AN INVESTIGATION
INTO THE POSSIBILITIES OF THE ELECTROLYTIC PRODUCTION OF METHYL ALCOHOL FROM FORMALDEHYDE

Thesis

by

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SURVEY OF PREVIOUS WORK

While formaldehyde has been the subject of many classical investigations, the greater part has been spent on oxidation, while few attempts have been made to reduce it to methyl alcohol. As a matter of fact, in the past the greater portion of the formaldehyde of commerce has been prepared from methyl alcohol, and as a result has been more expensive than the latter. But with the perfection of new and cheaper methods for the production of formaldehyde from natural gas*, the possibilities of working out a commercial process for the reduction of formaldehyde to alcohol present themselves. Hence, besides being of theoretical interest, the process might easily prove to be valuable. It is rather surprising that there is nothing available in the literature dealing with the electrolytic reduction of formaldehyde; consequently there was but little material to work from, and the results obtained in the following work are not as satisfactory as might be desired. Formaldehyde is very easily oxidized by many reagents as well as electrolytically, and, as previously stated, its oxidation has received a great deal of attention. Nevertheless, it is quite capable of being reduced, and perhaps the most familiar method is that of Sabatier**, in which a mixture of formaldehyde vapor and hydrogen is passed over a catalyst of finely divided nickel. This method can be made to give practically a quantitive yield if the flow is properly regulated. As is the case with many such catalysts, the nickel is rather easily contaminated and soon loses its activity.

In more recent years other methods of reduction have been proposed,

* Rideal-Comptes rendus de l'Academie des Sciences, 137 (302)

** Sabatier-Chemical Age (London) 4, 666-8 (1921) of which perhaps the most interesting is that of Erich Muller,[1] who employed finely divided Osmium as a catalysts and reduced that formaldehyde in aqueous solution. The mechanism of the reaction is thought to be rather involved, but the yields seem to indicate that three mols of formaldehyde react with one mol of water to form two mols of methyl alcohol and one mol of carbon dioxide. Hence, the maximum yield becomes 66.7% of the formaldehyde content. This method suggests the possibility of employing metallic Osmium in some form in the electrlytic reduction, as it seems to be a remarkably active catalytic agent, the reaction as indicated by Muller taking place at room temperature. The presence of a small amount of Osmium in the solution might serve to catalyze the reaction between formaldehyde and any molecular hydrogen dissolved or mechanically held by the swirling liquid.

Benzaldehyde has been the subject of some recent work by Carothers and Roger Adams[2] who obtained rather good results using molecular hydrogen. They employed as a catalyst platinum black in finely divided form but encountered a good deal of difficulty due to the tendency of the oxide to rapidly lose its activity. In the use of platinum black, oxygen is absolutely necessary to keep it active, and as most of the aldehydes take up oxygen very readily some method had to be devised to prevent this. This problem was apparently solved by the addition of small quantities of ferrous or ferric chloride to the mixture. This suggests the possibility of employing these agents in electrolytic methods. Some experiments were made, but with negative results.

[1] Erich Muller, Ber. Chem. Ges. Vol. 54, 3214 (1921)

[2] Amer. Chem. Soc., Vol. 45, 1071 (1923)

Difficulties encountered even in the attempt to obtain formaldehyde from methyl alcohol (the reverse of this investigation) were many. Investigations conducted in the last half of the nineteenth century by Renard, Jaillard, Habermann and Connel all failed to show the formation of formaldehyde in even small quantities. Lob' sums up the results as follows: in aqueous sulphuric acid solution; methyl formate, methyal, methyl acetate, acetic acid, methyl-sulphuric acid, some carbon dioxide and monoxide, but no formaldehyde. Later work by Elbs and Brunner'' prove that an 80% yield of formaldehyde could be obtained by electrolysis in sulphuric acid solution, using bright platinum anodes, in a porous cylinder and employing a current density of 3.75 amperes. It is easily seen that the effect of such factors as current density, voltage employed, anode and cathode materials, electrolyte, temperature, concentration of electrolyte, and concentration of formaldehyde have a marked effect upon the reactions which take place.

In the following work attempts were first made to reduce the formaldehyde without the use of a diaphragm, with rather meager results, the tendency towards oxidation seeming to be predominant in all cases. The method was suggested by that of Teeple* in the preparation of chloroform and iodoform from acetone; He used as an anode a platinum cylinder, while a fine platinum wire just touching the surface of the solution served as the cathode. This, of course, was reversed in the attempted reduction of formaldehyde, i.e., the cathode offered the largest surface, while a fine wire was employed as the anode in order to lessen so far as possible the tendency towards oxidation. The actual results will follow later in this paper. It might also be added here that previous to the work with formaldehyde, some experiments were carried out with acetone in the attempt to produce chloroform after the method of Teeple using a solution of Calcium Chloride as the electrolyte.

This method is dependent upon the electrolyte formation of calcium hypo chlorite and the subsequent chemical reaction with acetone to form chloroform. If some way could be found to overcome the resistance of the deposit which forms upon the anode this method might prove to be successful. It is not necessary to discuss the mechanism of the reaction in this paper, as it has no bearing upon the work with formaldehyde.

The fact that aldehydes occur among the reaction products of alcohol is perhaps the reason that they have rarely been chosen as the starting points in electrolyses. A more comprehensive treatment of this subject might prove highly remunerative, particularly with the aid of potential adjustments at certain values.[1]

THEORY OF THE REACTION.

While the theories as to the formation of some of the more complicated compounds have not been clearly advanced, nevertheless those of the formation of formic acid, carbon dioxide, and alcohol are readily understood. The passage of one Faraday of current is sufficient to liberate one equivalent of hydrogen (Faraday's Law) and if this hydrogen is all utilized according to the reaction

$$HCHO + H_2 = CH_3OH$$

a theoretical yield of alcohol might be obtained. However, when using a cell without a diaphragm, the reactions

$$HCHO + \frac{1}{2}O_2 = HCOOH$$

and

$$HCHO + O_2 = H_2O + CO_2$$

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[1] Lob. Electrochemistry of Organic Compounds, John Wiley & Sons. p. 67.

will also take place, in addition to more complicated reactions giving rise to the formation of such compounds as were mentioned on a previous page. Thus it is seen that the true current efficiency would be rather difficult to calculate.

It is not deemed necessary to go into a discussion of the theory of electrolysis, as this theory is well understood by scientific students and is obtainable in any volume on electrochemistry. However, some of the aspects of excess potential, or overvoltage effects, particularly so far as they influence reduction, will be discussed here, as in the following experimental work it is seen that the effect of excess potential is a large factor in the success of the experiment.

Excess potential is the excess of the discharge potential of hydrogen over the potential value of a hydrogen electrode in the corresponding electrolyte. The quantity of heat produced by the excess potential can be very considerable. According to Caspari' , these excess potentials have definite values for the individual metals, and in the table given by him, platinized platinum shows the smallest excess potential, while lead is very high on the list. Lob has shown that a high excess voltage or potential causes stronger concentrations of discharged reactive hydrogen ions to accumulate, so that the reduction of bodies reducible with difficulty, which does not occur at platinize, or platinum electrodes, may take place with ease at mercury or lead cathodes. Summed up, it might be said that the higher the excess potential the smaller the catalytic acceleration of the reaction, and hence the stronger the concurrent reduction.*

' Ztschr. f phys. Chem. 30,89 (1899)
* Ztschr. f Elektrochemie 9,642 (1903)

DESIGN OF APPARATUS.

Acting upon the suggestion of Teeple[1], the cell was first designed to be used without a diaphragm. The details of construction are perhaps more easily understood from an examination of the accompanying drawings than by an attempted description. Evolved gases could be carried off either through the side tube, or from the top of the reflux condenser, which was added in order to permit the attempted reduction at temperatures above the boiling point of methyl alcohol. The results obtained at these higher temperatures will be explained in detail later. A simple mercury seal was placed about the stirrer, and a small A. C. motor employed for power, drawing current from the 110 volt mains. During the earlier experiments a twelve volt D. C. motor was employed, drawing current from the same line as the cell, but this arrangement caused irregularities in both the speed of the motor and the current furnished the cell.

As cathode and anode materials a number of metals were tried out, the ones finally accepted as being the most suitable being lead. In the first experiments platinum was used at both terminals, but the tendency towards oxidation seemed to predominate in every case. Copper, nickel, and zinc were also tried but with poor results. As a final arrangement, a cylinder of rather heavy lead foil was employed as a cathode; the stirrer and the anode, a lead wire, projecting down thru the cylinder. This arrangement proved fairly satisfactory, except that oxidation of the formaldehyde to carbon dioxide was still too large a factor.

[1] Joun. Amer. Chem. Soc., 26, 536 (1904)

In most instances a strong solution of Sodium Sulphate was employed as the electrolyte, as the use of either acidic or basic solutions causes the polymerization of the formaldehyde solution.[*] A fairly strong solution of the sodium sulphate could be easily prepared, but the salt showed a decided tendency to crystalize out after standing, indicating supersaturation. Another difficulty encountered was the high voltage necessary to secure sufficient current to produce an appreciable action. Employing a single wire as an anode, and ten to twelve volts pressure, the highest current obtainable was about two amperes. Using a fairly strong, <u>6</u> normal, sulphuric acid solution as an electrolyte a much lower voltage could be employed, but the reasons for not using acid solutions are obvious, as referred to above.

An appreciable reduction being detected in the use of electrodes as last described led to the decision to radically alter the design of the cell for the last experiments. A porous cup of about one hundred and fifty cubic centimeters capacity was employed to hold the electrolyte to which the formaldehyde solution had been added. A cylinder of heavy lead foil was constructed to fit snugly in the inside of the cup, and on the outside of the cup, a similar cylinder was formed to serve as the anode. This then, cut the resistance of the cell down to a minimum, a large area being offered by both electrodes. The porous cup was then set inside a glass cylinder, which contained about three normal sulphuric acid as an electrolyte. The cup contained the previously employed sodium sulphate solution. With this cell a current as high as three and a half to four amperes could be obtained using a potential of only five volts. This seemed desirable, as the reduction seemed to be favored at lower voltages, while oxidation was predominant at the higher voltages. An interesting example of this is furnished by Lowy*, showing the effect of slight changes of voltage, and also covering the effect of the changes due to difference in concentration of electrolyte, etc.

" Beilstein. Handbuch der Org. Chemie, Vol. 1. 558-70 (1918)
* Alexander Lowy. Jour. Ind. and Eng. Chem., 15, 15 (1923)

METHODS OF ANALYSIS

Accurate determination of the products formed in the course of the electrolysis was almost impossible due to the lack of exact methods for the determination of methyl alcohol in the presence of formaldehyde and formic acid. Hence, most of the analytical work is of an indirect nature, and necessarily involves a good many assumptions. The method finally adopted as the most suitable for the determination of formaldehyde was that given by Griffin', in which hydrogen peroxide is employed to oxidize the formaldehyde to formic acid, which is then neutralized with an excess of sodium hydroxide solution, and the excess base titrated back with standard acid solution. The method in full is given on an accompanying page.

Formic acid may be determined either by direct titration, if other acids are known to be absent, or by the method of H. L. Jones*, using potassium permanganate. This latter method, however, is influenced by the presence in the solution of methyl alcohol, and the method of Griffin was usually employed. No attempts were made to accurately analyze the gases evolved because of the many difficulties met with, but only rough estimations made. In most cases any methyl alcohol formed was removed from the solution by fractional distillation, and the percentage present determined by measuring the specific gravity with a Westpahl balance. The tables used were those given in Van Nostrand's Annual, for density of mixtures of methyl alcohol and water at 15° C. In all the formaldehyde used some methyl alcohol was already present, but in rather small quantity. The alcohol was originally added to the alcohol to prevent polymerization.

' Griffin, Technical Methods of Analysis, McGraw Hill Co., 80 (1921)

* H. C. Jones, Amer. Chem. Journ. 17, 539 (1895)

EXPERIMENTAL WORK

Platinum Cathode.

In the first run, 225 grams of $Na_2SO_4 \cdot 10H_2O$ dissolved in 300 ccs. of water was employed as the electrolyte, and 50 ccs. of a 40% aqueous solution of formaldehyde added. A fine platinum wire was employed as the anode, and a bright platinum plate having an area of about 25 sq. cm. as the cathode. Analysis of the solution showed a formaldehyde content of 0.039 grams per cc. before electrolysis, and no formic acid. A pressure of eleven volts was used, giving a current of 1.25 to 1.5 amperes, or a cathode density of 5-6 amps. per sq. dcm.

The electrolysis was allowed to procced for three hours, the cell being cooled by circulating water, and then the solution again analyzed. During the electrolysis of the solution, CO_2 was evolved in considerable quantity, was also hydrogen, showing that oxidation was predominant. Analaysis showed a formaldehyde content of 0.023 grams per cc. a formic acid content of 0.007 grams per cc. Thus, about forty per cent of the formaldehyde had disappeared from solution, either as CO_2, alcohol, or other products of oxidation. Using the same solution, another run was made, all conditions being the same expcet the temperature, which was maintained in the neighborhood of 80° C. Results of this run showed a still grater evolution of CO_2, and a decrease in the amount of formic acid formed.

Nickel Cathode.

In the next run a nickel plate of about the same size as the platinum was substituted, a slightly stronger electrolyte, (200 grams of salt to 200 ccs. of water) employed, and 60 ccs. of 40% formaldehyde added. A portion of this mixture was then placed in the cell, and a voltage of nine volts applied, producing a current of 0.9 to 1.0 amperes. The original solution contained 0.048 grams per cc. of formaldehyde, and no formic acid. After three hours, analysis showed a formaldehyde content of only 0.032 grams, and a trace of formic acid. CO_2 evolution in the course of the electrolysis had been copious, as was also that of hydrogen. Several additional runs using the nickel electrode were made, small quantities of other salts such as stannous chloride, ferrous chloride, etc. being added, to notice their effect, if any, The results were not improved, and the only noticeable effect was the contamination of the cathode with other metals, formed by the reduction of the salts in the solution. From the results of these several runs it was decided to discard nickel as a possible cathode material.

Copper and zinc cathodes.

Several runs were made employing either copper or zinc as the cathode metal, but the results were not illuminating. They did not differ materially from those obtained with the platinum or nickel, though in the use of zinc the evolution of hydrogen did not seem as pronounced as in the other cases. It was realized that the conditions to be sought for were those in which the evolution of both CO_2 and hydrogen were reduced to a minimum and that of the oxygen raised to the maximum limit. Results up to this time had been rather discouraging, and the possibility of obtaining any appreciable reduction in a cell without a diaphragm did not seem bright. However, it was decided to try lead as a cathode material, and as a matter of fact in the following experiments, lead was employed for both the cathode and the anode.

Lead cathode.

Three hundred grams of sodium sulphate were dissolved in 300 ccs. of water, and 75 ccs. of the 40% formaldehyde added. The electrolysis was carried out for about three hours at approximately room temperature. Analysis of the original solution showed no formic acid, but a formaldehyde content of 0.046 grams or cc. After electrolysis, a second analysis showed a trace of formic acid present, and the formaldehyde content decreased to 0.016 grams per cc. This, then, looked more encouraging, as the evolution of hydrogen seemed to have dimished greatly, although carbon dioxide was still present in the gases evolved. A second run was made using these same electrodes, the solution being slightly weaker in formaldehyde content, 0.025 grams per cc. Between three and four volts were employed, giving a current of 0.5-0.75 amps, or a current density of 0.8-1.0 amps., add the cell kept at a temperature of about 25° C. After four hours running, analysis showed only a trace of formaldehyde left, and a trace of formic acid. In this run the evolution of hydrogen from the cathode was closely watched and for the first ten or fifteen minutes appeared negligible, increasing slowly till at the end of the four hours considerable quantities were being evolved. This is what would actually be the case if reductimwere taking place at the cathode, for as the strength of the remaining formaldehyde diminished, some hydrogen would in all probability be given off in the molecular form. Any attempt at exact-current efficiency in this type of cell is impossible, due to the variety of products that may be formed, and the variation in the current drawn by the cell, the latter due to temperature differences in the solution.

A third run employing these electrodes were made, using an electrolyte of 250 grams of sodium sulphate in 250 ccs. of water, to which was added 30 ccs. of formaldehyde. A current of 0.3-0.6 amperes was drawn at 4.5 volts, and the electrolysis of the solution continued till analysis showed no formaldehyde left in solution. Carbon dioxide in the exit gases was absorbed by saturated barium hydroxide solution, and determined as barium carbonate. The weight of barium carbonate was 3.84 grams, corresponding to 0.585 grams of formaldehyde decomposed, not nearly enough to account for the total. The solution was then fractionated using a tall Hempel column and 20 ccs. of the distillate collected. Using the Westphal balance, a specific gravity of 0.974 at 15° C. was obtained, corresponding to a methyl alcohol content of 16% by weight, or 3.15 grams. This value is considerably in excess of the theoretical current yield, showing that there was already some alcohol present in the formaldehyde solution.

In view of the rather improved results employing a lead cathode in the cell without a diaphragm, it was decided to employ a diaphragm cell, whereby the yield and current efficiency might better be calculated.

EXPERIMENTS WITH DIAPHRAGM CELL.

Lead cathode and anode, first run.

The cell used was as described in a previous section of this paper, and the porous cup contained 125 ccs. of a solution made up of 150 grams of sodium sulphate, 150 ccs. of water, and 60 ccs. of 40% formaldehyde solution. A current of two amperes at five volts was employed, and the electrolysis carried out for four hours. Originally the solution analyzed 0.058 grams of formaldehyde per cc., while after the electrolysis the presence of formaldehyde could not be detected. Results on this run were materially affected, however, as the porous cup was allowed to stand in the glass cylinder containing three-normal sulphuric acid over the week-end, and much of the formaldehyde and alcohol diffused thru into the outer solution, while the acid diffused into the cup. Electrolysis using the porous cup causes the formation of sodium hydroxide within the cup, as the sulphate ion passes out into the anode portion, while the sodium ion discharges at the cathode, liberates hydrogen and forms OH^3 ion. As has been stated the presence of a strong acid or base causes polymerization of the formaldehyde, and some arrangement should be devised to keep the electrolyte neutral for best results.

Both portions of the electrolyte were fractionated with a Hempel column as before, 20 ccs. collected and the specific gravity determined as before. The value of 0.974 at 15° C. showed a methyl alcohol content of 3.15 grams. The theoretical current yield would be 4.5 grams, while the original solution contained the equivalent of 7.2 grams. It is evident therefore that much of the formaldehyde must have diffused through the porous cup between the time of electrolysis and analysis, and undergone polymerization.

Lead cathode, second run.

A second run was made using electrolyte of the same concentration as before, but analyzing 0.153 grams per cc. of formaldehyde, the whole solution then containing 15.6 grams. A current of 3 amps. at 4 volts was employed, the run lasting five hours and thirty minutes. At the end of that time the electrolyte was removed from the porous cup and again analyzed for formaldehyde. This analysis showed a content of 0.079 grams per cc., or 9.8 grams in the whole solution, a decrease of 5.7 grams. Theoretical current yield would give a reduction of 8.9 grams. Hence the current efficiency was 64%. The solution was then fractionated and 25 ccs. collected as before. This portion showed a density of 0.933 at 15° C., and the computed weight of methyl alcohol was 9.8 grams. This again showed that some alcohol was already present in the formaldehyde solution.

In both these runs employing the diaphragm cell the lead anode was attacked by the sulphuric acid solution and partially disintegrated by the end of the run. Oxidation takes place at the face of the anode, lead peroxide being formed as would naturally be the case.

SUMMARY

Though there was no record of any previous work on the electrolytic reduction of formaldehyde, it was believed that so long as it was possible to reduce it chemically it would probably also be possible to affect its reduction electrolytically. Platinum electrodes were used in the first trials, a solution of sodium sulphate being employed for the electrolyte, and the formaldehyde concentration about 6%. Oxidation was predominant, with little if any tendency towards reduction. Nickel, copper, and zinc were also tried as cathode metals, but gave little better results, with the exception of zinc, which seemed to lessen somewhat the evolution of hydrogen. Conditions sought were those in which the evolution of hydrogen and carbon dioxide were reduced to a minimum, while that of oxygen was raised to its maximum value.

Having a high over potential value, lead was then tried as a cathode material, a lead wire serving as the anode. Results seemed somewhat improved, the evolution of hydrogen at the cathode having decreased noticeably, though carbon dioxide was still evolved at the anode. In order to combat this oxidation it was decided to employ a diaphragm cell.

Using a current density of 2-3 amperes at 4 volts with a diaphragm cell, very good results were obtained. The porous cup contained an electrolyte of sodium sulphate as before, while the outer solution was three-normal sulphuric acid. Reduction took place readily at the cathode, and good yields were obtained. The metal of the anode was rapidly disintegrated under the influence of the electric current.

TABULATION OF RESULTS.

SIMPLE CELL

Cathode Metal.	Voltage	Current Density	Products.
Platinum	11.0-15.0	5-6	Large amount of CO_2 Small amount HCOOH No alcohol
Nickel	9.0	4.0	Same as above
Copper	10.0	4.5	Same as above
Zinc.	10.0	4.5	CO_2 Trace of HCOOH Probably some CH_3OH
Lead	3.4	0.8-1.0	Much less CO_2 No HCOOH Small amount CH_3OH

DIAPHRAGM CELL.

Lead	4.5	2.5-3.0	No CO_2 No HCOOH Good yield of CH_3OH

CONCLUSIONS.

The following conclusions are to be drawn from the results of this investigation:

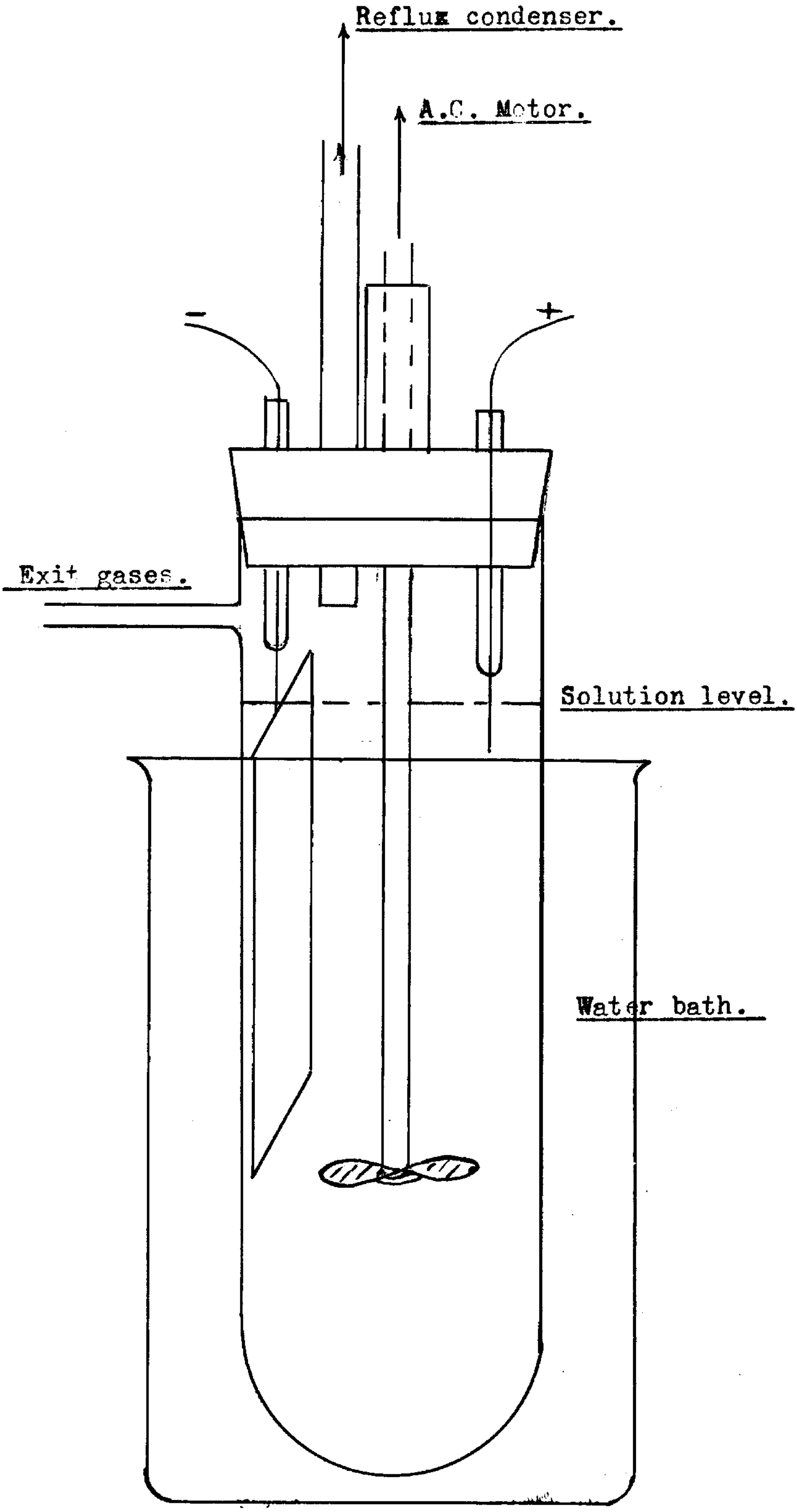
That formaldehyde is quite capable of being reduced electrolytically if the proper cathode metal is employed.

The reduction seems to take place more easily at a fairly low voltage, i.e., 5-10 volts, and a current density of 2-3 amps.

Only one electrolyte was employed in the investigations, but the choice of electrolyte is limited in that it must be a neutral solution, due to the tendency of formaldehyde to polymerize in acidic or basic solutions.

It is probably not necessary that the anode be of any particular metal; in fact carbon would probably prove to be very satisfactory, as most metals would be attacked by the action of the sulphuric acid during electrolysis.

Metals with a high over-voltage value should be employed as the cathode, that is, zinc, mercury or lead. This overvoltage effect retards the evolution of molecular hydrogen and increases the tendency towards reduction.


Reflux condenser.
A.C. Motor.
−
+
Exit gases.
Solution level.
Water bath.