10510CHEM311000-Analytical Chemistry (I)

分析化學一

Final Examination

Date: 10-01-2017, 10:10 am to 12:10 pm

Answer **all 8 questions** (total 106%). You have **2** hours to finish this paper.

1. Please draw two diagrams to illustrate Galvanic cells (voltaic cells) and electrolytic cells filled with 0.02 M $CuSO_4$ and 0.02 M $AgNO_3$ electrolyte solutions? You should indicate all the essential components of the cells and electron flow direction. Standard Electrode Potential: $E_{Cu^{2+}/Cu}$ = 0.337 V, $E_{Ag^+/Ag}$ = 0.799 V. **[16%]**

Ans: **Galvanic Cells**
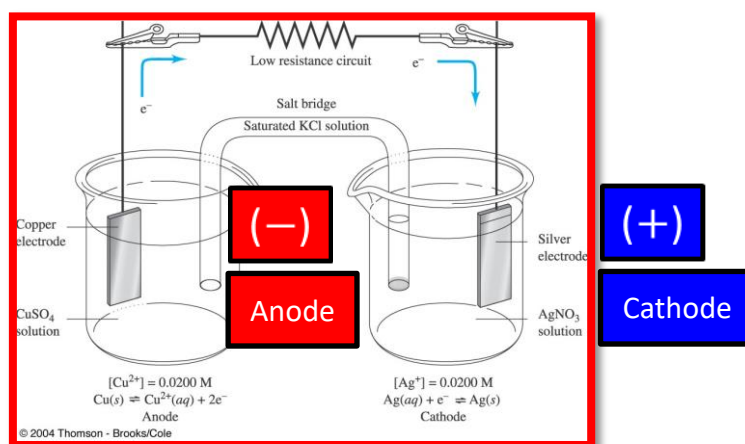
Electrolytic Cells
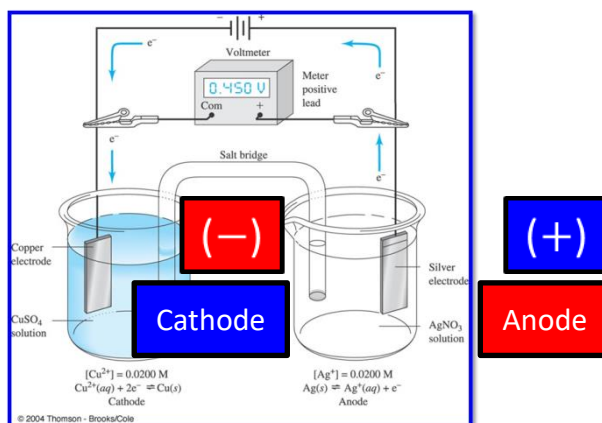
$$E_{Cu2+/Cu} = E^0_{Cu2+/Cu} - \frac{0.0592}{2}\log\frac{1}{[Cu2+]} = 0.337 - 0.0296\log\frac{1}{0.02} = 0.2867V$$

$$E_{Ag+/Ag} = E^0_{Ag+/Ag} - \frac{0.0592}{1}\log\frac{1}{[Ag+]} = 0.799 - 0.0591\log\frac{1}{0.02} = 0.6984V$$

$$E\text{ galvanic cell} = E_{Ag+/Ag} - E_{Cu2+/Cu} = 0.4117V$$

2. Please describe in detail four limitations to Beer's Law. **[16%]**

Answers:
1. **Real limitations**
2. **Chemical Deviations**
3. **Instrumental Deviations** _due to Polychromatic Radiation_
4. **Instrumental Deviations** _due to Stray Radiation_

Real Limitations:
- Beer's law is suitable for relatively low analyte concentration.(Limiting Law)
- For high concentration (>0.01 M)=> molecular interaction, such as solute-solute, solute-solvent interaction or H-bond, varies the absorptivity.
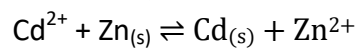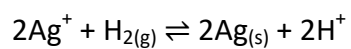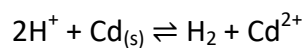
Chemical Deviations:
-Analyte dissociates, associates or reacts with a solvent _to produce a product with different absorption spectrum._

Instrumental Deviations: Polychromatic Radiation: Beer's law strictly applied only when measurements are made with monochromatic source radiation.

**Instrumental Deviations**: Stray radiation:
- is radiation from the instrument that is outside the nominal wavelength chosen for the measurement.
- stems from scattering and reflection.
- does not pass through the sample.
- causes deviation at high absorbance.

3.   The following reactions are spontaneous and thus proceed to the right, as written:

$$2H^+ + Cd_{(s)} \rightleftharpoons H_2 + Cd^{2+}$$
$$2Ag^+ + H_{2(g)} \rightleftharpoons 2Ag_{(s)} + 2H^+$$
$$Cd^{2+} + Zn_{(s)} \rightleftharpoons Cd_{(s)} + Zn^{2+}$$

Please rank the species in order from the strongest oxidant to the weakest oxidant.（沒有部份給分） **[5%]**

Ans:

$$Ag^+ > H^+ > Cd^{2+} > Zn^{2+}$$
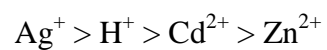
4. Please write the corresponding Nernst expressions for the following half-cell reactions.

(a) $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ **[5%]**

(b) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$ **[5%]**
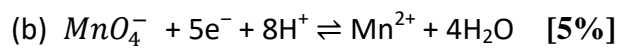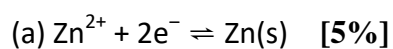
Answers:

(a)

$$E = E° - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

(b)

$$E = E° - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

5. Calculate the potential of a copper electrode immersed in

(a) 0.0380 M $Cu(NO_3)_2$ **[5%]**

(b) 0.0650 M in NaCl and saturated with CuCl   **[5%]**

Standard Electrode Potential and solubility product:

$E_{Cu^{2+}/Cu}$ = 0.337 V, K_{CuCl} = 1.9 X 10^{-7}, $E_{Cu^{+}/Cu}$ = 0.521 V

Ans:

(a)
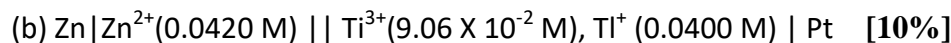
$$E_{Cu} = 0.337 - \frac{0.0592}{2} \log\left(\frac{1}{0.0380}\right) = 0.295 \text{ V}$$

(b)

$$K_{CuCl} = 1.9 ? \ 10^{-7} = [Cu^{+}][Cl^{-}]$$

$$E_{Cu} = 0.521 - \frac{0.0592}{1}\log\left(\frac{1}{[Cu^{+}]}\right) = 0.521 - \frac{0.0592}{1}\log\left(\frac{[Cl^{-}]}{K_{CuCl}}\right)$$

$$= 0.521 - \frac{0.0592}{1}\log\left(\frac{0.0650}{1.9 ? \ 10^{-7}}\right) = 0.521 - \frac{0.0592}{1}\log(3.42 ? \ 10^{5})$$

$$= 0.521 - 0.328 = 0.193 \text{ V}$$

6. Calculate the theoretical potential of the following cells. Indicate whether the reaction will proceed spontaneously in the direction considered or whether an external voltage source is needed to force this reaction to occur.

(a) $Pb|Pb^{2+}(0.120 \text{ M}) || Cd^{2+}(0.0500 \text{ M}) | Cd$ **[10%]**

(b) $Zn|Zn^{2+}(0.0420 \text{ M}) || Ti^{3+}(9.06 \times 10^{-2} \text{ M}), Tl^{+} (0.0400 \text{ M}) | Pt$ **[10%]**
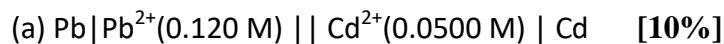
Standard Electrode Potential:

$E_{Pb^{2+}/Pb} = -0.126\text{V}, \ E_{Cd^{2+}/Cd} = -0.403\text{V}, \ E_{Zn^{2+}/Zn} = -0.763\text{V}, \ E_{Tl^{3+}/Tl^{+}} = 1.25\text{V}$

Answers:

(a)
$$E_{right} = -0.403 - \frac{0.0592}{2}\log\left(\frac{1}{0.0500}\right) = -0.442 \ \text{V}$$

$$E_{left} = -0.126 - \frac{0.0592}{2}\log\left(\frac{1}{0.1200}\right) = -0.153 \ \text{V}$$

$$E_{cell} = E_{right} - E_{left} = -0.442 - (-0.153) = -0.289 \ \text{V}$$

Because E_{cell} is negative, the spontaneous reaction is not oxidation on the left and reduction on the right. An external source would be needed to force this reaction to occur.

(b)

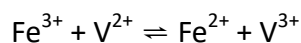$$E_{right} = 1.25 - \frac{0.0592}{2}\log\left(\frac{0.0400}{9.06 \times 10^{-2}}\right)$$

$$E_{left} = -0.763 - \frac{0.0592}{2}\log\left(\frac{1}{0.0420}\right) = -0.804 \ \text{V}$$

$$E_{cell} = E_{right} - E_{left} = 1.26 - (-0.804) = 2.06 \ \text{V}$$

Because E_{cell} is positive the reaction would proceed spontaneously in the direction considered (oxidation on the left, reduction on the right).

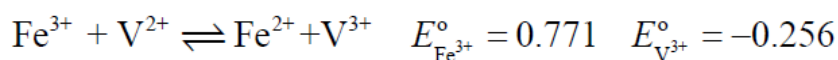**7.** (a) Calculate the equilibrium constant for the reaction below. **[7%]**

$$Fe^{3+} + V^{2+} \rightleftharpoons Fe^{2+} + V^{3+}$$

(b) Calculate the electrode potential of the system at the equivalence point for the reaction above. **[7%]**

Standard Electrode Potential: $E_{Fe^{3+}/Fe^{2+}} = 0.771$ V, $E_{V^{3+}/V^{2+}} = -0.256$ V.

Ans:

(a)

$$Fe^{3+} + V^{2+} \rightleftharpoons Fe^{2+} + V^{3+} \quad E^\circ_{Fe^{3+}} = 0.771 \quad E^\circ_{V^{3+}} = -0.256$$

$$0.771 - 0.0592 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right) = -0.256 - 0.0592 \log\left(\frac{[V^{2+}]}{[V^{3+}]}\right)$$

$$\frac{0.771 - (-0.256)}{0.0592} = \log\left(\frac{[Fe^{2+}][V^{3+}]}{[Fe^{3+}][V^{2+}]}\right) = \log K_{eq} = 17.348$$

$$K_{eq} = 2.23 \times 10^{17} \ (2.2 \times 10^{17})$$

(b)

At the equivalence point, $[Fe^{2+}] = [V^{3+}]$ and $[Fe^{3+}] = [V^{2+}]$

$$2E_{eq} = 0.771 + (-0.256) - 0.0592 \log\left(\frac{[Fe^{2+}][V^{2+}]}{[Fe^{3+}][V^{3+}]}\right)$$

$$E_{eq} = \frac{0.771 - 0.256}{2} = 0.258 \text{ V}$$

8. $K_2Cr_2O_7$ and $KMnO_4$ have overlapping absorption spectra in $1M$ H_2SO_4. $K_2Cr_2O_7$ has an absorption maximum at 440 nm, and $KMnO_4$ has a band at 545 nm. A mixture is analyzed by measuring the absorbance at these two wavelengths with the following results: $A_{440}=0.405$, $A_{545}=0.712$ in a 1-cm cell. Calculate the concentrations of $K_2Cr_2O_7$ and $KMnO_4$ in the sample solution. **[15%]**

The absorbances of pure solutions of $K_2Cr_2O_7$ (1.00×10^{-3} M) and $KMnO_4$ (2.00×10^{-4} M) in $1M$ H_2SO_4, using the same cell gave the following result: $A_{Cr,440}=0.374$, $A_{Cr,545}=0.009$, $A_{Mn,440}=0.019$, $A_{Mn,545}=0.475$.

Solution

Using Beer's Law and b=1,

$$0.374 = \varepsilon_{Cr,440} \times 1.00 \times 10^{-3} \qquad \varepsilon_{Cr,440} = 374$$

$$0.009 = \varepsilon_{Cr,545} \times 1.00 \times 10^{-3} \qquad \varepsilon_{Cr,545} = 9$$

$$0.019 = \varepsilon_{Mn,440} \times 2.00 \times 10^{-4} \qquad \varepsilon_{Mn,440} = 95$$

$$0.475 = \varepsilon_{Mn,545} \times 2.00 \times 10^{-4} \qquad \varepsilon_{Mn,545} = 2.38 \times 10^3$$

$$A_{400} = \varepsilon_{Cr,440}\left[Cr_2O_7{}^{2-}\right] + \varepsilon_{Mn,440}\left[MnO_4{}^-\right]$$

$$A_{545} = \varepsilon_{Cr,545}\left[Cr_2O_7{}^{2-}\right] + \varepsilon_{Mn,545}\left[MnO_4{}^-\right]$$

$$0.405 = 374\left[Cr_2O_7{}^{2-}\right] + 95\left[MnO_4{}^-\right]$$

$$0.712 = 9\left[Cr_2O_7{}^{2-}\right] + 2.38 \times 10^3\left[MnO_4{}^-\right]$$

Solving simultaneously,

$$\left[Cr_2O_7{}^{2-}\right] = 1.01 \times 10^{-3}\ M \qquad \left[MnO_4{}^-\right] = 2.95 \times 10^{-4}\ M$$

Note that for Cr at 545 nm, where it overlaps the main Mn peak, the absorbance was measured to only one significant figure since it was so small. This is fine. The smaller the necessary correction, the better. Ideally, it should be zero.

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