Uranyl nitrate, uranyl carbonate, and alkali solutions of U(VI) have been examined at 77°K at $4.2 \times 10^{-7}$ to $8.4 \times 10^{-4}$ M. The state of U(VI) in these solutions is determined.

U(VI) in aqueous solution shows a complicated behavior due to hydrolysis and formation of complexes. The hydrolysis of U(VI) has been examined several times [1-6] by cryoscopic, acid-base, electrochemical, polarographic, spectrophotometric, and fluorescence methods [5, 6]. The ionic state of U(VI) is known from these for concentrations above 1.5 mM [6]. Kraus [3] notes that the state of U(VI) in dilute solution is of interest in relation to the possible formation of products such as $\text{UO}_2\text{OH}^+$. The problem is [7] also of interest in relation to the fluorescence yield. We have examined the fluorescence at $4.2 \times 10^{-7}$ to $8.4 \times 10^{-4}$ M at low temperatures, which provided a sensitivity about 8 times that found at room temperature. This range was chosen because the fluorescence of U(VI) above the upper limit is complicated by concentration quenching [8], while the lower limit was set by the sensitivity of the apparatus.

Experimental. Pure solutions of uranyl nitrate, uranyl carbonate, and uranium in alkali were used. The initial solution was prepared by dissolving 0.4 g of uranium turnings (99.7%) in hot nitric acid. The solution was evaporated to dryness, and the residue was taken up in water to a concentration of 0.4 g/liter, this stock solution being diluted to $8.4 \times 10^{-4}$, $2.1 \times 10^{-5}$, $4.2 \times 10^{-6}$, $2.1 \times 10^{-6}$, $4.2 \times 10^{-7}$ M. The carbonate solutions were prepared by the addition of a solution of sodium carbonate (AR grade), and the alkali solutions by the addition of NaOH (AR grade).

The solutions were used in 2 ml lots in quartz tubes ($d = 1$ cm, $h = 4$ cm) in a Dewar filled with liquid nitrogen, the measurements being made with the tube in a fixed position. The light source was a DRSh-250 lamp with UFS-1 filter, the spectra being recorded with an FEP-1 photoelectric attachment to an ISP-51 spectrograph (FEU-17A phototube).

Figure 1 shows spectra at $-190^\circ$ C, the spectra being corrected for the spectral sensitivity of the apparatus. The pH were measured with an LP-5 meter. At 2.1 µM there are four not very prominent bands. The maxima shift to longer wavelengths and alter somewhat in relative strength as the concentration is raised. There is little change in the range $4.2 \times 10^{-5}$ to $4.2 \times 10^{-4}$ M (Fig. 2 shows the spectrum for 0.84 mM).

Published data [6, 9] indicate that $\text{UO}_2\text{NO}_3^+$ and $\text{UC}_2(\text{NO}_3)_2$ would not be formed in the range $4.2 \times 10^{-7}$ to $8.4 \times 10^{-4}$ M. Komar and Tret'yak [9] concluded that uranyl-nitrate complexes either do not occur at 4 mM or are present in amounts too small to be determined from the optical density. At room temperature, fluorescence bands due to $\text{UC}_2\text{NO}_3^+$ are apparent above 0.8 M; they also occur at 0.08 M in 30% HNO$_3$. Bands due to $\text{UC}_2(\text{NO}_3)_2$ occur in 75% HNO$_3$ [6].

The present effects must therefore relate solely to formation of hydrolysis products from U(VI). The composition of these was deduced by using a fixed U(VI) concentration with increasing NaOH concentrations, the solutions being allowed to stand for 24 hr after the addition of alkali (Fig. 2). The results with U(VI) : NaOH of 4 : 1 and 2 : 1 were as for the solution free from NaOH, but at higher NaOH concentrations there was a shift to longer wavelengths, with increase...
in the intensity of the long-wave bands. The effects most pronounced for \( \text{U(VI)} : \text{NaOH} = 1 : 2 \), which were due to formation of \( \text{UO}_2(\text{OH})_2 \), while at 1 : 5 there was a marked fall in intensity, which was due to onset of formation of solid phase. At 1 : 50 there was an orange precipitate having an orange fluorescence with peaks at 562 and 577 nm. The composition of the precipitate, as judged from the fluorescence spectrum, did not vary with NaOH content within the limits used (up to 1 : 200).

The powder pattern of the precipitate after washing to remove excess NaOH (see table) indicated that the material had a crystalline structure, since there were 9 broad lines. The sodium content of the precipitate was determined by flame photometry, while the uranium content was determined by fluorescence, the result being \( \text{Na : U(VI)} = 1 : 2 \), which corresponds to the composition \( \text{Na}_2\text{U}_4\text{O}_{12} \) [11].

Solutions with \( \text{U(VI)} : \text{NaOH} \) of 1 : 1 to 1 : 6 had a characteristic green fluorescence at room temperature, which was absent for all the other solutions. This spectrum consisted of two strongly overlapping bands with peaks at 510 and 529 nm. Curve 4 of Fig. 2 shows this solution at \(-190^\circ \text{C}\); the spectrum is then shifted to longer wavelengths.

The complex \( [\text{UO}_2(\text{CO}_3)_{3}]^{4-} \) was chosen as being [12] stable in solutions with ratios of \( \text{CO}_3^{2-} \) to \( \text{UO}_2^{2+} \) in excess of 3 and being negligibly hydrolyzed when the ratio is there. Figure 3 shows the fluorescence spectrum of this. A \( \text{U(VI)} : \text{Na}_2\text{CO}_3 \) ratio of 1 : 1 gave a spectrum as for solutions containing NaOH (Fig. 2); this solution also fluoresced at room temperature. The general form of the spectrum was unaltered by raising the \( \text{Na}_2\text{CO}_3 \) concentration to 0.5 M. The general position of the spectrum of this complex lies at shorter wavelengths than that from 0.84 mM uranyl nitrate. In addition, solutions 0.5 M in \( \text{Na}_2\text{CO}_3 \) and 2.1 \( \mu \text{M} \) to 0.24 mM in \( \text{U(VI)} \) gave spectra independent of the uranium concentration.

The carbonate ion forms the complex with \( \text{U(VI)} \) even if the latter is partly hydrolyzed; also, curve 2 of Fig. 3 (ratio of \( \text{U(VI)} \) to \( \text{Na}_2\text{CO}_3 \) of 1 : 1) and Fig. 2 (NaOH present) are analogous, so the tri-carbonate complex is probably formed via the hydrolyzed state of \( \text{U(VI)} \).

**Discussion.** The room-temperature fluorescence of \( \text{U(VI)} \) in dilute solution is due to \( \text{UO}_2(\text{OH})_2 \): at \(-190^\circ \text{C}\) \( \text{U(VI)} \) fluoresces whether hydrolyzed or not. The spectrum shifts to longer wavelengths as the \( \text{OH} \) concentration increases, and the shortwave bands become much weaker (Fig. 2). The separation of the shortwave peaks in either state (hydrolyzed or not) is \( \sim 2800 \text{ cm}^{-1} \) (curve 1 of Fig. 3 and curve 4 of Fig. 2). The spectra of dilute hydrolyzed solutions cannot be considered as arising by superposition of bands corresponding to two different states (Fig. 2). The changes in the bands give evidence on the state of \( \text{U(VI)} \) and the mechanism of complexing.