IV.—CHEMISTRY.

Art. LII.—*On an Allotropic Form of Zinc and Cobalt Salts.*

By William Skey, Analyst to the Geological Survey Department.

[*Read before the Wellington Philosophical Society, 4th December*, 1880.]

In testing some ores for certain metals, I obtained reactions with both the ferro- and ferri-cyanide of potassium, which, according to our present knowledge, indicated the presence of lead and copper, although further analytical processes showed both metals to be altogether absent.

Upon taking a retrospect of my operations throughout, I found that the solution which I had prepared for my tests were either uniformly alkaline or, if acid, *had been at one time in an alkaline condition.* The idea therefore occurred to me that alkalies modify the basic portion of these salts—that is, their metallic oxides, and that the forms to which they are thus modified possess sufficient stability to enable them to withstand the disintegrating effect of acid; and upon testing the matter, facts were elicited which, as will be seen, conclusively prove that this idea is correct. Thus I found—

1. That a solution of any zinc-salt alkalized with a fixed alkali, even at a common temperature, and then acidified with nitric, sulphuric, hydrochloric, or acetic acid, gives, upon the addition thereto of potassic-ferri-cyanide, a yellow precipitate, which shortly turns white, or else a white precipitate at once, instead of the brownish one which all text-books on chemistry teach us to expect.

2. That the solution thus prepared with either hydrochloric or sulphuric acid afford the brownish precipitate with a ferri-cyanide after being boiled for a short time, or after being kept two or three weeks in the dark or in light.

3. That the solution with nitric acid, after boiling, gives a yellow precipitate with the ferri-cyanide.

4. That the solution with acetic acid, when boiled, still gives the white precipitate with this salt.

5. That the white precipitate produced in the above operations is the ferro-cyanide of zinc; not the ferri-cyanide, as would be anticipated.

6. That a solution of cobalt when boiled with ammonia in excess affords with potassic ferro-cyanide, a precipitate which is of a rich brown colour

instead of being yellowish green, as our present knowledge upon the matter would lead us to expect.

7. That if the ammoniacal solution prepared as above is acidified *before* the application of the ferro-cyanide thereto, the precipitate which then ensues is of the colour we should look for that is yellowish-green.

8. That as far as I have yet examined this dark precipitate, it appears to be the ferri-cyanide of cobalt.

It thus appears that both zinc and cobalt oxides may, when in contact with certain salts, give us reactions which are altogether different to those which we have hitherto been cognizant of; consequently these oxides are capable of, and actually do in these cases, assume an allotropic form.

The characteristic of these oxides when in this form, is that they change the quantivalence or degree of basicity of ferro- and ferri-cyanic acids, so that they are transformed the one into the other (the acids themselves being, as you may remember, isomeric). Thus accomplishing that for which an oxidation or de-oxidation process has hitherto been deemed necessary.

I should in this connection inform you that manganese oxide, in solution, when boiled with ammonia in excess refuse to afford a precipitate with potassic ferri-cyanide. We only get this by acidifying the solution.

It seems therefore that careful cognizance should be taken of these facts by anyone making a qualitative analysis for the metals referred to, and using for this either of the tests above-named. The urgent necessity there may be for "acidifying" and then "boiling" the solution in the one case and of acidifying in the other, is clearly shown. If these precautionary operations are not taken zinc may be mistaken for lead, and cobalt for copper.

Art. LIII—*On a Periodide and an Iodo-Carbonate of Lead.*

By William Skey, Analyst to the Geological Survey Department.

[*Read before the Wellington Philosophical Society, 4th December*, 1880.]

If to a solution of a lead-salt and borax iodine dissolved in an aqeous solution of potassic-iodide is added a crystaline precipitate copiously forms, and which differs from the only plumbic-iodide which we now know in being of a brick-red colour (instead of yellow), and in being far less soluble in water than it.

I have not had time to fully analyse this new compound, but it is undoubtedly the per-iodide of lead. I merely note it here and the manner of its production, as it forms the basis of the salt which I desire especially to bring before your notice.