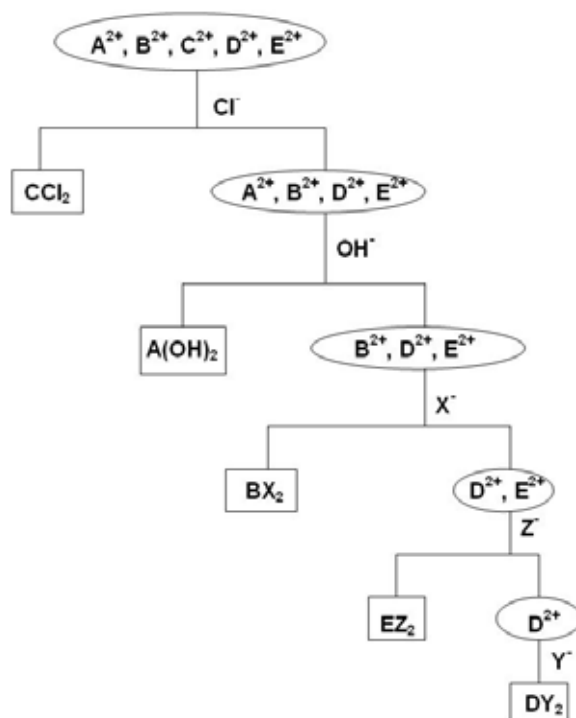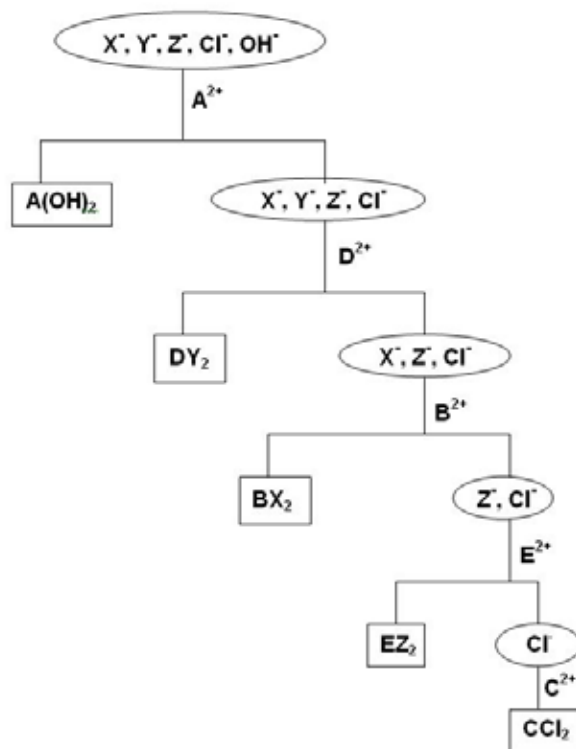# Answer 1: Separation and Identification of Ions

1-1 For example

$A^{2+}, B^{2+}, C^{2+}, D^{2+}, E^{2+}$

— Cl^- —

- CCl_2
- $A^{2+}, B^{2+}, D^{2+}, E^{2+}$

  — OH^- —
  - $A(OH)_2$
  - B^{2+}, D^{2+}, E^{2+}

    — X^- —
    - BX_2
    - D^{2+}, E^{2+}

      — Z^- —
      - EZ_2
      - D^{2+}

        — Y^- —
        - DY_2

1-2 For example

$X^-, Y^-, Z^-, Cl^-, OH^-$
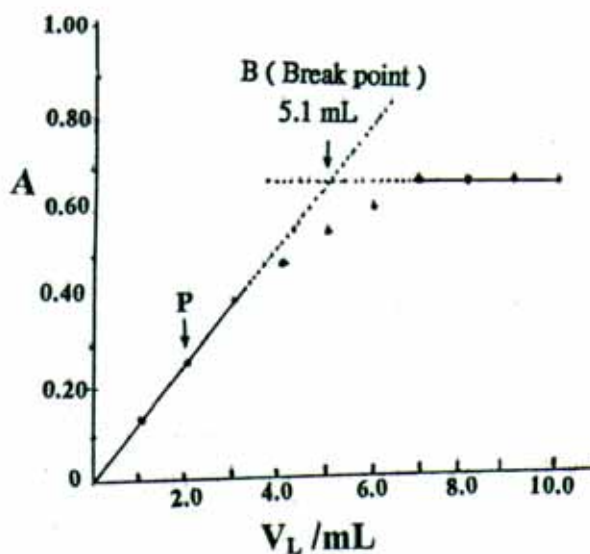
— A^{2+} —

- $A(OH)_2$
- X^-, Y^-, Z^-, Cl^-

  — D^{2+} —
  - DY_2
  - X^-, Z^-, Cl^-

    — B^{2+} —
    - BX_2
    - Z^-, Cl^-

      — E^{2+} —
      - EZ_2
      - Cl^-

        — C^{2+} —
        - CCl_2

1-3-1 BY_2 $=$ B^{2+} $+$ $2Y^-$ $K_{sp} = (S_1)(2S_1)^2 = 3.20 \times 10^{-8}$

                        S_1 $2S_1$

          $4S_1^3 = 3.20 \times 10^{-8}$, S_1(solubility of BY_2) $= 2.0 \times 10^{-3}$ M

1-3-2 CY_2 $=$ C^{2+} $+$ $2Y^-$ $K_{sp} = (S_2)(2S_2)^2 = 2.56 \times 10^{-13}$

                        S_2 $2S_2$

          $4S_2^3 = 2.56 \times 10^{-13}$, S_2(solubility of CY_2) $= 4.0 \times 10^{-5}$ M
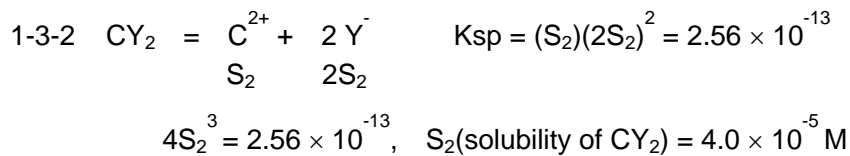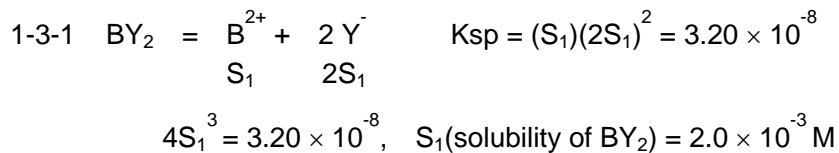
1-4-1   Plot of Absorbance (A) vs Volume (V_L) of L added as follows:

From the volume of L at Break point B (all B^{2+} ions form complex with L) in the plot, n can be calculated:

$n/1 = $ (# of moles of L) / (# of moles of B^{2+})

     $= (5.1 \text{ mL} \times 1.0 \times 10^{-2}) / (2.0 \text{ mL} \times 8.2 \times 10^{-3})$

     $\cong 3$

It means that B^{2+} forms BL_3^{2+} complex with L.

1-4-2   (1) Calculation of Molar Absorption Coefficient ε

        At Break point, A $= 0.66 = \varepsilon \times 1 \times$ (concentration of BL_3^{2+})

        And $\varepsilon = 0.66 / (2.0 \text{ mL} \times 8.2 \times 10^{-3} / 50 \text{ mL}) = 2.01 \times 10^3$

       (2) Choose a point in the curve of the plot, for example:

        At Point P (2.0 mL of L added): A = 0.26

          A $= 0.26 = \varepsilon \times 1 \times [BL_3^{2+}]$

$$[BL_3^{2+}] = 0.26 \, / \, \varepsilon = 0.26 \, / \, (2.01 \times 10^3) = 1.29 \times 10^{-4} \text{ M}$$

$$[B^{2+}] = (2.0 \text{ mL} \times 8.2 \times 10^{-3} - 50 \text{ mL} \times 1.29 \times 10^{-4} \text{ M}) \, / \, 50 \text{ mL}$$

$$[B^{2+}] = 1.99 \times 10^{-4} \text{ M}$$

$$[\,L\,] = (2.0 \text{ mL} \times 1.0 \times 10^{-2} - 3 \times 50 \text{ mL} \times 1.29 \times 10^{-4} \text{ M}) \, / \, 50 \text{ mL}$$

$$[\,L\,] = 1.3 \times 10^{-5} \text{ M}$$

[Calculation of formation constant]

So $\quad K_f = [BL_3^{2+}] \, / \, ([B^{2+}][\,L\,]^3) = (1.29 \times 10^{-4}) \, / \, ((1.99 \times 10^{-4})(1.3 \times 10^{-5})^3)$

$\quad K_f = 8.74 \times 10^{11}$

1-5-1　For CY_2: $Ksp = [C^{2+}] \, [Y^-]^2 = 2.56 \times 10^{-13}$

$\quad [Y^-] = ((2.56 \times 10^{-13}) \, / \, 0.05)^{1/2} = 2.26 \times 10^{-6} \text{ M}$　　When CY_2 begins to form

For BY_2: $Ksp = [B^{2+}] \, [Y^-]^2 = 3.20 \times 10^{-8}$

$[Y^-] = ((3.20 \times 10^{-8}) \, / \, 0.05)^{1/2} = 5.66 \times 10^{-4} \text{ M}$　　When BY_2 begins to form

$\quad CY_2$　forms first

1-5-2　The precipitation of C^{2+} as CY_2 considered to be completed at $[C^{2+}] = 10^{-6}$ M

Thus $\qquad Ksp = [C^{2+}] \, [Y^-]^2 = 2.56 \times 10^{-13}$

and $\quad [Y^-] = ((2.56 \times 10^{-13}) \, / \, 10^{-6})^{1/2} = 5.06 \times 10^{-4} \text{ M}$

It means that $[Y^-] = 5.06 \times 10^{-4}$ M, when CY_2 precipitates completely.

When $[Y^-] = 5.06 \times 10^{-4}$ M, for BY_2 :

$\quad [B^{2+}] \, [Y^-]^2 = (0.1) \, (5.06 \times 10^{-4})^2 = 2.56 \times 10^{-8} < Ksp$ of BY_2 (3.20×10^{-8})

$\quad BY_2$ (ppt) can not be formed at $[Y^-] = 5.06 \times 10^{-4}$ M and $[B^{2+}] = 0.1$ M

when CY_2 precipitates completely.

It means that it is possible to separate B^{2+} and C^{2+} ions by precipitation method with Y^- as a precipitating agent.

Answer 2: Preparation and Applications of Radioisotopes

2-1

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$$

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{3}_{1}T + ^{12}_{6}C$$

2-2-1 $A = \varepsilon \lambda N$, $A_o = \varepsilon \lambda N_o$ and $N = N_o e^{-\lambda t}$

$A / A_o = N / N_o = e^{-\lambda t}$

and $A = A_o e^{-\lambda t}$

2-2-2 $N = N_o e^{-\lambda t}$

If $N = 1/2 N_o$, $t = t_{1/2}$

then $1/2 N_o = N_o e^{-\lambda t_{1/2}}$

$\lambda = 2.303 \log 0.5 / t_{1/2} = 0.693 / t_{1/2}$

For C-14, $\lambda = 0.693 / 5730 = 1.2 \times 10^{-4}$

Also $A = A_o e^{-\lambda t}$

$10.2 = 16.5 e^{-1.2 \times 10^{-4} t}$

and $t = 4008$ years

2-3-1 $A = Rp - Rd = N \quad - N \quad (e^{-\lambda t}) = N \quad (1- e^{-\lambda t})$

and $\lambda = 0.693 / (14.3 \times 24 \times 60 \times 60) = 5.61 \times 10^{-7}$

$N = [(10 \times 10^{-3}) / 98] \times 6 \times 10^{23} = 6.12 \times 10^{19}$

$A = N \quad (1- e^{-\lambda t}) = (6.12 \times 10^{19})(1.00 \times 10^{13})(0.9 \times 10^{-24})(1-e^{-5.61 \times 10^{-7} \times 60 \times 60})$

and $A = 1.11 \times 10^{6}$ cps $= 1.11 \times 10^{6} / (3.7 \times 10^{10})$ Ci $= 3 \times 10^{-5}$ Ci $= 0.03$ mCi
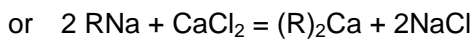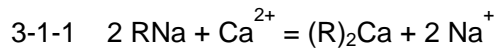
2-3-2   Total amount of P-32 is constant after and before the injection,

so, $V_o A_o = V_x A_x$ (V = volume,   A = Activity,   x for pool water)

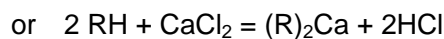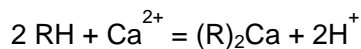2.0 x 1.0 = V_x (12.4 / (3.7 x 10^{10}))

and V_x(pool water) = 5.97 x 10^9 mL = 5.97 x 10^6 L

Answer 3: Ion Exchangers

3-1-1 $2\ RNa + Ca^{2+} = (R)_2Ca + 2\ Na^+$

or $2\ RNa + CaCl_2 = (R)_2Ca + 2NaCl$

3-1-2(a)   The tap water contains trace HCl after the adsorption of Ca^{2+} by the ion exchanger R^-H^+ and the chemical equation of the adsorption is:

$2\ RH + Ca^{2+} = (R)_2Ca + 2H^+$

or $2\ RH + CaCl_2 = (R)_2Ca + 2HCl$

3-1-2(b)   RNa is suitable for drinking purpose.   Because the product of the adsorption of Ca^{2+} by RNa is Na^+ or NaCl while the product is H^+ or HCl after the adsorption of Ca^{2+} by RH.
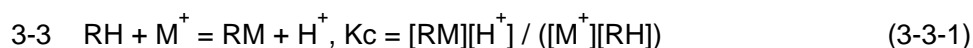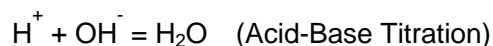
3-2-1   The removal of H^+ can be achieved by using the anionic ion exchanger R^+OH^- with the equation:

$ROH + HCl = R^+Cl^- + H_2O$
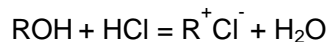
3-2-2   Firstly, the anionic ion exchanger R^+OH^- is used to adsorb the SO_4^{2-} ion with the equation :

$2\ ROH + SO_4^{2-} = (R^+)_2SO_4^{2-} + 2\ OH^-$
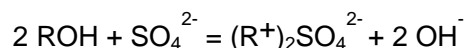
Secondly, a standard solution of HCl can be used for the titration of the OH^- in the solution after adsorption of SO_4^{2-} by the anionic ion exchanger R^+OH^-.

$H^+ + OH^- = H_2O$ (Acid-Base Titration)

3-3 $RH + M^+ = RM + H^+$, $Kc = [RM][H^+] / ([M^+][RH])$ (3-3-1)

$K_d = [RM] / [M^+]$ (3-3-2)

$S = ([RM] + [RH]) \times 10^{-3}$ (3-3-3)

We substitute Equations (3-3-1) and (3-3-2) into Equation (3-3-3) and obtain:

65

$$S = (Kd[M^+] + [RM][H^+] / Kc[M^+]) \times 10^{-3}$$

$$= (Kd[M^+] + Kd[M^+][H^+] / Kc[M^+]) \times 10^{-3}$$

$$= (Kd[M^+] + Kd[H^+] / Kc) \times 10^{-3}$$

$$S \, Kc \, 10^3 = Kd \, Kc \, [M^+] + Kd[H^+]$$

$$1 / Kd = [M^+] / (S(10^3)) + [H^+] / (S \, Kc \, (10^3)) \qquad\qquad (3\text{-}3\text{-}4)$$

3-4-1 $N_1 = 16 \, (t_1 / \omega_1)^2 = 16 \, (10 / 1.0)^2 = 1600$

$N_2 = 16 \, (t_2 / \omega_2)^2 = 16 \, (14 / 1.5)^2 = 1394$
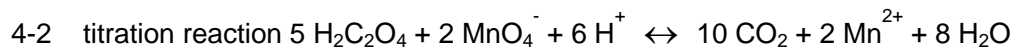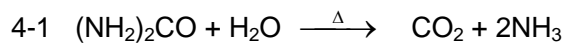
$N = (N_1 + N_2) / 2 = (1600 + 1394) / 2 = 1497$

3-4-2 $H = L / N = 30 / 1497 = 0.021$ cm

3-4-3 $R = 2 \, (t_2 - t_1) / (\omega_1 + \omega_2) = 2 \, (14 - 10) / (1.0 + 1.5) = 3.2$

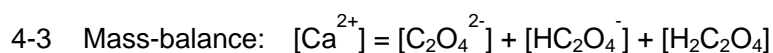3-4-4 $\alpha = (t_2 - t_0) / (t_1 - t_0) = (14 - 1) / (10 - 1) = 1.44$

3-5-1 $Z\text{-}Na^+ + Ca^{2+} = Z\text{-}Ca^{2+} + Na^+$

3-5-2 $Z\text{-}Na^+ + K^+ = Z\text{-}K^+ + Na^+$
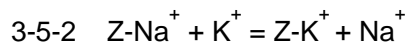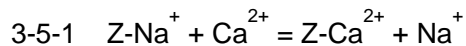
Answer 4: Determination of Calcium Ion by Precipitation Followed by Redox Titration

4-1 $(NH_2)_2CO + H_2O \xrightarrow{\Delta} CO_2 + 2NH_3$

4-2 titration reaction $5 \, H_2C_2O_4 + 2 \, MnO_4^- + 6 \, H^+ \leftrightarrow 10 \, CO_2 + 2 \, Mn^{2+} + 8 \, H_2O$

$[Ca^{2+}] = 2.5 \times 10^{-3} \, M \times 0.02741 \, L \times \frac{5}{2} \, / \, 0.025 \, L$

$= 6.85 \times 10^{-3}$ M

4-3 Mass-balance: $[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$

$$= [C_2O_4^{2-}] (1 + [H^+] / K_2 + [H^+]^2 / K_1 K_2)$$

$$[C_2O_4^{2-}] = [Ca^{2+}] / (1 + [H^+] / K_2 + [H^+]^2 / K_1 K_2) \qquad (1)$$

Substituting (1) into $[Ca^{2+}] [C_2O_4^{2-}] = K_{sp}$

$$[Ca^{2+}] = 1.92 \times 10^{-4} \text{ M}$$

4-4　$C_{Ca} = [Ca^{2+}] + [CaC_2O_{4(aq)}] + [Ca(C_2O_4)_2^{2-}]$

$$= K_{sp} \left(\frac{1}{[C_2O_4^{2-}]} + K_{f1} + K_{f1} K_{f2} [C_2O_4^{2-}] \right)$$

$$\frac{dC_{Ca}}{d[C_2O_4^{2-}]} = 0 = - K_{sp} \frac{1}{[C_2O_4^{2-}]^2} + K_{sp} K_{f1} K_{f2}$$

$$[C_2O_4^{2-}] = 1.0 \times 10^{-2} \text{ M}$$

$$[Ca^{2+}] = K_{sp} / [C_2O_4^{2-}] = 1.3 \times 10^{-6} \text{ M}$$

4-5　Charge balance: $2[Ca^{2+}] + [H^+] = 2[C_2O_4^{2-}] + [HC_2O_4^-] + [OH^-] \qquad (1)$

Mass balance: $[Ca^{2+}] = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4] \qquad (2)$

Because K_{b2} is too small, $[H_2C_2O_4]$ can be neglected.

Comparing (1), (2), $[HC_2O_4^-] = K_w / [H^+] - [H^+] \qquad (3)$

$$[C_2O_4^{2-}] = (K_2 K_w) / [H^+]^2 - K_2 \qquad (4)$$

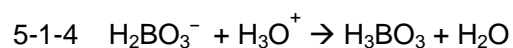$$[Ca^{2+}] = K_{sp} / [C_2O_4^{2-}] = K_{sp} [H^+]^2 / (K_2 K_w - K_2 [H^+]^2) \qquad (5)$$
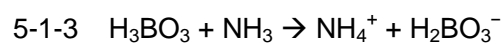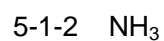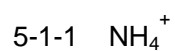
Substituting (3), (4), (5) into (2)

$$K_2 [H^+]^5 + (K_2^2 - K_{sp}) [H^+]^4 - 2 K_2 K_w [H^+]^3 - 2 K_2^2 K_w [H^+]^2 + K_2 K_w^2 [H^+] + K_2^2 K_w^2 = 0$$
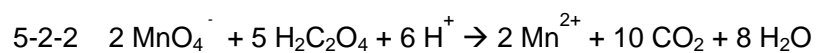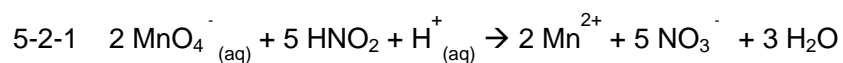
Solving $[H^+]$, $[H^+] = 5.5 \times 10^{-8}$ M (or pH = 7.26)

Substituting $[H^+]$ into (5), $[Ca^{2+}] = 1.04 \times 10^{-4}$ M

Answer 5: Nitrogen in Wastewater

5-1-1 NH_4^+

5-1-2 NH_3

5-1-3 $H_3BO_3 + NH_3 \rightarrow NH_4^+ + H_2BO_3^-$

5-1-4 $H_2BO_3^- + H_3O^+ \rightarrow H_3BO_3 + H_2O$

5-1-5   Methyl orange.   At the equivalence point, the solution contains boric acid and ammonium ion, therefore, an indicator with an acidic transition interval is required.

5-2-1 $2\ MnO_{4\ (aq)} + 5\ HNO_2 + H^+_{(aq)} \rightarrow 2\ Mn^{2+} + 5\ NO_3 + 3\ H_2O$

5-2-2 $2\ MnO_4 + 5\ H_2C_2O_4 + 6\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

5-2-3 $A = [\ 5\ (\ B \times C) - 2\ (\ D \times E\ )\ ] \times 7\ /\ F$

Answer 6: Use of Isotopes in Mass Spectrometry

6-1   0.77

6-2   Corrected signal = (m / z 136 signal) - 1.03 (m / z 138 signal)