STUDIES IN THE SPONTANEOUS OXIDATION OF ZINC AND THE NATURE OF "PYROPHORIC" ZINC.

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By "pyrophoric" zinc it is proposed to indicate zinc which undergoes spontaneous oxidation in air, with incandescence. It has often been observed that, when large masses of zinc dust have been used in reduction reactions, and then left in a damp state after separation from the other reagents, they become hot and oxidise, and may even be a source of fire: but no investigation of this phenomenon appears to have been recorded.

Zinc sponge prepared by electrolysis has been known for many years,[1] and it has been found that spongy zinc deposits, obtained under certain conditions, exhibit "pyrophoric" properties on drying. Zinc dust prepared by drying zinc sponge has been described,[2, 3] and the product used commercially: but although mention has been made of the tendency of such zinc dust to oxidise, when prepared under certain conditions, the matter does not appear to have undergone fuller investigation.

The following paper describes experiments which have been carried out in investigation of the spontaneous oxidation of zinc, and of the conditions for the zinc to become "pyrophoric" or to oxidise spontaneously with incandescence.

Experimental.

Experiments with Finely Divided Zinc, prepared Electrolytically.

Zinc was deposited in a spongy condition by the electrolysis of solutions of various zinc salts, under conditions of low metal ion content and high current density, as described by previous workers.[3] At the conclusion of the electrolysis, the non-adherent spongy deposit was removed from the cathode, by means of a glass rod, to a watch-glass.

The electrolytes considered comprised the following: zinc sulphate; zinc chloride (each in aqueous solution at concentrations between 0·5 per cent. and 5 per cent.); zinc nitrate; dilute solutions of zinc oxide in excess ammonium hydroxide solution; solutions of zinc hydroxide in sodium hydroxide formed by adding excess sodium hydroxide to zinc sulphate solutions; solutions of zinc hydroxide in ammonium hydroxide formed by adding excess ammonium hydroxide to zinc sulphate solutions; zinc sulphate solutions containing sodium sulphate; zinc sulphate solutions containing ammonium sulphate. Electrolysis was carried out in still

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[1] Mylius and Fromm, *Z. anorg. Chem.*, **9**, 164, 1895; Foerster and Gunther, *Z. Elektrochem.*, **5**, 20, 1898; **6**, 301, 1899; L. Glaser, *Z. Elektrochem.*, **7**, 368 and 381, 1900.

[2] *D.R.P.*, 276984, 3/5/13; Patentschrift 282234, 1/10/20; Chemische Fabrik Griesheim-Elektron.

[3] Morgan and Ralston, *Trans. Amer. Electrochem. Soc.*, **30**, 220, 1916.

solutions, using a vertical anode and cathode, of electrolytic rolled sheet zinc.

The deposits obtained as described above were in each case divided into three portions.

Excess electrolyte was removed from one portion of the deposit, by pressing it between filter papers; the slightly damp mass thus obtained was left exposed to the air on a watch glass for a few minutes, and was kept under observation. In all cases where the deposit had been obtained from solutions containing either sodium hydroxide or sodium salts likely to yield sodium hydroxide by electrolysis at the high current densities employed, in the absence of agitation, the damp mass was observed to get hot very rapidly, vigorous oxidation accompanied by incandescence finally occurring at the end of a few minutes.

The deposits obtained from the solutions of zinc salts free from sodium ions, and also from those containing ammonium ions, when examined under these conditions, did not exhibit this phenomenon of vigorous rapid oxidation, but oxidised only very slowly, with no appreciable rise in temperature.

The second portion of the deposit was transferred to a beaker, and was washed several times, by decantation, with distilled water, until free from adhering electrolyte; the surplus water was removed by pressing between filter paper and the damp mass exposed to the air on a watch-glass, as before. Under these conditions, it was found that in no case did spontaneous oxidation of the deposits occur, nor was any noticeable rise in temperature observed. Upon subsequently moistening with a few drops of 10 per cent. sodium hydroxide solution, vigorous and rapid oxidation, accompanied by incandescence, was observed in each case.

The remainder of the deposit was washed free from electrolyte by decantation with distilled water, followed by a final wash with alcohol and ether. It was then transferred to a Gooch crucible, sucked dry, and finally dried in an oven at 90° C. The nature of the deposit was found to be such as to permit the use of a Gooch crucible without the customary filter mat of asbestos or similar material, hence contamination of the deposit by foreign matter was avoided. The dried residue thus obtained was found to be a very fine powder, and, in the dry state, was very stable under ordinary atmospheric conditions; when heated on a crucible lid, it readily ignited, and burned with a brilliant bluish flame. On being moistened with a few drops of 10 per cent. sodium hydroxide solution, considerable heat was evolved, and vigorous oxidation, with incandescence, took place. Potassium hydroxide solution produced the same effect, but when sodium carbonate and potassium carbonate solutions were used, the phenomenon was not observed, nor did noticeable oxidation occur when ammonium hydroxide was used. Moistening with concentrated solutions of ammonium chloride produced no result, but it was found that when the deposit, moistened with ammonium chloride solution, was heated on a crucible lid, it did not ignite, but melted, to form small globules of metallic zinc. Dilute acids were then tried, but moistening the deposit with these resulted only in evolution of hydrogen.

A quantity of the deposit was next taken and excess water added to produce a suspension. The mixture was transferred to a test tube, and saturated with nitrogen gas. A few drops of 10 per cent. sodium hydroxide solution were added, and the mixture was evaporated to dryness in the test tube, warm dry nitrogen being passed through the tube until all moisture was expelled. No incandescence took place, even after the dried mass was transferred into the air and moistened with water. The sodium hydroxide originally added appeared to have been transformed into sodium zincate, which was, however, not peptised by the water added. On moistening the mass with a few drops of 10 per cent. sodium hydroxide solution, however, and removing excess moisture by means of filter paper, the mass became very hot, and oxidised rapidly.

Experiments with Zinc Dust.

To Render Zinc Dust " Pyrophoric."—About 50 grams of zinc dust, of the quality used for laboratory reductions, was moistened with 10 per cent. sodium hydroxide solution, and thoroughly mixed to form a stiff paste. Excess moisture was then removed by pressing between filter papers. The mass was then placed on a sheet of asbestos board, and exposed to the air of the laboratory. After about ten minutes steam began to rise rapidly, and after fifteen minutes the mass commenced to glow brightly, with vigorous oxidation, the incandescence spreading rapidly. The experiment was repeated, using different samples of zinc dust, and a positive result was obtained each time.

Experiments in Inert Atmosphere.—The experiments which were carried out in an inert atmosphere, as described above, were repeated, with commercial zinc dust in place of the electrolytic zinc. Similar results were obtained, but the reaction was not quite so vigorous as when the more finely divided electrolytic material was employed.

The Solubility of Zinc Oxide and Zinc Dust in 10 Per Cent. Aqueous Sodium Hydroxide Solution.—Five grams each of zinc oxide (British Drug Houses A.R. Quality) before and after ignition for 1 hour over a blast, and commercial zinc dust, were separately shaken vigorously with 50 c.c. of 10 per cent. sodium hydroxide solution, at the temperature of the laboratory. In each case the suspension was filtered, and zinc was determined in the filtrate by titration with potassium ferrocyanide in the usual manner. The amounts dissolved are shown in the table. When zinc dust was employed, no visible evolution of hydrogen was observed.

	Zinc content of filtrate (expressed as Zn).
Zinc oxide (before ignition)	0·445 grams.
Zinc oxide (after ignition)	0·425 ,,
Zinc Dust	0·125 ,,

The content of metallic zinc in the zinc dust was estimated in the usual manner, by measurement of the amount of hydrogen evolved from a weighed sample, when treated with dilute acid under standard conditions. The zinc dust was found to contain 94·7 per cent. metallic zinc, the remainder being composed of oxide, hydroxide, and basic carbonate of zinc.

It thus appears that treatment of zinc dust with 10 per cent. sodium hydroxide solution, in the cold, results in solution of the oxide, etc., present, and not of the metal: and that 100 c.c. of 10 per cent. sodium hydroxide solution at room temperature is capable of dissolving about 1 gram of zinc oxide. Special experiments showed that when an excess of sodium hydroxide solution is taken, the whole of the zinc oxide dissolves in the cold.

The Effect of Moistening Various Finely Divided Metals with 10 Per Cent Sodium Hydroxide Solution.

The metals cadmium, lead, and copper were obtained in a finely divided state by the employment of similar methods to those used for the electrolytic preparation of zinc dust; spongy deposits of the metals were obtained by electrolysing dilute solutions of suitable salts, the resulting sponge being washed with water, alcohol and ether successively, sucked dry in a Gooch crucible and finally dried at 85° C. The dried powder was moistened with 10 per cent. sodium hydroxide solution, excess moisture being removed by pressing between filter papers. In the case of copper and lead, no reaction was observed; cadmium so treated, however, grew hot and darkened somewhat in colour, but could not be made to glow.

It was not found possible to prepare finely divided aluminium by electrolysis: but when commercial aluminium powder, previously freed from oil by washing in benzene, was moistened with even very dilute sodium hydroxide solution, visible and rapid evolution of hydrogen occurred, but no incandescence.

Observations and Deductions.

(1) When finely divided zinc, either the ordinary zinc dust of commerce, or that prepared electrolytically, is moistened with 10 per cent. sodium or potassium hydroxide solution, in the presence of air or oxygen, the excess moisture being removed by expression, a reaction takes place, considerable heat is evolved, and the metal is oxidised to zinc oxide with incandescence.

(2) This phenomenon is not observed when the operation takes place in an inert atmosphere (nitrogen) or when solvents for zinc oxide and hydroxide other than potassium or sodium hydroxides are employed (dilute acids, ammonium hydroxide, ammonium chloride).

(3) The presence of a small amount of sodium or potassium hydroxide, moisture, and oxygen is essential for the reaction to take place.

(4) The mechanism of the reaction appears to be as follows: Sodium and potassium hydroxides dissolve the surface film of oxide and hydroxide from the metallic zinc forming the respective sodium and potassium zincates. The combined effects of the heat of this reaction and the removal of the protecting oxide film from the naturally reactive zinc cause further oxidation to take place: the resultant new oxide film is again removed by the caustic alkali, hence the reaction $Zn+O \rightarrow ZnO$ proceeds with acceleration, until the temperature is sufficient to cause incandescence.

As regards other solvents for zinc oxide, dilute acids also attack the metal, liberating hydrogen, which protects the metal from oxidation, while in the case of ammonia and its salts, gaseous ammonia is always present, again protecting the metal from oxidation by acting as an inert atmosphere.

With cadmium, the reaction takes place with much less vigour. This is probably due to the smaller affinity of cadmium for oxygen, and to the fact that cadmium oxide is not attacked by alkalis to the same extent as is zinc oxide, sodium cadmiate being formed only by solution of cadmium oxide in molten sodium hydroxide.[4] With aluminium, no effects such as those described were observed, in spite of its greater

[4] J. W. Mellor, *Theoretical and Inorganic Chemistry*, Vol. IV, p. 530.

affinity for oxygen. In this case the hydrogen liberated by the reaction of the sodium hydroxide solution with the metal most probably protects it from oxidation.

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