

THERMAL ANALYSIS AT LOW TEMPERATURES.<sup>1</sup>

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## SYNOPSIS.

*Cooling and Heating Curves for Water Solutions of Uranyl Nitrate between 0° and -70° C.*—A thermo-junction was placed in 0.5 cc. of a solution of known concentration and galvanometer readings were taken every 10 seconds during the cooling. At about -35° a rapid evolution of heat took place accompanied by expansion sufficient to break the glass tube if the solution filled more than the rounded bottom. On heating the solution a corresponding absorption of heat was observed at -20°. From the observed temperature changes and the specific heat the amount of heat evolved or absorbed was computed. The results of 67 experiments in which the concentration was varied from 10 to 55 per cent. were plotted and show a sharp maximum at 48.0 per cent. for the evolved heat and at 47.5 per cent. for the absorbed heat.

*New Compound Discovered by Thermal Analysis, Uranyl Nitrate Icositetrahydrate.*—The above results point to the formation at -35° of the compound  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , which has a less density than the hexahydrate and which decomposes spontaneously at -20°. This compound is of special interest in connection with the study of the relation between composition and the fluorescence and absorption of the spectra uranyl hydrates.

THE study of chemistry and chemical reactions is usually restricted to those compounds which are stable or in a state of false equilibrium at room temperatures. As a result, many compounds which might be stable at very high or very low temperatures are never discovered. The present article serves to illustrate how such compounds may be studied by means of cooling and heating curves. The cooling curve might be regarded as a method of determining the composition by synthesis, whereas the heating curve might be regarded as a method of analysis.

When a water solution of uranyl nitrate is cooled to the temperature of liquid air, it is possible to get various distinct fluorescence spectra from it, depending in general on the rate of cooling. H. L. Howes<sup>2</sup> has described what seemed to him to be five distinct spectra, varying from a sharp-line spectrum in the case of slow cooling to a broad-banded spectrum in the event that the solution was plunged directly into liquid air. The other spectra were the results of other chance intermediate methods. As far as we know today, the emission and absorption spectra

<sup>1</sup> Paper presented to American Physical Society (see abstract in *PHYS. REV.*, 11, p. 245, 1918).

<sup>2</sup> *PHYS. REV.* (2), Vol. VI., p. 192, 1915.

of elements and compounds are very characteristic at any given temperature, so that it would seem quite impossible to obtain more than one fluorescence spectrum for a given compound. The only logical explanation that the author could advance for the anomaly observed by Mr. Howes was that the uranyl nitrate formed one or more definite hydrates at low temperatures, the transformation taking place entirely in the solid phase. Professor Edward L. Nichols drew the author's attention to the work of Mr. Howes, and the research here discussed was carried out in order to prove or disprove the above conclusion.

Temperatures were measured by means of a copper-advance thermojunction in series with a resistance of about nine thousand ohms and a sensitive d'Arsonval galvanometer. The filament of a Nernst lamp was focused on a wall opposite the galvanometer at a distance of about five meters. The maximum deflection read was of the order of one meter, so that a linear relation between deflection, voltage, and temperature could be assumed. Accordingly deflections are used constantly in what follows, without any transformation to temperatures except in the final results of range of stability. One junction was kept packed in ice, while the other was placed directly in the specimen under examination while still in a liquid state.

Preliminary tests showed that if water solutions of uranyl nitrate were cooled in a carbon-dioxide-ether mixture, the tube was usually broken. The heavier the walls and the smaller the bore of the tube, the more completely was the container shattered. Using a thick walled capillary tube was found to prevent the breaking. However, when a thermojunction was placed in the solution in a tube that would break, a sudden rise in temperature was indicated by the galvanometer at the same instant that the tube gave way. In the case of a strong capillary tube no such rise was noted. Inasmuch as it would be valuable to heat and cool the same specimen frequently, as well as to use the same tube for specimens of different concentrations, it was necessary to permit the expansion as well as to prevent the breaking of the tube. To accomplish this, a test tube of such a diameter was used that one half cubic centimeter of solution would all be contained in the lower hemispherical volume. Thus the expansion could all take place upwards, and the same tube could be used for all experiments. Since the fused end of the thermojunction was no larger than a pin head, the small volume offered no difficulty.

A constant temperature gradient was obtained by placing the tube containing the specimen in two larger concentric test tubes which were all separated by cork rings and cotton. This gave two air chambers between the inner tube and the carbon-dioxide-ether mixture.

The best obtainable C.P. uranyl nitrate was recrystallized as the hexahydrate, and water solutions varying from ten to sixty per cent. by weight anhydrous salt were prepared and preserved in glass-stoppered bottles. An accurately calibrated half cubic centimeter pipette was used to measure out the samples to be tested. Since we are measuring the amount of chemical reaction by means of the quantity of heat liberated, we should always deal with the same total number of mols or molecules of water and uranyl nitrate. It is more simple, however, to deal with the same volume of the various solutions. We are justified in doing this since the result is the same in either case. In this particular case the curve may be different but the maximum will be the same. The heat liberated in any case would be the continuous product of the specific heat  $c$ , the mass  $m$  and the change in temperature  $t$ . The quantity of heat with which we would be concerned would be this product divided by the total number of mols of water and salt  $M$ , or heat per mol solution =  $cm/M$ .

Plotting values of  $t$  as ordinates and values of percentage as abscissæ, we obtain a curve showing a sharp maximum. The values of  $c$  and  $M$  decrease while  $m$  increases with increasing concentration. The value of  $cm/M$  is almost constant. The product of the ordinates of a curve showing a maximum by values differing only slightly from a constant gives a curve whose maximum has the same value of the abscissa as the original curve. Accordingly we are justified in this particular case in plotting values of  $t$  against per cent. of  $UO_2(NO_3)_2$ .

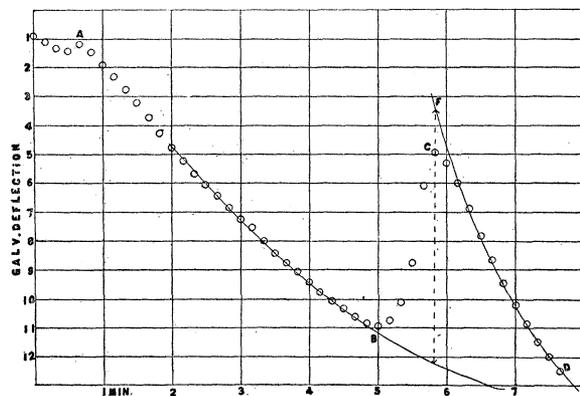


FIG. 1.  
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Referring to Fig. 1 we can get an idea of the appearance of the various cooling curves. At  $A$  the solidification of uranyl nitrate as hexahydrate and ice is complete, and we have the heterogeneous solid cooling uni-

formly to *B*. At this point a rapid evolution of heat takes place simultaneously with the expansion previously mentioned, bringing the temperature back up to *C*. Here the cooling again begins, and we finally arrive along a smooth cooling curve at *D*. Galvanometer deflections were read every ten seconds. By extrapolating the curves *AB* and *CD*, and drawing the line *EF* vertically through *C*, we obtain a length *EF* which is proportional to the heat liberated and consequently proportional to the chemical reaction. Similar curves were run for 20, 30, 45, 46.47, 47.75, 48, 49, 50, 52, and 55 per cent. The number of determinations for each percentage varied from two to ten. It is obvious that zero per cent., representing pure water, would give a zero value of *t*, and would be a point on the curve. Similarly there could be no rise in temperature if we use a concentration such as we have in the pure hexahydrate, which is the normal hydrate at ordinary temperatures. The compound  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  contains 78.48 per cent., by weight of uranyl nitrate and accordingly this value with  $t = 0$  would also be a point on the curve.

Fig. 2 is the weighted least square curve of all the observations. The

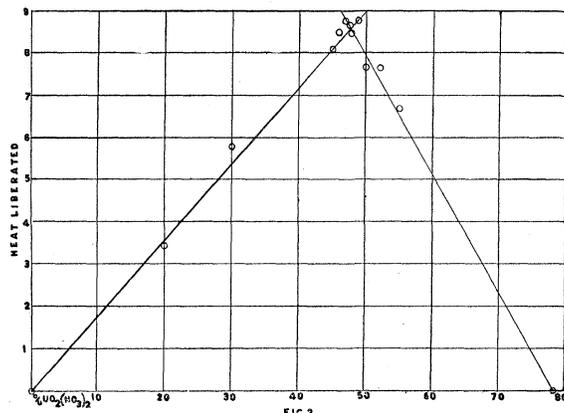


Fig. 2.

curve represents the results of forty-nine experiments. No values were discarded. The two lines, which are sensibly straight, intersect at 48.00. Multiplying all the ordinates of these lines by the respective values of  $cm/M$ , which remain practically constant, would give a curvature to the lines, but, as shown before, the abscissa of the maximum would remain the same.

If we now take a specimen which had been transformed, and allow it to warm up slowly with a definite temperature gradient, and take readings of the galvanometer as before, we obtain a curve of the type of Fig. 3. In this case the amount of chemical transformation would be evidenced

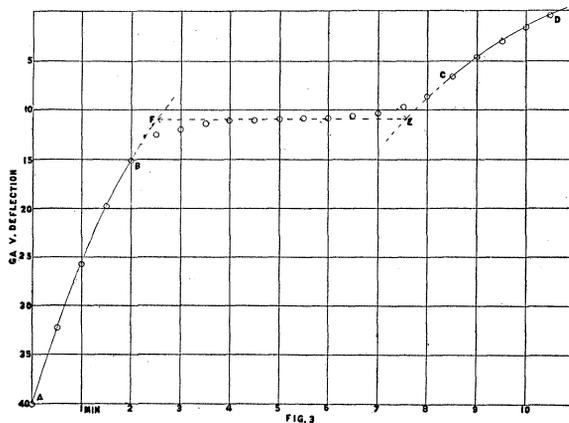


Fig. 3.

by a length of time  $FE$  of constant temperature. Here again galvanometer readings were taken every ten seconds. The points  $o$  and  $78.48$  may again be used with  $t = 0$ , together with the six other points determined experimentally. Each of these points is the average of three

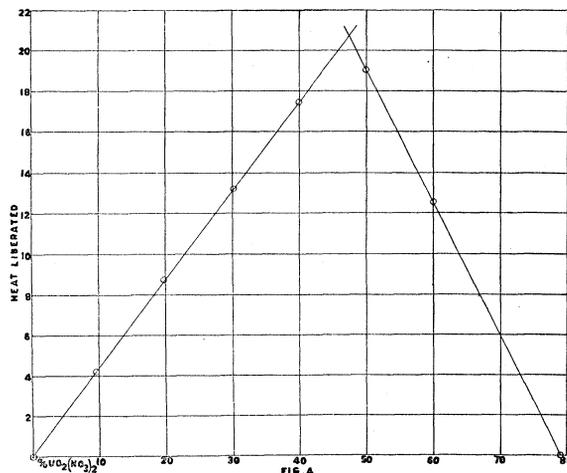


Fig. 4.

determinations. Hence Fig. 4 represents a total of eighteen experiments. As will be seen from the curve, the points fall almost exactly on the two straight lines, which intersect at  $47.50$ . The experiments involved in the formation of Fig. 2 were not as accurate, as the methods of procedure had not been well worked out. It would seem logical, therefore, to assign equal weights to the two curves. The probable error would be  $\pm 0.17$ , so that the composition of the hydrate formed would

be  $47.75 \pm 0.17$  per cent. A hydrate containing twenty-four molecules of water would consist of 47.69 per cent. uranyl nitrate, which falls within the limits mentioned. Twenty-three and twenty-five molecules of water would be equivalent to 48.70 per cent. and 46.70 per cent. uranyl nitrate respectively. We are therefore led to the conclusion that a hydrate exists whose composition given by  $47.75 \pm 0.17$  per cent. uranyl nitrate, and whose formula is  $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ . The name of the compound would be uranyl nitrate icositetrahydrate.

Since the icositetrahydrate forms spontaneously while in the presence of the hexahydrate, it is probable that it also crystallizes in the rhombic system, which is the system of the hexahydrate. Due to the low temperatures involved, it was impossible to determine this with ease, so that phase of the work was not followed up. It is also probable that another hydrate of some other crystalline system exists between the hexahydrate and the icositetrahydrate, but which was not observed because of the absence of seed crystals of the correct form.

The icositetrahydrate forms spontaneously at about  $-35^\circ$  C. and decomposes at about  $-20^\circ$  C. It could consequently never be studied at ordinary temperatures and pressures. The cooling curves were actually studied down to about  $-70^\circ$  C. The explanation of the anomalies observed by Mr. Howes are now obvious. Slow cooling of a 47 to 48 per cent. solution of uranyl nitrate would give almost a pure-line spectrum of the icositetrahydrate. Rapid cooling of the same might give a spectrum of the hexahydrate in the case of a complete suppression of the transformation, and a mixed spectrum in the case of a partial transformation. It is obvious that many possibilities are offered by different concentrations, and it is not strange that at least five fairly distinct types were picked out as actually existing.

The discovery of this new compound is of more than passing interest, since it adds another member to a series of hydrates studied by Nichols and Merritt in a paper entitled "The Influence of Water of Crystallization upon the Fluorescence and Absorption Spectra of Uranyl Nitrate."<sup>1</sup>

The above research work was done in the laboratories of the Department of Physics of Cornell University while the author was a Carnegie Research Associate. The author wishes to express his gratitude to Professor Nichols for suggesting the problem and to Professor Hutchinson of the Department of Engineering Mathematics of the University of Colorado for valuable suggestions in connection with the curves.

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December 6, 1921.

<sup>1</sup> PHYSICAL REVIEW (2), Vol. IX., pp. 113-126, 1917.