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THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE

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Technical Division
Sylvan Cromer, Superintendent

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ABSTRACT

The thermal decomposition of uranyl nitrate hexahydrate was studied at 41.8°C., 75.6°C., and 126.3°C. by observing the equilibrium pressure over the salt as the water of hydration was gradually removed. Constant equilibrium pressures were observed which corresponded to the hexahydrate, trihydrate, and dihydrate phases.

For the transition $UO_2(NO_3)_2 \cdot 6\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 3\ H_2O + 3\ H_2O(g)$, the variation of the equilibrium water vapor pressure with temperature is described by the equation

$$\log P = -\frac{2396}{T} + 9.010,$$

where P is in millimeters and T is the absolute temperature.

The heat of dehydration calculated from this relation was 10.9 kcal. per mole of water.

The trihydrate decomposed according to the following equation:

$$UO_3(NO_3)_2 \cdot 3\ H_2O \longrightarrow UO_3(NO_3) \cdot 2\ H_2O + H_2O(g).$$

The plot of log P vs 1/T showed curvature in this case, but the data may be approximately represented by the equation

$$\log P = -\frac{3277}{T} + 10.926\ ,$$

where the units are the same as above.

The average heat of this dehydration was 15.0 kcal. per mole of water released.

The decomposition pressure of the dihydrate at 126.3°C. was approximately 20 mm. Visible quantities of brown nitrogen tetroxide fumes were observed during this decomposition, but the vapor withdrawn was largely water. The main decomposition reactions can be represented by the following equations:

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_2(NO_3)_2 + 2\ H_2O(g) \quad \text{and}$$

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + N_2O_4(g) + 2\ H_2O(g) + 1/2\ O_2(g).$$

THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE

The study of the thermal decomposition of uranyl nitrate hexahydrate was undertaken in support of development work being done on the decomposition (1) of uranyl nitrate solutions to uranium trioxide. Information was desired on the nature of the individual reactions which took part in the overall decomposition reaction.

Early workers (12,13,18) established that uranyl nitrate hexahydrate could be dehydrated to the trihydrate and finally to the dihydrate at room temperature in a desiccator containing sulfuric acid or phosphoric anhydride. The rate of dehydration slowed markedly after the trihydrate stage was reached. The existence of the two stable lower hydrates was confirmed by subsequent studies of vapor pressure at room temperature (8,11), of phase relationships (4,15) in the uranyl nitrate-water system, and of the behavior of the hydrates in a stream of inert gas at elevated temperature (6,14).

There was less agreement in the literature on the nature of the decomposition of uranyl nitrate dihydrate. de Forcrand (6) claimed that a monohydrate was produced after 4 hours in a carbon dioxide stream at 120 to 125°C., with only slight loss of nitrogen content. Other workers report "nitrous fumes" at temperatures as low as 100°C. Phase studies indicated that the dihydrate was stable up to 180°C. (15). Marketos (14) reported that anhydrous uranyl nitrate could be produced by passing dry nitric acid over the trihydrate at 170 to 180°C. de Forcrand, on the other hand, stated that an oxide-free anhydrous salt could not be obtained in a nitric acid stream above a temperature of 130°C. Misciatelli (16) claimed the preparation of an anhydrous uranyl nitrate by treating the hexahydrate with nitrogen pentoxide (N_2O_5). He measured equilibrium pressures for the supposed reaction:

$$UO_2(NO_3)_2 \longrightarrow UO_3 + 2\ NO_2 + O_2\ .$$

The later work of Gibson and Katz (9) on the reaction of liquid nitrogen dioxide (NO_2) with uranium oxides to give addition compounds of the type $UO_2(NO_3)_2 \cdot 2\ NO_2$, $UO_2(NO_3)_2 \cdot NO_2 \cdot 2\ H_2O$ and $UO_2(NO_3)_2 \cdot 2\ NO_2 \cdot H_2O$ casts doubt on Misciatelli's work. The addition compounds were labile and gave off nitrogen dioxide easily, as did the preparation of Misciatelli.

The vapor pressure of water over uranyl nitrate hexahydrate and trihydrate had not been measured at elevated temperatures. There was sufficient uncertainty concerning literature values for the heats of hydration of the various hydrates that satisfactory extrapolation from the measured vapor pressures at room temperature could not be made. Therefore, the first object of this work was the measurement of the equilibrium water vapor pressure over the hexahydrate and over the trihydrate at various temperatures.

It was planned to make a similar study for the dihydrate in a temperature range where the uranyl nitrate part of the dihydrate remained unaffected, then to raise the temperature and determine the concentration of the various decomposition products in the gas phase. Unfortunately, it was not possible to carry out the dihydrate decomposition study in detail without equipment modifications. Data were obtained on the total decomposition pressure over the dihydrate at only one temperature.

EXPERIMENTAL

Preliminary Experiments

It became evident in exploratory experiments that an all-glass system was required for the decomposition study. The presence of metal in the experimental system gave rise to undesirable side reactions with the small amounts of nitric acid liberated at temperatures as low as 35°C. Under these conditions a steady equilibrium pressure was not observed. For this reason, a metal valve could not be used for withdrawing samples of vapor from the heated part of the system. A glass stopcock was also unsatisfactory since a stopcock grease could not be found which would maintain a gas-tight seal at elevated temperatures. Therefore a glass bellows valve with a silver chloride seat was constructed. The design and construction of this valve are described in the appendix.

A mercury manometer was used for measuring decomposition pressures, although a glass diaphragm pressure transmitter or glass Bourdon gauge would have been more satisfactory. However, the reaction of mercury with nitrogen oxide vapors was not excessively rapid, and pressures remained fairly steady.

Material

Mallinckrodt C. P. uranyl nitrate hexahydrate was used in this study. Analysis of the compound indicated 47.35% uranium (theoretical: 47.41%).

Apparatus

A schematic diagram of the apparatus used in the decomposition study is shown in figure 1. The thermostated section comprised a 150 ml. Erlenmeyer flask which contained the uranyl nitrate, a mercury manometer and the glass valve. The auxiliary manifold consisted of a small mercury manometer, a thermocouple gauge, a glass cold trap, a calibrated Merriam manometer, 1/4 in. HGP Crane valves, and 10 mm. standard taper stopcocks. The removable cold trap was attached to the manifold by ground glass joints. A two-stage mercury diffusion pump was used in conjunction with a Welch Duo Seal vacuum pump to evacuate the system.

The thermostated box was heated by two 250 watt strip heaters. The heating current was controlled by an Emil Greiner mercury thermoswitch which actuated an Emil Greiner electronic relay. The air in the heated box was circulated by a conventional laboratory blower. A copper-constantan thermocouple, with a Rubicon potentiometer and a portable General Electric galvanometer, was used to measure the temperature of the salt container. The thermocouple was calibrated against a Bureau of Standards mercury thermometer to a precision of ±0.2°C.

The calibrated Merriam manometer was used to calibrate the system manometer at operating temperatures. This calibration was necessary since the arm of

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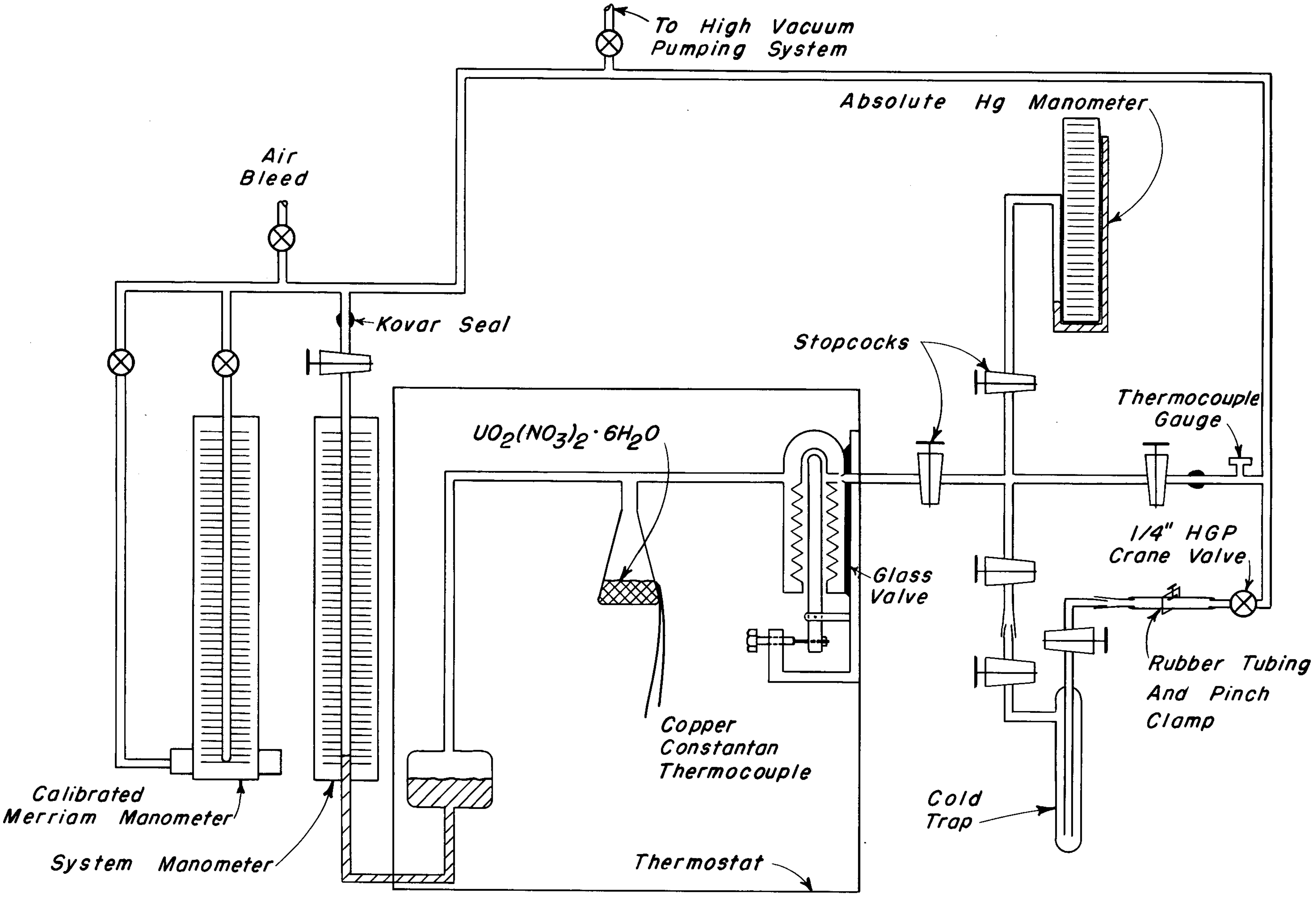


THERMAL DECOMPOSITION APPARATUS
FIGURE 1

the system manometer inside the thermostated section was at a higher temperature than the outside arm. A cathetometer was used in reading the manometers.

The volume of the thermostated section of the system up to the seat of the glass valve was 381 ml., as determined by the expansion of dry nitrogen from a bulb of known volume. The volume, similarly determined, of the auxiliary manifold between the glass valve seat and the stopcocks to the pumping line (including the small mercury manometer) was 15.2 ml.

Procedure

Approximately 65 grams of uranyl nitrate hexahydrate was accurately weighed into the Erlenmeyer flask and the flask was sealed to the system. A Dewar flask containing dry ice-trichloroethylene slush was placed around the Erlenmeyer flask and the system was evacuated to a pressure of 5×10^{-6} mm. The glass valve was closed, the coolant removed, and the thermostated box heated to the desired temperature. The temperatures used in this work were 41.8°, 75.6°, and 126.3°C. When equilibrium was reached, as indicated by constancy of system pressure, the pressure was recorded. The system was usually allowed to equilibrate for one day. The glass valve was then opened slightly, allowing the system vapor to condense into the tared cold trap, which was maintained at approximately 10°C. During the withdrawal of vapor, the system pressure was lowered only a few millimeters below its equilibrium value. After a small quantity of water (less than one gram, on the average) had been removed, the cold trap was detached from the system, and weighed. The contents of the trap were titrated to the methyl red endpoint with 0.01 normal sodium hydroxide. This titer was a measure of the quantity of nitrogen oxides and nitric acid in the decomposition products. At 41.8°C. and 75.6°C., the withdrawals were continued until the dihydrate stage was reached. The pressure then dropped to unmeasurable values and no water could be condensed into the cold trap even when it was cooled with dry ice. At 126°C. the withdrawals continued beyond the dihydrate stage.

A pressure versus temperature analysis of the system gases was occasionally made prior to and after withdrawals. A sample of gas was isolated in the auxiliary manifold at room temperature. The pressure (usually approximately 25 mm.) was read on the small absolute manometer and the pressures were then observed when the cold trap was cooled in ice water, dry ice-trichloroethylene (-75°C.), and liquid nitrogen (-196°C.). The color of the condensed materials was observed.

Several vapor samples from the decompositions at the higher temperatures were submitted for infrared absorption analysis.

EXPERIMENTAL RESULTS

The decomposition data at 41.8°, 75.6°, and 126.3°C. are given in tables I, II, and III, respectively, and are shown graphically in figures 2, 3, and 4, respectively. In agreement with the literature cited above, the data indicate three definite hydrate phases: the hexahydrate, the trihydrate, and the dihydrate. A fairly constant water vapor pressure corresponded to each phase at a particular temperature.

TABLE I

THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 41.8°C.

Sample Number	Equilibration Time, days	Equilibrium[a] Pressure, mm.	Weight Sample Withdrawn, g.	Acid Content[b], mole %	Initial Ratio[c], moles H_2O/mole U	Phases Present
1	4	40.5	0.1436	0.34	5.944	solid and vapor
2	1	25.2	0.5674	0.010	5.887	solid and vapor
3	1	25.4	0.3953	0.008	5.651	solid and vapor
4	3	26.7	1.1632	0.007	5.486	solid and vapor
5	2	26.8	1.0289	0.003	5.003	solid and vapor
6	1	25.5	1.9083	0.003	4.575	solid and vapor
7	1	25.5	1.1286	0.008	3.782	solid and vapor
8	1	25.5	0.7219	0.012	3.313	solid and vapor
9	1	4.2	0.4041	0.540	3.016	solid and vapor
10	1	4.3	1.2185	0.089	2.848	solid and vapor
11	1	4.3	0.8250	0.049	2.342	solid and vapor
12	3	<1.0	0	0	2.000	solid and vapor

[a] The pressure was read after the noted equilibration time and before the sample was withdrawn.

[b] The acid content was calculated as HNO_3. Actually, the sample contained mainly NO_2 and N_2O_4 as acidic constituents.

[c] The tabulated ratio of moles H_2O/mole U was calculated for the composition before withdrawal of the sample, taking into account the quantity of water vapor in the 381 ml. system volume.

TABLE II

THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 75.6°C.

Sample Number	Equilibration Time, days	Equilibrium[a] Pressure, mm.	Weight Sample Withdrawn, g.	Acid Content[b], mole %	Initial Ratio[c], moles H_2O/mole U	Phases Present
1	8	146.6	0.7005	0.42	5.684	liquid and vapor
2	5	142.8	1.8586	0.13	5.379	solid and liquid and vapor
3	1	139.0	1.6284	0.05	4.569	solid and liquid and vapor
4	1	137.1	1.7702	0.04	3.859	solid and vapor
5	4	135.8	0.2877	0.20	3.087	solid and vapor
6	1	128.0	0.9294	0.11	2.963	solid and vapor
7	2	52.8	1.2995	0.08	2.568	solid and vapor
8	4	43.8	0.0335	0.94	2.002	solid and vapor
9	2	$<$1.0	0	----	1.993	solid and vapor

[a] The pressure was read after the noted equilibration time and before the sample was withdrawn.

[b] The acid content was calculated as HNO_3. Actually, the sample contained mainly NO_2 and N_2O_4 as acidic constituents.

[c] The tabulated ratio of moles H_2O/mole U was calculated for the composition before withdrawal of the sample, taking into account the quantity of water vapor in the 381 ml. system volume.

TABLE III

THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 126.3°C.

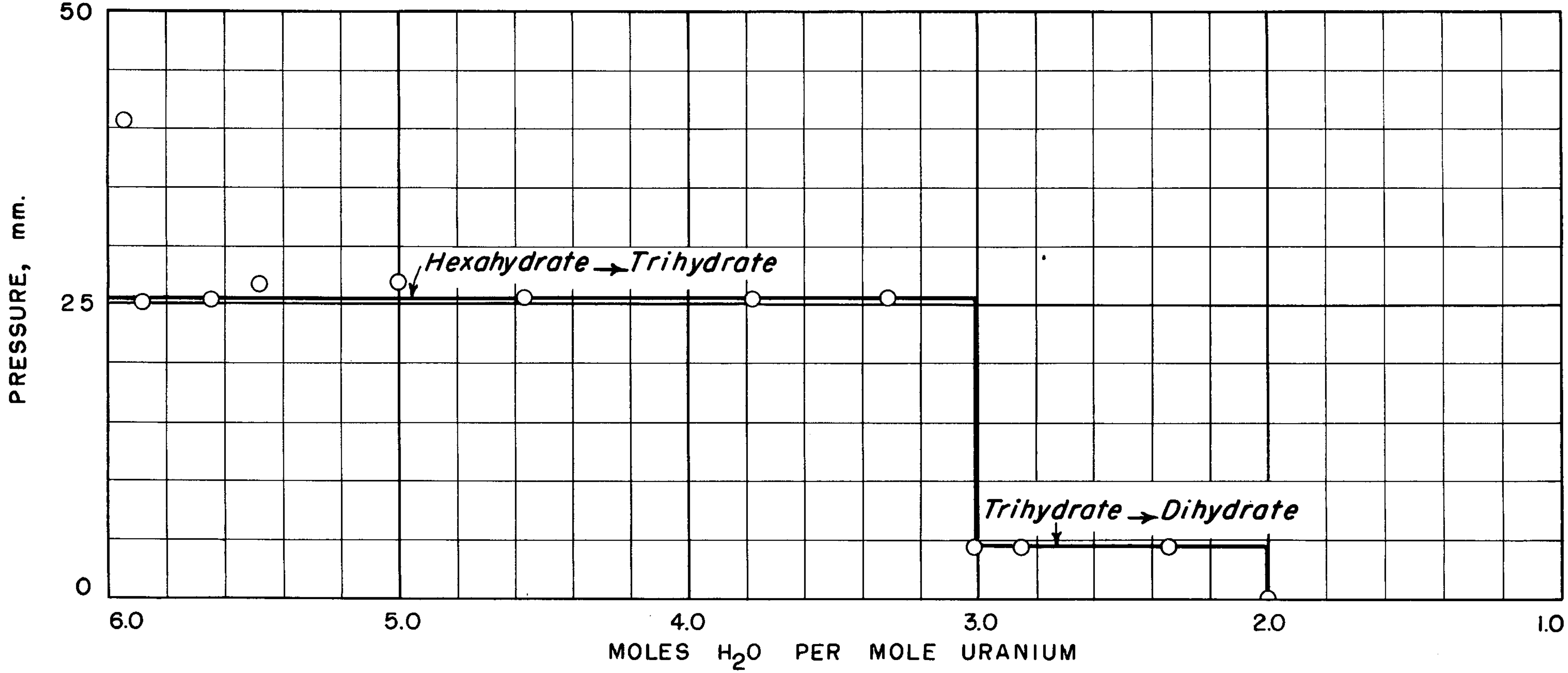
Sample Number	Equilibration Time, days	Equilibrium[a] Pressure, mm.	Weight Sample Withdrawn, g.	Acid Content[b], mole %	Initial Ratio[c], moles H_2O/mole U	Phases Present
1	5	968.3	0.4032	1.8	5.838	liquid and vapor
2	2	899.0	1.1369	0.67	5.641	liquid and vapor
3	1	791.2	1.6430	0.48	5.073	liquid and vapor
4	3	627.7	2.6677	1.1	4.253	liquid and vapor
5	1	304.0[d]	1.6730	0.50	2.929	solid and vapor
6	1	400.5	0.2928	0.75	2.055	solid and vapor
7	1	33.8	0.4410	4.9	1.957	solid and vapor
8	1	19.2	0.2533	9.1	1.733	solid and vapor
9	3	60.5	0.0865	41.2	1.597	solid and vapor
10	1	21.8	0.0592	14.0	1.558	solid and vapor
11	1	24.0	------	----	1.527	solid and vapor

[a] The pressure was read after the noted equilibration time and before the sample was withdrawn.

[b] The acid content was calculated as HNO_3. Actually, the sample contained mainly NO_2 and N_2O_4 as acidic constituents.

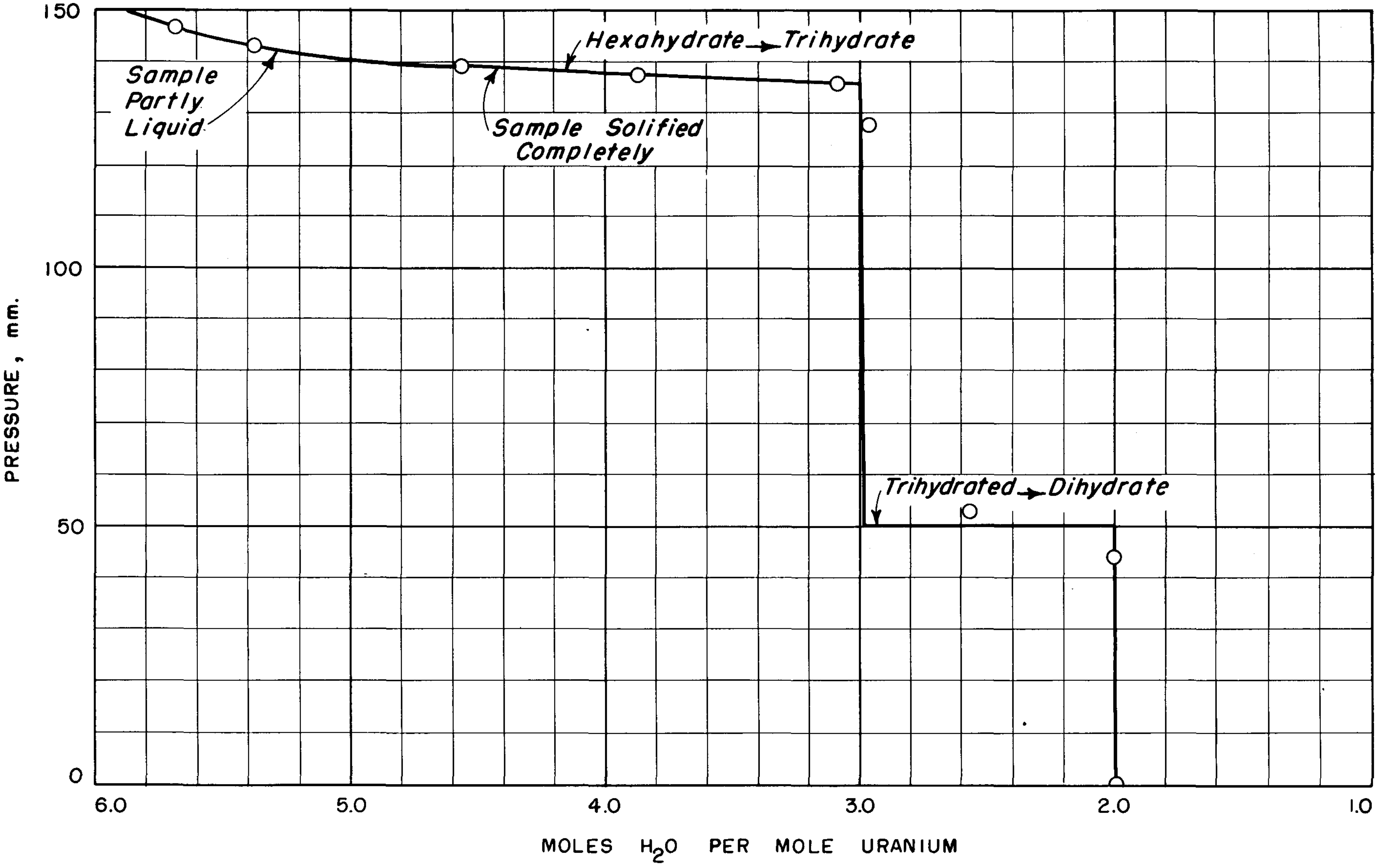
[c] The tabulated ratio of moles H_2O/mole U was calculated for the composition before withdrawal of the sample, taking into account the quantity of water vapor in the 381 ml. system volume.

[d] This pressure reading was made while the sample was liquid. During subsequent withdrawal, the salt solidified.



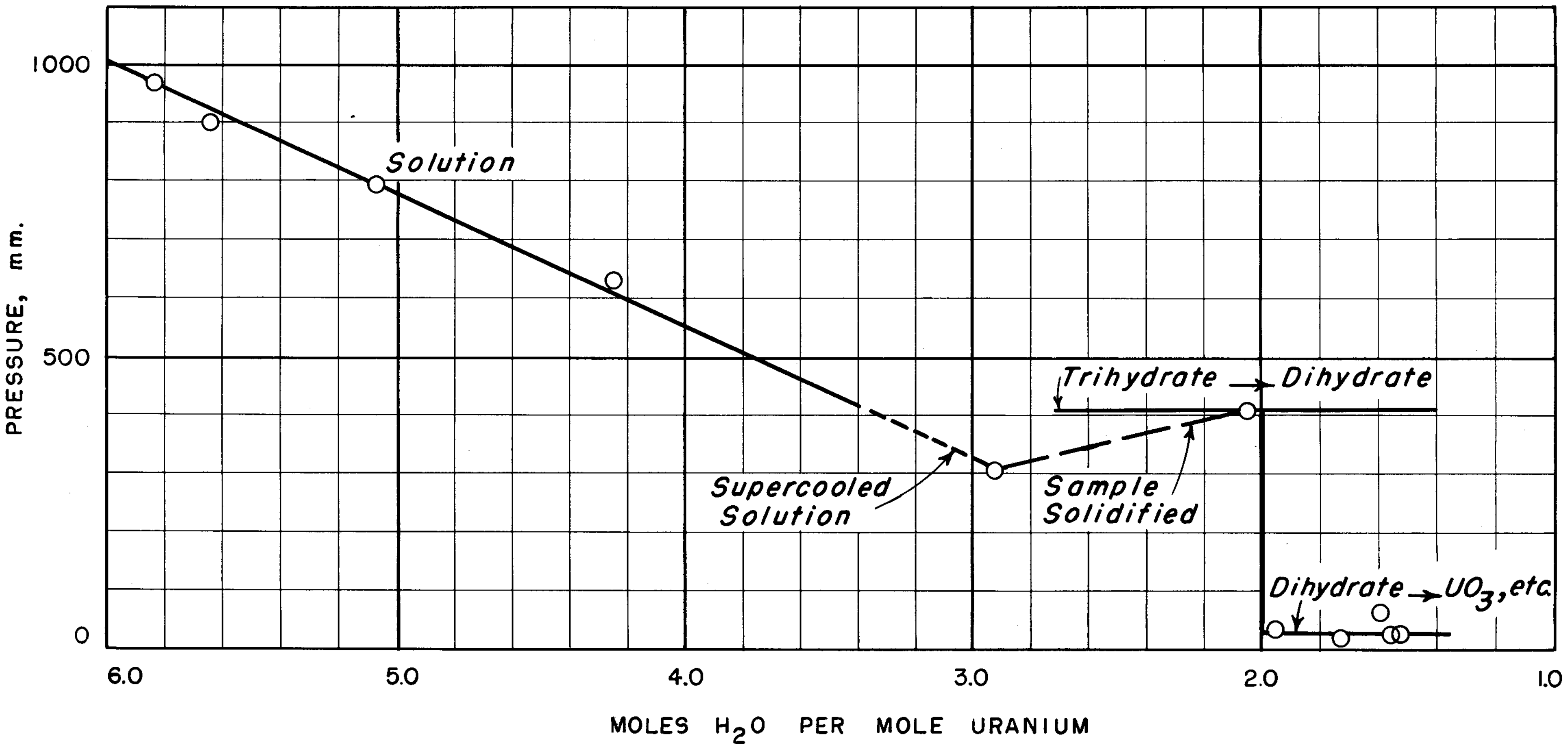
THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 41.8°C.

FIGURE 2



THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 75.6°C.

FIGURE 3



THERMAL DECOMPOSITION OF URANYL NITRATE HEXAHYDRATE AT 126.3 °C.

FIGURE 4

At 41.8°C., the main reactions observed were the dehydrations of the hexahydrate to the trihydrate and of the latter to the dihydrate. The data in the fifth column of table I show, however, that some acidic nitrogen compounds were evolved even at this low temperature, and that the rate of evolution increased after the trihydrate began to decompose.

At 75.6°C., the sample was liquid. The first withdrawal of water (0.3 mole) caused solid to appear. The sample was completely solid after approximately two moles of water had been removed from the hexahydrate. The solid must have been a mixture of the hexahydrate and the trihydrate. When the mole ratio of water to uranyl nitrate reached the value of three, the vapor pressure showed a marked drop. The pressure dropped again when the dihydrate stage was reached. The pressure over the dihydrate was less than one millimeter and could not be accurately measured. When the system was evacuated, and the glass valve closed, no pressure rise was observed after a few minutes. The data in the fifth column of table II show that more acidic materials were produced at 75.6°C. than at 41.8°C. A faint brown coloration in the gas phase was discernible to the eye, indicating nitrogen tetroxide (N_2O_4).

At 126.3°C., the sample was liquid until the mole ratio of water to uranyl nitrate decreased to approximately 2.5. The sample completely solidified during the conversion of the trihydrate to the dihydrate. The liquid, over which the 304 mm. pressure reading was taken just before solidification, was probably supercooled. Vapor pressures corresponding to the trihydrate and dihydrate phases were observed. The considerable degree of nitrate decomposition at this temperature caused the pressure to rise continuously (though slowly). The gas over the salt was a distinct brown-orange color. Infrared analysis of the gas indicated that the brown coloration was due to nitrogen dioxide. The data in the fifth column of table III show that the quantity of the acidic components in the decomposition gases increased markedly when the dihydrate stage was reached and continued to increase as the dihydrate decomposed. The pressure-temperature analyses made on occasional samples of the system vapor confirmed the titration results.

DISCUSSION OF RESULTS

The thermodynamics of a dehydration reaction may be completely determined, theoretically, by measurements of the vapor pressure of water in equilibrium with a given hydrate at various temperatures. The equilibrium constant (K), free energy (ΔF), heat (ΔH), and entropy (ΔS), of a dehydration reaction are calculated from the following expressions:

$$K = P^n_{H_2O} \quad \text{(where n = the number of moles of water produced),}$$

$$\Delta F = - RT \ln K = \Delta H - T\Delta S,$$

and

$$\ln K = - \frac{\Delta H}{RT} + C = n \ln P_{H_2O} \ .$$

From the last expression, it is seen that if the heat of dehydration is known, the equilibrium pressure at any temperature may be calculated from that at one temperature.

In table IV are given the equilibrium pressures at various temperatures for the dehydration of the hexahydrate to the trihydrate and of the trihydrate to the dihydrate. The values at 23.4°C. were taken from the work of Germann and Frey (8).

TABLE IV

EQUILIBRIUM PRESSURES IN THE URANYL NITRATE-WATER SYSTEM

Reaction	Equilibrium Pressure, mm., at			
	23.4°C.	41.8°C.	75.6°C.	126.3°C.
$UO_2(NO_3)_2 \cdot 6\ H_2O \rightleftharpoons UO_2(NO_3)_2 \cdot 3\ H_2O + 3\ H_2O(g)$	8.66	25.5	139	(Liquid)
$UO_2(NO_3)_2 \cdot 3\ H_2O \rightleftharpoons UO_2(NO_3)_2 \cdot 2\ H_2O + H_2O(g)$	0.62	4.3	50	400

Plots of the logarithm of the pressure versus the reciprocal of the absolute temperature for these equilibria are shown in figure 5. It is seen that the three points for the hexahydrate-trihydrate equilibrium (upper line) are in excellent alignment. This equilibrium is accurately represented by the equation:

$$\log P = \frac{2396}{T} + 9.010\ ,$$

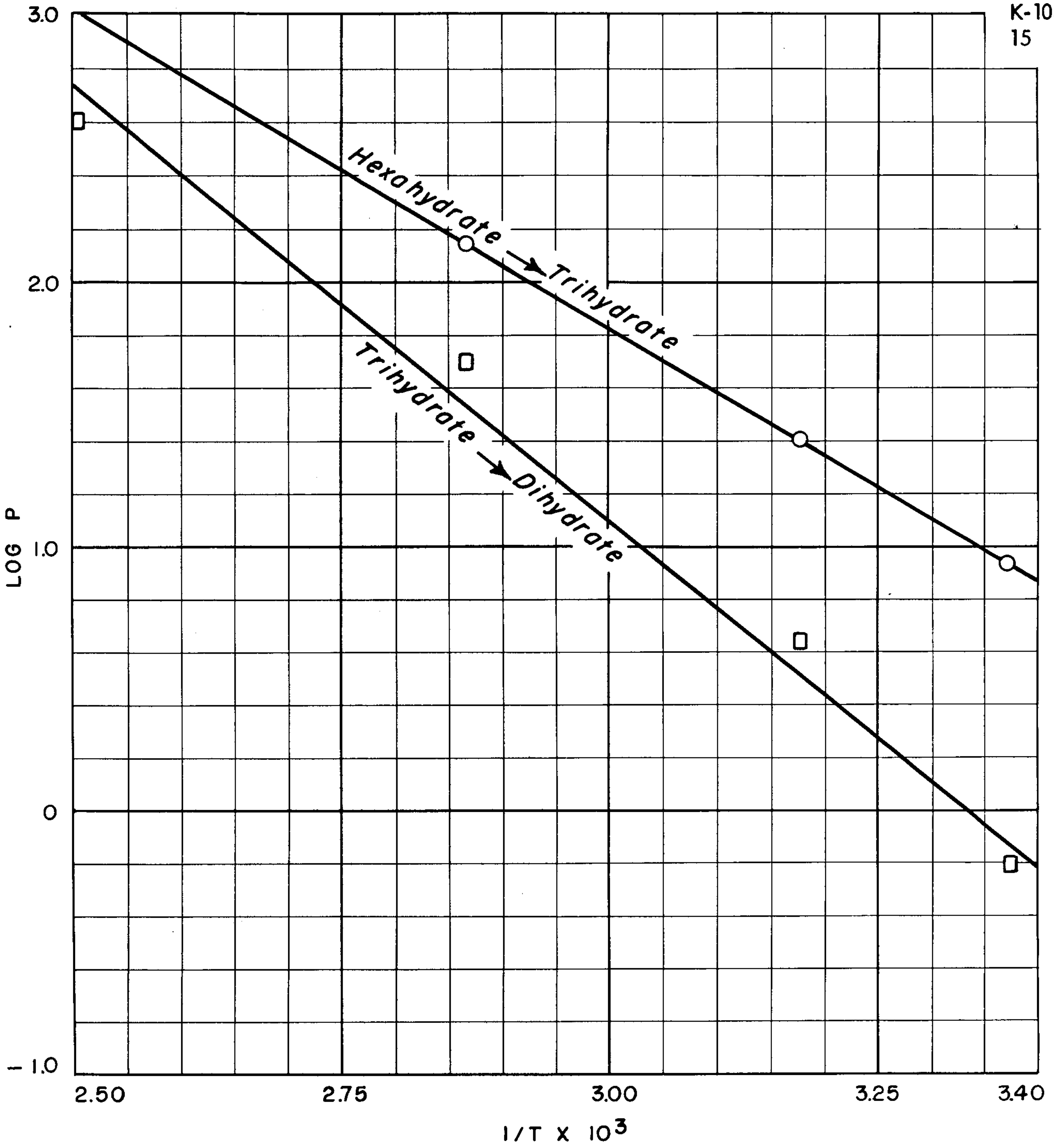
where P is the pressure in millimeters and T is the absolute temperature.

The heat of dehydration calculated from the slope of the line was 10.9 kcal. per mole of water released, a value somewhat lower than expected. (The heat of vaporization of water is 10.2 kcal. per mole at 50°C.) The points in the lower curve of figure 5 are not so well aligned. It is believed that the curvature is real; otherwise experimental error in the pressure measurements would be improbably great. The data are approximated by the equation:

$$\log P = -\frac{3277}{T} + 10.926\ .$$

The average heat of dehydration calculated from this line is 15.0 kcal.

Heat values calculated in this way may be compared with values obtained from heats of solution of the various hydrates. Heats of solution have been measured by several investigators and are given in table V.



LOG P VS I/T PLOTS FOR THE EQUILIBRIA: $UO_2(NO_3)_2 \cdot 6H_2O \rightarrow UO_2(NO_3)_2 \cdot 3H_2O + 3H_2O\,(g)$ AND $UO_2(NO_3)_2 \cdot 3H_2O \rightarrow UO_2(NO_3)_2 \cdot 2H_2O + H_2O\,(g)$

FIGURE 5

TABLE V

HEATS OF SOLUTION OF THE HYDRATES OF URANYL NITRATE

	Heat of Solution, kcal. Per Mole Uranyl Nitrate*				
Investigator	UN·6 H_2O	UN·3 H_2O	UN·2 H_2O	UN·1 H_2O	UN, anh.
Katzin, et al. (10) (25°C.)	+5.48 ± 0.03	-1.66 ± 0.05	-5.37 ± 0.06		
de Forcrand (7) (12°C.)	+5.45	-1.35	-5.05	-11.87	-19.0
Marketos (14)	+4	-1.96	-5.42		-16
Coulter, et al. (5)	+5.25				

*UN = $UO_2(NO_3)_2$; anh. = anhydrous

From these values, the heat changes in passing from one hydrate to another may be calculated. Using the data of Katzin et al. in table V, for example:

$$UO_2(NO_3)_2 \cdot 6\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 3\ H_2O + 3\ H_2O(1),\ \Delta H = 5.48 - (-1.66) = 7.14 \text{ kcal.}$$

Adding the heat of vaporization of water at 50°C., 10.2 kcal./mole: $UO_2(NO_3)_2 \cdot 6\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 3\ H_2O + 3\ H_2O(g)$, $\Delta H = 7.14 + 3\ (10.2) = 37.7$ kcal. per mole of $UO_2(NO_3)_2$, or 12.6 kcal. per mole of water. If the data of de Forcrand are used, the resulting heat change is 12.5 kcal. per mole of water released. There is thus a discrepancy of approximately 1.6 kcal. per mole between these calorimetric values and the 10.9 kcal. value obtained from the equilibrium pressure determinations.

In similar fashion, the heat change for the reaction: $UO_2(NO_3)_2 \cdot 3\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 2\ H_2O + H_2O(g)$ may be calculated. The results are 13.7, 13.7, and 13.5 kcal. per mole of water released, using the data of Katzin et al., de Forcrand, and Marketos, respectively (see table V), and using the heat of vaporization of water at 75°C., 10.0 kcal./mole. The average heat change calculated from the equilibrium pressure data was 15.0 kcal. per moles of water released, but at higher temperatures the slope of the log P vs. 1/T plot corresponded to a lower heat change. Thus, the magnitude of the heat change for the dehydration of the trihydrate to the dihydrate is approximately the same when calculated from calorimeteric and from equilibrium pressure data. Some of the discrepancies may be due to the fact that the heats of solution were measured at 25°C. (Katzin et al.) and 12°C. (de Forcrand). Therefore any pecularities of the system at higher temperatures could not be predicted.

Decomposition pressures of the dihydrate at 41.8°C. and 75.6°C. were so low that they could not be accurately measured. At 126.3°C., a pressure in the neighborhood of 20 mm. was observed when the system was allowed to equilibrate overnight. (One value of 60 mm. was obtained when the equilibration time was 3 days). As seen in table III, considerable quantities of acidic materials were present in the decomposition gases, with 5, 9, 41, and 14 mole per cent acid in the successive samples withdrawn. These observations suggest that the following reactions occur in the decomposition: $UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_2(NO_3)_2 + 2\ H_2O$ and $UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + N_2O_4 + 2\ H_2O + 1/2\ O_2$.

There are the further possibilities: $UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot H_2O + H_2O$ (de Forcrand claimed to have isolated the monohydrate) and $UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + 2\ HNO_3 + H_2O$. It is likely that all of these reactions take part in the decomposition with the major contributions from the first two reactions.

It is not possible to calculate the heat of this decomposition from the one experimental point. It may be calculated from de Forcrand's heat of solution data that the simple dehydration of the dihydrate (to produce gaseous water) would require approximately 17.0 kcal. per mole of water released. From the data in Bichowsky and Rossini (2), the heats of the following reactions were calculated:

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + N_2O_4 + 2\ H_2O + 1/2\ O_2; \quad \Delta H = 82 \text{ kcal.}$$

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + 2\ HNO_3 + H_2O; \quad \Delta H = 54.8 \text{ kcal.}$$

Therefore, a high temperature coefficient for these reactions is to be expected. From the fact that considerable decomposition of the uranyl nitrate was observed at 126.3°C., it may be predicted that at higher temperatures the decomposition would be rapid. This is in accord with all of the decomposition studies reported in the literature.

A complete study of the dihydrate decomposition would require the analysis of the decomposition gases to determine the partial pressures of each component at several temperatures. The work reported represents an exploratory experiment in this direction.

SUMMARY

The thermal decomposition of uranyl nitrate hexahydrate has been studied at 41.8, 75.6, and 126.3°C. The equilibrium pressure of water vapor in the system was measured after successive fractions of the water of hydration were removed. Constant equilibrium pressures were observed corresponding to the hexahydrate, the trihydrate, and the dihydrate phases, confirming previous work which postulated these three stable uranyl nitrate hydrates.

The hexahydrate decomposed according to the following equation:

$$UO_2(NO_3)_2 \cdot 6\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 3\ H_2O + 3\ H_2O(g)\ .$$

The equilibrium pressure of water vapor during this transition is represented by the equation:

$$\log P = -\frac{2396}{T} + 9.010\ ,$$

where P is the pressure in millimeters and T is the absolute temperature.

The heat of dehydration calculated from the slope of this line is 10.9 kcal. per mole of water released.

The decomposition of the trihydrate is described by the equation:

$$UO_2(NO_3)_2 \cdot 3\ H_2O \longrightarrow UO_2(NO_3)_2 \cdot 2\ H_2O + H_2O(g)\ .$$

The plot of log P vs. 1/T was not a straight line in this case, the slope decreasing as temperature increased. A straight line approximating the behavior of the system is given by:

$$\log P = -\frac{3277}{T} + 10.926$$

The heat of dehydration calculated from the slope of this line is 15.0 kcal. per mole of water released.

The decomposition pressure of the dihydrate at 126.3°C. was approximately 20 mm. At 41.8°C. and 75.6°C., the pressure was too low for accurate measurement (less than 1 mm.). The decomposition of the dihydrate at 126.3°C. produced visible quantities of brown nitrogen tetroxide fumes. The vapor withdrawn was largely water, however. It is indicated that the main reactions were:

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_2(NO_3)_2 + 2\ H_2O(g) \text{ and}$$

$$UO_2(NO_3)_2 \cdot 2\ H_2O \longrightarrow UO_3 + N_2O_4(g) + 2\ H_2O(g) + 1/2\ O_2(g)$$

Literature data indicated that the heat of dehydration of the dihydrate should be approximately 17.5 kcal. per mole of water removed. The high heat of decomposition to nitrogen tetroxide indicated that the equilibrium would shift toward the right rapidly with increasing temperature.

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Experimental work was completed January 27, 1950.

APPENDIX A

DESIGN AND CONSTRUCTION OF THE GLASS VALVE

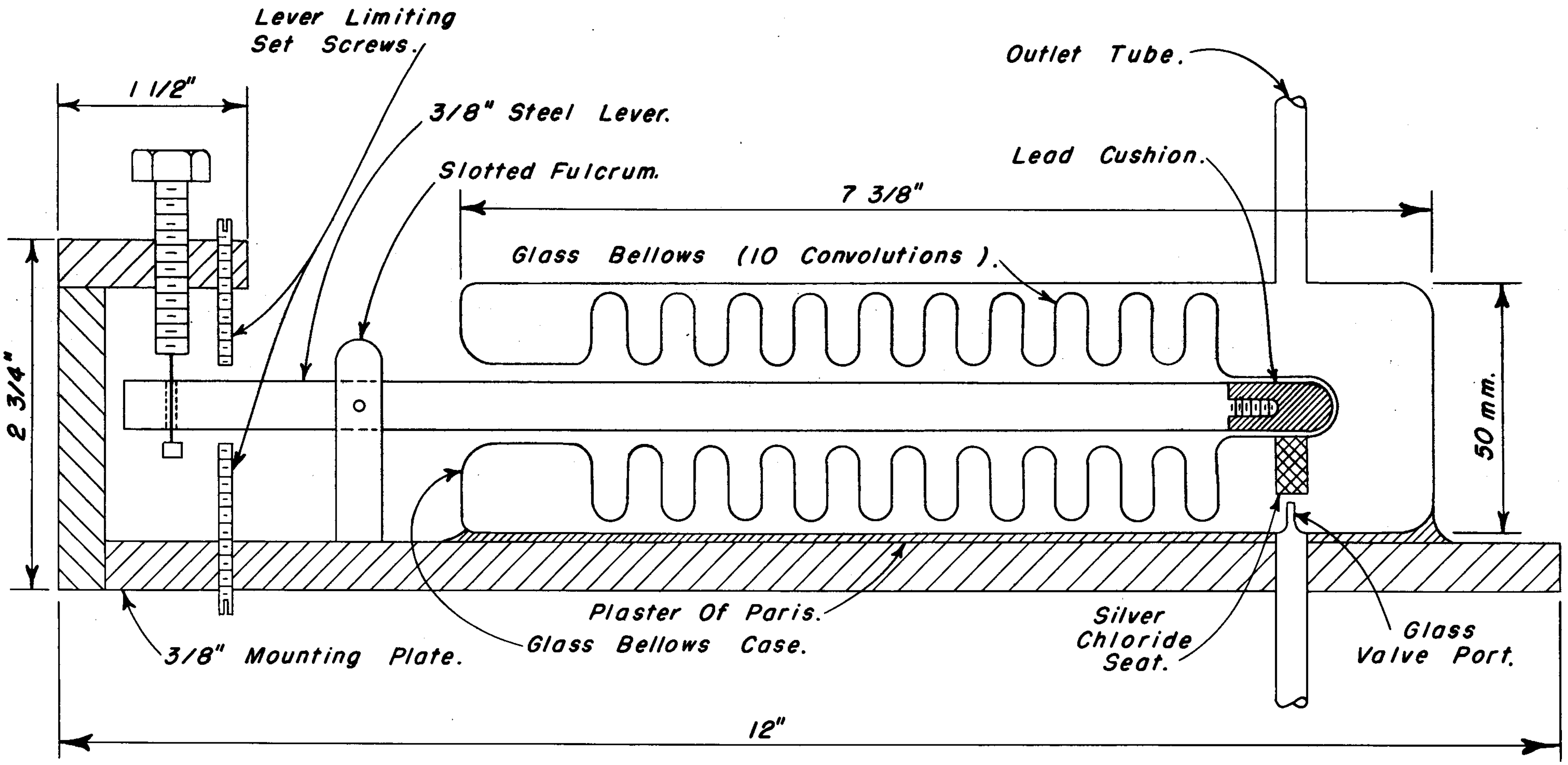
The glass valve used in this study is similar to those described by Bodenstein (3) and Ramsperger (17). The latter two valves were constructed so that the movement of the seating surface required the elongation of the bellows. In the present valve, advantage was taken of the fact that glass bellows may be displaced by bending more easily than by stretching.

The mounted valve and its operating mechanism are shown in figure 1-A. The valve body was attached to a brass mounting plate (12 x 6 x 3/8 inches) by means of Plaster of Paris and metal straps. The end of the 3/8 in. steel rod lever arm was enclosed in lead foil as a cushion between the glass and steel. The set screws limited the motion of the lever arm to eliminate the possibility of excessive strain on the glass bellows.

The bellows part of the valve was blown from 25 mm. heavy wall glass tubing. The convolutions were doughnut-shaped, approximately 10 mm. in thickness and 40 mm. O.D. A small cup, 12 mm. long and 12 mm. O.D., with a flat ground lip was sealed to the end of the bellows assembly. The small cup was filled with the seating material. Silver chloride was chosen as the seating material since it is soft , has a high melting point (455°C.), and is chemically resistant to water, nitrogen oxides, and nitric acid. Chemically pure silver chloride was melted at approximately 460°C. and formed into sticks by pouring the melt down a cool inclined glass tube. The sticks were carefully melted into the glass cup which was maintained at 460°C. Overheating caused the chloride to decompose and form an undesirable scum on its surface. Silver chloride was added, with repeated warming and cooling of the cup, until the sealing material extended about 1/16 in. above the lip of the cup. The cup was then slowly cooled to room temperature. Excess silver chloride was removed with a razor blade, and the seat was polished flat with grade 000 emery paper.

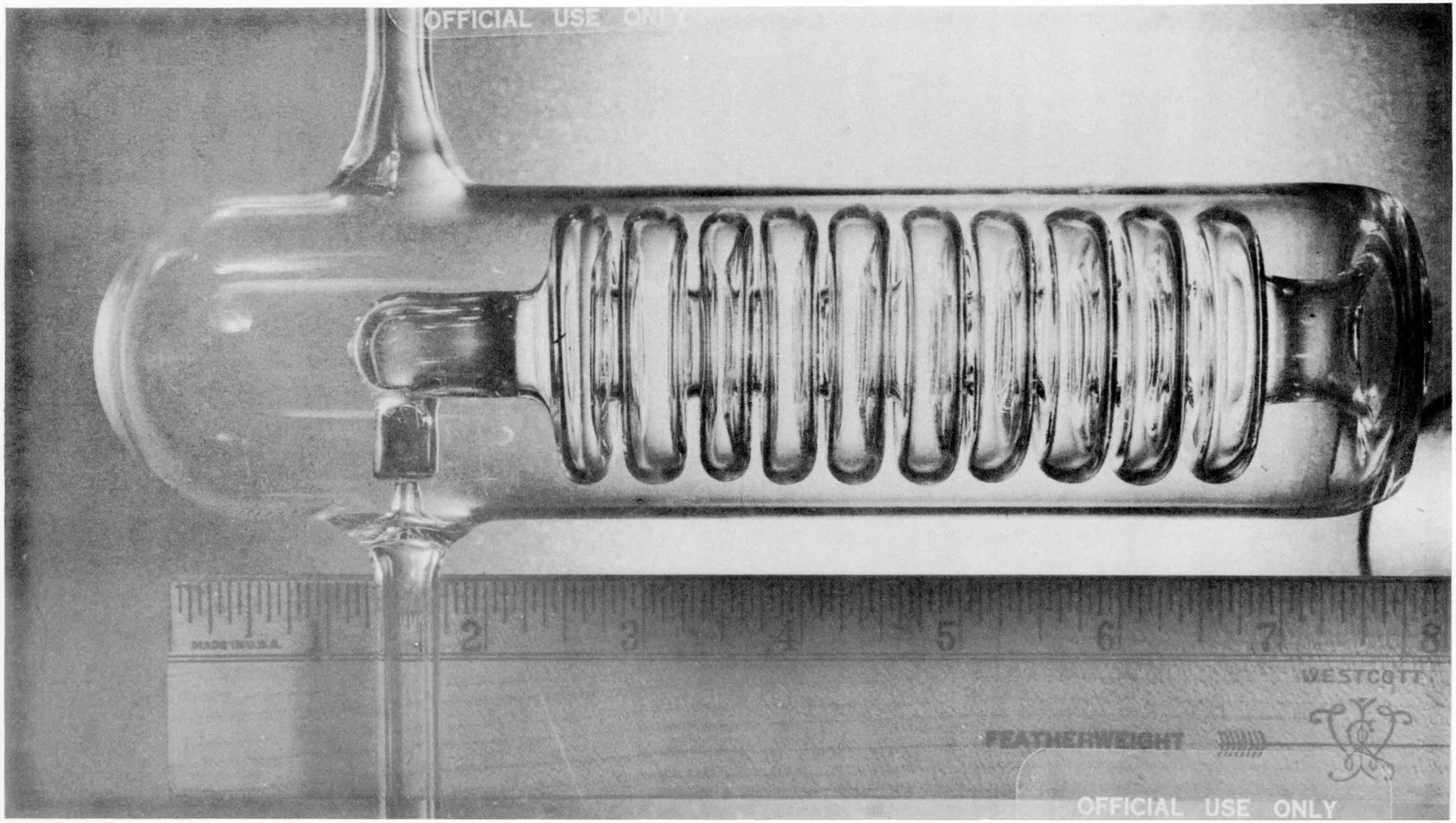
The outer jacket for the valve was constructed from 60 mm. heavy wall glass tubing. The outlet port was constructed from 10 mm. heavy wall tubing drawn down to 5 mm. at the seat end. The lip was ground flat so that the seating surface was an annular ring 5 mm. O.D. and approximately 1 mm. wide. This tube was sealed through the jacket wall at a position corresponding to the silver chloride seat. On the opposite side of the jacket, the 10 mm. inlet tube was sealed. The valve was finally assembled by attachment of the outer jacket to the bellows by means of a Dewar seal. Care was taken to align the seating surfaces properly during the final sealing operation. A photograph of the unmounted valve is given in figure 2-A.

To close the valve, a torque wrench force of 7.5 in. lb. on the lever screw was required. The leak rate was less than 0.01 micron liter per minute with a pressure differential of one atmosphere across the seat. Inspection of the seat after repeated usage showed that it was not deformed.



GLASS VALVE

FIGURE I-A



GLASS VALVE
FIGURE 2-A