REACTIONS OF GOLD AND SILVER IN CYANIDE

REACTIONS OF GOLD AND SILVER IN CYANIDE SOLUTIONS

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by

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HISTORICAL INTRODUCTION

Early History

The chemistry, of the cyanides in general, dates from the early eighteenth century, but the action of aqueous solutions of cyanide on gold was not noted until 1840. At that time the Elkingtons (20) obtained a patent for gold plating electrolytically, using for the electrolyte a solution made by dissolving gold in potassium cyanide with the aid of an electric current.

Three years later Prince Bagration (2) found that gold dissolves slowly without the aid of an electric current in alkaline solutions of either sodium or potassium cyanide. He found also that a solution of potassium ferrocyanide has the same effect but that the action is less rapid. In all three cases more rapid solution of the gold was effected if the reaction mixture was heated and free access of air allowed.

Glassford and Napier (27), at about the same time, studied the formation of potassium aurocyanide, $KAu(CN)_2$. In their work aurous oxide, Au_2O, was dissolved in potassium cyanide rather than metallic gold. The existence, formula, and properties of $KAu(CN)_2$ were well established by them.

This preliminary work led Elsner in 1846 to make the first comprehensive study of the action of cyanide solutions on metals in general. (21) He noted reaction with a number of metals and advanced a mechanism. Metals were divided into two classes; one, a class which reacted with the liberation of hydrogen, reaction occurring without the

aid of oxygen. Copper, nickel, iron, and zinc were believed to belong to this class, a type equation being,

$$Cu + 4\ KCN + 2\ H_2O \longrightarrow K_2Cu(CN)_4 + 2\ KOH + H_2\ ;$$

second, one which required the presence of oxygen for reaction to proceed as,

$$4\ Au + 8\ KCN + O_2 + 2\ H_2O \longrightarrow 4KAu(CN)_2 + 4\ KOH,$$

gold, silver, and cadmium belonging to this class. In the case of gold the final product upon evaporation of the solution was identified as colorless, octahedral crystals of potassium aurocyanide identical with those of Glassford and Napier.

Faraday (24) in 1857, apparently knowing nothing of any previous work on the subject, remarked that gold leaf floating on the surface of a potassium cyanide solution dissolved quite readily.

Developement of the Cyanide Process

The reaction next achieved commercial importance as the basis of the cyanide "process" for the extraction of gold from low grade ores.

Gold occurs most commonly in the uncombined or "native" state, and has been known and used from the earliest times. The first gold mines were deposits of free gold in fairly large particles, or nuggets. These were dug out by hand and worked into whatever shape they were desired. Then as deposits of this kind became scarce, the metal was found as very small grains in the beds of running streams and dried-up watercourses. These sands were shaken in a pan with water, the heavier grains of gold settling to the bottom and the lighter ones of sand being decanted off with the water.

Such a procedure lost a large quantity of the lighter particles of gold. A practice then developed of putting some metallic mercury in the

bottom of the pan. The gold amalgamated with the mercury and there was practically no loss upon decantation.

When gold was discovered in certain quartz rocks, this same "amalgamation process" was adopted in various modified forms. It was suitable however only for very rich ores, and when these became exhausted the need for a less expensive "chemical process" became apparent.

Prior to the appearance of the "cyanide process" only one such had been developed. This, known as the "Cassel process" depended upon the action of electolytically produced chlorine to dissolve the gold. It was not a success, for base metals were dissolved as well, and the steps necessary to separate these were too expensive to make the process practicable upon a commercial scale.

The "cyanide process" though offered a complete solution, and upon its introduction into the South African gold fields in 1890, a complete regeneration of gold mining was accomplished. Where before huge dumps of tailings, assaying twenty dollars to the ton, had accumulated around each plant, now, by the use of the cyanide process nearly a hundred per cent of the metal could be recovered (11). From South Africa the use of the process spread over the entire world until today it has been adopted and modified for use with every kind of gold and silver ore.

The story of the development of the process is a very interesting one from an historical as well as a chemical viewpoint. As early as 1866 we find Wurtz mentioning in a letter that the reaction of potassium cyanide solution upon gold might well be used for its extraction from ores(69).

The next year a patent was issued in the United States to J.H.Rae (55), marking the first commercial utilization of the reaction. The

process patented combined the action of the cyanide with the use of an electric current. It is doubtful if Rae understood the significance of the cyanide reaction because of the emphasis he placed upon the necessity of using a current in conjunction with it. His process is said to have been tried commercially but no report upon its success is available. If it had first been used upon a suitable ore and work continued upon it no doubt our modern cyanide process would have developed some twentyfive years before it did actually.

Another ten years passed before there can be found any further mention of the reaction. Skey (61) then observed that when potassium cyanide was used to clean amalgam plates a good deal of the gold was lost. It was undoubtedly this observation that led Dixon (17) to do some experimental work on the solution of gold in potassium cyanide and ferrocyanide solutions. He found the action slow unless bleaching powder or manganese dioxide were present, and concluded that a solution of neither salt was a good solvent.

In 1880 there were brought out in the United States, three patents (14),(25),(57), for variations in the amalgamation process using cyanide products in various forms. Then in 1885, Simpson and Parnell (60) patented a process for treating crushed gold ores with solutions of potassium cyanide and ammonium carbonate. The gold was recovered by suspending zinc plates in the solution and precipitating it out as metallic gold. They emphasized the use of ammonium carbonate in their process and also emphasized Rae's belief that if only potassium cyanide were used that an electric current must be used in conjunction.

The mining literature of the next few years contained a good many polemicals between these American patent holders, but the significance of

their work is shown to be small by the fact that O'Driscoll (52) in 1889 brought out a pamphlet devoted to ridiculing the utility of a cyanide process for the treatment of gold ores.

By the close of the eighties development of the process had come to a standstill. It was known generally that reaction took place between gold and cyanide solutions, but there was no comprehension of its metallurgical possibilities. But in 1887, J.S.MacArthur and the brothers R.W. and W.Forrest brought out a patent (40) covering the use of the reaction in what is essentially the modern process.

This patent was the result of work done by MacArthur in the private laboratory of the Forrests who were Glasgow medical practitioners. The three had made a number of diverse chemical investigations previously and in 1885 they tried the effect of various chemical reagents upon gold ores, with the hope of finding something which would be an improvement upon the chlorination method developed shortly before by Cassell (42) which involved the use of an electric current. In 1886 they brought out a patent (42) for a process which depended upon the action of chlorine or bromine to dissolve the gold in the presence of salts which caused the precipitation of the base metals. The method did not work very well for no salt could be found which moderated the action of the halogen so that no appreciable amount of base metal was dissolved.

The failure of this process led MacArthur to study the use of other solvents. The action of potassium cyanide was stumbled upon quite accidently (42). In 1886 he had treated ores with potassium cyanide and had afterward attempted to reduce and precipitate any dissolved gold with hydrogen sulphide. When no gold was precipitated he assumed a negative result for the use of the cyanide. Nearly a year later MacArthur had occasion to attempt the precipitation of gold from a known solution by means of hydrogen sulphide

and finding no action he recalled immediately his experiment of a year earlier with potassium cyanide. Further investigations were then made which resulted in the cyanide process of today.

A syndicate was next formed and patents were obtained throughout the world. In MacArthur's process two points were established ~~were~~ constitute his real contribution to the developement of the process. First, solution of the gold took place due to action of potassium cyanide alone. No other agent was considered necessary either to play a direct part in the reaction or to act as a catalyst. This point is in contra-distinction to that of the prior Simpson patent which emphasized the addition of ammonium carbonate to the reacting solution. Second, there was emphasized the use of dilute solutions rather than the strong ones used in previous methods.

It is of historical interest only, to note that all of these MacArthur patents were declared invalid by 1897, and that no permanent financial reward resulted from them. Too much was known of the reaction before MacArthur's discovery for him to claim full priority. And it is not possible to patent "concentrations" of chemical solutions. Simpson's patent had anticipated MacArthur's definitely in all of the legal requirements. The greatest contribution from MacArthur's work was the act of bringing the metallurgical possibilities of the reaction before the world.

The appearance of this process created so much interest in the reactions involved that a large number of scientific and engineering papers dealing with the subject appeared in the nineties and early nineteen hundreds. Statements made by MacArthur regarding the lack of any role that oxygen might play in the reaction led a number of workers in all parts of the world to study this point. Most indications were contrary to this belief as will be seen later.

An almost limitless amount of work was done in attempting to find catalysts or accelerators for the reaction. The one most often utilized appears to be hydrogen peroxide. Haloid cyanides, such as bromo- and chloro-cyanogen were also reported as catalysts quite frequently. Sodium and barium peroxides, as one might expect, were found to have an action similar to that of hydrogen peroxide. All of these substances are strong oxidizing agents and there are many disadvantages in their use. Opinions as to their utility vary, the best of them being, it is believed, those which give off oxygen slowly, as do the heavy metal peroxides.

By 1907 the process was developed about as it is today. Julian and Smart published at that time the first and most comprehensive text on the subject. (36)

Role of Oxygen

The appearance in 1888 of the MacArthur and Forrest patents (4) and of an article by MacArthur in 1890 (41), in which it was claimed, that hydrogen is formed during the course of the reaction, marks the beginning of an important chapter in the history.

L. Janin (34), (35) working independently, came to this same conclusion. According to these workers reaction takes place with the evolution of hydrogen as in the following equation:

$$2\ Au + 4\ KCN + 2\ H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH + H_2$$

Here gold is shown to react just as Elsner believed metals which he classified as class 1 did. Experimental evidence for the above is very weak however.

MacArthur mentioned in his paper, that according to Elsner's work either oxygen must be absorbed or hydrogen evolved for reaction to take

place. But it was stated that he had never observed the former and was unable to prove the latter which he believed to be true. Oxygen should oxidize the cyanide to cyanate as in the equation;

$$2\ KCN + O_2 \longrightarrow 2\ KCNO$$

Nascent hydrogen would be much less likely to react upon the cyanide, and hence as the reaction proceeds quite normally as far as the cyanide is concerned, it should, for this reason, most properly be considered as reacting with the formation of hydrogen. But regardless of what part oxygen plays in the solution of pure gold by cyanide, MacArthur claimed to have proved that it plays no part in dissolving gold from ores. He treated an ore with cyanide in free excess of air, and paralleled it with boiled solution, filling the bottle in each case to the stopper with ore and solution. Extraction was the same in each case. No experimental figures are given in this paper.

Butters and Clennell (9) writing in 1892 agreed with MacArthur in his idea of the action of the oxygen on the cyanide. They had found in practice that a much greater amount of potassium cyanide is needed than theory requires, but for the reaction with gold they accepted Elsner's equation rather than MacArthur's and Janin's.

In the same year Skey (62) showed that the following proportions are needed for the reaction; 130 parts KCN: 8 parts O_2: 196.8 parts Au, which translated into moles gives 4 Au: 8 KCN: O_2. Attention was called also to the fact that this proportion of oxygen was so small that the amount normally dissolved in solution or adhering to the surface of the gold is sufficient to cause the dissolution of a measurable amount of gold.

MacLaurin, in 1893, (44) published the first paper treating the reaction as a purely chemical problem.

Eight experiments were made in which gold foil was placed in bottles containing previously boiled potassium cyanide solution. Four of these were stoppered full, two were left open to the air, and two stoppered while containing oxygen gas. Results were obtained as follows:

	1	2	3	4	5	6	7	8
Type	92 hrs. in stoppered bottles				96 hrs. with O_2		68 hrs. in open	
H_2O	125	121.15	123.7	127.6	125 g	125 g	125 g	16 g
KCN	1	1	1	1	1 g	1 g	1 g	4 g
Amt. Au diss.	.0018	.0025	.00295	0.00265	0.23995	0.24140	0.09175	0.03225

From these data it is obvious that the reaction is accelerated by the presence of air, and even more by the presence of oxygen. These data MacLaurin considered as only qualitative. Experiments 1 - 4 might well have contained traces of air.

To prove O_2 necessary for solution to take place gold foil was placed in a retort containing boiled cyanide solution and its vapor, which was sealed off.

Loss in weight of gold was noted after twenty-four hours. The retort was then opened and the gold allowed to stand in the same solution under an atmosphere of air for twenty-four hours. Data obtained is as follows:

	I		II
	Sealed vessel	Open vessel	Sealed vessel
Au lost	.0002 g	.00835 g	0.0003 g

In a second paper by MacLaurin (13) the work was refined by noting the time required to dissolve traces of gold impregnated in paper. This was prepared by steeping filter paper in gold trichloride solution containing 0.1% Au, then suspending over a current of ammonia gas, forming the oxide, which was reduced by immersing in hot oxalic acid. On washing

and drying the paper had a pink color. A Dumas bulb was filled two-third's with 5% potassium cyanide and a piece of the gold paper introduced into the limb. The end was drawn out to a fine point and the solution boiled then the limb was sealed and the solution cooled. The paper was shaken down into solution, and eight days time was noted before the color faded. Then the limb was broken, air admitted and a similar piece of gold paper placed in the solution. Only two minutes were required to fade all trace of color.

No result was obtained in which absolutely no reaction was observed.

MacLaurin reported also an attempt to discover the stoichiometrical relationship between gold dissolved and oxygen. Using an apparatus of a U-tube design, previously boiled potassium cyanide, gold foil, and free oxygen were brought into contact. The reaction was allowed to continue for twenty-four hours and the amounts of oxygen present at the beginning and end observed, together with the loss in weight of the gold. The results are tabulated below. Assuming Elsner's equation to be correct.

$4\,Au + 8\,KCN + 2\,H_2O + O_2 \longrightarrow 4\,KAu(CN)_2 + 4\,KOH$ the factor to convert Au into O_2 is 0.04054.

Temp. 58° F.

Time in days	2	3	3	3
% KCN	1	1	2	2
Loss wt. Au.	0.13062	0.28128	0.17833	0.16802
A. Loss × 0.04054 = O_2 wt. reacted	0.0052953	0.011403	0.0072285	0.00681153
Vol O_2 absorbed S.T.P.	3.733	7.263	4.897	4.424
B. Wt. O_2 absorbed	0.005339	0.0103881	0.00700408	0.0063275
Ratio B/A.	1.0086	0.911	0.9688	0.9289

MacLaurin believed that these experiments showed two atoms of gold to require one of oxygen. The fact that the ratio is less than one is accounted for by noting the oxygen pressure to be slightly reduced towards the end. This work gave ample support to Elsner's equation.

This work was not sufficiently controlled to give results of the highest accuracy. No provision was made for stirring so as to insure uniform contact between gold and solution at all times. Nor was any provision made for thermostating the apparatus. Inasmuch as the measurement of the amount of oxygen reacting, involved gas measurements, the failure of providing adequate temperature control throws great doubt upon the reliability of the results.

Goyer (30) corroborated Elsner's equation at this time,but his experimental work was not comparable with MacLaurin's in quality.

The next important paper published was by Bodlander in 1896 (7). Having noted the difference between the equations of MacArthur and MacLaurin he attempted to differentiate between them. Potassium cyanide solution was placed in the half of a V-shaped retort and spongy gold in the bend. The whole was evacuated with a mercury pump and sealed off. The gold was then dropped into the solution and allowed to stand for fourteen days with frequent shaking. A parallel experiment of equal quantities of reagents was carried out in a loosely stoppered flask for an equal time. The author points out that according to MacArthur's equation,

$$Au + 4\ KCN + 2\ H_2O \longrightarrow K_2\ Au\ (CN)_4 + 2\ KOH : H_2$$

in the evacuated retort the amount of potassium cyanide present should give rise to 18.45 cc of H_2 gas at S.T.P. gold being present in excess.

Actually, one-half cc.of gas was found which did not give an analysis as hydrogen. Bodlander believed this gas to be nitrogen from dissolved air which had not been removed by the pumping process. For the gold a loss in weight of 0.0164 g was noted. A fact which the author explained by believing oxygen to have been present in small quantity from dissolved air.

In the parallel experiment 0.2818 g. of gold was found to have dissolved. No notice of the cyanide concentration at the conclusion was taken, nor were the two experiments duplicated. However, the work does indicate that MacArthur and Janin were wrong and Elsner's equation is the true one.

Dixon in 1897 (18) corroborated Elsner's equation in a qualitative manner.

Bettel in 1898 (5) treated gold leaf in an atmosphere of hydrogen with potassium cyanide solution and found that no reaction took place.

No further work was done until 1918 when Crowe (15) made some rather qualitative experiments under vacuum which convinced him that if oxygen is removed no gold will dissolve. The vacuum could have been no greater than aqueous vapor pressure for he evacuated above the solution. He pointed out the difference in oxygen content of air dissolved in water and atmospheric air, the former containing 35% oxygen to the latter's 21%.

Hay in 1926 (43) published two papers discussing the cyanide-gold problem and agreed that oxygen is necessary but did not give accurate experimental evidence of the fact.

Theories of Mechanism

MacLaurin published (44) (45) the first discussion of a possible mechanism for the action of oxygen in the reaction. Three hypotheses were advanced and one selected as being most probable.

(1) The gold might first be reacted upon by the oxygen of the solution and the oxide formed be dissolved by the cyanide as:

$$4\ Au + O_2 \longrightarrow 2\ Au_2O$$

$$Au_2O + 4\ KCN + H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH.$$

This mechanism MacLaurin rejected, for no evidence for formation of the intermediate aurous oxide had been found.

Skey (61) had given someevidence for this in reporting that in the presence of water and oxygen gold becomes coated with a film of oxide.

(2) The oxygen might oxidize the KCN to KCNO as

$$2\ KCN + O_2 \longrightarrow 2\ KCNO$$

Then $2\ Au + 4\ KCNO + H_2O \longrightarrow 2\ Au\ CN.KCN + 2KOH$

or $2\ Au + 3\ KCN + KCNO + H_2O \longrightarrow 2\ KAu(CN)_2 + 2\ KOH$

might be a more plausible explanation.

Making runs in stoppered bottles with boiled solution, MacLaurin found the addition of potassium cyanate to have no effect in accelerating reaction.

Figures obtained are as follows:

92 hours in stoppered bottles

	gs.	gs.	gs.	gs.
H_2O	125	121.15	123.7	127.6
KCN	1.0	1.0	1.0	1.0
KCNO	0.25	0.25	---	---
Loss wt. Au	0.0018	0.00255	0.00295	0.00265

(3) The mechanism finally accepted by MacLaurin, was that the Au is

dissolved by simultaneous action of oxygen and cyanide ion. The explanation being, that the "affinity" of Gold for Cyanide ion and Oxygen for Potassium ion is greater than that of potassium ion for cyanide ion. This conception is greatly clarified if modern concepts are utilized.

Bodlander after proving the validity of the Elsner equation, postulated the formation of hydrogen peroxide as an intermediate step in the reaction (7) as

$$2\ Au + 4\ CN + 2\ H_2O + O_2 \longrightarrow 2\ KAu(CN)_2 + 2\ KOH + H_2O_2,$$

most of the peroxide being used up again in a second reaction in which gold dissolves without absorption of oxygen.

$$2\ Au + 4\ KCN + H_2O_2 \longrightarrow 2\ KAu(CN)_2 + 2\ KOH$$

The combination of the two equations gives the Elsner equation. As the second reaction would follow the first simultaneously, we would not expect the concentration of hydrogen peroxide to build up. Bodlander removed it as fast as formed by precipitating as CaO_2 in an excess of lime, or causing it to react with an excess of indigo carmine. In this manner about 70% of the theoretical amount of hydrogen peroxide was accounted for.

Bettel (6) in 1898 suggested that $KAu(CN)_4$ was formed as an intermediate product, as

$$2\ H_2O + 2\ Au + O_2 + 6\ KCN \longrightarrow KAu(CN)_2 + KAu(CN)_4 + 4\ KOH$$

followed by

$$KAu(CN)_4 + 2\ Au + 2\ KCN \longrightarrow 3\ KAu(CN)_2$$

In 1895 Christy (12) stated that he believed the reaction to take place due to the formation of free cyanogen. That is, gold would dissolve in a potassium cyanide solution, if any substance were added which would cause the formation of nascent cyanogen. He found nearly all oxidizing agents to be effective in promoting the reaction.

The effect of bromo-cyanogen was explained as follows:

$$Br\ CN + KCN \longrightarrow K\ Br + (CN)_2$$

$$2\ KCN + 2\ Au + 2\ CN \longrightarrow 2\ KAu\ (CN)_2$$

combining

$$3\ KCN + 2\ Au + Br\ CN \longrightarrow 2\ KAu\ (CN)_2 + K\ Br.$$

Adding Bromine to a reaction mixture gave a similar result and increased reaction as:

$$2\ KCN + Br_2 \longrightarrow 2\ K\ Br + (CN)_2 + 2\ Au + (CN)_2 + 2\ KCN$$

$$\longrightarrow 2\ KAu\ (CN)_2 \quad \text{or} \quad 4\ KCN + Br_2 + 2\ Au \longrightarrow KAu\ (CN)_2 + K\ Br.$$

Christy did not believe oxygen to be necessary in this reaction as had Mulholland (50) who summarized it as:

$$4\ Au + 8\ KCN + Br_2 + H_2O + 70 \longrightarrow 4\ KAu\ (CN)2 + 2\ K\ Br\ O_3 + 2\ KOH.$$

A similar result was obtained using chlorine in the reaction mixture.

In 1902 Christy published a further work (31) (32) in which he altered his views entirely, and advancing an electro-chemical explanation, gave the first "modern" treatment of this problem.

When metallic gold is placed in a solution some gold dissolves leaving the remainder negatively charged as:

$$\underset{\text{(Metallic foil)}}{Au} \quad \overset{o}{\longleftarrow\!\!\longrightarrow} \quad \underset{\text{(Foil Negatively charged)}}{\overset{-}{Au}} \; + \; \underset{\text{(ion)}}{\overset{+}{Au}}$$

Equilibrium is set up between gold ions tending to plate out from solution (osmotic pressue) and gold ions in the foil tending to go into solution (electrolytic solution tension). This is, of course, the familiar Nernst theory of the origin of emf.

If any other substance is present which removes the gold ions from solution as fast as they enter no osmotic pressure is set up, hence equi-

librium is not established, the metal dissolves, and the electro-potential increases.

Cyanide ion removes gold ions with those of other metals so that gold dissolves in a potassium cyanide solution although absolutely inert in distilled water. This effect completely alters the sequence of metals in the electro-chemical series if they are set up in order of their ease of solution in potassium cyanide.

According to Christy the sequences are comparable as follows:

	6.5% KCN		Dist. H_2O
(1)	Zn		Zn
(2)	Cu		Pb
(3)	Au		Fe
(4)	Ag		Cu
(5)	Pb	Decreasing potential	Ag
(6)	Hg		Hg
(7)	Fe		Au

Only one side of the picture is presented thus far. In the initial formation of gold ions in the metal and subsequent solution the foil assumes a negative charge due to free electrons being deposited upon its surface. Even though gold ions are removed by the cyanide ion due to formation of a complex, further solution will not take place until the negative charge on the foil becomes discharged.

It is here that oxygen plays a role as it tends to assume the ionic state, in the presence of water, forming hydroxyl provided an electron is furnished it.

Traube (67) suggests this as a mechanism for the solution of all metals in the presence of oxygen. $O_2^0 + 2\ H_2O + 2e \longrightarrow 4\ OH^- \longrightarrow 2H_2O_2$

The hydrogen peroxide necessarily formed is accounted for in Bodlander's work.

Julian and Smart (36) in their well known textbook set forth a rather different viewpoint. When the gold is dissolved a miniature cell is set up in which one portion of the foil is a negative and the other a positive electrode. When gold dissolves a current is set up and as a result hydrogen gas plates out on the cathode or negative portion which in turn sets up a back emf. and effectively polarizes the cathode. Oxygen depolarizes this cathode forming hydrogen peroxide allowing solution to proceed.

This conclusion was based on work done by these authors using a cell composed of a gold foil anode and a pyrite cathode, each being suspended in a potassium cyanide solution divided into two portions by means of a porous partition.

By means of a galvanometer the current set up is ~~rated~~ measured. Bubbling oxygen over the pyrite cathode had a marked effect, increasing the current, while no effect occurred if oxygen was bubbled over the gold foil anode.

Further proof for this theory was found in the fact that gold was found to dissolve much more rapidly when in contact with iron than in the pure state

A second conclusion (36) reached by these authors was that as the temperature of reaction is increased less polarization occurrs and hence there must be a temperature at which polarization becomes zero and above which gold reacts in the total absence of oxygen due to the evolution of hydrogen.

This conclusion was reached by comparing the solubility of oxygen in water varying with temperature with the variation of rate of dissolution of gold. A maximum for the latter was reached at 85° C. If, as according to Julian and Smart the reason for gold not dissolving in the absence of

oxygen is due to polarization we may regard the mechanism as follows.

Gold dissolving has a certain emf.which is counter-balanced by the emf.of the polarizing hydrogen on the cathode portion of the gold. As the solution is heated this opposing emf. becomes less until that of the anodic portion is greater and gold will dissolve in the absence of oxygen.

Engler and Weissberg (23) in 1904 stated that they believed gold peroxide to be an intermediate product in the solution of gold in potassium cyanide. Reichinstein (56) expressed the same belief.

All of the publications from this date on seem to be mere elaborations upon the mechanism as established in Julian and Smart's book. Watts and Whipple (68) in publishing a paper on the solution of various metals in acids, state that they believe oxygen to be necessary because gold is a metal of the second class in dilate cyanide solutions. Keith (37) analyzed Elsner's equation and settled the MacArthur-MacLaurin controversy by stating that gold has a higher affinity for cyanide than potassium but that some third substance must be present to receive the electrons. White (69) accepted previous work but noted that in very dilute solution a brownish red stain appeared on gold foil. This he believed to be aurous cyanide but did not analyze the material. Copper gives the same effect giving a white precipitate of cuprous cyanide. The aurous cyanide obtained by the action of FeSCN or metallic Au is identical in appearance with that obtained on the plates mentioned above.

Studies of Rate of Solution

Because of obvious metallurgical importance considerable interest has been taken in the study of the rate of solution in this reaction.

The most substantial part of this interest has been concerned with the effect produced in varying the concentrations of the cyanide solution used. MacLaurin in his two papers (58) (59) studied this phase thoroughly. In the first of these it was shown experimentally that the rate of solution passes through a maximum in going from dilate to more concentrated solutions. This was explained by assuming the rate of solution as dependent upon two factors.

(1) Concentration of cyanide ions per unit volume.

(2) Concentration of oxygen moles in same volume.

The maximum effect in the rate of solution is due to decrease in solubility of oxygen as the concentration of potassium cyanide increases. A study of the solubility of oxygen in various strengths of potassium cyanide was reported in the same paper.

In the second paper (59) the work was extended somewhat further, the value for the concentration of potassium cyanide producing the maximum rate of solution, being established as 0.25%. The same effect was observed with silver in identical degree as with gold. The variation in rate was observed as not being influenced directly by the concentration of potassium cyanide except in very dilute solutions but as being due entirely to the variation in solubility of oxygen in the various concentrations. The amount of gold dissolved was found to be nearly proportionate to the absorption coefficients of oxygen in such solution. The failure for this rate to be exactly proportionate is due probably to the increased viscosity of cyanide solutions as the concentration increases. This belief was substantiated somewhat by adding inert substances to the more dilate solutions and obtaining appropriate results. The amount of gold dissolved is proportionate to the coefficient of viscosity of the solution as well as

to the variation in concentration of oxygen and cyanide ion.

Bodlander in 1896 (7) rejected MacLaurin's work and found that the rate rises rapidly to 0.25% and then falls off rising less steeply. But the maximum at 0.25% was not observed.

Christy in 1902 (13) showed the minimum concentration of potassium cyanide in which gold will dissolve at all. This is, of course, electrochemically, the point at which the solution pressure is just balanced by the osmotic pressure of the ions in solution, or where the electromotive force is zero. This point of concentration was found to be $\frac{M}{2,000} - \frac{M}{4,000}$ or 0.00325% - 0.0016% KCN.

Julian and Smart (36) modified MacLaurin's explanation in the light of their theory by stating that the maximum as established by MacLaurin must necessarily vary with different sets of conditions owing to the charges in potential and degree of polarization on the cathode portions of the metal. These authors showed that in dealing with a gold plate in a cyanide solution the difference in potential at any two points of its surface is about $\frac{1}{150}$ of the difference between gold and marcasite. Pure gold is then correspondingly much less soluble than gold in ores from the viewpoint of reaction rate.

In 1919 White (69) published a paper differing experimentally from results of MacLaurin's work. For gold leaf immersed in potassium cyanide solution he found from .02 - .03% to give the maximum speed of reaction. But for gold leaf floating on the surface 6.8% was most effective. It was noted as well that conditions are altered when contact occurrs between gold and any iron or carbon.

Two papers by Hay (31) appeared in 1926 - 1928 dealing in part with this question but they are in full agreement with the previous work.

Barsky, Swainson and Hedley (3) in 1934 using sodium cyanide found the maximum rate at 0.05% sodium cyanide and also by determining the solubility of oxygen in solutions ranging from 0.0 to 2.00 showed that it does not vary and therefore the fact that strong cyanide solutions do not dissolve gold as rapidly as weak ones does not depend on this factor. For silver 0.10% solution was found most effective.

Effect of Temperature and Light

The question of temperature effect is most adequately discussed by Julian and Smart in their book (36) as they explain the increased velocities of the cyanide ion and oxygen molecules with rise in temperature increases the rate of reaction. This effect is counter-balanced at rather high temperature by the fact that the solubility of oxygen in solution decreases with temperature. Still a maximum effect is noticeable which these authors place at about 85° C.

Two authors, Berthelot (4) and Caldecott (10) have found that cyanide solution is more active in dissolving metals in the presence of light. The former explains the increased activity by saying it is due probably to increased rate of absorption of oxygen by the potassium cyanide solution.

Effect of Added Substances

Work done upon studying the effect of adding foreign substances is best classified by the chemical nature of these substances.

It was noted during the earliest history of the "Cyanide Process" that Cyanogen Halides, as Bromo-cyanogen and Chloro-cyanogen, have an accelerating effect upon the rate of this reaction. Early patents appeared (26) (49) and a number of journal articles have reviewed this question. The former appears to be the best accelerator some doubt ex-

isting as to whether or not the chloride has any effect.

Stevens and Blackett (63) believe the effect to be due to substitution of bromine for oxygen as the oxidizing agent.

One patent (29) and a number of papers (31) (32) (33) have appeared discussing the uses of hydrogen peroxide as an accelerator. Its action is quite obvious of course.

Other peroxides were found to have a catalylic effect as one would naturally expect. Sodium peroxide (29) (35), barium peroxide (36) and persulphates have all been studied in this connection. Andrejeff (39) has noted that ozonized oxygen increased the rate of reaction with gold from one to one and one-fourth times the observed rates of air and that increasing the proportion of ozone accelerates the action.

Other and milder oxidizing agents might be expected to have some effect upon the reaction and this has been found to be the case though no very clear cut results have been obtained. Potassium permanganate (5) (6) has been used, as well as chromates (47), ferricyanide (60) (47) and the free halogen (60) (57) (6).

Parkes (53) has patented the use of a ~~solvated~~ mixture of bromine and potassium bromide with potassium cyanide, potassium dichromate and sulphuric acid. Noelting and Forel (51) have noted an accelerating effect with organic oxidizing agents as picric acid and nitroso naphthol. Keith summarizes the whole situation (37) by saying that any oxidizing agent is theoretically an accelerator in the light of Julian and Smart's mechanism.

Owing to the very nature of their action we should expect little work to have been done by previous investigators, nearly all of whom were activated by commercial interest, upon negative catalysts or acceler-

ators upon this reaction.

Reducing agents would be expected to have this effect though Pasuchin (54) claims to have proven that the presence of sulfides has no effect upon the reaction.

Barsky, Swainson, and Hedley (3) have noted that calcium hydroxide has a marked accelerating effect which they were unable to explain.

Purpose

From the foregoing survey of the literature it seems evident that dissolution of gold in alkali cyanide solution proceeds with the absorption of oxygen rather than with the liberation of hydrogen.

Nevertheless, in the 1921 edition of Julian and Smart's textbook on the Cyanide process, after a discussion of the literature dealing with this point, there appear the statements:

"(1) Gold and Silver are capable of dissolving at ordinary atmospheric temperatures and pressures to a limited extent without the addition of oxygen.

(2) For the continued dissolution of gold and silver at ordinary atmospheric temperatures and pressures, oxygen is desirable if not absolutely essential."

In view of the uncertainty which apparently still persists in spite of the work of MacLaurin (44) and Bodlander (7) already quoted, it seemed worth while to investigate the question further.

Some preliminary experiments were made by treating gold in an atmosphere of nitrogen with cyanide solutions which had been freed of oxygen by prolonged boiling. Some gold appeared to dissolve. This result, which in the light of later work was presumably due to incomplete removal of oxygen, led to the construction of an apparatus in which gold and cyanide solution could be brought together with oxygen rigidly excluded. This is described in Part I of the Experimental section.

In the complete absence of oxygen, no gold was found to dissolve. The next step was to investigate the stoichiometrical proportions of gold, oxygen and potassium cyanide. Some experiments were made with the apparatus described in Part I but the results were unsatisfactory. The amounts of oxygen involved are quite small, since from Elsner's

equation, one mg. of gold requires only about 1/35 cc. of oxygen under standard conditions.

An apparatus was devised by which the consumption of oxygen could be followed by the pressure change in a reaction vessel of known volume immersed in an accurately controlled thermostat. This is described in Part II of the experimental section.

It was anticipated that the rate of the reaction could be followed by observing the changes in oxygen pressure. However, it was found that the conditions under which the reaction proceeded favored the formation of hydrogen peroxide so that the ratio of gold dissolved to oxygen consumed was not a constant quantity unless some reagent was added to effect rapid decomposition of the hydrogen peroxide. The results obtained are in agreement with the work of Bodlander (7).

Since this work was undertaken, the same problem has been attacked from a very different point of view by Barsky, Swainson and Hedley (3). They have calculated the free energy changes for various hypothetical reactions and have shown that the two stages involving the formation and decomposition of hydrogen peroxide which were postulated by Bodlander and which when combined correspond to Elsner's equation, should occur readily while on the other hand the reaction proposed by MacArthur involving evolution of hydrogen is impossible from the point of view of the free energy change involved.

Experimental Section

Materials Used

The materials used in this work were pure gold and pure potassium cyanide. The cyanide used was Merck's Blue Label "Reagent" grade.

The gold foil was prepared specially for the work, using a method of purification given by Mallett as modified in this laboratory previously by Toole (66).

1. The crude gold was dissolved in aqua regia, and the solution evaporated down with excess hydrochloric acid till all the nitric acid was destroyed. A solution of hydrobromic acid was added and the solution diluted until the acidity was about three normal. It was then allowed to stand for thirty days to ensure precipitation of traces of silver.

2. The silver bromide precipitate was filtered off, and sulphur dioxide bubbled through the filtrate to precipitate the gold. This was redissolved as above and the solution allowed to stand again for seven days.

3. The gold was then precipitated with sulphur dioxide, dried and covered with concentrated sulphuric acid. The latter was evaporated off until the gold was merely moistened with it. This was followed by washing thoroughly with hot distilled water.

4. The gold was then dried and fused with potassium bisulphate to remove any traces of palladium.

5. It was again washed and dried and fused with potassium nitrate to remove any possible traces of iridium andruthenium.

6. After washing again it was redissolved in aqua regia, boiled down with hydrobromic acid and precipitated with sulphur dioxide.

7. The precipitated gold was then fused on a quartz plate using borax as a flux, by means of a hand torch with an oxygen flame.

8. The resulting gold ingot was rolled out into foil just thick enough to hold its shape when rolled into little spiral cylinders.

Other methods similar in procedure are given by Kruss (38), and Thorpe and Lourie (65).

The gold which had been used was recovered from the cyanide solution as follows:

9. The potassium aurocyanide was decomposed by making the solution acid with hydrochloric acid adding a few grams of potassium bromate and boiling down to crystallization.

10. The solution was then made acid with hydrobromic acid and allowed to stand as in 1 and 2. The only possible contaminating metal now is silver which is present of course from analyses of the gold solutions for cyanide by means silver nitrate.

11. The gold was dissolved in aqua regia, allowed to stand in hydrobromic acid and precipitated with sulphur dioxide some three times before fusing as in 7.

Preliminary Experiments

A 5% solution of potassium cyanide was boiled down in a flask from 300 cc. to 100 cc. with a stream of nitrogen bubbling through it. It was cooled, a weighed amount of pure precipitated gold was added, and the stream of nitrogen continued. The nitrogen was freed from oxygen by passing through two gas washing towers containing pyrogallol solution which was prepared by Benedict's method (16). At the end of one hour the gold was filtered off and weighed.

Three runs were made in this way and, for comparison, two were made using air instead of nitrogen and without boiling the solution.

The results are as follows:

Run No.	Wt. Au added	Wt. Au recovered	% dissolved of Au added	Gas used
1	0.~~0765~~ .2703 g.	0.2614 g.	3.29%	Water Vapor
2	0.3412 g.	0.3336 g.	1.02%	Nitrogen
3	0.3314 g.	0.3280 g.	2.49%	Nitrogen
4	0.2007 g.	0.1957 g.	2.22%	Air
5	0.2902 g.	0.2740 g.	5.58%	Air

While these experiments gave no conclusive result they seemed to indicate that the reaction might proceed in the absence of oxygen. To settle this point definitely a new apparatus was built and extreme precautions were taken to exclude oxygen completely from the reaction vessel in which the gold and cyanide were brought together.

PART I

Design of Apparatus

The method employed was to introduce the gold and solid potassium cyanide into the reaction bulb, then after removal of the air, to distil in a suitable amount of oxygen-free water and seal off the bulb. The gold could then be brought in contact with the cyanide solution for any desired length of time.

A diagram of the apparatus is shown in Fig. 1. It was constructed entirely of pyrex glass. A reservoir of water was permanently connected to the system. This consisted of a three-litre pyrex flask. It was filled about two-thirds full of water which had been freshly re-distilled in a current of nitrogen. The water was boiled in the flask for ten minutes and then the neck was promptly sealed off. Connected to the reservoir through Tap 1 was a "freezing bulb" which contained a stirrer consisting of a small glass rod with a coil of nichrome wire at the bottom. The latter was to prevent breakage of the stirrer when the contents of the bulb were frozen. The upper part of the stirrer was a short length of glass tubing into which was sealed an iron nail so that the stirrer could be raised by a solenoid. A mechanical "make and break" in the solenoid circuit caused the stirrer to rise and fall.

For each run a suitable amount of water was distilled into the freezing bulb. It was first evacuated as completely as possible, with Tap 1 closed, by means of a Langmuir mercury pump backed by a Hyvac oil-pump. Then Tap 2 was closed, Tap 1 opened, a Dewar flask containing acetone-carbon-dioxide placed in position so that the lower part of the bulb was immersed in the freezing mixture, and the water in the reservoir was heated. When the desired amount of water had condensed Tap 1 was closed

VACUUM
TO MCLEOD GAUGE
TO MERCURY PRESSURE VALVE
HYDROGEN
SOLENOID WITH MAGNETIC STIRRER
4
5
6
7
1
2
3
WATER RESERVOIR
FREEZING BULB
X
Y
REACTION BULB TYPE 1
REACTION BULB TYPE 2

Figure 1.

and the bulb again evacuated. With Tap 2 closed the bulb was allowed to warm up, the stirrer being set in operation as the ice melted. When all signs of ebullition had ceased, the water was frozen again and the bulb once more pumped out. Three repetitions of this procedure served to free the water thoroughly from any dissolved gases.

The reaction vessel was a cylindrical bulb of about 75 cc. capacity. A weighed amount of potassium cyanide was placed in the bottom of it and a piece of gold foil about 5 x 2 cm. was weighed, then rolled loosely into a cylinder and introduced into the small side tube or, in a later form (Type II) fixed in the neck of the bulb. The bulb was then sealed to the capillary leading to Tap 3. The S-bend served to prevent any tap grease from finding its way into the reaction bulb. Control experiments showed this to be a necessary precaution since traces of tap grease seemed to influence the reaction.

Tap 2 being closed, the bulb and connecting tubing were thoroughly evacuated with the Langmuir pump. Hydrogen could be admitted through Taps 4 and 5 and pumped out again. Three repetitions of this procedure were found sufficient to sweep the air out of the system. In earlier runs the additional precaution was taken of bringing an electric furnace into place surrounding the bulb and heating the bulb and contents to about 500° C. This temperature is below the softening point of pyrex but high enough to cause any traces of oxygen to react with the hydrogen. Excess pressure was prevented by allowing hydrogen to escape through a mercury trap.

The hydrogen was then pumped out and the air-free water distilled in from the freezing bulb through Taps 2 and 3 by immersing the lower part of the reaction bulb in the acetone-carbon-dioxide mixture.

Care was necessary to prevent ice formation choking the capillary entrance to the bulb. Only the bottom of the bulb was immersed in the freezing mixture at first and the Dewar flask was gradually raised as the ice accumulated. When about 30 cc. of water had distilled over, the bulb was sealed off at the lower end of the capillary.

The distillation of water vapor through capillary spaces proceeds slowly. To facilitate the operation the Taps 1, 2 and 3 were of large (2 mm.) bore. It is essential that the evacuation be very thorough as traces of permanent gas block the diffusion of the water vapor. For this reason the pressure was brought down to 0.04 mm. before each distillation, the pressure being observed on a McLeod gauge.

Considerable difficulty was encountered in overcoming leakage of the stopcocks. Experience showed that Pyrex stopcocks are not suitable for high vacuum work without careful re-grinding. Difficulties were also encountered in finding a suitable stopcock lubricant. A preparation supplied by the Fisher Scientific Company and named "Cello-grease" was found most effective. It retained its consistency well over a considerable temperature range, though it was found to dry out rather rapidly, necessitating frequent re-greasing. The tubing was sloped as shown in Fig. 1 so that excess tap grease would not choke the tube leading to the reaction bulb. The freezing bulb could be easily removed and cleaned when necessary.

The sealed reaction bulb was allowed to warm up to room temperature, the potassium cyanide dissolving in the water but the gold being kept out of contact with the resulting solution.

The bulb was then placed in the shaking apparatus illustrated in Fig. 2, the gold shaken out of the side arm into the cyanide solution, and the time noted.

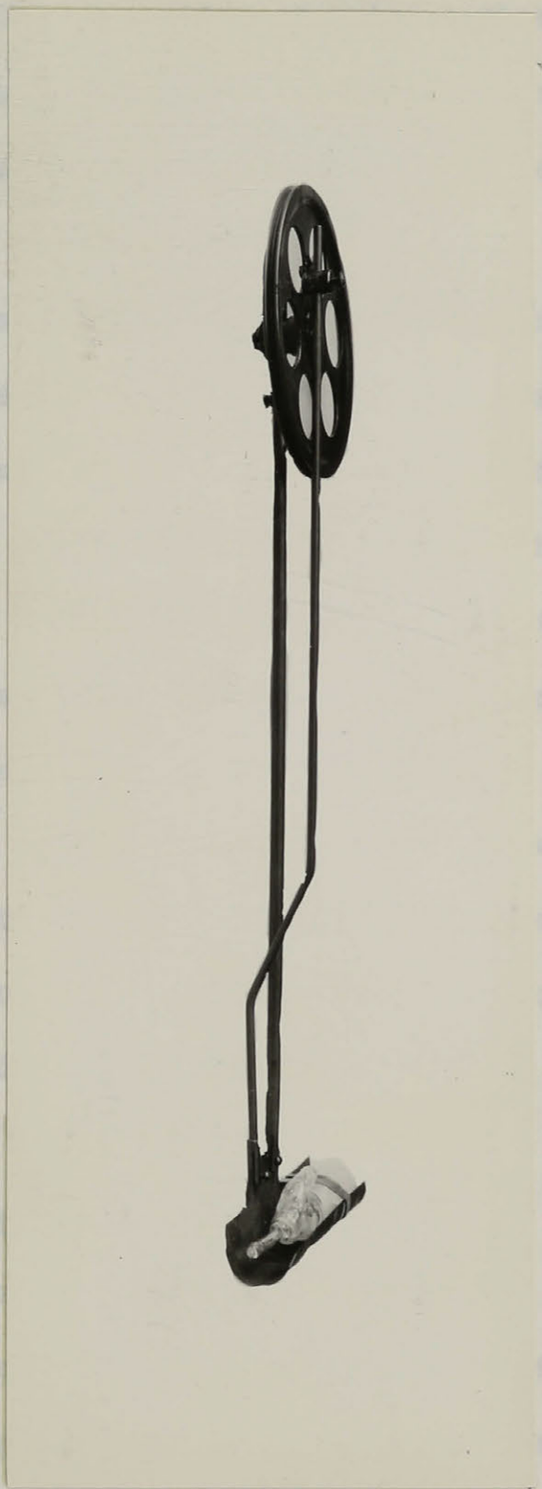


Figure 2.

The shaker operated in a constant temperature bath a plan of which is shown in Fig. 3. The precaution of using a thermostat was taken to have identical temperature conditions in case any reaction should take place. No reaction was found to occur so that this precaution proved to be unnecessary.

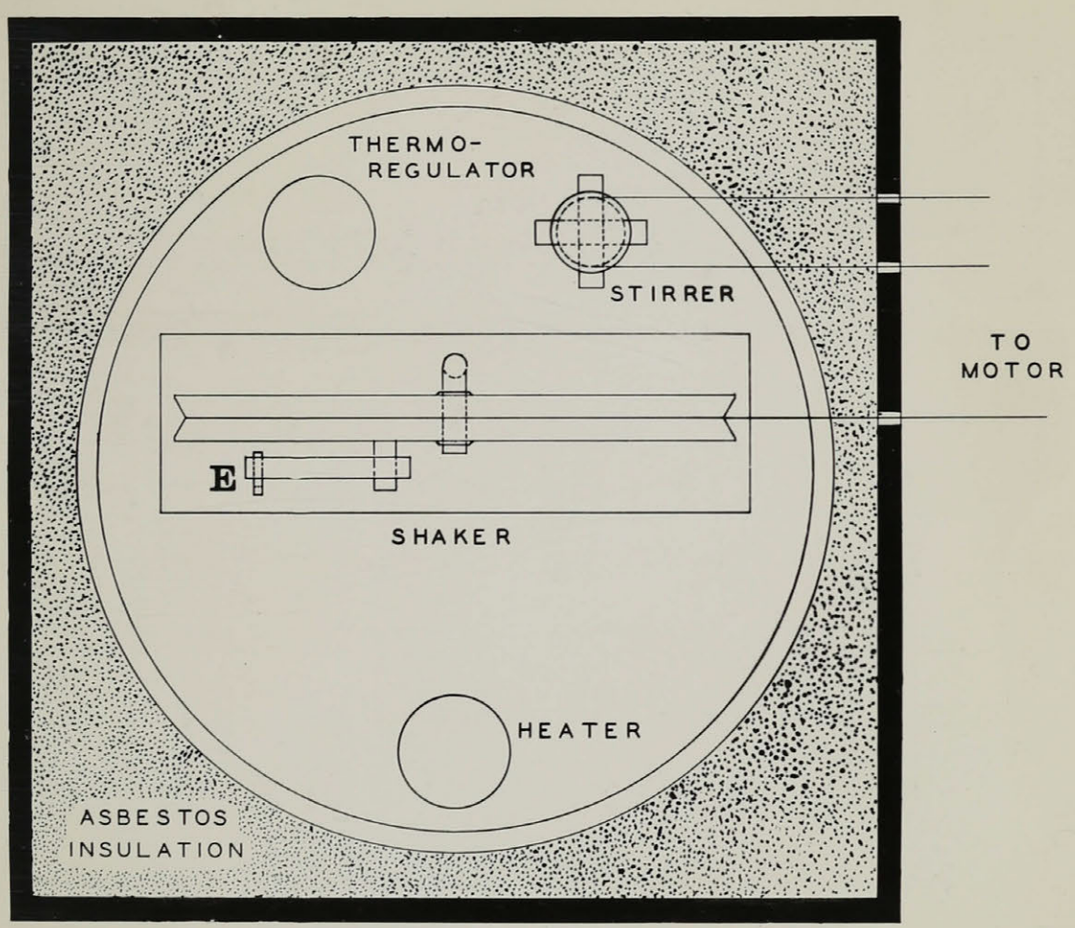
At the end of a measured period of time the bulb was removed from the bath, and the gold foil shaken into the side arm and drained of solution.

The entire tube and contents were then weighed. The bulb was opened and the gold foil and cyanide solution removed. The gold foil was washed with distilled water, alcohol and ether just as before starting the run and then weighed. The cyanide solution was titrated in aliquot parts to give the amount of cyanide remaining in solution. The empty glass tube and cap as broken off were then washed, dried and weighed. The weight of water distilled into tube was thus obtained by subtracting from the weight of the tube, and all its contents, the sum of the weights of gold foil, potassium cyanide and empty glass tube.

Description of Runs Made

Five runs were made as just described using a reaction bulb of Type I. A slight loss of gold was shown in each of these runs. It was suspected from the appearance of the gold that this might be attributable to mechanical abrasion as the cylinder of gold foil slid back and forth in the tube as it was shaken. This suspicion was confirmed by a control run (# 6) which was made with distilled water in place of the cyanide solution. The foil showed a loss in weight similar in amount to those found in the previous runs.

The results of these six runs are given in the following table.



PLAN DIAGRAM OF BATH

Figure 3.

Run No.	Loss in Wt.of foil	Area of foil	Mg. lost per cm^2	Hours Shaken	Strength KCN used
1	0.7 mg.	20 cm^2	0.035 mg.	6	--
2	1.0 mg.	21.04 cm^2	0.047 mg.	15	5.5%
3	8.1 mg.	12.44 cm^2	0.650 mg.	16	11.2%
4	3.0 mg.	9.28 cm^2	0.320 mg.	38	3.6%
5	5.1 mg.	13.26 cm^2	0.380 mg.	65	2.8%
6	6.6 mg.	19.98 cm^2	0.330 mg.	76	Dist. H_2O

It is evident from comparison with run #6 that the loss of weight of the gold in the cyanide solution might well be due to mechanical abrasion alone.

Runs #7 and #8 were made with the same type of bulb but were not shaken at all.

Run No.	Loss in Wt. of foil	Area of foil	Mg. lost per cm^2	Length of time in contact with KCN	Strength KCN used
7	0.1 mg.	17.56 cm^2	0.0057 mg.	13½ days	3%
8	1.0 mg.	17.56 cm^2	0.0570 mg.	22 days	3%

A slight reaction seems to have occurred.

According to Elsner's equation one milligram of gold is equivalent to 0.04 mg. of O_2 which in a 75 cc. bulb, as these reaction bulbs averaged, would give a pressure of about half a millimeter in the space above solution, say 50 cc. volume.

A very slight leakage of one of the taps during the distillation of the water could evidently account for reaction of the magnitude indicated by these losses in weight.

A bulb of Type II in which the gold was held firmly in position in the neck by small ridges in the glass was devised to eliminate mechanical rubbing of the foil and two runs using it were made with the utmost care

to prevent leakage during the distillation. All of the taps were thoroughly cleaned and re-greased and the period of time required for distillation kept at a minimum. Before distillation the system was evacuated beyond theregister of the McLeod gauge. A perfectly negative result ~~is obtainable~~ was obtained.

Run No.	Total Au lost	Hours Shaken	Strength KCN by wt.
9	0.0000	75½ hrs.	1.88%
10	0.0000	108 hrs. 4½ days	1.20%

As a control to show that nothing in the various procedures could prevent reaction from taking place a run was made following the same procedure exactly but air was admitted before sealing off the bulb.

Run No.	~~Gm.~~ Mg. Au lost per cm^2	Hours Shaken	Air Pressure	Strength KCN
11	17.41	62½ hrs.	650 mm.	1.64%

Julian and Smart suggested that reaction should take place in the absence of oxygen at higher temperatures. Run #8 was heated for four hours to 100° C. and subsequently remained sealed for twenty-two days. The slight loss in weight of the gold led to runs#12 and 13 being made. These were not shaken but remained, one at room temperature and the other in an oven at 105° C. for ten days.

Run No.	Mg. Au diss. per cm^2	Temperature	Hours Run	Strength KCN
8	0.057	100° C.	4 hrs. at 100° C. Not shaken	---
12	0.004	Room Temp.	10 days	3.25%
13	0.000	105° C.	10 days	3.4%

There is no evidence that heating to 100° C. produces any change in the character of the reaction.

Conclusion: It was concluded that sufficient evidence had been obtained to confirm definitely the views that the reaction between gold

and aqueous potassium cyanide solution does not proceed in the absence of oxygen or other oxidizing agent.

Liquid Ammonia Work

Some experiments were attempted also with a solution of potassium cyanide in liquid ammonia. The salt is extremely soluble in this solvent and the condition of almost complete absence of oxygen from air makes this solution of considerable interest. Three experiments were made. One by dropping a piece of gold foil into a solution of pure KCN in anhydrous ammonia, second by repeating and adding also a little free iodine, the common oxidizing agent for liquid ammonia, and third a stream of oxygen was bubbled through a solution containing a piece of gold foil.

No reaction was obtained in any case which is worthy of note. Reaction would be expected to occur in the presence of an oxidizing agent such as free iodine.

A red precipitate was observed to form when oxygen was bubbled through a cyanide solution. Time did not permit an attempt to isolate and identify this substance but the phenomenon undoubtedly merits further investigation.

The actual experimental data from which all of these figures are drawn are given in the following tables.

Tabulated Results

Run #1 Type #1 Bulb Fused

Wt. Au foil used	-	1.5581 g.
Area of foil	-	20.0 cm^2. roughly.
Wt. lost in gs.	-	0.0007 gs.
Wt. Au lost per cm^2.	-	.035 mg.
Wt. KCN in bulb	-	0.994 g.
Wt. bulb - contents	-	splintered on opening.
Wt. empty bulb	-	----
Wt. water in bulb	-	----
Strength KCN solution	-	----
Time fused	-	1 hour at dull red heat.
Time shaken	-	6 hours.

Run #2 Type #1 Bulb Fused

Wt. Au foil used	-	1.7614 g.
Area of foil	-	21.04 cm^2.
Wt. lost in gs.	-	0.0010 g.
Wt. lost per cm^2.	-	0.047 mg.
Wt. KCN in bulb	-	1.575 g.
Wt. bulb - contents	-	106.6 g.
Wt. empty bulb	-	75.8 g.
Wt. contents	-	30.8 g.
Vol. liquid in bulb	-	28.5 cc.
Strength KCN sol.	-	5.5% by wt.
Time fused	-	1 hour at dull red heat.
Time shaken	-	15 hours.

Run #3 Type #1 Bulb Fused

Wt. Au foil used	-	0.7781 g.
Area of foil	-	12.44 cm^2.
Wt. lost in gs.	-	0.0081 gs.
Wt. lost per cm^2.	-	0.65 mg.
Wt. KCN in bulb	-	1.520 g.
Wt. bulb - contents	-	105.43 g.
Wt. empty bulb	-	89.60 g.
Wt. contents	-	15.83 g.
Vol. liquid in bulb	-	13.55 cc.
Strength KCN sol.	-	11.2% KCN
Time fused	-	One hour at dull red heat.
Time shaken	-	Sixteen hours.

Run #4 Type #1 Bulb Fused

Wt. Au foil used	-	0.4020 g.
Area of foil	-	9.28 cm^2.
Wt. lost in grams	-	0.0030 g.
Wt. lost per cm^2.	-	0.32 mg.
Wt. KCN in bulb	-	1.398 g.
Wt. bulb - contents	-	110.5 g.
Wt. empty bulb	-	70.2 g.
Wt. contents	-	40.3 g.
Vol. liquid in bulb	-	38.6 cc.
Strength KCN sol.	-	3.6% KCN
Time fused	-	1 hour at dull red heat.
Time shaken	-	38 hours.

Run #5 Type #1 Bulb Fused

Wt. Au foil used	-	0.8844 g.
Area of foil	-	13.26 cm^2.
Wt. lost in grams	-	0.0051 g.
Wt. lost per cm^2.	-	0.38 mg.
Wt. KCN in bulb	-	1.206 g.
Wt. bulb - contents	-	122.0 g.
Wt. empty bulb	-	78.2 g.
Wt. contents	-	44.8 g.
Vol. liquid in bulb	-	42.8 cc.
Strength KCN sol.	-	2.8% KCN
Time fused	-	1 hour at bright red heat.
Time shaken	-	65 hours.

Run #6 Type #1 Bulb Control run with distilled water.

Wt. Au foil used	-	0.9534 g.
Area of foil	-	19.98 cm^2.
Wt. lost in gs.	-	0.0066 g.
Wt. lost per cm^2.	-	0.33 mg.
Vol. dist. H_2O	-	Bulb 1/3 full.
Time shaken	-	76 hours.

Run #7 Type #1 Bulb Fused

Wt. Au foil used	-	1.2097 g.
Area of foil	-	17.56 cm^2.
Wt. lost in grams	-	0.0001 g.
Wt. lost per cm^2.	-	0.0057 mg.
Time of fusion	-	1 hour at dull red heat.
Time shaken	-	Remained quiescent at room temperatures throughout for 13½ days.

Run #8 Type #1 Bulb Not Fused

Wt. Au foil used	-	1.2111 g.
Area of foil	-	17.56 cm^2.
Wt. lost in grams	-	0.0010 g.
Wt. lost per cm^2.	-	0.057 mg.
No fusion attempted.		
Time shaken	-	Bulb quiescent for most of 22 days. Heated to 100° C. for 4 hours. Remainder of time at room temperature.

Run #9 Type #2 Bulb Not Fused

Wt. Au foil used	-	1.4533 g.
Wt. lost in grams	-	0.0000 g.
Wt. KCN in bulb	-	0.3847 g.
Wt. bulb - contents	-	65.29 g.
Wt. empty bulb	-	43.39 g.
Wt. contents	-	21.90 g.
Vol. liquid in bulb	-	20.06 cc.
Strength KCN sol.	-	1.88% by wt.
No fusion attempted.		
Time shaken	-	75½ hours.

Run #10 Type #2 Bulb Not Fused

Wt. Au foil used	-	1.5908 g.
Wt. lost in grams	-	0.0000 g.
Wt. KCN in bulb	-	0.4059 g.
Wt. bulb - contents	-	88.76 g.
Wt. empty bulb	-	53.02 g.
Wt. contents	-	35.74 g.
Wt. liquid in bulb	-	33.74
Strength KCN sol.	-	1.20% by wt.
No fusion attempted.		
Time shaken	-	4-1/4 days.

Run #11 Type #1 Bulb Fused

Wt. Au foil used	-	0.8916 g.
Area of foil	-	13.60 cm^2.
Wt. lost in grams	-	0.2368 g.
Wt. lost per cm^2.	-	0.017.41 g. - 17.41 mg.
Wt. KCN in bulb	-	0.947 g.
Wt. bulb - contents	-	136.9 g.
Wt. empty bulb	-	78.2 g.
Wt. contents	-	58.7 g.
Wt. liquid in bulb	-	56.8
Strength KCN sol.	-	1.64% KCN by wt.
Time fused	-	1-1/4 hrs. bright red heat
Time shaken	-	62½ hours.

Run #12 Type #1 Bulb Not Fused
Not Shaken Kept at Room T.

Wt. Au foil used	-	0.6736 g.
Area of foil	-	20.40 cm^2.
Wt. lost in grams	-	0.0001 g.
Wt. lost per cm^2.	-	0.004 mg.
Wt. KCN in bulb	-	1.570 g.
Wt. bulb - contents	-	119.8 g.
Wt. bulb empty	-	70.8 g.
Wt. contents	-	49.0 g.
Wt. liquid in bulb	-	46.7 g.
Strength KCN	-	3.25%
Time run	-	10 days standing at room temp.

Run #13 Type #1 Bulb, Not Fused No Shaking
Kept at 105° C.

Wt. Au foil used	-	0.6502 g.
Area of foil	-	13.26 cm^2.
Wt. lost in grams	-	0.0000 g.
Wt. lost per cm^2.	-	0.0000 g.
Wt. KCN in bulb	-	1.353 g.
Wt. bulb - contents	-	105.2 g.
Wt. bulb empty	-	64.5 g.
Wt. contents	-	40.7 g.
Wt. liquid in bulb	-	38.6
Strength KCN	-	3.4%
Time ran	-	10 days standing at 105° C.

Experiments in Liquid Ammonia.

Run #1 Simple solution.

Reagents - 1 g. KCN dissolved in 200 cc. anhydrous liquid ammonia, contained in Dewar flask.

Wt. Au foil - 0.5036 g.

Wt. lost in grams 0.0004 g.

Remarks: Brownish white precipitate settled out of solution but also settled out of a similar solution containing no gold foil.

Run #2 Effect of I_2 on action.

Reagents - 1 g. KCN dissolved in 200 cc. anhydrous liquid ammonia contained in Dewar flask. 1 gm. iodine added

Wt. Au foil - 0.5032 g.

Wt. lost in grams - 0.0000 g.

Remarks: No change at all.

Run #3

Reagents - 1 g. KCN in 200 cc. liquid ammonia. Stream of oxygen bubbled through for one hour.

No loss in weight. Considerable quantity of red precipitate obtained.

PART II

Preliminary Work

Using the same apparatus as in the previous part, a number of runs were made with bulbs containing added oxygen. These were found to be entirely unsatisfactory. They were prepared as before with the exception that just before sealing off oxygen was admitted to some desired pressure. A mercury manometer was connected to the apparatus to measure this.

The bulbs were shaken for about three days in the bath which was thermostated at 25°C. They were then opened, the foil weighed, and the cyanide solution titrated.

Seven runs were made in this manner giving results as tabulated below.

Run No.	Hours Shaken	Moles Au dissolved	Moles O_2 present	Moles KCN reacted	Ratio Au/O_2	Ratio KCN/Au
1	70 hrs.	0.0046	0.0020	0.00082	2.04	1.8
2	70 hrs.	0.0012	0.00057	0.00381	2.11	2.1
3	70 hrs.	0.0011	0.00060	0.00291	1.84	2.6
4	70 hrs.	0.00051	0.00019	0.00229	2.68	1.5
5	70 hrs.	0.0047	0.0019	0.00805	2.47	1.7
6	70 hrs.	0.00033	0.00015	--	2.08	---
7	140 hrs.	0.00040	0.00016	—	2.65	---

The last two runs, numbers 6 and 7, were opened under water to see if any gas remained in the bulb. Such was found to be the case and subsequent attempts were made to collect this and analyze if for oxygen by means of a micro-burette. No success was attained. In the runs above only half of the oxygen present appeared to have reacted. In #7 the time of reaction was doubled and the ratio of gold dissolved to oxygen present

was increased somewhat. According to Elsner's equation this ratio should be 4 and that of cyanide to gold 2, as,

$$4\ Au + 8\ KCN + O_2 + 2\ H_2O \longrightarrow 4\ K\ Au\ (CN)_2 + 4\ KOH$$

In order to determine the exact stoichiometric relationships in this reaction an apparatus had to be devised which could measure the quantity of oxygen present in a reaction bulb initially and finally. The amount of oxygen reacting per unit of gold is so small that the problem presented was rather difficult of solution. Such an apparatus was devised and is described.

Design of Apparatus.

The apparatus was designed so that gold could be brought into control with a potassium cyanide solution of any desired strength under an atmosphere of oxygen. The reaction chamber was connected to a differential manometer so that the changes in pressure which occur due to reaction could be followed.

The apparatus is shown in diagram in Fig. 4. The entire construction was of Pyrex glass. The reaction bulb consisted of a cylindrical glass bulb fitted with a capillary tube at the bottom which could be opened or sealed at the point A. At the top of the bulb was sealed a glass tube fitted with a ground glass cap. At the junction of this tube and the reaction chamber a side tube was sealed which was constructed so as to connect with the remainder of the system at C and with the capillary tubing from the base of the reaction chamber at B. Taps 1 and 2 were placed in this tube so that the remainder of the system could be closed off if desired.

Within the reaction chamber was a stirrer made of glass rod sealed on to a glass tube sealed in turn around an iron nail. This could be

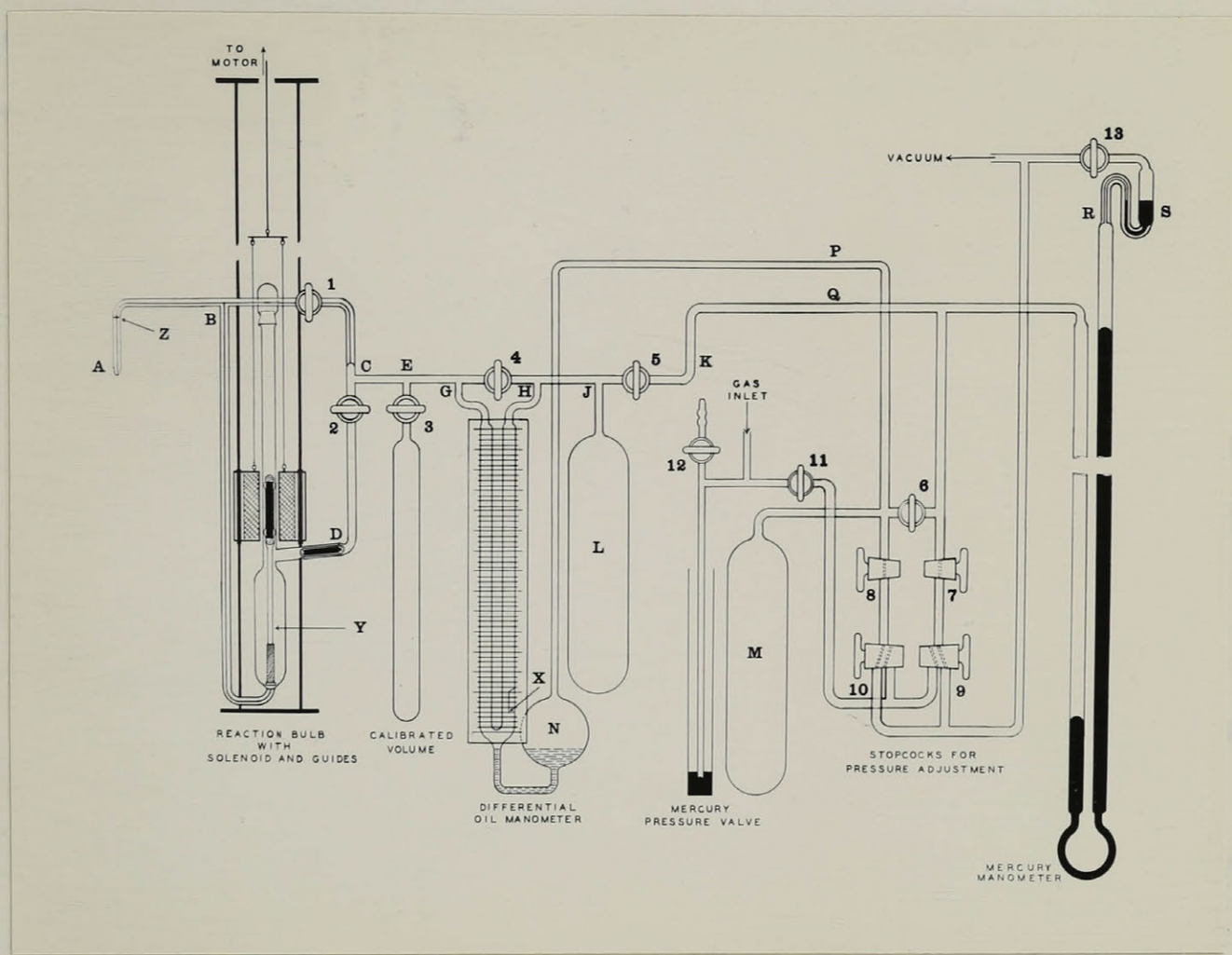

TO MOTOR
VACUUM
13
R
S
P
Q
1
Z
B
A
C
E
4
5
K
G
H
J
GAS INLET
2
3
12
11
6
D
L
M
8
7
Y
X
N
10
9
REACTION BULB WITH SOLENOID AND GUIDES
CALIBRATED VOLUME
DIFFERENTIAL OIL MANOMETER
MERCURY PRESSURE VALVE
STOPCOCKS FOR PRESSURE ADJUSTMENT
MERCURY MANOMETER

Figure 4.

raised up and down by means of a solenoid guided by two brass rods which passed through its frame. By means of this stirrer gold foil placed upon the lower end could be alternately dipped into and removed from a cyanide solution contained in the lower portion of the bulb. The raising of the solenoid was accomplished by gearing it on to the motor used in stirring the bath.

Connected at C was a line running to the differential manometer and to a mercury manometer. The differential manometer was filled with Cenco "Hyvac" oil and was provided with a leveling bulb N operated by means of the double Tap 10 and single Tap 8. On the right hand side a glass pointer X was sealed in so that the manometer on this side could be brought to the same level on successive occasions. The levels of the oil on both sides of the manometer were read from a mirror scale on which it was mounted. Tap 4 was sealed between the two halves so that when desired the pressure on each side could be equalized merely by opening it.

At the point E a calibrated volume of about 200 cc. was sealed into the system. This was used in calibrating the actual volume of the reaction chamber and connecting tubing up to Tap 4 and various levels of the oil in the left hand side of the manometer. Tap 3 was provided so that it could be shut on or off at will.

Tap 5 was provided so that the pressure above the right half of the manometer could be kept constant. If this were not done the difference in level between the halves would not represent a change in pressure within the reaction chamber.

L was a large bulb of about one liter capacity, provided so that when the level was adjusted on the right side there would be sufficient

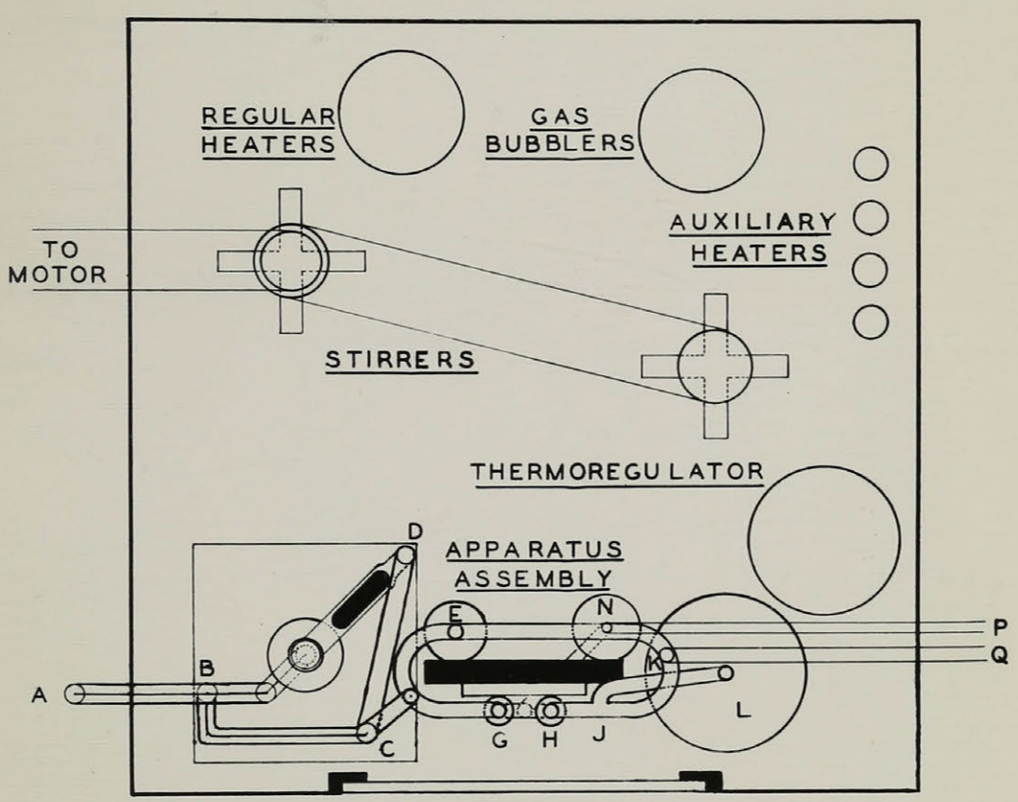
volume above the oil to prevent an error of measurable magnitude on the left side due to slight errors in adjustment at the level of the pointer X.

A mercury manometer was connected to the system through tubing as shown at points K and Q. It was used in getting an absolute reading of the initial pressure in the reaction chamber. The construction of this manometer was unique in that the evacuated side was not sealed off. Constructed as shown, the right hand side was evacuated, pressure applied on the left so that the mercury was forced up into the U-tube. Then Tap 13 was closed and the pressure released. The mercury thread in the capillary of the right broke leaving a mercury sealed vacuum.

The pressure within the apparatus was varied at will by the system of taps for pressure adjustment. Oxygen was admitted at the gas inlet, a constant flow being permitted by the mercury pressure valve. A vacuum from a Cenco "Hyvac" pump was maintained in the line marked "vacuum". Taps 10 and 9 were two-way taps allowing either pressure or vacuum to be exerted on either of the system or the manometer leveling bulb. Taps 8 and 7 were connected as guards against mishap in using 10 and 9.

M was a large compensating volume connected to the leveling bulb line in order to counter-act the pressure effect of L on the other side of the differential manometer. Tap 6 was connected between the system and oil leveling bulb so that both could be evacuated simultaneously.

The entire apparatus was thermostated in a water bath at 25° C. with the exception of the mercury manometer and the pressure adjustment stop-cocks. Points K, P, and Q, represent roughly the points at which the connections leave the bath. Fig. 5 is a plan diagram of the bath assembly.



TOP VIEW DIAGRAM OF ASSEMBLED BATH

Figure 5.

The letters represent the same points as in Fig. 4. The bath consisted of a sheet iron tank about 15 in. square and 26 in. in depth. On one side a plate glass window about 10 in. wide was inserted which ran the whole depth. The apparatus was so assembled that the mirror scale of the differential manometer could be read through this window. In order to bring the large volume of water to approximately 25° C. a series of four coils of nichrome wire were used as auxiliary heaters with about 20 amps. passing through them. These were manipulated by a hand switch. To maintain the temperature at 25° C. a 100 watt lamp bulb was used in series with a double-relay circuit governed by an ether-mercury contact thermoregulator. A wiring diagram of this circuit is given in Fig. 6, which is self explanatory. The bath was stirred by means of two shafts with five paddles each, distributed throughout the full depth.

The actual assembly of this apparatus differed somewhat from the linear impression one might gather from Fig. 4. The mirror scale and differential manometer were fastened to the flat side of a board. On the left of this was fastened the frame and guides for the solenoid within which rested the reaction chamber. Fig. 7 is a front view of this assembly, photographed as used. To the right can be seen the large volume L. The calibrated volume and point E in the line together with the leveling bulb N were fastened to the reverse side of the same board. Fig. 8 is a photographic view of this rear assembly. The bulb L and the solenoid guides can be seen here as well. Fig. 4 contains a diagram of this circular form of assembly.

Fig. 9 is a photograph showing the connections between the apparatus set up for use in the bath, with the stopcock assembly and mercury manometer.

In Fig. 10 the bath is shown in place and the apparatus connected ready for us.

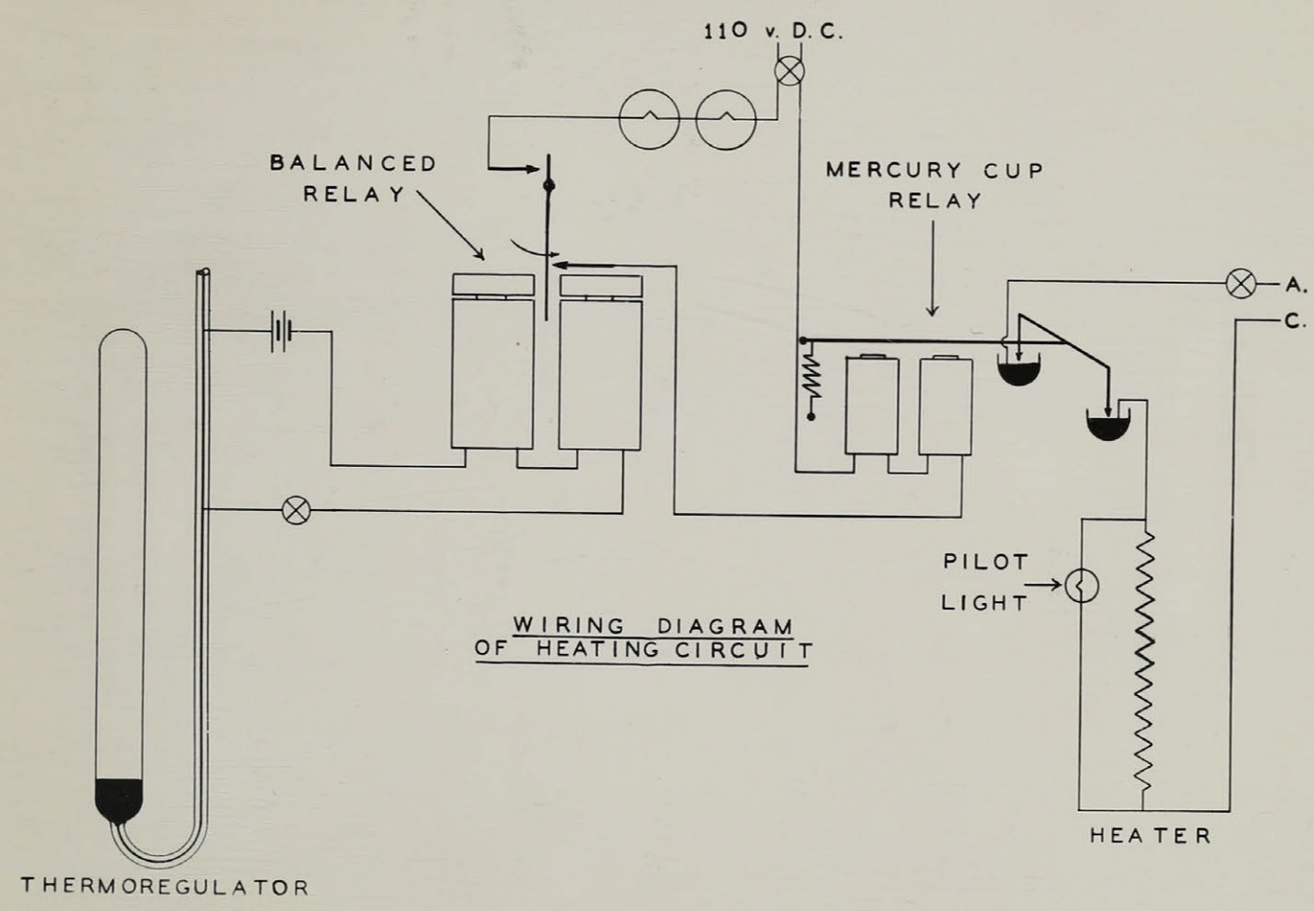

110 v. D.C.
BALANCED RELAY
MERCURY CUP RELAY
A.
C.
PILOT LIGHT
WIRING DIAGRAM OF HEATING CIRCUIT
HEATER
THERMOREGULATOR

Figure 6.

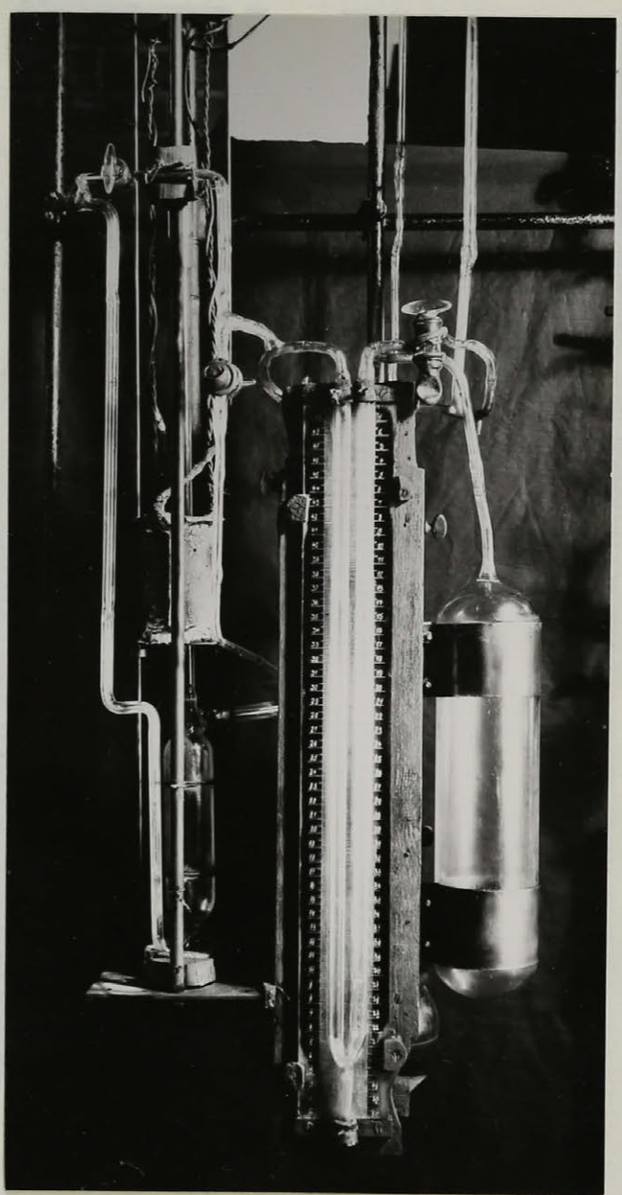


Figure 7.

Figure 8.

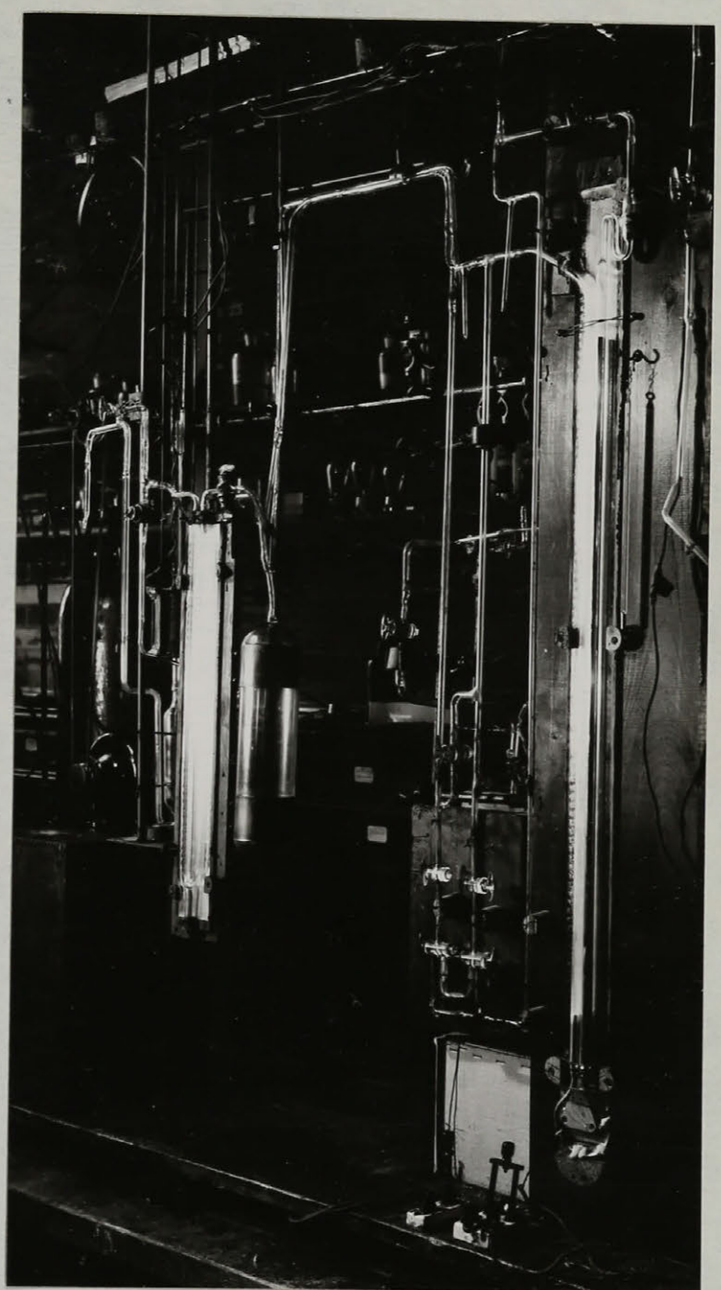


Figure 9.

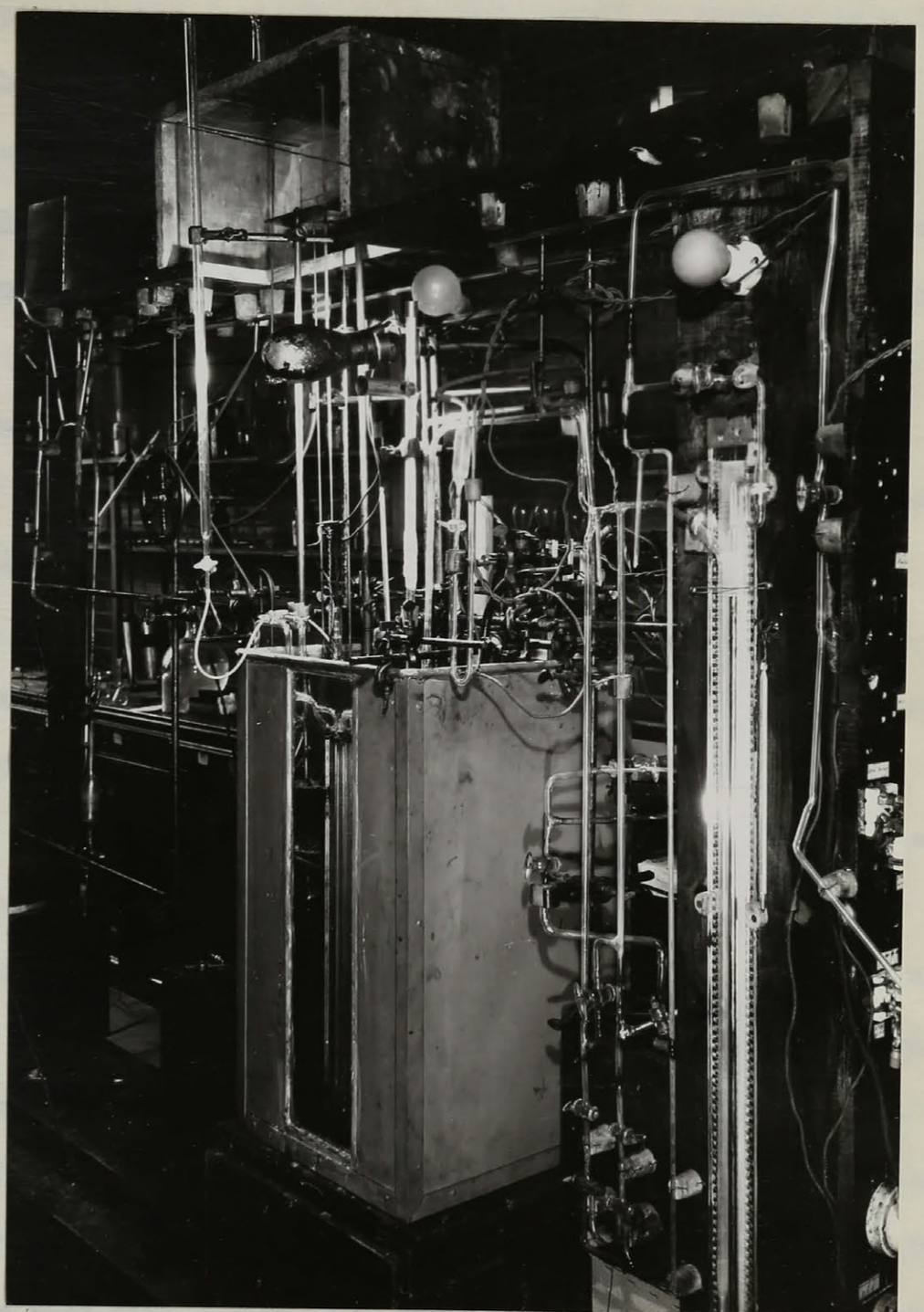


Figure 10.

Calibration of the Apparatus

The apparatus was designed to measure pressure changes in a known volume so that by means of the fundamental gas law, the amount of oxygen which reacted could be calculated.

The initial pressure was measured directly by means of the mercury manometer, using it against an 800 mm. mirror scale, giving an accuracy of 0.4 mm. Changes in pressure were measured by means of the oil differential manometer using a mirror scale of the same accuracy.

At the beginning of a run the oil level on both sides was brought to the level X. Then as reaction proceeded the level on the left was raised. In so doing a change in volume took place so that at the end of the reaction the system was not only at a different pressure but occupied a different volume.

Before making any runs the apparatus was calibrated, by means of an expansion from the calibrated volume, for any oil level in the left hand side of the manometer. This procedure was as follows: The capillary tubing was sealed off at A. The stirrer was placed in the reaction bulb and the ground glass cap greased and fitted into place. All of the Taps 1, 2, 3, 4, 5, 6, were opened wide and the system evacuated and flushed with oxygen dried by passing over phosphorus pentoxide. The pressure was read upon the mercury manometer when filled completely with dried oxygen at approximately atmospheric pressure. Tap 3 was then closed and the system evacuated completely. By means of Taps 10 and 8 the oil level in the manometer was raised as high as was possible. Tap 4 was closed. Tap 3 was opened so that the gas within the calibrated volume expanded very slowly. As expansion proceeded the left hand side of the oil manometer was forced down. By means of Taps 10 and 9 pressure

was then admitted to both the right side and the leveling bulb so that a constant level in both sides was maintained. When expansion through Tap 3 was complete then the levels in the manometer were matched exactly and the pressure on the right hand side read from the mercury manometer. This was equal to the pressure on the left hand side. By means of the ~~leveling~~ reservoir bulb the oil level was run down the mirror scale so that an equivalent pressure could be read for various levels.

The volume of the system at each of these levels was calculated as follows:

$$P_1 V_1 = P_2 (V_1 + V_2)$$

where P_1 - Pressure in calibrated volume.

P_2 - Pressure in system after expansion.

V_1 - Volume of calibrated volume.

V_2 - Volume of system less that of the calibrated volume.

V_1 was calibrated by weighing when empty, and when filled with distilled water. It was found to contain 194.67 cc. at 25° C.

The values for P_1 and P_2 were corrected for temperature variation from tabular data taken from the Eleventh Edition of the "Chemical Rubber Company 'Handbook'."

Four calibrations of the apparatus were made and data obtained giving the volume at various levels. The volume obtained was plotted against the reading on the mirror scale of the oil manometer. A photograph of such a curve is given in Fig. 11. After completion of a run the volume was read directly from such a curve.

The calibration extends to the line marked Z on the capillary tubing. The length below this line is measured and its volume obtained by

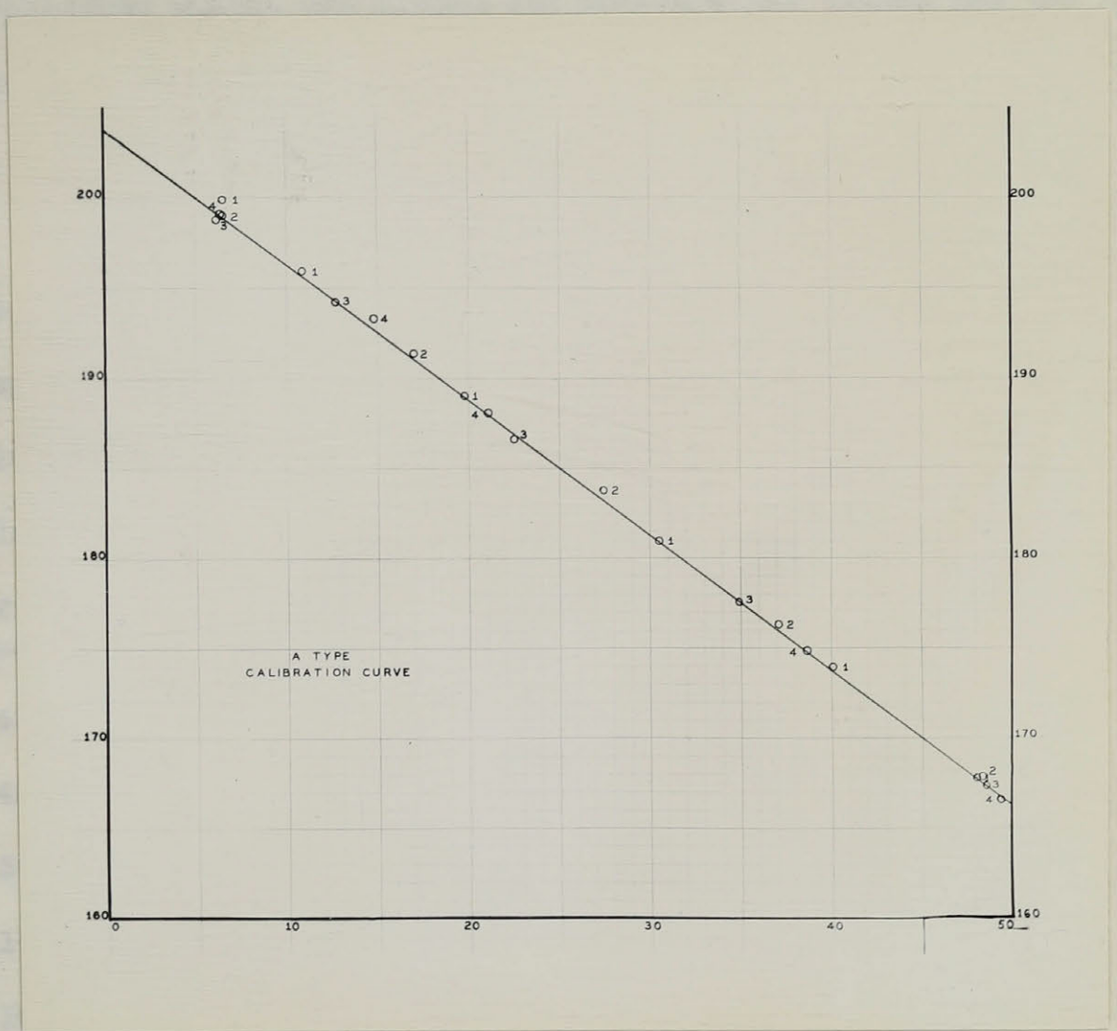


Figure 11.

multiplying the volume in cc. per mm. by the length. The volume per mm. was obtained by calibration with mercury and is 0.000464 cc.

Data from which this curve was constructed is given in the following. In the following tables the values for Pressure and Volume are the corrected ones.

Calibration Run #1.

Pressure in Calibrated Volume - 76.07

Temperature - 25° C.

Volume of Calibrated Volume - 194.67

Volume of capillary below Z - 0.49 cc.

Diff. Man. Reading	Pressure in System	$V_1 + V_2$	V_2
48.07	40.80	362.95	167.79
40.10	40.12	369.11	173.95
30.52	39.37	376.14	180.98
19.78	38.54	384.24	189.08
10.87	37.86	391.14	195.98
6.52	37.58	394.05	199.89

Calibration Run #2.

Pressure in Calibrated Volume - 75.28

Temperature - 25° C.

Volume of Calibrated Volume - 194.67 cc.

Volume of capillary below Z - 0.49 cc.

Diff. Man. Reading	Pressure in System	$V_1 + V_2$	V_2
48.39	40.37	363.01	167.85
37.01	39.45	371.48	176.32
27.29	38.67	378.98	183.82
17.00	37.92	386.58	191.42
6.58	37.18	344.16	199.00

Calibration Run #3.

Pressure in Calibrated Volume - 75.63

Temperature - 25° C.

Volume of Calibrated Volume - 194.67 cc.

Volume of capillary below Z - 0.49 cc.

Diff. Man. Reading	Pressure in System	$V_1 + V_2$	V_2
48.56	40.65	362.19	167.03
34.88	39.52	372.71	177.55
22.46	38.57	381.72	186.56
12.71	37.81	389.39	194.23
6.09	37.38	393.96	198.80

Calibration Run #4.

Pressure in Calibrated Volume - 75.58

Temperature - 25° C.

Volume of Calibrated Volume - 194.67 cc.

Volume of capillary below Z. - 0.49 cc.

Diff. Man Reading	Pressure in System	$V_1 + V_2$	V_2
49.42	40.68	361.69	166.53
38.67	39.76	370.05	174.89
27.98	38.88	378.43	183.27
21.04	38.39	383.26	188.10
14.81	37.86	388.63	193.47
6.41	37.31	394.35	199.19

Use of the Apparatus.

A number of special manipulations were developed in the use of the apparatus, which are best described in sequence as they occur in the course of preparing a run. It is for this reason that the following description of a typical run is given.

The reaction bulb was opened by removing the ground-glass cap and cutting the tip off of the capillary tubing at A. The stirrer was removed, Taps 1 and 2 were closed, all others opened, and the system evacuated up to 1 and 2. 50 cc. of potassium cyanide solution of known composition was introduced into the reaction bulb from a calibrated burette by means of a rubber catheter tube attached to the tip of the burette and thrust down into the reaction chamber. After delivery of the solution was complete the rubber tubing was drawn out care being taken to prevent wetting of the upper walls.

The trigger D consisting of an iron core enclosed in glass tubing was moved so as to obstruct the base of the tubing above the reaction chamber. A weighed piece of gold or silver foil was then placed on the end of the stirrer which was in turn lowered by means of the solenoid so that it rested securely on the obstruction presented by D at the base of the upper tube.

Oxygen was then passed into the chamber through the capillary tube, and bubbling up through the solution. This was done to displace air from the reaction vessel. In order to prevent the loss of any cyanide by volatilization of any hydrolyzed material, this stream of gas was passed previously through two gas washing bottles connected in series and containing about 100 cc. of the same cyanide solution. These were contained in the thermostat as shown in Fig. 5.

The ground glass cap was then put in place and Tap 2 opened slowly so that a flow of gas passed through the side tubing into the evacuated system. When the side tube was flushed free of air Tap 2 was closed and the system beyond evacuated again.

After a high vacuum, 0.2 mm., had been reached Tap 2 was opened as before and oxygen let into the system till atmospheric pressure was obtained. Tap 1 was opened to equalize the pressure between the capillary tubing and remainder of the system. The rubber connection to the gas bubblers was removed and the capillary sealed at A.

Oil was forced up in the differential manometer until both sides were level at X. The pressure was then read on the mercury manometer, a value for the temperature of the bath was taken on a Beckmannthermometer, and the exact level of the oil on either side was read.

Tap 3 was closed to cut off the volume of the calibrated bulb, and Taps 4 and 5 were closed to put the differential manometer into operation. The oil was forced further up into the arms of the oil manometer to prevent the right hand side from getting too low during reaction.

Then the stirrer was raised off the trigger which was pulled out of the obstructive position. The adjustments of the stirring were made so that the foil on the end of the rod dipped in and out of solution continuously. The course of reaction could then be followed by bringing the right hand oil level to the value of the pointer X and noting the rise of that on the left hand side.

When reaction had proceeded as long as was deemed necessary the stirrer was raised out of solution and again held in position in the upper tube by means of the trigger D. The system was then allowed to come to equilibrium so that all the solution wetting the gold had reacted.

Then a final reading for the oil manometer was read giving the change in pressure. The capillary was broken at A, the stirrer removed so that the foil could be weighed, and the cyanide solution forced into a container from which it could be analyzed.

Discussion of Results

The first investigation made with this apparatus was a study of the simple stoichiometrical proportions of the three reactants.

The amount of gold reacting was observed by weighing the foil before and after. The cyanide was titrated in 10 cc. portions at the commencement and end of each run. The amount of oxygen observed in each run was calculated as follows. The initial amount of oxygen in the system could be calculated from

$$P_1 V_1 = n_1 R T$$

The amount present at the end of the run was,

$$P_2 V_2 = n_2 R T$$

so the amount absorbed is

$$n_1 - n_2 = \frac{P_1 V_1 - P_2 V_2}{R T}$$

P_1 - initial pressure in atmosphere read on the mercury manometer.

V_1 - volume of system at level X, less 50 cc. the volume of added KCN solution.

P_2 - P_1 less the change of pressure indicated by the rise of the oil level in the differential manometer.

V_2 - volume of system at the final level of the oil.

R - gas constant in cc. atmosphere.

T - temperature of bath.

In order to use the oil manometer the specific gravity of the "Cenco Hyvac" oil had to be measured. It was found to be 0.89316 by making three weighings in a specific gravity bottle. To convert oil pressures to centimeters of mercury the ratio $\frac{\text{Density oil}}{\text{Density Hg}}$ for 25° C. was used to

multiply the oil reading. This was found to be equal to $\frac{b}{15.222}$.

Twelve runs were made in identical manner. In some of them the concentration of the cyanide solution was varied to see if any effect upon the stoichiometrical proportions could be observed. No marked effect was noticeable. Results in tabulated form are as follows.

Run No.	Av. % Strength KCN	Moles Au Dissolved x 10^{-4}	Moles O_2 Reacted $\times 10^{-4}$	Moles KCN Reacted $\times 10^{-4}$	Ratios $\frac{Au}{O_2}$	$\frac{KCN}{\frac{O_2}{Au}}$	$\frac{KCN}{O_2}$
1	0.44	28.14	9.25	58.66	3.04	2.08	6.34
2	0.49	21.52	7.12	43.26	3.02	2.01	6.08
3	0.53	21.65	7.05	44.68	3.07	2.06	6.34
4	0.56	19.84	6.24	39.94	3.18	2.01	6.40
5	0.76	14.05	4.35	29.42	3.23	2.09	6.76
6	0.98	11.35	3.49	22.97	3.25	2.02	6.58
7	1.20	13.38	4.28	27.00	3.13	2.02	6.31
8	1.47	18.31	5.26	36.46	3.31	1.99	6.93
9	1.95	19.57	5.79	40.84	3.39	2.09	6.52
10	2.48	21.19	6.68	43.54	3.16	2.05	6.52
11	4.92	15.62	5.12	27.62	3.05	1.77	5.39
12	8.81	16.89	5.23	41.90	3.22	2.48	8.01
			Average		3.16	2.06	6.51

Three blank runs were made with the apparatus using different concentrations of cyanide. No pressure change was observed over a twenty-four hour period in any case.

The ratio for gold to oxygen here is in the neighborhood of three with little tendency to alter with increasing concentration of cyanide.

Comparing with the ratios involved in Elsner's equation where

$$\frac{Au}{O_2} = 4 \qquad \frac{KCN}{Au} = 2 \qquad \frac{KCN}{O_2} = 8$$

from $4\ Au + 8\ KCN + O_2 + 2\ H_2O \longrightarrow 4\ KAu\ (CN)2 + 4\ KOH$

it is apparent that some conflicting reaction is occurring which is removing oxygen in addition to reaction with gold. The average cyanide oxygen ratio obtained here bears out this point also.

The value for the cyanide gold ratio seems to be established in agreement with Elsner's equation. The slightly high value may be ascribed to error in titration.

Two theories can be offered in explanation for the low value of gold to oxygen. First, gold may be dissolving with the formation of potassium auricyanide, $KAu\ (CN)_4$, as well as potassium aurocyanide, $KAu\ (CN)_2$, as

(1) $4\ Au + 16\ KCN + 3O_2 + 6H_2O \longrightarrow 4\ KAu\ (CN)_4 + 12\ KOH$

(2) and $4\ Au + 8\ KCN + O_2 + 2H_2O \longrightarrow 4\ KAu\ (CN)_2 + 4\ KOH.$

The fact that the cyanide gold ratio found in this work is more in accordance with equation #2 than equation #1 could be explained as due to lack of technique in analyzing for auricyanide which might decompose into aurocyanide upon titration with silver nitrate. If the reaction chamber contained products of both of these reactions some such set of values as were obtained are possible. Second, the theory of Bodlander in which he postulates formation of hydrogen peroxide as an intermediate would also explain the results obtained, as

(3) $2\ Au + 4\ KCN + O_2 + 2\ H_2O \longrightarrow 2\ KAu\ (CN)_2 + H_2O_2 + 2\ KOH$ followed by

(4) $2\ Au + 4\ KCN + H_2O_2 \longrightarrow 2\ KAu\ (CN)_2 + 2\ KOH$

Summation of the two gives Elsner's equation. If all of the hydrogen peroxide did not react when formed results, such as were obtained, could be explained.

To distinguish between the two theories, two runs were made using silver foil. This foil was rolled from commercial c.p. grade silver without attempt at further purification. Results obtained were in complete agreement with those obtained in the gold runs.

Run No.	Av. Strength KCN	Moles Ag	Moles O_2	Moles KCN	Ratios $\frac{Ag}{O_2}$	$\frac{KCN}{Ag}$	$\frac{KCN}{O_2}$
13	1.08%	22.32	7.32	46.57	3.5	2.08	6.36
14	1.13%	23.12	7.42	58.52	3.11	2.53	7.88

There is no possibility in the case of silver of there being formed a compound of more than one valence of metal. The indication is therefor that Bodlander's theory is the correct explanation.

To check for the formation of hydrogen peroxide a number of runs were made in the presence of an excess of Calcium and Barium oxides. Figures for the stoichiometrical proportions of these runs were irregular but results from them definitely established the formation of peroxide during reaction.

A white precipitate formed on the surface of the foil, which gave a positive test for peroxide with starch iodide. It was evidently calcium or barium peroxide as no test for silver was obtainable. The cyanide solution containing excess of calcium or barium hydroxides as a precipitate also gave a positive test for peroxide with starch iodide which it did not before reaction.

As a result of these qualitative tests some runs were made as before, but in the presence of a quantity of precipitated manganese dioxide, MnO_2. These were made in the hope that the peroxide formed would be decomposed immediately due to the catalytic effect of the manganese dioxide. If so a value of 4 for the gold-oxygen ratio should be found.

Four runs with silver and three with gold were made and such a result was obtained. The data of the following table shows the values obtained.

Run No.	Metal Used	Moles Metal	Moles O_2	Ratio $\frac{\text{Metal}}{O_2}$
15	Ag	29.58	7.39	4.002
16	Ag	18.24	4.64	3.92
17	Ag	21.39	5.28	4.04
18	Ag	23.19	5.80	4.04
19	Au	16.91	4.23	3.97
20	Au	20.47	5.13	3.99
21	Au	15.64	3.91	4.00

A blank run was also made with added manganese dioxide. No reaction took place.

No concern was taken of the cyanide ratios as proper value was obtained in the first twelve runs.

In conclusion, it is evident from this work that gold dissolves in an aqueous solution of potassium cyanide to form hydrogen peroxide and potassium aurocyanide in accordance with the views of Bodlander. Some of the peroxide formed reacts with more gold to form additional aurocyanide. All of the peroxide formed does not react however ~~within a measurable period of time~~. The reaction occurs in full accordance with Elsner's equation only if some catalytic agent is present which is capable of decomposing the peroxide as fast as formed.

The data for these runs are given in the following tables.

Tabulated Results

Run #1

Values for Gold.

Amount dissolved		0.5551 g.
Moles gold reacted		0.002814

Values for Oxygen.

Initial Pressure	-	74.71 cm. at 23.4° C.
Temp. Corrected Press.	-	74.41
Pressure change due to reaction		27.81 cm. oil
Pressure change	-	1.827 cm. mercury
Volume initially	-	149.18 cc.
Volume finally	-	128.58 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.000925

Values for Cyanide.

Titration Value per 10 cc. - Initially - 6.68 cc. Finally - 0.49 cc.

Normality of $AgNO_3$ used	-	0.09454 N.
Moles cyanide reacted	-	.005866

Run #2

Values for Gold

Amount dissolved	0.4243 g.
Moles gold reacted	0.002152

Values for Oxygen

Initial Pressure	-	75.34 cm. at 23.0° C.
Temp. Corrected Press.	-	75.04
Pressure change due to reaction		21.11 cm. oil
Pressure change	-	1.3868 cm. mercury
Volume initially	-	149.18 cc.
Volume finally	-	133.51 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.000712

Values for Cyanide

Titration Value per 10 cc.	-	Initially	- 6.31 cc.
		Finally	- 1.73 cc.
Normality of $AgNO_3$ used	-	0.09454 N.	
Moles cyanide reacted	-	.004326	

Run #3

Values for Gold

Amount dissolved	0.4269 g.
Moles gold reacted	0.002165

Values for Oxygen

Initial Pressure	-	74.13 cm. at 22° C.
Temp. Corrected Press.	-	73.85
Pressure change due to reaction		21.20 cm. oil
Pressure change	-	1.3928 cm. mercury
Volume initially	-	149.22 cc.
Volume finally	-	133.50 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0007047

Values for Cyanide

Titration Value per 10 cc.	-	Initially	- 6.70 cc.
		Finally	- 1.98 cc.
Normality of $AgNO_3$ used	-	0.09454 N	
Moles cyanide reacted	-	0.004468	

Run #4

Values for Gold

Amount dissolved	0.3910 g.
Moles gold reacted	0.001984

Values for Oxygen

Initial Pressure	-	75.88 cm. at 23° C.
Temp. Corrected Press.	-	75.58
Pressure change due to reaction		18.40 cm. oil
Pressure change	-	1.2087 cm. mercury
Volume initially	-	149.20 cc.
Volume finally	-	135.57 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.000624

Values for Cyanide

Titration Value per 10 cc.	- Initially	- 6.73 cc.
	Finally	- 2.05 cc.
Normality of $AgNO_3$ used	-	0.09454 N
Moles cyanide reacted	-	0.003994

Run #5

Values for Gold

Amount dissolved	0.2771 g.
Moles gold reacted	0.001405

Values for Oxygen

Initial Pressure	-	75.86 cm. at 21° C.
Temp. Corrected Press.	-	75.58
Pressure change due to reaction		12.65 cm. oil
Pressure change	-	0.83104 cm. mercury
Volume initially	-	149.09 cc.
Volume finally	-	139.35 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.000435

Values for Cyanide

Titration Value per 10 cc.	-	Initially	- 7.75 cc.
		Finally	- 4.64 cc.
Normality of $AgNO_3$ used	-	0.09454 N	
Moles cyanide reacted	-	0.002943	

Run #6

Values for Gold

Amount dissolved	0.2236 g.
Moles gold reacted	0.001135

Values for Oxygen

Initial Pressure	-	75.97 cm. at 19° C.
Temp. Corrected Press.	-	75.72
Pressure change due to reaction		8.40 cm. oil
Pressure change	-	0.5518 cm. mercury
Volume initially	-	344.13 cc.
Volume finally	-	337.82 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0003490

Values for Cyanide

Titration Value per 10 cc.	- Initially	- 8.20 cc.
	Finally	- 6.05 cc.
Normality of $AgNO_3$ used	-	0.10662 N
Moles cyanide reacted	-	0.002297

Run #7

Values for Gold

Amount dissolved	0.2638 g.
Moles gold reacted	0.001338

Values for Oxygen

Initial Pressure	-	75.79 cm. at 21° C.
Temp. corrected press.	-	75.51
Pressure change due to reaction		12.49 cm. oil
Pressure change	-	0.8205 cm. mercury
Volume initially	-	148.35 cc.
Volume finally	-	139.06 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0004275

Values for Cyanide

Titration Value per 10 cc.	-	Initially -- 11.24 cc.
		Finally - 8.35 cc.
Normality of $AgNO_3$ used	-	0.09454 N
Moles cyanide reacted	-	0.001350

Run #8

Values for Gold

Amount dissolved	0.3608 g.
Moles gold reacted	0.001831

Values for Oxygen

Initial Pressure	-	76.08 cm. at 21° C.
Temp. corrected press.	-	75.80
Pressure change due to reaction		16.05 cm. oil
Pressure change	-	1.0544 cm. mercury
Volume initially	-	149.99 cc.
Volume finally	-	138.67 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0005256

Values for Cyanide

Titration Value per 10 cc.	- Initially	- 12.23 cc.
	Finally	- 8.87 cc.
Normality of $AgNO_3$ used	-	0.10662 N
Moles cyanide reacted	-	0.003646

Run #9

Values for Gold

Amount dissolved	0.3858 g.
Moles gold reacted	0.001957

Values for Oxygen

Initial Pressure	-	76.32 cm. at 21.8° C.
Temp. corrected press.	-	76.03
Pressure change due to reaction		16.93 cm. oil
Pressure change	-	1.112 cm. mercury
Volume initially	-	149.43 cc.
Volume finally	-	136.89 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0005788

Values for Cyanide

Titration Value per 10 cc.	- Initially -	15.86 cc.
	Finally -	12.14 cc.
Normality of $AgNO_3$ used	-	0.10662 N
Moles cyanide reacted	-	0.002042

Run #10

Values for Gold

Amount dissolved	0.4177 g.
Moles gold reacted	0.002119

Values for Oxygen

Initial Pressure	-	76.28 cm. at 21.8° C.
Temp. corrected press.	-	75.99
Pressure change due to reaction		19.61 cm. oil
Pressure change	-	1.2883 cm. mercury
Volume initially	-	148.27 cc.
Volume finally	-	133.75 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0006683

Values for Cyanide

Titration Value per 10 cc.	-	Initially -	19.91 cc.
		Finally -	15.82 cc.
Normality of $AgNO_3$ used	-	0.10662 N	
Moles cyanide reacted	-	0.002177	

Run #11

Values for Gold

Amount dissolved	0.3151 g.
Moles gold reacted	0.001562

Values for Oxygen

Initial Pressure	-	78.02 cm. at 23.5° C.
Temp. corrected press.	-	77.70
Pressure change due to reaction		12.14 cm. oil
Pressure change	-	0.7975 cm. mercury
Volume initially	-	344.14 cc.
Volume finally	-	335.05 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0005117

Values for Cyanide

Titration Value per 10 cc.	-	Initially -	36.73 cc.
		Finally -	34.15 cc.
Normality of $AgNO_3$ used	-	0.10662 N	
Moles cyanide reacted	-	0.002762	

Run #12

Values for Gold

Amount dissolved	0.3329 g.
Moles gold reacted	0.001689

Values for Oxygen

Initial Pressure	-	75.86 cm. at 24° C.
Temp. Corrected Press.	-	75.55
Pressure change due to reaction		15.18 cm. oil
Pressure change	-	0.99724 cm. mercury
Volume initially	-	149.53 cc.
Volume finally	-	139.10 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0005232

Values for Cyanide

Titration Value per 10 cc.	-	Initially -	67.18 cc.
		Finally -	62.54 cc.
Normality of $AgNO_3$ used	-	0.10662 N	
Moles cyanide reacted	-	0.00419	

Run #13

Values for Silver

Amount dissolved	0.2408 g.
Moles silver reacted	0.002232

Values for Oxygen

Initial Pressure	-	76.92 cm. at 19° C.
Temp. corrected Press.	-	76.67
Pressure change due to reaction		20.82 cm. oil
Pressure change	-	1.3677 cm. mercury
Volume initially	-	149.53 cc.
Volume finally	-	133.79 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0007322

Values for Cyanide

Titration Value per 10 cc.	-	Initially -	10.84 cc.
		Finally -	6.46 cc.
Normality of $AgNO_3$ used	-	0.1066 N	
Moles cyanide reacted	-	0.004657	

Run #14

Values for Silver

Amount dissolved	0.2494 g.
Moles silver reacted	0.0023118

Values for Oxygen

Initial Pressure	-	77.11 cm. At 22° C.
Temp. corrected press.	-	76.82
Pressure change due to reaction		21.35 cm. oil
Pressure change	-	1.4026 cm. mercury
Volume initially	-	149.36 cc.
Volume finally	-	133.36 cc.
Temp. of Reaction	-	25° C.
Moles oxygen reacted	-	0.0007427

Values for Cyanide

Titration Value per 10 cc.	-	Initially -	10.76 cc.
		Finally -	5.27 cc.
Normality of $AgNO_3$ used	-	0.1066 N	
Moles cyanide reacted	-	0.005852	

Run #15 MnO_2 added

Values for Silver

Amount dissolved	0.3191 g.
Moles silver reacted	0.002958

Values for Oxygen

Initial Pressure	-	75.24 cm. at 22° C.
Temp. corrected press.	-	74.96
Pressure change due to reaction		21.77 cm. oil
Pressure change	-	1.4302 cm. mercury
Volume initially	-	149.13 cc.
Volume finally	-	132.81 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0007394

Run #16 MnO_2 added

Values for Silver

Amount dissolved	0.1968 g.
Moles silver reacted	0.001824

Values for Oxygen

Initial Pressure	-	75.11 cm. at 21° C.
Temp. corrected press.	-	74.84
Pressure change due to reaction		13.68 cm. oil
Pressure Change	-	0.8987 cm. mercury
Volume initially	-	149.09 cc.
Volume finally	-	138.88 cc.
Temp. of reaction	-	25° C
Moles oxygen reacted	-	0.0004643

Run #17 MnO_2 added

Values for Silver

Amount dissolved		0.2307 g.
Moles silver reacted		0.002139

Values for Oxygen

Initial Pressure	=	75.04 cm. at 26° C.
Temp. Corrected Press.	=	74.70
Press. change due to reaction		15.66 cm. oil
Pressure change	=	1.0288 cm. mercury
Volume initially	=	152.41 cc.
Volume finally	=	140.70 cc.
Temp. of reaction	=	27° C.
Moles oxygen reacted	=	0.0005278

Run #18 MnO_2 added

Values for Silver

Amount dissolved	=	0.2499 g.
Moles silver reacted	=	0.002318

Values for Oxygen =

Initial Pressure	=	75.77 cm. at 27° C.
Temp. corrected press.	=	75.42
Press. change due to reaction		17.01 cm. oil
Pressure change	=	1.118 cm. mercury
Volume initially	=	152.36 cc.
Volume finally	=	139.60 cc.
Temp. of reaction	=	27° C.
Moles oxygen reacted	=	0.0005798

Run #19 MnO_2 added

Values for Gold

Amount dissolved		0.2299 g.
Moles silver reacted		0.0011664

Values for Oxygen

Initial Pressure	-	74.62 cm. at 23.5° C.
Temp. corrected press.	-	74.32
Press. change due to reaction		9.44 cm. oil
Pressure change	-	0.6202 cm. mercury
Volume initially	-	152.48 cc.
Volume finally	-	145.37 cc.
Temp. of reaction	-	25° C.
Moles oxygen reacted	-	0.0003237

Run #20 MnO_2 added

Values for Gold

Amount dissolved		0.3332 g.
Moles silver reacted		0.001690

Values for Oxygen

Initial Pressure	-	76.48 cm. at 25.5° C.
Temp. corrected press.	-	76.14
Press. change due to reaction		15.11 cm. oil
Pressure change	-	0.9920 cm. mercury
Volume initially	-	152.11 cc.
Volume finally	-	142.80 cc.
Temp. of reaction	-	27° C.
Moles oxygen reacted	-	0.0004231

Run #21 MnO_2 added

Values for Gold

Amount dissolved		0.4034 g.
Moles silver reacted		0.002046

Values for Oxygen

Initial Pressure	=	75.31 cm. at 26° C.
Temp. corrected press.	=	74.97
Press. change due to reaction		12.29 cm. oil
Pressure change	=	0.8074 cm. mercury
Volume initially	=	152.08 cc.
Volume finally	=	140.72 cc.
Temp. of reaction	=	27° C.
Moles oxygen reacted	=	0.0005132

SUMMARY

The following contributions to the field have been made.

1. An apparatus was devised for the rigid exclusion of gases from aqueous solutions.

2. An apparatus was devised which makes possible the study of a three phase system in which the solid phase is metallic.

3. A method was developed for following small changes in pressure in a system, a pressure range of from one to eighty centimeters of mercury.

4. It has been established beyond possibility of doubt that the presence of oxygen is necessary for the solution of gold in aqueous potassium cyanide.

5. The reaction has been shown to take place in two steps, as

(1) $2\,Au + 4\,KCN + O_2 + 2H_2O \longrightarrow 2KAu(CN)_2 + KOH + H_2O_2$

(2) $2\,Au + 4\,KCN + H_2O_2 \longrightarrow 2\,KAu(CN)_2 + 2\,KOH$

which, when summarized, gives

(3) $4\,Au + 8\,KCN + O_2 + 2H_2O \longrightarrow 4\,KAu(CN)_2 + 4\,KOH.$

6. Under ordinary conditions the second reaction, equation 2, does not go to completion.

7. In the presence of manganese dioxide, the reaction has been shown to proceed in absolute accordance with the summarized equation.

8. A study of the reaction velocity by means of rate of absorption of oxygen was found impracticable due to this formation of hydrogen peroxide.

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