BERYLLIUM HALIDES AND PSEUDOHALIDES

N. A. Bell

Department of Chemistry, Sheffield Polytechnic, Sheffield, England

I. Introduction

The recent interest in the chemistry of beryllium and its compounds perhaps stems from its wide applications currently being developed, having moved from the nuclear power orientation, prevalent in 1961, to one which now explores aerospace and instrument applications. Beryllium possesses a generous supply of unique chemical and physical properties. It and the beryllides have great scientific and practical interest owing to the low neutron capture cross section of beryllium, their high melting points, relatively low specific gravities, hardness, high strengths at high temperature (ten times that of ceramics) and resistance to corrosion, these properties making them useful in aviation, rocket, and nuclear technology. This area of beryllium chemistry has recently been reviewed (*127, 413, 416, 461*), as also has the beryllium oxide system (*55, 99, 127*). Several articles (*25, 29, 31, 142, 347, 498*) cover various aspects of the organic chemistry of beryllium, and two books (*122, 139*) contain sections devoted to this topic. While Russian work on beryllium fluoride and the fluoroberyllates has been reviewed up to 1959 (*330*), these and the other halides have only been the subject, in recent years, of sections in Everest's book (*139*), covering many aspects of beryllium chemistry, and in a book devoted almost entirely to the analytical chemistry of beryllium (*333*). This present review deals with all the major aspects of the halide and pseudohalide chemistry of beryllium; the literature has been covered up to the middle of 1970. Beryllium fluorides and chlorides are important industrially, as intermediates in the preparations of metallic beryllium. Beryllium chloride has also been used in diagnosing tuberculosis; sodium beryllium fluoride has been used in the manufacture of glass having high ultraviolet permeability, as a flux in certain porcelain enamels, and in coating special welding rods.

Beryllium is normally divalent in its compounds, the first ionization potential ($Be^0 \rightarrow Be^+$) being 9.32 eV, the second ($Be^+ \rightarrow Be^{2+}$), 18.21 eV, and its standard electrode potential $E^\ominus_{Be^{2+}/Be}$, −1.70 volts. Although the atomic radius of beryllium is 0.93 Å, its ionic radius is only 0.31 Å; because of its high ionic potential of 6.45 (cf. 1.05 for the sodium ion), beryllium has a tendency to form covalent rather than ionic compounds. The ability of the group II elements to form complex ions is greatest with beryllium and thus it resembles aluminum in its chemistry rather than magnesium. Using the Pauling relationship, the percentage ionic character of the Be–X bond (where X = F, Cl, Br, I) is 80, 42, 35, and 25%, respectively (*264*). Thus the fluoride has considerable ionic character and forms no stable complexes with neutral ligands (L) of the type L_xBeF_2, but forms many stable anionic fluoride complexes. In contrast, the other three halides behave as though they are essentially covalent and form numerous stable complexes with neutral ligands. The Be–F bond is thermodynamically stable in aqueous solution because the bond energy is greater than that of Be–O, whereas the Be–X (X = Cl, Br, I) bond energies are less than for Be–O, hence thermodynamic instability. Because of these differences, beryllium fluoride is discussed separately from the other three halides.

Compounds containing beryllium–halogen bonds are extremely sensitive to moisture. Thus, some difficulty in handling these compounds exists and it is perhaps for this reason that variable melting points have been reported for some compounds and the authenticity of some compounds must be in doubt.

II. Beryllium Fluorides

A. ANHYDROUS BERYLLIUM FLUORIDE

1. *Preparation*

Beryllium fluoride cannot be isolated from aqueous solution since as for the other halides, hydrolysis takes place during dehydration with the formation of a thick syrupy liquid which continues to hydrolyze with the elimination of HF. A spongy mass of an oxyfluoride of indefinite composition is finally produced (*46*, *221*, *276*). The process discovered by Lebeau (*272*) as early as 1898, involving the thermal decomposition of ammonium tetrafluoroberyllate, is used most widely for the production of the anhydrous fluoride. Although decomposition takes place slowly at 125°,* in practice it is normally carried out at 900°–1100°, glassy BeF_2 being produced (*422*). The fluoride may also be obtained from $Be(OH)_2$ and HF (*4*, *272*) or from NH_4HF_2 and BeO, $Be(OH)_2$, or basic beryllium acetate (*2*, *237*, *314*, *315*, *390*, *518*). Fluorination of BeO with F_2 or ClF_3 gives poor results (*221*). The fluorination of beryllium sheet with F_2 follows a parabolic rate law and a protective coating of BeF_2 is produced (*357*); however, the equipment problem involved in the fluorination of BeO with HF makes this process unattractive (*3*, *221*, *237*). The product obtained from the digestion of BeO in 40% HF is low in fluorine content (*221*), further confirming that hydrolysis of BeF_2 readily takes place.

Sublimation at 1038° of BeF_2 at 1 mm pressure in the presence of 2% beryllium metal has been used for purification on a small scale, but this has not been so effective in large-scale preparations [experiments undertaken by the Brush Beryllium Co., quoted in (*313*)].

2. *Properties and Polymorphism*

Much of the work on beryllium fluoride has been carried out by the Russians Novoselova and co-workers in Moscow, and Toropov and Grebenshchikov in Leningrad.

Beryllium fluoride is a hygroscopic solid (*276*) existing in several crystalline forms and has low conductivity in the fused state (*269*, *324*), indicating that although more ionic in nature than the other halides, it still has considerable covalent character. Addition of alkali metal fluorides produces conducting materials which on electrolysis yield beryllium metal (*269*, *536*). It oxidizes when heated in an oxygen current,

---

* Temperatures are in °C except where otherwise stated.

forming the volatile compound $2BeO \cdot 5BeF_2$, and with water vapor, BeO and HF are formed; the pyrohydrolysis commences at 420° with a maximum reaction rate at 800°–1000° (*363*). Though slightly soluble in absolute ethanol, it is very soluble in ethanol–water solutions of high water content, but the solution process is slow (*276*). Further, it is only sparingly soluble in liquid HF (*225*), indicating that BeF_2 is a stronger base in HF than is $Be(OH)_2$ in water.

A variety of melting points have been ascribed to BeF_2, 542° ± 3° (*185*), 543° ± 5° (*408*), 545° (*87, 112, 447*), 821° (*341*), ca. 800° (*337, 446*), 590° (*337*), 545°–550° (*324*), 555° (*503*); boiling point, 1327° (*238*). The most recently quoted value of 555° (*503*) was obtained using very pure distilled BeF_2 and the melting behavior was confirmed by several methods. An inflection (*341, 446*) in the vapor pressure/temperature curve at ca. 800° was believed to be due to fusion of BeF_2, since it had earlier been noted that although BeF_2 softens at about 560°, it does not become free-flowing until ca. 800° (*87, 334, 350*). It has since been suggested that this inflection is indicative of depolymerization of BeF_2 to form a free-flowing liquid and that the true melting temperature is 555° (*503*).

The vapor pressure (*vp*) of BeF_2 has been measured by the flow (*185, 341, 446, 447*), torsion (*185, 210*), gravimetric (*185*), and manometric methods and by a differential variant of the Knudsen method (*53, 239*); the available data are somewhat discordant. At 627°, the *vp* is 0.0155 (*53*), 0.013 (*239*), and 0.019 mm (*210*); at 827°, 3.3 (*447*), 3.45 (*446*), ca. 5.0 (*185*), and 3.7 mm (*341*); and the partial pressure of Be_2F_4 in equilibrium with liquid beryllium fluoride at 627° is 8.8×10^{-6} mm (*53*). The constants in the vapor pressure equation $\log p_{\mathrm{mm}} = A - B/T$ (T in ° abs.) for BeF_2 are shown in Table I and for Be_2F_4 in the range 617°–704°, $A = 11.532$, $B = 14927$ (*53*).

The composition of the vapor has been determined qualitatively by mass spectrometry (*53, 58, 210*). Associated molecules are only minor constituents of the saturated vapor and the ion of highest molecular weight $Be_2F_3^+$, found in low abundance, indicates the presence of Be_2F_4 molecules. The saturated vapor at molecular effusion pressures has been estimated to contain less than 1 mole % Be_2F_4 (*210*).

The "model principle" has been used by Goldschmidt (*180*) to compare members of an isomorphous series in which structures are of the same type, even though the charge on corresponding ions or the ionic radii or both, are different. A common type of "model structure" is that in which the radii and polarizing properties of the ions in one structure are nearly the same as those in the second, but the charges on the ions in the two structures are not the same. The structure having the lower

TABLE I

VAPOR PRESSURE DATA FOR BeF_2 $\log p_{mm} = A - B/T$ (T in °abs.)

A	B	Temperature range (°C)	Ref.
11.596	12134	573–676	(*239*)
10.466	10943	802–1025	(*447*)
11.822	12385	740–803	(*446*)
10.651	11121	803–968	(*446*)
10.622	11189	542–704	(*53*)
11.125	11555	547–667	(*210*)
13.041	13762	767–821	(*341*)
9.904	10268	821–1002	(*341*)

charges is referred to as the weakened model and the other the reinforced model. As the fluoride ion has a radius nearly identical with that of the oxide ion but one-half the charge and similarly for the Be^{2+} and Si^{4+} ions, beryllium fluoride and silica, the fluoroberyllates and silicates show remarkable structural similarities. Beryllium fluoride thus behaves as a weakened model of silica, as demonstrated by the lower melting point, solubility, and hardness, and greater reactivity relative to SiO_2. Likewise, the fluoroberyllates behave as weakened models of the silicates, provided that the cations have similar ionic radii and polarizability and that the charge numbers on the cation in the fluoroberyllate is one-half that on the cation in the silicate; e.g., the $NaF–BeF_2$ system behaves as a weakened model of the $CaO–SiO_2$ system. The weakened character of the beryllium systems is due to the smaller electrostatic attractions resulting from the lower charge numbers of the ions relative to those in the silicate systems.

Like both silica and germania, BeF_2 has a radius ratio of about 0.3, a figure which Goldschmidt (*180*) believes will allow compounds of the AX_2 type to form glasses. Beryllium fluoride like silica has a tendency to supercool and is difficult to crystallize; rapid cooling of the melt produces vitreous BeF_2 (for further discussion, see Section II, C).

Silica exists in three crystalline forms: quartz (stable to 870°), tridymite (stable from 870°–1470°), and cristobalite (stable from 1470° to the melting point 1710°). Each of the polymorphic forms exists in two subsidiary forms, low (α) and high (β) temperature modifications with transition points at 573° for quartz, 120°–160° for tridymite, and 200°–275° for cristobalite. The structure of silica consists of a three-dimensional network of SiO_4 tetrahedra, joined so that each oxygen is common to two tetrahedra. The relationship between cristobalite and tridymite corresponds to that between zinc blende and wurtzite, although neither has a close-packed structure. In quartz, the tetrahedra are so linked that they acquire a spiral formation and this form is optically active. In each case, the α and β forms differ only by slight alteration in the disposition of the SiO_4 tetrahedra, and there is no difference in the way the tetrahedra are linked together. These alterations are thus easy to effect and are readily reversible.

By analogy with silica, the structures of the three crystalline forms of BeF_2 are presumably composed of BeF_4 tetrahedra. The quartz- and cristobalite-like polymorphs are well established and there is evidence for low and high temperature modifications. Our present knowledge of the stability ranges and transition points of the different forms leaves something to be desired, partly since the BeF_2 system is more difficult to study than the SiO_2 system owing to the sensitivity of the fluoride to moisture. Conversions between the crystalline forms are sluggish since they require bond rupture, followed by rearrangement, before the relinking of the BeF_4 units; such processes in the solid state are always slow. Russian workers, whose results up to 1959 are summarized in ref. (*330*), consider that the β-quartz form is the stable form at room temperature (corresponding to the α-quartz form of SiO_2) and this is transformed into the α-quartz form at ca. 220° (*334*, *409*). The α-quartz form when slowly heated is transformed at 420°–450° into what is possibly a tridymite form. At ca. 680°, this phase is converted to the α-cristobalite form of BeF_2 (corresponding to the β-cristobalite form of SiO_2), the β- to α-transformation of the cristobalite forms occurring at 130° (*334*). Decomposition of $(NH_4)_2BeF_4$ *in vacuo* below 450° produces the cristobalite modification (*89, 94*), which is also obtained by crystallization from glasses of high BeF_2 content at temperatures of 450° or lower and is converted into the quartz form by heating to high temperature (*410*). The quartz form is also obtained if $(NH_4)_2BeF_4$ is decomposed in a quartz crucible or when the decomposing mixture is fused toward the completion of the removal of NH_4F (*334*). The cristobalite form is partly inverted to the quartz form in 3 weeks at 340° or 430°, but persists in cristobalite form at 516° or above (*408*). The high temperature quartz form exists in equilibrium with liquid in binary fluoride systems up to the melting point of BeF_2, and the cristobalite form appears to have a metastable existence (*409*). During a study of the kinetics of the fluorination of beryllium sheet, it was noted that the α-quartz form is produced below 525°, but above this temperature the film has the rhombic tridymite structure (*357*). Further evidence for the existence of the tridymite form was obtained by heating BeF_2 in the presence of 4% ZrF_4 to 590°–600°

for several hours, and powder data indicate a close analogy between this and the tridymite form of SiO_2 (*253*). The quartz form of BeF_2 is hexagonal (*350*) and the cristobalite form has a tetragonal unit cell (*89*), like the low temperature form of cristobalite SiO_2. At 130°, this is transformed into a cubic structure, corresponding to the high temperature form of cristobalite SiO_2 (*240*).

In view of the above inconsistencies, the beryllium fluoride system requires further investigation before firm conclusions concerning the stability relations of the different crystalline forms can be safely drawn.

3. *Reactions*

In contrast to the other halides, complexes of beryllium fluoride with only one neutral ligand, namely, ammonia, are known. In 1927 Biltz and Rahlfs (*68*) obtained at −78.5° BeF_2NH_3 which decomposed at higher temperatures. The BeF_2 used in this preparation was probably contaminated with oxyfluoride as it was obtained from aqueous solution. However, BeF_2 prepared by a more reliable method, though sparingly soluble in liquid ammonia, forms the complex BeF_22NH_3, formulated as $[Be(NH_3)_4]^{2+}[BeF_4]^{2-}$ from spectroscopic data. Thermal decomposition proceeds at lower temperature than for the adduct of the corresponding chloride, but is not accompanied by appreciable ammonolysis. The first ammonia molecule is lost at 80°–130° and the second at 130°–150° (*191*).

Heating BeF_2 with B_2O_3 (*40*) produces Be_2FBO_3, isostructural with

$$2BeF_2 + B_2O_3 \rightarrow BF_3 + Be_2FBO_3 \qquad (1)$$

the mineral hambergite Be_2OHBO_3, whose structure (*560*) consists of BO_3 triangles and deformed BeO_4 tetrahedra involving three oxygen atoms and an OH group. The OH groups are bonded only to two beryllium atoms, while each of the oxygens surrounding a boron atom also belongs to two BeO_4 tetrahedra. Fusion of K_2BeF_4 with B_2O_3 at 600°–800° or KBF_4 and BeO at 550°–700° produces the water-insoluble double salt $KBe_2F_2BO_3$ (*40*).

$$2K_2BeF_4 + B_2O_3 \rightarrow KBe_2F_2BO_3 + BF_3 + 3KF \qquad (2)$$

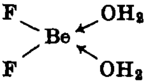
$$KBF_4 + 3BeO \rightarrow KBe_2F_2BO_3 + BeF_2 \qquad (3)$$

$$3KBF_4 + 3BeO \rightarrow KBe_2F_2BO_3 + 2BF_3 + K_2BeF_4 \qquad (4)$$

The solubility of BeF_2 in methanol increases with increasing HF concentration. At 25.15% HF, a solid phase, formulated as $[MeOH_2]^+[BeF_3]^-$, is obtained (*107*), but this compound has not been studied in detail. The complex molecule Be_2OF_2 has been identified by mass spectrometry in the BeO–BeF_2 system above 1327° (*137*).

B. Aqueous Chemistry of Beryllium Fluoride

The anhydrous fluoride is hygroscopic and very soluble in water (cf. SiO_2). Solutions of beryllium fluoride may also be obtained by dissolving the metal in hydrofluoric acid; the dissolution rate decreases linearly with decreasing acid concentration (*199*). Evaporation of these solutions leads to the elimination of HF with consequent formation of basic residues (*276*). The limiting solubility is ca. 18 moles/liter at 25° corresponding to a ratio of 2 moles of water per mole of BeF_2, hence the suggestion for the formation of the complex



in *saturated* solution (*256*, *276*). The existence of this complex is also supported by ^{9}Be magnetic resonance studies of *saturated* aqueous solutions of BeF_2; solutions at saturation are clear and viscous (*276*). Since aqueous solutions do not form a precipitate with calcium chloride, the low concentration of F^- in solution is demonstrated (ionization of BeF_2 in 1 and 2×10^{-4} *M* solutions has been estimated as 2 and 6%, respectively (*276*)). On addition of $BaCl_2$ solution, 50% of the beryllium is precipitated as $BaBeF_4$ and, thus, autocomplex formation is believed to take place in aqueous solution (*32*). However, ^{19}F NMR spectroscopy

$$2BeF_2 + 4H_2O \rightarrow [Be(H_2O)_4]^{2+}[BeF_4]^{2-} \qquad (5)$$

indicates that *dilute* solutions containing fluoride and beryllium in the ratio 2:1 contain BeF^+ and BeF_3^-, as well as the predominant (60%) species BeF_2 (*108*), all presumably solvated. Conductivity and emf data also support the presence of such species in *dilute* solutions of BeF_2 (*389*). Addition of ethylenediamine or triethanolamine to beryllium fluoride solutions precipitates beryllium hydroxide, leaving solutions from which the tetrafluoroberyllates $(H_2NCH_2CH_2NH_3)_2BeF_4$ or $[HN(CH_2CH_2OH)_3]_2BeF_4$ may be isolated (*32*). Passage of a beryllium fluoride solution through a hydrogen ion-exchange column produces a solution containing fluoroberyllic acid, H_2BeF_4 (*32*).

Beryllium fluoride (*276*), in contrast to the chloride (*32*, *200*), is a weak electrolyte in aqueous solution. Although all the aforementioned species are probably present in equilibrium in aqueous solutions of beryllium fluoride, if the autocomplex predominates, the weak electrolytic nature suggests the existence of hydrogen bonds between $[Be(H_2O)_4]^{2+}$ and $[BeF_4]^{2-}$ ions (*32*).

Conductometric measurements on $NH_4F/BeSO_4$ solutions have indicated the presence of the ions $[BeF_3]^-$, $[BeF_4]^{2-}$, $[BeF_5]^{3-}$, and $[BeF_6]^{4-}$ (*390*). Not surprisingly, later workers (*443*) have been unable to find evidence for the existence of these last two ions. The species $[BeF]^+$, BeF_2, $[BeF_3]^-$, and BeF_4^{2-} are present in solutions containing both beryllium and fluoride and the relative concentration of the ions depends on the F:Be ratio and on the pH (*443*, *490*); these ions are probably hydrated, e.g., $[BeF(H_2O)_3]^+$ (*489*) and $[BeF_3H_2O]^-$ (*140*). The particularly stable ion $[BeF_4]^{2-}$ is produced in the presence of excess fluoride (*396*) and evidence that the beryllium is present in the form of the complex anion has been obtained from the failure of $Be(OH)_2$ to precipitate on the addition of ammonia and by the concentration of beryllium at the anode on electrolysis (*414*). The formation of the stable tetrafluoroberyllates accounts for the ability of beryllium salts to solubilize sparingly soluble fluorides, e.g., Ca and Li, and to demask reaction systems which are masked by fluoride (*367*, *492*). No stable entity containing BeF^+ has yet been isolated.

The pH of a solution of HF increases in the presence of BeF_2 due to the formation of the fluoroberyllate ions (*488*). However, the pH of

$$BeF_2 + HF \rightarrow BeF_3^- + H^+ \tag{6}$$

$$BeF_3^- + HF \rightarrow BeF_4^{2-} + H^+ \tag{7}$$

an HF solution of beryllium chloride is lower than that of beryllium fluoride of the same concentration and the plot of pH against the ratio of HF to $BeCl_2$ shows a distinct bend at an HF:$BeCl_2$ ratio of 1:1 corresponding to either

$$BeCl_2 + HF \rightarrow BeClF + HCl \tag{8}$$

or

$$Be(aq)^{2+} + HF \rightarrow BeF^+ + H^+ \tag{9}$$

Stepwise formation constants (k) together with their method of determination for the beryllium–fluoride species are shown in Table II. Recent results obtained by measurements of the redox potential in the Fe^{3+}/Fe^{2+}–Be^{2+}/F^- system and of the pH in the $[BeF_4]^{2-}$–H^+ system at ionic strength 0.5 (*106*) and by a potentiometric method using a lanthanum fluoride solid state electrode (*297*) show substantial agreement. No evidence has been found for the presence of polynuclear species in solution, nor of species of composition $[Be_xF_y(OH)_z]^{(2x-y-z)+}$ (*297*). By a distribution procedure, the consecutive reaction constants K_n, defined as $[BeF_n][H^+]/[BeF_{n-1}][HF]$, have been determined: $\log K_1 = 1.99$, $\log K_2 = 1.12$, $\log K_3 = 0.32$ (*198*).

TABLE II

STEPWISE FORMATION CONSTANTS FOR BERYLLIUM SPECIES

$\log k_1$ (BeF^+)	Ref.	$\log k_2$ (BeF_2)	Ref.	$\log k_3$ (BeF_3^-)	Ref.	$\log k_4$ (BeF_4^{2-})	Ref.
3.64[d]	(*386*)	2.29[d]	(*386*)	1.83[d]	(*386*)	1.1[f]	(*140*)
4.29[a]	(*489*)	2.40[a]	(*493*)	2.788[c]	(*297*)	1.426[c]	(*297*)
4.71[c]	(*106*)	3.61[c]	(*106*)	2.80[c]	(*106*)	1.86[d]	(*386*)
4.90[c]	(*297*)	3.762[c]	(*297*)	2.97[c]	(*70*)	1.99[e]	(*243*)
5.06[c]	(*70*)	3.78[c]	(*70*)	3.56[e]	(*243*)	2.27[c]	(*106*)
5.40[b]	(*23*)	4.94[e]	(*243*)				
5.64[a]	(*493*)						
5.89[b]	(*243*)						

[a] Solubility.
[b] Spectrophotometrically.
[c] Potentiometrically.
[d] Ion exchange.
[e] Calculated.
[f] NMR.

Beryllium fluoride dissociates only slightly in solution (*243*, *276*, *488*, *489*, *490*, *493*) and not surprisingly behaves differently from other beryllium salts in solution. Hydrolysis in the BeF_2–NaOH system proceeds in two stages:

$$2BeF_2 + 2NaOH \rightarrow Na_2BeF_4 + Be(OH)_2 \tag{10}$$

$$Na_2BeF_4 + 2NaOH \rightarrow 4NaF + Be(OH)_2 \tag{11}$$

The formation of Na_2BeF_4 was confirmed by chemical analysis (*441*, *444*). This work invalidates Prytz's comments that the addition of NaOH lowers the solubility of BeF_2, but does not precipitate $Be(OH)_2$ (*388*, *389*). When the hydrolysis is carried out with carbonate or bicarbonate solutions, basic beryllium carbonates appear to be formed (*443*). Novoselova (*329*) has shown that $Be(OH)_2$, containing variable amounts of fluoride, begins to precipitate with NaOH from 0.1 M beryllium fluoride solution at pH 6 and is complete at pH 11.6–11.9 after 1.8 equivalents of alkali have been added, whereas precipitation from Na_2BeF_4 and $(NH_4)_2BeF_4$ begins only at pH 7.5–8.0. Precipitation of $Be(OH)_2$ from solutions of the fluoride takes place at higher pH than from solutions of other salts such as the chloride and sulfate (*329*). For sulfate solutions, precipitate begins to form at $n (= \text{NaOH}:\text{Be}) > 1$, but with dilute BeF_2 solutions, hydroxide appears at $n = 0.2$. At $n = 1$, 50%

of the beryllium is precipitated and as with the sulfate, precipitation is complete at $n = 1.8$. This suggests that at $n < 0.2$, the soluble basic salt $Be(OH)_xF_{2-x}$ is formed and from $n = 0.2$–1.8, the insoluble basic salt $9Be(OH)_2BeF_2$ is formed, and then with further addition of NaOH, a reaction occurs in the solid phase. This reaction is slightly reversible and

$$9Be(OH)_2BeF_2 + 2NaOH \rightarrow 10Be(OH)_2 + 2NaF \qquad (12)$$

a slight excess of NaOH is necessary for complete formation of $Be(OH)_2$, which dissolves to form beryllate as more NaOH is added. When an excess of fluoride is present in solution, much more than two equivalents of NaOH are necessary for complete precipitation (*491*). If a stoichiometric amount of ammonia is added to a BeF_2 solution, only 65% of the beryllium is precipitated. Complete precipitation of beryllium, even by 30% excess of NH_4OH, can only be attained if the F:Be ratio is at most 2. When this ratio is greater than 2, the amount of hydroxide precipitated decreases and when the F:Be ratio in the initial mixture is 6, no hydroxide is deposited. The quantity of beryllium precipitated by NH_4OH depends not only on the relative proportions of beryllium and fluoride in solution, but also on the absolute fluoride concentration (*329*, *451*).

C. Beryllium Fluoride and Fluoroberyllate Glasses

From X-ray diffraction studies (*547*), satisfactory agreement has been obtained between calculated and experimental scattering curves on the assumption of a random network structure for vitreous BeF_2 in which each beryllium is tetrahedrally surrounded by four fluorines and each fluorine in turn, is bonded to two beryllium atoms. Such a three-dimensional network is analogous to those found for vitreous silica and germania. Beryllium hydride is also amorphous (*27*, *204*) and it doubtless consists of a three-dimensional network similar to that of vitreous BeF_2, although in the case of the hydride, the bonding is likely to be electron-deficient in nature. Infrared spectroscopic measurements indicate the weakened structure of glassy BeF_2 relative to SiO_2 (*562*). The formation of halide glasses is uncommon and Zachariasen (*559*) has discussed the criteria for glass formation and Turnbull and Cohen (*513*) have explained, on the basis of kinetic considerations, the failure of some pure liquids to crystallize. The latter workers have shown that for a free-flowing liquid, free of nucleating singularities, crystallization will not take place if the kinetic barrier to nucleation exceeds, in the case of BeF_2, 48 $kcal \cdot mole^{-1}$. In a network liquid, interatomic bonding must be ruptured for flow to occur and in this case, the free energy of activation, estimated from viscosity data is ca. 50 kcal·mole^{-1}; thus glass formation is easily explained (*513*). The network structure is further supported by the high specific resistance and viscosity and the magnitude of the corresponding energies of activation of the liquid. Liquid BeF_2, like liquid SiO_2 and GeO_2, is highly associated, even at elevated temperatures. At a temperature 200° above the melting point, the energy of activation for viscous flow (E_Z) is greater than the heat of vaporization. The extrapolated viscosity at the melting point is at least 10^6 poise and the extrapolated E_Z at least 100 kcal·mole^{-1} (*278*). For most metal halides, at temperatures not far above the melting point, the viscosity is of the order 10^{-2} poise and E_Z seldom exceeds 10 kcal·mole^{-1} (*201*). The specific resistance is many orders of magnitude smaller than for most ionic halides (*278*) and this further demonstrates the structural differences between BeF_2 and the other halides. The low conductivity is somewhat surprising in view of the high ionic character of the Be–F bond.

Addition of alkali metal fluorides to molten BeF_2 causes a reduction in the viscosity, due to breaking of fluoride bridges, and therefore the degree of polymerization decreases. The stoichiometric end point for this process is at the composition M_2BeF_4 (*284*). There is also a corresponding increase in the electrical conductivity due to breaking down the network structure which also accounts for the positive enthalpies of mixing in LiF–BeF_2 mixtures (*216*).

On long standing in air, beryllium fluoride glasses become covered with a thin, cloudy film, as also do glasses containing only KF and BeF_2, but the addition of bivalent metal fluorides remarkably decreases the hygroscopicity of the glasses (*42, 224*). Whereas the BaF_2–BeF_2 system is characterized by an immediate crystallization of all its melts, the other alkaline earth fluoride systems show a tendency to form homogeneous glasses in the concentration range 0–30% for CaF_2 and MgF_2 and 0–10% for SrF_2 (*538*).

The fluoride glasses have a wide range of transmission without absorption (*408*), but contamination with BeO makes the glasses turbid (*537*). Beryllium fluoride is nontransparent for short wavelengths 30–220 mμ; with an increase in the wavelength the transparence of the glasses increases. Glass samples with a complex composition BeF_2–KF, BeF_2–KF–AlF_3, BeF_2–KF–MF_2 (M = Mg, Ca, Sr, or Ba), and BeF_2–KF–CaF_2–MgF_2 are transparent for all the wavelength regions mentioned. In the infrared, glassy BeF_2 is characterized by a region of transparency up to 5.5 μ, but is nontransparent from 5.5 to 15 μ (*42*). Fluoride glasses have low refractive indices, commonly lower than that of water (1.33), e.g., BeF_2 1.2747 (*378*), and the index increases for MF–BeF_2 glasses along the series Na < Li < K < Rb (*224, 537*). Although

BeF_2 is structurally and crystal chemically a complete analog of SiO_2, glasses on its basis have a higher percentage of ionic bonds than in silicate glasses and show a greater degree of ordering on solidification. In spectra of fluoroberyllate glasses, activated with rare-earths, more detailed resolution than for silicate glasses, similarly activated, may be the result of a more even ionic matrix or lower crystalline field strengths. The use of a beryllium fluoride glass matrix shows up a higher luminescence level ($^5D_1$), owing to the higher optical clarity and low dissipation of light on irradiation (*564*, *565*). The ESR spectra of some transition metal ions in fluoroberyllate glasses have been recorded (*1*).

D. ANHYDROUS FLUOROBERYLLATES

In the early work, great emphasis was given to general comparisons of fluoride and silicate systems, with principal interest in the structures of the intermediate compounds, rather than to precise determination of liquid–solid phase transitions, i.e., interest centered around the relationship of the fluoroberyllate systems to the silicate systems. As mentioned earlier, the fluoroberyllates and silicates show structural similarities, although there is considerable difference in melting points and hardness. The tetrafluoroberyllates (BeF_4^{2-}), analogous to the orthosilicates (SiO_4^{4-}), are the most stable fluoroberyllates, but neither sheet nor framework models are known. Beryllium fluorides cannot be handled in silica containers and special techniques and container materials are required for handling these materials (*216*, *240*); under an SiF_4 pressure, attack on silica by beryllium fluorides is considerably reduced (*26*).

For use in thermal breeder reactors, materials must satisfy stringent requirements with respect to their nuclear, physical, and chemical properties (*192*). Consequently, choice of useful solvents for fissile and fertile species is restricted to a very small number of inorganic fluorides of which ^7LiF–BeF_2 mixtures provide chemically stable fluids with excellent physical properties, low viscosity, vapor pressure, cross section, and melting temperature, and this system has gained preeminence as a solvent for fissile and fertile materials in the development of the molten salt reactor (MSRE) in the United States (*503*). The LiF–BeF_2 system has attracted the attention of many workers, but the results are diverse with respect to the liquidus, the existence of intermediate compounds formed by the components, and the polymorphism exhibited by the crystalline phases. Utilization of this as an ingredient in the MSRE has necessitated a restudy of this system and Thoma *et al.* (*503*) have published an excellent article on this system. Their phase results are shown in Fig. 1. The diversity in this system has been attributed to metastable nucleation or to exposure of the solutions to water vapor which causes hydrolysis.

$$2F^- + H_2O(g) \rightarrow O^{2-} + 2HF \qquad (12a)$$

The solubility of BeO in the melt is low (ca. 200 ppm) in the range 30–50 mole % BeF_2 at 600°–700° and the solubility increases with increasing BeF_2 content, but does not exceed 500 ppm (*212*, *450*). The reverse reaction, in which oxide impurities are removed from the melt by sparging with HF, has been used as a standard purification treatment (*448*).

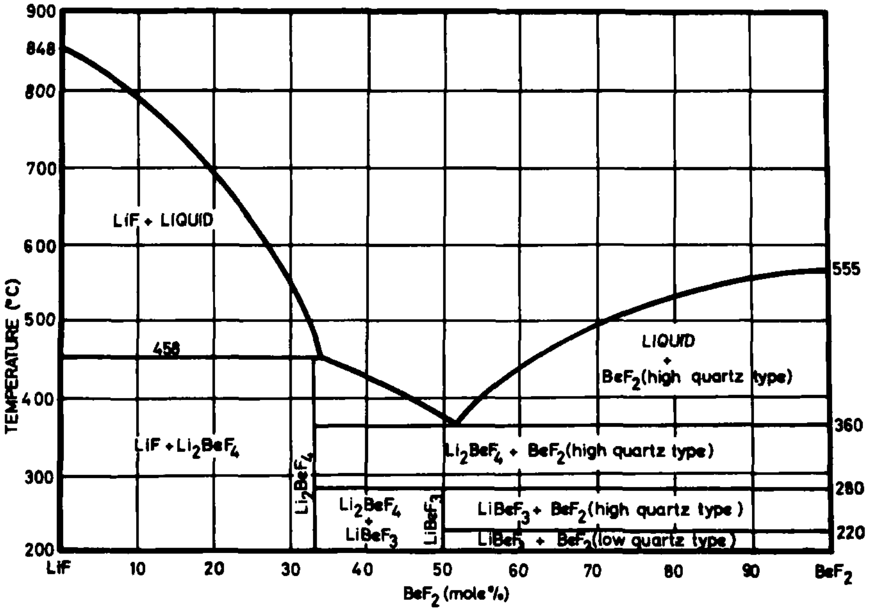


FIG. 1. The LiF–BeF_2 system [from (*503*), reproduced with permission].

Early claims (*348*, *350*, *500*) for the existence of Li_3BeF_5, $Li_3Be_2F_7$, Li_4BeF_6, and Li_5BeF_7 have not been substantiated and only Li_2BeF_4, $LiBeF_3$, and possibly $LiBe_2F_5$ exist (*410*, *503*). The trifluoroberyllate, m.p. 365° (*500*), is related to the pyroxene group (silicates in which SiO_4 tetrahedra share two corners to form long chains). Reports (*348*, *350*) that Li_2BeF_4 exists in three polymorphic forms have not been corroborated, nor does it melt congruently [(*410*), cf. (*408*, *500*)]. At 455°, a single crystal decomposes to a slurry of LiF and a liquid which coexist for the next 15°–20°; then above ca. 480°, the crystals dissolve in the melt, and the sequence is reversed on cooling (*503*). The LiF–BeF_2 system has been likened to the MgO–SiO_2 (*500*) and ZnO–SiO_2 (*408*) systems. Although Li_2BeF_4 was believed to resemble the silicates phenacite (Be_2SiO_4) (*197*, *348*, *410*, *558*), willemite (Zn_2SiO_4) (*197*, *408*, *410*, *558*), and forsterite (Mg_2SiO_4) (*408*, *410*), diffraction work clearly shows that the structure of Li_2BeF_4 is isotypic with that of Be_2SiO_4 (*105*). The structure (Fig. 2) consists of a chain of Li_2BeF_4 molecules, each metal ion being coordinated to four fluoride ions and these tetrahedra all share their corners to form a three-dimensional network (*105*). The average Be–F bond length is 1.55 Å, similar to the value of 1.57 Å found in $Li_6BeF_4ZrF_8$ (*423*). Owing to the difference in the Li–F and Be–F bond lengths, the tetrahedra are slightly distorted. The beryllium-containing ions BeF^+, $BeF_2{}^+$, $Be_2F_3{}^+$, and $LiBeF_2{}^+$ have been observed in the mass spectrum of an equimolar LiF–BeF_2 mixture; the binding energy of LiF to BeF_2 at ca. 630° is approximately 53 kcal·mole^{-1} (*58*).

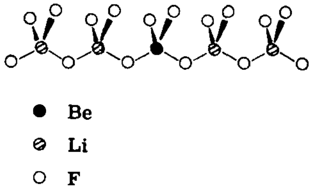


FIG. 2. Chain of tetrahedra along the C-axis of Li_2BeF_4 [from (*105*) reproduced with permission].

Molten mixtures of UF_4 and ThF_4, together with fluorides of alkali metals and BeF_2 or ZrF_4, are potential fuels for a fluid-fueled nuclear reactor that can operate at high temperature in low pressure systems (*504*, *549*), and certain molten fluoride mixtures are of value in the reprocessing of spent and therefore highly reactive elements for nuclear reactors (*39*). In connection with the utilization of such materials, equilibrium diagrams for the individual components and the binary and ternary mixtures have been obtained. In the BeF_2–MF_4 (M = Zr, Th, U) systems, compound formation has not been detected (*233*, *503*, *548*); eutectic points occur at 2 mole % ThF_4 and 0.5 mole % UF_4, indicating the comparatively low solubility of BeF_2 in melts of these fluorides (*233*, *548*) and the solubility of PuF_3 in fused alkali metal fluoride–BeF_2 mixtures is also quite low (*38*). Molten mixtures of BeF_2 and ThF_4 containing more than ca. 75% BeF_2 become very viscous at temperatures near the liquidus and equilibrium is reached only slowly, but the addition of small amounts of alkali metal fluorides reduces the viscosity, such that equilibrium is attained more rapidly (*504*). The phase boundaries for the $LiF–BeF_2–MF_4$ ($M = Th, U$) systems have been determined; no evidence has been obtained for the formation of ternary compounds (*504*, *506*) and in the $NaF–BeF_2–MF_4$ ($M = Th, U$) systems, the incongruently melting compounds $NaFBeF_23MF_4$ exist (*505*). The addition of BeO to fluoride melts causes precipitation of certain of the components as oxides, e.g., Pa, U, and Ce. Such reactions are of interest as a means of removing

$$2CeF_3 + 3BeO \rightleftharpoons Ce_2O_3 + 3BeF_2 \qquad (13)$$

reactor poisons from molten fluoride fuels, although BeO is an undesirable impurity. In fluoride melts, the order of affinity for oxygen is $UO_2 \sim ThO_2 > BeO > 1$. Thus it is possible to remove uranium from fluoride melts by passing it down a BeO column, where UO_2 is precipitated and held on the column; use of 30 gm of BeO per kg of molten salt ($LiF–BeF_2–ThF_4$) reduces the uranium in solution from 1800 ppm to less than 1 ppm (*449*).

The present version of a molten salt reactor (*279*) operates with a mixture of $^7LiF–BeF_2–ZrF_4$ as solvent and diluent for $^{235}UF_4$. Successful operation of this reactor, development of chemical reprocessing methods, and specification of safety practices dictate the need for accurate and detailed knowledge concerning crystallization and phase behavior in the $^7LiF–BeF_2–ZrF_4$ and $^7LiF–BeF_2–ZrF_4–^{235}UF_4$ mixtures. In the former system (*503*, *506*), in which the electrochemical oxidation of U(IV) has been studied (*281*), the complex compounds Li_2BeF_4, Li_2ZrF_6, Li_3ZrF_7, $Li_3Zr_4F_{19}$, and $Li_6BeF_4ZrF_8$ exist. The crystalline ternary compound, $Li_6BeF_4ZrF_8$, stable at room temperature, exhibits a property, uncommon among complex fluorides, in that the unit cell contains two discrete anion groupings, a tetrafluoroberyllate and an octafluorozirconate ion (*423*). These discrete ions are connected by a shared lithium ion and the lithium ions share fluoride ligands in such a way as to achieve a set of fluorine neighbors, best described as distorted octahedral. The Be–F distance is 1.57 Å and in the ZrF_8^{4-} dodecahedra, there are two independent Zr–F bonds (2.05 and 2.16 Å) (*423*). This complex compound melts semicongruently at 470° and undergoes no polymorphic transitions. In the subsystem $Li_2ZrF_6–BeF_2–ZrF_4$, the existence of three-component liquid immiscibility, not previously described in fluoride systems, has been observed (*503*).

The salts $NaBeF_3$, Na_2BeF_4, $NaBe_2F_5$, Na_3BeF_5, and $Na_3Be_2F_7$ are believed to exist in the $NaF–BeF_2$ system (*337*, *338*), which has been likened to the $CaO–SiO_2$ system (*197*, *409*, *502*), but the existence of $NaBe_2F_5$ has not been verified (*408*). There is little agreement about the melting behavior of these compounds (*337*, *338*, *502*). Only two modifications of $NaBeF_3$ have been identified, one having a structure similar to wollastonite (β-$CaSiO_3$) (*348*, *408*) below 343°, with only a slight difference in structure above that temperature (*409*). The existence of several structural modifications of Na_2BeF_4 has been established (*195*, *228*, *321*, *349*, *354*, *409*, *501*, *502*, *509*, *563*), but Thilo and co-workers (*228*, *501*) prepared Na_2BeF_4 in HF solution and their product was doubtlessly contaminated with fluorosilicates, and indeed $2Na_2BeF_4 \cdot Na_2SiF_6$ has since been obtained from which SiF_4 is eliminated at 540° to form Na_3BeF_5 (*499*). The basic structure for Na_2BeF_4 consists of a two-layer close-packed array of fluorine atoms, in which half the octahedral holes are taken by sodium atoms and a quarter of the tetrahedral holes by beryllium atoms (*195*). Na_2BeF_4 reacts with SiO_2 at ca. 730° forming phenacite (*332*); in the NaF–Na_2BeF_4–Na_3ZrF_7 system, only simple eutectics are present (*110*).

The partial pressure of BeF_2 and NaF above Na_2BeF_4, in the range 1008°–1197° is given by $\log p_{\mathrm{mm}} = 8.6881 - 10939/T$ for BeF_2 and $\log p_{\mathrm{mm}} = 8.4370 - 10623/T$ (T in °Abs.) for NaF, i.e., over the range studied, Na_2BeF_4 dissociates in the melt (*341*) only to an insignificant degree according to

$$Na_2BeF_4 \rightleftharpoons NaF + NaBeF_3 \tag{14}$$

Vapors above NaF–BeF_2 contain the complex molecule $(NaBeF_3)_2$, as well as NaF and BeF_2. The enthalpy of dissociation of the dimer is 51.1 ± 5 kcal·mole^{-1} and the standard heat and free energy of dissociation at 811° for the gas phase reaction $NaBeF_3 \rightarrow NaF + BeF_2$ are 63.1 ± 4 and 32.4 ± 2 kcal·mole^{-1}, respectively (*54*, *447*, *457*).

When equimolar melts of Na_2BeF_4 and Li_2BeF_4 are allowed to cool slowly, LiF starts to crystallize at 460°, and below 320° $Na_2LiBe_2F_7$ is formed. When a similar mixture is rapidly cooled from 550°–600° to below 240°, $NaLiBeF_4$ is formed (*226*) existing in a single modification and melting at 350° (*512*). The structure of $Na_2LiBe_2F_7$, which may also be obtained by heating $NaLiBeF_4$ above 240° or from NaF–LiF–BeF_2 (*226*, *408*), is similar to that of the melilite hardystonite, $Ca_2ZnSi_2O_7$ (*408*). Also present in the Na_2BeF_4–Li_2BeF_4 system is $Na_3Li(BeF_4)_2$, isotypic with merwinite, $Ca_3Mg(SiO_4)_2$ (*227*, *512*).

The existence of compounds $MBeF_3$, M_2BeF_4, MBe_2F_5 [M = K (*87*, *336*), Rb (*182*, *223*, *322*, *509*, *510*, *511*), Cs (*91*, *92*)], and M_3BeF_5 [M = K (*87*, *336*), Cs (*91*, *92*)] have been established in the MF–BeF_2 systems, some existing in several polymorphic modifications. Potassium tetrafluoroberyllate is isotypic with K_2SO_4 and Be_2SiO_4, having four molecules in the unit cell (*355*). The same basic structure persists for K_2BeF_4, Rb_2BeF_4, and Cs_2BeF_4 as for Na_2BeF_4, all similar to larnite, γ-Ca_2SiO_4, and olivine, (Fe, Mg)SiO_4, but slight deviations are found as the cation size increases (*10*, *164*, *195*, *321*). The tendency for bond formation between the cation and the fluorine valence orbitals increases as the cation size increases, accounting for the rising thermal stability of the tetrafluoroberyllates with increasing size of the cation (*10*). The Be–F distances in the alkali tetrafluoroberyllates are ca. 1.45–1.53 Å, which is slightly longer than that found from an electron diffraction study of BeF_2 vapor (*7*), corresponding to the change from *sp* hybridization in BeF_2 vapor to sp^3 hybridization in the tetrafluoroberyllate ion (*182*, *322*, *434*, *509*, *510*). The coordination numbers of the two cations (M_1 and M_2) in the tetrafluoroberyllates are shown in Table III (*10*, *164*).

TABLE III

COORDINATION NUMBERS OF THE CATIONS (M_1 AND M_2) IN M_2BeF_4

M	M_1	M_2
Na	6	6
K	8	8
Rb	6	8
Cs	10	8

A hindered motion of the BeF_4 group has been established in M_2BeF_4 (M = Na, K, Rb) in the range 10°–200° from ^{19}F magnetic resonance spectra of polycrystalline samples (*11*). Above room temperature, there is a reorientation of BeF_4 tetrahedra around the 3-fold axis, perpendicular to the plane of densest packing. This kind of movement above 70° changes to isotropic reorientation of the tetrahedra around the center of gravity. However, only in the cesium compound is the region of reorientation of the tetrahedra around the 3-fold axis, separate from the region of isotropic reorientation by a noticeable temperature interval (ca. 30°). The potential barrier for each kind of motion is 12.7 ± 0.5 and 14.5 ± 0.5, kcal·mole^{-1}, respectively (*9*).

The dimetafluoroberyllates (MBe_2F_5; M = Li, Na, K) decompose before melting, whereas the rubidium and cesium salts are stable (*330*). The structure of $RbBe_2F_5$ consists of compressed RbF_6 octahedra with almost ideal hexagonal symmetry. Between the layers of octahedra is a double network of BeF_4 tetrahedra, infinite in two directions (Fig. 3), corresponding to the Si–O network in the dimetasilicates, e.g., talc and micas, which have an infinite two-dimensional network of Si_2O_5 units (*222*, *223*).

The K_2BeF_4–K_2SO_4 system consists of a continuous series of solid solutions and of the respective α and β states of the two salts (*275*); in the KF–K_2BeF_4–K_3ZrF_7 (*280*) and KF–K_2BeF_4–LaF_3 (*112*) systems, neither Be–Zr- nor Be–La-containing compounds exist.

The two salts are completely miscible in the MgF_2–BeF_2 system, which plays an important role in the industrial production of beryllium. The system is like the TiO_2–SiO_2 system, especially in the absence of compound formation (*124*, *535*), quite surprising in view of the report that magnesium tetrafluoroberyllate can be isolated from aqueous solution (*376*).

Barium tetrafluoroberyllate exists in three modifications (*241*); the α-form has a rhombic lattice and is isostructural with the sulfate. The cell parameters agree well with those obtained for $BaBeF_4$ prepared in aqueous solution, and this compound has been examined as a possible host lattice for $RaBeF_4$ as a reproducible, controllable source of neutrons (*407*).

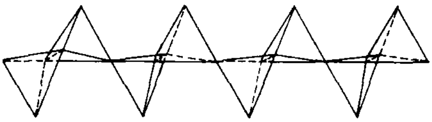


FIG. 3. x, z Projection of Be_2F_5 units in $RbBe_2F_5$. The beryllium units lie at the centers of the tetrahedra and the fluorine units at the vertices.

Strontium tetrafluoroberyllate exists in several modifications and forms a eutectic with SrF_2. When prepared by fusion of the components, the γ-modification is obtained, but when precipitated from aqueous solution, the β-form, which has high and low temperature forms, together with a small admixture of the γ-form is obtained (*93*). Evaporation of BeF_2 begins at 850° (*93*) and dissociation at 1010°–1145° occurs according to the equation:

$$SrBeF_4(\text{melt}) \rightleftharpoons SrF_2(\text{in melt}) + BeF_2(g) \qquad (15)$$

$$\log K_p\ (\text{mm}) = 4.6970 - \frac{6392}{T}\ (T \text{ in °abs.})$$

where the heat of dissociation is $29.0 \pm 3.0\ \text{kcal}\cdot\text{mole}^{-1}$ (*340*).

The CaF_2–BeF_2 system behaves as a weakened model of the MO_2–SiO_2 (M = Zr, Th) systems; the binary compound, $CaBeF_4$, formed in this system being a model for zircon ($ZrSiO_4$) [see also ref. (*197*)]. This tetrafluoroberyllate, which may also be obtained from aqueous solution (*398*), has a tetragonal lattice and melts incongruently as do the only compounds $MSiO_4$ (M = Zr, Th), formed in the above two systems (*124*).

Two compounds $3PbF_2 \cdot BeF_2$ and $PbBeF_4$ exist in the PbF_2–BeF_2 system (*410*), but these have not been studied in detail.

E. AQUEOUS CHEMISTRY OF THE FLUOROBERYLLATES

Contrary to chloroberyllates, many fluoroberyllates can be prepared in, and isolated from, aqueous solution. The tetrafluoroberyllates are the most stable and whereas the alkali metal and ammonium tetrafluoroberyllates may be obtained from aqueous solution, the dimetafluoroberyllates are generally only formed under anhydrous conditions. The ions BeF_4^{2-} and SO_4^{2-} are isoelectronic, isosteric, and similar in size; consequently, there is great similarity between sulfates and tetrafluoroberyllates (*376, 396, 397*). Barium tetrafluoroberyllate, isomorphous with the sulfate (*397*), is insoluble in water and is used for the gravimetric determination of beryllium (*136, 173, 437, 439*), and $CaBeF_4$ in its solubility behavior is like $CaSO_4$ (*303*). The sulfates and fluoroberyllates of Li, Rb, Cs, Tl, Ba, Ag, Pb, and NH_4 are known (*397, 414*) and the fluoroberyllates of K, Rb, Tl, and NH_4 are isomorphous among themselves, as well as with the corresponding sulfates (*37, 318*)

The acid, H_2BeF_4, from which other tetrafluoroberyllates are readily obtained, is known only in aqueous solution. Such solutions, which are fairly stable, are obtained by passage of BeF_2 down an ion exchange column (*32*) or by the reaction of Ag_2BeF_4 with HCl (*168*). Conductometric and pH titrations of solutions of the acid reveal inflections at points corresponding to the formation of $HBeF_4^-$ and BeF_4^{2-} (*167*).

The existence of $(NH_4)_2BeF_4$ and NH_4BeF_3 has been demonstrated in the NH_4F–BeF_2–H_2O system; the former may be obtained by dissolution of BeO or $Be(OH)_2$ in HF, followed by the addition of NH_4OH or $(NH_4)_2CO_3$ (*242, 331*) or by dissolving Be or BeO in NH_4F (*199*) or NH_4HF_2 (*422*). It is purified by recrystallization at low temperature, since it is very soluble in water at room temperature (*331*), although less soluble in propanol and butanol (*405*). The trifluoroberyllate is obtained from $(NH_4)_2BeF_4$ and BeF_2 and its solubility is greater than the tetrafluoroberyllate (*496*). Both ammonium fluoroberyllates exist in rhombic modifications, with four molecules in their unit cells; other modifications may exist as the diffraction data obtained for the rhombic modifications (*462*) differs from that of Thilo and Schröder (*502*). NMR studies (*140, 146, 254*) indicate that the fluoride ion is absent from aqueous solutions of $(NH_4)_2BeF_4$, that all the fluorine nuclei are equivalent, and that the tetrafluoroberyllate ion has a tetrahedral structure which has also been suggested for the solid from infrared and Raman measurements (*273, 297*). However, the NMR spectrum of the solid indicates that there are four structurally nonequivalent fluorine nuclei, located at the corners of a nearly true tetrahedron in the $(NH_4)_2BeF_4$ unit cell (*12*).

Thermal decomposition of $(NH_4)_2BeF_4$ takes place in three stages:

$$2(NH_4)_2BeF_4 \xrightarrow{-NH_4F} 2NH_4BeF_3 \xrightarrow{-NH_4F} NH_4Be_2F_5 \xrightarrow{-NH_4F} BeF_2$$

The intermediates have all been isolated and characterized (*94, 496*; cf. *502*). The dimetafluoroberyllate may also be obtained in solution by the reaction (*496*):

$$(NH_4)_2BeF_4 + 3BeF_2 \rightarrow 2NH_4Be_2F_5 \tag{16}$$

The salt $(NH_4)_2Mn(BeF_4)_2 \cdot 6H_2O$ is formed when NH_4BeF_3 and NH_4MnF_3 solutions are mixed (*43*); using $(NH_4)_2BeF_4$ instead of NH_4BeF_3, compound formation was not detected (*41*).

In the $NaF–BeF_2–H_2O$ system, the binary salts $NaBeF_3$, Na_2BeF_4, and $4NaF \cdot 3BeF_2 \cdot 2H_2O$ exist. The tetrafluoroberyllate may be recrystallized from water (*353*) in which it ionizes (*540*). The solubility of

$$Na_2BeF_4 \rightarrow 2Na^+ + BeF_4^{2-} \tag{17}$$

Na_2BeF_4 (*541*) is considerably reduced by the presence of NaF, whereas the solubility of NaF is little affected by Na_2BeF_4 (*328*). Other salts, $2Na_2BeF_4 \cdot NaHF_2$ (*102*), $3NaF \cdot 2BeF_2$, $5NaF \cdot 4BeF_2 \cdot 2H_2O$, and $4NaF \cdot 3BeF_2 \cdot 2H_2O$ (*100*) have been prepared as well as the previously mentioned mixed salts, $NaLiBeF_4$ (*512*), which has a structure (*226, 356*) similar to monticellite ($CaMgSiO_4$), and $Na_3Li(BeF_4)_2$ (*227*). The hydrate, $Li_2BeF_4 \cdot H_2O$, can be readily dehydrated at 100° (*397*).

In the $MF–BeF_2–H_2O$ systems (M = K, Rb), the solid phases $MBeF_3$, M_2BeF_4, and MBe_2F_5 are present. The tetrafluoroberyllates dissolve in water without decomposition, but the tri- and dimetafluoroberyllates decompose in water (*352, 397, 487*). Cesium tetrafluoroberyllate is more soluble in water than the corresponding potassium and rubidium salts (*397, 486*).

Calcium tetrafluoroberyllate dissolves in both water and hydrochloric acid without decomposition, the solubility increasing as the acidity increases. The solubility polytherms and structures of $CaSO_4$ and $CaBeF_4$ are similar (*303*). The magnesium analog is obtained from a soluble metal salt and a hot, nearly saturated solution of $(NH_4)_2BeF_4$, provided that the salt is not kept too long in the boiling solution; it decomposes quantitatively into MgF_2 and BeF_2 (*376*).

Several other tetrafluoroberyllates (see below) have been obtained from aqueous solution, in most cases containing the same number of water molecules as the corresponding sulfates. It is not known whether these compounds exist in more than one polymorphic form—$MBeF_4$ [$M = N_2H_5$, Pb (*397*), $(NH_3CH_2–)_2$, $NH_3CH(CH_3)CH_2NH_3$, $(NH_3C_6H_4–)_2$ (*168*)], $MHBeF_4$ [$M = Me_4N$ (*397*)], M_2BeF_4 [$M = Me_4N$, Ag, Tl (*397*), NH_3OH (*34*)], $MBeF_4 \cdot xH_2O$ [M = Ni, $x = 6, 7$ (*398, 497*); Co, $x = 4, 6, 7$ (*398*); Zn, $x = 7$ (*398, 497*); Fe, $x = 7$ (*398*), Cd, $x = 8/3$ (*398*), Cu, $x = 5$ (*398, 497*)], $M_2(BeF_4)_3$ [M = Al, Cr, $x = 18$ (*33, 171*); Fe, $x = 7$ (*36*)]. Many ammine complexes, e.g., $[Zn(NH_3)_4]BeF_4$, $[Ag(NH_3)_2]_2BeF_4$, and $[Co(NH_3)_4BeF_4]BeF_4$ have been prepared by Ray and his co-workers (*33, 169, 172, 175, 395, 402*).

The alums, $M_2^1 M_2^2 (BeF_4)_4 \cdot 24H_2O$ [M^2 = Al, $M^1 = NH_4$, K, Rb, Cs, Tl, N_2H_5, Me_4N, NH_3OH (*33, 34*); M^2 = Fe, M^1 = Rb, Cs (*36*); M^2 = Cr, $M^1 = NH_4$, H, K, Rb, Cs (*35, 170, 174*)] and schönite analogs, $M_2^1BeF_4M^2SO_4 \cdot 6H_2O$ [M^2 = Ni, Co, Zn, Fe, Mg, Mn, Cd, $M^1 = NH_4$; M^2 = Ni, Co, Cu, Zn, M^1 = K (*414*)] and $M_2^1M^2(BeF_4)_2 \cdot 6H_2O$ [$M^1 = NH_4$, M^2 = Cd, Co, Cu, Fe, Mn, Ni, Zn; M^1 = K, M^2 = Co, Ni; M^1 = Rb, M^2 = Cd, Co, Cu, Fe, Ni, Zn; M^1 = Cs, M^2 = Ni; M^1 = Tl, M^2 = Cd, Co, Cu, Ni, Zn (*43, 318, 399, 400, 401, 495*)] are obtained in aqueous solution and are isomorphous with the corresponding sulfates. A series of sulfatofluoroberyllates, $(NH_4)_2Cu(SO_4)_{2-x}(BeF_4)_x \cdot 6H_2O$, $0 \leqslant x \leqslant 2$, have also been obtained (*495*) and in the $(NH_4)_2BeF_4–H_2SO_4–H_2O$ system, evidence has been obtained for the existence of $(NH_4)_2BeF_4 \cdot H_2SO_4$, $3(NH_4)_2BeF_4 \cdot H_2SO_4$, and $(NH_4)_2BeF_4 \cdot 3H_2SO_4$ (*135*).

The close analogy between sulfates and fluoroberyllates is further exemplified by the similar ferroelectric behavior of some fluoroberyllates and sulfates. Ammonium tetrafluoroberyllate (*374*) and the sulfate (*292*), with which it is isomorphous at room temperature (*318*), become ferroelectric below the Curie points, $-97°$ and $-49.5°$, respectively. At these temperatures, phase transitions appear, but the direction of the spontaneous polarization ferroelectric axis in the sulfate is at 90° to that in the fluoroberyllate (*362*) and the Curie–Weiss constants are very small compared to those of other ferroelectrics (*358*). Structural changes occurring in the vicinity of the ferroelectric transition points are accompanied by only small changes in proton magnetic absorption. The two compounds have similar absorption lines at room temperature, but entirely different ones at low temperature, and this may be due to the ferroelectric phases not being isomorphous (*362*). Above $-180°$, no line-width transition is found, showing that the hydrogen bonds, $N–H \cdots F$ are weak. Splitting of some bands in the infrared at temperatures below the Curie point indicates deformation of BeF_4^{2-} and NH_4^+ ions, but the distortion is so small that it does not result in any significant redistribution of electron density in the Be–F bonds (*77*) and the phase transition is not accompanied by a change in the parameters of the H · · · F–Be bond (*12*). A necessary but not sufficient condition for a solid to be ferroelectric is the absence of a center of symmetry (*77*), and the presence of hydrogen bonds are essential in the polarization of some ferroelectrics.

Triglycine fluoroberyllate $(CH_2NH_2COOH)_3H_2BeF_4$ is also ferroelectric (*375*), like the sulfate and selenate (*291*). Substitution of BeF_4^{2-} for SO_4^{2-} in the triglycine salts raises the Curie temperature from 47° in the sulfate (22° in the selenate) to 73° (*552*) in the fluoroberyllate; the values of spontaneous polarization are of the same order of magnitude. The transition energies and entropy changes for transitions to the ferroelectric phase are, for the sulfate, 0.15 $\mathrm{kcal \cdot mole^{-1}}$ and 0.48 $\mathrm{cal \cdot mole^{-1} \cdot degree^{-1}}$, and for the fluoroberyllate, 0.40 $\mathrm{kcal \cdot mole^{-1}}$ and 1.17 $\mathrm{cal \cdot mole^{-1} \cdot degree^{-1}}$ (*218*). Triglycine fluoroberyllate has been doped with both Cs_2BeF_4 and Tl_2BeF_4 in order to prepare a habit-modified salt; but irrespective of crystalline habit, the Curie temperature is 73°. Crystalline imperfections, introduced during growth, are distributed anisotropically and have a marked effect upon the dielectric and ferroelectric polarization process (*552*).

The formation of complex fluoroberyllate oxalates has been indicated by the increased solubility of ammonium and alkali metal oxalates in beryllium fluoride solutions. From these solutions, hydrated salts $M_2[BeF_2C_2O_4]\cdot xH_2O$, which are also obtained from beryllium oxalate and alkali metal fluoride solutions, have been isolated. Analogous compounds containing malonate, salicylate, formate, acetate, or chloroacetate groups have not been obtained (*440*, *445*). Thermal decomposition at ca. 400° of the alkali metal oxalatofluoroberyllates yields the tetrafluoroberyllate, the oxalate, and BeO [cf. (*249*)]. At higher temperatures, the oxalate decomposes too, and the resulting carbonate reacts with fluoroberyllate to form the alkali metal fluoride and BeO (*101*).

$$\begin{tikzcd} \mathrm{2K_2[BeF_2C_2O_4]\cdot H_2O} \arrow[r, "160^\circ"] & \mathrm{2K_2[BeF_2C_2O_4]} \arrow[r, "360^\circ"] & \mathrm{[K_2BeF_4 + K_2C_2O_4] + BeO + CO + CO_2} \arrow[dl, "400^\circ"] \\ \mathrm{4KF + BeO + CO_2} & \mathrm{[K_2BeF_4 + K_2CO_3] + CO} \arrow[l] & \end{tikzcd} \qquad (18)$$

The formation of monohydroxytrifluoroberyllates and basic beryllium fluoroberyllates, described by Mitra and Ray (*306–311*), Sen-Gupta (*442*), and Pascal (*370*), has been the subject of some controversy. Sen-Gupta (*438*) has pointed out inherent discrepancies in this work and disputes the formation of some of these compounds. Kolditz and Bauer

(*249*) believe that the monohydroxytrifluoroberyllates are really tetrafluoroberyllates and that the preparative method described by Pascal (*370*) for the preparation of one of these compounds, utilizing KF, BeF_2, and $Be(OH)_2$ in the ratio 4:1:1, proceeds in the manner:

$$8KF + 2BeF_2 + 2Be(OH)_2 \rightarrow 3K_2BeF_4 + Be(OH)_2 + 2KOH \qquad (19)$$

Although Mitra (*306*) interpreted his results from the thermometric titration of K_2BeF_4 with NaOH as indicating the formation of K_2BeF_3OH, Sen-Gupta (*438*) states that in the hydrolysis of BeF_4^{2-} with NaOH, $Be(OH)_2$ is precipitated according to

$$K_2BeF_4 + 2NaOH \rightarrow Be(OH)_2 + 2KF + 2NaF \qquad (20)$$

III. Beryllium Chlorides, Bromides, and Iodides

A. ANHYDROUS SYSTEMS

1. *Preparation*

Beryllium halides* are deliquescent and cannot be obtained from their hydrates, since on heating or on reaction with $SOCl_2$ or $COCl_2$, hydrolysis occurs with consequent formation of basic halides (*17*, *18*, *205*, *436*, *544*). A variety of methods are available for the preparation of the halides and the most convenient are by heating beryllium in a stream of dry halogen (*5*, *19*, *24*, *160*, *219*, *231*, *302*, *393*, *555*) or hydrogen halide (*158*, *181*, *215*, *219*, *393*, *430*) at 400°–600°. Reductive halogenation procedures of the oxide have been extensively employed using carbon and halogen (*56*, *141*, *214*, *289*, *298*, *379*, *380*, *419*, *474*, *508*, *553*), carbonyl halide (*84*, *111*, *285*, *286*, *418*, *419*), or carbon tetrachloride (*160*, *289*, *300*, *346*, *474*) and using beryllium carbide and halogen or hydrogen halide (*215*, *231*, *271*, *285*, *298*). Ether solutions containing mainly solvated beryllium halides are obtained by the reaction of beryllium metal with halogen or hydrogen halide in ether (*17–19*, *516*, *521*, *524*). The equilibrium for the reversible reaction lies over to the left except

$$BeO + 2HCl \rightleftharpoons BeCl_2 + H_2O \qquad (21)$$

at very high temperatures (*60*, *473*) and although beryllium chloride is also formed from BeO and sulfur (*88*, *289*) or phosphorus chlorides (*289*), these reactions are less favorable; the halides have also been obtained by metathesis (*109*, *118*, *271*, *430*).

---

* In Section III, the use of the word halide refers only to the chloride, bromide, and iodide.

2. *Properties*

The halides, which are insoluble in benzene (*555*) and usually only dissolve in solvents with which they react, may be isolated and purified by sublimation as colorless, crystalline needles, extremely sensitive to moisture and susceptible to oxidation on heating (*144, 160, 393, 430, 553*). Silicon tetrahalides and BeO are formed when beryllium halides are heated in glass apparatus (*160, 187, 215, 219, 397, 465*).

$$2BeCl_2 + SiO_2 \rightarrow 2BeO + SiCl_4 \qquad (22)$$

A variety of melting and boiling points have been ascribed to the halides (see tabulation below).

Halide	M.p. (°C)	B.p. (°C)	d_4^{25} (gm/ml)
$BeCl_2$	399.2[a] (*160*), 404 (*418*), 405 (*144, 393*), 410 (*432*), 416 (*244*), 425 (*264*), 440 (*271*)	482.3[b] (*160*), 488 (*393*), 510 (*264*), 520 (*473*)	(α'-modification), 1.899 (*214, 264*), 1.901 (*298*)
$BeBr_2$	487 (*144*), 488 (*393*), 490 (*271*), 506–509 (*430*)		(α-modification), 3.465 (*285, 430*)
BeI_2	480 (*144, 393*), 510 (*271*)		(α-modification), 4.325 (*298, 430*)

[a] Average of 20 results spread over an 8° range. Numbers underlined are considered most reliable.

[b] Average of 12 results spread over a 3° range.

Data on the density and thermal coefficient of cubic expansion of $BeCl_2$ have been summarized by Klemm *et al.* (*244–246*). The fused chloride is a poor conductor of electricity (*66, 69, 282, 539*); the specific conductance at 451° is about one-thousandth that of sodium chloride (*539*).

The chloride, which is isomorphous with SiS_2 and Me_2Be, has four $BeCl_2$ molecules in the orthorhombic unit cell. Its structure (Fig. 4)

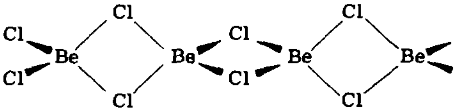


FIG. 4. The structure of solid $BeCl_2$.

consists of continuous chains with essentially tetrahedral configuration about each beryllium atom (*411*). The Cl–Be–Cl bond angle is 98.2°, which is less than the tetrahedral bond angle, as is also found for SiS_2 (*104*), instead of more (114°) as in Me_2Be (*472*), indicating all the bonds in $BeCl_2$ contain electron pairs with each chlorine atom using nearly pure *p* orbitals, i.e., $BeCl_2$ is not electron deficient. The Be–Cl distance is 2.02 Å [sum of covalent radii, 1.84 Å (*371*)]. The chains pack rather like circular cylinders with the Cl–Cl distance between chains about 3.85 Å (*411*).

Electron diffraction studies (*7*, *8*) on BeX_2 (X = F, Cl, Br, I) showed two radial distribution peaks which were interpreted as Be–X and X–X distances in the monomeric species (Table IV). No evidence for the presence of Be_2X_4 or BeX was found. The monomeric species are linear and, as expected, there is a shortening of the Be–Cl distance in going from the solid to the vapor, corresponding to the change from sp^3 to sp hybridization [see also (*434*)]. The Be–X distance is considerably less than the sum of the ionic radii, but approximates to the sum of the covalent radii; hence this must be regarded as direct confirmation that the Be–X bonds have a low degree of ionic character. Interatomic distances for MX_2 (M = Group II metal, X = F, Cl, Br, I) are given in references (*7*, *8*).

TABLE IV

INTERATOMIC DISTANCES IN BeX_2

X	Be–X (Å)	X–X (Å)	$\Sigma_{\text{covalent radii}}$ (Å)	$\Sigma_{\text{ionic radii}}$ (Å)
F	1.40	2.80	1.61	1.71
Cl	1.75	3.51	1.84	2.16
Br	1.91	3.84	1.99	2.30
I	2.18	4.22	2.23	2.51

$BeCl_2$ exhibits several polymorphic transitions (*264*), but only the fibrous (α′) modification, formed on sublimation, has been studied to any appreciable extent [see (*411*)]. The $BeCl_4$ tetrahedra can be packed in ways other than linear chains to form different polymorphic modifications with small heat changes and, consequently, with very small rates of mutual conversion. On heating freshly sublimed $BeCl_2$, the exothermic effects at 250° and 340° correspond to monotropic polymorphic transitions and the endothermic effect at 405° to an enantiotropic transition. During cooling of the melt, only one exothermic effect, corresponding to solidification of the liquid, was observed. When previously fused $BeCl_2$ is repeatedly heated, only one enantiotropic transition is detected at 405°, besides the fusion effect. On rapid cooling of the melt or on crystallization of the gaseous phase, a metastable α'-modification arises which on subsequent heating, is converted at 250° into a cubic β'-modification and at 340° into a β-form which is orthorhombic, like the α'-modification:

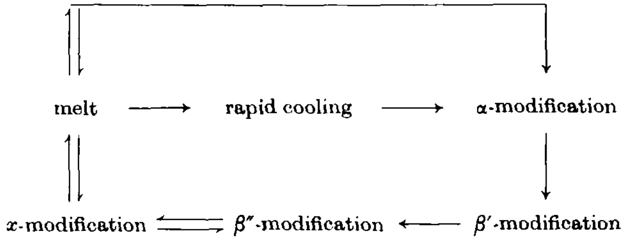
$$\alpha'\text{-}BeCl_2 \xrightarrow{250^\circ} \beta'\text{-}BeCl_2 \xrightarrow{340^\circ} \beta\text{-}BeCl_2$$

On slow cooling of the melt,

$$\text{Melt} \xrightleftharpoons{425^\circ} \alpha\text{-}BeCl_2 \xrightleftharpoons{405^\circ} \beta\text{-}BeCl_2$$

It is possible that the structure of the α- and α'-modifications are identical (*264*).

Freshly sublimed bromide (α-modification) does not undergo any polymorphic conversion up to the melting point. This modification, like the α-modification of the iodide, is isostructural with the α'-form of $BeCl_2$ (*430*). Several forms of BeI_2 are known (*231*, *430*) which are stable in different temperature intervals.



The presence of these modifications of the beryllium halides may well account for the variety of melting points which have been found for them.

There is ample evidence for association in the vapor phase. The vapor of the iodide contains dimeric molecules; the equilibrium constants for the dimer–monomer equilibrium are 53.3 at 766° and 19.5 at 636° and the heat of dissociation is 14.8 kcal·mole^{-1} (*252*). The bromide is also associated in the vapor (*393*), but accurate data regarding its composition are not known. The data on the vapor composition of the chloride are somewhat confusing and should be treated with caution. The vapor is calculated to contain 23% dimer at 562° (*393*), whereas at 500°, it is presumed to consist largely of dimer, and calculations from Brewer's data (*95*) show only monomer is present at 1000°. Büchler and Klemperer have found evidence for associated species, which they have suggested are dimers (Fig. 5), from spectroscopic studies of the vapor (*103*). Mass spectra studies (*412*) of the vapor composition, over the narrow temperature range 223°–305°, indicate dimer as well as monomer to be present. The dimer fraction under these conditions is 0.5–1.5% of the total number of molecules and increases with temperature, but it has since been pointed out that the possible contribution to the $BeCl_2^+$ peak, due to fragmentation of the dimer, was neglected (*247*). Transpiration studies combined with torsion–effusion experiments show the composition of the vapor over solid $BeCl_2$ contains 65% dimer at 198° and 90% at 410°, although a correction had to be applied in this work owing to the presence of water in the solid which was weighed out in air (*247*). A statistical analysis of torsion–effusion data indicates essentially monomeric species are present at effusion pressures at 197°–237° (*187*). Vapor pressure data for the halides are shown in Table V.

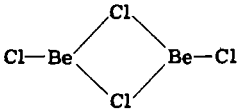


FIG. 5. Beryllium chloride dimer.

TABLE V

VAPOR PRESSURE DATA FOR BERYLLIUM HALIDES

$\log p_{\text{mm}} = A - B/T$ (T in °abs.)

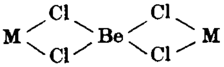
Halide	A	B	Temperature range (°C)	Ref.
$BeCl_2$	11.61	6564	340–405	(*393*)
	10.64	5908	405–460	(*393*)
	11.83	7200	167–327	(*187*)
	11.83	7260	197–237	(*187*)
	11.559	7093	187–231	(*211*)
$BeBr_2$	11.68	6564	351–422	(*393*)
BeI_2	10.64	5908	305–430	(*393*)

The anhydrous halides may be reduced to the metal in varying degrees of purity by Li, Na, K, Mg, or Ca (*237*, *271*, *419*), but only the fluoride reduction by magnesium (*236*, *316*, *422*, *534*) and, less widely, electrolysis of chloride melts (*419*, *553*, *554*) are of industrial importance. Reduction of BeI_2 with hydrogen (*215*), its thermal decomposition (*252*, *299*, *465*, *533*), and electrodeposition from a variety of solutions of beryllium halides are not satisfactory sources of the metal (*83–86*, *220*, *555*). Electrolysis of $BeCl_2$–alkali metal chloride systems proceeds in two stages: (1) primary deposition of Be on the cathode, and (2) secondary deposition of the metal by electrically produced alkali metal (*261, 262*). The introduction of fluoride anions into chloride melts displaces the beryllium equilibrium potential by 0.6–0.8 volts compared with that in chloride electrolytes. This suggests a considerable strengthening of the bond between beryllium and the anion on going from Be^{2+}–Cl^- to Be^{2+}–F^- (*469*).

3. *Halide Complexes*

The relative strength of halide complexes is as expected if the complex formation were due to essentially electrostatic forces. In such cases, strong bonds should be formed by ligands combining slight polarizability with small ionic radii. These factors decrease monotonically from I^- to F^- and, therefore, the sequence of halide complexes is shown to be $F^- \gg Cl^- > Br^- > I^-$ (*6*). Whereas fluoroberyllates are known both in aqueous solution and in the solid state, owing to hydrolysis, chloroberyllates are formed only under anhydrous conditions, while neither bromo- nor iodoberyllates are known, perhaps for steric reasons.

The phase diagram of NaCl–$BeCl_2$ indicates the existence of Na_2BeCl_4, isostructural with the sulfate, like one of the modifications of Na_2BeF_4 (*427, 563*). The tetrachloroberyllate undergoes a polymorphic transformation at 221°, marked by a sharp volume change, but without evident change of crystal structure; the existence of a metastable phase, $NaBeCl_3$, has been established (*160, 418, 432*). The ion $BeCl_4^{2-}$ is believed to be present in fused MCl–$BeCl_2$ ($M = K$, Cs) mixtures (*263, 468*), but evidence has been obtained for the presence of both anionic and cationic beryllium complexes in the fused NaCl–$BeCl_2$ system (*129*). Lithium and sodium tetrachloroberyllates differ from the potassium analog in crystal structure and thermal stability. Potassium tetrachloroberyllate crystallizes with the ionic type of lattice of K_2SO_4, whereas the structure of Na_2BeCl_4 can be regarded as intermediate between the predominantly ionic structure of K_2BeCl_4 and the molecular lattice containing bridging units of the type



There is some distortion of the $BeCl_4^{2-}$ tetrahedra in the tetrachloroberyllates on going from the sodium to the lithium salt (*260, 433*), although the symmetry of $BeCl_4^{2-}$ differs little from tetrahedral (*427, 428*). The Be–Cl stretching force constant is 1.81×10^5 dynes·cm^{-1} and the bond length (1.89 Å) in the isolated $BeCl_4^{2-}$ ion (*427*) is considerably less than the bond length (2.02 Å) in crystalline $BeCl_2$ (*411*), in which all the chlorine atoms form bridge bonds and are essentially divalent.

TABLE VI

$BeCl_2$–METAL HALIDE PHASE SYSTEMS

Metal halide	Eutectic temperature	Composition of eutectic	Complex formed in system
LiCl	300	56	Li_2BeCl_4
NaCl	215	51	Na_2BeCl_4
AgCl	235	40	None
TlCl	370	18	Tl_2BeCl_4 and $TlBe_2Cl_5$
	ca. 300	55	
	ca. 350	85	
$MgCl_2$	—	—	Solid solution formed with possible isodimorphism
$CdCl_2$	327	85	None
$CaCl_2$	355	85	Inconclusive
$BaCl_2$	372	87	$BaBeCl_4$
$PbCl_2$	292	47	None

A summary of $BeCl_2$–anhydrous metal chloride phase systems (*418*) is given in Table VI. Vapor over $BeCl_2$–$AlCl_3$ mixtures contain the species $BeAlCl_5$ (Fig. 6) and $Be_2Al_2Cl_{10}$ (Fig. 7) (*431*).

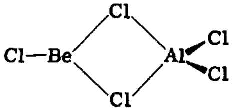


FIG. 6. The $BeAlCl_5$ structure.

The addition of hydrogen halide to ethereal beryllium chloride solutions produces the liquid complexes $HBeCl_2X{\cdot}2Et_2O$ (X = Cl, Br);

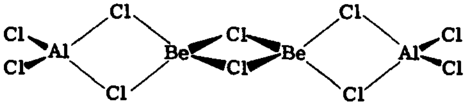


FIG. 7. The $Be_2Al_2Cl_{10}$ structure.

pyridine displaces the ether molecules yielding the corresponding pyridine complexes. The compounds are formulated as $[D \cdots H \cdots D]^+$-

$[BeCl_2X]^-$ (D = pyridine, ether; X = Cl, Br) (*304*), like the similar compounds formed by the halides of Zn, Cd, Hg, Al, Ga, In, Tl, and Sb (*161–163*).

B. AQUEOUS CHEMISTRY OF THE HALIDES

All the anhydrous halides dissolve in water with considerable heat evolution, forming solutions containing the hydrated beryllium ion, which may also be obtained from Be or BeO and dilute acids (*81*, *248*). Viscosity, freezing point, and conductivity data show the beryllium ion is more strongly hydrated than ions of other bivalent metals, which is in accordance with the large heat of solution of $BeCl_2$ and its small volume contraction when dissolved (*155*, *208*, *456*). The strong hydration of the beryllium ion can be partly explained by its formation of coordinate links with water molecules, the coordinate links being formed by donation of the electrons of the oxygen lone-pairs into vacant sp^3 beryllium orbitals (Fig. 8). Ions such as Ba^{2+} do not form such bonds; the solvation forces here are ion–dipole and electrostatic in origin.

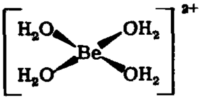


FIG. 8. The $[Be(H_2O)_4]^{2+}$ ion.

The solubility of $BeCl_2$ in water increases with temperature (*72*, *274*), but decreases in solutions of HCl and LiCl (*351*), whereas the presence of NH_4Cl does not appreciably affect its solubility (*343*). NaCl, KCl, and $AlCl_3$ are readily salted out of aqueous solution by $BeCl_2$ (*73*, *74*). The coordination number of the beryllium ion in solution is about 4; the lifetime of water molecules in the first coordination sphere of the Be^{2+} ion at room temperature is approximately 3×10^{-4} sec (*143*). The structure of beryllium chloride and bromide in concentrated aqueous solutions are thought to consist of polymeric chains of varying complexity (*78*, *79*). However, because $BeCl_2$, unlike BeF_2, is a strong electrolyte in solution (*200*, *265*, *391*), it is therefore likely that such solutions will also contain ionic species of the type $[Be(H_2O)_4]^{2+}$, as described earlier.

The solid hydrate, $BeCl_2 \cdot 4H_2O$, which is extremely hygroscopic and stable up to 70°, is obtained by concentration of aqueous beryllium chloride solutions. Partial hydrolysis of the hydrated salt or an aqueous solution of the salt, takes place with HCl evolution (*20*, *125*, *274*, *301*, *368*, *556*). Other workers (*436*), who were only able to obtain $BeCl_2 \cdot 4.5H_2O$, suggested that as a greater number of ligands were attached to beryllium than corresponds to its coordination capacity, such compounds must be formed as a result of inclusion of excess ligand into the cavities in the crystal lattice of the 1:2 compound, analogous to the inclusion compounds formed by urea with hydrocarbons. In view of the difficulty in obtaining $BeCl_2 \cdot 2H_2O$ (*274*), it is quite likely that the tetrahydrate can be formed containing the tetraaquoberyllium(II) ion which is present in the structure of $BeSO_4 \cdot 4H_2O$ (*45*, *126*, *459*). The ease of hydrolysis increases from the fluoride to the iodide; consequently, although $BeBr_2 4H_2O$ has been isolated, the corresponding iodide could not be obtained (*125*).

Basic chlorides, e.g., $BeCl_2 \cdot Be(OH)_2 \cdot 3H_2O$ and $BeO \cdot BeCl_2 \cdot 5H_2O$, are formed by heating $BeCl_2 \cdot 4H_2O$, by dissolving $Be(OH)_2$ in concentrated HCl solution, and by evaporation of aqueous solutions of beryllium chloride containing excess beryllium ions (*369*, *392*, *544*). Compounds in which ether molecules replace water molecules in the beryllium halide hydrates and the basic hydrates have also been reported, e.g., $[Be(H_2O)_3Et_2O]Cl_2$, $[Be(H_2O)_2(Et_2O)_2]I_2$, and $5Be(H_2O)_3$(dioxane)-$Cl_2 \cdot Be(OH)_2$ (*125*, *368*, *435*, *545*), but these have not been investigated in detail.

Hydrolysis of the Be(II) ion has been extensively studied, polynuclear species being formed. The addition of alkali to beryllium solutions causes precipitation to begin when $OH{:}Be > 1$, for the halides, precipitation is complete when OH:Be is 2, and for the sulfate and nitrate when the ratio is ca. 1.8–1.9, i.e., the deposit contains some of the oxoanion. The formulas of the soluble complex ions, several having the general formula $[Be_n(OH)_n]^{n+}$ (*293*), formed on hydrolysis, are in some doubt. Be_2O^{2+} (*176*, *387*, *388*), $Be(OH)^+$ (*359*, *387*), $Be_2(OH)_2^{2+}$ (*359*, *387*), $Be_3(OH)_3^{3+}$ (*59*, *234*, *290*, *296*, *359*, *360*, *417*, *455*), Be_2OH^{3+} (*59*, *234*, *296*, *359*, *455*), $Be_5(OH)_7^{3+}$ (*296*), $Be(OH)_2$ (*59*, *234*, *359*, *455*), and $Be_4O_2^{4+}$ or $Be_4(OH)_4^{4+}$ (*415*) have all been suggested and, in some cases, formation constants have been derived. The main hydrolysis product in aqueous (*59*) and dioxane–water (*359*, *360*) solutions is $Be_3(OH)_3^{3+}$, doubtlessly solvated (Fig. 9) (*234*), together with $Be_2(OH)^{3+}$; but there is disagreement over the contribution due to $Be(OH)_2$.

There is no evidence for the existence of anionic chloroberyllate complexes in aqueous solution, analogous to fluoroberyllates, from electrochemical measurements (*389*) or from solubility isotherms of $BeCl_2$–metal halide–water systems (*72–76*, *84*, *335*, *343*, *351*, *391*). However, from anion exchange experiments in chloride media, it has been proposed that the beryllium exists in the form of $BeCl_3^-$ in such solutions and from both the elution behavior on cation exchange resins and the distribution of beryllium between HCl and phosphoric acid esters, it has also been suggested that polynuclear cationic chloroberyllium complexes are also formed in solution (*82, 132, 198, 251, 257, 361*).

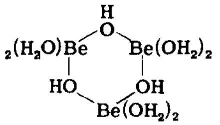


FIG. 9. The solvated $[Be_3(OH)_3]^{3+}$ ion.

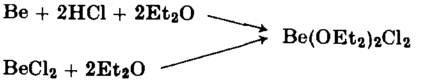
In the compounds $BeX_2 \cdot HgX_2 \cdot 5H_2O$, $Be(OH) \cdot HgX_3 \cdot 2H_2O$ ($X = Cl$, Br), $3Be(OH) \cdot 12HgI_2 \cdot 6H_2O$ (*475*), $2BeCl_2 \cdot M_2Cl_6 \cdot 2H_2O$ ($M = Fe$, Cr), and $3BeCl_2 \cdot 2TlCl_3$ (*325*), the beryllium is more likely to be in the form of a cationic species than an anionic halide complex.

C. COORDINATION COMPLEXES

The beryllium halides are Lewis acids and form many coordination compounds with oxygen-, sulfur-, and nitrogen-containing donor molecules. Usually only two ligands coordinate to beryllium, the beryllium–halogen covalent bond remaining intact, but with strong donors having small steric requirements, ionization of the beryllium–halogen bond takes place and the tetracoordinated Be(II) ion is formed. The known complexes of the halides are listed in Table VII, together with some of their properties.

1. *Oxygen and Sulfur Complexes*

The hydrate, ether–hydrate, and dioxane–hydrate complexes have been discussed earlier (Section III,B). Beryllium halide–diethyletherate systems have been extensively studied and have been the subject of several publications by the Russian workers Turova, Novoselova, and Semenenko. Beryllium chloride reacts exothermically with anhydrous ether, forming a two-phase solution from which colorless crystalline prisms of the bisetherate are deposited on cooling or evaporation of the solvent (*460*). This compound (*521*) and the analogous dimethyletherate



$$\left.\begin{array}{l} Be + 2HCl + 2Et_2O \\ BeCl_2 + 2Et_2O \end{array}\right\} \longrightarrow Be(OEt_2)_2Cl_2 \qquad (23)$$

m.p. 43° (*521, 522*), 43°–44.5° (*323*)

b.p. 105°–110° dec. (*522*)

TABLE VII

BERYLLIUM HALIDE AND PSEUDOHALIDE COORDINATION COMPLEXES[a]

Complex	M.p. (°C)	Properties	Solubility	Ref.
Dichloro adducts				
$Be(H_2O)_4Cl_2$	96	Colorless hygroscopic prisms	s(a)	(*125, 274*)
$Be(H_2O)_{4.5}Cl_2$	—	Orthorhombic tablets evolving HCl on heating	s(a)	(*402*)
$Be(H_2O)_3(Et_2O)Cl$	—	Colorless needles	—	(*125*)
$Be(H_2O)_4(Et_2O)$-$Cl_2 \cdot 0.25HCl$	—	Deliquescent acicular crystals	—	(*435*)
$5Be(H_2O)_3(dioxane)$-$Cl_2 \cdot Be(OH)_2$	—	Colorless hygroscopic crystals	s(a)	(*545*)
$Be(Me_2O)_2Cl_2$	63–64 dec.	Colorless hygroscopic crystals	s(b)(c)(d)	(*524*)
$[Be(Et_2O)Cl_2]_2$	116–118	Colorless needles	s(c)	(*97*)
$Be(Et_2O)_2Cl_2$	43–44.5	Colorless crystalline prisms	s(c)(e)	(*21, 149, 323, 460, 521, 522, 555*)
$Be(Et_2O)_3Cl_2$	—	Colorless acicular crystals stable in Et_2O solution below −2°	s(e)	(*522*)
$Be(THF)_2Cl_2$	150	Colorless needles	s(c)(f)	(*425, 520*)
$Be(THF)_3Cl_2$	—	Solid, stable below −2°	—	(*520*)
$Be(THP)_2Cl_2$	161	White needles	s(c)(f)	(*524*)
$Be(dioxane)Cl_2$	—	White deliquescent crystalline solid	s(g); ss(c)(e)(h)	(*342, 524*)
$Be(PhOMe)_2Cl_2$	—	White hygroscopic needles	s(a)(c)(e)	(*153*)
$Be(Cl(CH_2)_4OMe)_2Cl_2$	—	Colorless rods	s(e)	(*24*)
$Be(MeOC_2H_4OMe)Cl_2$[b]	237–244 dec.	White crystalline hygroscopic solid	i(c)(e)(j)	(*118, 524*)
$Be(Me_2CO)_2Cl_2$	—	Colorless crystals	—	(*154*)

$Be(Me_2CO)_2Cl_2 \cdot 4C_6H_6$	—	Colorless crystals	s(g)	*(154)*
$Be(Ph_2CO)_2Cl_2$	—	Colorless needles	s(e)	*(153)*
$Be(PhCHO)_2Cl_2$	—	White microcrystalline hygroscopic solid	s(g)(k); ss(c)(e)(l)(m)	*(149)*
$Be(PhCH{:}CHCHO)_2Cl_2$	—	White hygroscopic needles, $\mu = 7.33$ D	s(c)	*(153, 229)*
$Be(HCOOEt)_2Cl_2$	—	Viscous liquid	—	*(295)*
$Be(MeCOOMe)_2Cl_2$	—	White crystalline solid	—	*(295)*
$Be(MeCOOEt)_2Cl_2$	—	White solid	—	*(295)*
$Be(MeCOOPr^n)_2Cl_2$	—	Colorless viscous liquid	—	*(295)*
$Be(MeCOOPr^i)_2Cl_2$	—	White crystalline solid	—	*(295)*
$Be(MeCOOBu^n)_2Cl_2$	—	Light brown viscous liquid	—	*(295)*
$Be(MeCOOBu^s)_2Cl_2$	—	Brown viscous liquid	—	*(295)*
$HBeCl_3(Et_2O)_2$	—	Green liquid, fumes in air	—	*(304)*
$HBeCl_2Br(Et_2O)_2$	—	Green liquid, fumes in air	—	*(304)*
$BeCl_2 \cdot 3POCl_3$	58–58.5	White prisms	s(c)(e)(n)	*(527)*
$Be(S_2N_2O)Cl_2$	288–301	Yellow solid	—	*(28)*
$BeCl_2 \cdot GaCl_3 \cdot 3Et_2O$	61	White solid	s(e)	*(426)*
$BeCl_2 \cdot AlCl_3 \cdot 3Et_2O$	55	White solid, $\mu = 6.29$ D	s(e)	*(514, 515)*
$[Be(Me_2S)Cl_2]_2$	135	Colorless prisms	s(c)	*(118)*
$Be(Me_2S)_2Cl_2$	55, 117–119	White hygroscopic crystalline solid	s(c)(e)(f)(p)	*(118, 464)*
$Be(Me_2S)_3Cl_2$	—	White needles, stable below 5°	—	*(464)*
$Be(MeSC_2H_4SMe)Cl_2$	—	Colorless needles	ss(c)	*(118)*
$Be(Et_2S)_3Cl_2$	—	White needles at low temp., liquid at room temp.	—	*(464)*
$Be(Bu^i_2S)_3Cl_2$	—	White needles at low temp., liquid at room temp.	—	*(464)*
$Be(quinoline)_2(H_2O)Cl_2$	—	Colorless hygroscopic needles	—	*(404)*
$Be[CO(NH_2)_2]_4Cl_2$	213–214	White solid	—	*(385)*
$Be(PhCONH_2)_2Cl_2$	107–109	White solid	—	*(385)*

(continued)

TABLE VII—*continued*

Complex	M.p. (°C)	Properties	Solubility	Ref.
$Be[o\text{-}C_6H_4(OH)NH_2]_2Cl_2$	—	Dark brown solid	i(c)(d)(e)	*(384)*
$Be[m\text{-}C_6H_4(OH)NH_2]_2Cl_2$	—	Ash-colored solid	i(c)(d)(e)	*(384)*
$Be[o\text{-}C_6H_4(COOH)NH_2]_2Cl_2$	—	Light pink solid	i(c)(d)(e)	*(384)*
$Be[m\text{-}C_6H_4(COOH)NH_2]_2Cl_2$	—	Brown solid	s(a); i(c)(d)(e)	*(384)*
$Be[p\text{-}C_6H_4(NO_2)NH_2]Cl_2$	—	Yellow solid	s(g)	*(384)*
$Be[o\text{-}C_6H_4(OMe)NH_2]_2Cl_2$	—	Light gray solid	—	*(381)*
$Be[p\text{-}C_6H_4(OMe)NH_2]_2Cl_2$	—	Light gray solid	—	*(381)*
$Be[o\text{-}C_6H_4(OEt)NH_2]_2Cl_2$	—	Light gray solid	—	*(381)*
$Be[p\text{-}C_6H_4(OEt)NH_2]_2Cl_2$	—	Light gray solid	—	*(381)*
$Be[-C_6H_3(OMe)NH_2]_2Cl_2$	—	Ash solid	—	*(381)*
$Be(cocaine)_2Cl_2$	—	Colorless crystals	s(a)	*(364)*
$Be[CS(NH_2)_2]_2Cl_2$	—	Yellow hygroscopic solid	—	*(385)*
$Be(PhNHCSNH_2)Cl_2$	—	Light yellow solid	—	*(385)*
$Be(o\text{-}tolyl\text{-}NHCSNH_2)Cl_2$	—	Light pink solid	—	*(385)*
$Be(m\text{-}tolyl\text{-}NHCSNH_2)Cl_2$	—	Light pink solid	—	*(385)*
$Be(p\text{-}tolyl\text{-}NHCSNH_2)Cl_2$	—	Light pink solid	—	*(385)*
$Be(PhNHCSNHPh)Cl_2$	—	Light yellow solid	—	*(385)*
$Be(o\text{-}tolyl\text{-}NHCSNH\text{-}o\text{-}tolyl)Cl_2$	—	Pink solid	—	*(385)*
$Be(m\text{-}tolyl\text{-}NHCSNH\text{-}m\text{-}tolyl)Cl_2$	—	Pink solid	—	*(385)*
$Be(p\text{-}tolyl\text{-}NHCSNH\text{-}p\text{-}tolyl)Cl_2$	—	Pink solid	—	*(385)*
$Be(NH_3)_4Cl_2$	—	Colorless hygroscopic crystals	—	*(57, 67, 149, 301)*
$Be(NH_3)_xCl_2$	—	$x = 12$, 6, and 2	—	*(57, 67, 301)*
$BeCl_2 \cdot Be(NH_2)_2 \cdot xNH_3$	—	Colorless solid	ss(q)	*(57)*

$BeCl_2 \cdot 2NH_3 \cdot Me_2CO$	—	Solid, poor analysis	—	(*149*)
$Be(MeNH_2)_4Cl_2$	—	White powder	—	(*149*)
$Be(Me_3N)_2Cl_2$	—	White solid	—	(*381*)
$Be(Me_3N)_{1.5}Cl_2$	171–174	White solid	—	(*97*)
$Be(Et_2NH)_2Cl_2$	—	White crystalline needles	—	(*153*)
$Be(Bu^nNH_2)_2Cl_2$	—	Colorless microscopic crystals	s(c)(e)(l)	(*153*)
$Be(en)_2Cl_2$	—	White powder	—	(*150*)
$Be(PhNH_2)_2Cl_2$	—	Crystalline needles	s(k)	(*149*)
$Be(PhNMe_2)_2Cl_2$	—	Green solid	—	(*281*)
$Be(PhNEt_2)_2Cl_2$	—	Pink solid	—	(*281*)
$2BeCl_2 \cdot 3Ph_2NH$	—	Pink crystals	—	(*281*)
$Be(PhNHEt)_2Cl_2$	—	Light yellow solid	—	(*281*)
$Be(\alpha\text{-}C_{10}H_7NH_2)_2Cl_2$	—	Light ash solid	—	(*281*)
$Be(\beta\text{-}C_{10}H_7NH_2)_2Cl_2$	—	Light ash solid	—	(*281*)
$Be(p\text{-}CH_3C_6H_4NH_2)_2Cl_2$	—	Yellow needles	s(a)(g)(k); ss(c)(e)	(*153*)
$Be(m\text{-}CH_3C_6H_4NH_2)_2Cl_2$	—	Light gray solid	—	(*281*)
$Be(o\text{-}CH_3C_6H_4NH_2)_2Cl_2$	—	Light red needles	s(g)(k)	(*151*)
$Be(PhCH_2NH_2)_2Cl_2$	—	White solid	—	(*381*)
$Be[Ph(PhCH_2)NH]_2Cl_2$	—	Gray solid	—	(*381*)
$Be[Ph(Et)(PhCH_2)N]_2Cl_2$	—	Brown solid	—	(*381*)
$Be[(CH_2)_6N_4]_2Cl_2$	—	Colorless acicular crystals, $d_4^{20} = 1.23$	—	(*196*)
$Be[p\text{-}C_6H_4(NH_2)_2]Cl_2$	—	Dark red solid	—	(*381*)
$Be[1,2\text{-}C_{10}H_6(NH_2)_2]Cl_2$	—	Violet solid	—	(*381*)
$Be[p\text{-}C_6H_4(NEt_2)NH_2]Cl_2$	—	Black solid	—	(*381*)
$Be[p\text{-}C_6H_4(NEt_2)NH_2]_2Cl_2$	—	Black solid	—	(*381*)
$Be(PhNHNH_2)_3Cl_2$	—	White hygroscopic solid	s(g)(k)	(*149*)
$Be(PhNHNH_2)_4Cl_2$	—	Yellowish solid	—	(*150*)
$Be(pyridine)_2Cl_2$	152	White crystals	—	(*97, 153, 154*)
$Be(piperidine)_2Cl_2$	—	Microcrystalline white solid	—	(*148*)
$Be(\alpha\text{-picoline})_2Cl_2$	—	White crystals	ss(c)(g)	(*148*)

(*continued*)

TABLE VII—*continued*

Complex	M.p. (°C)	Properties	Solubility	Ref.
$\mathrm{Be(lepidine)_2Cl_2}$	—	White hygroscopic solid	s(g); ss(c)(e)	(*153*)
$\mathrm{Be(quinoline)_2Cl_2}$	—	Yellow solid	s(g); ss(c)(e)	(*151*)
$\mathrm{Be(quinaldine)_2Cl_2}$	—	White microcrystalline solid	s(g)(l); ss(e)(h)(l)	(*148*)
$\mathrm{Be(2,2'\text{-}bipyridyl)Cl_2}$	—	Colorless needles, dec. > 330°	ss(e)	(*117*, *118*)
$\mathrm{HBeCl_3(pyridine)_2}$	108	White crystals	—	(*304*)
$\mathrm{HBeCl_2Br(pyridine)_2}$	115	White crystals	—	(*304*)
$\mathrm{Be(1\text{-}phenyl\text{-}3\text{-}methyl\text{-}pyrazolone)_2 \cdot (Et_2O)_2Cl_2}$	—	White microcrystals; little evidence this is a pure compound	—	(*148*)
$\mathrm{Be(HCN)_4Cl_2}$	—	White prisms	s(a)(g)	(*151*)
$\mathrm{Be(C_2H_4(CN)_2)Cl_2}$	—	White hygroscopic solid	s(c)(e)	(*151*)
$\mathrm{Be(MeCN)_2Cl_2}$	—	Colorless crystals	—	(*154*)
$\mathrm{Be(EtCN)_2Cl_2}$	—	Colorless hygroscopic prisms	s(c)(e)	(*151*)
$\mathrm{Be(EtCN)}_x\mathrm{Cl_2}$	—	$x = 2, 3, 4, 5, 7$	—	(*152*)
$\mathrm{Be(Me_2CHCH_2CH_2CN)}_x\mathrm{Cl_2}$	—	Silvery lustrous flakes	s(c)(e)(g)	(*151*)
$\mathrm{Be(Me_2CHCH_2CH_2CN)}_x\mathrm{Cl_2}$	—	$x = 2, 3, 4$	—	(*152*)
$\mathrm{Be(PhCN)_2Cl_2}$	—	Colorless needles	s(e)(g)(k)	(*154*)
$\mathrm{Be(PhCH_2CN)_2Cl_2}$	151.5	White needles	s(c)(e)	(*151*, *153*)
$\mathrm{Be(}p\mathrm{\text{-}MeC_6H_4CN)_2Cl_2}$	—	Colorless crystals	s(e)(g); ss(c)	(*151*)
$\mathrm{Be(}p\mathrm{\text{-}MeC_6H_4CN)}_x\mathrm{Cl_2}$	—	$x = 2, 3, 4, 5, 7$	—	(*152*)
$\mathrm{Be(\alpha\text{-}C_{10}H_7CN)_2Cl_2}$	—	Yellow crystals	s(e)(g)	(*151*)
$\mathrm{Be(PhNO_2)_2Cl_2}$	—	Colorless crystals	s(g)(k); ss(c)(e)(l)	(*149*)
$\mathrm{Be(8\text{-}nitronaphthylamine)_2Cl_2}$	—	Orange solid	ss(d)(g)(h)(l)	(*148*)
$\mathrm{Be(2,4\text{-}dinitrophenylhydrazine)Cl_2}$	—	Chocolate solid prepared at 100°	—	(*384*)
$\mathrm{Be(2,4\text{-}dinitrophenylhydrazine)_2Cl_2}$	—	Chocolate solid prepared at 0°	—	(*384*)

Monochloro adducts				
$[Be(OBu^t)Cl]_4$	—	White solid, decomp. from 170°	s(e)(c)	(*14*)
$[Be(OBu^t)(Et_2O)Cl]_2$	88–90	Colorless crystals	s(c)	(*14*)
$[Be(OBu^t)(THF)Cl]_2$	—	Colorless crystals	—	(*14*)
$Be(OEt)Cl \cdot 0.7CH_3COOEt$	—	Viscous liquid	—	(*295*)
$Be(OPr^i)Cl \cdot 0.5CH_3COOPr^i$	—	Viscous liquid	—	(*295*)
EtBe(2,2′-bipyridyl)Cl	—	Orange-yellow solid dec. 167°	ss(e)	(*47*)
$[Bu^tBe(Et_2O)Cl]_2$	79–80	Colorless needles	s(c)(e)	(*204, 406*)
$[(p\text{-tolyl})_2C{:}NBeCl]_2$	168–170	Colorless crystals	—	(*484, 543*)
$[(p\text{-tolyl}(Bu^t)C{:}NBeCl]_2$	160–165 dec.	Colorless crystals	—	(*484, 543*)
$[Ph_2C{:}NBeCl]_2$	120–121	Crystalline solid	s(f)	(*484, 543*)
$\{Be[o\text{-}C_6H_4(NH_2)O–]Cl\}_2$	—	Black solid	—	(*384*)
$\{Be[m\text{-}C_6H_4(NH_2)O–]Cl\}_2$	—	Dark ash solid	—	(*384*)
$[Be(o\text{-}C_6H_4NH_2COO–)Cl]_2$	—	Light ash solid	—	(*384*)
$[Be(m\text{-}C_6H_4NH_2COO–)Cl]_2$	—	Light brown solid	—	(*384*)
Dibromo adducts				
$Be(H_2O)_4Br_2$	—	Prismatic hygroscopic crystals	—	(*125*)
$Be(H_2O)_3(Et_2O)Br_2$	—	Light yellow crystals	—	(*125*)
$Be(Me_2O)_2Br_2$	70–72 dec.	Hygroscopic yellow crystals, sensitive to oxygen and light	—	(*516*)
$Be(Et_2O)_2Br_2$	49, 53	Colorless rhomboidal crystals, four molecules in unit cell	—	(*323, 425, 521, 523, 532*)
$Be(Et_2O)_3Br_2$	—	Stable below −4°	—	(*523*)
$Be(THF)_2Br_2$	130 dec.	Flat crystalline tablets	—	(*516*)
$Be(dioxane)Br_2$	—	Colorless solid	s(g); ss(c)(e)(h)	(*342*)
$Be(CH_3COOEt)_2Br_2$	—	Brown viscous liquid	—	(*295*)
$Be(H_2S)_2Br_2$	—	Dissociation pressure 24.5 mm at −20	—	(*64*)
$Be(NH_3)_4Br_2$	—	Colorless crystals	—	(*57, 67*)
$Be(NH_3)_xBr_2$	—	$x = 6, 10$	—	(*67*)

(*continued*)

TABLE VII—*continued*

Complex	M.p. (°C)	Properties	Solubility	Ref.
$BeBr_2 \cdot 3Be(NH_2)_2 \cdot 4NH_3$	—	White crystals	ss(q)	(*57*)
$BeBr_2 \cdot 3Be(NH_2)_2 \cdot 8NH_3$	—	White crystals	—	(*57*)
$2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$	—	White crystals	s(q)	(*57*)
$Be(2,2'\text{-bipyridyl})Br_2$	—	Pale cream solid	ss(e)	(*117*, *118*)
Monobromo adducts				
$HBeCl_2Br(Et_2O)_2$	—	Green liquid, fumes in air	—	(*304*)
$HBeCl_2Br(\text{pyridine})_2$	115	White crystalline solid	—	(*304*)
$[Be(OBu^t)(Et_2O)Br]_2$	—	Colorless crystals	s(c)(e)	(*14*)
$[Be(OBu^t)(THF)Br]_2$	—	Colorless crystals decomp. 230°	s(e)	(*14*)
$Be(OEt)(CH_3COOEt)Br$	—	Brown viscous liquid	—	(*295*)
$[Bu^tBe(Et_2O)Br]_2$	55–56	Colorless needles	s(c)(e)	(*406*)
Diiodo adducts				
$Be(H_2O)_2(Et_2O)_2I_2$	—	Brown solid, poor analysis	—	(*125*)
$Be(Me_2O)_2I_2$	—	Pale brown solid	—	(*516*)
$Be(\text{dioxane})I_2$	—	Pale yellow solid	—	(*516*)
$Be(4\text{-aminoantipyrine})_2I_2$	—	Light yellow solid	—	(*133*)
$Be(H_2S)_2I_2$	—	Not fully characterized	—	(*64*)
$Be(NH_3)_xI_2$	—	$x = 4, 6, 13$	—	(*67*)
$2BeI_2 \cdot 3NH_3$	—	Crystalline solid	s(q)	(*271*)
$BeI_2 \cdot 3Be(NH_2)_2 \cdot 4NH_3$	—	Crystalline solid	s(q)	(*57*)
$BeI_2 \cdot 5Be(NH_2)_2 \cdot 4NH_3$	—	Colorless crystals	s(q)	(*57*)
$Be(2,2'\text{-bipyridyl})I_2$	—	Yellow solid	ss(e)	(*117*, *118*)

Monoiodo adducts				
$[Be(OBu^t)(Et_2O)I]_2$	—	Colorless crystals, dec. from 120°	s(c)(e)	(*14*)
$[Be(OBu^t)(THF)I]_2$	167–168 dec.	Colorless crystals	s(c)	(*14*)
Pseudohalide adducts				
$Be(4\text{-aminoantipyrine})_2(SCN)_2$	—	Pale yellow solid	s(a)(k)	(*133*)
$Be(Et_2O)_2(SCN)_2$	37–38	White acicular crystals	s(c)(e)(g)(k)	(*345*)
$Be(dioxane)_2(SCN)_2$	—	Pale yellow crystals	—	(*345*)
$[MeBeCN\cdot Me_3N]_n$	—	Air-sensitive white solid	—	(*120*)

---

[a] Key to abbreviations:

s = soluble
i = insoluble
ss = sparingly soluble

a = water
b = dimethyl ether
c = benzene
d = carbon tetrachloride
e = diethylether
f = toluene
g = ethanol
h = dioxane

j = xylene
k = acetone
l = chloroform
m = carbon disulfide
n = phosphorus oxychloride
p = dimethyl sulfide
q = ammonia

[b] Incorrectly described in ref. (*524*) as $Be(MeOC_2H_4OMe)_2Cl_2$, but analysis correct for $Be(MeOC_2H_4OMe)Cl_2$.

(*524*) may also be prepared by reaction of the metal suspended in the ether with dry hydrogen chloride. Unlike beryllium chloride, the diethyl ether complex is appreciably soluble in C_6H_6, CS_2, and CCl_4, although insoluble in petroleum ether (*522*). The hexagonal prisms are converted into a more stable modification on grinding, the properties of which differ from the former modification, being almost insoluble in ether and decomposing without melting. The melting point of the etherate crystals falls with time. Ether solutions, stored for a long time at room temperature, form a crystalline film or a flocculent precipitate whose composition is close to $Be(OEt_2)_2Cl_2$ and is structurally identical to the previously mentioned stable modification. The transformation is thought to be related to a change in configuration of the $Be(OEt_2)_2Cl_2$ molecule to form a more polar molecule which is less soluble in ether (*522*). After prolonged treatment of the dietherate *in vacuo* a crystalline dimeric monoetherate is formed, association occurring doubtless via chlorine bridges (*97*) (Fig. 10).

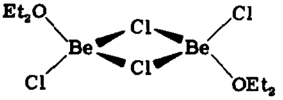


FIG. 10. The structure of $[Et_2OBeCl_2]_2$.

Anhydrous beryllium chloride dissolves in ether forming a two-phase system, the lower layer being a solution of ether in the complex and the upper layer being a solution of the etherate complex in ether. The composition of the top and bottom layers does not substantially change with temperatures between 15° and 80°. On cooling a dilute solution to about −70°, $BeCl_2 \cdot 3Et_2O$ crystallizes and this is stable below −2°; between −2° and 15°, the dietherate, which melts under ether solution at 14.5°–15.0° forming the lower immiscible layer, is the stable phase. The heats of solution of the di- and trietherates are −9.55 and −2.30 $kcal \cdot mole^{-1}$, respectively, being slightly higher than those for the corresponding tetrahydrofuranates (*520*, *522*).

The bromide dietherate may be obtained in similar fashion to the analogous chloride by crystallization from its ethereal solutions. Such solutions are prepared by dissolving anhydrous beryllium bromide in ether or by the reaction of beryllium metal with HBr or Br_2 in ether (*425*, *521*). Brominated ethers are produced in the reaction of beryllium, bromine, and ether when carried out under refluxing conditions (*17*–*19*). The bromide dietherate has four molecules in the unit cell and is not isomorphous with the chloride (*425*). The melting point of $Be(OEt_2)_2Br_2$, in contrast to the chloride, does not alter with time. The existence of a trietherate has been demonstrated and this reverts to the dietherate above −4°. The heats of solution for the di- and trietherates are −7.35 and −1.90 kcal·mole^{-1}, respectively. Crystals of the bromide–dietherate melt under ether at 37°, when a lower layer of a solution of ether in the dietherate is formed; layering of the solution remains up to 160° (*523*).

Iodine also reacts with beryllium in ether, heat being required for the completion of the reaction, but a solid etherate could not be isolated (*521*).

Decomposition of the chloride dietherate begins at 55°–60° and is complete at 220°–240°, whereas the bromide analog starts to decompose at 70° and decomposition is complete by 160°–170° (*530*). No definite intermediary thermal decomposition products are formed, but it may be inferred that decomposition takes place by the route

$$Be(OEt_2)_2Cl_2 \rightarrow EtOBeCl + EtCl + Et_2O \qquad (24)$$

The bromide and chloride dietherates have dipole moments of 7.52 and 6.74 D [6.23 D quoted in ref. (*514*)], respectively, in benzene solution at 20° indicating the tetrahedral nature of the compounds (*323*, *532*). Dielectric measurements on a number of molecular complexes of Be, Zn, Cd, and Hg halides have also been interpreted in terms of a tetrahedral configuration for undissociated complexes (*229*). Interaction between ether dipoles and the large dipoles of the beryllium halide bisetherates accounts for the existence of the weak trietherate complexes.

Beryllium halide etherates are poor conductors of electricity, the chloride being the best of the series. Electrolysis of an ethereal solution of the chloride yields 92% pure beryllium metal and electrolysis of a bromide solution yields a less pure metal (*555*). For ethereal solutions of beryllium chloride and bromide, the conductivity of the upper layer increases with concentration, but that of the lower layer decreases. There is a sharp increase in molar conductivity (100-fold) and viscosity in passing from the upper to the lower layer. The bromide and chloride dietherates are associated in benzene, but, since all the bonding orbitals are occupied, association must be weak, involving electrostatic or polarization forces. The degrees of association (α) increase linearly with concentration up to $\alpha = 2$–2.5 after which the increase is rather slow up to $\alpha \sim 3$ (*525*), whereas the ether addition compounds of aluminum chloride and bromide exist mainly as monomers up to very high concentrations (*531*). Isopiestic measurements in ether at concentrations bordering the heterogeneous region show the following degrees of association (*525*) as tabulated below.

Complex	Temp. (°C)	α
$Be(OEt_2)_2Cl_2$	20	3.0
$Be(OEt_2)_2Br_2$	20	2.9
$Be(OEt_2)_2Br_2$	37	3.0

The structure of the trimeric associate based on dipole–dipole interaction does not account for the large increase in conductivity and so it has been suggested that ion pairs of the type $[Be_3Cl_3(Et_2O)_6]^{3\delta+}[Cl^{\delta-}]_3$ are present (*526*).

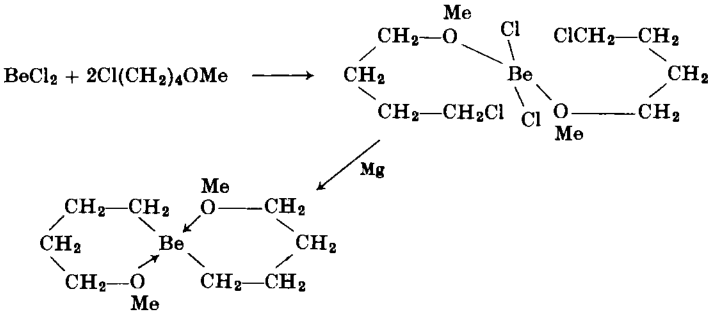
Although dimethyl ether, tetrahydrofuran, and tetrahydropyran complexes of beryllium chloride have been isolated as crystalline solids, a dibutyl ether complex could not be obtained (*520*, *524*). The tetrahydrofuran complexes $Be(THF)_2Cl_2$ and the corresponding bromide are isomorphous; an iodide complex could not be isolated (*425*, *516*). Both "monoglyme" and dioxane readily replace diethyl ether; the dioxane complexes of the chloride and bromide are sparingly soluble in ether, dioxane, and benzene, indicating a polymeric structure for the adducts in which each of the two oxygen atoms in the dioxane molecule is coordinated to different metal atoms as in $Mg(dioxane)Br_2$ (*118*, *342*, *524*).

The thio analog of monoglyme, $MeSC_2H_4SMe$, will not replace ether in beryllium chloride–ether complexes, sulfur being a weaker donor than oxygen to beryllium, but it forms a 1:1 chelate complex with beryllium chloride in benzene solution (*118*).

The thermal stability of the chloride complexes with monoethers increases sharply from open chain to cyclic ethers. Melting points and thermal stability of dimethyl- and diethyletherates show some tendency to increase as the atomic weight of the halide increases. Beryllium bromide and iodide complexes with aliphatic ethers are light-sensitive (*516*, *524*).

The structures of some of the "onium" compounds formed by beryllium halides have been discussed and estimates made for the interatomic distances and bond angles in these adducts. The infrared vibrations in these complexes have been tabulated, but beryllium–halogen vibrations have not been assigned (*434*, *517*, *529*), although beryllium–oxygen vibrational frequencies are well known (*157*).

Beryllium chloride forms an interesting colorless crystalline 1:2 complex with 4-chlorobutylmethyl ether which is reduced by magnesium in ether forming the spiran-type compound beryllium bis-(δ-methoxybutyl) which may also be prepared directly from the Grignard reagent of the chloroether and $BeCl_2$ (*24*).



(25)

The rate of exchange of complexed and uncomplexed solvent, dimethylformamide, at 290°K varies from 2 sec^{-1} for $AlCl_3$ to 150 sec^{-1} for $BeCl_2$. The primary solvation number for the Be(II) ion is four, oxygen being the donor atom and the activation energy for the exchange process is ca. 16 kcal·$mole^{-1}$ (*147*, *294*).

Beryllium halides form 1:2 complexes with aldehydes, ketones, and esters (*149*, *153*, *154*, *229*, *295*). The adducts are usually prepared from anhydrous beryllium halides and the Lewis base, although ester complexes have also been obtained from the reaction of beryllium alkoxides with excess acetyl halides (*295*).

$$Be(OR)_2 + 2CH_3COX \rightarrow Be(CH_3COOR)_2X_2 \qquad (26)$$

$$R = Et, Pr^i; X = Cl, Br$$

At 5°, solutions of $BeCl_2$ in Me_2CO/C_6H_6 deposit the unusual complex $Be(Me_2CO)_2Cl_2 \cdot 4C_6H_6$, which readily loses benzene (*154*). Beryllium chloride also reacts with $POCl_3$ forming the crystalline complex $BeCl_2 \cdot 3POCl_3$ (*527*) and with S_4N_4 in thionyl chloride producing the yellow complex $Be(S_2N_2O)Cl_2$ and thiodithiazyl dioxide ($S_3N_2O_2$) (*28*), but the structures of these chlorides are not clearly established.

The conductivity of $BeCl_2 \cdot AlCl_3 \cdot 3Et_2O$ is greater by three orders of magnitude than that of $Be(OEt_2)_2Cl_2$ and is three times that of $Al(OEt_2)Cl_3$ in benzene solution. It shows no sign of dissociation into its components in organic solvents and forms a two-phase system in benzene and ether, even at high dilution, with the complex almost entirely concentrated in the lower phase. The complex which melts congruently at 55°, has been formulated with the ionic structure $[Be(OEt_2)_3Cl]^+[AlCl_4]^-$ on the basis of its infrared spectrum (*514*, *515*). Phase studies of the $Be(OEt_2)_2Cl_2$–$Ga(OEt_2)Cl_3$ system over the whole range of concentration of components showed the existence of a 1:1

compound, melting congruently at 61°, isostructural with the corresponding aluminum compound and which may, therefore, be formulated as $[Be(OEt_2)_3Cl]^+[GaCl_4]^-$ (*426*).

Solutions containing adducts of beryllium halides with thioethers have been prepared by reaction of the halide with the donor and by reaction of beryllium metal in the donor solvent with hydrogen halide; reactions are less vigorous in thioethers than in ordinary ethers (*118*, *464*).

$$Be + 2HCl + 2R_2S \rightarrow Be(SR_2)_2Cl_2 + H_2 \tag{27}$$

$R = Me, Et, Bu^i$

R_2S = thiophene

Only the bisdimethyl sulfide complex of beryllium chloride has actually been isolated; Coates and Green (*118*) reported its melting point as 117°–119°, while other authors (*464*) state that its vapor pressure is negligible up to its melting point (55°), but that it decomposes from 65° with the formation of alkyl halide. The complex di-μ-chlorodichlorobis(dimethylsulfide)diberyllium (Fig. 11) is obtained on evaporation *in vacuo* of a toluene solution of $Be(SMe_2)_2Cl_2$ (*118*).

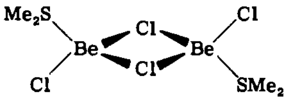


FIG. 11. The structure of $[Me_2SBeCl_2]_2$.

Trithioetherates, $Be(SR_2)_3Cl_2$ ($R = Me, Et, Bu^i$), have been obtained as white needles at low temperature, but these liquefy below room temperature (*464*). Although weak adducts of $BeBr_2$ and BeI_2 with H_2S have been obtained from which the H_2S may readily be recovered, the chloride does not dissolve in, nor react with, H_2S (*64*). BeI_2 reacts with H_2S on heating to form beryllium sulfide (*270*).

Amide and thioamide complexes of beryllium chloride have also been obtained (*385*). In the urea and thiourea complexes, oxygen and sulfur, respectively, are the donor atoms since the former forms an inner tetracoordinated beryllium complex and the latter a 2:1 complex in which the beryllium–halogen bond is retained; oxygen is a stronger donor to beryllium than sulfur and the presence of the NH_2 groups enhances the donor character of the oxygen and sulfur atoms, whereas the carbonyl and thiocarbonyl group decreases the basicity of the nitrogen atoms. Spectroscopic studies have shown that oxygen and sulfur, respectively, coordinate to the metals in urea and thiourea complexes of zinc and other metal halides (*373*, *557*). Steric factors are believed to preclude the formation of 2:1 complexes with symmetrical and asymmetrical substituted thioureas, although 1:1 complexes have been obtained in which sulfur rather than nitrogen is believed to be the donor atom, since these adducts are hygroscopic, unlike nitrogen coordinated complexes (*385*).

The Raman spectrum of the $BeCl_2$–glycine system in aqueous solution is quite different from the spectra of the zinc- and cadmium–glycine systems. At low pH, a large shift in the C–C stretching frequency indicates strong coordination of the ligand to beryllium. Also, since the spectrum indicates that the amino group is protonated, it seems glycine binds only through the carboxyl oxygen and that Be(II) coordinates only two glycine molecules in solution. With increasing pH, hydrolysis of the Be(II) ion takes place with consequent breaking of the metal ligand bond (*259*).

2. *Nitrogen Complexes*

Beryllium halides form a series of ammonia complexes which increase in stability with increasing atomic weight of the halogen (*65*). The tetrammine, $Be(NH_3)_4Cl_2$, whose lattice parameters (*424*) differ little from those of K_2BeCl_4, may be prepared by reaction of the anhydrous chloride with ammonia or by reaction of the metal in liquid ammonia with two equivalents of ammonium chloride (*57*, *67*, *149*, *301*). On heating above about 250°, the tetrammine splits out NH_4Cl (*138*) but *in vacuo* at 210°–255° the bisammine, melting at about 350°, is obtained (*138*). Experiments using a tensieudiometer have shown that beryllium chloride forms weak complexes with 12 and 6 molecules NH_3 at low temperatures, as well as the 4:1 and 2:1 complexes. Likewise the bromide and iodide have been shown to form adducts containing 10, 6, and 4 molecules NH_3 and 13, 6, and 4 molecules NH_3 per beryllium atom, respectively (*67*), and the unusual complex $2BeI_2 \cdot 3NH_3$ has also been reported (*271*). The tetrammines are the most stable and the adducts containing more than 4 molecules NH_3 are found only at low temperatures (*57*, *67*). The dissociation pressures, total and partial heats of formation of the beryllium halide–ammine complexes, and the heats of solution in hydrochloric acid have been determined; $Be(NH_3)_4Cl$ has a slightly greater heat of formation than has $Be(H_2O)_4Cl_2$ (*65*, *67*).

A solution of NH_4Cl in liquid ammonia dissolves beryllium to form $BeCl_2$, which, in turn, reacts with excess metal to form a very slightly soluble ammonobasic beryllium chloride of approximate composition $BeCl_2 \cdot Be(NH_2)_2 \cdot xNH_3$. Similar reactions of $BeBr_2$ with NH_4Br yield $BeBr_2 \cdot 3Be(NH_2)_2 \cdot 4NH_3$, $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$, and $BeBr_2 \cdot 3Be(NH_2)_2 \cdot 8NH_3$, whereas the iodides produce $BeI_2 \cdot 3Be(NH_2)_2 \cdot 4NH_3$, which gradually dissolves beryllium metal forming a colorless, crystalline complex $BeI_2 \cdot 5Be(NH_2)_2 \cdot 4NH_3$ (*57*).

Beryllium halides form a series of complexes with primary, secondary, and tertiary amines (*97, 149, 151, 153, 381*), diamines (*150*), and nitrogen-containing heterocycles (*97, 117, 118, 148, 151, 153, 154*). Aromatic amine complexes are normally colored and do not melt below 250° (*149, 151, 153, 381*). The diamines usually form 1:1 complexes in which ligands such as 1,2-naphthalenediamine act as chelating agents, whereas ligands like *p*-phenylenediamine probably act as catenating ligands. Ethylenediamine and benzidine produce complexes containing between 1 and 2 molecules of amine per beryllium (*150*), while 4-aminoantipyrine forms chelate complexes with beryllium bromide, iodide, and thiocyanate (*133*). Phenylhydrazine forms 4:1 and 3:1 complexes with $BeCl_2$, the former being formed with a vast excess of donor and the latter when the ratio of $BeCl_2$:ligand is 1:3 (*149, 150*). The hexamethylenetetrammine–$BeCl_2$ complex is soluble in water and, on heating the aqueous solution, formaldehyde is produced (*196*).

American workers have observed some unusual reactions of beryllium chloride with amines. Tetramethylhydrazine and beryllium chloride react in ether yielding a white precipitate from which at 120° *in vacuo* $Me_2NNMe_2 \cdot 1.5HCl$ sublimes. In similar fashion, tribenzylamine and trimethylamine hydrochlorides have been obtained from the corresponding amines. In the absence of solvent, pyridine yielded $C_5H_5N \cdot HCl$, but in benzene solution $Be(pyridine)_2Cl_2$ was obtained. The fate of the beryllium in these reactions, where amine hydrochloride is formed, has not been established. These same authors suggest that the 2:1 amine complexes of $BeCl_2$ have characteristics indicating their ionic nature and the ease with which the amine hydrochloride is formed supports their formulation as $[L_4Be]^{2+}[BeCl_4]^{2-}$. Further work is obviously necessary to establish the nature of the amine complexes of the beryllium halides.

Coates and Green (*117, 118*) have prepared a series of colored 2,2′-bipyridyl complexes of beryllium halides and organoberyllium compounds. All are chelate complexes with high intensity bands in the 220–300 mμ region, similar to those in free bipyridyl; the long-wavelength absorption bands only are given in Table VIII, together with the molar extinction coefficients. For absorptions giving visible color, there is a small decrease in λ_{max}, together with a marked decrease in extinction coefficient in passing from the less to the more electronegative halogen. For the organic derivatives the trend is in the same direction as the electronegativity of the organic group increases. The colors are due to electron transfer from one of the Be–X bonds to the lowest unoccupied orbital of the bipyridyl. Thus, in the excited state of the complex, the

Be–X bond is acting as an electron donor. The donor character will be greater if the electrons in the bond are relatively loosely held, as in beryllium alkyls, than if bonding were strong, as is probable in the beryllium halides, although it is possible for the halide complexes that the electron source is one of the nonbonding orbitals of the halogen.

TABLE VIII

2,2′-BIPYRIDYL COMPLEXES OF BERYLLIUM COMPOUNDS[a]

X in Be(bipy)X_2	Color	λ_{max} (mμ)	Molar extinction coefficient × 10^{-3}
Cl	White	352 infl.	1.2
Br	Pale cream	364	2.4
I	Yellow	368	7.0
Ph	Yellow	353 infl.	0.5
Me	Yellow	395	2.7
Et	Red	461	3.7

[a] From Coates (*118*), reproduced with permission.

Lithium bipyridyl reacts with beryllium chloride forming the green solid bisbipyridylberyllium which is also formed from dilithium bipyridyl and Be(bipy)$_2$Cl$_2$. This complex is formulated as (bipy$^-$)$_2$Be^{2+} from magnetic and esr measurements (*98, 118*).

$$2\text{Li bipy} + \text{BeCl}_2 \xrightarrow{-2\text{LiCl}} (\text{bipy})_2\text{Be} \xleftarrow{-2\text{LiCl}} \text{Li}_2\text{bipy} + \text{Be(bipy)Cl}_2 \qquad (28)$$

Many years ago, $BeCl_2 \cdot 2$quinoline$\cdot H_2O$ was reported (*404*), but other workers (*151*) have not been able to substantiate the existence of this compound. Hydrazine hydrate gives complexes of the type $2BeCl_2 \cdot 3N_2H_4 \cdot 4H_2O$ and $2BeCl_2 \cdot 5N_2H_4 \cdot 2H_2O$, which are probably mixtures of beryllium–aquo and beryllium–hydrazine complexes (*150*).

Nitrobenzene forms a bis complex with $BeCl_2$, but nitromethane reacts with the evolution of HCl (*149*). With nitriles, usually 2:1 adducts are formed. Succinonitrile forms a 1:1 chelate, whereas HCN forms a 4:1 complex, but cyanogen does not form a stable adduct (*151, 154*). In the $BeCl_2$(nitrile)$_2$–nitrile systems, the existence of adducts containing 3 and 4 moles of isocapronitrile and 3, 4, 5, and 7 moles of propionitrile and *p*-toluinitrile per beryllium atom has been demonstrated. Aceto- and naphthonitriles readily char in the presence of beryllium chloride (*152*). Complexes of metal halides with alkyl cyanides have been reviewed up to 1965 (*546*).

Aminophenols, aminobenzoic acids, nitroanilines, and 2,4-dinitrophenylhydrazine form 2 : 1 complexes which are usually insoluble in most organic solvents. The latter also forms a 1 : 1 complex with $BeCl_2$ at 100°. Heating $BeCl_2$ with the aminophenol or aminobenzoic acid complexes in a 1 : 1 ratio results in the liberation of HCl and the proposed structures for the products are shown in Figs. 12 and 13 (*384*). Evidence to substantiate these structures has not been presented.

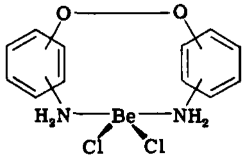


FIG. 12. Proposed structure of $Be_2[C_6H_4(NH_2)O]_2Cl_2$.

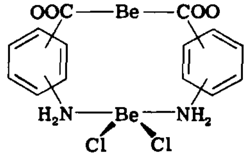


FIG. 13. Proposed structure of $Be_2[C_6H_4(NH_2)COO]_2Cl_2$.

D. HYDRIDO- AND ORGANOBERYLLIUM HALIDES

There are few references in the literature to the hydrido- and organoberyllium halides. Reactions between beryllium dialkyls and hydrogen halides, iodine, or beryllium halides and between the metal and alkyl halides, both in the presence and absence of ethers, produce the organoberyllium halides (*114*, *134*, *177*, *178*, *420*, *561*). The ether-free products are insoluble in alkyl halides and are doubtless coordination polymers. The beryllium–alkyl groups in such compounds add across carbonyl bonds producing, after hydrolysis, alcohols (*561*) in similar fashion to the addition of beryllium dialkyls to carbonyl compounds (*145*).

t-Butylberyllium chloride monoetherate (Fig. 14), obtained from di-*t*-butylberyllium etherate and beryllium chloride, is dimeric in benzene solution, though monomeric in ether solution. The analogous bromide has also been obtained. It is surprising that a bisetherate has not been isolated, although it probably exists in ether solution, but steric crowding round the beryllium may preclude its formation (*204*, *406*).

Ashby has provided conclusive evidence for the redistribution of BeX_2 ($X = Cl$, Br) with R_2Be ($R = Me$, Et, Ph) in ether (*18*, *19*). The product is formulated as RBeX [cf. (*130*)], analogous to the Grignard reagent (*16*, *131*). The degree of association of MeBeBr in ether is 1.0–1.1 in 0.05–0.10 *M* solution; Me_2Be, MeBeCl, and PhBeBr are also essentially monomeric in the same concentration range. The ^1H magnetic resonance spectrum of a 2 : 1 mixture of Me_2Be and $BeBr_2$ in ether at −78° indicates the presence of Me_2Be species, mixed with the redistribution product, MeBeBr (*18*, *19*). Dimethyl sulfide solutions of $BeCl_2$ and excess Me_2Be at −45° are believed to contain the species $MeBeCl(SMe_2)_2$; whether $BeCl_2$–Me_2S adducts are also present in such solutions has not been established (*255*). Coordination complexes of RBeX with dioxane and 2,2′-bipyridyl have been isolated from R_2Be–BeX_2 mixtures (*18*, *19*, *47*) and thus the Schlenk equilibrium (*177*) lies well to the right in ether

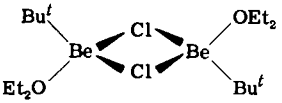


FIG. 14. The structure of $[Bu^tBe(Et_2O)Cl]_2$.

$$R_2Be + BeX_2 \rightleftharpoons 2RBeX \tag{29}$$

at room temperature. Beryllium reacts much faster with acid halides than with alkyl halides. The products of the former reaction have not been isolated in a pure state, but their structure as acylberyllium halides [RC(O)–Be–X] was established by the character of their chemical reactions. With water, acid halides, and ketones, these halides form aldehydes, α-diketones, and α-hydroxyketones, respectively (*266*, *267*).

Strohmeier and co-workers have prepared a series of crystalline diethylberyllium salts, having the general formula $MX(BeEt_2)_n$ (Table IX), where MX is an alkali metal halide or pseudohalide or a quaternary ammonium halide and $n = 1$, 2, or 4. Complexes with LiF, NaCN, and CsCl could not be obtained (*476*–*478*, *481*). The ease of complex formation is related to the lattice energy of MX and increases with increasing radius of the cation, but decreases with increasing size of the anion (*478*), as has been found for a similar series of salts of the aluminum alkyls (*566*). Ether-free diethylberyllium is liberated on heating most of the 2 : 1 complexes *in vacuo* or in hot benzene solution. In some cases 1 : 1 complexes are formed; $RbF(BeEt_2)_2$ on heating in benzene yields the 1 : 1 complex and an unusual complex $RbF(BeEt_2)_3$ (*481*). The structures

TABLE IX

COMPLEX DIETHYLBERYLLIUM SALTS $MX(BeEt_2)_n$

MX	n	M.p. (°C)	MX	n	M.p. (°C)
KF	2	83	Me_4NF	2	80–90 dec.
KF	1	46–48	Me_4NCl	2	Liquid
RbF	2	61–63	Et_4NCl	2	Liquid
CsF	2	29–31	$PhCH_2(Me)_3NF$	2	Liquid
KCN	4	52–53	$PhCH_2(Me)_3NCl$	2	Liquid

of the 2:1 complexes are probably similar to that of $KF(AlEt_3)_2$ (Fig. 15) (*13*). The specific conductivity of these salts lies in the range 10^{-2}–10^{-3} mhos·cm^{-1} at 80° and the decomposition potentials, which decrease with increasing temperature, are considerably larger than the polarization potentials (*480*, *481*). Beryllium metal, containing 20–30% beryllium carbide, is electrically deposited from the 2:1 complexes at 60°–100° (*479*, *483*). The following mechanism has been proposed for the electrolysis of $KF(BeEt_2)_2$. The deposited beryllium contains both Be_2C and polycrystalline K. Evidence for the radical intermediate $EtBe^{\bullet}$ is provided from the fact that when the electrolysis is carried out in the presence of pyridine at 80°, the formation of the radical complex $(pyBeEt)^{\bullet}$ is indicated by ESR (*482*).

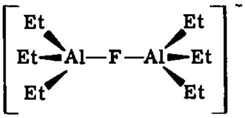


FIG. 15. The ion $[(AlEt_3)_2F]^-$ in $KF(AlEt_3)_2$; the fluorine atom is octahedrally surrounded by six potassium ions.

$$\begin{array}{llllll}
\textit{Cathode}: & \mathrm{K}^+ & \xrightarrow{e} & \mathrm{K} & & \\
 & \mathrm{K} + \mathrm{Et_2Be} & \longrightarrow & \mathrm{KEt} + \mathrm{EtBe}^{\bullet} & & \\
 & \mathrm{K} + \mathrm{EtBe}^{\bullet} & \longrightarrow & \mathrm{KEt} + \mathrm{Be} & & \\
\textit{Anode}: & [\mathrm{BeEt_2F}]^- & \xrightarrow{-e} & \mathrm{BeEt_2F} & \longrightarrow & \mathrm{EtBeF} + \mathrm{Et}^{\bullet} \\
 & 2\mathrm{Et}^{\bullet} & \longrightarrow & \mathrm{C_2H_4} + \mathrm{C_2H_6} & &
\end{array}$$

Although the hydridoberyllium halides have not yet been formed, a recent disclosure (*454*) reveals the formation of their tertiary amine complexes. These complexes, HBeX·L ($X = Cl$, Br, I; L = tertiary amine), are essentially dimeric in benzene solution (where molecular weights have been measured). Thus, the structures of these compounds (Fig. 16) contain a double hydrogen bridge between two beryllium atoms like the similar complexes formed by the organoberyllium hydrides (*48–50*). The adducts are useful intermediates for the production of pure beryllium hydride, a useful component for propellants, and can be decomposed thermally to pure metallic beryllium. Reaction with olefins results in the formation of organoberyllium halide–amine complexes; reduction of aldehydes, ketones, nitriles, and esters can also be effected.

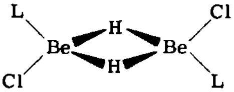


FIG. 16. Hydridoberyllium chloride–amine complexes (L = tertiary amine).

E. ALKOXY- AND KETIMINOBERYLLIUM HALIDES

The literature gives little information about the alkoxyberyllium halides. Acetyl halides react exothermically with beryllium alkoxides yielding ester complexes of the alkoxyberyllium halides.

$$Be(OR)_2 + CH_3COX \rightarrow Be(OR)X\cdot xCH_3COOR + (1 - x)CH_3COOR \qquad (30)$$

$$R = Et,\ Pr^i;\ X = Cl,\ Br;\ x = 0.5\text{–}0.7$$

With excess acetyl halide, ester complexes of the beryllium halides are produced (*295*).

Dimeric *t*-butoxyberyllium halide etherate complexes (*14*) have been obtained by similar routes used for the formation of dimeric alkoxymagnesium halide etherates (*119*). Tetrahydrofuranates, prepared from the etherates by displacement reactions, are also dimeric in benzene solution. $[Be(OBu^t)(Et_2O)Br]_2$ is also dimeric in the solid state, its structure (*453*) being similar to that of the corresponding magnesium complex (*317*) with butoxy, rather than halogen bridges (Fig. 17) as expected, since beryllium– and magnesium–halogen bridge bonds do not often persist in the presence of ethers. The ether-free chloride (*14*) is

$$\left.\begin{array}{l} Me_2Be + BeX_2 + 2Me_2CO + 2Et_2O \\ Me_2Be + BeX_2 + 2Bu^tOH + 2Et_2O \\ 2LiOBu^t + 2BeX_2 + 2Et_2O \end{array}\right\} \longrightarrow [Be(OBu^t)\ (Et_2O)Br]_2 \qquad (31)$$

$$X = Cl,\ Br,\ I$$

tetrameric in benzene solution like many alkylberyllium alkoxides (*145*) having probably a cubane-type structure like $(MeZnOBu^t)_4$ (*452*).

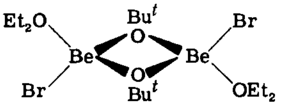


FIG. 17. The structure of $[Be(OBu^t)(Et_2O)Br]_2$.

An unusual series of compounds, $X_2Be_3(OBu^t)_4$ (X = Cl, Br, I, Me, Bu^t, PhC≡C, N_3, and BH_4), has recently been obtained (*14*). The structures of the chlorine member of this series (*453*) and $[(Me_2N)_2Be]_3$ (*22*) are very similar (Fig. 18). In this latter compound, the terminal nitrogen and beryllium atoms are free to form a dative π bond. Beryllium–chlorine π bonding may be present in $Cl_2Be(OBu^t)_4$ and also in the ketiminoberyllium chloride dimers $(R_1R_2C{=}NBeCl)_2$, which contain bridging ketimino groups (*484, 543*).

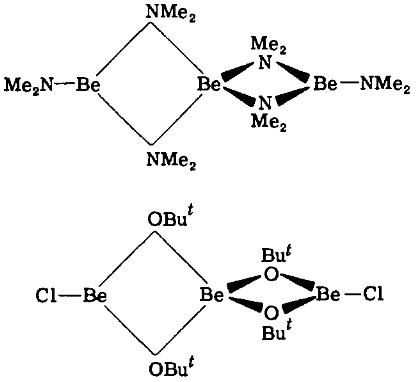


FIG. 18. Structures of $[(Me_2N)_2Be]_3$ and $Cl_2Be_3(OBu^t)_4$.

F. MISCELLANEOUS REACTIONS

Reactions of the halides, especially the chloride, with Grignard or lithium reagents or with organoaluminum compounds have been used for the preparation of beryllium alkyls and aryls (*115, 116, 177, 179, 181, 258, 312, 377*). With sodium hydridodiethylberyllate, or with R_2Be (R = alkyl, aryl) and LiH or $NaBEt_3H$ in ether, solutions are obtained from which organoberyllium hydride complexes may be isolated (*48–50, 121*).

Beryllium bromide has been used as a catalyst for the bromination of several organic molecules (*365*, *366*, *485*). The chloride acts as a Friedel–Crafts catalyst and as a catalyst in the polymerization of olefins, but it is less effective than either $AlCl_3$ or $ZrCl_4$ (*90*, *123*, *194*).

Beryllium dialkyls usually react readily with donor molecules containing a reactive hydrogen atom, liberating alkane and forming associated compounds. The halides require more vigorous treatment before hydrogen halide is liberated in similar reactions. With organic acids and anhydrides, the normal or basic salts are formed (*141*, *158*, *382*, *429*) and with alcohols or alkali metal alkoxides, beryllium alkoxides are produced (*15*, *30*, *51*, *149*, *159*, *383*, *519*, *528*).

G. UNIVALENT BERYLLIUM HALIDES

Although beryllium usually exhibits a charge number of two, there is some evidence, especially spectroscopic evidence (Section V), for the existence of Be(I) halides.

The readily oxidizable intermediate, formed by the anodic dissolution of beryllium in halide solutions, is thought to be a Be(I) derivative (*207*, *268*, *466–468*), but the equilibrium concentration of Be^+ at 25° is very small and thus suggestions (*80*, *81*, *166*) that Be(I) may form at ordinary temperatures must be doubtful. Beryllium iodide reacts with beryllium at 400°, as shown by the disappearance of the metal, which is replaced by a fine white powder having a Be:I ratio of 1:1.4, but there is some doubt concerning the reliability of the beryllium analysis in this work (*215*).

In view of other unconfirmed reports of metals exhibiting unusual valency states, further work is necessary before the existence of Be(I) at ordinary temperatures can be substantiated.

IV. Beryllium Pseudohalides

A. CYANIDE

The product of the reaction between beryllium iodide and cyanogen at ca. 500° probably contains beryllium cyanide, since it dissolves in water forming a viscous solution which shows reactions characteristic of aqueous cyanide solutions (*271*). The anhydrous cyanide is precipitated from solution when ethereal dimethylberyllium is added to excess HCN in benzene. It does not react with trimethylamine nor dissolve in solvents with which it does not react since it, no doubt, has a cross-linked polymeric structure (*120*, *283*). Equimolar quantities of the above reactants form methylberyllium cyanide, which is associated like its trimethylamine complex (*120*).

B. AZIDE

Beryllium azide, $Be(N_3)_2$, is precipitated as a white, water-sensitive solid in the reaction of HN_3 with Me_2Be at low temperature. It is reasonably stable like the alkaline earth azides (*551*).

C. THIOCYANATE

An aqueous solution of $Be(SCN)_2$ is obtained from the reaction of $BeCO_3$ and HSCN. From such solutions, a viscous or vitreous material is obtained, dissolving readily in donor solvents (*339*). Bisether, bisdioxane, and bis-4-aminoantipyrine complexes of $Be(SCN)_2$ and the double salt $Cs_2Be(SCN)_4 \cdot 2H_2O$ have been prepared and characterized (*133*, *339*, *344*, *345*). The extraction of beryllium from aqueous ammonium thiocyanate solutions into organic solvents has been studied with a view to using this as a means of separating Be from other metal ions (*61–63*). The highest distribution coefficient ($Be^{2+}_{org.}/Be^{2+}_{aq.}$) was found when the organic phase was alcohol, ester, or ketone at pH 2–3; the beryllium extracts, as does Li^+, Mn^{2+}, Al^{3+}, or Fe^{3+}, as the simple thiocyanate salt (*61*).

V. Spectroscopic Studies

Studies by Klemperer and co-workers (*550*), using electric quadrupole deflections of molecular beams to detect dipole moments, indicate that in the case of the gaseous group II dihalides, the linear form is found for light metal–heavy halogen, whereas the bent form is favored for light halogen–heavy metal combinations. The observed trends in the geometry of these halides has been explained on orbital energy considerations (*203*). The linear geometry of the beryllium halides has been confirmed by infrared spectroscopy (*470*).

Using the matrix isolation technique, the infrared spectra of the halides have been recorded by Snelson (*470*, *471*); his assignments and calculated force constants, which are close to those found for the monohalides, are shown in Table X. Other bands at 1250 and 825 cm^{-1} in the fluoride and 570 and 750 cm^{-1} in the bromide are believed to be due to associated species [see also (*103*)]. A preliminary report (*403*) of the emission spectrum of $BeBr_2$ has appeared in the literature. The force constant (1.1 mdynes/Å) in glassy BeF_2 is much smaller than for the gaseous linear molecule (*562*) and the main band at ca. 770 cm^{-1} in glassy BeF_2 is attributed to the Be–F stretching vibration in the BeF_4 tetrahedron (*44*, *52*).

For the Be–Cl molecule, two electronic states, $X^2\Sigma$ and $A^2\Pi$, are known. Herzberg (*206*) applied new physical constants and conversion factors to the spectral data of Friedrickson and Hogan (*156*) and obtained a value of 4.2 eV for the dissociation energy of BeCl. Gaydon (*165*) applied further corrections and obtained a value of 3.0 eV. In 1960, Novikov and Tunitskii (*327*) obtained a new set of spectral data for BeCl and derived a value of 5.9 eV for the dissociation energy. The doublet in the band spectrum of BeI in the 4100–4500 Å region is analogous to the $^2\Pi$–$^2\Sigma$ system of the other monohalides (*320*). The band spectrum of the BeF molecule was investigated in emission by Datta (*128*) and Jenkins (*230*), and only one band system in the UV region (3393–2812 Å) has been attributed to this molecule. The system, designated an A–X, has been attributed to arise from a $^2\Pi$–$^2\Sigma$ transition, for which the Franck–Condon factors, r-centroids, and vibrational constants have been evaluated (*235*, *305*, *319*, *494*). A band in the visible region is also attributable to the $^2\Sigma$–$^2\Pi$ transition [cf. (*394*)]. In the emission spectrum in the vacuum ultraviolet (*326*), four band systems are ascribed to the Be–F radical. The rotational constants of BeF in the $C^2\Sigma$ state are close to the values found by Rao and Rao (*394*), who incorrectly assigned their band system to the $B^2\Sigma$–$A^2\Pi$ transition, instead of to a $C^2\Sigma$–$A^2\Pi$

TABLE X

INFRARED ASSIGNMENTS FOR THE BERYLLIUM HALIDES

	BeF_2		$BeCl_2$		$BeBr_2$		BeI_2
Matrix	ν_2	ν_3	ν_2	ν_3	ν_2	ν_3	ν_3
Neon	330	1542	238	1122	207	993	878, 872
Argon	309	1528		1108		985	877, 867
Estimated gas-phase frequency	345	1555	250	1135	220	1010	873
Stretching force constant (mdynes/Å)	5.15		3.28		2.53		1.96
Bending force constant (mdynes/Å)	0.12		0.08		0.06		0.04

transition (*326*). Several conflicting values [5.4 (*319*), 8.0 (*494*), 4.0 (*463*), 5.85 (*209*), and 6.4 eV (*186*)] for the dissociation energy of the BeF molecule have been reported, most having been obtained by a Birge–Sponer extrapolation from vibrational analysis of electronic spectra, but the results are inherently of a low order of accuracy as a result of this very long extrapolation. From mass spectrometric study of vapor species, produced by the fluorination of beryllium with CaF_2 and BF_3 in a Knudsen effusion cell, the value 5.85 ± 0.1 eV was derived for the BeF dissociation energy. This thermochemical value clearly establishes that the dissociation products of the $X^2\Sigma$ state of BeF are Be(^1S) and F (^2P), while those of the $A^2\Pi$ state are Be(^3P) and F(^2P) (*209*).

The vibrational spectrum of $Be(NH_3)_4Cl_2$ shows bands at 914, 493, and 290 cm^{-1} in the infrared, which are assigned to vibrations of the BeN_4 tetrahedron; the weak band at 493 cm^{-1} has been attributed to a slight distortion of the tetrahedron in the crystal lattice (*188*, *190*). Bands assigned to Be–O vibrations lie in the region 860–930 cm^{-1} in a series of complexes of $BeCl_2$ with oxygen donors (*529*).

Two intense bands at ca. 386 and 800 cm^{-1} are observed in the absorption spectrum of K_2BeF_4 which are ascribed to the triply degenerate vibrations, the former due to deformation (ν_4) and the latter to the valence vibration (ν_3). In the Raman spectrum, the intense band at 560 cm^{-1} is due to the totally symmetrical vibration and another weak band at 388 cm^{-1} is ascribed to ν_4; repeated exposure yielded a weak band of the triply degenerate vibration at ca. 800 cm^{-1}, and the splitting of this band is explained by the lowering of the symmetry of the BeF_4^{2-} ion in the crystal field from T_d to C_{3v}. In accordance with this, a weak band in the infrared exactly corresponding to the total symmetrical band (ν_1) in the Raman spectrum is found at 560 cm^{-1}. A similar split of ν_3 also probably occurs in the spectra of rubidium and cesium fluoroberyllates, since these compounds also exhibit weak bands at 550 and 540 cm^{-1}, respectively (*189*, *372*) (Table XI).

In the Raman spectrum of $(NH_4)_2BeF_4$, relatively weak peaks at 543 and 800 cm^{-1} are assigned to ν_1 and ν_3, respectively, and very broad, low intensity peaks occur in the 300–400 cm^{-1} region. From the presence of peaks at 575 and about 420 cm^{-1}, it has been suggested (*191*) that $BeF_2 \cdot 2NH_3$ should be formulated as $[Be(NH_3)_4]^{2+}[BeF_4]^{2-}$.

The force constants for tetrahedral beryllium compounds of similar type increase regularly in the order Be–N, 2.38 (*188*, *190*); Be–O, 3.04 (*190*); and Be–F, 3.50 md/Å (*189*).

The band at 540 cm^{-1} in the absorption spectrum of K_2BeCl_4 corresponds to the triply degenerate stretching vibration of the $BeCl_4^{2-}$ ion. The Raman band at 210 cm^{-1} is probably due to the triply degenerate deformation vibration, while two equally intense maxima in the region of the triply degenerate stretching vibration in the absorption spectrum of Na_2BeCl_4 are ascribed to strong interion dipole–dipole interactions in the crystal lattice and not to slight distortion of the tetrahedra (*427*).

Although the literature contains reports of the ^9Be wide line spectra of the solids beryl (*202*), chrysoberyl (*421*), and beryllium oxide (*217*), there are only two reports (*254*, *256*) of the NMR signal of the ^9Be nucleus in solution. The spectra of beryllium chloride in ether, the acetylacetonate and 8-hydroxyquinaldinate in chloroform, and beryllium sulfate in water showed a single resonance line whose width at half-height was generally 5–10 Hz. No chemical shift from basic beryllium acetate standard was observed. Stronger bases in the adducts of beryllium species shift beryllium resonance signals to higher fields. The chemical shifts of beryllium chloride in the solvents Me_2S, Et_2O, and NH_3 occur at −5.5, −3.1, and −1.7 ppm, respectively, relative to $[Be(H_2O)_4]^{2+}$ consistent with the known relative base strengths of these solvents. The adduct $MeBeCl(SMe_2)_2$ exhibits a resonance signal at −4.2 ppm. The only spin-spin coupling observed between ^9Be and other nuclei is for aqueous solutions of BeF_2 and $(NH_4)_2BeF_4$. The tetrafluoroberyllate ion gives a 5-line spectrum, $J_{^9Be-^{19}F} = 33 \pm 2$ Hz. All the compounds mentioned except BeF_2 are tetrahedral and thus the electric field surrounding the beryllium nucleus is relatively symmetrical and quadrupolar coupling is minimized and therefore narrow lines are observed. The beryllium-9 resonance of *saturated* aqueous beryllium fluoride solutions consists of a rather broad triplet centered at 0.8 ppm relative to $[Be(H_2O)_4]^{2+}$ with $J_{^9Be-^{19}F} = 28$ Hz, favoring the presence of a tetrahedral species ($BeF_2 \cdot 2H_2O$) in such solutions (*256*) as proposed by Linnell and Haendler (*276*). However, conductivity emf and

TABLE XI

SPECTROSCOPIC ASSIGNMENTS FOR THE ALKALI METAL TETRAFLUOROBERYLLATES

Metal	ν_1	ν_3	ν_4
Li	616	785, 809, 864	364, 330
Na	550, 567	767, 858	376
K	560	805, 835	386
Rb	550	797	379
Cs	540	780	372

TABLE XII: THERMODYNAMIC PROPERTIES OF BERYLLIUM MONO- AND DIHALIDES[a]

Property[b]	BeF_2	$BeCl_2$	$BeBr_2$	BeI_2	BeF	BeCl	BeBr	BeI
$\Delta H^{\ominus}_{\mathrm{f(298°K)}}$	−241.2 (a) (*250*)	−109.2 (*458*)	−88.8 (*96*)	−50.6 (*96*)	−14 (*542*)	34 (*542*)	48 (*542*)	67 (*542*)
	−244.3 (b) (*113*)	−112.6 (*302*)						
	−245.44 (c) (*113*)	−117.1 (f) (*193*)						
		−117.5 (e) (*193*)						
		−118.03 (*232*)						
		−118.25 (*507*)						
		−119.0 (d) (*193*)						
		−155.0 (*379*)						
$\Delta H^{\ominus}_{\mathrm{f(298°K)gaseous}}$	−183.8 (*210*)	−84.33 (*247*)						
	−184.4 (*96*)	−86.0 (*96*)			−40.0 (*209*)	2.0 (*184*)		
	−187.0 (*210*)	−86.1 (*211*)	−58 (*96*)	−20.6 (*96*)	−48.3 (*186*)	3.7 (*184*)		
	−191.2 (*71*)	−196.3 (g) (*247*)			−52.6 (*186*)	13.1 (*211*)		
	−191.3 (*71*)	−197.18 (g) (*247*)						
$\Delta H_{\mathrm{SUB(298°K)}}$	55.3 (h) (*210*)	32.0 (*96*)						
	55.4 (h) (*210*)	32.1 (*187*)						
	56.0 (*210*)	32.5 (*211*)	31 (*96*)	30 (*96*)				
	56.8 (*96*)	33.0 (*247*)						
	58.1 (*71*)	33.1 (*187*)						
		35.1 (g) (*247*)						
		37.49 (g) (*247*)						
		38.38 (g) (*247*)						
ΔH_{SUB}	54.63 (*137*) (755°K)	30 (*393*) (613°–733°K)	30 (*393*) (624°–695°K)	27 (*393*) (578°–703°K)				
	55.20 (*239*) (0°K)	32.2 (*247*) (471°K)						
	55.56 (*137*) (0°K)	32.9 (*187*) (440°–600°K)						
	56.6 (*71*) (750°K)	34 (g) (*412*) (496°–578°K)						
	56.64 (*446*) (740°–803°K)	36.0 (g) (*247*) (663°K)						
	63.0 (*341*) (767°–821°K)	44 (*412*) (496°–578°K)						

$\Delta H_{\text{vap.}}$	40.98 (*341*) (1094°–1275°K) 50.1 (*447*) (1075°–1298°K) 50.88 (*446*) (1076°–1241°K) 53.22 (*185*) (823°–1223°K) 55.51 (*239*) (846°–950°K)				
ΔH_{fusion}	<2 (*213*)	2.07 (f) (*277*)			
$\Delta H_{\text{diss}^{\text{n}}\text{ of dimer}}$	32.9 (*53*) 34.5 (*53*)	24 (*412*)	14.8 (*252*)		
$\Delta H_{\text{solution}}$		−44.5 (*379*) −50.38 (*260*) −51.1 (*288*)			
$S^{\ominus}_{(298°\text{K})}$	52.3 (*183*) 52.4 (*183*)	18.12 (d) (*277*) 19.76 (e) (*277*) 92.51 (g) (*247*)		51.2 (*186*)	53.0 (*184*)
$\Delta H_{\text{SUB}(298°\text{K})}$	47.8 (*71*)	43.2 (*187*) 52.99 (*247*)			
ΔH_{SUB}	44.9 (*71*) (*750*°K)	42.7 (*187*) (440°–600°K) 48.04 (*247*) (663°K)			
S	68.1 (*471*) (880°K) 69.0 (*210*) (880°K)	66.6 (*470*) (500°K)			
$\Delta S_{\text{vap.}}$	38.7 (*185*) (550°–950°K)				

---

[a] Key to abbreviations: (a) β-cristobalite modification (b) amorphous modification (c) quartz modification (d) β-modification (e) α′-modification (f) α-modification (g) dimer (h) α-quartz modification

[b] Entropy values in cal·mole^{-1}·degree^{-1}; enthalpy values in kcal·mole^{-1}.

^{19}F magnetic resonance studies support the presence of other fluoroberyllium species in *dilute* solution (*108*, *389*).

The ^{19}F spectrum (*146*, *254*) of aqueous ammonium tetrafluoroberyllate at 20° showed a single quartet, all four components equally intense and, therefore, all fluorine nuclei are equivalent; $J_{^{9}Be-^{19}F} = 33.2 \pm 1.2$ (*254*), 33.7 ± 0.2 (*146*), and 34.0 Hz (*108*). A quadruplet in the spectrum of commercial $(NH_4)_2BeF_4$ has been attributed (*140*) to BeF_3^-, consistent with the formulation $[BeF_3 \cdot H_2O]^-$. The spectra of aqueous beryllium solutions (*108*) containing variable amounts of fluoride show a quartet for each species present in solution. When $F:Be = 0.5$, only BeF^+ was detected; when $F:Be = 1.0$, both BeF^+ (65%) and BeF_2 (35%) were detected; when $F:Be = 2.0$. BeF^+, BeF_2 (60%) and BeF_3^- [see also (*140*)] were present, and when $F:Be = 4.0$, BeF_3^- (22%) and BeF_4^{2-} (78%) were the only species in solution. The coupling constant increases with decrease in the number of fluorine atoms in the complex, but the line-widths in the multiplets do not substantially change from BeF_4^{2-} to BeF^+.

VI. Thermodynamic Properties

The increasing interest in beryllium and its compounds in such fields as rocket propellants and nuclear reactors has dictated the necessity for obtaining accurate thermodynamic and physical data for its compounds. The known thermodynamic parameters for the beryllium di- and monohalides are listed in Table XII, and it is obvious that the monohalides are unstable with respect to disproportionation and could not exist in an ionic lattice. The evaluation of the enthalpies of formation and the entropies of metal dihalides is discussed by Brewer and co-workers (*96*).

The heat of solution of anhydrous BeF_2 is -24.17 kcal·mole^{-1} (*250*), which may be compared with the heats of solution of Be and BeO in hydrofluoric acid of 94.25 and 23.3 kcal·mole^{-1}, respectively, (*287*). Values for the corresponding chloride systems are 13.65, 87.9 (*287*), and -89.2 kcal·mole^{-1} (*507*), respectively. The standard heats of formation of some alkali metal tetrachloroberyllates, M_2BeCl_4 (M = Li, -315.50; Na, -316.54; K, -336.22 kcal·mole^{-1}), have been derived (*260*) via the enthalpies of reaction for

$$2MCl + BeCl_2 \rightarrow M_2BeCl_4$$

ACKNOWLEDGMENT

I wish to express my thanks to Professor G. E. Coates for encouraging my interest in beryllium chemistry and for providing criticisms of the draft of this article.

REFERENCES

1. Abdrashitova, E. I., and Petrovskii, G. T., *Dokl. Akad. Nauk SSSR* **175**, 1305 (1967).
2. Adamoli, C., Can. Patent 383,438 (1939).
3. Adamoli, C., U.S. Patent 2,303,783 (1942).
4. Adamoli, C., and Panebianco, G., Can. Patent 383,440 (1939).
5. Addison, C. C., and Walker, A., *J. Chem. Soc., London* p. 1220 (1963).
6. Ahrland, S., *Acta Chem. Scand.* **10**, 723 (1956).
7. Akishin, P. A., and Spiridonov, V. P., *Sov. Phys.-Crystallogr.* **2**, 472 (1957).
8. Akishin, P. A., Spiridonov, V. P., and Sobolev, G. A., *Dokl. Akad. Nauk SSSR* **118**, 1134 (1958).
9. Aleksandrova, I. P., *Sov. Phys.-Crystallogr.* **14**, 268 (1969).
10. Aleksandrova, I. P., and Afanas'ev, M. L., *J. Struct. Chem. (USSR)* **9**, 807 (1968).
11. Aleksandrova, I. P., Falaleeva, L. M., Ilyukhin, V. V., and Aleksandrov, K. S., *Sov. Phys.-Crystallogr.* **13**, 871 (1969).
12. Aleksandrova, I. P., Zherebtsova, L. I., and Leibovich, T. I., *Sov. Phys.-Crystallogr.* **14**, 218 (1969).
13. Allegro, G., and Perego, G., *Acta Crystallogr.* **16**, 188 (1963).
14. Anderson, R. A., Bell, N. A., Coates, G. E., and Francis, B. R., personal communication.
15. Arora, M., and Mehrotra, R. C., *Indian J. Chem.* **7**, 399 (1969).
16. Ashby, E. C., *Quart. Rev. Chem. Soc.* **21**, 259 (1967).
17. Ashby, E. C., and Arnott, R. C., *J. Organometal. Chem.* **14**, 1 (1968).
18. Ashby, E. C., Carter, J. H., and Sanders, J. R., *J. Amer. Chem. Soc.* **90**, 6385 (1968).
19. Ashby, E. C., Sanders, R., and Carter, J., *Chem. Commun.* p. 997 (1967).
20. Atterberg, A., *Bull. Soc. Chim.* **19**, 497 (1873).
21. Atterberg, A., *Ber. Deut. Chem. Ges.* **9**, 855 (1876).
22. Atwood, J. L., and Stucky, G. D., *J. Amer. Chem. Soc.* **91**, 4426 (1969).
23. Babko, A. K., and Shimadina, L. G., *Russ. J. Inorg. Chem.* **4**, 482 (1959).
24. Bähr, G., and Thiele, K. H., *Chem. Ber.* **90**, 1578 (1957).
25. Balueva, G. A., and Ioffe, S. T., *Russ. Chem. Rev.* **31**, 439 (1962).
26. Bamberger, C. E., Baes, C. F., and Young, J. P., *J. Inorg. Nucl. Chem.* **30**, 1979 (1968).
27. Banford, L., and Coates, G. E., *J. Chem. Soc., London* p. 5591 (1964).
28. Bannister, A. J., and Padley, J. S., *J. Chem. Soc.* **A**, 658 (1969).
29. Barabas, A., *Stud. Cercet. Fiz.* **30**, (1965).
30. Barabas, A., *Rev. Roum. Chim.* **11**, 751 (1966).
31. Barabas, A., *Stud. Cercet. Chim.* **14**, 87 (1966).
32. Baral, A. K., Saha, H. K., and Ray, N. N., *J. Inorg. Nucl. Chem.* **29**, 2490 (1967).
33. Baral, A. K., Saha, H. K., and Ray, N. N., *J. Indian Chem. Soc.* **45**, 90 (1968).
34. Baral, A. K., Saha, H. K., and Ray, N. N., *J. Indian Chem. Soc.* **45**, 652 (1968).
35. Baral, A. K., Saha, H. K., and Ray, N. N., *J. Indian Chem. Soc.* **45**, 855 (1968).
36. Baral, A. K., Saha, H. K., and Ray, N. N., *J. Indian Chem. Soc.* **45**, 858 (1968).

37. Barker, T. V., *J. Chem. Soc., London* p. 2484 (1912).

38. Barton, C. J., *J. Phys. Chem.* **64**, 306 (1960).

39. Barton, C. J., Friedman, H. A., Grimes, W. R., Insley, H., Moore, R. E., and Thoma, R. E., *J. Amer. Ceram. Soc.* **41**, 63 (1958).

40. Batsanova, L. R., Egorov, V. A., and Nikolaev, A. V., *Dokl. Chem.* **178**, 153 (1968).

41. Batsanova, L. R., and Novoselova, A. V., *Zh. Obshch. Khim.* **26**, 1827 (1956).

42. Batsanova, L. R., and Novoselova, A. V., *Izv. Vyssh. Uchebn. Zaved. Khim. Tekhnol.* **2**, 751 (1959).

43. Batsanova, L. R., Novoselova, A. V., and Simanov, Y. P., *Zh. Neorg. Khim.* **1**, 2368 (1956).

44. Batsanova, L. R., Yure'v, G. S., and Doronina, V. P., *Zh. Strukt. Khim.* **9**, 79 (1968).

45. Beevers, C. A., and Lipson, H., *Z. Kristallogr. Mineral. Petrogr. Abt. A* **82**, 297 (1932).

46. Beja, M., U.S. Patent 1,992,854 (1935).

47. Bell, N. A., *J. Organometal. Chem.* **13**, 513 (1968).

48. Bell, N. A., and Coates, G. E., *Proc. Chem. Soc., London* p. 59 (1964).

49. Bell, N. A., and Coates, G. E., *J. Chem. Soc., London* p. 692 (1965).

50. Bell, N. A., and Coates, G. E., *J. Chem. Soc.* **A**, 1069 (1966).

51. Bell, N. A., and Coates, G. E., *J. Chem. Soc.* **A**, 823 (1968).

52. Bell, R. J., Bird, N. F., and Dean, P., *Proc. Phys. Soc., London* (*Solid State Phys.*) **1**, 299 (1968).

53. Belousov, V. I., Sidorov, L. N., Akishin, P. A., and Komarov, S. A., *Russ. J. Phys. Chem.* **41**, 1598 (1967).

54. Belousov, V. I., Sidorov, L. N., and Akishin, P. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* p. 131 (1968).

55. Belyaev, R. A., "Okis Berilliya. Svoistva i Primenenie." Gos. Izd. Lit. v Oblasti At. Nauki i Tekh., Moscow, 1962.

56. Berengard, A. S., and Glushkova, M. T., *Zh. Strukt. Khim.* **9**, 79 (1968).

57. Bergstrom, F. W., *J. Amer. Chem. Soc.* **50**, 657 (1928).

58. Berkowitz, J., and Chupka, W. A., *Ann. N.Y. Acad. Sci.* **79**, 1073 (1960).

59. Bertin, F., Thomas, G., and Merlin, J. C., *Bull. Soc. Chim. Fr.* p. 2393 (1967).

60. Besson, J., *Bull. Soc. Chim. Fr.* p. 1175 (1950).

61. Biermann, W. J., and McCorkell, R., *Can. J. Chem.* **40**, 1368 (1962).

62. Biermann, W. J., and McCorkell, R., *Can. J. Chem.* **41**, 112 (1963).

63. Biermann, W. J., and McCorkell, R., *Can. J. Chem.* **45**, 2846 (1967).

64. Biltz, W., and Keunecke, E., *Z. Anorg. Allg. Chem.* **147**, 171 (1925).

65. Biltz, W., Klatte, K. A., and Rahlfs, E., *Z. Anorg. Allg. Chem.* **166**, 339 (1927).

66. Biltz, W., and Klemm, W., *Z. Anorg. Allg. Chem.* **152**, 267 (1926).

67. Biltz, W., and Messerknecht, C., *Z. Anorg. Allg. Chem.* **148**, 157 (1925).

68. Biltz, W., and Rahlfs, E., *Z. Anorg. Allg. Chem.* **166**, 351 (1927).

69. Bjerrum, N., *Chem. Ber.* **62**, 1091 (1929).

70. Bjerrum, J., Schwarzenbach, G., and Sillén, L. G., "Stability Constants." Chem. Soc., London, 1957.

71. Blauer, J. A., Greenbaum, M. A., and Farber, M., *J. Phys. Chem.* **69**, 1069 (1965).

72. Blidin, V. P., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 400 (1954).

73. Blidin, V. P., *Zh. Neorg. Khim.* **1**, 2093 (1956).

74. Blidin, V. P., *Zh. Obshch. Khim.* **26**, 1281 (1956).

75. Blidin, V. P., *Zh. Neorg. Khim.* **2**, 1149 (1957).
76. Blidin, V. P., Gordienko, V. I., and Shalverova, O. K., *Zh. Neorg. Khim.* **1**, 2623 (1956).
77. Blinc, R., and Levstek, I., *J. Phys. Chem. Solids* **12**, 295 (1960).
78. Bobovich, Y. S., *Opt. Spectrosc.* (*USSR*) **11**, 85 (1961).
79. Bobovich, Y. S., *Opt. Spectrosc.* (*USSR*) **13**, 382 (1962).
80. Bodforss, S., *Z. Phys. Chem. Stoechiom. Verwandschaftslehre* **124**, 66 (1926).
81. Bodforss, S., *Z. Phys. Chem. Stoechiom. Verwandschaftslehre* **130**, 82 (1927).
82. Bonner, O. D., Jumper, C. F., and Rogers, O. C., *J. Phys. Chem.* **62**, 6 (1958).
83. Booth, H. S., and Merlub-Sobel, M., *J. Phys. Chem.* **35**, 3303 (1931).
84. Booth, H. S., and Torrey, G. G., *J. Phys. Chem.* **35**, 2465 (1931).
85. Booth, H. S., and Torrey, G. G., *J. Phys. Chem.* **35**, 3111 (1931).
86. Booth, H. S., Torrey, G. G., and Merlub-Sobel, M., U.S. Patent 1,893,221 (1933).
87. Borzenkova, M. P., Novoselova, A. V., Simanov, Y. P., Chernykh, I., and Yarembash, E. I., *Zh. Neorg. Khim.* **1**, 2071 (1956).
88. Bourion, F., *C. R. Acad. Sci.* **145**, 62 (1907).
89. Brandenberger, E., *Schweiz. Mineral. Petrogr. Mitt.* **13**, 243 (1932).
90. Bredereck, H., Lehmann, G., Schonfield, C., and Fritzsch, E., *Ber. Deut. Chem. Ges. B* **72**, 1414 (1939).
91. Breusov, O. N., Novoselova, A. V., and Simanov, Y. P., *Dokl. Chem.* **118**, 935 (1958).
92. Breusov, O. N., and Simanov, Y. P., *Russ. J. Inorg. Chem.* **4**, 1190 (1959).
93. Breusov, O. N., Trapp, G., Novoselova, A. V., and Simanov, Y. P., *Russ. J. Inorg. Chem.* **4**, 304 (1959).
94. Breusov, O. N., Vagurtova, N. M., Novoselova, A. V., and Simanov, Y. P., *Russ. J. Inorg. Chem.* **4**, 1008 (1959).
95. Brewer, L., *in* "The Chemistry and Metallurgy of Miscellaneous Materials" (L. L. Quill, ed.), pp. 197, 215. McGraw-Hill, New York, 1950.
96. Brewer, L., Somayajula, G. R., and Brackett, E., *Chem. Rev.* **63**, 111 (1963).
97. Brinckmann, F. E., Fetter, N. R., and Peters, F. M., *U.S. Govt. Res. Develop. Rep.* **40**(17), S21 (1965); AD 283306 (1962).
98. Brown, I. M., and Weissman, S. I., *J. Amer. Chem. Soc.* **85**, 2528 (1963).
99. Budnikov, P. P., and Belyaev, R. A., *Zh. Vses. Khim. Obshchest.* **6**, 629 (1961).
100. Budzinski, H., *Z. Anorg. Allg. Chem.* **347**, 248 (1966).
101. Budzinski, H., and Kolditz, L., *Z. Anorg. Allg. Chem.* **342**, 46 (1966).
102. Budzinski, H., and Thilo, E., *Z. Anorg. Allg. Chem.* **327**, 8 (1964).
103. Büchler, A., and Klemperer, W., *J. Chem. Phys.* **29**, 121 (1958).
104. Büssem, W., Fischer, H., and Gruner, E., *Naturwissenschaften* **23**, 740 (1935).
105. Burns, J. H., and Gordon, E. K., *Acta Crystallogr.* **20**, 135 (1966).
106. Buslaev, Y. A., and Gustyakova, M. P., *Zh. Neorg. Khim.* **10**, 1524 (1965).
107. Buslaev, Y. A., Gustyakova, M. P., and Tamm, N. S., *Russ. J. Inorg. Chem.* **11**, 83 (1966).
108. Buslaev, Y. A., and Petrosyants, S. P., *Zh. Strukt. Khim.* **10**, 726 (1969).
109. Chaigneau, M., *Bull. Soc. Chim. Fr.* p. 886 (1957).
110. Ch'ang, M., and Novoselova, A. V., *Vestn. Mosk. Univ., Khim.* **19**, 37 (1964).
111. Chauvenet, E., *C. R. Acad. Sci.* **152**, 87 (1911).
112. Ch'ih-tsu, H., and Novoselova, A. V., *Russ. J. Inorg. Chem.* **6**, 1097 (1961).
113. Churney, K. L., and Armstrong, G. T., *J. Res. Nat. Bur. Stand., Sect. A* **73**, 281 (1969).

114. Coates, G. E., Glockling, F., and Huck, N. D., *J. Chem. Soc., London* p. 4512 (1952).

115. Coates, G. E., and Glockling, F., *J. Chem. Soc., London* p. 22 (1954).

116. Coates, G. E., and Glockling, F., *J. Chem. Soc., London* p. 2526 (1954).

117. Coates, G. E., and Green, S. I. E., *Proc. Chem. Soc., London* p. 376 (1961).

118. Coates, G. E., and Green, S. I. E., *J. Chem. Soc., London* p. 3340 (1962).

119. Coates, G. E., Heslop, J. A., Redwood, M. E., and Ridley, D., *J. Chem. Soc.* **A**, 1118 (1968).

120. Coates, G. E., and Mukherjee, R. N., *J. Chem. Soc., London* p. 229 (1963).

121. Coates, G. E., and Tranah, M. *J. Chem. Soc.* **A**, 615 (1967).

122. Coates, G. E., Wade, K., and Green, M. L. H., "Organometallic Chemistry." Methuen, London, 1967.

123. Colclough, R. O., Gee, G., Higginson, W. C. E., Jackson, J. B., and Litt, M., *J. Polymer Sci.* **34**, 171 (1959).

124. Counts, W. E., Roy, R., and Osborn, E. F., *J. Amer. Ceram. Soc.* **36**, 12 (1953).

125. Cupr, V., and Salanský, H., *Z. Anorg. Allg. Chem.* **176**, 241 (1928).

126. Dance, I. G., and Freeman, H. C., *Acta Crystallogr., Sect. B* **25**, 304 (1969).

127. Darwin, G. E., and Buddery, J. H., *in* "Beryllium." Butterworth, London, 1960.

128. Datta, S., *Proc. Roy. Soc., Ser. A* **101**, 187 (1922).

129. Delimarskii, Y. K., Sheiko, I. N., and Feshchenko, V. G., *Zh. Fiz. Khim.* **29**, 1499 (1955).

130. Dessy, R. E., *J. Amer. Chem. Soc.* **82**, 1580 (1960).

131. Dessy, R. E., and Handler, G. S., *J. Amer. Chem. Soc.* **80**, 5824 (1958).

132. Diamond, R. M., *J. Amer. Chem. Soc.* **77**, 2978 (1955).

133. Dick, J., and Maurer, A., *Stud. Cercet. Chim.* **10**, 61 (1963).

134. Durand, J. F., *C. R. Acad. Sci.* **182**, 1162 (1926).

135. Dutta, R. K., *Sci. Cult.* **18**, 599 (1953).

136. Dutta, R. K., and Sen-Gupta, A. K., *J. Indian Chem. Soc.* **33**, 146 (1956).

137. Efimenko, J., *J. Res. Nat. Bur. Stand., Sect. A* **72**, 75 (1968).

138. Ephraim, F., *Z. Phys. Chem. Stoechiom. Verwandschaftslehre* **81**, 513 (1913).

139. Everest, D. A., "The Chemistry of Beryllium." Elsevier, Amsterdam, 1964.

140. Feeney, J., Haque, R., Reeves, L. W., and Yu, C. P., *Can. J. Chem.* **46**, 1389 (1968).

141. Feild, G. P., *J. Amer. Chem. Soc.* **61**, 1817 (1939).

142. Fetter, N. R., *Organometal. Chem. Rev., Sect. A* **3**, 1 (1968).

143. Fiat, D. N., and Connick, R. E., *J. Chem. Phys.* **29**, 1349 (1963).

144. Fischer, W., and Rahlfs, O., *Z. Elektrochem.* **26**, 5239 (1932).

145. Fishwick, A. H., and Coates, G. E., *J. Chem. Soc.* **A**, 477 (1968).

146. Francis, P. E., and Lawrenson, I. J., *J. Inorg. Nucl. Chem.* **26**, 1462 (1964).

147. Fratiello, A., Schuster, R. E., and Miller, D. P., *Mol. Phys.* **12**, 111 (1967).

148. Fricke, R., *Z. Anorg. Allg. Chem.* **253**, 173 (1947).

149. Fricke, R., and Havestadt, L., *Z. Anorg. Allg. Chem.* **146**, 121 (1925).

150. Fricke, R., and Havestadt, L., *Z. Anorg. Allg. Chem.* **152**, 357 (1926).

151. Fricke, R., and Rode, O., *Z. Anorg. Allg. Chem.* **152**, 347 (1926).

152. Fricke, R., and Rode, O., *Z. Anorg. Allg. Chem.* **163**, 31 (1927).

153. Fricke, R., and Röbke, F., *Z. Anorg. Allg. Chem.* **170**, 25 (1928).

154. Fricke, R., and Ruschhaupt, F., *Z. Anorg. Allg. Chem.* **146**, 103 (1925).

155. Fricke, R., and Schützdeller, H., *Z. Anorg. Allg. Chem.* **131**, 130 (1923).

156. Friedrickson, W. R., and Hogan, M. E., *Phys. Rev.* **46**, 454 (1934).

157. Funck, E., *Ber. Bunsenges. Phys. Chem.* **68**, 617 (1964).

158. Funk, H., and Römer, F., *Z. Anorg. Allg. Chem.* **239**, 288 (1938).

159. Funk, H., and Rogler, E., *Z. Anorg. Allg. Chem.* **252**, 323 (1944).

160. Furby, E., and Wilkinson, K. L., *J. Inorg. Nucl. Chem.* **14**, 123 (1960).

161. Galinos, A. G., *J. Amer. Chem. Soc.* **82**, 3032 (1960).

162. Galinos, A. G., *J. Inorg. Nucl. Chem.* **19**, 69 (1961).

163. Galinos, A. G., *J. Inorg. Nucl. Chem.* **24**, 1555 (1962).

164. Ganem, A., Pobedimskaya, E. A., and Belov, N. V., *Sov. Phys.-Crystallogr.* **13**, 1071 (1968).

165. Gaydon, A. G., "Dissociation Energies and Spectra of Diatomic Molecules." Chapman & Hall, London, 1947.

166. Getmon, F. H., *J. Electrochem. Soc.* **66**, 143 (1934).

167. Ghose, T. K., Chakrabarty, T. N., and Ray, N. N., *J. Indian Chem. Soc.* **42**, 847 (1965).

168. Ghosh, A. K., *Z. Anorg. Allg. Chem.* **300**, 98 (1959).

169. Ghosh, A. K., Mitra, G., and Ray, N. N., *J. Indian Chem. Soc.* **30**, 221 (1953).

170. Ghosh, A. K., and Ray, N. N., *J. Indian Chem. Soc.* **31**, 729 (1954).

171. Ghosh, A. K., and Ray, N. N., *Sci. Cult.* **20**, 603 (1955).

172. Ghosh, A. K., and Ray, N. N., *J. Indian Chem. Soc.* **32**, 209 (1955).

173. Ghosh, A. K., and Ray, A. B., *Anal. Chim. Acta* **14**, 112 (1956).

174. Ghosh, A. K., and Ray, N. N., *Z. Anorg. Allg. Chem.* **300**, 102 (1959).

175. Ghosh, A. K., and Ray, N. N., *Z. Anorg. Allg. Chem.* **300**, 109 (1959).

176. Gilbert, R. A., and Garrett, A. B., *J. Amer. Chem. Soc.* **78**, 5501 (1956).

177. Gilman, H., and Schulze, F., *J. Chem. Soc., London* p. 2663 (1927).

178. Gilman, H., and Schulze, F., *J. Amer. Chem. Soc.* **49**, 2904 (1927).

179. Glaze, W. H., Selman, C. M., and Freeman, C. H., *Chem. Commun.* p. 474 (1966).

180. Goldschmidt, V., *Skr. Nor. Vidensk.-Akad. Oslo, I. Mat.-Naturv. Kl.* **8**, 7 (1926).

181. Goubeau, J., and Rodewald, B., *Z. Anorg. Allg. Chem.* **258**, 162 (1949).

182. Grebenshchikov, R. G., *Dokl. Chem.* **114**, 485 (1957).

183. Greenbaum, M. A., Arin, M. L., and Farber, M., *J. Phys. Chem.* **67**, 1191 (1963).

184. Greenbaum, M. A., Arin, M. L., Wong, M., and Farber, M., *J. Phys. Chem.* **68**, 791 (1964).

185. Greenbaum, M. A., Foster, J. N., Arin, M. L., and Farber, M., *J. Phys. Chem.* **67**, 36 (1963).

186. Greenbaum, M. A., Yates, R. E., Arin, M. L., Arshadi, M., Weiher, J., and Farber, M., *J. Phys. Chem.* **67**, 703 (1963).

187. Greenbaum, M. A., Yates, R. E., and Farber, M., *J. Phys. Chem.* **67**, 1802 (1963).

188. Grigorev, A. I., Evseeva, N. K., and Sipachev, V. A., *J. Struct. Chem. USSR* **10**, 387 (1969).

189. Grigorev, A. I., Orlova, Y. V., Sipachev, V. A., and Novoselova, A. V., *Dokl. Phys. Chem.* **152**, 762 (1963).

190. Grigorev, A. I., Sipachev, V. A., and Novoselova, A. V., *Dokl. Phys. Chem.* **160**, 40 (1965).

191. Grigorev, A. I., Sipachev, V. A., and Novoselova, A. V., *Russ. J. Inorg. Chem.* **12**, 319 (1967).

192. Grimes, W. R., *Nucl. News (Hinsdale, Ill.)* **7**, 3 (1964).

193. Gross, P., Hayman, C., Greene, P. D., and Bingham, J. T., *Trans. Faraday Soc.* **62**, 2719 (1966).

194. Grosse, A. V., and Ipatieff, V. N., *J. Org. Chem.* **1**, 559 (1936).

195. Guseinov, G. G., Ilyukhin, V. V., and Belov, N. V., *Sov. Phys.-Dokl.* **10**, 594 (1965).

196. Gyunner, E. A., and Mel'nichenko, L. M., *Russ. J. Inorg. Chem.* **11**, 232 (1966).

197. Hahn, T., *Neues Jahrb. Mineral., Abh.* **86**, 1 (1953).

198. Hardy, C. J., Greenfield, B. F., and Scargill, D., *J. Chem. Soc., London* p. 174 (1961).

199. Hardy, C. J., and Scargill, D., *J. Chem. Soc., London* p. 2658 (1961).

200. Harned, H. S., and Owen, R. B., "The Physical Chemistry of Electrolyte Solutions." Reinhold, New York, 1950.

201. Harrap, B. S., and Heymann, E., *Chem. Rev.* **48**, 45 (1951).

202. Hatton, J., Rollin, B. V., and Seymour, E. F. W., *Phys. Rev.* **83**, 672 (1951).

203. Hayes, E. F., *J. Phys. Chem.* **70**, 3740 (1966).

204. Head, E. L., Holley, C. E., and Rabideau, S. W., *J. Amer. Chem. Soc.* **79**, 3687 (1957).

205. Hecht, H., *Z. Anorg. Allg. Chem.* **254**, 37 (1947).

206. Herzberg, G., "Spectra of Diatomic Molecules." Van Nostrand, New York, 1950.

207. Heusler, K. E., *Z. Elektrochem.* **65**, 192 (1961).

208. Heydweiller, A., *Z. Phys. Chem. Stoechiom. Verwandschaftslehre* **89**, 281 (1915).

209. Hildenbrand, D. L., and Murad, E., *J. Chem. Phys.* **44**, 1524 (1966).

210. Hildenbrand, D. L., and Theard, L. P., *J. Chem. Phys.* **42**, 3230 (1965).

211. Hildenbrand, D. L., and Theard, L. P., *J. Chem. Phys.* **50**, 5350 (1969).

212. Hitch, B. F., and Baes, C. F., *Oak Ridge Rep.* **ORNL-4076** (1967).

213. Hitch, B. F., and Baes, C. F., *Inorg. Chem.* **8**, 201 (1969).

214. Hönigschmid, O., and Birckenbach, L., *Ber. Deut. Chem. Ges.* **55**, 4 (1922).

215. Holley, C. E., and Lemons, J. F., *Los Alamos Rep.* **LA-1660** (1954).

216. Holm, J. L., and Kleppa, O. J., *Inorg. Chem.* **8**, 207 (1969).

217. Hon, J. F., *Phys. Rev.* **124**, 1368 (1961).

218. Hoshino, S., Mitsui, T., Jona, F., and Pepinsky, R., *Phys. Rev.* **107**, 1255 (1957).

219. Humpidge, T. S., *Proc. Roy. Soc., London* **39**, 1 (1886).

220. Hurley, H., and Wier, T. P., *J. Electrochem. Soc.* **98**, 203 (1951).

221. Hyde, K. R., O'Conner, D. J., and Wait, E., *J. Inorg. Nucl. Chem.* **6**, 14 (1958).

222. Ilyukhin, V. V., and Belov, N. V., *Sov. Phys.-Dokl.* **6**, 851 (1962).

223. Ilyukhin, V. V., and Belov, N. V., *Sov. Phys.-Crystallogr.* **6**, 685 (1962).

224. Imaaka, M., and Mizusaua, S., *Yogyo Kyokai Shi* **61**, 13 (1953).

225. Jache, A. W., and Cady, G. H., *J. Phys. Chem.* **56**, 1106 (1952).

226. Jahn, W., *Z. Anorg. Allg. Chem.* **276**, 113 (1954).

227. Jahn, W., *Z. Anorg. Allg. Chem.* **277**, 274 (1954).

228. Jahn, W., and Thilo, E., *Z. Anorg. Allg. Chem.* **274**, 72 (1953).

229. Jain, S. R., and Soundararajan, S., *J. Inorg. Nucl. Chem.* **26**, 1255 (1964).

230. Jenkins, F. A., *Phys. Rev.* **35**, 315 (1930).

231. Johnson, R. E., Staritzky, E., and Douglas, R. M., *J. Amer. Chem. Soc.* **79**, 2037 (1957).

232. Johnson, W. H., and Gilliland, A. A., *J. Res. Nat. Bur. Stand., Sect. A* **65**, 59 (1961).

233. Jones, L. V., Etter, D. E., Hudgens, C. R., Huffman, A. A., Rhinehammer, T. B., Rogers, N. E., Tucker, P. A., and Wittenberg, L. J., *J. Amer. Ceram. Soc.* **45**, 79 (1962).

234. Kakihana, H., and Sillén, L. G., *Acta Chem. Scand.* **10**, 985 (1956).

235. Katti, M. R., and Sharma, H. D., *Indian J. Pure Appl. Phys.* **6**, 458 (1968).

236. Kawecki, H. C., *J. Electrochem. Soc.* **89**, 133 (1946).

237. Kawecki, H. C., *in* "The Metal Beryllium" (D. W. White and J. E. Burke, eds.), p. 63. Amer. Soc. Metals, Cleveland, Ohio, 1955.

238. Kellogg, H. H., *in* "The Metal Beryllium" (D. W. White and J. E. Burke, eds.), p. 49. Amer. Soc. Metals, Cleveland, Ohio, 1955.

239. Khandamirova, N. E., Evseev, A. M., Pozharskaya, G. V., Borisov, E. A., and Nesmayanov, A. N., *Russ. J. Inorg. Chem.* **4**, 998 (1959).

240. Kirkina, D. F., Novoselova, A. V., and Simanov, Y. P., *Dokl. Akad. Nauk SSSR* **107**, 837 (1956).

241. Kirkina, D. F., Novoselova, A. V., and Simanov, Y. P., *Zh. Neorg. Khim.* **1**, 125 (1956).

242. Kjellgren, B. R. F., *J. Electrochem. Soc.* **93**, 122 (1948).

243. Kleiner, K. E., *Zh. Obshch. Khim.* **21**, 18 (1951).

244. Klemm, W., *Z. Anorg. Allg. Chem.* **152**, 235 (1926).

245. Klemm, W., *Z. Anorg. Allg. Chem.* **152**, 295 (1926).

246. Klemm, W., Tilk, W., and Müllenheim, S., *Z. Anorg. Allg. Chem.* **176**, 1 (1928).

247. Ko, H. C., Greenbaum, M. A., Farber, M., and Selph, C. C., *J. Phys. Chem.* **71**, 254 (1967).

248. Koch, G., *Ber. Bunsenges. Phys. Chem.* **69**, 141 (1965).

249. Kolditz, L., and Bauer, K., *Z. Anorg. Allg. Chem.* **325**, 196 (1963).

250. Kolesov, V. P., Popov, M. M., and Skuratov, S. M., *Russ. J. Inorg. Chem.* **4**, 557 (1959).

251. Kolosova, I. F., and Belyavskaya, T. A., *Vestn. Mosk. Univ., Khim.* **18**, 52 (1963).

252. Kopelman, B., and Bender, H., *J. Electrochem. Soc.* **98**, 89 (1951).

253. Korenev, Y. M., Simanov, Y. P., and Novoselova, A. V., *Dokl. Chem.* **147**, 1052 (1962).

254. Kotz, J. C., Schaeffer, R., and Clouse, A., *Inorg. Chem.* **6**, 620 (1967).

255. Kovar, R. A., and Morgan, G. L., *J. Amer. Chem. Soc.* **91**, 7269 (1969).

256. Kovar, R. A., and Morgan, G. L., *J. Amer. Chem. Soc.* **92**, 5067 (1970).

257. Kraus, K. A., Nelson, F., and Smith, G. W., *J. Phys. Chem.* **58**, 11 (1954).

258. Krause, E., and Wendt, B., *Ber. Deut. Chem. Ges.* **56**, 466 (1923).

259. Krishnan, K., and Plane, R. A., *Inorg. Chem.* **6**, 55 (1967).

260. Krivtsov, N. V., Kedrova, N. S., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **12**, 1734 (1967).

261. Kuroda, T., and Matsumoto, O., *Bull. Tokyo Inst. Technol.* **61**, 29 (1964).

262. Kuroda, T., and Matsumoto, O., *J. Electrochem. Soc. Jap.* **33**, 29 (1965).

263. Kuroda, T., and Yamada, O., *J. Electrochem. Soc. Jap.* **35**, 124 (1967).

264. Kuvyrkin, O. N., Breusov, O. N., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Phys. Chem.* **34**, 160 (1960).

265. Landolt, H. H., and Bornstein, R., "Physikalisch-Chemische Tabellen," Vol. II, p. 1086. Springer-Verlag, Berlin and New York, 1923.

266. Lapkin, I. I., Anvarova, G. Y., and Povarnitsyna, T. N., *J. Gen. Chem. USSR* **36**, 1945 (1966).

267. Lapkin, I. I., and Povarnitsyna, T. N., *J. Gen. Chem. USSR* **38**, 96 (1968).

268. Laughlin, B. D., Kleinberg, J., and Davidson, A. W., *J. Amer. Chem. Soc.* **78**, 559 (1956).

269. Lebeau, P., *C. R. Acad. Sci.* **126**, 744 (1898).

270. Lebeau, P., *C. R. Acad. Sci.* **126**, 1227 (1898); *Ann. Chim. Phys.* **7**, 16 (1899).

271. Lebeau, P., *C. R. Acad. Sci.* **126**, 1272 (1898).

272. Lebeau, P., *C. R. Acad. Sci.* **126**, 1418 (1898).

273. Lecomte, J., Duval, C., and Wadier, C., *C. R. Acad. Sci.* **249**, 1991 (1959).

274. Leikina, B. N., and Novoselova, A. V., *J. Gen. Chem. USSR* **7**, 241 (1937); *Chem. Abstr.* **31**, 4568 (1937).

275. Levina, M. E., Novoselova, A. V., Simanov, Y. P., and Bakina, L. I., *Zh. Neorg. Khim.* **1**, 1638 (1956).

276. Linnell, R. H., and Haendler, H. M., *J. Phys. Colloid Chem.* **52**, 819 (1948).

277. McDonald, R. A., and Oetting, F. L., *J. Phys. Chem.* **69**, 3839 (1965).

278. McKenzie, J. D., *J. Chem. Phys.* **32**, 1150 (1960).

279. MacPherson, H. G., *Power Eng.* **71**, 2 (1967).

280. Mai, C. N., Korenev, Y. M., and Novoselova, A. V., *Zh. Neorg. Khim.* **10**, 1683 (1965).

281. Manning, D. L., and Mamantov, G., *J. Electroanal. Chem.* **18**, 137 (1968).

282. Markov, B. F., and Delimarskii, Y. K., *Ukr. Khim. Zh.* **19**, 255 (1953); *Ref. Zh. Khim.* No. 17860 (1954).

283. Masthoff, R., *Z. Chem.* **3**, 269 (1963).

284. Mathews, A. L., and Baes, C. F., *Inorg. Chem.* **7**, 373 (1968).

285. Matignon, C., and Cathala, J., *C. R. Acad. Sci.* **181**, 1066 (1925).

286. Matignon, C., and Cathala, J., *C. R. Acad. Sci.* **182**, 601 (1926).

287. Matignon, C., and Marchal, G., *C. R. Acad. Sci.* **183**, 927 (1926).

288. Matignon, C., and Marchal, G., *Bull. Soc. Chim. Fr.* **39**, 167 (1926).

289. Matignon, C., and Piettre, M., *C. R. Acad. Sci.* **184**, 853 (1927).

290. Matijevic, E., *J. Colloid Sci.* **20**, 322 (1965).

291. Matthias, B. T., Miller, C. E., and Remeika, J. P., *Phys. Rev.* **104**, 849 (1956).

292. Matthias, B. T., and Remeika, J. P., *Phys. Rev.* **103**, 262 (1956).

293. Mattock, G., *J. Amer. Chem. Soc.* **76**, 4835 (1954).

294. Matwiyoff, N. A., and Movius, W. G., *J. Amer. Chem. Soc.* **89**, 6077 (1967).

295. Mehrotra, R. C., and Arora, M., *J. Less-Common Metals* **17**, 181 (1969).

296. Mesmer, R. E., and Baes, C. F., *Inorg. Chem.* **6**, 1951 (1967).

297. Mesmer, R. E., and Baes, C. F., *Inorg. Chem.* **8**, 618 (1969).

298. Messerknecht, C., and Biltz, W., *Z. Anorg. Allg. Chem.* **148**, 152 (1925).

299. Metcalfe, W. J., Perry, G. S., and Turner, K. H., *U.K. At. Energy Auth., Rep.* **AWRE 0-21/62** (1962).

300. Meyer, L., and Wilkens, R., *Ber. Deut. Chem. Ges.* **20**, 681 (1887).

301. Mieleitner, K., and Steinmetz, H., *Z. Anorg. Allg. Chem.* **80**, 71 (1913).

302. Mielenz, W., and von Wartenberg, H., *Z. Anorg. Allg. Chem.* **116**, 267 (1921).

303. Mikheeva, L. M., Novoselova, A. V., and Biktimirov, R., *Zh. Neorg. Khim.* **1**, 499 (1956).

304. Miliotis, J. A., Galinos, A. G., and Tsangaris, J. M., *Bull. Soc. Chim. Fr.* p. 1413 (1961).

305. Mishra, R. K., and Khanna, B. N., *Indian J. Pure Appl. Phys.* **7**, 63 (1969).

306. Mitra, G., *J. Indian Chem. Soc.* **32**, 241 (1955).

307. Mitra, G., *J. Indian Chem. Soc.* **32**, 246 (1955).

308. Mitra, G., *J. Indian Chem. Soc.* **33**, 45 (1956).

309. Mitra, G., *J. Indian Chem. Soc.* **34**, 728 (1957).

310. Mitra, G., and Ray, N., *Sci. Cult.* **16**, 216 (1950).

311. Mitra, G., and Ray, N., *J. Indian Chem. Soc.* **32**, 43 (1955).

312. "Montecatini," Brit. Patent 928,716 (1963); *Chem. Abstr.* **59**, 14022 (1963).

313. Moore, R. E., *U.S. At. Energy Comm.* **ORNL-2938** (1960).

314. Morana, S. J., and Simons, G. F., U.S. Patent 2,804,372 (1957).

315. Morana, S. J., and Simons, G. F., Brit. Patent 848,345 (1960).

316. Morana, S. J., and Simons, G. F., *J. Metals* **14**, 571 (1962).

317. Moseley, P. T., and Shearer, H. M. M., *Chem. Commun.* p. 279 (1968).

318. Mukherjee, P. L., *Indian J. Phys.* **18**, 148 (1944).

319. Mulliken, R. S., *Phys. Rev.* **38**, 836 (1931).

320. Murty, P. S., and Rao, P. T., *Curr. Sci.* **38**, 187 (1969).

321. Mustafaev, N. M., Ilyukhin, V. V., and Belov, N. V., *Sov. Phys.-Dokl.* **9**, 1047 (1965).

322. Mustafaev, N. M., Ilyukhin, V. V., and Belov, N. V., *Sov. Phys.-Dokl.* **10**, 490 (1965).

323. Nespital, W., *Z. Phys. Chem. Abt. B* **16**, 153 (1932).

324. Neumann, B., and Richter, H., *Z. Elektrochem.* **31**, 484 (1925).

325. Neumann, G., *Justus Liebigs Ann. Chem.* **244**, 329 (1888).

326. Novikov, M. M., and Gurvich, L. V., *Opt. Spectrosc. (USSR)* **23**, 173 (1967).

327. Novikov, M. M., and Tunitskii, L. N., *Opt. Spectrosc. (USSR)* **8**, 396 (1960).

328. Novoselova, A. V., *J. Gen. Chem. USSR* **4**, 1206 (1934); *Chem. Abstr.* **29**, 3223 (1935).

329. Novoselova, A. V., *J. Gen. Chem. USSR* **16**, 509 (1946); *Chem. Abstr.* **41**, 1167 (1947).

330. Novoselova, A. V., *Usp. Khim.* **28**, 33 (1959).

331. Novoselova, A. V., and Averkova, M. Y., *J. Gen. Chem. USSR* **9**, 1063 (1939); *Chem. Abstr.* **33**, 7687 (1939).

332. Novoselova, A. V., and Azhikina, Y. Z., *Izv. Akad. Nauk SSSR, Neorg. Mater.* **2**, 1604 (1966).

333. Novoselova, A. V., and Batsanova, L. R., "Analytical Chemistry of Beryllium" (Engl. Transl. by J. Schmorak). Isr. Program Sci. Transl. Jerusalem, 1966.

334. Novoselova, A. V., Breusov, O. N., Kirkina, D. F., and Simanov, Y. P., *Zh. Neorg. Khim.* **1**, 2670 (1956).

335. Novoselova, A. V., Danilevich, R., and Tikhonova, A., *J. Gen. Chem. USSR* **16**, 439 (1946); *Chem. Abstr.* **41**, 904 (1947).

336. Novoselova, A. V., Korenev, Y. M., and Borzenkova, M. P., *Russ. J. Inorg. Chem.* **9**, 1103 (1964).

337. Novoselova, A. V., Levina, M. E., and Savel'eva, M. P., *Zh. Neorg. Khim.* **3**, 2562 (1958).

338. Novoselova, A. V., Levina, M. E., Simanov, Y. P., and Zhasmin, A. G., *J. Gen. Chem. USSR* **14**, 385 (1944); *Chem. Abstr.* **39**, 4542 (1945).

339. Novoselova, A. V., Mikheeva, L. M., Pochkaeva, T. I., and Tamm, N. S., *Vestn. Mosk. Univ., Khim.* **21**, 46 (1966).

340. Novoselova, A. V., Muratov, F. S., and Reshetnikova, L. P., *Vestn. Mosk. Univ., Khim.* **17**, 36 (1962).

341. Novoselova, A. V., Muratov, F. S., Reshetnikova, L. P., and Gordeev, I. V., *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz. Khim.* **13**, 181 (1958).

342. Novoselova, A. V., and Pashinkin, A. S., *Vestn. Mosk. Univ., Ser. Fiz.-Mat. Estestv. Nauk* No. 3, p. 75 (1954); *Chem. Abstr.* **48**, 13514 (1954).

343. Novoselova, A. V., Pashinkin, A. S., and Semenenko, K. N., *Vestn. Mosk. Univ., Ser. Fiz.-Mat. Estestv. Nauk* No. 10, p. 49 (1955).

344. Novoselova, A. V., Pochkaeva, T. I., Tamm, N. S., and Tomashchik, A. D., *Vestn. Mosk. Univ., Khim.* **24**, 70 (1969).

345. Novoselova, A. V., Pochkaeva, T. I., Tamm, N. S., and Tomashchik, A. D., *Russ. J. Inorg. Chem.* **14**, 316 (1969).

346. Novoselova, A. V., and Semenenko, K. N., *Zh. Neorg. Khim.* **3**, 2213 (1958).

347. Novoselova, A. V., Semenenko, K. N., and Turova, N. Y., *Vestn. Mosk. Univ., Ser. Mat., Mekh., Astron., Fiz. Khim.* **13**, 139 (1958).

348. Novoselova, A. V., and Simanov, Y. P., *Uch. Zap. Mosk. Gos. Univ.* **174**, 7 (1955).

349. Novoselova, A. V., Simanov, Y. P., and Kovba, L. M., *Dokl. Akad. Nauk SSSR* **126**, 93 (1959).

350. Novoselova, A. V., Simanov, Y. P., and Yarembash, E. I., *Zh. Fiz. Khim.* **26**, 1244 (1952).

351. Novoselova, A. V., and Sosnovskaya, I. G., *J. Gen. Chem. USSR* **21**, 893 (1951); *Chem. Abstr.* **48**, 1789 (1954).

352. Novoselova, A. V., Tamm, N. S., and Vorob'eva, O. I., *Khim. Redk. Elem., Akad. Nauk SSSR, Inst. Obshch. Neorg. Khim.* No. 2, p. 3 (1955).

353. O'Daniell, H., and Tscheischwili, L., *Z. Kristallogr. Mineral. Petrogr., Abt. A* **103**, 178 (1941).

354. O'Daniell, H., and Tscheischwili, L., *Z. Kristallogr. Mineral. Petrogr., Abt. A* **104**, 124 (1942).

355. O'Daniell, H., and Tscheischwili, L., *Z. Kristallogr. Mineral. Petrogr. Abt. A* **104**, 348 (1942).

356. O'Daniell, H., and Tscheischwili, L., *Neues Jahrb. Mineral., Monatsh.* **48**, 65 (1944).

357. O'Donnell, P. M., *J. Electrochem. Soc.* **114**, 1206 (1967).

358. Ohshima, H., and Nakamura, E., *J. Phys. Chem. Solids* **27**, 481 (1966).

359. Ohtaki, H., *Inorg. Chem.* **6**, 808 (1967).

360. Ohtaki, H., and Kata, H., *Inorg. Chem.* **6**, 1935 (1967).

361. Ohtaki, H., and Yamasaki, K., *Bull. Chem. Soc. Jap.* **31**, 6 (1958).

362. Okaya, Y., Vedam, K., and Pepinsky, R., *Acta Crystallogr.* **11**, 307 (1958).

363. Ozhigov, E. P., *Tr. Dal'nevost. Filiala Akad. Nauk SSSR, Ser. Khim.* **5**, 24 (1961).

364. Pace, E., *Arch. Farmacol. Sper. Sci. Affini* **42**, 35 (1926).

365. Pajeau, R., *C. R. Acad. Sci.* **202**, 1795 (1936).

366. Pajeau, R., *C. R. Acad. Sci.* **204**, 1202 (1937).

367. Palei, P. N., and Karalova, Z. K., *Zh. Anal. Khim.* **17**, 528 (1962).

368. Parsons, C. L., *J. Amer. Chem. Soc.* **26**, 721 (1904).

369. Parsons, C. L., and Robinson, W. O., *J. Amer. Chem. Soc.* **28**, 567 (1906).

370. Pascal, P. (ed.), *Nouveau Traite de Chimie Minèrale (IV)*, Masson, Paris p. 39 (1957).

371. Pauling, L., "The Nature of the Chemical Bond." Cornell Univ. Press, Ithaca, New York, 1942.

372. Peacock, R. D., and Sharp, D. W. A., *J. Chem. Soc., London* p. 2762 (1959).

373. Penland, R. B., Mizushima, S., Curran, C., and Quagliano, J. V., *J. Amer. Chem. Soc.* **79**, 1575 (1957).

374. Pepinsky, R., and Jona, F., *Phys. Rev.* **105**, 344 (1957).

375. Pepinsky, R., and Okaya, Y., *Bull. Amer. Phys. Soc.* **2**, 220 (1957).

376. Perfect, F. H., *Proc. Penn. Acad. Sci.* **26**, 54 (1952).

377. Peters, F. M., *J. Organometal. Chem.* **3**, 334 (1965).

378. Pincus, A. G., *J. Opt. Soc. Amer.* **35**, 92 (1945).

379. Pollock, J. H., *J. Chem. Soc., London* **85**, 603 (1904).

380. Potvin, R., and Farnham, G. S., *Trans. Can. Inst. Mining Met.* **49**, 525 (1946).

381. Prasad, S., and Srivastava, K. P., *J. Indian Chem. Soc.* **34**, 317 (1957).

382. Prasad, S., and Srivastava, K. P., *J. Indian Chem. Soc.* **35**, 261 (1958).

383. Prasad, S., and Srivastava, K. P., *J. Indian Chem. Soc.* **35**, 263 (1958).

384. Prasad, S., and Srivastava, K. P., *J. Indian Chem. Soc.* **35**, 653 (1958).

385. Prasad, S., and Srivastava, K. P., *J. Indian Chem. Soc.* **35**, 793 (1958).

386. Presnyakova, O. E., and Prishchenko, R. S., *Russ. J. Inorg. Chem.* **11**, 767 (1966).

387. Prytz, M., *Z. Anorg. Allg. Chem.* **180**, 355 (1929).

388. Prytz, M., *Z. Anorg. Allg. Chem.* **197**, 103 (1931).

389. Prytz, M., *Z. Anorg. Allg. Chem.* **231**, 238 (1937).

390. Purkayastha, B. C., *J. Indian Chem. Soc.* **24**, 257 (1947).

391. Purkayastha, B. C., *J. Indian Chem. Soc.* **25**, 81 (1948).

392. Quinet, M. L., *C. R. Acad. Sci.* **218**, 675 (1944).

393. Rahlfs, O., and Fischer, W., *Z. Anorg. Allg. Chem.* **211**, 349 (1933).

394. Rao, K. M., and Rao, P. T., *Indian J. Pure Appl. Phys.* **3**, 177 (1965).

395. Ray, A. B., Banerjee, S., and Ray, N. N., *J. Indian Chem. Soc.* **31**, 731 (1954).

396. Ray, A. K., *Naturwissenschaften* **44**, 279 (1957).

397. Ray, N. N., *Z. Anorg. Allg. Chem.* **201**, 289 (1931).

398. Ray, N. N., *Z. Anorg. Allg. Chem.* **205**, 257 (1932).

399. Ray, N. N., *Z. Anorg. Allg. Chem.* **206**, 209 (1932).

400. Ray, N. N., *Z. Anorg. Allg. Chem.* **227**, 32 (1936).

401. Ray, N. N., *Z. Anorg. Allg. Chem.* **227**, 103 (1936).

402. Ray, N. N., *Z. Anorg. Allg. Chem.* **241**, 165 (1939).

403. Reddy, Y. P., and Rao, P. T., *Curr. Sci.* **36**, 399 (1967).

404. Renz, C., *Z. Anorg. Allg. Chem.* **36**, 100 (1903).

405. Reshetnikova, L. P., Novoselova, A. V., and Zhakarova, B. S., *Vestn. Mosk. Univ., Khim.* **19**, 30 (1964).

406. Roberts, P. D., and Coates, G. E., *J. Chem. Soc.* **A**, 2651 (1968).

407. Rollier, M. A., *Gazz. Chim. Ital.* **84**, 663 (1954).

408. Roy, D. M., Roy, R., and Osborn, E. F., *J. Amer. Ceram. Soc.* **33**, 85 (1950).

409. Roy, D. M., Roy, R., and Osborn, E. F., *J. Amer. Ceram. Soc.* **36**, 185 (1953).

410. Roy, D. M., Roy, R., and Osborn, E. F., *J. Amer. Ceram. Soc.* **37**, 300 (1954).

411. Rundle, R. E., and Lewis, P. H., *J. Chem. Phys.* **20**, 132 (1952).

412. Ryabchikov, L. N., and Tikhinskii, G. F., *Phys. Metals Metallogr. (USSR) 10*, 146 (1960).

413. Samsonov, G. V., *Russ. Chem. Rev.* p. 339 (1966).

414. Sarkar, P. B., and Ray, N., *J. Indian Chem. Soc.* **6**, 987 (1929).

415. Schaal, R., and Faucherre, J., *Bull. Soc. Chim. Fr.* **14**, 927 (1947).

416. Schetky, L. M., and Johnson, H. A., eds., "Metallurgical Society Conferences. Vol. 33: Beryllium Technology." Gordon & Breach, New York, 1966.

417. Schindler, P., and Garett, A. B., *Helv. Chim. Acta* **43**, 2176 (1960).

418. Schmidt, J. M., *Bull. Soc. Chim. Fr.* **39**, 1686 (1926).

419. Schmidt, J. M., *Ann. Chim. (Paris)* **11**, 351 (1929).

420. Schulze, F., *Iowa State Coll. J. Sci.* **8**, 225 (1933).

421. Schuster, N. A., and Pake, G. A., *Phys. Rev.* **81**, 886 (1951).

422. Schwenzfeier, C. W., *in* "The Metal Beryllium" (D. W. White and J. E. Burke, eds.), p. 71. Amer. Soc. Metals, Cleveland, Ohio, 1955.

423. Sears, D. R., and Burns, J. H., *J. Chem. Phys.* **41**, 3478 (1964).

424. Semenenko, K. N., *Vestn. Mosk. Univ., Khim.* **20**, 39 (1965).

425. Semenenko, K. N., *Vestn. Mosk. Univ., Khim.* **22**, 36 (1967).

426. Semenenko, K. N., and Gavrilova, S. S., *Russ. J. Inorg. Chem.* **12**, 1049 (1967).

427. Semenenko, K. N., and Grigorev, A. I., *Russ. J. Inorg. Chem.* **10**, 1410 (1965).

428. Semenenko, K. N., Kedrova, N. S., and Iofa, B. Z., *Russ. J. Inorg. Chem.* **10**, 1537 (1965).

429. Semenenko, K. N., and Kurdyumov, G. M., *Russ. J. Inorg. Chem.* **6**, 1298 (1961).

430. Semenenko, K. N., and Naumova, T. N., *J. Struct. Chem. USSR* 4, 59 (1963).

431. Semenenko, K. N., Naumova, T. N., Gorokhov, L. N., and Novoselova, A. V., *Dokl. Chem.* **154**, 103 (1964).

432. Semenenko, K. N., Surov, V. N., *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1**, 1982 (1965).

433. Semenenko, K. N., Surov, V. N., and Alymova, T. E., *Russ. J. Inorg. Chem.* **13**, 885 (1968).

434. Semenenko, K. N., and Turova, N. Y., *Russ. J. Inorg. Chem.* **8**, 1093 (1963).

435. Semenenko, K. N., and Turova, N. Y., *Russ. J. Inorg. Chem.* **9**, 559 (1964).

436. Semenenko, K. N., and Turova, N. Y., *Russ. J. Inorg. Chem.* **10**, 42 (1965).

437. Sen-Gupta, A. K., *Sci. Cult.* **21**, 687 (1956).

438. Sen-Gupta, A. K., *J. Indian Chem. Soc.* **33**, 433 (1956).

439. Sen-Gupta, A. K., *J. Indian Chem. Soc.* **34**, 725 (1957).

440. Sen-Gupta, A. K., *Sci. Cult.* **24**, 98 (1958).

441. Sen-Gupta, A. K., *Sci. Cult.* **23**, 492 (1958).

442. Sen-Gupta, A. K., *Sci. Cult.* **25**, 79 (1959).

443. Sen-Gupta, A. K., *J. Indian Chem. Soc.* **37**, 291 (1960).

444. Sen-Gupta, A. K., *J. Indian Chem. Soc.* **37**, 473 (1960).

445. Sen-Gupta, A. K., *J. Indian Chem. Soc.* **37**, 547 (1960).

446. Sense, K. A., Snyder, M. J., and Clegg, J. W., *J. Phys. Chem.* **58**, 223 (1954).

447. Sense, K. A., and Stone, R. W., *J. Phys. Chem.* **62**, 453 (1958).

448. Shaffer, J. H., *U.S. At. Energy Comm.* **ORNL-3708** (1964).

449. Shaffer, J. H., Grimes, W. R., Watson, G. M., Cunes, R., Strain, J., and Kelly, M. J., *U.S. At. Energy Comm.* **TID-7160** (1960).

450. Shaffer, J. H., Watson, G. M., and Grimes, W. R., *U.S. At. Energy Comm.* **ORNL-2931** (1960).

451. Shcheglova, E. P., Thesis, IONKh, 1959; Quoted in Novoselova and Batsanova, ref. *333*, p. 20.

452. Shearer, H. M. M., and Spencer, C. B., *Chem. Commun.* p. 194 (1966).

453. Shearer, H. M. M., and Twiss, J., personal communication.

454. Shepherd, L. H., U.S. Patent 3,483,219 (1969).

455. Shirvington, P. J., Florence, T. M., and Harle, A. J., *Aust. J. Chem.* **17**, 1072 (1964).

456. Sidgwick, N. V., and Lewis, N. B., *J. Chem. Soc., London* p. 1287 (1926).

457. Sidorov, L. N., Belousov, V. I., and Akishin, P. A., *Russ. J. Phys. Chem.* **43**, 39 (1969).

458. Siemonsen, H., *Z. Elektrochem.* **55**, 327 (1951).
459. Sikka, S. K., and Chidambaram, *Acta Crystallogr., Sect. B* **25**, 310 (1969).
460. Silber, P., *Ann. Chim.* (*Paris*) **7**, 182 (1952).
461. Silina, G. F., Zarembo, Y. I., and Bertina, L. E., "Berillii Khimicheskaya Tekhnologiya i Metallurgiya." Atomizdat, Moscow, 1960.
462. Simanov, Y. P., Smirnova, I. N., and Novoselova, A. V., *Zh. Fiz. Khim.* **29**, 287 (1955).
463. Singh, R. B., and Rai, D. K., *Indian J. Pure Appl. Phys.* **4**, 102 (1966).
464. Sitdykova, N. S., Turova, N. Y., Semenenko, K. N., and Novoselova, A. V., *Russ. J. Inorg. Chem.* **6**, 1271 (1961).
465. Sloman, H. A., *J. Inst. Metals* **49**, 365 (1932).
466. Smirnov, M. V., and Chukreev, N. Y., *Zh. Fiz. Khim.* **32**, 2165 (1958).
467. Smirnov, M. V., and Chukreev, N. Y., *Russ. J. Inorg. Chem.* **4**, 1168 (1959).
468. Smirnov, M. V., Chukreev, N. Y., and Komarov, V. E., *Tr. Inst. Elektrokhim., Akad. Nauk SSSR, Ural. Filial* **9**, 29 (1966).
469. Smirnov, M. V., Komarov, V. E., and Chukreev, N. Y., *Russ. J. Inorg. Chem.* **10**, 1089 (1965).
470. Snelson, A., *J. Phys. Chem.* **70**, 3208 (1966).
471. Snelson, A., *J. Phys. Chem.* **72**, 250 (1968).
472. Snow, A. I., and Rundle, R. E., *Acta Crystallogr.* **4**, 348 (1951).
473. Spitzin, V., *Z. Anorg. Allg. Chem.* **189**, 337 (1930).
474. Spitzin, V., and Shostak, N. Z., *Khim. Redk. Elem., Akad. Nauk SSSR, Inst. Obshch. Neorg. Khim.* **2**, 85 (1955).
475. Stavvo, A. V., *Zh. Obshch. Khim.* **22**, 374 (1952).
476. Strohmeier, W., and Gernert, F., *Z. Naturforsch. B* **16**, 760 (1961).
477. Strohmeier, W., and Gernert, F., *Z. Naturforsch. B* **17**, 128 (1962).
478. Strohmeier, W., and Gernert, F., *Chem. Ber.* **95**, 1420 (1962).
479. Strohmeier, W., and Gernert, F., *Z. Naturforsch. B* **20**, 829 (1965).
480. Strohmeier, W., and Haecker, W., *Ber. Bunsenges. Phys. Chem.* **70**, 838 (1966).
481. Strohmeier, W., Haecker, W., and Popp, G., *Chem. Ber.* **100**, 405 (1967).
482. Strohmeier, W., and Popp, G., *Z. Naturforsch. B* **23**, 38 (1968).
483. Strohmeier, W., and Popp, G., *Z. Naturforsch. B* **23**, 870 (1968).
484. Summerford, C., Wade, K., and Wyatt, B. K., *J. Chem. Soc.* **A**, 2016 (1970).
485. Taboury, M. F., and Pajeau, R., *C. R. Acad. Sci.* **202**, 328 (1936).
486. Tamm, N. S., Thesis, MGU, 1949; Quoted in Novoselova and Batsanova, ref. *333*.
487. Tamm, N. S., and Novoselova, A. V., *Zh. Neorg. Khim.* **2**, 1428 (1957).
488. Tananaev, I. V., and Deichman, E. N., *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **6**, 591 (1947).
489. Tananaev, I. V., and Deichman, E. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 144 (1949).
490. Tananaev, I. V., and Deichman, E. N., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* p. 26 (1951).
491. Tananaev, I. V., and Shcheglova, E. P., *Russ. J. Inorg. Chem.* **6**, 623 (1961).
492. Tananaev, I. V., and Vinogradova, A. D., *Zh. Anal. Khim.* **14**, 487 (1959).
493. Tananaev, I. V., and Vinogradova, A. D., *Russ. J. Inorg. Chem.* **5**, 155 (1960).
494. Tatevskii, V. M., Tunitskii, L. N., and Novikov, M. M., *Opt. Spektrosk.* **5**, 520 (1958).
495. Tedenac, J. C., Avinens, C., Cot, L., and Maurin, M., *C. R. Acad. Sci., Ser. C* **286**, 240 (1969).
496. Tedenac, J. C., and Cot, L., *C. R. Acad. Sci., Ser. C* **268**, 1687 (1969).

497. Tedenac, J. C., Granier, W., Norbert, A., and Cot, L., *C. R. Acad. Sci., Ser. C* **268**, 1368 (1969).

498. Thiele, K. H., and Zdunneck, P., *Organometal. Chem. Rev.* **1**, 331 (1966).

499. Thilo, E., and Budzinski, H., *Z. Anorg. Allg. Chem.* **320**, 177 (1963).

500. Thilo, E., and Lehmann, H. A., *Z. Anorg. Allg. Chem.* **258**, 332 (1949).

501. Thilo, E., and Liebau, F., *Z. Phys. Chem. (Leipzig)* **199**, 125 (1952).

502. Thilo, E., and Schröder, H., *Z. Phys. Chem. (Leipzig)* **197**, 39 (1951).

503. Thoma, R. E., Insley, H., Friedman, H. A., and Hebert, G. M., *J. Nucl. Mater.* **27**, 166 (1968).

504. Thoma, R. E., Insley, H., Friedman, H. A., and Weaver, C. F., *J. Phys. Chem.* **64**, 865 (1960).

505. Thoma, R. E., Weaver, C. F., Friedman, H. A., and Harris, L. A., *J. Amer. Ceram. Soc.* **43**, 608 (1960).

506. Thoma, R. E., Weaver, C. F., Insley, H., and Hebert, G. M., *U.S. At. Energy Comm.* **TID-7641** (1962).

507. Thompson, C. J., Sinke, G. C., and Stull, D. R., *J. Chem. Eng. Data* **7**, 380 (1962).

508. Tiede, E., and Goldschmidt, F., *Chem. Ber.* **62**, 758 (1929).

509. Toropov, N. A., and Grebenshchikov, R. G., *Zh. Neorg. Khim.* **1**, 1619 (1956).

510. Toropov, N. A., and Grebenshchikov, R. G., *Zh. Neorg. Khim.* **1**, 2686 (1956).

511. Toropov, N. A., and Grebenshchikov, R. G., *Russ. J. Inorg. Chem.* **6**, 469 (1961).

512. Toropov, N. A., and Shchetnikova, I. L., *Zh. Neorg. Khim.* **2**, 1855 (1957).

513. Turnbull, D., and Cohen, M. H., *J. Chem. Phys.* **29**, 1049 (1958).

514. Turova, N. Y., Grigorev, A. I., Novoselova, A. V., Arzamanova, I. G., and Gur'yanova, E. N., *Dokl. Chem.* **164**, 916 (1965).

515. Turova, N. Y., Kedrova, N. S., Semenenko, K. N., and Novoselova, A. V. *Russ. J. Inorg. Chem.* **9**, 496 (1964).

516. Turova, N. Y., and Novoselova, A. V., *Russ. J. Inorg. Chem.* **8**, 273 (1963).

517. Turova, N. Y., Novoselova, A. V., and Kedrova, N. S., *Vestn. Mosk. Univ., Khim.* **19**, 3 (1964).

518. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Zh. Neorg. Khim.* **1**, 2567 (1956).

519. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **4**, 453 (1959).

520. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **4**, 1104 (1959).

521. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **5**, 550 (1959).

522. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **5**, 56 (1960).

523. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **5**, 452 (1960).

524. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **5**, 828 (1960).

525. Turova, N. Y., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **7**, 56 (1962).

526. Turova, N. Y., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **11**, 545 (1966).

527. Turova, N. Y., Semenenko, K. N., and Novoselova, A. V., *Russ. J. Inorg. Chem.* 8, 1126 (1963).

528. Turova, N. Y., Semenenko, K. N., and Savost'yanova, R. I., *Russ. J. Inorg. Chem.* **4**, 249 (1959).

529. Turova, N. Y., Semenenko, K. N., and Novoselova, A. V., *Russ. J. Inorg. Chem.* **8**, 452 (1963).

530. Turova, N. Y., Sitdykova, N. S., Novoselova, A. V., and Semenenko, K. N., *Russ. J. Inorg. Chem.* **8**, 275 (1963).

531. Uhlich, H., *Z. Phys. Chem., Abt. A*, Bodenstein-Festband, 423 (1931).

532. Uhlich, H., and Nespital, W., *Z. Elektrochem.* **37**, 559 (1931).

533. Van Arkel, A. E., *Metallwirt., Metallwiss., Metalltech.* **13**, 405 (1934).

534. Veazy, W. R., U.S. Patent 1,515,082 (1924).

535. Venturello, G., *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Natur.* **76**, 556 (1941).

536. Vivian, A. C., *Trans. Faraday Soc.* **22**, 211 (1926).

537. Vogel, W., and Gerth, K., *Glastech. Ber.* **31**, 15 (1958).

538. Vogel, W., and Gerth, K., *Silikat Tech.* **9**, 353 (1958).

539. Voigt, A., and Biltz, W., *Z. Anorg. Allg. Chem.* **133**, 277 (1924).

540. Vorob'eva, O. I., and Novoselova, A. V., *Zh. Obshch. Khim.* **18**, 567 (1948).

541. Vorob'eva, O. I., Novoselova, A. V., Zhasmin, A. G., and Simanov, Y. P., *Zh. Neorg. Khim.* **1**, 516 (1956).

542. Waddington, T. C., *Advan. Inorg. Chem. Radiochem.* **1**, 157 (1959).

543. Wade, K., Summerford, C. J., and Wyatt, B. K., *Chem. Commun.* p. 61 (1969).

544. Walter-Levy, L., and Perrotey, J., *C. R. Acad. Sci.* **254**, 1803 (1962).

545. Walter-Levy, L., and Perrotey, J., *Bull. Soc. Chim. Fr.* p. 1965 (1968).

546. Walton, R. A., *Quart. Rev. Chem. Soc.* **19**, 126 (1965).

547. Warren, B. E., and Hill, C. F., *Z. Kristallogr. Mineral. Petrogr., Abt. A* **89**, 481 (1934).

548. Weaver, C. F., Thoma, R. E., Friedman, H. A., and Hebert, G. M., *J. Amer. Ceram. Soc.* **44**, 146 (1961).

549. Weaver, C. F., Thoma, R. E., Insley, H., and Friedman, H. A., *J. Amer. Ceram. Soc.* **43**, 213 (1960).

550. Wharton, L., Berg, R. A., and Klemperer, W., *J. Chem. Phys.* **39**, 2023 (1963).

551. Wiberg, E., and Michaud, H., *Z. Naturforsch. B* **9**, 502 (1954).

552. Wieder, H. H., and Parkerson, C. R., *J. Phys. Chem. Solids* **27**, 247 (1966).

553. Windecker, C. E., *in* "The Metal Beryllium" (D. W. White and J. E. Burke, eds.), p. 102. Amer. Soc. Metals, Cleveland, Ohio, 1955.

554. Wong, M. M., Campbell, R. E., and Baker, D. H., *U.S. Bur. Mines, Rep. Invest.* **RI-5959** (1962).

555. Wood, G. B., and Brenner, A., *J. Electrochem. Soc.* **104**, 29 (1957).

556. Wood, J. K., *J. Chem. Soc., London* **97**, 878 (1910).

557. Yamaguchi, A., Penland, R. B., Mizushima, S., Lane, T. J., Curran, C., and Quagliano, J. V., *J. Amer. Chem. Soc.* **80**, 527 (1958).

558. Zachariasen, W., *Nor. Geol. Tidsskr.* **9**, 65 (1926).

559. Zachariasen, W., *J. Amer. Chem. Soc.* **54**, 3841 (1932).

560. Zachariasen, W., Pletinger, H., and Marezio, M., *Acta Crystallogr.* **16**, 1144 (1963).

561. Zakharkin, L. I., Okhlobystin, O. Y., and Strunin, B. N., *Bull. Acad. Sci. USSR, Div. Chem. Sci.* p. 2114 (1961).

562. Zarzycki, J., and Naudin, F., *Verres. Refract.* **14**, 113 (1960).

563. Zhdanov, G. S., and Savost'yanov, N. G., *Dokl. Akad. Nauk SSSR* **22**, 170 (1939); *Chem. Abstr.* **33**, 9081 (1939).

564. Zhmyreva, I. A., Kovaleva, I. V., Kolobkov, V. P., Kudryashov, P. I., Mokeeva, G. A., Petrovskii, G. T., and Tsurikova, G. A., *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* p. 29 (1967).
565. Zhmyreva, I. A., Kovaleva, I. V., Kolobkov, V. P., Kudryashov, R. I., Mokeeva, G. A., Petrovskii, G. T., and Tsurikova, G. A., *Izv. Akad. Nauk SSSR, Ser. Fiz.* **31**, 814 (1967).
566. Ziegler, K., Köster, R., Lehmkuhl, H., and Reinert, K., *Justus Liebigs Ann. Chem.* **629**, 33 (1960).