

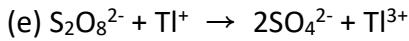
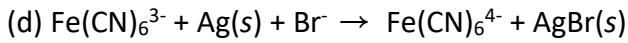
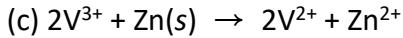
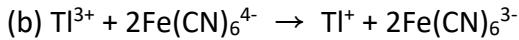
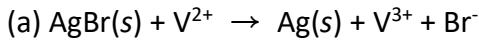
11310CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

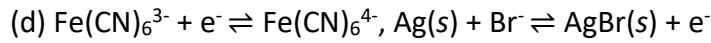
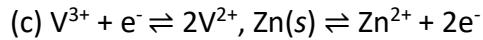
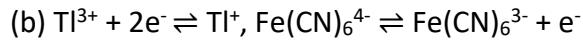
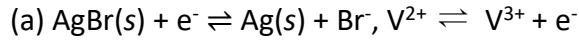
Date: 17-12-2024, 10:10 am to 12:30 pm

Answer all 10 questions (total 100%). You have 2 hours and 20 minutes to finish this paper.

1. Write each net process in terms of two balanced half-reactions for the following oxidation/reduction reactions: [10%]

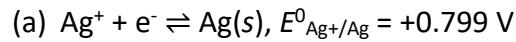


Solution:



2. Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^0_{\text{Ag}^+/\text{Ag}} = 0.799 \text{ V}$ and (b) $E^0_{\text{AgCl}/\text{Ag}} = 0.222 \text{ V}$. K_{sp} for AgCl = 1.82×10^{-10} . [10%]

Solution:



The Ag^+ concentration of this solution is given by

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} \text{ M}$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$

- (b) Write this last equation as

$$E = 0.222 - 0.0592 \log [\text{Cl}^-] = 0.222 - 0.0592 \log 0.0500 = 0.299 \text{ V}$$

3. Calculate the (a) thermodynamic potential of the following cell and the (b) free energy change associated with the cell reaction: [10%]

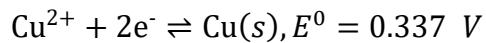
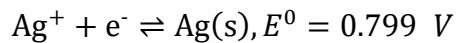


Refer to Table 1 for the standard reduction potential E^0 .

Faraday constant = 96485 C/mol.

Solution:

- (a) The two half-reactions and standard potentials are



The electrode potentials are

$$E_{\text{Ag}^+/\text{Ag}} = 0.799 - 0.592 \log \frac{1}{0.0200} = 0.6984 \text{ V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.337 - \frac{0.592}{2} \log \frac{1}{0.0200} = 0.2867 \text{ V}$$

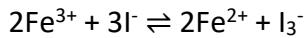
Note from the cell diagram that the silver electrode is the right-hand electrode and the copper electrode is the left-hand electrode. Therefore,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+/\text{Ag}} - E_{\text{Cu}^{2+}/\text{Cu}} = 0.6984 - 0.2867 \\ &= +0.412 \text{ V} \end{aligned}$$

- (b) The free energy change ΔG for the reaction $\text{Cu}(s) + 2\text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Ag}(s)$ is found from

$$\Delta G = -nFE_{\text{cell}} = -2 \times 96485 \text{ C} \times 0.412 \text{ V} = -79503 \text{ J} (18.99 \text{ kcal})$$

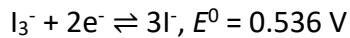
4. Calculate the equilibrium constant for the following reaction



Refer to Table 1 for the standard reduction potential E^0 .

[10%]

Solution:



We have multiplied the first half-reaction by 2 so that the number of moles of Fe^{3+} and Fe^{2+} will be the same as in the balanced overall equation. Write the Nernst equation for Fe^{3+} based on the half-reaction for a two-electron transfer, that is,

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

and

$$E_{\text{I}_3^-/\text{I}^-} = E_{\text{I}_3^-/\text{I}^-}^0 - \frac{0.0592}{2} \log \frac{[\text{I}^-]^3}{[\text{I}_3^-]}$$

At equilibrium, the electrode potentials are equal, and

$$\begin{aligned} E_{\text{Fe}^{3+}/\text{Fe}^{2+}} &= E_{\text{I}_3^-/\text{I}^-} \\ E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - \frac{0.0592}{2} \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} &= E_{\text{I}_3^-/\text{I}^-}^0 - \frac{0.0592}{2} \log \frac{[\text{I}^-]^3}{[\text{I}_3^-]} \end{aligned}$$

This equation rearranges to

$$\frac{2(E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - E_{\text{I}_3^-/\text{I}^-}^0)}{0.0592} = \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} - \log \frac{[\text{I}^-]^3}{[\text{I}_3^-]} = \log \frac{[\text{Fe}^{2+}]^2 [\text{I}_3^-]}{[\text{Fe}^{3+}]^2 [\text{I}^-]^3}$$

Recall that in this instance the concentration terms are *equilibrium concentrations*, and

$$\begin{aligned} \log K_{\text{eq}} &= \frac{2(E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - E_{\text{I}_3^-/\text{I}^-}^0)}{0.0592} = \frac{2(0.771 - 0.536)}{0.0592} = 7.94 \\ K_{\text{eq}} &= \text{antilog } 7.94 = 8.7 \times 10^7 \end{aligned}$$

5. Calculate the theoretical cell potential of the following cells. If the cell is short-circuited, indicate the direction of the spontaneous cell reaction: [10%]

- (a) $\text{Ag}|\text{Ag}^+(0.0575 \text{ M})|\text{H}^+(0.0333 \text{ M})|\text{O}_2(1.12 \text{ atm}), \text{Pt}$
 (b) SHE||HCOOH (0.1400 M), HCOO⁻(0.0700 M)|H₂(1.00 atm), Pt

Refer to Table 1 for the standard reduction potential E^0 .

Solution:

$$(a) E_{\text{right}} = 1.229 - \frac{0.0592}{4} \log \left(\frac{1}{1.12(0.0333)^4} \right) = 1.142 \text{ V}$$

$$E_{\text{left}} = 0.799 - 0.0591 \log \left(\frac{1}{0.0575} \right) = 0.726 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 1.142 - 0.726 = 0.416 \text{ V}$$

The spontaneous reaction would be oxidation on the left, reduction on the right.

$$(b) \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = 1.80 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]0.0700}{0.1400}$$

$$[\text{H}_3\text{O}^+] = \frac{(1.80 \times 10^{-4})(0.1400)}{0.0700} = 3.60 \times 10^{-4}$$

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2} \log \left(\frac{1.00}{(3.60 \times 10^{-4})^2} \right) = -0.204 \text{ V}$$

$$E_{\text{left}} = 0.000 \text{ V}$$

$$E_{\text{cell}} = -0.204 - 0.000 = -0.204$$

Because E_{cell} is negative, the reaction would not proceed spontaneously in the direction considered

6. A cell consisting of a saturated calomel electrode and a lead ion electrode developed a potential of -0.4706 V when immersed in 50.00 mL of a sample. A 5.00-mL addition of standard 0.02000 M lead solution caused the potential to shift to -0.4490 V. Calculate the molar concentration of lead in the sample. [10%]

Solution:

Assume that the activity of Pb^{2+} is approximately equal to $[\text{Pb}^{2+}]$. Thus,

$$p\text{Pb} = -\log[\text{Pb}^{2+}] = -\frac{E'_{\text{cell}} - C}{0.0592/2}$$

where E'_{cell} is the initial measured potential (-0.4706 V).

After the standard solution is added, the potential becomes E''_{cell} (-0.4490 V), and

$$\begin{aligned}-\log \frac{50.00 \times [\text{Pb}^{2+}] + 5.00 \times 0.0200}{50.00 + 5.00} &= -\frac{E''_{\text{cell}} - C}{0.0592/2} \\-\log(0.9091[\text{Pb}^{2+}] + 1.818 \times 10^{-3}) &= -\frac{E''_{\text{cell}} - C}{0.0592/2}\end{aligned}$$

Subtracting this equation from the first leads to

$$\begin{aligned}-\log \frac{[\text{Pb}^{2+}]}{(0.9091[\text{Pb}^{2+}] + 1.818 \times 10^{-3})} &= \frac{2(E''_{\text{cell}} - E'_{\text{cell}})}{0.0592} \\&= \frac{2[-0.4490 - (-0.4706)]}{0.0592} = 0.7297\end{aligned}$$

$$\frac{[\text{Pb}^{2+}]}{(0.9091[\text{Pb}^{2+}] + 1.818 \times 10^{-3})} = \text{antilog}(-0.7297) = 0.1863$$

$$[\text{Pb}^{2+}] = 3.45 \times 10^{-4} \text{ M}$$

7. The Na^+ concentration of a solution was determined by measurements with a sodium ion-selective electrode. The electrode system developed a potential of -0.2462V when immersed in 10.0 mL of the solution of unknown concentration. After addition of 1.00 mL of 2.00×10^{-2} M NaCl, the potential changed to -0.1994V. Calculate the Na^+ concentration of the original solution. [10%]

Solution:

$$\text{pNa} = -\log([\text{Na}^+]) = -\left(\frac{E'_{\text{cell}} - K}{0.0592}\right), \text{ where } E'_{\text{cell}} = -0.2462 \text{ V}$$

$$\text{After addition, } E''_{\text{cell}} = -0.1994 \text{ V}$$

$$-\log\left(\frac{10.00 \times [\text{Na}^+] + 1.00 \times (2.00 \times 10^{-2})}{10.00 + 1.00}\right) = -\frac{E''_{\text{cell}} - K}{0.0592}$$

$$-\log(0.9091[\text{Na}^{2+}] + 1.818 \times 10^{-3}) = -\frac{E''_{\text{cell}} - K}{0.0592}$$

Subtracting this latter equation from that of the initial potential gives

$$\begin{aligned} -\log([\text{Na}^+]) + \log(0.9091[\text{Na}^{2+}] + 1.818 \times 10^{-3}) &= -\left(\frac{E'_{\text{cell}} - K}{0.0592}\right) + \frac{E''_{\text{cell}} - K}{0.0592} \\ &= \frac{E''_{\text{cell}} - E'_{\text{cell}}}{0.0592} \end{aligned}$$

$$-\log \frac{[\text{Na}^{2+}]}{(0.9091[\text{Na}^{2+}] + 1.818 \times 10^{-3})} = \frac{-0.1994 + 0.2462}{0.0592} = 0.7905$$

$$\frac{[\text{Na}^{2+}]}{(0.9091[\text{Na}^{2+}] + 1.818 \times 10^{-3})} = \text{antilog}(-0.7905) = 0.16198$$

$$[\text{Na}^+] = 3.453 \times 10^{-4} \text{ M}$$

8. A solution containing the complex formed between Bi(III) and thiourea has a molar absorptivity of $9.32 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ at 470 nm.

- (a) What is the absorbance of a $5.67 \times 10^{-5} \text{ M}$ solution of the complex at 470 nm in a 1.00-cm cell? [3%]
- (b) What is the percent transmittance of the solution described in (a)? [3%]
- (c) What is the molar concentration of the complex in a solution that has the absorbance described in (a) when measured at 470 nm in a 2.50-cm cell? [4%]

Solution:

(a) $A = 9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 5.67 \times 10^{-5} \text{ mol L}^{-1} = 0.528$

(b) $\%T = 100 \times \text{antilog}(-0.528) = 29.6\%$

(c) $c = \frac{A}{\epsilon b} = \frac{0.528}{9.32 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 2.50 \text{ cm}} = 2.27 \times 10^{-5} \text{ M}$

9. $K_2Cr_2O_7$ 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.

The absorbance 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: $A_{Cr,440}=0.374$, $A_{Cr,545}=0.009$, $A_{Mn,440}=0.019$, $A_{Mn,545}=0.475$.

[10%]

Solution:

Using Beer's Law and $b = 1$ cm,

$$0.374 = \epsilon_{Cr,440} \times 1.00 \times 10^{-3}$$

$$\epsilon_{Cr,440} = 374 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$0.009 = \epsilon_{Cr,545} \times 1.00 \times 10^{-3}$$

$$\epsilon_{Cr,545} = 9 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$0.019 = \epsilon_{Mn,440} \times 2.00 \times 10^{-4}$$

$$\epsilon_{Mn,440} = 95 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$0.475 = \epsilon_{Mn,545} \times 2.00 \times 10^{-4}$$

$$\epsilon_{Mn,545} = 2.38 \times 10^3 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$A_{440} = \epsilon_{Cr,440}[Cr_2O_7^{2-}] + \epsilon_{Mn,440}[MnO_4^-]$$

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

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

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

Solving simultaneously,

$$[Cr_2O_7^{2-}] = 1.01 \times 10^{-3} M, \quad [MnO_4^-] = 2.95 \times 10^{-4} M$$

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.

10. Substances A and B have retention times of 16.40 and 17.63 minutes, respectively, on a 30.0-cm column. An unretained species passes through the column in 1.30 minutes. The peak widths (at base) for A and B are 1.11 and 1.21 minutes, respectively. Calculate [10%]

- (a) the column resolution
- (b) the average number of plates in the column
- (c) the plate height
- (d) the length of column required to achieve a resolution of 1.5
- (e) the time required to elute substance B on the column that gives an R_s value of 1.5.

Solution:

$$(a) R_s = \frac{2(17.63 - 16.40)}{1.11 + 1.21} = 1.06$$

$$(b) \text{ For Substance A, } N = 16 \left(\frac{16.40}{1.11} \right)^2 = 3493$$

$$\text{For Substance B, } N = 16 \left(\frac{17.63}{1.21} \right)^2 = 3397$$

$$N_{\text{avg}} = \frac{3493 + 3397}{2} = 3445$$

$$(c) H = \frac{L}{N} = \frac{30.0}{3445} = 8.7 \times 10^{-3} \text{ cm}$$

(d) The quantities k and α do not change greatly with increasing N and L . Thus,

$$\frac{(R_s)_2}{(R_s)_1} = \frac{\sqrt{N_1}}{\sqrt{N_2}}$$

Where the subscripts 1 and 2 refer to the original and longer columns, respectively. Substituting the appropriate values for N_1 , $(R_s)_1$, and $(R_s)_2$ gives

$$\frac{1.06}{1.5} = \frac{\sqrt{3445}}{\sqrt{N_2}}$$

$$N_2 = 3445 \left(\frac{1.5}{1.06} \right)^2 = 6.9 \times 10^3$$

But

$$L = NH = 6.9 \times 10^3 \times 8.7 \times 10^{-3} = 60 \text{ cm}$$

(e) Substituting $(R_s)_1$ and $(R_s)_2$ and dividing yield

$$\frac{(t_R)_1}{(t_R)_2} = \frac{(R_s)_1^2}{(R_s)_2^2} = \frac{17.63}{(t_R)_2} = \frac{(1.06)^2}{(1.5)^2}$$
$$(t_R)_2 = 35 \text{ min}$$

So, to obtain the improved resolution, the column length and thus the separation time must be doubled.

~ End of Paper ~

Table 1. Standard Reduction Potentials

Half Reaction	E^0 , V
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	1.229
$2H^+ + 2e^- \leftrightarrow H_2$	0
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.337
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	0.771
$I^-_3 + 2e^- \leftrightarrow I^-$	0.536
$Ag^+ + e^- \leftrightarrow Ag(s)$	0.799