

Letters to the Editor

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The Constitution of Nitrated Cellulose.

IN a recent publication (*Zeit. für physikal. Chem.*, **130**, 616; 1927), Herzog and von Náray-Szabó gave an account of the X-ray examination of ramie fibre nitrated in various ways, and concluded that for any nitrocellulose containing from 4.41 to 13.31 per cent of nitrogen the diffraction spots on the 'fibre diagrams' were produced mainly by the substance cellulose trinitrate, two spots from unchanged cellulose occasionally persisting, and that all nitrocelluloses were therefore principally mixtures of cellulose trinitrate and cellulose.

Two rather diffuse diagrams were given, one of which (for 12.99 per cent nitrogen) seems to show evidence of imperfect nitration. In the later paper by von Náray-Szabó and von Susich (*Zeit. für physikal. Chem.*, **134**, 264; 1928), this diagram, with the unit cell proposed for cellulose, is withdrawn and replaced by a new diagram in which the layer lines are closer together, but the claim is still made that the nitrocellulose diagram is always compounded of those of cellulose and its trinitrate. This theory is open to serious objections from many aspects of the chemistry and technology of nitrocellulose. Many of these have been presented by Brunswig in two interesting articles (*Zeit. für ges. Schiess- und Sprengstoffwesen*, **23**, 337 and 384; 1928).

In an investigation which has been carried on in these laboratories for more than a year, a complete range of samples of nitroramie nitrated in widely different mixed acids, together with their denitration products, has been examined by X-ray diffraction methods. The fibre diagrams of the nitrates are frequently lacking in definition and are difficult to interpret, but whenever measurements have been possible they have been found to afford only the slightest basis for Herzog's theory.

The nitration of cellulose in mixed acid is complicated by a loss of fibre structure which occurs with all mixed acids, for example, with those containing from about 30 per cent to 60 per cent of nitric acid, whenever the nitrogen content of the nitrocellulose reaches about 7.5 per cent. It continues until 10.5 per cent of nitrogen is exceeded. If the content of sulphuric acid is increased and the ratio H_2SO_4/H_2O has a certain value (about 1.7 to 1), the disintegration of the fibre structure may be greatly accentuated. It is therefore convenient to consider three groups.

The diagram of a nitroramie of less than 7.5 per cent of nitrogen shows the same spacings as that of its denitrated product but different relative intensities and is much weaker. The spacings remain constant with increasing degree of nitration. This type of diagram (*B*) may be contrasted with that of unaltered cellulose (*A*). It resembles that of fully mercerised cellulose, but excels it in sharpness and the intensities of the two are different. The diffractions characteristic of the trinitrate do not appear, although from a mixture of unnitrated ramie with comparatively little of the highly nitrated fibre it is quite easy to produce them.

In the second group (7.5 to 10.5 per cent) the nitrated material loses its fibre structure more or less, diffuse diffraction rings appear, but the denitrated product is still of type *B* and gives sharp lines.

As to the third and technically important class, sharper diagrams of which have been produced by

von Náray-Szabó (*loc. cit.*) and by Andress (*Berichte*, **61**, 603; 1928), nitration in acids of technical composition nearly always results in diffuse spots, and the most important factor in securing definition seems to be a high content of nitric acid, say 50 per cent of the nitration mixture. In the cases of both cotton and ramie, as the nitrogen content falls to about 11 per cent, certain spots from planes parallel to the fibre axis are altered in spacing through small ranges in which confusion with diffractions of remanent cellulose of either type is not possible. In some instances the diagrams show an equatorial spot which falls in the same position as the *A4* spot of cellulose, but its intensity is quite disproportionate to the possible cellulose content and its position changes on denitration. The denitration product from highly nitrated ramie is practically indistinguishable from that of pure cellulose (type *A*), but as the nitrogen content decreases to about 12 per cent, type *A* passes into type *B* more or less gradually, according to other conditions holding in the nitration.

It appears, therefore, that by the action of the mixed acid the cellulose residue is converted into type *B* for all but the highest degrees of nitration, and that the lines obtained in the range 10-12 per cent of nitrogen do not coincide with those given by the trinitrate or by cellulose of either type. Even if spots of type *B* were present it would not be certain, in view of the diffractions given by the less nitrated products, that they originated from unnitrated cellulose.

To account for these facts in a systematic way further data will be required, and it will probably be of great use to determine accurately the densities of certain nitrocelluloses and their denitration products and so obtain some indication of the closeness with which their structures are packed.

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Ardeer, Jan. 7.

The Distribution in Space of the Sunlit Aurora Rays.

SOME time ago (*NATURE*, Sept. 3, 1927) I discussed the position of the sunlit aurora rays with my colleague, Prof. Krogness, and he made the suggestion that the great heights of these rays might perhaps be explained by assuming that the sun's radiation pressure pushes away the upper atmosphere like a small tail of a comet, and if the corpuscular rays hit this tail they produce aurora at unusual heights.

As this idea seemed very promising, I again took up the calculations of the aurora rays in the period from 1911 to 1922, mentioned in my letter to *NATURE* of Sept. 3, 1927. The only two occasions when sunlit aurora rays were photographed simultaneously from two stations in order to obtain their altitude were during the nights of Mar. 22-23, 1920, and May 13-14, 1921.

In Fig. 1 we see the position of all the rays from these two nights compared with the position of the earth's shadow. The figure represents a vertical section of the earth, and the tangent to the earth's surface is the boundary between the sunlit and dark atmosphere. For each point of an aurora ray the position in the vertical plane through the centre of the earth and the sun is marked by a small circle for aurora of Mar. 22-23, and by a black dot for aurora of May 13-14. On each aurora ray two points are calculated and combined with a straight line representing the ray. This line is continued beyond the points as far as the photographs indicate. If the ray passes out of the photographic field it is marked by an arrow, and if the foot or summit can be seen on the photograph no arrow is given. Some rays form a