

11010CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 11-01-2022, 10:10 am to 12:30 pm

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

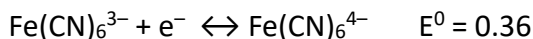
1. Calculate the potential of a platinum electrode immersed in a solution that is

(a) 0.0613 M in $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.00669 M in $\text{K}_3\text{Fe}(\text{CN})_6$ [5 %]

(b) Prepared by mixing 50.00 mL of 0.0607 M $\text{Ce}(\text{SO}_4)_2$ with an equal volume of 0.100 M FeCl_2 (assumed solutions were 1.00 M H_2SO_4 and use formal potentials). [5 %]

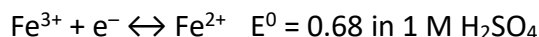
ANS:

(a)



$$E_{\text{Pt}} = 0.36 - 0.0592 \log \left(\frac{0.0613}{0.00669} \right) = 0.36 - 0.057 = 0.30 \text{ V}$$

(b)



$$\begin{aligned} \text{amount } \text{Ce}^{4+} \text{ consumed} &= \frac{0.0607 \text{ mmol } \text{Ce}(\text{SO}_4)_2}{\text{mL}} \times \frac{1 \text{ mmol } \text{Ce}^{4+}}{\text{mmol } \text{Ce}(\text{SO}_4)_2} \times 50.00 \text{ mL} \\ &= 3.04 \text{ mmol } \text{Ce}^{4+} \end{aligned}$$

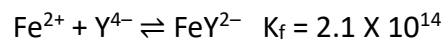
$$\text{amount } \text{Fe}^{2+} \text{ consumed} = \frac{0.100 \text{ mmol } \text{FeCl}_2}{\text{mL}} \times \frac{1 \text{ mmol } \text{Fe}^{2+}}{\text{mmol } \text{FeCl}_2} \times 50.00 \text{ mL} = 5.00 \text{ mmol}$$

$$\text{amount } \text{Fe}^{3+} \text{ formed} = \text{mmol } \text{Ce}^{4+} \text{ consumed} = 3.04 \text{ mmol } \text{Fe}^{3+}$$

$$\text{amount } \text{Fe}^{2+} \text{ remaining} = 5.00 - 3.04 = 0.196 \text{ mmol}$$

$$E_{\text{Pt}} = 0.68 - 0.0592 \log \left(\frac{1.965/100.0}{3.04/100.0} \right) = 0.68 - (-0.011) = 0.69 \text{ V}$$

2. Given the following formation constants



Calculate E^0 for the process: $\text{FeY}^{-} + \text{e}^{-} \rightleftharpoons \text{FeY}^{2-}$

[10 %]

ANS

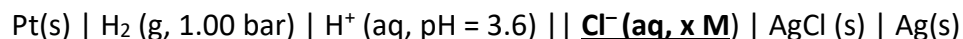
$$[\text{Fe}^{3+}] = \frac{[\text{FeY}^{-}]}{[\text{Y}^{4-}](1.3 \times 10^{25})} \quad \text{and} \quad [\text{Fe}^{2+}] = \frac{[\text{FeY}^{2-}]}{[\text{Y}^{4-}](2.1 \times 10^{14})}$$

$$\begin{aligned} E &= 0.771 - 0.0592 \log \left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \\ &= 0.771 - 0.0592 \log \left(\frac{[\text{FeY}^{2-}](1.3 \times 10^{25})}{[\text{FeY}^{-}](2.1 \times 10^{14})} \right) \end{aligned}$$

When $[\text{FeY}^{2-}] = [\text{FeY}^{-}] = 1.00$, $E = E_{\text{FeY}^{-}}^{\circ}$

$$E = 0.771 - 0.0592 \log \left(\frac{1.00 (1.3 \times 10^{25})}{1.00 (2.1 \times 10^{14})} \right) = 0.771 - 0.64 = 0.13 \text{ V}$$

3. The following cell can be used as a probe to find the concentration of Cl^- in the right compartment.

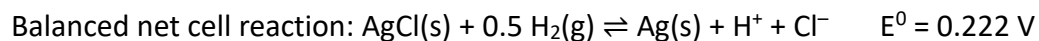
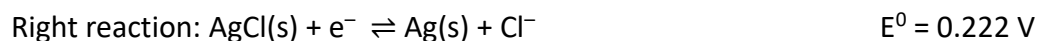


(a) Write reaction for each half-cell, a balanced net cell reaction, and the Nernst equation for the net cell reaction. [5 %]

(b) Given a measured cell voltage of 0.485 V, find $[\text{Cl}^-]$ in the right compartment. [5 %]

ANS:

(a)

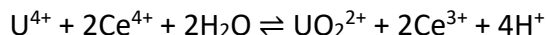


$$\text{Nernst equation for the net cell reaction: } E = 0.222 - 0.0592 \log \frac{[\text{H}^+][\text{Cl}^-]}{\sqrt{P_{\text{H}_2}}}$$

$$(b) 0.485 = 0.222 - 0.592 \log \frac{[10^{-3.6}][\text{Cl}^-]}{\sqrt{1.00}}$$

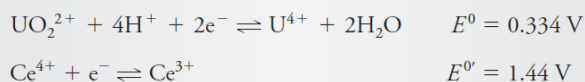
$$[\text{Cl}^-] = 0.143 \text{ M}$$

4. Derive an expression for the equivalence-point potential in the titration of 0.0500 M U^{4+} with 0.1000 M Ce^{4+} . Assume both solutions are 1.0 M in H_2SO_4 . [10 %]



ANS:

In Table 1, we find



For the oxidation of U^{4+}

$$E_{eq} = E_{UO_2^{2+}/U^{4+}}^0 - \frac{0.0592}{2} \log \frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

For the reduction of Ce^{4+}

$$E_{eq} = E_{Ce^{4+}/Ce^{3+}}^{0'} - \frac{0.0592}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

we multiply the first equation by 2 and combine the log term,

$$3E_{eq} = 2E_{UO_2^{2+}/U^{4+}}^0 + E_{Ce^{4+}/Ce^{3+}}^{0'} - 0.0592 \log \frac{[U^{4+}][Ce^{3+}]}{[UO_2^{2+}][Ce^{4+}][H^+]^4}$$

At equivalence: $[U^{4+}] = [Ce^{4+}]/2$ & $[UO_2^{2+}] = [Ce^{3+}]/2$.

Substituting these equations give the following equation.

$$\begin{aligned} E_{eq} &= \frac{2E_{UO_2^{2+}/U^{4+}}^0 + E_{Ce^{4+}/Ce^{3+}}^{0'}}{3} - \frac{0.0592}{3} \log \frac{2[Ce^{4+}][Ce^{3+}]}{2[Ce^{3+}][Ce^{4+}][H^+]^4} \\ &= \frac{2E_{UO_2^{2+}/U^{4+}}^0 + E_{Ce^{4+}/Ce^{3+}}^{0'}}{3} - \frac{0.0592}{3} \log \frac{1}{[H^+]^4} \end{aligned}$$

5. The Na^+ concentration of a solution was determined by measurements with a sodium ion-selective electrode. The electrode system developed a potential of -0.2462 V 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 -0.1994 V. calculate the Na^+ concentration of the original solution.

[15 %]

ANS:

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

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

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

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

Subtracting this latter equation from that for the initial potential gives

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

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

$$\text{or, } \log\left(\frac{[\text{Na}^+]}{0.9091[\text{Na}^+] + (1.818 \times 10^{-3})}\right) = -0.7905$$

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

$$[\text{Na}^+] = 0.1473[\text{Na}^+] + 2.945 \times 10^{-4}$$

$$[\text{Na}^+] = \underline{\underline{3.453 \times 10^{-4} \text{ M or rounding } 3.5 \times 10^{-4} \text{ M}}}$$

6. By how many volts will the potential of an ideal Mg^{2+} ion-selective electrode changed if the electrode is removed from $1.00 \times 10^{-4} \text{ M MgCl}_2$ and placed in $1.00 \times 10^{-3} \text{ M MgCl}_2$ at 25°C . [5 %]

ANS:

$$E_1 = \text{constant} + 0.0592/2 \log [1.00 \times 10^{-4}]$$

$$E_2 = \text{constant} + 0.0592/2 \log [1.00 \times 10^{-3}]$$

$$\Delta E = E_2 - E_1 = 0.0592/2 \log [1.00 \times 10^{-3}/1.00 \times 10^{-4}] = \underline{\underline{0.0296 \text{ V}}}$$

7. Identify factors that cause Beer's law relationship to be nonlinear. You should describe in detail the cause of this nonlinear relationship. [10 %]

ANS:

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 ($>0.01\text{ M}$) \Rightarrow 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.

8. The complex formed between Cu(I) and 1, 10-phenanthroline has a molar absorptivity of $7000 \text{ L cm}^{-1} \text{ mol}^{-1}$ at 435 nm, the wavelength of maximum absorption. Calculate

(a) the absorbance of a $6.17 \times 10^{-5} \text{ M}$ solution of the complex when measured in a 1.00-cm cell at 435 nm. [2.5 %]

(b) the percent transmittance of the solution in (a). [2.5 %]

(c) the concentration of a solution that in a 5.00-cm cell and has the same absorbance as the solution in (a). [2.5 %]

(d) the path length through a $3.13 \times 10^{-5} \text{ M}$ solution of the complex that is needed for an absorbance that is the same as the solution in (a). [2.5 %]

ANS:

$$(a) A = 7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 6.17 \times 10^{-5} \text{ mol L}^{-1} = 0.439$$

$$(b) \%T = 100 \times \text{antilog}(-0.439) = 36.4\%$$

$$(c) c = A/\epsilon b = 0.439/(7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 5.00 \text{ cm}) = 1.25 \times 10^{-5} \text{ M}$$

$$(d) b = A/\epsilon c = 0.439/(7000 \text{ L mol}^{-1} \text{ cm}^{-1} \times 3.13 \times 10^{-5} \text{ mol L}^{-1}) = 2.00 \text{ cm}$$

9. The distribution constant for **X** between *n*-hexane and water is 8.9. Calculate the concentration of **X** remaining in the aqueous phase after 50.0 mL of 0.200 M **X** is treated by extraction with the following quantities of *n*-hexane.

(a) one 40.0-mL portion. [1 %]

(b) two 20.0 mL portion. [1 %]

(c) four 10.0-mL portion. [1 %]

(d) eight 5.00-mL portion. [1 %]

ANS:

$$[X]_i = \left(\frac{V_{\text{aq}}}{V_{\text{org}}K + V_{\text{aq}}} \right)^i [X]_0$$

$$\text{(a)} [X]_1 = \left(\frac{50.0}{40.0 \times 8.9 + 50.0} \right) (0.200) = 0.0246 \text{ M}$$

$$\text{(b)} [X]_2 = \left(\frac{50.0}{20.0 \times 8.9 + 50.0} \right)^2 (0.200) = 9.62 \times 10^{-3} \text{ M}$$

$$\text{(c)} [X]_4 = \left(\frac{50.0}{10.0 \times 8.9 + 50.0} \right)^4 (0.200) = 3.35 \times 10^{-3} \text{ M}$$

$$\text{(d)} [X]_8 = \left(\frac{50.0}{5.0 \times 8.9 + 50.0} \right)^8 (0.200) = 1.23 \times 10^{-3} \text{ M}$$

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

length of packing	24.7 cm
flow rate	0.313 mL/min
V_M	1.37 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)
Nonretained	3.1	-
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

Calculate

- (a) the mean number of plates (N) from the four peaks. [2 %]
- (b) the plate height (H) for the column. [2 %]
- (c) the retention factor (k) for **B** and **C**. [2 %]
- (d) the distribution constant (K) for **B** and **C**. [2 %]
- (e) the resolution ($R_{b,c}$) for **B** and **C**. [2 %]
- (f) the selectivity factor ($\alpha_{b,c}$) for **B** and **C**. [2 %]
- (g) the length of column necessary to separate **B** and **C** with a resolution of 1.5. [2 %]
- (h) the time required to separate the two species on the column in part (g). [2 %]

ANS: (a) use the equation $N = 16(t_R/W)^2$ to calculate N for **A**, **B**, **C** and **D**, then average them.

	A	B	C	D
1	Problem 31-24			
2		t_r	W	N
3		5.4	0.41	2775.491
4		13.3	1.07	2472.041
5		14.1	1.16	2363.971
6		21.6	1.72	2523.31
7	Avg N			2533.703
8	Std. Dev N			174.3371
9	H	0.009749		
10	Spreadsheet Documentation			
11	Cell D3=16*(B3/C3)^2			
12	Cell D7=AVERAGE(D3:D6)			
13	Cell D8=STDEV.S(D3:D6)			
14	Cell B9=24.7/D7			

(b) $H = L/N = 0.0097 \text{ cm}$

(c) $k = (t_R - t_M)/t_M$

For **B**, $k_B = (13.3 - 3.1)/3.1 = 3.29$

For **C**, $k_C = (14.1 - 3.1)/3.1 = 3.55$

(d) $K = k V_M/V_S$

For compound **B**, $K_B = 3.29 \times 1.37/0.164 = 27$

For compound **C**, $K_C = 3.55 \times 1.37/0.164 = 30$

(e) $R_S = 2[(t_R)_C - (t_R)_B]/(W_B + W_C)$

$R_S = 2(14.1 - 13.3)/(1.07 + 1.16) = 0.717$

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

(g) $\frac{(R_S)_1}{(R_S)_2} = \frac{\sqrt{N_1}}{\sqrt{N_2}} = \frac{0.717}{1.5} = \frac{\sqrt{2534}}{\sqrt{N_2}}$

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

From (b) $H = 0.0097 \text{ cm/plate}$

$L = 11090 \times 0.0097 = 108 \text{ cm}$

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

$(t_R)_2 = [14.1 \times (1.5)^2]/(0.717)^2 = 61.7$

Table 1. Standard and Formal Electrode Potentials

Half Reaction	E ⁰ , V
$\text{Fe(CN)}_6^{3-} + \text{e}^- \leftrightarrow \text{Fe(CN)}_6^{4-}$	0.36
$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	0.68 in 1 M H ₂ SO ₄
$\text{Zn}^{2+} + \text{e}^- \leftrightarrow \text{Zn(s)}$	− 0.763
$\text{Co}^{2+} + \text{e}^- \leftrightarrow \text{Co(s)}$	− 0.277
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.000
$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	0.771
$\text{V}^{3+} + \text{e}^- \leftrightarrow \text{V}^{2+}$	− 0.256
$\text{V(OH)}_4^+ + 2\text{H}^+ + \text{e}^- \leftrightarrow \text{VO}^{2+} + 3\text{H}_2\text{O}$	1.00
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \leftrightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	0.334
$\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag(s)}$	0.799
$\text{AgCl(s)} + \text{e}^- \leftrightarrow \text{Ag(s)} + \text{Cl}^-$	0.222
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \leftrightarrow \text{U}^{4+} + 2\text{H}_2\text{O}$	0.334
$\text{Ce}^{4+} + \text{e}^- \leftrightarrow \text{Ce}^{3+}$	1.44