

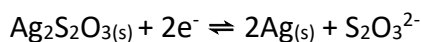
10610CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 11-01-2018, 10:10 am to 12:10 pm

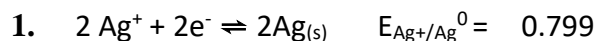
Answer **all 10 questions** (total 100%). You have **2** hours to finish this paper.

1. The solubility-product constant for Ag_2SO_3 is 1.5×10^{-14} . Calculate E^0 for the process below at the standard condition. **[10%]**



$$E_{\text{Ag}^+/\text{Ag}}^0 = 0.799 \text{ V}$$

Ans:



$$[\text{Ag}^+]^2 [\text{SO}_3^{2-}] = 1.5 \times 10^{-14} = K_{\text{sp}}$$

$$E = 0.799 - \frac{0.0592}{2} \log \left(\frac{1}{[\text{Ag}^+]^2} \right) = 0.799 - \frac{0.0592}{2} \log \left(\frac{[\text{SO}_3^{2-}]}{K_{\text{sp}}} \right)$$

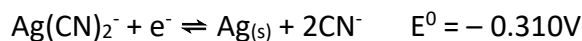
At standard condition, $[\text{SO}_3^{2-}] = 1.00$, Thus,

$$E = 0.799 - \frac{0.0592}{2} \log \left(\frac{1.00}{K_{\text{sp}}} \right) = 0.799 - \frac{0.0592}{2} \log \left(\frac{1.00}{1.5 \times 10^{-14}} \right) = 0.799 - 0.409 = 0.390 \text{ V}$$

2. (a) Calculate the voltage (E) of the cell [8%]



by considering the following reactions:



(b) Indicate the direction of electron flow. [2%]

Ans: 2

$$E = \left\{ -0.310 - 0.05916 \log \frac{[\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} \right\} - \left\{ 0.339 - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]} \right\}$$

We know that $[\text{Ag}(\text{CN})_2^-] = 0.010 \text{ M}$ and $[\text{Cu}^{2+}] = 0.030 \text{ M}$. To find $[\text{CN}^-]$ at pH 8.21, we write

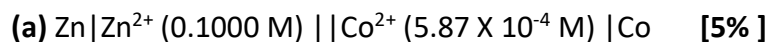
$$\frac{[\text{CN}^-]}{[\text{HCN}]} = \frac{K_a}{[\text{H}^+]}$$

$$[\text{CN}^-] = 0.10 [\text{HCN}]$$

Because $[\text{CN}^-] + [\text{HCN}] = 0.10 \text{ M}$, $[\text{CN}^-] = 0.0091 \text{ M}$. putting this concentration into the Nernst equation gives $E = -0.187 - (0.294) = -0.481 \text{ V}$

(b) Electrons flow from the more negative Ag electrode (-0.187 V) to the more positive Cu electrode (0.294 V).

3. Calculate the theoretical cell potential of the following cells. State the direction of the electron flow.



$$(E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.763 \text{ V}, E_{\text{Co}^{2+}/\text{Co}}^0 = -0.277 \text{ V})$$



$$(E_{\text{Hg}^{2+}/\text{Hg}}^0 = 0.854 \text{ V}, E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.771 \text{ V})$$

Ans: 3. (a)

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

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

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

Electrons flow from the more negative zinc electrode (-0.793V) to the more positive cobalt electrode (-0.373V) through the circuit.

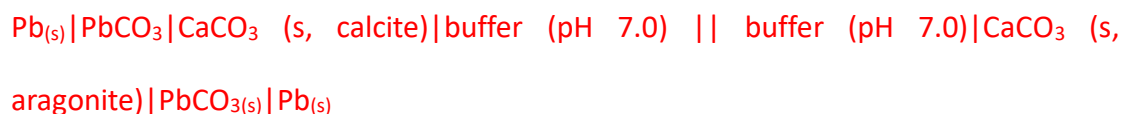
$$(b) \quad E_{\text{right}} = 0.854 - \frac{0.0592}{2} \log \left(\frac{1}{0.0350} \right) = 0.811 \text{ V}$$

$$E_{\text{left}} = 0.771 - \frac{0.0592}{1} \log \left(\frac{0.0700}{0.1600} \right) = 0.792 \text{ V}$$

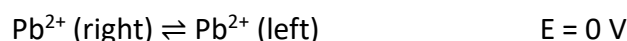
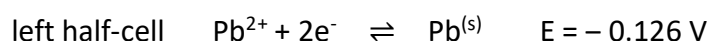
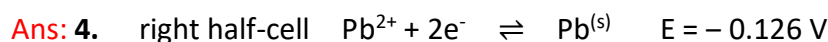
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.811 - 0.792 = \mathbf{0.019 \text{ V}}$$

Electrons flow from the more negative platinum electrode (-0.792V) to the more positive mercury electrode (0.811V) through the circuit.

4. The following cells were constructed to find the difference in K_{sp} between two naturally occurring forms of $\text{CaCO}_3(s)$, called calcite and aragonite.



Each compartment of the cell contains a mixture of solid PbCO_3 ($K_{sp} = 7.4 \times 10^{-14}$) and either calcite or aragonite, both of which have $K_{sp} \sim 5 \times 10^{-9}$. The measured cell voltage was -1.8 mV. Find the ratio of solubility products, K_{sp} (for calcite)/ K_{sp} (for aragonite). Hint: Use the concentration cell concept to solve the question. [10%]



Nernst equation for net cell reaction

$$-0.0018 \text{ V} = -\frac{0.05916}{2} \log \frac{[\text{Pb}^{2+}(\text{left})]}{[\text{Pb}^{2+}(\text{right})]}$$

$$\frac{[\text{Pb}^{2+}(\text{left})]}{[\text{Pb}^{2+}(\text{right})]} = 1.15$$

For each half-cell, we can write $[\text{CO}_3^{2-}] = K_{sp}(\text{PbCO}_3)/[\text{Pb}^{2+}]$

$$\frac{[\text{CO}_3^{2-}(\text{left})]}{[\text{CO}_3^{2-}(\text{right})]} = \frac{K_{sp}(\text{PbCO}_3)/[\text{Pb}^{2+}(\text{left})]}{K_{sp}(\text{PbCO}_3)/[\text{Pb}^{2+}(\text{right})]} = \frac{1}{1.15} = 0.87$$

In each compartment, the Ca^{2+} concentration is equal to the total concentration of all carbonate species (since PbCO_3 is much less soluble than CaCO_3). Let the fraction of all carbonate species in the form CO_3^{2-} be αCO_3^{2-} . Thus, $[\text{CO}_3^{2-}] = \alpha\text{CO}_3^{2-}[\text{total carbonate}]$. We can say that $[\text{Ca}^{2+}] = [\text{total carbonate}] = [\text{CO}_3^{2-}]/\alpha\text{CO}_3^{2-}$. Since the pH is the same, the value of αCO_3^{2-} is the same in both compartments. Now we can

write:
$$\frac{K_{sp}(\text{calcite})}{K_{sp}(\text{aragonite})} = \frac{[\text{Ca}^{2+}(\text{left})][\text{CO}_3^{2-}(\text{left})]}{[\text{Ca}^{2+}(\text{right})][\text{CO}_3^{2-}(\text{right})]} = \frac{\frac{[\text{CO}_3^{2-}(\text{left})]^2}{\alpha\text{CO}_3^{2-}}}{\frac{[\text{CO}_3^{2-}(\text{right})]^2}{\alpha\text{CO}_3^{2-}}} = (0.87)^2 = 0.76$$

5. The cell, SCE || H⁺ (*a* = *x*) | glass electrode, has potential of 0.2106 V when the solution in the right-hand compartment is a buffer of pH 4.006. The following potential are obtained when the buffer is replaced with unknowns: **(a)** – 0.2902 V and **(b)** + 0.1241 V. Calculate the pH and the hydrogen ion activity of each unknown.
[5% each]

Ans

5. Substituting the potential and pH data into the following Equation give

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

$$K = (4.006 \times 0.0592) + 0.2106 = 0.447755$$

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

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

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

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

6. When measured with a F^- ion-selective electrode, the potential due to F^- in the ground water in Taipei was 40.0 mV more positive than the potential of tap water in Hsinchu. We know that Hsinchu city maintains its fluoridated water at the recommended F^- level of 5.26×10^{-5} M. What is the concentration of F^- in Taipei groundwater? [10%]

Ans

$$6. [F^-]_{\text{Hsinchu}} = 5.26 \times 10^{-5} \text{ M.}$$

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

$$E_{\text{Taipei}} = \text{constant} - 0.05916 \log[F^-]$$

$$\Delta E = E_{\text{Taipei}} - E_{\text{Hsinchu}} = 0.040 \text{ mV} = -0.05916 \log[F^-] + 0.05916 \log[5.26 \times 10^{-5}]$$

$$[F^-]_{\text{Taipei}} = 1.11 \times 10^{-5} \text{ M}$$

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

(a) 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%]

(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%]

Ans:

7.

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

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

(c) $T = \text{antilog}(-0.238) = \mathbf{0.578}$

(d) $A = -\log(T) = -\log(0.578/2) = \mathbf{0.539}$

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

Ans: 8

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

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

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

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

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

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

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

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

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

Solving simultaneously,

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

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. An aqueous solution containing MgCl_2 and HCl was analyzed by first titrating a 25.00 mL aliquot to a bromocresol green end point with 17.53 mL of 0.02932 M NaOH . In the second experiment, a 10.00 mL aliquot of the sample was passed through a cation exchange resin. The eluate and washing required 35.94 mL of the 0.02932 M NaOH solution to reach the same end point. Report the molar concentration of HCl and MgCl_2 in the sample. [10%]

Ans:

9. In the first analysis, only HCl will react with NaOH but not the salt MgCl_2 .

In the second analysis, both HCl and MgCl_2 will be retained by the strong-acid ion exchange resin (bind to the H^+ and Mg^{2+}).

$$[\text{HCl}] = 17.53 \text{ mL} \times \frac{0.02932 \text{ mmol NaOH}}{\text{mL}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}} \times \frac{1}{25.00 \text{ mL}}$$

$$= 0.02056 \text{ mmol/mL}$$

$$\text{amount } \text{H}_3\text{O}^+/\text{mL from exchange} = 35.94 \text{ mL} \times 0.02932 \text{ mmol/mL} / 10.00 \text{ mL} = 0.10538 \text{ M.}$$

$$= (\text{no. mmol HCl} + 2 \times \text{no. mmol MgCl}_2) / \text{mL}$$

$$\text{mmol MgCl}_2/\text{mL} = (0.10538 - 0.02056) / 2 = 0.04241$$

The solution is thus 0.02056 M in HCl and 0.04241 M in MgCl_2 .

10. The selectivity factor for two compounds in gas chromatography is 1.068 on a column with a plate height of 0.520 mm. The retention factor for compound **1** is 5.16.

(a) Find the retention factor for compound **2** which is a strongly held solute. **[2.5%]**

(b) What length of column will separate the compounds with a resolution of 1.50? **[2.5%]**

(c) The retention time for air (t_m) is 2.00 minutes. If the number of plates is the same for both compounds, find t_r (retention time) and $W_{1/2}$ (half width) for each peak. **[5%]**

Ans: 10.

(a) we know that $\alpha = 1.068$ and $k_1 = 5.16$.

Since $\alpha = k_2/k_1$, $k_2 = \alpha k_1 = (1.068)(5.16) = 5.51$

$$(b) \text{ Resolution} = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_2}{1 + k_2} \right)$$

$$1.50 = \frac{\sqrt{N}}{4} \left(\frac{1.068 - 1}{1.068} \right) \left(\frac{5.51}{1 + 5.51} \right)$$

$$N = 1.24 \times 10^4 \text{ plates}$$

Required length = $(1.24 \times 10^4)(0.52 \text{ mm/plate}) = 6.45 \text{ m}$.

(c) The relation between the retention factor and retention time is

$$k_1 = (t_1 - t_m)/t_m$$

$$t_1 = t_m(k_1 + 1) = (2.00)(6.16) = 12.32 \text{ min}$$

$$t_2 = t_m(k_2 + 1) = (2.00)(6.51) = 13.02 \text{ min}$$

$$W_{1/2} = \frac{\sqrt{5.55}}{N} t_r = \frac{\sqrt{5.55}}{1.24 \times 10^4} 12.32 = 0.26 \text{ minute for compound 1.}$$

$$W_{1/2} = \frac{\sqrt{5.55}}{N} t_r = \frac{\sqrt{5.55}}{1.24 \times 10^4} 13.02 = 0.27 \text{ minute for compound 2.}$$

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