

On Causes which determine the Formation of Amorphous Sulphur. By Professor Alexander Smith, B.Sc., Ph.D.

(Read July 21, 1902.)

While the investigation of the freezing-point of sulphur, described in these *Proceedings* (vol. xxiv. p. 299), was in progress, some experiments on the maximum quantities of amorphous sulphur, formed at various temperatures from 130° to 448° , were being made. The results showed remarkable irregularities. It was also found that the addition of foreign bodies, which are for the most part without chemical action on sulphur, greatly magnified these disturbances, and led to the discovery of their source. The following is a condensed statement of the principal facts.

When sulphur, purified by recrystallisation from carbon disulphide, was heated for one and a half to two hours at 448° in an open tube, varying proportions of amorphous sulphur seemed to be formed. The tube was transferred rapidly to, and broken into a vessel of ice, so that no opportunity might be given for reversion to the soluble form. The variations, which ranged from 32 per cent. down to 10 per cent. of amorphous sulphur, appeared to depend in part upon the length of time intervening between the purification of a large lot and the use of a particular portion of it. Portions taken early gave, as a rule, less of the amorphous body.

Heating for a longer time than two hours seemed also to reduce the proportion. Part of a specimen gave, after two hours' heating, 31.8 per cent., while another part of the same specimen, after eight hours', gave only 2.6 per cent.

It seemed evident that sulphuric acid or sulphur dioxide, produced by the action of the air in variable but minute amount, was responsible for the differences. The more prolonged heating eliminated most of the sulphur dioxide.

Passing certain gases through the sulphur during the heating increased the yield of amorphous sulphur. Thus, dry air gave 34.5 per cent., dry sulphur dioxide 36.5 per cent., dry hydrogen chloride

38.5 per cent. Under these conditions, long continuance of the treatment did not cause any reduction in the yield. Addition of powdered glacial phosphoric acid had the same effect as these gases (37.3 per cent.).

On the other hand, certain other gases, when used from the beginning of the heating, seemed to prevent the formation of the amorphous sulphur. Nitrogen gave 4.7 per cent., carbon dioxide 4.5 per cent., hydrogen sulphide 0.8 per cent., ammonia 0 per cent. These gases also reduced the quantity to the same minima when, by use of air or sulphur dioxide, the larger amounts had already been formed. This remarkable fact was confirmed by repeated trial. In the case of phosphoric acid, however, treatment with carbon dioxide did not reduce the proportion, presumably because this acid is non-volatile. Conversely, air and sulphur dioxide restored the amorphous sulphur, which had already been destroyed by treatment with carbon dioxide. A little powdered potassium hydroxide had the same effect as the second class of gases.

From these observations it may be inferred that absolutely pure sulphur would altogether lack the power to form amorphous sulphur.

This work is being continued. The obviously cognate question of the supposed rule that sulphur precipitated from acid solutions is amorphous, and from neutral solutions is crystalline, will be examined. It is not advisable to offer any theory until further work has been done.

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