Qualitative and quantitative analysis in inorganic chemistry

Practical in Medical Biochemistry
General Medicine

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2024/25

Qualitative analysis

Task 1: Selected inorganic reactions

Reagents:

Ammonia, aqueous solution 70 g·l^{-1}

Ammonium molybdate, solution in nitric acid 100 g·l^{-1}

Barium nitrate, aqueous solution 60 g·l^{-1}

Calcium chloride, aqueous solution 50 g·l^{-1}

Calcium hydroxide, aqueous solution   (limewater)

Copper(II) sulfate, aqueous solution 0.3 mol·l^{-1}

Hydrochloric acid, aqueous solution 2 mol·l^{-1}

Hydrogen sulfide, aqueous solution   (sulfane water)

Iron(III) chloride (ferric chloride), aqueous solution 5 g·l^{-1}

Iron(II) sulfate (ferrous sulfate), heptahydrate

Lead(II) acetate, aqueous solution 10 mmol·l^{-1}

Mercury(II) nitrate, aqueous solution 5 mmol·l^{-1}

Phosphoric acid, aqueous solution 2 mol·l^{-1}

Potassium chromate, aqueous solution 50 g·l^{-1}

Potassium hexacyanoferrate(III) (ferricyanide), aqueous solution 100 g·l^{-1}

Potassium hexacyanoferrate(II) (ferrocyanide), aqueous solution 100 g·l^{-1}

Potassium iodide, aqueous solution 20 mmol·l⁻¹

Potassium thiocyanate, aqueous solution 50 g·l⁻¹

Silver nitrate, aqueous solution 20 g·l⁻¹

Sodium hydrogen carbonate

Sodium hydrogen phosphate, aqueous solution 50 g·l⁻¹

Sodium hydroxide, aqueous solution 100 g·l⁻¹

Sodium phosphate, aqueous solution 20 g·l⁻¹

Sulfuric acid, aqueous solution 2 mol·l⁻¹

1. Reactions of selected cations

1.1 Reactions of silver compounds

a) **$Ag^+ + HCl \rightarrow AgCl \downarrow + H^+$**
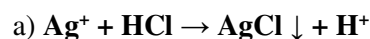
Mix about 0.5 ml of aqueous silver nitrate with 0.5 ml of diluted hydrochloric acid. A white precipitate of silver chloride is produced.

Add an excess of aqueous ammonia, the precipitate dissolves – a diamminesilver complex $[Ag(NH_3)_2]^+$ is formed.

The halides of silver, especially silver bromide, were used in photography. Following excitation with light they become more susceptible to reduction in alkaline medium, so that in the developer (alkaline solution of reducing agents) a metallic silver originates, which has a black color.

Precipitation with silver cations is one of very sensitive reactions; it can be employed to detect even traces of halides. It was used both in qualitative and quantitative analysis.

Note that if a metal becomes bound as a central atom of a complex compound, it often remains soluble even in the medium, where it would otherwise yield insoluble products – in this case the silver cations remain in the solution despite the presence of halogen anions, and despite the alkalinity (silver hydroxide is also insoluble). This is often utilized in various analytical or technological applications.

b) **2 Ag$^+$ + H$_2$S → Ag$_2$S ↓ + 2 H$^+$**
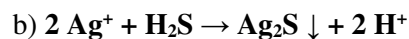
To about 0.5 ml of aqueous silver nitrate ⬦⬦⬦ add about 0.5 ml of aqueous sulfane ⬦⬦.
A black precipitate of silver sulfide is formed.

This reaction is behind tarnishing of silver jewelry. Many other transition metals form dark insoluble sulfides as well.

c) **2 Ag$^+$ + 2 NaOH → 2 [AgOH] + 2 Na$^+$ → Ag$_2$O ↓ + H$_2$O + 2 Na$^+$**
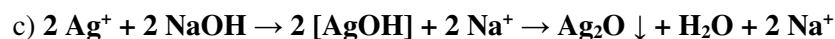
To about 0.5 ml of aqueous silver nitrate ⬦⬦⬦ add about 0.5 ml of aqueous sodium hydroxide
⬦. A brownish-black precipitate apppears.

Hydroxides of transition metals are usually insoluble. Often they display an intense coloration typical for each cation.

Add an excess of aqueous ammonia ⬦⬦⬦; the precipitate dissolves. Again, complex compounds collectively called ammoniacal silver are produced, especially the diamminesilver complex cation [Ag(NH$_3$)$_2$]$^+$.

d) **2 Ag$^+$ + K$_2$CrO$_4$ → Ag$_2$CrO$_4$ ↓ + 2 K$^+$**

To about 0.5 ml of aqueous silver nitrate ⬦⬦⬦ add about 0.5 ml of aqueous sodium chromate ⬦
⬦⬦⬦⬦. An intensely colored brownish-red precipitate appears.

This reaction is very sensitive. The coloration is visible already at silver ions concentrations orders of magnitude lower than are those needed for the precipitation of halides. Therefore, the reaction is useful as an indication reaction in quantitative analysis.

1.2   Reactions of lead compounds

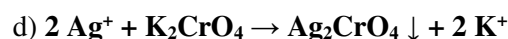a) **Pb^{2+} + H$_2$S → PbS ↓ + 2 H$^+$**
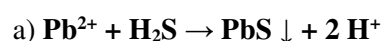
To a small amount of aqueous lead(II) acetate ⬦⬦ add a small amount of sulfane water ⬦⬦.
A black precipitate appears.

b) **Pb^{2+} + 2 I$^-$ → PbI$_2$ ↓**
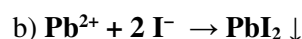
Mix equal amounts of aqueous lead(II) acetate ⬦⬦ and aqueous potassium iodide ⬦⬦⬦.
A yellow precipitate of lead(II) iodide originates. Heat the mixture to 100 °C in thermoblock;
the precipitate nearly dissolves. Then cool the solution quickly on ice. The lead(II) iodide crystallizes again, but this time the crystals resemble 'gold'.

Some lead compounds are strongly colored and were used as pigments – e.g. the white lead (basic lead carbonate, 2 PbCO$_3$ · Pb(OH)$_2$), or orange-red minium (red lead, lead (II,IV) oxide, 2PbO · PbO$_2$). But intensely colored pigments can be derived from other metals as well.

1.3 Reactions of copper compounds

a) $Cu^{2+} + H_2S \rightarrow CuS \downarrow + 2\ H^+$
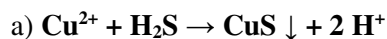
Mix a small amount of aqueous copper sulfate ◇◇ with sulfane water ◇◇. A brownish-black precipitate is produced.

Again we see that sulfides of many metals are insoluble and often dark colored.

b) $Cu^{2+} + 2\ NH_4OH \rightarrow Cu(OH)_2 \downarrow + 2\ NH_4^+$
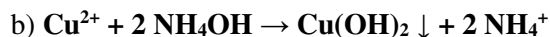
Take a small amount of aqueous copper sulfate ◇◇ and with constant vortexing add aqueous ammonia ◇◇◇ dropwise. First, a light blue gel-like precipitate of copper hydroxide appears.

Keep adding the ammonia. In excess of NH_4OH the precipitate dissolves to a dark blue solution of a complex tetraamminecopper $[Cu(NH_3)_4]^{2+}$. Again, we see that the complex compounds are often highly soluble. Majority of them are also strongly colored.

c) The fact that the presence of coordination covalent bonds in a compound often causes its color can be shown in the following experiment (**demonstration only!**).

About 0.5 g of copper sulfate pentahydrate $CuSO_4 \cdot 5\ H_2O$ ◇◇ is placed to a metal pot, and heated ⚠. At high temperature the water of crystallization evaporates and only the anhydrous copper sulfate remains in the pot. The anhydrate is practically colorless. The water of crystallization was in this case bound by coordination covalent bonds. In reality, the copper sulfate pentahydrate is a complex compound tetraaquacopper sulfate $[Cu(H_2O)_4]SO_4$. The 5th H_2O molecule is elsewhere in the crystal lattice.

If the anhydrous copper sulfate ⚠ is hydrated again, the characteristic blue color is restored.

d) Prepare again the precipitate of copper hydroxide and heat it to 100 °C ⚠. A nearly black copper(II) oxide originates. In analogy to sulfides, the oxides of some transition and heavy metals are also intensely colored.

1.4 Reactions of mercury compounds

$Hg^{2+} + 2\ KI \rightarrow HgI_2 \downarrow + 2\ K^+$
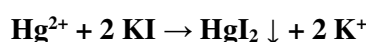
Mix the solutions of mercury(II) nitrate ◇◇◇◇ and potassium iodide ◇◇◇. An orange-red precipitate results.

With constant vortexing keep adding more aqueous iodide dropwise, until the precipitate dissolves. Take about 0.5 ml of the resulting solution and add approximately equal volume of aqueous sodium hydroxide ◇. The resulting product is known as Nessler's reagent, potassium tetraiodomercurate(II) K_2HgI_4.

Combine the prepared Nessler's reagent with just one drop of ammonia ⬦⬦⬦. Nessler's reagent is used for a sensitive detection of ammonium cations – together they form an orange precipitate of mercury(II) amido iodide complex:

$$NH_4^+ + 2\ [HgI_4]^{2-} + 4\ OH^- \rightarrow HgO \cdot [Hg(NH_2)I] \downarrow + 7\ I^- + 3\ H_2O$$

It is one of the few precipitation reactions that can be employed for detection of ammonium cations. It is still used in the environmental chemistry as a test for pollution of water with ammonia.

1.5   Reactions of iron compounds

a) $Fe^{2+} + 2\ NaOH \rightarrow Fe(OH)_2 \downarrow + 2\ Na^+$
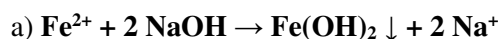
Prepare a fresh solution of ferrous ions by dissolving a small amount of iron(II) sulfate ⬦ in purified water. The solution must be used immediately, because the ferrous ions in the solution quickly undergo oxidation to ferric by reacting with the dissolved atmospheric oxygen.

Mix the freshly prepared solution of ferrous ions with aqueous sodium hydroxide ⬦. First a light green precipitate of iron(II) hydroxide forms. Its color gradually turns to rusty brown as the iron becomes oxidized to Fe(III) by oxygen, and the $Fe(OH)_2$ changes to $Fe(OH)_3$.

A viscid precipitation of iron(III) hydroxide is a typical deposit in the water pipes. Further reactions produce other ferric salts of similarly rusty appearance.

The color of iron compounds, like many other transition metals, depends on the metal oxidation number. In this case we could see that the Fe(II) compounds are usually green, whereas the Fe(III) are brown. The ability of transition metals to readily change their oxidation states and display it in the color of their compounds, is utilized in many analytical systems. Examples of some typical colors are in the table:

Copper	Cu(II)	Cu(I)
Iron	Fe(III)	Fe(II)
Manganese	Mn(VII)	Mn(VI)
Chromium	Cr(VI)	Cr(III)

b) $Fe^{2+} + K_3[Fe^{III}(CN)_6] \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3,\ KFe^{III}[Fe^{II}(CN)_6]$
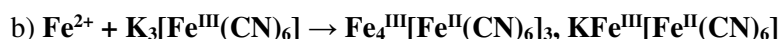
Combine the solution of ferrous ions ⬦ with hexacyanoferrate(III) ⬦⬦⬦. A dark blue precipitate of a complex salt iron(III) hexacyanoferrate(II), or potassium iron(III) hexacyanoferrate(II) results.

Essentially the same complexes will originate by a similar reaction, if the iron oxidation numbers in the reagents are swapped: try to mix also a solution of ferric ions (e.g. iron(III) chloride ⬦⬦) with potassium hexacyanoferrate(II) ⬦. Although in both cases the resulting substances contain the same complexes, differing only in contents of potassium and perhaps impurities, the obtained colors somewhat depend on the way of preparation. Therefore, in the past they were considered different, and the former was called Turnbull's blue, whereas the latter Berlin (Prussian) blue.

Notice that this is another case when the complex compounds are remarkably colored. Accordingly, Berlin blue has become an important pigment for painting.

c) $[Fe(H_2O)_6]^{3+} + KSCN \rightarrow [Fe(H_2O)_5(SCN)]^{2+} + H_2O + K^+$

Carry out the reaction of aqueous ferric cations ⬦⬦ with thiocyanate⬦⬦. Intensely red complexes result. Because of these typical reactions the thiocyanates are trivially named rhodanides (in ancient Greek rhódón = rose).

1.6   Reactions of calcium compounds

$3\ Ca^{2+} + 2\ PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \downarrow$
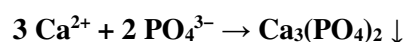
Mix the solutions of calcium chloride ⬦ and sodium phosphate ⬦. A white precipitate is formed.

By dropwise addition of phosphoric acid ⬦ (or another acid) the precipitate will gradually dissolve because of formation of calcium hydrogen phosphate, calcium dihydrogen phosphate, and other more complicated phosphates. In general, dihydrogen phosphates are much more soluble than hydrogen phosphates, which in turn are more soluble than phosphates.

Calcium phosphates and derived salts occur in many different forms. Typically they are insoluble in alkaline medium, whereas acidification easily turns them to soluble compounds. One of the more complicated salts of this group is hydroxyapatite, the mineral component of bone and teeth.

1.7   Reactions of ammonium cations

$NH_4^+ + NaOH \rightarrow NH_3 + Na^+ + H_2O$
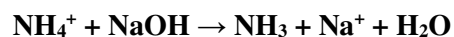
Mix about 0.5 ml of aqueous ammonia ⬦⬦⬦ with solution of sodium hydroxide⬦. A gaseous ammonia starts to release. It can best be demonstrated by placing a strip of universal pH indicator, pre-wet with pure water, to the test tube orifice – it will turn blue, showing a high pH as the ammonia re-dissolves in water used to wet the indicator.
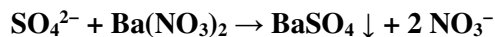
The proof of ammonium cation with Nessler's reagent was already performed (see 1.4).

2. Demonstration of selected elements with flame tests

The flame reactions will be demonstrated by your instructor.

3. Reactions of selected anions

3.1 Reactions of sulfates

$$SO_4^{2-} + Ba(NO_3)_2 \rightarrow BaSO_4 \downarrow + 2\ NO_3^-$$

Mix a small amount of diluted sulfuric acid ⬦ with aqueous barium nitrate ⬦⬦⬦. A white precipitate originates. Try to add more acid – the precipitate does not dissolve.

Barium sulfate is used as a radiocontrast agent for X-ray examinations of gastrointestinal tract (as a suspension, 'barium meal'). This usage is safe despite the fact that soluble barium salts are toxic – barium sulfate is virtually insoluble and would not release barium cations even in the acidic stomach juice.

3.2 Reactions of carbonates and hydrogen carbonates

This experiment will be demonstrated by your instructor.

In a flask heat about 1 g of solid sodium hydrogen carbonate ⬦⚠. Drain the originating gas through a hooked glass tubing to a beaker containing a solution of calcium hydroxide (limewater)⬦⬦.

The gas is carbon dioxide that gives a white turbidity in reaction with calcium hydroxide:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$
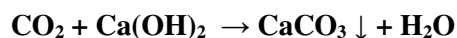
If no more gas emerges, allow the flask to cool down⚠. Then add aqueous hydrochloric acid ⬦⬦ and again close it with the plug with inserted hooked tubing. Once again a gas emerges and the reaction with limewater ⬦⬦ provides the proof that it is carbon dioxide as before.

The traditional trivial name for hydrogen carbonates is bicarbonates. The name stemmed from the demonstrated reactivity – by heating the hydrogen carbonate releases the 'first' molecule of carbon dioxide, the reaction with an acid can then be used to release the 'second' CO_2 molecule.

3.3   Reactions of phosphates

$$HPO_4^{2-} + (NH_4)_2MoO_4\ (in\ HNO_3) + heat \rightarrow ammonium\ phosphomolybdate,\ yellow\ precipitate$$

A small amount of aqueous sodium hydrogen phosphate (alternatively phosphoric acid ⬦ or sodium phosphate ⬦ can be used) is mixed with solution of ammonium molybdate ⬦⬦ and the test tube is heated in boiling water bath. A yellow precipitate of a stechiometrically complicated salt, which can be called ammonium phosphomolybdate, is formed (if the precipitate does not appear, repeat with a smaller amount of the phosphate).

Quantitative analysis

Task 2: Determination of molar and mass concentration of sulfuric acid solution by acid-base titration

Principle

$$H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$
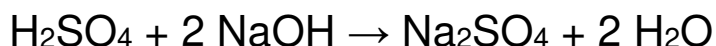
Reagents

1. Solution of sulfuric acid of unknown concentration

2. Titration reagent $c(NaOH) = 0.1$ mol/l, factor = 1.00

3. Phenolphthalein 2 g/l in ethanol

Procedure

Exactly 5.0 ml of H_2SO_4 solution of unknown concentration is measured to a pure titration flask and diluted with about 10-20 ml of distilled water. A few drops of indicator are added and solution is titrated with the titration reagent NaOH from burette. Titration is completed when a permanent tint of indicator, clearly different from the colorless state of the original solution, is achieved. Titration is repeated three times. The molar and mass concentration of sulfuric acid is calculated from the average of values of the second and third titrations.

Objectives

1. Write the equation in ionic form – the base of titration determination.
2. Give reasons for the used indicator.
3. Calculate molar and mass concentration of sulfuric acid in tested sample.