% 1-methyl-2-ethylbenzene, 0.15% 1-methyl-3-ethylbenzene, 0.08% xylenes, and other light hydrocarbons. Sulfur content was 0.3 p.p.m.

Disproportionation Reaction. The author used a continuous flow-type tubular reactor, consisting of a 50-cm. long, 0.635-cm. O.D. stainless steel tube. The tube held 0.5 ml. of 100 to 200 mesh catalyst. The catalyst used in most of the experiments was a commercial synthetic silica-alumina cracking catalyst. The catalyst contained 10 weight % alumina, 90 weight % silica, and 0.1 weight % Na_2O. The B.E.T. nitrogen surface area of the catalyst was 340 $m.^2$ per gram. The experiments were carried out at atmospheric pressure with a hydrogen diluent at a hydrogen-to-methylethylbenzene mole ratio of 3. Liquid feed rate was varied to obtain different conversion levels. The author collected the reaction products in an acetone–dry ice-cooled condenser. Reaction periods were 65 minutes long.

Product Analysis. A 300-foot long, 0.02-inch I.D. capillary column was used for the analyses of the liquid products. The column was packed with Ucon LB550-X polypropylene glycol. Sample sizes were between 2 and 5 μl. The analytical procedure is described in detail by Baumann and Csicsery (*2*).

ACKNOWLEDGMENT

The author thanks Chevron Research Company for permission to publish this work.

LITERATURE CITED

(1) Baddeley, G., Holt, G., Voss, D., *J. Chem. Soc.* **1952**, p. 100.
(2) Baumann, F., Csicsery, S.M., *J. Chromatog.*, to be published.
(3) Condon, F.E., in "Catalysis," P.H. Emmett, Ed., Vol. **VI**, Chap. 2, Reinhold, Baltimore, Md., 1958.
(4) Holm, V.C.F., Clark A., *J. Catalysis* **2**, 16 (1963).
(5) MacIver, D.S., Wilmost, W.H., Bridges, J.M., *Ibid.*, **3**, 502 (1964).
(6) Myers, C.G., Sibbett, D.J., Ciapetta, F.G., *J. Phys. Chem.* **63**, 1032 (1959).
(7) Rossini, F.D., Zwolinski, B.J., Canjar, L.N., Ries, H.J., Bitler, L.P., Kerr, J.T., Beery, W.T., Dunlap, A.B., "Selected Values of Properties of Hydrocarbons and Related Compounds," API Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1959.
(8) Streitwieser, A., Jr., Reif, L., *J. Am. Chem. Soc.* **82**, 5003 (1960).

RECEIVED for review July 11, 1966. Accepted October 17, 1966.

Enthalpies of Solution and Formation of Some Uranium Oxides

GEORGE C. FITZGIBBON, D. PAVONE, and CHARLES E. HOLLEY, Jr.
University of California, Los Alamos Scientific Laboratory, Los Alamos, N. M.

The enthalpies of formation of U_4O_9, β-U_3O_7, and γ-UO_3 have been determined to be $\Delta H_{f\ 298.15^\circ K.}$ = −1078.1 ± 3.6, −818.4 ± 2.8, and −292.3 ± 1.4 kcal. per mole, respectively. The method used consisted of combining the known enthalpies of formation of $UO_{2.028}$ and U_3O_8 with data obtained from enthalpy of solution measurements of samples of U_4O_9, U_3O_7, and U_3O_8 and of mixtures of $UO_{2.028}$ and $UO_{2.993}$ of corresponding compositions. An aqueous 0.057*M* $Ce(SO_4)_2$–1.5*M* H_2SO_4 solution was used as the solvent.

URANIUM forms many oxides, including UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3, of which several may exist in more than one polymorphic form. In addition, wide homogeneity ranges exist for some of these oxides at moderately elevated temperatures. The enthalpies of formation of the uranium oxides are of considerable practical and theoretical interest. This paper presents the results of some work on the measurement of the enthalpies of solution of several uranium oxides, and oxide mixtures, in aqueous $Ce(SO_4)_2$–H_2SO_4 solutions, from which, given the enthalpies of formation of UO_2 and U_3O_8, the enthalpies of formation of U_4O_9, U_3O_7, and UO_3, can be calculated.

A review of the phase diagram and the enthalpies of formation of the uranium oxides, as of 1962, has been given by Rand and Kubaschewski (*9*). Table I lists their assessed values along with some recently determined experimental values, including the results reported here.

EXPERIMENTAL

The method involved measurement in a solution calorimeter of the differences in the enthalpies of solution obtained when U_4O_9, U_3O_7, or U_3O_8 was dissolved in 1.5*M* H_2SO_4 which was also 0.057*M* in $Ce(SO_4)_2$ and the enthalpy change obtained when corresponding mixtures of $UO_{2.028}$ and $UO_{2.993}$ were dissolved in the same solvent. The details of the solution calorimeter, its operation, and the procedures have been described (*5*). Briefly, the calorimeter is an isothermal solution calorimeter whose environmental temperature may be kept constant at any setting between 23° and 33° to within 0.001° in an 800-liter thermostatically controlled bath. The vacuum-jacketed, silver-bodied, platinum-lined calorimeter reaction vessel has a volume of ~450 cc., a thermal leak modulus of 0.005 per minute, and a heat capacity of 420 cal. per degree.

Within the reaction chamber are a heater, a thermistor, a borosilicate glass rod to which is attached a platinum stirrer, and a glass sample bulb. The heater consists of a 15.24-cm. length of 0.64-cm. O.D. platinum tubing, the lower end gold soldered, the upper end sealed to glass tubing which extends through the calorimeter lid and carries the heater leads. The platinum tubing contains 23 ohms of bifilarly wound, helically coiled, silk-covered manganin wire with leads to measure the voltage drop, located at the solution level. A Fenwal 2300-ohm thermistor is used as the sensing element to measure temperature differences up to 1.6° to within 0.0001°. A Brown recorder was modified to an automatic-changing, multiscale, self-balancing Wheatstone bridge, whose arm position is an indication of the resistance of the thermistor.

The energy equivalent is determined by passing a current from a precision voltage-regulated supply through the calorimeter heater and a 0.1-ohm standard resistor in series and measuring the voltage drops using a Rubicon Type

Table I. The Enthalpies of Formation of the Uranium Oxides

	$\Delta H_{f\,298^\circ\,K}$, Kcal./Mole				
	UO_2	U_4O_9	β-U_3O_7	U_3O_8	γ-UO_3
Rand and Kubaschewski (9)	−259.0 ± 0.6	−1078 ± 4		−854.1 ± 2.0	−293 ± 2
Cordfunke and Ailing (2)					−293.5 ± 1.0[a]
Vidavskii *et al.* (*12*)					−295.80 ± 0.45
Mukaibo *et al.* (*8*)			−815.7 ± 2.4 or −821.1 ± 2.1		
Duquesnoy and Marion (*3*)		−1073.3[b]			
This work		−1078.1 ± 3.6	−818.4 ± 2.8		−292.3 ± 1.4

[a] Cordfunke (*1*) has recently measured the enthalpies of formation of the other UO_3 polymorphs by solution calorimetry based on this value for γ-UO_3. [b] Calculated from Duquesnoy and Marion's measurements of the dissociation pressure of U_4O_9 with the assumption that $\Delta C_p = 0$.

B potentiometer and a Rubicon reflecting galvanometer. The input time is read directly from an electronic decade counter whose time base is derived from a 100-kc. crystal-controlled oscillator, accurate and stable to 0.01%.

The uranium oxides used were of high purity containing no other cations in amounts greater than 0.01%. Two methods of analysis were used to determine the stotchiometric composition of the oxides. The first method involved determination of the change of weight of the oxide sample upon ignition to U_3O_8 in an oxygen atmosphere at 750° C. using a standard combustion analysis apparatus. The water absorption tube invariably collected a small quantity of water during the ignition. In the case of $UO_{2.028}$, it is uncertain whether this water indicates the presence of adsorbed hydrogen or of molecular water, and calculations of the composition have been made for both alternatives. This method will be referred to as "analysis by ignition." The second analytical method involved determination of the quantity of cerous ion produced upon dissolution of an oxide sample in a stock solution of 0.057*M* ceric sulfate in 1.5*M* sulfuric acid. The remaining ceric ion was titrated with standardized ferrous sulfate solution using Fe-o-phenanthroline indicator. The quantity of cerous ion produced is a measure of the average valence of the uranium in the oxide sample from which its stoichiometric composition may be determined. This method will be referred to as "analysis by titration." The uncertainties given in the formulas are twice the standard deviations of the means of the results of repeated analyses.

$UO_{2.028}$. The uranium dioxide was stock material which had been stored in the laboratory atmosphere for several months so that its composition was not changing. Analysis by the titration method gave the formula $UO_{2.028\,\pm\,0.003}$. Analysis by ignition to U_3O_8 also gave $UO_{2.028}$ if the water obtained was considered to have come from adsorbed hydrogen, and $UO_{2.016}$ if the water came from adsorbed water. The value $UO_{2.028}$ was taken as correct. X-ray analysis gave lines of UO_2 only with $a = 5.4690 \pm 0.0003$ A.

U_4O_9. This material was prepared by low temperature oxidation of UO_2. Analysis by titration gave the formula $U_4O_{8.996\,\pm\,0.009}$ while analysis by ignition to U_3O_8 gave the formula $U_4O_{9.003}$. The formula U_4O_9 was taken as correct. X-ray analysis showed a cubic cell with $a = 5.4421 \pm 0.0003$ A with some extra weak lines.

U_3O_7. This material is referred to by Westrum and Grønvold as β-U_3O_7 in their heat capacity work (*13*). Analysis by titration gave the formula $U_3O_{7.005\,\pm\,0.012}$ ($UO_{2.335\,\pm\,0.004}$) while analysis by ignition gave $U_3O_{6.990\,\pm\,0.003}$ ($UO_{2.330\,\pm\,0.001}$). The formula U_3O_7 was taken as correct. X-ray analysis showed only lines of tetragonal U_3O_7 with $a = 5.38 \pm 0.01$ A, $c = 5.55 \pm 0.01$ A, and $c/a = 1.032$. It thus corresponds to the phase sometimes designated as γ_1 (*11*).

U_3O_8. The U_3O_8 was stock material dried at 300° C. for 2 hours. Its stoichiometry was confirmed by titration and by ignition. X-ray analysis showed the lines for U_3O_8 only.

UO_3. This was stock material which had been dried at 700° C. for 2 hours. Analysis by titration gave the formula $UO_{2.993\,\pm\,0.006}$. X-ray analysis showed the lines for γ-UO_3 only.

RESULTS

The results are presented in Tables II and III.

CALCULATIONS

The results from Table II are shown plotted in Figure 1. As might be expected, the points fall nicely on a straight line, the equation of which was determined by least squares to be $-\Delta H_{\text{soln.}} = (118.1 \pm 1.1) - (32.59 \pm 0.42)x$ where x is the O/U ratio, and the uncertainties are twice the standard deviations. The data at O/U = 2.028 show a much wider range of values than at the other compositions. The deviations from the mean of the extreme high and low values are about equal and neither may be excluded on statistical grounds. The average value falls very near to the straight line. From the equation, the enthalpies of solution at various O/U ratios were calculated with the results shown in Table IV.

ENTHALPIES OF FORMATION

The values for the enthalpies of formation of the uranium oxides calculated from the results of these experiments are all based upon the enthalpy of formation of U_3O_8 and the difference between it and the enthalpy of formation of $UO_{2.028}$. These will be discussed first, followed by a calculation of the enthalpies of formation of the other oxides.

U_3O_8. The enthalpy of formation of U_3O_8 has been assessed by Rand and Kubachewski (*9*) and their value of −854.1 ± 2.0 kcal. per mole is accepted, which gives ΔH_f ($UO_{2.667}$) = −284.7 ± 0.7.

$UO_{2.028}$. The enthalpies of combustion of $UO_{2.014}$, $UO_{2.025}$, and $UO_{2.039}$ to U_3O_8 have been determined by Huber *et al.* to be −74.82 ± 0.07 (*4*), −74.31 ± 0.04 (*6*), and −73.25 ± 0.05 (*7*) kcal. per mole of U_3O_8 produced, respectively.

By interpolation, the value for $UO_{2.028}$ is found to be −74.0 ± 0.1 kcal. per mole U_3O_8. From this, the enthalpy of formation of $UO_{2.028}$ is calculated to be −260.0 ± 0.7 kcal. per mole.

Table II. Enthalpies of Solution of Uranium Oxides—Mixtures of $UO_{2.028}$ and $UO_{2.993}$

Solvent—475 grams of 1.5M H_2SO_4 + 0.057M $Ce(SO_4)_2$

$UO_{2.028}$ Mass of Oxide, G.	$UO_{2.993}$ Mass of Oxide, G.	Total Mmoles of Uranium as Oxide	Formula, O/U	Energy Equiv., Cal./Arbitrary Unit	ΔT, Arbitrary Unit	Energy from Solution Kcal./Mole U
2.8915		10.6902	2.028	18.56	30.397	52.774
2.8912		10.6891	2.028	18.35	30.456	52.284
2.8915		10.6902	2.028	18.37	30.013	51.574
2.8920		10.6920	2.028	18.74	30.437	53.347
2.8906		10.6868	2.028	18.37	30.266	52.026
2.8924		10.6935	2.028	18.49	29.433	50.893
2.1646	0.7644	10.6763	2.270	18.556	25.46	44.252
2.16465	0.7643	10.6760	2.270	18.249	25.64	43.827
2.1649	0.76415	10.6765	2.270	18.237	25.75	43.894
2.1641	0.7637	10.6719	2.270	18.170	25.81	43.944
2.16435	0.76415	10.6744	2.270	18.257	25.86	44.230
1.9570	0.9859	10.6834	2.339	18.597	24.000	41.778
1.95715	0.9859	10.6840	2.339	18.550	24.047	41.751
1.9569	0.9856	10.6820	2.339	18.576	23.935	41.623
1.9570	0.9860	10.6837	2.339	18.573	23.975	41.679
1.9568	0.9860	10.6830	2.340	18.464	24.087	41.631
1.9572	0.9860	10.6845	2.339	18.838	23.789	41.943
0.9777	2.0221	10.6870	2.667	18.208	18.216	31.036
0.9780	2.0216	10.6863	2.666	18.107	18.184	30.811
0.9779	2.0220	10.6873	2.667	18.180	18.307	31.142
0.9784	2.0222	10.6898	2.666	18.219	18.274	31.145
0.9777	2.0221	10.6870	2.667	18.231	18.373	31.343
0.9775	2.0217	10.6848	2.667	18.240	18.360	31.343
0.9627	2.03825	10.6878	2.672	18.400	18.096	31.037
0.9624	2.03813	10.6862	2.672	18.602	17.784	30.951
0.9636	2.03800	10.6905	2.671	18.550	17.858	30.977
0.9631	2.03800	10.6886	2.671	18.496	17.900	30.968
	3.0560	10.688	2.993	18.360	11.957	20.540
	3.0558	10.688	2.993	18.380	11.907	20.476
	3.0635	10.715	2.993	18.460	11.985	20.648
	3.06445	10.718	2.993	18.222	12.092	20.548
	3.0660	10.723	2.993	18.414	12.296	21.115
	3.0639	10.716	2.993	18.400	11.995	20.596

III. Enthalpies of Solution of Uranium Oxides—U_4O_9, U_3O_7, U_3O_8

Solvent—475 grams of 1.5M H_2SO_4 + 0.057M $Ce(SO_4)_2$

	Mass of Oxide, G.	Mmoles of Uranium as Oxide	Energy Equivalent, Cal./Arbitrary Unit	ΔT, Arbitrary Unit	Energy from Solution, Kcal./Mole U	Δ
U_4O_9	2.9285	10.687	18.759	24.494	42.994	0.345
	2.9288	10.688	18.450	24.587	42.443	0.206
	2.9286	10.687	18.770	24.248	42.587	0.062
	2.9287	10.687	18.727	24.232	42.462	0.187
	2.9283	10.686	18.250	25.037	42.760	0.111
				Av.	42.649	0.182
			2 × standard deviation of mean		0.21	
U_3O_7	2.9447	10.694	18.598	22.781	39.581	0.137
	2.9431	10.688	18.594	22.645	39.396	0.048
	2.9435	10.690	18.521	22.694	39.319	0.125
	2.9434	10.689	18.532	22.685	39.330	0.114
	2.9431	10.688	18.576	22.782	39.596	0.152
				Av.	39.444	0.115
			2 × standard deviation of mean		0.12	
U_3O_8	3.0002	10.685	18.683	15.873	27.755	0.063
	3.0002	10.685	18.573	15.832	27.520	0.298
	3.0009	10.688	18.762	15.861	27.842	0.024
	3.0002	10.685	18.742	16.018	28.096	0.278
	3.0003	10.686	18.612	16.007	27.879	0.021
				Av	27.818	0.145
			2 × standard deviation of mean		0.19	

γ-$UO_{2.993}$. The enthalpy of formation of $UO_{2.993}$ is found from the following set of reactions:

$$1.985\ UO_{2.993}(c) + 1.015\ UO_{2.028}\ (c) + 2H_2SO_4\ (aq.,\ 1.5M) + 2Ce(SO_4)_2(aq.,\ 0.057M) \rightarrow 3UO_2SO_4(aq.) + Ce_2(SO_4)_3(aq.) + 2H_2O(soln.),\ \Delta H_1 \quad (1)$$

$$U_3O_8\ (c) + 2H_2SO_4\ (aq.,\ 1.5M) + 2\ Ce(SO_4)_2\ (aq.,\ 0.057M) \rightarrow 3\ UO_2SO_4\ (aq.) + Ce_2(SO_4)_3\ (aq.) + 2H_2O(soln.),\ \Delta H_2 \quad (2)$$

Subtracting,

$$1.985\ UO_{2.993} + 1.015\ UO_{2.028} \rightarrow U_3O_8 \qquad \Delta H_3 = \Delta H_1 - \Delta H_2 \quad (3)$$

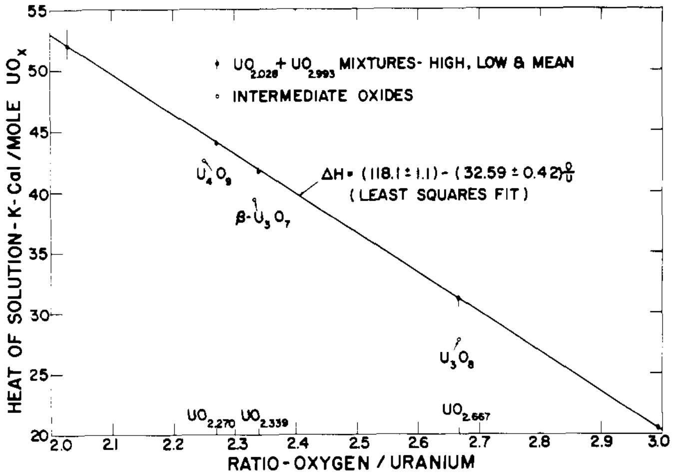

Figure 1. Heats of solution of uranium oxides

ΔH_1 is found from Table IV at O/U = 2.667 to be equal to 3(−31.17 ± 0.16) = −93.51 ± 0.48 kcal. ΔH_2 is found from Table III to be 3(−27.82 ± 0.19) = −83.46 ± 0.57 kcal.

Thus

$$\Delta H_3 = -10.05 \pm 0.75.$$

But

$$\Delta H_3 = \Delta H_f(U_3O_8) - 1.985\ \Delta H_f(UO_{2.993}) - 1.015\ \Delta H_f(UO_{2.028}),$$

from which

$$\Delta H_f(UO_{2.993}) = \frac{\Delta H_f(U_3O_8) - 1.015\ \Delta H_f(UO_{2.028}) - \Delta H_3}{1.985}$$

$$= -292.2 \pm 1.4 \text{ kcal. per mole}$$

The uncertainties in $\Delta H_f(U_3O_8)$ and $\Delta H_f(UO_{2.028})$ are not independent, since the latter depends upon the former.

U_3O_7. In a similar manner

$$\Delta H_f(U_3O_7) = 0.949\ \Delta H_f(UO_{2.993}) + 2.051\ \Delta H_f(UO_{2.028}) + \Delta H_4$$

where ΔH_4 is the difference between the enthalpies of solution of 0.949 $UO_{2.993}$ + 2.051 $UO_{2.028}$ and U_3O_7 as found in the tables.

From this

$$\Delta H_f(U_3O_7) = -818.4 \pm 2.8 \text{ kcal. per mole}$$

and

$$\Delta H_f(UO_{2.333}) = -272.8 \pm 0.9 \text{ kcal. per mole.}$$

U_4O_9. Again in a similar manner

$$\Delta H_f(U_4O_9) = 0.920\ \Delta H_f(UO_{2.993}) + 3.080\ \Delta H_f(UO_{2.028}) + \Delta H_5$$

where ΔH_5 is the difference between the enthalpies of solution of 0.920 $UO_{2.993}$ + 3.080 $UO_{2.028}$ and U_4O_9 as found in the tables. From this

$$\Delta H_f(U_4O_9) = -1078.1 \pm 3.6 \text{ kcal. per mole}$$

and

$$\Delta H_f(UO_{2.250}) = -269.5 \pm 0.9 \text{ kcal. per mole}$$

γ-UO_3. The values of the enthalpies of formation of the uranium oxides per gram atom of uranium were plotted *vs.* O/U ratio and the value for γ-UO_3 was found by extrapolation to be $\Delta H_f(\gamma\text{-}UO_3)$ = −292.3 ± 1.4 kcal. per mole.

Table IV. Enthalpies of Solution of $UO_{2.028}$ – $UO_{2.993}$ Mixtures at given O/U Ratios

O/U	$\Delta H_{\text{soln.}}$ Kcal./Mole U
2.028	−51.99 ± 0.24
2.250	−44.76 ± 0.17
2.333	−42.05 ± 0.15
2.667	−31.17 ± 0.16
2.993	−20.55 ± 0.26

DISCUSSION

The differences in the enthalpies of formation of the various uranium oxides are known with a considerably smaller uncertainty than the value for the enthalpy of formation of U_3O_8; thus, most of the uncertainty indicated comes from the uncertainty in the value for U_3O_8.

The results obtained in this work are in quite satisfactory agreement with previous measurements and estimates. The case of γ-UO_3, where other recent precise measurements are available, perhaps warrants a little discussion. These results and those of Cordfunke (2) differ by 1.2 kcal. per mole, both being based on the same value for U_3O_8. With their accompanying uncertainties, they appear to be in agreement, but when the uncertainty in the value for U_3O_8 is subtracted out, the remaining combined uncertainty is about 0.6 kcal. (0.2 kcal. for Cordfunke, 0.4 kcal. for the present measurements) so that the difference probably is significant. Cordfunke measured the dissociation pressure of γ-UO_3 at temperatures between 500° and 600° C. U_3O_8 has a trigonal modification above 400° C. (*10*), and a value of a few kilocalories for the enthalpy of transformation would provide agreement between his results and the authors'.

The value for the enthalpy of formation of γ-UO_3 obtained by Vidavskii *et al.* (*12*), is based on their measurements of the enthalpy of solution of γ-UO_3 in aqueous HF and literature values for the enthalpies of formation of H_2O, UF_6, aqueous HF, and the enthalpy of solution of UF_6, and is, thus, independent of the value for the enthalpy of formation of U_3O_8. Their results and the authors' for γ-UO_3 differ by somewhat more than the estimated uncertainties involved.

ACKNOWLEDGMENT

The authors are pleased to acknowledge the help of Helen D. Cowan, chemical analysis, and Finley Ellinger, x-ray analysis. The U_3O_7 was obtained from E. F. Westrum, Jr., of the University of Michigan.

LITERATURE CITED

(1) Cordfunke, E.H.P., *J. Phys. Chem.* **68**, 3353–6 (1964).
(2) Cordfunke, E.H.P., Ailing, P., *Trans. Faraday Soc.* **61**, 50–3 (1965).
(3) Duquesnoy, A., Marion, F., *Compt. rend.* **258**, 4550–2 (1964).
(4) Farr, J.D., Huber, E.J., Jr., Head, E.L., Holley, C.E., Jr., *J. Phys. Chem.* **63**, 1455 (1959).
(5) Fitzgibbon, G.C., Pavone, D., Huber, E.J., Jr., Holley, C.E., Jr., "A New Solution Calorimeter," Los Alamos Scientific Laboratory Report **LA-3031**, 1964.
(6) Huber, E.J., Jr., Head, E.L., Holley, C.E., Jr., *J. Phys. Chem.* **67**, 1730 (1963).
(7) Huber, E.J., Jr., Storms, E.K., Los Alamos Scientific Laboratory, Los Alamos, N. M., unpublished data.
(8) Mukaibo, T., Naito, K., Sato, K., Uchijimo, T., *Thermodyn. Nucl. Mater., Proc. Symp., Vienna,* **1962**, p. 723.
(9) Rand, M.H., Kubaschewski, O., "The Thermochemical Properties of Uranium Compounds," Interscience, New York, 1963.
(10) Siegel, S., *Acta Cryst.* **8**, 617–9 (1955).
(11) "Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases," C.E. Holley, Jr., Ed., Tech. Repts. Ser. No. **39**, International Atomic Energy Agency, Vienna, 1965.
(12) Vidavskii, L.M., Byakhova, N.J., Ippolitova, E.A., *Zh. Neorg. Khim.* **10**, 1746–7 (1965).
(13) Westrum, E.F., Jr., Grønvold, F., *Phys. Chem. Solids* **23**, 39–53 (1962).

RECEIVED for review July 11, 1966. Accepted October 20, 1966. Work done under the auspices of the U. S. Atomic Energy Commission.