Some Observations on the Isothermal Dehydration of Uranyl(VI) Nitrate Hexahydrate Above Room Temperature

By **Patrick T. Moseley** * and **Cathleen J. Seabrook**, Applied Chemistry Division, A.E.R.E., Harwell

The dehydration of uranyl(VI) nitrate hexahydrate to the trihydrate has been studied gravimetrically between 313 and 343 K at varying water-vapour pressures in flowing air. With crushed crystals the dehydration rate is controlled by diffusion of water through the powder bed, even when using very shallow bed depths; with single crystals the kinetics of dehydration conform to a contracting-interface model. The activation energy is higher than that reported for vacuum decomposition. *X*-Ray powder data for the hexa- and tri-hydrates of uranyl(VI) nitrate have also been recorded. Single crystals of the former grew with a similar habit to that found by earlier workers, but with a different orientation of the crystal axes. When partially dehydrated crystals were heated above the melting point of the hexahydrate (333 K), it was observed that the molten hexahydrate was encapsulated in a sheath of solid polycrystalline trihydrate. Under these conditions, the dehydration reaction became very slow but accelerated again on cooling below the hexahydrate melting point. This is a new observation, not previously reported for crystal hydrate decomposition.

Until recently, studies of the kinetics of decomposition of uranyl(VI) nitrate hexahydrate have been complicated by the use of continuously changing conditions of temperature and uncontrolled water-vapour pressure. Hence, although vapour-pressure [1] and thermogravimetric [2] studies have indicated a sequence of stable hydrates, hexahydrate → trihydrate → dihydrate, some of the dynamic-decomposition experiments [3-5] have failed to isolate one or more of the stable intermediate hydrates. More recent thermogravimetric analyses [6] have followed the decomposition through the trihydrate

---

[1] M. H. Rand and O. Kubaschewski, 'The Thermochemical properties of Uranium Compounds,' Oliver and Boyd, 1963, London.

[2] J. K. Dawson, E. Wait, K. Alcock, and D. R. Chilton, *J. Chem. Soc.*, 1956, 3531.

[3] W. W. Wendlandt, *Analyt. Chim. Acta*, 1956, **15**, 435.

[4] B. A. J. Lister and R. J. Richardson, A.E.R.E. Report C/R 2276, 1957.

[5] W. Lodding and J. Ojamaa, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1261.

[6] W. H. Smith, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1761.

and dihydrate stages and have also detected a monohydrate.

Thermodynamic relations between the hexa-, tri-, and di-hydrates have been examined by equilibrium vapour-pressure measurements.[7-10] Several descriptions of water-vapour pressure over each hydrate as a function of temperature are collected together in Figure 1. In 1961 the isothermal decompositions of the dihydrate and anhydrous uranyl(VI) nitrate were described[11] and the activation energy for the change $UO_2(NO_3)_2,2H_2O \longrightarrow UO_2(NO_3)_2$ was reported as 77·8 kJ mol^{-1} *in vacuo* compared with 53·5 kJ mol^{-1} for dehydration under nitrogen at 1 atm. The observation that reaction rates were much greater at atmospheric pressure than *in vacuo* was tentatively ascribed to catalytic activity by product gases.

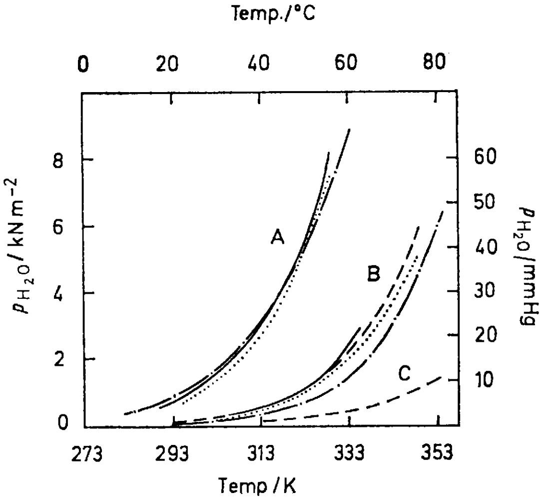

FIGURE 1 Vapour pressure data for uranyl(VI) nitrate hydrate complexes from refs. 7 (· · · ·), 8 (— · — · —), 9 (– – – –), and 10 (——): A, $UO_2(NO_3)_2,6H_2O$; B, $UO_2(NO_3)_2,3H_2O$; and C, $UO_2(NO_3)_2,2H_2O$

After some debate over the initial structural investigations,[12-14] the crystal structures of the hexahydrate[15] and the dihydrate[16] have been confidently described following neutron-diffraction studies. The only structural report on the trihydrate[17] is less complete, but there can be little doubt that this too is a distinct crystalline phase. The crystal structures of the hexa- and di-hydrates both contain units in which the metal atom is linked to two uranyl(VI) oxygen atoms, two water molecules, and two bidentate nitrate ions. The four extra 'structural' water molecules in the hexahydrate crystal structure are located in continuous sheets perpendicular to the *a* axis where they are hydrogen bonded to nitrate ions and to each other. A study of the self diffusion of water in uranyl(VI) nitrate hexahydrate[18] has shown that the four structural water molecules undergo diffusive exchange with D_2O, down to 225 K, although below 253 K only three water molecules are lost in vacuum dehydration.

The most up-to-date study of the hexahydrate decomposition[19] comprised isothermal dehydration experiments with atmospheric control. From these a much clearer picture has emerged of a rather unusual dehydration process. This work was carried out at low gas pressures and below 273 K. It was established that, under such conditions, the apparent reactant–product interface is not the site of the reaction, and it was suggested that desorption of water from the surface of the crystal samples is the slow step.

The observations described herein relate to the dehydration of uranyl(VI) nitrate hexahydrate between 313 and 343 K, at total gas pressures of 1 atm. The object of the investigation was to obtain information about the first stage of decomposition when the hexahydrate is heated in air.

EXPERIMENTAL

A uniform batch of uranyl(VI) nitrate hexahydrate powder was prepared by grinding AnalaR-grade crystals and seiving to a particle size between 200 and 350 μm. Samples were taken from this stock for gravimetric analysis before, during, and after the series of dehydration-rate measurements. The stock supply was preserved in an air-tight container with little atmosphere space [Found: U (as U_3O_8), 47·1, 47·4, and 47·2. Calc. for $UO_2(NO_3)_2,6H_2O$: U, 47·4%]. Single crystals of the hexahydrate were grown from a slightly acidified aqueous solution. The stoicheiometry of a few crystals from each batch was checked by gravimetric analysis for uranium as described

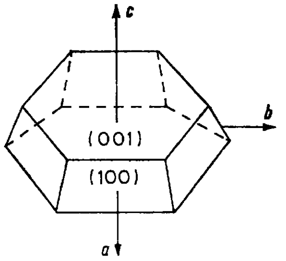

FIGURE 2 Habit of $UO_2(NO_3)_2,6H_2O$ crystal

---

[7] A. F. Kapustinsky and L. I. Baranova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1952, 112.

[8] W. S. Wendelkowski and S. S. Kirslis, U.S.A.E.C. Report K-1086, 1954.

[9] V. M. Vdovenko and A. P. Sokolov, *Radiokhimiya*, 1959, **1**, 117.

[10] E. H. P. Cordfunke, *I.A.E.A. Conf. Thermodynamics*, 1965, vol. II, 483.

[11] R. S. Ondrejcin and T. P. Garret, *J. Phys. Chem.*, 1961, **65**, 470.

[12] B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 1958, 3965.

[13] V. M. Vdovenko, E. V. Stroganov, A. P. Sokolov, and V. N. Zandin, *Radiokhimiya*, 1960, **2**, 24.

[14] J. E. Flemming and H. Lynton, *Chem. and Ind.*, 1960, **79**, 1416.

[15] J. C. Taylor and M. H. Mueller, *Acta Cryst.*, 1965, **19**, 536.

[16] N. K. Dalley, M. H. Mueller, and S. H. Simonsen, *Inorg. Chem.*, 1971, **10**, 323.

[17] V. M. Vdovenko, E. V. Stroganov, and A. P. Sokolov, *Radiokhimiya*, 1963, **5**(1), 97.

[18] M. L. Franklin and T. B. Flanagan, *J. Phys. Chem.*, 1971, **75**, 1272.

[19] M. L. Franklin and T. B. Flanagan, *J.C.S. Dalton*, 1972, 192.

above. All the crystals exhibited the same morphology as those used by Franklin and Flanagan,[18,19] but the orientation of the orthorhombic axes in our crystals (shown in Figure 2) is in a different sense from theirs.

Apparatus.—Dehydration runs were performed in a silica bucket suspended by a platinum wire in a glass vessel housed centrally in an oven (Figure 3). The atmosphere supplied to the apparatus was saturated with water in a U-tube immersed in a water-bath, the temperature of which determined the partial pressure of water vapour in the mixture. The effectiveness of this control was checked by inserting a weighed U-tube of magnesium(II) perchlorate 'down stream' of the water source and collecting the water pasing over at a known flow-rate for a timed period. The variation of water-vapour pressure with temperature thus measured compared well with that in the literature.[20] The temperature in the oven was measured by a mercury thermometer adjacent to the sample, and was controlled to $\pm 0{\cdot}5$ K.

Weight changes were measured using a C.I. Electronics microbalance with one arm placed vertically over a series of apertures in the apparatus to allow the introduction of the platinum suspension. Egress of air–water vapour through the top of the apparatus gave rise to no 'updraft' effects on the balance even at high flow-rates.

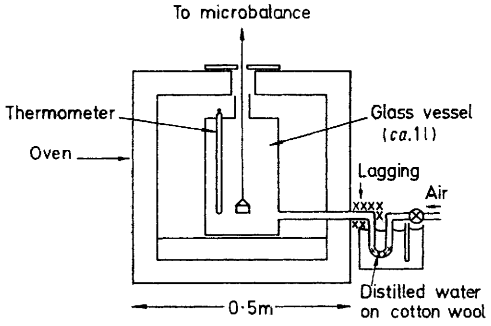

FIGURE 3 Dehydration apparatus

Varying the gas flow-rate between 50 and 500 ml min^{-1} through the apparatus did not affect the rate of dehydration and a standard flow-rate of 60 ml min^{-1} was used for the kinetic runs. Before each run the temperature of the water-bath and oven were held constant for a minimum of 2 h. At the start of each run the sample and suspension were introduced to the oven through the top hole, and a small time interval (*ca.* 1 min) before weight-loss began represented the time the crystal took to reach the temperature of its surroundings. The initial period during which the temperature was not constant probably accounts for the non-zero extrapolation in Figure 4.

X-Ray powder patterns were recorded using a Guinier focussing camera.

RESULTS

The validity of Figure 1 was demonstrated by successful prediction of the range of conditions of temperature and water-vapour pressure under which the dehydration hexahydrate ⟶ trihydrate was found to take place. The rate of hydration of a typical powder sample was almost linear over the first half of the reaction, but variation of the sample mass showed that, for all reasonably obtainable reaction conditions, the rate was controlled by diffusion of water vapour through the powder bed even for the shallowest bed depths. Since we wished to study the dehydration of uranyl(VI) nitrate hexahydrate and not the diffusion of water vapour through a powder bed of the hexahydrate, we turned our attention to single-crystal specimens.

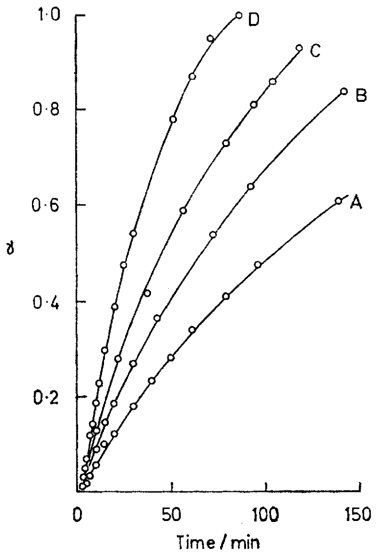

FIGURE 4 Dehydration of single crystals of $UO_2(NO_3)_2,6H_2O$ at $p_{H_2O} = 3{\cdot}3$ kN m^{-2}: A, 315·5 K, 179 mg; B, 320·5 K, 169 mg; C, 324 K, 164 mg; and D, 327·5 K, 159 mg

The α (fraction of reaction completed) against time plots for single crystals were not linear (Figure 4) but if the rates were interpreted in terms of a three-dimensional contracting-volume model, as $2kt = 1 - (1 - \alpha)^{1/3}$, then plots approached linearity for most of the reactions (Figure 5). The dependence of dehydration rate on partial pressure of water (p_{H_2O}) is shown in Figure 6 for both powder and single-crystal samples. No extrema due to impedance[21] were found and, in fact, the plots appear to be linear as in the case of other experiments performed at low pressures.[19]

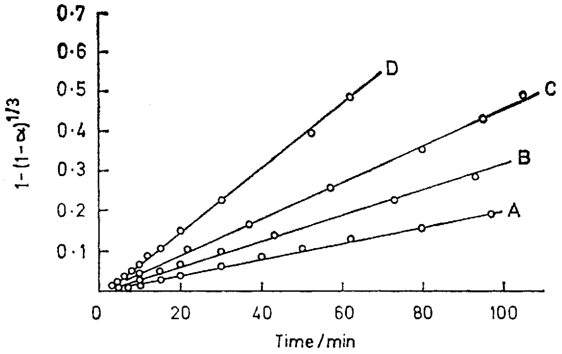

FIGURE 5 Dehydration of single crystal plotted as $1 - (1 - \alpha)^{1/3}$ against time. See Figure 4 for details

---

[20] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co. Ltd., 1964.

[21] 'Chemistry of the Solid State,' ed. W. E. Garner, Butterworths', 1955.

The absolute dehydration rates observed here are comparable to those found during low-temperature runs *in vacuo* for which self cooling was not considered to be a problem;[19] self cooling is not expected to be a difficulty in the present case either. When initial gradients of the α against time plots (Figure 4) were considered as proportional to reaction rates, a linear Arrhenius plot [Figure 7(*a*)] was obtained which indicates an activation energy for the early stages of dehydration (hexahydrate $\longrightarrow$ trihydrate), under a partial pressure of p_{H_2O} of 3·3 kN m^{-2}, of 79·3 kJ (mol hexahydrate)$^{-1}$. If gradients of $1 - (1 - \alpha)^{1/3}$ against time plots are substituted for the α against time gradients [Figure 7(*b*)], a higher activation energy [105·1 kJ (mol H_2O)$^{-1}$] results. Both these values are far greater than that [46 ± 4 kJ (mol H_2O)$^{-1}$] found *in vacuo*.[19]

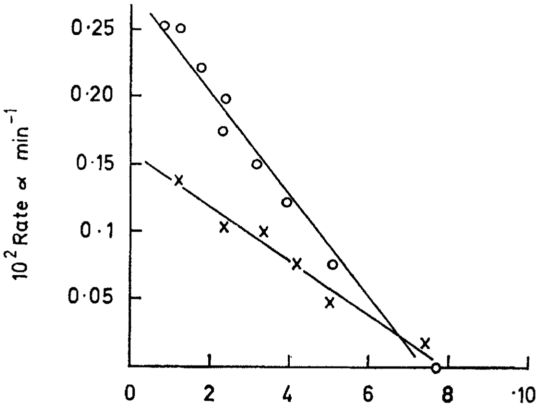

FIGURE 6 Dependence of the gradients of α against time plots on water vapour pressure at 328 K: (○), powder samples (320 ± 20 mg); and (×), single crystals (355 ± 10 mg)

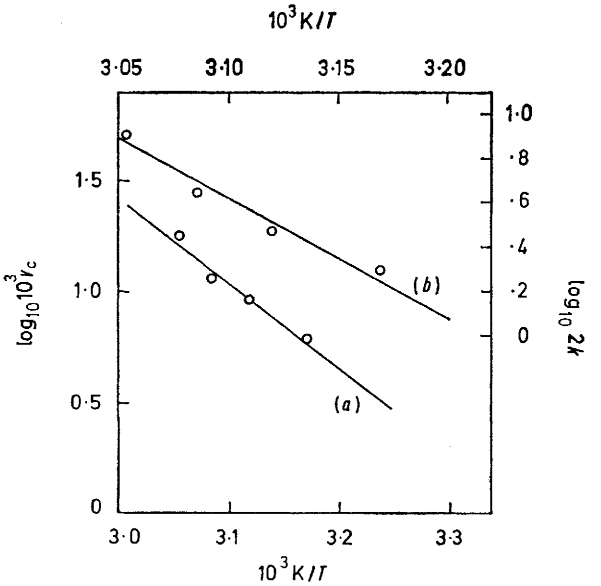

FIGURE 7 Arrhenius plot at p_{H_2O} = 3·3 kN m^{-2}: (*a*) rates (v_c) from α against time plots; (*b*) rates ($2k$) from $1 - (1 - \alpha)^{1/3}$ plots

The steady increase in dehydration rate with temperature in these experiments came to a halt in the region of the melting point of uranyl(VI) nitrate hexahydrate (333 K) when dehydration was found to cease. This effect is well illustrated by Figure 8 which shows a differential-thermogravimetric record of a dehydration at a rather low heating rate, in static air. The renewed increase in dehydration rate above 355 K is due to the onset of the trihydrate $\longrightarrow$ dihydrate transformation. Crystals withdrawn from the apparatus at temperatures above 333 K and sectioned quickly revealed a molten interior within a thin solid opaque shell which maintained the shape of the original crystal. A crystal in the apparatus above the melting point (at 336 K) restarted to lose weight when the temperature was reduced to 331 K, *i.e.* when the interior hexahydrate recrystallised.

When a single crystal of uranyl(VI) nitrate hexahydrate was dehydrated to a fraction α = 0·50 (as adjudged by weight loss), cooled, and sectioned, the fraction of dehydrated product as predicted from observation of the penetrating interface of opaque product corresponded only to α = 0·25. This observation parallels that[19] made by Franklin and Flanagan in that the interface is not the centre of the dehydration reaction. Such a result, together with an earlier observation[22] that the diffraction pattern of uranyl(VI) nitrate hexahydrate persists even when the weight-loss corresponds to complete dehydration to trihydrate, suggests a model for the reaction whereby a quasi-zeolitic water loss and recrystallisation to the crystal structure of the lower hydrate are not synchronous processes.

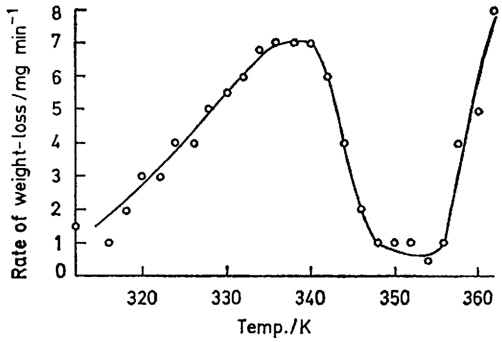

FIGURE 8 Differential-thermogravimetric run in static air: mass of crystal = 1·582 g; heating rate = 0·8 K min^{-1}

In view of the special arrangement of the structural water molecules in sheets perpendicular to the *a* axis in the crystal of uranyl(VI) nitrate hexahydrate, Franklin and Flanagan[19] examined the effects on the dehydration rate of coating the two large crystal faces [marked (100) in their paper] with a water impermeable plastic material. The results showed little difference in dehydration rate between this run and a run in which the other six faces were coated and the large faces were not. It was concluded that the layer arrangement of water molecules did not manifest itself in the form of an anisotropic dehydration mechanism. As mentioned earlier, our crystals, though similar to those of Franklin and Flanagan in habit, showed a different orientation of crystal axes, so that in our case a coating experiment based mainly on the large faces [marked (100) in Figure 2] would not provide conclusive evidence

[22] A. J. King, R. Pfeiffer, and W. Zeek, U.S. Report, NYO-6313, 1957.

about anisotropic effects due to the layer of water molecules. We, therefore, concentrated on each type of face in turn, leaving only the one pair of opposite faces uncoated for a kinetic run. The rates of dehyration were no different in the (100) direction and generally were proportional to the free surface area of crystal. It was also noticed that, when a partially dehydrated crystal was sectioned in two mutually perpendicular directions, the opaque–transparent interface had penetrated by a similar margin from all the crystal faces. It seems probable, therefore, that neither water loss nor recrystallisation are concentrated in particular crystallographic directions.

The ultimate trihydrate product of dehydrating a crystal of uranyl(VI) nitrate hexahydrate was polycrystalline and an *X*-ray oscillation photograph showed that, although the external form of the original crystal was retained, the trihydrate crystallites were randomly oriented. The trihydrate product rehydrated to the hexahydrate was also polycrystalline. Kinetic curves for a second dehydration of this rehydrated, polycrystalline hexahydrate resembled those for the original crystal but the absolute dehydration rates were increased by up to 30%. *X*-Ray powder data for the hexahydrate starting material and the trihydrate product are shown in the Table. The unit-cell parameters derived for the hexahydrate are in close agreement with the parameters determined by Flemming and Lynton.[14] Cell parameters for the trihydrate are close to those quoted by Vdocenko *et al.*[17]

X-Ray powder patterns of uranyl(VI) nitrate hexahydrate and trihydrate

			d/Å		
h	*k*		Observed	Calc.[a]	Intensity
			$UO_2(NO_3)_2,6H_2O$		
1	1	0	6·83	6·84	s
0	1	1	6·57	6·56	s
1	1	1	5·86	5·87	vs
0	0	2	5·72	5·72	s
3	0	0	4·38	4·38	s
2	0	2	4·31	4·31	s
1	2	0	3·83	3·83	w
0	2	1	3·77	3·78	m
1	2	1	3·64	3·63	m
1	1	3	3·33	3·33	ms
2	2	1	3·28	3·28	m
1	2	2	3·19	3·18	w
2	2	2	2·93	2·93	w
4	0	2	2·85	2·85	w
0	2	3	2·76	2·76	m
1	2	3	2·71	2·70	w
1	1	4	2·64	2·64	m
			$UO_2(NO_3)_2,3H_2O$ [b]		
0	1	0	6·23	6·20	s
0	0	1	5·66	5·65	s
0	−1	1	5·48	5·55	s
−1	0	1	5·12	5·19	s
1	0	0	4·93	4·88	s
1	1	−1	4·73	4·68	s
−1	1	0	4·03	4·04	s
−1	1	1	3·51	3·50	m
0	1	1	3·47	3·47	m
0	−2	1	3·41	3·40	w
0	−1	2	3·12	3·12	w
1	−1	1	3·09	3·09	vw
1	2	−1	3·04	3·06	vw
1	0	1	3·01	3·01	vw
1	2	−2	2·95	2·95	m
0	0	2	2·81	2·81	vw

[a] Unit-cell dimensions by a least-squares method (J. A. C. Marples and J. L. Shaw, A.E.R.E. Report R5210, 1966): $a = 13{\cdot}14 \pm 0{\cdot}03$; $b = 8{\cdot}01 \pm 0{\cdot}02$; and $c = 11{\cdot}43 \pm 0{\cdot}02$ Å. [b] Unit-cell dimensions: $a = 5{\cdot}63 \pm 0{\cdot}08$; $b = 6{\cdot}87 \pm 0{\cdot}10$; and $c = 7{\cdot}20 \pm 0{\cdot}09$ Å; $\alpha = 116{\cdot}3 \pm 0{\cdot}8$, $\beta = 120{\cdot}4 \pm 0{\cdot}8$, and $\gamma = 82{\cdot}0 \pm 0{\cdot}7$ °.

CONCLUSIONS

It has already been established [19] that the dehydration of uranyl(VI) nitrate hexahydrate *in vacuo* is unusual among dehydration processes which have been studied so far in that the extent of water loss and the position of the interface do not coincide. The model envisaged for the mechanism of dehydration requires the hexahydrate lattice to be able to accommodate a large density of water vacancies. It is also acknowledged that the high self-diffusion coefficient of water in the hexahydrate [18] is important. None of the four structural water molecules is crystallographically unique and yet, under suitable conditions (see Figure 1), one of these molecules remains in the lattice available for subsequent recrystallisation to the trihydrate. Precisely why this should be so is not clear, although evidently the lattice forces which retain the last member of the water layer are relatively strong.

Most of the conclusions drawn about the reaction mechanism of the dehydration of uranyl(VI) nitrate hexahydrate *in vacuo* may be extended to cover the conditions of the present experiments also, except in the details of the kinetics. *In vacuo,* the α against time plots [19] were linear for most of the reaction and it was concluded that the slow step in the dehydration was desorption of water from the surface of the crystals. At atmospheric pressure and temperatures of *ca.* 323 K, the activation energy is much greater and the rate plots are no longer linear. The form of the $1 - (1 - \alpha)^{1/3}$ against time plots suggests that under these conditions the dehydration is limited by a three-dimensional contracting-volume process.

The discontinuity in the dehydration of uranyl(VI) nitrate hexahydrate in the region of the melting point was observed only for single crystals. The dehydration rate of powder specimens continued to increase uniformly through the melting point up to at least 356 K. As already mentioned, the characteristics of the dehydration kinetics of the powdered hexahydrate are controlled by diffusion of water vapour through the powder bed. It seems that crystals greater than some critical size are important for inhibition of the dehydration and that this is observed only when melting of a central core of unreacted hexahydrate occurs within an envelope of dehydrated material.

Some difference in the tenacity with which the structural water molecules are retained by molten uranyl(VI) nitrate hexahydrate is to be expected. The plot of log *P* against $1/T$ given by Vdovenko [9] shows a change in gradient at 333 K, which indicates a slightly greater heat change (ΔH) for reaction $UO_2(NO_3)_2,6H_2O(s) \longrightarrow UO_2(NO_3)_2,3H_2O + 3H_2O$ than that for $UO_2(NO_3)_2,6H_2O$ (molten) $\longrightarrow UO_2(NO_3)_2,3H_2O + 3H_2O$. The difference between the entropy changes (ΔS) for the two reactions would tend to make the dehydration of the melt less favourable. However, in view of the dependence on the form of the sample exhibiting this type of inhibition, it is necessary to look beyond such straightforward thermodynamic considerations for an explanation.

The most likely mechanism seems to be a cementing process at the melt–dehydration product interface which seals the core from continued water loss. Such a seal would need to be destroyed during recrystallisation of the core in order for dehydration to recommence as the temperature dropped below the melting point once again. In the case of a powder we might expect that each particle would be too small to form a surface layer sufficiently thick for effective sealing of the core. So far as we are aware, the melting of a crystal hydrate within an external sheath of a solid lower hydrate during the course of its decomposition has not previously been recorded in the literature. We would expect such a phenomenon to be confined to crystal hydrates which lose water near their melting points.

We are grateful to Dr. R. M. Dell and Mr. V. J. Wheeler for many helpful discussions and to Mr. N. J. Bridger for carrying out the differential thermogravimetric experiment.

[2/2530 *Received, 8th November*, 1972]