

The reaction indicated in Equation 4 has also been studied by Foerster and others.⁴ Interaction between the items recorded in Equations 1, 4 and 5 account for the end products observed in our work.

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FORMATION OF COLLOID SOLUTIONS BY ELECTRICAL PULVERIZATION IN THE HIGH-FREQUENCY ALTERNATING CURRENT ARC

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One of the most general methods for preparing colloid solutions of the metals consists in pulverizing metallic electrodes in an electric arc immersed in a suitable liquid. The method was studied in some detail first for the direct current arc,¹ and subsequently decidedly improved by the substitution of the high-frequency arc for the direct current arc.² The use of high-frequency current of the order of magnitude of 10^6 in general not only increases the degree of dispersion in the resulting sol,³ but also makes it possible to disperse metals into organic liquids with decreased decomposition of the medium.² Various sources of high-frequency current, however, have been found to be of unequal merit, and yet it has not been possible to establish the causes for these differences. In previous studies of electrical pulverization, the discharge of a condenser through an oscillatory circuit and across a spark gap immersed in a liquid has been used invariably as the source of the high-frequency current. Under such conditions, as will be shown in this paper, there is superimposed upon the oscillatory condenser discharge across the spark gap the direct or low-frequency current which charges the condenser. In view of the inferiority in many ways of direct and low-frequency current methods for preparing colloids, it seems justifiable to suppose that the elimination of the direct or low-frequency components from the circuit in which colloid formation takes place would be advantageous. Accordingly, a study has been made of the electrical pulverization of metals with the Tesla coil as the source of current. For comparison purposes, parallel studies have been made of circuits in which the direct or low-frequency components were present in the pulverizing circuit. In this paper are presented the results of these

⁴ Foerster, *Z. anorg. Chem.*, **128**, 245 (1923).

¹ Bredig, "Anorganische Fermente," Engelmann, Leipzig, 1901.

² Svedberg, *Nova Acta Reg. Soc. Scient. Upsaliensis*, [4] **2**, No. 1 (1907).

³ Börjeson, *Dissertation*, Upsala, 1921, p. 117.

experiments and a discussion of the preparation of colloid solutions by means of the high-frequency alternating current arc.

Apparatus

The various types of electrical circuits either actually used or considered in the discussion are represented in a diagrammatic way in Figs. 1a-d.

Fig. 1a shows the construction of the Tesla coil.⁴ The transformer A was a 1kw. Thorardson "wireless" transformer with maximum secondary voltage of 25,000. The current from the secondary charged the condenser C, a petroleum-covered, copper foil and glass plate condenser with a capacity of 5.0×10^{-3} mf, which in turn discharged across the air-quenched silver spark gap S, and produced in Circuit I oscillations of a frequency approximating 1×10^6 . The spark gap was in the form of a cone and conical socket from the tip of which issued a blast of compressed air to quench the spark. The primary of the oscillation transformer O consisted of 3 turns of a helix 30 cm. in diameter made of 0.8cm. copper tubing. A turn or two of the secondary (constructed like the primary), a hot-wire ammeter and a micrometer spark gap P⁵ formed the "col-

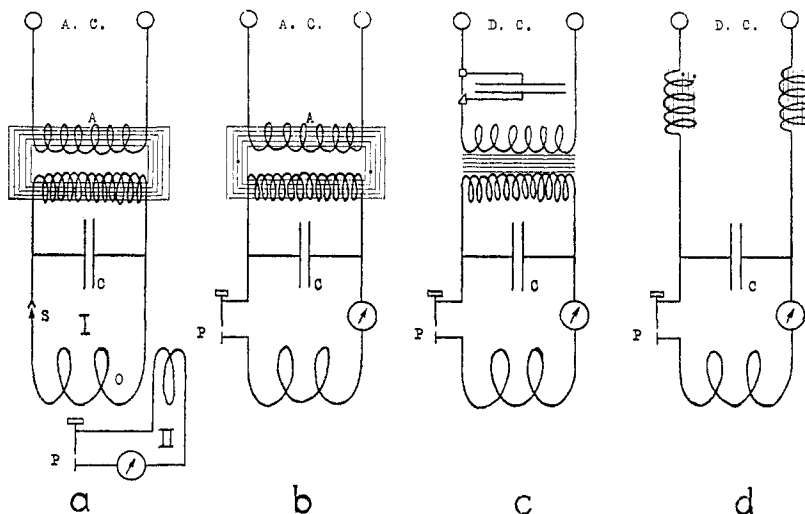


Fig. 1.

loid-forming" Circuit II. Cylindrical electrodes 5.8 mm. in diameter of the metal to be pulverized were mounted in the micrometer gap P and immersed in the liquid which was to form the dispersion medium of the colloid solution. During operation, 10 amperes flowed through the primary of the transformer A, the gap S was adjusted to give a bluish-white, crackling spark, and variation of the current in Circuit II was accomplished by changing the number of turns of the oscillation transformer included in the circuit.

In some of the experiments, an arrangement was used which may be called the "transformer circuit," schematically illustrated in Fig. 1b.⁶ The air-quenched spark

⁴ The authors are indebted to Mr. Wengel, a student, for the construction of the Tesla coil.

⁵ Ref. 2, p. 21.

⁶ A similar circuit has been used by Bodfors and Frölich, *Kolloidchem. Beihefte*, **26**, 301 (1922).

gap in the condenser circuit of the Tesla coil was replaced by the micrometer spark gap and the hot-wire ammeter, Circuit II of Fig. 1a being discarded. Therefore, with the exception of the change in the spark gap, the constants of the circuit (capacity and inductance) remained the same.

A modified Poulsen or "undamped wave circuit" was also used.⁷ In this circuit, the transformer of the transformer circuit was replaced by a 500-volt direct-current line protected by high inductive resistance from the high-frequency current in the oscillatory circuit. Fig. 1d shows the arrangement. In these last two circuits, the discharge of the condenser takes place across the same gap as that in which the pulverization of the electrodes occurs.

Experimental Part

The quantities of special interest in the electric pulverization of metals to form colloid solutions are (a) the rate of pulverization, (b) the ratio of sediment to total metal dispersed, (c) the extent of decomposition of the medium, and the dependence of these quantities on the current characteristics.

The rate of pulverization was found by determining the loss in weight of the electrodes in the micrometer spark gap corresponding to a known period of pulverization. Inasmuch as with the Tesla coil and the transformer circuit the loss in weight was equally divided between the two electrodes, the rate of pulverization is expressed in the tables simply as milligrams of metal per minute.

As pointed out by Börjeson,⁸ the total quantity of metal pulverized electrically may be divided into two distinct portions on the basis of size of particle and probable differences in the mechanism of formation. One portion consists of particles larger than a few tenths μ in diameter, and accordingly settles out in a comparatively short time. In the experiments reported in this paper, 20 hours were allowed for this coarser portion to settle out from layers about 4 cm. deep. The supernatant liquid was carefully removed and the quantity of metal in the sediment determined.

The decomposition of the medium was measured in terms of the gaseous decomposition products evolved. The gases were caught by placing over the electrodes an inverted glass bell leading to a gas buret containing the same liquid as the dispersion medium.⁹

The "specific decomposition"¹⁰ is defined as the ratio of the number of cubic centimeters of gas formed (reduced to N. T. P.) to the number of milligrams of metal pulverized under the same conditions. Since the sedimenting portion of the pulverized metal does not form a part of the final colloid solution, it is more significant to express the decomposition in terms of the "net specific decomposition" which is defined as the ratio of the vol-

⁷ See also Svedberg, *Physik. Z.*, **15**, 361 (1914). Ref. 3. Kohlschütter, *Z. Elektrochem.*, **25**, 309 (1919).

⁸ Ref. 3, p. 39.

⁹ Ref. 2, p. 33.

¹⁰ Ref. 2, p. 54.

ume of gas formed (in cubic centimeters under standard conditions) to the milligrams of fine-grained, non-sedimenting material.

For all three circuits, the frequency of the oscillations as determined with a resonance wave meter was 1.01×10^6 . Although the decrement of the oscillations in the colloid-forming circuit is not an entirely unique quantity because of the disturbing influence of the arc, approximate values were computed from the resonance curves. The values for the Tesla coil varied according to the conditions between 0.30 and 0.35, and for the transformer circuit averaged 0.75.

The frequency of discharge of the condenser in the Tesla coil was determined in the following way. A photographic plate was mounted upon an electric motor so that it could be revolved rapidly about an axis perpendicular to the plane of the plate. A fine discharge point connected conductively to the oscillating Tesla coil was drawn quickly across the face of the revolving plate from the center outwards. After development, the plate showed groups of spots recording the separate discharges arranged on a spiral, two groups for each cycle of the 60 cycle current charging the transformer. The number of discharges per half cycle varied between 20 and 30, and averaged 25, equaling 3000 per second.

In the following tables are recorded the data obtained upon pulverizing cadmium into alcohol, ether or water with the electrical arrangements already described. The alcohol and ether were carefully dehydrated with burnt lime and sodium, respectively. In Col. 1 of Tables I and II is given the effective current as registered by the hot-wire ammeter in series with the

TABLE I
PULVERIZATION WITH TESLA COIL OF CADMIUM INTO ALCOHOL
Arc length: 0.16-0.18 mm.

Current	M/min. Mg.	cc/min. Cc.	v ₀ /M
2.87	59.3	26.3	0.44
2.83	58.7	28.0	.48
2.47	47.8	23.7	.50
2.47	49.5
2.47	49.4
2.47	48.3	23.5	.49
2.06	37.3	18.8	.50
2.06	36.6	19.1	.52
1.75	30.0	12.1	.40
1.75	30.3	17.3	.57
1.75	29.5	13.8	.46
1.32	19.2	7.6	.40
1.30	19.3	8.8	.46
1.19	17.2	8.4	.49
1.15	16.2	8.2	.51
0.83	9.4	3.7	.40
0.81	9.7	3.3	.34

pulverizing arc; Col. 2 shows the rate of pulverization of cadmium in milligrams per minute; Col. 3 gives the rate of gas evolution in cc. per minute (N. T. P.); and Col. 4 contains the values for the specific decomposition.

According to Table I, the specific decomposition shows considerable fluctuation without any noticeable regularity. It seems legitimate, however, to consider the specific decomposition as essentially constant and to accept an average value of 0.46. The rather large experimental error is due to the difficulty of measuring gases accurately over such a volatile liquid as alcohol. The solubility of the gases in alcohol is another factor which cannot be corrected readily. The low values for the specific decomposi-

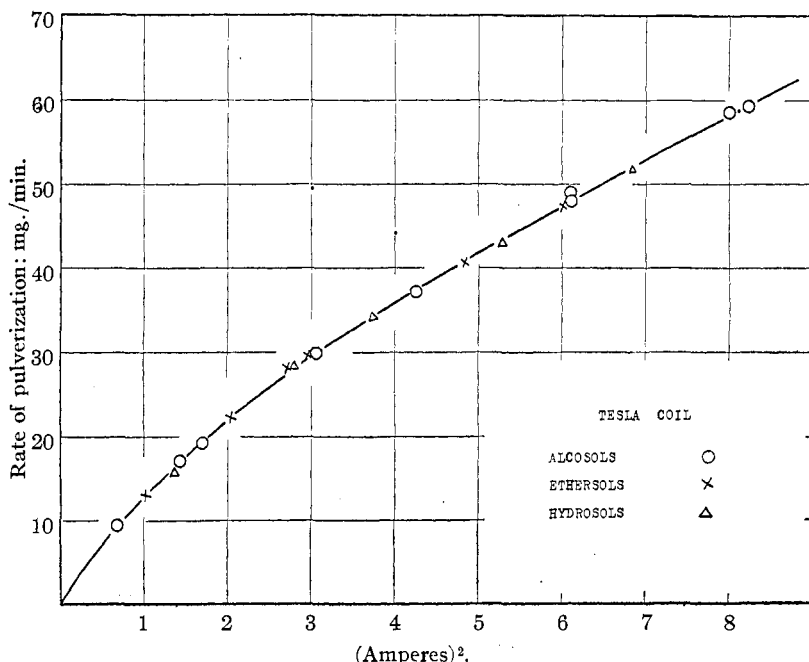


Fig. 2.—Pulverization of cadmium into alcohol, ether and water with the Tesla coil.

tion with small pulverizing currents are probably caused by this solubility error. In other series of experiments, the quantity of sediment was determined and found to be independent of current intensity (between 0.8 and 2.5 amperes). The average value was 54.0%. The relationship between the rate of pulverization and the square of the effective current is shown graphically in Fig. 2.

Entirely similar experiments were made in which cadmium was dispersed into anhydrous ether. Typical data are given in Table II.

The remarks made concerning the specific decompositions in Table I are applicable to the data of Table II. In this case, however, the average

TABLE II
PULVERIZATION WITH TESLA COIL OF CADMIUM INTO ETHER

Current	Arc length: 0.12-0.16 mm.		v_0/M
	$M/\text{min.}$ Mg.	$v_0/\text{min.}$ Cc.	
1.05	13.9	4.9	0.36
1.42	23.1	6.7	.38
1.65	28.4	6.6	.23
1.73	30.1	7.6	.25
2.20	40.2	14.4	.36
2.46	47.5	12.1	.25

specific decomposition was only 0.30, as might be expected in view of the greater chemical stability of ether. The instability of the ethersols at room temperatures prevented an estimate of the sediment from being made. Qualitatively, it appeared to be about the same as in the case of the alc-sols. Fig. 2 shows that for both alcohol and ether the same relationship exists between the rate of pulverization and the square of the effective current.

With the Tesla coil, it was even possible to disperse cadmium with ease into a liquid with an appreciable electrical conductivity such as ordinary tap water. A series of pulverizations was made in distilled water from which the air had been removed by boiling. The pulverization took place smoothly with the greater currents, but was somewhat unsteady with a current of 1 ampere and less. Data are given in Table III.

TABLE III
PULVERIZATION WITH TESLA COIL OF CADMIUM INTO WATER

Current.....	Arc length: 0.08-0.12 mm.							
	1.17	1.67	1.93	1.93	1.93	2.30	2.30	2.62
$M/\text{min. mg.}$	15.7	28.6	36.0	35.6	34.1	43.2	42.6	51.4

The data of Table III are incorporated into Fig. 2 from which it is apparent that the rate of pulverization into water is practically identical with the rates into alcohol and ether. The sediment was found to approximate 50%. These cadmium hydrosols prepared in air-free water showed the reflected black and the transmitted deep brown colors characteristic of the sols in organic media. When the hydrosols were protected from the air, they remained stable and apparently unchanged for a fortnight or more. In the presence of air, however, the color lightened noticeably in a few hours, and if undisturbed, the sol soon gelatinized. The chemical change—probably oxidation—did not cease until the gel disappeared, leaving only a white residue.

In air, the pulverization was quite slight. With a current of 1.5 amperes, the loss in weight of the electrodes was only 1 mg. per minute, increasing to 1.6 mg. for a current of 2.3 amperes.

Similar studies were made of the transformer circuit as the source of the

high-frequency current. Tables IV and V contain specimens of the data so obtained.

TABLE IV
PULVERIZATION OF CADMIUM INTO ALCOHOL WITH TRANSFORMER

Current.....	0.97	1.11	1.27	1.57
M/min, mg.....	18.0	21.9	27.7	43.6

In other runs, the specific decomposition was found to average 1.60 and the percentage of sediment to be 38.5. Fig. 3 shows that the rate of pulverization was greater with the transformer circuit than with the Tesla coil, and furthermore that it was directly proportional to the square of the effective current. This is in agreement with the results of Bodfors and Frölich.⁶

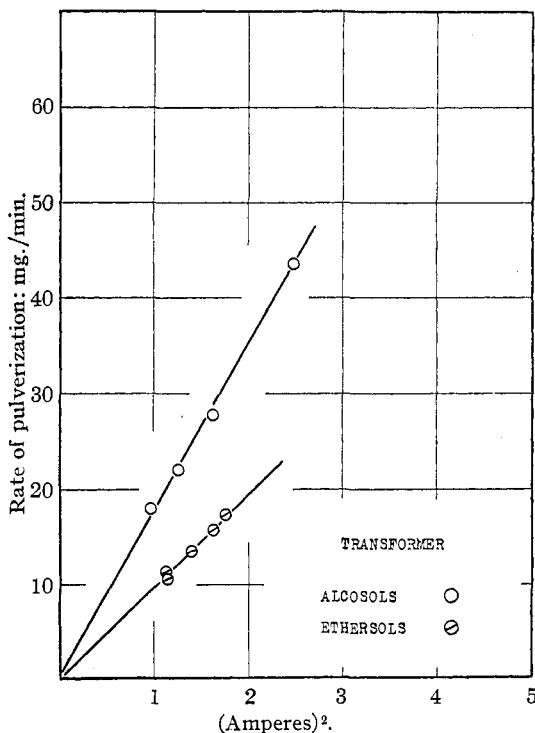


Fig. 3.—Pulverization of cadmium into alcohol and ether with the transformer circuit.

The average specific decomposition of the ether was 0.60. On account of the instability of the sols, the sediment was not determined. Tables IV and V and Fig. 3 show that the rates of pulverization of cadmium into alcohol and ether are not the same with the transformer circuit as they are with the Tesla coil. A possible explanation of this behavior will be given in the discussion.

The behavior of the modified Poulsen circuit is illustrated in the following averaged data. With a primary direct current of 0.2 ampere, an arc length of 0.06–0.08 mm. and an effective current of 1.17 amperes, 33.0 mg. of cadmium was pulverized into alcohol per minute and the specific decomposition was 1.43 (average of 7 runs).

TABLE V
PULVERIZATION OF CADMIUM INTO ETHER WITH TRANSFORMER

Current.....	1.06	1.06	1.18	1.27	1.32
M/min., mg.....	10.6	11.3	13.6	15.9	17.3

Thus, the rate of pulverization is greater for the modified Poulsen than for any of the other circuits used. The percentage of sediment is low and the decomposition of the liquid moderate, but for some unknown reason, sols prepared with this circuit tend to be less stable than the same type of sols prepared by means of one of the other circuits. Pulverization does not take place equally at the two electrodes with this arrangement. Under the conditions of these experiments, 73% of the total metal dispersed came from the anode, in agreement with the observations of Börjeson.¹¹ The proportion of sediment was estimated by analysis of the supernatant sol and was found to approximate 30%.

Discussion

To facilitate a comparison of the various types of electrical circuits which may be used, there has been added to Fig. 1 a diagrammatic scheme of the induction-coil circuit as used by one of the authors. Fig. 4 contains data for the pulverization with the induction coil of cadmium into alcohol (by Börjeson) and into ether (by Svedberg).

In order to have a basis for correlating the observations, it is necessary first to point out the peculiar and significant characteristics and differences in the electrical arrangements used,¹² particularly with respect to the current which flows through the pulverizing arc.

The source of the high-frequency oscillations in all four cases illustrated in Figs. 1a-d is in the discharge of a condenser through an oscillatory circuit.

In the case of the Tesla coil, the condenser discharge spark at S is rapidly and frequently extinguished or quenched by the air blast so that there is

¹¹ Ref. 3, p. 54.

¹² Reference must be made to Zenneck, "Elektromagnetische Schwingungen," Enke, Stuttgart, 1905, and Fleming, "Principles of Electric Wave Telegraphy," Longmans, Green and Co., London, 3rd ed., 1916, for details concerning high-frequency oscillations.

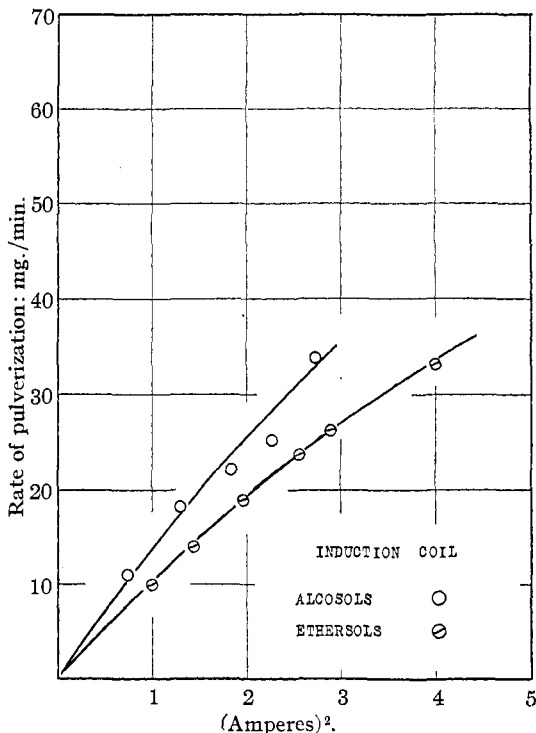


Fig. 4.—Pulverization of cadmium into alcohol and ether with the induction coil circuit according to observations of Svedberg and of Börjeson.

very little tendency to short-circuiting of the condenser through arc formation. The high-frequency oscillations of Circuit I are transmitted to Circuit II by means of the oscillation transformer O. The current in Circuit II is therefore a symmetrical one consisting of a train or series of groups of damped, high-frequency oscillations separated by relatively long periods during which the current is zero. For a given frequency, the duration of the intervals between successive groups is determined by the discharge frequency in Circuit I and the damping decrement of the oscillations in the pulverizing circuit. With a decrement of 0.30 and a frequency of 10^6 , the amplitude of the oscillations decreases to 1% of the maximum in 15 cycles. Since the discharge frequency was found to be about 3000 per second, only (15×3000) 45,000 oscillations (with an amplitude greater than 1% of the maximum) take place each second, but with a frequency of 10^6 per second. In other words, the arc burns probably less than 5% of the total time. Inasmuch as the hot-wire ammeter records merely the average effective current, the maximum instantaneous current intensities attain on this basis values at least 100 times as great as recorded by the hot-wire ammeter.

The transformer and induction-coil Circuits 1b and 1c are closely related, but differ decidedly from the Tesla coil. In the former a low-frequency, alternating current transformer charges the condenser, while in the latter the interruptions by means of a mercury turbine interrupter of the primary direct current produce in the secondary of the induction coil an intermittent, almost uni-directional current which charges the condenser. The important difference between these two circuits and the Tesla coil is the change in the conditions under which the condenser discharge occurs. In the transformer and induction coil circuits, the discharge takes place across a short gap (0.10–0.25 mm.) between the electrodes being pulverized. The quenching action of the surrounding liquid is insufficient to prevent partial short-circuiting of the transformer or induction coil. This allows the charging current to be superimposed upon the high-frequency discharge. At the same time, the maximum condenser voltage is lowered because of incomplete charging. Due to the much lower resistance of the secondary of the transformer, the intensity of the low-frequency component across the gap is probably considerably greater than in the induction coil circuit. The effect of the short-circuiting of the transformer is shown on the electrodes, in that the loss of metal is largely from the center where the quenching action is least, the short-circuiting most complete, and the low-frequency intensity is greatest. With the low-frequency components present, the arc actually burns for a greater part of the time than with the Tesla, and the maximum instantaneous current intensities are less. The current form in the transformer circuit is therefore a symmetrical one in which there is combined a low-frequency alter-

nating current with groups of high-frequency oscillations. The current form of the induction-coil circuit is more complex, consisting of an intermittent, complicated, highly unsymmetrical (almost uni-directional) current superimposed upon damped oscillations.

The high-frequency current furnished by the modified Poulsen circuit, Fig. 1d, is an undamped or slightly damped, alternating but non-symmetrical current of complex form, containing higher harmonics of the fundamental frequency.¹³ Its non-symmetrical character is due to the direct current from the primary d. c. source. The oscillations are of the third type described by Barkhausen¹⁴ in which the effective intensity of the current through the arc is considerably greater than that of the primary direct current, and re-ignition of the arc takes place when the direction of the oscillatory current is opposed to the primary direct current.

On the basis of these characteristics, the varying behaviors of the different circuits with respect to the pulverization of metals may be coordinated. The observations recorded in the tables and figures indicate that under comparable conditions the rate of pulverization at equal effective current intensities is greater with the modified Poulsen and transformer circuits than with the Tesla coil and induction coil. This appears to be due to the fact mentioned above that the interruptions, and therefore the periods during which the arc is not burning and cooling of the electrodes takes place, are shorter in the case of the wave current and the transformer circuits. Similarly, the decreased rate of pulverization of cadmium into ether with the transformer and induction-coil circuits is a result of the more effective quenching of the condenser discharge in the presence of the ether, and therefore a greater degree of elimination of the low-frequency components. In the case of the Tesla coil on the other hand, the character of the current through the pulverizing arc is practically independent of the nature of the liquid surrounding the electrodes, and the rate of pulverization is constant for different liquids, in spite of differences in specific heat, heat conductivity, viscosity, etc.

In his dissertation, Börjeson showed that the percentage of sediment increases with the number and duration of the interruptions in the pul-

TABLE VI
PULVERIZATION OF CADMIUM INTO ALCOHOL

Circuit	Sediment	Sp. decompn.	Net sp. decompn.
Wave current (Poulsen).....	30.0	1.43	2.0
Transformer.....	38.5	1.60	2.6
Induction coil ^a	40.0	2.36	3.9
Tesla coil.....	54.0	0.46	1.0

^a Results obtained by Börjeson, Ref. 3, pp. 35, 46.

¹³ Rönholm, *Arkiv Mat. Astron. Fysik*, **11**, No. 4 (1916).

¹⁴ Barkhausen, *Dissertation*, Göttingen, 1907.

verizing current, provided that these be not too short. This parallelism is shown by the results of this study as indicated in Table VI.

The wave-current circuit with relatively few interruptions shows the least sediment formation, while the Tesla coil with its frequent and protracted interruptions (between each two groups of oscillations) produces the greatest quantity of sediment. In the transformer and induction-coil circuits, the superimposed low-frequency partially closes up, as it were, the interruptions which the high-frequency alone would show, and therefore produces a quantity of sediment between that of the other two circuits.

Although it is not possible at the present time to specify the factors which determine the extent of decomposition of the medium, Table VI demonstrates in a convincing fashion the advantage of the Tesla coil in reducing the specific decomposition. The same advantage is shown in the pulverizations into ether; thus the specific decomposition with the Tesla coils is 0.30, with the transformer is 0.60, and with the induction coil 1.44.¹⁵ Since direct and low-frequency currents lead to great decomposition of organic media, it is probable that the absence of such components in the high-frequency current of the Tesla coil is the cause for the small decomposition accompanying its use.

As has already been pointed out, the net specific decomposition is of greater significance than the specific decomposition, because the former gives a measure of the relative purity of the final sol after the coarsely dispersed portion has settled out and been removed. The last column of Table VI contains the values for this quantity. In spite of the high percentage of sediment, the decomposition of the medium per milligram of finely dispersed, non-sedimenting metal is least for the Tesla coil.

The observations recorded in this paper lead to the conclusion that the Tesla coil arrangement, because of the absence of direct and low-frequency current components in the colloid-forming arc, is superior to any other circuit producing damped, high-frequency oscillations for preparing pure colloid solutions of metals in organic media by electrical pulverization. On account of the complexity of the wave current furnished by the modified Poulsen circuit, no judgment can be rendered concerning the relative merits of damped and undamped, high-frequency oscillations for this purpose until pulverization studies have been made with an apparatus for producing a symmetrical high-frequency current of constant amplitude. Preparations are being made for carrying out such an investigation in the laboratory at Upsala.

Summary

The electrical arrangements which have been used previously for the pulverization of metals in the high-frequency arc suffer from the defect that

¹⁵ Value obtained by Svedberg, Ref. 2, p. 37.

the generation of the high-frequency oscillations is disturbed and modified by the pulverization process which takes place in the same circuit and across the same discharge gap. These two processes are separated in the Tesla coil. In this investigation, a low-voltage type of Tesla coil has been used as a source of damped high-frequency oscillations for the pulverization of cadmium into various liquids. Rates of pulverization, sediment formation and decomposition of the medium have been studied. Parallel studies have been made with a modified Poulsen circuit and with a transformer circuit. It has been shown that the Tesla coil is superior to the other types of circuits studied for the production of colloid solutions with minimum decomposition of the medium, and therefore with maximum purity. A discussion of the possible causes underlying the various behaviors of the different circuits has been given. Particular emphasis has been placed upon the influence of the character of the condenser discharge upon the nature of the oscillatory current produced, and therefore upon the pulverization process.

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THE ELECTROLYSIS OF SODA-LIME GLASS. I EVOLUTION OF GAS AND ITS RELATION TO SORPTION AND CONDUCTIVITY

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Our meager knowledge of the nature of the conduction process in glass has been well indicated by the recent work of several investigators. Poole,¹ for example, found that Ohm's law is not obeyed at moderate temperatures and this would seem to indicate at these temperatures a different process of conduction from the purely electrolytic one occurring at higher temperatures.² Results have also been obtained by Bush and Connell³ which may be interpreted as indicating that the sorbed gases are primarily responsible for the conduction process at ordinary temperatures. We have, therefore, carried out several series of experiments for the purpose of clearing up if possible some of the chemical aspects of the problem and in particular those aspects which have a bearing on the probable behavior of glass in vacuum apparatus such as is now used for many electrical purposes.

Our work has shown that under certain conditions of electrolysis, gas is evolved and this gas is related to the sorbed water. The present paper is

¹ Poole, *Phil. Mag.*, **42**, 488 (1921).

² This has been pointed out by C. A. Kraus, "Properties of Electrically Conducting Systems," Chemical Catalog Co., **1922**, p. 352.

³ Bush and Connell, *J. Franklin Inst.*, **194**, 231 (1922).