LIX.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Mercuric Zinc Cyanide; a Study of the Mode of Formation and Properties of an Insoluble Double Salt.

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IN a paper communicated to the Pharmaceutical Society in 1890 (*J. Pharm.* [3], 20, 653; this Journal, Abstr., 1890, 855), I gave an account of the composition and properties of the white precipitate, resulting from the interaction of aqueous solutions of mercuric potassium cyanide and zinc sulphate, which was first observed by Rammelsberg [*Ann. Chim. Phys.* (Pogg.), 42, 131], and described by him in connection with the properties of the mercuric potassium cyanide he had then discovered. In recording this reaction, Gmelin (*Handbook*, 7, 424; 8, 24) mentions that the same precipitate may be obtained by adding mercuric chloride to a solution of zinc potassium cyanide, $\text{ZnK}_2(\text{CN})_4$, and since no hydrogen cyanide is produced, he suggests that double decomposition has occurred, and that the precipitate consists of mercuric zinc cyanide, $\text{HgZn}(\text{CN})_4$. This suggestion has been accepted by subsequent writers, the reaction being expressed by the equations—

It does not appear, however, that the precipitate was ever analysed.

In his search for a satisfactory antiseptic surgical dressing, Sir

Joseph Lister, after having found neither zinc cyanide nor mercuric cyanide free from objection, determined to examine the effect of the double cyanide of zinc and mercury described by Gmelin. Its action, as an antiseptic material, was found to be superior to that of any substance previously tried, having none of the corrosive properties of mercuric cyanide, whilst acting more efficiently as an antiseptic than zinc cyanide.

In the preparation of the substance on a somewhat large scale, it was observed that the greater part of the mercuric cyanide was dissolved by the water used in washing the precipitate, and that only a small proportion remained in the precipitate, which consisted chiefly of zinc cyanide. This fact, combined with the circumstance that the amount of mercuric salt retained in the precipitate was subject to variation, led to the suspicion that the substance might be a mixture of the two cyanides.

It was found, however, that an intimate mixture of the two salts did not act antiseptically in the same manner as the precipitate, since the mercuric cyanide was readily dissolved from the mixture, and exerted a corrosive effect.

The question as to the nature of the precipitate was eventually referred by Sir Joseph Lister to the present writer, who undertook to investigate it. The enquiry has led to the observation of a number of facts of considerable chemical interest, and goes to show that, in many respects, the precipitate is a remarkable substance.

Preparation of Pure Materials.

The potassium cyanide used in these experiments was prepared by passing the vapour of hydrogen cyanide into an alcoholic solution of pure potash. The crystalline precipitate was collected, washed with alcohol, and dried in a vacuum on a porous tile. Potassium cyanide thus prepared is, of course, free from cyanate, and will not contain any appreciable quantity of carbonate if the alcoholic potash used in its manufacture has been freshly prepared.

The mercuric potassium cyanide, $\text{HgK}_2(\text{CN})_4$, is prepared by dissolving finely powdered mercuric cyanide in a warm, concentrated, aqueous solution of potassium cyanide, containing rather more than the calculated amount of the salt. On evaporating the liquid, the double salt is deposited in crystals, which are once recrystallised from water. This compound is stable. If pure mercuric cyanide be not available, the double cyanide may be prepared by dissolving the calculated quantity of mercuric sulphate, in small portions at a time, in a slight excess of an aqueous solution of potassium cyanide. Mercuric chloride cannot be conveniently substituted for the sulphate

in this process, since a double salt containing chloride is also formed, from which the mercuric potassium cyanide cannot be completely separated by recrystallisation. In many instances, when both pure potassium and mercuric cyanides have been at hand, the aqueous solution of the double cyanide required for the experiment has been prepared by dissolving the proper quantity of mercuric cyanide in the solution of potassium cyanide.

When zinc cyanide was required, it was obtained by precipitating a solution of zinc acetate with aqueous hydrogen cyanide. The double cyanide of zinc and potassium, $\text{ZnK}_2(\text{CN})_4$, may be readily prepared by dissolving freshly precipitated zinc cyanide in a slight excess of aqueous potassium cyanide, or even more readily by adding aqueous potassium cyanide to a solution of zinc acetate until the precipitate at first formed is redissolved. The salt may be obtained pure by recrystallisation from water. If zinc sulphate is used instead of the acetate, considerable difficulty is experienced in completely separating the potassium sulphate.

Both mercuric potassium cyanide and zinc potassium cyanide are readily soluble in water, whilst zinc cyanide is insoluble. Mercuric cyanide, as is well known, is sparingly soluble in cold water.

Methods of Analysis.

The methods used in analysing the various products have not been exceptional in any important respect, and, therefore, only call for brief notice. The mercury, as a rule, has been estimated by heating the material with excess of lime in a combustion tube, and collecting the distilled mercury in the usual manner. When the amount of material was too small to admit of distillation of the metal, it has been estimated as sulphide. The zinc has been estimated by igniting a known weight of the substance at a low red heat until a constant weight of zinc oxide remained, a few drops of nitric acid being added when necessary, in order to facilitate the oxidation of the last traces of carbonaceous matter. Sometimes, when only a small quantity of material was available, and both zinc and mercury were to be estimated, the zinc, after removal of the mercury as sulphide, was precipitated with sodium carbonate and weighed as oxide. The correct determination of the amount of cyanide in the material was not at first found to be easy, for the reason that mercuric cyanide is very difficult to decompose. The direct conversion of the whole of the cyanogen into silver cyanide by heating the substance with dilute nitric acid and silver nitrate gave results which were much too low even when the operation was conducted in a closed tube at 100—120°. Ebullition with strong aqueous sodium carbonate, except after pro-

longed action, failed to afford the whole of the cyanogen in the form of sodium cyanide, especially when the material was rich in mercuric salt. This appears to be due to the combination of the sodium cyanide with mercuric cyanide to form the double salt, which is not readily decomposed by sodium carbonate.

Perfectly satisfactory determinations of the cyanogen were furnished by bringing the substance in contact with a mixture of zinc and dilute sulphuric acid from which hydrogen is being evolved, and conducting the resulting hydrogen cyanide into a solution of silver nitrate; the silver cyanide was collected and weighed. The indirect estimation of the cyanogen through the nitrogen, which was determined by Dumas' method, or through the ammonia obtained by the soda-lime method, also gave accurate results which agreed well with those furnished by the action of hydrogen. As a rule, it was most convenient to estimate the nitrogen by Dumas' method, the operation being conducted in a vacuum and the nitrogen collected through the limb of a Sprengel pump.

Formation and Composition of the Precipitate.

The first experiments were made to ascertain whether the composition of the precipitate, prepared by either of the two methods described by Gmelin, corresponds with the formula of the double salt $\text{HgZn}(\text{CN})_4$ which he considers is probably formed.

A solution of mercuric potassium cyanide was precipitated with a solution of zinc sulphate, the quantities used being calculated from the equation $\text{HgK}_2(\text{CN})_4 + \text{ZnSO}_4 = \text{HgZn}(\text{CN})_4 + \text{K}_2\text{SO}_4$. The precipitation was carried out in the following manner. Mercuric cyanide (12.5 grams) was dissolved in about 60 c.c. of water and mixed with 40 c.c. of a solution containing rather more than the calculated quantity of potassium cyanide. This solution of mercuric potassium cyanide was precipitated by the addition of the calculated amount of zinc sulphate dissolved in about 60 c.c. of water. The copious white precipitate was collected and washed with cold water (about 50 c.c.) until no more soluble mercuric salt could be detected in the washings by means of hydrogen sulphide. The precipitate was then dried at 100° . Its bulk had been very considerably reduced in washing. The calculated quantity of the hypothetical double compound producible from these quantities of the reacting salts is 18.5 grams; the amount actually obtained was rather more than 2 grams. On analysis, the substance was found to have the following composition:—

Zinc cyanide.....	94	per cent.
Mercuric cyanide.....	6.7	„

The substance also contained a small quantity of oxygen, estimated by ignition in a current of hydrogen, which appeared to be present as hydroxide of zinc. The amount of mercuric cyanide found is about one-tenth of that demanded by the formula $\text{HgZn}(\text{CN})_4$, which requires 68.29 per cent.

In another experiment, the same quantities of salts were used, but less water was employed in dissolving them. The precipitate was washed with cold water until free from mercuric salt. The yield of precipitate was larger than in the former experiment, and it contained more mercuric cyanide, namely, 17.7 per cent.

This quantity of mercuric salt is rather more than one-fourth of that required by the formula $\text{HgZn}(\text{CN})_4$.

These experiments were repeated, varying the quantities of the reacting salts and of the water used to dissolve them, but in no instance could the double salts consisting of equimolecular proportions of the two cyanides be prepared.

The second method which, according to Gmelin, probably furnishes this double cyanide was now tried. Zinc potassium cyanide (7 grams) was dissolved in water and the strong solution precipitated with 8 grams of mercuric chloride dissolved in water so that the following reaction might occur:—

The white precipitate was washed with cold water until free from soluble mercuric salt, then dried and analysed. It contained 9.67 per cent. of mercuric cyanide, the remainder being zinc cyanide with a little hydroxide. This quantity of mercuric salt corresponds with about one-seventh of that calculated from the formula $\text{HgZn}(\text{CN})_4$.

It is therefore evident that the white precipitate which Gmelin thought to be the equimolecular double cyanide of zinc and mercury is a compound or mixture containing much less mercuric cyanide than this double salt.

Attempts were now made to prepare this double cyanide by other methods. A solution was made containing equivalent quantities of zinc potassium cyanide and mercuric potassium cyanide. This was decomposed with exactly sufficient dilute sulphuric acid to convert the potassium of both salts into sulphate; zinc cyanide and mercuric cyanide would then be set free in the proper proportion to form the hypothetical double salt,

The precipitate was collected, washed free from soluble mercuric salt, and dried. It contained 8.46 per cent. of mercuric cyanide,

the rest being zinc cyanide. This quantity of mercuric salt is about one-eighth of that demanded by the formula $\text{HgZn}(\text{CN})_4$.

Lastly, a fourth method was tried in order to prepare the double salt. Equivalent quantities of mercuric oxide and zinc carbonate, both freshly precipitated, were dissolved in a slight excess of a saturated aqueous solution of hydrogen cyanide:—

Reaction immediately occurred, and a white precipitate gradually settled. After shaking and standing for some time in a closed bottle, the precipitate was collected, washed, dried, and analysed. It consisted almost entirely of zinc cyanide, and contained only a trace of mercuric salt.

It is proved by these experiments that the white precipitate obtained under the various conditions above described is principally composed of zinc cyanide, containing a variable quantity of mercuric cyanide, and is not the equimolecular double salt, as Gmelin suggested might be the case.

The properties of the precipitate were now examined, and further experiments were made in order to determine whether the mercuric cyanide is mixed with the cyanide of zinc, or if any evidence could be obtained of the existence of a chemical compound of the two cyanides.

Properties of the Precipitate.

Although the precipitate contains a variable quantity of mercuric cyanide, and in many respects resembles a mixture of the two salts, yet it presents some features of chemical interest. In the experiments of which an account has just been given, the amount of water present during precipitation was in every instance sufficient to dissolve only a small proportion of the mercuric cyanide produced. Nearly the whole of this salt is therefore precipitated with the insoluble cyanide of zinc. When the precipitate is washed with cold water, a large part of the mercuric salt is removed. It is, however, remarkable that although water, in a sufficient quantity of which mercuric cyanide dissolves without difficulty, should fail to extract the whole of the salt from the precipitate; a variable quantity, usually between 5 and 10 per cent., remains after the washings have ceased to react with hydrogen or ammonium sulphide. In what condition is this mercuric cyanide, which is so incorporated with zinc cyanide as to be insoluble in cold water?

The ability of cold water to completely dissolve mercuric cyanide from a mixture of it with zinc cyanide was demonstrated by wash-

ing an intimate mixture of these cyanides with cold water, when the whole of the mercuric salt passed into the filtrate, and left pure zinc cyanide on the filter. A specimen of the substance containing about 15 per cent. of mercuric cyanide was microscopically examined. It appeared to be a homogeneous, amorphous powder free from any crystalline particles.

Although the mercuric cyanide is not dissolved from the substance by washing with cold water, it is slowly removed by the action of boiling water. It was observed that if the precipitate is washed free from mercuric salt, and then dried at 100° , a small quantity of mercuric salt, usually from 2 to 3 per cent., can be dissolved from the dried substance by cold water. If this washed material is again dried at 100° , a further quantity of mercuric cyanide may be dissolved from it by cold water, and if the operation is repeated sufficiently often, the whole of the mercuric cyanide may be removed. The following results illustrate the course of this action. The material used had been washed free from mercuric cyanide and dried at 100° . A portion of it was then analysed, and the remainder washed and again dried. This series of operations was performed four times with the following results:—

After the first operation..	12.0	per cent. of mercuric cyanide.
„ second „ ..	10.46	„ „ „
„ third „ ..	9.09	„ „ „
„ fourth „ ..	8.26	„ „ „

The residue was finally boiled with water for some hours, when the remainder of the mercuric salt went into solution.

That the liberation of the mercuric cyanide is due to the action of hot water on the substance, and not alone to the rise in temperature, was proved by drying some of the washed precipitate in a vacuum desiccator over calcium chloride, and then heating it for some hours at 100° . Cold water dissolved no mercuric salt from the substance which had been dried in this manner.

Further experiments as to the action of cold water (13 – 15°) on the substance have shown that, although it fails to dissolve the mercuric salt under the ordinary conditions of washing, when the water is in contact with the substance for only a short time, by prolonged contact with cold water the mercuric salt slowly passes into solution, although at a diminishing rate. This gradual action is shown in the curve, Fig. 1, C, which has been plotted from the results of an experiment which lasted 172 days; the amount of mercuric cyanide dissolved being determined from time to time.

Action of Cold Water (Fig. 1, C).

Days.	Per cent. of $\text{Hg}(\text{CN})_2$ removed.
3	3.15
26	5.73
143	10.42

The aqueous liquid, on evaporation, deposited crystals which were proved by analysis to be mercuric cyanide. The residue left undissolved by the boiling water consisted of zinc cyanide and hydroxide, the hydroxide being the result of the hydrolysis which occurs when zinc cyanide is boiled with water.

Nature of the Precipitate.

Two suggestions may be made with reference to the condition of the mercuric cyanide in the precipitate.

1. The mercuric cyanide may be combined with the zinc cyanide in the form of a double salt decomposable by water.
2. The mercuric cyanide may be entangled and mechanically retained by the cyanide of zinc. In the precipitation the two cyanides are thrown out together, and since there is not sufficient water present to dissolve the whole of the mercuric cyanide, there must be particles of this salt intermingling with those of the zinc cyanide which are aggregating to form the precipitate. Under these circumstances it is conceivable that a certain number of particles of mercuric cyanide

may become encased by the insoluble zinc cyanide, and thus be protected from the solvent action of cold water, which would never come into actual contact with them, except perhaps after long digestion. Boiling water may be supposed to slowly disintegrate and break down these small masses, and set free the mercuric cyanide.

In order to decide between these possibilities, several points relating to the formation of the substance were more fully investigated. More information was obtained as to the influence of the quantity of water present during precipitation upon the composition of the substance. Previous experiments had shown that the amount of retained mercuric cyanide fluctuates with the quantity of water present whilst the action is taking place, but is not appreciably affected by the volume of water employed in washing the precipitate. The larger the quantity of water used to dissolve the reacting salts, the smaller is the amount of mercuric cyanide found in the washed precipitate, and *vice versa*.

Precipitation was now brought about by mixing very strong, but not quite saturated, solutions of the salts. The calculated quantity of pure potassium cyanide was dissolved in a small quantity of water, and the proper amount of finely powdered mercuric cyanide was dissolved in the warm liquid. The solution of mercuric potassium cyanide thus prepared was precipitated when cold by the addition of a concentrated solution of the equivalent quantity of zinc sulphate. The precipitate was collected and washed with cold water until all the soluble mercuric salt had been removed. It was then dried in a vacuum over calcium chloride, and analysed. The results were as follows:—

Mercuric cyanide	36·17 per cent.
Zinc cyanide	64·0 ,,

Experiments made later, which are alluded to subsequently, have proved that by reducing the amount of water used in dissolving the salt to a minimum, the percentage of mercuric cyanide may be raised about 2·5 per cent. above this amount. On the other hand, by gradually increasing the volume of this water, specimens of material may be prepared containing any percentage of mercuric cyanide from about 38 per cent. to less than 1 per cent.

Striking as these results are, they do not enable us to decide between the chemical and physical explanations referred to above, for although they may be attributed to the gradual decomposition of a double salt by water, they are also susceptible of a physical explanation, since the more water there is present to dissolve the mercuric cyanide the smaller would be the proportion encased by the zinc cyanide.

If zinc cyanide combines with mercuric cyanide to form a double

salt, which is readily decomposed by water, it seems possible that this salt might be formed under other circumstances than precipitation. An attempt was made to produce the compound by evaporating to dryness at 100° a mixture of freshly precipitated zinc cyanide with a strong aqueous solution of mercuric cyanide. The dried mass contained 10 per cent. of mercuric cyanide. Washing with cold water removed the whole of the mercuric salt, proving that no combination had taken place.

In other experiments an intimate mixture of the two cyanides was heated to various temperatures between 90° and 150° , but no combination occurred between the two salts.

Again, if the substance produced by precipitation contained an ordinary double salt decomposable by water, it seemed possible that this salt might be obtained in an almost pure state if the two cyanides were brought together in the absence of water. Equivalent quantities of freshly precipitated mercuric oxide and zinc carbonate* were suspended in a small quantity of absolute alcohol and the vapour of hydrogen cyanide passed into the mixture until the whole of the yellow mercuric oxide had disappeared and carbon dioxide had ceased to be evolved. On filtering the liquid and washing the precipitate with cold water, the mercuric cyanide was completely dissolved, and a residue of zinc cyanide remained. The conditions under which this experiment was made seemed to be most favourable to the formation of a compound of the two cyanides, but none was produced. So far, the facts might appear to lead to a physical rather than to a chemical explanation of the retention of the mercuric cyanide in the substance. When opportunity is afforded, as it is in precipitation, for the entanglement or encasement of mercuric cyanide by zinc cyanide to occur, the substance is formed. When the conditions are unfavourable to this action, but are, nevertheless, still conducive to chemical combination, as they are in the experiment just described, the substance is not produced. For these reasons, I suggested, in my former paper on the subject, that the phenomenon is probably physical and not chemical.

Further inquiries into the circumstances attending the formation and decomposition of the substance have, however, conclusively proved that the attachment of the mercuric cyanide to the zinc cyanide must be ascribed to chemical combination, which, however, does not occur to any appreciable extent when the two ready-made salts are brought together.

If the zinc cyanide entangles the undissolved mercuric cyanide during precipitation, and the action is purely mechanical and inde-

* The oxide was not used owing to the difficulty there is in preparing it pure by precipitation.

pendent of any chemical attraction between the molecules, it ought to be found that other salts, whose solubility is about the same as that of mercuric cyanide, should also be entangled when precipitated together with zinc cyanide in presence of insufficient water for their solution. Potassium sulphate appeared to be a very suitable salt to employ in this crucial experiment, since its solubility is nearly the same as that of mercuric cyanide; 100 parts of water at the ordinary temperature dissolve 12 parts of mercuric cyanide and 11 parts of potassium sulphate.

Three experiments were made in which zinc cyanide and potassium sulphate were precipitated together in presence of so little water that only a small proportion of potassium sulphate would be dissolved by it. Five grams of zinc potassium cyanide were dissolved in 24 c.c. of water, and precipitated with a cold saturated solution containing 5.75 grams of zinc sulphate. The reaction is represented by the equation

The precipitate was washed with cold water until no sulphate could be detected in the washings, and then dried. It now consisted entirely of zinc cyanide, and did not contain a trace of potassium sulphate. A similar experiment with potassium cyanide and zinc sulphate led to the same result. These experiments were now repeated, using zinc chloride instead of zinc sulphate, potassium chloride being formed instead of potassium sulphate, so that it might be ascertained whether this salt was entangled by the zinc cyanide precipitated with it. To diminish the solubility of potassium chloride in water, an alcoholic solution of zinc chloride was precipitated with a dilute alcoholic solution of potassium cyanide. The resulting precipitate was washed with dilute alcohol until the washings no longer contained chloride and then analysed. It consisted entirely of zinc cyanide, no potassium chloride having been retained.

These results conclusively show that zinc cyanide does not entangle salts which are precipitated with it. The retention of the mercuric cyanide by zinc cyanide must, therefore, be attributed to the existence of chemical attraction between the molecules of these salts, under the conditions which obtain during precipitation. The correctness of this conclusion has since been substantiated by a considerable mass of experimental evidence.

It has already been shown that cold water has no immediate action on the substance, but that after prolonged contact mercuric cyanide is very gradually dissolved. If the inability of the water to dissolve the mercuric cyanide is due to anything in the nature of a protective coating of zinc cyanide, a liquid in which zinc cyanide is insoluble

but which dissolves mercuric cyanide much more readily than water, should also be unable to dissolve mercuric cyanide from the substance, whereas, if the mercuric salt were loosely combined with the zinc cyanide, it might be more readily dissolved by this liquid, especially if it contained a salt capable of forming a stable compound with the mercuric cyanide. A number of experiments were made with the object of finding some solution which would serve this purpose. Exactly the proper liquid was at last found in a strong aqueous solution of potassium iodide, in which mercuric cyanide is far more soluble than it is in water, owing to the formation of a soluble crystalline double salt of the formula $\text{Hg}(\text{CN})_2, 2\text{KI}$. The effect was therefore tried of digesting a material containing 36.5 per cent. of retained mercuric cyanide with a strong aqueous solution of potassium iodide. A weighed quantity (1.3 grams) was left in contact with 15 c.c. of the solution, at the ordinary temperature, for 24 hours. The precipitate was collected, washed with cold water until free from soluble mercuric salt and dried. On analysis, it was proved that the substance now consisted almost entirely of zinc cyanide, only 0.8 per cent. of mercuric cyanide being present. It is thus shown that whilst cold water, after digestion with the material for 24 hours, dissolves only about 1 per cent. of the mercuric cyanide, a strong solution of potassium iodide, acting under the same conditions, dissolves 35.7 per cent. of the salt, that is, practically the whole of the retained mercuric cyanide. From the filtrate, crystals were obtained whose composition corresponded with the formula $\text{Hg}(\text{CN})_2, 2\text{KI}$.

This result negatives the suggestion that the mercuric cyanide is encased by the zinc cyanide, and is in accordance with the conclusion that the material contains a compound of the two cyanides.

The Conditions which influence the Retention of Mercuric Cyanide.

An extended series of observations, as to the conditions which affect the retention of the mercuric cyanide in the precipitate, has not only confirmed this conclusion, but has furnished evidence which makes it possible to ascertain with considerable certainty what the composition of the double cyanide is.

Experiments have been made in which the various conditions attending precipitation have been modified in order to ascertain to what extent they determine the composition of the substance. It has been found that the order in which the two solutions are mixed does not appreciably affect the composition of the precipitate. Working with saturated aqueous solutions containing equimolecular proportions of mercuric potassium cyanide and zinc sulphate, the addition of the solution of zinc sulphate to that of the mercuric

potassium cyanide furnished a precipitate which, after washing, contained 36.9 per cent. of mercuric cyanide, whilst when the mercuric potassium cyanide was added to the zinc sulphate the washed precipitate contained 37.7 per cent. of the mercuric salt.

A study of the influence of temperature has proved that the higher the temperature the smaller is the amount of mercuric cyanide retained by the precipitate. The experiments described above were repeated at 100°, boiling solutions of the reacting salts being mixed, so that the influence of temperature might be ascertained. The precipitate produced under these conditions contained 25.5 per cent. of mercuric cyanide, which is about 11 per cent. less than that resulting from interaction at about 15°. This difference probably corresponds with the increased solubility of the mercuric cyanide in the hot, as compared with the cold solution of potassium sulphate.

It now became of interest to determine the action of mass on the chemical change. For this purpose 1 mol. proportion of mercuric potassium cyanide was fractionally precipitated with 1 mol. proportion of zinc sulphate, the two solutions being prepared with as little water as possible, and the solution of zinc sulphate added in four equal parts. The precipitate was collected after the addition of each fourth part, and washed with cold water as before. The composition of the four precipitates was then ascertained by analysis. Two series of experiments were made in this way, the first at a rather lower temperature than the second, which accounts for the small differences in the two series of percentages. The details are given in the table, and the curves plotted from these results are shown in the diagram (Fig. 1).

Fractional Precipitation of Mercuric Potassium Cyanide (1 mol.) with Zinc Sulphate (1 mol. added in 4 equal parts). (Fig. 1, A and B.)

Series A. $t = 10-13^{\circ}$.		Series B. $t = 17-20^{\circ}$.	
$\frac{1}{4}$ mol. ZnSO_4 .	Per cent. $\text{Hg}(\text{CN})_2$ in precipitate.	$\frac{1}{4}$ mol. ZnSO_4 .	Per cent. $\text{Hg}(\text{CN})_2$ in precipitate.
1st	27.15	1st	25.7
2nd	31.95	2nd	31.2
3rd	34.37	3rd	34.0
4th	38.53	4th	38.0

The results show that there is a gradual increase in the percentage of retained mercuric cyanide in each fraction of the precipitate, the first fraction containing the least, and the last fraction the most, mercuric salt. When the reaction is carried out in this manner there are three variable conditions: (1) the amount of water, which increases with each addition of the solution of zinc sulphate; (2) the amount of

potassium sulphate, which is also augmented by each addition of zinc sulphate; and (3) the amount of mercuric potassium cyanide, which diminishes relatively with each addition of zinc sulphate; the first fraction of the precipitate is formed by the interaction of 1ZnSO_4 and $4\text{HgK}_2(\text{CN})_4$, the second by the interaction of 1ZnSO_4 and $3\text{HgK}_2(\text{CN})_4$, the third by the interaction of 1ZnSO_4 and $2\text{HgK}_2(\text{CN})_4$, whilst the fourth fraction results from the interaction of 1ZnSO_4 and $1\text{HgK}_2(\text{CN})_4$. The largest percentage of mercuric cyanide is retained when reaction occurs in equimolecular proportions, but even then a large quantity of the mercuric cyanide, nearly three-fourths of the total quantity, appears in the precipitate in the free state and is subsequently washed away.

The variations in the composition of the precipitates cannot be principally attributed to the action of the water, since former experiments have shown that the larger the quantity of water present during the precipitation the smaller is the quantity of mercuric cyanide retained, whilst here, although the volume of water increases with each fractional precipitation, the amount of retained mercuric cyanide also increases, the smallest quantity being found when the volume of water is smallest, and the largest amount when the volume of water is greatest. It is clear that there must be some other influence at work in the opposite direction. It is improbable that the increase in the mass of the potassium sulphate will do more than slightly enhance the amount of mercuric cyanide, since it can only act by dissolving in the water and rendering it incapable of removing so much mercuric salt.

There remains for consideration the variation in the mass of the mercuric potassium cyanide. That this salt exerts an important influence on the course of the change is evident from the circumstance that the size of the first fraction is very much smaller than that of the precipitates subsequently formed. It is observable that the larger the proportion of this salt to that of one molecule of zinc sulphate the smaller is the percentage of mercuric cyanide retained. The maximum percentage is reached when the two salts are present in equimolecular proportions; that is to say, when there is sufficient zinc sulphate present to decompose the whole of the mercuric potassium cyanide, in accordance with the equation

The action of excess of mercuric potassium cyanide on the precipitate appears to be represented by the equation

These results serve to exhibit the influence of excess of mercuric potassium cyanide on the composition of the precipitate. In another series the influence of excess of zinc sulphate was studied. In these experiments the action of one of the variables alluded to above was reduced to a minimum. The quantity of potassium sulphate was made as far as possible constant by saturating both the solution of mercuric potassium cyanide and that of zinc sulphate with this salt before mixing the two substances together, so that in every instance precipitation occurred in a liquid saturated with potassium sulphate. A cold saturated solution containing 45.5 grams (1 mol. proportion) of mercuric potassium cyanide was saturated with potassium sulphate. The volume of the solution was 75 c.c. Different volumes of the liquid were added to a saturated aqueous solution containing 9.8 grams (1 mol. proportion) of zinc sulphate; this solution being also saturated with potassium sulphate. The precipitates were collected, washed, dried, and analysed in the usual manner. The following are the results which were obtained; from them the curve in Fig. 2 has been plotted. Unlike the experiments in the former series, these do not represent a process of fractional precipitation; the solutions containing different amounts of the mercury salt being added each to a separate solution containing the 1 mol. proportion of zinc sulphate.

Precipitation of Solution of 1 mol. proportion of ZnSO_4 with varying quantities of $\text{HgK}_2(\text{CN})_4$. (Fig. 2.)

Mols. of $\text{HgK}_2(\text{CN})_4$ to 1 mol. ZnSO_4 .	Percentage of $\text{Hg}(\text{CN})_2$ retained in the precipitate.
0.146	31.58
0.30	34.02
0.446	35.82
0.7	37.74
0.9	38.40
1.0	38.50
1.31	38.44

In plotting these results the curve has been drawn, not by the free hand, but with a bent lath, in the manner suggested in his work on the properties of solutions by my friend Mr. Spencer Pickering, F.R.S., to whom I am indebted for much valuable information. It is interesting to observe that the first six experimental points lie perfectly on the curve made by the bent lath (the continuous line in Fig. 2), whereas the seventh point lies beyond this curve, thus indicating the existence of a change of curvature at or near the sixth point, which corresponds with the interaction of equimolecular proportions and the production of the maximum amount of retained mercuric cyanide. It is

FIG. 2.

clear that a change of curvature must occur here, for the conditions change at this point; the precipitation, which before was only partial, here becomes complete, and, of course, remains so at all points beyond. It may be inferred from the direction which the bent lath curve follows, that even if the conditions which obtained at the first six points before the equimolecular proportion was reached were continued, the maximum formation would still coincide with the point at which equimolecular interaction takes place, for the curve bends downwards after reaching the sixth point.

A comparison of Fig. 1 with Fig. 2 shows that excess of zinc sulphate, like excess of mercuric potassium cyanide, leads to the retention of less mercuric cyanide in the precipitate. The maximum quantity retained corresponds with that found in the previous series of experiments, namely, 38.5 per cent., and the precipitate containing the maximum quantity of mercuric cyanide is formed at exactly the same point, namely, when equimolecular proportions of mercuric potassium cyanide and zinc sulphate interact. The difference in the character of the two curves is to be attributed partly to the fact that the experiments to which they relate were not made in exactly the same manner, but chiefly to the circumstance that the environment of the precipitate is not the same in the two cases. In the first series, the salts in the solution surrounding the precipitate are potassium sulphate and mercuric potassium cyanide, whilst, in the second series, the solution which surrounds the precipitate contains potassium sulphate and zinc sulphate.

It has now been satisfactorily demonstrated that the phenomenon

under investigation is the formation of double cyanide of zinc and mercury, insoluble in, but partially decomposed by, water. Can any evidence be obtained as to the composition and formula of this double salt?

The maximum percentage of retained mercuric cyanide is near 38.5 per cent., and by no device has it been found possible to appreciably augment this quantity, which corresponds with the interaction of equimolecular proportions of the salts dissolved in the minimum quantity of water. Since water must be present in order that reaction may occur, some of the double cyanide will inevitably be decomposed, even if the water is at first saturated with potassium sulphate or mercuric cyanide; for as soon as precipitation takes place the water which previously held the reacting salts in solution will be set free to decompose the double salt or prevent its formation by dissolving mercuric cyanide. Having regard to the fact that some decomposition must occur, and that, therefore, the substance will always contain some free zinc cyanide, it is probable that the pure double salt contains somewhat more mercuric cyanide than the maximum actually obtainable, viz., 38.5 per cent. The simplest molecular proportion, representing somewhat more than 38.5 per cent. of mercuric cyanide, is $\text{Zn}(\text{CN})_2, \frac{1}{4}\text{Hg}(\text{CN})_2$ or $\text{Zn}_4\text{Hg}(\text{CN})_{10}$, which requires 40.65 per cent. of mercuric cyanide. Confirmatory evidence that this is really the formula of the double cyanide is

FIG. 3.

• = $\text{HgK}_2(\text{CN})_4$ mols. added to ZnSO_4 mols.

x = ZnSO_4 mols. added to $\text{HgK}_2(\text{CN})_4$ mols.

afforded by a closer examination of the curves representing the two series of results above described. For this purpose these two series of results have been plotted in one diagram (Fig. 3). In order to render this possible, the "percentage-molecular" plotting, suggested by Mr. Pickering, has been adopted in this diagram. The percentage numbers of molecules of mercuric potassium cyanide in the total number of reacting molecules are plotted against the percentages of mercuric cyanide retained in the precipitates. The numbers used are as follows:—

Left-hand curve.		Right-hand curve.	
Per cent. HgK ₂ (CN) ₄ mols. in the HgK ₂ (CN) ₄ + ZnSO ₄ mols.	Per cent. of Hg(CN) ₂ in precipitates.	Per cent. of HgK ₂ (CN) ₄ mols. in the HgK ₂ (CN) ₄ + ZnSO ₄ mols.	Per cent. of Hg(CN) ₂ in precipitates.
12·74	31·58	50·0	38·53
23·10	34·02	66·67	34·37
30·85	35·82	75·0	31·95
41·18	37·74	80·0	27·15
47·37	38·40	—	—
50·00	38·50	—	—
56·71	38·44	—	—

The following equations also illustrate the nature of the reaction depicted by the two branches and by the apex of the curves. In these equations the formula of the precipitate is assumed to be Zn₄Hg(CN)₁₀, although the facts which they indicate are independent of any particular formula.

A glance at these equations shows that the amount of water per molecule of precipitate formed is least, and therefore the percentage of mercuric cyanide in the precipitate (which is partially decomposed by water) must be greatest, when the reagents are present in equimolecular proportions, the $(x + y)\text{H}_2\text{O}$ present in this case being

always less than the $(nx + y)\text{H}_2\text{O}$ or $(x + ny)\text{H}_2\text{O}$ present in the other cases.

Moreover, reference to the diagram (Fig. 3) shows that, in accordance with this conclusion, the percentage of mercuric cyanide is actually greatest at the equimolecular proportion. As has already been pointed out, the two branches of the figure are not strictly comparable, owing chiefly to the presence of different substances in the two liquids in which the precipitate is formed; the results expressed by the right-hand branch are probably more complex than those of the left-hand branch, because of the presence in the former case of excess of mercuric zinc cyanide, which has a very marked action on the precipitate. The left-hand branch must, therefore, be taken as representing more simply the mass action of the water alone on the precipitate. Now the first three experimental points on this branch, where this action is further simplified by the smallness of the precipitate formed, lie on a nearly straight line; by prolonging this line (the dotted line in Fig. 3) to equimolecular proportions of the reagents, we arrive at the probable composition of the precipitate which would be formed in presence of the minimum quantity of water, if the reaction occurred under the same simple conditions which obtained in the first three experiments. The composition thus indicated is 40.5 per cent. of mercuric cyanide, a number which agrees almost exactly with the percentage (40.65) required by the formula $\text{Zn}_4\text{Hg}(\text{CN})_{10}$. It may, therefore, be safely concluded that this is the formula of the double salt.

In the course of the numerous experiments which this inquiry has involved, no evidence has been obtained of the existence of any other compound of the two cyanides than that now described. A special experiment was made to ascertain whether the formation of the decacyanide is preceded by the production of a salt richer in mercury, such as that assumed by Gmelin, $\text{ZnHg}(\text{CN})_4$. For it might be that this tetracyanide is formed according to the equation

and subsequently breaks up into mercuric cyanide and the double decacyanide $4\text{HgZn}(\text{CN})_4 = 3\text{Hg}(\text{CN})_2 + \text{Zn}_4\text{Hg}(\text{CN})_{10}$. A cold saturated solution of mercuric potassium cyanide was made to dissolve as much mercuric cyanide as possible, the liquid being digested for some hours with the mercuric salt finely powdered. A cold saturated solution of zinc sulphate was likewise made to absorb as much mercuric cyanide as it would take up. The solutions were then mixed, the precipitate collected and washed with a saturated aqueous solution of mercuric cyanide, and dried over calcium chloride and analysed. It contained 60 per cent. of mercuric cyanide; the formula $\text{HgZn}(\text{CN})_4$ requires

68.29 per cent. When washed with cold water the precipitate behaved as if it contained free mercuric cyanide, mercuric salt being quickly dissolved in large quantity. The washing was continued until no more mercuric cyanide was removed, when the remaining precipitate was dried and analysed. It contained 38.8 per cent. of mercuric cyanide, which is only very slightly higher than the maximum percentage already determined, namely, 38.5. There is, therefore, no evidence that these two cyanides can combine in any but the proportion $4\text{Zn}(\text{CN})_2:\text{Hg}(\text{CN})_2$. It is not to be expected that saturating the solutions with mercuric cyanide would prevent decomposition and cause any appreciable increase in the retention of mercuric cyanide, since directly precipitation commences the water in which the reacting salts were dissolved will be set free and will be able to attack the double salt and dissolve mercuric cyanide from it.

Attempts to Prepare the Double Salt in other ways.

It has already been shown that this double salt, $\text{Zn}(\text{CN})_2, \frac{1}{4}\text{Hg}(\text{CN})_2$, cannot be produced except by means of a process in which the two cyanides are precipitated together. It cannot be formed by heating at 100° the ready formed cyanides, either with or without water; neither does it result from the action of hydrogen cyanide on a mixture of mercuric oxide and zinc carbonate suspended in water or alcohol. These are the methods usually employed in forming soluble double salts.

It appears probable that the explanation of this remarkable fact may reside in the circumstance that combination cannot occur unless simple molecules, $\text{Zn}(\text{CN})_2$ and $\text{Hg}(\text{CN})_2$, are brought together. We know that these salts in the solid state are most probably composed of complex molecules of the formula $[\text{Hg}(\text{CN})_2]_n$ and $[\text{Zn}(\text{CN})_2]_n$. There seems to be no tendency on the part of these complexes to combine together. Similarly, the solid oxide of mercury and the solid zinc carbonate may be supposed to consist of complexes of the simple fundamental molecules HgO and ZnCO_3 ; and it appears that these are changed into masses of the solid cyanides by the action of hydrogen cyanide, and hence the double salt cannot be formed in this way. When, however, the two cyanides are precipitated from solution, we must suppose that at first the simple fundamental molecules are formed, and that combination takes place between them in the proportion $4\text{Zn}(\text{CN})_2:\text{Hg}(\text{CN})_2$ to an extent which is principally conditioned by the quantity of water present. Many of the fundamental molecules unite with each other to form the molecular aggregates which constitute the solid zinc cyanide; whilst those of the mercuric cyanide not required for the production of the

double salt also aggregate as solid particles, although some which would otherwise enter into combination with zinc cyanide dissolve in the water. When the precipitate is washed with cold water, the uncombined and undissolved solid particles of mercuric cyanide are removed, but the double salt, which is always mixed with zinc cyanide, is scarcely attacked by the cold water.

Several attempts have been made to experimentally verify the hypothesis that the formation of the double cyanide is the result of combination between fundamental molecules. The undoubted fact that dilute solutions contain these simple molecules suggested the possibility of preparing the compound by mixing dilute solutions of the two cyanides. Unfortunately this method cannot be actually carried out, for although a dilute solution of mercuric cyanide in several solvents can be made, it has not been found possible to dissolve zinc cyanide without at the same time decomposing it. This salt is insoluble in water, alcohol, and the usual solvents, and no liquid could be found in which it would dissolve without combination or decomposition. Spontaneous evaporation of a solution of mercuric cyanide with freshly precipitated zinc cyanide led to no result.

It is highly probable that a dilute solution of metallic zinc in mercury contains monatomic zinc molecules, and if the solution is heated it is likely that some monatomic molecules of mercury will also be formed. If, now, cyanogen gas were led into this hot solution and combination occurred, there would be present, at first at all events, fundamental molecules of the two cyanides of zinc and mercury which, it is to be expected, would combine to form the double salt. Many experiments have been made in this manner with dilute solutions of zinc in mercury at all temperatures up to and including the boiling point, but they all failed to afford any of the double salt. The white solid which separated from the mercury was found to be almost entirely zinc cyanide. The cyanogen had not combined with the mercury to any appreciable extent.

As both mercuric cyanide and zinc cyanide are resolved into the metal and cyanogen when strongly heated, it appeared possible that if a mixture of the two salts were heated in a closed and vacuous tube, so that a certain quantity of each cyanide is decomposed, that during the recombination which would take place on cooling some of the double cyanide might be produced. Numerous experiments of this kind failed, however, to afford any of the substance, owing, apparently, to the polymerisation of the cyanogen, which invariably occurred when the temperature was elevated enough to decompose zinc cyanide.

So far, then, it has not been found possible to prepare the double salt in any other way than by precipitation.

Search for Similar Double Cyanides of other Metals.

A large number of experiments have been made in order to ascertain whether any other insoluble double cyanide analogous to this mercuric zinc cyanide can be prepared by the union of mercuric cyanide with other metallic cyanides. These experiments were, as a rule, carried out in the following manner. A cold saturated solution of mercuric potassium cyanide was decomposed with a cold saturated solution containing an equimolecular proportion of the metallic salt, and any precipitate that formed was analysed after it had been washed with cold water.

Cadmium.

On the addition of a saturated solution of cadmium chloride to a saturated solution of mercuric potassium cyanide, a white precipitate is thrown down. When washed with cold water, this precipitate dissolves, and, on evaporating the solution at 100°, decomposition sets in with evolution of hydrogen cyanide. If, however, the precipitate is dissolved in water at 20° and the solution cooled below 0°, crystals separate. These were purified by recrystallisation, and dried over calcium chloride. They contained 56.9 per cent. of mercury; the formula $\text{Cd}(\text{CN})_2, 1\frac{1}{2}\text{Hg}(\text{CN})_2$ requires 55.35 per cent. The double cyanide of cadmium and mercury is, therefore, a soluble salt which differs from zinc mercuric cyanide both in composition and properties.

Nickel.

A cold saturated solution of mercuric potassium cyanide was decomposed with a saturated solution containing an equivalent quantity of nickel chloride. A bulky, green precipitate was thrown down which was washed with cold water. It was afterwards examined, but it contained no mercuric salt, all of which was found in the filtrate and washings.

Aluminium.

By the addition of a saturated solution of soda-alum to a saturated solution of an equivalent quantity of mercuric potassium cyanide, an abundant, gelatinous precipitate was thrown down, whilst much hydrogen cyanide was evolved. The washed precipitate contained no mercury.

Magnesium.

When saturated solutions containing equivalent quantities of magnesium sulphate and mercuric potassium cyanide are mixed, no pre-

precipitate is formed. On warming the solution, decomposition begins with evolution of hydrogen cyanide.

Silver.

A saturated solution of mercuric potassium cyanide was decomposed by adding a saturated solution containing an equivalent proportion of silver nitrite. An abundant, white precipitate resulted, and this, after washing with cold water, consisted of pure silver cyanide.

Lead.

On decomposing a saturated solution of mercuric potassium cyanide with a saturated solution of lead acetate, a small, white precipitate was obtained, which, after washing, contained no mercury.

Manganese.

Saturated solutions containing equivalent quantities of mercuric potassium cyanide and manganous chloride were mixed together in the cold. Much hydrogen cyanide was evolved, and only a small precipitate was obtained, which, after it had been washed, contained no mercury.

Copper.

A solution of copper sulphate energetically reacts with a solution of mercuric potassium cyanide; some gas is evolved, and the mixture becomes semi-solid. After washing the mass with cold water until it was free from soluble mercuric salt, no mercuric salt remained.

Tin.

The solution of mercuric potassium cyanide was decomposed with the equivalent quantity of stannic chloride, dissolved in the smallest possible quantity of water. A great deal of hydrogen cyanide was given off, and the precipitate which formed was almost entirely dissolved by washing with cold water, whilst the residue contained no mercury. On cooling the filtrate below 0°, flat, tabular crystals were deposited, which were dried in a vacuum over calcium chloride. These crystals fused when heated, a little water being evolved. By qualitative analyses they were found to contain mercury, potassium, cyanogen, and chlorine, but no tin. The percentage of mercury present in them was ascertained to be 59.75; the formula

requires 59.5 per cent.

From the negative results of these experiments with various metallic salts, it appears that the *tetrazincic monomercuric decacyanide*,

$\text{Zn}_4\text{Hg}(\text{CN})_{10}$, is an exceptional compound, no similar compound of mercuric cyanide with other metallic cyanides having been obtained when experiments were made under conditions exactly corresponding with those which led to the formation of the mercuric zinc cyanide, which this inquiry has shown must be included in the little known class of insoluble double salts.