THE DISTILLATION OF AMALGAMS AND THE PURIFICATION OF MERCURY.

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Distillation of Amalgams.

In a previous article,[1] it was shown that measurable quantities of some of the common metals distil over with the mercury vapor when they are present with the mercury in the still. It seems that in the distillation of amalgams, just as in the case of other liquid mixtures, that a complete separation is impossible. It was found, however, that when a little air was allowed to pass over with the mercury vapor during the distillation that most metallic vapors were odixized while mercury vapor was not affected. On distilling zinc amalgams with a little air bubbling up through the mercury and passing over with the vapors, no zinc was detected in the distillate although we were able to detect one part of zinc in 10^{10} parts of mercury.[2] Zinc amalgams were also distilled in an ordinary Weinhold still where the air was all displaced by mercury vapor and the distillation was carried on in a space which was free from all gases except mercury vapor. Under these conditions it was always possible to detect zinc in the distillate, even when there was only a trace of zinc in the mercury in the still.

The above experiments suggested that all readily oxidizable metals such as zinc, cadmium, bismuth, tin, copper, lead, etc., might be effectively removed by one distillation. The simplest method of accomplishing this result was to use an ordinary distilling flask with suction and so arranged that a little air bubbled through the mercury in the still and passed over with the vapors. This arrangement, just as for other liquids, prevented the troublesome bumping and spurting of the mercury.[3] The distillation was carried out in a flask where the air pressure was about 25 mm. or about 5 mm. partial pressure of oxygen, and the temperature was about 200° C. Any metallic vapor will completely oxidize under these conditions if the dissociation pressure of its oxide is less than the partial pressure of the oxygen maintained in the still. This is eminently true

[1] Phys. Rev., 21, 288.

[2] L. c., p. 391.

[3] The bumping does not seem to take place with mercury when the air is all removed, as in the case of the Weinhold still, but is very troublesome when a little air is present except when it is bubbled through the mercury.

of all the common base metals. These oxides collect on the distillate and when they are present in considerable quantity as in the case of quite impure mercury, the distillate may then look dirty but when filtered through a pinhole in a filter paper is found to be free from the metals, provided sufficient air passes over with the vapors.

Mercury vapor does not seem to oxidize under the conditions given above since kilograms of pure mercury may be distilled without a suggestion of oxide appearing on the top of the "Sprengle" column (Fig. 2), while the merest trace of oxide is very noticeable. When the partial pressure of the oxygen is much more than 5 mm., mercury oxide appears. The work of Pelabon[1] indicates a very low dissociation pressure of mercury oxide at 200° C., but this is an extrapolated value and may be considerably in error. The oxides of silver, gold and the platinum metals would not form under the conditions in our still so their vapors would condense with the mercury vapor and be found as amalgams. On the other hand the vapor pressure of these metals must be very small at 200° C. as their melting points are 960° for silver, 1063° for gold and 1750° for platinum, furthermore the partial pressures of these vapors from dilute solutions in mercury would be even less than the vapor pressures of the metals themselves and it was hardly to be expected they would distill over in detectable quantities, however, it seemed well to test this conclusion experimentally.

Silver amalgams were first studied. A still, such as is described below, was charged with 6,800 grams of pure mercury and 35 grams of purest silver. It was thought that this would form a saturated solution at 200° as the solubility of silver in mercury is very small. This amalgam was distilled with a slow current of air passing through the amalgam in tiny bubbles and there was no suggestion of bumping or spurting. The fact that oxidizable metals are completely removed by one distillation in this apparatus is evidence that none of the amalgam in the still is mechanically carried over as a spray. The residue left in the still was a white sponge of silver which contained some mercury. The distillate was brought into a clean flask and distilled again, there was a small residue of silver sponge about 5 mm. in diameter left in the still together with several white spots distributed about the lower part of the still. These residues were dissolved in a little nitric acid and the solution sucked up into a little specially made pipette and then transferred to a small weighed porcelain crucible. The flask was thoroughly washed with a little water which was removed with the pipette and this washing repeated several times. The solution and washings were evaporated and

[1] C. R., 128, 825.

glowed and then heated to the melting point of silver to expel the mercury. 12.7 milligrams of silver was recovered and as this amount distilled over with 6,775 grams of mercury it appears that the distillate contained one part of silver to 533,000 parts of mercury or not quite two parts in a million when distilled from a saturated silver amalgam. This distillate had furnished a second distillate which was redistilled and a residue amounting to .19 milligrams of silver was obtained so the second distillate contained some .03 parts of silver in a million. The third distillate left no visible residue on distillation. It would therefore appear to be necessary to distill mercury at least three times if it contains silver and it is quite impossible to entirely remove silver from mercury by chemical means or any other method. It was noticed that mercury containing these small traces of silver very readily became "dirty" when agitated and was noticeably different from pure mercury in its behavior.

A gold amalgam was next distilled. 6,750 grams of mercury from the above experiment was brought into the still together with 45.5 grams of pure gold which had been electrically refined. This amalgam was distilled as above, the gold was left behind as a beautiful sponge which contained some mercury. The distillate was redistilled and left a distinct gold stain in the bottom of the still which was about 4 mm. in diameter, together with several smaller stains. These stains were dissolved in a little aqua regia, evaporated, glowed and found to weigh .18 milligrams. This gold was dissolved and determined colorimetrically by the method of T. K. Rose.[1] The color obtained was slightly less than that given by .2 mg. of gold in the same volume but the comparison was not particularly sharp. Evidently the weight obtained was reliable so the distillate from a saturated gold amalgam contains .027 part of gold to a million of mercury. The second distillate left a barely visible residue of gold which was colorimetrically determined to be very much less than .01 mg.

6,700 grams of mercury were now brought into the still together with 12.25 grams of platinum foil. This was ordinary foil which had been etched with aqua regia and then glowed. Soon after the distillation began the foil amalgamated and sank to the bottom of the still. The 12.25 grams of platinum was much more than was necessary to saturate the mercury at 200° and it was largely left behind as foil at the end of the distillation. The last of the mercury clung to the platinum foil and as it distilled the foil assumed the appearance of having been platinized. The solubility of platinum in mercury at 200° is evidently very small but the mercury was at all times saturated with platinum and must have had

[1] Chem. News, 66, 271.

a partial pressure of platinum equal to the vapor pressure of platinum at the same temperature. The distillate was redistilled and left a very distinct stain of platinum which was collected as above, evaporated glowed and again dissolved in aqua regia. It was found by a colorimetric method to be .067 mg. of platinum. If a little stannous chloride is added to an acid solution of platinum a clear golden color is obtained when the platinum concentration is very small. This color is very stable and can be quite exactly duplicated with solutions containing known amounts of platinum. It appears therefore that mercury which distills from a platinum saturated amalgam at 200°, contains one part of platinum to one hundred million parts of mercury. The 6,700 grams of mercury distilled as a vapor occupied, at 200° and 25 mm. pressure, 39,540 liters and the .067 mg. of platinum in this volume would show a partial pressure of .00000026 mm., assuming that platinum, like the other metals is monatomic in the gaseous state. This figure then represents the vapor pressure of platinum at 200°, since the amalgam in the still was saturated with platinum. This is of course only to be regarded as giving the order of magnitude of this constant, but with proper precautions there seems to be no reason why a fairly reliable value for the vapor pressures of these metals might not be obtained in this way. If we take the value for the number of atoms in a cubic centimeter of a gas at standard temperature and pressure,[1] a calculation shows that with each cubic centimeter of mercury vapor which passed out of the still there were 5.3×10^9 atoms of platinum. From this then each cubic centimeter of space or gas which is in equilibrium with platinum at 200° contains some five billion atoms of platinum.

THE PURIFICATION OF MERCURY.

Mercury is one of the indispensable things in scientific work. Some properties which render it especially useful are its density and that it is a liquid with a negligible vapor pressure while gases are insoluble in it. Mercury is acted upon chemically by but a few substances and, due to its position in the voltaic series, it may be used in contact with most salt solutions and so has played a fundamental role in the development of electrochemistry. Mercury does not oxidize readily under ordinary conditions although the dissociation pressure of mercury oxide is very small at ordinary temperatures.[2] Evidently it is a question of rate for pure mercury will remain bright in contact with air or oxygen almost indefinitely but a little ozone soon causes the mercury to tarnish, also the presence of the merest traces of metals dissolved in mercury cause it to

[1] Millikan, PHYS. REV., 32, 396.

[2] Pelabon, C. R., 128, 825.

tarnish and readily assume the form of very small globules which do not coalesce with the main mass and so the mercury acquires a "dirty appearance" and wets or sticks to glass and other substances. It is assumed that the base metal oxidizes and forms a coating about the little mercury globules but the effect may be obtained when silver, gold or platinum are dissolved in mercury. It is quite possible that the foreign metals catalyse the oxidation of the mercury. The fact is that the merest traces of foreign metals have a most remarkable effect on the physical properties of mercury and very seriously interfere with its use in scientific instruments and investigations so it is necessary to have mercury of a higher degree of purity than any other substance we work with as evidenced by the very large number of methods which have been proposed for purifying mercury.

The chemical methods depend upon the property of most metals to displace mercury from solutions. When an amalgam is brought into contact with a solution which contains mercury, the metal in the amalgam will displace mercury from the solution, but these are reversible reactions and even in the case of such electropositive metals as zinc and cadmium the removal from mercury cannot be complete and to a much less degree in the case of such metals as copper, lead and tin which are much nearer mercury in the voltaic series while there is little to be gained in the case of such metals as silver, gold and platinum by the chemical methods and acid solutions. If we treat mercury or dilute amalgams with an oxidizing acid mercury goes into solution and we have a solution containing mercury, and while some of the base metal is directly oxidized, most of it simply displaces the mercury in solution. Making mercury anode in acid or salt solutions[1] leads to the same result. In cyanide solutions mercury as anode might loose some metals more completely than in acid solutions.[2]

The well-known apparatus of L. Meyer,[3] is a most convenient and effective device for the chemical purification of mercury. The mercury flows in a thin stream through a long column of dilute nitric acid, or better a nitric acid solution of mercurous nitrate and is delivered bright and dry. This apparatus was noticeably improved by J. H. Hildebrand,[4] by a modification which allows the mercury to flow faster and still to divide into much finer globules. If an outlet tube with a glass cock is sealed into the lower part of the bend in the "goose neck" the last of the mercury and the solution may be run out separately and the appa-

[1] Jaeger., Wied. Ann. 48, 209, 1893.

[2] Battel, Chem. News, 97, 158.

[3] Zeit. anal. Chem., 2, 241.

[4] J. Amer. Chem. Soc., 31, 933 and C. J. Moore, Jour Amer. Chem. Soc., 32, 971.

ratus may be easily cleaned even when it is fastened in a permanent position. Mercury left in contact with nitric acid or mercurous nitrate solution slowly forms basic salts which are insoluble and troublesome.

The method proposed by Crafts[1] of drawing air through a long column of mercury, causes some oxidation of the base metal. It also causes a great deal of the mercury to become finely divided. We caused filtered air to bubble through a dilute cadmium amalgam (1 in 10,000) at the rate of 3 cc. per minute for four days and were able to detect cadmium in the mercury after this treatment. It is less effective than the chemical method and not as convenient.

The chemical purification of mercury is sufficient for many uses and it is a very simple and convenient operation with the V. Meyer apparatus. The chemical purification may also be effectively carried out by bringing the mercury and an acid solution of mercurous nitrate into a separatory funnel and vigorously shaking for several minutes. The mercury is then run into a second separatory funnel which contains water and from thence onto a filter with a pinhole. The chemical purification should precede the distillation so as to avoid undue clogging of the still.

The only way to effectively remove metallic impurities from mercury is by distillation and from the results given in the first part of this paper, it would seem to require two or three distillations if silver, gold or the platinum metals are present. Silver is distinctly the most difficult to remove. In the case of such metals as zinc, cadmium, lead, tin and bismuth which have a very low melting point and greater vapor pressures, it would take many distillations to satisfactorily remove these metals if the distillation was carried out in a vacuum or a reducing atmosphere. An ingenious apparatus for distilling mercury in a vacuum was devised by Weinhold[2] and modified by many other investigators. The arrangement is such that all the gases are removed by the mercury vapor and the distillation is also continuous. After the mercury vapor removes all other gases the distillation proceeds quietly and satisfactorily but we have found[3] that low melting metals like zinc distil over with the mercury and may be detected in the distillate even when there is only a trace of the metal in the mercury in the still.

We have found, however, that all oxidizable metals may be effectively removed by a single distillation if a little air is allowed to bubble through the amalgam in the still and pass over with the mercury vapor. It appears that the oxidation of the base metal occurs in the vapor phase and not to any extent while the air is bubbling through the amalgam in

[1] Bull. Soc. Chim., Paris, 49, 856.

[2] Carls, Repertorium, 9, 69.

[3] L. c., 390.

the still since the distillate from concentrated amalgams was found to be pure mercury, although the amalgam in the still contained much more base metal than could be oxidized by the small amount of air which was admitted. The following experiment was also tried: 160 c.c. of a one to ten thousand cadmium amalgam was brought into the still and was heated for four hours with air bubbling through in the usual way. The condensed mercury was allowed to flow back into the still and at the end of this time the mercury in the still had shown only a slight decrease in cadmium concentration, so it is evident that only a little of the oxygen of the air is used up in passing through the mercury in the still but in the gas phase all metallic vapors of the base metals are completely oxidized.

The question of the solubility of oxygen in mercury has been brought up by T. W. Richards and J. H. Wilson.[1] In preparing mercury for their work on amalgam concentration cells these authors used our still but employed hydrogen instead of air. This of course defeats the main advantage of this form of still. Richards and Hunt feared that the mercury distilled with air, contained dissolved oxygen but they gave no experimental evidence to support this view. The absorption of oxygen by mercury has never been detected even where the gas has been in contact with mercury at great pressures. On releasing such systems an effect should have been observed at the surface of the mercury even if the solubility was very small. Amagat[2] investigated this question and could find no evidence of absorption of oxygen at ordinary temperatures and high pressures nor any oxidation even at 100° and considerable pressures provided that the mercury and oxygen were pure. Furthermore the Weather Bureau at Washington has under observation three barometers which have been in use for over thirty years. At present they give the same readings as new barometers so there has been no deterioration of the vacuum in these barometers, and .05 mm. would have surely been detected. Now the mercury in the cisterns of these barometers soon became "saturated" with oxygen at a pressure of 150 mm. as there was contact with the atmosphere. The variations of the barometric pressure and diffusion soon brought this mercury into the barometer tube and to the top of the column where it would loose any oxygen which had been dissolved and we would expect a continually deteriorating vacuum. If the volume of the space above the mercury column is 10 c.c., .05 mm. would require only .0008 mg. of oxygen. The fact that less than this amount of oxygen got in during thirty years will give some idea of the insolubility of oxygen in mercury. The merest trace of foreign metals

[1] Zeit. Phys. Chem., 72, 136.
[2] C. R., 91, 812, and 93. 308

in the mercury starts oxidation as evidenced by a tarnish that appears on the mercury, a most delicate test, but with really pure mercury we are of the opinion that the absorption or oxidation of oxygen by mercury does not occur or that it is an infinitesimal of a higher order.

The information gained in this and previous investigations give the essential conditions for obtaining pure mercury and it may be questioned whether any single substance may now be prepared in as high a state of purity as mercury. For small quantities of mercury a simple still may be constructed from materials found in any laboratory: Fig. 1 gives an idea of the essential details, *g* is a common "Asbestos Air Bath" with a hole in the bottom for the flame and above this there is fastened a shallow metal cup which supports the flask and on which the flame plays. The flask *a* is an ordinary round bottom flask holding from 250 to 500 c.c. The neck is drawn down short and the 20 cm. tube *b* sealed on and also the side tube *e* which is thin walled and 10 to 15 mm. in diameter and 50 cm. long, *e* serves as the air condenser. A tube *c* is selected of such a diameter that it will just nicely fit into the tube *b* and to this is sealed a glass cock while it is drawn out to a fine capillary at the lower end. This tube is slipped into the tube as indicated in the cut. The joint *d* where there is a slight enlargement of the tube *c*, is made tight with thin rubber bands which are about one centimeter wide. These bands are wrapped about the joint while stretched thus making a tight and simple joint. The asbestos shields *s*, *s* deflect the hot gases so that this joint never gets even warm to the hand. This is much simpler than a ground joint which may be used here. The glass cock regulates the rate at which the gas bubbles through the mercury in the still and if it is well ground no fat need be used on it. The end of the condensing tube *e* is sealed to the stopper of an ordinary Drexel Washing Bottle. The outlet tube from the Drexel bottle *f* is joined to an ordinary Sprengle suction pump and a manometer and a vacuum of 25 to 30 mm. maintained in the system while air is bubbling through the mercury in the still. When the still is once uniformly in operation it needs little attention and a couple of kilograms of mercury may be distilled in two or

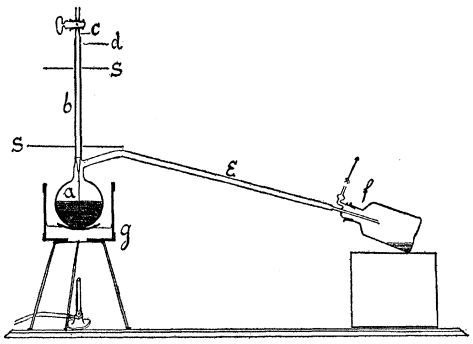

Fig. 1.

three hours. Steady gas and water pressures are desirable. It is best to avoid all organic matter, dust and fat. The ground joints may be readily made sufficiently tight by a little grinding with fine emery if they are not satisfactory to start with. The rubber joint at *d* never gives trouble if the tube fits well in the neck of the flask which is 20 or 30 cm. long.

In distilling large amounts of mercury we have found it necessary to use a larger still provided with an electric heater and arranged to permit of introducing mercury into the still during the distillation. The main features of the still we are using are represented by the sketch in Fig. 2. The flask *a* is about 15 cm. in diameter and into the bottom is sealed the glass tube *e* which connects with the reservoir *h*. The cock *g* is ordinarily open but is often found to be necessary. It was found that the air might be admitted from below through the side tube *s* instead of from above through the neck as in the proceeding still. *f* is a ground glass joint, the tube ends in a capillary which delivers the air well into the tube *e* where it bubbles up through the mercury and into the still. With this arrangement one can always observe the rate at which the air is passing into the mercury and control it with the cock *i*. Mercury is allowed to flow into the reservoir *h* at any desired rate and this controls the rate at which the mercury enters the flask *a*. The mercury vapor is condensed in the large "U" tube *c*, *c* which is made from 25 mm. thin-walled tubing and is 50 cm. long, thus giving a condensing tube one meter long. The tube *o* is joined to a Sprengle suction pump and manometer and a vacuum of 20 to 30 mm. maintained in the apparatus during distillation. The mercury condenses in the tube *c*, *c* and collects in the tube *d* and flows out at the bent up end. This tube *d* is about a meter long and 4 mm. in diameter.

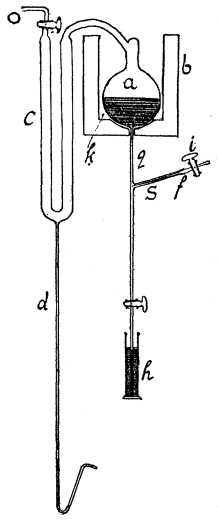

Fig. 2.

b, *b* is an electric heater made from asbestos, water glass and magnesium oxide cement. The heating coils are of "nichrome" ribbon and are located on the sides and bottom. The bottom part of the still is made from strips of asbestos 40 mm. wide and 1.5 mm. thick. The nichrome ribbon is placed along the edge of these strips and then they are rolled up together forming the ribbon into a spiral very close to one side of the " wheel " formed. The asbestos strips are well wetted with water and the waterglass-magnesium oxide mixture and after it is wound it may, while still wet, be dished to fit the form of the bottom of the flask. This

gives a good support to the flask and the heating coil is right where it will be most effective. A short piece of brass tubing is attached to the end of the nichrome ribbon as a convenience in starting the roll. This brass tube serves as a hole for the tube *e* and also as one terminal for this heating coil. For 110-volt circuits this coil should have a resistance from 12 to 15 ohms.

A thin piece of asbestos is wound on a cylindrical form of the desired diameter. The asbestos "wheel" just made is forced into one end of the cylinder and on the outside is wound nichrome ribbon to form the heater for the sides, about 5 or 6 ohms are needed here. About the cylinder is wound a layer of asbestos wet with the cement and over all several layers of asbestos for insulation. The top of the heater is also covered with asbestos and glass wool. Some more resistance will be needed if all the heat from the 110–volt circuit is to be used in the heater. This is easily accomplished by making a spiral of nichrome wire and placing it in the lower inside corner of the heater *k*, *k*. The resistance of this coil may be adjusted so that no external resistance need be used and when working normally the rate of distillation should be such that the mercury vapor is condensing over nearly the whole length of the condenser. Our still takes 4.6 amperes at 110 volts and distills about two kilograms an hour. The electrical energy used is thus about half a kilowatt hour for two kilograms of mercury and at the high rate of 10 cents per kilowatt hour this would cost only 2½ cents a kilo for the electrical energy. If the heat needed to evaporate a kilo of mercury is 62,000 calories it would seem that only about one third of the heat generated by the current was used in volatilizing mercury. The still needs little attention when once in operation and will easily distill 20 kilos a day.

This apparatus is fastened to an upright support which is part of a large tray, a bracket holds the heater. After using the still the last of the mercury is run out and acids drawn up into the flask *a* and the condensing tube if necessary. One to one nitric acid is best for this purpose and is followed with distilled water. The still is easily cleaned and dried without dismantling. The glass cocks should be well ground so as to avoid the use of fat or organic matter, the cocks need not be perfectly tight. In constructing and assembling this apparatus a hand blowpipe was found to be indispensable.

PRINCETON, N. J.,
July, 1911.