

CLII.—*The Chemical Action of Radium Emanation.  
Part II. On Solutions Containing Copper, and  
Lead, and on Water.*

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THE results of preliminary experiments relating to the action of radium emanation on water form the subject of the previous memoir (this vol., p. 931). It will be remembered that excess of hydrogen above that yielded by the decomposition of water was

always found. With the view of accounting for its origin, and with the idea that this *pseudo*-electrolysis, if applied to a copper salt, would give a deposit of metallic copper equivalent to the hydrogen, a solution of copper sulphate was treated with radium emanation in the manner described below. No copper was deposited; and on investigating the products, it was found that a trace of lithium was present in the copper solution along with a considerable amount of sodium. This experiment was carried out during the summer of 1906. The result was so unexpected that it was repeated during the autumn of that year and again in the spring of 1907, always with the same result. A solution of lead nitrate was also exposed to the action of emanation obtained as the maximum yield from 87.7 milligrams of radium as bromide and sulphate. And more recently, a prolonged experiment has been carried out on a specimen of copper nitrate, prepared from electrolytic copper with specially pure nitric acid, avoiding the use of glass as much as possible; the result was substantially the same, for a residue was obtained consisting chiefly of sodium salts, but showing the spectra of calcium and lithium. Simultaneously, a blank experiment was made with the same copper nitrate, leaving it to stand in a glass bulb under identical circumstances, but untreated with emanation. A second blank experiment was also made in which distilled water was treated with emanation with the view of excluding the formation of lithium from a possible alteration in the water, or in the glass of the bulb which contained the reacting substances.

No definite results have been obtained as yet from the experiment with lead nitrate, except that the minute residue after removal of lead from the solution consisted solely of sodium and calcium salts; it did not show the lithium spectrum. The glass of the bulbs employed contained both sodium and calcium; it was free from lithium.

From dry radium emanation, decomposing spontaneously, the inactive gas produced showed a brilliant spectrum of helium; it is possible that a trace of neon was present, but this is uncertain. A bright helium tube, which was exhibited to the Chemical Society in April, left no doubt that by far the major part of the inactive gas resulting from the dry emanation consists of helium.

The gas proceeding from the action of the emanation on a saturated solution of slightly acid copper nitrate was also analysed; it contained a large percentage of nitric oxide, and left a residue of 0.3 c.c. of nitrogen. This gas, when examined spectroscopically, contained argon, but no helium.

The gas, similarly collected from water on which emanation had

acted, when examined spectroscopically, after removal of ordinary gases, showed a brilliant spectrum of neon, in which all the visible lines of neon were identified by comparison with a neon tube. This gas also contained a trace of helium; the green, yellow, and red lines were feeble; the blue lines and the violet line were invisible, owing to the small quantity of helium present.

### EXPERIMENTAL.\*

*First Experiment, with Copper Sulphate.*—A specimen of ordinary "pure" copper sulphate was recrystallised four times. A saturated solution of this salt was treated in a small soda-lime-glass bulb with emanation from radium bromide (152 milligrams) and sulphate (10 milligrams), containing 87.7 milligrams of metal, on the suppositions that the atomic weight of radium is 225, that the bromide crystallises with 2 molecules of water, and that the sulphate is anhydrous. Only one dose, collected during four days, was introduced, corresponding to about 0.3 cubic millimetre of emanation. After standing for more than a month, the copper was removed from the treated solution with hydrogen sulphide, and the residue, after evaporation, consisted mainly of sulphates of sodium and calcium, the latter present in very small amount; it showed the red line of lithium when examined spectroscopically. The original specimen of copper sulphate, from which the crystallised sample used for the experiment had been prepared, was then examined in the same way; it was found to contain a trace of lithium. The recrystallised sample failed to show this test.†

*Second Experiment, with Copper Sulphate.*—For this experiment, the copper sulphate was produced by dissolving metallic

\* To save space, the description of the precautions taken during the first three experiments has been abbreviated; details relating to the fourth experiment are alone given.

† Mr. A. C. Egerton has been so obliging as to carry out a series of crystallisations of copper sulphate to which a small known quantity of lithium sulphate had been added. It was of interest to determine whether the double sulphate,  $\text{CuLi}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , could be easily separated from excess of copper sulphate by crystallisation. Two sets of experiments were made, in which both copper and lithium were determined in the first four fractions of a mixture of copper sulphate with a trace of lithium nitrate. The results are:

	Fraction 1.	2.	3.	4.
I. {	Copper... 0.760 gram	0.827 gram	0.843 gram	0.823 gram as metal.
	Lithium. trace	0.0001 ,,	0.0007 ,,	0.0015 ,, as sulphate.
II. {	Fraction 1.	2.	3.	4.
	Copper... 0.7008 gram	0.5065 gram	0.6426 gram	0.6401 gram as metal.
	Lithium. 0.0001 ,,	0.0004 ,,	0.0008 ,,	0.0029 ,, as chloride.

It appears unlikely, therefore, that, after four recrystallisations of an ordinary sample of copper sulphate, any lithium could be found in the recrystallised sample.

copper, deposited from the sulphate with a current of three volts potential, in sulphuric acid, which had been specially made in the laboratory for the purpose by the "contact" process. Glass vessels were used, but a careful analysis of the glass, in which the amyl alcohol method of separating lithium as chloride from the other alkalis was employed, failed to reveal the presence of lithium in it.

The same process was adopted, the amount of emanation introduced having been the same. After more than a month, the bulb was opened and its contents analysed, and again with the same result. The residue of sulphates weighed 1.1 milligrams; it gave a brilliant sodium spectrum, and it again showed the red line of lithium.

*Third Experiment, with Copper Nitrate.*—The copper sulphide obtained from experiment 2, after solution in nitric acid, was converted into acetylide with hydroxylamine hydrochloride, ammonia, and acetylene. This was the method employed to separate copper from all other metals of the sulphide group. The copper acetylide was dissolved in dilute nitric acid in a platinum basin, and the nitrate was evaporated to dryness. It was then dissolved in water and exposed to five doses of emanation, amounting in volume to 1.5 cubic millimetres. The solution was then allowed to stand for forty-one days, when practically all the emanation must have changed. The copper nitrate deposited a trace of basic salt. At the end of that time, all the nitrate was washed out of the bulb into a platinum basin, the purest obtainable water, kept in a steamed-out glass wash-bottle, being used, and a current of hydrogen sulphide, led in through a platinum tube, was used to throw down the copper. The filtrate from the copper sulphide was evaporated to dryness in a platinum basin and ignited; it weighed 2.48 milligrams. The spectrum was chiefly that of sodium, but the lithium red line was detected, and its position confirmed. It was undoubted.

The copper sulphide was dissolved in nitric acid, and the copper was precipitated as before in the form of acetylide (Erdmann and Makowka, *Zeitsch. anal. Chem.*, 1907, **46**, 128). The filtrate was dried and ignited to decompose salts of hydroxylamine; only a trace of iron was found in it, due probably to the acids employed.

*Fourth Experiment, with Copper Nitrate.*—During this experiment, the greatest care was taken to avoid the introduction of any possible impurity. The vessels used, with exception of the original bulb and of a glass pipette, were of platinum and silica. Only gaseous reagents were used in the whole work, up to obtaining the residue of alkali.

The source of the copper was "pure" laboratory copper sulphate; it was dissolved in distilled water, of which 20 c.c. gave a total unweighable residue. This solution was electrolysed, the current used being 1 ampere, and the E.M.F. 3 volts, and it was deposited on a rotating cathode of smooth platinum. After two and a half hours, the copper coating was washed several times with the purest water.

Pure redistilled nitric acid was the solvent for the copper; the residue from 50 c.c. weighed 0.4 milligram. About half the copper was dissolved; the solution was evaporated to dryness in a platinum basin over a water-bath, and the residue was heated for two hours longer to expel the last traces of nitric acid. This copper nitrate was dissolved in pure water and filtered into two glass bulbs, newly made from the same piece of tubing. One was exhausted and sealed (I); emanation which had collected for ten days was introduced on April 29th into the other bulb (II); emanation was again added on May 4th, 9th, and 14th. The bulb was then sealed off. The total quantity of emanation introduced was approximately 1.62 cubic millimetres.

After the first day, a slight cloudiness appeared in bulb II, whereas the contents of I were perfectly transparent. On the second day, the liquid in II was distinctly green, whilst the copper nitrate in I, naturally, remained clear blue. The green colour did not become more intense.

The residual gas from the emanation was collected as "copper gas." The method was: to freeze with liquid air the contents of the bulb, then to open the tap to the pump, and to evacuate the bulb; this yielded the "copper gas." Emanation with some hydrogen was then introduced into the bulb; the hydrogen was then pumped out, and examined subsequently. It may be stated here that this gas was used as a source of helium; it is possible that, when freshly prepared, some neon lines were present, but this is not certain.

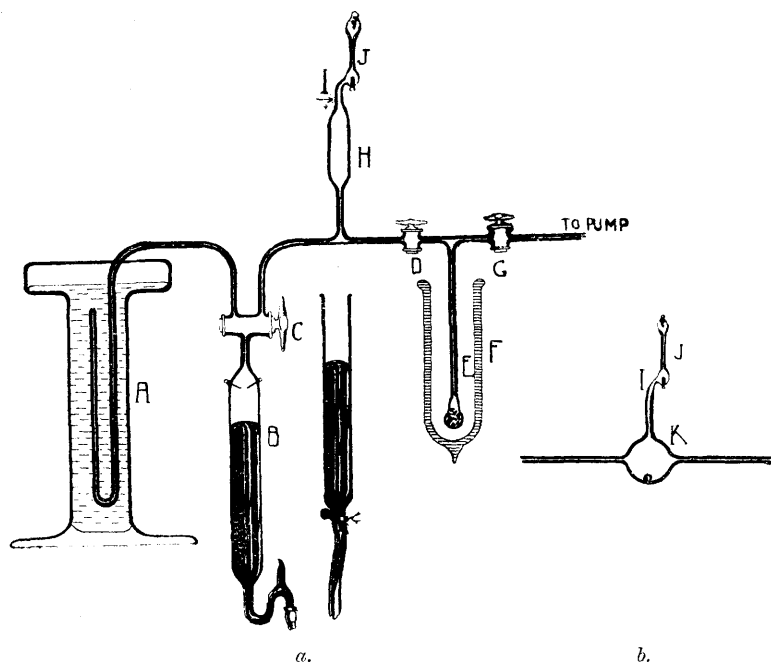
Both bulbs were finally opened on June 10th; from the untreated bulb nothing could be pumped off, as might have been supposed.

In order to gain some knowledge of the action of the emanation on glass alone, a similar bulb was charged with pure distilled water, and emanation was introduced on May 22nd and 29th, and on June 7th and 11th; in all, 1.44 cubic millimetres were added. The bulb was opened on June 29th. The liquid contents of the bulbs are left for after consideration; the gaseous contents alone will be now treated of.

*Investigation of the Gaseous Products.*—A curious circumstance now transpired. On pumping out the gaseous contents of the

bulb containing copper nitrate (the "copper gas") for the last time, it was naturally collected in the same tube into which it had previously been introduced; but the copper solution was not frozen with liquid air, in order that *all* gases might be removed, and not merely those volatile at the lower temperature. On mixing, red fumes were observed; the explanation evidently is that the nitric oxide, to which the nitrate ion had been reduced, had been frozen during the former extractions of gas, and had accumulated in the bulb. It is known that nitric

FIG. 1.



oxide forms unstable combinations with copper salts, and these, at the low temperature of liquid air, must have remained undissociated. This mixture of gases was then well shaken with mercury, in order to absorb the nitric peroxide, and the analysis of the residual gas was carried out. The deposit of mercurous nitrate was then treated with concentrated sulphuric acid, and the nitric oxide was thus liberated. In this manner, the analysis of the gaseous mixture was rendered complete.

The method of separating and examining the inactive gases was as follows. After the carbon dioxide had been removed with

potassium hydroxide, sparks were passed, and the hydrogen and oxygen, or carbon monoxide and oxygen, were made to unite. The residue was again treated with potash, so as to absorb any carbon dioxide formed from carbon monoxide. If necessary, this operation was repeated after a measured quantity of oxygen had been added. The oxygen was then absorbed by phosphorus, and the residue of nitrogen was introduced through the inverted siphon, *A*, Fig. 1 (*a*), into the burette, *B*. The rest of the apparatus was connected with the pump through *G* and evacuated; *G* was then closed. The stopcock, *C*, was then opened, and the gas under examination was allowed to enter, the mercury being raised just above the stopcock, which was then closed. The bulb, *E*, containing charcoal, previously heated to  $230^{\circ}$  in quinoline vapour and freed from adsorbed gases, was then cooled with liquid air; any argon and nitrogen present was condensed in *E*. A paper cup was then constructed round the tube, *H*, moistened with water, and, on pouring in liquid air, a vessel of ice was produced; by this means the tube, *H*, was cooled, so that the major part of the gas which had not condensed in the cooled charcoal was contained therein. The tap, *D*, was then closed, and mercury was forced up through *C* to the point *I*; here again a similar funnel of wet paper was constructed and charged with liquid air, so that, in sealing off, mercury vapour should be condensed, and should not give its spectrum in the vacuum tube. The vacuum tube, *J* (which had at the beginning of the operation been glowed out to remove hydrogen from the electrodes), was then sealed off.

The stopcock, *G*, was then opened, and the gas was pumped off; the charcoal was again surrounded by boiling quinoline, so as to make certain of extracting all the gas. Oxygen was added to the nitrogen, and by sparking in presence of potassium hydroxide, all nitrogen was removed. The gas was then admitted into a piece of apparatus similar to that already described, but differing, inasmuch as, instead of charcoal, phosphorus was placed in *K* to absorb the oxygen, the only residual gas besides those of the inactive group. After absorption of oxygen, mercury was allowed to enter and force the residual gas up into the little vacuum tube, where its spectrum could be examined after condensing mercury vapour as before.

The gases from the various solutions were examined as described. Their composition was:

	From copper nitrate solution, "treated."	From "treated" water.	From "treated" lead nitrate.
Nitric oxide, NO .....	1.12 c.c.	—	—
Nitrogen, N <sub>2</sub> .....	0.34 "	0.307 c.c.	0.032 c.c.
Carbon dioxide, CO <sub>2</sub> ...	0.27 "	0.065 "	0.009 "
Carbon monoxide, CO.	— "	0.030 "	— "
Hydrogen, H <sub>2</sub> .....	0.44 "	3.746 "	0.184 "
Oxygen, O <sub>2</sub> .....	1.12 "	1.562 "	0.700 "
	3.29 "	5.710 "	0.925 "

From the residue of nitrogen from the gas evolved by the emanation by its action on copper nitrate, the residual nitrogen was removed by sparking with oxygen over sodium hydroxide, and the excess of oxygen was removed, as already described, with phosphorus in the apparatus shown in Fig. 1 (*b*). The spectrum was that of pure argon; no helium or neon line could be observed. It must be noticed, however, that two red lines, of approximate wave-length 6739 and 6670, were observed, which were not present in the argon spectrum used for comparison. Now it is possible that air might have leaked in through the stopcocks, for the emanation was introduced during a period of fifteen days, and the bulb was then sealed off. But if the argon had been derived from the atmosphere alone, helium should still have been visible in the spectrum if it had been derived from the emanation; reckoning the nitrogen as entirely atmospheric, the corresponding amount of argon would have been approximately three cubic millimetres, and we know, from experiments on the emanation above that from 1.62 cubic millimetres of the emanation, the volume of helium to be expected should have been about 5 cubic millimetres, a quantity easily visible in the presence of so little argon. We regard it as more probable that there was no leakage, and that the nitrogen was derived from the copper nitrate. This point, however, cannot be regarded as settled until further experiments have been made, in which the possibility of leakage of air into the apparatus is completely excluded.

The gas from the water, treated with emanation, was examined by the help of cooled charcoal. The uncondensable gas, forced up into the small vacuum tube, gave a brilliant neon spectrum in which the helium spectrum was faintly visible. A comparison was made with a vacuum tube containing atmospheric neon, and every line of neon was identified in the gas from the "treated" water. With a helium tube for comparison, it could be seen that the yellow and green helium lines of wave-lengths 6677, 5876, and 5016 were present, but the other lines of helium were too faint to be visible. There were also other lines present, of which the approximate wave-lengths are:



Red	6242 strong	Yellow-green	5828 very feeble	
	6223 feeble	„	5806 „	
	6149 „	„	5720 „	
Yellow	6018 „	Green	5454 „	(Hg=5461)
	5912 „	„	5259 feeble	
		„	4893 very feeble	(H <sub>2</sub> =4861)
		„	4625 „	

As the gas from the lead nitrate was the product of only one dose of emanation, it was not thought worth while to examine the inactive residue. That must be left for further experiment.

*Investigation of the Copper Nitrate.*—Parallel experiments were carried out with the “treated” nitrate, and with a sample of the same solution, filtered into a bulb of similar glass, which was pumped empty and allowed to stand for the same length of time as the bulb containing the nitrate plus emanation. These will be termed I. and II. respectively.

I. contained a greenish-white deposit; II. was quite transparent. The mixed solid and liquid from I. were transferred to a weighed silica tube, which was constructed for centrifugalisation, and centrifuged. The liquid was poured into a platinum crucible. The solid was twice washed with pure water\* and the washings were added to the contents of the crucible. The residue, dried at 130°, weighed 4.11 milligrams. This residue was dissolved in nitric acid, distilled directly from a glass flask through a platinum tube sealed into the flask; it gave a blue solution. The nitric acid, thus prepared, gave no perceptible residue on evaporation. The acid solution was diluted with distilled water, and hydrogen sulphide, which had been allowed to stand for some hours in the Kipp's apparatus, was passed in through a platinum tube. A black precipitate was produced, which, with the liquor, was added to that obtained from the rest of the copper nitrate.

The liquid from the greenish-white precipitate, which was mainly a basic nitrate of copper, was also treated with hydrogen sulphide, using the same precautions as before. The precipitate of sulphides was separated by centrifugalisation in a silica tube, but a new glass pipette was used to transfer the supernatant liquid to a platinum capsule. The process was repeated so as to ensure the separation of all sulphide.

\* This water, which had also been used in the preparation of the copper nitrate and for treatment with emanation, was prepared as follows:—Ordinary distilled water was redistilled, using a tin condenser, into a Jena-glass flask. It was then frozen, being violently shaken in the shaking machine. Half the ice was allowed to melt and drain away, and the residue, when liquid, was stored in steamed-out Jena flasks. Previous to the copper nitrate analysis, 20 c.c. of this water gave a just visible total residue, absolutely unweighable, and invisible after ignition. The residue on evaporation, after the water had stood during the time required for the analysis, was perhaps perceptibly greater, but was still quite negligible.

The filtrate was evaporated nearly to dryness on a water-bath, and finally dried over a flame. The residue was dissolved in four drops of water, and transferred to a smaller capsule. Four drops and five drops of the purest redistilled water were successively used as wash-water; the solution was evaporated over a small glass water-bath, and finally dried at  $130^{\circ}$ . The capsule was transferred while still hot to a glass weighing-dish. The weight of the residue was 1.67 milligrams. Its spectrum consisted of sodium (very strong) and calcium (present, but weak), and the lithium red line was identified and compared with the spectrum of lithium chloride. The position of the line was undoubted. A mixture of sodium and lithium chlorides was made, so as to be able to estimate approximately the percentage of lithium present. When the lithium was present in such amount that it formed 0.01 per cent. of the sodium, the intensity of the lithium red line was comparable with that of the residue from the copper nitrate. The total quantity of lithium therefore may be estimated as 0.00017 milligram.

II. The blank experiment was treated in exactly the same manner. The residue weighed 0.79 milligram. The spectrum was that of sodium (very strong) and calcium (feeble); no trace of the lithium line could be observed. This was again repeated with identical results.

I. The copper sulphide was heated in a clean glass beaker with pure distilled hydrochloric acid. As there was now no necessity to exclude alkalis, ordinary distilled water and glass vessels were used. The precipitate dissolved, leaving a small residue of sulphur. The liquid was filtered into an Erlenmeyer flask, and ammonia was blown in until the cupric hydroxide, precipitated at first, had re-dissolved. Crystals of hydroxylamine hydrochloride were then added, and the solution was warmed; when it had become quite colourless, acetylene was passed in for some minutes. The cuprous acetylide was filtered off, and the process was repeated; the solution gave no further precipitate, even after standing overnight. The filtrate from the acetylide gave no precipitate with hydrogen sulphide, but, on acidifying with hydrochloric acid, a faint precipitate was produced, consisting largely of sulphur. This residue was digested with *aqua regia*; the solution gave no blue coloration with ammonia; it was evaporated to dryness, dissolved in hydrochloric acid, evaporated, and taken up with a drop of water. It gave a minute, black precipitate with hydrogen sulphide, too small for further investigation.

The copper acetylide was transformed into sulphate, and weighed as such. The weight corresponded to 0.815 gram of  $\text{Cu}(\text{NO}_3)_2$ , which was therefore the amount treated with emanation.

II. The blank experiment was treated in an exactly similar manner; the only difference was that in this case no trace of a black precipitate could be produced in the filtrate from the copper acetylide. The weight of nitrate taken was 0.968 gram of  $\text{Cu}(\text{NO}_3)_2$ . The black precipitate, if it is possible to produce it in greater amount, deserves investigation.

*Investigation of the Lead Nitrate.*—Here again a duplicate, untreated sample was examined along with the sample which had been exposed to the action of the emanation. As before, the treated sample will be termed I., and the untreated sample II.

I. The treated sample was transferred to a platinum crucible; the glass bulb was twice washed out with the purest distilled water;\* dilute sulphuric acid, produced in the laboratory by the contact process, and uncontaminated by alkali, was added, until no further precipitate fell. The precipitate was separated by centrifugalisation in a silica tube, and the sulphate residue was transferred to a glass beaker.

The liquid was transferred to a platinum capsule, and evaporated to dryness to remove sulphuric acid; water was added, and hydrochloric acid was then distilled in, in the state of gas. Hydrogen sulphide was then passed in, and the black precipitate of sulphide was centrifugalised. The liquid was decanted into a platinum capsule, and evaporated to dryness on a water-bath. Water was again added, hydrochloric acid again distilled in, and then ammonia was blown through the solution. There was a very slight reddish-brown precipitate, resembling ferric hydroxide. This was removed centrifugally in silica, and the solution was poured into a platinum capsule. This liquid was evaporated, and heated to volatilise ammonium salts. The residue weighed 0.45 milligram, but some had previously been removed for spectroscopic testing; the original weight was probably about 0.6 or 0.8 milligram. The spectrum was that of sodium only; no calcium or lithium was visible.

The reddish-brown precipitate gave the reactions of iron.

II. The blank experiment gave precisely similar results so far.

I. The precipitate of lead sulphate was dissolved in sodium hydroxide prepared from sodium with alcohol. (Iron was present as an impurity in this sodium hydroxide.) There remained a very small insoluble residue, distinct from the flocky precipitate of ferric hydroxide; the latter dissolved in hydrochloric acid, but some grains of a black powder remained. This was not observed in II.; the ferric hydroxide dissolved completely and at once.

I. The precipitate of lead sulphide, obtained by passing hydrogen

\* The wash-bottle was wholly of glass; no grease was used, and the flask was thoroughly steamed-out before the specially pure distilled water was introduced.

sulphide through the liquid from which the sulphate had been separated centrifugally, was dissolved by saturating the liquid with hydrogen chloride and heating. There remained a residue of six-sided, colourless tables, and some reddish-yellow grains. The whole liquid was evaporated to dryness, when lead chloride separated. Alcohol was added, and the lead chloride was separated centrifugally. The alcohol was evaporated in a silica capsule over a water-bath. The residue of white crystals still was seen, and also a yellow powder similar to that already described. Experiments made with the blank, II., gave no crystals and no yellow grains.

The residues, both from the copper and from the lead, are unfortunately so small that their investigation is exceedingly difficult. It is our intention to try to produce them in larger amount by using larger quantities of emanation and by employing a silica bulb. The latter is already in operation, and by its means the objections naturally attaching to glass bulbs will be removed. These experiments must be considered as preliminary. It is necessary first to find out where to search for the unknown before proper experiments can be made.

*Examination of the Water treated with Emanation.*—After exposure to the action of 1.422 cubic millimetres of emanation, the water, after gases had been removed, was shaken in the bulb with freshly distilled, pure ether. The ether was tested for hydrogen peroxide with titanium sulphate, and a yellow colour showed its presence in small amount. This contradicts the observation previously made, when the water was allowed to evaporate into phosphorus pentoxide and gave no gas; it might have been supposed that hydrogen peroxide would have been decomposed during such evaporation. It is possible, however, that it is absorbed by phosphorus pentoxide when its vapour slowly comes in contact with the anhydride.

The remaining water was evaporated to dryness in a platinum capsule; the residue was somewhat deliquescent; it weighed 0.71 milligram. The residue gave the spectrum of sodium (strong) and potassium (very faint), but no lithium.

It is to be inferred that the alkali residue, obtained from the blank copper and lead experiments and from the glass, all having approximately the same weight, is derived from the glass bulb. The greater weight of the residue of alkali salt from the treated copper nitrate may be noted. It can hardly be fortuitous, but some experiments with the silica bulb will show whether this excess is real and not a chance occurrence.

*Discussion of Results.*—That the radium emanation, during its

spontaneous change, parts with an enormous amount of energy, has already been emphasised in this series of papers. It has been suggested that this energy is due to the explosive emission of " $\alpha$ -particles," which may conceivably be identical with helium. Whether this last supposition be just or not, these particles may certainly be regarded as small masses of molecular dimensions moving with a very high velocity. It may be taken that, since the emanation presents a strong resemblance to the inactive gases of the argon series in the character of its spectrum, and in its indifference to chemical reagents, it belongs in all probability to that series, and we have already suggested that its atomic weight may be approximately 216.5. When left alone in an otherwise vacuous vessel, or when mixed with oxygen and hydrogen gases, it is known to yield helium as one of its products. This was first shown by Ramsay and Soddy, and the observation has been confirmed by Indrikson, by Debierne, by Giesel, by Curie and Dewar, and by Himstedt and Meyer.

It now appears that when dissolved in water, it yields almost exclusively neon as its gaseous educt; the trace of helium observed is produced, in all probability, from the undissolved and gaseous portion of the emanation. When a copper salt is simultaneously present in solution, helium, if present at all, cannot be detected, and argon is the main product, mixed possibly with a trace of neon. It may be contended that the argon formed in presence of copper sulphate is derived from atmospheric nitrogen which may have leaked in through the stopcocks. It is impossible at this stage to disprove this possibility, but the presence of argon does not account for the absence of helium, and it is remarkable that the amount of nitrogen is almost exactly the same both when water and when copper sulphate were present, although the conditions were by no means parallel.

We suggest (1) that helium and the  $\alpha$ -particle are not identical; (2) that helium results from the "degradation" of the large molecule of emanation by its bombardment with  $\alpha$ -particles; (3) that this "degradation," when the emanation is alone or mixed with oxygen and hydrogen, results in the lowest member of the inactive series, namely, helium; (4) that if particles of greater mass than hydrogen or oxygen are associated with the emanation, namely, liquid water, then the "degradation" of the emanation is less complete, and neon is produced; (5) that when molecules of still greater weight and complexity are present, as is the case when the emanation is dissolved in a solution of copper sulphate, the product of "degradation" of the emanation is argon. We are inclined to believe, too, that (6) the copper also is involved in

this process of degradation, and is reduced to the lowest term of its series, namely, lithium; at the same time, inasmuch as the weight of the residue of alkali, produced when copper nitrate is present, is double that obtained from the blank experiment, or from water alone, the supposition is not excluded that the chief product of the "degradation" of copper is sodium. It may be argued in favour of this view that, inasmuch as sodium is a much commoner element than lithium, it may be regarded as more stable, and therefore more likely to be produced.

It is to be noticed that the sodium "produced" from copper, if this suggestion is correct, corresponds to an enormously greater number of molecules than the helium. That is true, but it must be remembered that the chances of collision of a molecule of "disrupting" emanation with an atom of copper are almost infinitely greater than with one of its own atoms, because the number of copper ions in the solution is considerable.

Experiments confirmatory of the above view, in which it appears that an acid solution of thorium nitrate continuously produces carbon dioxide, are in progress. The observation has been made three times, at intervals of six months between the observations, but publication of an account of these experiments will be delayed until a fourth experiment has been made and a corresponding blank experiment has been studied.

It is evident that the research, of which the foregoing is a description, is merely a preliminary survey of the field to be explored, and that much work must be done before the tentative hypothesis which has been put forward can be substantiated.

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