of potassium chloride as catalyst to the potassium chlorate accelerated the reaction $4\ KClO_3 = 3\ KClO_4 + KCl$, but did not accelerate the reaction $2\ KClO_3 = 2\ KCl + 3O_2$.

These explanations concordant with the experimental data of Scobai substantiate his interpretations.

The velocity coefficient at constant temperature of the reaction, $4\ KClO_3 = 3\ KClO_4 + KCl$, conforms to the expression $K_1 = \frac{dy/dt}{C(a-x)}$ in which dy/dt is the instantaneous speed of the reaction, C the concentration of potassium chloride and $(a-x)$ the concentration of potassium chlorate.

The reaction, $2\ KClO_3 = 2\ KCl + 3\ O_2$, has been shown to be monomolecular.

The logs of the velocity coefficients K_1 and K_2 have been plotted against the reciprocals of the absolute temperatures and these points lie approximately on straight lines.

Cincinnati, Ohio

[Contribution from Kent Chemical Laboratory, the University of Chicago]

A METHOD FOR THE PREPARATION OF THE DOUBLE FLUORIDES OF THE METALS OF THE PLATINUM GROUP AND THE ABSORPTION SPECTRA OF THE HALOGENO PLATINATES

By H. I. Schlesinger and Mark W. Tapley[1]

Received September 27, 1923

In connection with other work being done in this Laboratory on complex inorganic compounds it was desired to obtain the absorption spectra of the halogeno platinates. Methods for the preparation of the chloro-, bromo- and iodoplatinates are well known but the fluoroplatinate has hitherto not been prepared. In this connection it may be pointed out that very little is known about the fluorides of the platinum group metals; the only ones which have been examined in detail are those of osmium and platinum. Consequently, some preliminary work was done to determine whether the method which we have developed for the preparation of potassium fluoroplatinate can be used for the other corresponding salts of this group in the hope that through them the simple fluorides could be obtained.

Occasional reference to complex fluorides of the group is found in the literature. Berzelius[2] states that he prepared potassium, sodium, and ammonium platinum fluorides as viscous, non-recrystallizable salts, soluble in water; the solution becomes acid and

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[1] The work herein reported constitutes the basis of a dissertation presented to the Graduate Faculty of the University of Chicago by Mark W. Tapley in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Berzelius, "Lehrbuch der Chemie," **1825**, vol. 2, p. 953.

leaves behind a basic salt. No method of preparation is given and, as will be seen later, his statements are incorrect. Mellor[3] in his discussion of the electrolytic preparation of fluorine says, "Possibly the fluorine first forms a platinum fluoride, PtF_4, which produces a double compound with the potassium fluoride. This compound is considered to be the electrolyte which on decomposition forms the two gases and a double potassium platinum fluoride which is deposited as a black mud." Since potassium fluoroplatinate is a pale yellow, crystalline compound, obviously it cannot be precipitated as a "black mud." Ruff,[4] in his attempts to make fluorine, observed that when he heated the double salt of lead tetrafluoride, $3KF \cdot HF \cdot PbF_4$,[5] in a platinum crucible, much platinum in the form of platinum tetrafluoride was found in the melt after the experiment. There is no description of any compound. In his work with osmium octafluoride, OsF_8, Ruff obtained what he believed to be a double fluoride of osmium and potassium but he did not prepare the pure substance.

Platinum unites with fluorine when heated with it. but attempts to prepare fluorides of platinum without employing elementary fluorine have hitherto proved unsuccessful. The fusion of the metal with potassium hydrogen fluoride, or the heating of the chloride in an atmosphere of anhydrous hydrogen fluoride, leads to no results.[6] Platinum difluoride and tetrafluoride were obtained by Moissan[7] by passing fluorine over platinum wire heated to 500–600°, in a thick platinum or fluorspar tube. The product is deep red when fused but yields yellow crystals. These are very hygroscopic and dissolve in water with considerable evolution of heat. The aqueous solution is unstable readily decomposing into hydrofluoric acid and a hydrated oxide of platinum.

The Preparation of Potassium Fluoroplatinate.—For the preparation of double fluorides of the platinum group, the method of heating a mixture of the finely divided metal and the alkali fluoride in a stream of fluorine suggests itself. This method, however, has the disadvantage that it is extremely difficult to find a suitable vessel in which to carry out the reaction. It occurred to us that this difficulty could be avoided by the use of the double salt of lead tetrafluoride which loses hydrogen fluoride at temperatures below 250°, and fluorine at higher temperatures. The use of this salt for experiments in which pure fluorine is desired is not very satisfactory because it is difficult to obtain fluorine free from hydrogen fluoride. For the work in question the presence of the latter could do no harm and it was found that fusion of finely divided platinum with the lead salt formed the desired compound.

The double salt of lead tetrafluoride, $3KF \cdot HF \cdot PbF_4$, was prepared according to the method described by Clark.[8] Platinum was purified from commercial samples by conversion into chloroplatinic acid, reduction of the acid by hydrazine sulfate which does not reduce the other members of the platinum group to the metallic state and then reconversion of the

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[3] Mellor, "Treatise on Inorganic Chemistry," Longmans, Green and Co., **1922,** vol. 2, p. 7.

[4] Ruff, "Die Chemie des Fluors," J. Springer, Berlin, **1920,** p. 54.

[5] Brauner, *Z. anorg. Chem.*, **7,** 1 (1894); **98,** 38 (1916).

[6] Ruff, *Ber.*, **46,** 920 (1913).

[7] Moissan, *Ann. chim. phys.*, [VI] **24,** 282 (1891).

[8] Clark, THIS JOURNAL, **41,** 1477 (1919).

precipitated platinum to the chloride. The last traces of iridium were removed by the method of Mylius and Mazzucchelli.[9]

Method.—The finely divided platinum is intimately mixed in a platinum dish with the calculated amount of the double salt of lead tetrafluoride. As heat is applied, the mixture gradually melts with effervescence to a red solution. When all of the platinum has apparently disappeared, the reaction is assumed to be complete. The cooled mass does not retain the red color of the melt but has a reddish-brown cast. It is extracted with hot, 48% hydrofluoric acid until further extractions are colorless. The yellow extract is filtered and to the filtrate are added a few drops of concd. sulfuric acid to precipitate lead. After the removal of the small amount of lead sulfate, the filtrate is concentrated on the water-bath until crystallization begins. Crystallization is completed at approximately 0°. The salt is recrystallized from hot water. To avoid the introduction of silica, the hydrofluoric acid solution is kept in platinum and all filtrations are carried out with hard rubber funnels.[10]

Properties.—Potassium fluoroplatinate is a pale yellow, crystalline compound. At 25° its solubility is 0.0023 g. in 100 g. of water, or 0.018 mole per liter. The solubility decreases rapidly with decrease in temperature. The complex fluoroplatinate ion is relatively stable. This is shown by the fact that when potassium iodide is added to an aqueous solution of the salt the characteristic red coloration of the iodoplatinate appears only slowly after the application of heat. Also, reduction with hydrazine hydrochloride in slightly alkaline solution takes place slowly. The compound is fairly stable towards heat but decomposes below red heat into potassium fluoride, platinum and fluorine.

Analysis of Potassium Fluoroplatinate.—Considerable trouble was encountered in devising a satisfactory method of analysis of the double platinum fluoride. It was found that of all the commonly used reducing agents, hydrazine hydrochloride was the most effective since it produced moderately rapid reduction of the platinum in a solution containing 0.5 mg. in 40 cc. of solution. Its effectiveness was not diminished by the presence of an excess of fluoride ion. Nevertheless, the weight of platinum obtained by reduction was low and variable and this method was used, therefore, only to remove platinum for analysis of potassium and fluorine. For the determination of platinum, three methods were finally

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[9] Mylius and Mazzucchelli, *Z. anorg. Chem.*, **89**, 1 (1914).

[10] The residue from the hydrofluoric acid extraction was washed with hot water to remove the acid and was then treated with hot 10% ammonium acetate solution and finally with a 50% solution of the ammonium salt. The latter extracted a small amount of yellowish material which could be precipitated from solution by 95% alcohol. The precipitate gave qualitative tests for lead, fluorine, and platinum, but the amount of material obtained from 1 g. of platinum in the original fusion did not warrant further study of this substance.

adopted which led to fairly concordant results. First, the compound is decomposed by heat into fluorine, potassium fluoride, and platinum, of which all but the last are volatilized at the temperature of a Meker burner and the residual platinum weighed. Second, the double salt is reduced by hydrogen. For this purpose the material, contained in a platinum boat, is heated in a stream of hydrogen in a Pyrex tube. The residue from this treatment contains platinum and potassium fluoride. The latter is removed by washing and is converted into sulfate with sulfuric acid. Third, a solution of the salt in the presence of 3% sulfuric acid is electrolyzed and the residual solution analyzed for potassium. Marie,[11] Senter,[12] and Ruer[13] have already shown that a small amount of an oxide of platinum is deposited on the anode which leads to low results. Potassium was determined as sulfate from solutions from which the platinum had been removed as mentioned and fluorine was determined as calcium fluoride by the method described by Ruff[14] in the solution obtained by reduction of the double salt by hydrazine hydrochloride.

TABLE I

RESULTS OF THE ANALYSES

FOR PLATINUM

	Wt. of sample G.	Wt. of platinum G.	Pt found %	Pt calc. (K_2PtF_6) %
By ignition	0.0877	0.0441	50.28	50.38
	.0730	.0367	50.27	
By electrolysis	.1354	.0678	50.01	
By reduction (H_2)	.1272	.0637	50.08	

FOR POTASSIUM

	Wt. of sample	Wt. of potassium	K found %	K calc. %
Double salt reduction with N_2H_4HCl	0.1104	0.0221	20.03	20.18
	.1354	.0273	20.14	
Reduction with H_2	.1272	.0257	20.25	

FOR FLUORINE

	Wt. of sample	Wt. of fluorine	F found %	F calc. %
Reduction with N_2H_4HCl	0.0661	0.0195	29.51	29.42
		Loss	% loss	% loss
Reduction with H_2	.1272	.0250	19.65	19.61

Thus the analyses show that the formula of the compound is K_2PtF_6.

Attempts were made to convert the potassium fluoroplatinate into other salts, especially into the barium salt, with the view of preparing the free acid, H_2PtF_6. Soluble metal fluorides such as those of barium, strontium,

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[11] Marie, *Compt. rend.*, **145,** 117 (1907).

[12] Senter, *Trans. Faraday Soc.*, **2,** 142 (1906).

[13] Ruer, *Z. Elektrochem.*, **14,** 302 (1908).

[14] Ref. 4, p. 89.

lead, silver and zinc failed to precipitate the corresponding fluoroplatinate from saturated aqueous solutions of the potassium salt.

It was found that the solubility of the potassium fluoroplatinate is greatly increased by the presence of ammonium fluoride. The absorption spectrum of this solution was photographed and compared with that of the potassium fluoroplatinate to determine whether the increased solubility of the potassium salt is due to compound formation. However, ammonium fluoride produced no change in the absorption spectrum; hence, the solubility of potassium fluoroplatinate in ammonium fluoride is probably due to the effect of the latter in increasing hydrolysis to fluoroplatinic acid.

The Preparation of Potassium and of Lead Fluoro-iridates.—Three difficulties were encountered in preparing potassium fluoro-iridate. In the first place, platinum vessels cannot be used for the fusion of iridium with the double salt of lead tetrafluoride without serious contamination of the product with platinum. To avoid this, a metal which does not form an insoluble complex fluoride must be used. Such a metal is nickel. The second difficulty is the insolubility of the lead salt. In the preparation of potassium fluoroplatinate practically no lead fluoroplatinate was formed, whereas the corresponding reaction with iridium converted most of the latter into an insoluble lead fluoro-iridate. Third, the potassium salt begins to decompose at 130°, while the reaction must be carried out at a temperature higher than 250° in order to liberate fluorine from the double salt of lead tetrafluoride.

Method.—A nickel crucible is coated with a thin film of potassium fluoride by fusing the latter in the crucible over a Meker burner. The coated crucible is cooled to dull redness and finely divided iridium sprinkled over the bottom. When the iridium has assumed the temperature of the crucible, the double salt of lead tetrafluoride is added slowly so as not to lower the temperature appreciably. The reaction begins immediately. While there is still undecomposed lead salt present, the crucible is chilled by plunging the bottom into cold water. If the fusion has been successful the material in the crucible has a deep lavender color.

This mass is extracted with hot water to remove the soluble potassium fluoro-iridate which dissolves readily, yielding a reddish solution. This is treated with 95% alcohol, which precipitates a pink crystalline solid. After washing this with alcohol, the solid is recrystallized from water.

When the hot water extract from the fusion described above is no longer colored, the residue still has a decided lavender appearance. This material is insoluble in hot hydrofluoric acid but practically all of it dissolves when treated with hot 10% ammonium acetate solution, yielding a red solution similar in appearance to the first aqueous solution. As the solution cools the pink lead fluoro-iridate separates. The precipitate is collected upon a filter, washed with water and recrystallized from 10% ammonium acetate.

When a platinum crucible was used for the fusion the yield was greatly improved. The appearance of the lavender color, especially where the iridium comes into contact with the platinum, seems to indicate catalytic action of the platinum. Iridium contaminated with a small amount of platinum was then tested using a nickel crucible for the fusion and in this case also, a marked increase in the yield was noted. The presence of the platinum also aided in the precipitation of the fluoro-iridate, for the pink salt, contaminated with potassium fluoroplatinate, separated from the hot water extract as it cooled, without the addition of alcohol.

Analysis of the Fluoro-iridates.—The salts were analyzed by reduction in a stream of hydrogen. Care was taken to avoid volatilization of potassium fluoride in the case of the potassium salt. This made it possible to determine the loss of weight on reduction as well as to determine iridium, potassium and fluorine by the methods used in the corresponding analysis of the platinum salt. In the case of the lead salt, lead fluoride, remaining after reduction by hydrogen, was converted into lead sulfate and weighed. While the analytical data are not in perfect agreement with the values calculated from the formulas, it will be seen that they agree as closely as is to be expected when the very small amount of material available for analysis is taken into consideration.

Subs., 0.0871: Ir, 0.0436; K, 0.0180; loss (F), 0.0158. Calc. for K_2IrF_6: Ir, 50.12; K, 20.29; loss (F) 19.71. Found: Ir, 50.06; K, 20.66; loss (F), 18.14.

Subs., 0.1420, 0.2426: Ir, 0.0531, 0.0921; Pb, 0.0580, 0.0981; loss (F), 0.0207, 0.0361. Calc. for $PbIrF_6$: Ir, 37.54; Pb, 40.28; loss (F), 14.77. Found: Ir, 37.39, 37.96; Pb, 40.85, 40.48; loss (F), 14.57, 14.88.

The analyses show that the compounds have the formulas K_2IrF_6 and $PbIrF_6$, respectively.[15]

When ruthenium was treated in a manner analogous to that for iridium, a pink solution with a purple cast was obtained upon extraction with hot water. When the residue was extracted with 10% ammonium acetate a similarly colored solution yielded a lavender precipitate upon cooling. The hot water extract decomposed when concentrated on the water-bath. When a portion of this hot water extract was made alkaline and then acidified, an ozone-like odor was developed, indicating that a derivative of octavalent ruthenium might be present.

Additional work on the complex fluorides of these metals is to be carried on in this Laboratory.

[15] When a solution of the potassium fluoro-iridate was treated with barium nitrate a pinkish-red precipitate was formed, coming down slowly as the concentration of barium was increased. This precipitate was collected on a filter, washed free from nitrate and dried over sulfuric acid. The compound gave qualitative tests for barium, iridium and fluorine. When it was treated with dil. sulfuric acid, a pinkish-white precipitate and a pink filtrate were obtained.

The Absorption Spectra of the Halogeno Platinates

The work on the absorption spectra was carried out according to the method of Hartly as modified by Baly and Desch.[16] An imported quartz spectrograph was used in conjunction with a Baly tube having quartz windows. The source of light was the arc and later the spark between carbon poles thoroughly impregnated with the oxides of uranium and molybdenum. For the ultraviolet, commercial "Seed 30" plates were used. When the visible as well as the ultraviolet regions were desired, "Wratten M" plates gave the most satisfactory results.

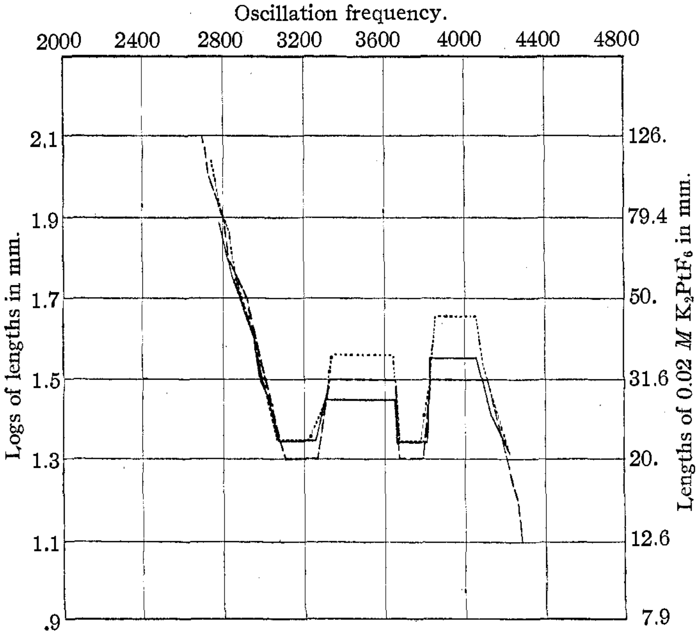

Fig. 1.—Absorption spectra of K_2PtF_6.
— — — 0.005 *M* K_2PtF_6. ——— 0.015 *M* K_2PtF_6.
- - - - - - - - - 0.025 *M* K_2PtF_6.

The absorption spectrum of one of the halogeno platinates is already known. Hantzsch[17a] found potassium chloroplatinate to have an absorption band in the ultraviolet region, the head being at an oscillation frequency[17b] of 3700. In order to have a basis of comparison with the results of Hantzsch, it was necessary to repeat his work on the chloroplatinate for one concentration; this resulted in complete agreement with his work. (Fig. 1.)

Potassium fluoroplatinate, prepared as described, has two very shallow

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[16] Baly and Desch, *J. Chem. Soc.*, **85**, 1039 (1904).

[17a] Hantzsch, *Ber.*, **41**, 1216 (1908); *Z. physik. Chem.*, **72**, 362 (1910).

[17b] Oscillation frequency is the reciprocal of the wave length.

bands in the ultraviolet region. The head of the first band is at an oscillation frequency of 3175 and the second at 3720. The latter is almost identical with the single band found in the absorption spectrum of the chloroplatinate. Upon varying the concentration over a wide range, Beer's law is shown to be obeyed. (Fig. 2.) The addition of ammonium fluoride to increase the solubility of the potassium fluoroplatinate showed no effect upon the spectrum.

Potassium bromoplatinate was prepared according to the method of Gutbier and Bauriedel.[18] Bromoplatinic acid was prepared by evaporating a solution of chloroplatinic acid six times with concd. hydrobromic acid and then thrice with the addition of aqueous bromine to the acid and finally dissolving the residue in dil. hydrobromic acid. The acid thus prepared was added to a concentrated solution of potassium bromide to precipitate potassium bromoplatinate. The latter was recrystallized from dil. hydrobromic acid.

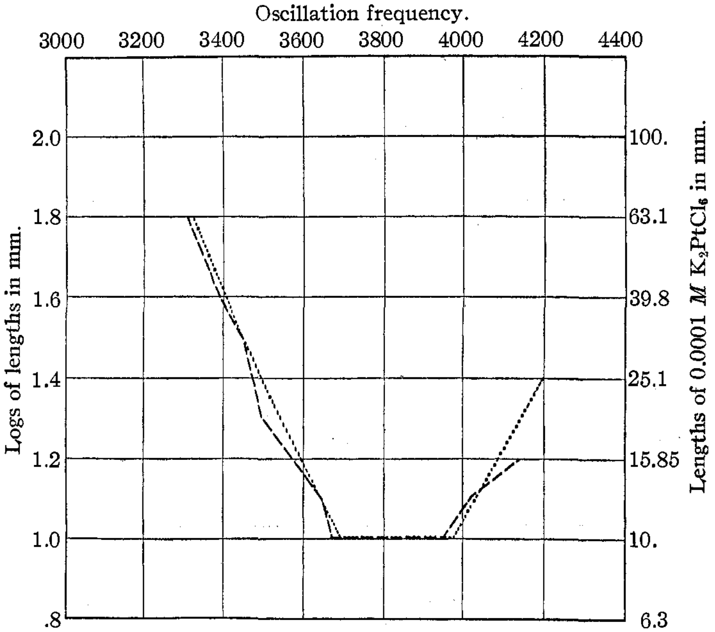

Fig. 2.—Absorption spectra of K_2PtCl_6.

————0.0001 *M* K_2PtCl_6. --------- 0.0001 *M* K_2PtCl_6. Hantzsch.

Potassium bromoplatinate gave an absorption spectrum showing one wide absorption band, the head being at an oscillation frequency of 3280. The spectra taken at various concentrations showed that the bromoplatinate obeys Beer's law. (Fig. 3.) In agreement with the work of Archibald and Gale[19] on the hydrolysis of potassium bromoplatinate, it

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[18] Gutbier and Bauriedel, *Ber.*, **42**, 4243 (1909).

[19] Archibald and Gale, *J. Chem. Soc.*, **121**, 2849 (1922).

was found necessary to take exposure immediately after making up the solution, as otherwise no band but only end absorption was observed.

Potassium iodoplatinate was prepared according to the method of Datta[20] by adding a 10% solution of chloroplatinic acid to a saturated solution of potassium iodide. The black salt obtained has a very intense wine-red color even in dilute solution, so that in order to have enough light transmitted a solution of such dilution had to be used that immediate decomposition took place. It was found, however, that the presence of a solution of potassium iodide, even as dilute as 0.0001 *M*, delays the decomposition sufficiently to make photography of the spectrum easily possible. The absorption spectrum of potassium iodide in solutions of the concentrations employed does not interfere with that of the complex platinum salt. It was found that variation of the concentration of the iodide did not affect the absorption spectrum—in fact, even solutions of the platinum salt in which decomposition had already set in gave the same spectrum as those of the undecomposed salt except for differences due to the change in concentration of the latter.

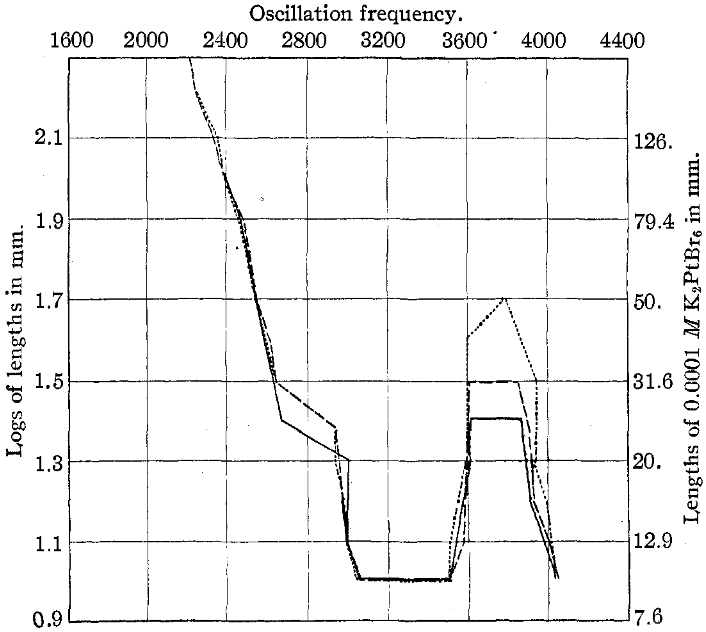

Fig. 3.—Absorption spectra of K_2PtBr_6.
———0.00005 *M* K_2PtBr_6. — — —0.0001 *M* K_2PtBr_6.
----------0.0002 *M* K_2PtBr_6.

The absorption spectrum of potassium iodoplatinate has two well-defined bands, one in the visible and the other in the ultraviolet region.

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[20] Datta, This Journal, 35, 1186 (1913).

The head of the former is at oscillation frequency 1960 and that of the other at 2920. The latter is close to the head of the band of the bromoplatinate but is not identical with it. The iodoplatinate, like the other halogeno platinates, obeys Beer's law in aqueous solutions. (Fig. 4.)

The distinct differences in the absorption spectra of the halogeno platinates suggest the possibility of employing an optical method for determining the relative stabilities of the complex ions involved. To determine the feasibility of this project, the spectra of the iodoplatinate dissolved in normal solutions of potassium fluoride, chloride and bromide, respectively, were photographed and are plotted with that of the iodoplatinate in 0.0001 *M* potassium iodide in Fig. 5. In the fluoride solution the absorption band of the iodoplatinate in the visible region has completely disappeared, indicating practically complete conversion of the iodo complex into the corresponding fluorine salt. In the bromide solution the band is almost eliminated, being noticeable only when the light falls through relatively long columns of solution while in the chloride solutions the band persists over quite a range of length of column, but does not have the persistency of the iodoplatinate band in the iodide solution. The band in the ultraviolet is eliminated in all of the mixtures;

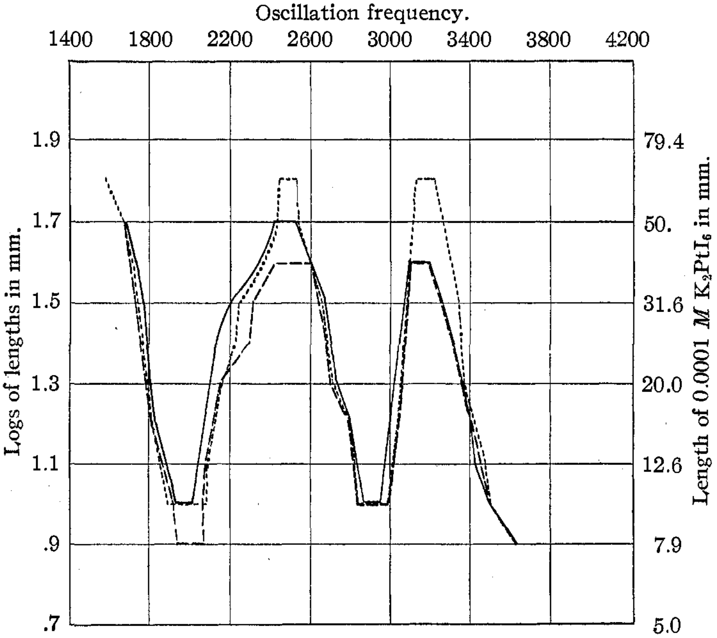

Fig. 4.—Absorption spectra of K_2PtI_6.
———— 0.00005 *M* K_2PtI_6. — — — — 0.0001 *M* K_2PtI_6.
- - - - - - - - - 0.0002 *M* K_2PtI_6.

the solution containing potassium bromide shows the band of the bromoplatinate. It is clear that the conversion of platinum compounds into iodoplatinates is a reversible reaction and that by a quantitative study of the changes in the absorption spectra described above the relative stabilities of the various ions can be determined. This work is to be undertaken in this Laboratory in the near future.

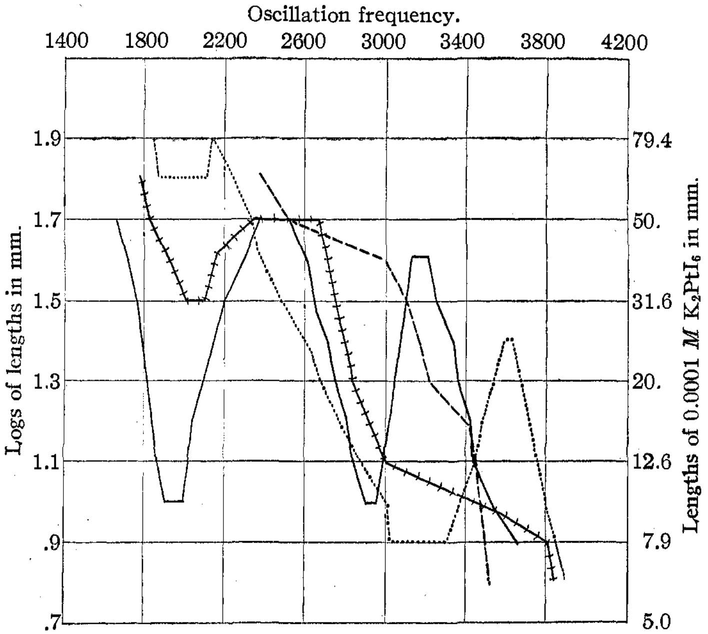

Fig. 5.—Absorption spectra of K_2PtI_6 in KF, KCl, and KBr.

———— 0.0001 *M* K_2PtI_6. +++++0.0001 *M* K_2PtI_6 in KCl.

— — — - 0.0001 *M* K_2PtI_6 in KF. -------0.0001 *M* K_2PtI_6 in KBr.

In conclusion, we take pleasure in acknowledging the courtesy of Goldsmith Brothers Smelting and Refining Company who put at our disposal the iridium, ruthenium and other metals used in this research. The expense of the spectrograph was met in part by a grant from the Bache Fund of the National Academy of Sciences.

Summary

1. A method is described for preparing complex fluorides of the platinum group metals. Potassium fluoroplatinate and potassium and lead fluoro-iridates have been obtained and are described.

2. Absorption spectra of all of the halogeno platinates have been photographed.

3. A study of the absorption spectra of potassium iodoplatinate in solutions of fluorides, chlorides and bromides, respectively, has demon-

strated that the formation of the complex salts from one another is a reversible reaction and that their relative stabilities can be determined by a spectroscopic method. Measurements will be reported in a later communication.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, UNIVERSITY OF LONDON, KINGS COLLEGE]

A METAL-TO-GLASS JOINT

BY H. N. RIDYARD

RECEIVED OCTOBER 5, 1923

Introductory

The author desired to obtain a joint which would unite glass and silica, and hold a vacuum for long periods, at temperatures at which the usual vacuum cements soften and become useless.

McKelvy and Taylor[1] describe a method of soldering glass to metal, after giving an account of previous work on this subject. These authors describe tests of this joint made at high pressures, and state that it was found suitable for vacuum work, but do not give any data as to degree of vacuum obtained, etc.

Later, Dundon[2] stated that he was unable to make joints of this type more than 8 mm. in diameter, and described a method of making a joint by electrodeposition of copper between a platinized glass tube and another of metal.

More recently, Meyers[3] describes joints of the soldered type up to 41 mm. in diameter.

Experimental Part

Attempts to use the first mentioned (soldered) joint for high-vacuum work were unsuccessful, the joint leaking at pressures below 10^{-2} mm.

Examination of joints after they were taken apart, showed that the solder or tin adhered to the glass only in places, so that contact between glass and solder in the joint appears to have been incomplete, thus accounting for the leak.

Experiments were then conducted to obtain a continuous film of metal over the glass, but were at first unsuccessful. It was found, however, that hot zinc chloride, used as a flux, appeared to cause disintegration of the platinum film.

Attempts to obtain films on the glass by dipping platinized tubes into a bath of molten tin were also unsuccessful; but at length lead was substituted for the tin and, after necessary conditions were worked out, continuous

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[1] McKelvy and Taylor, THIS JOURNAL, **42,** 1364 (1920).

[2] Dundon, *ibid.*, **45,** 716 (1923).

[3] Meyers, *ibid.*, **45,** 2135 (1923).