XXXVIII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XII.—*The action of finely divided metals on solutions of Ferric Salts, and a rapid method for the titration of the latter.*

By DOUGLAS J. CARNEGIE, B.A., Demonstrator in Chemistry, Gonville and Caius College.

1. It is universally admitted in text-books, that of existing methods for converting ferric salts into ferrous salts prior to titration with potassium permanganate, the safest and best, though by far the slowest, method is to boil the acidified ferric solution with zinc in an inert atmosphere. The more rapid methods (excluding the stannous chloride method, which is not applicable if permanganate titration be employed) are hampered by the facts that in their employment it is difficult to determine the point of exact reduction, and excess of the reducing agent is as fatal as defect.

It seemed to me that the safest method might be so modified as at the same time to make it a rapid one, by increasing the effective surface of the zinc through the employment of zinc-dust in the place of the usual granulated zinc. While experimenting in this direction, I found that zinc-dust *instantly* reduces ferric to ferrous salt, *and this even in neutral solutions*. At the same time, if the solution is neutral, iron is precipitated partly as ferrous, partly as ferric hydroxide. In acid solutions, no iron is precipitated, but the reduction is less rapid the more free acid there is present. In every case zinc goes into solution.

2. Very rapid and accurate estimations of ferric solutions are realised by the following method :—

The bottom of a dry and narrow beaker is covered with zinc-dust, which has been sifted through fine muslin. A known volume of ferric solution, previously nearly neutralised by ammonia, is now delivered into the beaker, and shaken briskly with the zinc-dust. Finally, a known volume of dilute sulphuric acid is added, and the contents of the beaker are once more shaken. It is essential for rapid reduction that the above order be observed; the nearly neutral ferric solution must *first* be added to the zinc, *then* the acid. In order to withdraw for titration a definite volume of the ferrous solution free from particles of undissolved zinc, I make use of the "reversed filter," figured, in which *a* is a glass tube; *c*, muslin; *d*, filter-paper, held in position by an india-rubber ring, *b*. When this filter is

immersed in the beaker, the clear ferrous solution rises in it to the same level as the liquid in the beaker, and may then be withdrawn by

a pipette. The object of the muslin, *c*, is to prevent rupture of the filter-paper by the narrow end of the pipette. A titration which formerly demanded an hour or more can be executed by this method in three or four minutes with an accuracy deducible from a comparison of the following numbers selected at random from a series of titrations in which no special refinements were employed:—

25 c.c. of an acidulated ferric chloride solution reduced by iron-free magnesium required 15·3 c.c. of a decinormal permanganate solution.	25 c.c. of same solution reduced as above required 15·2 c.c. of same permanganate solution.

If one is to judge from Aldendorff's analysis of a typical specimen of zinc-dust (Fremy's *Encyclopédie*), this substance is usually free from iron. The specimen with which I worked contained only 0·08 per cent. of iron, or rather reducing substance equivalent to 0·08 per cent. iron.

3. As to the nature of the reaction between zinc-dust and neutral ferric chloride, I was at first inclined to ascribe the efficacy of the dust in this respect to the occluded hydrogen which, as Greville Williams has shown, is always contained therein. I was all the more strengthened in this view by experiments which showed that hydrogen occluded by palladium quickly reduces ferric chloride in solution. It is interesting in this connection, coupled with the experiments of Gladstone and Tribe, to note that hydrogen occluded by platinum has no action on ferric salts.

To put this hypothesis to the proof, I heated some of the zinc-dust in a Sprengel vacuum till all the hydrogen was given off; I then

tried the action of the volatilised zinc crystals on ferric chloride. Their reducing power was unimpaired; hence I had to seek for a new explanation.

It is well known that ferric chloride in aqueous solution is in a state of partial dissociation, as is roughly represented in the equation—

It might be urged that on adding zinc-dust to such a system, the hydrochloric acid would be removed from the sphere of action, with formation of zinc chloride and hydrogen, and that the nascent hydrogen would reduce the ferric chloride existing as such, while the soluble hydrated iron oxide might in virtue of this upsetting of the mobile equilibrium be simultaneously transformed into an insoluble hydrated form. According to this explanation it would follow that more iron hydroxide would be precipitated the higher the temperature at which reduction takes place, for the dissociation of ferric chloride increases with the temperature. And, indeed, experiment proved that about twice as much iron is precipitated as insoluble hydroxide when the reduction is effected at 100° as when it takes place at ordinary temperatures. But according to this explanation, one would predict the improbability of reduction if absolute alcohol were substituted for water as the medium of the change; whereas experiment shows that even under these conditions reduction readily takes place with great rise of temperature.

4. I am thus driven to the conclusion that the zinc acts merely as a dechlorinating agent, much as stannous chloride acts—

and that the precipitate of iron hydroxides which occurs in neutral solutions is partly due to the zinc oxide which is always present in the dust to the extent of about 50 per cent., partly to the zinc hydroxide formed during the reduction by the action of water on the finely divided zinc. Zinc-dust merely effects instantaneously the dechlorination which I found zinc-foil required several hours to effect.

The change represented above is an exothermic one; the heat of formation in aqueous solution of ZnCl_2 [112,840] is greater than the negative thermal change in the passage from the system $\text{Fe}_2\text{Cl}_6, \text{Aq}$ to the system $\text{Fe}_2\text{Cl}_4, \text{Aq}$ [55,540].

5. If this explanation of direct dechlorination be valid, it seemed probable that all those metals whose chlorides have a heat of formation in aqueous solution greater than 55,540 gram-units would, in the finely-divided state, reduce ferric solutions. I have made many experiments in this direction, and I find that the following metals in

a finely-divided state reduce ferric solutions with varying degrees of rapidity:—iron, mercury, silver, aluminium, and copper, as well as zinc. Sometimes the metals were employed in the shape of foil [aluminium, copper, silver], sometimes in the state of fine division in which they are precipitated from boiling alkaline solutions of their formates, or from hot solutions of any of their salts by means of zinc-dust, followed by repeated digestion with dilute acids suited to the occasion. In the cases of aluminium and silver, it was definitely proved that no precipitation of a salt of iron occurred. This, without doubt, would be the case with all metals M'' where $M'' + H_2O = M''O + H_2$ represents an endothermic change. Platinum and gold do not reduce ferric solutions. Now, with the exception of the last two named, the heats of formation of the chlorides of all the foregoing metals are greater than 55,540. Nevertheless, the *rapidity* of reduction by a metal does not appear to be a function of the energy which runs down in the formation of its chloride, thus $[Al^3, Cl^e, Aq] = 475,650$, whilst $[Zn, Cl^2, Aq] =$ only 112,840; yet zinc reduces instantaneously, whilst aluminium reduces the most slowly of all the metals experimented with. But experiment showed it to be undoubtedly the case that those metals reduce the quickest which are the most readily attacked at ordinary temperatures by dilute chlorine-water. It is of interest to note that galena in a finely-divided state also reduces ferric chloride solution, whereas antimony sulphide has not this power.

6. From the whole of my experiments, I conclude that zinc-dust is practically the best reducing agent for the purpose in hand. True it is that zinc-dust may sometimes contain a little iron, and that titration with permanganate cannot be conducted in an acid solution containing zinc, but that the latter must be first removed. But, in the first place, zinc-dust contains so little iron, and so slight a solution of zinc takes place before titration by my method, that any error arising from this source is negligible. However, in the attempt to elaborate a method which would preclude *any* uncertainty on this point, I prepared zinc-dust free from zinc oxide, as recommended by Sabatier, by means of repeated digestion with dilute acid, and also by what I found to be a more rapid method, viz., by digestion with solutions of ammonium chloride and ammonia, in both cases finally drying the product on porous tiles in a vacuum. This purified zinc was shaken up with a standard ferric chloride solution *without the addition of any acid*; the ferrous solution was filtered off, acidified, and titrated; but the iron was not fully accounted for in the filtrate, so rapidly does water attack the finely-divided zinc with formation of hydrogen and zinc hydroxide; the latter precipitating solutions of iron salts in contact with it. In fact, in solutions of

several metallic salts, MgCl_2 , $\text{Al}_2(\text{SO}_4)_3$, $\text{Co}(\text{NO}_3)_2$, MnSO_4 , &c., finely-divided zinc very soon causes a precipitate either of the hydroxides or of basic salts of the metals present.

In the second place, even when the reduction is effected by metals which can easily be obtained absolutely free from iron, which are not oxidised by water, and which do not evolve hydrogen with dilute acids, separation from the finely-divided metal *must* always precede titration; for even silver and aluminium are attacked in feebly acid solutions by permanganate.

7. Mitscherlich (*Zeit. anal. Chem.*, 2, 72) has stated that in the reduction of ferric solutions it is absolutely necessary that the whole of the zinc should be dissolved before titration; the reason adduced being that iron is precipitated on the surface of the zinc, and does not dissolve until the last traces of the zinc themselves disappear. If this statement be accurate, objection may be taken to my method detailed above; but I much doubt its accuracy. Experiment showed that the titre of an acidulated iron solution was independent of the time it had remained in contact with the zinc-dust. This might be explained in this special case by supposing the finely divided zinc to be practically enveloped in a protecting layer of hydrogen, but other experiments would lead me to believe that such a supposition is unnecessary. Examination of pieces of granulated zinc free from iron removed either before or after complete reduction of both hot and cold ferric solutions, always failed to give evidence of iron. Beebe's method of reducing ferric solutions (*Chem. News*, 53, 269) would also be untrustworthy were Mitscherlich's statement correct. Without doubt the zinc in all cases becomes coated with a black deposit, which as Rodwell, Vogel, and others have shown, contains *in addition to the iron present originally in the impure zinc itself*, zinc combined with lead, sulphur, and carbon.

8. After the work of which this paper is a short account was finished, I casually came across a reference in Fremy's *Encyclopédie* to a paper by Brown, on the reduction of ferric compounds by zinc. I have procured the paper referred to (*Iron*, 1878, 361), and find that Brown's method consists in reducing iron ores directly by fusion with *pulverised* zinc (Hobson and Sylvester had shown that at a temperature of 205° zinc becomes so brittle that it may be powdered in a mortar). Brown has also used this pulverised zinc to reduce ferric salts in acid solutions; but that his method is founded, as is the current one, on the reducing action of nascent hydrogen, and not on the direct reducing powers of the zinc, is obvious from the following quotation :—"There should be but a very small excess of sulphuric acid present, so that at the *end of an hour or two* only about half the zinc will be dissolved." Brown is also of opinion that the whole of the zinc must be dis-

solved before titration, but he does not state his grounds for that opinion.

I prepared some pulverised zinc, by Hobson and Sylvester's method, but with three different specimens of zinc. I uniformly found that they did not become brittle at 205° but at higher temperatures, and also that it was impossible thus to obtain anything approaching the fine division of zinc-dust. The pulverised zinc obtained reduced neutral ferric solutions but slowly.

In conclusion, I would express my thanks to Mr. Pattison Muir for the kindly suggestive interest he has taken in the work detailed.