

# 11110CHEM311000-Analytical Chemistry (I) 分析化學一

## Second Midterm Examination

Date: 08-12-2022, 10:10 am to 12:10 pm

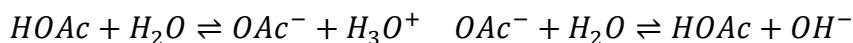
Answer all 10 questions (total 110%). You have 2 hours to finish this paper.

1. Consider solutions prepared by

- (a) dissolving 8.00 mmol of NaOAc in 200 mL of 0.100 M HOAc ( $K_a = 1.75 \times 10^{-5}$ ). [4%]
- (b) adding 100 mL of 0.0500 M NaOH to 100mL of 0.175 M HOAc. [4%]
- (c) adding 40.0 mL of 0.1200 M HCl to 160.0 mL of 0.0420 M NaOAc. [4%]

In what respects do these solutions resemble one another? How do they differ? [3%]

**Solution:**



$$(a) [OAc^-] = \frac{8.00 \text{ mmol}}{200 \text{ mL}} = 4 \times 10^{-2} \text{ M}$$

$$[HOAc] = 0.100 \text{ M}$$

$$pH = -\log(1.75 \times 10^{-5}) + \log \frac{4 \times 10^{-2}}{0.100} = 4.359$$

$$(b) 0.175 \text{ M } HOAc = \frac{0.175 \text{ mmol}}{\text{mL}} \times 100 \text{ mL} = 17.5 \text{ mmol}$$

$$0.0500 \text{ M } NaOH = \frac{0.0500 \text{ mmol}}{\text{mL}} \times 100 \text{ mL} = 5.00 \text{ mmol}$$

$$[HOAc] = \frac{(17.5 - 5.00) \text{ mmol}}{200 \text{ mL}} = 6.25 \times 10^{-2} \text{ M}$$

$$[OAc^-] = \frac{5 \text{ mmol}}{200 \text{ mL}} = 2.50 \times 10^{-2} \text{ M}$$

$$pH = -\log(1.75 \times 10^{-5}) + \log \frac{2.50 \times 10^{-2}}{6.25 \times 10^{-2}} = 4.359$$

$$(c) \ 0.0420 \text{ M } OAc^- = \frac{0.042 \text{ mmol}}{\text{mL}} \times 160 \text{ mL} = 6.72 \text{ mmol}$$

$$0.1200 \text{ M } HCl = \frac{0.1200 \text{ mmol}}{\text{mL}} \times 40 \text{ mL} = 4.80 \text{ mmol}$$

$$[OAc^-] = \frac{(6.72 - 4.80) \text{ mmol}}{200 \text{ mL}} = 9.6 \times 10^{-3} \text{ M}$$

$$[HOAc] = \frac{4.8 \text{ mmol}}{200 \text{ mL}} = 2.4 \times 10^{-2} \text{ M}$$

$$pH = -\log(1.75 \times 10^{-5}) + \log \frac{9.6 \times 10^{-3}}{2.4 \times 10^{-2}} = 4.359$$

The solutions all are buffers with the same pH, but they differ in buffer capacity with (a) having the greatest and (c) the least.

2. What mass of sodium formate (MW = 67.997 g/mol) must be added to 500.0 mL of 1.00 M formic acid ( $K_a = 1.8 \times 10^{-4}$ ) to produce a buffer solution that has a pH of 3.75? [10%]

**Solution:**

$$pH = 3.75 = pK_a + \log \frac{[HCOO^-]}{[HCOOH]} = -\log(1.8 \times 10^{-4}) + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$3.75 = 3.74 + \log \frac{[HCOO^-]}{[HCOOH]} \quad \frac{[HCOO^-]}{[HCOOH]} = 10^{0.01} = 1.02$$

$$500 \text{ mL} \times 1.00 \frac{\text{mmol HCOOH}}{\text{mL}} = 500 \text{ mmol HCOOH}$$

$$\text{So amount of HCOO}^- \text{ needed} = 1.02 \times 500 \text{ mmol} = 511.6 \text{ mmol}$$

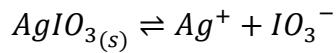
$$511.6 \text{ mmol} \times 10^{-3} \text{ mol/mmol} = 0.5116 \text{ mol HCOO}^-$$

$$\text{Mass HCOONa} = 0.5116 \text{ mol} \times 67.997 \text{ g/mol} = 34.79 \text{ g}$$

3. Calculate the solubilities of  $\text{AgIO}_3$  ( $K_{\text{sp}} = 3.1 \times 10^{-8}$ ) in a 0.0167 M solution of  $\text{Ba}(\text{NO}_3)_2$  using (1) activities and (2) molar concentrations. The activity coefficient for  $\text{Ag}^+$  is 0.80 and for  $\text{IO}_3^-$  is 0.82, respectively. [10%]

**Solution:**

$$\mu = \frac{1}{2} [0.0167 \times 2^2 + 2 \times 0.0167 \times 1^2] = 0.050$$



$$(1) \gamma_{\text{Ag}^+} = 0.80 \quad \gamma_{\text{IO}_3^-} = 0.81$$

$$[\text{Ag}^+][\text{IO}_3^-] = \frac{3.1 \times 10^{-8}}{\gamma_{\text{Ag}^+}\gamma_{\text{IO}_3^-}} = \frac{3.1 \times 10^{-8}}{(0.80)(0.81)} = 4.8 \times 10^{-8}$$

$$\text{Solubility} = S = [\text{Ag}^+] = [\text{IO}_3^-]$$

$$S^2 = 4.8 \times 10^{-8}$$

$$S = \sqrt{4.8 \times 10^{-8}} = 2.2 \times 10^{-4} \text{ M}$$

$$(2) S = \sqrt{3.1 \times 10^{-8}} = 1.8 \times 10^{-4} \text{ M}$$

4. Calculate the % relative error in hydronium ion concentration by using concentrations instead of activities in calculating the pH of the following buffer solutions using the thermodynamic constants: [10%]

0.175 M HOAc ( $K_a = 1.75 \times 10^{-5}$ ) and 0.275 M NaOAc.

Use  $\alpha_{H_3O^+} = 0.9$  and  $\alpha_{OAc^-} = 0.425$  to calculate the activity coefficient.

**Solution:**

In this buffer solution, we assume  $[HOAc] = c_{HOAc}$  and  $[OAc^-] = c_{NaOAc}$ . We also assume that the ionic strength is contributed solely by NaOAc, neglecting  $H_3O^+$  and  $OH^-$ .

$$\mu = \frac{1}{2} [0.275 \times 1^2 + 0.275 \times 1^2] = 0.275$$

$$-\log \gamma_{H_3O^+} = \frac{(0.51)(1)^2 \sqrt{0.275}}{1 + (3.3)(0.9)\sqrt{0.275}} = 0.1046 \quad \gamma_{H_3O^+} = 0.786$$

$$-\log \gamma_{OAc^-} = \frac{(0.51)(1)^2 \sqrt{0.275}}{1 + (3.3)(0.425)\sqrt{0.275}} = 0.1541 \quad \gamma_{H_3O^+} = 0.701$$

$$K_a = \frac{\gamma_{H_3O^+}[H_3O^+]\gamma_{OAc^-}[OAc^-]}{[HOAc]}$$

$$K_a' = \frac{[H_3O^+][OAc^-]}{[HOAc]} = \frac{K_a}{\gamma_{H_3O^+}\gamma_{OAc^-}} = \frac{1.75 \times 10^{-5}}{0.786 \times 0.701} = 3.176 \times 10^{-5}$$

$$[H_3O^+] = \frac{K_a'[HOAc]}{[OAc^-]} = \frac{3.176 \times 10^{-5} \times 0.175}{0.275} = 2.0 \times 10^{-5} M$$

$$pH = 4.69$$

With no activity corrections

$$[H_3O^+] = \frac{1.75 \times 10^{-5} \times 0.175}{0.275} = 1.1 \times 10^{-5} M$$

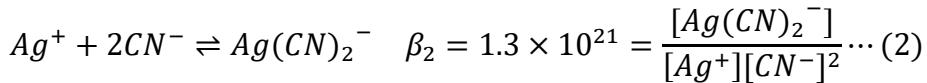
$$pH = 4.96$$

$$Relative\ error\ in\ [H_3O^+] = \frac{1.1 \times 10^{-5} - 2.0 \times 10^{-5}}{2.0 \times 10^{-5}} \times 100\% = -45\%$$

5. What mass of AgBr (MW = 187.7 g/mol,  $K_{sp} = 5.0 \times 10^{-13}$ ) dissolves in 200 mL of 0.200 M NaCN? [10%]



**Solution:**



It is readily shown that  $CN^- + H_2O \rightleftharpoons HCN + OH^-$  can be neglected in this problem so that only the two equilibria shown above need to be considered.

Mass balance requires that

$$[Br^-] = [Ag^+] + [Ag(CN)_2^-] \dots (3)$$

$$0.200 = [CN^-] + 2[Ag(CN)_2^-] \dots (4)$$

We now have 4 equations and 4 unknowns.

Because  $\beta_2$  is very large, let us assume that

$$[CN^-] \ll 2[Ag(CN)_2^-] \quad and \quad [Ag^+] \ll [Ag(CN)_2^-]$$

$$(4) \text{ becomes } [Ag(CN)_2^-] = \frac{0.200}{2} = 0.100$$

$$\text{and (3) becomes } [Br^-] = [Ag(CN)_2^-] = 0.100$$

To check the assumptions, we calculate  $[Ag^+]$  by substituting into (1)

$$[Ag^+] = \frac{5.0 \times 10^{-13}}{0.100} \cong 5 \times 10^{-12} \quad (5 \times 10^{-12} \ll 0.100)$$

To obtain  $[CN^-]$  we substitute into (2) and rearrange

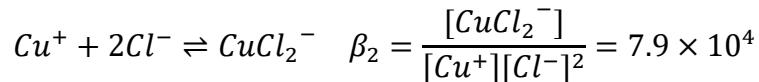
$$[CN^-] = \sqrt{\frac{0.100}{(5 \times 10^{-12})(1.3 \times 10^{21})}} = 3.9 \times 10^{-6} \quad (3.9 \times 10^{-6} \ll 0.100)$$

Thus, the two assumptions are valid and

$$Solubility = [Br^-] = 0.100 \text{ M}$$

$$\frac{\text{mass AgBr}}{200 \text{ mL}} = 0.100 \frac{\text{mmol}}{\text{mL}} \times 200 \text{ mL} \times \frac{0.1877 \text{ g}}{\text{mmol}} = 3.754 \text{ g}$$

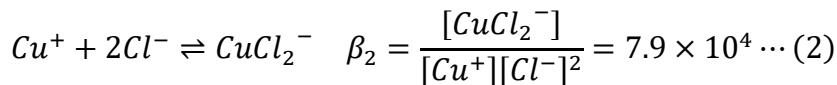
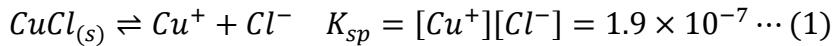
6. The equilibrium constant for formation of  $\text{CuCl}_2^-$  is given by



What is the solubility of CuCl ( $K_{sp} = 1.9 \times 10^{-7}$ ) in solutions having the following analytical NaCl concentrations: [15%]

- (a) 5.0 M?
- (b)  $5.0 \times 10^{-1}$  M?

**Solution:**



It is convenient to multiply (1) by (2) to give

$$\frac{[\text{CuCl}_2^-]}{[\text{Cl}^-]} = 1.9 \times 10^{-7} \times 7.9 \times 10^4 = 1.50 \times 10^{-2} \dots (3)$$

From a charge balance consideration, we can write (if we assume  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ )

$$[\text{Cu}^+] + [\text{Na}^+] = [\text{Cl}^-] + [\text{CuCl}_2^-] \dots (4)$$

By rearrange (1) and (3) and substituting into (4) we obtain

$$[\text{Cl}^-] = [\text{Na}^+] + \frac{1.9 \times 10^{-7}}{[\text{Cl}^-]} - 1.50 \times 10^{-2}[\text{Cl}^-]$$

which rearranges to the quadratic

$$0 = 1.015[\text{Cl}^-]^2 - [\text{Na}^+][\text{Cl}^-] - 1.9 \times 10^{-7} \dots (5)$$

By using  $[\text{Na}^+] =$  the NaCl analytical concentration, (5) can be solved to give the following  
[Cl<sup>-</sup>]

Note that the equilibrium  $[Cl^-]$  concentration is *larger* than the NaCl analytical concentration for part (e). The reason for this apparent anomaly is that the dissolution of CuCl to give  $Cu^+$  and  $Cl^-$  contributes significantly to the equilibrium  $[Cl^-]$  at the lower NaCl analytical concentrations.

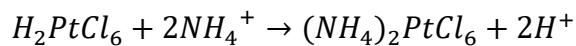
The solubility of CuCl can be obtained from the calculated  $[Cl^-]$  and the expression

$$S = [Cu^+] + [CuCl_2^-] = \frac{1.9 \times 10^{-7}}{[Cl^-]} + 1.50 \times 10^{-2}[Cl^-]$$

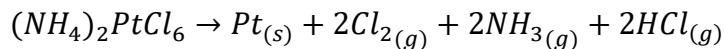
Solution of this equation for each of the  $[Cl^-]$  gives

- (a)  $7.4 \times 10^{-2} M$
- (b)  $7.4 \times 10^{-3} M$

7. Ammoniacal nitrogen can be determined by treatment of the sample with chloroplatinic acid; the product is slightly soluble ammonium chloroplatinate:



The precipitate decomposes on ignition, yielding metallic platinum and gaseous products:



Calculate the percentage of ammonia (MW = 17.0306 g/mol) in a sample if 0.1195 g gave rise to 0.2329 g of platinum (MW = 195.08 g/mol). **[10%]**

**Solution:**

$$M_{NH_3} = 17.0306 \frac{g}{mol} \quad M_{Pt} = 195.08 \frac{g}{mol}$$

$$\frac{0.2329 \text{ g } Pt \times (\frac{1 \text{ mol } Pt}{195.08 \text{ g}}) \times (\frac{2 \text{ mol } NH_3}{1 \text{ mol } Pt}) \times (\frac{17.0306 \text{ g } NH_3}{\text{mol}})}{0.1195 \text{ g } impure \text{ sample}} \times 100\% = 34.03\% \text{ } NH_3$$

8. A series of sulfate (MW = 96.064 g/mol) samples is to be analyzed by precipitation as  $\text{BaSO}_4$  (MW = 233.39 g/mol). If it is known that the sulfate content in these samples ranges between 20% and 55%, what minimum sample mass should be taken to ensure that a precipitate mass no smaller than 0.200 g is produced? What is the maximum precipitate mass to be expected if this quantity of sample is taken? [10%]

**Solution:**

$$M_{\text{BaSO}_4} = 233.39 \frac{\text{g}}{\text{mol}} \quad M_{\text{SO}_4^{2-}} = 96.064 \frac{\text{g}}{\text{mol}}$$

Let  $S_w$  = mass of sample in grams

$$0.200 \text{ g } \text{BaSO}_4 \times \frac{1 \text{ mol } \text{BaSO}_4}{233.39 \text{ g}} \times \frac{1 \text{ mol } \text{SO}_4^{2-}}{1 \text{ mol } \text{BaSO}_4} = 8.57 \times 10^{-4} \text{ mol } \text{SO}_4^{2-}$$

$$\frac{8.57 \times 10^{-4} \text{ mol } \text{SO}_4^{2-} \times \frac{96.064 \text{ g } \text{SO}_4^{2-}}{\text{mol}}}{S_w \text{ g sample}} \times 100\% = 20\% \text{ SO}_4^{2-}$$

$$S_w = \frac{8.57 \times 10^{-4} \text{ mol } \text{SO}_4^{2-} \times \frac{96.064 \text{ g } \text{SO}_4^{2-}}{\text{mol}} \times 100\%}{20\%} = 0.412 \text{ g sample}$$

The maximum precipitate weight expected given this sample weight is

$$0.412 \text{ g sample} \times \frac{55 \text{ g } \text{SO}_4^{2-}}{100 \text{ g sample}} \times \frac{1 \text{ mol } \text{SO}_4^{2-}}{96.064 \text{ g}} \times \frac{1 \text{ mol } \text{BaSO}_4}{1 \text{ g } \text{SO}_4^{2-}} \times \frac{233.39 \text{ g } \text{BaSO}_4}{1 \text{ mol}} \\ = 0.550 \text{ g } \text{BaSO}_4$$

9. A 24-hour urine specimen was diluted to 2.000 L. After the solution was buffered to pH 10, a 10.00-mL aliquot was titrated with 23.57 mL of 0.004590 M EDTA. The calcium in a second 10.00-mL aliquot was isolated as  $\text{CaC}_2\text{O}_4(s)$ , redissolved in acid, and titrated with 10.53 mL of the EDTA solution. Assuming that 15 to 300 mg of magnesium (MW = 24.305 g/mol) and 50 to 400 mg of calcium (MW = 40.08 g/mol) per day are normal, did this specimen fall within these ranges? [10%]

**Solution:**

$$\text{Amount } \text{Mg}^{2+} + \text{Ca}^{2+}$$

$$= \frac{0.004590 \text{ mmol EDTA}}{\text{mL}} \times 23.57 \text{ mL EDTA} \times \frac{1 \text{ mmol } (\text{Mg}^{2+} + \text{Ca}^{2+})}{\text{mmol EDTA}}$$

$$= 0.108186 \text{ mmol}$$

$$\text{Amnt Ca}^{2+}$$

$$= \frac{0.004590 \text{ mmol EDTA}}{\text{mL}} \times 10.53 \text{ mL EDTA} \times \frac{1 \text{ mmol Ca}^{2+}}{\text{mmol EDTA}} = 0.048333 \text{ mmol}$$

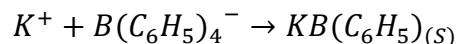
$$\text{Amnt Mg}^{2+} = 0.108186 - 0.048333 = 0.059854 \text{ mmol}$$

$$\frac{(0.048333 \text{ mmol Ca}^{2+} \times \frac{40.08 \text{ mg}}{\text{mmol}})}{10.00 \text{ mL} \times \frac{\text{L}}{1000 \text{ mL}} \times \frac{1}{2.000 \text{ L}}} = 387.4 \text{ ppm Ca}^{2+}$$

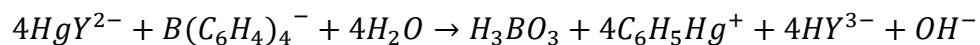
$$\frac{\left(0.059835 \text{ mmol Mg}^{2+} \times \frac{24.305 \text{ mg}}{\text{mmol}}\right)}{10.00 \text{ mL} \times \frac{\text{L}}{1000 \text{ mL}} \times \frac{1}{2.000 \text{ L}}} = 290.9 \text{ ppm Mg}^{2+}$$

Both fall within the normal ranges.

**10.** The potassium ion ( $MW = 39.098 \text{ g/mol}$ ) in a  $250.0\text{-mL}$  sample of mineral water was precipitated with sodium tetraphenylborate:



The precipitate was filtered, washed, and redissolved in an organic solvent. An excess of the mercury(II)/EDTA chelate was added:



The liberated EDTA was titrated with  $34.374 \text{ mL}$  of  $0.04813 \text{ M } Mg^{2+}$ . Calculate the potassium ion concentration in parts per million. **[10%]**

**Solution:**

$$\begin{aligned} 1 \text{ mmol } Mg^{2+} &\equiv 1 \text{ mmol EDTA} \equiv \frac{1}{4} \text{ mmol } B(C_6H_5)_4^- \equiv \frac{1}{4} K^+ \\ & \left( \frac{0.04813 \text{ mmol } Mg^{2+}}{\text{mL}} \times 34.37 \text{ mL } Mg^{2+} \times \frac{1 \text{ mmol } K^+}{4 \text{ mmol } Mg^{2+}} \times \frac{39.098 \text{ mg } K^+}{\text{mmol}} \right) \\ & \quad \frac{L}{250 \text{ mL} \times \frac{L}{1000 \text{ mL}}} \\ &= 64.68 \text{ ppm } K^+ \end{aligned}$$

**Table 1. Activity Coefficients for Ions at 25°C**

Ion	$\alpha_X, \text{nm}$	Activity Coefficient at Indicated Ionic Strength				
		0.001	0.005	0.01	0.05	0.1
H <sub>3</sub> O <sup>+</sup>	0.9	0.967	0.934	0.913	0.85	0.83
Li <sup>+</sup> , C <sub>6</sub> H <sub>5</sub> COO <sup>-</sup>	0.6	0.966	0.930	0.907	0.83	0.80
Na <sup>+</sup> , IO <sub>3</sub> <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> , OAc <sup>-</sup>	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH <sup>-</sup> , F <sup>-</sup> , SCN <sup>-</sup> , HS <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , BrO <sub>3</sub> <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> , MnO <sub>4</sub> <sup>-</sup>	0.35	0.965	0.926	0.900	0.81	0.76
K <sup>+</sup> , Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup> , CN <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , HCOO <sup>-</sup>	0.3	0.965	0.925	0.899	0.81	0.75
Rb <sup>+</sup> , Cs <sup>+</sup> , Ti <sup>+</sup> , Ag <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	0.25	0.965	0.925	0.897	0.80	0.75
Mg <sup>2+</sup> , Be <sup>2+</sup>	0.8	0.872	0.756	0.690	0.52	0.44
Ca <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> , Sn <sup>2+</sup> , Mn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Phthalate <sup>2-</sup>	0.6	0.870	0.748	0.676	0.48	0.40
Sr <sup>2+</sup> , Ba <sup>2+</sup> , Cd <sup>2+</sup> , Hg <sup>2+</sup> , S <sup>2-</sup>	0.5	0.869	0.743	0.668	0.46	0.38
Pb <sup>2+</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>3</sub> <sup>2-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.45	0.868	0.741	0.665	0.45	0.36
Hg <sub>2</sub> <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> , Cr <sub>4</sub> <sup>2-</sup> , HPO <sub>4</sub> <sup>2-</sup>	0.40	0.867	0.738	0.661	0.44	0.35
Al <sup>3+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , La <sup>3+</sup> , Ce <sup>3+</sup>	0.9	0.737	0.540	0.443	0.24	0.18
PO <sub>4</sub> <sup>3-</sup> , Fe(CN) <sub>6</sub> <sup>3-</sup>	0.4	0.726	0.505	0.394	0.16	0.095
Th <sup>4+</sup> , Zr <sup>4+</sup> , Ce <sup>4+</sup> , Sn <sup>4+</sup>	1.1	0.587	0.348	0.252	0.10	0.063
Fe(CN) <sub>6</sub> <sup>4-</sup>	0.5	0.569	0.305	0.200	0.047	0.020