

LXXXIX.—*The Dissociation of Chloride of Gold.*

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THIS investigation was undertaken in order to obtain information as to the dissociation of trichloride of gold, and also to endeavour to explain the somewhat contradictory results already published by various experimenters on the relations between gold and chlorine. It has been repeatedly affirmed and denied that AuCl_3 readily volatilises, and the temperatures at which the chlorides of gold are formed and decomposed have also been variously stated by different observers.

In the course of the work, the pressure of dissociation of gold chloride at different temperatures up to 332° , and the effect on this pressure of the removal of all traces of moisture were observed. The volatility of gold trichloride in chlorine at various temperatures up to 1100° , and the rate of decomposition of both chlorides in air at various temperatures were also examined.

The first reference to the volatility of gold chloride appears to have been made by Robert Boyle, who describes experiments (*Philosophical Works of Robert Boyle*. Abridged by Peter Shaw, M.D., London, 1738, 1, 263 and 377) in which he and his assistants “dissolved gold in a moderate heat, with a sufficient quantity of the *menstruum peracutum* (which consists of spirit of nitre, several times drawn from butter of antimony), and having carefully decanted the solution into a retort, we very gently, in a sand-furnace, distilled off the liquor The liquor being abstracted, we urged the remaining matter by degrees of fire; and in no stronger an one than may easily be given in a sand-furnace, a considerable quantity of the gold would be elevated to the upper part of the retort, and would fasten itself to the top and neck in the form of a yellow and reddish sublimate. Sometimes we had the neck of the retort enriched with numerous large, thin, red crystals, very like rubies, and glorious to behold, which would run in the air *per deliquium*. Nor can I see any cause to doubt that, by the reeffusions of fresh *menstruum* upon the dry calx of gold which remains behind, the whole body of the metal may be easily made to pass through the retort.” It should be noted that in this singularly interesting early experiment, the atmosphere inside the retort at the time of the sublimation must have mainly consisted of chlorine. Boyle also did not overlook the fact that these sublimed crystals could be shown to contain gold by various tests.

In the present century, but over 50 years ago, Mr. Lewis Thompson, in a paper read on November 1, 1838 (*Jour. Soc. of Arts*, 1840, **53**, part 1, 16), observed that his method of purifying gold "is founded on a circumstance long known to chemists, viz., that not only has gold no affinity for chlorine at a red heat, but that it actually parts with it at that temperature, although previously combined; that is to say the chloride of gold is reduced to the metallic state by heat alone [and] it cannot, therefore, possess any affinity for chlorine when red hot."

In a report appended to Mr. Thompson's paper by Mr. Arthur Aikin, who experimented on the same subject, it is stated that "in all the first trials the button of gold was found to weigh considerably less than before the process, and the accidental breaking of one of the tubes showed that in the part directly over the button several globules of gold adhered, having probably been thrown up thither by the ebullition of the alloy (of gold, with silver, copper, &c.) when the chlorine was first passed over it. Having thus discovered the cause of the failure, the process was twice more repeated, taking care to give only a low red heat in the beginning, and to pass the chlorine slowly. With these precautions, the button of gold remaining at the end of the process was found to be exactly equal to its original weight, as shown by a balance that indicated well to the 1/200th part of a grain."

In 1867, Mr. F. B. Miller (*Trans.*, 1868, **6**, 506) described his process for the separation of silver and other metals from gold by means of a current of chlorine passing through the molten alloy, the success of the process depending on the extremely small volatility shown under these conditions by gold alloyed with silver. Roberts-Austen proved (*First Mint Report*, 1870, 93) that the presence of copper did not increase the loss of gold.

In 1868, Prat (*Compt. rend.*, 1870, **70**, 840) stated that if a current of gaseous chlorine is passed over any chloride of gold heated "suitably," a volatile chloride is obtained, which can be condensed and collected in the form of a liquid which contains more chlorine than does gold trichloride.

Experimenting on the same subject, Debray (*Compt. rend.*, 1869, **69**, 984) found that at 200° gold trichloride is decomposed with the formation of metallic gold and gold monochloride, and above this temperature with the formation of gold and chlorine. If chlorine is passed over gold leaf which is being gradually heated, then, as the temperature rises, the gold is covered with a coating of the chloride far below 300°; but it is not until a temperature of nearly 300° is reached that volatilisation of the chloride begins to be sensible. The volatilised chloride can be condensed in voluminous

long needles in the cool part of the glass tube, the gold trichloride being kept from dissociating by chlorine vapour at atmospheric pressure.

In examining these statements in 1887, Krüss (*Ber.*, 1887, **20**, 211—213) obtained results which were considerably at variance with them. He placed precipitated gold, which had been dried at 180° , in a glass tube heated in an air-bath, passed a rapid stream of dry chlorine through the tube and heated it gradually, beginning at the ordinary temperature. At 140° to 150° , he observed the formation of red-brown fumes, a slight yellowish-red sublimate was formed, and the gold was converted into the red-brown auro-aurochloride, AuCl , AuCl_2 . At 180° to 190° , this was decomposed, and greenish gold monochloride, AuCl , was left behind, and a little trichloride was volatilised. At 220° , the AuCl was decomposed and a little trichloride was sublimed with the evolved chlorine; the sublimate consisted of shining reddish-brown needles, which were shown to consist entirely of AuCl_3 . It was collected in a cool part of the tube and subsequently dissolved in water and analysed. On heating from 220° to above 300° , no further change was observed, and on cooling similar appearances were observed, in reverse order, at the same temperatures as before. From no less than one hundred repetitions of the process, only 0.12 gram of the trichloride, AuCl_3 was sublimed and condensed from a length of 30 to 35 cm. of the powdered gold. From these experiments, Krüss concluded that both Prat and Debray were mistaken in thinking that gold chloride is readily volatilised at moderate temperatures. He observed, however, (*Ber.*, 1887, **20**, 2641), that at 1100° continuous, though slow, distillation of gold chloride could be effected by passing a current of chlorine over metallic gold; he states that this sublimation begins at 1000° , although chloride of gold is completely decomposed at 220° .

Lindet subsequently (*Bull. Soc. Chim.*, 1888, **49**, 450) showed that while gold trichloride begins to dissociate into the monochloride and chlorine at 175° , the completion of the operation is slow, so that a stream of chlorine passed over metallic gold at 200° to 220° gives an ultimate product consisting of :

Gold in the state of AuCl_3	65.0 per cent.
Gold in the state of AuCl	13.5 „
Gold not attacked	21.5 „

Finally, S. B. Christy (*Trans. Am. Inst. of Mining Engineers*, May, 1888) in the course of an investigation into the causes of loss of gold in the chloridising roasting of auriferous ores, made a number of experiments on the rate of volatilisation of gold in a current of damp chlorine. He heated buttons of pure gold in clay dishes in a muffle

furnace and passed a stream of chlorine through a pipe-stem, the bowl of which loosely covered the gold button. Under these circumstances the gold buttons always lost weight, the greatest loss being observed at 250°.

A. Smithells has lately shown (*Phil. Mag.*, 1895, **39**, 131) that "in presence of abundance of chlorine, gold chloride may be formed at a red heat, and so emit its characteristic spectrum."

It will be seen from these results how little the various statements confirm each other.

Pressure of Dissociation of Gold Trichloride.

The limited chemical action investigated is expressed by the equation $\text{AuCl}_3 \rightleftharpoons \text{AuCl} + \text{Cl}_2$.

The chloride of gold was prepared by heating finely divided gold in a current of dry chlorine.

The chlorine was generated from hydrochloric acid and manganese dioxide in the earlier experiments, and from sulphuric acid, salt and manganese dioxide in the later ones, the formation of the gas being more easily regulated when obtained in this manner. The gas thus obtained was passed successively through three wash-bottles containing a solution of sulphate of copper to free the gas from hydrochloric acid and chloride of manganese, and was then dried by sulphuric acid and subsequent passage through some U-tubes filled with calcium chloride, and then through one filled with phosphoric anhydride. The P_2O_5 tube was added for the reason given by Krüss, who states (*Ber.*, 1887, **20**, 212) that a stream of gas, dried by sulphuric acid only, causes gold chloride to be completely dissolved. In the latter experiments, sulphuric acid only was used for drying the gas, two Winkler's tubes, and one U-tube filled with pumice-stone moistened by sulphuric acid being employed. The drying apparatus proved adequate for the purpose, as the current of gas passed through it had no apparent effect on dark-red anhydrous crystals of AuCl_3 .

The purified and dried chlorine was tested at intervals by ascertaining to what extent mercury had power to absorb it. After agitation with mercury for fifteen minutes, the residue was usually about 5 per cent. of the original gas. In view of Shenstone's results (*Trans.*, 1892, **61**, 449), it may be assumed that part of this residue was chlorine, but as no perceptible absorption of the residue by water could be observed, it is also probable that it consisted chiefly of air, the presence of which was of no moment.

The gold used was precipitated, washed, and dried at about 200° with the precautions observed in preparing the very pure gold used

in the Royal Mint, in connection with the gold bullion assay, and was 1000 "fine." In the first series of experiments, the finely divided metal was dropped into the "gold chloride" tube shown in Fig. 1, and the tube then closed by the glass stopper, and heated at 180° in a slow stream of chlorine, which was at first completely absorbed. The chlorine was prevented from entering the manometer

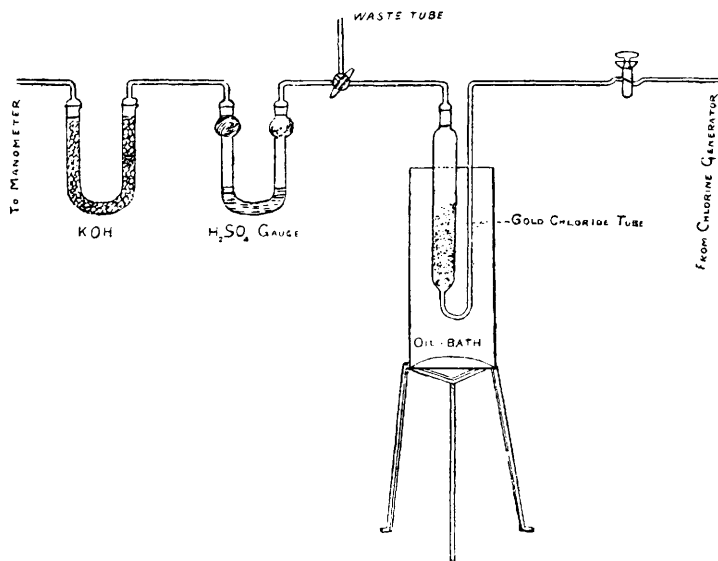


FIG. 1.—DISSOCIATION APPARATUS.

by the 3-way tap, which has a mercury cup and communicates with the "waste tube." The "gold chloride" tube was a little more than half filled by $1\frac{1}{2}$ oz. of precipitated gold, the quantity usually employed. The resulting chloride was in the form of dark-red shining plates and needle-shaped crystals which consisted chiefly of gold trichloride, AuCl_3 . Since the active mass of a solid is constant, it is immaterial what excess of AuCl may be present, provided that some AuCl_3 (indicated by its ruby colour) is also present.

The chlorine contained in the chloride was enough to fill the tube (which is 10 ins. long and $\frac{3}{4}$ in. in diameter) many times over at atmospheric pressure. Only about four-fifths of the tube was heated in the oil bath, but this was of little consequence, as the pressure would be the same in different parts of the apparatus, although the composition of the gaseous atmosphere might be different. The thermometer used was a mercury one filled with nitrogen; its readings were subjected to the usual corrections.

The communication between the heated tube and the manometer was through two U-tubes (Fig. 1), one of which contained sulphuric acid to keep the chlorine from passing further and to act as a gauge; whilst the other contained solid potash to absorb such chlorine as might pass through the acid, and so protect the mercury of the Sprengel pump and manometer. It was found that 25 mm. of sulphuric acid above the mercury in the manometer was not enough of itself to protect it from the action of an atmosphere consisting mainly of chlorine, so that when the manometer was put in direct

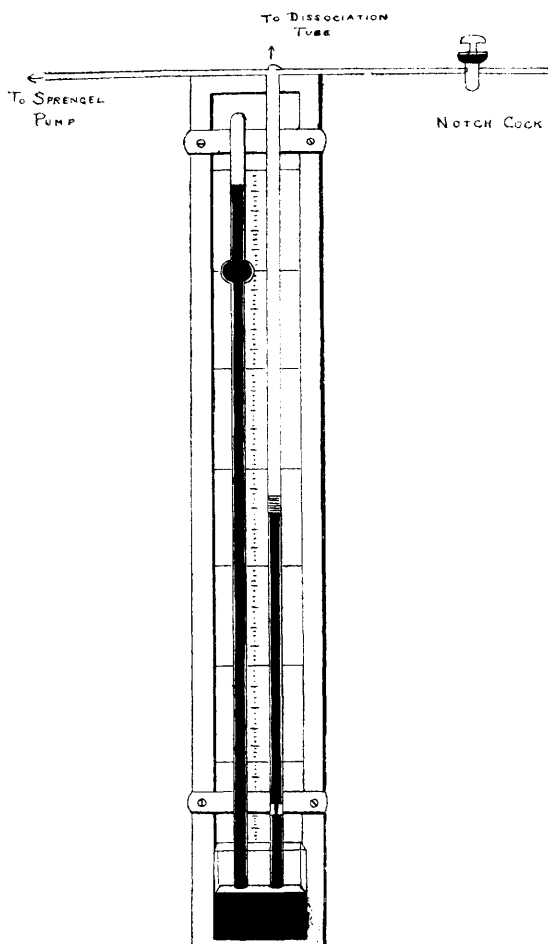


FIG. 2.—THE MANOMETER.

communication with the heated tube the results were not so exact. For very low pressures, the amount of sulphuric acid in the gauge was reduced to the smallest possible amount, but generally it was more convenient to keep about 30 mm. in each leg of the U-tube.

Measurement of the Pressure.—The arrangement of barometer and manometer, shown in Fig. 2, was suggested to me by Prof. Ramsay. Both tubes are furnished with air-traps, and the manometer and the upper part of the barometer are made from pieces of the same tube to avoid errors due to capillarity, whilst both dip into the same mercury vessel. These tubes are $12\frac{1}{2}$ mm. in diameter. The graduated mirror placed behind and parallel to them is 3 ins. wide and 1 metre long, divided into millimetres, parallax being avoided by bringing the mercury and its image in a line with the eye. It is not difficult with this arrangement to read to the tenth of a millimetre with unassisted vision. The pressure inside the apparatus is the difference between the two readings. The correction for temperature—0.000173 lt.—had to be applied to this difference.

The upper part of the manometer tube opens into a 4-way tube, leading to the Sprengel, to the dissociation apparatus, and to the notch-cock (used to admit air) respectively. In place of the notch-cock an ordinary stop-cock and a fine capillary tube was used in some of the experiments.

For pressures above 760 mm. a U-shaped mercury manometer of ordinary form, having both limbs open above and graduated in millimetres, was used; in this case, the sulphuric acid gauge was dispensed with, the dissociation tube being put in direct communication with the manometer.

Method of Operating.—When a vacuum had been attained, the level of the sulphuric acid in the two limbs of the gauge was made the same, and kept so by the notch-cock and Sprengel during the progress of the heating. The oil-bath was heated to a definite temperature which was maintained until the pressure showed no further appreciable variation; this usually took place in about 20 minutes, but occupied a shorter time at high than at low temperatures. After taking readings, the Sprengel was started and the pressure reduced by from 10 to 20 mm.; the manometer was then again allowed to become stationary, so that if at any point the maximum pressure first observed was not restored it might be at once apparent. The temperature was then again raised and made constant, and a series of readings thus obtained. Finally the apparatus was allowed to cool, and the pressures again noted at various points; in general, these were higher than those noted with an ascending temperature, the differences being especially marked if the cooling had been rapid.

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By slow cooling, however, and long waiting, readings only slightly higher than those previously recorded were obtained in some cases, so that the reaction seems to be completely reciprocating within the limits of temperature investigated.

The results obtained are given in the following table, and in the form of a curve in Fig. 3.

Temperature.	Pressure.	Temperature.	Pressure.
70°	0.0 mm.	218.0°	212 mm.
115	9.0	224.0	306
140	15.0	240.5	522
160	30.0	248.0	682
165	38.5	251.0	755
174	51.0	258.0	893
180	67.5	266.0	1021
191	98.0	273.0	1218
200	138.0	278.0	1354
207	161.0		

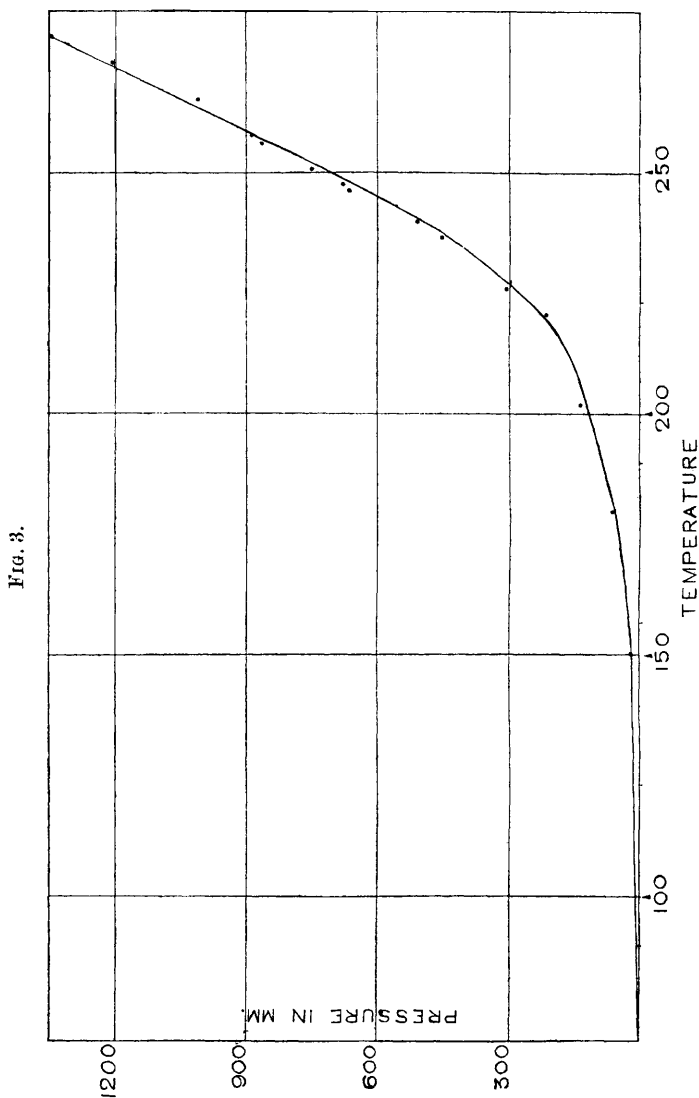
These are not single results, but the means of a number of fairly concordant ones. Other intermediate results were also obtained; for example, at 137° pressures of 15 mm. and 14.6 mm. were observed; at 138° a pressure of 14.8 mm.; at 139° a pressure of 14.7 mm.; at 140° pressures of 15.7 and 15.3 mm.; at 142° pressures of 16.0 and 17.0 mm. From these results, the pressure of 15 mm. at a temperature of 140° is taken for the table and the curve.

The results, of course, show the maximum pressures corresponding to various temperatures when equilibrium is established. It must be noted that the pressures given are not the true pressures of dissociation, but the sum of the partial pressures p and p_1 , where p = the pressure of dissociation, and p_1 = the vapour pressure of gold chloride.

The starting point of 70°, at which trichloride of gold is supposed to begin to dissociate, is somewhat arbitrarily chosen. At 66°, and at all lower temperatures, no pressure could be detected; at 74° the pressure is quite perceptible, but is less than 0.5 mm.; at 84° the rate at which chlorine is evolved in a vacuum is more than three times that observed at 74°, and the pressure is apparently between 1 and 2 mm., but the apparatus is obviously unsuitable for measuring very low pressures.

The observation of a pressure of 755 mm. at 251° is one in which special confidence may be placed, as this was confirmed several times, the temperature being on two occasions maintained for over three hours. Under these conditions attempts were made to obtain

a sample of the gases in the hot part of the dissociation tube. For this purpose, the stop-cock leading to the chlorine generator was cut



off, a partially exhausted flask was affixed by stout rubber tubing to the narrow tube leading from the bottom of the "gold chloride" tube, and the stop-cock of the flask was momentarily opened and then

closed. It was hoped that by the rush of gas into the flask, any chloride of gold existing in the state of vapour would be carried over as dust, even if it were condensed by being cooled. It was assumed that this expectation was realised, and the flask was found to contain on one occasion 0.0537 gram of gold and 0.0919 gram of chlorine; and in the case of another experiment 0.0576 gram of gold and 0.1001 gram of chlorine. If the whole of the gold was present in the state of trichloride, as might be expected from Krüss's results, and those with the hot and cold tubes described below, this would correspond to the presence in the vapours at 251° of 1 mol. (AuCl_3) of gold chloride to about $3\frac{1}{4}$ mols. of chlorine.

These numbers are made use of in the calculations given subsequently (p. 893), by which the pressures of dissociation at different temperatures are theoretically deduced.

Experiments at Higher Temperatures.—In these experiments, the gold chloride was enclosed in the horizontal part, *a*, of a glass tube bent as in Fig. 4, and sealed at both ends. The part, *a*, containing

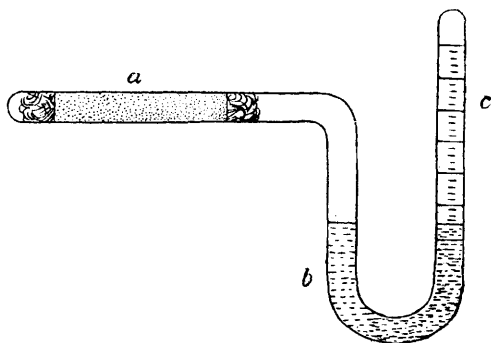
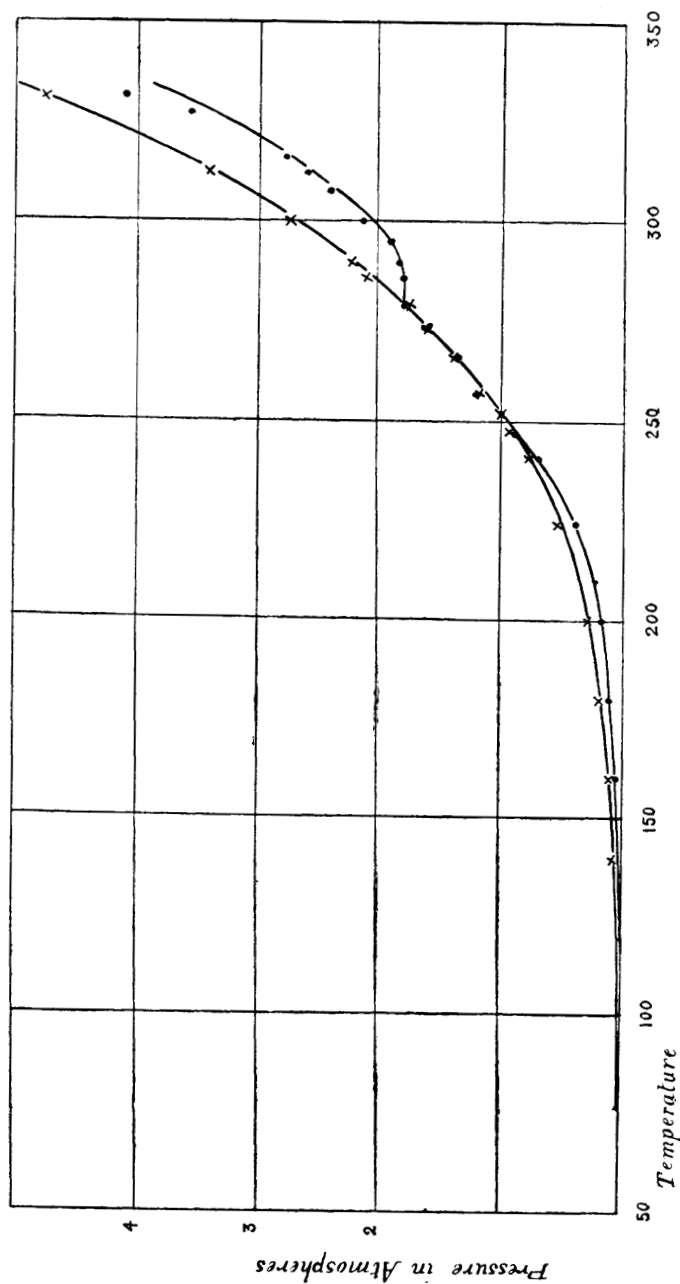


FIG. 4.

the chloride was heated in an air bath; the bent part, *b*, was partly filled with sulphuric acid, and the internal pressure was observed by noting the compression of the gas in the part of the tube marked *c*. The whole tube was filled with chlorine and the sulphuric acid saturated with it before the ends were closed.

The results were as follows.

FIG. 5.



Temp.	Pressure.
286° (the chloride now melting and bubbling)	1·81 atmospheres.
290	1·85 „
295	1·92 „
300	2·1 „
303	2·25 „
306	2·40 „
308	2·50 „
312	2·58 „
316	2·72 „
328	3·58 „
331	3·95 „
332	4·1 „

The accompanying curve, Fig. 5, shows both these results and those at lower temperatures. The dotted curve is obtained by calculation as explained below. It will be seen that while the agreement between the curves, obtained by observation and calculation respectively, is fairly close for all temperatures below the melting point of the chloride, the curves diverge above that point. This was to be expected, the constants being no doubt altered by the change in the physical state of the substance.

Calculation of the Pressure of Dissociation.—The pressure of dissociation can be calculated from the well-known formula

$$0\cdot002 \log_e p + L/T = 0\cdot0405$$

(given by H. le Chatelier, *Ann. des Mines*, 1888 [8], 13, 211), in which p = pressure in kilograms per square metre; L = latent heat of dissociation (or of vaporisation); T = absolute temperature.

It is practically impossible to measure the latent heats of dissociation and vaporisation of AuCl_3 at the temperatures employed; these values can, however, be calculated approximately from the data obtained at 251° by using the equation given above.

Thus p (vapour pressure of AuCl_3) = $178/760 \times 10333$.

p' (tension of dissociation of AuCl_3) = $577/760 \times 10333$.

$T = 524^\circ$.

By substituting these values in the equation, it is found that

L (latent heat of vaporisation) = 13·05 cal.

L' (latent heat of dissociation) = 11·82 „

By substituting these values in the equation (and assuming them to be unchanged throughout the range of temperature within which the experiments were made), the results given in the following table are obtained.

Tempera- ture.	Pressure in mm.			
	p .	p' .	$p + p'$.	
			Calculated.	Observed.
70°	0·2	1·5	1·7	0·0
115	2·0	11·0	13·0	9·0
140	6·0	27·0	33·0	15·0
160	13·0	54·0	67·0	30·0
180	25·0	98·0	123·0	67·5
200	46·0	171·0	217·0	138·0
224	90·0	312·0	402·0	306·0
240	137·0	453·0	590·0	522·0
248	165·0	538·0	703·0	682·0
251	178·0	577·0	755·0	755·0
258	210·0	670·0	880·0	893·0
266	250·0	790·0	1040·0	1021·0
273	295·0	910·0	1205·0	1218·0
278	330·0	1000·0	1330·0	1354·0

Tempera- ture.	Pressure in atmospheres; i.e., values of $p + p'$.	
	Calculated.	Observed.
286°	2·1	1·81
290	2·2	1·85
300	2·7	2·1
312	3·4	2·58
332	4·8	4·1

The comparative want of agreement between the calculated and observed values of the total pressure at temperatures from 140—240° would be explained if the maximum pressures of dissociation had not been attained between these limits. The agreement, however, is much closer below the melting point of the chloride than above it, as has been already pointed out.

Effect of the Removal of Moisture on the Pressure of Dissociation.—The following experiments were made at the suggestion of Professor Armstrong, who thought it probable that perfectly dry chloride of gold would not show fixed pressures of dissociation, for the reason that dry chlorine would perhaps not combine with dry gold.

The tube shown in Fig. 6 was substituted for the one previously employed. The gold was placed in the tube and the latter then drawn out at *a*. The bulbs *b, b* contained P_2O_5 , and the tube was

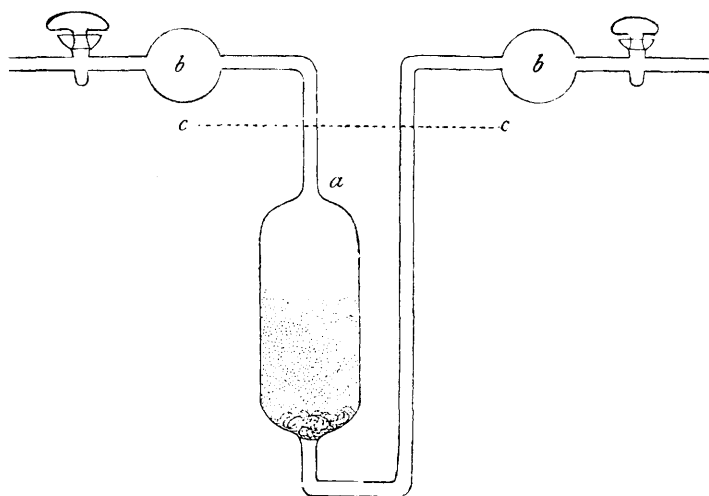


FIG. 6.

heated in the oil bath up to the line *c, c*. Gold chloride was then formed inside the tube as before, and the pressure of dissociation observed at a few temperatures, with the result that the previous values were confirmed. The tube was then exhausted and the vessel heated continuously at 180—200° during six weeks, some of the atmosphere of chlorine being pumped out occasionally. It was hoped that the traces of water contained in the gold chloride tube would be distilled off and be retained by the phosphoric anhydride. It was also expected that practically no moisture would pass through the sulphuric acid gauge, but even if it did, the air in the tubes on the other side of the gauge would also be eventually dried and the passage of moisture stopped. All the tubes were heated at intervals by a moving Bunsen flame. The pressures of dissociation subsequently taken were as follows.

After drying for 14 days:—

Temperature.	Pressure.	
	Dried chloride.	Undried chloride (from curve).
194°	86 mm.	108 mm.

After drying six weeks:—

177.5°	42 mm.	59 mm.
204.0	101 „	150 „

The pressures given by the dried chloride were only reached after several hours heating, whilst those of the undried chloride were attained in less than an hour. The dryness of the chloride of gold seemed, therefore, to retard in a marked way the attainment of the maximum pressures of dissociation.

The question was then approached from the opposite direction. The gold chloride in the tube was heated to about 270° , and the vessel kept partly exhausted until no more chlorine could be removed. The exhaustion was then completed, the vessel allowed to cool, and filled with chlorine which had been in contact with phosphoric anhydride in a glass flask for six weeks. The transfer was made through a glass tube which had been exhausted, and then heated for some time; the stop-cock closing the flask was open for a moment only, when a rush of gas into the tube containing the gold took place, and the pressure in it was found to have been raised to over 600 mm.

The apparatus was then heated, and a rise of pressure occurred due to expansion of the gas by heating, until the temperature reached about 75° when the pressure began to diminish, although the rise of temperature was continuous. It was clear, therefore, that the chlorine was already being taken up by the gold. In half an hour from the time of introducing the chlorine, with the temperature at 220° , the pressure had fallen to 350 mm. The experiment was then stopped.

The result shows that carefully dried chlorine readily attacks gold. Shenstone has already shown that it attacks mercury when very dry (Trans., 1892, **61**, 451), and he suggested that the action of chlorine may be conditioned not so much by the presence of moisture, although it has a distinct connection with this, as by that of traces of other impurities.

Further investigation is required with perfectly pure dry chlorine, if it can be prepared, before the actions in which it takes part can be shown to take place according to Armstrong's theory of chemical change.

I am indebted to Mr. H. Brereton Baker for advice regarding the drying of the vessels and gases.

Experiments on the Volatilisation of Gold Chloride.

According to Krüss, gold can be volatilised in a stream of chlorine at 1100° , the action beginning at 1000° , although at 220° gold chloride is completely decomposed. Now both chlorides are formed at ordinary temperatures with evolution of heat, the heat of formation of dry AuCl_3 being given by Thomsen as 22.8 cal. at 15° , and being calculated from the results given above as 11.8 at 251° .

But according to the law of the displacement of equilibrium with temperature, given by van't Hoff (*Études des Dynamique Chimique*, 1884, 161, Amsterdam,)* and subsequently extended by H. le Chatelier, every state of equilibrium between two different systems is displaced by a reduction of temperature towards that one of the two systems whose formation develops heat. It follows, therefore, that a compound in a state of equilibrium under constant pressure will be governed by the following laws.

- a. If it is formed with evolution of heat, then the higher the temperature, the more complete the dissociation of the compound will be.
- b. If it is formed with absorption of heat, then the higher the temperature, the greater the proportion of the compound that remains undissociated.

Moreover, J. Moutier had previously proved by means of thermodynamics (*Soc. Philomathique*, 1877, 3rd Series, 1, 39 and 96) the following particular case of the law of the displacement of equilibrium: "When action takes place under a fixed pressure, only one temperature exists for which the reaction is reversible: below that temperature the reaction always takes place with disengagement of heat; above that temperature it takes place with absorption of heat." Here, as before, "reaction" stands for any change of physical or chemical state.

Moutier showed that this principle afforded a simple explanation of the fact cited by Troost and Hautefeuille (*Compt. rend.*, 1877, 104, 946), that a number of compounds exist which can be formed at temperatures far above those at which they are decomposed, the only condition necessary to render the explanation valid being that these compounds should be endothermic. As a matter of fact, all the compounds cited, namely, silicon trichloride, chloride of platinum, ozone, oxide of silver, and several other bodies, are formed with absorption of heat.

It would appear, therefore, that, according to Krüss, gold chloride is an exception to the class of compounds which are re-formed at temperatures above those at which they are decomposed, and to the law by which their behaviour is explained. If Krüss were correct, then chloride of gold, on being heated, would dissociate more and more up to a certain point; then, on the temperature being further raised, a change (the recombination of gold and chlorine) would take place, which, by disengaging heat, would tend to raise the temperature still further, instead of tending to reduce it, as required by theory. Gold chloride would, therefore, belong to the same class of bodies as explosives, and the apparent equilibrium of

the system below 300° would be one of "false equilibrium," such as is observable in a mixture of oxygen and hydrogen below 500° .

It might, therefore, have been expected, that Krüss was mistaken in believing that gold chloride cannot exist between 220° and 1000° . Professor Christy's results tend to strengthen that expectation, and it was hoped that by the use of "hot and cold tubes" the matter might be settled.

The apparatus just named was devised by H. Sainte-Claire Deville (*Leçons de la Soc. Chim.*, 4, 316) and subsequently used by Troost and Hautefeuille (*Compt. rend.*, 1877, 84, 946). The exact form used in the experiments now to be described is as follows. When the temperature used was not above 300° , a glass tube $1\frac{1}{2}$ in. in diameter, containing 15 grams of finely divided gold placed in a porcelain boat, was heated in an oil-bath. The ends of the tube were closed with rubber corks, each provided with two holes; through one of these passed a little glass tube, serving for the introduction of a slow stream of dry chlorine, whilst at the other end a similar tube allowed it to escape. In addition, a thin tube of brass, coated with silver on the outside and 5-16 in. in diameter, was passed through the axis of the large glass tube; through the brass tube a rapid current of cold water was passed, and this was found to undergo no perceptible increase of temperature in passing through the apparatus. When the temperature of the oil-bath had remained stationary at the desired point for a few minutes, chlorine was introduced and passed over the gold for thirty minutes. The current of chlorine was then stopped, a rapid stream of dry air passed through until all the chlorine had been expelled, and the water then turned off, and the brass tube emptied and instantly withdrawn. After inspection, the tube was washed down into a capsule, and the washings analysed.

In the experiments at temperatures above 300° , the outer glass tube was replaced by one of glazed porcelain, and a thin glass tube 30 ins. long was used to convey the water, experience showing that it was perfectly safe and easier to wash clean. The temperatures were taken by the Le Chatelier pyrometer, the thermo-couple being placed close to the porcelain boat containing the gold. The couple was protected by being enclosed in a glazed porcelain tube sealed at the inner end, and placed inside the outer porcelain tube. The latter had its ends plugged with baked clay and sealed up, the arrangement of the tubes passing through the plugs being the same as in the other experiments described above.

The outer tube was heated in experiments Nos. 1, 2, and 3 (up to 300°) by an oil-bath; in experiments Nos. 4, 5, and 6 (up to 580°) in a gas furnace; and in the others (above 590°) in a coke furnace. In every case, a length of about 20 in. of the tube was heated.

By the use of the "hot and cold tubes" a portion of the hot vapours is suddenly cooled below the temperature at which any change of chemical composition can take place; a sample more or less representative of the condensible vapours existing in the hot tube is thus preserved, and can then be examined at leisure. The outer surface of the water tube remains cool, the heating action to which it is subjected being mainly due to radiation.

The results obtained were as follows.

Number.	Temperature.	Gold volatilised.		
		Lost from boat.	Recovered from water tube.	Percentage volatilised in 30 minutes.
		grams.	grams.	
1	180°	—	0·00105	0·007
2	230	—	0·0522	0·35
3	300	—	0·3473	2·32
4	390	0·2731	0·1748	1·82
5	480	0·1325	0·0884	0·88
6	580	0·0907	0·0624	0·60
7	590	0·0864	0·0590	0·58
8	805	0·0753	0·0518	0·50
9	965	0·2441	0·1672	1·63
10	1100	0·2895	0·2037	1·93

For purposes of comparison, it may be added that when gold is heated in air or coal gas, no gold is volatilised below 1050°, and only about 0·02 per cent. in 30 minutes at 1100° (Trans., 1893, 61, 717), or about one-hundredth part of that volatilised in chlorine.

In the table, the amounts "lost" by volatilisation include the amounts recovered from the water tube and the gold condensed on the inside of the outer tube; the latter sublimate was not recovered separately after each experiment.

In every case, the gold recovered from the water tube was associated with a little less chlorine than was required to form gold trichloride, and therefore presumably contained either some metallic gold or AuCl, or both; these doubtless resulted from the dissociation of some of the trichloride, when in the form of vapour.

The amounts volatilised vary according to two different factors. (1) The vapour pressure of gold trichloride, AuCl₃, which of course increases continuously as the temperature rises; and (2) the pressure of dissociation of the trichloride, which also rises continuously with the temperature, but not at the same rate as the vapour pressure. The rise of vapour pressure tends to raise, and that of the pressure

of dissociation to reduce the amount of gold volatilised as chloride. The vapour pressure increases more rapidly than the pressure of dissociation at temperatures below 300° , and also above 900° , but less rapidly at intermediate temperatures. Hence the curve showing the

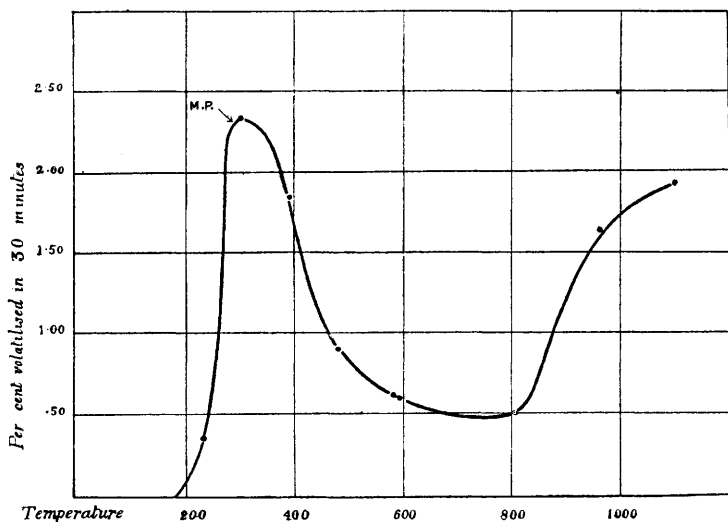


FIG. 7.

variation of volatilisation with temperature is irregular, passing through a maximum near 300° , and a minimum at a point somewhere below the melting point of gold. The first-named change in the direction of the curve possibly occurs at the melting point of the chloride, namely 288° . The second change is perhaps caused by the change of sign of the heat of formation of the trichloride AuCl_3 ; when this becomes negative, the pressure of dissociation of the compound would decrease, in accordance with the law of van't Hoff and Le Chatelier. However this may be, it is certain that when gold is heated in chlorine at atmospheric pressure, trichloride of gold is formed and volatilised at all temperatures above 180° , up to, and probably far beyond, 1100° .

It is thus shown to be improbable that gold chloride is an exception to the rule that a substance formed with evolution of heat exhibits a greater tendency to dissociate as the temperature rises. As already stated, several substances are known which, although they are completely decomposed at moderate temperatures, again become capable of formation at much higher ones, but these substances are all formed with absorption of heat. It is doubtful whether a substance formed by an exothermic change could behave

in this way: for example, in spite of the results of C. Langer and V. Meyer (*Ber.*, 1879, **12**, 2202) on the behaviour of platinous chloride, which is stated to be capable of existing only below 300° and above 1300° , it is probable that its properties in this respect resemble those of gold chloride. This will be investigated subsequently by the "hot and cold tube."

Repetition of Krüss's Experiments.

As Krüss's results did not agree with those given above, it was thought desirable to repeat his experiments on the volatilisation of gold chloride (*Ber.*, 1887, **20**, 212). A glass tube was therefore filled with precipitated gold for a length of about 10 cm., and the empty part of the tube drawn out at several places. A slow current of chlorine, prepared as before, was then passed through the tube, and the part of the latter containing the gold gradually heated in an air-bath. The appearances noted by Krüss at temperatures below 180° were readily seen, but there was no further agreement with his observations. As the temperature rose higher, the sublimed crystals of chloride of gold formed more rapidly in the cool part of the tube, and the part which was being heated became darker in colour, until at 270° it was almost black, consisting of lustrous crystals, apparently composed of AuCl_3 . At 285° , signs of decomposition of the chloride were perceptible, but even at 300° the rate at which dissociation was taking place seemed to be very slow. On cooling, the red colour gradually returned, and volatilisation became less by degrees. The stream of chlorine passing into the tube was, on the other hand, absorbed more and more, the greatest rate of absorption of the gas being observed at about 225° .

In a similar tube, but with a smaller quantity of gold, the rate of volatilisation at 260° was tested with a view to determine if it were really continuous. The following results were obtained.

Duration of experiment.	Amount of AuCl_3 sublimed.	
	Total.	Per hour.
1 hour	0.0926 gram	0.0926 gram.
$3\frac{1}{2}$ hours	0.3188 "	0.0911 "

The sublimation is thus seen to be perfectly continuous at 260° .

With regard to Krüss's observations, it may be noted that he made no attempt to ascertain whether the decomposition of either AuCl_3 into AuCl and chlorine at 180° to 190° , or that of AuCl into gold and chlorine at 220° , was complete at the temperature named. He trusted to inspection through the glass, although the thickness of the layer of gold in the tube was considerable. If the film next the glass were

changed in the manner stated, the absence of change in the remainder would not be detected, and Krüss could thus merely observe the *beginning* of actions, which are incomplete until much higher temperatures are attained.

Rate of Decomposition of the Chlorides of Gold at Different Temperatures.

In this investigation, the method adopted was to heat a mixture of the chlorides of gold to various temperatures and for various lengths of time, (a) in the air, and (b) in an atmosphere of chlorine, and then to analyse the products. As pure dry chloride of gold, free from acids, is difficult to prepare in large quantity, a mixture of the chlorides was prepared as follows. One ounce of pure precipitated gold was heated in a stream of pure dry chlorine until no more was absorbed at 210–220°. The tube containing the gold chloride was then sealed up, heated to 300°, and the melted chloride shaken up, allowed to cool in a mass, and sampled. It was found to contain, by analysis,

Metallic gold	Nil.
AuCl	18·81 per cent.
AuCl ₃	81·19 „

Portions were heated in porcelain crucibles in a water-oven and in an air-oven; the crucible being placed in a pipe-clay triangle supported on asbestos, and the bulb of the thermometer inserted in the crucible. In the “atmosphere of chlorine,” the samples were placed in short glass tubes sealed up at one end and drawn out to fine capillaries about 7·5 cm. long, at the other; chlorine, generated by the decomposition of the chlorides, expelled the air from these tubes, and as long as the temperature was not allowed to fall, no subsequent entrance of air into them took place, except by diffusion, which would not be rapid under such conditions. Nevertheless, the pressure of chlorine in the bulb could not be expected to be quite equal to that of the atmosphere.

The results are given in the following table. The total weight of gold used in each experiment varied from about 0·5 to 2·5 grams. The chlorides were not weighed out at the beginning and the loss by volatilisation was neglected.

In addition to these experiments, some of the fused chloride was heated for seven days in an atmosphere of chlorine at 220°. The product, which was not analysed, consisted of two parts, a large quantity of volatilised dark red AuCl₃ in crystals, which were kindly examined and described by Mr. W. J. Pope (see succeeding paper, p. 906), and a residue, consisting, apparently, of a mixture of metallic gold and

Table of Experiments on Decomposition of Chloride of Gold.

Temperature.	Time of treatment.	Analysis of product. Percentages.			Percentage of AuCl ₃ decomposed per hour.
		Metallic gold.	Gold as AuCl.	Gold as AuCl ₃ .	
In atmosphere of chlorine					
165°	4 hours	—	20·11	79·89	0·40
188	18 „	—	21·86	78·14	0·21
190	8 „	—	27·06	72·94	1·27
190	24 „	—	37·30	62·70	0·95
In air					
100°	7 days	—	24·33	75·77	0·04
165	4 hours	—	28·60	71·40	3·015
168	18 „	—	59·59	41·41	2·72
190	10 „	0·12	99·88	—	—
190	24 „	57·88	42·12	—	—
175—180°	6 days	100·00	—	—	—
155—163	7 „	52·23	47·77	—	—

gold monochloride, AuCl . The crystals of AuCl_3 did not change in appearance during the last five days, and seemingly were more stable than the AuCl_3 cooled from fusion.

The analyses were made, except in the last four cases, by digesting the product with ether, treating the residue with water, and estimating the gold in the two solutions and in the undissolved part. In the four cases mentioned, the preliminary treatment with ether was dispensed with, as the product was pale yellow and appeared to be free from the trichloride. The complete decomposition of the monochloride was ensured by digesting it with water for 48 hours, then gently warming it and washing the residue first with cold and then with hot water. The gold in solution was precipitated by sulphurous acid, and the chlorine estimated by precipitation as silver chloride. In every case, nearly 3 atoms of chlorine were found for each atom of gold in the portion soluble in water.

From the table, it is seen that AuCl_3 , as it cools from fusion, suffers slow decomposition at as low a temperature as 165°, in an atmosphere consisting almost entirely of chlorine, and the decomposition is about five times as rapid if the temperature is 190°. In these experiments, the initial decomposition is much more rapid, as it takes place in an atmosphere of air until the latter has been driven out.

Gold trichloride, AuCl_3 , prepared in a similar manner, is slowly decomposed in air at 100°, although not so rapidly as was observed

by Lowe (*Ding. Polyt. Jour.*, 1891, **279**, 167) in the case of a solution of the trichloride; he states that 4 grams of gold trichloride, when heated in a porcelain basin on a boiling water bath, can be completely transformed into the monochloride, although not until after the lapse of several days. Monochloride of gold suffers slow decomposition in air at about 160° , and the decomposition is complete if it is heated at 175 – 180° for six days.

By making use of the formula $\alpha_1/\alpha_2 = (\tau_1/\tau_2)^m$, given by Harcourt and Esson (Bakerian Lecture, "On the Laws of Connection between the Conditions of Chemical Change and its Amount," read at the Royal Society, May 9, 1895), the following results are obtained. Taking the initial decomposition of gold trichloride in air at 165° as at the rate of 3.21 per cent. per hour, and at 100° as at 0.0411 per cent. per hour (the rates calculated from the first two experiments in air), the value of m for this chemical action is found to be about 27. Hence the rate of decomposition of gold trichloride should be about 0.365 per cent. in a year at 15° .

The value of m is about the same in the decomposition of gold trichloride in chlorine as in air. That is to say, the effect of temperature on the rate of decomposition of gold trichloride is about the same whether the latter is heated in air or in chlorine.

General Conclusions.

The results of the experiments prove that gold chloride shows fixed pressure of dissociation, the attainment of which is greatly delayed by very careful drying. The pressure of dissociation is insignificant below 70° , and becomes equal to that of the atmosphere at about 265° . As, however, the vapour pressure of AuCl_3 , which is just perceptible at 100° , rises rapidly with the temperature, and becomes considerable between 200° and 300° , it follows that the pressure of dissociation combined with the vapour pressure of AuCl_3 is equal to that of the atmosphere at 251° .

The change of state of the chloride of gold from solid to liquid, which occurs at 288° , causes a decided check to be given to the rate of increase with temperature both of the pressure of dissociation and of the vapour pressure, but the greater effect seems to be produced on that of the latter.

The decomposition and volatilisation of gold trichloride take place in accordance with these properties. When the pressure of chlorine is kept constant at about 760 mm., the continuous volatilisation of AuCl_3 is readily observed at 180° , and increases rapidly until about the melting point. The rate of volatilisation then falls slowly as the temperature rises through several hundred degrees, but shows a

minimum at about 800° and again increases, owing to the falling-off of the pressure of dissociation as compared with vapour pressure. Probably the heat of formation of AuCl_3 passes through zero and becomes negative at between 800° and 1000° . This could only be determined with certainty by calculation, using the specific heat of the substance, which is not known, and those of its elements. The change of sign of the heat of formation would readily account for a diminution in the pressure of dissociation, and consequent increase in the observed rate of volatilisation at high temperatures.

The decomposition of gold trichloride in air might be expected to become perceptible at 70° , requiring, however, about 25 years for its nearly complete change into the monochloride, AuCl , at this temperature. The observed rate of decomposition at 100° shows that a similar change would require about 1,000 days at this temperature, while it results from calculation, using Harcourt and Esson's formula, that at 200° , 36 hours, and at the melting point, namely, 288° , less than one minute suffices for the complete decomposition of AuCl_3 in air.

There might appear at first sight to be a discrepancy between the results obtained on the one hand by heating gold trichloride, and on the other by passing a stream of chlorine over metallic gold. In the former case, the pressure of dissociation becomes equal to four atmospheres at about 332° , and by the direction of the curve between 300° and 330° might be expected to become enormous at a bright red heat. Nevertheless, by the use of the "hot and cold tubes," gold trichloride is condensed from the stream of chlorine at atmospheric pressure at all temperatures between 180° and 1100° . The reason for this is partly to be found in the change of the heat of formation of AuCl_3 with temperature, but mainly in the extreme slowness with which the last traces of a compound are dissociated, even when it is much above its mean temperature of dissociation. This is, of course, attributable to the differences in the movements of the atoms in the different molecules in a given mass at a definite temperature. As already stated, there is reason to believe that at the ordinary atmospheric pressure, there is no temperature at which it is impossible to form gold chloride.

The Royal Mint.
