LXIX.—*On the Action of Oxides on Salts.* Part III.

By EDMUND J. MILLS, D.Sc., F.R.S., and C. W. MEANWELL.

27. IN pursuance of previous researches,* we directed our attention to the important cases considered below.

A. *Silica and Alkaline Sulphates.*

Sodic chloride, purified by precipitation with hydric chloride and washing with distilled water, was evaporated with hydric sulphate and ignited; towards the end of the ignition, some ammoniac carbonate was added. This treatment was repeated until the last traces of chlorine were expelled. The residue, which was persistently acid to litmus, was neutralised with caustic soda freshly prepared from sodium, ignited again, powdered and sifted. It was always ignited once more before use.

In order to prepare pure potassic sulphate, we submitted the chlorate to repeated crystallisation and ignited it, first alone, then after treatment with hydric sulphate, and, lastly, after exact neutralisation with pure potassic carbonate. This salt was always treated before use, in the same manner as the sodic sulphate. The silica was part of the stock referred to in previous memoirs.

Five grams of either of the sulphates were now mixed with 1 gram of silica, in a small platinum crucible, which was enclosed by another of the same material, and kept from actual contact with it by a few fibres of asbestos. To this arrangement heat was applied by means of a Fletcher's burner for periods of three hours; at first very gently, but afterwards very intensely, and with the aid of a draught. In another series of experiments the outer crucible was removed, and the highest temperature again resorted to. In the first series, the outer crucible was of glazed porcelain.

28. Throughout these experiments we invariably observed either that the mixture underwent no change of weight, or that, in the event of its doing so, the platinum was attacked, and a soluble alkaline sulphide produced. We accordingly infer that at all temperatures up to bright redness at least, pure silica is without action on potassic or sodic sulphate.

This remarkable result, to ourselves wholly unexpected, induced us to try the action of alumina upon the sodic sulphate.

* For Part II, see Journal (1879) i, p. 336.

B. Alumina and Sodid Sulphate.

29. The sodic sulphate was a portion of the sample used in the experiments with silica.

The alumina was prepared as follows:—Some potash alum, which gave no reaction with potassic ferrocyanide, and in which we failed to detect any other impurity having influence on our work, was dissolved in a large quantity of distilled water, and to this rather more ammonia was added than would be sufficient for complete precipitation. After washing by decantation until soluble sulphate was no longer present, the precipitate was dissolved in pure hydric chloride, again thrown down with ammonia, and washed as before. It was then dried at 100° and strongly ignited in a platinum crucible enclosed within an earthen one; the fuel used being paraffin still coke, which is free from sulphur and ash.

In carrying out the experiments, a constant weight of sulphate (1·5 gram) was mixed in a small platinum crucible, with varied weights of one sample of alumina, thus prepared. The crucible was placed in a platinum saucer, from which it was separated by a few fibres of asbestos; the object of the saucer being to prevent as far as possible the intrusion into the crucible of reducing gases. Beneath the saucer, at a suitable distance, was a specially constructed blow-pipe. Coal-gas was supplied to this instrument through a cone regulator, and air from an injector driven by a water-supply at constant pressure through an elastic bag. Every effort was thus made to maintain constant conditions. The temperature was that of light redness, and the duration of incandescence six hours.

30. We now always encountered, without the formation of sulphide, an appreciable amount of chemical change, this being indicated both by the loss of weight and the alkaline reaction of the mixture. Our results are comprised in the following table:—

TABLE X.

Gram of alumina.	<i>x.</i>	Gram of sulph. oxide expelled.	<i>e.</i>	Remaining sulphate.	<i>y_r.</i>	<i>a.</i>
0·25	·0024529	·1649	·0020625	1·2071	·0085001	8·7190
0·50	·0049056	·1257	·0015722	1·2767	·0089904	4·1201
1·00	·0098115	·1201	·0015022	1·2867	·0090604	2·7354
1·50	·014718	·0762	·00095310	1·3647	·0096095	1·4194
2·00	·019623	·0155	·00019387	1·4725	·0103688	0·28051
2·50	·024529	·0156	·00019512	1·4723	·0103675	0·26280

In order to convert grams into chemical units, we have used $\text{Al}_2\text{O}_3 = 101.92$, $\text{Na}_2\text{SO}_4 = 142.01$, and $\text{SO}_3 = 79.95$ as divisors.

31. If e represent chemical effect, measured by units of sulphuric anhydride, expelled, x the alumina taken, y the sulphate employed, y_r the residual sulphate (all similarly measured), and α be the factor of condition, then, in accordance with the usual formula—

$$e = \frac{\alpha xy}{x + y_r}.$$

We have calculated the values of α , which are not constant, and have given a list of them in the table. In the accompanying figure, we have graphically represented them as a function of x .

In this figure it at once becomes apparent that the action of alumina is most energetic when a comparatively small mass of the oxide is used. There are, moreover, three distinct stages in the action. In the first, the value of α clearly takes the form $(A - \mu B)$, B being the number of grams of alumina; but we are unable to assign the values of A and μ . In the second, α is also linear, and proves to have the value—

$$\alpha = 4.1200 - 2.67 (B - 0.5).$$

In the third stage, α is sensibly constant and equal to 0.27166.

The maximum value of x in the second stage is obtained by putting $\alpha = 1 = 4.1200 - 2.67 (B - 0.5)$, whence $B = 1.67$ gram. The figure in fact shows that this point must lie somewhat beyond 1.50 gram.

At first, then, the action of alumina upon sodic sulphate is such as to give rise to a polysodic aluminate or polysodic aluminates of very high order; this kind of action diminishing until $3\text{Al}_2\text{O}_3$ approximately expel SO_3 . In like manner the second stage terminates nearly, when $100\text{Al}_2\text{O}_3$ expel SO_3 ; and in the third stage a still greater effort is required. It is also evident that beyond about $126\text{Al}_2\text{O}_3$, the further addition of alumina produces no useful effect.

32. In Part II, where the action of ferric oxide on potassic carbonate was described, it was pointed out that there are three stages also in that action. Of these the first exactly resembles the first stage of the action of alumina on sodic sulphate; in the second, however, α is constant, while in the present case it diminishes linearly with the weight of oxide; in the third stage, it is in each case constant. On the other hand, when alumina acts on potassic carbonate, the factor of chemical effect undergoes linear increase with the mass of the oxide. The behaviour of an oxide with a salt is thus demonstrated to depend both on the oxide and the salt; so that no general inference can be drawn, in the comparison of a pair of oxides, from their deportment with a single salt.