

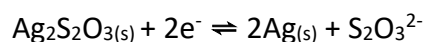
10810CHEM311000-Analytical Chemistry (I) 分析化學一

Final Examination

Date: 07-01-2020, 10:10 am to 12:10 pm

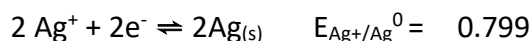
Answer **all 10 questions** (total 105%). You have **2 hours** to finish this paper.

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:



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

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

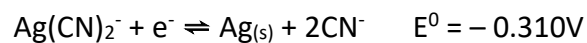
At standard condition, $[\text{S}_2\text{O}_3^{2-}] = 1.00$, Thus,

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

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

$\text{Cu}_{(s)} | \text{Cu}^{2+} (0.030 \text{ M}) || \text{K}^+ \text{Ag}(\text{CN})_2^- (0.010 \text{ M}), \text{HCN} (0.10 \text{ M}), \text{buffer to pH } 8.21 | \text{Ag}_{(s)}$

by considering the following reactions:



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

Ans:

$$E = \left\{ -0.310 - 0.0592 \log \frac{[\text{CN}^-]^2}{[\text{Ag}(\text{CN})_2^-]} \right\} - \left\{ 0.339 - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]} \right\}$$

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

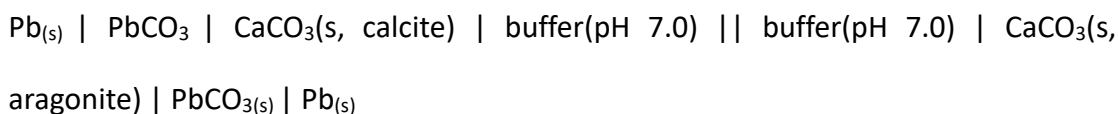
$$\frac{[\text{CN}^-]}{[\text{HCN}]} = \frac{K_a}{[\text{H}^+]}$$

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

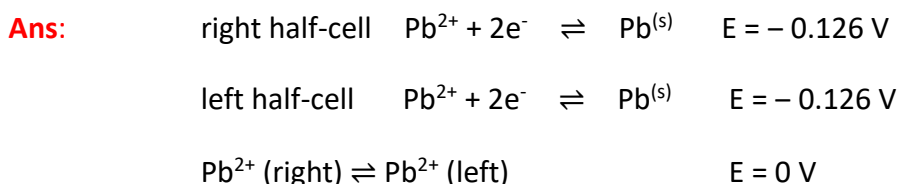
Because $[\text{CN}^-] + [\text{HCN}] = 0.10 \text{ M}$, $[\text{CN}^-] = 0.0091 \text{ M}$. Putting this concentration into the Nernst equation gives $E = -0.187 - (0.294) = \underline{\underline{-0.481 \text{ V}}}$

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

3. 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 $[\text{CO}_3^{2-}] = K_{sp} (\text{PbCO}_3) / [\text{Pb}^{2+}]$

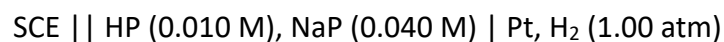
$$\frac{[\text{CO}_3^{2-}(\text{left})]}{[\text{CO}_3^{2-}(\text{right})]} = \frac{K_{sp}(\text{PbCO}_3)/[\text{Pb}^{2+}(\text{left})]}{K_{sp}(\text{PbCO}_3)/[\text{Pb}^{2+}(\text{right})]} = \frac{1}{1.15} = 0.87$$

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:

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

4. Calculate the dissociation constant K_{HP} for the weak acid HP if the cell



Develops a potential of -0.591 V. **[10%]**

Ans:

The diagram for this cell indicates that the saturated calomel electrode is the left-hand electrode. Thus,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} = E_{\text{right}} - 0.244 = -0.591 \text{ V} \\ E_{\text{right}} &= -0.591 + 0.244 = -0.347 \text{ V} \end{aligned}$$

We then apply the Nernst equation for the hydrogen electrode to find that

$$\begin{aligned} -0.347 &= 0.000 - \frac{0.0592}{2} \log \frac{1.00}{[\text{H}_3\text{O}^+]^2} \\ &= 0.000 + \frac{2 \times 0.0592}{2} \log [\text{H}_3\text{O}^+] \\ \log [\text{H}_3\text{O}^+] &= \frac{-0.347 - 0.000}{0.0592} = -5.86 \\ [\text{H}_3\text{O}^+] &= 1.38 \times 10^{-6} \end{aligned}$$

By substituting this value of the hydronium ion concentration as well as the concentrations of the weak acid and its conjugate base into the dissociation constant expression, we obtain

$$K_{\text{HP}} = \frac{[\text{H}_3\text{O}^+][\text{P}^-]}{[\text{HP}]} = \frac{(1.38 \times 10^{-6})(0.040)}{0.010} = 5.5 \times 10^{-6}$$

5. 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:

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

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

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

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

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

6. 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:

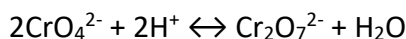
(a) $A = 7.00 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.00 \text{ cm} \times 3.40 \times 10^{-5} \text{ mol L}^{-1} = \mathbf{0.238}$

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

7. The equilibrium constant for the reaction



is 4.2×10^{14} . The molar absorptivity for the two principal species in a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ are

| λ (nm) | ϵ_1 (CrO_4^{2-}) | ϵ_2 ($\text{Cr}_2\text{O}_7^{2-}$) |
|----------------|--------------------------------------|---|
| 345 | 1.84×10^3 | 10.7×10^2 |
| 370 | 4.81×10^3 | 7.28×10^2 |
| 400 | 1.88×10^3 | 1.89×10^2 |

A 4.00×10^{-4} M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ was prepared in water with a pH of 5.6. Calculate the theoretical absorbance values (1.00 cm cell) for the solution at each wavelength.

[10%]

Ans:

$$[\text{Cr}_2\text{O}_7^{2-}] / \{[\text{CrO}_4^{2-}][\text{H}^+]^2\} = 4.2 \times 10^{14}$$

$$[\text{H}^+] = \text{antilog}(-5.60) = 2.51 \times 10^{-6}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = c_{\text{K}_2\text{Cr}_2\text{O}_7} - [\text{CrO}_4^{2-}] / 2$$

$$\frac{c_{\text{K}_2\text{Cr}_2\text{O}_7} - 0.500[\text{CrO}_4^{2-}]}{[\text{CrO}_4^{2-}]^2 \times (2.51 \times 10^{-6})^2} = 4.2 \times 10^{14}$$

$$c_{\text{K}_2\text{Cr}_2\text{O}_7} - 0.500[\text{CrO}_4^{2-}] = 2.65 \times 10^3 [\text{CrO}_4^{2-}]^2$$

$$[\text{CrO}_4^{2-}]^2 + 1.887 \times 10^{-4} [\text{CrO}_4^{2-}] - 3.774 \times 10^{-4} c_{\text{K}_2\text{Cr}_2\text{O}_7} = 0$$

$$\text{When } c_{\text{K}_2\text{Cr}_2\text{O}_7} = 4.00 \times 10^{-4}$$

$$[\text{CrO}_4^{2-}]^2 + 1.887 \times 10^{-4} [\text{CrO}_4^{2-}] - 1.510 \times 10^{-7} = 0$$

$$[\text{CrO}_4^{2-}] = 3.055 \times 10^{-4} \text{ M}$$

$$[\text{Cr}_2\text{O}_7^{2-}] = 4.00 \times 10^{-4} - 3.055 \times 10^{-4} / 2 = 2.473 \times 10^{-4}$$

$$A_{345} = 1.84 \times 10^3 \times 3.055 \times 10^{-4} + 10.7 \times 10^2 \times 2.473 \times 10^{-4} = 0.827$$

$$A_{370} = 4.81 \times 10^3 \times 3.055 \times 10^{-4} + 7.28 \times 10^2 \times 2.473 \times 10^{-4} = 1.649$$

$$A_{400} = 1.88 \times 10^3 \times 3.055 \times 10^{-4} + 1.89 \times 10^2 \times 2.473 \times 10^{-4} = 0.621$$

8. 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%]

Ans:

(a) Fraction remaining $q = \frac{V_1}{V_1 + KV_2}$

$$0.01 = \frac{10}{10 + 4.0V_2}$$

$$V_2 = \mathbf{248 \text{ mL}}$$

$$(b) 0.01 = \left(\frac{10}{10 + 4.0V_2} \right)^3$$

$$V_2 = 9.1 \text{ mL}$$

$$\text{Total volume} = 9.1 \times 3 = \mathbf{27.3 \text{ mL}}$$

9. 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:

(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

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

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

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

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

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

10. Consider a chromatography experiment in which two components with retention factors $k_1 = 4.00$ and $k_2 = 5.00$ are injected into a column with $N = 1.00 \times 10^3$ 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} . **[5%]**

(b) Find $w_{1/2}$ (width at half height) and w (width at the base) for peak 1 and 2. **[5%]**

(c) Calculate the resolution of the two peaks. **[2.5%]**

(d) Supposing the two peaks have the same amplitude (height), sketch the chromatogram and indicate the half-widths accurately. **[2.5%]**

Ans:

$$(a) k_1 = \frac{t_{r1} - t_m}{t_m}$$

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

$$t_m = 10/5 = 2.00 \text{ minutes}$$

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

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

$$\sigma_1 = \frac{t_{r1}}{\sqrt{N}} = \frac{10}{\sqrt{1000}} = 0.316 \text{ minutes}$$

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

$$w_{1/2} (\text{peak 1}) = 2.35\sigma_1 = 0.74 \text{ minutes}$$

$$w (\text{peak 1}) = 4\sigma_1 = 1.26 \text{ minutes}$$

$$\sigma_2 = \frac{t_{r2}}{\sqrt{N}} = \frac{12.00}{\sqrt{1000}} = 0.379 \text{ minutes}$$

Using the same method, we can find

$$w_{1/2} (\text{peak 2}) = 2.35\sigma_2 = 0.89 \text{ minutes}$$

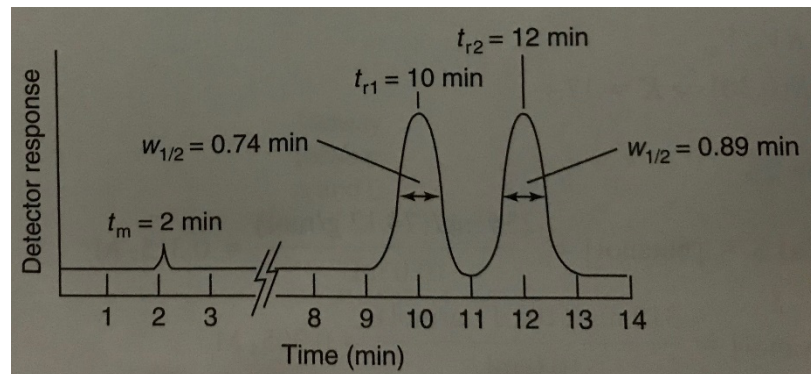
$$w (\text{peak 2}) = 4\sigma_2 = 1.52 \text{ minutes}$$

(c) Resolution $R_s = \frac{2[(tr_1)-(tr_2)]}{w_1+w_2}$

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

$= 1.44$

(d)



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