

A STUDY OF PLATINUM GLYOXIME AS A SUITABLE SUBSTANCE  
FOR THE  
ESTIMATION OF THE ATOMIC WEIGHT OF THE METAL

by

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" A Study of Platinum Glyoxime as a Suitable Substance for the  
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Table of Contents.

	Page.
I. Introduction.	
II. Review of Earlier Determinations.	3.
III. Comparison of Mass Spectrum Measurements with the Chemical Atomic Weight.	4.
IV. Purification of Reagents.	5.
V. Calibration of Apparatus.	7.
VI. Preliminary Investigation with Nickel Glyoxime.	8.
VII. Chloroplatinic Acid.	12.
VIII. Chloroplatinic Acid with Dimethylglyoxime.	15.
IX. Chloroplatinous Acid with Dimethylglyoxime.	20.
X. Chlorides and Oxides of Platinum.	25.
XI. Summary.	27.
XII. Acknowledgment.	27.
XIII. Bibliography.	28.

## Figures

### Facing page

1. Hydrogen treatment of Nickel Glyoxime.	9.
2. Chlorine treatment of Nickel Glyoxime.	10.
3. Oxygen treatment of Nickel Glyoxime.	10.
4. Reduction of Potassium Chloroplatinate.	11.
5. Electrolysis Apparatus.	12.
6. Weber's Electrolytic Cell.	13.
7. Electric heater.	15.
8. Treatment of brown precipitate in Carbon Dioxide.	16.
9. Treatment of brown precipitate in CO <sub>2</sub> at reduced pressure.	17.
10. Nitrogen treatment of brown material.	17.
11. Chlorine treatment of brown material.	18.
12. Treatment of Platinous Dimethylglyoxime.	23.

" A Study of Platinum Glyoxime as a Suitable Substance for the Estimation of the Atomic Weight of the Metal".

Introduction.

The atomic weight of platinum was studied by Dr. E.H. Archibald(1) some thirty years ago by an analysis of potassium and ammonium chloroplatinates and bromoplatinates. The value obtained in this determination is the atomic weight accepted by the International Committee (1937). However, as this value is based entirely on the atomic weights of chlorine, silver, potassium and bromine, it was thought that it would be of considerable interest if another set of ratios could be established with constants quite independent of those previously used. Further, a great many improvements in the technique that has to do with atomic weight determinations have been introduced and by following these modifications a more exact value for the constant in question might be obtained.

Since organic compounds are used successfully in determining the atomic weights of metals, it was thought, if a suitable reagent could be obtained, that platinum might be precipitated in combination with this substance in a form that could be weighed with accuracy and precision and whereof the platinum content could be exactly estimated. The high degree of purity and the reduced cost of organic reagents lend support to this proposal.

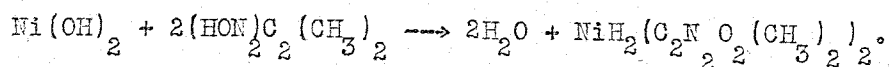
Dimethylglyoxime is one instance of an organic compound that

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(1) Archibald, E.H., Proc. Roy. Soc. Edinburgh XXIX., 721-747, (1909).

(2)

has proven to be particularly useful in analytical work. It is used in nickel determinations and in quantitative estimations of palladium. Addition of dimethylglyoxime to an ammoniacal solution of a salt of nickel gives a brilliant red precipitate of an acid salt.



The precipitate is insoluble in water(2) and is very slightly soluble in alcohol and glacial acetic acid. The compound will sublime at 250° C. and shows marked stability at this temperature(3).

By using an organic reagent, such as dimethylglyoxime, it should be possible to prepare the platinous salt as well as the platonic salt. Previous investigations were chiefly a study of platonic salts.

The formation of an insoluble and stable compound would make the determinations comparatively simple assuming that the compound can be purified. Many experimental errors incident to the usual atomic weight estimations would thus be eliminated.

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(2) Brunck, O., Z. Angew Chem. 20, 3844(1907), Chem. Ab. 2:240(1908).

(3) Brunck, O., ibid 20, 834 (1907), Chem. Ab. 2:46 (1908).

Review of earlier determinations.

The study of the atomic weight of platinum is recorded in the works of J.J. Berzelius(4), T. Andrews, K. Seubert, W. Halberstadt, W. Dittmar, J. McArthur and E.H. Archibald and covers a period of investigations dating from 1826 to 1909. Berzelius and Andrews obtained values that were more than one percent above those of later investigators. J.S. Stas pointed out the difficulty involved in removing the last traces of water from potassium chloroplatinate and suggested this as a possible source of error. Berzelius analyzed the double salt of potassium chloride and platinic chloride and found ratios between the salt and its constituents. Andrews also worked with potassium chloroplatinate, decomposing the salt by means of zinc and water. K. Seubert decomposed ammonium chloroplatinate and potassium chloroplatinate in a stream of hydrogen and determined the several ratios between the salts and silver chloride. Seubert's results were confirmed by W. Halberstadt, who studied the ammonium and potassium salts of bromoplatinic and of chloroplatinic acids. Seubert's and Halberstadt's values were 195.22 and 195.05 respectively. Analyses of potassium chloroplatinate by W. Dittmar and J. McArthur involved corrections for hydrolysis. They held that the salt was seldom pure because of the tendency for chlorine to be replaced by hydroxyl and for potassium to be replaced by hydrogen. The results which they obtained give a value of 195.5. E. H. Archibald obtained ratios from the analyses of

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(4) Mellor, Comp. Treatise on Inorg. and Theoretical Chem. Vol XVI.

potassium and ammonium chloroplatinates and bromoplatinates and compared platinum and its salts with silver and its halides. Conversion of the metal into the salts of bromoplatinic and chloroplatinic acid by electrolysis removed any source of contamination from nitric acid. Precaution was taken against hydrolysis by heating to expel any absorbed and occluded moisture. The best representative value from E.H. Archibald's determination is 195.23.

#### Comparison of Mass Spectrum Measurements with the Chemical Atomic Weight.

It is only recently that values for the atomic weight of platinum have been determined by mass-spectrum analysis. Sampson and Bleakney(5) used a new type of ion source and a mass spectrograph of extremely high resolving power to find the relative frequency of platinum isotopes. The following measurements were obtained in their analysis:

Mass number	192	194	195	196	198
Percentage abundance	0.8	30.2	35.3	26.6	7.2

By assuming a packing fraction from Aston's curve(6) of 0.5, they obtained a value which is identical with the accepted atomic weight. O. Hahn<sup>(7)</sup> obtained  $195.11 \pm 0.5$  by using the same percentage frequency, but a different conversion factor, of 1.000275, in place of the Mercke and Child's factor (1.00022). The argument in favor of a change in the conversion factor is that the values based on measurements of isotopic masses will be, for most of the elements, in closer agreement with the chemically determined constants.

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(5) Sampson and Bleakney, Phy. Rev., L.8. 734 (1936)

(6) Aston F.W. Mass Spectra and Isotopes (1933)

(7) Hahn O., Ber. 71.1 (1938)

Purification of Reagents.

Water: Redistilled water was used throughout the investigation.

Hookey and Phillips' apparatus(8) was used in the second distillation.

Alcohol: 95% ethyl alcohol was put into a 2-liter flask, lumps of quicklime were added and the flask shaken every few hours for several days. Some of the alcohol was transferred to a dry flask and distilled. The first and last portions of the distillate were discarded.

Dimethylglyoxime: A preliminary test of the relative solubility of the compound in cold and hot alcohol was made by treating the substance with 10 c.c. of alcohol. It was found that 0.163 grams of solute dissolved in 10 c.c. on shaking the mixture for one hour at 27°C. and that 0.60 grams dissolved at 78°C. These weights, however, do not express the absolute solubility at these two temperatures, since insufficient time was allowed for complete saturation.

Adams and Kamm's method of crystallization(9) was used in purifying the compound. 25 grams of dimethylglyoxime were added to 300 c.c. of distilled alcohol and a hot saturated solution prepared. The solution was filtered by suction through a heated funnel and the filtrate obtained was cooled rapidly with frequent shaking. The crop of white crystals was washed into a porcelain Gooch crucible, filtered by suction, washed with alcohol and dried for several hours

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(8) Hookey and Phillips, J. Chem. Educ. 11, 376 (1934).

(9) Adams and Kamm, J. Am. Chem. Soc. 40, 1281-9, (1918)



at 120°C. The alcoholic filtrates were used repeatedly in preparing more crystals.

Potassium chloroplatinate: The salt used in the investigation was purified by Dr. E.H. Archibald from purified potassium chloride and chloroplatinic acid. The potassium chloride was twice precipitated from solution by gaseous hydrogen chloride and washed and dried by centrifuge. The salt was used in the precipitation of potassium chloroplatinate, which in turn was reduced to potassium chloride and the metal. A pure product was obtained by precipitating the potassium chloride twice from solution by hydrogen chloride. Chloroplatinic acid was made by dissolving spongy platinum in concentrated hydrochloric acid by an electrolytic method. The potassium chloroplatinate was formed by adding dilute chloroplatinic acid slowly to a dilute solution of pure potassium chloride. The precipitates were thoroughly washed with water and alcohol. The product obtained was reduced in pure hydrogen and the platinum again dissolved and precipitated as before. This operation was repeated four times. The potassium chloroplatinate used by Noyes and Weber(10) was made from electrolytically prepared chloroplatinic acid.

Hydrochloric acid: Concentrated C.P. acid was distilled from Pyrex, quarter the first and last portions being discarded.

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(10) Noyes and Weber, U.S. Bureau of Stand., Bulletin, 4, 347, (1907-8).

Sodium Oxalate: Two methods of purification were recommended by Sorensen(II), e.g., crystallization from water and precipitation from aqueous solution by alcohol. Alcoholic precipitation has the disadvantage of yielding a product which is more hygroscopic than that crystallized from water. The Bureau of Standards reports that two crystallizations from water are sufficient to effect purification. 60 grams of sodium oxalate were added to one liter of water and the mixture was boiled for 10 minutes. ( The solubility is 3 grams at 20°C. and 6 grams per 100 ml. at 100°C.) The hot solution was decanted and cooled to room temperature. The mother liquor was poured off the crystals. 275 c.c. of water were added to the crystal mass, the temperature was raised and the whole operation repeated. The crystals were dried at 70°C.

#### Calibration of Apparatus.

##### Calibration of pipettes:

First pipette: average weight of water for three trials is 4.6417 g.

Temperature is 18 $\frac{1}{2}$ °C.

4.6417 g. of water at 18 $\frac{1}{2}$ °C. occupy 4.6673 ml.

Second pipette: average weight of water for four trials is 4.9854 g.

Temperature is 18 $\frac{1}{2}$ °C.

4.9854 g. of water at 18 $\frac{1}{2}$ °C. occupy 5.0129 ml.

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(II) U.S. Bureau of Stand. Circular No. 381, Feb. 20, 1930.

Calibration of volumetric flask:

Average volume for three trials is 100.0652 ml.

<u>Apparent weight</u>	<u>Temp.</u>	<u>Vol. of 1 g. of water</u>	<u>Vol. for recorded wt.</u>
99.6981 g.	23°C.	1.0035 ml.	100.0459 ml.
99.6774 g.	26°C.	1.0042 ml.	100.0960 ml.
99.7247 g.	22°C.	1.0033 ml.	100.0538 ml.

Preliminary investigation with nickel glyoxime.

A few of the experiments of other investigators having to do with nickel glyoxime as a form in which to precipitate and weigh nickel are here set forth.

O. Brunck's method of determining nickel by dimethylglyoxime precipitation was found by Congdon and Belge(12) to give a value for precipitated nickel agreeing with the theoretical value. Parr and Lindgren's method(13) of treating the nickel salt with dimethylglyoxime in large excess seemed unnecessary and the amount used in this determination was slightly less than twice the amount required for complete precipitation. A sample of nickel sulphate weighing 6.6686 grams was dissolved in 505 ml. of water containing 5 ml. of concentrated sulphuric acid. 50 ml. of solution was drawn off for the determination. The solution was diluted to 120 ml., heated nearly to boiling and treated with 100ml. of alcoholic solution of dimethylglyoxime. 2 grams of ammonium acetate were added to buffer the

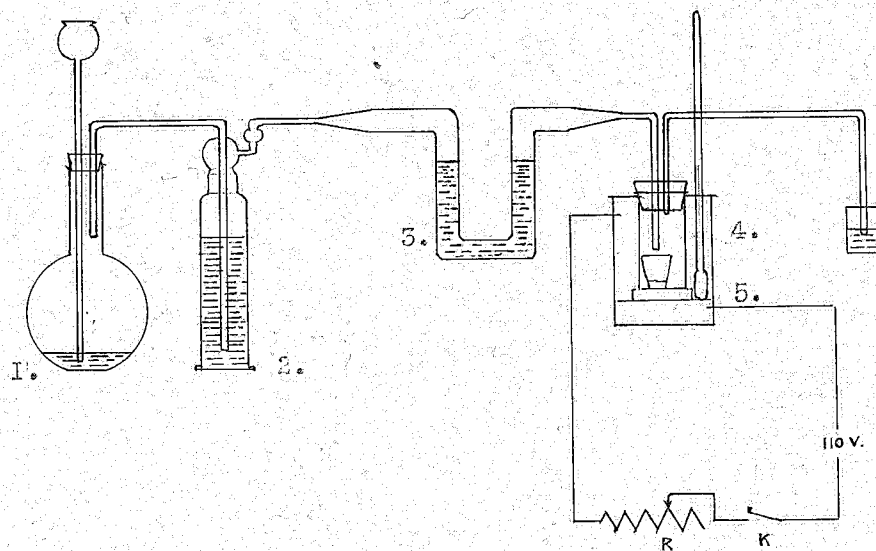
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(12) Congdon and Belge, Chem. News 128, 67-8 (1924)

(13) Parr and Lindgren, Trans. Am. Brass Founders' Assn. 5, 120-9

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Figure 1.



1. Zinc and hydrochloric acid.
2. Wash bottle with water.
3. U-tube containing caustic potash.
4. Beaker containing crucible and nickel compound.
5. Electric heater.

(9)

solution, then ammonium hydroxide was added to completely neutralize the solution. The slightly alkaline solution was heated until precipitation was complete. The precipitate was collected and washed in a weighed platinum Gooch crucible. Then the precipitate was dried for 7 to 9 hours at  $140^{\circ}\text{C}$ . and weighed. The following results were obtained in three trials using 0.6602 grams of nickel sulphate in each:

No.	Wt. of Ni-Glyoxime	Wt. of Nickel	Exptal % Ni	Error
1.	0.7205 g.	0.1464 g.	22.17%	0.67%
2.	0.7170 g.	0.1457 g.	22.00%	1.07%
3.	0.7156 g.	0.1454 g.	22.04%	1.25%

Possible sources of error include the slight solubility of the precipitate(14) and slight loss of material in the transfer from flask to crucible.

#### Treatment of Nickel Dimethylglyoxime.

The scarcity of reliable information concerning the properties of the nickel compound led us to examine its behaviour under conditions that were likely to obtain when we were dealing with the corresponding platinum salt. To a certain degree the properties could be expected to be analogous and information regarding the glyoxime of nickel could be transferred to the platinum compound. In particular we wished to find out how it would behave when heated in certain of the common gases.

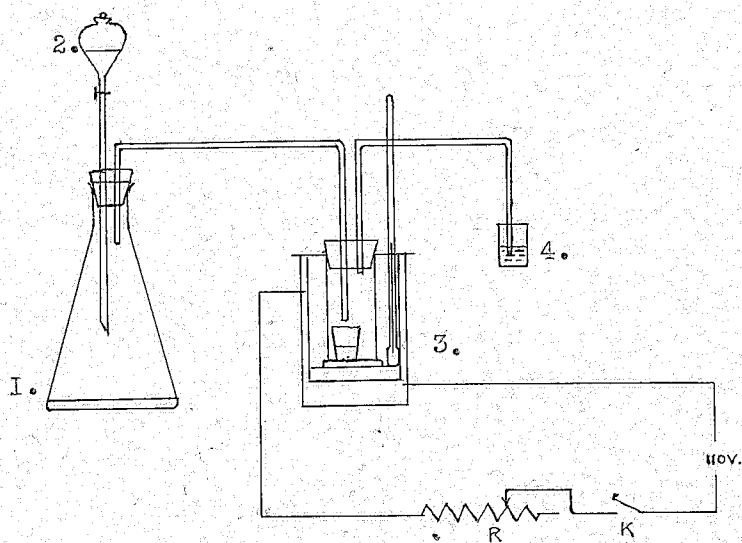
Hydrogen: The gas was passed over nickel glyoxime for  $3\frac{1}{2}$  hours at  $190^{\circ}\text{C}$ . No appreciable change in weight was recorded and no change

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(14) Waka B., Z. Anal. Chem. 91, 29-32, (1932)

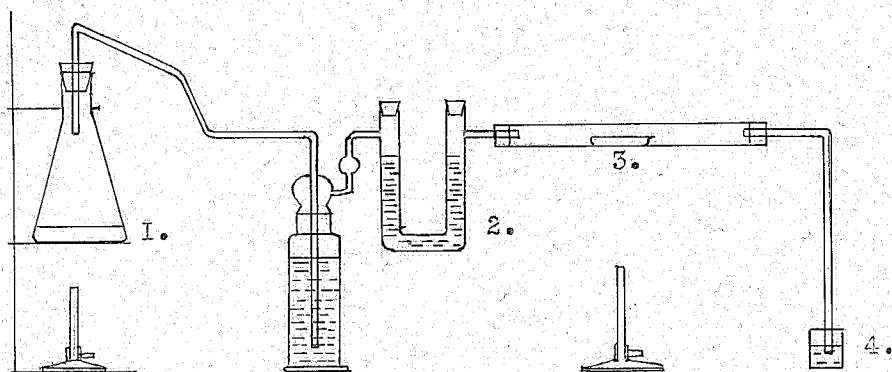
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Figure 2.



1. Potassium permanganate.
2. Conc. hydrochloric acid.
3. Nickel dimethylglyoxime.
4. Sodium hydroxide solution.

Figure 3.



1. Potassium chlorate and manganese dioxide.
2. Potassium hydroxide.
3. Boat containing black residue.
4. Calcium hydroxide.

was observed in the appearance of the material.

Oxygen: The compound was heated in an atmosphere of oxygen as follows:

60 minutes at  $210^{\circ}\text{C}$ . without any change in appearance or in weight.

60 minutes at  $270^{\circ}\text{--}277^{\circ}\text{C}$ . without any change in appearance or in weight.

Chlorine: The gas was generated by dropping concentrated hydrochloric acid on potassium permanganate crystals (Figure 2). Chlorine reacted with the nickel compound at  $90^{\circ}\text{C}$ . producing dense white fumes. The temperature was raised to  $135^{\circ}\text{C}$ . without further change. A black residue remained in the crucible. Loss in weight was 0.2302 grams.

Oxygen treatment of the black residue from the above experiment.

Oxygen was passed over the residue heated to several temperatures. No carbon dioxide was produced at  $212^{\circ}\text{C}$ . and no change in weight was recorded after heating at this temperature for one hour.

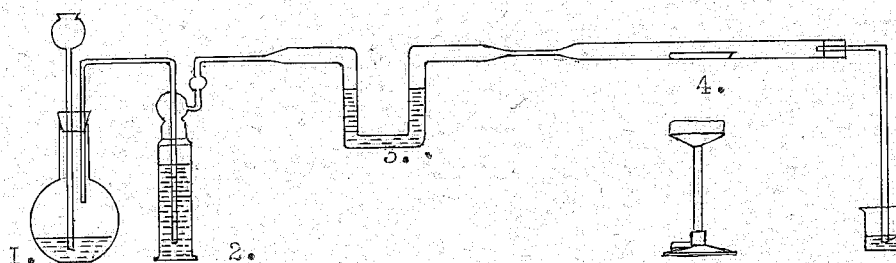
Hydrogen treatment of the black residue: Hydrogen was passed over the black residue for 2½ hours at  $210^{\circ}\text{C}$ . without any change taking place.

Oxygen treatment in the ignition tube (Figure 3). The residue in the platinum Gooch crucible was transferred to porcelain boats. A stream of oxygen was passed over the black residue and the temperature was raised slowly. Part of the residue turned gray, then became orange-colored at a higher temperature. Intense heating caused volatilization of part of the residue leaving a white deposit. The loss in weight was 0.1316 grams.

Hydrogen treatment in the ignition tube: The orange-colored material turned gray when treated with hydrogen. Continued heating for 30 minutes caused no further change. The loss in weight was 0.0545 grams.

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Figure 4.



1. Hydrogen generator.
2. Wash bottle.
3. Potassium hydroxide.
4. Potassium chloroplatinate.



(II)

Chlorine treatment in the ignition tube.

Chlorine converted the gray ash to the orange-colored body. The gain in weight was 0.0371 grams.

Hydrogen treatment in the ignition tube: The operation was repeated producing the gray ash. Heating was continued for two hours after the formation of the gray body. The loss in weight was 0.0437 grams.

Conclusion regarding nickel dimethylglyoxime.

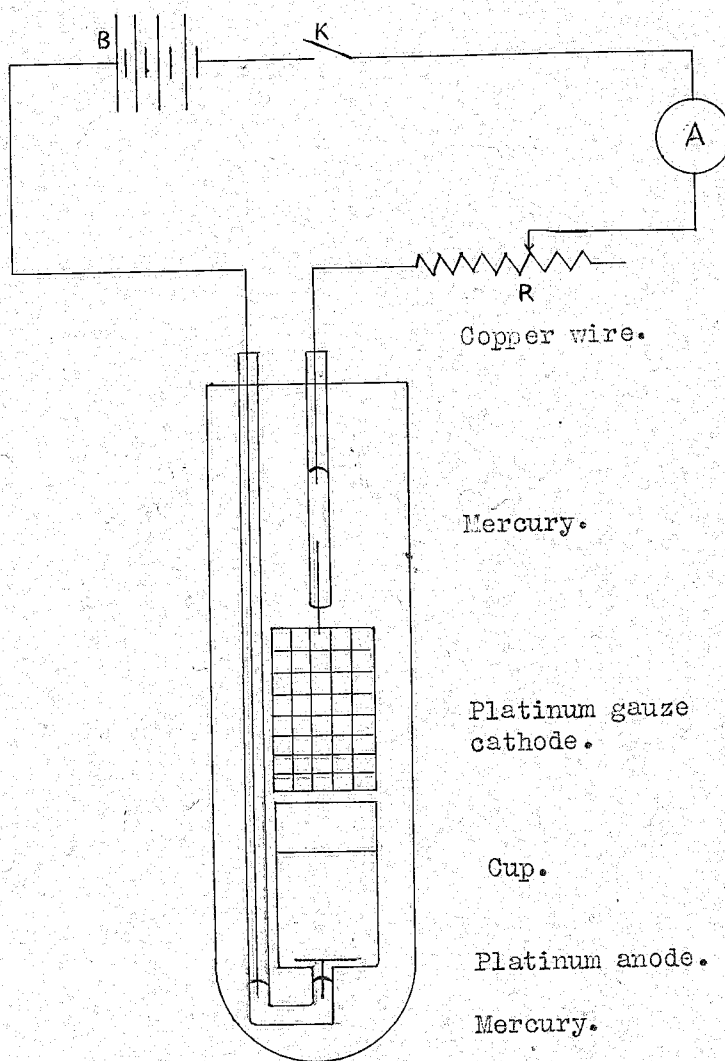
1. The formula of the compound produced by treating nickel sulphate with dimethylglyoxime is  $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$ .
  2. The compound is stable. No decomposition takes place in oxygen at  $277^\circ\text{C}$ .
  3. The compound is insoluble in water and in alcohol.
  4. Nickel dimethylglyoxime reacts with chlorine. Oxygen and hydrogen react with the product obtained by the chlorine treatment.
  5. The results of the preceding series of experiments suggest a procedure for reducing platinum dimethylglyoxime to the metal.
- Once the compound is obtained in a pure state it can be treated with chlorine and the product reduced with hydrogen.

Reduction of Potassium Chloroplatinate.

Potassium chloroplatinate was reduced to spongy platinum by heating the yellow salt in hydrogen. The train, which is represented in Figure 4, includes: 1. Hydrogen generator. 2. Wash bottle. 3. Drying tube. 4. Ignition tube. All joints were sealed except for the rubber stoppers in the generator and at the exit from the

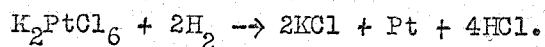
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Figure 5.



(12)

ignition tube. The hydrogen was generated by the action of dilute hydrochloric acid (Baker's C.P. acid) on zinc metal (Baker's C.P. granular). The gas was washed in distilled water and dried by caustic potash pellets. Cautious heating of the salt converted some of the yellow powder to platinum black. Increased heating in a steady stream of hydrogen converted the remainder of the salt to platinum black. Complete reduction was assured by heating the salt in hydrogen for 60 minutes. Most of the platinum black was converted to spongy platinum at the higher temperature. A series of runs were made to get enough spongy platinum for a determination. The reaction takes place as follows:

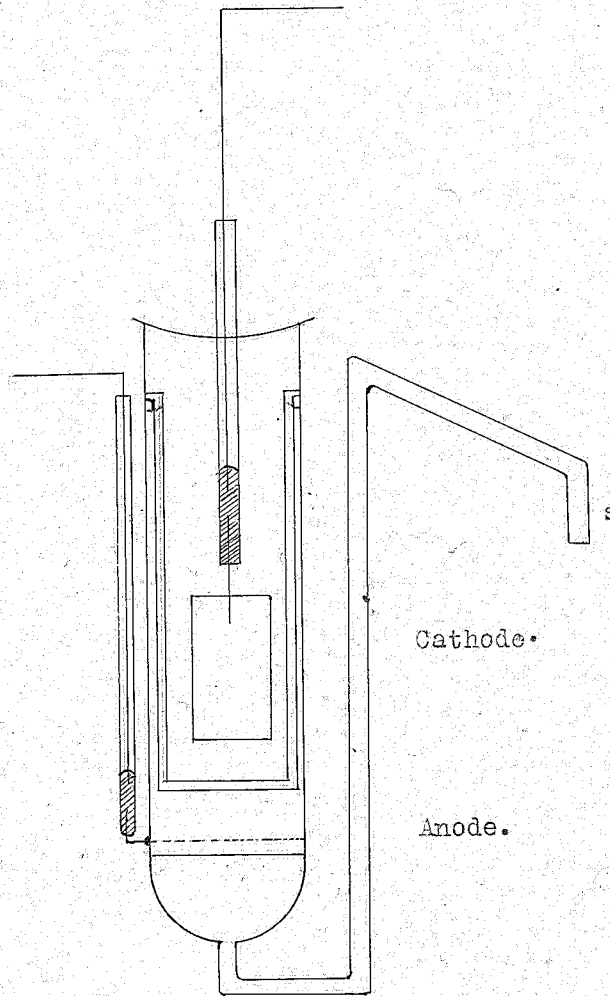


The potassium chloride was separated from the platinum by repeated washing. The treatment was continued until no trace of chloride ion could be detected with silver nitrate solution.

#### Preparation of Chloroplatinic Acid.

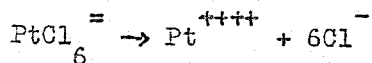
Platinum was brought into solution electrolytically. Apparatus for the purpose was kindly loaned by Dr. E.H. Archibald. It consisted of a platinum-gauze cathode and a glass cup fitted with a platinum anode (Figure 5). Spongy platinum was put into the cup of the cell and lowered into the glass tube containing redistilled hydrochloric acid. The cathode was put into the acid and a current of 0.6 amperes was passed through the solution. The chloroplatinic acid was formed in the cup as an orange-red solution which diffused slowly through the hydrochloric acid. The accumulation of chlorine at the base of the cup made it necessary to use a weak current. The deposition of platinum on the

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Figure 6.



(13)

cathode was due to dissociation of some chloroplatinic ions,  $\text{PtCl}_6^{=}$ .



When nearly all the platinum had been dissolved the orange solution was drawn off by a pipette and filtered. The volume of the solution was reduced from 400 c.c. to 100 c.c. by evaporation under reduced pressure. Weber prepared chloroplatinic acid in an electrolytic cell (15) of slightly different construction. His cell consisted of a cylindrical tube drawn out into a siphon. A sheet or disk of perforated platinum was fitted into the glass tube (Figure 6) for an anode. A piece of platinum wire was welded to the disk and at the other end the wire was led through a glass tube containing mercury. Notches at the top of the cylindrical tube supported the cathode chamber which consisted of a porous porcelain filter. The platinum cathode was suspended from a watch glass which also served as a cover for the apparatus. The chloroplatinic acid was siphoned from the cell.

#### Reduction of Chloroplatinic Acid by Hydrogen.

The following experiment was performed in order to find the weight of platinum contained in a given volume of chloroplatinic acid solution. 4.667 ml. of solution were run into two weighed porcelain boats. The solution was evaporated slowly to dryness on a hot-plate. Orange-colored crystals remained. The boats were transferred to an ignition tube and hydrogen was passed over the orange crystals, forming a gray product. The weights obtained were as follows:

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(15) Weber, W.C.P. U.S. Bureau of Stand., Bulletin, 4, 365, (1907-8)

(14)

First solution:

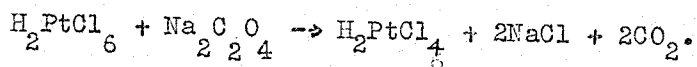
Weight of boats 1,2.	= Weight of counterpoise + 0.4800 g.
Weight of boats and Pt.	= Weight of counterpoise + 0.6003 g.
Weight of platinum	0.1203 g.

Second solution:

Weight of boats 1,2	= Weight of counterpoise + 0.3570 g.
Weight of boats + Pt.	= Weight of counterpoise + 0.5896 g.
Weight of platinum	0.2326 g.

Reduction of Chloroplatinic Acid by Sodium Oxalate.

Chloroplatinous acid and chloroplatinic acid were both used in the preparation of insoluble platinum salts. The former solution was obtained from chloroplatinic acid by reduction with sodium oxalate(16). 2.26 grams of recrystallized sodium oxalate were dissolved in 75 c.c. of water at 70°C. The solution, at 60°C., was added to the chloroplatinic acid solution, which was at the same temperature. The resulting mixture was kept at 60°C. for one hour, then allowed to cool slowly. It appeared to be somewhat lighter in color after standing for 18 hours. The volume of the solution was reduced to 40 c.c. by slow evaporation at 75°C. The equation for the reaction is:



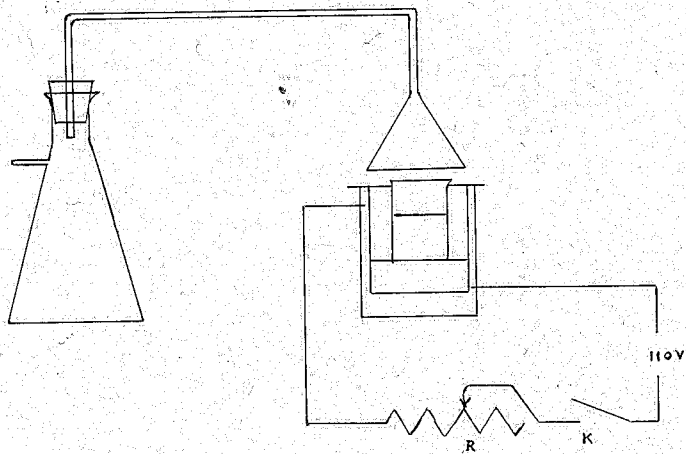
In a preliminary test on the reduction of chloroplatinic acid, a crystal of oxalic acid was added to three drops of chloroplatinic acid solution diluted with an equal volume of water. The solution was kept at 70°C. for 15 minutes without any noticeable change. Then, the

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(16) Hopkins, Chemistry of the Rarer Elements, page 358.

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Figure 7.



solution was divided into two equal parts and one part treated with sodium hydroxide. Next, dimethylglyoxime was added to each solution and the temperature kept at 45°C. for 48 hours. An insoluble brown material formed in each solution, with greater precipitation occurring in the alkaline solution.

Treatment of Chloroplatinic Acid with Dimethylglyoxime.

65.338 ml. of chloroplatinic acid solution were measured out with a calibrated pipette. The volume of the solution was reduced to 40 c.c. by slow evaporation and the temperature was brought to 40°C. The warm acid was added to 300 c.c. of an alcohol solution, containing 4.5 grams of recrystallized dimethylglyoxime. The amber-colored solution was cooled to zero°C. and kept at this point for 8 hours. A fine crystalline material appeared in the solution. Then, the temperature was kept at 35°C. for five days, producing a flocculent brown precipitate. The volume of the mixture was reduced to 175 c.c. by warming at 70°C. Thompson, Beamish, and Scott(17), in their study of platinic glyoxime, heated the mixture on a steam bath, whereas in our investigation the temperature was kept constant by using an electric heater (Figure 7). The precipitate was separated by filtration and the residue washed with 20 c.c. of alcohol at 70°C. The lustrous precipitate was digested in 25 c.c. of alcohol for 40 minutes at 64°C., then refiltered. A brown crystalline mass separated from the filtrate after standing for one week.

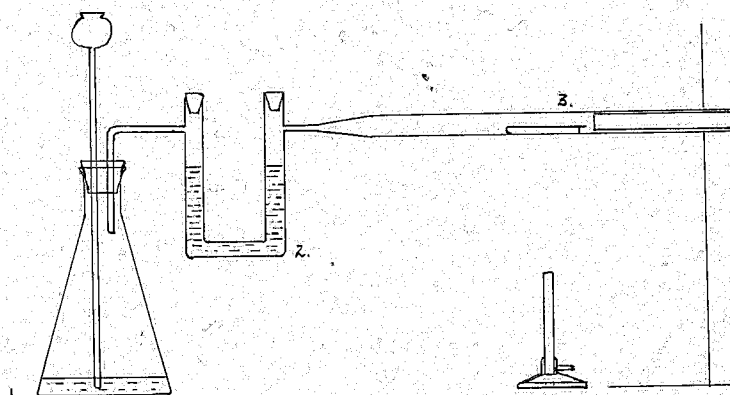
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(17) Thompson, Beamish and Scott, J. of Ind. and Eng. Chem., Anal. Ed.  
Sept., 1937.



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Figure 8



1. Calcium carbonate and hydrochloric acid.
2. Calcium chloride.
3. Boat containing brown residue.

Treatment of the brown residue.

Solubility.

Water: The solubility of the residue was slight at both zero°C. and at 100°C. The filtrate from the digested material had a blue color and on reducing the volume a blue body separated. With further reduction the blue material became finely dispersed. A flocculent bluish-black material separated on standing.

Acetone: A small portion of residue was digested in acetone for 20 minutes at 65°C. The mixture was filtered and the filtrate was set aside. A yellow crystalline material separated from the filtrate. The solution was decanted and used again to digest the residue; no crystals appeared on cooling the solution.

Hydrochloric acid: The solubility in hydrochloric acid was slight, producing a yellow solution.

Sublimation in Carbon Dioxide.

The behaviour of the brown precipitate when heated in carbon dioxide, nitrogen, chlorine and hydrogen was next examined.

A stream of carbon dioxide was passed over a small quantity of brown residue contained in a porcelain boat (Figure 8). Part of the material sublimed with cautious heating and a blue deposit formed in the condenser tube. The rest of the material turned black.

The results of the preliminary test suggest a possible means of purifying platinum dimethylglyoxime. If most of the brown material can be sublimed and if the blue substance is homogeneous and is the compound that we are seeking, then the purification of the

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Figure 9.

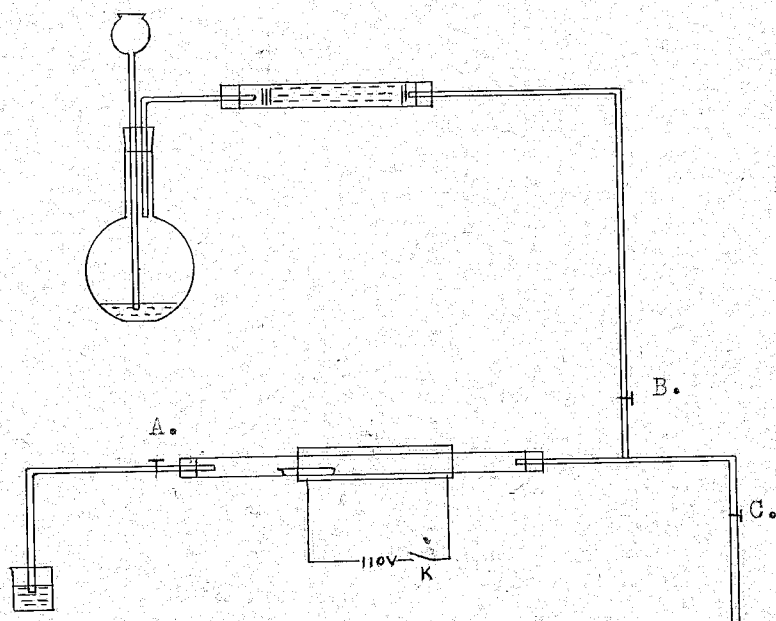
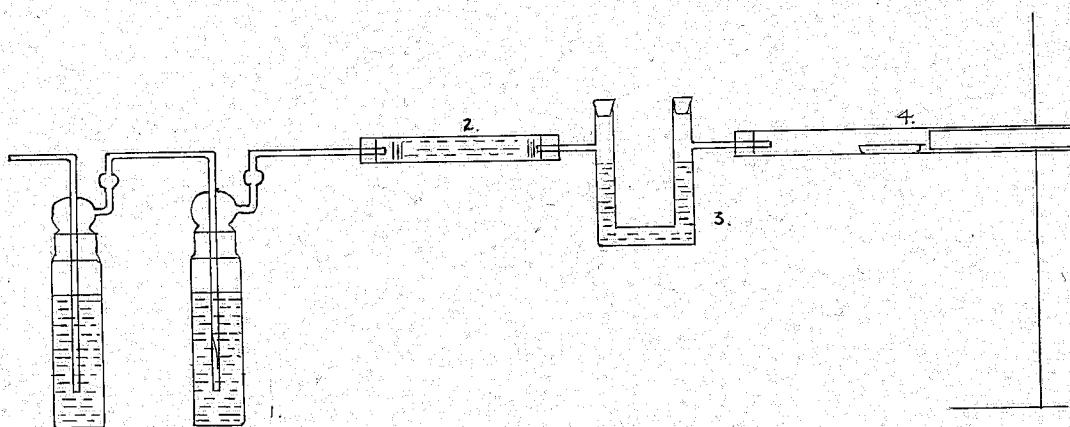


Figure 10.



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|----------------------|-------------------------|
| 1. Pyrogallol.       | 3. Potassium hydroxide. |
| 2. Calcium chloride. | 4. Brown residue.       |

compound should offer little difficulty.

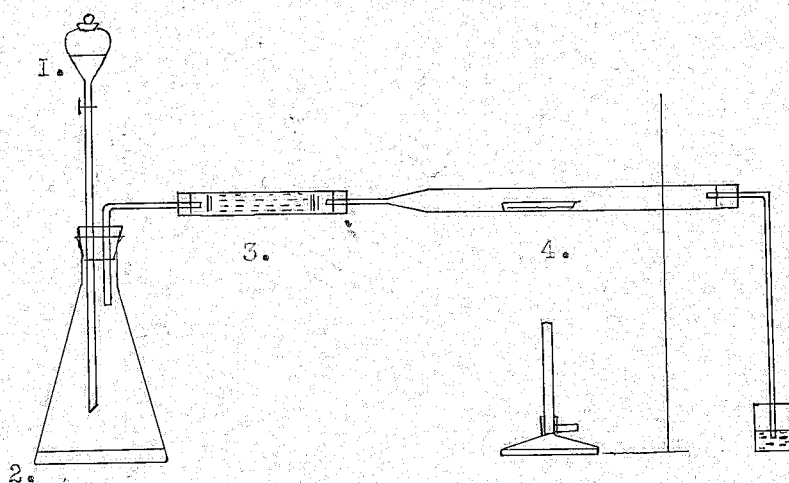
The carbon dioxide treatment was repeated allowing ample time for all air to be removed. On warming the ignition tube the blue sublimate and black residue were formed as in the first trial. Treatment with carbon dioxide under pressure was also tried but the black residue was produced again. A resistance coil was placed around the ignition tube in an attempt to get better temperature control and the work was repeated using carbon dioxide at atmospheric pressure and at reduced pressure. Treatment under reduced pressure was carried out in the following way. The gas was passed through the ignition tube for 30 minutes, the temperature was raised slowly. Next, switch K (Figure 9) was opened and stopcocks A and B were closed, the generator was disconnected and stopcock C was opened to the pump. No change was observed. Then switch K was closed and the temperature was raised until there was a puffing of the compound. A blue deposit formed on the walls of the tube and black material remained in the boat. Similar products were obtained in the carbon dioxide treatment at atmospheric pressure. The temperature was controlled in the last trial by closing and opening the switch at regular intervals.

#### Nitrogen treatment (Figure 10).

The brown material, when heated in an atmosphere of nitrogen, turned black without showing any sign of puffing. A gray body was left in the boat after intense heating. There was, however, no blue deposit formed in the condenser tube. A white film was produced on

Facing page 18.

Figure II.



- 1. Conc. hydrochloric acid.
- 2. Potassium permanganate.
- 3. Calcium chloride.
- 4. Brown residue.

(18)

on the walls of the ignition tube. Subsequent treatment of the gray body with hydrogen caused evolution of heat and the formation of considerable liquid within the ignition tube. The liquid turned anhydrous copper sulphate blue.

Chlorine treatment of the brown residue.

A preliminary test with chlorine produced explosively a black material which did not change at a higher temperature. It reacted with hydrogen forming a gray mass.

Platinum dimethylglyoxime was dried at  $133^{\circ}\text{C}$ . for 10 hours, weighed in a quartz boat, then treated with chlorine. A steady stream of the gas was passed along the train (Figure II) for ten minutes before any heat was applied. The temperature was raised slowly and after 10 minutes of cautious heating there was a puff and some material was discharged from the boat. The temperature was increased without any further change taking place. The tube was cooled after 15 minutes of intense heating.

The black mass was treated with hydrogen for several hours.

A gray body was formed which glowed on exposure to air.

Weight of Quartz boat	8.7521 g.
Weight of boat and brown residue before drying	9.9988 g.
Weight of boat and brown residue after drying	9.9700 g.
Weight of brown residue	1.2179 g.
Weight of boat and gray body	9.2451 g.
Weight of gray body	0.4930 g.
Experimental percentage of platinum	40.47 %
Theoretical value	45.89%

Hydrogen treatment of the brown residue.

A blue deposit appeared in the collecting tube and the contents of the boat turned black. At a higher temperature the blue deposit also became black.

Treatment of the black material obtained in heating the brown precipitate in carbon dioxide.

Carbon dioxide was passed over the material which remained in the boat and heating was continued for 4½ hours. The black material was partly decomposed to a gray mass.

Treatment of the blue deposit.

The blue material, which collected in the condenser tube, was scraped into a porcelain boat, then it was treated with chlorine. Gentle heating produced a rapid reaction accompanied by a flash of light. A black residue was left in the boat. Subsequent treatment with hydrogen gave a gray body.

Discussion.

The following suggestions are offered as possible explanations for the behaviour of the brown precipitate when subjected to the treatment outlined in the preceding group of experiments.

The blue sublimate, which formed in carbon dioxide, is probably platinum dimethylglyoxime, because it behaves in a manner similar to that of nickel glyoxime when treated, first with chlorine and later with hydrogen. It may be either the platinic or platinous compound. The formation of the latter type of compound is suggested since the blue deposit is also formed in hydrogen. If, on the other hand, the brown precipitate is platinic dimethylglyoxime, then the

blue deposit is more likely the platinum compound. The black residue which remains in the boat may be either a decomposition product of dimethylglyoxime or of platinum glyoxime. If the former assumption is correct, then the brown precipitate is heterogeneous. The puffing of the brown residue may be accounted for by assuming catalytic action of platinum. Sufficient heat may be generated to volatilize part of the original substance, giving the blue deposit. The product obtained on passing chlorine over the blue substance is probably a chloride, since subsequent treatment with hydrogen produces a gas which fumes in moist air. The same chloride may form on treating the brown precipitate with chlorine because the product reacts with hydrogen to produce the white fumes and a gray body similar to that obtained with the blue substance.

#### Chloroplatinous acid with Dimethylglyoxime.

R.A. Cooper (18) prepared platinum dimethylglyoxime by reducing platinum chloride directly, then adding dimethylglyoxime to the platinum salt.

In our investigation, 40 c.c. of chloroplatinic acid containing 1.86 grams of platinum was added to 85 c.c. of alcoholic solution of dimethylglyoxime containing 2.8 grams of the glyoxime. The solutions were mixed at 65°C. and the temperature was kept at this point for 15 minutes, then lowered to 45°C. The solution, which remained clear after two hours at this temperature was removed from the water bath and left overnight at room temperature. The appearance of a brown crystalline precipitate was noted. Later, the

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(18) Cooper R.A. , J. Met. & Min. Soc. of S.A. 25, 296-7 (1925)



mixture was heated to 45°C. and kept at this temperature for several days, then filtered, and the residue washed with 15 c.c. of alcohol at 10°C.

Solubility of Platinous Dimethylglyoxime.

The solubility of the compound was tested at 60°C. in each of the following solvents:

<u>Solvent</u>	<u>Solubility</u>
Acetone	Slight
Ethyl acetate	Slight
N. butyl alcohol	Insoluble
Iso butyl alcohol	Insoluble
Iso amyl alcohol	Insoluble
Benzene	Slight
Chloroform	Fairly soluble
Ethyl ether	Insoluble
Water	Insoluble

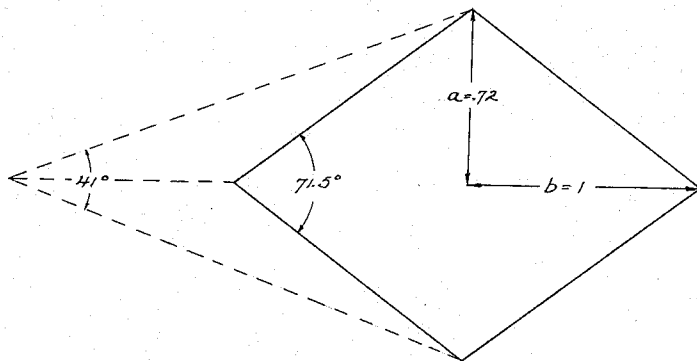
A solution of platinum glyoxime in chloroform was prepared by adding the platinum compound in small portions to 160 c.c. of the solvent. The mixture was kept at 58-60°C. for 8 hours and was shaken frequently.

Recrystallization of Platinum Dimethylglyoxime.

A saturated solution of the platinum compound was cooled slowly from 60°C. to room temperature, kept at this point for 16 hours then cooled to zero°C. for 8 hours. Small crystals appeared at room

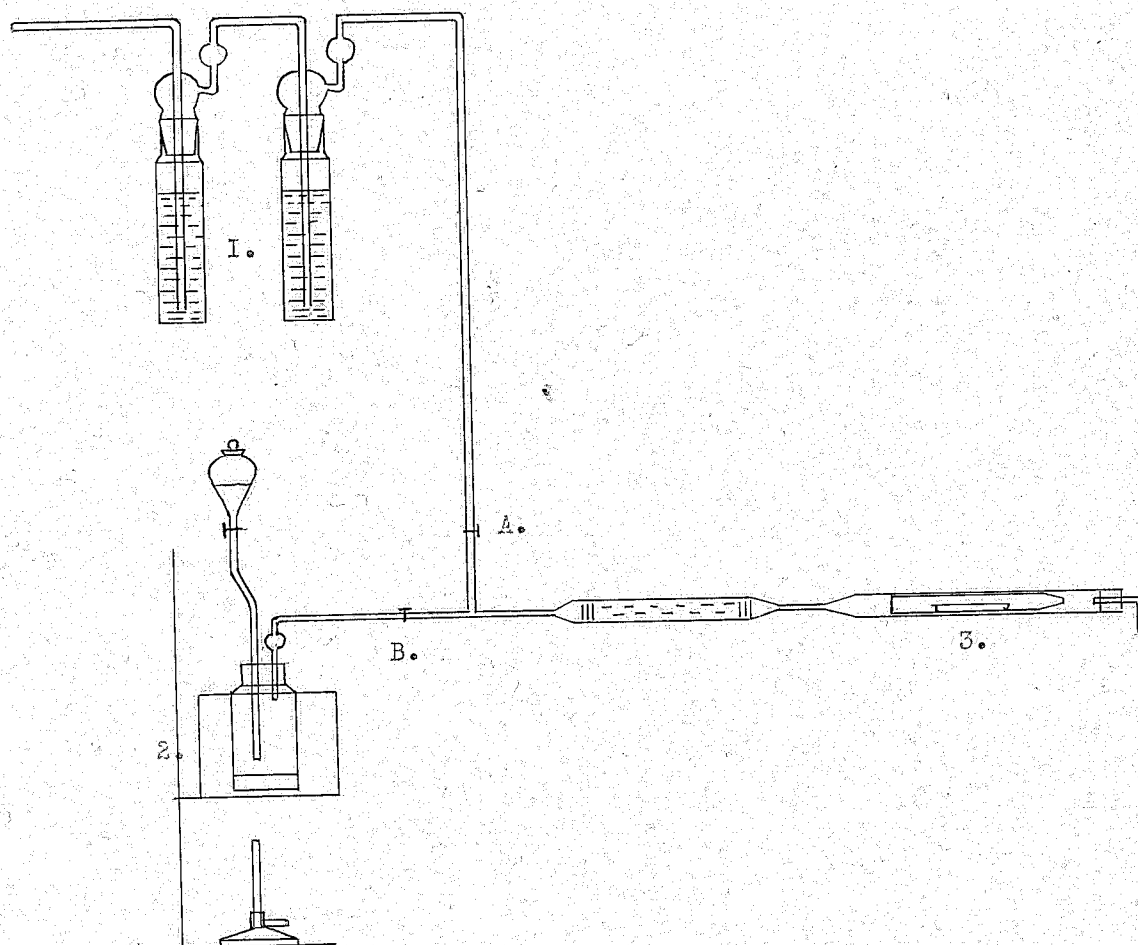
temperature and more material separated at zero°C. The mixture was not filtered because of possible contamination with dimethylglyoxime. Instead, the crystals were redissolved at 60°C. and the solution was cooled no lower than 30°C. Filtration through a Gooch crucible, at this temperature, left orange-colored crystals on the filter paper. These were washed with 5 c.c. of alcohol at 15°C, and dried slowly at room temperature.

Professor C.O. Swanson has kindly examined a specimen and finds that the crystal is orthorhombic, with smaller superimposed crystals imbedded in the faces of the larger crystal. Evidence for the orthorhombic symmetry is indicated by the perfectly centred interference figure. The angles between the faces and the axial ratios are shown in the diagram below:



Facing page 23.

Figure 12.



1. Pyrogallol.
2. Chlorine generator.
3. Platinous compound.

Chlorine treatment of Platinous Dimethylglyoxime.

The behaviour of the purified platinous compound when heated in chlorine and nitrogen was next examined.

Crystals of the compound were spread out in a weighed porcelain boat and dried at 120°C. for 2 hours. The boat and contents were transferred to a combustion tube and chlorine was passed over the crystals for one hour without any change except a slight tendency for crystals to decrepitate on warming. A tube, drawn out at one end, was inserted to collect any products lost from the boat. Chlorine was again passed through the tube and after thirty minutes of cautious heating the crystals were observed to vibrate and turn black. A few seconds after this change there was a flash of light, followed by a puffing. A yellow deposit formed on the collecting tube and some material discharged into the delivery tube. The yellow powder turned black when heated to a higher temperature in chlorine.

White fumes appeared when dry hydrogen was passed over the black material, but no further change resulted on continued heating.

Nitrogen and Chlorine Treatment.

The following procedure was tried as a means of removing occluded air from the crystals. Nitrogen was passed through the ignition tube (Figure 12) to remove air from the apparatus. Stopcock A was closed and B was opened. Then a stream of chlorine was passed through the tube and the temperature was kept at 20°C.

Next, nitrogen was passed over the crystals and the temperature was raised slowly, causing slight decrepitation. Finally, chlorine was sent through the tube and the temperature was elevated. Only a slight rise in temperature was needed to cause a rapid reaction, yielding products similar to those obtained in the initial treatment.

Reduction of Platinum Dimethylglyoxime to metal.

1 c.c. portions of platinum glyoxime solution were treated with the following reagents: 3% hydrogen peroxide, alkaline solution of sodium formate and alkaline solution of sodium oxalate. The hydrogen peroxide produced no change, but the formate and oxalate gave, in each case, a black film at the interface of chloroform and aqueous solution. Partition of the yellow solute from chloroform to alkaline solution took place and the change was accompanied by a gradual darkening of the solution.

Discussion;

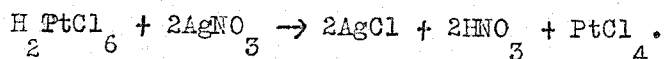
The crystals are evidently activated in chlorine at the time decrepitation starts since they turn black, then, after a short induction period, react explosively. This change may be brought about by the catalytic action of platinum.

The yellow product and black residue formed in the chlorine treatment are probably the result of decomposition. They may be either chlorides or decomposition products of platinumous dimethylglyoxime.

Chlorides and Oxides of Platinum.

Chlorides and oxides were studied in a search for some compound which could be readily purified and would be suitable for an atomic weight determination, but no suitable substance was found. A synopsis follows on methods of preparation and properties of these two types of compounds.

Platinum tetrachloride was first obtained in an anhydrous state by W. Pullinger(19), who passed dry hydrogen chloride over chloroplatinic acid at 165°C. The hydrated form of the tetrachloride was prepared by S.A. Norton by adding 2 moles of silver nitrate solution to 1 mole of chloroplatinic acid and separating the platinum chloride by evaporation of the filtered liquid.



Dehydration of this chloride gives the anhydrous salt(20), which on heating above 350°C. dissociates to form progressively the trichloride, dichloride and metal. F.C. Phillips(21) observed that hydrogen reduces solid hydrated platinum tetrachloride below 80°C. with evolution of water and hydrogen chloride.

(19) Pullinger W., J. Chem. Soc. 61, 423 (1892)

(20) Mellor, Inorganic and Theoretical Chem. XVI. 292-6 (1937)

(21) Phillips, F.C., Am. Chem. Journal 16, 255 (1894).

Voorhees and Adams obtained platinum dioxide(22) by fusing a mixture of chloroplatinic acid and sodium nitrate at 300°C. McKinney(23) prepared the oxide by the same method, then reduced it with carbon monoxide. An explosion occurred after an induction period of several hours at room temperature. At higher temperatures there were shorter induction periods, but the transition from slow to rapid reaction always took place quickly. Adams and Shriner(24) reduced the oxide with hydrogen, producing metallic platinum. Mellor refers to the works of von Meyer and Wohler, in discussing the reduction of platinum dioxide by hydrogen. The former observed that hydrogen reduces platinum dioxide energetically at ordinary temperatures. He also found that a hydrate,  $\text{PtO}_2 \cdot \text{H}_2\text{O}$ , can be prepared from platinum tetrachloride by evaporating to dryness a mixture of the salt and excess sodium carbonate. Wohler observed that hydrogen reduces this hydrate at slightly elevated temperatures.

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(22) Voorhees and Adams, J. Am Chem. Soc. 44, 1397 (1922)

(23) McKinney P.V.                      *ibid*                      56,2577 (1934)

(24) Adams and Shriner                *ibid*                      45,2171 (1923)

Summary.

The results of this investigation may be summarized briefly as follows:

1. Chloroplatinic acid reacts with dimethylglyoxime to form an insoluble and fairly stable compound, which can be reduced to metal by treatment, first with chlorine and later with hydrogen. It is a problem, however, to get a suitable method of purifying the material.
2. Chloroplatinic acid can be reduced to chloroplatinous acid by sodium oxalate.
3. Platinous dimethylglyoxime can be prepared in purified form by recrystallization from chloroform solution. The transparent orange-brown crystals exhibit orthorhombic symmetry.
4. The crystals decrepitate when heated in nitrogen, and subsequent treatment with chlorine produces a rapid reaction accompanied by the discharge of a yellow material and the formation of a black residue.
5. Alkaline solutions of sodium formate or sodium oxalate reduce platinous dimethylglyoxime to the metal.

Acknowledgment.

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## Bibliography

(26)

1. Adams, R. and Kamm, O., "Dimethylglyoxime", J. Am. Chem. Soc., 40, 1261-9, (1918).
2. Adams, R. and Shriner, R.L., "Platinum Oxide as a Catalyst in the Reduction of Organic Compounds", *ibid*, 45, 2171, (1923).
3. Archibald, E.H., "The Atomic Weight of Platinum", Proc. Roy. Soc. Edin., 29, 722-747, (1909).
4. Aston, F.W., "Mass Spectra and Isotopes", (1933).
5. Brunck, O., "Use of Dimethylglyoxime for the Determination of Nickel", Z. Angew Chem. 20, 3844, (1907), Chem. Ab. 2, 240, (1908).
6. Brunck, O., "A New Method for the Quantitative Determination of Nickel", *ibid*, 20, 384, (1907), Chem. Ab. 2, 46, (1908).
7. Congdon, L.A. and Belge, C.H., "Critical Studies on Analysis of Nickel", Chem. News, 128, 67-8, (1924).
8. Cooper, R.A., "Note on Platinum and Palladium Dimethylglyoximes", Journ. of Chem., Met., and Min. Soc. of South Africa, 25, 296-7, (1925).
9. Hahn, O., "Die Chemischen Elemente und natuerlichen Atomarten nach dem Stande der Isotope und Kernforschung", Ber. 71, 1, (1938).
10. Hooley, J.G. and Phillips, N.W.F., "A Convenient Water Still", J. Chem. Educ., 11, 376, (1934).
11. Hopkins, B.S., "Chemistry of the Rarer Elements."
12. Mellor, "Comp. Treatise on Inorg. and Theoretical Chem." Vol. XVI.
13. McKinney, P.V., "Reduction of Platinum Oxide by Carbon Monoxide", J. Am. Chem. Soc., 56, 2577, (1934).
14. Nuka, P., "Zur Loslichkeit des Nickeldimethylglyoxims", Z. Anal. Chem., 91, 29-32, (1932).

15. Noyes, W.A. and Weber, H.C.P., "Atomic Weight of Chlorine".  
Bull. U.S. Bureau of Stand. , 4, 347 (1907-8)
16. Parr and Lindgren, "Detn. of Nickel in Alloys",  
Trans. Am. Brass Founders' Assn. 5, 130-9, Chem. Ab. 23, 6:1579.
17. Phillips, F.C., Am. Chem. Journal, 16, 355, (1894)  
"Researches upon Phenomena of Oxidation and Chem. props. of Gases".
18. Pullinger, W. "Platinum Tetrachloride", J. Chem. Soc. 61, 425 (1892).
19. Sampson and Bleskney, "Relative Abundance of Isotopes of Mn.,  
Cb, Pt, Pd, Ir, Rh, Co", Phy.Rev. 50, 734 (1936)
20. Thompson, S.O., Beamish F.H., Scott, M., " Detn. of Gold and  
Platinum and Detection of Pt metals", J. Ind. and Eng. Chem.  
Analyt. Ed. Sept, 1937.
21. U.S. Bureau of Standards, "Sodium Oxalate as a Standard in  
Volumetric Analysis", Circ. No. 381, Feb 20, 1930.
22. Voorhees and Adams, "Oxides of Platinum for Reduction of Organic  
Compounds", J. Am. Chem. Soc, 44, 1597 (1922).
23. Weber H.C.P., "Prep. of Chloroplatinic Acid by Electrolysis of  
Platinum black", U.S. Bureau of Stand. , Bulletin  
4, 365, (1907-8)