

THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME ORGANIC AMALGAMS

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Although ammonium amalgam was first prepared a little over a century ago,¹ it remained until very recently the sole representative of its class. Shortly after its discovery, Davy² concluded that this unique substance was a compound of the pseudometal ammonium with mercury and while this view was shared by many chemists, others believed the so-called amalgam was only mercury inflated with ammonia and hydrogen. The true metallic nature of the substance was finally proved beyond question by the researches of LeBlanc,³ Coehn⁴ and G. M. Smith.⁵ The experiments of LeBlanc also indicated very forcibly the possibility of the existence of substituted ammonium amalgams; and though LeBlanc concluded he had firmly established this point yet the supposed new amalgams had so transient an existence under the conditions of his experiments that they were not isolated and no evidence of their existence, other than that based on polarization potentials, was obtained.

The preparation of two new synthetic amalgams has recently been described.⁶ These new substances are monomethylammonium amalgam and tetramethylammonium amalgam. The first of these is much like ammonium amalgam in its physical and chemical properties. The second differs markedly in several important particulars. As obtained by McCoy and Moore, it appeared as a crystalline mass mixed always with an excess of liquid mercury. It was of characteristic metallic lustre. At a temperature of zero degrees or lower it was fairly stable in the absence of

¹ Seebeck: *Ann. Chim. Phys.*, **66**, 191 (1808).

² *Phil. Trans.*, **100**, 37 (1810).

³ *Zeit. phys. Chem.*, **5**, 467 (1890).

⁴ *Zeit. anorg. Chem.*, **25**, 430 (1900); *Zeit. Elektrochemie*, **12**, 609 (1906).

⁵ *Jour. Am. Chem. Soc.*, **29**, 844 (1907).

⁶ McCoy and Moore: *Jour. Am. Chem. Soc.*, **33**, 273 (1911).

moisture. Chemically it resembles the alkali amalgams, but is far more active than that of sodium. It reacts with water with great energy and rapidly gives hydrogen and the corresponding base, tetramethylammonium hydroxide. From solutions of salts of copper and zinc, these metals are precipitated at once; while from solutions of salts of sodium and potassium the corresponding amalgams are formed. With a solution of ammonium chloride, the characteristic inflated mass of ammonium amalgam is produced. The very high solution tension indicated by these reactions was confirmed by direct potential measurements. The value obtained, for similar conditions was about 0.6 volt higher than that found recently by Lewis and Kraus¹ for sodium amalgam. The properties of the new synthetic amalgams presented so many novel and interesting features that the study of the subject has been continued by us with the results herewith presented.

The first object of the research was to find an improved method of preparation and preservation of tetramethylammonium amalgam which was at the same time the more interesting of the two new bodies and the more difficult to prepare. The method of McCoy and Moore consisted in the electrolysis of an absolute ethyl alcohol solution of tetramethylammonium chloride using a mercury cathode and a silver plated platinum gauze anode. The silver united with, and so prevented secondary actions by, the liberated chlorine. The electrolysis was usually made at zero C or at about -10° to -15° . It was found that absolute alcohol reacted with the amalgam rather rapidly even at zero, about 5 percent being destroyed per minute.² As this action during electrolysis decreased the yield very greatly, we designed a vessel (Fig. 1) in which the electrolysis could be conducted at the temperature of boiling liquid ammonia, -34° . At this temperature, the action of the alcohol on the amalgam was much slower than at 0° C. We also found that a platinum anode

¹ Jour. Am. Chem. Soc., 32, 1459 (1910).

² McCoy and Moore: Loc. cit.

could be substituted for the one of silver, as the chlorine set free no longer attacked the amalgam at this low temperature.

The glass vessel shown in Fig. 1 had outside dimensions of 13.5×5.5 cm. One of the side tubes of the jacket was joined by a rubber tube to a steel cylinder containing 50 pounds of commercial liquid ammonia.

This jacket could be readily filled with liquid ammonia from the steel cylinder. After the vessel had become cold and coated externally with frost, the ammonia boiled away only slowly. The second side tube was joined to two large bottles partly filled with water for the absorption of the waste ammonia gas. The inner chamber of the vessel was closed by a close fitting rubber stopper carrying the electrodes and a tube filled with calcium chloride. The glass tube with the stopcock leading downward from the inner chamber was intended to allow us to draw off the amalgam without exposing it to the air. However, the usual procedure with this apparatus yielded so much solid amalgam that another method of removing the product proved more expedient.

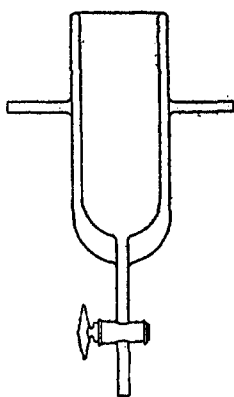


Fig. 1

The preparation of the amalgam was carried out as follows: Seventy-five grams of clean, dry mercury were put into a piece of white muslin, 15 cm square, and lowered into the vessel (Fig. 1). Forty cc of absolute alcohol containing 1.5–2.0 grams of dissolved salt were poured in and the cloth made to stand up snugly against the damp walls of the vessel. The stopper and electrodes were adjusted and the jacket filled with liquid ammonia from the tank. The electrolysis was usually conducted with an E. M. F. of 35–40 volts, which gave a current of 0.3 ampere. After the electrolysis the cloth together with the semi-solid amalgam was then raised above the solution and the alcohol drained off while the whole was still in the electrolysis chamber, the low temperature

of which prevented decomposition of the amalgam. The latter, while still held in the cloth, was rinsed in ice-cold carbon tetrachloride. This liquid has no action on the amalgam and proved very effective in removing the alcohol and preventing decomposition by the moisture of the air. If kept at zero degrees under carbon tetrachloride, the amalgam undergoes but little change in the course of several hours.

As thus obtained, tetramethylammonium amalgam is a semi-solid mass of crystals and excess of liquid mercury, the former being but slightly soluble in the latter. By filtration, with suction, through a plug of cotton, the crystals are easily freed from most of the excess of mercury and the amalgam is left as a solid, crystalline, metallic mass, weighing about 15 grams. During filtration the temperature must be kept at or below 10° and the amalgam protected from the air by a layer of carbon tetrachloride. Unless otherwise stated all experiments in the following pages were made with *solid* amalgam which had been freed from excess of uncombined mercury.

Even at -34° , the use of absolute alcohol as a solvent during electrolysis was not wholly satisfactory. By reason of the action of the alcohol on the amalgam, the yield of the latter was only about 15 percent of that corresponding to the quantity of electricity passed through the cell. In the hope of finding a solvent that would give a better yield than did ethyl alcohol, fifteen other liquids were tried. Those selected were such as dissolved the salt and had high dielectric constants. Only two solvents gave appreciably better results, in some respects, than did ethyl alcohol; even these solvents had their disadvantages. Propyl alcohol acts on the amalgam more slowly than ethyl alcohol, but the solution has a lower conductivity, which necessitates the use of a smaller electrolyzing current. Acetonitril behaves much like propyl alcohol. Very good preparations could be obtained from each of these solvents but no decided advantage was to be gained by using either in place of absolute ethyl alcohol.

Almost all of the experimental work represented by this

paper was carried out in an unheated room which had three large windows on each of two opposite sides. Most of the experiments requiring exposure of the amalgam to the air were made during the winter, so that with open windows, the temperature of the room was usually between 0° and 10° C.

Physical Properties.—The amalgam is a silver-white, granular solid. In its preparation, when the anode has been allowed to touch the cloth, large crystals will usually be found adhering tightly to the outside of the latter. These crystals will stand considerable pressure without breaking and in cold dry winter weather, their crystalline form is maintained for several minutes even though exposed to the air.

Density.—McCoy and Moore had observed that the solid amalgam floats on the excess of mercury and stated that the density of the amalgam is somewhat less than that of mercury. We made determinations at zero degrees of the density of several solid preparations of tetramethylammonium amalgam by the pycnometer method, using carbon tetrachloride as the accessory liquid. The weight of the amalgam alone was in some cases found by direct weighing, with the material exposed to the air, when the weather was very cold and the air dry. An alternative method consisted in weighing a beaker containing amalgam covered with carbon tetrachloride, transferring the amalgam to the pycnometer and finding the weight of amalgam removed by difference. The weight of the bottle filled jointly with amalgam and carbon tetrachloride and again when filled with the latter alone, gave, together with a knowledge of the density of the carbon tetrachloride, the required data.

After each determination, the amalgam was immediately put into water and the weight of the colloidal mercury, thus obtained, divided by the weight of the mercury, was taken as a measure of the concentration of the amalgam present.¹ The following results were obtained:

¹ See McCoy and Moore, *Loc. cit.*

Percent colloidal mercury	Density at 0° C
0.0	13.6 (pure mercury)
1.2	11.8
1.0	11.7
1.0	11.6
2.0	11.1
2.4	10.6

Electrical Resistance.—The electrical resistance was measured by the Wheatstone bridge principle. Three resistance boxes were connected, as in the Post Office box bridge, by means of entirely negligible leads and the lack of balance was detected with a sensitive D'Arsonval galvanometer. Even though the resistance measured was very small, yet with the ratio of 1,000-1 in two of the boxes, the galvanometer was sufficiently sensitive to give an accuracy of one-fifth of 1 percent.

The solid, but somewhat plastic amalgam was put into a funnel that was connected to a narrow U-shaped glass tube and was drawn into the latter by means of a water aspirator. The tube was 37.7 cm long and 0.047 sq. cm in cross section. The entire manipulation was, in each experiment, carried out in a very cold room; during the electrical measurement the temperature of the amalgam was kept at 0° C. The resistance of the wires connecting the amalgam to the boxes was also measured with the ends of the wires placed near together in mercury and this resistance subtracted from the total. The concentration of the amalgam was determined as above from the weight of the colloidal mercury produced when it was added to water. The following results were obtained, the specific resistance being expressed in ohms per linear centimeter and one square centimeter cross section.

Percent colloidal mercury	Specific resistance
0.0	0.000094 (pure mercury)
2.0	0.000110
2.8	0.000110
5.0	0.000131
—	0.000133
—	0.000139

The percent of colloidal mercury was not determined in the last two samples. The leads dipped a short distance below the surface of the amalgam and it was therefore difficult to get at the true length of the column of material. This, together with the difficulty of working with the material, would not make the results given accurate to more than 1 or 2 percent. It is to be observed that the higher the amalgam content, the greater is the resistance, and that the most concentrated amalgam has a resistance about one and one-half times that of mercury.

Electrical Behavior of the Amalgams.—Coehn¹ discovered that ammonium amalgam discharged a charged electroscope, but that the discharge takes place only if the electroscope is charged electro-negatively. We had no difficulty in confirming Coehn's observations on the discharge of negative electricity, and in addition, contrary to Coehn, we found that a small though decisive effect was always produced when the leaf of the electroscope was positively charged. We have also found that organic amalgams have similar properties. Monomethylammonium amalgam discharges both positive and negative electricity, the effect being, as in the case of ammonium amalgam, several times greater with negative electricity. On the other hand, tetramethylammonium amalgam discharges rapidly the positively charged electroscope but has no effect when the electroscope is negatively charged.

The electrical behavior of the last named amalgam is suggestive of that of the alkali metals and their amalgams. It is a well-known fact that many metals give off electrons under the influence of ultraviolet light.² This action is the more pronounced the greater the electropositive nature of the metal. It is small with mercury, but is very marked with sodium and potassium. In case of the alkali metals, a strong source of ultraviolet light is unnecessary, even the light of a kerosene lamp is sufficient, while rubidium is still more sensi-

¹ Zeit. Elektrochemie, 12, 609 (1906).

² Thomson: "Conduction of Electricity through Gases," Chap. X.

tive and gives off negative electricity in the presence of a red hot glass rod. As the electrolytic solution tension of tetramethyl ammonium amalgam is about 0.6 volt greater than that of sodium amalgam and about equal to that of potassium amalgam,¹ we might expect, therefore, that the organic amalgam would lose electrons under similar conditions. An account of our study of the electrical behavior of synthetic amalgams is given in the following pages.

The electroscope used was like that described by McCoy and Ashman,² excepting that there was no condenser, C, nor plate L, to increase the electrostatic capacity. The instrument was one that had been used for several years in this laboratory for the quantitative measurement of radioactivity. The ionization chamber is 20 cm square and 14 cm high; the gold leaf chamber, 9 cm square and 10 cm high. The gold leaf system is insulated by an amber plug and carries at its lower end a circular brass plate or electrode 8 cm in diameter. The motion of the leaf is observed through a pair of glass windows by means of a micrometer microscope. With the aid of two switches and a battery of small dry cells, the leaf could be instantly grounded or charged positively or negatively to about 300 volts. The discharge of the electroscope by an amalgam is most readily distinguishable from that by a radioactive substance in two noticeable particulars: (1) the rate of discharge by the amalgam is erratically variable, (2) it also depends on the sign of the electric charge on the gold leaf system. However, the rate of discharge by an amalgam, though irregular, may be observed and measured in precisely the same way as in the case of a radioactive substance. This rate of discharge may readily be expressed in term of that produced by a standard film of uranium oxide. Such a film, which produced an ionization current of 2.15×10^{-11} amperes as shown by comparison with one of McCoy and Ashman's standards,³ was used

¹ McCoy and Moore: *Jour. Am. Chem. Soc.*, **33**, 289 (1911).

² *Am. Jour. Sci.*, **26**, 521 (1908).

³ McCoy and Ashman: *Loc. cit.*

throughout this work and will be referred to as the "standard." In measuring the rate of discharge, the uranium film or the amalgam held in a shallow platinum dish was placed under the electrode on an earthed metallic support the distance of which below the electrode could be varied up to 8 cm. The micrometer scale of the reading microscope had 60 divisions; the standard discharged the electroscope at the constant rate of 42 divisions per minute. The natural leak amounted to about one-half division per minute.

The behavior of ammonium amalgam may be first considered. We made this amalgam by the electrolysis of an ice-cold aqueous solution of ammonium sulphate. In one experiment 80 grams of mercury were used and a current of 0.3 ampere was run for 10 minutes. When the amalgam was placed in the electroscope and the gold leaf system charged negatively, the rate of discharge was so great that it could not be measured with much accuracy, but was approximately equal to 6 times the uranium standard. After several repetitions of this measurement with concordant results, the gold leaf system was charged positively; the rate of discharge was now much slower but still many times as fast as the minimum that could have been detected with certainty. The rate for the positive discharge was 0.26 that of the standard. At other times three other samples of ammonium amalgam were prepared and studied in the manner just described. The results were in all cases much like those recorded: a small rate of discharge of the positively electrified leaf and a 20-50-fold greater rate for one negatively charged.

The rate of discharge of the electroscope by tetramethylammonium amalgam was studied in a large number of experiments. The detail of a few of these will fully illustrate the nature of the results observed. (1) A sample of the amalgam made in the manner already described and filtered from the excess of mercury was placed in the electroscope on a large platinum crucible lid. The positively charged gold leaf system was repeatedly discharged at a rapid rate. The motion of the gold leaf was very irregular and often

jerky, in notable distinction to the behavior when the discharge is caused by a radioactive substance. Five consecutive determinations of the rate of discharge in terms of that of the uranium standard as unity gave the following figures: 0.6, 1.6, 1.7, 2.9, 2.9, the charge on the gold leaf in all cases being positive. Immediately after the last of the above measurements, the gold leaf system was charged negatively: no discharge took place, although one one-hundredth of the rate shown in the last measurement with a positively charged system could not have escaped notice. After several minutes the sample still discharged a positive charge as fast as the uranium standard. This experiment was made on December 21st and therefore during cold weather, with the room unheated. Although the electroscope used was capable of giving activity measurements accurately to a small fraction of 1 percent, of the standard¹ the erratic variability of the rate of discharge by tetramethylammonium amalgam made it useless to express the results with greater apparent accuracy than they are here recorded. The enormous variation from one determination to another is therefore a real one and is not due to any appreciable inaccuracy of the method of measurement. This was further shown by the fact that substitution of the uranium film for the amalgam led, as is always found, to entirely concordant constant readings for the rate of discharge.

(2) On February 20, 1911, a very good preparation of tetramethylammonium amalgam was made by a current of 0.32 ampere for 1.5 hours. At a room temperature of almost exactly zero the following rates of discharge of the positively charged electroscope were observed: 0.30, 0.16, 0.38, 0.06, 0.19, all in terms of the uranium standard as unity. The gold leaf system was then charged negatively, but no discharge occurred. With a positive charge the following additional rates were observed: 0.41, 0.10, 0.25. The last rate in each of the two series with this sample is much greater than the one immediately preceding it. In each case the

¹ See McCoy and Ashmann: *Loc. cit.*

sample was stirred immediately before the reading was taken. A similar effect was often noticed.

(3) On March 1, 1911, a sample was made by a current of 0.4 ampere for 1 hour. This was filtered and placed in the electroscope. At a room temperature of 6° the following rates of discharge were observed in the six successive determinations made in the course of 4 or 5 minutes: 1.6, 7.0, 1.7, 3.3, 1.4, 0.38.

(4) On May 4, 1911, a current of 0.3 ampere for 2 hours and 5 minutes gave a large yield of amalgam of excellent quality. The filtered product placed in the electroscope at a room temperature of 12° caused discharge of the positively charged gold leaf system at a very great rate, too fast to be measured. No effect was produced when the charge was negative. The large portion of this sample was covered with carbon tetrachloride and kept on ice until later in the day. The balance was used to find the effect on the rate of discharge of the distance between the amalgam and the electrode of the gold leaf system. The charge was positive in all cases. The successive rates of discharge were as follows: Far, 1.8, 0.9; near, 1.8, 0.50; far, 0.14; near, 0.40, 0.14; far, 0.08; near, 0.12. The distances designated as far and near were 3.7 cm and 1.5 cm, respectively. In spite of the fact that the rate was decreasing rapidly, it is easy to see that the effect is greater when the amalgam is near the electrode. The significance of this is discussed later. The portion of the sample kept on ice under carbon tetrachloride was tested after the lapse of about an hour; immediately upon being placed in the electroscope, the rate of discharge was enormous: as close an estimate as could be made indicated an activity 25-30 times that of the uranium standard. This very great activity continued for about 5 minutes. The temperature of the room was 12° at the time.

These experiments show conclusively that tetramethyl-ammonium amalgam causes a discharge of positive electricity only. The rate of discharge is irregular for a given preparation under constant conditions and varies from one

preparation to another. Temperature has an enormous effect on the activity of the amalgam. Thus in experiments 2, 3, and 4, the room temperatures were 0, 6, and 12 respectively and the maximum rates of discharge 0.38, 7.0 and 30 times the standard.

A large crystal that had been found adhering to the outside of the cloth on a cold, dry, winter day was placed in the electroscope. It showed no signs of decomposition for several minutes and it also had no effect on the charged leaf. It then slowly began to show evidence of decomposition and also began to have a slight effect on the leaf which increased to about 0.1 the rate of the standard and continued thus for several hours. This seems to indicate that the phenomenon is not an intrinsic property of the crystalline amalgam but is concomitant with its decomposition. On the other hand it was frequently found that after the electrical activity had entirely ceased, the residue would give colloidal mercury with water, showing that decomposition was not yet complete.

With a positive charge on the leaf, the amalgam discharges the electroscope very similarly to a true radioactive substance. There is not the slightest doubt, however, that the phenomenon is not one of radioactivity. A radioactive substance discharges both positive and negative charges at the same rate; moreover this rate is not erratically variable and is not affected by temperature. An additional fact also differentiates the phenomenon from that due to radioactive ionization: for the production of the maximum ionization current, a given radioactive substance must be at least a certain distance from the electrode. This minimum distance is the range¹ of the alpha rays of the substance. If the radioactive film is much nearer the electrode than the distance represented by the range of its alpha rays, its rate of discharge is much less than the maximum. For moderate distances greater than the range the ionization current is not appreciably lower than the maximum. In experiment 4

¹ Bragg: *Phil. Mag.*, [6] 8, 726 (1904).

above we found that the rate of discharge by the amalgam was greater at 1.5 cm than at 3.7 cm. As the ranges of the alpha rays of radioactive substances lie between 2.6 cm and 8.0 cm this is further evidence of the difference between the behavior of the amalgam and a radioactive substance.

The facts so far mentioned indicate either (1) the liberation by the amalgam of electrons with velocities too low to cause ionization of the air or (2) the production of an electro-negatively charged gas. Since the escape of electrons from a metal is enormously accelerated by the action of ultraviolet light, we next studied the behavior of the amalgam in this respect.

The effect of daylight on the rate of discharge of the electroscope by tetramethylammonium amalgam was shown by the following experiments. A large quantity of solid amalgam was placed in the electroscope and the door of the ionization chamber left open and directed toward the window of the room. The rates of discharge were 0.30 and 1.7 times the standard. The brass door of the ionizing chamber was then closed, thus leaving the amalgam in total darkness, and the following rates of discharge observed: 1.6, 2.9 and 1.1. The experiment shows that the phenomenon occurs in the dark as well as in the light. In fact many of the results already recorded were obtained when the amalgam was in complete darkness. In several experiments, magnesium ribbon was burned close to the open door of the ionization chamber and the light, rich in ultraviolet rays, allowed to fall upon the amalgam; but no acceleration of the rate of discharge was produced.

A more elaborate study of the effect of ultraviolet light on the behavior of tetramethylammonium amalgam was greatly facilitated through the generous coöperation of Dr. J. R. Wright, of Ryerson Physical Laboratory of this University. At the time we were engaged in this research, Dr. Wright, working with Professor Millikan, was investigating the effect of ultraviolet light upon aluminium. Dr. Wright's paper on the results has just appeared in the

Physikalische Zeitschrift, 12, 338 (1911) under the title: "The Positive Potential of Aluminium as a Function of the Wave Length of the Incident Light." For his own work Dr. Wright had a very powerful source of ultraviolet light produced by the spark discharge between zinc electrodes in parallel with eight Leyden jars and operated by the secondary current of a Seidel transformer, through the primary of which a current of 10 amperes at 25 volts was passed. Dr. Wright's installation also included a Dolezalek quadrant electrometer with the wires leading to it surrounded by earthed brass tubes. As this apparatus was admirably suited for the purpose of testing the effect of ultraviolet light on our amalgam we were very glad to have the privilege of its use in making the following experiments. For his courtesy in this respect and for his valued coöperation in the experiments we wish to express to Dr. Wright our sincere thanks.

The immediate object of our experiments was to find the nature and potential of the charge which the amalgam when insulated and in contact with very cold, dry air might acquire under the influence of ultraviolet light. From the electro-scope experiments, we should expect such a charge to be electropositive. This also would be in accord with the behavior of the alkali metals.¹ The insulated amalgam was connected to the quadrant electrometer by a wire which passed with sulphur insulation through a brass tube 6 cm in diameter. The terminal of this wire together with the amalgam and its support were shielded from the spark by means of large sheet metal screens. One of these screens had an opening 2×4 cm which was covered by a piece of cardboard having an opening 2 mm square. The light from the spark passed through this opening and illuminated the amalgam. The needle of the electrometer was charged to 120 volts and held its charge perfectly for hours. One pair of quadrants of the electrometer was earthed; a charge of

¹ Thomson: Loc. cit.

1 volt on the other pair gave a scale deflection of 3.4 cm. When the amalgam was absent and the spark going, the agitation of the needle due to static effects was not over 1 mm on the scale. In the preliminary experiments the amalgam rested on a watch glass supported by a vulcanized rubber stand.

Before making an experiment, all four quadrants of the electrometer were earthed; when all was ready, the earth connection of one pair of quadrants was lifted and this pair connected to the amalgam, appropriate switches being used. In all cases the amalgam took on a positive charge; a maximum potential of about 2.4 volts was usually reached in a few minutes. There was some doubt, however, whether the result was due to the ultraviolet light. It seemed possible that the amalgam might have acquired a positive charge spontaneously in the absence of the light.

In the final experiments the amalgam was contained in the glass tube represented by Fig. 2. This tube was 9 by 1.3 cm and had a small side tube closed with a quartz glass window. The spark passed through the 2 mm opening in the screen and through the quartz window and illuminated the amalgam. During an experiment, the lower part of the tube holding the amalgam was surrounded by ice and water.

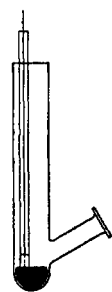


Fig. 2

The first trial with the amalgam in the tube Fig. 2 was begun before the spark was started. During the first 3 minutes, the positive potential of the amalgam rose slowly to 0.2 volt; the spark was now started and allowed to illuminate the amalgam. It seemed to have no effect on the rate of increase of potential. It was soon turned off without noticeable effect, for the amalgam continued to increase in positive potential until the electrometer deflection indicated 2.7 volts. In three subsequent trials in which the spark giving the ultraviolet light was not running, the amalgam took on potentials of 2.7, 2.8, and 3.8 volts respectively. The maxima were usually reached in 5-10 minutes. The

charge on the amalgam was positive in all cases. These results made it clear that the taking on of a positive charge by an insulated portion of tetramethylammonium amalgam is a spontaneous action which is not caused by the illumination with ultraviolet light. However, it is still possible that the ultraviolet light may be able to cause a smaller additional effect, which in our experiments in which the light also acted was masked by the larger spontaneous one.

The acquirement of a positive charge by the insulated amalgam can only mean that it loses spontaneously negative electricity. This fact is in complete accord with that of the discharge of the positively charged electroscope in the presence of the amalgam. The carriers of the negative electricity given off by the amalgam may be either (1) electrons or (2) ions, consisting of electronegatively charged molecules or larger groups or in general terms an electronegatively charged gas.

Photographic Experiments.—The difference between the activity of tetramethylammonium amalgam and that of the typical radioactive element uranium was clearly shown by the behavior of each toward photographic plates. For the experiments, Lumière Sigma dry plates were used. (This make is known to be rapid.) These were exposed with all usual and necessary precautions for known periods to the action of the rays from a quantity of uranium oxide which discharged the electroscope about as fast as the average sample of the amalgam. A plate exposed to the uranium oxide for 15 minutes showed distinctly a uniform black spot of the same size as the 3 cm hole in the piece of sheet iron which shielded the balance of the plate from the action of the alpha and beta rays of the uranium. Longer exposures gave blacker spots. One of the same kind of plates was also exposed, under strict photographic conditions, to the action of the amalgam in place of the uranium, all else being the same. Seven preparations of solid (filtered) amalgam were allowed to act on the plate successively in the course of 12 days. The total weight of the solid amalgam so used was 115 grams;

its preparation had required a total of 4.85 ampere hours. Upon development, this plate was found to be "fogged" in the centre, the intensity being about equal to that caused by 30 minutes' exposure to the uranium. The "fogged" portion of the plate was not sharply defined, corresponding to the hole in the sheet iron, as in the case of exposure to uranium rays. This fact suggested some other cause than the action of a radiation from the amalgam: possibly the dim red light used in the dark room or the action of mercury vapor during the long exposure. The first possibility was excluded by the fact that plates exposed to the red light for much longer periods than the total possible exposure to the same source in the amalgam experiment showed no effect at all upon development. On the other hand, a plate exposed for 13 days to the action of pure mercury under the same conditions as used in the case of the amalgam showed a distinct circular spot, fully as dark, if not darker, than that on the plate which had been exposed to amalgam. These experiments show clearly that the apparent photographic action of the amalgam was due simply to mercury vapor and that the amalgam has no photographic activity.

The experiments on the electrical behavior of the amalgam and the fact that this was not influenced by ultraviolet light, together with the negative results of the photographic experiments, are all best explained by the assumption that the amalgam gives rise to an electronegatively charged gas. In the electroscope, the electronegative ions are attracted to the positively charged electrode and so discharge the gold-leaf system. On the other hand, the negative charge of the ions comes from the amalgam; so that, if the latter is insulated, as in the quadrant electrometer experiments, it acquires a positive potential. The cause of the electrification of the air or gas is not certain although the following explanation seems probable. It is shown (in the following section) that the spontaneous decomposition of the dry amalgam gives, besides mercury, trimethylamine and hydrocarbon gases, from 40-60 cc resulting from a single prepara-

tion. Now Lenard¹ has found that air bubbled through or shaken with mercury becomes negatively electrified. From this, it would seem very probable that the gases formed by the decomposition of the amalgam would escape from the interior of the mass in an electrified condition. It might seem that this explanation would require that the gas from every amalgam should have the same kind of electrification, whereas this is not the case. However, it is not improbable that mercury may behave like water which electrifies gases bubbled through it either negatively or positively according to the nature of the solution and the gas.² The fact already mentioned that the amalgam does not lose electricity except when it is decomposing is further evidence in favor of this view. Also the fact mentioned in an earlier paragraph that the rate of discharge of the electroscope by the amalgam is greater when the latter is near the electrode is entirely in accord with the view that a charged gas is given out by the amalgam, since, under such conditions, fewer of the gaseous ions will fail to reach the electrode. The effect would be very different if a radiation capable of causing ionization were given out by the amalgam. Further evidence in this direction is also furnished by the following experiment.

A very good preparation of the amalgam that had been obtained with a current of 0.5 ampere for an hour and a half was freed from excess of mercury and put in a small crystallizing dish, $3\frac{3}{4}$ cm in diameter and $1\frac{1}{4}$ cm high, and placed in the electroscope with the gold leaf system charged positively. The discharge rate was 0.63 of the standard. A piece of aluminum leaf 0.0044 cm thick was now quickly sealed with wax over the mouth of the dish. The covered amalgam had no effect whatever on the positively charged gold leaf system. The aluminum leaf was now removed and the amalgam again placed in the electroscope. The discharge rate was 0.19 of the standard. A second trial with the

¹ Wied. Ann., 46, 584 (1892).

² Kelvin: Proc. Roy. Soc., 57, 335 (1894). Kusters: Wied. Ann., 69, 12 (1899).

aluminum leaf over the amalgam resulted like the first, and when the leaf was again removed the discharge rate was 0.33 of the standard. This experiment was repeated on several different occasions with other preparations of amalgam with exactly similar results. It is thus seen that the charged particles that arise from the amalgam can not pass through aluminum leaf of the thickness used. On the other hand, this aluminum leaf would absorb only a small fraction of a beta radiation such as that of uranium, but would completely prevent the passage of gaseous ions of all sorts.

The carriers of electricity or the ions of a gas electrified by bubbling have much smaller velocities in an electric field and much smaller speeds of diffusion than have ions produced by radioactive radiations. The former sort of ions are therefore much more persistent than the latter so that the gas remains charged for a relatively long time. It also retains much of its charge after passing through glass-wool, etc. The following experiments show that the negative electrification of the gas from tetramethylammonium amalgam is present as persistent ions. The rate of discharge of the electroscope by a sample of amalgam contained in a porcelain boat was determined in the usual way. The boat and amalgam were then brought into a straight "calcium chloride tube" outside of the electroscope and a current of air blown over the amalgam and into the electroscope, the air emerging near and toward the electrode, and the rate of discharge again noted. As a mean of four such independent experiments, it was found that the rate of discharge was 95 percent as great in the second case as in the first. In a similar experiment in which uranium oxide was substituted for the amalgam, the rate of discharge by the air current was only 28 percent of that when the uranium was in the ionization chamber. It was also found, in several trials, that an appreciable part of the electrification of air blown over the amalgam would pass through a 6 cm layer of glass wool or a narrow copper tube 30 cm long and 0.2 cm in diameter, while

if the path of the air current included both of these the electrification was all removed.

In beta ray radioactive changes, at least one electron is liberated by the disintegration of each atom. It is easy to calculate roughly how much electricity is contained in the electrified gas produced during the decomposition of the amalgam and to compare this quantity with that if each molecule of the amalgam decomposed gave off one electron. A quantity of amalgam, the decomposition of which would yield 50 cc of gas of which 29 cc would be trimethylamine, would on the average discharge the positively charged electroscope at a rate equal to that of the standard for a period of about 10 minutes. Since the standard produces an ionization current of 2.15×10^{-11} amperes and 1 cc of a univalent gas would represent 4 coulombs, it follows that only one electron is given off for every 10^{10} molecules of amine gas formed! This fact is itself sufficient to show that this phenomenon has nothing in common with that due to a radioactive transformation. If a few drops of water be added to the amalgam while it is in the electroscope, with the gold leaf system positively charged, the discharge becomes very rapid for about 1 minute and then suddenly stops. The duration of the rapid discharge depends on the quantity of amalgam present and it is a particularly significant fact that the rate of electrical discharge is evidently dependent on the rate of decomposition of the amalgam.

The action of water on tetramethylammonium amalgam gives hydrogen and tetramethylammonium hydroxide.¹ In the absence of water the amalgam decomposes spontaneously giving a mixture of gases having the intense fishy odor, characteristic of trimethylamine. The speed of decomposition varies greatly with the temperature. At zero it is very slow; at 25° it is much faster, the decomposition being practically complete in about an hour. A quantitative velocity determination was made by the use of a Lunge gas burette fitted with a water jacket through which water at the

¹ McCoy and Moore: Loc. cit.

constant temperature of 27° flowed. A quantity of the amalgam, made and washed as usual but not filtered, was freed from carbon tetrachloride as thoroughly as possible by means of filter paper and brought into the burette. Before introducing the amalgam, the burette and leveling tube were carefully dried and filled with dried mercury. As time went on, the amalgam began to decompose and the gas to accumulate in the burette over the amalgam; its volume at atmospheric pressure was read off at frequent intervals with results as shown in the following table:

VELOCITY OF DECOMPOSITION OF DRY TETRAMETHYLAMMONIUM AMALGAM AT 27° , K' AND K BEING CALCULATED BY THE MONOMOLECULAR FORMULA

Time in minutes	Volume of gas formed cc	K' $t_0 = 8 \text{ min.}$	K $t_0 = 13 \text{ min.}$
0	0.0	—	—
8	2.0	—	—
9	2.8	0.060	—
11.5	5.5	0.083	—
13	7.2	0.094	—
15	9.5	0.110	0.155
17	11.3	0.124	0.161
19	12.7	—	0.168
21	13.5	—	0.163
23	14.1	—	0.160
25	14.5	—	0.155
29	15.0	—	0.145
33	15.5	—	0.160
46	15.75	—	—
56	15.85	—	—
			Mean, 0.158

During the washing and drying of the amalgam and its introduction into the burette, it was kept as cold as possible. Its temperature at the moment it was inclosed was therefore far below that of the water jacket, 27° . It must have required considerable time (perhaps 10 minutes or more) for the amalgam to have reached this higher temperature. For this reason the velocity constant, K , of the rate of decom-

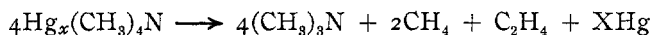
position was calculated from the time 13 minutes after the start. A calculation based on the 8th minute as zero gave the values under the heading K' , $t_0 = 8$ minutes. The results after the 13th minute show that the reaction is monomolecular. The initial velocity is very low, owing to the low temperature of the amalgam at the start. A second disturbing factor at the start was due to the fact that the gas did not separate from the amalgam readily, due no doubt to its being present in the minute bubbles. This resulted in a swelling of the material without the appearance, for several minutes, of a gaseous layer. Two additional velocity determinations under similar conditions gave results essentially like that just discussed. In an attempted velocity determination at 0° , no gas had separated in the course of 4 hours, although some increase of volume of the amalgam seemed to have taken place. At the end of the 4th hour, the temperature was raised to 25° whereupon the decomposition occurred as usual and was complete in the course of an hour. The amalgam used in this experiment had been prepared by a current of 0.21 ampere for 1 hour and 50 minutes; the amount of mercury used was about four times the usual amount, the object being to obtain a more fluid product than usual.

The gas obtained by the spontaneous decomposition of this sample of amalgam measured 63.4 cc. It was transferred quantitatively to another burette over mercury and a known volume of 0.1 normal HCl introduced. The basic portion of the gas was absorbed by the acid solution; the volume remaining was 26.5 cc, corresponding to an absorption of 58.2 percent. In several analyses, the uncombined standard acid was titrated and a comparison made with the shrinkage in volume when the acid was added. For instance, in another experiment 40.15 cc of gas shrank to 16.1 cc when the acid was added. The shrinkage was thus 24.05 cc. The titration of the uncombined standard acid showed 9.47 cc to have been neutralized by the 24.05 cc of gas absorbed. If this gas were univalent, it should have required 9.53 cc of the standard acid. Similar measurements in other analyses gave equally

concordant results, and show that the gas absorbed is a univalent amine or a mixture of such amines.

The solutions of the amine hydrochlorides from several determinations were united, made alkaline with caustic soda and the amines distilled off and absorbed in water. The solution was neutralized with hydrochloride acid, treated with platinic chloride and alcohol and the resulting yellow precipitate washed thoroughly with absolute alcohol.¹ In the analysis of the substance, 0.1308 gram gave upon ignition 0.0470 gram of platinum, equal to 35.93 percent; trimethylamine chlorplatinate requires 36.94 percent. Dimethylamine and monomethylamine chlorplatinate require 39.0 and 41.32 percent of platinum, respectively. In spite of the somewhat low value found, there is little doubt that the gas is trimethylamine.

The gas insoluble in the standard acid was analyzed by means of the usual Hempel apparatus; 14.05 cc of it was exploded with 41.4 cc of pure oxygen. After the explosion 27.4 cc of gas remained. This consisted of 16.16 cc of carbon dioxide, soluble in 30 percent KOH, and 11.24 cc of oxygen soluble, excepting a minute bubble, in alkaline pyrogallol. These results indicate that the decomposition of the tetramethylammonium radical occurs as follows:



This reaction would give 57.1 percent by volume of trimethylamine while the experiment described gave 58.2 percent of soluble gas and the average for 8 additional experiments was 58.3 percent. Each cc of the amine-free gas should require 2.33 cc of oxygen and produce 1.33 cc of carbon dioxide. This particular experiment showed 2.15 cc and 1.15 cc respectively while the mean of four such determinations gave 2.21 cc and 1.20 cc, respectively. Theoretically also each cc of the amine-free gas should require an equal volume of oxygen to unite with the hydrogen of the methane and ethylene; in the experiment the oxygen consumed, in excess

¹ Eisenberg: *Liebig's Ann.*, 205, 142 (1880).

of that needed for the carbon, was 1.01 cc per cc of original gas. However, a more thorough study of the decomposition products will be necessary before the reaction suggested can be considered as definitely established.

Monomethylammonium Amalgam.—McCoy and Moore made this amalgam by electrolysis of both aqueous and alcoholic solutions of its salts and made potential measurements with it just as with tetramethylammonium amalgam. In the attempt to increase the yield we tried a large number of additional solvents. There was amalgam formation in methyl alcohol and glycerol solutions as well as traces in some of the others. Although the current is small with the glycerol, the crystalline character of the amalgam is well marked. However, water as solvent gives the best results. The amalgam decomposes rapidly in all cases during the electrolysis giving off a gas with a strong ammoniacal odor, obviously monomethylamine. While the current is on, a dense white cloud persists in the electrolyzing chamber. Neutral liquids, such as carbon tetrachloride or benzene, exercised no protective action on the amalgam nor did low temperatures appreciably increase its stability. A fair preparation was obtained in one experiment at 75° and that made at -34° was little if any superior to the one obtained when the temperature was kept at 0°.

Monomethylammonium amalgam increases greatly in volume as it undergoes spontaneous decomposition, in which respect it closely resembles ammonium amalgam. In each case the compact amalgam constitutes without doubt the alloy with mercury of the metallic form of the radical, while the distended material is only mercury inflated with the gaseous decomposition products. As stated in the introduction, monomethylammonium amalgam discharges the electroscope when the latter is charged either positively or negatively, the rate being several times greater for a negative charge. In several experiments a rate of discharge 3-4 times that of the uranium standard was observed for a negative charge on the gold leaf. The effect of the distance of

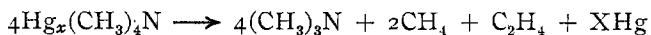
the amalgam from the electrode of the electroscope was tried as in the case of tetramethylammonium amalgam. In one such experiment the rate was 1.6 times the standard for a distance of 1.5 cm and 0.8 for 3.7 cm, the leaf being negatively charged.

Summary

(1) An improved method of making tetramethylammonium amalgam has been worked out, and the substance obtained in solid form. Determinations of its density and electrical resistance have been made.

(2) The amalgam causes the discharge of a positively charged electroscope, behaving in this respect like a radioactive substance. That the phenomenon is not one of radioactivity was shown by the following facts: a negatively charged electroscope is not discharged; the rate of discharge of a positive charge is erratically variable, temperature having an enormous effect; the rate is greater when the amalgam is closest to the electrode of the electroscope, thus showing the absence of an ionizing radiation. A thin aluminium leaf placed over the amalgam prevents the discharge and so proves the absence of a beta radiation. The same conclusion is supported by the fact that the amalgam has no photographic activity. The phenomenon is distinguished from that shown by the alkali metals in that it is not appreciably influenced by ultraviolet light. The facts here summarized as well as some others of minor importance are best explained as follows: The amalgam decomposes spontaneously into mercury and gaseous products. The gas escaping from the mercury in minute bubbles is negatively electrified, just as in the case of air bubbled through mercury as shown by Lenard. The ions of the negatively charged gas cause the discharge of the positively charged electroscope.

(3) The spontaneous decomposition of the amalgam which takes place very slowly at 0° but quite rapidly at 25° seems to occur according to the equation:



The fact that a velocity determination of the speed of decomposition showed the reaction to be monomolecular indicates that the change takes place in stages.

(4) The method of preparation and the properties of monomethyl amalgam were also studied.

(5) The further study of the properties of organic amalgams, as described in this paper, has served to support the hypothesis that free radicals, formed by the electrical neutralization of the positive ions of salts, would have metallic properties.¹

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University of Chicago, Dec., 1911*

¹ McCoy and Moore: Loc. cit. McCoy: Science, 34, 138 (1911).