



ANALYTICAL CHEMISTRY OF  
**BERYLLIUM**

A. V. NOVOSELOVA and L. R. BATSANOVA

Translated by J. SCHMORAK



ANN ARBOR-HUMPHREY SCIENCE PUBLISHERS

ANN ARBOR · LONDON · 1969

ANN ARBOR-HUMPHREY SCIENCE PUBLISHERS, INC.  
Drawer No. 1425 Ann Arbor, Michigan 48106

ANN ARBOR-HUMPHREY SCIENCE PUBLISHERS, LTD.  
5 Great Russell Street London W.C. 1

© 1968 Israel Program for Scientific Translations Ltd.

Library of Congress Catalogue Card Number 72-103811  
SBN 024 87591 6 (USA)  
SBN 250 399113 (UK)

This book is a translation of  
ANALITICHESKAYA KHIMIYA BERILLIYA  
Izdatel'stvo "Nauka"  
Moskva 1966

Printed in Israel  
Manufactured at the Israel Program for Scientific Translations, Jerusalem

ANALYTICAL CHEMISTRY OF ELEMENTS

ANALYTICAL CHEMISTRY OF BERYLLIUM

# *Analytical Chemistry of Elements*

Series prepared by the Vernadskii Institute of Geochemistry and Analytical Chemistry  
USSR Academy of Sciences

A. P. VINOGRADOV, *Editor*

English translation by ISRAEL PROGRAM FOR SCIENTIFIC TRANSLATIONS, Jerusalem

---

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.

*Editorial Board*

CHIEF EDITOR

Academician A. P. Vinogradov

EDITORIAL BOARD

I. P. Alimarin, A. K. Babko, A. I. Busev, A. P. Vinogradov  
A. N. Ermakov, V. I. Kuznetsov, P. N. Palei,  
D. I. Ryabchikov, I. V. Tananaev, Yu. A. Chernikhov

EDITOR OF THIS VOLUME

A. N. Ermakov

ADDRESS OF THE EDITORIAL BOARD

Moskva, V-334, Vorob'evskoe shosse, 47a,  
Institut Geokhimii i Analiticheskoi Khimii im. Vernadskogo  
Akademii Nauk SSSR

## TABLE OF CONTENTS

FOREWORD . . . . .	1
Chapter I: PHYSICAL, CHEMICAL AND ANALYTICAL CHARACTERISTICS OF BERYLLIUM AND ITS COMPOUNDS . . . . .	1
Physicochemical properties of beryllium . . . . .	3
Beryllium compounds . . . . .	4
Chapter II: DETECTION OF BERYLLIUM . . . . .	29
The more important analytical reactions of beryllium . . . . .	31
Chapter III: DETERMINATION OF BERYLLIUM . . . . .	44
Chemical methods . . . . .	44
Gravimetric methods . . . . .	44
Volumetric methods . . . . .	52
Physicochemical methods . . . . .	61
Photometric methods . . . . .	61
Polarographic methods . . . . .	80
Radiochemical methods . . . . .	82
Physical methods . . . . .	84
Spectroscopic methods . . . . .	84
Activation methods . . . . .	107
Fluorimetric methods . . . . .	113
Chapter IV: SEPARATION AND CONCENTRATION OF BERYLLIUM . . . . .	119
Extraction methods . . . . .	121
Chromatographic methods . . . . .	132
Separation of beryllium by precipitation reactions . . . . .	147
Electrolytic separation of interfering elements from beryllium . . . . .	155
Other separation methods . . . . .	156
Chapter V: DETERMINATION OF BERYLLIUM IN NATURAL AND INDUSTRIAL MATERIALS . . . . .	157
Determination of beryllium in minerals, ores, and industrial concentrates . . . . .	157
Determination of beryllium in alloys and metals . . . . .	165
Determination of beryllium in biological materials and in the atmosphere . . . . .	176
Chapter VI: DETERMINATION OF IMPURITIES IN BERYLLIUM AND ITS COMPOUNDS . . . . .	180
BIBLIOGRAPHY . . . . .	195
SUBJECT INDEX . . . . .	221



## CHAPTER I

# Physical, Chemical and Analytical Characteristics of Beryllium and its Compounds

Beryllium heads Group II of the periodic system; its atomic number is 4, and its atomic weight 9.0122. The known beryllium isotopes have mass numbers 7, 8, 9, 10, and 11, but only  $\text{Be}^9$  is stable (Table 1).

Beryllium readily emits neutrons following irradiation with  $\gamma$ -rays,  $\alpha$ -particles, and deuterons:  $\text{Be}^9 (\alpha, n) \text{C}^{12}$ ,  $\text{Be}^9 (\gamma, n) \text{Be}^8$ ,  $\text{Be}^9 (d, n) \text{B}^{10}$ .

Table 1  
RADIOACTIVE ISOTOPES OF BERYLLIUM [1-5]

Isotope	Radiation emitted	Radiation energy, MeV	Half-life	Reaction of formation
$\text{Be}^7$	$\gamma$	0.485	52.9 days	$\text{Li}^7 (p, n)$ $\text{B}^{10} (p, \alpha)$ $\text{Li}^6 (p, \gamma)$ $\text{B}^{10} (d, \alpha, n)$
$\text{Be}^8$	$\alpha$	0.047	$\approx 10^{-16}$ sec	$\text{Be}^9 (\gamma, n)$ $\text{C}^{12} (\gamma, \alpha)$
$\text{Be}^{10}$	$\beta$	0.555	$2.7 \cdot 10^6$ yr	$\text{Be}^9 (\alpha, p)$ $\text{Be}^9 (n, \gamma)$ $\text{C}^{13} (n, \alpha)$ $\text{B}^{10} (n, p)$
$\text{Be}^{11}$	$\beta$	$> 5$	14.1 sec	$\text{B}^{11} (n, p)$

## 2 CHARACTERISTICS OF BERYLLIUM AND ITS COMPOUNDS

Beryllium has a small thermal neutron capture cross section (0.009 barn/atom) and has a large scattering power (6.9 barns/atom).

The most important of the radioisotopes is  $\text{Be}^7$ , which is used as a radioactive tracer. The isotopes  $\text{Be}^7$  and  $\text{Be}^{10}$  have been identified in rainwater and melted snow, and it is thought that they are formed in the atmosphere by the action of cosmic rays on oxygen and nitrogen atoms, possibly  $\text{N}^{14}(n, \chi)\text{Be}^7$ ,  $\text{N}^{14}(p, 2\alpha)\text{Be}^7$ , etc. [6-8]. The amount of natural isotope  $\text{Be}^7$  at a height of 9-10 km above the Earth's surface is estimated at 245 atoms/liter [9]. The natural long-lived isotope  $\text{Be}^{10}$  would probably be of interest in studies on the age of rocks [10].

Beryllium was discovered by L. Vauquelin in 1798. Metallic beryllium was obtained by F. Woehler, and independently by A. Bussy, in 1828.

Beryllium is a lithophilic element; its content in the Earth's crust is  $6 \cdot 10^{-4}\%$  [11]. Beryllium is a constituent of more than twenty minerals, of which beryl is of industrial importance. The other minerals are of relatively rare occurrence (phenacite, chrysoberyl, helvite, etc.) (Table 2). Silicates, and also borates and phosphates, occur most frequently. Beryl is usually associated with pegmatite veins, and appears in industrial concentrates together with quartz, feldspars, micas, and other minerals. Until recently, enrichment was carried out by hand-picking coarsely crystalline beryl ores. However, large beryl deposits are rare. Accordingly, mechanical enrichment methods (flotation) are now often used, with the result that finely disseminated beryl ores and secondary minerals have become more important [12-14].

Table 2  
THE MOST IMPORTANT BERYLLIUM MINERALS

Mineral	Composition	BeO content, %
Beryl	$\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}(3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2)$	14.0
Phenacite	$\text{Be}_2\text{SiO}_4$	45.5
Chrysoberyl	$\text{Al}_2\text{BeO}_4$	19.8
Helvite	$\text{Mn}_8[\text{BeSiO}_4]_6 \cdot \text{S}_2$	11 - 14.2
Gadolinite	$\text{Y}_2\text{FeBe}_2\text{Si}_2\text{O}_{10}$	10.0
Euclase	$\text{BeAlSiO}_4(\text{OH})$	17.3
Bertrandite	$\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$	39.6 - 42.6
Danalite	$\text{Fe}_8[\text{BeSiO}_4]_6 \cdot \text{S}_2$	12.7 - 14.7
Bromellite	BeO	98.02

Beryllium is one of the lightest, most heat resistant, and hardest metals. In addition, it has a small neutron capture cross section and a high scattering power. This combination of properties makes it irreplaceable by any other metal for industrial purposes, especially in the technology of the future.

The two main uses of beryllium are metallurgy and nuclear technology. Beryllium is chiefly used in the manufacture of alloys, of which the most important are copper-beryllium alloys, because of their high mechanical parameters, such as hardness, strength, and resistance to corrosion. Beryllium bronzes are used to produce important machine parts (springs, contact, engine parts, bearings, electrodes, etc.) [15]. The introduction of beryllium into aluminum-magnesium alloys improves their strength and resistance to heat, and reduces their tendency to oxidize. Owing to their low density, these alloys are of potential interest in the production of planes and rockets.

An important field of application is the beryllization of various objects (surface cementation) in order to impart surface hardness.

In nuclear technology beryllium is used as a component of neutron sources, since the beryllium nucleus disintegrates quite easily under the action of  $\alpha$ -radiation.

Neutron sources usually consist of a mixture of beryllium with radium, with a yield of 460 neutrons per  $10^6$  disintegrations. A recent, more stable neutron source is the compound of the long-lived isotope of plutonium,  $\text{Pu}^{239}$ , with beryllium,  $\text{PuBe}_3$  (yield  $7 \cdot 10^4$  neutrons/sec  $\cdot$  g [16, 17]). In atomic reactors Be and also its oxide and carbide are employed as neutron reflectors and neutron moderators.

Beryllium is used in the manufacture of windows of X-ray tubes and radioactive counters owing to its high transparency to  $\gamma$ -rays.

Among the beryllium compounds, the oxide is of industrial importance due to its high thermal conductivity and low electrical conductivity. Beryllium oxide is used not only in nuclear technology, but also in the manufacture of chemically-resistant refractories and electrical and radio insulators.

A number of recently published monographs [14, 18, 19] give detailed information on the technology of beryllium and beryllium oxide, and the fields of application of these substances.

## PHYSICOCHEMICAL PROPERTIES OF BERYLLIUM

Beryllium is a light, high-melting, brittle, light-gray metal. The low-temperature modification of beryllium has a hexagonal lattice:  $a = 2.285 \text{ \AA}$ ,  $c = 3.583 \text{ \AA}$  [20]. No polymorphic transformations of beryllium are observed below  $1200^\circ$ . The transition of  $\alpha$ -Be into the cubic  $\beta$ -Be takes place at  $1254^\circ$  [21]. The physical constants of beryllium are given below [14]:

Density	1.847 g/cm <sup>3</sup>
Melting point	1283°C
Boiling point	2970°C
Specific heat (30–100°)	0.425–0.516 cal/g $\cdot$ deg
Heat of fusion	$2.8 \pm 0.5$ kcal/g-atom
Electrical conductivity	38.0–43.1
Brinell hardness	97–114 kg/mm <sup>2</sup>
Elasticity modulus	29,280–30,000 kg/mm <sup>2</sup>

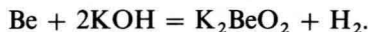
#### 4 CHARACTERISTICS OF BERYLLIUM AND ITS COMPOUNDS

In its chemical compounds beryllium is bivalent. Its ionization potential ( $\text{Be}^0 \rightarrow \text{Be}^{2+}$ ) is 27.4 eV; the first potential ( $\text{Be}^0 \rightarrow \text{Be}^+$ ) is 9.32 eV, while the second ( $\text{Be}^+ \rightarrow \text{Be}^{2+}$ ) is 18.21 eV.

Compounds of monovalent beryllium are unstable;  $\text{BeCl}$  is probably formed during the anodic dissolution of beryllium in molten beryllium chloride [22–24].

In its chemical properties beryllium resembles aluminum and zinc, and differs from magnesium. This is due to the small ionic radius of  $\text{Be}^{2+}$  (0.32 Å) and consequently the high potential of the cationic field ( $e/r^2 = 17$ ). Hence beryllium has a tendency to covalent bonding.

When immersed in cold or hot water, beryllium is practically unaffected; the corrosive action of water on beryllium varies greatly with the purity of the metal and of the water. Beryllium is soluble in dilute hydrochloric and sulfuric acids. Beryllium is passivated by cold concentrated nitric acid; it reacts with both concentrated and dilute nitric acid when heated. It dissolves in hot alkalis with the formation of beryllates:



At high temperatures beryllium forms compounds with oxygen ( $\text{BeO}$ ), sulfur ( $\text{BeS}$ ), nitrogen ( $\text{Be}_3\text{N}_2$ ), carbon ( $\text{Be}_2\text{C}$ ), halogens ( $\text{BeHal}_2$ ), and other elements. In the compact state beryllium resists the action of atmospheric oxygen up to 600°. It reacts with fluorine at room temperature. It is oxidized by carbon dioxide at 600° according to  $2\text{Be} + \text{CO}_2 \rightleftharpoons 2\text{BeO} + \text{C}$ , with the formation of beryllium carbide [14, 25]:



Beryllium reacts with gaseous ammonia with the formation of beryllium nitride. It dissolves in solutions of ammonium bifluoride [26]. It does not react with hydrogen directly. Beryllium hydride  $\text{BeH}_2$  is obtained by the decomposition of organoberyllium compounds, and is a solid which dissociates into the constituent elements above 200° [27, 28].

A chemical description of a number of beryllium compounds which are important for its chemical analysis is given below. Inorganic beryllium compounds will be discussed first.

### BERYLLIUM COMPOUNDS

#### Beryllium hydroxide $\text{Be}(\text{OH})_2$

The hydroxide is one of the least soluble beryllium compounds. It may be obtained by the action of alkalis, ammonia, and organic bases on solutions of beryllium salts. The hydroxide is amphoteric. When ammonia is added to dilute solutions of beryllium salts in the cold, the amorphous beryllium hydroxide  $\text{Be}(\text{OH})_2 \cdot x\text{H}_2\text{O}$  precipitates

out, and on standing is transformed into the metastable crystalline  $\alpha$ -Be(OH)<sub>2</sub>; the latter in turn is transformed into the stable  $\beta$ -modification on shaking with a solution of alkali [29].

The hydroxide begins to precipitate at pH 5.7 [30] (see below); the solubility of the amorphous hydroxide increases with increase in the concentration of ammonia. According to Moser and Singer [31], its solubility in water and in a solution of ammonium chloride at room temperature is  $2 \cdot 10^{-3}$  g or  $0.8 \cdot 10^{-4}$  moles BeO/liter of solution. The solubility of the amorphous hydroxide in a 1% solution of ammonia is as high as  $4 \cdot 10^{-3}$  g or  $1.8 \cdot 10^{-4}$  moles BeO/liter. Freshly precipitated beryllium hydroxide is readily soluble in dilute acids and in solutions of alkalis with the formation of beryllates. When dilute beryllate solutions are boiled, the crystalline  $\beta$ -beryllium hydroxide precipitates out [32].

Freshly precipitated beryllium hydroxide is soluble in concentrated solutions of alkali carbonates and ammonium carbonate with the formation of soluble complex carbonates. Amorphous beryllium hydroxide absorbs carbon dioxide from the atmosphere with the formation of a basic carbonate. Because of its amorphous nature, beryllium hydroxide tends to form colloidal solutions, and has a high adsorption capacity. The amorphous beryllium hydroxide becomes crystalline on aging; this transition may be accelerated by boiling the amorphous hydroxide in a solution of ammonia or alkali hydroxide [29, 33, 34].

The stable  $\beta$ -Be(OH)<sub>2</sub> modification may be obtained by boiling the  $\alpha$ -form for 24 hours in an autoclave at 160° [35], and also by saturating hot 40% NaOH with the freshly precipitated beryllium hydroxide and cooling the solution. At 105–110°,  $\beta$ -Be(OH)<sub>2</sub> crystallizes from the solution [36].

The  $\beta$ -form may also be obtained directly by the reaction between beryllium sulfate and sodium hydroxide [37]. The  $\beta$ -form is also obtained by the action of gaseous ammonia on solutions of beryllium sulfate heated to 95–98° at pH 7.5 [14, p. 22]. The  $\beta$ -form is orthorhombic ( $a = 4.61$ ,  $b = 7.02$ ,  $c = 4.52$  Å) with four formula units in the unit cell [36].

The crystalline modifications of beryllium hydroxide have a much smaller adsorptive capacity and are much less soluble in acids and alkalis than the amorphous form [29, 38]. The solubility of the crystalline hydroxide ( $\alpha$ -form) in water is less than  $10^{-7}$  moles/liter of water [34].

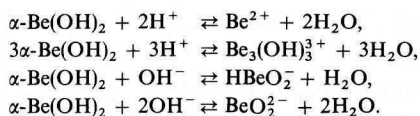
The solubility product of beryllium hydroxide has been determined by numerous workers [34, 38, 40–42], but the results are very discrepant ( $7.3 \cdot 10^{-22}$ ,  $2 \cdot 10^{-20}$ ,  $2 \cdot 10^{-18}$ ,  $2 \cdot 10^{-26}$ ).

Numerous literature data on the dissociation constants of beryllium hydroxide are available (Table 3). This is because aggregates of dissociation products are formed in solution, with the formation of polynuclear hydroxo- or oxo-complexes, which have been assigned various compositions [43–50].

The dissolution of the  $\alpha$ -form in dilute solutions of sodium hydroxide and acids [34] takes place mainly

## 6 CHARACTERISTICS OF BERYLLIUM AND ITS COMPOUNDS

by the reactions between  $\text{Be}(\text{OH})_2$  and the solid phase:



The equilibrium constants of these reactions ( $25^\circ$ ,  $\mu = 0$ ) are  $7.3 \cdot 10^{-6}$ ,  $2.1 \cdot 10^{-12}$ ,  $3.2 \cdot 10^{-3}$ ,  $2.0 \cdot 10^{-3}$ , respectively [34, 39].

The solubility values of crystalline  $\text{Be}(\text{OH})_2$  in solution of  $\text{NaOH}$  [29] are given below:

Solid phase $\beta\text{-Be}(\text{OH})_2$		Solid phase $\text{BeO} \cdot \text{NaOH} \cdot \text{H}_2\text{O}$	
$\text{NaOH}$ , %	$\text{BeO}$ , %	$\text{NaOH}$ , %	$\text{BeO}$ , %
14.10	0.159	36.92	3.22
16.20	0.197	39.00	3.04
19.52	0.352	40.04	3.06
24.16	0.780	43.38	3.35
28.27	1.66	46.47	3.78
31.00	2.95		
34.10	4.66		

Table 3  
BASIC AND ACID DISSOCIATION CONSTANTS OF  $\text{Be}(\text{OH})_2$

Reaction	$K_1$	$K_2$	$K_1 \cdot K_2$	pH	References
<i>Basic dissociation constants</i>					
$\text{Be}(\text{OH})_2 \rightleftharpoons \text{BeOH}^+ + \text{OH}^-$	$5.2 \cdot 10^{-11}$				[51]
	$(1.5 \pm 0.2) \cdot 10^{-11}$			6.2–5.4	[46]
$\text{Be}_2\text{O}(\text{OH})_2 \rightleftharpoons \text{Be}_2\text{O}^{2+} + 2\text{OH}^-$	$4 \cdot 10^{-19}$				[43]
or					
$2\text{Be}(\text{OH})_2 \rightleftharpoons \text{Be}_2(\text{OH})_2^{2+} + 2\text{OH}^-$		$3.3 \cdot 10^{-8}$			[45]
$\text{BeOH}^+ \rightleftharpoons \text{Be}^{2+} + \text{OH}^-$					
$\text{Be}_2\text{O}^{2+} + \text{H}_2\text{O} \rightleftharpoons 2\text{Be}^{2+} + 2\text{OH}^-$		$(1-6) \cdot 10^{-22}$			[43, 44]
or					
$\text{Be}_2(\text{OH})_2^{2+} \rightleftharpoons 2\text{Be}^{2+} + 2\text{OH}^-$		$(4.9 \pm 0.3) \cdot 10^{-22}$		5.1–3.8	[46]
$\text{Be}_3(\text{OH})_3^{3+} \rightleftharpoons 3\text{Be}^{2+} + 3\text{OH}^-$		$5 \cdot 10^{-32}$			[47]
		$(9.4 \pm 0.7) \cdot 10^{-34}$		5.1–3.8	[46]
$\text{Be}(\text{OH})_2 \rightleftharpoons \text{Be}^{2+} + 2\text{OH}^-$			$9.1 \cdot 10^{-15}$		[41]
			$7.3 \cdot 10^{-22}$		[34]
<i>Acid dissociation constants</i>					
$\text{Be}(\text{OH})_2 \rightleftharpoons \text{HBeO}_2^- + \text{H}^+$	$3.2 \cdot 10^{-17}$				[34]
$\text{Be}(\text{OH})_2 \rightleftharpoons \text{BeO}_2^{2-} + 2\text{H}^+$			$2.0 \cdot 10^{-31}$		[34]
			$2 \cdot 10^{-30}$		[52]

During the precipitation of beryllium hydroxide, basic salts are formed as intermediate products. The separation of the precipitate is complete when the pH is close to 8 [53]. In this respect the behavior of beryllium resembles that of aluminum hydroxide, but the latter dissolves in alkali at pH 9.75 [54, 55], and the dissolution begins immediately with the appearance of excess alkali in solution. Beryllium hydroxide, on the other hand, dissolves at pH above 10 after a certain excess of NaOH has accumulated [53, 56], and, as was shown by Tananaev and Shcheglova [57], in the presence of 0.025 mole/liter excess of NaOH. This difference can be employed for only an incomplete separation of aluminum from beryllium [54, 57].

When beryllium hydroxide is heated, it loses water and is converted to the oxide, which is the weighing form in the gravimetric determination of beryllium. Heating to 150–180° yields the anhydrous hydroxide; decomposition of the hydroxide begins at 240–300°. The water loss at this temperature is 90% [58]. The remaining water can be eliminated by raising the temperature to at least 500°. Traces of water are more difficult to remove [59–62].

The minimum temperature at which the bound water can be eliminated from the hydroxide depends on the conditions of precipitation of the hydroxide [59]. Beryllium hydroxide precipitated by ammonia in the cold is ignited at 850°, that precipitated from a hot solution at 595°, and that precipitated by  $\alpha$ -picoline at 817°, etc. (see also Chapter III). To obtain nonhygroscopic beryllium oxide, the hydroxide is ignited at 1000–1200° [62, 63].

### Beryllium oxide

Beryllium oxide is obtained by igniting the hydroxide, or beryllium salts (nitrate, basic carbonate, sulfate, oxyacetate, etc.). It is a white, amorphous powder, whose density varies between 2.86 and 3.02, depending on the ignition temperature.

Crystalline beryllium oxide is formed at very high temperatures by distillation or from melts. The crystalline form is of the wurtzite type (ZnS) (hexagonal,  $a = 2.698$ ,  $c = 4.377$  Å, density 3.025 g/cm<sup>3</sup>) [64]. The parameters of the elementary cell vary a little when the oxide is heated. The melting point of beryllium oxide is 2500°, and its boiling point is around 4000°. Beryllium oxide has a high heat conductivity, which decreases with increase in temperature (from 0.6 to 0.05 cal/cm · sec · deg between 100 and 1000°) but is still higher than that of aluminum and magnesium oxides.

Beryllium oxide is practically insoluble in water. According to Remy and Kuhlman [40, 65], when water is saturated with beryllium oxide at 25°, the resulting solution contains  $5 \cdot 10^{-4} - 2 \cdot 10^{-5}$  moles of Be(OH)<sub>2</sub> per liter. The solubility of beryllium oxide in acids and alkalis depends on the temperature of preparation and the grain size of the compound [66–68]. Ignition at high temperatures gives an oxide with a large grain size, which is particularly marked if the oxide is heated to 1100°. The

average particle size of the oxide heated from 800 to 1400° increases fortyfold [68].

Beryllium oxide ignited at low temperatures (400–500°) is very reactive; it is readily soluble in acids, and less so in solutions of alkalis. Beryllium oxide heated to temperatures above 1000° dissolves only in hydrofluoric acid, hot concentrated sulfuric acid, or when fused with carbonates, alkalis and alkali pyrosulfates, at a much slower rate than the oxide ignited at a low temperature.

Fluorine reacts with beryllium oxide at 400°, while other halogens react at higher temperatures. Carbon reacts with BeO above 2000° to give beryllium carbide  $\text{Be}_2\text{C}$ . At high temperatures in the presence of water vapor BeO is very volatile [14, 69].

Beryllium oxide is hygroscopic, and its hygroscopicity depends to a large extent on the ignition temperature [70]:

Ignition temperature, °C	Water adsorption, %
Nonignited oxide	34.27
900	3.27
1100	2.13
1300	0.21
1500	0.18

### Beryllium basic carbonates

When aqueous solutions of alkali carbonates and ammonium carbonate react with solutions of beryllium salts, compounds of variable composition  $\text{BeCO}_3 \cdot n\text{Be}(\text{OH})_2$  ( $n = 2-5$ ) are formed, which contain varying amounts of water. The basic carbonate of beryllium is soluble in acids and also in excess precipitant, with the formation of complex compounds. When a solution of the complex compound is boiled, the basic carbonate precipitates out. The basic carbonate is slightly soluble in hydrazine and guanidine carbonates [71, 72]. The solubility of complex beryllium carbonates is utilized in analytical chemistry (and in technology) to separate beryllium from aluminum and iron. The basic carbonate is also formed by the reaction between the freshly precipitated beryllium hydroxide and gaseous carbon dioxide. The basic carbonates are very unstable to heat, and when heated readily evolve water and gaseous  $\text{CO}_2$ . The thermal decomposition of a basic carbonate with the composition  $\text{BeCO}_3 \cdot 4\text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  was studied by Shargorodskii and Shor [73]. The thermograms indicated two endothermal effects: at 100–120° and 240–255°. The first effect was attributed to the elimination of water (with partial decomposition of  $\text{Be}(\text{OH})_2$ ), and the second to the decomposition of the carbonate and of the residual hydroxide.

When the basic carbonate reacts with crystalline ammonium carbonate or with its saturated solution, a complex compound of variable composition  $x(\text{NH}_4)_2\text{Be}(\text{CO}_3)_2 \cdot$



$\cdot \text{Be}(\text{OH})_2 \cdot y\text{H}_2\text{O}$  is formed. The compound may be precipitated by alcohol and isolated as a crystalline substance. The composition of the complex anion in 0.1 M ammonium carbonate, as determined by ion exchange, corresponds to the formula  $[\text{Be}(\text{CO}_3)_2]^{2-}$  [74].

The soluble complex beryllium carbonate reacts with hexamminecobalt (III) chloride to form the insoluble  $[\text{Co}(\text{NH}_3)_6] [\text{Be}_2(\text{CO}_3)_2(\text{OH})_3(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  [75], or according to [76]  $[\text{Co}(\text{NH}_3)_6]_2 \cdot [\text{Be}_4\text{O}(\text{CO}_3)_6] \cdot 10\text{H}_2\text{O}$ . It was shown by Vinogradov, Apirina and Cherstvenkova [77] that the latter composition is more correct. The compound can be utilized in the gravimetric determination of beryllium [75, 77a, 77b].

When beryllium hydroxide is dissolved in excess sodium or potassium bicarbonate, the ion  $[\text{Be}_4\text{O}(\text{CO}_3)_6]^{6-}$  is formed, and salts with this anion  $\text{Me}_6[\text{Be}_4\text{O}(\text{CO}_3)_6]$  can be isolated from solution [76].

Normal beryllium carbonate  $\text{BeCO}_3$  can probably be obtained by saturating the basic carbonate in water with  $\text{CO}_2$  for a long time, and evaporating the solution in an atmosphere of carbon dioxide.

### Beryllium phosphates

Beryllium orthophosphate  $\text{Be}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$  is obtained by the reaction between beryllium salts and bisubstituted sodium phosphate [78] or ammonium phosphate in an acetic acid medium (pH 5–5.5) [79] at a component ratio of 2:1. The solubility product of this compound is  $1.9 \cdot 10^{-38}$ . Its solubility increases markedly with temperature [80]. The variation in the solubility of the compound as a function of the pH of the medium at 19–20° [81] is given below:

pH	$[\text{Be}^{2+}]$ , g-ion/liter	pH	$[\text{Be}^{2+}]$ , g-ion/liter
4.15	$7.7 \cdot 10^{-4}$	2.90	$6.5 \cdot 10^{-3}$
3.20	$4.7 \cdot 10^{-3}$	2.70	$1.2 \cdot 10^{-2}$

When an alkali orthophosphate is added to a solution of beryllium sulfate, basic beryllium phosphates are formed [78].

The most important phosphate in analytical chemistry is beryllium ammonium phosphate  $\text{NH}_4\text{BePO}_4$ , which is also sparingly soluble ( $\text{SP} = 2.2 \cdot 10^{-20}$ ) [81]. This compound is formed by the action of excess bisubstituted ammonium phosphate on solutions of beryllium salts [82].

The freshly formed precipitate of  $\text{NH}_4\text{BePO}_4 / \text{H}_2\text{O}$  is amorphous, and its composition is often different from the stoichiometric due to the precipitation of  $\text{BeHPO}_4$ . The conditions of precipitation of beryllium ammonium phosphate have been studied by a number of workers [83–85]. A crystalline precipitate of a definite composition