CH 223 – Worksheet 4

1. Calculate the solubility of silver(I) oxalate ($Ag_2(C_2O_4)$), Ksp = 5.40×10^{-12} a) in pure water and b) in 0.010 M $AgNO_3$.

$$Ag_2(C_2O_4)(s) \rightleftharpoons 2\,Ag^+(aq) + C_2O_4^{2-}(aq)$$

0   0

2x   x

$$K_{sp} = [Ag^+]^2[C_2O_4^{2-}] = 4x^2 = 5.40\times10^{-12}$$

$(2x)^2$ x

$$x = \left(\frac{5.40\times10^{-12}}{4}\right)^{1/3} = 1.11\times10^{-4}\ \frac{mol}{L}$$

molar mass = $303.8\ \frac{g}{mol}$

$$\left(1.11\times10^{-4}\ \frac{mol}{L}\right)\left(303.8\ \frac{g}{mol}\right) =$$

Solubility $\frac{g}{L}$

$\boxed{0.0336\ \frac{g}{L}}$

2. The graph below shows the titration of 20.00 mL of a weak acid, H_2A, with 0.09950 M NaOH.

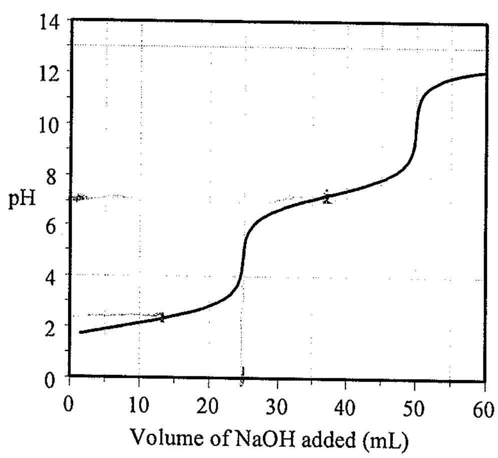
$pH = pKa + \log\frac{[A^-]}{[HA]}$

$2.2 = pH_1$

$\boxed{pKa_1 = 10^{-2.2} = 6.31\times10^{-3}}$

$pH_2 = 7.1$

$\boxed{pKa_2 = 10^{-7.1} = 7.94\times10^{-8}}$



a) What is the molarity of the H_2A solution?   b) What are K_{a1} and K_{a2} for H_2A?

$$(0.025\,L\ NaOH)\left(0.09950\ \frac{mol}{L}\ NaOH\right)\left(\frac{1\ mol\ H_2A}{1\ mol\ NaOH}\right) = 2.49\times10^{-3}\ mol\ H_2A$$

$$\frac{2.49\times10^{-3}\ mol\ H_2A}{0.020\ L} = \boxed{0.1245\ \frac{mol}{L}\ H_2A}$$

3. Calculate the pH when 24.9 mL of 0.100 M HNO_3 has been added to 25.0 mL of a 0.100 M KOH solution.

$$(0.0249\,L)\left(0.100\ \frac{mol}{L}\ HNO_3\right) = 2.49\times10^{-3}\ mol\ H^+$$

$$(0.0250\ L)\left(0.100\ \frac{mol}{L}\ KOH\right) = 2.5\times10^{-3}\ mol\ OH^-$$

$1.0\times10^{-5}\ mol\ OH^-$

$$\frac{1.0\times10^{-5}\ mol\ OH^-}{4.99\times10^{-2}\ L} = 2.0\times10^{-4}\ \frac{mol}{L} \quad \therefore\ pOH = -\log\left(2.0\times10^{-4}\ \frac{mol}{L}\right)$$

$pOH = 3.70$

$pH = 14 - 3.70 = 10.30$

4. What are the geometries most commonly associated with (a) coordination number 4, (b) coordination number 6?

a) tetrahedral, square planar

b) octahedral

5. For each of the following polydentate ligands, determine (i) the maximum number of coordination sites that the ligand can occupy on a single metal ion and (ii) the number and type of donor atoms in the ligand: (a) ethylenediamine (en), (b) thiocyanate ion, (c) the oxalate anion ($C_2O_4^{2-}$), (d) $[EDTA]^{4-}$

a) 2 sites, N: atoms $H_2\ddot{N}-CH_2CH_2-\ddot{N}H_2$

d) EDTA :N & $\ddot{O}$ 6 sites

b) $:\ddot{S}=C=\ddot{N}:$ 1 site :N or S: donates

c) $HO-C(=O)-C(=O)-OH$ 2 sites $\ddot{O}$ donates

6. As shown in Figure 24.26 of the course textbook, the *d-d* transitions of $[Ti(H_2O)_6]^{3+}$ produces an absorption maximum at a wavelength of 500 nm. (a) What is the magnitude of Δ for $[Ti(H_2O)_6]^{3+}$ in kJ? (b) What is the spectrochemical series? How would the magnitude of Δ change if the H_2O ligands in $[Ti(H_2O)_6]^{3+}$ were replaced with NH_3 ligands?

a) $\Delta = \dfrac{hc}{\lambda} = \dfrac{(6.626\times10^{-34}\ J\cdot s)(3.0\times10^{8}\ \frac{m}{s})}{500\ nm\left(\frac{1\times10^{-9}\ m}{1\ nm}\right)} = 3.98\times10^{-19}\ J$

b) A series of ligands in order of increasing or decreasing field (Δ) strength $F^- < NH_3 < CO$ etc.

When H_2O is replaced with NH_3 Δ will increase.

7. Draw the crystal-field energy-level diagrams and show the placement of electrons for the following complexes: (a) $[Mn(H_2O)_6]^{2+}$ (high spin), (b) $[IrCl_6]^{2-}$ (low spin).

$Mn(H_2O)_6$ — Mn: +2, H_2O: 0

$4s^2 3d^5$ remove s electrons

Ir: +4, Cl: −6

$6s^2 5d^7$ remove 4e⁻

∴ $5d^5$

↑ ↑ high spin

↑ ↑ ↑

— — low spin

↑↓ ↑↓ ↑