THE FLUORESCING SODIUM URANYL PHOSPHATE.

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IN an early article¹ by G. G. Stokes on the ultra-violet spark spectra of the metals mention is made of a powerfully fluorescent screen made from the phosphate of uranium. Since the ordinary phosphate is only slightly fluorescent it seemed of interest to prepare the phosphate employed by Stokes and to determine the nature of its fluorescence. The Stokes method of preparation is to treat the ordinary phosphate with a solution of phosphoric acid and sodium or ammonium phosphate. The non-fluorescent salt, which is a yellow amorphous insoluble powder, is changed into the fluorescent double salt as the mass dries out. The addition of sufficient of the reagents to produce strong fluorescence does not produce any visible change in the uranyl phosphate except to make the color lighter and more greenish due to the fluorescence.

The chemical problem is to find the composition of the fluorescent double salt. Although Stokes used the acid double phosphate as indicated above, the following specimens were prepared to determine whether the "neutral" sodium uranyl double salt was fluorescent. For specimen No. 1 a mixture was made consisting of uranyl phosphate and sodium phosphate in the ratio of four molecular weights of $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ to one molecular weight of HNa_2PO_4 . The proportions for specimen No. 2 were two to one and for No. 3 were one to one. It will be seen by referring to Fig. 1 that these three specimens, when cooled to -186°C ., yielded precisely similar spectra on excitation with the carbon arc.

To ascertain the rôle played by phosphoric acid, several specimens were prepared by mixing increasing amounts of phosphoric acid with sodium uranyl phosphate. Specimen No. 4 was made by adding one molecule of phosphoric acid to two molecules of uranyl phosphate and one molecule of sodium phosphate, giving the composition $\text{H}_3\text{NaUO}_2(\text{PO}_4)_2$. This was a powder resembling specimen No. 2. The spectrum of this specimen consists partly of lines occupying approximately the same positions as in the spectrum of specimen No. 1, 2 and 3; and partly of a broad band series. Specimen No. 5 was made by adding one molecule of

¹ Phil. Trans. Roy. Soc. Lond., 152, 599-617 (1862); Chem. News, 7, 147-149, (1863); Abstract Proc. Roy. Soc., 12, 166 (1862); Jahrsbericht Fortsch. Chem., 106 (1863).

phosphoric acid to one molecule of uranyl phosphate and two molecules of sodium phosphate. When dried this contained much free sodium phosphate. Specimen No. 6 was made by adding two molecules of phosphoric acid to one molecule of uranyl phosphate and one molecule of sodium phosphate. This specimen did not dry but remained syrupy at room temperature and appeared to be vitreous at -180° C. The spectrum consisted entirely of broad bands. Specimen No. 7 was made

Fig. 1.

by dissolving some uranyl phosphate in syrupy phosphoric acid. This gave a great excess of acid and no sodium. The specimen presented a clear glassy appearance even at 20° C. The spectrum, like that of No. 6, consisted of one series of broad bands.

In examining the spectra the specimens were mounted in glass, immersed in liquid air, and excited by the carbon arc. A wave-length spectrometer was used in locating the bands. In Fig. 1 the bands are plotted to a frequency scale, *i. e.*, $(1/\lambda) \times 10^3$ is one frequency unit when μ is the unit of wave-length. Thus the abscissa 1,800 corresponds to $\lambda = 5,555$ A. U.

It will be seen that the spectra of specimens 1, 2 and 3 consist of recurring groups of bands. Careful measurements show that the homologous members of these groups form constant interval series. The interval of any one of the line series has a value lying between 80 and 81 units, which is the shortest interval yet observed in the study of the fluorescence spectra of the uranyl salts. The broad bands of Specimens 4 and 5 form series with a constant interval of 82.5 units. Evidently the increase in the proportion of phosphoric acid tends to suppress the strongest line series and merge the dimmer series into broad bands. With the increasing predominance of the broad bands,—caused by the increasingly larger proportion of acid present,—there is a simultaneous increase in interval from 82.5 units to 85.1 units for Specimen No. 6, and 87.0 units for specimen No. 7.

A comparison of the spectra of uranyl nitrate in nitric acid solutions¹ with the spectra of sodium uranyl phosphate in phosphoric acid solutions shows a striking resemblance in the matter of resolution when the proportion of acid is increased. In each of these solutions the acid acts as the solvent even at low temperatures, and this fact may well be the cause of the vitreous appearance. If the acid were crystalline at low temperatures presumably the broad bands would not appear. Evidence gained from the study of several other uranyl salts, having different crystalline forms or no crystalline form, leads us to believe that a crystalline form is a necessity where a resolved spectrum is to be obtained.

Since Stokes used an acid powder to make his screen, he could not have used specimens Nos. 1, 2 or 3, since they are neutral. Again, since he used a powder he could not have used specimens No. 6 or No. 7 because they are semi-solid solutions; hence he must have employed No. 4 or No. 5. Either of these specimens is extremely brilliant; the fluorescence being more intense in fact than that of the average uranyl salt; it appears therefore that Stokes employed, for the purpose of making his fluorescence screen, one of the best substances he could have obtained.

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December 2, 1915.

¹ H. L. Howes, *Phys. Rev.*, Vol. VI., No. 3, pp. 202–203, Sept., 1915.