CXXXIX.—*Observations on the Phenomena and Products of Decomposition when Normal Cupric Acetate is Heated.*

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*"Ce ne sont pas toujours les résultats des opérations chimiques qui fournissent le plus de lumières aux Chimistes-observateurs ; l'examen des différens phénomènes qui accompagnent ces opérations, est souvent un moyen de saisir des vérités fugitives, pour ainsi dire, qu'il aurait été impossible d'apercevoir autrement."**

THE changes which verdigris, or cupric acetate, undergoes when heated, attracted the attention of chemists during a long period,† the heating of this salt being in use as a method of preparing concentrated acetic acid.

In 1754, M. de Courtanvaux, happening to rectify on a very cold day some "radical vinegar" obtained from Dutch verdigris, observed with surprise the freezing of the distillate. Another winter, eight years later, he repeated this observation, and made others. The first six fractions from a distillation of five pounds of verdigris were successively more dense and more acid, the seventh was more acid but less dense ; and, unlike the others, when it was heated it gave off an inflammable vapour.

In 1773, M. de Lassone observed that the weight of cupric acetate

* M. de Lassone. Sur les phénomènes que présentent la distillation du Verdet et du sel de Saturne (*Histoire de l'Académie Royale des Sciences*, 1773, 26).

† Previous papers on the same subject :

Courtanvaux, *Memoires de l'Académie*, 1754.

Lassone, *Histoire de l'Acad. Royale des Sciences*, 1773, 26, and *Memoires*, 60 ; also Crell, *Chem. Journal*, 1780, 4, 103.

Chaptal, *Annales de Chimie*, 1793, 25, 321 ; 1798, 28, 113.

Adet, " " 1798, 27, 299.

Proust, " " 1799, 32, 35.

Darracq, " " 1802, 41, 264.

Fourcroy, " " 1802, 42, 225.

Proust, *Journal de Physique, de Chimie, et d'Histoire Naturelle. Messidor, An. 13.*

Derosnes, *Annales de Chimie*, 1807, 63, 267.

Mollerat, " " 1808, 68, 88.

Chenevix, " " 1809, 69, 1.

Gehlen, *Schweigger's Journal für Chemie und Physik*, 1812, 4, 23.

Vogel, *Journal de Pharmacie*, 1815, 1, 339.

Berzelius, *Poggendorff's Annalen*, 1824, 2, 252.

Wöhler, *Liebig's Annalen*, 1836, 17, 137.

Roux, *Revue Scientifique et Industrielle*, 1846, [ii], No. 8, p. 5.

Foerster. *Ber.* 1892, 25, 3419.

subjected to distillation exceeded that of the liquid product and solid residue, and inferred that some gas had escaped. He also noticed and described a white, crystalline sublimate, lighter than flowers of zinc, which was a cuprous salt.

Between 1798 and 1802, several chemists took part in a controversy as to whether the acetous acid of vinegar and the acetic acid, or radical vinegar, obtained by the destructive distillation of cupric acetate, were different, as had hitherto been believed, or identical. Chaptal, Fourcroy, and Berthollet supported the old view. Crystallised verdigris was copper acetite. When this substance was heated, there were carbon and copper in the residue. By an elimination of carbon and by taking oxygen which had been in combination with the copper, the acetous acid of the salt was changed into the acetic acid of the distillate. Chaptal also prepared from ordinary vinegar and from radical vinegar two acids of the same density, but differing in their power of neutralising potash and in several other properties. It had not yet been observed that a more and a less dilute acetic acid may have the same density.

Adet, Proust, and Darracq maintained and proved the identity of the two acids. "Acetous" acid, distilled with sulphurous acid to preclude oxidation, resembled that from the distillation of copper "acetite" and yielded similar salts. Copper acetate, prepared by saturating radical vinegar with copper oxide, had the same crystalline form, and decomposed when heated with the same phenomena as copper "acetite" extracted from verdigris. With mercury, lead, iron, and tin, the behaviour of the two acids is the same. Copper "acetite" precipitated by sulphuretted hydrogen gives acetic acid, and here there can have been no oxidation. Distillation of vinegar from calcium chloride yields an acid exactly resembling that from copper acetate, and there is no separation of carbon. Finally, Fourcroy and Berthollet admit that they are convinced.

Some years later, 1806--1809, Proust, the brothers Derosnes, Mollerat, and Chenevix made further observations on the distillation of cupric acetate. For shortness' sake, we will again summarise a group of observations. The white sublimate was observed, but mistaken for dehydrated cupric acetate. About 20 kilos. of "verdet" yielded on distillation nearly 10 kilos. of liquid and left a residue, mistaken for copper oxide, weighing $6\frac{2}{3}$ kilos. The variations in density of the liquid distillate, which did not correspond to the variations in acidity, and the formation of an inflammable liquid were observed. Soon after, the discovery was made that when acetic acid is progressively diluted with water, the density first increases and then diminishes. The inflammable liquid, called pyroacetic ether or spirit, was acetone. It was well shown by Chenevix that the copper in the residue is metallic copper, and that

it is associated with a small proportion of a black substance which he regarded as carbon.

Further observations of these changes were made in 1812 by Gehlen, who showed that the light sublimate was anhydrous cuprous acetate, and that the gases evolved were not hydrogen or hydrocarbons, as previous observers had stated, but consisted of carbon dioxide and carbon monoxide. In 1815, A. Vogel published fresh observations on the distillation of acetate of copper. He notes, as others had, that the salt decrepitates, and does not fuse in its water of crystallisation. The white crystals which formed in the neck and at the bottom of the retort he takes to be anhydrous acetate, since in damp air it became of a blue colour; the gas evolved is carbon dioxide mixed with one-fifth its bulk of a hydrocarbon; the residue consists of copper, cuprous oxide, and carbon. In 1824, Berzelius observed that when verdigris is gradually heated there is obtained at a certain period a white sublimate which fills the body of the retort with a light, woolly crystallisation. He states that this substance is cuprous acetate, and that it did not change on exposure to moist air. Attempts made by him and by previous observers to produce the same substance by the reduction of cupric acetate with copper were unsuccessful.

The last observations we have found were made by Roux in 1846. He heated copper acetate in an open tube, the lower part of which was plunged in a bath of fusible alloy. Up to 140° , water with but little acid was given off. He gives also the temperatures at which acetic acid is formed and at which the white sublimate and the gaseous products appear; these temperatures are much higher than the temperatures at which such changes occur when heat is applied very slowly and the substance is in a vacuum.

To the many sets of observations of which a summary has been given, containing much that is contradictory and not much that is quantitative, the authors have added another, which, though still incomplete, will, they hope, add materially to our insight into a change of an interesting but very complex character, and contribute some useful suggestions of apparatus and methods for the prosecution of similar inquiries.

When a few crystals of normal cupric acetate, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ (prepared from the commercial salt by recrystallisation of a hot aqueous solution acidified with acetic acid), are heated in a test-tube, acetic acid is given off and condenses on the walls of the tube, copious brown fumes are evolved, and a bright, continuous, metallic coating of copper is deposited on the bottom and sides of the tube. As the coating is produced where the salt is not in immediate contact with the glass, it must be deposited from some volatile compound containing copper. The nature of this volatile compound was first investigated.

For this purpose, some of the salt was placed in a porcelain boat in a horizontal glass tube, which was connected through a smaller tube, in which a bulb had been blown, with a second similar tube. The bulb was filled with cotton wool. The tube containing the boat was gradually heated, and the second tube, through which any gaseous products would pass, was kept at a temperature a little below a red-heat. To exclude air, hydrogen was passed slowly through the apparatus during the heating. When the salt was heated, moisture was evolved and a slight, copper-coloured mirror, which did not afterwards increase, was formed in the heated part of the second tube. The contents of the boat became partially white, and a white deposit was observed above the boat on the tube. When this white deposit was heated, it was destroyed and a deposit of copper appeared on the glass tube. No brown fumes were evolved. It appeared probable from this that the white substance was a volatile copper compound; that the slight mirror at first formed was due to the decomposition of a little of the compound which was carried forward, and that the non-increase of the coppery mirror might be due to the cotton-wool becoming wet with acetic acid and thus decomposing the sublimate and preventing it travelling forward.

In a second experiment, the salt was heated gradually up to the boiling point of water, but no change in its appearance could be noted; on heating it to a higher temperature in an air-bath while dry hydrogen was passed over it, the white deposit was again observed, and in this case it was distinctly crystalline. The temperature of the bath when the white substance appeared was 195—200°. In a subsequent experiment, in which the temperature was raised more gradually, sublimation commenced at 173°.

In these experiments, only small quantities of the white substance were obtained, and transmission of steam and of the vapour of acetic acid caused no increase.

The behaviour of the salt when heated in a vacuum tube was next investigated. A tube of the shape shown in Fig. 1 (p. 1389) was made, and the lower compartment filled with the salt. The apparatus was then exhausted by means of a Sprengel pump, and the small tube by which the pump had been attached was drawn off and sealed. The tube containing the salt was then immersed, as shown, in a bath of melted paraffin (Fig. 2, p. 1389).

The side-tube and bulb were to collect the liquid given off, the bulb being immersed in a dish of cold water to promote condensation. With this apparatus, no change was observed up to 130°, when a little liquid collected in the bulb. The next change noticed was a slight coppering of the faces of the crystals, which occurred at about 195°. The temperature was allowed to rise fairly quickly; at 235°, the copper-

ing appeared to be slightly redder, especially on the parts of the salt touching the sides of the glass. No further change was noted until 245° , when the salt appeared dull and paler. The redness had not increased or spread to any portion not in contact with the glass.

At 246° , a sublimate appeared for the first time on the top of the crystals. The red patches disappeared (possibly owing to their being coated over with the white substance), and the whole of the salt lost its blue tint and became of a warm grey colour. Liquid continued to distil over, and no other change was noted until 260° , when some very small, glittering, crystalline particles appeared which disappeared again

FIG. 1.

FIG. 2.

at 273° . The top of the upper compartment of the apparatus had in the meantime become coated with sublimate, but this was washed down from time to time by condensed liquid; finally, however, the distillation of liquid ceased, and the top of the apparatus remained coated with sublimate. The whole of the substance in the lower bulb appeared of a chocolate-brown colour. After allowing the apparatus to cool, it was divided into three parts by sealing off at the side tube and in the middle. On heating the tube to seal off, the softened glass blew out, showing that a volume of fixed gas in excess of the capacity of the tube had been formed.

To investigate these products, and in particular to collect the gases formed and to prevent contact between the liquids which are condensed and the sublimate, a different form of apparatus was needed. The form which was finally adopted may be seen by reference to Fig. 3 (p. 1391).

Description of Apparatus shown in Fig. 3.

The tube in which the salt is heated is divided into two compartments, *A* and *U*, by a constriction, in which a small bulb, *H*, is placed, to prevent the salt falling down into the lower or sublimate chamber, *U*. The sublimate chamber is drawn out below into a narrow tube, bent as shown, *J*, and terminating in a capillary point, *V*. The tube is fixed by means of a rubber cork, *W*, into a wider tube, *B*. The tube *B* is filled with oil, and is heated by means of a ring-burner consisting of a series of hard, glass tubes, *Z*, seven in number, of the shape shown in the figure, which allows of their being set close to, or further from, the tube *B*. The burner tubes fit into a wide glass chamber, *I*, which is supplied with gas by an inlet tube, *T*. The gas, after a preliminary regulation by a gas-governor, passes through the regulator, *F*, before entering the inlet tube *T*. This regulator, *F*, allows of the temperature being kept constant for a long time at any desired point. For this purpose, the temperature is set approximately by taking out or putting in oil at *X*, and the final adjustment is made by raising or lowering the fine tube *A'*; a pin hole, *B'* in *A'*, acts as a by-pass when the expansion of the oil in *B* raises the mercury in the regulator up to the end of the tube *A'*, and so prevents the burners from being put out. By this vertical arrangement of the tube in the oil-bath, different zones of temperature are obtained, the object of which is to allow the sublimate to condense at a point where the temperature is still sufficiently high to prevent the acetic acid condensing also. Below the level of the burner-tips, the temperature of the sublimate chamber falls off rapidly, and the acetic acid and water condense at the bottom, apart from the sublimate, and flow down into the drawn out tube and thence into the washing bulbs. The tube *B* is supported by a clamp (not shown in the figure) at the narrow portion of the neck, below the two side tubes *X* and *Y*.

D and *D'* are two semicircular sheets of tin plate, partly shutting in the space enclosed by the wide, outer glass cylinder, *C*, which keeps up the temperature and prevents a draught from disturbing the flames. A thermometer, *G*, registers the temperature of the bath. *E* is a plate of mica to act as a shield.

The drawn out tube, *J*, is fitted by a gas-tight mercury joint (shown in section in Fig. 4, about its actual size), so that the capillary tube, *V*, delivers the liquid freely from its point into the tube of the washing

bulbs, *R*. The washing bulbs, *R*, are six in number, and are so arranged that when held by one end there is a continual fall from the first to the last bulb, so that they may be conveniently washed out. The three bottom bends form three points of a triangle, and allow of the bulbs standing on the balance pan or any flat surface without support.

The bulbs are charged with water (3 or 4 c.c. in each pair), rather less being placed in the pair of bulbs nearest the capillary, as the main quantity of acetic acid and water from the decomposition of the salt is arrested there. By keeping the three portions of water separate, the washing is made much more complete, since only that portion of the acetic acid vapour which escapes from the first pair of bulbs after the water in it is nearly saturated passes into the second pair, and only the residue of this into the third pair. The result is that practically the whole of the acetic acid is stopped, whereas this is not the case if the three portions of liquid are in communication. To prevent the distillation of liquid which is apt to occur when the vacuum is good and the atmosphere moderately warm, the bulbs are enclosed in a bath of ice and water which is wrapped round in cotton wool, *P*. As the contact of the glass of the bulbs with the zinc of the bath, *O*, has sometimes caused fracture, some folds of flannel, *Q*, are placed on the bottom of the bath. The bulbs are connected by another mercury joint, *L*, with a drying tube, *S*, containing pumice moistened with sulphuric acid in the upper part and sulphuric acid in the lower. The drying tube, *S*, is connected by another mercury joint, *M*, with the Sprengel pump by which the gases are drawn off and collected. The washing bulbs and drying tube are of a form convenient for weighing.

The Action of Heat on Copper Acetate.

The first result of the action of heat on the salt is a formation of liquid. With the apparatus described, it is somewhat difficult to determine exactly the temperature at which this occurs, but in one experiment it was observed at 115°. When the temperature has reached 150—160°, the surface of the salt appears coppered in parts. This coppering occurs also when the salt is heated in carbon dioxide or hydrogen. It appears on the parts of the salt immediately touching the glass, and spreads somewhat irregularly over the surface of the salt, but never becomes uniform over the entire surface. The coppery deposit appears a long time before any trace of sublimate is seen, and occurs whether the salt is powdered or in crystals; in the latter case, however, the smooth surfaces of the crystals give the coppering a more metallic appearance.

The next noteworthy change is the deposition of sublimate and the

evolution of gas. These two changes occur together, and the temperature at which they occur is about 230° . In some experiments, the sublimate has been observed at 215° , and in others lower than this. The formation of sublimate is, however, so extremely slow that a complete experiment at these lower temperatures is impracticable. In one instance, the experiment was continued for a week and the temperature kept below 212° the whole time; it was afterwards found that the decomposition was even then incomplete, and on reheating the residue at a higher temperature a small additional sublimation occurred. For this reason, in the later experiments, the temperature was allowed to rise fairly rapidly to 230° , at which temperature the decomposition can be completed in a reasonable time. When about 8 grams of salt are used and the gas is pumped out at a convenient rate, the experiment can be completed in about $9\frac{1}{2}$ hours after the appearance of the sublimate. If the pressure of the gases is allowed to rise, the decomposition is retarded.

The sublimate always appears at a point in the sublimate chamber just below the level of the tips of the burners, and spreads downwards. At this part, there is a very steep gradient of temperature. In one experiment, the temperatures of the extreme limits within which sublimate was being deposited were approximately determined by raising and lowering the thermometer. At the lower limit of the sublimate, the temperature was 103° , and at the upper limit 170° ; the width of this zone was only 8 or 10 mm.

The first portions of the sublimate are almost invariably crystalline; as sublimation becomes more rapid, its appearance changes: it becomes granular and nodular, growing out from the sides of the tube until a cake is formed at the top by the sublimate meeting in the centre. After this cake is formed, the sublimate increases upwards slightly, but only for a very short distance. After a time, the bottom of the deposit gradually becomes moist through a condensation of acetic acid, and a green band is formed which spreads slowly upwards. Finally, if the experiment is prolonged, the top of the sublimate becomes of a darker colour. Condensation of liquid and evolution of gas go on more and more slowly, and finally the decomposition comes to an end, and all that remains of the salt is a reddish-brown residue in the top chamber. The drawn out tube, *J* (Fig. 3), is then sealed off, the burner extinguished, and the apparatus allowed to cool. After the tube has been removed from the oil-bath, the chambers *A* and *U* (Fig. 3) are separated by sealing off.

The following tables give the results of the experiments so far as the amounts of the different products obtained are concerned; afterwards the different products are dealt with separately:

Salt taken, in grams.	Experiment 32.		Experiment 34.		Experiment 35.	
	10.5094.	Per cent. 100.	8.5886.	Per cent. 100.	8.7741.	Per cent. 100.
Residue	3.4628	32.95	2.7904	32.49	2.9221	33.31
Sublimate	0.3581	3.41	0.3616	4.21	0.2247	2.56
Acetic acid	4.807	45.73	3.5960	46.04	4.069	46.38
Water + a trace of acet. one	0.7712*	7.34	0.6331	7.40	0.6637	7.57
Carbon dioxide	0.8935	8.50	0.7333	8.54	0.7822	8.91
Carbon monoxide	0.1526	1.45	0.1235	1.44	0.1142	1.30
Total.....	10.4452	99.38	8.5979	100.12	8.7759	100.03

* The amount of acetone formed in this experiment was found to be 0.0013 gram, or 0.01 per cent.

The Gases from Copper Acetate heated in a Vacuum.

Although many chemists have observed the evolution of gas which occurs when cupric acetate is heated, no two of them agree as to the composition of the gaseous mixture. Thus, Gehlen finds the mixture to be 6 vols. of carbon dioxide and 5 vols. of carbon monoxide; Vogel, 4 vols. of carbon dioxide and 1 vol. of carburetted hydrogen; Roux, a mixture of carbon dioxide and a combustible gas; Chenevix, 2 vols. of carbon dioxide and 3 of hydrocarbon.

In the present experiments, the gases collected after washing with water consisted only of carbon dioxide and carbon monoxide, approximately 4 volumes of the former to 1 of the latter. In some of the earlier experiments, it was found that the gases contained some acetic acid vapour, which had to be washed out before they were analysed. When the last form of washing bulbs (shown in Fig. 3) was used, the acetic acid was completely stopped. As none of the chemists above-mentioned washed the gases with water, it is probable that some acetic acid vapour was mixed with the permanent gases and constituted the "hydrocarbon" which several mention.

The method of analysis was as follows. The gas was collected over mercury at the exit of the Sprengel pump in tubes holding about 40 c.c. The amount of carbon dioxide was estimated by absorption with potash and the residue exploded with an excess of oxygen. A second absorption by potash and, in some cases, an estimation of the residual oxygen by absorption with pyrogallol or explosion with hydrogen, completed the analysis. We found, as others must, that when the

gas in which oxygen is to be estimated by pyrogallol is unmixed oxygen, the potash used must be very strong.

In some cases, one portion of gas was divided into two parts and each half analysed separately. Portion XI, Expt. 32, and Portion II, Expt. 34, were treated in this way, and the numbers obtained were :

	First part.	Second part.	First, per cent.	Second, per cent.
Portion XI, 32 :				
Taken for analysis.. .. .	45·05	47·50	100	100
Carbon dioxide	34·51	36·41	76·60	76·65
Carbon monoxide	10·39	10·93	23·06	23·01
	<u>44·90</u>	<u>47·34</u>	<u>99·66</u>	<u>99·66</u>
Portion II, 34 :				
Taken for analysis.....	42·67	51·64	100	100
Carbon dioxide	35·51	42·93	83·22	83·16
Carbon monoxide	7·00	8·46	16·42	16·39
	<u>42·51</u>	<u>51·39</u>	<u>99·64</u>	<u>99·55</u>

A table is given on p. 1396 which shows the results of the analyses of the gases from different experiments, from which it will be seen that the mean ratio $\text{CO}_2 : \text{CO}$ is approximately 4 : 1, that in the first portions of gas collected the proportion of carbon dioxide is invariably greater than this, and that it then diminishes as the decomposition of the salt proceeds.

The temperature of the salt was kept within a degree or two of 230° and the pressure of gases upon it at 2 or 3 cm. The time required for the collection of each portion of gas was about three-quarters of an hour. The evolution was rather more rapid at the beginning and showed a sudden decrease at the end.

In most cases, the gas was collected under as low a pressure as possible. It was found inexpedient to reduce the pressure below about a couple of centimetres of mercury, because water then evaporated quickly from the washing-tube into the sulphuric acid drying-tube and there was a danger of sulphuric acid spirting back into the bulbs. In Expt. 35, an attempt was made, by collecting the gases at different pressures, $1/3$, $2/3$, &c., of an atmosphere, to see whether the pressure influenced the ratio of carbon dioxide to carbon monoxide. It was found that at the higher pressures the proportion of carbon dioxide was slightly increased.

EXPT. 30.

No. of sample.	I.	II and III.	IV and V.	VI and VII.	VIII and IX.	X, XI and XII.	Mean.	I.	II.	III.	IV.	V.	Mean.
CO ₂	87.7	80.2	77.8	78.1	77.5	77.3	78.9	81.68	77.80	79.32	77.64	82.90	79.87
CO	12.3	19.8	22.2	21.9	22.5	22.7	21.1	17.99	22.00	20.44	22.32	17.38	20.03
Total ..	—	—	—	—	—	—	—	99.67	99.80	99.76	99.96	100.28	99.90

EXPT. 32.*

No. of sample.	I.	II.	III.	IV.	V.	VI.	VII.	X.	XI.	XII.	XIII.	XIV.	Mean.
CO ₂	85.90	81.70	79.09	78.75	77.54	77.73	76.40	75.71	76.61	76.64	76.49	77.94	78.74
CO	14.10	18.04	20.91	21.25	22.21	22.27	23.60	24.17	23.04	23.36	23.51	21.72	21.17
Total	—	99.74	—	—	99.75	—	—	99.88	99.65	—	—	99.66	99.91

EXPT. 34.

No. of sample.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	Mean.
CO ₂	86.04	83.19	80.57	78.86	78.40	79.01	77.40	77.04	76.49	76.42	76.07	79.91	79.12
CO	13.96	16.40	19.43	21.14	21.40	20.99	22.60	22.86	23.51	23.58	23.62	20.09	20.79
Total	—	99.59	—	—	99.80	—	—	99.90	—	—	99.69	—	99.91

EXPT. 35.

No. of sample.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	Mean.
CO ₂	89.80	84.47	80.01	75.95	78.96	78.63	79.01	81.46	83.09	82.50	80.01	81.26
CO	10.20	15.32	19.99	24.05	20.81	21.37	20.75	18.60	16.91	17.50	19.90	18.67
Total	—	99.79	—	—	99.77	—	99.76	—	—	—	99.91	99.93
Pressure of dry gas in mm. of mercury, during Expt. 35.	30	40	40	40	264	264	507	507	507	72	207	—

* The results of the analyses of portions VIII and IX have been omitted for convenience of printing. They are included in the mean.

As the gas formed and collected consecutively in separate tubes had been found to consist wholly of carbon dioxide and carbon monoxide, in the later experiments only a few complete analyses were made, and in most cases the carbon dioxide was absorbed and the residue taken to be carbon monoxide. Where, in the tables, the numbers would add up to 100 exactly and the spaces have been left blank, the carbon monoxide was determined by difference.

In Expt. 30, the analysis was made, during the repair of the gas analysis apparatus, by absorbing and weighing the carbon dioxide present, passing the rest through a tube over red hot copper oxide, and absorbing and weighing the carbon dioxide produced.

It will be seen that the differences in the proportion of the two gases, in portions collected successively, far exceed the differences shown by two analyses of the same portion. There are, therefore, at least two changes, of which the gases are products, whose relative rates vary slightly as the decomposition of the salt proceeds, but are not greatly affected by changes of temperature or pressure.

The Liquid Products.

The liquid products of the decomposition of normal copper acetate at a gradually increasing temperature are water, acetic acid, and a trace of acetone. The amount of acetone found in these experiments is extremely small, for example, in Expt. 32, it was 0.01 per cent. With some other acetates, for example, lead and calcium, acetone is the principal product, and some previous observers, working on a large scale, have obtained acetone from copper acetate. The brothers Derosnes, using more than 20 kilograms of the salt, got several ounces of acetone. The cause of the difference would seem to be that in distillations on a large scale substances produced at a lower temperature come into contact subsequently with the sides of the retort and with other substances at a much higher temperature, and thus secondary changes occur. This complication is avoided when we work with small quantities and raise the temperature very gradually. In the present experiments, it has been noticed that if the experiment is prolonged the top of the sublimate becomes discoloured, and if greatly prolonged, some of it is destroyed and a coppery deposit is formed on the sides of the sublimate chamber. In a good experiment, the amount of this decomposition is very small, and is probably comparable in amount with the trace of acetone formed. If the acetone were a primary product of the decomposition of the cupric acetate, it would not be formed in such very small quantities. If, however, it is a product of the decomposition of the sublimed cuprous acetate, which is itself only a small product of the reaction and is only decomposed

to a small extent, the minute amount of acetone formed is accounted for. A possible equation is :

Estimation of Water, Acid, and Acetone.

After the washing-bulbs had been weighed, they were emptied and washed, the liquid was made up to a known volume, and a portion taken for titration with standard alkali.

The acetone was estimated in another portion by Messinger's method, which depends on the conversion of the acetone into iodoform by a standard solution of iodine in presence of potash solution, and estimation of the residual iodine by standard sodium thiosulphate and starch. Three molecules of iodine are required to convert one molecule of acetone into iodoform. The method was first tested with known quantities of acetone and found to be satisfactory.

The water was estimated by difference.

The Sublimate.

The white substance, here called the sublimate, has been known for a long time as a product of this decomposition. Originally described as "flowers of copper" it was afterwards found to be cuprous acetate. The small amount of it formed (1/1280 of the amount of the salt decomposed is given as the quantity by Lassone) has, however, hitherto prevented any analysis of it being made. The amount obtained varies in different experiments; the largest amount obtained in these experiments was 4.21 per cent. (Expt. 34). Also it is very easily decomposed. As ordinarily prepared, by heating cupric acetate, it is apt to contain traces of acetic acid, and this causes it to turn green when exposed to the air; if it is free from acetic acid, it is fairly permanent. Water turns it yellow, forming cuprous oxide or hydroxide. When it is obtained by heating the salt in a tube through which hydrogen is passed, it forms beautiful, transparent, leafy crystals, and the first portion that appears when the salt is heated in a vacuum is always crystalline. It can be resublimed in a current of gas (hydrogen, carbon monoxide, &c.), but decomposes on strong heating, leaving a coppery deposit.

The analysis of the sublimate was made as follows. The sublimate chamber, after being sealed off, was cleansed from all traces of oil. A file mark was then made near one end and a crack led nearly round it, so as to allow air to enter slowly. After the air had entered, it was weighed. The tube was then parted at the crack and the contents washed out into a porcelain dish. The sublimate resisted the action of the water for a short time (it was not very easily wetted by water)

and then turned orange and red and also partly green. As the sublimate could not be wholly removed from the glass by water, a little dilute hydrochloric acid was used to dissolve it off. After having been washed and dried, the tube was weighed, the difference giving the amount of sublimate taken for analysis. As the amount of sublimate was small, not more than 0.2 to 0.3 gram, the whole of it was generally used for an estimation of the copper. A little nitric acid was added to produce the cupric salt and the liquid diluted and heated to boiling. The copper was precipitated with caustic soda and estimated as copper oxide. Two determinations of different samples gave 52.15 per cent. and 51.57 per cent. of copper respectively, the theoretical amount in cuprous acetate, $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_2$, being 51.78.

The Residue.

The residue is a soft, light, reddish-brown powder. When crystals of the salt have been heated, they retain their form more or less in the residue. Under a magnifying glass, numerous glittering particles can be seen, and if one of the little nodules of the residue is pressed with a spatula on a flat surface so as to crush it, it is seen to consist, in addition to the small metallic specks, of a brownish-black, amorphous substance resembling some form of carbon. If the residue is powdered and then washed with a stream of water, a partial separation of the metallic particles from the carbonaceous material can be effected. This separation, however, is not complete enough for analysis.

When ignited in a crucible open to the air, the carbonaceous material glows and burns away, while the copper is converted into copper oxide. The copper appears to be entirely in the metallic state, and is only mechanically mixed with the carbonaceous matter. The residue amounts almost exactly to one-third of the salt taken. It varies, however, slightly in amount in different preparations, and this variation is connected with the variation in the amount of sublimate obtained; the greater the amount of sublimate, the less is the amount of residue, as may be seen by reference to the table of the results of experiments 32, 34, and 35.

Although this residue has often been examined, and is stated to contain copper, cuprous and cupric oxides, and carbon, no analyses of it have been given beyond a statement of the percentage of a substance "which had all the properties of carbon." It was hoped to determine the composition of this substance by a combustion. It was found, however, that in no case did the amount of carbon, obtained as carbon dioxide, suffice to make up with the copper the full amount of substance taken; also a little water was always formed. The black substance

must therefore contain oxygen and hydrogen as well as carbon. The numbers obtained in the combustions were :

	Copper.	Carbon.	Hydrogen.	Oxygen by diff.	Total.
Expt. 32.....	90.39	6.02	0.237	3.353	100
Expt. 34.....	90.14	5.83	0.30	3.73	100
Expt. 35.....	91.58	6.00	0.21	2.21	100

It was noticed during the combustion in Expt. 34 that moisture appeared in the calcium chloride tube before there was any sign of carbon dioxide, and before the substance, which was placed in a porcelain boat, had begun to glow. This pointed to the substance containing moisture, and on trial it was found to be hygroscopic and to lose weight over sulphuric acid. When a little of the residue was placed on blue litmus paper and moistened with distilled water, a red spot appeared. The black substance is slightly soluble and may have an acid reaction, or it may have retained or recovered from the contents of the nearly vacuum tube a little water and acetic acid.

Carbon dioxide, being one of the products of the reaction, seemed a suitable gas to employ for passing over the residue to assist in removing whatever is volatile. Accordingly, in order to prepare some quantity of the residue and examine the carbonaceous material, an experiment was made on a larger scale, in which about 46 grams of the salt were taken instead of the usual 5 or 10 grams, and dry carbon dioxide was passed through during the whole of the heating, which was continued during three days; the residue obtained had the usual appearance.

Dilute nitric acid of semi-normal strength was employed to extract the copper. The results showed that the extraction was complete. After the usual washing and drying, the substance was placed in a porcelain boat within a glass tube heated to 105° and a stream of dry air was passed over it for five hours.

The combustion still showed deposition of water before the substance began to burn visibly. There was no residue of cupric oxide in the boat, or sublimate in the combustion tube above. The presence of a little water would throw the carbon too low, and the hydrogen and oxygen too high; in view of this, the formula which best represents the composition of the substance is $C_{11}H_4O_4$:

Found C = 65.30 ; H = 2.11 ; O = 32.59 per cent.

$C_{11}H_4O_4$ requires C = 65.99 ; H = 2.01 ; O = 32.00 „

That water is given off before a compound of carbon, hydrogen, and oxygen enters into visible combustion is, of course, no evidence that the hydrogen and oxygen which form the water were not constituents of the substance. If, however, it be assumed that all the water

collected in the combustion was attached as water to the actual substance, and the mass taken for combustion be reduced accordingly, there remains, as the actual substance, a compound of carbon and oxygen of which the most probable formula is $C_{11}O_2$:

Found C = 80.56 ; O = 19.44 per cent.

$C_{11}O_2$ requires C = 80.50 ; O = 19.50 „

The composition of the residue may also be arrived at by subtracting from the quantities of copper, carbon, oxygen, and hydrogen in the copper acetate originally taken, the quantities of each element in all the volatile products. It will be seen that the composition thus calculated accords well with the results of analysis, leaving no doubt that the black substance, which, in admixture with metallic copper, forms the residue after prolonged heating of the salt in a vacuum, contains a considerable amount of oxygen.

Experiments 34 and 35. Masses of each element from 100 of $Cu(C_2H_3O_2)_2, H_2O$.

	Copper.	Carbon.	Hydrogen.	Oxygen.
In sublimate {	2.18 1.33	0.82 0.5	0.10 0.06	1.10 0.67
In acetic acid {	— —	18.42 18.55	3.07 3.09	24.55 24.73
In water {	— —	— —	0.82 0.84	6.58 6.72
In carbon dioxide {	— —	2.33 2.43	— —	6.21 6.48
In carbon monoxide {	— —	0.62 0.56	— —	0.82 0.74
Sum of two experiments (to be divided by 2)	3.51	44.23	7.98	78.60
Total	1.75	22.11	3.99	39.30
In 100 of $Cu(C_2H_3O_2)_2, H_2O$	31.78	24.06	4.04	40.11
Hence, in residue	30.03	1.95	0.05	0.81
In residue, by analysis..... (Mean of Expts. 34 and 35)	29.9	1.94	0.08	0.98

The excess of oxygen and hydrogen in the composition of the residue

shown by analysis is doubtless due to the hygroscopic character of the substance and the small quantity available for analysis.

The authors hope to make a similar examination of the phenomena and products when copper formate is gradually heated in a vacuum.

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