Fourier's series to determine the electron density at points in the unit cell of a crystal, the coefficients of the series being evaluated from the measured intensities of X-ray reflection. This method, when applied to mercurous chloride, mercurous bromide and mercurous iodide, sets the values of the parameters at $u = 0.116$, $v = 0.347$ in the unit cell containing two molecules of mercurous halide with mercury atoms at $00u$; $00\bar{u}$; $^1/_2, {}^1/_2, {}^1/_2 + u$; $^1/_2, {}^1/_2, {}^1/_2 - u$; and halogen atoms at $00v$; $00\bar{v}$; $^1/_2, {}^1/_2, {}^2/_2 + v$; $^1/_2, {}^1/_2, {}^-{}^1/_2 - v$.

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NOTES

Reaction of "Aluminon" with Hydroxides of Beryllium, Rare Earths, Zirconium and Thorium.—The new reagent for aluminum, proposed by Hammett and Sottery[1] and now on the market under the trade name "Aluminon," has proved very satisfactory in our Laboratory. Its value for the detection of very small amounts of aluminum has been shown recently by Lundell and Knowles.[2]

It appears worth recording that lakes are formed by this reagent with the hydroxides or basic acetates of beryllium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium and thorium. All these are deeper red than the aluminum lake, the color being a rich bright crimson, that with cerous hydroxide much darker than the others. All, except that of beryllium, are either dissolved or decolorized by moderate additions of ammonium carbonate. Accordingly, the reagent does not distinguish aluminum from beryllium in mixtures of the two hydroxides. The lakes are not affected by moderate concentrations of ammonia except that of zirconium which is partially decolorized and flocculates as a rose-pink precipitate. All are distinctly more insoluble than the corresponding hydroxides or basic acetates.

From the commercial pure nitrates, solutions were made up containing approximately 10, 1 and 0.1 mg. of the element per cc., except the beryllium solutions which contained 2, 0.2 and 0.02 mg. of the element per cc. To 1 cc. of these solutions was added 5 cc. of 1 N hydrochloric acid, 5 cc. of 3 N ammonium acetate, 5 cc. of 0.1% Aluminon solution and, after mixing, 3 cc. of 6 N aqueous ammonia. Further addition of 2 cc. of 9 N aqueous ammonium carbonate sufficed to dissolve or decolorize the precipitates except in the case of beryllium. Distinct precipitates were formed by 1 mg. of each of the elements tested (0.2 mg. of beryllium). Pink solutions, but no precipitates formed when 0.1 mg. (0.02 mg. of beryllium) was taken. The pink color of these very dilute solutions was not

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[1] Hammett and Sottery, THIS JOURNAL, **47**, 142 (1925).

[2] Lundell and Knowles, *Ind. Eng. Chem.*, **18**, 60 (1926).

altered by aqueous ammonia even after several days, except in the case of zirconium where aqueous ammonia rapidly discharged the color.

The following experiments show the smaller solubilities of the lakes compared with the solubilities of the corresponding hydroxides or basic acetates. Mixtures of 1 cc. of solution (10 mg. of the element), 5 cc. of 1 *N* hydrochloric acid and 5 cc. of 3 *N* ammonium acetate became distinctly turbid as soon as 5 cc. of Aluminon solution was added, except in the cases of aluminum and erbium which remained clear for several hours, but on standing overnight deposited precipitates. Precipitation in all these cases was incomplete and the supernatant liquids remained red or pink. The fraction precipitated seemed to vary between roughly one-fifth and one-third. The zirconium lake precipitated under these conditions was brilliant scarlet-red in contrast to the rose-pink color of that formed in the presence of ammonia. Likewise the aluminum lake similarly precipitated is deep crimson, much darker than that formed in the presence of ammonia. It appears that ammonia exerts an appreciable bleaching action on both of these lakes. Mixtures in which the Aluminon solution was replaced by an equal volume of water all remained perfectly clear after 24 hours.

The beryllium lake is much less soluble in ammonium carbonate than is beryllium hydroxide. A precipitate of the latter containing 2 mg. of the element dissolved completely when the liquid was made 3 *N* in ammonium carbonate while the lake containing the same amount of element was only partially dissolved when the liquid was made 5.5 *N* in carbonate.

A peculiar action was observed in the case of the lanthanum solution and in this alone. In the presence of ammonia the crimson lake settled rapidly, leaving the supernatant liquid colorless. Thereafter a considerable amount of pure white precipitate gradually flocculated which settled slowly and tended to cling to the walls of the vessel. After 24 hours a sharp line of demarcation between the heavier red and lighter white precipitates was visible. The cause of this phenomenon is not immediately apparent since impurities likely to be found in a lanthanum preparation should adsorb the dye equally well.

Thallic hydroxide is not precipitated in the presence of ammonium acetate but when the usual addition of Aluminon was made before adding ammonia the solution remained red for some days and a small amount of reddish precipitate was gradually deposited.

A scandium salt was not available. It would be of interest to know the behavior of Aluminon toward scandium hydroxide.

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The Isomeric Chlororutheniates.—In a recent number of THIS JOURNAL Howe and Haynes[1] have referred to my paper on the potassium chlororutheniates[2] and it is necessary for me to correct certain inaccuracies in their communication.

According to Howe and Haynes "Briggs considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which ruthenium has a coördination number of 6," also "Briggs gives to the aquo salt the formula $2K_2RuCl_5.3H_2O$......It is difficult to see how so slight a difference in hydration could occasion so profound a difference in properties."

As a matter of fact the third paragraph of my paper reads as follows: "It has been found that in Miolati's series (alpha series) there are at least two compounds having the formulae $K_2RuCl_5.H_2O$ and $2K_2RuCl_5.3H_2O$, respectively. In Howe's series (aquo series) the only salt prepared in the pure state had the formula $2K_2RuCl_5.3H_2O$, although some slight evidence was obtained for the existence of other compounds having the formulae $K_2RuCl_5.H_2O$ and $K_2RuCl_5.2H_2O$." In the seventh paragraph of my paper I expressed the view that ruthenium probably functions with the coördination number 8 in all these compounds. Reference was also made to the possibility that the coördination number may be different in the two series, namely, seven in the one and eight in the other, but *nowhere* have I suggested a coördination number six as stated by Howe and Haynes.

Again, in referring to the compound $K_2RuCl_5.K_2RuCl_5OH$ which I obtained from the aquo salt by bubbling air through the heated, strongly acid solution, Howe and Haynes suggest "This would seem to be the ordinary alpha salt, partially in the anhydrous form and partly the monohydrate." The oxidation product, however, is quite different in properties (crystalline form, solubility and color) from the alpha salt.

The existence[2] of such substances as $2K_2RuCl_5.3H_2O$ (with constitutional water), $K_2RuCl_5.K_2RuCl_5OH$ and $K_5Ru_3Cl_{14}.3H_2O$ shows that in the chlororutheniates there is a polynuclear complex in which chloride ions or water molecules are shared by the ruthenium ions. Various cases of isomerism are then possible according to the particular components which are shared.

Assuming a binuclear complex and coördination number of eight, then if the coördinated ions or molecules are arranged around the ruthenium ion, not at the corners of a cube but at the corners of the polyhedron obtained by rotating one face of a cube in its own plane[3] through 45°, either two, three or four components may be shared, the two polyhedra in the complex having a common edge, a common triangular face or a common square face respectively. With a common edge the formula would be $2K_2RuCl_5.4H_2O$.

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[1] Howe and Haynes, THIS JOURNAL, **47**, 2920 (1925).

[2] Briggs, *J. Chem. Soc.*, **127**, 1042 (1925).

[3] This figure gives the stable arrangement of eight electrons around a positive core according to Föppl [see J. J. Thomson, *Phil. Mag.*, **41**, 515 (1921)].

A common triangular face would give $2K_2RuCl_5.3H_2O$, and a common square face $2K_2RuCl_5.2H_2O$. Owing to the comparatively slight solubility of the alpha salts, and the ease with which both series undergo hydrolysis in neutral solution, molecular-weight determinations would have little value, and I therefore suggested in my paper the desirability of an X-ray investigation of these substances which I personally, however, am not in a position to undertake.

Charonnat's Views.—The suggestion made by Charonnat[4] that the alpha series contain quadrivalent ruthenium appears improbable for the following reasons in addition to those mentioned by Howe and Haynes: (1) the alpha series is formed directly from $RuCl_3$ and KCl as observed by Miolati and Tagiuri[5] and by Gutbier, Falco and Vogt;[6] (2) a reducing agent is not necessary to convert the alpha salt into the aquo salt; this change can be brought about by hydrochloric acid alone;[2] (3) by oxidizing the aquo salt with oxygen the alpha salt is not obtained, but instead a totally different substance having the formula $K_2RuCl_5.K_2RuCl_5OH$.

Finally, I would stress the following conclusions at which I arrived after a careful and protracted investigation of the potassium chlororutheniates.

1. No deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during the analysis. It is quite useless to determine one or two constituents only.
2. Water cannot be determined by merely heating the compounds. The only satisfactory method is to determine hydrogen by combustion over lead chromate in an atmosphere of oxygen. If air is used the results obtained are liable to be too low.

Addendum

Owing to the kindness of the Editor, I have had an opportunity of reading the Note by Professor Howe, which follows.

If the compound formulated as K_2RuCl_5 had a binuclear complex as in the formula $K_4(Cl_4RuCl_2RuCl_4)$, the coördination number of the ruthenium would be six. A formula can also be devised with coördination number eight, the complex being quadrinuclear with four ruthenium ions in a ring, each pair of ruthenium ions sharing three chloride ions. At present we have no knowledge of the actual molecular weight of the compound.

It would appear from Professor Howe's references to the water content of his preparations that there are at least two "aquo"-salts in accordance with the suggestions made in my paper. If his preparations have consisted chiefly or entirely of the compound $K_2RuCl_5.H_2O$, whereas mine were

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[4] Charonnat, *Compt. rend.*, **180**, 1271 (1925).

[5] Miolati and Tagiuri, *Gazz. chim. ital.*, **30**, II, 511 (1900).

[6] Gutbier, Falco and Vogt, *Z. anorg. Chem.*, **115**, 225 (1921).

certainly $2K_2RuCl_5.3H_2O$, the difference in behavior on chlorination might possibly be explained.

BIRSTALL, NR. LEEDS, ENGLAND S. H. C. BRIGGS

RECEIVED MARCH 3, 1926
PUBLISHED AUGUST 5, 1926

The Isomeric Ruthenium Chlorides.—The statement in the recent paper of Howe and Haynes[1] that "Briggs considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which the ruthenium has a coördination number of 6," was based on a misunderstanding of his paper. He there states:[2] "It is evident that the coördination number of ruthenium is greater than 6 in the compound $2K_2RuCl_5.3H_2O$." It was wrongly assumed that in $K_2RuCl_5.H_2O$ he considered the number to be 6, as would naturally be expected. There is no reason for assuming a higher coördination number for ruthenium in this compound. On the other hand, the anhydrous form, K_2RuCl_5, which seems undoubtedly to exist, would call for a coördination number of 5.

With Briggs' conclusion that "no deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during analysis," I should heartily agree, if the sentence were qualified by writing it "no *complete* deduction." In practically all of our recent analyses of the halo-ruthenium salts, we have heated the salt in hydrogen, recovering the evolved halogen in silver nitrate solution. Thus, for example, in the analysis of $K_2RuCl_5.H_2O$ ("aquo" salt), $2KCl + Ru$ is left in the boat, and Cl_3 collected as silver chloride. There can be no more water than is indicated by loss, and as this has in no case amounted to $1^1/_2$ H_2O, we have been unable to accept Briggs' formula, $2K_2RuCl_5.3H_2O$, for the "aquo" salt.

CONTRIBUTION FROM JAS. LEWIS HOWE
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RECEIVED MARCH 23, 1926
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The Reaction between Selenium Tetrachloride and Copper.—The reactions between the chlorides of selenium and copper are comparatively much simpler than those between the oxychloride and the same metal.[1] We have determined the course of the reactions both with the monochloride and with the tetrachloride, by analysis. Our results with the former compound agree with those obtained about the same time by Lenher and Kao.[2] On account of qualitative observations we consider that the reaction probably proceeds according to Equations 3 and 4 below.

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[1] Howe and Haynes, THIS JOURNAL, **47**, 2920 (1925).

[2] Briggs, *J. Chem. Soc.*, **127**, 1042 (1925).

[1] Ray, THIS JOURNAL, **45**, 2090 (1923).

[2] Lenher and Kao, *ibid.*, **48**, 1550 (1926).

Selenium tetrachloride, made in the usual manner from selenium kindly supplied by the Baltimore Copper Company, was transferred to a bulb at the bottom of a glass tube. This was then bent at an obtuse angle, a weighed roll of freshly reduced copper gauze was introduced, the whole was evacuated through a tube containing phosphorus pentoxide and sealed to the pump. It was then heated for some hours at 105°. The selenium tetrachloride disappeared, and was replaced by drops of a brown liquid (the dichloride, Se_2Cl_2); finally these also were absorbed. The copper gauze was ground in a mortar, and the unchanged copper was picked out. Samples of the total product, and of the soluble and insoluble parts of this, were analyzed separately, and the combined copper, selenium and chlorine were compared with the weight of the selenium tetrachloride taken. All checks, for which analytical data are supplied in our complete paper, agree satisfactorily with the equation,

$$SeCl_4 + 4\ Cu = Cu_2Se + 2\ CuCl_2 \qquad (1)$$

Summary.—By combining the qualitative with the quantitative results, we conclude that the reactions proceed in the following stages,

$$2\ SeCl_4 + 3\ Cu = 3\ CuCl_2 + Se_2Cl_2 \qquad (2)$$
$$Se_2Cl_2 + 5\ Cu = 2\ Cu_2Se + CuCl_2 \qquad (3)$$

and with an excess of the chlorides thus

$$2\ Cu_2Se + 4\ Se_2Cl_2 = 4\ CuCl_2 + 10\ Se \qquad (4)$$

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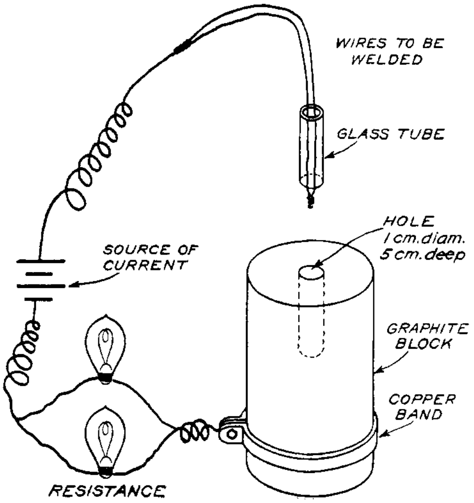
A Device for Arc-Welding Easily Oxidizable Wires.—I have found the following device very serviceable in welding thermocouples. A hole 1 cm. in diameter and 5 cm. deep is bored in a graphite block. The block forms one terminal and the wires to be welded the other terminal. A drop of "oil-dag," or of common lubricating oil, is dropped into the hole, and the wires are placed in the hole to make a contact with the oil. The wires are then quickly pulled out a very little and the resulting arc, in a reducing atmosphere, gives a very good weld.



A glass tube, open at both ends, may be slipped over the wires to prevent contact with the block at any other place except the very ends, which are twisted together.

Lamps of suitable resistance are placed in parallel. One ampere with 230 volts is sufficient to weld the common wires employed as thermocouples. However, wires of larger gage may be welded by decreasing the resistance.

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RECEIVED JUNE 17, 1926
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO ALKYL TIN COMPOUNDS. I. SOME STANNOETHANES. II. TRIMETHYLBENZYL STANNANE

BY CHARLES A. KRAUS AND RALPH H. BULLARD[1]

RECEIVED JULY 24, 1925 PUBLISHED AUGUST 5, 1926

I. Some Stannoethanes

Introduction.—The elements of the fourth group of the periodic system (not including titanium) form compounds of the type $R_3M.MR_3$, where M is an element of the fourth group and R is an organic group or hydrogen. In these compounds the stability of the bond between the atoms of the element M depends upon the nature of the central element as well as upon that of the substituent groups R. In general, the more electronegative the central element M, the more stable is the bond between the atoms of that element. Thus, tin atoms are bonded much more loosely than are atoms of germanium or silicon. The bond between carbon atoms is extremely stable with the exception of compounds in which the substituents R are aryl or very heavy alkyl groups. The stability of a bond between two carbon atoms in these compounds is the weaker the heavier the substituent groups.

In the case of carbon, these compounds are spoken of as methyls as, for example, triphenylmethyl, the idea being that these compounds consist actually of the free substituted methyl groups. Here there is an attempt to differentiate between the C—C bond as it occurs in the methyls on the one hand and carbon-chain compounds on the other. Such differentiation appears somewhat arbitrary, particularly in the case of other elements of the fourth group, such as lead, tin, germanium and silicon. Little is known with regard to the stability of the Pb—Pb bond. In the case of tin compounds, the Sn—Sn bond is fairly stable, particularly when phenyl groups are the substituents. The Ge—Ge bond appears to be very stable. Probably the stability of the Si—Si bond is even higher than that of germanium.

In view of the gradation in the strength of the bonds of the type M—M

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[1] Rice Fellow in Chemistry at Brown University.