Some visual and microscopic observations were made on systems enclosed in evacuated glass cells and capillaries.[1] Only the t_i points, the temperatures at which, on heating, the optically anisotropic systems become isotropic, could be reproduced repeatedly, and also a few observations below this temperature. The latter (t_g-) points seem to represent transitions from a highly viscous to a much less viscous state, the system however remaining anisotropic. Below the t_g point the magnetically-operated stirrer left a wake which did not heal while above this point healing was increasingly rapid. The observed properties of these states conformed with McBain's definitions[11] of the gel and jelly states, respectively, and they are labeled accordingly in Fig. 4. Although these data should be useful for filling in the missing boundaries of a phase diagram, we feel that we have not sufficient data to construct a complete diagram of this type.

Comparison of Figs. 3 and 4 shows that at soap concentrations below 50%, addition of solvent depresses the visual t_i points markedly without having a corresponding effect on the ultimate transition temperature observed in the thermal analysis. An experiment made with a similar system[12] shows that structural anisotropy, at low concentrations, can exist up to the ultimate transition temperatures, where optical anisotropy no longer exists.

Small amounts of water affect not only the transition temperatures, but also the visual aspect of the system. At lower soap concentrations, the substantially anhydrous systems separate on cooling, at temperatures of 100° and below, into a soap curd and virtually pure cetane; the addition of water ($\sim$0.1%) will cause these mixtures to appear as turbid white gels, which completely retain the cetane. There is a marked difference between the anhydrous and the damp systems when they are viewed between crossed polarizers. The system containing traces of water exhibits a somber yellowish-red glow up to temperatures in the neighborhood of 125°; the anhydrous system shows very bright yellow coarse granules with variegated edges. Valid conclusions regarding the phase diagram can be drawn only from observations made on rigorously dried substances.

The latent heats of the individual phase changes have been evaluated by means of differential thermal analysis. In spite of the only moderate accuracy of the measurements, it can be seen from Table I that the latent heats of the phase changes are fairly constant throughout the concentration range studied. The probable error of the individual latent heats is ±5 to 8% depending on the sharpness of the peak. Where several peaks were superimposed, the individual heats could not be resolved and appear lumped together in the table. The sum of the heats of transition from the solid state at room temperature to the solution in cetane at the t_i point amounts to an average of 10,700 gram calories per mole of soap.

EMERYVILLE, CALIF. RECEIVED DECEMBER 18, 1950

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[11] J. W. McBain, K. J. Mysels and G. H. Smith, *Trans. Faraday Soc.*, **42B**, 173 (1946).

[12] Mr. R. J. Moore of these laboratories has followed the viscosity-temperature relation with a Brookfield viscosimeter at a concentration of about 9% soap in a light oil, and has found the viscosity to decrease sharply with temperature until the temperature corresponding to the ultimate transmission observed by differential thermal analyses was reached. At this point the temperature coefficient of viscosity suddenly decreased, and the viscosity decrease of the system became essentially that of the oil.

[CONTRIBUTION FROM THE DIVISION OF ANALYTICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

A Method for the Preparation of Rhenium(VI) Oxide[1]

BY H. NECHAMKIN[2], A. N. KURTZ AND C. F. HISKEY

Rhenium(VI) oxide is formed by the thermal decomposition of a neutralization product of rhenium(VII) oxide and dioxane. The dioxane complex appears to be $Re_2O_7 \cdot 3C_4H_8O_2$. Exact quantitative studies of the rhenium(VI) oxide disproportionation have been made and confirm a previously reported reaction.

Rhenium(VI) oxide was first prepared by Biltz and Lehrer[3,4] who interacted the metal and yellow rhenium(VII) oxide at 300°. By repeated cooling and grinding of the reagent mixture it was possible to get the reaction to go to completion in a number of days. Even then the product was not uniform, but had compositions ranging between $ReO_{2.4}$ and $ReO_{3.13}$.

A red rhenium(V) oxide also has been reported by Briscoe, *et al.*,[5] confirmed by Roth and Becker[6] and even described in Druce's recent monograph.[7] It now seems certain however that this substance was also the (VI) oxide and that this error has come into the literature largely because these authors did not have analytical methods sufficiently precise to distinguish between Re_2O_5(82.3% Re) and ReO_3-(79.5% Re). Biltz's claims for ReO_3 however rest upon more satisfactory analytical evidence, including a crystal structure determination by X-ray diffraction.

In view of the indefiniteness of composition of Biltz's preparations, it was decided to develop an

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[1] Based on the thesis research of Howard Nechamkin for the Degree of Master of Science in Chemistry at the Polytechnic Institute of Brooklyn, June, 1949. Some of this material was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September 19, 1949.

[2] Department of Chemistry, Pratt Institute, Brooklyn, N. Y.

[3] W. Biltz, A. A. Lehrer and K. Meisel, *Nachr. Ges. Wiss. Gottingen, Math.-Physik. Klasse*, 191 (1931).

[4] W. Biltz, A. A. Lehrer and K. Meisel, *Z. anorg. allgem. Chem.*, **207**, 113 (1932); **214**, 225 (1933).

[5] H. V. A. Briscoe, P. L. Robinson and A. J. Rudge, *J. Chem. Soc.*, 3087 (1931); *Nature*, **129**, 618 (1932).

[6] W. A. Roth and G. Becker, *Z. phys. Chem.*, **A159**, 27 (1932).

[7] J. G. F. Druce, "Rhenium," Cambridge University Press, 1948, p. 32.

alternative method for the preparation of this compound. After several preliminary studies had been made using carbon monoxide and sulfur dioxide to reduce rhenium(VII) oxide, a satisfactory synthesis was achieved by means of a thermal decomposition of the acid–base neutralization product of dioxane and rhenium(VII) oxide.

Preparation of Materials

Rhenium(VII) Oxide.—Two grams or less of powdered rhenium metal is placed at the sealed end of a length of Pyrex tubing about 10 cm. long and 9 mm. in diameter. The tube is sealed to an apparatus in which the metal is burned to the oxide, distilled and collected. The apparatus consists of a three-way stopcock, a ballast bulb, a manometer and a distillation receiver. The entire apparatus is evacuated, flamed carefully, checked for leaks and filled with pure dry oxygen. During the flaming operation, care must be taken not to heat the powdered metal too rapidly, since entrapped gas bubbles may, at times, be violently ejected and the metallic powder be spread through the apparatus. This sequence is repeated twice and finally a pressure of oxygen about 6 cm. above that of atmospheric is maintained. A horizontal tube furnace or cone heater, previously heated to about 450° is slipped over the length of tubing containing the metal so that about 5 cm. are heated strongly. After about two hours, the heater is advanced another 5 cm. and heating is continued for another two hours or more. A product of bright yellow appearance results. It is found that inclining the reaction tube slightly to permit the heavy oxide vapor to flow downward away from the metal speeds the reaction. With the aid of a bunsen burner the rhenium(VII) oxide is sublimed into the receiver. The yield is in excess of 99%.

Dioxane.—The C.P. solvent was dehydrated by refluxing over sodium and then distilled. The other organic reagents were usually C.P. and freshly distilled before use.

Tetraphenylarsonium Chloride.—This reagent was purchased from Eastman Kodak Co. and recrystallized from absolute alcohol. It was also prepared according to the procedure of Blicke and Monroe.[8] It has a melting point of 256–257°.

Experimental

The experimental approach that soon proved to be most promising was one which entailed the use of an anhydrous solvent for the rhenium(VII) oxide. Most of those chosen were reducing in character and basic in the G. N. Lewis sense. It was thought that by preventing ionization of the acid anhydride, to give the perrhenate ion, that the general character of the reduction process would be different from what it is in aqueous solution. In this way it was hoped that a method might be found to stop the reduction at the hexavalent state.

In general, it was found that alcohols, esters and anhydrides reduce the rhenium(VII) oxide to the black rhenium(IV) oxide. Ethers, however, gave more promising results since they caused reduction to the trioxide although generally in poor yield and of questionable purity. The ethers tested as solvent reductants included diethyl ether, anisole, diphenyl ether and dioxane. The best product of ReO_3 was obtained by refluxing with the dioxane, in which case a 40% yield of rhenium(VI) oxide of good purity was obtained. It was also noted that not only were the best products obtained using dioxane as solvent but dioxane solutions of rhenium(VII) oxide, evaporated to dryness on the hot-plate, deposited rhenium(VI) oxide, of fair purity. In fact this was a most effective method for making large quantities of a crude product.

In the preliminary experiments on the reduction of rhenium(VII) oxide with dioxane it was noted that a white deposit appeared at the junction of the solid and liquid phases. A further study of this substance and attempts at its pyrolysis were considered necessary in connection with the preparation of rhenium(VI) oxide. This approach proved to be the successful one.

Rhenium heptoxide was placed in a test-tube and dioxane, which had previously been refluxed over sodium was added to it. A white neutralization product formed, increasing in quantity with prolonged time of contact. Upon careful warming with constant agitation, the white material and the unchanged rhenium(VII) oxide went into solution. Cooling this solution resulted in the precipitation of a heavy, pearly-white crystalline deposit. The mixture was chilled in an ice-water bath to obtain maximum precipitation of the neutralization product and the dioxane was then decanted from the solid material. Excess dioxane was removed by vacuum drying in a desiccator at room temperature. The product thus prepared was a gray-white powder melting indefinitely in the range of 90–100°.

The neutralization product was analyzed by gravimetric rhenium precipitation and by molecular weight determination. Facilities, unfortunately, were lacking for carbon and hydrogen determination immediately after preparation. This would have been necessary since the compound is not only extremely hygroscopic but also unstable.

The gravimetric analyses were performed by the method of Willard and Smith[9] involving the precipitation of rhenium as tetraphenylarsonium perrhenate. The results showed a mean value for rhenium of 49.7 ± 0.1%. The theoretical per cent. of rhenium calculated for the neutralization product $Re_2O_7 \cdot 3C_4H_8O_2$ is 49.8%. This suggests a composition of the complex which is represented by one mole of Re_2O_7 associated with three moles of dioxane. Further quantitative studies in this connection produced similar results. The molecular weight determinations on the neutralization product were obtained from freezing point data in acetophenone, a solvent in which the complex was soluble. An average molecular weight of 655 was determined by this method which compares well with the anticipated 661 expected for the complex with the composition suggested.

The complex, on standing in a vacuum desiccator, became insoluble and darker in color. Analysis of the complex at intervals during the drying operation disclosed it to have lost weight to the extent of one mole of dioxane per mole of complex after 50 hours. Further loss in weight with prolonged exposure to vacuum was significantly slower.

Heating the neutralization product to about 145° resulted in rapid transformation to a beautiful brick-red product, presumably rhenium(VI) oxide. There was not the slightest trace of a blue tinge which would have indicated the presence of other oxides. During the pyrolysis gaseous products were emitted and investigation of them disclosed the presence of dioxane, aldehydes, carbon(II) oxide, carbon(IV) oxide and oxalic acid. The entire process of burning approximately two grams of metallic rhenium to rhenium(VII oxide, conversion to the dioxane neutralization product and final decomposition of the latter to rhenium(VI) oxide gave a yield of trioxide which was 98.6% based on the weight of rhenium metal used.

The product was analyzed quantitatively for rhenium content to determine its purity. The rhenium(VI) oxide was taken into solution with a few drops of nitric acid and 30% hydrogen peroxide. The solution was diluted and the rhenium precipitated as tetraphenylarsonium perrhenate. The rhenium content was found to be 79.47 ± 0.04% (theoretical for ReO_3 is 79.51%) based upon six analyses of samples weighing from 0.03 to 0.11 g.

When prepared as described here, it is a bright maroon-red solid possessing tiny glistening surfaces. If the oxide is observed by the transmitted light through very thin layers, it appears to be green. These properties are similar to those listed previously by Biltz, Lehrer and Meisel.[4,10]

Although the trioxide is chemically inert, it may be reduced with the lower alcohols and aldehydes. Heating in air or oxygen at elevated temperatures causes oxidation but at 110° it may be heated in air for several hours without a weight change.

An attempt was also made to develop a suitable gas phase reduction reaction using sulfur(IV) oxide and carbon(II) oxide. To accomplish this the heptoxide vapor was confined in a small vertical reaction tube where it remained by virtue of its great vapor density while the reducing gases were afforded an opportunity of reacting with it and precipitating the trioxide. It was found possible to convert oxide samples, 100 mg. in weight, in this way using an atmosphere of reducing gas pressure and a heating operation commencing at 180° with the temperature slowly increasing

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[8] F. F. Blicke and E. Monroe, THIS JOURNAL, **57**, 720 (1935).

[9] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, **11**, 305 (1939).

[10] K. Meisel, *Z. anorg. allgem. Chem.*, **207**, 121 (1932).

to 250° over a two-hour period. Although tedious for laboratory use it might easily be adapted for larger production. The product obtained is also red in color. Details of this process may be found in the literature.[11]

The presence of a bluish color or cast in the trioxide preparation appears to be due to incomplete reduction to the hexavalent state rather than to a state of subdivision of the compound as Biltz has argued.[12] There are several reasons for believing the above statement to be true: In the first place there is the sequence of color changes during the reduction process. This may be demonstrated by taking a single hexagonal platelet of the heptoxide and subjecting it to the reducing action of the above gases or, better yet, to controlled amounts of dioxane vapor. When this is done, it may be observed that the color changes from yellow through green to blue. The blue color steadily darkens and then changes to the red of the trioxide. This suggests that the red trioxide is the concluding stage of the reduction process and that the rhenium blue is intermediate. If the red oxide is reduced further it becomes black and does not pass through a blue colored stage.

In the second place, these observations do not differ from Biltz's[12] except in interpretation. It will be recalled that he contended that the rhenium blues were a different subdivision of the trioxide. This argument was based upon (a) X-ray diffraction data and (b) upon rhenium analyses.

With respect to the first point it must be remembered that only crystalline phases are observed so that a colloidal blue of intermediate rhenium valency would not be detected. Indeed Biltz himself reports the preparation of blues which showed no diffraction patterns whatsoever.

With respect to his analytical data the following comments are appropriate. The rhenium was determined by the nitron perrhenate method of Geilmann and Voigt.[13] Where sample weights are listed by Biltz they have a value of about 13 mg. For this size of sample the uncertainty would be according to Geilmann about 1%. Biltz's data suggest that his uncertainty is of this magnitude also. Now, if it is remembered that there is only a 2.6% difference between the rhenium contents of the tri- and the heptoxide, it is seen that rhenium blues reported as pure rhenium(VI) oxide by Biltz could have been contaminated to a considerable extent with the higher oxide without detection by his method of study.

From such considerations, it seems evident that the exact composition of these substances remains as an unsolved problem.

Biltz had observed that when rhenium(VI) oxide is heated in a vacuum at temperatures in excess of 300°, rhenium(VII) oxide is produced and a black residue of rhenium(IV) oxide remains. He formulated the reaction as

$$3ReO_3 \longrightarrow Re_2O_7 + ReO_2$$

but gave no quantitative data to support this formulation. In view of the state of the analytical techniques at that time, it seemed desirable to repeat the work in a very careful way. A large quantity of the rhenium(VI) oxide which possessed an average composition of $ReO_{2.959 \pm 0.006}$ was available and was used in this experiment.

An apparatus was so constructed that rhenium(VI) oxide was heated under vacuum conditions and the volatile rhenium (VII) oxide was separated from the rhenium(IV) oxide. Relatively large samples of rhenium(VI) oxide were used in this study and were heated at about 450° for from 16 to 28 hours during the decomposition. The weight of the two oxides produced, together with the original weight of the rhenium(VI) oxide used, and the analytical determination of the rhenium distribution between the two resultant oxides were used as criteria for the validation of Biltz' proposed equation. In Table I material balance data on the reaction are presented.

TABLE I

RHENIUM(VI) OXIDE DISPROPORTIONATION

Sample	Sample, g.	Re_2O_7 found	ReO_2 found	Re_2O_7 + ReO_2	Material balance
A	0.2947	0.1954	0.0991	0.2954	−0.0002
B	1.4108	0.9362	.4749	1.4111	.0003
C	2.2317	1.4826	.7489	2.2315	− .0002
D	1.8132	1.2026	.6108	1.8134	.0002
E	0.5811	0.3857	.1956	0.5813	.0002
F	1.6139	1.0698	.5440	1.6138	− .0001

It is apparent from these data that the original rhenium(VI) oxide disproportionates into the two other oxides without a detectable loss of oxygen. In each case the weight of oxides produced equals that of the original oxide decomposed within the limits of error imposed upon the study by the weighing technique. As a further check, it was decided to determine the purity of the oxides produced by the decomposition and to establish precisely the ratio of rhenium in each of the oxide phases. In Table II the data obtained are listed.

TABLE II

PURITY OF THE ReO_3 AND THE Re_2O_7 PHASES

Sample	$(C_6H_5)_4As^+$ ppt. of Re_2O_7	$\frac{Re_2O_7}{(C_6H_5)_4As\,ReO_4}$	$(C_6H_5)_4As^+$ ppt. of ReO_7	$\frac{ReO_2}{(C_6H_5)_4As\,ReO_4}$	$\frac{\text{Wt. of Re (as } Re_2O_7)}{\text{Wt. of Re (as } ReO_2)}$
A	0.5124	0.3813	0.2875	0.3447	1.776
B	2.4518	.3813	1.3790	.3443	1.776
C	3.8839	.3817	2.1762	.3441	1.784
D	3.1512	.3816	1.7693	.3452	1.782
E	1.0112	.3814	0.5677	.3445	1.780
F	2.8008	.3820	1.5784	.3447	1.778
Av. value		0.3816 ± 0.0002		0.3446 ± 0.0003	
Theo. value		0.3824		0.3445	1.778

From an inspection of columns three and five where the conversion factors for tetraphenylarsonium perrhenate to rhenium(VII) and rhenium(IV) oxides, respectively, are given, it can be seen that purity of these compounds is very good. Consequently there is justification for concluding that there are no

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[11] "Inorganic Syntheses," Vol. III.

[12] W. Biltz, F. W. Wrigge and K. Meisel, *Nachr. Ges. Wis. Gottingen Math.-Physik. Klasse, Fachgruppe III.* (*N. F.*), **1**, 161 (1936).

[13] W. Geilmann and A. Voigt, *Z. anorg. allgem. Chem.*, **193**, 311 (1930).

other disproportionation reactions occurring, *i.e.*, $4ReO_3 \rightarrow Re_2O_7 + Re_2O_5$, etc.

It will be observed that in spite of the high precision of these analytical data the value of the conversion factor $Re_2O_7/(C_6H_5)_4AsReO_4$ is low by about 0.2%. No satisfactory explanation for this discrepancy suggests itself.

If pure ReO_3 disproportionates according to the reaction

$$3ReO_3 \longrightarrow Re_2O_7 + ReO_2$$

the ratio of rhenium metal present at the end of the reaction as the (VII) oxide to that as the (IV) oxide should be exactly 2.000. Since the oxide used had a composition corresponding to $ReO_{2.96}$, the over-all equation should be

$$3ReO_{2.96} \longrightarrow 0.96\ Re_2O_7 + 1.08\ ReO_2$$

in which case the same ratio would be 1.777. The actual rhenium distribution between the two oxides was determined and the ratio (listed in column 6 of Table II) was calculated and found to be that expected. This indicates that not only does the disproportionation involve the four and seven valence states but that the rhenium oxide preparation $ReO_{2.96}$ very probably was contaminated with dioxide and not with any other phase.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA]

The Hydrates of Beryllium Sulfate

BY A. N. CAMPBELL, A. J. SUKAVA AND J. KOOP

The transition temperature for the change, $BeSO_4 \cdot 4H_2O \rightarrow BeSO_4 \cdot 2H_2O$ + solution, has been found to be 89.0°. Below this temperature the stable solid phase is the tetrahydrate, and above it the dihydrate. The normal boiling point of saturated aqueous beryllium sulfate solution is 108.2°, the equilibrium solid phase being the dihydrate. The existence of a monohydrate of beryllium sulfate has been disproved by X-ray diffraction studies. It is possible that a discontinuous series of solid solutions exists between the dihydrate and the anhydrous salt, with a miscibility gap lying between 19 and 11% water. The X-ray equipment was not sufficiently sensitive to decide this point, however, and it is also possible that the solid phases at the high temperature transition are simply dihydrate and anhydrous salt. This transition occurs at 270°, under an equilibrium pressure of 9.38 atm.

The literature concerning the hydrates of beryllium sulfate is summarily dealt with by Sidgwick,[1] and extensively by Gmelin.[2] Of the possible hydrates which have been claimed at various times, only the tetrahydrate, dihydrate and anhydrous forms can be said to be definitely proved to exist. A paper by Rohmer[3] has recently appeared in which the claim is made that the dihydrate has no stable existence and that the transition is from tetrahydrate to monohydrate. This claim we have disproved.

In order to complete (both verifying and correcting) available information, for the determination of lower hydrates and of their transition points, various equilibrium measurements were undertaken: solubilities in ternary systems with sulfuric acid and with alcohols, dilatometry, vapor pressure and X-ray examination.

I. Experimental Procedure

Preparation and Purification of Starting Material.—The tetrahydrate of beryllium sulfate was prepared from the carbonate (British Drug Houses "glucinum carbonate") by treating with excess sulfuric acid. The procedure of separation and purification was similar to that employed by Parsons[4] and by Krauss and Gerlach.[5] Analysis of the product always showed good agreement when the beryllium sulfate content was calculated from separate estimations of both sulfate and beryllium ion, and it indicated that the tetrahydrate was reasonably free from occluded sulfuric acid.

The dihydrate was prepared from the tetrahydrate by dehydration. The density of the dihydrate does not appear in the literature and, since we required it to calculate the expansion in the dilatometer accompanying the transformation of tetrahydrate to dihydrate, we determined it as 1.865 g. per ml. at 25°.

The Ternary System: Beryllium Sulfate–Sulfuric Acid–Water.—The determination of the transition temperature of beryllium sulfate tetrahydrate to the next lower hydrate was accomplished by us by an investigation of the ternary system beryllium sulfate–sulfuric acid–water. The compositions of the saturated solutions of beryllium sulfate in aqueous sulfuric acid of varying concentrations were determined at different temperatures, together with those of the equilibrium solid phases. Working at successively higher temperatures, an isotherm was finally obtained on which tetrahydrate did not occur as solid phase. The transition temperature was then interpolated. The intersection of the tie-lines indicated clearly that the next lower hydrate was the dihydrate.

This investigation was pushed to a concentration of sulfuric acid of 80 weight per cent. It could not be carried to a higher concentration of sulfuric acid, because the high viscosity of the solutions made it impossible to separate the solid phase from the liquid phase in a satisfactory manner.

The solubility isotherms were determined at 25, 50, 75, 85 and 95°, employing Schreinemakers' method of the "wet rest," for the determination of the composition of the equilibrium solid phase. The saturated solution was separated from the wet rest in a specially designed apparatus employing a fritted glass filter, and operating at the temperature of the thermostat. The sulfate ion was estimated by precipitation as barium sulfate. Despite the well known objections to this method, it was shown by analysis of pure material that the method is satisfactory in this case. For the estimation of beryllium a method suggested by Bleyer and Boshard[6] was employed. The beryllium ion was precipitated as the hydroxide with ammonia in the presence of ammonium chloride, filtered by ordinary methods, and ignited to the oxide.

The isothermally invariant solutions (tetrahydrate–dihydrate–solution) were obtained by addition of tetrahydrate to solution saturated with dihydrate; both solids were evident at the end, the tetrahydrate as long transparent crystals, the dihydrate finely divided and settling slowly.

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[1] Sidgwick, "The Elements and their Compounds," Vol. 1, Clarendon Press, New York, N. Y., 1950, p. 207.

[2] Gmelin, "Handbuch der anorganischen Chemie," 8 edit., No. 26, Beryllium, 1930, pp. 133–137.

[3] R. Rohmer, *Bull. soc. chim.* [5] **10**, 468 (1943).

[4] C. L. Parsons, THIS JOURNAL, **26**, 1433 (1904).

[5] F. Krauss and H. Gerlach, *Z. anorg. allgem. Chem.*, **140**, 61 (1924).

[6] B. Bleyer and K. Boshard, *Z. anal. Chem.*, **51**, 748 (1912).