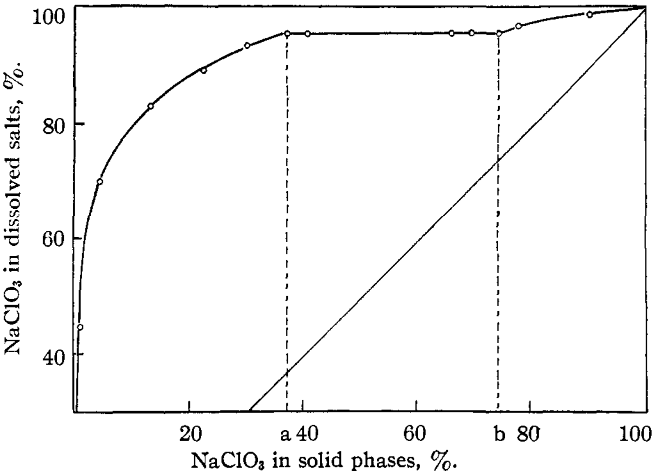

Fig. 2.—System $AgClO_3$-$NaClO_3$-H_2O at 25°; distribution diagram.

however, show no tendency to converge at this point, and hence do not suggest, as they do in the corresponding system of the bromates,[1] a tendency for compound formation between the components in the solid state. It is to be expected, therefore, that the limit (point a) will probably vary with temperature.

Since the percentage of $NaClO_3$ in the dissolved salts is always higher than it is in the solid solution, the system is an example of type V in the Roozeboom classification.[6] Evaporation at this temperature therefore always leads, under equilibrium conditions, to a solid richer in $AgClO_3$ than were the dissolved salts. This means that a sample of $AgClO_3$ containing $NaClO_3$ can be purified by a sufficient number of recrystallizations at this temperature. Moreover, since the tie-lines near the $AgClO_3$ side converge markedly toward the $AgClO_3$ corner, or since the solid phase at equilibrium is almost pure $AgClO_3$ for an appreciable concentration of $NaClO_3$ in the aqueous solution, this purification by recrystallization is rapid and efficient. In contrast, $NaClO_3$ containing some $AgClO_3$ could not thus be purified by recrystallization, since the solid obtained would be still richer in $AgClO_3$.

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[6] B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL CHEMISTRY, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION]

Barium Chloride Metaphosphate

BY F. R. HARTLEY AND A. D. WADSLEY

Barium chloride metaphosphate $Ba_4P_4O_{12}Cl_4$ has been prepared in a crystalline condition by the passage of chlorine over barium orthophosphate–carbon briquettes heated to 800°. As the result of a chemical method designed to distinguish the different classes of phosphate ion in insoluble compounds, this substance is considered to be an association of barium, chloride and metaphosphate radicals. Unit cell dimensions and possible space groups, together with some optical properties, have been determined.

The preparation of chlorophosphates has been claimed by several workers[1,2,3] but their claims are not supported by chemical or microscopical evidence. No anion of the type $(PO_3Cl)^=$ has been described hitherto, though there are well defined series of salts containing the complex anions $(PO_3F)^=$ and $PO_2F_2{}^-$ as intermediates in the series $(PO_4)^{\equiv}$ to POF_3.[4]

While investigating the mechanism of reaction of chlorine with a barium orthophosphate–carbon mixture at an elevated temperature, some crystals were isolated which had an empirical formula $BaPO_3Cl$ equivalent to barium chlorophosphate. In view of the lack of evidence for a compound of this nature, it was felt to be worthy of further investigation.

Experimental

Reagents.—Barium orthophosphate was prepared from Reagent Grade chemicals by the simultaneous addition of 500 ml. each of 1 *M* $BaCl_2$ and 0.67 *M* $(NH_4)_2HPO_4$ to 1 liter of a solution of 80 ml. of NH_4OH (sp. gr. 0.880) and 30 g. of NH_4Cl heated to 70°. After 1 hour the precipitation was complete, and the barium orthophosphate was washed by decantation, filtered, dried and ignited at 800°.

Anal. Found: Ba, 68.3; PO_4, 31.5. Calcd. for $Ba_3(PO_4)_2$: Ba, 68.5; PO_4, 31.5.

Barium "polyphosphate" was precipitated from a cold solution of barium chloride at *p*H 2.3 by the slow addition of an equivalent amount of commercial Graham salt.[5] After washing with water the dried cryptocrystalline material was heated to 800° and the melt allowed to cool slowly to below 400°. Prepared by this method, barium metaphosphate is a vitreous crystalline compound, insoluble in water. Analysis indicated that it contained only minor amounts of residual polyphosphate radicals.

Anal. Found: Ba, 46.7; PO_3, 52.5. Calcd. for $Ba(PO_3)_2$: Ba, 46.5; PO_3, 53.5.

Intensities and spacings from its powder pattern have been measured and are available in microfilm.[6]

Phosphorus oxychloride had been prepared as a by-product in some earlier work.[7] It was distilled before use, the fraction boiling between 104.5° and 105.5° being retained.

Chlorination of Barium Orthophosphate.—Barium orthophosphate and charcoal in the ratio 4.5 to 1 by weight were formed into briquettes with starch as bonding agent. These were heated at 800° in a current of chlorine in an apparatus which has been previously described.[7] A charge consisted of sufficient briquettes to contain 40 g. of ortho-

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[1] A. Ditte, *Compt. rend.*, **99**, 791 (1884).

[2] L. V. R. Ouvrard, *Ann. chim. phys.*, [6] **16**, 289 (1889).

[3] M. Berthelot, *ibid.*, [7] **25**, 197 (1902).

[4] W. Lange, *Ber.*, **62B**, 793 (1929).

[5] L. T. Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

[6] For detailed material supplementary to this article order Document 3030 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.50 for photocopies (6 × 8 inches) readable without optical aid.

[7] F. R. Hartley and A. W. Wylie, *J. Soc. Chem. Ind.*, **69**, 1 (1950).

phosphate through which a total of 25 g. of chlorine was passed at a rate of 0.14 g./min. Carbon monoxide appeared as an exhaust gas after 5 g. of chlorine had been passed. After 15 g. of chlorine had been used, phosphorus vapor in addition to carbon monoxide appeared at the exit tube, followed soon afterwards by PCl_3 and $POCl_3$ vapors which could be readily condensed.

The charge on removal from the furnace was powdery in texture and very distinctly zoned. The lower portion weighing 18.5 g., which was almost completely water soluble, consisted chiefly of barium chloride containing little unreacted charcoal. The upper half, which still contained much charcoal, was finally crystalline with some free barium chloride and unreacted barium orthophosphate. These latter compounds could readily be dissolved by digesting with an excess of 1 *N* nitric acid for an hour at 70°. Most of the carbon was removed by flotation with a kerosene–water mixture containing a trace of pine oil.

The fine colorless crystals left after these treatments were analysed chemically by dissolving a weighed amount in boiling 5 *N* nitric acid. The chloride evolved was absorbed in dilute sodium hydroxide and subsequently determined by Volhard's method. Barium, phosphorus and residual chloride were estimated by standard procedures on the nitric acid solution.

Anal. Found: Ba, 53.9; PO_3, 31.9; Cl, 13.9. Calcd. for $BaPO_3Cl$: Ba, 54.6; PO_3, 31.3; Cl, 14.1.

A list of spacings and intensities for the X-ray diagram of some finely ground crystals is available on micro film.[6]

The crystals could be fused at a temperature near 930° with some loss of chlorine, and formed a white vitreous solid on cooling.

Preparation of $BaPO_3Cl$ by Direct Heating.—Equimolar parts of barium metaphosphate and barium chloride were heated in a nickel crucible at 800°. After washing with hot 1 *N* nitric acid to remove unreacted matter, the finely divided material gave an X-ray powder pattern identical with that of the crystals prepared by chlorination. A chemical analysis also corresponded closely to the formula $BaPO_3Cl$. The X-ray diffraction pattern of a powder prepared in a similar manner from barium chloride and ammonium dihydrogen phosphate, contained several additional lines believed to be due to barium pyrophosphate, present as an impurity.

Each of these products exhibited a feeble yellow-brown fluorescence when illuminated with ultraviolet radiation (2800–3000 Å.). This is thought to be due to some nickel introduced as an impurity from the crucible, as the crystals prepared by chlorination did not exhibit this property.

Mechanism of the Chlorination Reaction.—Neglecting the carbon dioxide which may be formed, the reaction for complete chlorination may be represented by three equations

$$Ba_3(PO_4)_2 + 3Cl_2 + 8C \longrightarrow 3BaCl_2 + {}^1/_2P_4 + 8CO \quad (1)$$

$$Ba_3(P_4)_2 + 6Cl_2 + 8C \longrightarrow 3BaCl_2 + 2PCl_3 + 8CO \quad (2)$$

$$Ba_3(PO_4)_2 + 6Cl_2 + 6C \longrightarrow 3BaCl_2 + 2POCl_3 + 6CO \quad (3)$$

Accordingly each g.-atom of phosphorus in the gaseous products should be equivalent to 3 g.-atoms of chlorine fixed in the solid.

Analysis of the preparations from the experimental chlorination gave a ratio of 12.2 g.-atoms of chlorine in the briquettes for one g.-atom of phosphorus envolved. Attention is drawn to the appearance of considerable carbon monoxide prior to any phosphorus evolution.

As crystals of $BaPO_3Cl$ were isolated from the charge, these facts could be explained by postulating an initial reaction (4).

$$Ba_3(PO_4)_2 + 2Cl_2 + 2C \longrightarrow 2BaPO_3Cl + BaCl_2 + 2CO \quad (4)$$

Riban[8] proposed a similar mechanism for the chlorination of calcium orthophosphate. He concluded that calcium metaphosphate was formed as a mixture with calcium chloride.

On further chlorination, reaction (4) would yield barium chloride and a volatile phosphorus compound by means of a reaction such as (5).

$$2BaPO_3Cl + 4Cl + 4C \longrightarrow 2BaCl_2 + 2POCl_3 + 4CO \quad (5)$$

The sharp zoning of the charge observed on removal from the furnace indicates that (5) must proceed slowly.

An alternative hypothesis for the formation of $BaPO_3Cl$ may be found if it is assumed that the phosphorus oxychloride produced in the lower half of the charge is able to form $BaPO_3Cl$ directly from barium orthophosphate as in equation (6).

$$Ba_3(PO_4)_2 + POCl_3 \longrightarrow 3BaPO_3Cl \quad (6)$$

This reaction was verified by an experiment in which phosphorus oxychloride vapor, carried by a stream of nitrogen, was passed over powdered barium orthophosphate in an alundum boat, heated in a tube furnace at 800°. After washing with 1 *N* nitric acid, an X-ray powder photograph of the finely divided material was identical with that of $BaPO_3Cl$. No macroscopic crystals were found.

Crystallographic Examination.—Microscopical examination showed that the crystals of $BaPO_3Cl$ consisted of fibrous needles often aggregated into spherical or fan shaped particles. As they were rarely terminated, no reliable measurements of interfacial angles were made. The average length was 50 to 100 microns although some exceeded 0.5 mm. in length. The majority of particles were acicular, consisting of groups of parallel fibers, the average width of an individual fiber being 3 to 5 μ. Some were more plate-like with a width of 30 to 40 μ, and in this form appeared to be true single crystals too small, however, for handling on a goniometer.

With polarized light, the crystals were anisotropic with parallel extinction. The plate-like single crystals with convergent light gave a biaxial figure almost parallel to an optic axis. γ was found to be parallel to the needle axis (X-ray *b* axis) giving a refractive index n_D 1.658. The crystals were optically positive, $2V$ being large.

X-Ray examination of a crystal of dimensions approximately 0.5 × 0.1 × 0.2 mm. by oscillation and moving film methods showed that $BaPO_3Cl$ crystallizes in the monoclinic system with the unit cell dimensions: $a = 8.39$, $b = 4.54$, $c = 11.39$ Å., $\beta = 82.8°$ (Cu Kα radiation $\lambda = 1.542$ Å.) The unit cell contains $(BaPO_3Cl)_4$ giving a calculated density 3.93. (Found 3.79 for the crystals, 3.83 for the powder obtained by reaction of $POCl_3$ with $Ba_3(PO_4)_2$.) Moving films were taken about the zero, first and second levels of the *b* axis and the zero level of the *a* axis on a Weissenberg goniometer of new design.[9] As there are no systematic extinctions the space group must be P2, Pm or P2/m. Although the crystal for this examination was selected with great care, the moving films showed it to consist of a group of smaller crystals approximately parallel to each other. No struc-

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(8) J. Riban, *Bull. soc. chim.*, **39**, 14 (1883).

(9) A. McL. Mathieson, *J. Sci. Inst.*, in press.

TABLE I

RATIOS OF BASICITIES OF PHOSPHORUS IN PHOSPHATE SALTS

1, Graham salt B.D.H. reagent; 2, Graham salt after fusion with NaCl; 3, Barium orthophosphate after NaCl fusion; 4, Barium metaphosphate after NaCl fusion; 5, $(BaPO_3Cl)_4$ after NaCl fusion; 6, "Anhydrous" Na_3PO_4 (Merck and Co., Inc., grade dehydrated at 1000°); 7, As 6 after passing $POCl_3$ at 800° (similar to $Ba_3(PO_4)_2$ treatment in text); 8, $BaPO_3F$ dissolved in 0.5 *N* H_2SO_4 and filtered; 9, $BaPO_3F$ after NaCl fusion.

Per cent. phosphorus as	1	2	3	4	5	6	7	8	9
Ortho	0.3	0.0	73.5	4.2	7.0	97.3	48.8	0.3	0.0
Pyro	15.3	27.0	23.5	38.4	49.4	2.6	25.6	98.0	100.0
Meta	84.4	73.0	3.0	57.4	43.6	0.1	25.6	1.7	0.0
Solution coagulated egg albumin + acetic acid	Yes	Yes	No	Yes	Yes	No	Yes	No	No

ture analysis has been attempted on account of the poorly developed crystals, and the resultant difficulty of obtaining accurate intensity measurements.

The Nature of the (PO_3Cl) Complex.—Apart from the chlorophosphates mentioned briefly by Ditte,[1] Ouvrard[2] and Berthelot,[3] compounds containing the orthophosphate ion and a halogen are well known. The group of minerals collectively known as apatite possesses the formula $R_5(PO_4)_3X$ where R is an alkaline earth metal (or lead in the case of the mineral pyromorphite) and X may be $(OH)^-$, F^- or Cl^-. Although this formula admits a very wide range of constitution, each member of the group crystallizes in the hexagonal system with axial ratios differing little for each member.

It is clear that the compound $(BaPO_3Cl)$ is not a member of this important group of substances, and it is tempting to suggest that it is the barium salt of monochlorophosphoric acid. However, although the existence of salts of monofluorophosphoric acid has been convincingly demonstrated by Lange,[4] attempts to prove that the $(PO_3Cl)^{=}$ ion may exist in solution have not been successful. Meerwein and Bodendorff[10] were unable to detect this ion by titrating phosphorus oxychloride with barium hydroxide, although they found evidence for the transient existence of the dichlorophosphate ion $(PO_2Cl_2)^-$. If it existed in the solid state the chlorophosphate ion would be expected to hydrolyze to an acid orthophosphate ion and a chloride ion

$$PO_3Cl^{=} + H_2O \longrightarrow HPO_4^{=} + Cl^- + H^+$$

A solution of a chlorophosphate would therefore give the characteristic tests for orthophosphate. Alternatively if $(BaPO_3Cl)_4$ contains both metaphosphate and chloride as acid groups, an aqueous solution would give the reactions of a condensed phosphate.

However the compound is virtually insoluble in water and cold dilute acids. Heating with acid has been shown to destroy the complex releasing chloride and orthophosphate, and this therefore fails to distinguish between these two alternative compositions.

Solution was effected by quickly fusing with previously melted sodium chloride, followed by an extraction with sodium sulfate solution to prevent reprecipitation of the phosphate. The filtered solution was titrated electrometrically with standard sodium hydroxide solution by the procedure of Gerber and Miles[11] to estimate the relative amounts of ortho-, pyro- and metaphosphate ions present in the solution. Experiments were made under similar conditions with Graham salt (before and after fusion with NaCl), barium metaphosphate "anhydrous" sodium orthophosphate, barium orthophosphate and barium fluorophosphate prepared by Lange's method.[4]

It must be emphasized that this test is applied from a semi-empirical point of view, and no attempt is made to predict the quantitative behavior of condensed phosphates under the thermal conditions employed.

The results are given in Table I.

There seems little doubt that this procedure correctly indicates whether the solid, prior to fusion with sodium chloride, contains ortho or condensed phosphate radicals. $(BaPO_3Cl)_4$ is seen to belong to the class containing condensed phosphate radicals and the ions $P_4O_{12}^{4-}$ and $4Cl^-$ which are present in the solid state must therefore be unassociated. The formation of this compound by heating together barium metaphosphate and barium chloride supports this view. The compound should therefore be called barium chloride metaphosphate in accordance with the views of the International Union of Chemistry.[12] It is perhaps best classed with those substances in which the apparently coördinated complex ion does not persist in solution. These have been called lattice compounds,[13] although the term does not yet appear to be universally accepted. Substances possessing asymmetrical coördination numbers, some double salts and many addition compounds involving neutral molecules belong to this group.

Barium fluorophosphate will be seen from Table I to behave as a pyrophosphate. Since the $(PO_3F)^{=}$ ion is relatively stable in solution, this is in accord with the accepted views on the dissociation of the phosphorus acids which have *pK* values of approximately 4.4 and 9.0. Gerber and Miles' analytical procedure effectively estimates the phosphorus acids radicals but, although distinguishing between ortho-, meta- and pyrophosphates, is unable to differentiate the pyrophosphate from divalent anions. Since the fusion treatment did not effect any material change in barium fluorophosphate, it obviously is a true

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[10] H. Meerwein and K. Bodendorff, *Ber.*, **62B**, 1952 (1929).

[11] A. B. Gerber and F. T. Miles, *Ind. Eng. Chem., Anal. Ed.*, **10**, 519 (1938); also **13**, 406 (1941).

[12] See for instance A. D. Mitchell, "British Chemical Nomenclature," Arnold & Co., London, 1948, p. 17.

[13] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Routledge & Sons, Ltd., London, 1938, p. 80.

coördinated complex, in no way related to barium chloride metaphosphate. This is emphasized by the behavior of these two apparently similar compounds toward cold dilute acids. Barium fluorophosphate is readily soluble; the chloride metaphosphate is not.

Bengtsson[14] found that an X-ray powder photograph of one form of barium fluorophosphate prepared by Lange's method closely resembled that of barium sulfate. On this evidence he assumed the two substances to be isomorphous. This infers that the oxygen and fluorine atoms have a similar tetrahedral arrangement about the phosphorus atom as the oxygen atoms have about the sulfur atom in $BaSO_4$, a not unlikely arrangement in view of the similarity in size of the oxygen and fluorine ions. A powder photograph of barium fluorophosphate prepared by Lange's method was made, spacings and intensities being available on microfilm.[6] The obvious differences between it and that of barium chloride metaphosphate show a more fundamental difference than would be expected if these two substances differed merely by the substitution of chlorine for fluorine in the PO_4 tetrahedron.

The crystal structures of only two metaphosphates have been determined. Pauling and Sherman[15] showed that aluminum metaphosphate contains ions of the composition $P_4O_{12}{}^{4-}$ grouped in a ring. This grouping has recently been confirmed by an X-ray analysis of ammonium tetrametaphosphate.[16] It is indeed regrettable that the barium chloride metaphosphate crystals were not suitable for a structure analysis, since metaphosphates as a rule are difficult to crystallize, their glassy or rubbery state being generally attributed to rings or chains of the empirical composition $(PO_3)_n$ analogous to the metasilicates.

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(14) E. Bengtsson, *Arkiv Kemi. Mineral Geol.*, **156**, No. 7 (1941).

(15) L. Pauling and J. Sherman, *Z. Krist.*, **96**, 481 (1937).

(16) C. Romers, J. A. A. Ketelaar and C. H. MacGillavry, *Nature*, **164**, 960 (1949).

MELBOURNE, AUSTRALIA RECEIVED MAY 19, 1950

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ZAGREB]

Coagulation Effects of Thorium Nitrate on Aqueous Sols of Silver Halides in *Statu Nascendi*. I. The Coagulation Curve and the Coagulation Value of Thorium Nitrate

BY B. TEŽAK, E. MATIJEVIĆ AND K. SCHULZ

The effect of thorium nitrate in various concentrations on systems of silver nitrate–hydrobromic acid, and silver nitrate–potassium bromide in aqueous solution, respectively, have been investigated by means of tyndallometrical measurements. By systematic dilution of thorium nitrate, the coagulation curve shows four distinct regions, two stabilization regions and two coagulation regions. For the diluted, negatively charged silver bromide sols in *statu nascendi* (5×10^{-4} N $AgNO_3$–2×10^{-3} N HBr) the first limit of coagulation–stabilization (0.02 N) represents the critical concentration of coagulation where the coagulating ion is nitrate ion, while the stabilizing action is caused by the thorium complexes of positive sign in adsorbed state. Under otherwise same conditions (2×10^{-4} N $AgNO_3$–4×10^{-4} N HBr and 4×10^{-3} N $Th(NO_3)_4$) the coagulation concentration is shifted from 2×10^{-2} N of potassium nitrate to 6×10^{-4} N of potassium sulfate. The second limit of stabilization–coagulation ($\sim 1 \times 10^{-3}$ N $Th(NO_3)_4$) is very much influenced by the initial concentration of the thorium nitrate solution and the acidity of the medium. The third limit of coagulation–stabilization ($\sim 3 \times 10^{-5}$ and $\sim 3 \times 10^{-6}$ N $Th(NO_3)_4$) gives the coagulation values of thorium complexes (probably trivalent and tetravalent, respectively) on the negatively charged silver bromide sol.

In accordance with the Schulze–Hardy rule, owing to its high electric charge, the effect of thorium ion on negatively charged sols is characterized by a small coagulation value. In many cases, however, this strong coagulating power is overshadowed either by the stabilization effect caused by the adsorption of this multivalent ion and the subsequent reversal of the original negatively charged sol into a positive one, or by the formation of variously charged complexes between thorium ion and other components of the system (*e.g.*, ionic parts of the protolytic reactions of water, various anions, etc.). Such examples were found by Gorochowsky and Protass,[1] Bosch and Haemers,[2] Gillis and Eeckhout,[3] Kruyt and Troelstra,[4] and others for coagulation of silver halide sols. The cited investigations gave evidence also that the state of the thorium ion in aqueous solution is far from a simple one, its reactions depending on the concentration and the "age" of the solution of thorium salt, and on the nature of other ionic components, especially those of anionic character. All these factors control the stabilizing effects. As the physical chemistry of aqueous solutions of ions of higher valency is the object of numerous newer investigations,[5] it would be worthwhile to give some results obtained by the tyndallometrical observations of the precipitation of silver halides in presence of thorium nitrate. Especially, it might be of interest to attempt to answer some open questions on this field using the experimental procedure already applied on the similar coagulating systems with ions of lower valency.[6]

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(1) G. N. Gorochowsky and J. R. Protass, *Z. physik. Chem.*, **A174**, 122 (1935).

(2) F. Bosch and H. Haemers, *Natuurw. Tijdschr. Belg.*, **18**, 90 (1936).

(3) J. Gillis and J. Eeckhout, *ibid.*, **19**, 49 (1937).

(4) H. R. Kruyt and S. A. Troelstra, *Kolloid-Beihefte*, **54**, 262 (1943).

(5) M. Kasha and G. E. Sheline, Natl. Nuclear Energy Ser., Div. IV. Transuranium Elements, Pt. I (1949), p. 180; M. Kasha, *ibid.*, p. 295; J. C. Hindman and D. P. Ames, *ibid.*, p. 348; J. C. Hindman, *ibid.*, pp. 370, 388, 405. J. Sutton, *J. Chem. Soc.*, S 275 (1949); R. H. Betts and R. K. Michels, *ibid.*, S 286 (1949); E. Glueckauf, H. A. C. McKay and A. R. Mathieson, *ibid.*, S 299 (1949).

(6) B. Težak, *Kolloid-Z.*, **68**, 60 (1934); *Z. physik. Chem.*, **A176**, 219 (1935); *ibid.*, **A191**, 270 (1942); *Arhiv kem.*, **19**, 19 (1947); B. Težak and E. Matijević, *ibid.*, **19**, 29 (1947); B. Težak, E. Matijević and K. Schulz, *ibid.*, **20**, 1 (1948).