Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and 1 bar and at higher temperatures--Preliminary models for the origin of coffinite deposits

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Abstract

Thermodynamic values for 110 uranium-bearing phases and 28 aqueous uranium solution species (298.15 K and 1 bar) are tabulated based upon evaluated experimental data (largely from calorimetric experiments) and estimated values. Molar volume data are given for most of the solid phases. Thermodynamic values for 16 uranium-bearing phases are presented for higher temperatures in the form of and as a supplement to U.S. Geological Survey Bulletin 1452 (Robie et al., 1979).

The internal consistency of the thermodynamic values reported herein is dependent upon the reliability of the experimental results for several uranium phases that have been used as secondary calorimetric reference phases. The data for the reference phases and for those phases evaluated with respect to the secondary reference phases are discussed.

A preliminary model for coffinite formation has been proposed together with an estimate of the free energy of formation of coffinite. Free energy values are estimated for several other uranium-bearing silicate phases that have been reported as secondary uranium phases associated with uranium ore deposits and that could be expected to develop wherever uranium is leached by groundwaters.

I: Evaluation of experimental and estimated thermodynamic data, and properties at 298.15 K and 1 bar (10^5 Pascals). Preliminary models for the origin of coffinite deposits.

Introduction

Several reviews of the thermodynamic properties of uranium bearing phases and aqueous species have been published recently (e.g., Wagman, et al., 1981; Lemire and Tremaine, 1980; Langmuir, 1978; and Cordfunke and O'Hare, 1978). These reviews draw upon the same experimental data and, in general, the same interpretation of the experimental data for those phases evaluated in two or more of these studies. Although there has been moderate experimental activity on phases bearing uranium in the last twenty years, many of the naturally occurring phases have not been studied. Where data are lacking it has been necessary to estimate thermodynamic properties and where the experimental data is sparse or poorly defined, it has been necessary to make simplifying assumptions in order to calculate thermodynamic values.

This report contains a review of some of the experimental data and interpretations for uranium phases and aqueous species that may be of importance in evaluating the origin of uranium ore bodies or the evolution of such ore bodies, in developing programs for the solution mining of low grade uranium deposits or mine dumps, in the study of radioactive waste and in the containment of such waste, and finally, that may be of importance in reactions within breeder reactors.

The thermodynamic data listed in Tables 1 and 2 represent, to the extent possible, an internally consistent data set that has been evaluated and developed by the stepwise or sequential method. The majority of data are tied to the enthalpy of formation of U_3O_8 as given by Huber and Holley (1969) or to secondary standards such as -UO_3, UO_2Cl_2, UCl_4, and UO_2. Consequently, few cross links are available within the system that would allow the use of the simultaneous regression approach of Haas and Fisher (1976) to identify erroneous data. Where a reaction involving a reference phase is found to be in error, all thermodynamic data based upon that reaction must be corrected. In order to facilitate that process, a brief description of the reaction scheme for each phase is provided in this study along with a reference to the experimental study that contains a detailed description of the thermochemical cycle.

Ancillary thermodynamic values required in the thermochemical cycles cited in this study are from Robie et al. (1979) unless otherwise stated. The atomic weights and physical constants are also taken from Robie et al.

U_3O_8

Triuranium octaoxide is the primary reference compound in this network. Selection of this material was predicated by its use as the reference phase for γ-UO_3 and UO_2Cl_2, the two phases to which most other

Table 1. Thermodynamic properties of selected uranium bearing phases at 298.15 K and 1 bar. Estimated values are enclosed in parentheses. Uncertainties are listed below values

Name formula and (references)*	Entropy	Molar volume	Enthalpy of formation	Gibbs free energy of formation
	J/(mol·K)	cm^3	kJ/mol	kJ/mol
Oxides, hydroxides and multiple oxides				
Uraninite:	77.03	24.618	-1084.910	-1031.710
UO_2 (133;133;133)	0.24	0.014	1.000	1.000
Triuranium heptaoxide (alpha):	247.65	71.93		
U_3O_7 (158;74;)	0.75	0.10		
Triuranium heptaoxide (beta):	250.53	71.63	-3425.400	-3191.200
U_3O_7 (158;74;49)	0.75	0.10	11.700	11.700
Tetrauranium ennanoxide:	335.91	96.57	-4512.000	-4276.900
U_4O_9 (120;116;49)	0.67	0.10	15.100	15.200
Triuranium octaoxide:	282.59	100.32	-3574.800	-3369.400
U_3O_8 (157;45;23)	0.50	0.03	1.000	1.200
Hydrated uranium dioxide:				
$UO_2 \cdot 2H_2O$ (crystals) (;;166)				(-1494.600)
				(4.000)
$UO_2 \cdot 2H_2O$ (amorphous) (;;166)				(-1483.000)
				(8.000)
Uranium peroxide dihydrate:		72.46	-1782.400	
$UO_4 \cdot 2H_2O$ (;152;30)		0.05	4.200	
Studite:		102.60	-2384.500	
$UO_4 \cdot 4H_2O$ (;152;30)		0.05	2.100	
Uranyl trioxide (gamma):	96.11	35.56	-1223.800	-1145.700
UO_3 (156;133;23)	0.20	0.04	1.220	1.250
Uranyl trioxide (beta):	96.32	34.46	-1220.054	-1142.000
UO_3 (156;45;34)	0.21	0.05	2.100	2.100
Uranyl trioxide (alpha):	99.41	34.05	-1216.700	-1141.700
UO_3 (156;45;25)	0.21	0.02	2.100	2.100
Uranyl trioxide (delta):			-1209.200	
UO_3 (;;25)			2.100	

Table 1. continued.

Name formula and (references)*	Entropy J/(mol·K)	Molar volume cm^3	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
Uranyl trioxide (epsilon):		32.76	-1216.500	
UO_3 (;45;25)		0.10	2.100	
Uranyl trioxide (amorphous):			-1207.500	
UO_3 (;;25)			2.100	
Uranyl trioxide (cubic):		42.92	-1217.500	
$UO_{2.9}$ (;151;25)		0.03	2.100	
Uranyl trioxide hemihydrate**:		42.57	-1379.900	
$UO_3\cdot 0.5H_2O$ (;116;30)		0.06	1.300	
Dehydrated schoepite**:	(150.)	45.5	-1491.600	(-1370.500)
$UO_3\cdot 0.85H_2O$ (166;41;25)	(10.)	0.1	1.300	(4.000)
Dehydrated paraschoepite**:	(134.)	52.29	-1533.400	(-1397.100)
β-$UO_3\cdot H_2O$ (166;116;25)	(8.)	0.10	1.200	(4.000)
Dehydrated schoepite**:	(156.)	46.40	(-1534.500)	(-1404.900)
α-$UO_3\cdot H_2O$ (166;116;166)	(8.)	0.10	(4.000)	(4.000)
Paraschoepite**:	(174.)	68.07	(-1826.000)	(-1632.000)
α-$UO_3\cdot 2H_2O$ (166;17;166)	(8.)	0.20	(4.000)	(4.000)
Schoepite**:	(190.)	66.70	-1827.200	(-1638.200)
β-$UO_3\cdot 2H_2O$ (166;17;25)	(5.)	0.20	2.100	(3.000)
Uranyl trioxide dihydrate:		54.68	-1530.900	
ϵ-$UO_3\cdot 2H_2O$ (;27;25)		0.06	1.200	
Non-stoichiometric UO_3 hydrates:				
$UO_{2.86}\cdot 0.5H_2O$ (;;30)			-1366.900	
			4.200	
$UO_{2.86}\cdot 1.5H_2O$ (;;30)			-1666.100	
			1.700	

Table 1. continued.

Name formula and (references)*	Entropy	Molar volume	Enthalpy of formation	Gibbs free energy of formation
	J/(mol·K)	cm^3	kJ/mol	kJ/mol
Sulfides, selenides, selenates, selenites, and tellurides				
Uranium monosulfide:	77.99	24.84	-306.300	-305.080
US (160;116;160)	0.21	0.03	14.600	14.600
Uranium disulfide (beta):	110.54	37.47	-527.000	-526.000
US_2 (70;116;173)	0.21	0.03	10.000	10.000
Uranium trisulfide:	138.45	57.55	-549.400	-547.240
US_3 (70;116;173)	0.21	0.03	2.000	2.000
Uranium selenide:	96.52	28.47		
USe (156;116;)	0.22	0.03		
Uranium diselenide:	133.8	45.69		
USe_2 (156;116;)	0.2	0.05		
Uranium triselenide:	(177.0)	65.40		
USe_3 (99;116;)	(8.0)	0.04		
Uranyl selenate (alpha):			-1539.300	
UO_2SeO_4 (;;32)			3.600	
Uranyl selenite:			-1522.200	
UO_2SeO_3 (;;32)			0.900	
Uranium telluride:	(111.7)	35.02	(-182.400)	
UTe (99;116;99)	(12.0)	0.04	(20.000)	
Uranium ditelluride:	(150.6)	48.50	(-318.000)	
UTe_2 (99;116;99)	(12.0)	0.06	(60.000)	
Halides				
Uranium tetrabromide:	238.50	100.5	-802.500	-767.790
UBr_4 (173;45;173)	0.80	0.1	0.500	0.600
Uranium trichloride:	158.95	62.04	-866.500	-799.130
UCl_3 (65;45;173)	0.40	0.06	4.000	2.000
Uranium tetrachloride:	196.60	77.60	-1018.390	-928.990
UCl_4 (65;45;35,48)	0.50	0.03	4.200	4.200

Table 1. continued.

Name formula and (references)*	Entropy J/(mol·K)	Molar volume cm^3	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
Uranium trifluoride:	123.4	32.95	-1508.500	-1439.600
UF_3 (173;45;33)	0.5	0.08	5.500	6.000
Uranium tetrafluoride:	151.67	46.88	-1920.000	-1829.300
UF_4 (15;45;33)	0.17	0.08	3.700	4.000
Uranium hexafluoride:	227.6	69.55	-2197.700	-2069.200
UF_6 (12;45;79)	1.2	0.02	1.800	2.000
Uranyl bromide:	(170.)		-1137.200	(-1038.500)
UO_2Br_2 (166;;127)	(6.)		1.300	(2.500)
Uranyl bromide hydrate:	(212.5)		-1455.600	(-1300.100)
$UO_2Br_2 \cdot H_2O$ (166;;127)	(6.0)		1.300	(2.500)
Uranyl bromide dihydrate:	(255.)		-1958.500	(-1746.100)
$UO_2Br_2 \cdot 2H_2O$ (166;;127)	(6.)		1.300	(2.500)
Uranyl bromide trihydrate:	(297.5)		-2057.700	(-1788.400)
$UO_2Br_2 \cdot 3H_2O$ (166;;127)	(6.)		1.300	(2.500)
Uranyl chloride:	150.54	63.20	-1243.070	-1145.280
UO_2Cl_2 (68;116;35,23)	0.42	0.03	2.100	2.200
Uranyl fluoride:	135.55	47.98	-1653.900	-1557.700
UO_2F_2 (29;162;31,29)	0.50	0.04	1.200	1.200
Uranyl iodide:	(182.)		(-1000.000)	(-943.500)
UO_2I_2 (166;;127)	(10.)		(4.000)	(6.000)
Carbonates and nitrates				
Rutherfordine:	(142.7)	57.69	-1704.100	(-1577.000)
UO_2CO_3 (166;18;166)	(2.0)	0.10	2.000	(2.100)
Sharpite:	(192.)		(-1982.300)	-1800.400
$UO_2CO_3 \cdot H_2O$ (166;;166)	(10.)		(12.000)	4.000
Liebigite:				-6226.000
$Ca_2UO_2(CO_3)_3 \cdot 10H_2O$ (;;170)				12.000
Swartzite:				-6607.000
$CaMgUO_2(CO_3)_3 \cdot 12H_2O$ (;;170)				10.000

Table 1. continued.

Name formula and (references)*	Entropy J/(mol·K)	Molar volume cm^3	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
Bayleyite:				-7924.000
$Mg_2UO_2(CO_3)_3 \cdot 18H_2O$ (;;170)				10.000
Andersonite:				-5651.000
$Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$ (;;170)				24.000
Rabbittite:				(-13525.000)
$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18H_2O$ (;;166)				(30.000)
Schroeckingerite:				(-8094.000)
$NaCa_3(UO_2)(CO_3)_3(SO_4)F \cdot 10H_2O$ (;;166)				(30.000)
Voglite:				(-5791.400)
$Ca_2Cu(UO_2)(CO_3)_4 \cdot 6H_2O$ (;;166)				(35.000)
Uranyl nitrate:	(240.)		-1368.000	(-1122.800)
$UO_2(NO_3)_2$ (30;;30)	(5.)		17.000	(20.000)
Uranyl nitrate hydrate:	(297.)		(-1674.000)	
$UO_2(NO_3)_2 \cdot H_2O$ (166;;166)	(5.)		(17.000)	
Uranyl nitrate dihydrate:	334.70		-1978.600	-1622.500
$UO_2(NO_3)_2 \cdot 2H_2O$ (30;;30)	7.10		2.500	2.500
Uranyl nitrate trihydrate:	361.50		-2281.500	-1863.900
$UO_2(NO_3)_2 \cdot 3H_2O$ (30;;30)	3.80		1.300	1.300
Uranyl nitrate hexahydrate:	505.60	182.08	-3168.100	-2584.800
$UO_2(NO_3)_2 \cdot 6H_2O$ (30;45;30)	2.50	0.05	2.100	2.100
Sulfates and phosphates				
Uranium sulfate:	(180.)		-2309.600	(-2084.600)
$U(SO_4)_2$ (30;;30)	(21.)		12.600	(15.000)
Uranium sulfate tetrahydrate:	(338.)	139.39	-3483.200	(-3027.200)
$U(SO_4)_2 \cdot 4H_2O$ (166;45;30)	(21.)	0.06	6.300	(6.800)

Table 1. continued.

Name formula and (references)*	Entropy	Molar volume	Enthalpy of formation	Gibbs free energy of formation
	J/(mol·K)	cm^3	kJ/mol	kJ/mol
Uranium sulfate octahydrate: $U(SO_4)_2 \cdot 8H_2O$ (;;30)			-4662.600 6.300	
Uranyl sulfate (beta): UO_2SO_4 (30;;32,30)	(163.) (8.)		-1845.100 1.200	(-1685.700) (2.000)
Uranyl sulfate 2.5-hydrate: $UO_2SO_4 \cdot 2.5H_2O$ (30;;30)	245.60 7.5		-2607.500 1.200	-2298.900 1.500
Uranyl sulfate trihydrate: $UO_2SO_4 \cdot 3H_2O$ (166;45;30)	(266.8) (10.0)	108.34 0.06	-2748.900 4.200	(-2411.800) (5.000)
Uranyl sulfate 3.5-hydrate: $UO_2SO_4 \cdot 3.5H_2O$ (30;;30)	287.90 7.50		-2901.600 1.200	-2536.100 1.500
Artificial zippeite: $(UO_2)_3(OH)_2(SO_4)_2 \cdot 8H_2O$ (166;45;166)	(760.) (10.)	331.73 0.10	(-7625.000) (10.000)	(-6703.000) (12.000)
Zippeite: $K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$ (;;169)				-12603.000 20.000
Sodium zippeite: $Na_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$ (;;169)				-12523.000 20.000
Cobalt zippeite: $Co_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$ (;;169)				-12695.000 20.000
Nickel zippeite: $Ni_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$ (;;169)				-12983.000 20.000
Magnesium zipperite: $Mg_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$ (;;169)				-13506.000 20.000
Zinc zippeite: $Zn_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$ (;;169)				-12870.000 20.000
Hydrogen-autunite: $HUO_2PO_4 \cdot 4H_2O$ (89;134;89)	(330.5) (5.0)	134.2 0.1	(-4621.900) (6.000)	-4217.500 6.000

Table 1. continued.

Name formula and (references)*	Entropy J/(mol·K)	Molar volume cm^3	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
		Uranates		
Barium monouranate:	153.97	58.08	-1997.100	-1887.070
$BaUO_4$ (108;116;108,107)	0.31	0.02	2.100	2.100
Calcium monouranate:	(144.3)	45.91	-2001.700	(-1895.000)
$CaUO_4$ (107;116;107)	(8.0)	0.04	2.100	(3.000)
Cesium monouranate:	219.66	85.44	-1929.800	-1807.140
Cs_2UO_4 (117;45;110,108,30)	0.45	0.09	1.500	1.500
Cesium diuranate (beta):	(331.8)		-3219.400	(-3023.400)
$Cs_2U_2O_7$ (30;;113,108)	(8.2)		8.000	(10.000)
Lithium uranium trioxide:		38.24	-1522.100	
$LiUO_3$ (;116;167)		0.04	1.700	
Lithium monouranate:	(133.)	43.95	-1970.100	(-1855.000)
Li_2UO_4 (111;116;111,108)	(6.)	0.10	4.000	(6.000)
Magnesium monouranate:	131.90	44.70	-1857.000	-1749.300
$MgUO_4$ (30;116;106)	0.50	0.04	1.300	1.300
Potassium uranium trioxide:		47.55	-1522.900	
KUO_3 (;116;167)		0.03	1.600	
Potassium monouranate:	(180.3)	74.12	-1920.300	(-1798.100)
K_2UO_4 (111;45;111,108)	(6.3)	0.08	4.000	(5.000)
Sodium uranium trioxide:	132.84	42.36	-1494.600	-1412.200
$NaUO_3$ (93;116;166)	0.13	0.03	1.600	1.600
Sodium monouranate (alpha):	166.00	58.55	-1890.200	-1771.800
Na_2UO_4 (119;45;109,28)	0.30	0.07	4.500	4.500
Sodium monouranate (beta):	(166.8)	60.84	-1880.000	(-1761.800)
Na_2UO_4 (166;45;109,28)	(2.0)	0.07	4.500	(4.700)
Sodium diuranate:		95.34	-3195.300	
$Na_2U_2O_7$ (;45;28)		0.05	2.500	
Trisodium uranium tetraoxide:	198.20		-2021.700	-1897.600
Na_3UO_4 (118;;115)	0.40		6.000	6.000

Table 1. continued.

Name formula and (references)*	Entropy	Molar volume	Enthalpy of formation	Gibbs free energy of formation
	J/(mol·K)	cm^3	kJ/mol	kJ/mol
Tetrasodium uranium pentaoxide:		80.21	-2454.800	
Na_4UO_5 (;28;28)		0.10	2.500	
6-sodium 7-uranium 24-oxide:			-11348.000	
$Na_6U_7O_{24}$ (;;28)			8.000	
Rubidium uranium trioxide:		48.65	-1520.900	
$RbUO_3$ (;116;167)		0.05	1.700	
Rubidium monouranate:	(202.9)	78.62	-1923.000	(-1823.300)
Rb_2UO_4 (111;116;111,108)	(6.3)	0.07	4.000	(5.000)
Strontium monouranate (alpha):		53.60	-1985.300	
Sr_2UO_4 (;116;30)		0.02	2.100	
Strontium monouranate (beta):			-1986.600	
Sr_2UO_4 (;;30)			2.100	
Distrontium uranium pentaoxide:		77.85	-2625.900	
Sr_2UO_5 (;116;30)		0.04	2.500	
Distrontium triuranium 11-oxide:			-5234.200	
$Sr_2U_3O_{11}$ (;;30)			3.300	
Tristrontium uranium hexaoxide:		94.83	-3248.000	
Sr_3UO_6 (;116;30)		0.03	2.500	
		Silicates		
Coffinite:		46.12		(-1886.000)
$USiO_4$ (;45;166)		0.06		(20.000)
Soddyite:				(-3685.000)
$(UO_2)_2(SiO_4)\cdot 2H_2O$				(20.000)
(;45;166)				
Uranophane:***		224.9		(-6213.000)
$Ca(H_3O)_2(UO_2)_2(SiO_4)_2\cdot 3H_2O$		0.1		(25.000)
(;141;166)				

Table 1. continued.

Name formula and (references)*	Entropy J/(mol·K)	Molar volume cm^3	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
Boltwoodite:*** $K(H_3O)UO_2(SiO_4)$ (;;166)				(-2695.000) (20.000)
Sodium boltwoodite:*** $Na_{.7}K_{.3}(H_3O)UO_2(SiO_4)\cdot H_2O$ (;;166)				(-2919.500) (20.000)
Kasolite:*** $Pb(UO_2)SiO_4\cdot H_2O$ (;;166)				(-2480.000) (20.000)
Sklodowskite:*** $Mg(H_3O)_2(UO_2)_2(SiO_4)_2\cdot 4H_2O$ (;;166)				(-6319.000) (25.000)
Cuprosklodowskite:*** $Cu(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$ (;;166)				(-5827.000) (25.000)
Weeksite:*** $K_2(UO_2)_2(Si_2O_5)_3\cdot 4H_2O$ (;;166)		273.5 0.2		(-9043.000) (25.000)
Haiweeite:*** $Ca(UO_2)_2(Si_2O_5)_3\cdot 5H_2O$ (;;166)				(-9396.000) (25.000)

* References: Reference numbers are given in the form (A;B;C), where A represents references to the entropy, B to the molar volume, and C to the enthalpy or Gibbs free energy of formation. Multiple references to a property are separated by a comma.

** The structures of β-$UO_3\cdot 2H_2O$, α-$UO_3\cdot H_2O$, and $UO_3\cdot 0.5H_2O$ are related and should be expressed as β-$U_2O_5(OH)_2\cdot 3H_2O$, α-$U_2O_5(OH)_2\cdot H_2O$, and $U_2O_5(OH)_2$ (see text and Porte et al.,1962). The structures of α-$UO_3\cdot 2H_2O$ and β-$UO_3\cdot H_2O$ are also related and should be given as α-$UO_2(OH)_2\cdot H_2O$ and β-$UO_2(OH)_2$ (see text and Porte et al.,1962).

*** The formulas are based upon the work of Stohl and Smith (1981).

Table 2. Thermodynamic properties of selected aqueous uranium species. The reference state is the hypothetical ideal solution with unit molality. Estimated values are enclosed in parentheses. Uncertainties are listed below values

Aqueous species (references)*	Entropy J/(mol·K)	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
U^{4+}	414.	-591.200	-530.950
(56;56)	20.	3.200	2.200
UOH^{3+}	(192.)	(-828.000)	-764.000
(89;89)	(10.)	(4.000)	4.000
$U(OH)_5^-$			(-1630.400)
(;166)			(6.000)
UO_2^{2+}	-97.0	-1018.800	-952.650
(23;23)	3.8	2.500	2.500
$UO_2(OH)^+$			-1160.500
(;44)			3.000
$(UO_2)_2(OH)_2^{2+}$			-2347.500
(;7)			3.000
$(UO_2)_3(OH)_5^+$			-3954.500
(;7)			3.000
$UO_2CO_3^\circ$			-1532.700
(;19,166)			3.000
$(UO_2)_3(OH)_3CO_3^+$			-4113.300
(;19,166)			8.000
$(UO_2)_{11}(OH)_{12}(CO_3)_6^{2-}$			(-16700.000)
(;19,166)			(30.000)
$(UO_2)_3(CO_3)_6^{6-}$			-6312.200
(;168,166)			15.000
$UO_2(CO_3)_3^{4-}$			-2658.500
(;168,89)			5.000

Table 2. continued.

Aqueous species (references)*	Entropy J/(mol·K)	Enthalpy of formation kJ/mol	Gibbs free energy of formation kJ/mol
UF^{3+}			-861.900
(;89)			3.000
UF_2^{2+}			-1177.000
(;89)			3.000
UF_3^{+}			-1485.000
(;89)			3.500
UF_4°			-1792.500
(;89)			3.500
UF_5^{-}			-2083.000
(;89)			3.500
UO_2F^{+}			-1263.500
(;89)			4.000
$UO_2F_2^{\circ}$			-1567.500
(;89)			4.000
$UO_2F_3^{-}$			-1862.500
(;89)			4.000
$UO_2F_4^{2-}$			-2151.500
(;89)			4.000
$UO_2SO_4^{\circ}$			-1713.000
(;89)			4.000
$UO_2(SO_4)_2^{2-}$			-2466.000
(;89)			4.000

Table 2. continued.

Aqueous species (references)*	Entropy	Enthalpy of formation	Gibbs free energy of formation
	J/(mol·K)	kJ/mol	kJ/mol
$UO_2HPO_4^\circ$			-2090.000
(;89)			4.000
$UO_2(HPO_4)_2^{2-}$			-3235.500
(;44)			4.000
$UO_2H_2PO_4^+$			-2100.500
(;89)			4.000
$UO_2(H_2PO_4)_2^\circ$			-3244.500
(;89)			4.000
$UO_2(H_2PO_4)_3^-$			-4385.000
(;89)			5.000

* Reference numbers are given in the form (A;C) as discussed in Table 1.

uranium phases are referenced. Any improvement in the enthalpy of formation of U_3O_8 will change the values throughout the network.

Cordfunke and Aling (1965), Goto (1968), Huber and Holley (1969), Ackermann and Chang (1973), Dharwadkar and Chandrasekharaiah (1973), and Cordfunke et al. (1975) have shown that U_3O_8 is not necessarily stoichiometric. Ackermann and Chang (1973) have shown that $P_{O_2} > 1$ atm is required to maintain the stoichiometric oxide above 840 K. Consequently, the large scatter in the high temperature heat-capacity and heat-content data of Powers (1949), Khomyakov et al. (1964) and Maglic and Herak (1970) may be attributable to differences in sample stoichiometry resulting from preparation under varied conditions and subsequent loss of oxygen in the heat-content experiments. Ackermann and Chang (1973) state that the composition of U_3O_8 heated above 870 K prior to an experiment must be questioned, suggesting that the composition will depend upon the thermal history of the oxide sample. Stoichiometric U_3O_8 heated to 1300 K in air partially dissociates. These samples are reluctant to return to the stoichiometric composition (Ackermann and Chang, 1973). Also, chemical analyses for uranium based upon determination of U_3O_8 at temperatures above 1000 K would be subject to error (Ackermann and Change, 1973).

Huber and Holley (1969) were careful to determine the composition of their reaction products and to extrapolate (by least squares) the results to stoichiometric U_3O_8. They obtained -3574.8 ± 2.5 kJ/mol for the heat of formation of U_3O_8 at 298.15 K. Combining this value with the entropy of U_3O_8, $S^\circ_{298} = 282.6$ J/mol•K, determined by Westrum and Gronvold (1959) and Girdhar and Westrum (1968) yields the Gibbs free energy of formation at 298.15 K, $\Delta G_{f,298} = -3369.4 \pm 2.5$ kJ/mol.

The heat capacity of α-U_3O_8 has been measured from 5 to 350 K by Westrum and Gronvold (1959). Girdhar and Westrum (1968) measured the heat capacity of U_3O_8 between 300 and 555 K defining the α-β transition at 482.7 K. Powers (1949) and Khomyakov et al. (1964) measured the heat capacity of U_3O_8 between 477 and 1254 K and 623 and 1273 K, respectively. The data of Powers (1949) and of Khomyakov et al. (1964) are of low quality. The heat content of U_3O_8 has been measured by Maglic and Herak (1970) between 482 and 927 K.

γ-UO_3

The enthalpy of formation of γ-UO_3 at 298.15 K has been determined from U_3O_8 by two thermochemical cycles. Fitzgibbon et al. (1967) determined the heat of solution of mechanical mixtures of $UO_{2.028}$ and γ-$UO_{2.993}$, extrapolating their results to stoichiometric γ-UO_3. U_3O_8 was dissolved in the same solvent (0.057 M ceric sulfate in 1.5 M sulfuric acid). Based upon the difference in the heats of solution of γ-UO_3 and U_3O_8 (corrected to the value given above), Fitzgibbon et al. (1967) obtained -1223.4 ± 2.5 kJ/mol for the enthalpy of formation of γ-UO_3 at 298.15 K. The second thermochemical cycle involved the measurement of the dissociation pressure of reaction (1) by Cordfunke and Aling (1965) and the extrapolation of the heat of the reaction (Cordfunke et al., 1975) to 298.15 K by the third law method, equation (2).

$$3\gamma\text{-}UO_{3(c)} = U_3O_{8(c)} + 1/2\ O_{2(g)} \qquad (1)$$

$$\Delta H^\circ_{r,298} = 1/2RT \ln P_{O_2} - \int_{298.15}^{T} \Delta C^\circ_p dt + T \left[\Delta S^\circ_{298} + \int_{298.15}^{T} \Delta(C^\circ_p/T)dt \right] \qquad (2)$$

Cordfunke et al. (1975) obtain -1223.8 ± 0.8 kJ/mol for the enthalpy of formation of γ-UO_3 at 298.15 K based upon the enthalpy of formation of U_3O_8 given above.

The weighted average of these results, -1223.7 ± 2.1 kJ/mol combined with the entropy for γ-UO_3 (S_{298} = 96.11 J/mol•K, Westrum, 1966) yields -1145.6 ± 2.1 kJ/mol for the Gibbs free energy of formation of γ-UO_3 at 298.15 K.

An additional determination of the heat of formation of γ-UO_3 not dependent upon the heat of formation of U_3O_8 was made by Vidavskii et al. (1965). The thermochemical cycle involved the dissolution of γ-UO_3 in hydrofluoric acid and literature values for the enthalpy of formation of UF_6 and aqueous HF and the enthalpy of hydrolysis of UF_6 in water. Using the heat of solution for γ-UO_3 given by Vidavskii et al. (1965), the enthalpy of hydrolysis of UF_6 in water (Popov et al., 1957), the enthalpy of formation of HF•44.5 H_2O (Johnson et al., 1973), UF_6 (Settle et al., 1963), and H_2O (Wagman et al., 1968), one obtains the enthalpy of formation of γ-UO_3 at 298.15 K as -1219 ± 7.5 kJ/mol. Johnson et al. (1973) have used the Vidavskii et al. (1965) cycle in reverse in order to calculate the heat of formation of HF•10 H_2O. The value derived from this cycle, assuming the heat of formation of γ-UO_3 to be -1223 ± 6 kJ/mol as was done by Johnson et al., is in good agreement with, but at the more positive end of a narrow range of values derived from twelve other Hess cycles. If the heat of formation of aqueous HF is taken from the JANAF Tables (Stull and Prophet, 1971), the enthalpy of formation of γ-UO_3 as determined by the Vidavskii cycle becomes -1225.5 ± 7.5 kJ/mol or -1224.6 ± 7.5 kJ/mol if the enthalpy of hydrolysis of UF_6 given by Rand and Kubaschewski (1963) is chosen. Consequently, within the limits of the experimental error, the value of the heat of formation of γ-UO_3 obtained from U_3O_8 and from UF_6 are in agreement.

Johnson (1979) has redetermined the enthalpy of formation of UF_6 and using this value, corrected the Hess cycle discussed above. Johnson obtained -1224.1 ± 2.6 kJ/mol for the enthalpy of formation of γ-UO_3 in excellent agreement with Cordfunke et al. (1975).

Jones, Gordon, and Long (1952) reported low-temperature heat-capacity measurements for a sample of UO_3 prepared by heating uranyl nitrate for eight hours at 300°C. Moore and Kelley (1947) used the same sample for heat-content measurements covering the temperature range from 415 to 886 K. Moore and Kelley noted that the sample obtained from Jones, Gordon, and Long contained 1.17 percent water which could not be removed by heating the sample to 120°C. The sample was purified by heating the material seventy-nine hours at 550° to 600°C in dry oxygen. Moore and Kelley noted that this treatment did not alter the orange-yellow color of the material.

Neither group of investigators appear to have been aware that several polymorphs of UO_3 existed. Hoekstra and Siegel (1961) have described five crystalline polymorphs of UO_3 together with details of how each phase may be prepared and of the relative stability of the UO_3 polymorphs.

Westrum (1966) measured the low-temperature heat capacities of three polymorphs of UO_3. Westrum presented his measured results in the form of a difference plot in which the heat capacities of the α-UO_3 phase were used as the reference values. Westrum included the results of Jones et al. (1952) for comparison.

A comparison of the shape of the difference plots given by Westrum (1966) for γ-UO_3 and β-UO_3 and for the data of Jones et al. (1952) suggests that the sample used by Jones and coworkers was a mixture of both γ-UO_3 and β-UO_3 (Westrum, 1966). This interpretation is further supported by the work of Hoekstra and Siegel (1961). Hoekstra and Siegel have shown that dehydration of $UO_2(NO_3)_2 \cdot 6H_2O$ before denitration will result in the formation of an amorphous UO_3 rather than the γ-UO_3 phase produced by decomposition at higher temperatures. Furthermore, Hoekstra and Siegel suggest that amorphous UO_3(A) will follow the reaction series $UO_3(A) \rightarrow \alpha\text{-}UO_3 \rightarrow \beta\text{-}UO_3 \rightarrow \gamma\text{-}UO_3$ when held at higher temperatures in an oxidizing environment.

The heat capacities of UO_3 reported by Jones et al. (1952) are larger, at all temperatures, than the results reported by Westrum (1966) for the β- and γ-UO_3 polymorphs. Giauque and Archibald (1937) have shown that the heat capacity of an amorphous powder (MgO in this case) can be as much a 1% greater than its crystalline equivalent. Consequently, the UO_3 sample used by Jones et al. may have contained a substantial portion of amorphous UO_3.

In view of the uncertainty associated with the sample used by Jones et al. (1952), it is recommended that the data of Westrum (1966) be used for the UO_3 polymorphs. The entropy of γ-UO_3 selected by CODATA (1977) is the value as given by Westrum.

UF_6

The enthalpy of formation of UF_6 has been determined by Johnson (1979). The new value of -2197.7 kJ/mol represents a substantial revision from previously accepted values.

UO_2

The enthalpy of formation of UO_2 was determined from the enthalpy of combustion of $UO_{2.055}$ to U_3O_8 by Huber and Holley (1969) combined with earlier studies of the enthalpy of combustion of several UO_{2+x} compositions and the enthalpy of formation of U_3O_8. The enthalpy of formation of UO_2 at 298.15 K is -1084.9±0.8 kJ/mol. Combining this value with the entropy of UO_2 at 298.15 K (Parker et al., 1976) yields -1031.8±1.3 kJ/mol for the free energy of formation of UO_2 at 298.15 K.

UCl_4

The enthalpy of formation of UCl_4 at 298.15 K has been determined by solution calorimetry from uranium metal and UO_2 (Fitzgibbon et al., 1971, and Cordfunke et al., 1976). Fitzgibbon et al. (1971) determined the enthalpy of formation of UCl_4 from the dissolution of uranium metal and UCl_4 in both 4M and 6M HCl which had been carefully purged of dissolved oxygen. Previous experiments purporting to measure the heat of solution of uranium metal in HCl (see for example Argue et al., 1961) also measured the additional oxidation of the uranium by the oxygen dissolved in the acid solvent (Fitzgibbon et al., 1971). Argue et al. (1961) note that the heat of solution of uranium is as much as 62.8 kJ/mol larger when the experiment is performed in air.

The enthalpy of formation of UCl_4 has been determined from a reaction scheme involving the heat of solution of UO_2 by Fitzgibbon et al. (1971) and by Cordfunke et al. (1976). The same general thermochemical cycle was used in each investigation. Fitzgibbon et al. (1971) and Cordfunke et al. (1976) give -1020.9±4.2 and -1017.8±2.7 kJ/mol, respectively, for the enthalpy of formation of UCl_4. Although these results are in fairly good agreement the values given by Fitzgibbon et al. (1971) scatters by a somewhat larger difference than one would like to see. Fitzgibbon et al. (1971) list the heat of solution data for UCl_4 in Table 6 of their paper. One of these values differs from the mean of all the heat of solution values by more than twice the standard deviation of the mean. If this value is discarded, the enthalpy of formation of UCl_4 as determined with the data given by Fitzgibbon et al. (1971) becomes -1020.0±4.0 kJ/mol.

A weighted average of the enthalpy of formation data given by Fitzgibbon et al. (1971) and Cordfunke et al. (1976) yields -1018.4±3.3 kJ/mol for UCl_4 at 298.15 K. Using the entropy at 298.15 K given by Ginnings and Corruccini (1947), the Gibbs free energy of formation of UCl_4 is calculated to be -928.8±4.0 kJ/mol.

UO_2Cl_2

Cordfunke et al. (1976) have determined the enthalpy of formation of UO_2Cl_2 from two reaction schemes, called the γ-UO_3 and Shchukarev cycles. The enthalpy of formation UO_2Cl_2 based upon the γ-UO_3 cycle is -1243.1±2.2 kJ/mol.

The Shchukarev cycle (Shchukarev et al., 1958) is based upon the heat of solution of UCl_4 in a hydrochloric acid solution containing ferric chloride as an oxidizing agent. The enthalpy of formation of UO_2Cl_2 determined by the Shchukarev cycle by Cordfunke et al. (1976) is -1247.2±4.2 kJ/mol. Since complete oxidation of U^{4+} is not guaranteed by this reaction scheme and since Cordfunke et al. did not determine the extent of oxidation of U^{+4} to U^{+6}, the value of the enthalpy of formation obtained from this cycle cannot be considered as accurate as the value based upon the γ-UO_3 thermochemical cycle.

The entropy of UO_2Cl_2 at 298.15 K is given by Kelley and King (1961) as 150.5±0.4 J/mol•K. Combining this value with the enthalpy of formation of UO_2Cl_2 from the γ-UO_3 cycle yields -1145.2±-2.1 kJ/mol for the free energy of formation of UO_2Cl_2 at 298.15 K.

Phases referenced to U_3O_8, γ-UO_3, and UO_2Cl_2

The thermodynamic properties of several of the reference phases have been revised as either better samples became available or as errors or problems with earlier studies were recognized. Further revision of these values will result in changes in the thermodynamic properties of the phases that reference uranium through them.

The thermodynamic properties of the secondary uranium reference materials UO_2 and γ-UO_3 have been determined from reactions involving U_3O_8. The enthalpies of formation of $NaUO_3$, $LiUO_3$, KUO_3, and $RbUO_3$ are based upon thermochemical cycles referenced to U_3O_8.

The reaction schemes used by several laboratories to obtain values for the thermodynamic properties of β-UO_3, δ-UO_3, α-UO_3, ε-UO_3, UO_3 (amorphous, A), $UO_2^{++}{}_{(aq)}$, UO_3,$\cdot 2H_2O$, $\beta UO_3 \cdot H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 3H_2O$, U_4O_9, β-U_3O_7, and $CaUO_4$ have been corrected to conform to the selected enthalpy of formation of γ-UO_3.

The thermochemical cycles used by several investigators to determine the thermodynamic properties of Na_3UO_4, α-Na_2UO_4, $NaUO_3$, α-Li_2UO_4, K_2UO_4, Rb_2UO_4, Cs_2UO_4, $Cs_2U_2O_7$, $Na_2U_2O_7$, $K_2U_2O_7$, $Rb_2U_2O_7$, and $BaUO_4$, have been corrected to be consistent with the selected enthalpy of formation of UO_2Cl_2. In addition, the data of O'Hare et al. (1972), O'Hare and Hoekstra (1973, 1974a, b, and c; 1975) have been corrected for an error in the impurity correction to the heat of solution of UO_2Cl_2 (O'Hare et al., 1980).

The enthalpy of formation of the alkali and calcium monouranates determined by Ippolitova et al. (1964) are substantially different than the results obtained by Osborne et al. (1974), O'Hare et al. (1976) and O'Hare and Hoekstra (1973; 1974a, b, and c). Time was not spent attempting to identify the source of the discrepancies since the article by Ippolitova et al. (1964) did not give the values of the auxillary data used in their thermochemical cycles.

The $NaUO_3$ problem

O'Hare and Hoekstra (1974c) have compared the reported data for the enthalpy of formation of $NaUO_3$ and found it to be in good agreement. The values reported by O'Hare and Hoekstra (1974c) were -1495.8±3.3, -1494, -1492.4±8.0, and -1440±17kJ/mol from O'Hare and Hoekstra (1974c), King et al. (1971), Cordfunke and Loopstra (1971), and Battles et al. (1972, ΔH_f at 1000 K), respectively. Cordfunke et al. (1976) have published a revised value for the heat of formation of UO_2Cl_2 calculated from two thermochemical cycles. O'Hare and Hoekstra (1974c) used UO_2Cl_2 as the reference uranium phase in determining the heat of formation of $NaUO_3$, consequently, their value must be corrected for the revised value for UO_2Cl_2. Since the correction is about -23 kJ/mol, the apparently consistent data set is shown to contain erroneous data. The data given by King et al. (1971) and Battles et al. (1972) may be disregarded from the present discussion because of the relatively large uncertainties associated with each set of data (O'Hare and Hoekstra, 1974c). The thermochemical cycle utilized by Cordfunke and Loopstra (1971) is based upon the heat of formation of β-UO_3 which is in turn based upon γ-UO_3 and upon U_3O_8.

Cordfunke and Ouweltjes (1981) have redetermined the enthalpy of formation of $NaUO_3$ confirming the earlier result of Cordfunke and Loopstra (1971). They were unable to identify the source of the difference between these data and those given by O'Hare and Hoekstra (1974c).

The source of the discordant enthalpy of formation data for $NaUO_3$ was not determined by Cordfunke and O'Hare (1978). They averaged the results given by O'Hare and Hoekstra (1974c) and Cordfunke and Loopstra (1971) after supplementing the data of Cordfunke and Loopstra with the enthalpy of solution of $NaSO_4$ in 1.7M H_2SO_4 in order to provide a more complete thermochemical cycle. Following the procedures of Cordfunke and O'Hare we obtain -1496.2 and -1519.6 kJ/mol, respectively, for the data of Cordfunke and Loopstra and for that of O'Hare and Hoekstra (1974c).

The enthalpy of formation of $NaUO_3$ derived from the data of Cordfunke and Loopstra (1971) is referenced to the enthalpies of solution and formation of U_3O_8 and β-UO_3. One may also derive the enthalpy of formation of $NaUO_3$ from the enthalpy of solution and formation of UO_2 under nearly identical conditions from the work of Cordfunke et al. (1976) if we assume that the enthalpy of solution of UO_2 in 1.5M H_2SO_4 and 1.7M H_2SO_4 are not appreciably different. This assumption would appear logical because Cordfunke et al. have shown that the enthalpy of solution of β-UO_3 (-87.9±0.1) in 1.5M H_2SO_4 is nearly identical to the enthalpy of solution in 1.7M H_2SO_4 (-88.1 ± 1.0, Cordfunke and Loopstra). Following the thermochemical cycle based upon UO_2 we obtain -1502.9 kJ/mol for the enthalpy of formation of $NaUO_3$.

The source causing the differences in the enthalpies of formation of $NaUO_3$ cannot be resolved from the data available at this time. An average of these results would appear an unreasonable solution to this problem.

Instead, the values based upon the work of Cordfunke and Loopstra (1971) have been chosen since the enthalpies of solution of each phase other than $NaUO_3$ has been confirmed elsewhere and since the thermochemical cycles used can be tied directly to the two secondary reference phase UO_2Cl_2 and γ-UO_3 and to UO_2 and U_3O_8. If this value proves to be in error for any reason other than a problem related to the purity of the $NaUO_3$ sample, the entire net of thermodynamic data for the uranium phases would have to be reevaluated.

Cordfunke and Ouweltjes (1981) have redetermined the enthalpy of formation of $NaUO_3$. Their result (-1494.6±1.6 kJ/mol) is in good agreement with the result given by Cordfunke and Loopstra (1971). However this result does not clarify the descrepancy cited above. As the procedures followed by Cordfunke and Ouweltjes are straightforward, their result will be accepted for $NaUO_3$.

Revised enthalpy of solution of UO_2Cl_2

O'Hare, Flotow and Hoekstra (1980) have revised the enthalpy of formation of $BaUO_4$ based upon a revised value for the enthalpy of solution of UO_2Cl_2. O'Hare et al. accept -101.7±0.8 kJ/mol in place of the corrected value given earlier by O'Hare, Boerio, and Hoekstra (1976) of -92.8±0.6 kJ/mol. It is important to note that the enthalpies of formation of Li_2UO_4, K_2UO_4, Rb_2UO_4, $Cs_2U_2O_7$, and Cs_2UO_4 are also depend upon the enthalpy of solution of UO_2Cl_2 that has been revised. Because the most likely source of the difference in the enthalpy of solution of UO_2Cl_2 cited above would be the impurities cited by O'Hare et al (1976), a correction to the thermodynamic cycles used for Na_3UO_4, Na_2UO_4, and $NaUO_3$ would also appear likely. If the corrections are applicable to the thermochemical cycles used for $NaUO_3$ the magnitude would be small and consequently not alter the discussion presented in the preceeding section.

O'Hare and Hoekstra (1974) reported a value of -1897.3±3.3 kJ/mol for the enthalpy of formation of Cs_2UO_4. Cordfunke and O'Hare (1978) report unpublished experimental results from which they obtained -1930.7±1.2 kJ/mol (Cordfunke, 1975) for the enthalpy of formation of Cs_2UO_4. If we correct the results of O'Hare and Hoekstra for the enthalpy of solution and formation of UO_2Cl_2 used in their study, the resulting enthalpy of formation for Cs_2UO_4 is -1928.8±3.5 kJ/mol. Thus the two results are in excellent argeement lending support to the justification for correcting the enthalpy of solution of UO_2Cl_2 in 1MHCl as proposed by Parker (1980, cited in O'Hare et al., 1980). Consequently, the thermochemical cycles reported by O'Hare and coworkers for Li_2UO_4, K_2UO_4, Rb_2UO_4, Cs_2UO_4 and $Cs_2U_2O_7$ have been corrected to the enthalpy of solution of UO_2Cl_2 reported by Parker (1980, cited in O'Hare et al., 1980).

UO_2^{2+}

The enthalpy of formation of UO_2^{2+} may be calculated from the enthalpy of formation and heat of solution of $UO_2(NO_3)_2 \cdot 6H_2O$ following the reaction scheme listed in Table 3. The enthalpy of formation of $UO_2(NO_3)_2 \cdot 6H_2O$ may be calcualted from the heats of solution of γ-UO_3 and $UO_2(NO_3)_2 \cdot 6H_2O$

(Cordfunke, 1964), the enthlpy of formation of γ-UO_3 (this report), and the enthalpies of formation of H_2O and various concentrations of nitric acid (Wagman et al., 1968) by the reaction scheme outlined in Table 4. The heat of solution of $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.0004m HNO_3 is 4.73 kcal/mol (Bailey and Larson, 1971). The very dilute acid solution was used to prevent hydrolysis of UO_2^{2+}.

The enthalpy of formation of UO_2^{2+} calculated in this report confirms the tentative value given by CODATA (1977). The CODATA (1977) value is accepted in this report.

Schoepite, paraschoepite and their dehydration products

Seven hydrates of UO_3 have been discussed in the literature (e.g., Wheeler et al., 1964). These phases include three dihydrates (Christ and Clark, 1960), three monohydrates (e.g., Cordfunke and Debets, 1964), and a hemihydrate (e.g., Dawson et al., 1956). Some earlier workers reported four monohydrate phases (e.g., Katz and Rabinowitch, 1951), however Cordfunke and Debets suggest that two were structurally identical and varied only in water content.

Several of the UO_3 hydrates are inferred to be structurally related because they are related through a thermal dehydration (in air) sequence. One series is represented by β-$UO_3 \cdot 2H_2O$, α-$UO_3 \cdot H_2O$, $UO_3 \cdot 0.8H_2O$, $UO_3 \cdot 0.5H_2O$, and finally a UO_3 polymorph that Dawson et al. (1956) suggest is monoclinic. The second series (note that the series does not contain a hemihydrate phase) involves α-$UO_3 \cdot 2H_2O$, β-$UO_3 \cdot H_2O$ and a simple cubic UO_3 polymorph that can be oxygen difficient (with the limit about $UO_{2.88}$, Dawson et al.).

Porte et al. (1962) have studied the proton magnetic resonance spectra for β-$UO_3 \cdot 2H_2O$ and β-$UO_3 \cdot H_2O$ suggesting the compounds are β-$U_2O_5(OH)_2 \cdot 3H_2O$ and β-$UO_2(OH)_2$, respectively. They further suggest that the hemihydrate should be designated as $U_2O_5(OH)_2$.

Based upon these findings, it is logical to assume that α-$UO_3 \cdot H_2O$ should be given as α-$U_2O_5(OH)_2 \cdot H_2O$ and α-$UO_3 \cdot 2H_2O$ should be α-$UO_2(OH)_2 \cdot H_2O$.

Dawson et al. (1956) and Debets and Loopstra (1963) found only one X-ray pattern for $UO_3 \cdot 2H_2O$ and assigned the pattern to β-$UO_3 \cdot 2H_2O$. The cell volume and constants are identical to those given by Christ and Clark (1960) for schoepite II. However, Christ and Clark concluded that schoepite II was an intermediate phase between schoepite (designated schoepite I) and paraschoepite (designated schoepite III). It is reasonable to assume that the β-$UO_3 \cdot 2H_2O$ phase studied by Dawson et al. and Debets and Loopstra, as well as that sample upon which the enthalpy of formation of β-$UO_3 \cdot 2H_2O$ is based (Cordfunke, 1964) represented a mixture of the phases paraschoepite and schoepite as found by Christ and Clark.

Schoepite and paraschoepite should represent the ideal β- and α-$UO_3 \cdot 2H_2O$ phases discussed above. The relationship of masuyite ($UO_2(OH)_2 \cdot H_2O$, Donnay and Ondik, 1973) to these phases is unknown.

Table 3. Reaction scheme and enthalpy values used to calculate the enthalpy of formation* of UO_2^{2+} at 298.15 K.

1. $UO_2(NO_3)_2 \cdot 6H_2O_{(c)} \rightarrow UO_{2(aq)}^{2+} + 2NO_{3(aq)}^{-} + 6H_2O_{(\ell)}$ $\Delta H_1 = 19.8 \pm 0.1$

2. $6H_2O_{(\ell)} \rightarrow 6H_{2(g)} + 3O_{2(g)}$ $\Delta H_2 = 1715.1 \pm 0.3$

3. $2NO_{3(aq)}^{-} \rightarrow N_{2(g)} + 3O_{2(g)}$ $\Delta H_3 = 414.7 \pm 0.2$

4. $U_{(c)} + 7O_{2(g)} + N_{2(g)} + 6H_{2(g)} \rightarrow UO_2(NO_3)_2 \cdot 6H_2O_{(c)}$ $\Delta H_4 = -3170.0 \pm 2.5$

5. $U_{(c)} + O_{2(g)} \rightarrow UO_{2(aq)}^{2+}$ $\Delta H_5 = -1020.4 \pm 2.5$

*This value differs by -1.6 kJ/mol from the value listed in Table 1. This difference arises from the differences in the enthalpy of formation given in Table 4 and used in reaction 4 in this thermochemical cycle.

Table 4. Reaction scheme and enthalpy values used to calculate the enthalpy of formation* of $UO_2(NO_3)_2 \cdot 6H_2O$ at 298.15 K.

1. $\gamma\text{-}UO_{3(c)} + [211.7HNO_3 \cdot 1957.9H_2O]_{(aq)} \rightarrow [UO_2^{2+} + 2NO_3^- + 209.7HNO_3 \cdot 1958.9H_2O]_{(aq)}$ $\Delta H_1 = -71.3 \pm 0.1$

2. $[UO_2^{2+} + 2NO_3^- + 211.7HNO_3 \cdot 1963.9H_2O]_{(aq)} \rightarrow UO_2(NO_3)_2 \cdot 6H_2O_{(c)} + [211.7HNO_3 \cdot 1957.9H_2O]_{(aq)}$ $\Delta H_2 = -39.9 \pm 0.2$

3. $[UO_2^{2+} + 2NO_3^- + 209.7HNO_3 \cdot 1958.9H_2O]_{(aq)} + [2HNO_3 \cdot 5H_2O]_{(aq)} \rightarrow [UO_2^{2+} + 2NO_3^- + 211.7HNO_3 \cdot 1963.9H_2O_{(aq)}$ $\Delta H_3 = -10.8 \pm 0.1$

4. $H_{2(g)} + N_{2(g)} + 3O_{2(g)} + 5H_2O_{(P)} \rightarrow [2(HNO_3 \cdot 2.5H_2O)]_{(aq)}$ $\Delta H_4 = -395.0 \pm 0.2$

5. $U_{(c)} + 3/2\ O_{2(g)} \rightarrow \gamma\text{-}UO_{3(c)}$ $\Delta H_5 = -1223.8 \pm 2.1$

6. $5H_{2(g)} + 5/2\ O_{2(g)} \rightarrow 5H_2O_{(P)}$ $\Delta H_6 = -1429.2 \pm 0.3$

7. $U_{(c)} + 6H_{2(g)} + N_{2(g)} + 7O_{2(g)} \rightarrow UO_2(NO_3)_2 \cdot 6H_2O_{(c)}$ $\Delta H_7 = -3170.0 \pm 2.5$

*This value differs by -1.6 kJ/mol from the value obtained from solubility studies (see Cordfunke and O'Hare, 1978).

Estimated thermodynamic properties of rutherfordine, sharpite, schoepite, and dehydrated schoepite

Eight enthalpy of solution measurements (in $HCl\cdot 10.01H_2O$) were made on rutherfordine samples obtained from two preparations. No evidence of major deviations of the enthalpy of solution from within or between the samples was apparent. The average of the eight measurements was -11680 ± 118 J/mol, based upon the chemical formula $UO_2(CO_3)_{.86}(OH)_{.28}\cdot 0.57H_2O$ obtained from chemical anlayses yielding UO_3 of 84.5%, CO_2 of 11.2% and H_2O of 3.8% (analyses by Floyd Brown and John Marinenko, USGS).

The enthalpy of formation of rutherfordine was calculated from the observed enthalpy of solution cited above, the enthalpy of solution of β-$UO_3\cdot H_2O$ in $HCl\cdot 10.01H_2O$ calculated from the data of Cordfunke (1964), the enthalpy of solution of γ-UO_3 and H_2O in $HCl\cdot 10.01H_2O$ from Cordfunke et al. (1976), the enthalpy of formation of CO_2 and H_2O from Robie et al. (1979), and the enthalpies of formation of γ-UO_3 and β-$UO_3\cdot H_2O$ given by Cordfunke and O'Hare (1978). The enthalpy of solution of CO_2 in $HCl\cdot 10.01H_2O$ and corrections for the vaporization of the solvent into the CO_2 gas formed in the reaction were calculated from the data of Robb and Zimmer (1968). The enthalpy of formation of rutherfordine, $UO_2(CO_3)_{.86}(OH)_{.28}\cdot 0.57H_2O$, calculated from the afore mentioned data was -1833.5±2.0 kJ/mol.

The thermochemical cycle used in this study ties the thermodynamic properties of rutherfordine directly to those of γ-UO_3 and to UO_2Cl_2 since the enthalpy of formation of UO_2Cl_2 was determined by Cordfunke et al. (1976) using $HCl\cdot 10.01H_2O$ as a solvent and γ-UO_3 as the reference uranium phase.

Rutherfordine is described as an anhydrous UO_2CO_3 (Frondel, 1958; Bullwinkle, 1954; and Clark and Christ, 1956), but most chemical analyses for rutherfordine show small amounts of H_2O to be present (Frondel and Meyrowitz, 1956; Miller, Pray and Munger, 1949; and Chernyaev, Golovnya, and Ellert, 1956). Vaes (1947) proposed the mineral name diderichite for a slightly hydrated uranyl carbonate found as crusts of fibers and laths in Katanga, Zaire. Frondel and Meyrowitz (1956) noted the similarity in the optical properties and X-ray powder diffraction patterns of a specimen of diderichite and those of rutherfordine and suggested that the minerals were identical. Some of the chemical analyses reported by Frondel and Meyrowitz were corrected for impurities of Pb, Ca, Si and Fe by assuming these elements to be present as hydrous phases which may bias their corrected analyses toward anhydrous uranyl carbonate.

Christ and Clark (1960) have discussed the similarity in the structure of UO_2CO_3, $UO_2(OH)_2$, UO_2F_2, $CaUO_2O_2$, and $UO_2(OH)_2\cdot H_2O$ and Frondel and Barnes (1958) disucssed $PbUO_2O_2$. Water is not essential to the rutherfordine structure, but the similarity in structures allows hydroxyl to substitute for carbonate in the structure.

A comparison of the X-ray powder diffraction data for the calorimetric rutherfordine sample with the rutherfordine samples studied by Frondel and Meyrowitz (1956), Chernyaev et al. (1956) and by Clark and Christ (1956) can be made using the data given in Table 5. The X-ray powder diffraction patterns for these samples are identical within the experimental limitations of each study. No evidence was found to indicate that the sample used in this study was a mechanical mixture of UO_2CO_3 and $UO_2(OH)_2\cdot H_2O$.

Sharpite, $UO_2CO_3\cdot H_2O$, is the only recognized hydrated uranyl carbonate (Frondel, 1958, and Chernyaev et al., 1956). Sharpite is less stable than rutherfordine (Frondel, and Chernyaev et al.) and undergoes thermal decomposition to CO_2 gas, steam, and amorphous UO_3 (orange in color) at 600 K (Frondel, 1958). No X-ray powder diffraction data are available for sharpite, but Chernyaev et al. have synthesized the phase at 413 K from a concentrated aqueous solution of uranyl nitrate at elevated CO_2 gas pressure. The lower thermal stability of sharpite compared to rutherfordine and the color change (from yellow to orange) associated with the thermal decomposition of sharpite preclude its presence as a contaminant in the rutherfordine sample studied here.

The synthesis of rutherfordine has followed two reaction schemes, either UO_3(solid) + CO_2 (gas) + steam → UO_2CO_3 + steam or $UO_2(OH)_2\cdot nH_2O$ (solid) + CO_2 (gas) → $UO_2CO_3 + nH_2O$. Miller et al. (1949) and Chernyaev et al. (1956) followed the former procedure obtaining $UO_2(CO_3)_{.95}(OH)_{.1}\cdot 0.15H_2O$ and $UO_2(CO_3)_{.95}(OH)_{.1}\cdot 0.1H_2O$, respectively, for the rutherfordine phases at 373 and 298 K, also respectively. Blake et al. (1956) also followed the former procedure and reported 0.97 moles of CO_3 per mole of U in the product formed at about 373 K and 200 bars CO_2 pressure (no analysis for H_2O given). The latter reaction was utilized by Bullwinkel (1954), Frondel and Meyrowitz (1956), Sergeyeva et al. (1972) and in this study. Frondel and Meyrowitz obtained a phase with the composition $UO_2(CO_3)_{.9}(OH)_{.2}$ at 573 K. Bullwinkel did not report a full chemical analysis of the rutherfordine sample which he prepared, but did note that the ratio of U/CO_2 was approximately 1. The sample of rutherfordine prepared by Chernyaev et al. was dried at 373 K in air prior to chemical analysis and consequently may have lost some water present at the time of crystallization. Sergeyeva et al. do not provide analyses of their samples prepared at 298 K and at higher temperatures.

The data provided by Sergeyeva et al. (1972) have been assumed to represent anhydrous UO_2CO_3 and have been used to derive the enthalpy and free energy of formation of rutherfordine (e.g., Cordfunke and O'Hare, 1978; and Langmuir, 1978). Cordfunke and O'Hare obtained a value of -1561.9 kJ/mol for the free energy of formation of rutherfordine from the solubility of rutherfordine reported by Sergeyeva et al. Langmuir obtained -1563.1 kJ/mol from the same data. Cordfunke and O'Hare estimated the entropy of UO_2CO_3 (139 J/mol·K) from Latimer's Rules and calculated the enthalpy of formation of rutherfordine as -1686.1 ± 4.2 kJ/mol. Langmuir estimated the entropy of rutherfordine as 142.7 J/mol·K and calculated -1689.9 kJ/mol for the enthalpy of formation of UO_2CO_3. Cordfunke and O'Hare also calculated the enthalpy of formation of rutherfordine (-1696.2±7.5 kJ/mol) from the phase equilibria data given by Sergeyeva et al.

Table 5. X-ray powder diffraction data for several rutherfordine samples

Calculated* hkl	d_{hkl}	Chernyaev, et al. (1956)	Frondel and Meyrowitz (1956)	Clark and Christ (1956)	Present study
020	4.603	4.64	4.60	4.61	4.60
110	4.287	4.33	4.29	4.30	4.29
011	3.893	3.90	3.90	3.92	3.86
101	3.214	3.22	3.21	3.23	3.20
121	2.635	2.65	2.64	2.64	2.63
200	2.423	2.42	2.41	2.42	2.42
040	2.301	2.31	2.32	2.309	2.30
002	2.148	2.14	2.15	2.156	2.14
220	2.144				
211	2.057	2.06	2.05	2.062	2.05
original rutherfordine cell parameters					
a		4.84	4.82	4.84	4.84
b		9.28	9.20	9.20	9.20
c		4.28	4.30	4.29	4.28
cell parameters for rutherfordine fired to constant weight at 523 K					
a					4.82
b					9.12
c					4.28
cell parameters for rutherfordine fired to constant weight at 700 K**					
a					4.82
b					9.06
c					4.28

* Data calculated by Clark and Christ (1956)

**Sharpite, $UO_2CO_3 \cdot H_2O$ reacts to form CO_2 gas, steam, and amorphous UO_3 at 600 K (Frondel, 1958). Therefore, the sample is not sharpite (see discussion in text).

In order to compare these results we must examine the validity of the estimates of the entropy of rutherfordine. As a first approximation we may plot the entropy of several related phases against their gram formula weight and examine the consistency of the entropy estimates for rutherfordine. Three "families" of data are presented in Figure 1 as carbonates, chlorides, and sulfates. In each "family" the phases represented contain Ca, Sr, Ba, Pb, and UO_2. The values given for the uranyl phases are consistent with the linear trends of the related phases, however, both the uranyl sulfate and carbonate values are estimated as is the value for $SrSO_4$. The entropy values were taken from Robie et al. (1979), Kelley and King (1961), or Cordfunke and O'Hare (1978). It should also be noted that the carbonate phases selected were the orthorhombic aragonite group. Thus, within the precision of the data for the carbonate group and within the limits of this simple model, the values of the entropy of anhydrous rutherfordine are reasonable.

Lemire and Tremaine (1980) estimated the entropy of rutherfordine as 194 J/mol•K from the solubility data reported by Nikolaeva (1976). This estimate appears to be too large for the anhydrous carbonate, but agrees with the estimated entropy for sharpite listed in Table 1.

The uncertainties of the two values for the enthalpy of formation of rutherfordine calculated by Cordfunke and O'Hare (1978) barely overlap. Cordfunke and O'Hare took a weighted average of these values as the best value for the enthalpy of formation of rutherfordine (-1690.3±8.4 kJ/mol), a value which is close to that given by Langmuir (1978), but derived from different values of the entropy and Gibbs free energy of rutherfordine.

If we correct the enthalpy of formation of the rutherfordine sample, $UO_2(CO_3)_{.86}(OH)_{.28}\cdot 0.57H_2O$ (this study), to anhydrous rutherfordine assuming no enthalpy of mixing terms, we obtain -1691.6 ± 4.0 kJ/mol based upon corrections for 0.43 H_2O and $0.14(UO_3\cdot 2H_2O)$. This value is in good agreement with the values obtained by Langmuir (1978) and Cordfunke and O'Hare (1978).

A more appropriate correction to the anhydrous composition UO_2CO_3 may be made if we estimate the enthalpy of hydration for the 0.57 H_2O. A portion of the sample was heated to constant weight at 523 K to remove the 0.57 H_2O. This temperature was chosen on the basis of differential scanning calorimetry temperature traces combined with weight loss determinations made with a microbalance.

Two measurements of the enthalpy of solution of the $UO_2(CO_3)_{.86}(OH)_{.28}$ sample yielded -17099 J/mol in $HCl\cdot 10.01\ H_2O$. Combining this value with the enthalpy of solution of the rutherfordine sample discussed previously and the enthalpy of solution of H_2O (Cordfunke et al., 1976) in $HCl\cdot 10.01\ H_2O$ allowed the calculation of the enthalpy of hydration, -5.42 kJ/ 0.57 moles of H_2O.

The enthalpy of formation of UO_2CO_3 may be calculated from the enthalpy of hydration previously calculated and the enthalpies of formation of H_2O and

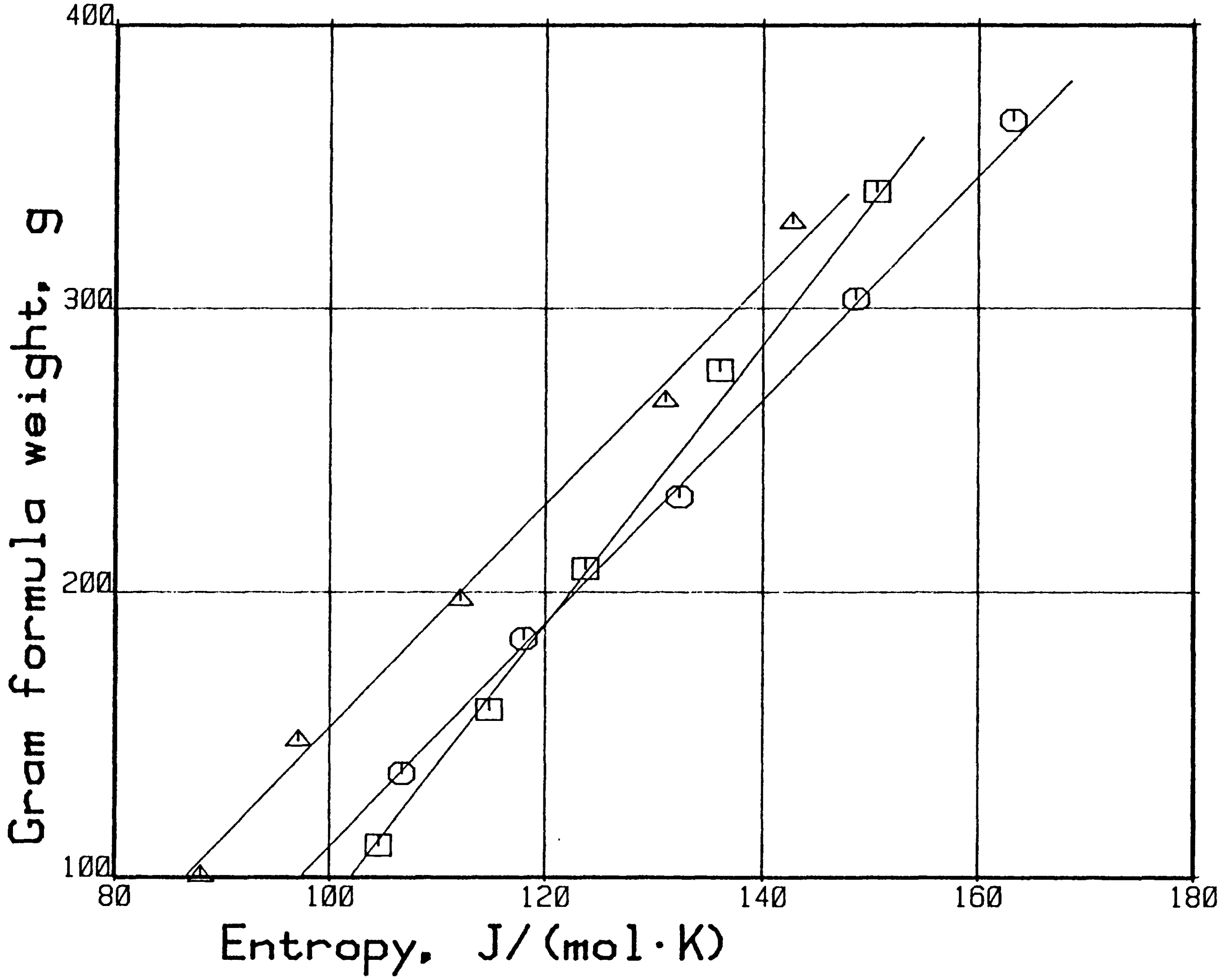


Figure 1: A comparison of a linear approximation relating the gram formula weights and entropies (at 298.15 K) of several families of phases. The three families shown are chlorides, sulfates, and carbonates, represented by squares, octagons, and triangles, respectively. The associated cations representing the phases plotted along each curve are Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, and the uranyl ion UO_2^{2+}, respectively, from the lowest to the greatest gram formula weight. Only members of the orthorhombic aragonite group of carbonate minerals were used.

$UO_3 \cdot H_2O$, again assuming no other enthalpy of mixing terms. Following these assumptions, the enthalpy of formation UO_2CO_3 is -1704.1±2 kJ/mol. Using the estimate of the entropy of rutherfordine, 142.7 J/mol, given by Langmuir (1978) and the ancillary thermodynamic data from Robie et al. (1979), the free energy of formation of rutherfordine may be calculated from the derived enthalpy of formation as -1577.0 kJ/mol with an estimated uncertainty of ±2 kJ/mol. These results are significantly different from earlier estimates.

There are several lines of evidence to suggest that the control of dissolved uranium (VI) in solutions saturated with CO_2 gas at 1 bar is maintained by different phases in the nominally acidic and basic regions.

Ciavatta, Ferri, Grimaldi, Palombari, and Salvatore (1979) have shown that in weakly acid solutions the complexes $UO_2(OH)_2CO_2^{\circ}$ and $(UO_2)_3(OH)_5CO_2^+$ are formed. They further conclude that the species $(UO_2)_3(OH)_3CO_3^+$ results from the substitution of CO_3^{2-} for two OH^- without a substantial structural change from the uranyl hydrolysis species, $(UO_2)_3(OH)_5^+$.

Scanlan (1977) has shown the distribution of uranyl species as a function of pCO_3^{2-} and has shown the variation of pCO_3^{2-} with pH and concentration of $NaHCO_3$. Similar data are presented by Babko and Kodenskaya (1960). From Scanlan's data we may predict that the solutions studied by Sergeyeva et al. (1972) would be dominated by the monouranyl species discussed by Ciaratta et al. (1979) where the pH was less than 5.3 (at pH 5.3 and P_{CO_2} = 1 bar, concentration of monouranyl species = concentration of uranyl dicarbonate complex).

Scanlan (1977) has presented spectral data for the uranyl dicarbonate complex which differs substantially from that given by Bullwinkel (1954). Scanlan has shown that the solutions used by Bullwinkel (and consequently by Sergeyeva et al.) allowed hydrolysis of the uranyl solution species.

Finally, the shape of the solubility curve for rutherfordine (Sergeyeva et al., 1972) is similar to the solubility curve for aluminum in solutions of variable phosphate concentration given by Goldshmid and Rubin (1978) and shown in Figure 2. A double minimum was found in the curve for aluminum solubility similar to that shown in the curve for uranium solubility. Goldshmid and Rubin examined the precipitates in equilibrium with the acidic and basic solutions finding sodium taranakite precipitating from the acidic solutions and $AlPO_4$ precipitating from the basic region.

The results presented by Cole and Jackson (1950) perhaps have greater relevance to this study, because of the procedures followed in preparing their solutions for study (note the discussions of Hemingway, 1982, in this regard). Cole and Jackson excluded sodium from the phases which precipated from solutions similar to those studied by Goldshmid and Rubin (1978). Cole and Jackson found variscite, $Al(OH)_2H_2PO_4$, to be the major phase to precipitate at a pH of 3.8 and wavellite (labelled stenethite) $[Al(OH)_2]_3HPO_4H_2PO_4$, the major phase at a pH of 5.5, both identified by electron diffraction (the precipitates were amorphous to X-rays).

The shape of the solubility curve for rutherfordine (see Figure 2) suggests, by analogy to the aluminum-phosphate system, that two phases controlled the uranium concentration in the studies of Sergeyeva et al. (1972). Also by analogy with the aluminum phosphate system we may suggest that the phase controlling the uranium solubility in the acidic pH region (here pH <5) was sharpite.

The presence of sharpite in the solutions studied by Sergeyeva et al. (1972) cannot be proven because these authors assumed equilibrium with rutherfordine was maintained and therefore did not look for other phases during their experiments. However, this hypothesis is consistent with the very limited natural occurrence of sharpite, the association of sharpite with uranophane (Frondel, 1958), and with the synthesis of sharpite by Chernyaev et al. (1956). Uranophane is thought (Frondel) to form through the interaction of meteoric water and primary or secondary uranium minerals in the zone of oxidation. Chernyaev et al. grew sharpite in an aqueous solution of uranyl nitrate and carbon dioxide at 413 K.

Although relatively good agreement was noted between the thermodynamic parameters for rutherfordine derived from the solubility data and from the relatively meager high temperature phase equilibrium data, substantial questions remain regarding the validity of the several assumptions required in the calculations. The major assumption, of course, is that the same phase is present in each set of experiments.

Cordfunke and O'Hare (1978) calculated the free energy of formation of rutherfordine from the average value of the equilibrium constant ($8.0 \pm 4.0 \times 10^3$) calculated for pH < 4.4 reported by Sergeyeva et al (1972) for reaction (3). Langmuir (1978) calculated the free energy of rutherfordine for a fit of eleven of the twelve solubility results reported

$$UO_2CO_{3(c)} + 2H^+_{(sol)} = UO^{2+}_{2(sol)} + H_2O_{(l)} + CO_{2(g)} \qquad (3)$$

by Sergeyeva et al. assuming the solution species UO_2^{2+}, $UO_2CO°$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ and selected values for β_1, β_2 and β_3 (the overall stability constant, e.g., $\beta_2 = [UO_2(CO_3)_2^{2-}]/[UO_2^{2+}][CO_3^{2-}]^2$). Langmuir omitted the value given by Sergeyeva et al. for the lowest pH (3.22) experiment whereas Sergeyeva et al. gave the value double weight, assuming it to be more accurately determined. The solution species $UO_2CO_3°$ was assumed to be the only uranyl species other than UO_2^{2+} present in the experiments having low pH and corrections to zero ionic strength were made in each set of calculations.

Ciavatta et al. (1979) have estimated the value of β_{121} ($\log \beta_{121} = -8.99 \pm .05$) for reaction (4)

$$UO_2^{2+} + 2H_2O\ (l) + CO_2\ (g) = UO_2(OH)_2CO_2^{\circ} + 2H^+ \qquad (4)$$

under conditions similar to those under which Sergeyeva et al. (1972) determined the solubility of rutherfordine. (Sergeyeva$_{\circ}$et al. estimated that $\log \beta_1 = -9.87$ for the uranyl carbonate monomer UO_2CO_3.) Ciavatta et al. have calculated the average number of H^+ generated through reaction (4), as the pH and uranyl concentration of the solution are varied and with P_{CO} fixed at 0.98 bars. It is apparent from the data presented by Ciavatta et al. that an accurate definition of uranyl carbonate complex is necessary if the solubility

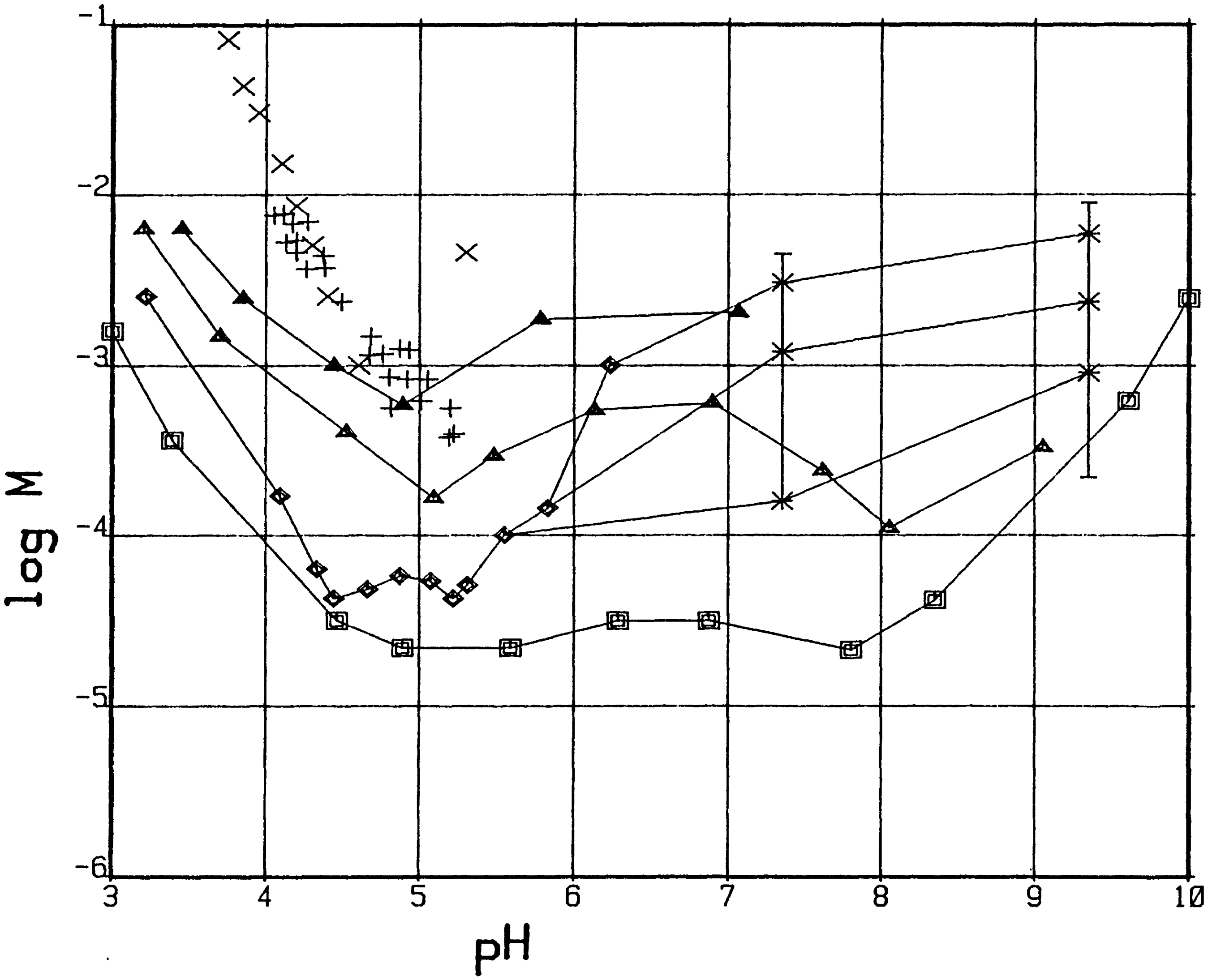


Figure 2: The molar concentration of aqueous aluminum or uranyl solution species (M) as a function of pH. The data of Goldshmid and Rubin (1978) for aluminum are shown as squares, and open and filled triangles, where the solutions contained 0.1, 0.5, and 1.0 M phosphate, respectively. The + and x symbols represent the data of Gayer and Leider (1955) and Babko and Kodenskaya (1960), respectively, for the solubility of $UO_3 \cdot 2H_2O$. The diamonds represent the data of Sergeyeva et al. (1972) for the solubility of rutherfordine. The * symbols represent the data of Babko and Kodenskaya (1960) for the solubility of uranyl carbonate at several concentrations of CO_3^{2-} (0.005, 0.01 and 0.02 M from lowest to highest concentration of uranyl ions at each pH) and are connected to the data values of Sergeyeva et al. (1972) measured at equivalent values of dissolved CO_3^{2-}. The range of values obtained by Babko and Kodenskaya (1960) are shown by the vertical bars at pH 7.3 and 9.3.

experiments having solutions with a pH > 3.5 are to be properly interpreted. The problem is minimized however if only the experiment conducted in a solution having a pH of 3.22 is used.

Sergeyeva et al. (1972) have calculated the activity of UO_2^{2+} in equilibrium with "rutherfordine" at a pH of 3.22 to be 1.66×10^{-3}. From this result we may estimate the free energy of reaction (3) as -20.9 kJ and the free energy of "rutherfordine" as -1563.3±4 kJ/mol. This estimate for the free energy of rutherfordine is significantly less negative than that calculated from the calorimetric data. It is assumed here that the phase controlling the solubility at low pH is sharpite. The free energy of formation of sharpite calculated from the data given by Sergeyeva et al. is -1800.4±4 kJ/mol.

Results similar to those of Sergeyeva et al. (1972) have been published by Nikolaeva (1976). Interpretation of these results would follow the arguments applied to the results of Sergeyeva et al. The entropy of rutherfordine (194 J/mol•K) calculated from the data of Nikolaeva by Lemire and Tremain (1980) appears excessively large, probably indicating improper phase identification in the reaction studied.

In order to interpret the results presented by Sergeyeva et al. (1972) for reaction (5)

$$UO_2CO_3 + H_2O_{(l)} = UO_2(OH)_2 + CO_{2\,(g)} \tag{5}$$

several assumptions must be made regarding the crystalline phases involved in the reaction. Sergeyeva et al. did not attempt to reverse reaction (5). Instead, they studied the formation of UO_2CO_3 from the other components of the reaction as P_{CO} and T were varied. The composition of the rutherfordine phase was assumed to be UO_2CO_3 and the uranyl hydroxide has been assumed to be β-$UO_2(OH)_2$.

Wheeler et al. (1964) and Cordfunke and Debets (1964) have found evidence for three uranyl monohydrates and two uranyl dihydrates. The brief description of the synthesis procedures followed by Sergeyeva et al. (1972) indicates the phase they produced as a starting material for their experiments was schoepite. Cordfunke and Debets have shown that schoepite will be converted to α-$UO_2(OH)_2$ in several days at 373 K. Sergeyeva et al. reported that the conversion of uranyl hydrate to UO_2CO_3 was completed in less than 24 hours. Consequently, the reaction studied by Sergeyeva et al. at 373 K was most likely reaction (6)

$$UO_2CO_3 + 2H_2O_{(l)} = UO_3 \cdot 2H_2O + CO_{2\,(g)} \tag{6}$$

rather than reaction (5).

The data presented by Sergeyeva et al. (1972) for temperatures of 423 and 473 K most likely involved reaction (5) with the uranyl hydroxide of the α-$UO_2(OH)_2$ form rather than the β-$UO_2(OH)_2$ form assumed by Langmuir (1978) and Cordfunke and O'Hare (1978). Wheeler et al. (1964) have shown that α-$UO_2(OH)_2$ is converted to β-$UO_2(OH)_2$ in aqueous solutions at temperatures above 473 K and that schoepite is dehydrated at temperatures above 413 K forming α-$UO_2(OH)_2$. It must be assumed that the dehydration reaction occurred at a faster rate than did the conversion of the uranyl hydrate to rutherfordine.

The enthalpy of formation of rutherfordine may be calculated from the limited data given by Sergeyeva et al. (1972) by assuming that the two points defining reaction (5) give a reasonably valid estimate of the equilibrium change of P_{CO_2} with temperature. The equilibrium constant calculated for reaction (5) is log $K_{(5)}$ = 8.43 - 3293/T and from this relationship, the enthalpy of reaction (5) is 63.0 kJ and the enthalpy of formation of rutherfordine is -1705±6 kJ/mol, both at 298.15 K. This estimate of the enthalpy of formation of rutherfordine is in remarkable agreement with the estiamte based solely upon the calorimetric data given earlier ($\Delta H^\circ_{f,298}$ = -1704.1±2 kJ/mol). The enthalpy of formation of α-$UO_2(OH)_2$ required in this calculation (-1534.5 kJ/mol) was estimated from the calorimetric value for the enthalpy of formation of the partially dehydrated form, $UO_3 \cdot 0.85H_2O$.

The entropy of dehydrated schoepite or α-$UO_2(OH)_2$ may be estimated from the experimental data for reaction (5) given by Sergeyeva et al. (1972), the estimated entropy and free energy of formation of rutherfordine derived in this paper, and other ancillary thermodynamic data from Robie et al. (1979). The free energy of reaction (5) at 298.15 K, 14.9 kJ, may be calculated from the equilibrium constant given above. The free energy of formation of dehydrated schoepite or α-$UO_2(OH)_2$ is estimated to be -1404.9 kJ/mol and the entropy to be 156.6 J/mol•K.

The entropy estimate for α-$UO_2(OH)_2$ is considerably larger than the value estimated from Latimer's rules by Cordfunke and O'Hare (1978) for β-$UO_2(OH)_2$ of 134±8 J/mol•K or that estimated by Langmuir (1978) for β-$UO_2(OH)_2$ from the presumed equilibrium between scheopite and β-$UO_2(OH)_2$ at 333 K. However, this is not unreasonable because Zachariasen (1948) has shown that UO_2F_2, having a similar structure to $UO_2(OH)_2$, commonly exhibits stacking disorder in samples prepared at low temperature (that are removed upon heat treatment of the sample). Also, Porte, Gutowsky, and Boggs (1962) interpreted the broad band proton magnetic resonance spectrum of β-$UO_2(OH)_2$ and schoepite to represent the structures $UO_2(OH)_2$ for the monohydrate and $U_2O_2(OH)_2 \cdot 3H_2O$ for the dihydrate. The estimates of the entropy of β-$UO_2(OH)_2$ given by Langmuir and by Cordfunke and O'Hare are based upon an ordered structure while thermal dehydration of schoepite probably results in some initial disorder between oxygen deficiency and H_2O distribution similar to the oxygen deficiency which exists in some $UO_{2.9}$ formed by thermal decomposition (e.g., Wheeler et al., 1964). Also, Dawson et al. (1956) have shown that α-$UO_2(OH)_2$ has a smaller unit cell volume, 307.1 $Å^3$, than β-$UO_2(OH)_2$ (351 $Å^3$, where Z = 4 for each phase).

Heat Capacities of Rutherfordine and Dehydrated Schoepite by Differential Scanning Calorimetry

The heat capacities of rutherfordine as $UO_2(CO_3)_{.86}(OH)_{.28}$ and dehydrated schoepite as $UO_3 \cdot 0.77H_2O$ were measured by differential scanning calorimetry to near the limits of their thermal stability, 700 and 500 K, respectively. The experimental results are listed in table 6 together with estimates of the heat capacities of UO_2CO_3, $UO_3 \cdot 0.85H_2O$ and $\alpha\text{-}UO_2(OH)_2$ based upon these results.

The experimental heat capacities of dehydrated schoepite were corrected to the compositions $UO_3 \cdot 0.85H_2O$ and (see table 7) $\alpha\text{-}UO_2(OH)_2$ through addition of the heat capacity of the appropriate amount of H_2O as steam at the temperature of the experimental data point. Because the H_2O behaves like zeolitic water (Porte et al., 1962) this approximation is probably valid within the experimental error of the differential scanning calorimetric values (i.e., ±1.0 percent). Smoothed values of heat capacity estimates for each phase are listed in table 6.

The heat capacities of the rutherfordine sample were corrected for $0.14\alpha\text{-}UO_2(OH)_2$ assuming no excess heat capacity terms in this temperature range. Smoothed heat capacity estimates for temperatures between 298.15 and 700 K are given in Table 6. The calculated heat capacity values for rutherfordine are significantly smaller than the estimated values given by Lemire and Tremaine (1980).

Schoepite and dehydrated schoepite: Uranyl nitrate trihydrate (reagent grade) was decomposed in a circulating air oven at 503 K yielding orange, amorphous UO_3. The amorphous UO_3 was mixed with distilled water and aged several days at room temperature. A portion of the sample was removed and air dried. An x-ray diffraction pattern of the dried sample matched the data given by Christ and Clark (1960) for schoepite and Dawson et al. (1956) for $UO_3.2H_2O$. This sample will be called schoepite.

Analysis of the schoepite sample indicated there were 2.02 H_2O/UO_3. Dehydration of this sample at 500 K in a differential scanning calorimeter (sample heated until constant isothermal baseline observed) yielded a sample containing 0.77 H_2O/UO_3. The sample was stable in air (i.e., changes in relative humidity did not change the weight of the dehydrated sample).

Rutherfordine: The rutherfordine sample was prepared by the procedures used by Bullwinkel (1954) and by Sergeyera et al. (1972). Briefly, a stream of CO_2 was vigorously bubbled through a ceramic frit (to produce very fine bubbles) into the solution containing aged schoepite. The solution was rapidly stirred during the 24 to 36 hour period and the beaker was covered thus providing a CO_2 pressure of about 1 bar.

An X-ray diffraction pattern of the material is given in table 5. The powder diffraction pattern for the synthetic rutherfordine is in good agreement with that given by Clark and Christ (1956) and by Frondel and Meyrowitz (1956) for natural rutherfordine.

The synthetic rutherfordine was prepared in two batches (one for 24 hours the other for 36 hours). Neither the enthalpy of solution or X-ray powder diffraction data indicated a difference in these samples.

Table 6. Experimental and calculated heat capacities of rutherfordine and dehydrated schoepite

	Rutherfordine		Dehydrated Schoepite		
Temperature	$UO_2(CO_3)_{.86}(OH)_{.28}$	UO_2CO_3	$UO_3 \cdot 0.77H_2O$	$UO_3 \cdot 0.85H_2O$	$\alpha UO_2(OH)_2$
K	J/g•K	J/mol•K	J/g•K	J/mol•K	J/mol•K
298.15		106.5		107.0	109.0
360	.363	117.4	.3851	117.7	120.0
360			.3829		
380	.370	120.5	.3946	120.9	123.2
380			.3917		
400	.379	123.3	.4035	123.9	126.3
400	.378		.4024		
420	.387	125.9	.4146	126.8	129.3
420			.4132		
440	.395	128.4	.4234	129.6	132.0
440	.394		.4211		
460	.405	130.6	.4328	132.1	134.6
460			.4346		
480	.411	132.7	.4399	134.6	137.0
480	.408		.4409		
500	.417	134.7	.4430	136.8	139.3
500	.414		.4477		
520	.422	136.5		138.9	141.4
540	.426	138.2		140.8	143.4
560	.429	139.7		142.6	145.2
580	.435	141.2		144.2	146.8
600	.438	142.5		145.7	148.3
620	.441	143.7		147.0	149.7
620	.445				
640	.448	144.8		148.2	150.9
650	.450	145.3		148.8	151.5
700	.455	147.6		151.0	153.9

Table 7. Molar thermodynamic properties of (alpha) $UO_3 \cdot 0.85H_2O$

Temp.	Heat Capacity	Entropy	Enthalpy Function	Gibbs energy Function
T	C°_p	S°_T	$(H^\circ_T-H^\circ_{298})/T$	$-(G^\circ_T-H^\circ_{298})/T$
Kelvin		J/(mol·K)		
298.15	107.0	150.7	0.0	150.7
320	110.9	158.4	7.4	151.0
340	114.3	165.2	13.6	151.6
360	117.7	171.9	19.3	152.5
380	120.9	178.3	24.6	153.7
400	123.9	184.6	29.5	155.1
420	126.8	190.7	34.0	156.7
440	129.6	196.7	38.3	158.4
460	132.1	202.5	42.3	160.1
480	134.6	208.2	46.1	162.0
500	136.8	213.7	49.7	164.0
520	138.9	219.1	53.1	166.0
540	140.8	224.4	56.3	168.1
560	142.6	229.5	59.4	170.2
580	144.2	234.6	62.3	172.3
600	145.7	239.5	65.0	174.5
620	147.1	244.3	67.7	176.6
640	148.2	249.0	70.2	178.8
660	149.3	253.6	72.5	181.0
680	150.2	258.0	74.8	183.2
700	151.0	262.4	77.0	185.4

Estimated Thermodynamic Properties of Coffinite

Natural coffinite samples usually contain dispersed, fine-grained uraninite, quartz, and organic material (Nord, 1977). Synthetic coffinite prepared by Fuchs and Hockstra (1959) contained excess silica and some uraninite. Thus preparation of a coffinite sample (natural or synthetic) that has sufficient purity, mass, or that can be properly characterized for calorimetric studies appears improbable. Therefore, the thermochemical properties of coffinite must be estimated from the qualitative experiments and geological information available to us.

Brookins (1975) and Langmuir (1978) have estimated the free energy of formation of coffinite as -1907.9±10.9 and -1891.2 kJ/mol, respectively. Brookins' estimate was based upon the method of differences and used the thermodynamic properties for uraninite, zircon, baddeleyite, thorite, and thorianite in the model. From this model, Brookins predicted that uraninite would be unstable with respect to coffinite where the log of the activity of $H_4SiO_4^o$ was greater than -6.9. Langmuir felt that Brookins' model predicted an unreasonably low equilibrium silica activity for coffinite and uraninite and noted that coffinite would be stable with respect to uraninite in all natural waters, a point at variance with the common occurrance of uraninite and quartz. Langmuir assumed that the average value of the concentration of silica (about 10^{-3}) found in ground waters draining the Grants mineral belt in New Mexico, where both uraninite and coffinite occur in uranium ore deposits, would represent a better estimate of the equilibrium silica activity for reaction (7).

$$USiO_4 + 2H_2O = UO_2 + H_4SiO_4^o \qquad (7)$$

Brookins (1975) and Langmuir (1978) have each assumed that coffinite is more stable than the component oxides uraninite and quartz at 298.15K. However, qualitative evidence from synthesis experiments and from petrographic studies of coffinite ore suggest that this assumption may not be valid.

Brookins (1975) rationale for assuming that the free energy for reaction (8) as calculated by Schuiling

$$ZrO_2 + SiO_2 = ZrSiO_4 \qquad (8)$$

$$UO_2 + SiO_2 = USiO_4 \qquad (9)$$

et al. (1976) could be used for ΔG_r of reaction (9) was based upon his hypothesis that U and Zr are ideally diadochic and upon literature data which implied that both coffinite and zircon break down to their respective oxides at high temperature. If U and Zr were ideally diadochic, a complete solid solution between zircon and coffinite should exist. However, Mumpton and Roy (1961) found that only 4±2 mole percent of coffinite dissolved in zircon and that only 8±2 mole percent of baddeleyite dissolved in uraninite (both studies at 1623 K and in controlled oxygen atmospheres).

Curtis and Sowman (1953) concluded that zircon decomposed at 1813 K. Earlier, Geller, and Lang (1949) had reported that zircon underwent incongruent melting at 2048 K. Mumpton and Roy (1961) prepared zircon from zirconia and silica gels at 1573 K (24 hour heating) and heated the zircon at 1773 and 1873 K for 72 hours. Mumpton and Roy observed peaks for ZrO_2 in the X-ray pattern for the sample heated at the higher temperature and concluded that this represented unequivocal proof that Curtis and Sowman were correct. However, Harris (1959) synthesized huttonite under conditions similar to those followed by Mumpton and Roy and concluded that the reaction was so sluggish that as many as five homogenization runs were required to attain equilibrium. In all of the X-ray data taken for huttonite samples prepared at temperatures above 1673 K, a pattern for ThO_2 was clearly evident. Thus the appearance of an X-ray pattern for ZrO_2 in the data of Mumpton and Roy does not provide unequivocal evidence of the temperature of thermal decomposition for zircon, but more likely represents incomplete reaction of the initial components.

Knowledge of the temperature of thermal decomposition of zircon and huttonite combined with the observation that coffinite decomposed to uraninite and anorphous silica at 1518 K, and with the estimated values for the free energy formation of zircon and huttonite given by Schuiling et al. (1976) should allow us to make a better estimate of the free energy of formation of coffinite. Schuiling et al. have estimated that the free energies of reactions (9) and (10) at 1000 K and 1 kbar where quartz is the SiO_2 phase were between the limits $- 22.1\ \mathrm{kJ} < \Delta G < -14.3\ \mathrm{kJ}$ based upon the study of 19 go, no-go type reactions involving the phases ZrO_2, SiO_2, ThO_2, $ZrSiO_4$ and $ThSiO_4$ among others.

$$ThO_2 + SiO_2 = ThSiO_4 \qquad (10)$$

These results are consistent with decomposition temperatures for huttonite and zircon above 2000 K and with the silicates more stable than the oxide components at 298.15 K.

The thermal stability of coffinite is not well known. Fuchs and Hoekstra (1959) observed complete dissociation of coffinite to uraninite and amorphous silica at 1518 K and placed the upper limit of thermal stability at 1273 K (for coffinite heated in a vacuum) based upon short term (3 to 4 hours) heating experiments at 473, 673, 873, and 1073 K. On the basis of these observations we may estimate that the free energy of reaction (9), where the SiO_2 phase is approximated by silica glass, is zero at 1273 K. Using the heat capacities of quartz (α-βtransition removed) and uraninite to approximate the heat capacity of coffinite between 298.15 and 1273 K and using ancillary thermochemical data from Robie et al. (1979), the free energy of coffinite is estimated to be -1886±6 kJ/mol at 298.15 K. Coffinite, so defined, would be less stable than quartz and uraninite at 298.15 K and at higher temperatures.

A Model for the Deposition of Coffinite and Some Uraninites

At this point, it must be determined whether the estimate for the free energy of coffinite is realistic in light of our knowledge of the natural occurrence of coffinite. Cuney (1978) has made a detailed study of the Bois Noirs - Limouzat uranium vein, Forez, France, and discussed a six stage paragenetic sequence. Stage 1 began with the precipitation of fibrous quartz and large quartz crystals. Hematite and sericite were frequently trapped in quartz. Colloform pitchblende (nominally uraninite) coated the quartz and was, in turn, coated with pyrite. The half-spherules of pitchblende show mutual integrowths with quartz. This sequence was followed by several cyclic periods of deposition of marcasite that was coated by pyrite. Evidence for simultaneous preciptitation of marcasite and pitchblende was not observed. Stage 2 began with the precipitation of microcrystalline quartz and chalcedony which were colored red by microcrystalline hematite. Older pitchblende coatings frequently broke off and became brecciated inclusions in the precipitated silica. Concretionary coffinite precipitated on quartz surfaces toward the end of stage 2. Marcasite, precipitated in stage 1, underwent strong corrosion and stage 1 pyrite was corroded around the pitchblende spherules during stage 2. In addition, adularia grew on K-feldspar surfaces during stage 2. Stages 3 and 4 were characterized by precipitation of chalcopyrite, hematite, goethite, galena, and white to smokey quartz followed by precipitation of carbonates. Bismuth minerals were precipitated with quartz, chalcopyrite, pyrite and some hematite in stage 5. Uranium was remobilized in stage 6 and deposited as hexavalent uranium along joints in the brecciated previous mineralization and in the granite.

The paragenetic sequence described by Cuney (1978) indicates that uraninite and quartz were precipitated contemporaneously. The geologic record would suggest that the free energies of formation of coffinite estimated by Brookins (1976) and Langmuir (1978) overstate the stability of coffinite. Cuney has shown that the activity of silica rose high enough for chalcedony to precipitate (log a(H_4SiO_4) = -3.68 based upon the free energy of formation of chalcedony from Walther and Helgeson, 1977, and ancillary thermochemical data from Robie et al., 1979). Using the free energy of coffinite derived in this report and the ancillary thermochemical data from Robie et al., the equilibrium silica activity defined by reaction (7) would be log a(H_4SiO_4)= -3.59, a value in good agreement with the activity of silica necessary to precipitate contemporaneous chalcedony as observed by Cuney.

The value of the log of the activity of silica in equilibrium with coffinite and uraninite is in general agreement with the value [log a(H_4SiO_4)= -3.0] postulated by Langmuir (1978). However, the free energy of formation of coffinite given by Langmuir is not consistent with his estimate for the equilibrium silica activity for reaction (7).

Leroy (1978) has described the Margrac and Fanay uranium deposits (western Massif Central, France) and noted a similar paragenetic sequence to that observed by Cuney (1978). An important observation reported by Leroy was that transformation of uraninite precipitation to coffinite precipitation was contemporaneous with the formation of montmorillonite. Kittrick (1970) observed silica activities of $10^{-2.38}$ to $10^{-3.53}$ in solubility studies of montmorillonite samples. These results support the equilibirum silica activity for reaction (7) and free energy of formation for coffinite derived above.

Although uraninite and coffinite are common in sandstone-host uranium ore deposits, paragenetic sequences for these ore bodies have not been developed (Ludwig and Grauch, 1980). However, a review of some of the literature describing the mineralized zones of the Colorado Plateau uranium ores clearly associates coffinite precipitation with an increase in silica activity in the local depositional environment. For example, Garrels et al. (1959) have noted that precipitation of overgrowths on quartz preceeded mineralization at the Virgin No. 3 mine, Montrose County, Colorado, and that mineralization began with the deposition of vanadiferous clays. A similar increase in silica activity can be inferred from the description of the ore deposit at the J. J. mine, Montrose County, Colorado, reported by Elston and Botinelly (1959). Finally, Dahlkamp (1978) studied the Key Lake U-Ni deposits, Northern Saskatchewan, Canada, and found that coffinite always occurred with kaolinite and chlorite as a coating on earlier pitchblende deposits.

In several of the natural occurrences of coffinite cited above the mode of deposition suggests a preliminary colloidal gel precipitation followed by crystallization of coffinite (also see Noench, 1962, and Ludwig and Grauch, 1980). Coffinite also occurs intermixed with uraninite, both of very small crystal size, as a matrix replacing woody material (Gas Hills District, Wyoming) or as alternating concentric bands with uraninite (South Power River basin, Wyoming) as shown by Ludwig and Grauch.

Fuchs and Hoekstra (1959) had great difficulty finding a procedure to prepare synthetic coffinite while others were completely unsuccessful (e.g., Mumpton and Roy, 1961). Fuchs and Hoekstra found that coffinite could only be obtained from runs which were buffered between pH 8 and 10.5 and which contained a sample that represented a coprecipitate of U^{4+} and silica gel. Gast (1977) has shown that silica has a maximum in ligand exchange capacity (OH^- or H_2O are displaced from surfaces allowing the formation of partial covalent bonds with cations) near a pH of 9.5. It is suggested that the formation of coffinite in the runs prepared by Fuchs and Hoekstra were only successful where the covalent bonding between U^{4+} and $H_3SiO_4^-$ was strong enough to allow the coffinite structure to form as water was expelled. Under such conditions, the formation of large crystals through the process of diffusion would be greatly limited as dehydration and fragmentation of the gel structure progressed during crystallization of coffinite.

Several attempts (in this study) to produce coffinite from crystalline and noncrystalline mixtures of uranyl and silica were unsuccessful. Fresh precipitates of crystalline material obtained from basic solutions of sodium metasilicate and uranyl nitrate yielded an X-ray diffraction pattern similar to that for kasolite ($PbO_3 \cdot UO_3 \cdot SiO_2 \cdot H_2O$) although the solution contained no lead. Heating the kasolite-like phase for 3 days at 518 K yielded a phase which produced an X-ray diffraction pattern similar to soddyite. Soddyite and the kasolite-like material heated to 523 K (for about 3 weeks) at a pressure of 80 bars of hydrogen gas decomposed yielding uraninite, amophous silica and some quartz (Nord, written communication, 1979). Freshly precipitated uranyl silicate gel mixed with sodium thiosulfate in a slightly acidified solution yielded a greenish gray solid with an X-ray diffraction pattern similar to that of natural boltwoodite (the presence of Na in the structure was not confirmed). Similar negative results were obtained using methane and hydrogen plasma (Irving Breger, written communication, 1978) as the reducing agents for soddyite. Freshly precipitated uranyl silicate gel placed in a bomb for 24 hours at 523 K and a pressure of 50 bars of hydrogen gas yielded several black chunks that had several light blue patches on the surfaces. A few areas appeared dark blue where uraninite was mixed into the blue material. This material resembles the coffinite described by Fuchs and Hoekstra (1959), but was not produced in sufficient quantity to allow a positive identification to be made (X-ray data non-conclusive). Evidence collected in this brief set of experiments, suggest that U^{6+} must be reduced to U^{4+} before or shortly after the uranium is absorbed on the amorphous silica surface in order to form coffinite. Reduction of uranium in a crystalline uranyl silicate will result in the formation of uraninite and quartz when the uranyl silicate is decomposed.

Jones and Uehara (1973) have studied amorphous coatings on mineral surfaces using electron microscopy. They observed that after 6 months, finely crushed quartz particles develop a gel coating which coalesced forming coat-of-paint appearance. Similar features were seen on kaolin particles and particularly in soils developed from volcanic ash. It is suggested here that a silica gel coating such as that observed by Jones and Uehara is a necessary first stage in the formation of natural coffinite.

Mark et al. (1970) used radio-tracer ($^{233}UO_2^{2+}$) techniques to study the absorption of aqueous uranyl species on the surface of glass scintillators at various pH, temperature, and uranyl concentration values. They concluded the surface coverage was a monolayer or less thick. It is assumed here that the study by Mark et al. could be extended to the interaction of agueous uranyl species and silica gel. Stanton and Maatman (1963) have studied the strong interaction of aqueous uranyl species and the surface of silica gel.

The following model of coffinite formation has been derived from the preceeding discussion and from some additional experimental studies that are discussed below. The initial stage in the formation of coffinite is the precipitation of a gel coat (containing both uranium and silica gel) on the surfaces through which the ore forming solutions pass. Both gels continue to accumulate with older portions of the precipitated gels recrystallizing. Coffinite formation occurs where temperature and pressure conditions do not result in rapid dehydration and alteration of the precipitated gel structure. Coffinite precipitation ceases where the Eh of the solution causes oxidation of U^{4+} to U^{6+}, or where crystallization of UO_2 occurs before bonding between the uranium gel and silica gel components can be established. Excess silica or uranium will be excluded from the precipitating coffinite and crystallize as quartz (or another silica polymorph) or uraninite (under reduced conditions).

Uranium is generally considered to have been transported as the uranyl ion or a complexed uranyl species (Reynolds and Goldhaber, 1978; Brookins, 1976; Langmuir, 1978; and Weeks and Garrels, 1959), for unmetamorphosed deposits which are younger than about 2200 m.y. and to have been of detrital origin in older deposits (Robertson et al., 1978). Robertson et al. and Cloud (1976) have suggested that the first appearance of red beds at about 2000 m.y. indicated a major change in oxidation potential of the atmosphere and Robertson et al. further suggest that this change in atmospheric conditions led to increased solubility of uranium (as uranyl species) and the loss of uraninite as a stable phase under surface weathering conditions. Dissolved uranium is deposited and concentrated under unique sedimentary conditions where either sedimentary or structural conditions developed a permeable zone through which the oxidized uranium bearing solutions were channeled, and within which, chemical conditions resulted in the reduction of U^{6+} to U^{4+}. The mechanisms by which the uranyl species may be reduced have been extensively discussed in the literature (e.g. Reynolds and Goldhaber, 1978; Brookins, 1976; and Moench, 1962) and, therefore, will not be discussed in detail here.

The two commonly cited mechanisms by which uranyl ions may be reduced are through the oxidation of sulfides and of organic material. Humic and fulvic acids form complexes with UO_2^{2+} (Kribek and Podlaha, 1980) and with Th(IV) (Nash and Choppin, 1980). Nash and Choppin have shown that desolvation of aqueous Th(IV) is an important result of complexation by fulvate and humate. It may be assumed that this effect is important in the uranyl-humic complexes as well.

The desolvation associated with uranyl-humic complexes may be an important contributing factor to the high correlation of coffinite and organic material in the uranium ore bodies of the Colorado Plateau. Dalton et al. (1962) have shown that ion exclusion from the pores of silica gel is directly related to the charge density of the cation. Desolvation of the uranyl ion followed by reduction of U^{6+} to U^{4+} and destruction of the bonding with fulvate or humate may allow penetration of U^{4+} into existing silica gel rather than limiting the association to a strictly surfacial reaction. This mechanism could allow coffinites precipitated in and near organic material to occur in relatively massive volumes of uraninite, coffinite, and quartz mixtures while coffinites developed in vein deposits would tend to be built from thin coatings.

Corrosion of early sulfide precipitates and a lack of evidence of coprecipitation of uraninite or coffinite and sulfides (e.g. Leroy, 1978; and Cuney, 1978) have been cited as proof that sulfides play an important role in reducing U^{6+} from solutions that have transported uranium. Miller (1958) qualitatively studied this process by investigating the conditions under which pitchblende precipitated from solutions of uranyl fluoride, sulfate, carbonate, and hydroxide as these solutions were saturated with H_2S. Miller's observations combined with the X-ray analysis of natural uraninites and a few of Miller's synthetic uraninite samples (Croft, 1956) support this idea.

Croft (1956) noted that the common morphologies for uraninite were the cube, octahedron, and cubo-octahedron. The cube was the most commonly occurring crystal habit in pegmatite deposits of uraninite. Croft's X-ray data showed that the major development in crystals in vein type UO_2 deposits and in botryoidal pitchblende was in the [111] direction. Miller (1958) noted that Croft had found that pitchblende that precipitated directly as hemispherical and botryoidal masses from uranyl sulfate solutions saturated with H_2S also showed elongation in the [111] direction. Croft also found that the fine-grained material that precipitated originally as a uranyl sulfide (in Miller's experiments) and then reacted to form uraninite showed elongation in the [001] direction. Where elongation in the [111] direction was observed; Croft determined that the adjacent fibers were randomly oriented with respect to rotation about [111].

The theory may then be advanced that crystal growth in the [111] direction would be consistent with an accumulation of linear UO_2^+ molecules from the solution on the (111) plane. Reduction of UO_2^{2+} to UO_2^+ is rapid and reversible (Ahrland et al., 1973), while reduction to U^{4+} requires the breaking of metal-oxygen bonds and proceeds at a lower rate. UO_2^+ has the same linear structure as UO_2^{2+} and could easily be accommodated on a (111) growth surface. Final reduction of U^{5+} to U^{4+} could then proceed during the change in oxygen-uranium bonding as each O - U - O is incorporated into the growing crystal.

A similar sequence would allow the development of bonding between O - U - O and silica gel. Thus, natural coffinite may form (in the absence of organic catalysts) only where UO_2^+ is absorbed on a silica gel surface and then reduced to U^{4+}. The occurrance of uraninite and quartz in pegmatites where the uranium was presumably carried in a reduced state (U^{4+}) and the lack of coffinite deposition from these reduced high silica solutions supports this theory. In addition, the occurrance of hematite (e.g. Cuney, 1978) in hydrothermal veins associated with pegmatites or granite, preceeding the deposition of uranium phases, suggests some oxidation of the ore forming fluids from which the coffinite and uraninite (elongated in the [111] direction) were precipitated, also in support of this theory.

The theory is also supported by studies conducted on the related system Zr-O-H-Si. Clearfield (1964) and Garvie (1965) have shown that ZrO_2 would crystallize in a metastable tetragonal form that is elongated in the [111] direction when ZrO_2 is precipitated from aqueous solutions at low temperature. Wells (1975) and Teufer (1962) describe tetragonal ZrO_2 as having four oxygen in a flattened tetrahedron and four oxygen in an elongated tetrahedron, rotated at 90° with respect to the former tetrahedron, surrounding the Zr. This distorted cubic arrangement is similar to the structure in $ZrSiO_4$ as noted by both Teufer and by Wells.

Because Zr^{4+} and U^{5+} have similar ionic radii (Shannon and Prewitt, 1969), U^{5+} can be expected to react similar to Zr^{4+} in nucleation and early crystallization. The smaller ionic radius of U^{5+} compared to U^{4+} (Shannon and Prewitt) would cause initial distortion of the oxygen bonding at the growing surface that would favor the growth of uraninite in the [111] direction or favor bonding to form coffinite.

Ahrland et al. (1973) have shown that uranium ions with the highest charge are stabilized with respect to other uranium species through hydrolysis. Both UO_2^{2+} and U^{4+} are stabilized with respect to UO_2^+ in this manner. In contrast to U^{4+} and UO_2^{2+}, the actual charge on the UO_2^+ ion is small enough that protons are not split off from the hydration shell in acidic solutions. Thus reduction of UO_2^{2+} to UO_2^+ would decrease the stability of the dissolved uranium and favor the incorporation of the uranium species into either uraninite or coffinite crystals.

The model for coffinite deposition may then be summarized as follows. Uranium must be transported into a zone in which reduction from U^{6+} proceeds through a two step reaction. Initial reduction of UO_2^{2+} to UO_2^+ decreases the solubility of the dissolved uranium leading to adsorption of the linear UO_2^+ molecule onto a boundary surface. Reduction of U^{5+} to U^{4+} results in the bonding of the linear O - U - O molecule to the surface. If the boundary surface is an amorphous silica coating, bonding between the linear O - U - O molecule and the silica may result in the formation of coffinite. The absence of amorphous silica as the boundary layer or a rapid influx of hexavalent uranium would lead to the crystallization of uraninite (elongated in the [111] direction). Variations in the rate of adsorption of these components (as a consequence of a change in Eh or a change in mass transport) could lead to the deposition of alternating bands of uraninite and coffinite with or without bands of a silica polymorph. The tendency for the linear UO_2^+ molecule to be adsorbed with its pole parallel to the surface and at a thickness of a monolayer provides the necessary proximity for coffinite formation as thin coatings.

The proposed model of coffinite formation does not depend upon the presence of either impurity cations (e.g. Ca^{2+}) or anions (e.g. OH^-). However, the metastable nature of the crystals initially formed and the distorted bonding on the growth surfaces presumably would promote the formation of many nuclei of crystallization and prevent these crystallites from becoming very large. Such surfaces may easily accommodate ions of an appropriate size and charge although they may not be necessary to stabilize the structure.

Finally, coffinite is metastable with respect to uraninite and quartz at all geologically important temperatures.

Estimated values for the free energy of formation of selected uranyl silicates

Models for estimating the Gibbs free energy and enthalpy of formation of geologically important phases have been developed using several methods (Slaughter, 1966; Karpov and Kashik, 1968; Kittel, 1971; Eugster and Chou, 1973; Tardy and Garrels, 1974; Chen, 1975; Nriagu 1976, and Tardy and Garrels, 1976 and 1977). Slaughter and Kittel have used models to predict crystal lattice energies while the other studies have attempted to correlate differences in energy between a series of phases and reference substances through regression analysis.

A complete review of the various models by which free energies or enthalpies of formation have been estimated is beyond the scope of this paper. The method followed by Chen (1975), however, will be examined in some detail. Chen calculated the free energy of a phase (called here the standard phase) by summation of several types of reference materials and assigned an integer value, x, between 0 and about 6 representing what he called the order or degree of complexity of the reaction (several examples are provided in table 8). The estimated free energies, G_E, were fit to an equation of the form $G_E=ae^{bx}+c$ where a, b, and c were obtained through regression analysis and where c represented the estimated free energy of the phase. Alternatively, Chen's model predicts that the free energy of reaction, Δ Gr, from the selected reference phases will vary as ae^{bx}.

Karpov and Kashik (1968) and Nriagu (1976) calculated non-standard state values for simple reference oxide and/or hydroxide componenets which partitioned the free energy of reaction from these reference phase in their standard states among these oxide and/or hydroxide reference substances. Estimated values of the free energy of formation of several phases using the non-standard state reference values yield values between 0.5 and 1.0 percent different than the best current experimentally derived values for the same phase. There is an equal probability that the model will overestimate or

Table 8. Examples of the procedure suggested by Chen (1975) for estimating the free energies of formation for silicate minerals. The sums of the free energies of the reference phases, G_E, are fit to an equation of the form $G_E = ae^{bx} + c$, where the values of a, b, and c were obtained thru regression analysis and x was the order assigned to the reaction

Standard Phase*	Reference Phases*	$G*_F$ kJ/mol	Order	$\Delta G**_r$ kJ
Low albite $NaAlSi_3O_8$	$0.5Na_2O+0.5Al_2O_3+3SiO_2$	-3548.023	0	163.698
measured -3711.720	$0.5Na_2O+0.5Al_2SiO_5+2.5SiO_2$	-3548.711	0	163.010
	$0.5Na_2SiO_3+0.5Al_2SiO_5+2SiO_2$	-3666.222	1	45.498
calculated -3705.0	$0.5Na_2Si_2O_5+0.5Al_2SiO_5+1.5SiO_2$	-3666.478	1	45.242
difference 0.2%	$NaAlSiO_4 + 2SiO_2$	-3690.074	2	21.646
	$NaAlSi_2O_6 + SiO_2$	-3707.122	3	4.598
Jadeite $NaAlSi_2O_6$	$0.5Na_2O + 0.5Al_2O_3 + 2SiO_2$	-2691.735	0	159.099
measured -2850.834	$0.5Na_2O + 0.5Al_2SiO_5 + 1.5SiO_2$	-2692.423	0	158.411
	$0.5Na_2SiO_3 + 0.5Al_2SiO_5 + SiO_2$	-2809.934	1	40.900
calculated -2839.5	$0.5Na_2Si_2O_5 + 0.5Al_2SiO_5 + 0.5SiO_2$	-2810.190	1	40.644
difference 0.4%	$NaAlSiO_4 + SiO_2$	-2833.786	2	17.048
Paragonite $NaAl_2[AlSi_3O_{10}](OH)_2$	$0.5Na_2O + 1.5Al_2O_3 + 3SiO_2 + H_2O$	-5367.392	0	187.509
	$0.5Na_2SiO_3+1.5Al_2SiO_5+SiO_2+H_2O$	-5486.967	1	67.933
measured -5554.900	$NaAlSiO_4 + Al_2SiO_5 + SiO_2 + H_2O$	-5510.819	2	44.081
calculated -5532.500	$NaAlSi_2O_6 + Al_2SiO_5 + H_2O$	-5527.867	3	27.033
difference 0.4%	$NaAlSi_3O_8 + Al_2O_3 + H_2O$	-5531.089	4	23.811

Standard Phase*	Reference Phases*	G^*_F kJ/mol	Order	ΔG^{**}_r kJ
Microcline $KAlSi_3O_8$ measured -3742.330 calculated -3746.0 difference 0.1%	$0.5K_2O + 0.5Al_2O_3 + 3SiO_2$	-3521.022	0	221.309
	$0.5K_2SiO_3 + 0.5Al_2SiO_5 + 2SiO_2$	-3660.412	1	81.918
	$KAlSiO_4 + 2SiO_2$	-3718.551	2	23.779
	$KAlSi_2O_6 + SiO_2$	-3732.178	3	10.152

*The thermodynamic data are taken from Robie et al., (1979), Stull and Prophet (1971), and Robie and Hemingway (1981, unpublished data for paragonite).

**The calculated difference between the sum of the free energies of the reference phases and the measured free energy of the standard phase.

underestimate the stability of the standard phase.

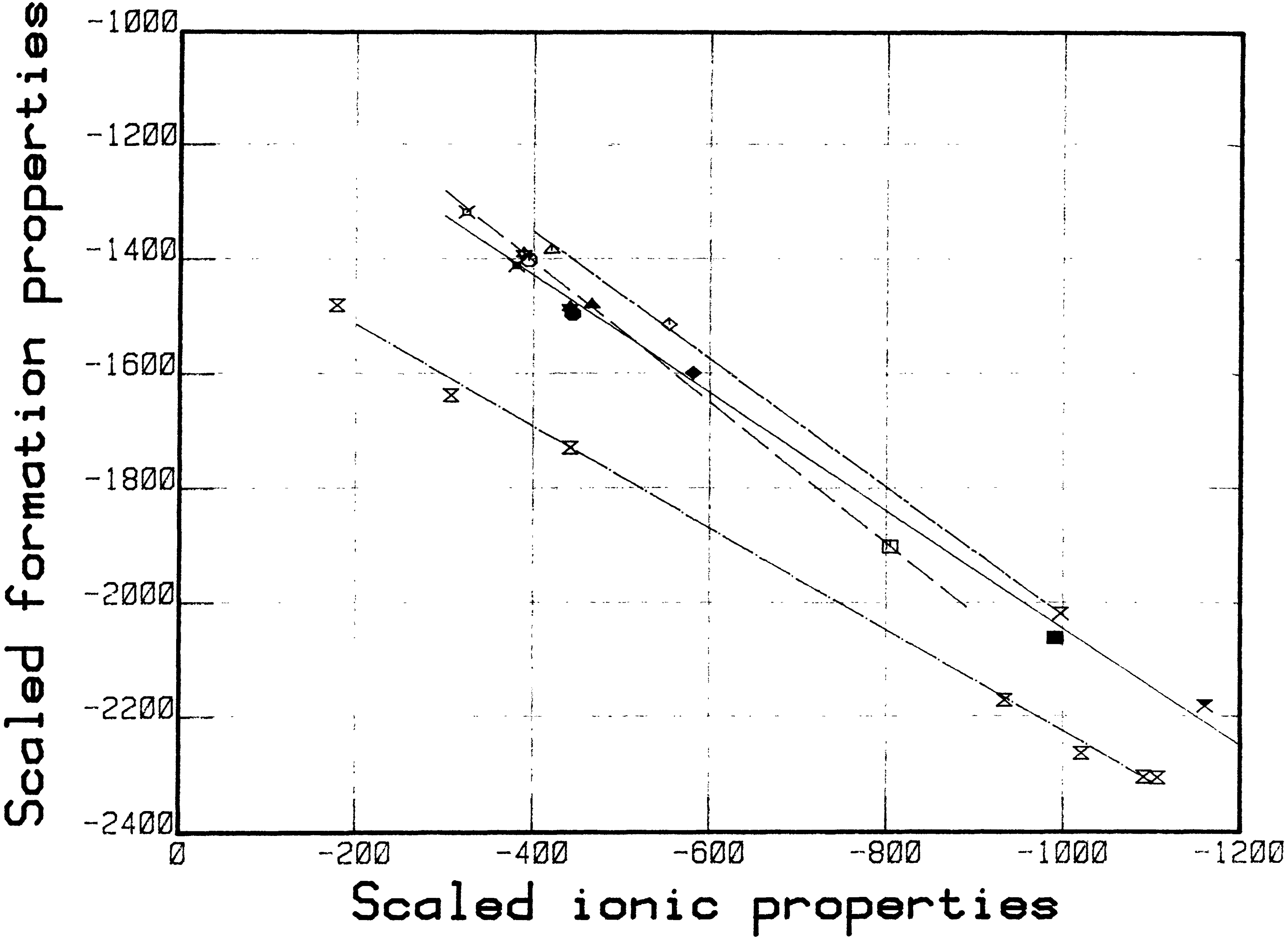
Eugster and Chou (1973) estimated the enthalpy of formation of several phyllosilicates from a linear relationship between the enthalpy of formation of a phyllosilicate divided by the number of tetrahedrally coordinated silicon and aluminum atoms in the structure and the sum of the enthalpies of formation of the aqueous ions representing the octahedral and exchangeable ions in the structure, also divided by the number of tetrahedrally coordinated silicon and aluminum ions. The experimental values used to develop the linear relationships scattered by less than 1.0 percent. A revised figure showing this relationship is included as figure 3. The thermodynamic data were taken from Robie et al.(1979) and Robie and Hemingway (1981, unpublished data).

A procedure similar to that followed by Euster and Chou (1973) was used by Tardy and Garrels (1976). Tardy and Garrels developed a linear relationship between the free energy of formation of ortho- and metasilicates from an oxide reference state and the average difference in free energy between the oxide components and the free energy of the common aqueous cation. Care must be exercised when examining or using the data of Tardy and Garrels because the several sets of free energy values are derived from largely the same experimental data but contain slight to major differences in the free energy values for the reference oxides. These differences cancel out in the procedures followed by Tardy and Garrels to obtain their linear relationship, but do not cancel out in the absolute magnitude of the free energies of formation from the elements.

Of those methods described above, the method of Chen (1975) and that of Eugster and Chou (1973) appear the most readily adaptible in providing estimates of the free energy of formation of the uranyl silicate phases. The method of Eugster and Chou was modified such that the free energies of formation rather than the enthalpies of formation were used. The results for the free energy calculations are shown in Figure 3. These results appear as valid as the correlation provided by Eugster and Chou. However, the estimated free energies of formation for the uranyl silicates derived from the relationship shown in Figure 3 were consistently of equal magnitude to the summation of the component oxide values. The fact that the method of Eugster and Chou does not appear to provide a good estimate for the free energies of the uranyl silicates is not supprising nor is it a reflection in the usefulness of the procedure. Rather, it reflects the degree to which the model is dependent upon the structural similarity of the phases. To illustrate this point, data for several ortho- and metasilicates are also shown in Figure 3, that are based upon similar calculations.

The method of Chen (1975) was applied by using a summation of oxide component free energies for the order 0 reaction, using meta-silicate, water, chalcedony, and schoepite values for the order 1 reactions, and using uranate, water, chalcedony, and schoepite values for the order 2 reactions. No reactions greater than order 2 were used. The data for the magnesium uranate and meta-silicate phases produced a reversal of the reaction order (as defined by Chen) with respect to the other cations examined that may indicate an error in one of these values. The estimated values for the uranyl silicates are listed in Table 1.

Figure 3: The linear relationship between scaled formation properties and scaled ionic properties as an example of the procedure followed by Eugster and Chou (1973) to estimate enthalpies of formation of several phyllosilicates. The scaled formation properties represent the enthalpy or free energy of formation (in J/mol) divided by the number of tetrahedrally coordinated silicon and aluminum atoms in the structure. The scaled ionic properties represent the sum of the enthalpies or free energies of formation of the octahedral or exchangeable ions in the structure divided by the number of tetrahedrally coordinated silicon and aluminum atoms. The hour glass shaped symbols and dash-dot line represent a modification of the procedure for ortho- and metasilicate phases (fayalite, willemite, tephroite, forsterite, monticellite, distrontium silicate, and larnite, respectively from left to right on the figure). Other phases represented are paragonite, star; chrysolite, inverted triangle with extended sides; pyrophyllite, squares with extended lines at corners; talc, triangles; and fluorphlogopite, diamonds. The open symbols represent enthalpy of formation values and the filled symbol represent free energy data. The solid curve represents the trend of the enthalpy of formation values. The dashed lines represent the free energy of formation results. As can be seen in the results presented for the free energy data, the values obtained from phases that have Al in the octahedral sites (dash pattern) represent a different trend than those containing Mg in the octahedral sites (long-short dash pattern).


Scaled formation properties
-1000
-1200
-1400
-1600
-1800
-2000
-2200
-2400
0
-200
-400
-600
-800
-1000
-1200
Scaled ionic properties

Uranyl Carbonate Complex Ions

The uranyl carbonate aqueous species have commonly been assigned the composition $UO_2(CO_3)_3^{4-}$(UTC),$UO_2(CO_3)_2^{2-}$(UDC) and UO_2CO_3 (e.g. Langmuir, 1978; Scanlan, 1977; Sergeyeva et al. 1972; and Bullwinkel, 1954). Other workers (see Ciavatta et al. 1979, for a concise summary) have considered mixed or polynuclear species such as $(UO_2)_2(OH)_2(CO_3)_2^{2-}$,$(UO_2)_2(OH)_3CO_3^-$, and $UO_2OHCO_3^-$. Recently, Ciavatta et al. (1979 and 1981) have proposed that in addition to the uranyl hydrolysis species present in highly acid solutions, the uranyl carbonate complexes are UO_2CO_3, $(UO_2)_3(OH)_3CO_3^+$, and $UO_2(CO_3)_3^{4-}$ with two polynuclear complexes, $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$ and $(UO_2)_3(CO_3)_6^{6-}$ appearing in those special conditions just preceeding the initiation of precipitation of uranyl carbonate. Although some questions still remain regarding the exact composition of the uranyl carbonate complexes, the results provided by Ciavatta et al. appear to be in better agreement with the chemistry of the natural uranium system than those provided by Langmuir, Scanlan, or Bullwinkel.

Scanlan (1977), Bullwinkel (1954), and Blake et al. (1956) examined the uranyl carbonate complex ions in aqueous solutions that contained additional carbonate added as sodium carbonate or HCO_3^-. Ciavatta et al. (1979 and 1981) examined changes in the aqueous uranyl species associated with changes in the concentration of initial dissolved uranium and with variations in the pressure of CO_2 gas in equilibrium with the solution, but in the absence of added carbonate or bicarbonate ions. Scanlan has shown that the difference in these experimental procedures is reflected in the absorption spectra for the uranyl carbonate solution. Where the concentration of $NaHCO_3$ was less than 0.03M, Scanlan found an increase in the intensity in the absorption spectrum at a wavelength of 425 nm. Sutton (1949) has shown this absorption peak to be associated with the hydrolysis of the uranyl ion.

Bullwinkel (1954) measured the absorption spectrum of uranyl carbonate solutions in the wavelength range of 340 to 490 nm for solutions with pH from 9 to 5. Bullwinkel identified the structure of the spectrum observed for the more basic solutions as that belonging to UTC. A shift in the position of the absorption peaks with the addition of H^+ was interpreted by Bullwinkel to indicate a second mono-uranyl complex that he suggested was UDC. The loss of the fine structure of the absorption spectra upon further addition of H^+ was interpreted by Bullwinkel as indicating that no other uranyl carbonate complexes were present in the solutions he studied. His final spectra at the lowest pH he studied was similar to that given by Sutton (1949) for the uranyl hydrolysis species.

Scanlan (1977) refined the absorption spectra for UDC and studied the variation of the UDC spectra with changes in the concentration of sodium bicarbonate. Scanlan did not alter the interpretation of the absorption spectra for UDC and UTC as given by Bullwinkel (1954), but did note that when the pressure of CO_2 was 1 bar, the concentration of $NaHCO_3$ was less than 0.03m, and the solution pH was lower than 6.5 significant hydrolysis of the uranyl species could be observed. Scanlan assumed that UO_2CO_3 was an additional uranyl carbonate species, but offered no additional proof that the aqueous species was present in the solutions he studied.

Ciavatta et al. (1981) made potentiometric measurements of uranyl carbonate solutions having pH>5.7. They concluded that two uranyl carbonate species were present in these solutions, $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$. This interpretation retains the ratio of U/C found in UDC, but suggests a polynuclear species forms as the solution containing UTC is acidified to the point at which precipitation of UO_2CO_3 begins. Preliminary ^{13}C nuclear magnetic resonance (NMR) data cited by Ciavatta et al. suggest that a single NMR peak was representative of equivalent bonding between the three coordinated carbonate groups of $UO_2(CO_3)_3^{4-}$ and that the two NMR peaks observed in the solutions containing the polynuclear complex, $(UO_2)_3\ (CO_3)_6^{6-}$, represented both bridging and terminal carbonate groups. Ciavatta et al. found no evidence for aqueous species of the form $(UO_2)_x(OH)_y(CO_3)_z$ or for the species $UO_2(CO_3)_2^{2-}$.

Ciavatta et al. (1979) have also made potentiometric measurements of uranyl carbonate solutions with a pH<5. Ciavatta et al. have shown that their data is consistent with the assumption of the aqueous species $UO_2CO_3^{o}$,$(UO_2)_3(OH)_3CO_3^{+}$ and a large polynuclear species with an estimated composition of $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$ that occurs in the solutions as the pH is raised to the point where uranyl carbonate precipitation results. Ciavatta, et al. suggests that the species $(UO_2)_3(OH)_3CO_3^{+}$ may be viewed as having about the same structure as the uranyl hydrolysis species $(UO_2)_3(OH)_5^{+}$ with CO_3^{2-} substituting for $2OH^-$.

One may readily postulate that the uranyl carbonate phase that precipitates from aqueous uranyl carbonate solutions will have a composition that varies in the ratio of UO_2^{2+} to H_2O, OH^- and CO_3^{2-} as pH, P_{CO_2}, pCO_3^{2-}, pUO_2^{2+}, and temperature change. As the precipitation of uranyl carbonate is approached from the basic pH region, rutherfordine would be expected to be the phase that precipitated. As the precipitation point is approached from the acidic pH region, the initial uranyl carbonate phase to precipitate would be sharpite. The composition of the sharpite phase would be expected to show greater variability in CO_3^{2-}, OH^- and H_2O than would the rutherfordine phase because of the greater influence of hydrolysis in the more acidic solutions. This theory is developed in a previous section of this study.

Ciavatta et al. (1979) have provided the equilibrium constants for the aqueous uranyl species $UO_2CO_3^{o}$,$(UO_2)_3(OH)_3CO_3^{+}$, and $(UO_2)_{11}(OH)_{24}(CO_2)_6^{2-}$ as log $\beta_{1,2,1}$ = -9.02, log $\beta_{3,5,1}$ =-16.34, and log $\beta_{11,24,6}$ = -72.0, respectively, from which we may calculate the free energy of formation of each species. Ciavatta et al. (1981) provide a value for the equilibrium constant $*\beta_{3,12,6}$ (for the reaction of UTC to $(UO_2)_3(CO_3)_6^{6-}$ or $(UO_2)_3(OH)_{12}(CO_2)_6^{6-}$) of log $*\beta_{3,12,6}$ =-6.43±0.08, but they were unable to calculate the formation constants $\beta_{1,6,3}$ and $\beta_{3,12,6}$ from their data. Consequently, we must rely upon the free energy of formation of UTC calculated by Langmuir (1978) to obtain a free energy value for the species $(UO_2)_3\ (CO_3)_6^{6-}$. Langmuir calculated a value for the free energy of formation of UDC from the equilibrium constants of Tsymbal (1969) and Scanlan (1977). If we assume that both sets of measurements refer to the species $(UO_2)_3\ (CO_3)_6^{6-}$ defined by Ciavatta et al. (1981) the free energy of formation of UDC may be recalculated to reflect this change in aqueous species representation. The corrected free energy of formation of 3 UDC is 4 kJ/mol greater than the free energy of $(UO_2)_3(CO_3)_6^{6-}$

calculated from the data of Ciavatta et al., well within the uncertainty of the several data sets cited above and in good agreement with the results of Lemire and Tremaine (1980), again corrected to $(UO_2)_3(CO_3)_6^{6-}$.

U^{4+} hydrolysis products and $UO_2 \cdot 2H_2O$

Langmuir (1978) has reported estimated values for the thermodynamic properties of the aqueous species $U(OH)_2^{2+}$, $U(OH)_3^+$, $U(OH)_4$, and $U(OH)_5^-$. Langmuir based his estimate upon the solubility of $UO_2 \cdot 2H_2O$ in basic solutions (Gayer and Leider, 1957), an estimate of the free energy of formation of $UO_2 \cdot 2H_2O$ (ie. $\Delta G_r = 0$ for $UO_2 + 2H_2O = UO_2 \cdot 2H_2O$), and upon assuming a regular progression of stepwise stability constants. Langmuir's assumption that the free energy of $UO_2 \cdot 2H_2O$ is equivalent to the sum of the free energy of $2H_2O$ and UO_2 is clearly incorrect.

Miller (1958) has shown that freshly precipitated $UO_2 \cdot 2H_2O$ maintains a uranium concentration of 3.4 - 6x 10^{-3}M for several months at room temperature and pH values of 8.5 to 4.6. Upon heating the system to 573 K, the solid phase recrystallizes to uraninite and the concentration of uranium drops below 10^{-6}M when the solution is cooled and maintained at 298.15 K. Freshly precipitated $UO_2 \cdot 2H_2O$ is amorphous to X-rays and precipitates have the characteristics of a gel. Drying the gel-like material at room temperature yields microcrystalline uraninite (Miller).

Gayer and Leider (1957) prepared $UO_2 \cdot 2H_2O$ by two procedures obtaining samples with different characteristics. The first sample was prepared by adding NaOH to a solution of U^{4+} sulfate. This procedure was similar to that followed by Miller (1958) and yielded a solid that was very fine grained. A coarser grained sample was prepared by the reaction of NaOH with crystalline $U(SO_4)_2 \cdot 4H_2O$. The second sample was used in the solubility experiment referenced by Langmuir (1978) as discussed above. The first sample yielded higher solubility values, comparable with those found by Miller.

Because Langmuir (1978) referenced the free energy of $U(OH)_5^-$ to UO_2 (by assuming that $\Delta G_r = 0$ as discussed above) by using the data of Gayer and Leider (1957) that gave an equilibrium concentration for dissolved uranium of about 4.5×10^{-5}M in basic solutions over $UO_2 \cdot 2H_2O$, and because Miller (1958) has shown that the concentration of uranium in equilibrium with uraninite in basic solutions is less than 10^{-6}M, Langmuir has overestimated the stability of $U(OH)_5^-$ and, most likely, the other hydrolysis species.

Based upon the preceeding discussion, we may estimate that ΔG_r=11.4 kJ for the reaction uraninite plus 2 water = well crystallized $UO_2 \cdot 2H_2O$ and that $\Delta G_{f,298} = -1494.6 \pm 4.0$ kJ/mol for well crystallized $UO_2 \cdot 2H_2O$. We may also estimate the free energy of amorphous $UO_2 \cdot 2H_2O$ as $\Delta_{f,298} = -1483 \pm 8$kJ/mol. Finally, we may estimate the free energy of formation of $U(OH)_5^-$ as $\Delta G_{f,298} = -1630.4 \pm 6.0$ KJ/mol using the estimated free energy of $UO_2 \cdot 2H_2O$ derived above and the equilibrium constant given by Gayer and Leider (1957).

Part II. Properties at higher temperatures.

Introduction

The thermodynamic properties reported in this study at temperatures above 298.15 K were derived from the properties of these phases at 298.15 K listed in Part I of this report and from heat-content or heat-capacity data. The heat-content or heat-capacity data were fit to an equation of the form suggested by Haas and Fisher (1976) and used by Robie et al. (1979). Data for sixteen phases are tabulated in the format used by Robie et al. and included in this section.

Methods of calculation

The methods and procedures followed in this study were largely those followed by Robie et al. (1979). The tables of thermodynamic properties were calculated using the FORTRAN IV programs of Hemingway and Robie (1975, unpublished software for IBM 370 or MULTICS computer systems) and the thermodynamic data base of Robie et al.

Problem data sets

1. U_3O_8: Several investigations of the heat capacity or heat content of U_3O_8 at temperatures above 298.15 K are available in the literature (Girdhar and Westrum, 1968; Maglic and Herak, 1970; Popov et al., 1958; Powers, 1949; and Khomyakov et al., 1961). Westrum and Gronvold (1959) measured the heat capacity of U_3O_8 from 5 to 350 K.

Girdhar and Westrum (1968) and Westrum and Gronvold (1959) used the same sample of U_3O_8, but used different calorimetric systems for their experiments. The results reported by Girdhar and Westrum are 1 percent larger in heat capacity and 0.8 percent larger in H_{350}-H_{298} than the results given by Westrum and Gronvold. The calculated value of H_{550}-H_{350} obtained from the data of Girdhar and Westrum is 0.6 percent larger than the value calculated from the data of Maglic and Herak. Consequently, the data of Girdhar and Westrum were not weighted as heavily as the values given by Maglic and Herak and by Westrum and Gronvold.

The results reported by Powers (1949), Popov et al. (1958) and Khomyakov et al. (1961) show substantial scatter within each data set and significant deviations from the selected data sets.

The table of high temperature thermodynamic data for U_3O_8 is terminated at 1000 K. Khomyakov et al. (1961) found evidence for transitions in the heat capacity of U_3O_8 at 1046 and 1213 K. However, Ackermann and Chang (1973) have shown that the pressure of O_2 gas must exceed 1.01 bars at 840 K to maintain stoichiometric U_3O_8. Ackermann and Chang have shown that requilibration proceeds slowly following dissociation at temperatures above 1000 K. Consequently, heat-content and heat-capacity data reported for temperatures above 1000 K must be considered as suspect for stoichiometric U_3O_8.

2. U_4O_9: Osborne et al. (1957) measured the heat capacity of U_4O_9 from 5 to 310 K. Westrum et al. (1965) using the sample of U_4O_9 previously studied by Osborne et al. extended the heat capacity measurements on this sample to about 400 K. Gronvold et al. (1970) measured the heat capacity of U_4O_9 in the temperature range of 300 to 1000 K. Finally, Macleod (1972) measured the heat content of U_4O_9 from 845 to 1568 K.

Westrum et al. (1965) defined a λ-type transition in U_4O_9 with a maximum at 348 K. Gronvold et al. (1970) confirmed this transition, but reported values of the heat capacity of U_4O_9 which were about 1 percent greater than those of Westrum et al. in the temperature range of 300 to 330 K. Such differences are not unexpected because the shape of λ-type heat-capacity curves are known to vary with the measurement technique, the particle size of the sample and with radiation damage within the sample.

Gronvold et al. (1970) observed an increase in the heat capacity of their U_4O_9 sample above 800 K. They interpreted this result as representing evidence for a transition in U_4O_9 in the region of 900 to 950 K. Macleod (1972) found no evidence to support the interpretation of Gronvold et al. However, Macleod found evidence for a disorder-disproportionation transition at about 1398K that is consistent with the phase diagram constructed by Roberts and Walter (1961). Furthermore, if the heat-capacity data given by Gronvold et al. are smoothed and the smoothed function is integrated to yield heat-content values that may be compared with the data of Macleod, one finds that the data of Gronvold et al. yield values 2 percent or more larger than those of Macleod.

Macleod (1972) attributed much of the difference between his results and those of Gronvold et al. (1970) to the slight difference in oxygen content in the two samples (2.248±.003 O/U for Macleod and 2.254 O/U for Gronvold et al.) Macleod, using the data of Affortit and Marcon (1972) for the UO_{2+x} phase, estimated that a difference of 0.01 O/U yields a difference of 1.5 percent in the heat capacity. Gronvold et al. estimated that a difference of 0.017 O/U yielded a difference of 0.7 percent in the heat capacity. However, both estimates are based upon data for uraninite with compositions between UO_2 and $UO_{2.1}$ and probably are not realistic models for U_4O_9. That is, the energy changes associated with the changes occurring during the initial oxidation of uraninite may be assumed to be greater than those associated with small deviations from the more oxidized form U_4O_9.

Because the results of Gronvold et al. (1970) are 1 percent larger than those of Westrum et al. (1965), whose sample was considered stoichiometric or 2.250 O/U, and about 2 percent larger than the results of Macleod (1972) a difference attributable to the variation in oxygen cannot be discounted. However, another process may be of equal or greater significance in explaining the divergent results of Gronvold et al. and Macleod. Ackermann et al. (1960), Macleod (1972), and Roberts and Walter (1961) have shown that gaseous uranium oxide can be observed over solid uranium oxides at 1000 K.

The thermal effect of the volatilization of small amounts of UO_3 gas (or oxygen) would be negligible at 1000 K for heat-content experiements, but could have a significant effect on heat capacity results. The heat capacity results of Gronvold et al. for temperatures above 900 K show significant scatter and a lack of reproducibility that is characteristic of the evoluation of a gaseous phase. Therefore, rather than observing a transition in the heat capacity of U_4O_9 Gronvold et al. more likely observed apparently higher heat capacities associated with the development of the UO_3 gas phase.

The results of Roberts and Walter (1961) provide some support for the foregoing interpretation. Roberts and Walter studied the oxygen pressure in equilibrium with uranium oxides with compositions from O/U of 2.221 to 2.250 and in the temperature range of 1175 to 1475 K. Significant volalility of UO_3 gas was found only in the sample with the highest O/U ratio (the final composition of the sample was O/U = 2.249). Gronvold et al. (1970) analyzed their U_4O_9 sample after completing the heat capacity experiments and obtained the ratio O/U = 2.254, well into the O/U range were the data of Roberts and Walter suggests the formation of UO_3 gas could be significant.

Blank and Ronchi (1968) examined electron diffraction patterns of thin foils of U_4O_9 taken between room temperature and 1275 K. They concluded that U_4O_9 underwent a partial disorder transformation between 825 and 1175 K. The variation in the temperature at which the superstructure lines disappeared was inferred to be related to the degree to which U_4O_9 was reduced (phase designated as U_4O_{9-y}). As y increased, the temperature of the transformation decreased. In support of this conclusion, Blank and Ronchi noted that Ferguson and Street (1963) had shown that the transformation temperature of a single sample (with O/U = 2.235) was lowered by 150 K when powdered platinum was added to the sample (sample reduction by the platinum was assumed).

The data presented by Blank and Ronchi (1968) would support the conclusion of Gronvold et al. (1970) regarding the interpretation of the heat capacity data in the 900 to 1000 K temperature region. However, Gronvold et al. reported a composition with O/U = 2.254 which would suggest the highest transition temperature (that is, the transition would have occurred above the temperature range studied by Gronvold et al.) and the transition has not been shown to occur in U_4O_9 samples which are not somewhat oxygen difficient (that is, U_4O_{9-y}).

In support of the interpretation of Gronvold et al. (1970) it should be noted that Gronvold (1967) was in the practice of sealing his calorimeter under a reduced pressure of hydrogen gas. If that procedure had been followed by Gronvold et al., then we may infer from the data of Ferguson and Street (1963) that partial reduction of the sample by the hydrogen gas could result in a lowering of the transition temperature for a portion of the calorimetric sample. Macleod (1972) sealed his sample under a reduced pressure of helium gas that would not support an equivalent reduction of his calorimetric sample.

The interpretation by Blank and Ronchi (1968) of their electron microscope data is not straightforward. Blank and Ronchi were aware that the thin foils of U_4O_9 underwent reduction in the electron beam and obtained sufficient reduction in some experiments to observe precipitation of the UO_{2+x} phase in their sample as they passed into the two phase region $UO_{2+x}+U_4O_{9-y}$. The interaction between the electron beam and the thin foil may have increased the vaporization of UO_3 and O_2 gasses and that may have resulted in loss of the superstructure data observed in the fresh foils rather than a change in structure of an intact sample mass. Ferguson and Street (1963) have concluded that the transformation that they observed represented the change from the stability field for the U_4O_{9-y} phase to the 2 phase field of UO_{2+x} + U_4O_{9-y} in contrast to the interpretation proposed by Blank and Ronchi.

Although a clear resolution to the problem of incompatible heat-capacity and heat-content data is not available, it appears reasonable to assume that the "transition" observed by Gronvold et al. (1970) in the temperature region 900 to 1000K is not characteristic of the stoichiometric phase U_4O_9. Furthermore, the heat-content data provided by Macleod (1972) will overestimate the heat capacity and heat content of U_4O_9 above 1000K because of the generation of significant pressure of O_2 and UO_3 gas during the drop calorimetric experiments.

3. UO_2F_2: Cordfunke et al. (1979) measured the heat content of UO_2F_2 from 374.8 to 810.8 K. They fit their data with an equation of the form $a + bT + cT^2 + d/T$ and concluded that their results were not consistent with the earlier heat capacity data for UO_2F_2 reported by Wacker and Cheney (1947). The two data sets were fit with a five term equation where the additional term was $eT^{1/2}$. The statistics of the fit show the $T^{1/2}$ term to be more important than the T^2 or T^{-1} terms. The total data set (Cp values from 200 to 425K and heat-content values from 374 to 800 K) was fit with an average deviation of 0.20 percent. The heat capacity data of Wacker and Cheney were analytically smoothed and the smoothed values were integrated to provide heat-content data that were fit with the values given by Cordfunke et al. The results agree within the experimental error of each experiment.

Table 9. The thermodynamic properties of 16 selected uranium-bearing phases at 298.15 K and at higher temperatures and at 1 bar.

URANINITE

FORMULA WEIGHT 270.028

UO_2: Crystals 298.15 to 1800 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_p	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	77.03	77.03	63.60	-1084.910	-1031.710	180.752
UNCERTAINTY		0.24	0.24		1.000	1.000	0.175
400	17.350	97.00	79.65	71.59	-1083.913	-1013.685	132.374
500	28.626	113.43	84.80	75.50	-1082.685	-996.270	104.080
600	36.660	127.43	90.77	78.01	-1081.500	-979.098	85.238
700	42.709	139.61	96.90	79.92	-1080.490	-962.120	71.795
800	47.464	150.39	102.93	81.54	-1079.732	-945.260	61.719
900	51.333	160.08	108.75	83.02	-1079.292	-928.480	53.888
1000	54.572	168.90	114.33	84.42	-1081.628	-911.568	47.616
1100	57.347	177.01	119.66	85.78	-1085.433	-894.363	42.470
1200	59.772	184.53	124.76	87.11	-1084.167	-877.048	38.177
1300	61.926	191.55	129.62	88.44	-1082.804	-859.828	34.548
1400	63.864	198.16	134.30	89.77	-1081.348	-842.760	31.444
1500	65.638	204.40	138.76	91.09	-1089.212	-825.152	28.734
1600	67.271	210.32	143.05	92.42	-1088.504	-807.576	26.365
1700	68.789	215.96	147.17	93.76	-1087.685	-790.048	24.275
1800	70.213	221.36	151.15	95.09	-1086.756	-772.566	22.419

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 2.4618 J/bar

24.618 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = 62.867 + 1.4610\times10^{-2}\ T + 2.7429\times10^{2}\ T^{-0.5} - 1.7341\times10^{6}\ T^{-2}$$

(EQUATION VALID FROM 298 - 1800 K)

REFERENCE 133 133 133 COMPILED 3-19-81

TETRAURANIUM ENNEAOXIDE FORMULA WEIGHT 1096.111

U_4O_9: Alpha phase 298.15 to 348 K. Beta phase 348 to 1400 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	335.93	335.93	293.34	-4512.000	-4276.900	749.298
UNCERTAINTY		0.67	0.67		15.100	15.200	2.663
400	116.000	466.10	350.10	314.49	-4490.884	-4198.439	548.262
500	130.410	503.26	372.85	328.19	-4498.191	-4122.126	430.637
600	164.118	563.89	399.77	336.63	-4492.499	-4047.453	352.364
700	189.243	616.29	427.05	343.20	-4487.688	-3973.684	296.521
800	208.871	662.52	453.65	349.32	-4483.994	-3900.502	254.678
900	224.822	704.02	479.20	355.66	-4481.607	-3827.715	222.156
1000	238.249	741.85	503.60	362.59	-4490.258	-3754.478	196.115
1100	249.896	776.76	526.86	370.30	-4504.634	-3680.141	174.756
1200	260.282	809.34	549.06	378.91	-4498.469	-3605.450	156.942
1300	269.768	840.04	570.27	388.50	-4491.561	-3531.277	141.889
1400	278.621	869.22	590.60	399.12	-4483.801	-3457.769	129.012

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	9.6570 J/bar 96.570 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATIONS

$$C^\circ_P = 4.5153792\times10^{5} - 7.04127\times10^{2}\,T + 0.55685234\,T^{2} - 5.4159017\times10^{6}\,T^{-0.5} + 2.0308879\times10^{9}\,T^{-2}$$

(EQUATION VALID FROM 250 - 348 K)

$$C^\circ_P = 366.62 - 5.5972\times10^{-2}\,T + 5.81885\times10^{-5}\,T^{2} - 6.2481\times10^{6}\,T^{-2}$$

(EQUATION VALID FROM 348 - 1400 K)

REFERENCE 120,71 120 49 COMPILED
159,94 3-20-81

TRIURANIUM OCTAOXIDE FORMULA WEIGHT 842.082

U_3O_8: Crystals 298.15 to 1000 K. A reversible lambda-type thermal anomaly is present at 482.7 K. The alpha-beta transition temperature is 1043 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	282.59	282.59	238.36	-3574.800	-3369.400	590.307
UNCERTAINTY		0.50	0.50		1.000	1.200	0.210
400	64.200	356.49	292.29	263.65	-3569.973	-3299.938	430.930
500	105.700	417.14	311.44	276.27	-3564.302	-3233.132	337.764
600	133.363	466.69	333.33	269.17	-3559.792	-3167.345	275.743
700	152.833	508.26	355.43	271.20	-3556.752	-3102.206	231.490
800	168.022	544.88	376.86	278.08	-3554.600	-3037.408	198.323
900	180.767	578.17	397.40	287.80	-3553.094	-2972.849	172.540
1000	192.036	609.08	417.04	299.27	-3559.328	-2907.948	151.896

MELTING POINT		K	BOILING POINT		K
ENTHALPY OF MELTING		kJ	ENTHALPY OF VAPORIZATION		kJ
$H^\circ_{298} - H^\circ_0$		kJ	MOLAR VOLUME	10.0320	J/bar
				100.320	cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATIONS

$$C^\circ_P = 3.3931\times10^2 + 3.9418\times10^{-2}\ T - 1.6164\times10^3\ T^{-0.5} - 1.6973\times10^6\ T^{-2}$$

(EQUATION VALID FROM 200 - 482.70 K)

$$C^\circ_P = 1.2170\times10^2 + 0.15877\ T + 1.8796\times10^7\ T^{-2}$$

EQUATION VALID FROM 482.70 - 1800 K)

REFERENCE	157,95 66	157	23	COMPILED 3-20-81

URANIUM TRIOXIDE (GAMMA) FORMULA WEIGHT 286.027

UO_3: Crystals 298.15 to 900 K.

					FORMATION FROM THE ELEMENTS		
TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	96.11	96.11	84.72	-1223.800	-1145.700	200.723
UNCERTAINTY		0.21	0.21		1.220	1.250	0.219
400	22.025	121.49	99.47	88.55	-1222.445	-1119.239	146.158
500	35.736	141.70	105.96	92.53	-1221.064	-1093.609	114.249
600	45.467	158.85	113.38	95.54	-1219.732	-1068.241	92.999
700	52.773	173.74	120.97	97.53	-1218.588	-1043.091	77.837
800	58.447	186.84	128.39	98.68	-1217.754	-1018.070	66.473
900	62.944	198.50	135.56	99.14	-1217.351	-993.144	57.641

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	3.5560 J/bar 35.560 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = 215.00 - 3.8496\times10^{-2}\ T - 2.5272\times10^{3}\ T^{-0.5} + 2.4500\times10^{6}\ T^{-2}$$

(EQUATION VALID FROM 298 - 900 K)

REFERENCE 133 156 23 COMPILED 3-19-81

ALPHA $UO_2(OH)_2$ FORMULA WEIGHT 304.042

$UO_2(OH)_2$: Dehydrated schoepite crystals 298.15 to 700 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	156.60	156.60	109.00	-1534.500	-1404.900	246.134
UNCERTAINTY		8.00	8.00		4.000	4.000	0.701
400	30.050	191.15	161.10	126.33	-1534.410	-1360.602	177.677
500	50.664	220.81	170.15	139.30	-1533.231	-1317.281	137.616
600	66.242	247.06	180.82	148.33	-1531.407	-1274.247	110.934
700	78.403	270.38	191.98	153.87	-1529.349	-1231.555	91.900

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 4.6400 J/bar

46.400 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = -302.61 + 29.0152\ T^{0.5} - 0.47663\ T + 1.5717\times10^4\ T^{-1}$$

(EQUATION VALID FROM 298 - 700 K)

REFERENCE 166 166 166 COMPILED 3-12-81

URANIUM TRICHLORIDE FORMULA WEIGHT 344.388

UCl_3: Crystals 298.15 to 1000 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_p	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	158.95	158.95	101.73	-891.190	-823.820	144.330
UNCERTAINTY		0.40	0.40		4.000	5.000	0.876
400	26.125	188.69	162.57	104.23	-888.957	-800.997	104.600
500	41.912	212.14	170.23	105.71	-886.882	-779.257	81.409
600	52.643	231.52	178.88	107.02	-885.031	-757.910	65.982
700	60.569	248.18	187.61	109.43	-883.364	-736.854	54.985
800	66.891	263.01	196.12	113.09	-881.785	-716.025	46.752
900	72.278	276.60	204.32	117.92	-880.223	-695.417	40.361
1000	77.130	289.32	212.19	123.75	-881.003	-674.803	35.248

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 6.2040 J/bar

62.040 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = -175.29 + 0.13399\ T + 5.4565\times10^{3}\ T^{-0.5} - 7.5036\times10^{6}\ T^{-2}$$

(EQUATION VALID FROM 298 - 1000 K)

REFERENCE 133 65 133 COMPILED 3-19-81

URANIUM TETRACHLORIDE FORMULA WEIGHT 379.841

UCl_4: Crystals 298.15 to 700 K.

					FORMATION FROM THE ELEMENTS		
TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	196.60	196.60	119.89	-1018.390	-928.990	162.756
UNCERTAINTY		0.50	0.50		4.200	4.200	0.736
400	31.625	233.05	201.42	127.29	-1015.723	-898.855	117.379
500	51.174	261.90	210.73	131.32	-1013.001	-869.951	90.884
600	64.878	286.21	221.33	135.62	-1010.255	-841.596	73.268
700	75.347	307.50	232.15	140.87	-1007.420	-813.708	60.720

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	7.7600 J/bar 77.600 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = -80.231 + 0.12983\ T + 3.6987\times10^3\ T^{-0.5} - 4.6948\times10^6\ T^{-2}$$

(EQUATION VALID FROM 298 - 700 K)

REFERENCE 133 65 48 COMPILED 3-19-81

URANYL CHLORIDE FORMULA WEIGHT 340.934

UO_2Cl_2: Crystals 298.15 to 800 K.

					FORMATION FROM THE ELEMENTS		
TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	150.54	150.54	107.86	-1243.070	-1145.280	200.649
UNCERTAINTY		0.42	0.42		2.100	2.200	0.385
400	28.475	183.36	154.89	115.28	-1241.155	-1112.167	145.235
500	46.348	209.63	163.28	120.01	-1239.083	-1080.158	112.844
600	58.913	231.82	172.91	123.28	-1237.037	-1048.565	91.286
700	68.286	251.01	182.72	125.63	-1235.148	-1017.308	75.913
800	75.567	267.90	192.33	127.34	-1233.512	-986.296	64.399

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	6.3200 J/bar 63.200 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = 1.7418\times10^{2} - 9.6124\times10^{-3}\ T - 1.1107\times10^{3}\ T^{-0.5} + 7.7166\times10^{4}\ T^{-2}$$

(EQUATION VALID FROM 298 - 800 K)

REFERENCE 29 68 35 23

COMPILED 3-18-81

URANYL FLUORIDE FORMULA WEIGHT 308.025

UO_2F_2: Crystals 298.15 to 800 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	135.55	135.55	103.20	-1653.900	-1557.700	272.904
UNCERTAINTY		0.50	0.50		1.200	1.200	0.210
400	27.450	167.17	139.72	111.64	-1652.147	-1525.087	199.157
500	44.836	192.67	147.83	116.79	-1650.226	-1493.546	156.030
600	57.135	214.29	157.15	120.25	-1648.341	-1462.389	127.313
700	66.334	233.02	166.69	122.66	-1646.639	-1431.536	106.823
800	73.487	249.52	176.03	124.37	-1645.221	-1400.901	91.470

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 4.7980 J/bar

47.980 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = 174.31 - 1.1443\times10^{-2}\ T - 1.1491\times10^{3}\ T^{-0.5} - 1.0228\times10^{5}\ T^{-2}$$

(EQUATION VALID FROM 200 - 800 K)

REFERENCE 29 29 31 COMPILED

29 3-18-81

RUTHERFORDINE FORMULA WEIGHT 330.037

UO_2CO_3: Crystals 298.15 to 700 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	142.70	142.70	106.50	-1704.100	-1577.000	276.285
UNCERTAINTY		2.00	2.00		2.000	2.100	0.368
400	29.400	176.50	147.10	123.30	-1703.863	-1533.621	200.271
500	49.382	205.32	155.94	134.68	-1703.010	-1491.165	155.782
600	64.292	230.61	166.32	142.48	-1701.953	-1448.888	126.137
700	75.854	252.99	177.14	147.57	-1700.975	-1406.800	104.977

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 5.7690 J/bar

57.690 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = -87.541 + 115.7163\ T^{0.5} - 0.257862\ T - 1.3463\times10^2\ T^{-1}$$

(EQUATION VALID FROM 298 - 700 K)

REFERENCE 166 166 166 COMPILED 2- 4-81

BARIUM MONOURANATE FORMULA WEIGHT 439.367

$BaUO_4$: Crystals 298.15 to 1100 K.

					FORMATION FROM THE ELEMENTS		
TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	153.97	153.97	125.27	-1997.100	-1887.070	330.608
UNCERTAINTY		0.31	0.31		2.100	2.100	0.368
400	33.425	192.46	159.03	136.34	-1995.768	-1849.680	241.545
500	54.758	223.70	168.94	143.44	-1994.784	-1813.295	189.434
600	69.978	250.32	180.34	148.45	-1994.461	-1777.017	154.704
700	81.466	273.49	192.02	152.15	-1993.383	-1740.877	129.906
800	90.485	294.00	203.52	154.96	-1992.996	-1704.822	111.314
900	97.778	312.38	214.60	157.14	-1992.476	-1668.818	96.856
1000	103.800	329.03	225.23	158.84	-1994.748	-1632.715	85.285
1100	108.868	344.24	235.37	160.19	-2006.890	-1595.497	75.764

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 5.8080 J/bar

58.080 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

BARIUM..... ALPHA-BETA 643, M. P. BETA 983, B. P. 2169 K.

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = 215.49 - 8.8192\times10^{-3}\,T - 1.5125\times10^{3}\,T^{-0.5}$$

(EQUATION VALID FROM 298 - 1100 K)

REFERENCE 108 108 108 COMPILED
107 3-18-81

CALCIUM MONOURANATE FORMULA WEIGHT 342.107

$CaUO_4$: Crystals 298.15 to 1000 K. Small solid-phase transition at 1025 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_p	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	144.30	144.30	129.56	-2001.700	-1895.000	331.998
UNCERTAINTY		8.00	8.00		2.100	3.000	0.526
400	33.600	183.04	149.44	134.33	-1999.848	-1858.812	242.737
500	54.212	213.52	159.31	139.02	-1998.084	-1823.769	190.529
600	68.737	239.28	170.54	143.70	-1996.468	-1789.054	155.752
700	79.779	261.78	182.00	148.38	-1995.077	-1754.606	130.931
800	88.646	281.90	193.25	153.06	-1994.696	-1720.240	112.321
900	96.067	300.20	204.13	157.74	-1993.812	-1685.978	97.852
1000	102.465	317.06	214.59	162.42	-1995.855	-1651.635	86.273

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	4.5910 J/bar 45.910 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

CALCIUM.... ALPHA-BETA 737, M. P. BETA 1123, B. P. 1755 K.

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = 115.60 + 4.6820\times10^{-2}\ T + 0.12838\ T^{-0.5}$$

(EQUATION VALID FROM 298 - 1000 K)

REFERENCE 107 107 107 COMPILED 4- 2-81

DICESIUM MONOURANATE FORMULA WEIGHT 567.837

Cs_2UO_4: Crystals 298.15 to 1100 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	219.66	219.66	152.76	-1929.800	-1807.144	316.605
UNCERTAINTY		0.45	0.45		1.500	1.500	0.263
400	40.100	265.87	225.77	161.47	-1934.867	-1763.695	230.316
500	64.968	302.55	237.58	167.13	-1934.238	-1720.963	179.789
600	82.350	333.39	251.04	171.17	-1932.696	-1678.428	146.121
700	95.266	360.02	264.75	174.21	-1930.847	-1636.210	122.096
800	105.287	383.44	278.15	176.56	-1929.236	-1594.220	104.092
900	113.311	404.35	291.04	178.43	-1928.384	-1552.402	90.099
1000	119.904	423.23	303.33	179.93	-2063.092	-1502.284	78.472
1100	125.418	440.44	315.02	181.16	-2065.015	-1446.100	68.670

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 8.5440 J/bar

85.440 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

CESIUM..... M. P. 301.55 K, B. P. 942 K.

HEAT CAPACITY EQUATION

$$C^\circ_P = 221.62 - 4.8832\times10^{-3}\ T - 1.1639\times10^{3}\ T^{-0.5}$$

(EQUATION VALID FROM 298 - 1100 K)

REFERENCE 51 117 110,30 COMPILED
108 3-18-81

MAGNESIUM MONOURANATE — FORMULA WEIGHT 326.332

$MgUO_4$: Crystals 298.15 to 1400 K.

					FORMATION FROM THE ELEMENTS		
TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_p	ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	131.90	131.90	128.10	-1857.000	-1749.300	306.471
UNCERTAINTY		0.50	0.50		1.300	1.300	0.228
400	33.400	170.40	137.00	133.91	-1855.206	-1712.722	223.660
500	53.950	200.77	146.82	138.27	-1853.474	-1677.314	175.229
600	68.312	226.30	157.99	141.89	-1851.911	-1642.223	142.969
700	79.053	248.42	169.37	145.05	-1850.609	-1607.393	119.946
800	87.482	267.98	180.50	147.89	-1849.629	-1572.717	102.688
900	94.344	285.55	191.21	150.51	-1849.032	-1538.128	89.271
1000	100.082	301.53	201.45	152.96	-1860.231	-1502.671	78.492
1100	104.995	316.22	211.22	155.29	-1863.902	-1466.725	69.649
1200	109.279	329.83	220.55	157.51	-1862.454	-1430.683	62.276
1300	113.072	342.52	229.45	159.65	-1860.861	-1394.760	56.042
1400	116.471	354.43	237.96	161.73	-1986.089	-1355.389	50.570

MELTING POINT	K	BOILING POINT	K
ENTHALPY OF MELTING	kJ	ENTHALPY OF VAPORIZATION	kJ
$H^\circ_{298} - H^\circ_0$	kJ	MOLAR VOLUME	4.4700 J/bar 44.700 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

MAGNESIUM.. M. P. 922, B. P. 1361 K.

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = 154.55 + 1.5352\times10^{-2}\ T - 5.3568\times10^{2}\ T^{-0.5}$$

(EQUATION VALID FROM 298 - 1400 K)

REFERENCE 106 30 106 COMPILED 3-18-81

DISODIUM MONOURANATE FORMULA WEIGHT 348.006

Na_2UO_4: Alpha crystals 298.15 to 1193 K. Beta crystals 1193 to 1300 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	166.00	166.00	146.60	-1890.200	-1771.800	310.413
UNCERTAINTY		0.30	0.30		4.500	4.500	0.788
400	39.000	210.91	171.91	158.74	-1894.917	-1730.986	226.045
500	63.790	247.25	183.46	166.78	-1894.035	-1690.110	176.565
600	81.468	278.20	196.73	172.65	-1892.743	-1649.437	143.597
700	94.831	305.17	210.34	177.17	-1891.289	-1608.993	120.065
800	105.356	329.07	223.71	180.77	-1889.853	-1568.765	102.430
900	113.900	350.54	236.64	183.71	-1888.592	-1528.710	88.724
1000	121.013	370.03	249.02	186.17	-1890.027	-1488.617	77.758
1100	127.034	387.87	260.84	188.26	-1892.942	-1448.301	68.774
1200	149.918	421.92	272.00	224.68	-2064.386	-1403.731	61.103
1300	155.669	439.27	283.60	224.68	-2057.076	-1348.157	54.170

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME 5.8550 J/bar

58.550 cm^3

TRANSITIONS IN REFERENCE STATE ELEMENTS

SODIUM..... M. P. 370.98, B. P. 1175 K.

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATIONS

$$C^\circ_P = 237.73 - 2.1460\times10^{-3}\ T - 1.5626\times10^{3}\ T^{-0.5}$$

(EQUATION VALID FROM 298 - 1193 K)

REFERENCE 51 166 109 COMPILED

28 3-18-81

TRISODIUM MONOURANATE FORMULA WEIGHT 370.996

Na_3UO_4: Crystals 298.15 to 1200 K.

TEMP.	$(H^\circ_T-H^\circ_{298})/T$	S°_T	$-(G^\circ_T-H^\circ_{298})/T$	C°_P	FORMATION FROM THE ELEMENTS ENTHALPY	GIBBS FREE ENERGY	LOG K
K	J/mol·K	J/mol·K	J/mol·K	J/mol·K	kJ/mol	kJ/mol	
298.15	0.000	198.20	198.20	173.00	-2021.700	-1897.600	332.453
UNCERTAINTY		0.40	0.40		6.000	6.000	1.051
400	46.100	251.32	205.22	187.01	-2029.252	-1854.625	242.190
500	74.994	293.81	218.82	193.46	-2028.710	-1811.030	189.198
600	95.115	329.48	234.36	197.77	-2027.848	-1767.568	153.881
700	110.046	360.24	250.19	201.42	-2026.883	-1724.245	128.665
800	121.686	387.37	265.68	204.91	-2025.942	-1681.085	109.764
900	131.133	411.71	280.58	208.44	-2025.123	-1638.024	95.069
1000	139.042	433.86	294.82	212.07	-2026.926	-1594.896	83.309
1100	145.851	454.24	308.39	215.83	-2030.080	-1551.493	73.675
1200	151.844	473.19	321.35	219.72	-2320.251	-1501.921	65.377

MELTING POINT K BOILING POINT K

ENTHALPY OF MELTING kJ ENTHALPY OF VAPORIZATION kJ

$H^\circ_{298} - H^\circ_0$ kJ MOLAR VOLUME J/bar

TRANSITIONS IN REFERENCE STATE ELEMENTS

SODIUM..... M. P. 370.98, B. P. 1175 K.

URANIUM.... ALPHA-BETA 941, BETA-GAMMA 1048, M. P. 1405 K.

HEAT CAPACITY EQUATION

$$C^\circ_p = 111.37 + 5.3940\text{x}10^{-2}\ T + 1.6134\text{x}10^{3}\ T^{-0.5} - 4.2576\text{x}10^{6}\ T^{-2}$$

(EQUATION VALID FROM 298 - 1200 K)

REFERENCE 50 118 115 COMPILED 3-19-81

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