Recap

- Introduction Gravimetry

It is a process of isolation and weighing of an element or compound of element in pure form as possible

- Common Ion Effect

To a weak electrolyte, when another electrolyte containing common ion is added, then degree of dissociation of weak electrolyte is suppressed.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$$

Recap

- Ionic product and Solubility product

Ionic Product

It is the product of ionic concentration in an unsaturated or saturated solution. (i.e. actual concentration of ions in the solution)

Solubility product (Ksp)

In a saturated solution of sparingly soluble salt (electrolyte), the product of ionic concentration when raised to proper power is constant at a given temperature.

When ionic product > solubility product

solution is supersaturated and precipitation is take place.

Recap

- Co-precipitation and Post-precipitation

Coprecipitation:

The contamination of precipitate by substances which are soluble in mother liquor is termed as coprecipitation.

Ex. Adsorption of silver acetate over silver iodide

Post precipitation

The process in which precipitation of some component occur on the surface of the main precipitate after its formation is called post precipitation.

Ex. During the formation of calcium oxalate magnesium oxalate can form afterwards

SESSION AGENDA

- Factors affecting solubility of precipitate
- Precipitation from Homogeneous Solution
- Operations involve in gravimetric analysis
- Organic Precipitants

LEARNING OBJECTIVES

Students should able to understand

- various factors affecting solubility of precipitate
- Technique of precipitation from Homogeneous Solution
- Various operations involve in gravimetric analysis
- Use of organic precipitating agents

Factors affecting Precipitation

A) Effect of acid on solubility of precipitate

In general similar to salt effect solubility of sparingly soluble salt increases on addition of acid

Consider the sparingly soluble salt MA, it dissociate as

$$MA \rightleftharpoons M^{+} + A^{-}$$

When strong acid HCl

$$HCl \longrightarrow H^{+} + Cl^{-}$$

H^{+} from acid combine with A^{-} of salt to form

$$H^{+} + A^{-} \rightleftharpoons HA$$

As no. of A^{-} ions in solution decreases, dissociation of MA increases to produce more A^{-}

Factors affecting Precipitation

B) Effect of Solvent

- Polar solutes are more soluble in polar solvent while non polar solutes are soluble in non polar solvent.
- Inorganic salts are soluble in water while organic compounds are soluble in organic solvent.
- Solubility of Precipitate in solvent can be controlled by selecting suitable solvent.

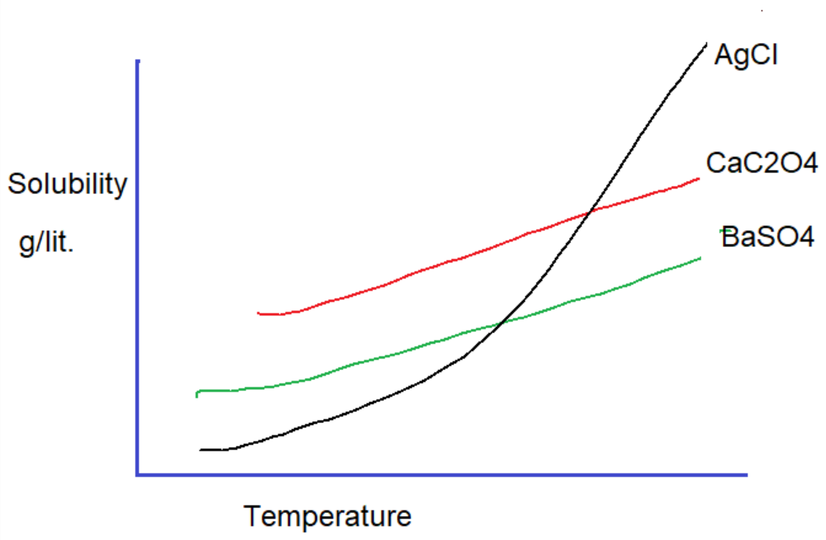
Factors affecting Precipitation

C) Effect of temperature on solubility of precipitate

Dissociation of salt is an endothermic process hence solubility of precipitate increases as temperature increases.

Examples

- Solubility of AgCl at 10ºC is 1.72mg/liter while at 100ºC is 21.1 mg/lit
- Solubility of $BaSO_4$ at 10ºC is 2.2mg/liter while at 100ºC is 3.9 mg/lit



Precipitation from Homogeneous Solution

Homogeneous precipitation is a process by which the precipitate is formed within the solution.

Precipitating reagent is not added directly but slowly generated by homogeneous chemical reaction taking place within the solution.

Precipitate formed by homogeneous precipitation is pure and have larger particle size.

Precipitation from Homogeneous Solution

Example 1
Urea is used for generation of OH^- (precipitating agent) and can be used for formation of precipitate of metal cation Al^{3+}, Fe^{+3} etc.

$$CO(NH_2)_2 + 3\ H_2O \rightarrow CO_2(g) + 2\ NH_4^{\ +} + 2\ OH^-$$

$$\boxed{Al^{3+} + 3OH^- \longrightarrow Al(OH)_3}$$

Example 2
Sulphamic acid is used for generation of SO4 $^{2-}$ as precipitating agent.

$$NH_2SO_3H + 2H_2O \rightarrow NH_4^{\ +} + H_3O^+ + SO_4^{2-}$$

$$\boxed{Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4}$$

Operations involve in gravimetric analysis

1) Precipitation
2) Digestion
3) Filtration
4) Washing
5) Drying and ignition
6) Weighing
7) Calculation

Operations involve in gravimetric analysis

1) Precipitation

Determination of Ag as AgCl

$$Ag^{+} + Cl^{-} \longrightarrow AgCl_{(s)}$$

Determination of Pb as PbCl2

$$Pb^{2+} + 2Cl^{-} \longrightarrow PbCl_{2(s)}$$

Operations involve in gravimetric analysis

2) Digestion/ Ostwald ripening

- The precipitate is allowed to stand for 10-24 hours at room temperature is called digestion
- Sometime precipitate is warm with mother liquor and allowed to stand.
- In digestion dissolution of smaller particles and formation of larger particle result in particle growth.
- It is useful for reducing coprecipitation.

Operations involve in gravimetric analysis

3)Filtration

- Filter paper:

Generally filter papers with low ash content are used, these are called as ashless fitter paper.

- 2) Hardened filter paper:

They have very small ash content , greater mechanical strength and more resistance to acid and alkali.

- 3) Whatman filter paper:

Whatman filter paper 40 and 42 are used for filtration of fine particles, whereas No.41 is used for filtering gelatinous precipitate.

Operations involve in gravimetric analysis

3)Filtration

- 4) Filter pulp:

It is prepared by vigorously shaking an ordinary filter paper with hot acidic solution.

- 5) Filtering crucibles:

Some precipitate can not be filtered by simple filter paper, these precipitates are easily undergo reduction and decomposes on heating for such precipitates filtering crucibles are used.

Porcelain Gooch crucible , Platinum Gooch crucible, Silica Gooch crucible, Sintered glass crucible

Operations involve in gravimetric analysis

4) Washing

a) Solution which prevent the precipitate from becoming colloidal

Washing of precipitate remove the impurities present on the surface of precipitate.

Choice of washing liquid depends upon type of precipitate

Gelatinous and curdy precipitates are washed with solution containing electrolyte or dilute acid.

Example: precipitate of oxide of Al and Fe are washed with 1% ammonium nitrate solution

Operations involve in gravimetric analysis

4) Washing

b) Solution which reduce solubility of precipitate

When precipitate is soluble in washing liquid then it’s solubility is reduced by using mixture of solvent.

Example: Precipitate of calcium oxalate is washed with dilute solution of ammonium oxalate.

3) Solution that prevent the hydrolysis of salts of weak acids and bases

Example: Addition of acid to washing liquid will prevent hydrolysis of ferric or similar salts.

Operations involve in gravimetric analysis

5) Drying and ignition

Precipitate is heated until the mass of precipitate becomes constant.

Heating is essential for removing solvent and other volatile species.

Drying: when precipitate is dried below 250°C then it is called as drying.

Ignition: When precipitate is dried in between 250°C to 1200°C is called ignition.

Operations involve in gravimetric analysis

6) Weighing and Calculation

Accurate weight of completely dried ppt is taken and used for calculations.

Calculation
Calculation of Ag From AgCl
Molecular weight of AgCl =143.32
Molar mass of Ag 107. 86

If wight of precipitate is 0.5g then weight of Ag can be calculated as
107.86 x 0.5 / 143.32
= 0.372 g of Ag

Fractional Precipitation

Precipitation of one component / element in presence of other is possible.

Example

When $AgNO_3$ is added to Solution containing Cl^- and I^-

Selective precipitation of AgI can be achieved by using solubility product concept.

Ksp of AgCl

$[Ag^+] [Cl^-] = 1.2 \times 10^{-10}$

Ksp of AgI $[Ag^+] [I^-] = 1.7 \times 10^{-16}$

Thus AgI is less soluble than AgCl

Hence AgI will be precipitated first

Organic Precipitants

- They are used for precipitating various metal ions.

- They have the ability to coordinate with many metals as they contain acidic or basic groups having unpairs electrons on hetero atoms.

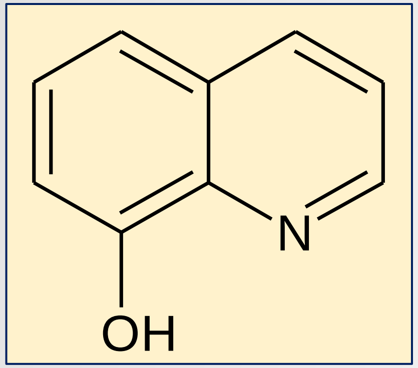
- They have high molecular weight, hence small amount of metal can produce large amount (weight) of precipitate.

Organic Precipitants

- Many of organic precipitants are selective, and form precipitates with selective cation in presence of other cation.

- By controlling pH and the concentration of masking reagents, the selectivity of an organic reagent can be enhanced.

8- hydroxy quinoline (oxine)



C_9H_7ON

By controlling pH, it can be used for precipitation of many elements.

It forms $M(C_9H_6ON)_2$ type complex with Mg, Zn, Cu, Cd, Pb

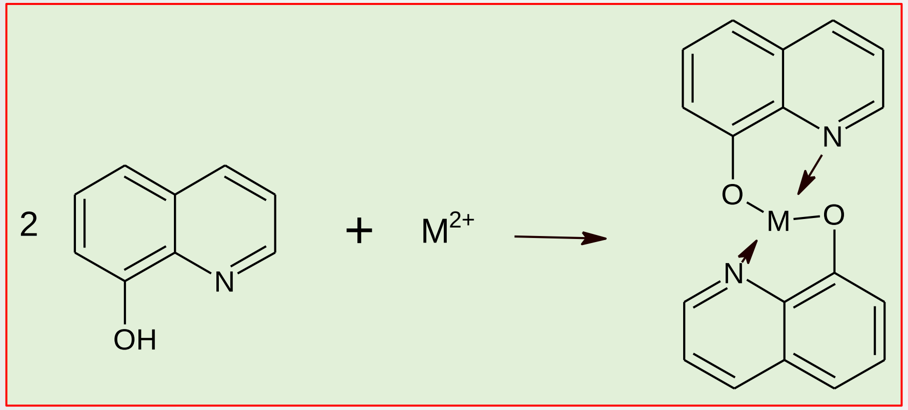
It forms $M(C_9H_6ON)_3$ type complex with Al, Fe, Bi, Ga

It forms $M(C_9H_6ON)_4$ type complex with Zr and Th

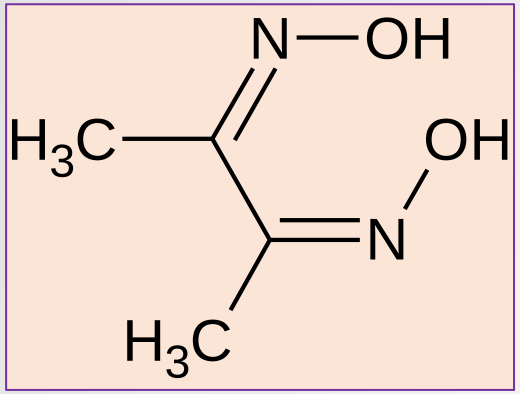
8- hydroxy quinoline (oxine)

Reagent

- 2 gram of 8 Hydroxyquinoline was dissolved in 100ml 2M acetic acid.
- Dropwise ammonia solution was added till turbidity persist.
- Few drops of acetic acids were added to get clear solution



Dimethyl glyoxime (DMG)

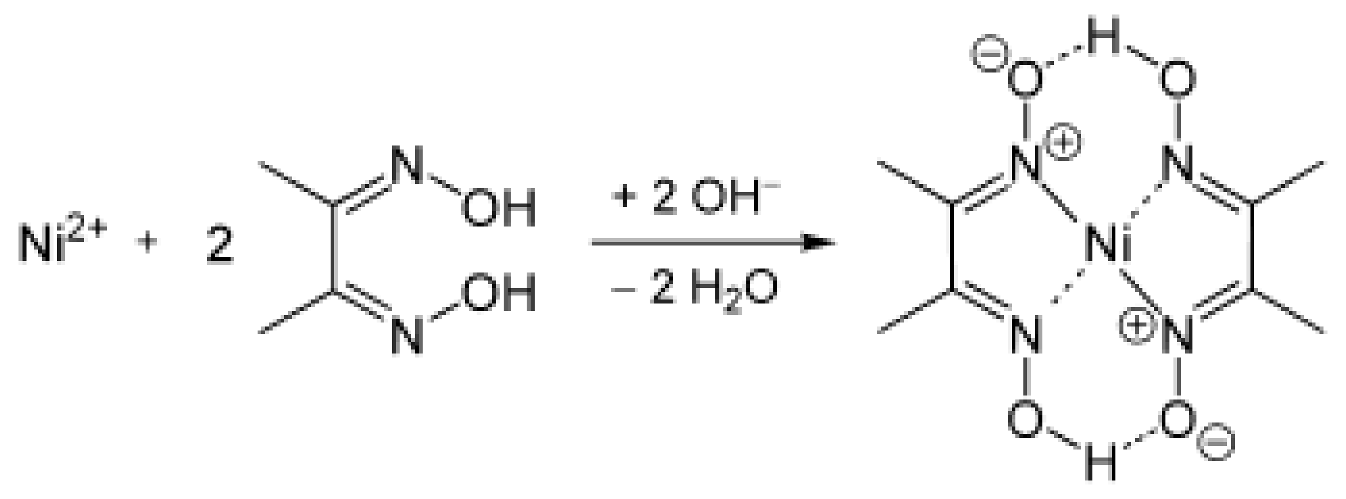


$C_4H_8O_2N_2$

1% solution in ethanol is used as a reagent

It form bright red colored complex with Ni metal.
$Ni(C_4H_7N_2O_2)_2$

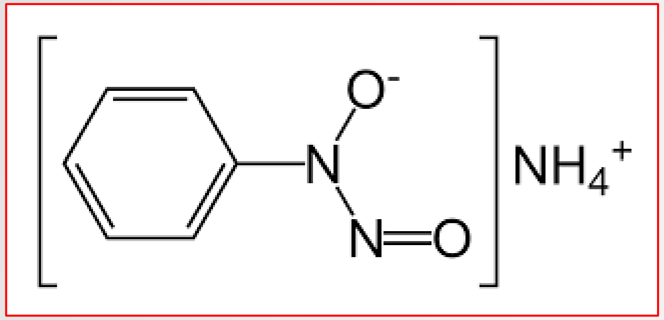
Dimethyl glyoxime (DMG)



Nickel bis(dimethylglyoximate) Complex

Reference:
https://en.wikipedia.org/wiki/Nickel_bis(dimethylglyoximate

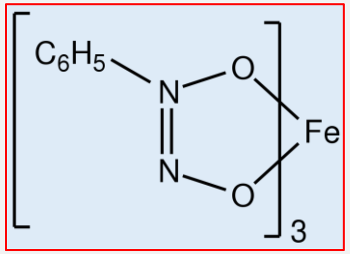
Cupferron (ammonium salt of N-nitroso-N-phenyl-hydroxylamine)



$C_6H_9N_3O_2$

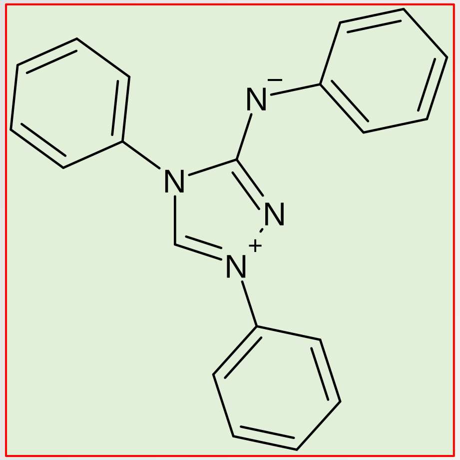
5-10 % acidic solution is used as a reagent
Specially Used for determination of Fe(III)

Also used for other elements like V(V), Ti (IV), Zr(IV), Ce(V)



Reference: https://en.wikipedia.org/wiki/Nickel_bis(dimethylglyoximate

Nitron

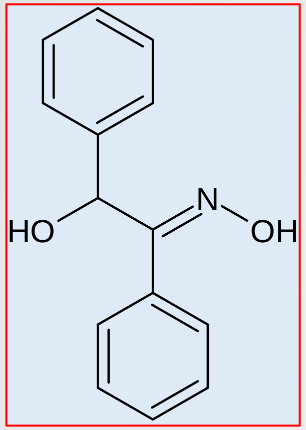


$C_{20}H_{16}N_4$

It is yellow crystalline solid (m.p. 189^0C)
10 % reagent in 5 % acetic acid is used as a reagent

Used for determination of Nitrate and other anion
$C_{20}H_{16}N_4HNO_3$

Cupron (Benzoin-alfa-oxime)



$C_{14}H_{13}O_2N$

It is white crystalline solid
2 % solution in ethanol is used as a reagent

Specially used for determination of copper

$CuC_{14}H_{11}O_2N$ (Green complex)

Student Assignment

1. Explain the precipitation from homogeneous solution with example.
2. Explain the different operations involved in gravimetry.
3. What is organic precipitants?

SUMMARY

- Factors affecting the solubility of precipitate
- Precipitation from Homogeneous Solution
- Operations involved in gravimetry
- Organic Precipitants

Precap

- Applications of Gravimetry
- Numerical problems based on Gravimetry

RECAP

Factors affecting Solubility of Precipitate

1) Effect of addition of acid
In general similar to salt effect solubility of sparingly soluble salt increases on addition of acid

2) Effect of Solvent

3) Effect of temperature

Example: Solubility of AgCl at 10°C is 1.72mg/liter while at 100°C is 21.1 mg/lit

Recap

Precipitation from Homogeneous Solution

Precipitating reagent is not added directly but slowly generated by homogeneous chemical reaction taking place within the solution.

Example

Urea is used for generation of OH^- (precipitating agent) and can be used for formation of precipitate of metal cation Al^{3+}, Fe^{+3} etc.

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$$\boxed{Al^{3+} + 3OH^- \longrightarrow Al(OH)_3}$$

RECAP

Operations involve in gravimetric analysis

1) Precipitation
2) Digestion
3) Filtration
4) Washing
5) Drying and ignition
6) Weighing
7) Calculation

RECAP

Organic Precipitants

- They are used for precipitating various metal ions.
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- They have high molecular weight, hence small amount of metal can produce large amount (weight) of precipitate.
- Many of organic precipitants are selective, and form precipitates with selective cation in presence of other cation.

SESSION AGENDA

- Applications of Gravimetry
- Numerical Problems

LEARNING OBJECTIVES

Students should able to understand various applications of gravimetry.

Student should able to solve numerical problems based on gravimetric analysis

Applications of Gravimetry

Determination of Al(III) by 8-Hydroxyquinoline

Aluminum can be separated from beryllium and magnesium by using 2-5% solution of oxine

Reagent

- 2 gram of 8 Hydroxyquinoline was dissolved in 100ml 2M acetic acid.
- Dropwise ammonia solution was added till turbidity persist.
- Few drops of acetic acid were added to get clear solution

Procedure: For practice,

- Take 0.45 g of aluminium ammonium sulphate and dissolve it in water containing about 1 mL of conc. hydrochloric acid and dilute to about 200 mL.

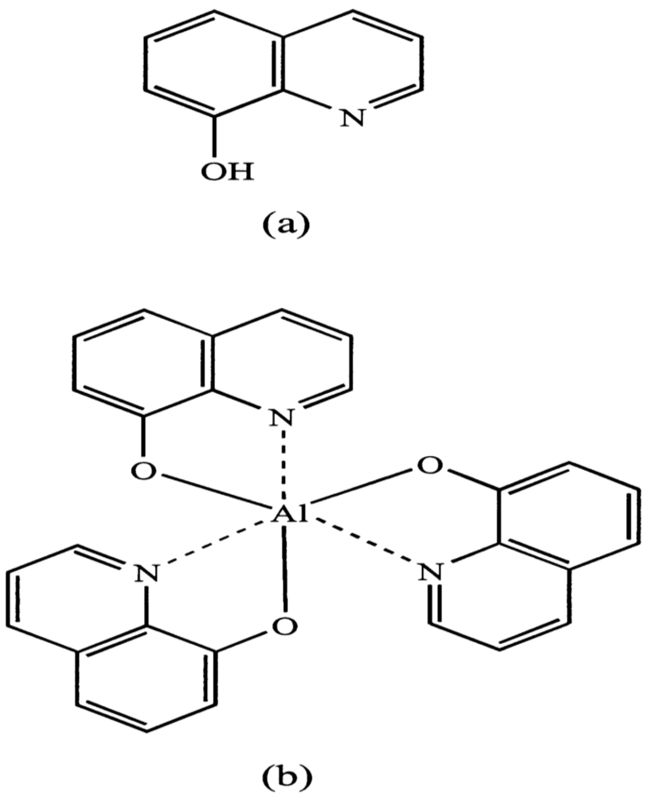
Applications of Gravimetry

Determination of Al(III) by 8-Hydroxyquinoline

- Add 5-6 mL of oxine reagent (10 per cent solution in 20 per cent acetic acid) and 5 g of urea.
- Cover the beaker and heat at 95°C for 2.5 hours.
- Precipitation is completed when greenish yellow solution become orange-yellow.
- Allow to cool and collect the precipitate in a sintered-glass filtering crucible.
- Wash with a little hot water and finally with cold water.
- Dry at 130 °C. Weigh as $Al(C9H6ON)_3$

Applications of Gravimetry

Determination of Al(III) by 8-Hydroxyquinoline



Applications of Gravimetry

Determination of calcium as oxalate

Calcium can be determine by using oxalate in basic medium. Precipitate of calcium oxalate ($CaC_2O_4{\cdot}H_2O$) is formed.

$$Ca^{2+} (aq.) + C_2O_4{}^{2-} (aq.) + H_2O (l) \rightarrow CaC_2O_4{\cdot}H_2O (s)$$

Procedure.

- Take sample containing 0.2 g of calcium into a 500mL beaker.
- Add 10 mL water, followed by 15 mL 1:1 hydrochloric acid.
- Heat to dissolve, and boil gently for several minutes to expel carbon dioxide.
- Dilute the solution to 200 mL and add 2 drops of methyl red indicator.
- Heat the solution to boiling, and add slowly a warm solution of 2.0 g of ammonium oxalate in 50 mL of water.

Applications of Gravimetry

Determination of calcium as oxalate

- To this hot solution (about 80 ^{O}C) add 1:1 ammonia solution dropwise and with stirring until the mixture become neutral or slightly alkaline (colour change from red to yellow).
- Allow to stand the solution at room temperature for at least an hour.
- After the precipitate has settled, test the solution for complete precipitation with a few drops of ammonium oxalate solution.
- Filter and dry the precipitate at $105^{0}C$ for 30 minutes.
- Determine Calcium from calcium oxalate ($CaC_2O_4 \cdot H_2O$)

Applications of Gravimetry

Determination of Potassium as potassium tetraphenyl borate.

Sodium tetraphenyl borate($NaB(Ph)_4$) is the best precipitant for potassium.

$$K^+ + NaB(Ph)_4 \rightarrow KB(Ph)_4 + Na^+$$

Procedure: For practice

- weigh out accurately about 0.10 g potassium chloride and dissolve it in 50 mL distilled water.
- Add 10 mL of 0.1M hydrochloric acid.
- Slowly add 40 mL sodium TPB reagent with constant stirring.

Applications of Gravimetry

- Throughout the experiment, maintain the temperature below 20^0C.
- Allow the precipitate to settle down for 1 hour.
- Collect the precipitate on a sintered-glass filtering crucible.
- Wash with saturated potassium TPB solution (5-10 mL in small portions) and finally with 1-2 mL ice-cold distilled water.
- Dry at 120^0C and weight as $K[B(C_6H_5)_4]$

Numerical Problems

Problem 1

Calculate solubility of $BaSO_4$ in water if solubility product is 1.41×10^{-10} mole/lit

Let us consider solubility of $BaSO_4$ in water as x

$$BaSO_4 \longrightarrow Ba^{2+} + SO_4^{2-}$$

$$\qquad\qquad\quad x \qquad\quad x$$

$$Ksp = [Ba^{2+}]\,[SO_4^{2-}]$$

$$Ksp = x^2$$

$$Ksp = x^2 = 1.41 \times 10^{-10}$$

$$x = \sqrt{1.41 \times 10{-}10}$$

$$x = 1.187 \times 10{-}5 \text{ mol/l}$$

Solubility in gram per liter $= 1.187 \times 10{-}5 \times 233$

$= 2.76 \times 10^{-3}$ g/l

Numerical Problems

Problem 2

Solubility of AgCl is 0.0030 g/liter. Calculate the solubility product. [molecular weight of AgCl is 143.5]

Solubility of AgCl is 3 x10^{-3} g/liter and molecular weight of AgCl is 143.5

Thus solubility in moles /liter $= \frac{3 \text{ x } 10-3}{143.5}$

$= 2.09 \text{ x } 10^{-5}$

Dissociation of AgCl take place as

$$AgCl_{(s)} \longrightarrow Ag^{+}_{(l)} + Cl^{-}_{(l)}$$

One mole of AgCl give one mole of Ag^+ and one mole of Cl^-

Thus Solubility product of AgCl is $Ksp = [Ag^{+}][Cl^{-}]$

$Ksp = 2.09 \text{ x } 10^{-5} \text{ X } 2.09 \text{ x } 10^{-5}$

$Ksp = 4.36 \text{ x } 10^{-10}$

Numerical Problems

Problem 3

The solubility of $Mg(OH)_2$ at 300 K is 1.75×10^{-4} mol/liter. Calculate the solubility product.

The equilibrium is:

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

One mole of $Mg(OH)_2$ produce one mole of Mg^{2+} and 2 mole of OH^-

$Ksp = [Mg^{2+}]\,[OH^-]^2$

$[Mg^{2+}] = 1.75 \times 10^{-4}$ mole/liter,

$[OH^-] = 2 \times 1.75 \times 10^{-4} = 3.50 \times 10^{-4}$ mole/liter

$Ksp = 1.75 \times 10^{-4} \times [3.50 \times 10^{-4}]^2$

$Ksp = 1.75 \times 10^{-4} \times 12.25 \times 10^{-8}$

$Ksp = 2.143 \times 10^{-11}$

Numerical Problems

Problem 4

Calculate the solubility product of silver chromate. [Given molecular weight of Ag_2CrO_4 is 331.7 and solubility is 2.54×10^{-2} g/liter]

Given : Solubility of Ag_2CrO_4 is 2.54×10^{-2} g/liter and molecular weight of Ag_2CrO_4 is 331.7

$$\text{Thus solubility in moles /liter} = \frac{2.54 \text{ x } 10-2}{331.7}$$

$$= 7.76 \times 10^{-5}$$

One mole of Ag_2CrO_4 give two moles of Ag^+ and one mole of CrO_4^{2-}

Thus Solubility product of Ag_2CrO_4 is

Ksp = $[Ag^+]^2 \, [CrO_4^{2-}]$

Numerical Problems

Problem 4

$[Ag^{+}] = 2 \times 7.76 \times 10^{-5}$

$[Ag^{+}] = 1.55 \times 10^{-4}$

$[CrO4^{2-}] = 7.76 \times 10^{-5}$

$Ksp = [Ag^{+}]^{2}\,[CrO_4^{2-}]$

$Ksp = [1.55 \times 10^{-4}]^{2} \times 7.76 \times 10^{-5}$

$Ksp = 2.40 \times 10^{-8} \times 7.76 \times 10^{-5}$

$Ksp = 1.86 \times 10^{-12}$

Numerical Problems

Problem 5

How much gram zinc should be added to 0.03 mol $AgNO_3$ solution to displace all the silver from the solution?

Reaction

$Zn + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2Ag$

Moles of $AgNO_3$ in the solution = 0.03

Moles of Zn to be added to solution = 0.015

(As $AgNO_3$ and Zn are reacting the molar ratio of 2 : 1)

Hence Mass of Zn to be added to solution = 0.015 × 65.4 = 0.3981 g

Numerical Problems

Problem 6

Solubility product of magnesium hydroxide is 2.10 x 10^{-11} mol/ lit. at 300 K, calculate its solubility in mol/lit at that temperature.

Consider the solubility of magnesium hydroxide as x

$[Mg2+]$ = x mol/ lit and $[OH-]$ = 2x mol/lit

$Ksp = [Mg^{2+}] [2OH^{-}]^2$

$Ksp = [x][2x]^2 = 4x^3$

$2.10 \times 10^{-11} = 4x^3$

$X^3 = = \frac{2.10 \times 10-11}{4}$

$X^3 = 5.25 \times 10^{-12}$

$X = \sqrt[3]{5.25} \times 10^{-12}$

$X = 1.74 \times 10^{-4}$ mol/lit

Student Assignment

1. Explain the procedure for Determination of Potassium as potassium tetraphenyl borate.
2. Explain the procedure for Determination of phosphate as ammonium molybdophosphate
3. Explain the procedure for calcium as calcium oxalate

SUMMARY

- Applications of gravimetry
- Numerical problems based on gravimetry

Thank You so Much