)_2$. The electrolyte in B is 1.00 M $Sn(NO_3)_2$. Which half-cell houses the cathode? What is the voltage of the cell?
   (Answer: Compartment B houses the cathode and the cell voltage is +29.6 mV.)

5) A voltaic cell with Mn/Mn^{2+} and Cd/Cd^{2+} half-cells has the following starting concentrations: $[Mn^{2+}] = 0.010$ M and $[Cd^{2+}] = 0.100$ M.

   a) What is the initial ε_{cell}? **(Answer: $\varepsilon_{cell} = +0.81$ V)**
   b) What is ε_{cell} when $[Mn^{2+}] = 0.055$ M? **(Answer: $\varepsilon_{cell} = +0.78$ V)**
   c) Calculate K_{eq} and the concentrations of the ions at equilibrium.
      (Answers: $K_{eq} \approx 1 \times 10^{26}$ and $[Mn^{2+}] = 0.110$ M and $[Cd^{2+}] = 1 \times 10^{-27}$ M)

6) The following reactions occur at 25°C with all soluble substances present in 1 M concentrations:

   $Zn(s) + 2Eu^{3+}(aq) \longrightarrow Zn^{2+}(aq) + 2Eu^{2+}(aq)$
   $Zr(s) + 2Zn^{2+}(aq) \longrightarrow Zr^{4+}(aq) + 2Zn(s)$
   $4Sc(s) + 3Zr^{4+}(aq) \longrightarrow 4Sc^{3+}(aq) + 3Zr(s)$

   From this information alone, predict whether the following reactions will occur under similar conditions:

   a) $Sc(s) + 3Eu^{3+}(aq) \longrightarrow Sc^{3+}(aq) + 3Eu^{2+}(aq)$
   b) $Zr^{4+}(aq) + 4Eu^{2+}(aq) \longrightarrow Zr(s) + 4Eu^{3+}(aq)$
   c) $2Sc(s) + 3Zn^{2+}(aq) \longrightarrow 3Zn(s) + 2Sc^{3+}(aq)$

   YOUR ANSWERS MUST BE RATIONALIZED BY INDICATING A RELATIVE SCALE OF EMF FOR THE FOUR ELEMENTS IN QUESTION.
   (Answers: (a) YES (b) NO (c) YES)

7) Explain why copper is oxidized by nitric acid and not by hydrochloric acid.
   (Answer: Copper cannot be oxidized by HCl because for the reaction $Cu + 2H^+ \longrightarrow H_2 + Cu^{2+}$ the ε°cell is less than zero. However for the reactions $Cu + HNO_3 \longrightarrow Cu^{2+} + NO_2$ or NO the ε°cell is greater than zero.)

8) The corrosion of iron involves oxidation of the metal and the subsequent formation of the oxide. Which metal, zinc or nickel, will provide the better protection against corrosion if coated in a thin layer on the iron?
   (Answer: Zinc would be better than nickel because it has a more positive value for its oxidation potential than does iron, and thus would be oxidized more readily than iron. However if it were coated with nickel, the iron would be oxidized before the nickel and thus would not protect the iron.)

9) A solution contains the following metal ions: $[Au^{3+}] = 1.0 \times 10^{-6}$ M, $[Fe^{3+}] = 1.0$ M and $[Ni^{2+}] = 1.0 \times 10^{-4}$ M. What metal will plate out first if this solution is electrolyzed? (HINT: Use the Nernst equation to calculate ε for each half-reaction.)
(Answer: For $[Au^{3+}] = 1.0 \times 10^{-6}$ M the $\varepsilon_{half\text{-}cell} = +1.38$ V
For $[Fe^{3+}] = 1.0$ M the $\varepsilon_{half\text{-}cell} = -0.037$ V
For $[Ni^{2+}] = 1.0 \times 10^{-4}$ M the $\varepsilon_{half\text{-}cell} = -0.37$ V
Since the $\varepsilon_{half\text{-}cell}$ for the Au^{3+}/Au is the most positive it will be the first metal to plate out of the solution.)

10) A voltaic cell employs the following two half-reactions:

$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^{-1}$ $\quad \varepsilon° = 0.00$ V
$Hg_2Cl_2(s) + 2e^{-1} \rightleftharpoons 2Hg(l) + 2Cl^{-1}(aq)$ $\quad \varepsilon° = +0.28$ V

Write the overall cell reaction and calculate ε_{cell} if the pH = 4.00 and all other substances are at standard conditions. **(Answer: $\varepsilon_{cell} = +0.52$ V)**

11) Hydrolysis of molten $MgCl_2$ is the final production step in the isolation of magnesium from seawater by the Dow process. Assuming that 48.6 g of Mg forms:

a) How many moles of electrons are required?
b) How many coulombs are required?
c) How many amps will produce this amount in 11 hours?
(Answers: (a) 4.0 mol e^{-1} (b) $4 \times 9.65 \times 10^4$ C ≈ 4×10^5 C (c) about 10 A)

12) Zinc plating (galvanizing) is an important means of corrosion protection. Although the process is done customarily by dipping the object into molten zinc, the metal can also be electroplated from aqueous solutions. How many grams of zinc can be deposited on a steel tank from a $ZnSO_4$ solution when a 0.965 A current flows for 2.3 days (approx. 2.0×10^5 seconds)?
(Answer: 1 mole zinc ≈ 65 g zinc)

13) Car manufacturers are developing engines that use H_2 as fuel. In Iceland, Sweden, and other parts of Scandinavia, where hydroelectric plants produce inexpensive electric power, the H_2 can be made industrially by the electrolysis of water.

a) How many coulombs are needed to produce 2.5×10^6 L of H_2 gas at 10.0 atm and 25°C? (Assume the ideal gas law applies.)
b) If the coulombs are supplied at 1.5 V, how many joules are produced?
c) If the combustion of oil yields 4.0×10^4 kJ/kg, what mass of oil must be must be burned to yield the number of joules in part (b)?
(Answers: (a) 2.0×10^{11} C (b) 3.0×10^{11} J (c) 7.5×10^3 kg oil)

14) Electrodes used in electrocardiography are disposable, and many incorporate silver. The metal is deposited in a thin layer on a small plastic "button", and then some is converted to AgCl:

$$Ag(s) + Cl^{-1} \rightleftharpoons AgCl(s) + e^{-1}$$

a) If the surface area of the button is 2.0 cm^2 and the thickness of the silver layer is 7.0×10^{-6} m, calculate the volume (in cm^3) of Ag used in one electrode.
b) The density of silver metal is 10.5 g/cm^3. How many grams of silver are used per electrode?
c) If the silver is plated on the button from an Ag^+ solution with a current of 10.0 mA, how many minutes does the plating take?
d) If bulk silver costs $5.50 per troy ounce (31.10 g), what is the cost (in cents) of the silver in one disposable electrode?
(Answers: (a) 1.4×10^{-3} cm^3 (b) 1.5×10^{-2} g Ag (c) about 25 min (d) about 0.3 cents)

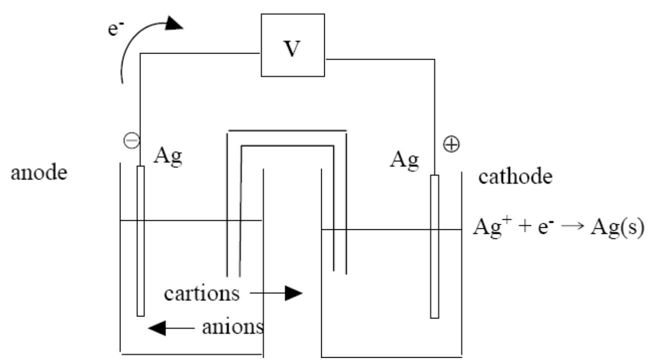
15) Given the following standard reduction potentials at 25°C

$Ag(S_2O_3)_2^{-3}(aq) + e^{-1} \longrightarrow Ag(s) + 2S_2O_3^{-2}(aq)$ $\quad \varepsilon° = +0.017$ V
$Ag^+(aq) + e^{-1} \longrightarrow Ag(s)$ $\quad \varepsilon° = +0.799$ V

a) Calculate the value of the equilibrium constant at 25°C for the reaction:

$$Ag^+(aq) + 2S_2O_3^{-2}(aq) \rightleftharpoons Ag(S_2O_3)_2^{-3}(aq)$$

(Answer: $K_{eq} = 1 \times 10^{13}$)
b) Write the conventional cell notation for the cell you have sketched.
(Answer: $Ag(s)|S_2O_3^{-2}(aq)$,cations(aq),$Ag(S_2O_3)_2^{-3}(aq)||Ag+(aq)$,anions(aq)$|Ag(s)$)
c) Sketch the voltaic cell in which the above chemical equation is the overall reaction. Your sketch should clearly indicate the following: anode, cathode, electrode signs, electron movement as well as the reactions taking place both the anode and cathode.
Answer:



$Ag(s) + 2S_2O_3^{-2}(aq) \longrightarrow Ag(S_2O_3)_2^{-3}(aq) + e^{-1}$ $\quad$ $Ag^+ + e^{-1} \longrightarrow Ag(s)$