10710CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 08-01-2019, 10:10 am to 12:30 pm

Answer **all 10 questions** (total 110%). You have 140 minutes to finish this paper.

1. (a) In Figure 1, the right half-cell contains 0.50 M Ag(NO$_3$)$_{(aq)}$ and the left half-cell contain 0.010 M Cd(NO$_3$)$_{2(aq)}$.

(a) Write the net cell reaction. [**5%**]

(b) Find the voltage of the cell and state whether the reaction is spontaneous in the forward or reverse direction. [**10%**]

$E^0_{Ag+/Ag} = 0.799\ V,\ E^0_{Cd2+/Cd} = -0.402\ V$
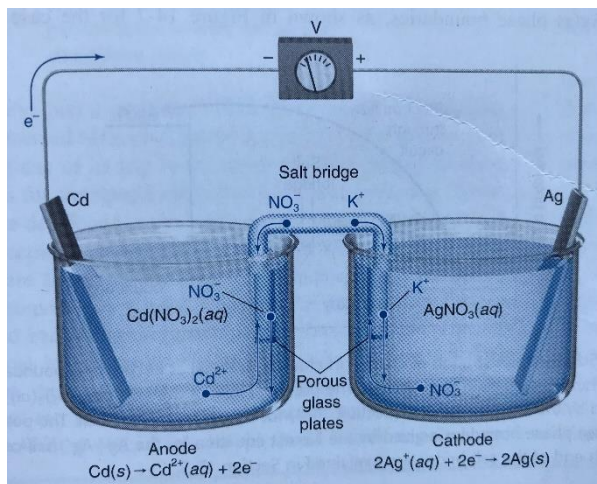
Figure 1.

Solution:

(a) Net cell reaction

Right electrode: 2Ag$^+$ +2e$^-$ $\longleftrightarrow$ 2Ag(s)   E^o = 0.799V

Left electrode: Cd^{2+} + 2e$^-$ $\longleftrightarrow$ Cd(s)   E^o = −0.4.02 V

Net cell reaction: Cd(s) + 2Ag$^+$ $\longleftrightarrow$ Cd^{2+} + 2Ag(s)
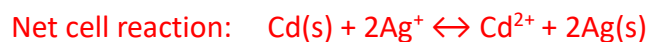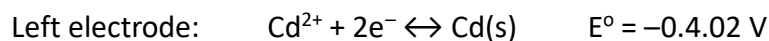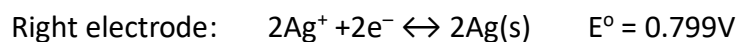
(b) Nernst equation for the right electrode:

$$E_{right} = E^o - \frac{0.0592}{2} log \frac{1}{[Ag+]^2}$$

$$= 0.799 - \frac{0.0592}{2} log \frac{1}{[0.50]^2}$$

$$= 0.781V$$

Nernst equation for the left electrode:

$$E_{left} = E^o - \frac{0.0592}{2} log \frac{1}{[Cd2+]}$$

$$= -0.402 - \frac{0.0592}{2} log \frac{1}{[0.010]}$$

$$= -0.461V$$

Cell voltage E = E_{right} − E_{left} = 0.781 − (−0.461) = 1.242 V

The voltage is positive, so the reaction is spontaneous in the forward direction.

2. Find the equilibrium constant for the reaction below: [**10%**]

$$Cu_{(s)} + 2Fe^{3+} \leftrightarrow 2Fe^{2+} + Cu^{2+}$$
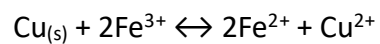
$E^0_{Fe3+/Fe2+} = 0.771 \ V, \ E^0_{Cu2+/Cu} = 0.339 \ V$

Solution:

Right cell electrode: $2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+}$ E° = 0.771

Left cell electrode: $Cu^{2+} + 2e^- \leftrightarrow Cu(s)$ E° = 0.339

To find E° of the net reaction
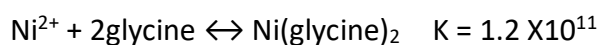
E° = E$_{right}$ − E$_{left}$ = 0.771 − 0.339 = 0.432V
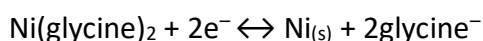
E° = $\frac{0.0592}{2} log K$

0.432 = $\frac{0.0592}{2} log K$

K = 10$^{(2)(0.432)(0.0592)}$

   = 4 X 10^{14}

3. The formation constant of $Ni(glycine)_2$ and the reduction potential E^o for $Ni^{2+}/Ni_{(s)}$

are shown below:

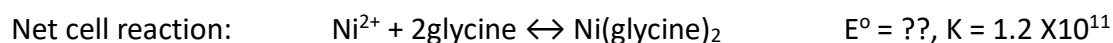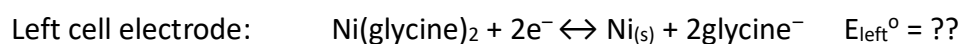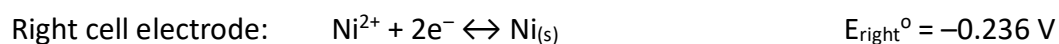$$Ni^{2+} + 2glycine \leftrightarrow Ni(glycine)_2 \quad K = 1.2 \times 10^{11}$$

$$Ni^{2+} + 2e^- \leftrightarrow Ni_{(s)} \qquad\qquad E^o = -0.236 \text{ V}$$

Based on the above data, calculate the value of E^o for the reaction below **[10%]**

$$Ni(glycine)_2 + 2e^- \leftrightarrow Ni_{(s)} + 2glycine^-$$

Solution:

We need to see the relation among the three reactions:

Right cell electrode: $\quad Ni^{2+} + 2e^- \leftrightarrow Ni_{(s)}$ $\qquad\qquad\qquad$ $E_{right}^o = -0.236$ V

Left cell electrode: $\quad Ni(glycine)_2 + 2e^- \leftrightarrow Ni_{(s)} + 2glycine^-$ $\quad$ $E_{left}^o = ??$

Net cell reaction: $\quad Ni^{2+} + 2glycine \leftrightarrow Ni(glycine)_2$ $\qquad$ $E^o = ??, K = 1.2 \times 10^{11}$

We know that $E_{right}^o - E_{left}^o$ must equal E^o, so we can deduce the value of E_{left}^o if we

can find E^o. But, E^o can be determined from the equilibrium constant of the net

reaction:

$E^o = \dfrac{0.0592}{2} log K = \dfrac{0.0592}{2} \log(1.2 \times 10^{11}) = 0.328$ V

Hence, the standard reduction potential for the left half reaction is

$E^o = E_{right}^o - E_{left}^o$

$0.328 = -0.236 - E_{left}^o$

$E_{left}^o = -0.564$ V

4. 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 X10^{-2} M NaCl, the potential changed to −0.1994V. Calculate the Na$^+$ concentration of the original solution. [**10%**]

Solution:

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

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

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

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

Subtracting this latter equation from that for the initial potential gives

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

$$= \left(\frac{E_{\text{cell}}'' - E_{\text{cell}}'}{0.0592}\right)$$

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

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

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

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

[Na$^+$] = 3.453 × 10^{-4} M or rounding 3.5 × 10^{-4} M

5. Explain why a silver electrode can be used as an indicator electrode for Ag^+ and for halides. [**5%**]

Solution:

A silver electrode serves as an indicator for Ag^+ by virtue of the equilibrium

$Ag^+ + e^- \leftrightarrow Ag(s)$ that occurs at its surface. If the solution is saturated with silver halide, then [Ag+] is affected by changes in halide concentration. Therefore, the electrode is also an indicator for halide.

6. The detection of Li^+ with Li^+ ion-selective electrode can be interfered by high concentration of H^+. The selectivity coefficient ($K_{Li+,H+}^{Pot}$) for the Li^+ ion-selective electrode is 4×10^{-4}. When this electrode is placed in a 3.44×10^{-4} M Li^+ solution at pH 10, the potential is $-0.333V$ versus SCE reference electrode. What would be the potential if the pH were lowered to 1.1 and the ionic strength were kept constant? [**10%**]

Solution:

At pH 10, the effect of H^+ will be negligible because $[H^+] << [Li^+]$

$-0.333V$ = constant + $0.0592 \log [3.44 \times 10^{-4}]$

Constant = $-0.128V$

At pH 1.1, ($[H^+] = 0.079$ M), we must include the interference by H^+

E = $-0.128 + 0.0592 \log [3.44 \times 10^{-4} + (4 \times 10^{-4})(0.079)]$ = $-0.331V$

7. At 580 nm, the wavelength of its maximum absorption, the complex $Fe(SCN)^{2+}$ has a molar absorptivity of 7.00×10^3 $Lcm^{-1}mol^{-1}$. Calculate

(a) The absorbance of a 3.40×10^{-5} M solution of the complex at 580 nm in a 1.00 cm cell. **[2.5%]**

(b) The absorbance of a solution in which the concentration of the complex is twice that in (a). **[2.5%]**

(c) The transmittance of the solutions described in (a). **[2.5%]**

(d) The absorbance of a solution that has half the transmittance of that described in (a). **[2.5%]**

Solution:

(a) $A = 7.00 \times 10^3$ L mol^{-1} cm^{-1} $\times 1.00$ cm $\times 3.40 \times 10^{-5}$ mol L^{-1} = **0.238**

(b) A $= 7.00 \times 10^3 \times 1.00 \times 2 \times 3.40 \times 10^{-5}$ = **0.476**

(c) T = antilog(-0.238) = **0.578**

(d) $A = -\log(T) = -\log(0.578/2)$ = **0.539**

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. **[10%]**

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,

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

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

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

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

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

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

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

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

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.

9. A solute with a partition coefficient of 4.0 is extracted from 10 mL of phase 1 to phase 2.

(a) What volume of phase 2 is needed to extract 99% of the solution in single extraction? [**5%**]

(b) What is the total volume of phase 2 needed to remove 99% of the solute in three equal extractions? [**5%**]

Solution:

(a) Fraction remaining q = $\dfrac{V1}{V1+KV2}$

$0.01 = \dfrac{10}{10+4.0V2}$

V2 = 248 mL

(b) $0.01 = (\dfrac{10}{10+4.0V2})^3$

V2 = 9.1 mL

Total volume = 9.1*3 = 27.3 mL

10. Consider a chromatography experiment in which wo components with retention factors k_1 = 4.00 and k_2 = 5.00 are injected into a column with N = 1.00×10^3 theoretical plate numbers. The retention time for the less-retained component is t_{r1} = 10.0 minutes.

(a) Calculate t_m (dead time) and t_{r2}. Find $w_{1/2}$ (width at half height) and w (width at the base) for each peak. [**10%**]

(b) Calculate the resolution of the two peaks. [**5%**]

(c) Supposing the two peaks have the same amplitude (height), sketch the chromatogram and indicate the half-widths accurately. [**5%**]

Solution:

(a) $k_1 = \frac{tr1 - tm}{tm}$

$4.00 = \frac{10 - tm}{tm}$

t_m = 10/5 = 2.00 minutes

t_{r2} = t_m(k_2 +1) = 2.00(5.00 +1) = 12.00 minutes

N = $(t_{r1}/\sigma)^2$

$\sigma_1 = \frac{tr1}{\sqrt{N}} = \frac{10}{\sqrt{1000}}$ = 0.316 minutes

N = 5.54 $(t_{r1}/w_{1/2})^2 = (t_{r1}/\sigma_1)^2$

$w_{1/2}$ (peak 1) = 2.35σ1 = 0.74 minutes

w (peak 1) = 4σ1 = 1.26 minutes

$\sigma_2 = \frac{tr2}{\sqrt{N}} = \frac{12.00}{\sqrt{1000}}$ = 0.379 minutes

Using the same method, we can find
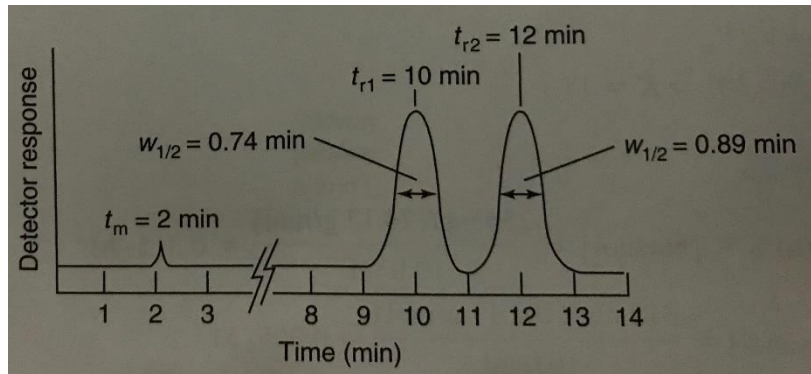
$w_{1/2}$ (peak 2) = 2.35σ2 = 0.89 minutes

w (peak 2) = 4σ2 = 1.52minutes

(b) Resolution Rs = $\frac{2[(tr1)-(tr2)]}{w1+w2}$

   = $\frac{2[12-10]}{1.26+1.52}$

   = 1.44

(c)

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