

Analytical Chemistry

(Gravimetric)

Lecturer 1

Analytical chemistry is mainly concerned with determining the chemical composition of substances or compounds and determining their quantitative ratio. It includes:

1- Qualitative analysis: - In which substances (compounds or elements) are detected and the quantity of these substances is not concerned

2- Quantitative analysis: It includes determining the amounts or quantities of materials to be analyzed and it is divided into:

A- Volumetric analysis methods: It depends on the volumes of materials, so tools with exact standard sizes must be used.

B- Gravimetric analysis methods: It aims to arrive at separating the components of a substance and knowing its concentration in terms of weight, provided that the substance has a known chemical composition.

C- Instrumental analysis:- In which the material is quantitatively estimated by measuring one or some of its physical or chemical properties such as density, color or conductivity.

*The gravimetric analysis depends on isolating the substance of the known chemical composition in a completely pure manner and weighing it with a sensitive analytical balance, and despite the long time that these methods require to accomplish and the many shortcomings they suffer from, they are still the standard methods that are reliable in the determination of chemical elements and compounds.

*The accuracy of these methods approaches (0.01-0.02)%, and the sensitivity and selectivity of these methods have been developed using organic precipitants.

Sensitivity of weighing methods

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Some things effect on the sensitivity of the gravimetric methods including:

- 1- The difficulty of separating a small amount in the precipitate from a relatively large volume of a solution that contains high concentrations of other components.
- 2-Loss in the sediment due to dissolution or during the filtration and washing processes
- 3- It is preferable to use these methods when the concentration of the component to be deposited is more than 1% and it is not recommended if the concentration is less than 0.1%

***Accuracy of gravimetric analysis methods**

Gravimetric analysis methods are no less accurate than other methods when the concentration of the component to be deposited is more than 1% in simple models where the error rate is less than one or two parts per thousand. The accuracy of these methods decreases with the increase in the complexity of the model, as the error rate increases

The steps followed by a chemical analyzer in quantitative gravimetric analysis

1-Solubility and weight: The model is accurately weighed with a sensitive scale, with an accuracy of 0.1 mg, and the appropriate solvent is selected, for example:

A-Water because it is more available and cheaper

b- Dilute acids such as HCl, HNO₃

C- Concentrated acids, including royal water

D-HF to dissolve silica

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E - Melting - is by mixing the form with NaOH or $\text{NaNO}_3 + \text{Na}_2\text{CO}_3$, crushing it well and then melting it at high temperatures so that it turns into a molten formula that can be dissolved with water or diluted acids to facilitate analysis.

2- Precipitation - is the process of creating a new solid phase as a result of a chemical reaction by adding a precipitating agent to the component to be precipitated, thus producing a poorly soluble compound called the precipitate.

3- Filtering and washing the precipitate - the correct steps must be followed in the filtration process to prevent any part of the precipitate being lost. The precipitate to reduce solubility and not to interfere with the precipitate and not to return it to the colloidal state if it was colloidal

4-Drying and burning the sediment - some sediments are dried at moderate temperatures before weighing and others require high temperatures

5- Weighing the precipitate - the precipitate is weighed with a sensitive scale after it has cooled in the dryer and some calculations are made to determine its percentage in the original form

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Qualities that must be present in the precipitate

1-Chemical composition: The chemical formula of the precipitate must be known and fixed so that it is possible to know the percentage of the dissolved element in the compound (in the precipitate) and that it is not variable, for example, Ba^{+2} precipitates in the form of BaSO_4

*Not all precipitates are known and fixed in composition. For example, aluminum hydroxide, which is an unstable aqueous oxide, therefore burned and converted into a stable substance with a known composition, which is aluminum oxide.

2 -Solubility: The sediment must be very poorly soluble so that the sedimentation can be completed. This is usually done by adding an excess of the precipitating agent.

3-Crystal formation: Precipitates are preferred that lead to the formation of a precipitate with a large crystalline formation so that the precipitate can be separated by filtration without passing through the filter paper.

4-Purity: The more pure the sediment is without the presence of impurities, the better the results, and the purity can be increased by paying attention to the method of sedimentation, washing and filtration.

5 -Thermal stability: The sediments must be thermally stable within the thermal range used and not disintegrate into other compounds.

6- Molecular weight of the precipitate: it should be large, which provides an opportunity to estimate trace amounts of the element and reduce damage.

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Chemical composition of the precipitate and calculations in quantitative gravimetric analysis

We have explained that gravimetric analysis depends on measuring the weight of a substance with a known composition that has a chemical relationship to the analyzed substance, that is, the weight of a specific substance separated by sedimentation in a pure chemical state or in the form of another substance with a known chemical composition that contains the ion or substance to be determined. poorly soluble precipitate

*Where a certain exact weight is taken from the model and dissolved in an appropriate solvent, and an appropriate chemical reagent is added to the formed solution that interacts with one of the components of the model, which is the element or ion to be specified in the model, and with it a pure, poorly soluble precipitate with known chemical formula separated from the rest of the model, i.e. obtaining (precipitation formula). When the separated sediment is filtered and washed with an appropriate scrubber to remove some of the impurities that dissolve in it, it is dried or burned in a suitable flask at a high temperature until it is stable and weighed by a sensitive scale, i.e., the weight formula is obtained.

Q/ Define the following 1- the precipitation formula 2- the gravimetric formula

Q: Give examples that show the precipitation formula and the weight

Water loses and turns into Fe_2O_3 , which is weighed by this formula, and on this basis we distinguish two formulas in gravimetric analysis, the precipitation formula $\text{Fe}(\text{OH})_3$ and the gravimetric formula Fe_2O_3

Q/ Do all materials have a sedimentary formula different from their gravimetric formula?

C/ No, there are substances whose sedimentation formula is the same as the gravimetric formula. For example, the barium ion Ba^{+2} , for example, is precipitated by a dilute H_2SO_4 solution in the form of barium sulfate, filtered, dried, burned and cooled in the form of barium sulfate BaSO_4 also

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because its chemical composition does not change as a result of burning at very high temperatures.

*In order to find out the quantity of the substance to be estimated, the calculations are carried out using ratio and proportion and as follows:

Weight of the material to be estimated = Weight of the weighted material x weight factor

Q/ What is the gravimetric factor?

It is a factor that shows or relates the molecular weight of the substance to be estimated (i.e. the substance from which it is sent) to the numerator and the molecular weight of the weighted substance (ie, the precipitate) in the denominator in order to find the percentage or weight of the substance to be estimated (researched for). It can also be considered as the factor of converting the weight of the compound into the weight of the element.

Example/A sample weighing 1.5 g containing chloride is analyzed. AgNO₃ was added to its solution and a precipitate of AgCl was formed by weight. What is the percentage of chloride in the sample?

Wt of chlorid =atom weight Cl/M.wt AgCl x wt. of AgCl

$$=35.46/143.34 \times 0.9214$$

$$= 0.2282 \text{ g of Cl}^-$$

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Solubility of precipitates

*Solubility or solubility is defined as the disappearance of atoms, molecules or ions of the solute between the atoms or molecules of the solvent. That is, the process is a homogeneous molecular mixture of two or more substances that do not react with each other chemically.

As for solubility, which is defined as the amount of solute soluble in a given volume of solvent at a given temperature. It is considered an important susceptibility in gravimetric analysis because it is a measure of the quantitative nature of the sedimentation process. It is also possible to distinguish between the quantitative and non-quantitative process by increasing the solubility.

The solubility of the sediment used in the quantitative analysis should be as low as possible so as not to lead to a significant loss in the amount of the sediment

*To avoid errors that result from solubility, optimum conditions must be chosen so that the solubility does not exceed 10^{-6} mol/L by controlling the volume of the precipitation and washing solution. Note: There is information available about solubility in tables found in books, including physical compounds.

*Solubility Product (K_{sp})

The solubility product of a poorly soluble salt (its solubility is less than 0.01 mol/L) is defined by the product of the molar concentration of the ions present in the solution raised to the power of the number of ions involved in the chemical equilibrium equation for a saturated dipole electrolyte solution that ionizes to- :



In a solution containing the poorly soluble compound AB, a state of equilibrium arises between the solid part of this compound and its ions, and

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this state of equilibrium is subject to the law of mass action, and the equilibrium constant is calculated as follows:

$$K_{eq} = \frac{[A^+] [B^-]}{[AB]}$$

*That is, the product of the activities of the resulting materials divided by the product of the activities of the input materials and it is equal to a fixed quantity— :

That is, the effectiveness of the solid part $1 = a_{AB}$

The equation can be written in the following form:

$$K_{eq} = a_{A^+} a_{B^-}$$

The solvation product is used instead of a constant when placing the concentrations instead of the activities, where the equation becomes:

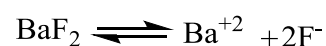
$$K_{sp} = [A^+] [B^-]$$

That is, the solubility product, K_{sp} , is not a constant quantity except in dilute solutions, because the higher the concentration of the ions, the greater the solubility due to the attraction effect of the ions.

Examples of the solubility product of some salts



$$K_{sp} = [Ag^+] [Br^-]$$



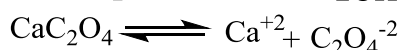
$$K_{sp} = [Ba^{+2}] [F^-]^2$$



$$K_{sp} = [Pb^{+2}]^3 [PO_4^{-3}]^2$$



$$K_{sp} = [Pb^{+2}] [OH^-]^2$$



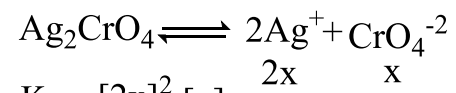
$$K_{sp} = [Ca^{+2}] [C_2O_4^{-2}]$$



$$K_{sp} = [Bi^{+3}] [I^-]^3$$

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Example / a- Calculate the concentration of Ag⁺ ions in a solution saturated with Ag₂CrO₄ silver chromate that has K_{sp} = 3.4 x 10⁻¹² ?



$$K_{\text{sp}} = [2x]^2 [x]$$

$$K_{\text{sp}} = 4x^3$$

$$x^3 = \frac{3.4 \times 10^{-12}}{4} = 8.5 \times 10^{-13}$$

$$x = 9.47 \times 10^{-5} \text{ M}$$

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Lecture 5

Factors affecting solubility

1- The effect of the volume of solute particles 2- Temperature 3- The nature of the solute 4- The nature of the solvent 5- The common ion 6- Effect of ionic strength 7- Effect of pH

1- The effect of the size of the solute particles - for many solid materials, the solubility of their small crystals is much greater than the solubility of their large crystals

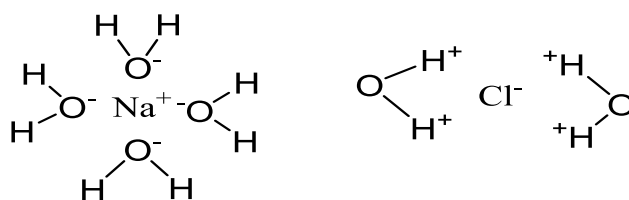
Example/ The solubility of small barium sulfate crystals is 1000 times greater than that of large crystals, while there is no appreciable difference in the solubility of large and small AgCl particles

This property can be taken advantage of in obtaining a precipitate with large and regular crystals by performing the so-called (precipitate digestion), which is the process of leaving the precipitate with the mother solution for a long period of time after heating it.

2 - The effect of temperature on solubility - the dissolution process requires heat absorption to overcome the forces of attraction between molecules and ions of the solid to be dissolved

Dissolution process (dissolution): It is the process of diffusion or union of particles of a solute between or with particles of a solvent.

Example: Dissolving table salt in water



lattice energy (UMA) is the force or energy of attraction between positive and negative ions within the crystal lattice of a molecule.

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Sodium chloride crystals do not dissolve in carbon tetrachloride or benzene, but they do dissolve well in water

Answer / Because these solvents do not have a high dielectric constant and do not have a large dipole moment to overcome the energy of the crystal lattice and isolate positive ions (Na⁺) from negative ions (Cl⁻), unlike water, which is a polar solvent with a high dielectric constant

If the hydration energy released is equal to or greater than the energy of the crystal lattice needed to break the UMA bond, solubilization occurs

In the case of NaCl, the hydration energy is equal to the energy of the crystal lattice, so the dissolution is not accompanied by the release of energy or a change in the temperature of the solution.

$$\Delta H_{\text{solution}} = \sum \Delta H_{\text{hyd.}} + U_{\text{MA}}$$

Q/why the solubility increases with increasing temperature

Answer/ Because the energy of hydration is usually less than the energy of the crystal lattice (UMA), so the melt needs heating heat and increases with its increase

*Why the dissolution of Na₂SO₄ Sodium sulfate is accompanied by an increase in the temperature of the solution

The answer is / because the heat of its hydration is higher than the energy of its crystal lattice, so its dissolution is accompanied by the liberation of energy

3-The nature of the dissolved substance - the amount of solubility depends on (UMA), and the higher it is, the salt is less soluble, and (UMA) is overcome by the enthalpy of solubility (the heat resulting from dissolution or enclosing or union of solute ions with water molecules

$$K = \frac{1}{D} \times \frac{e_1 e_2}{r^2}$$

(Coulomb's law)

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*The force required to separate two minutes or two ions with different charges from each other is directly proportional to the product of the charges and inversely proportional to the square of the distance between them

e_1, e_2 positive and negative ion charge

r The distance between them

D is a solvent-specific constant called the dielectric constant

It is clear from this that the solubility decreases with the increase in the charge of the ion

It increases with increasing distance or pitch

The dielectric constant of the solvent increases with increasing

The solubility of alkaline earth salts, calcium and magnesium salts, is lower than the solubility of alkaline metal salts such as sodium and potassium salts.

The solubility of aqueous oxides and hydroxides of quaternary metals is less than that of tertiary and is less than that of binary

Quaternary tin hydroxide can be precipitated from a moderate environment of nitric acid, while ferric hydroxide is precipitated from an acidic medium $\text{pH} = 3$, while magnesium is precipitated from a basic medium $\text{pH} = 11$

*The solubility of the salts of the metals of one group in the periodic table increases with the increase of the ion (atomic weight), and this is theoretically correct and the examples are few



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But in many cases, the opposite happens, that is, the solubility increases with a decrease in purity, and one of the reasons is-

A-Blocking and the effect of hydration energy on solubility. Small cations that carry a high charge have a hydrosphere of 6-4) molecules of water. As for the anions, they hydrate much less than cations, and their hydration envelope consists of (2-1) water molecules. In general, the largeness and stability of the hydrosphere It decreases with increasing atomic number or radius (within one group), which means a decrease in shielding and leads to a decrease in solubility.



In other words:



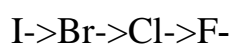
The same is true for the nitrates, bromides and iodides of these cations, as well as the halides of Hg^{+2} , Cd^{+2} , Zn^{+2} .

Note: cations = positive ions

anions = negative ions

Halides = chlorides, bromides

b- polarizability and solubility: simple ions such as (OH^- , I^- , Br^- , Cl^- , S^{2-} , O^{2-} , CN^-) contain a wide electron shell that is easily deformed by cations, which leads to the polarization of the atom or ion To form the electron shell, the symmetric molecules such as SO_4^{2-} , NO_3^- , ClO_4^- , PO_4^{3-} , CO_3^{2-} do not have the ability to polarize, but it is clear in the halides, where the polarizability increases with increasing ion purity



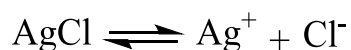
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4 -Nature of the solvent: Polar solvents are solvents for many ionic salts because the higher the polarity of the solvent, the greater the attraction between it and the dissolved (salt) ions, in addition to the fact that the forces of attraction of salt solute ions to each other within the crystal lattice are inversely proportional to the dielectric constant of the solvent

5-The effect of the combined ion: the solubility of sediments or salts decreases in a solution that contains a common ion with the ions of the precipitate according to the Les Chatelet rule.

Example: The solubility of AgCl decreases when there is an increase in Cl⁻, Ag⁺ ions in the solution because



If an excess of Cl⁻ ions is added to this balanced system, the balance will be disturbed and for the sake of

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Lecture 6

6 -Effect of pH on solubility

The solubility of the precipitates in quantitative gravimetric analysis is affected by the acidity of the solution. For example, the solubility of hydroxides decreases with an increase in the concentration of the hydroxide ion-OH⁻ in the solution due to the separation of the common ion. Therefore, the complete precipitation of metal hydroxide depends on the pH of the solution.

Example: Magnesium hydroxide Mg(OH)₂ begins to precipitate at pH = 9.6 and completes its precipitation at pH = 11, meaning that the complete precipitation of the magnesium ion in the form of hydroxide takes place at pH = 11

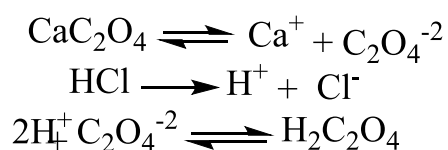
Example/ Ferric hydroxide begins to precipitate at pH = 2 and completes precipitation at pH = 3.5

*The solubility increases with increasing acidity and decreases with increasing concentration of OH⁻

Q/Why the solubility of weak acid deposits and salts such as carbonates CO₃²⁻, oxalates C₂O₄²⁻, phosphates PO₄³⁻, chromates CrO₄⁼, sulfates SO₄⁼ and F-fluorides increases when the concentration of acidic hydrogen ion in solution increases?

Answer: The hydrogen ion in the solution combines with the negative ion resulting from the dissolution of the salt or the precipitate, leading to the formation of a weakly dissociated acid, which leads to an imbalance and displacement of the reaction towards the dissolution of the salt, i.e. an increase in the solubility of the solid part of the salt

Example: Calcium oxalate CaC₂O₄ its solubility increases when HCl is added to it



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The amount of increase in the solubility of the salts when adding the same amount of acid varies with the quality of the salt

Example: The relative increase in the solubility of the following salts when the same amount of acid is added to it



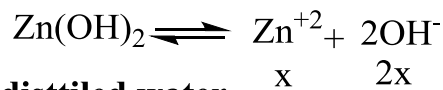
The reason is that carbonic acid formed from BaCO_3 is weaker than oxalic acid formed from BaC_2O_4 and the second dissociation of oxalic acid is less than the second dissociation of sulfuric acid

It is clear that the sediment ions used in the analysis, such as OH^- , $\text{CO}_3^{=}$, $\text{SO}_4^{=}$, $\text{CrO}_4^{=}$, F^-

It behaves like a Bröchtsted base, as it combines with H^+ to form weakly dissociated acids, which leads to an increase in the solubility of these salts. Therefore, the quantitative precipitation depends on the pH of the solution. Therefore, it is necessary to know the pH with which the precipitation begins for the metal, the pH at which the precipitation completes, i.e. the so-called precipitation pH limits.

Example/ Calculate the solubility of a solution of $\text{Zn}(\text{OH})_2$ in 1- distilled water 2- pH=6 3- pH=9 if ($K_{\text{sp}}=2 \times 10^{-17}$)?

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1- in distilled water

$$\begin{aligned} K_{sp} &= [\text{Zn}^{+2}][\text{OH}^-]^2 \\ 2 \times 10^{-17} &= (x)(2x)^2 \\ 2 \times 10^{-17} &= 4x^3 \\ x &= 1.7 \times 10^{-6} \text{ M} \end{aligned}$$

2- pH=6

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 6 = 8 \implies \text{pOH} = -\log[\text{OH}^-] \implies [\text{OH}^-] = 10^{-8}$$

$$2 \times 10^{-17} = (x)(2x + 10^{-8})^2 \implies x = 0.2 \text{ M}$$

3-pH=9

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 9 = 5 \implies \text{pOH} = -\log[\text{OH}^-] \implies [\text{OH}^-] = 10^{-5}$$

$$2 \times 10^{-17} = (x)(2x + 10^{-5})^2 \implies x = 0.2 \times 10^{-7} \text{ M}$$

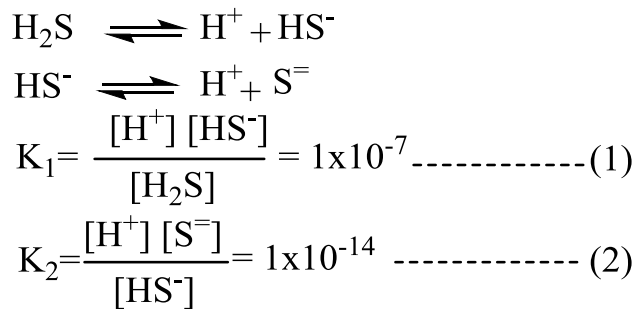
*It is noted that the solubility increases in the acidic medium compared to distilled water, and also decreases in the basic medium

The effect of the acid function on the precipitate and separation of ions

1 -Effect of acid function on precipitation of sulphides

We will discuss the precipitation of divalent metal ions in the form of sulfides from a saturated solution of hydrogen sulfide (as a precipitating agent) with a concentration $[\text{H}_2\text{S}] = 0.1 \text{ M}$. The concentrations of metal ions to be precipitated are often 10^{-2} M , knowing that the precipitation of the metal ion is complete if the remainder of the The concentration of the metal ion in the solution does not exceed the range 10^{-5} M

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And by multiplying equation (1) x equation (2)

$$\begin{aligned} K_1 \cdot K_2 &= \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \times \frac{[\text{H}^+][\text{S}^-]}{[\text{HS}^-]} = 1 \times 10^{-21} \\ \frac{[\text{H}^+]^2 [\text{S}^-]}{[0.1]} &= 1 \times 10^{-21} \\ [\text{S}^-] &= \frac{1 \times 10^{-22}}{[\text{H}^+]^2} \text{----- (3)} \end{aligned}$$

Equation (3) shows that the concentration of sulfide ions is inversely proportional to the square of the hydrogen ions concentration in the solution. Let us take divalent metal sulfide MS, the solubility product constant

$$K_{sp} = [\text{M}^{+2}] [\text{S}^-] \text{.....(4)}$$

Substituting $[\text{S}^-]$ from equation (3) into equation (4), we get:

$$\begin{aligned} K_{sp} &= [\text{M}^{+2}] \frac{1 \times 10^{-22}}{[\text{H}^+]^2} \\ \frac{K_{sp}}{[\text{M}^{+2}]} &= \frac{1 \times 10^{-22}}{[\text{H}^+]^2} \\ [\text{H}^+]^2 &= \frac{[\text{M}^{+2}] \times 10^{-22}}{K_{sp}} \end{aligned}$$

Taking the logarithm of both sides, we get:

$$2 \log [\text{H}^+] = -22 \log 10 + \log [\text{M}^{+2}] - \log K_{sp}$$

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By multiplying both sides of the equation (-1) and converting the logarithm of concentration to the corresponding functions, we get:

$$2\text{pH} = 22 - \log [M^{+2}] + \log [K_{sp}]$$

And if the concentration of the remaining metal ion in the solution is not more than 10^{-5} M

$$\text{pH} = \frac{22 - \log 10^{-5} + \log K_{sp}}{2} = \frac{22 + 5 + \log K_{sp}}{2}$$

$$\text{pH} = \frac{27 + \log K_{sp}}{2}$$

The pH value extracted from the last equation is considered the minimum acidity function. If the metal ion is precipitated at $\text{pH} = 1$, it can be precipitated at $\text{pH} = 2$ or 3 etc. But if the pH value is negative, the metal ion can precipitate in any acidic function.

Example/in any acidic function MnS can completely precipitate. Note that the solubility product constant is ($K_{sp}\text{MnS} = 14 \times 10^{-15}$)?