11210CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 11-1-2024, 10:10 am to 12:10 pm

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

1. Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (a) $E^\circ_{Ag^+/Ag} = 0.799$ V and (b) $E^\circ_{AgCl/Ag} = 0.222$ V. For AgCl, $K_{sp} = 1.82 \times 10^{-10}$. **[5 % each]**

Solution:

(a) $Ag^+ + e^- \rightleftharpoons Ag_{(s)}$ $\qquad\qquad E^\circ_{Ag^+/Ag} = +0.799$ V

The Ag^+ concentration of this solution is given by

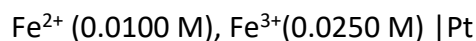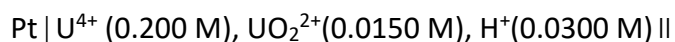$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9} \text{ M}$$

Substituting into the Nernst expression gives

$$E = 0.799 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$
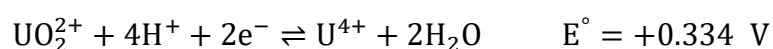
(b) Write this last equation as

$$E = 0.222 - 0.0592 \log[Cl^-] = 0.222 - 0.0592 \log 0.0500$$

$$= 0.299$$

2. Calculate the potential of the following cell, and indicate the reaction that would occur spontaneously if the cell were short-circuited. **[10 %]**

$$Pt \mid U^{4+} (0.200 \text{ M}), UO_2{}^{2+}(0.0150 \text{ M}), H^+(0.0300 \text{ M}) \parallel$$

$$Fe^{2+} (0.0100 \text{ M}), Fe^{3+}(0.0250 \text{ M}) \mid Pt$$

Solution:

The two half-reactions are

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad\qquad\qquad\qquad E^\circ = +0.771 \text{ V}$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^\circ = +0.334 \text{ V}$$

The electrode potential for the right-hand electrode is

$$E_{right} = 0.771 - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= 0.771 - 0.0592 \log \frac{0.0100}{0.0250} = 0.771 - (-0.0236)$$

$$= 0.7946 \text{ V}$$

The electrode potential for the left-hand electrode is

$$E_{left} = 0.334 - \frac{0.0592}{2} \log \frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$= 0.334 - \frac{0.0592}{2} \log \frac{0.200}{(0.0150)(0.0300)^4}$$

$$= 0.334 - 0.2136 = 0.1204 \text{ V}$$

and

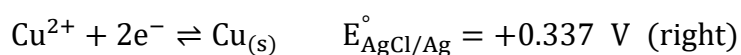$$E_{cell} = E_{right} - E_{left} = 0.7946 - 0.1204 = 0.6742 \text{ V}$$

The positive sign means that the spontaneous reaction is the oxidation of U^{4+} on the left and the reduction of Fe^{3+} on the right, or

$$U^{4+} + 2Fe^{3+} + 2H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 4H^+$$
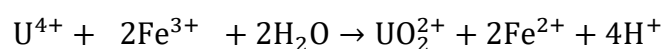
3. Calculate the potential required to initiate deposition of copper from a solution that is 0.010 M in CuSO$_4$ and contains sufficient H$_2$SO$_4$ to give a pH of 4.00. **[10 %]**

Solution:

The deposition of copper necessarily occurs at the cathode, which according to IUPAC convention is the right-hand electrode. Since there is not a more easily oxidizable species than water in the system, O$_2$ will evolve at the anode. The two half-reactions and their corresponding standard electrode potentials are

$$Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\circ_{AgCl/Ag} = +0.337 \text{ V (right)}$$

$$O_{2(g)} + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^\circ_{O_2/H_2O} = +1.229 \text{ V (left)}$$

The electrode potential for the Cu electrode is

$$E_{Cu^{2+}/Cu} = +0.337 - \frac{0.0592}{2} \log \frac{1}{0.010} = +0.278 \text{ V}$$

If O$_2$ is evolved at atmospheric pressure, or 1.00 atm, which is likely close to the barometric pressure in most laboratories the electrode potential for the oxygen electrode is

$$E_{O_2/H_2O} = +1.229 - \frac{0.0592}{4} \log \frac{1}{P_{O_2}[H^+]^4}$$

$$= +1.229 - \frac{0.0592}{4} \log \frac{1}{(1 \text{ atm})(1.00 \times 10^{-4})^4}$$

$$= +0.992 \text{ V}$$

and the cell potential is thus

$$E_{cell} = E_{right} - E_{left} = E_{Cu^{2+}/Cu} - E_{O_2/H_2O} = +0.278 - 0.992 = -0.714 \text{ V}$$

The negative sign shows that the cell reaction

$$2Cu^{2+} + 2H_2O \rightarrow O_{2(g)} + 4H^+ + 2Cu_{(s)}$$
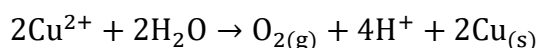
is nonspontaneous and that, to cause copper to be deposited according to the preceding reaction, apply a negative potential slightly greater than -0.714 V.

4. Calculate the equilibrium constant for the reaction   **[10 %]**

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

Solution:

$$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+} \qquad\qquad E^\circ = 0.771 \ V$$

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad\qquad E^\circ = 0.536 \ V$$
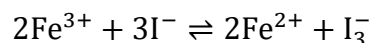
We have multiplied the first half-reaction by 2 so that the number of moles of Fe^{3+} and

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,

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

and

$$E_{I_3^-/I^-} = E^\circ_{I_3^-/I^-} - \frac{0.0592}{2} \log \frac{[I^-]^3}{[I_3^-]}$$

At equilibrium, the electrode potentials are equal, and

$$E_{Fe^{3+}/Fe^{2+}} = E_{I_3^-/I^-}$$

$$E^\circ_{Fe^{3+}/Fe^{2+}} - \frac{0.0592}{2} \log \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} = E^\circ_{I_3^-/I^-} - \frac{0.0592}{2} \log \frac{[I^-]^3}{[I_3^-]}$$

This equation rearranges to

$$\frac{2(E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{I_3^-/I^-})}{0.0592} = \log \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} - \log \frac{[I^-]^3}{[I_3^-]}$$

$$= \log \frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} + \log \frac{[I_3^-]}{[I^-]^3}$$

$$= \log \frac{[Fe^{2+}]^2[I_3^-]}{[Fe^{3+}]^2[I^-]^3}$$

Notice the change in the sign of the second logarithmic term by inverting the

fraction. Further arrangement gives

$$\log \frac{[Fe^{2+}]^2[I_3^-]}{[Fe^{3+}]^2[I^-]^3} = \frac{2(E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{I_3^-/I^-})}{0.0592}$$

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

concentrations, and

$$\log K_{eq} = \frac{2(E^{\circ}_{Fe^{3+}/Fe^{2+}} - E^{\circ}_{I_3^-/I^-})}{0.0592} = \frac{2(0.771 - 0.536)}{0.0592} = 7.94$$

$$K_{eq} = \text{antilog } 7.94 = 8.7 \times 10^7$$

Round the answer to two figures because log K_{eq} contains only two significant figures

(the two to the right of the decimal point).

5. 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 $[Pb^{2+}]$ and apply Equation

$$pX = -\log a_X = -\frac{(E_{cell} - C)}{0.0592/n}$$

Thus,

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

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

$$-\log\frac{50.00 \times [Pb^{2+}] + 5.00 \times 0.0200}{50.00 + 5.00} = -\frac{E''_{cell} - C}{0.0592/2}$$

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

Subtracting this equation from the first leads to

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

$$= \frac{2[-0.4490 - (-0.4706)]}{0.0592}$$

$$= 0.7297$$

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

$$[Pb^{2+}] = 4.08 \times 10^{-4} \text{ M}$$

6. The complex formed between Cu(I) and 1,10-phenanthroline has a molar absorptivity of 6850 L cm⁻¹ mol⁻¹ at 435 nm, the wavelength of maximum absorption. Calculate **[2.5 % each]**

(a) The absorbance of a 4.42×10^{-5} M solution of the complex when measured in a 1.00-cm cell at 435 nm.

(b) The percent transmittance of the solution in (a).

(c) The concentration of a solution that in a 5.00-cm cell has the same absorbance as the solution in (a).

(d) The path length through a 2.21×10^{-5} M solution of the complex that is needed for an absorbance that is the same as the solution in (a).

Solution:

(a)

$$A = 6850 \text{ L mol}^{-1}\text{cm}^{-1} \times 1.00 \text{ cm} \times 4.42 \times 10^{-5} \text{ mol L}^{-1} = 0.303$$

(b)

$$\%T = 100 \times \text{antilog}(-0.303) = 49.8\%$$

(c)

$$c = \frac{A}{\epsilon b} = \frac{0.303}{(6850 \text{ L mol}^{-1}\text{cm}^{-1} \times 5.00 \text{ cm})} = 8.85 \times 10^{-6} \text{ M}$$

(d)

$$b = \frac{A}{\epsilon c} = \frac{0.303}{(6850 \text{ L mol}^{-1}\text{cm}^{-1} \times 2.21 \times 10^{-5} \text{ mol L}^{-1})} = 2.00 \text{ cm}$$

7. Substances A and B have retention times of 16.40 and 17.63 minutes, respectively, on a 30-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 (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, and (e) the time required to elute substance B on the column that gives an Rs value of 1.5. **[2 % each]**

Solution:

(a)

Using Equation

$$(R_s = \frac{\Delta Z}{\frac{W_A}{2} + \frac{W_B}{2}} = \frac{2\Delta Z}{W_A + W_B} = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B})$$

give

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

(b)

Equation ($N = 16(\frac{t_R}{W})^2$) permits computation of N:

$$N = 16 \times (\frac{16.40}{1,11})^2 = 3493 \qquad \text{and} \qquad N = 16 \times (\frac{17.63}{1,21})^2 = 3397$$

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

(c)

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

(d) The quantities κ and α do not change greatly with increasing N and L. Thus, substituting N_1 and N_2 into Equation ($R_s = \frac{\sqrt{N}}{4}(\frac{\alpha-1}{\alpha})(\frac{\kappa}{1+\kappa})$) and dividing one of the resulting equations by the other yield

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

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

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

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

But

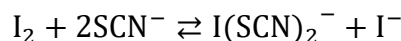$$L = NH = 6.9 \times 10^3 \times 8.7 \times 10^{-3} = 60 \ cm$$

(e)

Substituting $(R_s)_1$ and $(R_s)_2$ into Equation ($t_R = \frac{16Rs^2H}{\mu}(\frac{\alpha}{\alpha-1})^2\frac{(1+\kappa)^3}{\kappa^2}$) and dividing yield

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

$$(t_R)_2 = 35 \ min$$

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

8. To determine the equilibrium constant for the following reaction: **[5 % each]**

$$I_2 + 2SCN^- \rightleftarrows I(SCN)_2^{\ -} + I^-$$

25.0 mL of a 0.0100 M aqueous solution of I_2 was extracted with 10.0 mL of $CHCl_3$.

After extraction, spectrophotometric measurements revealed that the I_2

concentration of the aqueous layer was 1.12×10^{-4} M. An aqueous solution that

was 0.0100 M in I_2 and 0.100 M in KSCN was then prepared. After extraction of

25.0 mL of this solution with 10.0 mL of $CHCl_3$, the concentration of I_2 in the $CHCl_3$

layer was found from spectrophotometric measurement to be 1.02×10^{-3} M.

(a) What is the distribution constant for I_2 between $CHCl_3$ and H_2O?

(b) What is the formation constant for $I(SCN)_2^-$?

Solution:

(a)

$$[I_2]_{aq} = 1.12 \times 10^{-4} M$$

$$[I_2]_{org} = \frac{(mol \ I_{2tot} - mol \ I_{2aq})}{10 \ mL}$$

$$[I_2]_{org} = \frac{(25.0)(0.0100) - (25.0)(1.12 \times 10^{-4})}{10 \ mL} = 0.0247 \ M$$

$$K = \frac{[I_2]_{org}}{[I_2]_{aq}} = \frac{0.0247}{1.12 \times 10^{-4}} = 221$$

(b) After extraction,

$$[I_2]_{aq} = \frac{[I_2]_{org}}{K} = \frac{(1.02 \times 10^{-3})}{221} = 4.62 \times 10^{-6} \ M$$

$$[(SCN)_2^{\ -}] = [I^-] = \frac{(mmols \ I_{2tot} - mmols \ I_{2aq} - mmols \ I_{2org})}{25.0 \ mL}$$

$$[(SCN)_2^{\ -}] = [I^-]$$

$$= \frac{(25.0)(0.0100) - (25.0)(4.62 \times 10^{-6}) - (10.0)(1.02 \times 10^{-3})}{25.0}$$

$$= 0.0095874 \ M$$

$$[SCN^-] = (mmols \ SCN^-_{tot} - 2 \times mmols \ I(SCN)_2^{\ -})/(25.0 \ mL)$$

$$[\text{SCN}^-] = \frac{(25.0)(0.100) - 2 \times (25.0)(0.0095874)}{25.0} = 0.080825$$

$$K_f = \frac{[\text{I(SCN)}_2{}^-][\text{I}^-]}{[\text{I}_2][\text{SCN}^-]^2} = \frac{(0.0095874)^2}{(4.62 \times 10^{-6} \times (0.080825)^2)} = 3.05 \times 10^3$$

9. When measured with a F⁻ ion-selective electrode with a Nernstian response at 25°C, the potential due to F⁻ in unfluoridated groundwater in Foxboro, Massachusetts, was 40.0 mV more positive than the potential of tap water in Providence, Rhode Island. Providence maintains its fluoridated water at the recommended level of 1.00±0.05 mg F⁻/L. What is the concentration of F⁻ in mg/L in groundwater in Foxboro? (Disregard the uncertainty) **[10 %]**

(Atomic mass of F = 18.998 u)

Solution:

$[F^-]_{Providence} = 1 \ mg \ F^-/L = 5.26 \times 10^{-5} \ M$

$E_{Providence} = constant - 0.05916 \times log[5.26 \times 10^{-5}]$

$E_{Foxboro} = constant - 0.05916 \times log[F^-]_{Foxboro}$

$\triangle E = E_{Foxboro} - E_{Providence} = 0.0400 \ V$

$= -0.05916 \times log\dfrac{[F^-]_{Foxboro}}{5.26 \times 10^{-5}} \Rightarrow [F^-]_{Foxboro} = 1.11 \times 10^{-5} \ M = 0.211 \ mg/L$

10. The following data are for a liquid chromatographic column:

Length of packing	24.7 cm
Flow rate	0.313 mL/min
V_M	1.7 mL
V_s	0.164 mL

A chromatogram of a mixture of species A, B, C and D provided the following data:

	Retention Time, min	Width of Peak Base(W), min	Plate Number(N)
Nonretained	3.1	▬	▬
A	5.4	0.41	2775.491
B	13.3	1.07	2472.041
C	14.1	1.16	2363.971
D	21.6	1.72	2523.310

From those data, calculate for species B and C   **[2.5 % each]**

(a) the resolution

(b) the selectivity factor

(c) the length of column necessary to separate the two species with a resolution of

   $1.5(\bar{N} = 2534)$

(d) the time required to separate the two species on the column in part c

Solution:

(a)

$$R_s = \frac{2[(t_R)_C - ((t_R)_B)]}{W_B + W_C}$$

$$R_s = \frac{2(14.1 - 13.3)}{(1.07 + 1.16)} = 0.717 = 0.72$$

(b)

$$\alpha_{C,B} = \frac{(t_R)_C - t_M}{(t_R)_B - t_M} = \frac{14.1 - 3.1}{13.3 - 3.1} = 1.08 = 1.1$$

(c)

$$\frac{(R_s)_1}{(R_s)_2} = \frac{\sqrt{\overline{N}}}{\sqrt{N_2}} = \frac{0.717}{1.5} = \frac{\sqrt{2534}}{\sqrt{N_2}}$$

$$N_2 = \frac{2534 \times (1.5)^2}{(0.717)^2} = 11090 = 1.11 \times 10^4$$

$$H = \frac{L}{N} = \frac{24.7}{2534} = 9.75 \times 10^{-3} \text{ cm/plate}$$

$$L = 11090 \times 9.75 \times 10^{-3} = 108 \text{ cm}$$

(d)

$$\frac{(t_R)_1}{(t_R)_2} = \frac{(R_S)_1}{(R_S)_2} = \frac{14.1}{(t_R)_2} = \frac{(0.717)^2}{(1.5)^2}$$

$$(t_R)_2 = \frac{[14.1 \times (1.5)^2]}{0.717^2} = 61.7 = 62 \text{ min}$$

Table 1

Standard Electrode Potentials*	
Reaction	E^0 **at 25°C, V**
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017
$\mathbf{2H^+ + 2e^- \rightleftharpoons H_2(g)}$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763