KEY TO EXAMINATION 1
September 24 2001
Q1. (20 points) Define, or explain, the following (use equations or examples where appropriate):

a) Principle of the Fajans titration for Cl⁻ using an adsorption indicator
b) Why the pH of a solution of 1.0 x 10⁻¹⁰ M HCl is 7.00
c) Relationship between $K_a$ for a weak acid and $K_b$ for its conjugate base, and $K_w$
d) Why supersaturation should be avoided during precipitation in gravimetric analysis
e) Back titration and why it is sometimes necessary

a) In titration, an indicator dye is added. Dye has a charge. Before equivalence point, AgCl(s) adsorbs Cl⁻ ions in solution. Just after end point, precipitate AgCl(s) adsorbs Ag⁺ ions and becomes negatively charged. Indicator dye, In⁻, adsorbs and gives precipitate a pink color.

b) $H^+$ from H₂O dissociation is much greater than from the 1.0 x 10⁻¹⁰ M HCl. Hence $[H^+] ≈ 1.0 \times 10^{-7} \text{M}$, i.e. pH ≈ 7.00

c) $K_w = K_a \times K_b$

d) Supersaturation results in large number of crystal nuclei being formed rather than slow crystal growth of nuclei. A colloid is often formed which is difficult to filter.

e) Back titrations often used when direct titration results in poorly observed end point or when direct titration reaction is slow to reach equilibrium.
Q.2. Both chloride ion and chromate ion can be precipitated with $Ag^+$ in a precipitation titration. You have a solution containing 0.0100 M $Cl^-$ and 0.0100 M $CrO_4^{2-}$ and a solution of $AgNO_3$ is slowly added:

a) Calculate whether $AgCl$ or $Ag_2CrO_4$ will precipitate first and what the $[Ag^+]$ in the solution will be when the first precipitate forms.

b) Can 99% of the first anion to precipitate be precipitated without any precipitation of the second? You must show your calculations.

c) Can 99.9% of the first anion be precipitated without precipitation of the second? Show calculations.

$K_{sp}$ for $AgCl = 1.8 \times 10^{-10}$; $K_{sp}$ for $Ag_2CrO_4 = 1.2 \times 10^{-12}$

**Part (a):** Solid which will precipitate first will have the lowest $[Ag^+]$ at initiation of precipitation

For $AgCl$: $K_{sp}$ for $AgCl = 1.8 \times 10^{-10}$

$$[Ag^+]^2 = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.0100} = 1.8 \times 10^{-8} M$$

For $Ag_2CrO_4$: $K_{sp}$ for $Ag_2CrO_4 = 1.2 \times 10^{-12}$

$$[Ag^+]^2 = \frac{K_{sp}}{[CrO_4^{2-}]} = \frac{1.2 \times 10^{-12}}{0.0100} = 1.2 \times 10^{-10}$$

$$[Ag^+] = \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} M \Rightarrow 1.1 \times 10^{-5} M$$

Ans: Hence $AgCl$ will precipitate first.

**Part (b):** Can 99% of $AgCl$ (i.e., $Cl^-$) be precipitated without precipitation of $Ag_2CrO_4$?

If 99% of $Cl^-$ is precipitated (i.e., as $AgCl$)

The 1% remains in solution

$$[Cl^-] = 0.0100 \times 1.0 \times 10^{-3} = 1.0 \times 10^{-5} M$$

Now

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-5}} = 1.8 \times 10^{-5} M$$

This is not sufficient to precipitate $Ag_2CrO_4$.

Since $1.8 \times 10^{-5} M < 1.1 \times 10^{-5} M$, Ans: No.

**Part (c):** For 99.9% precipitation of $Cl^-$

$$[Cl^-]_{solution} = 0.0100 \times 1.0 \times 10^{-3} = 1.0 \times 10^{-5} M$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-5}} = 1.8 \times 10^{-5} M$$

Since $1.8 \times 10^{-5} M > 1.1 \times 10^{-5} M$, $Ag_2CrO_4$ will precipitate.

Ans: 99.9% $Cl^-$ cannot be precipitated free of $Ag_2CrO_4$. 
Q.3. (20 points) Calculate the pH of the following solutions (all species strong acids or bases):

a) A solution containing 0.50 M HCl and 0.2000 M HNO₃
b) 5.0 x 10⁻³ M Ca(OH)₂
c) 10.00 M H₂SO₄ (assume both protons completely dissociated)
d) 1.0 x 10⁻¹² M HCl

a) Both HCl and HNO₃ are strong acids.

\[ [H^+] = (0.50 \text{ M})_{\text{HCl}} + (0.20 \text{ M})_{\text{HNO}_3} \]

\[ = 0.70 \text{ M} \quad \text{(note 2 s.f.)} \]

\[ \text{pH} = -\log 0.70 = 0.50 \quad \text{(2 s.f.)} \quad \text{Ans} \]

b) 5.0 x 10⁻³ M Ca(OH)₂ — strong base

\[ \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \]

\[ [\text{OH}^-] = 2(5.0 \times 10^{-3}) \quad \text{m} = 1.0 \times 10^{-2} \text{ M} \]

\[ \text{pOH} = 2.00 \quad ; \quad \text{pH} = \text{pK}_w - \text{pOH} \]

\[ \text{pH} = 14.00 - 2.00 \]

\[ \text{pH} = 12.00 \quad \text{Ans} \quad (2 \text{ s.f.)} \]

c) If both protons are completely dissociated

\[ \text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \]

\[ [\text{H}^+] = 2 \times 10.00 \quad \text{m} = 20.00 \text{ M} \]

\[ \text{Ans} \quad \text{pH} = -1.30 \text{ s.f.)} \]

*Note: The second proton is not completely dissociated*

d) 1.0 x 10⁻¹² M HCl

\[ \text{pH} = 2.00 \quad \text{Ans} \]

Solution: pH is due almost entirely to H₂O dissociation.
Q.4. (20 points) A 25.00 mL solution of La\(^{3+}\) was treated with excess sodium oxalate, Na\(_2\)C\(_2\)O\(_4\), to precipitate La\(_2\)(C\(_2\)O\(_4\))\(_3\), which was filtered off, washed, dissolved in acid and titrated with 12.34 mL of 0.004321 M KMnO\(_4\) to reach a purple end point. Find the molarity of the La\(^{3+}\) solution. The reaction between oxalate and permanganate is:

\[
5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ = 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}
\]

Need to work this problem backwards.

Since \((0.004321 \text{ mol MnO}_4^-/L) \times 0.01234 \text{ L} = \text{ mol MnO}_4^- \text{ used} = 5.332 \times 10^{-5} \text{ mol MnO}_4^-\)

From reaction stoichiometry:

\[
\text{mol C}_2\text{O}_4^{2-} = \frac{5.332 \times 10^{-5} \text{ mol MnO}_4^-}{2 \text{ mol MnO}_4^-}
\]

\[
= 1.333 \times 10^{-4} \text{ mol C}_2\text{O}_4^{2-}
\]

This is the amount of C\(_2\)O\(_4\)\(^{2-}\) in the La\(_2\)(C\(_2\)O\(_4\))\(_3\) precipitate.

\[
\text{mol La}^{3+} = \frac{1.333 \times 10^{-4} \text{ mol C}_2\text{O}_4^{2-} \times 2 \text{ mol La}^{3+}}{3 \text{ mol C}_2\text{O}_4^{2-}}
\]

\[
= 8.887 \times 10^{-5} \text{ mol La}^{3+}
\]

Since solution volume = 25.00 mL

\[
\left[\text{La}^{3+}\right] = \frac{8.887 \times 10^{-5} \text{ mol}}{0.02500 \text{ L}} = 3.555 \times 10^{-3} \text{ M La}^{3+}
\]

Ans \(3.555 \times 10^{-3} \text{ M La}^{3+}\) (4 s.f.)
Q.5. (20 points) 50.00 mL of a solution of H₂SO₄ of unknown concentration was treated with 0.0100 mol of solid NaOH which gives an excess of NaOH (assume no volume change in the solution). Both protons are neutralized according to the reaction:

\[ \text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

The excess NaOH was then back titrated with standard 0.0500 M HCl and the volume required to reach the end point was 20.20 mL.

a) What is the concentration of the H₂SO₄ solution?

b) What is the value of the equilibrium constant for the reaction of H₂SO₄ with NaOH?

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(a) As for Q.4, this problem needs to be worked in reverse.

\[ \text{mol HCl used to titrate excess NaOH} = 0.2020 \text{ L} \times 0.0500 \text{ mol HCl/L} = 1.010 \times 10^{-3} \text{ mol HCl} = \text{mol NaOH in excess} \]

Since amount of NaOH added = 0.0100 mol NaOH

\[ \text{mol NaOH reacted with H}_2\text{SO}_4 = 0.0100 - 1.010 \times 10^{-3} = 8.990 \times 10^{-3} \text{ mol} \]

Since 1 mol H₂SO₄ = 2 mol H⁺ = 2 mol OH⁻

\[ \text{mol H}_2\text{SO}_₄ = 8.990 \text{ mol NaOH} \times \frac{1 \text{ mol H}_2\text{SO}_₄}{2 \text{ mol NaOH}} = 4.495 \times 10^{-3} \text{ mol H}_2\text{SO}_₄ \]

Concentration of H₂SO₄ in original solution:

\[ \frac{4.495 \times 10^{-3} \text{ mol H}_2\text{SO}_₄}{0.0500 \text{ L}} = 8.99 \times 10^{-2} \text{ M} \]

Ans. \( 9.0 \times 10^{-2} \text{ M} \) (2 s.f.)

(b) Reaction is neutralization of strong acid with strong base.

\[ \text{H}_2\text{SO}_₄ + 2\text{NaOH} \rightarrow 2\text{Na}^+ + \text{SO}_₄^{2-} + 2\text{H}_2\text{O} \]

or \( \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \)

Ans. \( K_w = \frac{1}{K_a} = 1.00 \times 10^{14} \)