

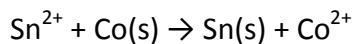
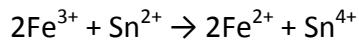
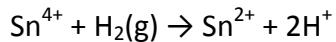
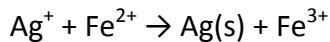
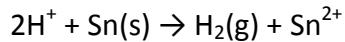
10910CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 05-01-2021, 10:10 am to 12:10 pm

Answer all 10 questions (total 110%). You have 2 hours and 20 minutes to finish this paper.

1. Consider the following oxidation/reduction reactions:

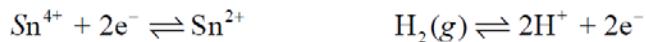


(i) Write each net process in term of two balanced half-reactions. [5 %]

(ii) Identify the reduction half-reaction and arrange them in the order of increasing reduction potential. [5 %]

Ans:

(i)



(ii)

Reactions	E°
$\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag(s)}$	0.799
$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	0.771
$\text{Sn}^{4+} + 2\text{e}^- \leftrightarrow \text{Sn}^{2+}$	0.154
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	0.00
$\text{Sn}^{2+} + \text{e}^- \leftrightarrow \text{Sn(s)}$	-0.136
$\text{Co}^{2+} + 2\text{e}^- \leftrightarrow \text{Co(s)}$	-0.277

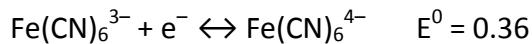
2. Calculate the potential of a platinum electrode immersed in a solution that is

(i) 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 %]

(ii) 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 %]

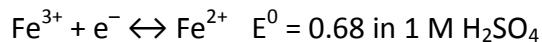
Ans:

(i)



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

(ii)



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

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

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

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

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

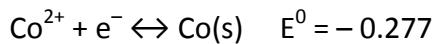
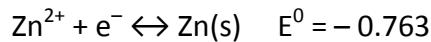
3. Calculate the theoretical cell potential of the following cells. If the cell is short-circuited, indicate the direction of the spontaneous cell reaction.



$$K_a(\text{HCOOH}) = 1.8 \times 10^{-4}, \text{SHE} = \text{Standard Hydrogen Electrode}$$

ANS:

(i)



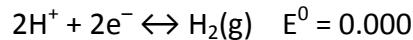
$$E_{\text{right}} = -0.277 - \frac{0.0592}{2} \log\left(\frac{1}{5.87 \times 10^{-4}}\right) = -0.373 \text{ V}$$

$$E_{\text{left}} = -0.763 - \frac{0.0592}{2} \log\left(\frac{1}{0.100}\right) = -0.793 \text{ V}$$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.373 - (-0.793) = 0.420 \text{ V}$$

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

(ii)



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

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

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

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

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

Because E_{cell} is negative, the reaction would not proceed spontaneously in the direction considered (reduction on the left, oxidation on the right).

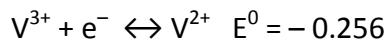
4. Generate equilibrium constant expressions for the following reactions and calculate the K_{eq} values of the two reactions.



ANS:

(i)

Note that in these calculations, it is necessary to round the answers to either one or two significant figures because the final step involves taking the antilogarithm of a large number.



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

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

$$K_{\text{eq}} = 2.23 \times 10^{17}$$

(ii)



$$1.00 - \frac{0.0592}{2} \log\left(\frac{[\text{VO}^{2+}]^2}{[\text{V(OH)}_4^+]^2 [\text{H}^+]^4}\right) = 0.334 - \frac{0.0592}{2} \log\left(\frac{[\text{U}^{4+}]}{[\text{UO}_2^{2+}] [\text{H}^+]^4}\right)$$

$$\frac{(1.00 - 0.334) 2}{0.0592} = \log\left(\frac{[\text{VO}^{2+}]^2 [\text{UO}_2^{2+}]}{[\text{V(OH)}_4^+]^2 [\text{U}^{4+}]}\right) = \log K_{\text{eq}} = 22.50$$

$$K_{\text{eq}} = 3.2 \times 10^{22}$$

5. Answer the following questions:

- (i) Calculate $E_{\text{AgIO}_3}^{\circ}$ for the process: $\text{AgIO}_3(s) + e^- \leftrightarrow \text{Ag}(s) + \text{IO}_3^-$. The solubility constant for Silver iodate is $K_{\text{sp}} = [\text{Ag}][\text{IO}_3^-] = 3.1 \times 10^{-8}$. [5 %]
- (ii) Use the shorthand notation to describe a cell consisting of a saturated calomel reference electrode ($E^{\circ} = 0.244$) and a silver indicator electrode that could be used to measure pIO_3^- . [5 %]
- (iii) Develop an equation that relates the potential of the cell in (ii) to pIO_3^- . [5 %]
- (iv) Calculate pIO_3^- if the cell in (ii) has a potential of 0.306 V. [5 %]

ANS:



$$E_{\text{Ag}} = 0.799 - 0.0592 \log \left(\frac{1}{[\text{Ag}^+]} \right) \quad K_{\text{sp}} = [\text{Ag}^+][\text{IO}_3^-] = 3.1 \times 10^{-8}$$

$$E_{\text{Ag}} = 0.799 - 0.0592 \log \left(\frac{[\text{IO}_3^-]}{K_{\text{sp}}} \right)$$

When $[\text{IO}_3^-] = 1.00$, E_{Ag} is equal to $E_{\text{AgIO}_3}^{\circ}$ for the reduction of AgIO_3 , that is,

$$E_{\text{AgIO}_3}^{\circ} = 0.799 - 0.0592 \log \left(\frac{1.00}{3.1 \times 10^{-8}} \right) = 0.354 \text{ V}$$

(ii) SCE || $\text{IO}_3^- (\text{x M})$, $\text{AgIO}_3(\text{sat'd})$ | Ag SCE = saturated calomel electrode

(iii)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{AgIO}_3}^{\circ} - E_{\text{SCE}} \\ &= (0.354 - 0.0592 \log ([\text{IO}_3^-]) - 0.244) \\ &= 0.110 + 0.0592 \text{pIO}_3 \end{aligned}$$

$$\text{pIO}_3 = \frac{E_{\text{cell}} - 0.110}{0.0592}$$

(iv) $\text{pIO}_3 = \frac{0.306 - 0.110}{0.0592} = 3.31$

6. The cell

SCE || H⁺ (a = x) | glass electrode

has a potential of 0.2106 V when the solution in the right-hand compartments is a buffer of pH 4.006. The following potentials are obtained when the buffer is replaced with unknowns. Calculate the pH and the hydrogen ion activity of each unknown.

(i) – 0.2902 V [2.5 %]

(ii) + 0.1241 V [2.5 %]

(iii) Assuming an uncertainty of 0.002 V in the junction potential, what is the range of hydrogen ion activities for (a) within which the true value might be expected to lie? [5 %]

ANS:

$$\text{pH} = -\frac{1(E_{\text{cell}} - K)}{0.0592} \quad \text{and} \quad 4.006 = -\frac{(0.2106 - K)}{0.0592}$$
$$K = (4.006 \times 0.0592) + 0.2106 = 0.447755$$

(i) $\text{pH} = -\frac{(-0.2902 - 0.447755)}{0.0592} = 12.47$

$$a_{\text{H}^+} = \text{antilog}(-12.4655) = 3.42 \times 10^{-13} \text{ M}$$

(ii) $\text{pH} = -\frac{(0.1241 - 0.447755)}{0.0592} = 5.47$

$$a_{\text{H}^+} = \text{antilog}(-5.4671) = 3.41 \times 10^{-6} \text{ M}$$

(iii) For part (i)

$$\text{If } E = -0.2902 + 0.002 = -0.2882 \text{ V}$$

$$\text{pH} = -\frac{(-0.2882 - 0.447755)}{0.0592} = 12.43$$

$$a_{\text{H}^+} = \text{antilog}(-12.4317) = 3.70 \times 10^{-13} \text{ M}$$

$$\text{If } E = -0.2902 - 0.002 = -0.2922 \text{ V}$$

$$\text{pH} = -\frac{(-0.2922 - 0.447755)}{0.0592} = 12.50$$

$$a_{\text{H}^+} = \text{antilog}(-12.4992) = 3.17 \times 10^{-13} \text{ M}$$

Thus pH should be 12.43 to 12.50 and a_{H^+} in the range of 3.17 to $3.70 \times 10^{-13} \text{ M}$

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

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

(ii) The absorbance of a solution in which the concentration of the complex is twice that in (i).

[2.5 %]

(iii) The transmittance of the solutions described in (i) and (ii). [2.5 %]

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

ANS:

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

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

(iii) For part (i), $T = \text{antilog}(-0.238) = 0.578$

For part (ii), $T = \text{antilog}(-0.476) = 0.334$

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

8. A solution with a “true” absorbance [$A = -\log(P_0/P)$] of 2.10 was placed in a spectrophotometer with a stray light percentage (P_s/P_0) of 0.75.

(a) What absorbance A' would be measured? [5 %]

(b) What percentage error would result? [5 %]

ANS:

(i) $2.10 = -\log(P/P_0)$ $P/P_0 = 0.0079433$

$$P = 0.007943 P_0$$

$$P_s/P_0 = 0.0075$$

$$P_s = 0.0075 P_0$$

$$\begin{aligned} A' &= \left(\frac{P_0 + P_s}{P + P_s} \right) = \log \left(\frac{P_0 + 0.0075P_0}{0.007943P_0 + 0.0075P_0} \right) = \log \left(\frac{1.0075P_0}{0.015443P_0} \right) = \log(65.2139) \\ &= 1.81 \end{aligned}$$

(ii) Error = $[(1.81 - 2.10)/2.10] \times \%100 = -13.6\%$

9. To determine the equilibrium constant for the following reaction



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. Subsequently, 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.

(i) What is the distribution constant for I_2 between $CHCl_3$ and H_2O ? [5 %]

(ii) What is the formation constant for $I(SCN)_2^-$? [5 %]

ANS:

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

$$[I_2]_{org} = (\text{mols } I_2_{tot} - \text{mols } I_2_{aq})/(10.0 \text{ mL})$$

$$[I_2]_{org} = \frac{(25.0)(0.0100) - (25.0)(1.12 \times 10^{-4})}{10.0} = 0.0247 \text{ M}$$

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

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

$$[I(SCN)_2^-] = [I^-] = (\text{mmols } I_2_{tot} - \text{mmols } I_2_{aq} - \text{mmols } I_2_{org})/(25.0 \text{ mL})$$

$$[I(SCN)_2^-] = [I^-] = \frac{(25.0)(0.0100) - (25.0)(4.62 \times 10^{-6}) - (10.0)(1.02 \times 10^{-3})}{25.0} = 0.0095874 \text{ M}$$

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

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

$$K_f = \frac{[I(SCN)_2^-][I^-]}{[I_2][SCN^-]^2} = (0.0095874)^2 / (4.62 \times 10^{-6} \times (0.080825)^2) = 3.05 \times 10^3$$

10. The total cation content of natural water is often determined by exchanging the cations for hydrogen ions on a strong-acid ion-exchange resin. A 25.0 mL sample of a natural water was diluted to 100 mL with distilled water, and 2.0 g of a cation-exchange resin was added. After stirring, the mixture was filtered and the solid remaining on the filter paper was washed with three 15.0 mL portions of water. The filtrate and washings required 15.3 mL of 0.0202 M NaOH to give a bromocresol green end point.

- (i) Calculate the number of millimoles of cation present in exactly 1.00 L of sample. [5 %]
(ii) Report the results in terms of milligrams of CaCO₃ (MW = 100.087 g/mol) per liter. [5 %]

ANS:

(i) amount H⁺ resulting from exchange = 15.3 mL × 0.0202 mmol/mL = 0.3091 mmol

mmols H⁺ = mol cation = 0.3091 in 0.0250 L sample

0.3091 mmol cation/0.0250 L = 12.36 mmol cation/L

(ii) $\frac{12.36 \text{ mmol cation}}{\text{L}} \times \frac{1 \text{ mmol CaCO}_3}{2 \text{ mmol cation}} \times \frac{100.087 \text{ mg CaCO}_3}{\text{mmol CaCO}_3} = 619 \text{ mg CaCO}_3/\text{L}$

~ End of Paper ~

Table 1. Standard and Formal Electrode Potentials

Half Reaction	E^0 , V
$\text{Fe}(\text{CN})_6^{3-} + \text{e}^- \leftrightarrow \text{Fe}(\text{CN})_6^{4-}$	0.36
$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	0.68 in 1 M H_2SO_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