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CHEMISTRY OF THE CYANIDE PROCESS

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Presented to both Houses of the General Assembly by Command of His Excellency.

THE great and the growing importance of the cyanide process for extracting gold from its matrices makes anything that is explanatory of the chemistry of this process interesting, and more or less valuable according to its precise nature.

In this place I would first refer to the fact that, in 1895, in the annual Report of the Mines Department is a copy of a report of mine to the Hon. the Minister of Mines, in which I describe certain singular effects that occur when a piece of gold-leaf is partly immersed in an aqueous solution of potassic cyanide, also other phenomena, and which appeared to me at that time not easily explainable; and, being then pressed for time, I let these matters stand over, but I promised a further investigation of them, and a statement of the results thereof, at the first opportunity. I have since spent a good deal of time in following up these subjects, and have communicated some results thereon to the public at various times, but not in the Mines Reports. I now, therefore, make a special report of these results, together with other later ones of mine that have not yet been published, so as to give a complete and connected account of my investigations of the subject since the publication of the report referred to (1895). For this purpose I shall not keep to the order of time, but shall arrange the facts brought out by them, so that they shall be stated in a natural sequence, and in such a way that their comprehension by the reader may be as easy as possible. I will first deal with those results that bear upon the question—

HOW IS THE CYANIDING OF GOLD EFFECTED?

Every chemist of our cyanide plants is now very well aware that to do this profitably a very weak solution of potassic cyanide, or its chemical equivalent, free oxygen, and, of course, a sufficiency of gold in a rather fine state of division, are necessary; and he further knows that it so happens that the gold he wins is won as the *auro-cyanide of potassium*, but the precise way in which this happy event comes about he does not know. A good deal he knows, and he has several plausible-looking theories to choose from for his guidance and information; but (as it appears to me, at least) there are certain facts underlying the whole process—certain phenomena—hitherto unknown, which, if circumstances were unfavourable for their occurrence, would make any attempt to cyanide gold at all a complete failure. It is these facts that I shall endeavour to show as clearly as I can, and, as it so happens that the experimental results upon which my evidence for these facts is grounded were initiated by the study of a remarkable phenomenon first noticed by Professor Faraday, I commence my subject by reference to this.

It was in the year 1857, in his Bakerian Lecture, that this eminent chemist informed the scientific world that gold-leaf, as resting on the surface of a solution of potassic cyanide, dissolves about one hundred times quicker than gold-leaf that is wholly immersed therein—a fact that is now taken advantage of by cyaniders for a rough and ready test of the strength of their cyanide-solution. The difference is, indeed, marvellous, and there are at present two theories proposed to account for this. The first in time is that of Faraday himself, to which, indeed, great weight should attach notwithstanding its antiquity. It has not (to my knowledge, at least), hitherto been directly challenged. It is, as stated in his own words, "air voltaic currents are formed in these cases" (the cyaniding of gold resting on the solution), "and the gold is dissolved almost entirely under their influence."

The next theory is one which, if not yet precisely formulated in a public print, is, as far as I can learn, the popular one among the cyaniders, as it really appears to exactly fit the facts of the case. Taking cognisance of the fact that oxygen is a necessary factor in the process, and is far more plentiful at the surface of the cyanide-solution than in the solution itself, it claims that this rapid dissolution of gold at the surface is simply due to the plentiful supply of this gas. In this connection, it is right that I should take cognisance of the fact that Mr. Maclaurin, F.C.S., has given us a theory to explain the rapid action of cyanide-solutions on gold so placed that, as he suggests, it may be considered as only an extension of the under-surface of gold in the position described, and consequently is a theory that, if true, goes to explain the particular phenomenon under consideration here, and therefore has to be noticed in this communication. This theory, then, maintains that there is generated at the surface of the cyanide-solution on which gold is resting a current of electricity, and that this current causes the solution of the gold (at least, the gold immediately under that having contact with atmosphere)—that, in his own words, "the solution of this gold is due to electrolytic action obtained by the action of the cyanide and the oxygen of air."*

This is the theory that Mr. Maclaurin offers us to explain the rapid dissolution of the underparts of gold resting on a cyanide-solution. However, as previous to the reading of the paper embodying this theory I had shown that the current which does obtain in this case is just in the reverse direction to what he affirms it to be, I need not do more than state the fact that this gold is not brought into solution by an electrical current at all. There is therefore no necessity for me to treat this theory separately, so I proceed with my discussion of the theory first stated—that of Professor Faraday.

In regard, then, to this theory, it appears to me that this scientist, in his eagerness to pursue the main investigation—the real object of his labour—contented himself here to take a course very unusual for him—to make, as it were, a snapshot; for had his mind not been so preoccupied he would certainly have followed up the matter, and just as certainly he would have solved the enigma—nay, it is my firm belief that he, with the wonderful all-round faculties he had for scientific investigation, the great capacity he had for entertaining and successfully grappling with phenomena, whether those of astronomical magnitude or those equally difficult and no less entertaining, so minute as almost to elude not only investigation but even perception itself—it is, I say, my firm belief that he would have followed up his labours in this direction, and crowned them by the discovery of the extraordinary, the unexpected potency of the weak cyanide-solution, and then, in his own good time, have conferred a gift to the world that would have anticipated that miner, to us unknown, who, in sheer desperation to make the cyanide process a workable one, blundered to the discovery of this strange potency of the weak solution. However, Faraday lost the opportunity to benefit the miner in this way, but only to take opportunities of serving man in the higher reaches of science, leaving us only, as I have said, a bare theory to interpret the phenomenon that he discovered, and which I have here to discuss.

Now, as to this matter, I would like to know the *modus operandi* of the production of these "air voltaic currents" that this scientist states are the agents for thus rapidly dissolving gold lying in the solution. As I take it, an air voltaic current is one that can exist in the air alone, or is produced there by the assistance of this surface gold and the cyanide-solution; but how is the current formed, and, when formed, how does it promote the solution of the gold? But, whatever answers may be framed to these questions, the following facts certainly appear to show that the "air voltaic current" theory is not tenable. If the gold-leaf and the surrounding cyanide-solution be covered with a thick layer of kerosene or gasoline the dissolution of that gold is but little retarded.† Ether can be substituted for these oils with like effects if only the cyanide-solution is very strong or has been heavily salted to prevent the downward diffusion of the ether, and so favour the existence of a hard line of demarcation between the two liquids. All these substances are, I find, slowly permeable by oxygen; still, apparently, not notably more so than water is: but the same results happened when they were depleted of their contained gases by passing coal-gas through them, and even when the gold-leaf itself was also depleted more or less of the air lodged in its pores by the same gas.

These facts, then, I think, clearly prove that, for the rapid dissolution of gold-leaf on the cyanide solution, a body of air resting on that solution is not at all necessary. They show, on the other hand, that there is entangled in the pores of the gold-leaf,‡ or mechanically absorbed by it, a sufficiency of oxygen to provide for a rapid dissolution of the metal. These facts, to my mind, strike, and fatally, at one and the same time at both the theory of Faraday and the popular theory that the profuse supply of oxygen has largely to do with this rapid dissolution of gold.

Now, the result just stated, while, as I think, disproving the two theories specified, raises a question of great pertinency to the subject—one which, if fairly answered, should lead to the settlement of the question that I set out with, How is the cyaniding of gold effected? And it is this: Why should gold-leaf in a cyanide-solution be very much longer in dissolving than gold-leaf lying on the surface, and under a layer of oil or ether, the necessary supply of oxygen being in each case, as it were, afoot—that is, lodged in the gold-leaf? Well, the answer—and I believe the only answer—to this question is one that rests largely for support on results and deductions therefrom which were started by the observation of another phenomenon almost as singular as the one that we have been attempting to explain, and which I announced in 1895,§ and it is this: A piece of gold (say gold-leaf) that is immersed in a cyanide partly-solution, weak or strong, not only dissolves rapidly at the surface of that liquid, as Faraday announced, but also rapidly—often just as rapidly—in the liquid itself, and even at those parts that are quite distant from the surface.

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* "On the Action of Potassium-cyanide Solution upon Gold." (Trans. N.Z. Inst., Vol. xxviii., Art. lxxiii.).

† Trans. N.Z. Inst. for 1896, p. 581.

‡ Faraday shows this leaf is full of pores.

§ Mines Report, 1895, pp. 186–9.

Here, then, to me, as it would have been to any other chemist, was a very suggestive fact, and a means offered whereby the singular phenomenon that Faraday discovered might be hopefully investigated. Now, the part of the gold-leaf that is immersed in the cyanide-solution may be viewed as merely an extension of the under-surface of the gold-leaf that lies on the surface of this solution, and so I was led to suppose that the phenomenon had, as it were, an electrical side—was, in fact, if not produced electrically, at least contemporaneous, and connected with a current of electricity; so, acting on this idea, I connected a square of gold-leaf that laid on the cyanide solution with a square of the leaf submerged therein through a galvanometer, when an electric current manifested its presence, the direction of which would have been a surprise to Faraday himself, for it indicated that the current proceeded from the submerged gold. Thus the idea of the rapid dissolution of gold lying on a cyanide-solution being due to electromotive force generated at the surface, as Faraday supposes, receives a very rude shock.

Following up this new line of investigation it was soon found that gold in strong solutions of the cyanide is always positive to gold in weak solutions of this salt, and that the current thus generated is sufficiently strong to give electrolytic effects—*e.g.*, the deposition of copper and gold from their sulphate and chloride respectively. These results, while showing clearly and undeniably that the rapidity with which gold dissolves when lying on a cyanide-solution is not due to the generation of any electrical current at all, shows just as clearly the fact of the potency of cyanide-solutions of different strengths in contact with the gold for accelerating the cyaniding of the metal; and the inference I would make from this is, that the rapidity with which this surface gold dissolves is in greater part, if not wholly, due to the action of cyanide of different strengths—in fact, to the action of the stronger solution on the under-surface of the leaf, its upper surface forming in the weaker cyanide the negative pole.

Now, that the solutions in the vicinity of the gold-leaf as there situated are, or soon get to be, of different strength, appears certain for the following reasons:—Gold-leaf is, as Faraday long ago pointed out, very porous, and it is easily conceivable that the easily-decomposable cyanide-solution, rising through the capillary pores of the metal, and subjected therein to oxygen condensed on their sides, would undergo a partial decomposition. There is this, too, to be taken cognisance of, and that helps to perpetuate this difference in cyanide strength: The solution next the air cannot so well be recuperated from the normal solution as can the solution underneath, the former being almost cut off from the underlying solution.

In this connection I would state that my experiments show a very small negative pole will serve for quite a large positive pole, reckoning by superficies. Therefore, a local weakening of the solution at any point would give us a general dissolution of gold over the parts of the metal that have still contact with the normal solution. If any one should reply to this theory for the dissolution of gold that by the same rule a solid body—say, glass—placed over the gold-leaf should also favour the production of the heterogeneity in the solution which my theory requires, and *which it does not*, I would answer that solid substances thus placed prevent the escape of air out of the capillary cavities or pores of the gold-leaf, and so keep the cyanide-solution from that contact with the surface-gold necessary to complete the interpolar connection between its upper and lower surfaces.

Now, if differentiation of the strength of the cyanide-solution does explain the rapidity with which gold, as placed on a cyanide-solution, is dissolved, differentiation in strength must be a factor in the dissolution of gold in the cyanide process generally. I conceive it, indeed, to be the key, the mainstay, of the process as worked at the mines. The initiation of this is easy, and easy to understand: the percolation of the cyanide-solution through the charge—this "drip, drip, drip,"—and in a damp atmosphere, is all very favourable for its production, also for its maintenance. Thus the cyaniding of gold appears to be eminently an electric process: not that the gold is dissolved therein by means of electric currents (not even in the case of gold on the cyanide), but that, on the other hand, it generates these currents—gives us, in fact, electro-motive power; and if the mechanical fixings are not present which are necessary for the setting-up of these voltaic currents, no dissolution occurs. In reality, the dissolution of gold in the cyanide is analogous to the dissolution of zinc in the sulphuric acid of a Smee's cell. If means are not present for the production of the voltaic circle no pronounced, no regular, action takes place—it is merely a difference in the construction and the arrangement of the cell. Thus, in the Smee's cell it is one solution and two metals, but in the cyanide process one metal and one solution at the start, which solution, from the causes I have named, and probably others in conjunction, becomes of various strength, and so fulfils the condition necessary to insure the existence of the voltaic circle.

THE THEORIES OF DR. KEITH AND DR. HOOD.

In this connection it is proper that I note, and shortly discuss, two theories that I just learn from the second edition of Rose's "Metallurgy of Gold" have been constructed to show how the chemical actions obtaining in the cyanide process are initiated and brought about. Dr. Keith suggests, in "Engineering" for 1895, page 379, "that the action of oxygen (in this process) is due to its strongly electric negative relation to gold in the cyanide-solution." Making use of Dr. Gore's table of the electro-motive power of certain metals in these solutions as compared among themselves,* he selected carbon for experiment to support the theory, and, as he states, found that it greatly accelerated the dissolution of gold—a fact that twenty years before I had stated would occur.

In regard to this supposed capability of oxygen to act the part of a negative pole—to substitute a metal—say, mercury—in the voltaic cell—I must, however, strongly dissent from him, and would

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* My own table for this purpose was published two years before Dr. Gore's table was. The tables pretty well agree as far as they go; but, as Dr. Gore's was published in the Transactions of the Royal Society, it takes precedence over mine in the editorial mind.

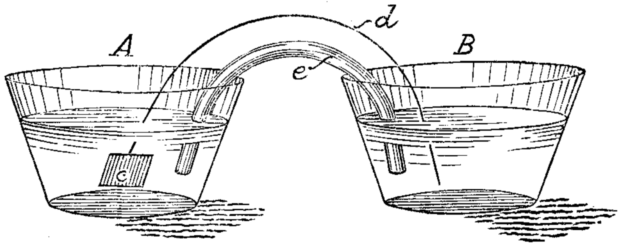
remind him that oxygen at ordinary temperatures is not an electric conductor; it is therefore physically incapable of acting the part here assigned to it.

By the way, I would remark that the use of a mercuric cyanide in the potassic-cyanide solution, feasible—nay, profitable—as it should be on theoretical grounds, is not likely to be successful, and for the reason I have stated in 1895.* The fact is, that, though the gold becomes quickly amalgamated, and there is every sign of a rapid dissolution of the gold, these are appearances only, as the deposited mercury greatly interferes with the passage of the underlying gold through it to the cyanide-solution, nor, indeed, "does it," as I say, "entirely go before all the mercury thus deposited has also been dissolved." The process is really retarded instead of being accelerated by this chemical amalgamation of the gold. These statements of mine have since received confirmation as to their absolute correctness by the results of certain experiments of the author of the work on metallurgy that I quoted from (Dr. Kirke Rose, D. Sc., A.R.S.M., F.C.S., &c.).

The next theory, that of Dr. Hood, claims that the cyanodizing of gold is always effected by a displacement of another metal from the cyanide used by it—that, in fact, as he goes on to say, "pure alkaline cyanides cannot dissolve gold"—meaning, of course, in the oxygenated solution. To meet this theory, I need only ask him, I think, what metal or metals are likely to be in the cyanide, or even in the auriferous mine-stuff itself, that gold could displace from a cyanide-solution. The table of mine referred to only names the metals platina, iron, lead, and mercury as being negatives to gold in cyanide-solutions; but certainly platina is out of the question, while iron would not be replaceable. There only, then, remains mercury and lead, and neither of these are present in cyanide-solutions except on very rare occasions. But, independent of this, we know that gold absolutely pure (as prepared from its pure chloride by oxalic acid) is dissolvable by the weak cyanide. Clearly, then, this theory is disproved by fact.

THE ACTUAL CHEMICAL DECOMPOSITIONS THAT OCCUR IN THE PROCESS.

Two theories have been formulated to explain how gold becomes dissolved in the cyanide process. One is that given by a joint patentee of the process, Mr. McArthur. This assumes that water is decomposed, its oxygen being used to replace the cyanogen necessary to cyanide the gold, while its hydrogen is evolved. Now, this theory is that of the minority, and is still, I believe, held by its author. My own experiments in this matter gave, as I have already stated,† results entirely against it, and I have seen no reason to alter my expressed opinion in this matter—that is, as regards the practical working of the process; but by an apparently trivial and unimportant variation in cyaniding gold we actually do get a liberation of hydrogen. For this it is only necessary to so arrange that the negative gold of the cyanide apparatus (the voltaic cell, as it really is) shall be placed in an acid solution—say, in hydrochloric, sulphuric, or acetic acid. The diagram here given explains what I mean. A is a vessel containing potassic cyanide of any strength, in which is a sheet of gold-leaf (gummed to paper). B is another vessel, containing the acid in water heavily salted to drive out the oxygen that might interfere with the result. In this vessel is a gold wire *d*, which is connected with the gold-leaf *c*. Interpolar connection is completed by the bent glass tube *e* that is full of hydrated, but almost solid, gelatine, slightly salted for conducting purposes, if necessary.



Soon after this arrangement is set up a stream of gas may be observed issuing from the gold or platina wire. This is hydrogen, and the evolution goes on continuously till all the gold-leaf is dissolved. It is necessary to have a small cathode and a large anode to be certain of success in the experiment, as cyanodizing is at the best a slow process, and even concentrated solutions of the acids and salts let in oxygen fast enough to oxidize hydrogen to a notable extent, and thus prevent its liberation being noticed. It is a singular fact that if potash, or any alkaline solution, were substituted for the acid in B, I was unable to observe any evolution of gas, yet the currents formed appear as strong as when the acid was used. It is possible, however, that potash, by its great affinity for water, so rapidly determines the oxidation of hydrogen that none is to be seen escaping.

These results, while they clearly show the unexpected fact to many that hydrogen can be liberated in a cyanide process, show just as clearly that in the process as carried on at the mines the gas is never evolved, but is, so to speak, only transferred in a liquid form to the oxygen present at the anode. The process there demands that the oxygen shall be present there and in quantity, while the alkalinity of the solutions around them favours the rapid union of this gas with oxygen before it can assume the gaseous form, or even before it can in reality become free.

It should be stated that a brisk evolution of hydrogen is afforded by cyanodizing copper, even when the anode is in an alkaline solution. This branch of the investigation requires further researches.‡

The next theory, and the popular one, to explain the chemistry of the process involves the decomposition of potassic cyanide, the cyanogen combining with the gold as before, while its potassium combines with oxygen gas as present in the solution. This view appears reasonable,

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* Twenty-ninth Annual Laboratory Report, p. 44. † Mines Report for 1895, p. 88. ‡ Regarding the gold used in this experiment, I should state that it did not contain silver, copper, or iron.

and, indeed, unassailable, until we take cognisance of the fact that we can, by the very slight modification in the process just described, get an evolution of hydrogen—that is, by transferring the negative gold—the negative pole—from its alkaline to an acidic solution. A careful consideration of this fact leads me to think it is not in reality the potassic cyanide but the hydrocyanic acid that is decomposed.

We must consider that in the cyanide-solution we have not the simple compound potassic cyanide to deal with, but the hydrocyanide of potash, corresponding to the hydrochloride of potash. As I have already stated, the cyaniding of gold produces electricity, thus necessitating for its continuance the presence of an electrolyte, and for this hydrocyanic acid should, I think, be as well suited as hydrochloric acid, which, as we well know, is capable of acting this part, although not so easy to decompose as the former acid. Why not, then, look upon this compound as the one that is decomposed in the process? It is true that the decomposition of potassic cyanide may also result in the liberation of hydrogen by a secondary action in which water is decomposed, as McArthur's theory supposes; but to my mind this is hypothecating a complexity in the process that we have no necessity and no warranty for doing.

On the hypothesis I have here advanced the cyanodizing of gold is a very simple operation, or, rather, a combination of two very simple operations. The affinity of gold for cyanogen and that of oxygen for hydrogen in the presence of an alkali conjointly determine the decomposition of the hydrocyanic acid, a gold-cyanide forming at the one pole and water at the other. This constitutes the first operation. The dissolution of the cyanide by a portion of the remaining potassic cyanide is the second operation. In the first operation there is no precedence in action at either pole; the electric action at each pole commences simultaneously. True it is that to the old idea of voltaic electricity as a current (a false idea which our every-day use of old terms perpetuates) it is not easy to reconcile one's-self to the thought of a simultaneous start of electricity at each pole; but by charging one's-self with a full and a trusting belief in Faraday's theory, that such electricity is only a polarisation, one clearly perceives that this is the only way the action is started.

NOT ALWAYS THE "DILUTE SOLUTION" THAT MOST RAPIDLY ATTACKS GOLD.

A very singular phenomenon may be observed in regard to the action of the cyanide-solution upon gold such as that which Professor Faraday used for his experiment. This gold is deposited from very weak solutions of its chloride by phosphorus or hydrogen[*] in such finely-divided particles that they are indistinguishable—in fact, invisible—under the highest-powered microscope of that time, and they are able to remain in suspension in water for an indefinite period, and it is only by reflected light Faraday could observe them. Now, if we neutralise, or slightly alkalize, this red-looking auriferous fluid (we cannot designate it as a solution), then divide into two parts, and mix one part with, say, three volumes of the dilute solution, and mix the other part with a strong cyanide-solution—say, the concentrated solution—it will be found that it is the gold in the strong cyanide that first disappears from view. Nor is it a neck-and-neck affair by any means, for in the strong solution three seconds may suffice to complete the operation, while in the case of the orthodox dilute solution the time required will be about five minutes—that is, about one hundred times longer. This is, of course, just what one would have expected a few years ago, before our working cyaniders had taught us the extraordinary potency of the dilute solution over the strong solution as a gold-dissolver. Both the blue and the red gold of Faraday give these results.[†]

These results clearly prove that even in the supposed inert solutions of the cyanide the strong solutions rapidly act upon gold to a limited extent. It is not a matter of superior causticity, for it was found that strongly alkalizing the weak cyanide did not hasten the dissolution.

The explanation of this enigma is, I think, this: In the strong solution cyaniding goes on at once, but only so far as to produce a colourless cyanide of gold that is insoluble, or but very slowly soluble, in the liquid. I have before[‡] shown that gold taken out of a strong cyanide-solution refuses to amalgamate, or, at least, but very slowly amalgamates, showing, as I said, that an insoluble saline film of some gold-cyanide has enveloped it. In further support of this idea I would note here the fact (which may or may not have been observed before) that gold-leaf upon a strong cyanide-solution, in disappearing, leaves floating thereon a pale white ghostly-looking figure of its departed self, exact to the shape, and reminding the student of ancient history of the sad metamorphosis of Lot's wife. In the case before us, however, there is no transmutation of a vast number of metals—nor even of one: the white floating mass left by the gold is its cyanide, and it is this substance that, I believe, always forms upon gold in strong cyanide-solution, thus preventing or retarding its dissolution.

In the strong solution, then, we have not only the limited supply of oxygen against the cyanider, as Maclaurin has shown, but we have also the rapid enfilming of the gold by a salt that is but very slowly removed therefrom.

THE RELATIVE SPEED AT WHICH THE CYANIDE DISSOLVES FINELY-DIVIDED GOLD AND GOLD IN THE MASSIVE FORM.

It will be taken as granted that the finer the state of division in which gold is presented to the cyanide-solution the more speedily, weight for weight, will it dissolve—that it is all a matter of superficies. No cyanider would, I think, doubt this any more than some eight years ago he would have doubted the statement that generally the stronger the solution of the cyanide the quicker would any gold therein dissolve. However, as I have before remarked, "the chemistry of the cyanide process is full of surprises," and I think that another surprise awaits our cyanider here. Thus, if to any one of those blue- or red-coloured liquids of Faraday's, containing gold diffused

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[*] Coal-gas may conveniently be substituted for hydrogen.

[†] The blue gold that Faraday got by the administration of salt to the red gold reverts to the red gold in weak cyanide, also chlorine—a change that Faraday failed to produce, though he long sought for it.

[‡] Twenty-ninth Laboratory Report, 1895, p. 45.

through them in extremely fine particles, he adds sufficient alkali to feebly alkalize it, and afterwards adds thereto, say, three volumes of a 0·3-per-cent. solution of the cyanide, he will find that, as a rule, there will not be a complete dissolution of the gold until five minutes has elapsed; and he will further find that the disappearance of the gold—*i.e.*, the discolouration of the fluid—is progressively slower as the operation goes on—that the last traces of gold linger, as it were, in the liquid in a very marked manner, instead of vanishing from sight in an abrupt manner, as we should expect. These were, at any rate, my experiences of the matter, and I took great care to prevent either any excess of auric chloride or any compound of phosphorus interfering with the experiment.

In a test experiment I made for comparative purposes, I had a square inch of gold-leaf dissolved, and the solution of gold resulting was then decomposed and made up to 6 cubic inches of the gold-fluid; and the gold in this fluid was found to be dissolved by three volumes of the 0·3-per-cent. cyanide in five minutes. Now, were the gold-leaf I took only divided by the precipitating-agent into cubes of the same thickness as that of the gold-leaf—say, $\frac{1}{280000}$ in.—the speed of dissolution should, if regulated by the extent of gold-superficies exposed to the cyanide, have taken place in about one minute, because the same kind of gold-leaf that I used in this case was dissolved as in its oxygenated state in eighteen minutes, and by the same stock solution of cyanide that I used for my former test. The gold-leaf, therefore, as thus divided, is three times longer in dissolving than the gold-leaf was. But it is certain that the gold has been much more finely divided than this; therefore it is certain that the retardation of the dissolution of gold by such a division of it as we have in these solutions, or, rather, auriferous liquids, is very much greater than the results of these calculations show; consequently the rate of dissolution for similar areas exposed is still more in favour of the leaf-gold. The fact should be noted that it is the finely-divided gold, which is, of the two, the most liberally supplied with oxygen.

As an abundance of time is given at the mines for dissolving fine gold, the fact I have here described does not concern the cyanider, and I only give it as being of possible interest to the chemist.

To present a complete record of all the experimental results that since my report to the Mines Department I have obtained in my investigation of the chemistry of the cyanide process, I insert here the following extracts from the Twenty-ninth Annual Laboratory Report, 1894–95:—

"1. In the exercise of selective action of potassic cyanide for gold, when paired with a conducting metallic sulphide, there is only a very slight conservation of that sulphide—so slight, indeed, as to be hardly appreciable.

"Now, this is exactly what any one would expect when he considers that the electric current—the very existence of the voltaic pair here—is founded upon an oxidizing process only, the oxidation either of the gold or the potassium of the cyanide by atmospheric oxygen; the gold or the potassium (as the case may prove) being more easily oxidized in this way than the metallic sulphide used. As I have proved (and shall show in due course), the solution of the sulphide in potassic cyanide which simultaneously occurs produces no electricity—at least, no dynamic electricity: it melts in the cyanide as sugar melts in water. Whether the sulphur of the ore goes to the basic side of the salt to form potassic sulphide, or to the acidic side to form a radical—sulpho-cyanogen*—it is all the same, no electric current is produced.

"2. Generally, any salt added to a good working-solution of potassic cyanide acts the same as an equal quantity of the cyanide in retarding or preventing dissolution of gold. Sugar and glycerine produce the same effects.

"3. Albumen added to a solution of potassic cyanide of 0·26 per cent., in quantity sufficient to well froth such solution when whipped with it, did not appear to exercise any retarding effect on the dissolution of gold.

"4. Potash when added to an aqueous solution of potassic cyanide does not, as is now authoritatively alleged, destroy the cyanogen of that salt by hydrolysis or in any other way, but, on the other hand, conserves it.

"Thus we see that, instead of being, as it is termed, a cyanicide, potash is a preservative; consequently the excess of it in the cyanide-solution that we are now urgently warned against we need not fear to have. Far better the excess, even to a great excess, than the deficiency, even if but slight. There is only this point to consider: that, as potash, soda, and salts generally (see 2) retard the dissolution of gold in potassic cyanide, it is certainly right that no large excess of it should be used.

"5. Ammonia, whether in large or in small proportion, decomposes the cyanogen of potassic-cyanide solutions, and this whether it is applied in its combined state, as the chloride, &c., or in its uncombined state.

"Here, then, is the cyanicide that the worker of cyanide plants should be warned against—this, the ever-present enemy that he has to contend with, and not caustic potash, one of his best friends.

"6. Ammonia decomposes the potassic cyanide of these solutions, gradually taking off the cyanogen as a part of ammonium-cyanide. Salts of ammonia effect the same decomposition.

"7. Contrary to what is now alleged, nitrogen does not decompose potassic cyanide and carry hydrocyanic acid off when it is passed over or through a solution of this salt.

"These results (Nos. 6 and 7) would seem to show that, in the case where a loss of cyanogen occurred by passing nitrogen through a cyanide solution, such loss was entirely due to the action of ammonia, this compound being frequently present in cyanide-solutions that have been made for some time. It is also present in all soils and many rocks, and would be taken up by potassic-cyanide solutions.

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* I believe that I was the first to show that the cyanogen of potassic cyanide in dissolving metallic sulphides formed with a part of their sulphur sulpho-cyanogen (see "On the Production of Artificial Chromes," Trans. N.Z. Inst., Vol., xxi., p. 360).

"8. Ammonia does not, by the aid of an air-jet, carry off the cyanogen from either the auro-, cupro-, or zinco-cyanide of potassium, nor yet from the cyanide of strychnine.

"In regard to this, I may state that, as far as I have gone, it appears to me that it is only the cyanides of the alkalies and alkaline earths that are decomposed by ammonia.

"9. Hydrocyanic acid does not, as is now alleged, attack gold.

"10. Gaseous ammonium-cyanide attacks gold in presence of oxygen very rapidly if the contact takes place in air—the speed being about three times as great as that at which the most potent solutions of the potassic cyanide operate.

"11. Mercury and platinum are dissolved, though very slowly, by potassic-cyanide solutions; for mercury at least the dilute solutions are far more potent than the strong ones are.

"This is contrary to the teachings of Gmelin; and the fact that platinum is also soluble in the cyanide proves that wherever this metal exists along with the gold that is won by the cyanide process it will be found to a more or less extent in the bullion thus obtained.*

"12. Auric cyanide is a powerful accelerator in the cyanide process, and this whether it is used in the strong or the weak cyanide-solution. Platino-cyanide of potassium is also a powerful accelerator.

"It will be seen from this that, once the process of dissolution of gold starts, it is greatly assisted by the auro-cyanide thus formed.

"13. Mercuric cyanide of potassium, though a rapid accelerator in strong solutions of potassic cyanide, acts as a retarder in dilute solutions.

"This, no doubt, is quite contrary to the opinion of the patentee of this salt for the process; but the fact appears that, although the gold quickly becomes amalgamated,† and there is every sign of a rapid dissolution of gold, it is not so. The mercury that has been deposited does not allow the gold to go into solution at all freely, nor, indeed, does it entirely go before all the mercury thus deposited has also dissolved. The process is, as I have said, really retarded instead of being accelerated, and this because mercury takes longer to dissolve in the cyanide than gold does, being, as it is, the more negative of the two metals.

"14. The bichromate of potash (patented as an accelerator for the cyanide process) is considerably inferior to the ferri-cyanide of potassium in this respect.

"15. Ferri-cyanide of potassium is, as the patentee of it states, an accelerator in the cyanide process, reducing, as it did in my experiments, the time about half."

"DETAILS OF CERTAIN OF THESE EXPERIMENTS.

"(1.) Two pieces of covellite (a mineral representing the copper-sulphides) of the same shape, size, and weight were placed in separate cyanide-solutions of the same strength, volume, and shape. One of these pieces was connected voltaically with a gold plate, when, after the lapse of two hours, both the pieces of covellite were nearly dissolved, and I could only detect a very minute difference in the weight of their residues in favour of that piece of covellite that had had contact with gold. The weight of each piece of covellite was 6 gr.; that of the gold dissolved was ¼ gr.

"Clearly, then, covellite is but very slightly conserved by being voltaically connected with gold; it is only conserved so far as this: it does not oxidize. Still, all the time it is, as it were, quietly melting in the cyanide-solution, without producing any electric phenomena that we can detect.

"The covellite that I used for this experiment I prepared in very thin translucent sheets or films upon glass by the process that I published a few years ago in the Transactions N.Z. Institute, Vol. xxi., page 361. Films prepared in this way may be had of precisely the same thickness, and absolutely pure.

"(8.) Doubting the accuracy of the statement that nitrogen gas driven through a potassic-cyanide solution decomposes it and carries off the cyanogen, I tried the effect of this gas on a solution of the cyanide of 10 per cent. After two hours I tested the solution, and could not observe any loss of cyanogen by the colour test in the ferro-cyanide process. I then tried the effect of nitrogen, as admixed with oxygen in the air, in conjunction with ammonia, when, in five minutes, all the cyanogen was carried off from the solution.

"Now, as a current of air driven through an ammoniated solution of bicarbonate of soda only reduces this carbonate to the monocarbonate, the affinity of cyanogen for the alkalies is less than that of carbonic acid for these bodies."

"NOTES ON THE BROMO-CYANIDE PROCESS.

"This process was first invented by Dr. Gaze, as an 'improvement on the cyanide process,' and consists in bromodizing a part of the cyanogen present in a cyanide-solution before applying it therein. Now, this is a real invention, and it could only have been made after much careful research in a direction that required a fair acquaintance with the laws of chemistry, and so is very creditable to Dr. Gaze, as an experimentalist in science, and he certainly deserves a reward for his 'improvement,' if it can be successfully applied. But, unfortunately for him, his improvement necessitated the use of cyanogen, an article which, both singly and in all its combinations, had already been patented by the patentees of the cyanide process—a process which some people think should never have been patented, as being a patent for an application only—a patent for the sole use of a principle known long before, and with not the least trace of invention on their part in it. This is said despite the opinion of the bench of learned Judges who sat upon the cyanide case recently in

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* Since this report was written I was informed by Mr. Park, F.G.S., late Director of the School of Mines, Thames, that he has found mercury in some quantity in the cyanide-solutions that form with the tailings where mercury is present.

† This process was invented by myself in 1876 (see Trans. N.Z. Inst., Vol. viii.), and it was proposed by me as a good test for minute grains of gold in its matrices.

England, and in concurrence with the view of Mr. Justice Romer, who tried the case in the ower Court. But, however the rights of this may be, these are the points that I have ascertained in the bromo-cyanide process :—

"(1.) That when strong solutions of potassic cyanide are bromodized they act with even greater rapidity on gold than potassic cyanide does upon gold that is polarised;

"(2.) That, in the good working-solution of the cyanide, bromodizing has but very little accelerating effect, if, indeed, it has any at all—certainly far less than ferri-cyanide of potassium has;

"(3.) That a well-prepared solution of this agent has but an extremely slight effect on cupreous sulphides;

"(4.) That gold, even when sulphurised, is speedily attacked and dissolved by this bromodized-cyanide solution.

"These results show that the bromo-cyanide process, also variations of it with other haloids, seems especially applicable in those cases where the gold to be extracted is coarse or is admixed with metallic sulphides—cases where the ordinary cyanide process either completely fails or is not at all satisfactory."

"On the Position that Cyanogen holds in Relation to the Simple Radicals, and its Inability to combine directly with Silver or Gold. (By William Skey, Analyst to the Mines Department.)

"[Read before the Wellington Philosophical Society, 26th August, 1896].

"*Abstract.*

"In this communication I refer to the fact that in 1874 I gave a paper to this Society entitled 'On the Analogy of Cyanogen to Oxygen,'* in which I endeavoured to show that this compound radical should not, for certain reasons that I stated, be classed, as it now is, with the haloid elements chlorine, bromine, and iodine, but rather with oxygen; that, in fact, it is only when it is united with sulphur that we have a radical at all comparing with the elements here named. This theory when circulated in England did not meet with any favour—not that the facts I adduced in support of it were at all questioned, but that others were put forward which, as was stated, conflicted with them. Not then having any further facts to adduce I let the subject drop; but just recently, owing to the question assuming considerable importance, I took it up again, and I have, as a result, discovered further evidence, which, as I believe, is greatly in favour of my theory, and which I adduce. I therefore state this evidence, which is to the effect that cyanogen does not, as it is at present supposed, dissolve either silver or gold when administered to it as an aqueous solution, whether these are dilute or concentrated—that, indeed, as far as I have at present investigated the matter, cyanogen does not even attack either of these metals at all.

"The exhibits 1 and 2 on the table here show a little silver- and gold-leaf that have been in a strong solution (aqueous) of this gas for five days, and, for comparison, pieces of silver- and gold-leaf, from the same sheets respectively, that have not been in the solution. I do not think any one can discern any difference in the appearance of these—that is, any loss of either the gold- or silver-leaf that has been in the cyanogen; and I think that you will allow that this is a very severe test in the case of gold, when you consider that its thickness is not more than $\frac{1}{170000}$in. To get a still more crucial test I have coupled gold-leaf with chalcopyrites in the solution of cyanogen (as you may see in the exhibit No. 3), so as to have the benefit, the stimulating effect, that we get by allowing any electricity produced by chemical action to become current electricity. Still, you may see the result is the same; the gold remains, as far as we can see, *absolutely unaffected.*

"In all these experiments I feebly acidulate the cyanogen solution to counteract the decomposing effect produced by atmospheric ammonia or the alkali of the vessels that I use. Thus I completely avoid the production of gold-dissolvers—that is, the alkaline cyanides, which otherwise would interfere with the accuracy of investigations of this nature.

"Light does not appear to act on these solutions of cyanogen, at least so as to produce any solvent for gold, such as ammonium-cyanide.

I then assert that cyanogen gas, like oxygen, is far more soluble in water than in saline solutions generally that have no chemical effect on it, but that, as it now appears to me that this is a general character of gases, I do not count upon this fact to aid me in my contention. I then go on to state, in regard to the position of this compound radical among the elementary radicals, that wherever this is, it cannot be with the group of chlorine radicals, owing to the non-acidity of its hydride in water, the composition of its acidic compounds with oxygen, and, lastly, as here shown, its refusal to unite directly with certain metals.

"I then, in conclusion, state the position I would take in the controversy that I started, and it is this: that, while not disputing the correctness of the general opinion that cyanogen stands in close relation to the radical carboxyl, in which case it is monoatomic, and so comparing with the chlorous radicals, I still maintain that it is on certain occasions diatomic, and so comparable with oxygen. It has, in fact, as I believe, a varying atomicity or quantivalence, according to the nature of its environment.

"As you are aware, this compound can assume allotropic states—that is, like oxygen, it can combine with itself—and an intercombination such as this might, I think, give us cyanogen in the form of a 'dyad'; but this is a matter that requires further consideration.

"It is only right that I should inform you that Professor Black, of the Otago University, has proved by a series of experiments which are practically contemporaneous with mine that if cyanogen does dissolve gold it is only at a very slow rate as compared with the action of potassic cyanide on this metal. However, as it appears that a very suggestive query that I proposed bearing on this matter started these experiments, I feel sure that this gentleman will, with his accustomed magnan-

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* Trans. N.Z. Inst., Vol. vii., p. 379.

imity and feelings of good-fellowship for his brother-workers in the field of science, concede to me the position of leader in this investigation."

"FURTHER RESULTS SHOWING THAT FREE CYANOGEN DOES NOT DISSOLVE OR EVEN ATTACK GOLD.

(By WILLIAM SKEY, Analyst to the Mines Department.)

" [Read before the Wellington Philosophical Society, 7th October, 1896.]

"The scientific and other interests that attach to the statements I made before the Society a few weeks ago, that free cyanogen does not attack gold, has induced me to continue my investigations on the subject by the application of tests of a more severe character even than those were upon which I based this statement.

"I should premise the description of the results of this further investigation by informing you that soon after the paper referred to was read I learned that Mr. Park, late lecturer at the Thames School of Mines, had made a series of valuable experiments on the subject, in which he used the gravimetric method for determining whether there was not a dissolution of gold by aqueous solution of this gas.

"The results of these experiments do not confirm the correctness of this statement of mine (that cyanogen is unable to dissolve gold), but, still, they clearly show that, at least, solutions of this gas do not dissolve this metal at all readily. Mr. Park informs us that he performed his experiments with a button of pure 'parted' gold gently hammered to a coherent spongy mass of about $\frac{1}{8}$ in. in diameter, and weighing 0·340 grain. This button was placed in an aqueous solution of cyanogen, and the containing vessel loosely covered. Upon again weighing this button, at intervals of twenty-four hours, he found there was generally a loss of about $\frac{1}{330}$ of its weight at every weighing —that, in fact, about $\frac{1}{1000}$ gr. of gold dissolved per diem.

"This does not appear to be a great loss: still, it is very much more than I should have anticipated, but, knowing that the most recent works on chemistry to hand in the colony decide that cyanogen in water alone does not decompose to substances solvent of gold, this scientist could not support my contention as he desired to do.

"It was this unsatisfactory state of the case that induced me to make further researches in the matter. Now, as you are aware, cyanogen is a substance that in the presence of even minute traces of ammonia or potash is decomposed to form alkaline cyanides which are solvent of gold, and when once this action starts it proceeds with ever-increasing rapidity. The atmosphere of a laboratory in full operation is frequently alkaline; the vessels used for receptacles in chemical work are capable of yielding alkaline matter to cyanide-solutions. For these reasons any experimental results obtained in a laboratory are likely to be misleading.

"It is evident, therefore, that any method which requires considerable periods of time, such as the gravimetric method does, is not well adapted for this kind of research; one is required that will speedily give reliable results. Eschewing, therefore, the use of even the hypothetical just balance as an abomination in this case, I adhered to my old method, which is that of testing by sight alone whether any loss of gold does occur by the action of free cyanogen. For this I merely replaced the gold-leaf of my former experiments by gold-paper, which is a Swedish filter-paper, in which gold has been chemically precipitated in a very finely-divided state. A sample of this test-paper is tabled here for exhibition, and the red tint of its gold is easily perceptible in this paper, $\frac{1}{10}$ in. square, by contrasting it with the same kind of paper that has not been so treated. A few short statements showing the extreme tenuity of the gold in this paper may be interesting.

"A square inch of the paper contains $\frac{1}{10000}$ gr., and $\frac{1}{10}$ in. square contains $\frac{1}{1000000}$ gr. of gold. Were the gold in this paper agglomerated to a film having a like area with that of the containing paper, that film would be only $\frac{1}{50000000}$ in. thick—that is, 250 of these would be the thickness of gold-leaf. In the paper itself (being, as it is, $\frac{1}{120}$ in. thick) this film (of the $\frac{1}{50000000}$ in.) is broken up to occupy a volume 400,000 times that which it occupies in the form of a film.*

"It follows, therefore, that the gold in this paper, volume for volume, only weighs half as much as hydrogen gas.

"Broken up in this manner in the test-paper before you, it is in very truth fine gold—in fact, gold divided almost to its ultimate atom (if, indeed, atoms do exist)—gold in the cloud form, as it were, and therefore in the best condition that I know of for my purpose. Provided with a test so delicate as this is, we get results in an hour that, using the gravimetrical test for loss, would require several days, and so we avoid those errors that are apt to creep in and vitiate our results when long periods of time are required for experiments of this nature.

"Placing then in a porcelain vessel a strong aqueous solution of cyanogen, along with a little of this gold test-paper, I closed the vessel down airtight, and on examining at periodic intervals I found that even after the expiration of six hours, corresponding to sixty-two days for gold-leaf, there was no visible diminution of the colour of that test-paper. After this, however, the tint gradually faded, until in thirty hours it had quite disappeared. Thirty hours to dissolve the millionth of a grain of gold so finely divided as this gold was, shows that if cyanogen itself does dissolve gold it is only at an extremely low rate—at such a rate that ordinary gold-leaf would require about one year to become entirely dissolved therein.

"Now, this result is a very different one to those that I am faced with both by Professor Black and Mr. Park; still, while it is clearly shown that for gold-milling the gas cyanogen as a direct solvent is useless, it does show that there is an infinitesimal dissolution of gold either by cyanogen or its derivatives, and in the interest of exact science the question has to be decided which of these it is.

"Now, the cyanogen I used, though very carefully prepared, had a slight acid reaction; it contained traces of ammonia, hydrocyanic and hydrochloric acids, and this even when to avoid

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* The method for accomplishing this is given in the "Transactions of the New Zealand Institute," Vol. xxv., p. 383.

producing them I used the protochloride in place of the bichloride of mercury; and I may further state that the solution of this cyanogen kept persistently acid even when it was three weeks old and much of the gas decomposed; and, what is more singular still, the solution was far more solvent of gold at that time than just after it had been made. It was therefore apparent to me that it is not *any* degree of acidity in a cyanogen-solution that does, as is now supposed, conserve this gas—it is not a mild acidity that is always effective for this purpose. So I increased the acidity of the cyanogen-solution by adding to it a few drops of hydrochloric acid, and tried another gold test-paper therein, when I was unable to detect, even after the lapse of seven days, the slightest change of tint had been produced upon that test-paper. Hydrochloric acid had not any retarding effect upon the dissolution of gold in weak solutions of bromine.

"For supplementary and confirmative evidence on this point I next passed cyanogen gas through a weak solution of nitrate of silver to wash out any ammonia, hydrocyanic and hydrochloric acids contained therein, and the purified gas was then allowed contact with the gold test-paper both as gas and as aqueous solution of it, when I got results altogether confirmatory of those obtained in the previous experiment—that is, no perceivable effect was produced on the test-papers by seven days' contact. Subsequently I extended the time of contact to three months, but even then failed to discern any loss or change upon the gold.

"The results of these various experiments, taken collectively, appear to be positively overwhelming in favour of the correctness of the assertion I made before the Society last month—that aqueous solutions of free cyanogen have not the least solvent power upon gold; consequently they support the old contention of mine cited in the former paper, and alluded to here—that cyanogen does not, as is now generally supposed, compare with the haloids, chlorine, bromine, and iodine chemically—that, in fact, except that it appears to be a monad with these and a dozen or so more of the elements, it has no chemical relations to any of them.

"I should inform you that the gold I used for the experiments here detailed, also for those for my former paper to the Society, was practically pure; at least, it only contained minute traces of copper. Argentiferous gold, of which class most or all our native gold is, would, of course, if possible, be still less amenable to solutions of cyanogen than the gold I used, and for the reason that argentic cyanide, if formed at all, would always remain as a product quite insoluble in such cyanogen-solutions.

"That cyanogen would have very little tendency to form by its decomposition solvents for gold as used upon quartz, &c., at the gold-mines appears to me absolutely certain, as both air and water are generally acidic, and all the reef-quartz I have tested also gives an acidic reaction."

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