

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

A NEW HYDRATE OF URANYL NITRATE<sup>1</sup>

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Received April 3, 1922

It is a well-known fact that crystals of uranyl nitrate fluoresce strongly when cooled to liquid air temperatures. Nichols and Merritt<sup>2</sup> have mapped out the fluorescence and absorption spectra of the hexa-, tri- and dihydrates of uranyl nitrate in order to try to discover the influence of water of crystallization upon the position of the lines and bands of these spectra. They conclude that the fluorescence spectrum is made up of series in which the frequency intervals between bands are constant and the same for all of the series. The interval increases slightly but unmistakably as the amount of water of crystallization decreases. For the hexahydrate the interval is 86.0, for the trihydrate 86.8, and for the dihydrate 88.1.

In earlier work by the same authors<sup>3</sup> the fluorescence spectra of the frozen water solutions of uranyl nitrate were studied. The work was

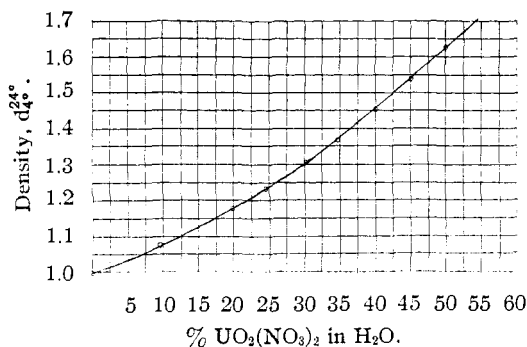


Fig. 1.

continued under their direction by Howes<sup>4</sup> who described 5 distinct fluorescence spectra as being obtained by cooling solutions of various concentrations, with varying speeds to the temperature of liquid air.

In order to explain this anomalous observation, the writer made up a series of solutions of uranyl nitrate of various concentrations, to be able to follow the variations in the spectra systematically. For a part of the work it became necessary to know accurately the densities of the various solutions, which were determined by means of a pycnometer, the temperature being maintained at 24° by means of a thermostat. The results are given in Fig. 1, which is of more than passing interest due to its strong curvature. The values, as read from the curve, are as follows.

%	d.	%	d.
5	1.035	30	1.302
10	1.076	35	1.376
15	1.126	40	1.457
20	1.178	45	1.540
25	1.236	50	1.626

<sup>1</sup> Germann, "Thermal Analysis at Low Temperatures," *Phys. Rev.*, **19**, 1922.

<sup>2</sup> Nichols and Merritt, *ibid.*, **9**, 113 (1917).

<sup>3</sup> Nichols and Merritt, *ibid.*, **3**, 457 (1914).

<sup>4</sup> Howes, *ibid.*, **6**, 192 (1915).

For each concentration, cooling curves of the type shown in Fig. 2 were made so that an average height EF could be determined. Temperatures were measured by means of a galvanometer, thermocouple and high resistance. The apparatus was adjusted so that galvanometer readings were directly proportional to temperatures. Consequently they were used directly, and transformed only in the event of determining the temperatures of transformation. Readings were taken every 10 seconds while the solution was immersed in a freezing mixture of carbon dioxide and ether. Slow cooling was obtained by placing the test-tube containing the solution within 2 other test-tubes, so that there were 2 air chambers separating the freezing mixture and the solution.

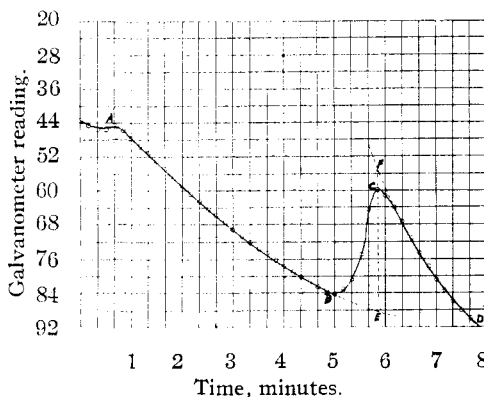


Fig. 2.

Fig. 3 is the result of plotting the average values of the elevation EF for each concentration, against the percentage. It is evident that pure water, or 0% would show a zero value of EF, so that the origin would be a point on the curve. Experiment also showed that a transparent crystal of uranyl nitrate hexahydrate, which contains 78.48% of anhydrous

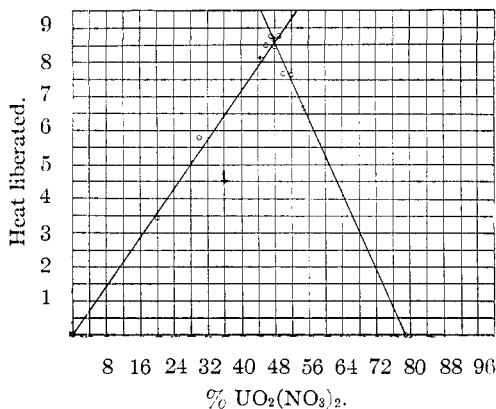


Fig. 3.

uranyl nitrate, remains unchanged when cooled to  $-80^{\circ}$ . Hence, there would be a point on the X-axis at the point 78.48%. The other values are experimental, each point representing from two to ten observations. The curves are weighted least-square lines. The intersection is at 48%.

Fig. 4 shows a sample of the heating curve after transformation had taken place. The curve from A to B is the normal heating curve, followed by CD. A short distance above D fusion takes place. In this case FE is a measure of the heat absorbed. Making a series of runs on each of the various concentrations and again plotting average values of FE against

the percentage of anhydrous uranyl nitrate we obtain the curve in Fig. 5. Here again 0% and 78.48% would be points. The intersection is

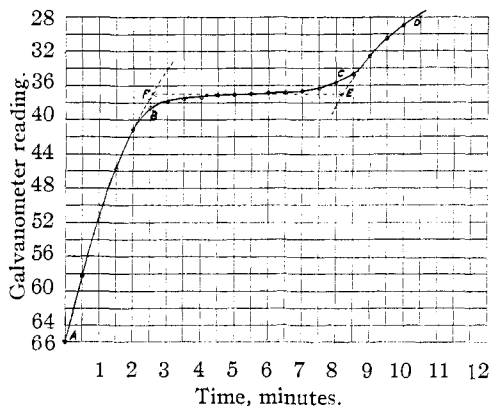


Fig. 4.

at 47.50%. Taking account of the number of observations involved in the formation of Curves III and V, as well as the accuracy with which they were determined, it seemed logical to assign equal weights to the two curves and consequently take the average point of intersection. This value  $47.75 \pm 0.17$ , agrees well with 47.69%, which is the theoretical percentage of anhydrous uranyl nitrate contained in a compound of the formula  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ . The compound forms spontaneously at about  $-35^\circ$  and decomposes at about  $-20^\circ$ . Its detection and analysis by the usual chemical procedure would, therefore, be impossible.

We have evidence, therefore, on the basis of both the heating and cooling curves of the existence of the above hydrate, which may be called uranyl nitrate icositetrahydrate. We also have an explanation of the anomalous group of spectra observed by Howes. As a matter of fact with rapid cooling, the part BCD of Fig. 2 never appeared and in such cases the part BC of Fig. 4 is also absent. Enclosing the sample to be cooled in a heavy-walled tube also prevented

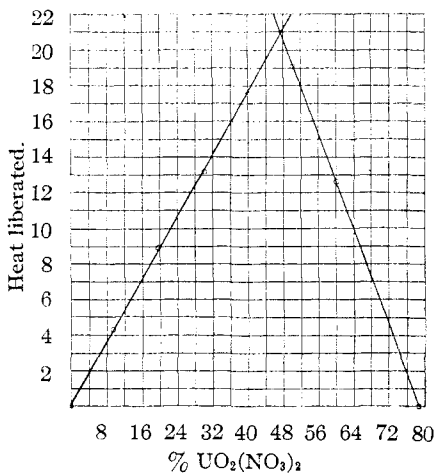


Fig. 5.

the change from taking place, as the transformation was always accompanied by a considerable volume change; the transformation was, therefore, always allowed to take place in the lower half of a spherical container. An analysis based on this volume change is at present in progress. The numerous spectra observed can be explained by assuming the pure spectrum of the hexahydrate, of the icositetrahydrate and of various mixtures of the two depending on the concentration, rate of cooling, etc.

### Summary

1. A curve showing the variation of density with concentration of uranyl nitrate has been constructed for 24°.
2. Uranyl nitrate icositetrahydrate has been shown to be capable of existing below -20°, forming spontaneously at about -35°.
3. Uranyl nitrate icositetrahydrate has been shown to exist by methods of thermal analysis: in one case by a cooling curve which might be compared to a method of synthesis, and in the other case by a heating curve, which might be regarded as a method of analysis.
4. The existence of the 5 distinct fluorescence spectra due to a single compound as published by Howes has been disproved and an explanation of the cause offered.
5. A new hydrate has been added to the uranyl nitrate series which will make possible an extension of the work on the effect of water of crystallization on the fluorescence and absorption spectra of these substances.

The experimental work was performed in the laboratories of the Department of Physics of Cornell University while the writer was a Carnegie Research Associate.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE KELLY-SPRINGFIELD TIRE COMPANY]

## SYMMETRICAL DIPHENYL-GUANIDINE AS A STANDARD IN ACIDIMETRY AND ALKALIMETRY

By C. A. CARLTON

Received April 10, 1922

Various substances have been proposed as standards for use in preparing solutions of acids and alkalies of known concentration for use in volumetric analysis. The accuracy attainable with the various methods and substances now in use depends upon the manipulative skill of the operator and upon the time at his disposal; but taking into account economy of time and ease of operation for the routine chemist these methods leave much to be desired.

All methods of standardization can be divided into two classes, direct and indirect. The direct method involves the use of standard pure substance which can be accurately weighed and directly titrated. This is the ideal method, as to both time necessary and accuracy of results, provided a thoroughly suitable standard substance is at hand.

Dodge,<sup>1</sup> in an article on the Standardization of Alkalimetric Solutions, gives the following requirements for an ideal standard substance: (1) the standard should be easily obtained in a state of sufficient purity; (2)

<sup>1</sup> Dodge, *J. Ind. Eng. Chem.*, 7, 29 (1915).