11210CHEM311000-Analytical Chemistry (I) 分析化學一

Second Midterm Examination

Date: 14-12-2023, 10:10 am to 12:10 pm

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

1. Which has the greater buffer capacity: (a) a mixture containing 0.100 mol of NH_3 and 0.200 mol of NH_4Cl or (b) a mixture containing 0.0500 mol of NH_3 and 0.100 mol of NH_4Cl? **[10 %]**

Solution:

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.7 \times 10^{-10}) + \log\frac{(0.100 \ M)}{(0.200 \ M)} = 8.943$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.7 \times 10^{-10}) + \log\frac{(0.050 \ M)}{(0.100 \ M)} = 8.943$$

Although the two solutions have identical pH values, the solution in (a) has the greatest buffer capacity, because it has the higher concentration of weak acid and its conjugate base.

2. What volume of 0.200 M HCl must be added to 500.0 mL of 0.300 M sodium mandelate to produce a buffer solution with a pH of 3.25? **[10 %]**

Solution:

Let HMn = mandelic acid, Mn^- = mandelate anion.

500 mL × 0.300 M NaMn = 150 mmol Mn.

For a pH of 3.25 need the ratio of Mn^- to HMn to be

$$\text{pH} = 3.25 = \text{pK}_a + \log\frac{[Mn^-]}{[HMn]} = 3.398 + \log\frac{[Mn^-]}{[HMn]}$$

$$\log\frac{[Mn^-]}{[HMn]} = 3.25 - 3.398 = -0.148$$

$$\frac{[Mn^-]}{[HMn]} = 0.711$$

$$\frac{\text{mmol } Mn^- - x \text{ mmol } HCl}{x \text{ mmol } HCl} = 0.711$$

$$0.711 \times x \text{ mmol } HCl = \text{mmol } Mn^- - x \text{ mmol } HCl$$

$$x = \text{mmol } Mn^-/1.711 = 150 \text{ mmol } Mn^-/1.711 = 87.66 \text{ mmol } HCl$$

Volume HCl = 87.66 mmol/(0.200 mmol/mL) = 438 mL

3. Calculate the ionic strength of a solution that is

(a) 0.025 M in $FeSO_4$. **[2.5 %]**

(b) 0.25 M in $(NH_4)_2CrO_4$. **[2.5 %]**

(c) 0.25 M in $FeCl_3$ and 0.15 M in $FeCl_2$. **[2.5 %]**

(d) 0.025 M in $La(NO_3)_3$ and 0.050 M in $Fe(NO_3)_2$. **[2.5 %]**

Solution:

(a) 0.025 M in $FeSO_4$

$$\mu = \frac{1}{2}[0.025 \times 2^2 + 0.025 \times 2^2] = 0.10$$

(b) 0.25 M in $(NH_4)_2CrO_4$

$$\mu = \frac{1}{2}[0.50 \times 1^2 + 0.25 \times 2^2] = 0.75$$

(c) 0.25 M in $FeCl_3$ and 0.15 M in $FeCl_2$

$$\mu = \frac{1}{2}[0.25 \times 3^2 + 0.75 \times 1^2 + 0.15 \times 2^2 + 0.30 \times 1^2] = 1.95$$

(d) 0.025 M in $La(NO_3)_3$ and 0.050 M in $Fe(NO_3)_2$

$$\mu = \frac{1}{2}[0.025 \times 3^2 + 0.075 \times 1^2 + 0.05 \times 2^2 + 0.10 \times 1^2] = 0.30$$

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

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

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^-.

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

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

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

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

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

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

$$pH = 4.69$$

With no activity corrections

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

$$pH = 4.96$$

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

5. Write the mass-balance expressions for a solution that is

(a) 0.25 M in NH_3. **[2.5 %]**

(b) 0.10 M in H_3PO_4. **[2.5 %]**

(c) 0.100 M in NaOH and saturated with $Zn(OH)_2$, which undergoes the reaction
$Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$. **[2.5 %]**

(d) saturated with $Ag_2C_2O_4$. **[2.5 %]**

Solution:

(a) 0.25 M in NH_3.

For $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$, we write

$0.25 = [NH_3] + [NH_4^+]$

(b) 0.10 M in H_3PO_4.

$0.10 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

(c) 0.100 M in NaOH and saturated with $Zn(OH)_2$, which undergoes the reaction
$Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$.
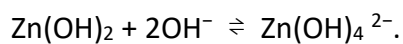
$0.100 = [Na^+] = [OH^-] + 2[Zn(OH)_4^{2-}]$

(d) saturated with $Ag_2C_2O_4$.

$[Ag^+] = 2([C_2O_4^{2-}] + [HC_2O_4^-] + [H_2CO_4])$

6. Silver ion is being considered for separating I⁻ from SCN in a solution that is 0.040 M in KI and 0.080 M in NaSCN. (For AgI, $K_{sp} = 8.3 \times 10^{-17}$, and for AgSCN, $K_{sp} = 1.1 \times 10^{-12}$)

(a) What Ag⁺ concentration is needed to lower the I⁻ concentration to 1.0×10^{-6} M?

[2.5 %]

(b) What is the Ag⁺ concentration of the solution when AgSCN begins to precipitate?

[2.5 %]

(c) What is the ratio of SCN⁻ to I⁻ when AgSCN begins to precipitate? **[2.5 %]**

(d) What is the ratio of SCN⁻ to I⁻ when the Ag⁺ concentration is 1.0×10^{-3} M?

[2.5 %]

Solution:

(a)

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.3 \times 10^{-17}}{1.0 \times 10^{-6}} = 8.3 \times 10^{-11} \ M$$

(b)

$$[Ag^+] = \frac{K_{sp}}{[SCN^-]} = \frac{1.1 \times 10^{-12}}{0.080} = 1.375 \times 10^{-11} \ M \approx 1.4 \times 10^{-11} \ M$$

(c)

$[I^-]$ when $[Ag^+] = 1.375 \times 10^{-11} M$

$$[I^-] = \frac{8.3 \times 10^{-17}}{1.375 \times 10^{-11}} = 6.0 \times 10^{-6} M$$

$$\frac{[SCN^-]}{[I^-]} = \frac{0.080}{6.0 \times 10^{-6}} = 1.3 \times 10^4$$

(d)
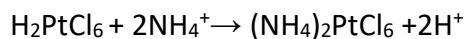
$$[I] = \frac{8.3 \times 10^{-17}}{1.0 \times 10^{-3}} = 8.3 \times 10^{-14} M$$

$$[SCN^-] = \frac{1.1 \times 10^{-12}}{1.0 \times 10^{-3}} = 1.1 \times 10^{-9} M$$

$$\frac{[\text{SCN}^-]}{[\text{I}^-]} = \frac{1.1 \times 10^{-9}}{8.3 \times 10^{-14}} = 1.3 \times 10^4$$

Note that this ratio is independent of [Ag$^+$] as long as some AgSCN$_{(s)}$ is present.

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

$$H_2PtCl_6 + 2NH_4^+ \rightarrow (NH_4)_2PtCl_6 + 2H^+$$

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

$$(NH_4)_2PtCl_6 \rightarrow Pt_{(s)} + 2Cl_{2(g)} + 2NH_{3(g)} + 2HCl_{(g)}$$
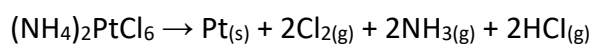
Calculate the percentage of ammonia in a sample if 0.1195 g gave rise to 0.2329 g of platinum. ($M_{NH_3} = 17.0306$ g/mol, $M_{Pt} = 195.08$ g/mol) **[5 %]**

Solution:

$$M_{NH_3} = 17.0306 \text{ g/mol}$$
$$M_{Pt} = 195.08 \text{ g/mol}$$

$$\frac{0.2329 \text{ g Pt} \times \left(\frac{1 \text{ mol Pt}}{195.08 \text{ g}}\right) \times \left(\frac{2 \text{ mol NH}_3}{1 \text{ mol Pt}}\right) \times \left(\frac{17,0306 \text{ g NH}_3}{\text{mol}}\right)}{0.1195\text{g impure sample}} \times 100\%$$

$$= 34.03\% \text{ NH}_3$$

8. A 50.0-mL portion of a solution containing 0.200 g of $BaCl_2 \cdot 2H_2O$ is mixed with 50.0 mL of a solution containing 0.300 g of $NaIO_3$. Assume that the solubility of $Ba(IO_3)_2$ in water is negligibly small and calculate.

(a) the mass of the precipitated $Ba(IO_3)_2$. **[5 %]**

(b) the mass of the unreacted compound that remains in solution. **[5 %]**

($M_{BaCl_2 \cdot 2H_2O} = 244.26$ g/mol, $M_{NaIO_3} = 197.89$ g/mol , $M_{Ba(IO_3)_2} = 487.13$ g/mol)

Solution:

$$0.200 \text{ g } BaCl_2 \cdot 2H_2O \times \frac{1 \text{ mol } BaCl_2 \cdot 2H_2O}{244.26 \text{ g}} \times \frac{1 \text{ mol } Ba^{2+}}{1 \text{ mol } BaCl_2 \cdot 2H_2O}$$

$$= 8.188 \times 10^{-4} \text{ mol } Ba^{2+}$$

$$0.300 \text{ g } NaIO_3 \times \frac{1 \text{ mol } NaIO_3}{197.89 \text{ g}} \times \frac{1 \text{ mol } IO_3^-}{1 \text{ mol } NaIO_3} = 1.516 \times 10^{-3} \text{ mol } IO_3^-$$

Because IO_3^- is the limiting reagent,

(a) the mass of the precipitated $Ba(IO_3)_2$.

$$\text{amount } Ba(IO_3)_2 = \frac{1.516 \times 10^{-3}}{2} = 7.580 \times 10^{-4} \text{ mol}$$

$$\text{mass } Ba(IO_3)_2 = 7.580 \times 10^{-4} \text{ mol} \times \frac{487.13 \text{g } Ba(IO_3)_2}{1 \text{ mol}} = 0.369 \text{ g } Ba(IO_3)_2$$

(b) the mass of the unreacted compound that remains in solution.

$$\text{amount } BaCl_2 \cdot 2H_2O \text{ remaining} = [(8.188 \times 10^{-4}) - (7.580 \times 10^{-4})] \text{ mol}$$
$$= 6.080 \times 10^{-5} \text{ mol}$$

$$\text{mass } BaCl_2 \cdot 2H_2O = 6.08 \times 10^{-5} \text{ mol } BaCl_2 \cdot 2H_2O \times \frac{244.26 \text{ g } BaCl_2 \cdot 2H_2O}{1 \text{ mol}}$$
$$= 0.0149 \text{ g}$$

9. A solution contains 1.569 mg of $CoSO_4$ (155.0 g/mol) per milliliter. Calculate

(a) the volume of 0.007840 M EDTA needed to titrate a 25.00-mL aliquot of this solution. **[5 %]**

(b) the volume of 0.009275 M Zn^{2+} needed to titrate the excess reagent after addition of 50.00 mL of 0.007840 M EDTA to a 25.00-mL aliquot of this solution. **[5 %]**

(c) the volume of 0.007840 M EDTA needed to titrate the Zn^{2+} displaced by Co^{2+} following addition of an unmeasured excess of ZnY^{2-} to a 25.00-mL aliquot of the $CoSO_4$ solution. The reaction is $Co^{2+} + ZnY^{2-} \rightarrow CoY^{2-} + Zn^{2+}$ **[5 %]**

Solution:

First calculate the $CoSO_4$ concentration

$$\frac{1.569 \text{ mg}}{mL} \times \frac{1 \text{ mmol } CoSO_4}{155.0 \text{ mg}} = 0.010123 \text{ M}$$

In each part 25 mL of this solution is taken,

so amount $CoSO_4 = 25.00 \text{ mL} \times \frac{0.010123 \text{ mmol}}{mL} = 0.25306 \text{ mmol}$

(a) The volume of 0.007840 M EDTA needed to titrate a 25.00 mL aliquot of this solution

$$\text{Vol. EDTA} = 0.25306 \text{ mmol } CoSO_4 \times \frac{1 \text{ mmol EDTA}}{\text{mmol } CoSO_4}$$

$$\times \frac{1 \text{ mL}}{0.007840 \text{ mmol EDTA}}$$

$$= 32.28 \text{ mL}$$

(b) The volume of 0.009275 M Zn^{2+} need to titrate the excess reagent after addition of 50.00mL of 0.007840 M EDTA to a 25.00mL aliquot of this solution.
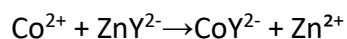
Amount excess EDTA

$$= \left(\frac{0.007840 \text{ mmol}}{mL} \times 50.00mL \right) - \left(0.25306 \text{ mmol } CoSO_4 \times \frac{1 \text{ mmol}}{\text{mmol } CoSO_4} \right)$$

$$= 0.1389 \text{ mmol}$$

$$\text{Vol.}\,Zn^{2+} = 0.1389 \ \text{mmol EDTA} \times \frac{1 \ \text{mmol} \ Zn^{2+}}{\text{mmol EDTA}} \times \frac{1 \ \text{mL}}{0.009275 \ \text{mmol} \ Zn^{2+}}$$

$$= 14.98 \ \text{mL}$$

(c) The volume of 0.007840 M EDTA needed to titrate the Zn^{2+} displace by Co^{2+} following addition of an unmeasured excess of ZnY^{2-} to a 25.00mL aliquot of the $CoSO_4$ solution. The reaction is

$Co^{2+} + ZnY^{2-} \rightarrow CoY^{2-} + Zn^{2+}$

$$\text{Vol.}\,EDTA = 0.25306 \ \text{mmol} \ CoSO_4$$

$$\times \frac{1 \ \text{mmol} \ Zn^{2+}}{\text{mmol} \ CoSO_4} \times \frac{1 \ \text{mmol EDTA}}{\text{mmol} \ Zn^{2+}} \times \frac{1 \ \text{mL}}{0.007840 \ \text{mmol EDTA}} = 32.28 \ \text{mL}$$

10. 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 $CaC_2O_{4(s)}$, redissolved in acid, and titrated with 10.53 mL of the EDTA solution. Assuming that 15 to 300 mg of magnesium and 50 to 400 mg of calcium per day are normal, did this specimen fall within these ranges? ($M_{Ca} = 40.08$ g/mol, $M_{Mg} = 24.305$ g/mol) **[10 %]**

Solution:

Amount $Mg^{2+} + Ca^{2+} =$

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

$$= 0.108186 \text{ mmol}$$

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

$$= 0.048333 \text{ mmol}$$

Amount $Mg^{2+} = 0.108186 - 0.048333 = 0.059854$ mmol

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

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

Both fall within the normal ranges.

~ End of Paper ~

Table 1. Activity Coefficients for Ions at 25°C

Ion	α_X, nm	Activity Coefficient at Indicated Ionic Strength				
		0.001	0.005	0.01	0.05	0.1
H_3O^+	0.9	0.967	0.934	0.913	0.85	0.83
Li^+, $C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4–0.45	0.965	0.927	0.902	0.82	0.77
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, MnO_4^-	0.35	0.965	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.965	0.925	0.899	0.81	0.75
Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+	0.25	0.965	0.925	0.897	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.756	0.690	0.52	0.44
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Phthalate^{2-}	0.6	0.870	0.748	0.676	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.869	0.743	0.668	0.46	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, $C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, Cr_4^{2-}, HPO_4^{2-}	0.40	0.867	0.738	0.661	0.44	0.35
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.737	0.540	0.443	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.587	0.348	0.252	0.10	0.063
$Fe(CN)_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020