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ANALYTICAL CHEMISTRY OF RUTHENIUM

T. D. AVTOKRATOVA



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ANALYTICAL CHEMISTRY OF ELEMENTS

ANALYTICAL CHEMISTRY OF RUTHENIUM

Analytical Chemistry of Elements

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ANALYTICAL CHEMISTRY OF BERYLLIUM
ANALYTICAL CHEMISTRY OF BORON
ANALYTICAL CHEMISTRY OF COBALT
ANALYTICAL CHEMISTRY OF GALLIUM
ANALYTICAL CHEMISTRY OF MOLYBDENUM
ANALYTICAL CHEMISTRY OF NICKEL
ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM
ANALYTICAL CHEMISTRY OF PLUTONIUM
ANALYTICAL CHEMISTRY OF POTASSIUM
ANALYTICAL CHEMISTRY OF PROTACTINIUM
ANALYTICAL CHEMISTRY OF RUTHENIUM
ANALYTICAL CHEMISTRY OF TECHNETIUM, PROMETHIUM, ASTATINE
AND FRANCIUM
ANALYTICAL CHEMISTRY OF THALLIUM
ANALYTICAL CHEMISTRY OF THORIUM
ANALYTICAL CHEMISTRY OF URANIUM
ANALYTICAL CHEMISTRY OF YTTRIUM AND THE LANTHANIDE ELEMENTS
ANALYTICAL CHEMISTRY OF ZIRCONIUM AND HAFNIUM

FOREWORD

The Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences has begun the publication of a series of monographs on the analytical chemistry of individual elements. This series, *Analytical Chemistry of Elements*, will include about fifty volumes, and it is planned to complete the publication during the coming five years. The necessity for such a project has been felt for a long time. We also have at our disposal the accumulated experience of numerous laboratories which now can (and should) be summarized. In this way the present series originated, the first of its kind. The analytical chemistry of any element with its different compounds is at present extremely varied; this is due to the complexity of the modern materials investigated and the wide range of concentrations determined, as well as to the variety of the methods employed.

With this in mind, a general plan has been worked out for the present series, both with respect to the contents and to the presentation of the material.

The monographs contain general information on the properties of the elements and their compounds, followed by a discussion of the chemical reactions which are the basis of the analytical work. The physical, physicochemical, and chemical methods for the quantitative determination of the element are given in the following order: first, the analysis of raw materials, next the analysis of the typical semi-manufactured products, and last, that of the finished products—metals or alloys, oxides, salts, and other compounds and materials. The underlying principles are always explained; whenever necessary, the exhaustive description of the entire analytical procedure is given. Due attention is paid to rapid analytical methods. A separate place is allotted to techniques for the determination of impurities in high purity materials.

Particular stress is placed on the accuracy and the sensitivity of the various methods, in view of the general tendency toward increased sensitivity of determination of traces of impurity elements.

The monographs contain an exhaustive and up-to-date bibliography. They are intended for a wide circle of chemists: in the first place, for the analysts of research institutes and industrial laboratories of various branches of the national economy, and also for teachers and students of chemistry in institutions of higher education.

Our most prominent experts participated in the preparation of the monographs, drawing upon their own extensive experience in the analytical chemistry of the element in question.

Each volume of the series will be published separately as soon as it has been made ready for publication. [A list of currently available volumes will be found facing the title page. Further titles are in preparation.]

We invite all our readers to send us their comments and criticisms on the monographs.

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PREFACE

The interest in the chemistry of ruthenium, and in particular in its analytical chemistry has lately been on the increase, mainly in connection with the processing of irradiated nuclear fuels. In spite of the fact that the properties of ruthenium compounds have been studied for over 100 years, very little is yet known of the state of ruthenium ions in hydrochloric, sulfuric and nitric acid solutions. Even less is known of the thermodynamic constants and physicochemical properties of a large number of ruthenium compounds, the knowledge of which is indispensable both for technological and for analytical purposes. For this reason we have included a considerable number of empirical data, which should nevertheless be redetermined with greater precision.

Since no monograph in Russian on the chemistry of ruthenium has been available until now, the chemistry of this element has been dealt with in somewhat greater detail than is the case in the other monographs [of this series] dealing with analytical chemistry of individual elements.

The most important chemical properties of a number of simple and complex compounds of ruthenium and their preparation are described in the appropriate sections. Thus, for instance, the ruthenium halides used in redox titrations are described in the section dealing with volumetric methods; the properties of ruthenates and perruthenates are found in the section on spectrophotometric methods, etc.

The book is intended for the use of analytical chemists working on the analyses of platinum group metals, and of the scientists of the appropriate research establishments.

The section on the radiochemical determination of ruthenium was compiled in collaboration with Yu. B. Gerlit.

The author wishes to express her gratitude to Academician I. V. Tananaev, and to D. I. Ryabchikov, Dr. Chem., for their valuable criticism during the discussion of the manuscript.

T. D. Avtokratova

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CHAPTER I

Physicochemical and Analytical Characteristics of Ruthenium and Its Compounds

Ruthenium was discovered by C. Claus in 1844 in waste products of Ural platinum ores. The history of this discovery has been described by numerous authors [8, 39, 46, 71, 614, 671]. Claus arrived at his discovery of ruthenium by separating an easily crystallizing and water-soluble compound, which for a long time was considered to be the complex hexachloride of ruthenium (IV); it subsequently proved to be potassium pentachloronitrosoruthenate, a representative of the most common type of ruthenium compounds. The characteristic bright-blue color acquired by the wastes of Ural platinum ores in reducing media (the color produced by ruthenium compounds) also served as an indication of the discovery of a new element.

The ruthenium content in the earth's crust is $5 \cdot 10^{-6}$ clarke [38]. In addition to the earth's crust, ruthenium has been detected in meteorites ($5 \cdot 10^{-4}$ clarke), in plants [30, 203], and in the sun [655].

Ruthenium, like all the other platinum metals, is contained in osmiridium in the heavy lower parts of the solid crystalline magma (dunite), and in pyroxenite or silicate rocks.

In the USSR, the bulk of ruthenium is concentrated in the osmium-ruthenium-iridium belt on the eastern slopes of the Urals [38]. The ruthenium content in various osmiridium deposits may be as high as 20%. For properties and composition of osmiridium, see [44, 149b, 218, 622]. Laurite, a mineral encountered in conjunction

with native platinum and gold, mainly contains ruthenium and osmium sulfides whose composition, according to various authors, may be expressed by the formulas RuS_2 , $(\text{Ru}, \text{Os})\text{S}_2$, $12\text{Ru}_2\text{S}_3 \cdot \text{OsS}_4$ [17, 765]. Artificially prepared ruthenium sulfides [242] have a pyrite crystal structure [583, 594]. Other ruthenium minerals contain the following amounts of this element: 4.7 to 19% in ruthenium nevyanskite; 10.2 to 18.3% in ruthenium siserskite; 5.5% in osmite, and 3.5% in aurosmirid [218].

Ruthenium, like other platinum metals, is encountered in placer deposits or native alloys which are often found with the so-called black sand consisting of magnetite, chromite, ilmenite, rutile, zircon, cassiterite, garnierite, and other heavy minerals [83]. The element is also found in rocks containing high-melting oxides of aluminum, magnesium, calcium, and other metals.

Platinum placer deposits contain 70 to 90% platinum metals, the maximum ruthenium content being 2.32% [38]. In some ores of base metals the ruthenium content is as follows (in mg/ton): 0.4 in antimonite, 0.01 to 0.02 in columbite, 0.006 in molybdenite, 0.004 in ilmenite, 0.002 in tantalite, 0.01 in rutile, and traces in cassiterite [38]. Qualitatively, ruthenium has been detected in gadolinite, gehlandite, monazite, pyrolusite, psilomelane, molakone, pink kaolin [716], and also in the compounds of lanthanide elements [743] occurring in nature.

The production of platinum metals in various countries is given by Cochrane [218]. In 1924 the price of ruthenium was US\$1.68 per gram [581].

Ruthenium is in the eighth group of Mendeleev's periodic table, and is one of the platinum elements. The configuration of its outermost electron shell is $4d\ 5s^1$ [74].

The valencies of ruthenium are 1, 2, 3, 4, 5, 6, 7, and 8; the compounds of ruthenium (III) and ruthenium (IV) are the most numerous and stable. Most of the ruthenium halide complexes, ruthenium dioxide, and others are compounds of ruthenium in these two oxidation states.

The known ruthenium isotopes have the mass numbers 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107 [111].

Unlike other platinum metals [171], ruthenium crystallizes in a hexagonal close-packed lattice (Figure 1). The coordination number of the crystal lattice is 6; the lattice constants of ruthenium are $a = 2.7015\text{\AA}$, $c/a = 1.5828$ [107]*. The dipole length is calculated from Ormont's formula [78].

Ruthenium exists both in the amorphous and the crystalline states. Amorphous ruthenium is a black powder which separates out when the metal is reduced from its solutions. Light-gray cubic crystals are obtained after recrystallization of amorphous ruthenium from a melt with 5- to 6-fold amount of tin and treatment of the melt with hydrogen chloride [243]. Jaeger and Rosenbohm [409, 410-412] showed that crystalline ruthenium exists in four polymorphous modifications, corresponding to α -, β -, γ -, and δ -types. The transitions between the various

* The lattice constants of osmium and ruthenium have also been published elsewhere [489, 599].

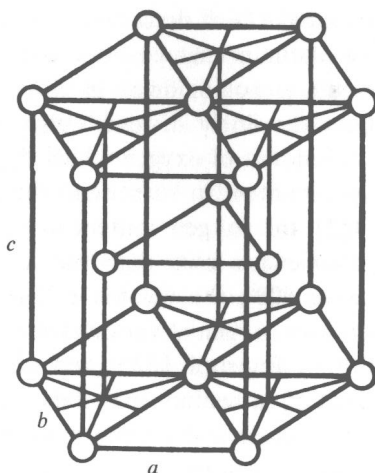


Figure 1
Crystal lattice of metallic ruthenium

modifications take place at the following temperatures: $\alpha \rightleftharpoons \beta$ at 1035° , $\beta \rightleftharpoons \gamma$ at 1190° , and $\gamma \rightleftharpoons \delta$ at about 1500° . It has been suggested [412] that a fifth allotropic form of ruthenium may exist at 310° . However, according to Rudnitskii and Polyakova, ruthenium does not undergo any polymorphous transformation below 1250° [107]. Compact ruthenium is a hard, brittle metal which cannot be pressure-worked even at high temperatures [107]. The atomic weight of ruthenium is 101.1 [757]. The specific weight of the metal is 12.2, the melting point 2500° , the boiling point 4900° , Brinell hardness 220, Mohs hardness 6.5 [74, 432]. The atomic radius of ruthenium is 1.30 \AA to 1.32 \AA [74, 330], and the ionic radius of Ru^{4+} is 0.657 \AA [74].

The atomic heat capacity of ruthenium is 1.01 [490]; for the entropy and other physical properties of ruthenium, see [491].

Data on the magnetic susceptibility of ruthenium have been published by several authors [109, 337, 361].

Finely dispersed ruthenium or ruthenium black are obtained by the reduction of ruthenium compounds with hydrazine hydrate or with hydrazine salts in acid or alkaline medium. The sorption of hydrogen and oxygen by ruthenium black has been studied by Bel'nevich [13]. The author has shown that the maximum amount of hydrogen which can be absorbed by ruthenium under definite conditions approximately corresponds to the formula RuH_2 [13]. At atmospheric pressure and at a pressure of 10^{-4} mm Hg and 20° , hydrogen is not sorbed by ruthenium; it is fully removed from the metal at 650° [566]. This fact is of considerable practical importance in analytical chemistry, since the final stage in the gravimetric determination of ruthenium is ignition in a stream of hydrogen and cooling of the metal in an atmosphere of carbon dioxide [544]. The sorption isotherms and isobars of

hydrogen on ruthenium black have been described in a number of papers [13, 359, 566]. For the application of platinum-metal blacks as catalysts, see [67].

Compact metallic ruthenium is not oxidized in either dry or humid air under standard conditions, whereas the finely divided metal is rapidly oxidized when heated in air. The maximum amount of oxygen which can be bound by ruthenium is 31.3%, whereas the oxygen content in ruthenium dioxide is 31.5%.

According to Gutbier [352], the oxygen content in the product of the reaction of ruthenium with oxygen is somewhat lower than that corresponding to the formula RuO_2 . At temperatures above 600° , the volatile ruthenium tetroxide is formed.

The reaction of ruthenium with oxygen at various temperatures and various times of reaction has been studied by Ranshoff [625] and other workers [344].

The normal redox potential of ruthenium may vary with the conditions of heat treatment [574], depending on whether the metal is in the active or in the passive state. The difference in potentials between the passive and the active forms of the metal may be as high as 0.86V. According to Biryukov [18], the normal potential of ruthenium is 0.92 V, whereas Latimer [64] gives it as 0.79 V. Ruthenium is highly inert to chemical reagents: in its compact state, the metal dissolves neither in alkalis, nor in acids, nor in aqua regia, whereas ruthenium alloys with platinum metals are partly soluble in aqua regia [673]. When ruthenium is fused with alkalis in the presence of oxidizing agents, a water-soluble ruthenate of the corresponding alkali metal is formed. The low solubility of amorphous ruthenium in molten sodium hydroxide and sodium carbonate has no practical importance [769]. Metallic ruthenium combines with oxygen, boron [199], silicon [199], germanium [731], zirconium [730], titanium [475], phosphorus [185], sulfur, selenium, and tellurium [770]. Phosphorus halides combine with ruthenium at 250 to 300° to give crystalline compounds of the composition $\text{Ru}_2\text{P}_5\text{Hal}_{13}$ which are soluble in organic solvents [678].

The oxygen compounds of ruthenium, other than the dioxide and the tetroxide, do not have a definite composition and have not been studied much. The most important oxygen compound of ruthenium is ruthenium tetroxide (for the properties of this compound, which is very important in analysis, and for the methods of its preparation see pp. 144ff).

Another highly stable oxygen compound of ruthenium is ruthenium dioxide which is obtained by heating the metal in a stream of oxygen, by reducing ruthenium tetroxide, and also by heating dry ruthenium sulfides. This compound can also be prepared by igniting chlorides, by decomposing ammonium ruthenate in contact with air, and by other methods [423, 466, 676, 767]. For the electron conductivity of ruthenium oxides, see [479].

Ruthenium dioxide, RuO_2 , is an amorphous black-brown powder which, on heating in vacuo to 958° , is converted to an indigo-blue crystalline form, isomorphous with the dioxides of osmium, iridium, tin, and titanium [506].

The crystal structure of ruthenium dioxide has been described by many authors [12, 331, 403, 623]. The heat of formation as calculated from the approximate Nernst formula is 52.9kcal/mole [633]; according to other data, its value is 72kcal/mole. The thermal dissociation of ruthenium dioxide begins at 930 to 950°. Ruthenium dioxide is fully reduced to metal by hydrogen [326].

Freshly dried ruthenium dioxide is readily soluble in hydrochloric acid; it is sparingly soluble in sulfuric and nitric acids. Ignited ruthenium dioxide is insoluble in acids, and can be dissolved only by fusing with alkalis and oxidants [326].

Beside the tetroxide and the dioxide of ruthenium, the oxide Ru_2O_5 may possibly exist; it has been obtained by the anodic oxidation of ruthenium (III) sulfate, and according to the author [342], this is actually a solid solution of ruthenium (IV) and ruthenium (VI) compounds. This oxide was also prepared by oxidizing $\text{Ru}(\text{OH})_2$ with atmospheric oxygen, and by reducing RuO_4 in hermetically sealed vessels [632].

The existence of the oxides RuO , Ru_2O_3 , Ru_5O_6 , Ru_4O_9 and RuO_3 has not been proved. It has been suggested that RuO and Ru_2O_3 can be obtained by dehydrating ruthenium (II) and ruthenium (III) hydrates in a stream of carbon dioxide, or by fusing ruthenium (II) salts with carbonates [50]. Ru_5O_6 has been considered as the mixture $3\text{RuO} + \text{Ru}_2\text{O}_3$ which may form when metallic ruthenium is heated to white heat. Ru_4O_9 has been prepared by heating ruthenium tetroxide to 100° [423], RuO_3 by heating $\text{H}_2[\text{RuO}_2\text{Cl}_4]$ or $(\text{NH}_4)_2[\text{RuCl}_6] \cdot 0.5\text{H}_2\text{O}$ to 540° [146].

Oxygen compounds of ruthenium have been described by many authors [50, 234, 235, 244, 360, 632, 652].

Ruthenium hydroxides, which are of major importance in analytical practice, are described in Chapter III, in the section *Determination of ruthenium as hydroxides*.

Halogen compounds of ruthenium (I), (II), (III), (IV), (V), and (VI) are known.

According to Manchot [520–522], compounds of ruthenium (I) are present in solutions obtained by reducing chlorides or cyanides of ruthenium (II). The $\text{Ru}^{1+}/\text{Ru}^{2+}$ oxidation potential in 0.1 N HCl is + 0.03 to 0.05 V [339].

The dark-brown ruthenium dichloride, a compound insoluble in water, acids, alkalis, or absolute alcohol, but soluble in 25% alcohol, is obtained by dry chlorination of the metal in the presence of carbon monoxide [395]. The reaction product, apparently, does not correspond to the stoichiometric composition, since dry chlorination may yield a mixture of various chlorides [377, 430].

Ruthenium dichloride is also obtained by electrolysis of ruthenium trichloride solutions [328, 522], or by reduction of this compound by amalgams [290, 638, 639]. Electrolysis of ruthenium trichloride yields a blue solution stable in 2N HCl. Bluish-black crystalline powdery RuCl_2 (soluble in water) separates from this solution on evaporation in vacuo in a hydrogen atmosphere. In less acid solutions ruthenium disproportionates as follows [339]:



The $\text{Ru}^{2+}/\text{Ru}^{3+}$ oxidation potential in 1.53 to 6.8 *N* HCl is $+ 0.084 \pm 0.005$ V [339].

The crystal structure of ruthenium dichloride is analogous to the structure of the dichlorides of platinum, palladium, manganese, and iron [603].

Ruthenium dibromides and ruthenium diiodides [289] and also PBr_5 -addition products of ruthenium dibromide [678] have been described.

Ruthenium trichloride is prepared by dry chlorination of the metal [457, 518]. According to latest data [51], the product of the reaction of ruthenium with chlorine (at a chlorine pressure of 1 atm and at 850°) is ruthenium trichloride, which is known to exist in two crystalline forms. An amorphous soluble form of ruthenium trichloride has also been obtained. Until recently it has been maintained that it is difficult to prepare ruthenium tribromides and triiodides in the pure state. Ruthenium triiodide is known in two allotropic forms, one of which is soluble in water. When compounds of ruthenium (III) are boiled with potassium iodide, RuI_3 is formed, which is insoluble in water, alcohol, or excess of KI [212]. Ruthenium tribromide has recently been prepared by treating the metal with bromine for 30 to 35 hours at 450° and 15 to 20 atm. The reaction product is insoluble in water, sodium hydroxide, mineral acids, alcohol, benzene, ether, carbon tetrachloride, and other solvents. Unlike the halides of some elements, ruthenium trihalides are not extractable with ether. All the compounds of this class have a tendency to enter into addition reactions; the compounds of the type $\text{RuHal}_3 \cdot 7\text{NH}_3$, where $\text{Hal} = \text{Cl}^-$, Br^- , are used as dyestuffs because of their characteristic bright colors.

$\text{RuCl}_4 \cdot 5\text{H}_2\text{O}$ is the only halogen compound of ruthenium (IV) so far described in the literature. This compound forms red hygroscopic crystals which are readily soluble in water and can be prepared by heating a solution of $\text{H}_2[\text{RuO}_2\text{Cl}_4] \cdot 3\text{H}_2\text{O}$ in concentrated hydrochloric acid over a steam bath in a stream of chlorine [147–149]*.

Evaporation on a steam bath of HCl solutions of ruthenium tetroxide gives $\text{RuCl}_4 \cdot n\text{H}_2\text{O}$, where $n < 5$. The number of molecules of the water of crystallization depends on the duration of evaporation and on temperature [212]. Halogen compounds of ruthenium (IV) are easily hydrolyzed, and ruthenium hydroxychloride RuOHCl_3 is formed in aqueous, alcoholic, and HCl solutions of RuCl_4 [640, 644]. The formation of oxyhalides is characteristic of ruthenium (VI). Ruthenyl chloride, RuO_2Cl_2 , is formed in the reaction of ruthenium tetroxide with hydrogen chloride [146]. A reaction product of ruthenyl chloride with hydrogen chloride is also known. This compound fits the formula $\text{H}_2[\text{RuO}_2\text{Cl}_4] \cdot 3\text{H}_2\text{O}$, melts at 120°, and is readily decomposed by water [146]. This compound can also be obtained as red, acicular crystals in the reaction between ruthenium tetroxide, hydrogen chloride, and chlorine. All compounds of this type are diamagnetic.

* The existence of this compound is doubtful.

The formation of complex halides is highly characteristic of ruthenium; the structure of these complexes has not yet been sufficiently studied. Complex fluorides, chlorides, bromides, and iodides of ruthenium are known. Brief information on ruthenium fluorides is given on p. 214. Complex halides of ruthenium (III) and ruthenium (IV), which are highly characteristic of this element, are described in Chapter III under *Volumetric methods*.

Complex halides of ruthenium (II) correspond to the general formula $\text{Me}_2[\text{RuHal}_4]$, where $\text{Me} = \text{Rb}^+$, Cs^+ and NH_4^+ , and $\text{Hal} = \text{Cl}^-$ and Br^- . Ruthenium (II) also forms the compound $\text{K}_3[\text{RuH}_2\text{OCl}_5]$ whose method of preparation is remarkable: irradiation of an HCl solution of ruthenium tetroxide with ultraviolet light [468]. Addition of organic molecules is characteristic of the complex halides of ruthenium (II), (III), and (IV).

Compounds of the type $\text{H}_2[\text{RuCl}_4] \cdot \text{A}$, where A is a molecule of pyridine, ethylenediamine, or dipyridyl, are obtained by adding the reagent to solutions of ruthenium (II) salts [328].

The following formulas are attributed to the reaction products of ruthenium (III) and ruthenium (IV) halides with amines: $\text{H}_2[\text{RuHal}_5] \cdot 2\text{A}$, $\text{H}_2[\text{RuHal}_5] \cdot 4\text{A}$ and $\text{H}_2[\text{RuHal}_6] \cdot 2\text{A}$, where $\text{Hal} = \text{Cl}^-$ and Br^- ; $\text{A} = \text{NH}_2\text{R}$, NHR_2 , NR_3 , and $[\text{NR}_4]\text{X}$; $\text{R} = \text{CH}_3$, C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} . A may also be a molecule of pyridine, ethylenediamine, quinoline, or another organic ligand [347, 349, 350, 355–357, 784].

Ruthenium sulfates are also important in the analytical chemistry of this element, since ruthenium tetroxide, on the formation of which the various methods for the separation of ruthenium from other elements are based, often precipitates from sulfate solutions. The green ruthenium (VI) sulfate, containing the ion $[\text{RuO}_2(\text{SO}_4)_2]^{2-}$, is obtained by reducing ruthenium tetroxide in a dilute solution of sulfuric acid by such reducing agents as NaNO_2 , Na_2SO_3 , FeSO_4 , N_2H_4 , and NH_2OH [529]. The reaction of ruthenium tetroxide with sulfuric anhydride under ultraviolet radiation gives $\text{RuO}_2\text{S}_2\text{O}_7$ which, when dissolved in dilute sulfuric acid at 0° produces $[\text{RuO}_2(\text{SO}_4)_2]^{2-}$. If the compound is dissolved at room temperature, a solution of ruthenium (IV) sulfate is obtained and a precipitate of ruthenium dioxide [370] separates out.

A solution of ruthenium (IV) sulfate can also be obtained by reacting barium ruthenate with excess sulfuric acid [143]. When gaseous SO_2 is passed through, the solution first becomes violet, then sky-blue, and finally a light-yellow solution of RuS_2O_6 is formed, which is stable at high temperatures [142]. RuSO_4 is obtained as an intermediate product [142] which, in excess SO_2 , is converted to yellowish-bluish water- and acid-soluble ruthenium dithionate. This compound does not react with excess sulfurous acid; at 80° it splits off sulfurous anhydride, and at higher temperatures, sulfuric anhydride.

Complex nitrites of platinum metals, and in particular complex ruthenium nitrites,