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CHEMICAL ENGINEERING DIVISION
REACTOR SAFETY AND PHYSICAL PROPERTY STUDIES
SEMIANNUAL REPORT
January—June 1972

by

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S. D. Gabelnick, L. Leibowitz,
A. D. Tevebaugh, and R. C. Vogel

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ABSTRACT

A report of the work on Reactor Safety and Physical Properties Studies performed in the Chemical Engineering Division at Argonne National Laboratory is given for the period January through June 1972. The report includes the following: final results for the measurement of the enthalpy of Na_2O from 500 to 1300°K; matrix isolation studies of infrared spectra of species above UO_2 ; computer calculations of fission-product and fuel vapor pressures over mixed-oxide fuels up to 6000°K; a calculated P-V-T diagram for sodium; thermal diffusivity measurements for tungsten from 1870 to 3300°C and UO_2 at 1600°C; solubility data for UO_2 in molten basalt, and information on development of equipment to measure viscosities and densities of molten UO_2 -basalt solutions.

SUMMARY

Resistance-Heated Drop Calorimetric System

The compound Na_2O was studied in an effort to understand the chemical interactions among fuel, sodium coolant, and cladding of a liquid-metal fast-breeder reactor. The enthalpy (relative to 298.15°K) of Na_2O was measured from 500 to 1300°K . Values of $(H_T^\circ - H_{298}^\circ)$, C_p° , and $(S_T^\circ - S_{298.15}^\circ)$ are tabulated.

Induction-Heated Drop-Calorimetric System

Experimentation is continuing on the measurement of the enthalpy of $(\text{U,Pu})\text{O}_2$. Work in progress is directed toward measurement of the enthalpy of liquid mixed oxide. Apparent enthalpy values of empty capsules needed for this work have been measured. Filled capsules have shown decreasing enthalpies with repeated measurements. Examination of the contents of heated capsules is in progress to determine the cause of this effect.

Matrix Isolation Spectroscopy

Further evidence is presented which supports our assignments of the features of the infrared spectrum of vapor species found over UO_{2+x} to the molecules UO , UO_2 , and UO_3 . In particular, the infrared spectra of uranium oxide species trapped in a krypton matrix are compared with similar results obtained using argon matrices. A normal coordinate analysis of the peaks assigned to the UO_2 stretching modes is consistent with a linear structure for UO_2 and agrees with observed frequencies to within experimental uncertainties. The relative intensities of the $\text{U}^{16}\text{O}^{18}\text{O}$ stretching frequencies are explained in terms of the normal coordinate analysis; the excellent agreement with the observed intensities further substantiates our assignments.

Theoretical Extrapolation of Measured Physical Property Data to Higher Temperatures

Vapor pressures above fuel/fission-product systems for temperatures up to 6000°K have been recalculated on the basis of new thermodynamic data for vapor-phase uranium oxides, a separation of the plutonium oxide and uranium oxide vapor-pressure contributions, and a revised model for the oxygen pressure above the U-Pu-O system.

A P - V - T diagram for the saturated, superheated vapor and subcooled liquid regions of the sodium system has been calculated by revising some of the relationships used in the NAPROP computer code originally developed by D. Miller (Reactor Analysis and Safety Division, ANL).

Thermal Diffusivity of Reactor Materials

Values of thermal diffusivity of UO_2 in the liquid state are important to the reactor safety program. Thermal diffusivity will be determined from the phase change in a thermal wave, produced by a sinusoidally modulated electron beam, which has passed through a sample. The thermal diffusivity, heat capacity, and density are used to calculate the thermal conductivity.

Measured phase shifts have been used in a computer program to calculate the thermal diffusivity of tungsten from 1870 to 3300°C and the thermal diffusivity of UO_2 at 1600°C. It was found that above 2000°C the electron beam damages and erodes the surface of UO_2 , and it is necessary to enclose the UO_2 in tungsten to make measurements at higher temperatures. Experiments above the melting point of UO_2 are now being carried out. A thermal-diffusivity formulation has been derived for the complex case of UO_2 encapsulated in a tungsten disk, and the equations are being programmed for computer solution.

Reactor Materials--Fuel Phase Studies at High Temperature

Knowledge of the interaction of phases and the distribution of fission products to the phases which are produced in the event of a hypothetical meltdown of the core of an LMFBR is required to predict the heat distribution after an accident. The information will be used to assure that means are available for cooling the products of a meltdown.

If basalt should be used as a diluent for molten reactor fuel, it will be necessary to know the extent to which the fuel components dissolve in molten basalt. The solubility of UO_2 in molten basalt is being determined. Experimental work on the distribution of fission products between UO_2 -basalt and iron is in progress, and involves the fission products Mo, Nb, Ce, and Ru.

Physical Properties of Interaction Products

Work is proceeding on the viscometer calibration and the viscosity measurements of basalt-urania solutions in a temperature range of 1500-2000°C. The system for determining the density of molten basalt and molten basalt-urania mixtures has been tested with potassium chloride and barium chloride. The measured values are within 0.5% of the reported values for these materials. The tungsten crucibles and bobs necessary for the temperatures of measurement have been received. The W-5%Re/W-26%Re thermocouples are being calibrated.

REACTOR SAFETY AND PHYSICAL PROPERTY STUDIES

The primary objective of these studies is to provide physical-property data for use in evaluating the safety of various fast-breeder-reactor materials. The property data obtained experimentally at temperatures above normal operating conditions of a fast-breeder reactor will also be extrapolated to the much higher temperatures involved in hypothetical accident situations. Reactor material-fuel phase studies at high temperatures are under way to provide chemical information needed on fission-product distribution between molten fuel and other reactor materials for use in post-accident heat-removal calculations. The physical properties of interaction products that may be important in post-accident heat-removal analysis are also under study.

I. ENTHALPIES AND HEAT CAPACITIES BY DROP CALORIMETRY (M. G. Chasanov)

Three complementary calorimetric systems for the measurement of high-temperature enthalpy increments are available for our use. Depending on the material to be studied and the temperature range to be covered, one may choose (1) the resistance-heated drop-calorimetric system (500-1600°K), (2) the electron-beam-heated drop-calorimetric system (1300-2500°K) or (3) the induction-heated drop-calorimetric system (2500-3600°K). During this report period, systems (1) and (3) have been used for making measurements.

A. Resistance-Heated Drop-Calorimetric System (D. R. Fredrickson)

The program for this system is oriented toward obtaining physical-property data primarily for materials of interest in reactor technology and secondarily for materials useful in high-temperature technology.

The compound Na_2O was studied in an effort to understand the chemical interactions among fuel, sodium coolant, and cladding of a liquid-metal fast-breeder reactor. The literature is rather sparse concerning high-temperature heat-content data for Na_2O . Naylor¹ estimated the heat content for Na_2O by using the Neumann-Kopp rule in conjunction with experimental data for Na_2TiO_3 , $\text{Na}_2\text{Ti}_2\text{O}_5$, $\text{Na}_2\text{Ti}_3\text{O}_7$, and TiO_2 . Grimley and Margrave² made a limited number of heat-content measurements on a sample of Na_2O containing Na_2CO_3 and Na_2O_2 to the extent of 3.24%.

Na_2O has an antifluorite crystal structure³ in which the anions are in positions of cubical close packing (face-centered cubic) with the cations in tetrahedral holes. Dworkin and Bredig⁴ postulated the existence of diffuse transitions in antifluorite-type compounds and predicted a rapid rise in C_p° at some elevated temperature due to the disordering of the Na^+ ions. This type of rapid increase in C_p° has been observed by us for Na_2O . Our enthalpy data are currently represented below by two empirical equations, one for temperatures below 1023°K and another for temperatures above 1023°K.

Recently at ANL, P. A. G. O'Hare⁴ determined the standard enthalpy of formation of Na_2O by solution calorimetry. A portion of the sample used by O'Hare was used for the high-temperature enthalpy measurements reported here. The sodium oxide was purchased from Alfa Inorganic, Beverley, Massachusetts. The sample was heated under vacuum at 510°C for 40 hr to remove excess sodium and any NaOH present. The material was then charac-

terized by titrimetric analysis and emission spectrography. Hydrolysis products were shown to contain $99.9 \pm 0.2\%$ of the amount of NaOH that would be produced by pure Na_2O . The details of the purification and characterization of the sodium oxide are presented in detail by P. A. G. O'Hare.⁵

For the calorimetric studies, a cylindrical Pt-10% Rh capsule with 0.4-mm wall thickness and 1.25-cm dia. was used to contain the sample. The internal volume was 5 cm^3 and the capsule length was 5 cm. The capsule had a filling tube with 0.5-cm OD, 0.25-mm wall thickness, and 3-cm length. The capsule contained 4.4438 g of Na_2O (mol wt = 61.979) sealed under vacuum. All of the loading and sealing operations were carried out in a glovebox filled with flowing high-purity helium.

The experimentally measured enthalpies for Na_2O above the reference temperature of 298.15°K are given in Table 1. Reported in this table are 31 drops covering the temperature range from 512 to 1285°K . The results are best expressed by two empirical equations, one for the temperature range $300\text{--}1023^\circ\text{K}$ and another for the temperature range $1023\text{--}1400^\circ\text{K}$.

The following equations, with the constants determined by the method of least squares, represent the data over their respective temperature ranges.

(a) $512\text{--}1023^\circ\text{K}$:

$$(\bar{H}_T^\circ - \bar{H}_{298.15}^\circ) = 16.0343T + 2.80598 \times 10^{-3}T^2 - 5222.57 \text{ cal mol}^{-1} \quad (1)$$

The standard deviation for Eq. 1 is 34 cal mol^{-1} or 0.39% .

To provide an equation applicable down to 298.15°K , the constraint that $(\bar{H}_T^\circ - \bar{H}_{298.15}^\circ) = 0$ when $T = 298^\circ\text{K}$ was added with the resulting equation being

(b) $298\text{--}1023^\circ\text{K}$:

$$(\bar{H}_T^\circ - \bar{H}_{298.15}^\circ) = 17.5509T + 2.1545 \times 10^{-3}T^2 + 2.8217 \times 10^5T^{-1} - 6370.72 \text{ cal mol}^{-1} \quad (2)$$

The standard deviation for Eq. 2 is 36 cal mol^{-1} or 0.43% .

(c) $1023\text{--}1400^\circ\text{K}$:

$$(\bar{H}_T^\circ - \bar{H}_{298.15}^\circ) = -24.9346T + 2.2864 \times 10^{-2}T^2 + 15,763.75 \text{ cal mol}^{-1} \quad (3)$$

The standard deviation for Eq. 3 is 28 cal mol^{-1} or 0.16% .

The derived heat-capacity equations from Eqs. 2 and 3, respectively, are

(d) $298\text{--}1023^\circ\text{K}$:

$$C_p^\circ = 17.5509 + 4.3089 \times 10^{-3}T - 2.8217 \times 10^5T^{-2} \text{ cal mol}^{-1} \text{ } ^\circ\text{K}^{-1} \quad (4)$$

(e) $1023\text{--}1400^\circ\text{K}$:

$$C_p^\circ = -24.9346 + 4.5727 \times 10^{-2}T \text{ cal mol}^{-1} \text{ } ^\circ\text{K}^{-1} \quad (5)$$

The smooth enthalpies from Eqs. 2 and 3, along with the derived high-temperature heat capacities and entropy increments, are given in Table 2. These values are provisional and may be changed by evaluation of the data in terms of Dworkin and Bredig's theory of the diffuse transition.

Table 1. Enthalpy of Na_2O

Temp, °K	Total Measured Heat, cal	Pt-10% Rh Capsule, cal	$H_T^0 - H_{298}^0$, cal/sample	Obs. $H_T^0 - H_{298}^0$, cal mol ⁻¹	Calc. $H_T^0 - H_{298}^0$, cal mol ⁻¹	% Dev (calc-obs)
From Equation 1						
511.8	380.37	113.79	266.58	3718.04	3718.81	+0.02
520.0	394.46	118.28	276.18	3851.94	3874.03	+0.57
567.5	487.14	144.34	342.80	4781.10	4780.61	-0.01
568.0	488.04	144.62	343.42	4789.75	4790.22	+0.01
614.1	576.79	170.03	406.76	5673.16	5682.32	+0.16
653.1	658.16	191.63	466.53	6506.79	6446.33	-0.93
697.1	739.50	216.10	523.39	7299.82	7318.54	+0.26
697.4	741.52	216.28	525.24	7325.63	7324.53	-0.02
709.7	765.39	223.14	542.25	7562.87	7570.31	+0.10
729.7	808.21	234.31	573.90	8004.30	7971.78	-0.41
802.5	952.61	275.19	677.42	9448.11	9452.07	+0.04
876.4	1102.50	316.99	785.51	10955.66	10985.15	+0.27
951.3	1261.55	359.68	901.87	12578.56	12570.24	-0.07
951.8	1255.68	359.97	895.71	12492.64	12580.93	+0.71
975.4	1313.36	373.49	939.87	13108.55	13086.96	-0.17
991.4	1347.45	382.67	964.78	13455.98	13431.81	-0.18
1007.0	1381.17	391.64	989.53	13801.17	13769.43	-0.23
From Equation 3						
1025.5	1422.36	402.29	1020.07	14227.12	14237.83	+0.08
1050.1	1478.21	416.49	1061.72	14808.02	14791.85	-0.11
1074.9	1532.01	430.84	1101.17	15358.23	15378.38	+0.13
1099.9	1595.07	445.33	1149.74	16035.65	15998.11	-0.23
1123.4	1649.29	459.00	1190.29	16601.21	16606.71	+0.03
1149.3	1715.16	474.09	1241.07	17309.45	17306.72	-0.02
1176.4	1781.54	489.92	1291.62	18014.48	18072.01	+0.32
1200.8	1852.99	504.22	1348.77	18811.56	18789.77	-0.12
1216.8	1896.28	513.61	1382.67	19284.37	19275.22	-0.05
1234.5	1943.68	524.01	1419.67	19800.42	19825.88	+0.13
1243.5	1974.00	529.31	1444.69	20149.37	20111.37	-0.19
1254.4	2003.12	535.73	1467.39	20465.98	20462.10	-0.02
1266.6	2039.28	542.93	1496.35	20869.89	20861.09	-0.04
1285.1	2092.55	553.86	1538.69	21460.41	21479.11	+0.09

Table 2. Thermodynamic Functions of Na_2O

Temp, °K	$H_T^\circ - H_{298}^\circ$ cal mol ⁻¹	C_p cal mol ⁻¹ °K ⁻¹	$S_T^\circ - S_{298}^\circ$ cal mol ⁻¹ °K ⁻¹
298.15	0	15.66	0
300	29.02	15.71	0.10
400	1699.78	17.51	4.89
500	3507.68	18.58	8.92
600	5405.70	19.35	12.38
700	7373.69	19.99	15.41
800	9401.56	20.56	18.12
900	11483.71	21.08	20.57
1000	13616.80	21.58	22.82
$S_T^\circ - S_{1023}^\circ$			
1023	14183.08	21.84	0
1025	14226.86	21.94	0.04
1100	16000.65	25.37	1.71
1150	17326.07	27.65	2.89
1200	18765.81	29.94	4.12
1250	20319.87	32.22	5.38
1300	21988.24	34.51	6.69
1350	23770.94	36.80	8.04
1400	25667.95	39.08	9.42

In related work, Bouaziz⁶ reported DTA measurements on Na_2O indicating transitions at 1023 and 1243°K. Our heat-content data do not indicate the transitions observed by Bouaziz. Henry *et al.*⁷ recently ran DTA on a sample having the composition Na_2O -5 wt % NaOH and reported seeing neither the 1023°K nor the 1243°K transformation reported by Bouaziz.

B. Induction-Heated Drop-Calorimetric System (L. Leibowitz, D. F. Fischer)

Experimentation is continuing on the measurement of the enthalpy of $(\text{U,Pu})\text{O}_2$. Values have been obtained up to about 3000°K and these results have been already reported.⁸ To extend this work to higher temperatures for measurements on the molten oxide, it is necessary to use a double-walled capsule, as we found in our earlier work on liquid UO_2 . This capsule design provides for both greater temperature uniformity and lowered heat loss during the drop. Accordingly, a series of measurements of the apparent enthalpy of empty double-walled capsules was carried out. These apparent enthalpies are subtracted from values obtained in using identical capsules loaded with the experimental material to find the enthalpy of the contents of the capsule. Following successful completion of the empty-capsule series, measurements were begun using loaded capsules. After a number of measurements had been performed, it became apparent that the measured enthalpies for the mixed oxide were decreasing as repeated measurements were made. For example, at about 3050°K, the enthalpy for the mixed oxide fell from about 75 kcal

mol^{-1} to about 66 kcal mol^{-1} over the course of 14 runs at various temperatures (maximum temperature attained was about 3300°K). Attempts to heat capsules to temperatures higher than 3300°K resulted in failure of the tungsten capsule and release of plutonium-containing oxide to the inside of the furnace.

Examination of various heated samples is currently being carried out. Preliminary indications are that considerable reaction between the oxide and the tungsten container had occurred. Reduction in O/M ratio as the series measurements progressed may be responsible for the enthalpy effects observed. Further work on this aspect is in progress.

II. MATRIX ISOLATION SPECTROSCOPY (M. G. Chasanov)

The thermodynamic properties of the vapor species of fuel oxides are important in determining equation-of-state relationships used in projecting the results of certain fast-breeder-reactor core-disruptive accidents. Application of statistical-mechanical techniques to spectroscopic data for these species presents a useful way of determining their thermodynamic properties at temperatures beyond the range of direct experimental measurements. Consisting of trapping molecules in frozen inert-gas lattices, the matrix isolation method allows low-temperature pseudo-gas-phase studies to be carried out on molecules that would normally be present in high gas-phase concentrations only at very high temperatures. Because the population of excited rotational quantum levels is eliminated under these low-temperature conditions, interpretation of the simplified infrared and visible spectra is greatly facilitated.

A. UO_2 (S. D. Gabelnick, G. T. Reedy)

The thermodynamic properties of gas-phase oxides of uranium are important to many aspects of reactor safety and analysis and to our general understanding of the vaporization behavior of refractory-oxide systems. Examination of the infrared spectra of these oxides enables one to compute the vibrational contributions to the various thermodynamic functions. Further study of isotopically substituted molecules allows one to determine certain geometric properties (such as bond angles) that are important in the calculation of the rotational contributions to the thermodynamic functions.

Assignment of the features of the infrared spectra of uranium oxide species isolated in argon matrices has been discussed previously.⁹ Additional data that support those assignments are reported below. The infrared spectrum of vapor species in equilibrium with $\text{U}^{16,18}\text{O}_{2+x}$ isolated in a krypton matrix is shown in Fig. 1. A comparison of the frequencies of all major peaks (except matrix splittings) observed in the two matrix gases is given in Table 3. The four peaks assigned as UO_2 features are noted to have differences in their shifts of $7.6 \pm 0.7 \text{ cm}^{-1}$ compared with shifts of $4.2 \pm 0.3 \text{ cm}^{-1}$ for the peaks assigned to $\text{UO}_3(\nu_3)$ and $4.75 \pm 0.15 \text{ cm}^{-1}$ for $\text{UO}_3(\nu_1)$.

Determinations of the O-U-O bond angle (α), based on ratios of $\text{U}^{16}\text{O}_2(\nu_3)/\text{U}^{18}\text{O}_2(\nu_3)$ observed in both argon and krypton, are consistent within experimental uncertainties with a value of 180° . The results of a complete normal

Fig. 1. Vapor from Hyperstoichiometric Sample of Urania with $^{16}\text{O}/^{18}\text{O} \approx 1/1$ Matrix Isolated in Krypton

Table 3. Comparison of Observed Frequencies (cm^{-1}) of Uranium Oxides Isolated in Argon and Krypton Matrices

Argon	Krypton	Difference	Assignment
852.55	848.10	4.45	$\text{U}^{16}\text{O}_3(\nu_3)$
847.55	843.40	4.15	$\text{U}^{16,18}\text{O}_3$
842.50	838.15	4.35	$\text{U}^{16,18}\text{O}_3$
818.35	814.45	3.90	$\text{U}^{16,18}\text{O}_3$
809.95	805.80	4.15	$\text{U}^{18}\text{O}_3(\nu_3)$
800.65	796.75	3.90	$\text{U}^{16,18}\text{O}_3?$
745.60	740.70	4.90	$\text{U}^{16}\text{O}_3(\nu_1)$
731.80	727.00	4.80	$\text{U}^{16,18}\text{O}_3$
720.50	715.90	4.60	$\text{U}^{16,18}\text{O}_3$
712.60	708.00	4.60	$\text{U}^{16,18}\text{O}_3$
705.15	700.50	4.65	$\text{U}^{18}\text{O}_3(\nu_1)$
776.10	767.97	8.15	$\text{U}^{16}\text{O}_2(\nu_3)$
771.60	764.05	7.55	$\text{U}^{16}\text{O}^{18}\text{O}(\nu_3)$
737.10	729.40	7.70	$\text{U}^{18}\text{O}_2(\nu_1)$
728.40	721.50	6.90	$\text{U}^{16}\text{O}^{18}\text{O}(\nu_1)$
820	815.4	4.6	U^{16}O

Table 4. Normal Mode Analysis for Matrix-Isolated UO_2 ($\alpha = 180^\circ$)

Assignment	Observed Frequency, cm^{-1}	Calculated Frequency, cm^{-1}	Normal Coordinate Eigenvector
1. Argon.			
$\text{U}^{16}\text{O}_2(\nu_3)$	776.10	776.1	$0.2663(\Delta r_1 - \Delta r_2)$
(ν_1)		765.4	$0.2500(\Delta r_1 + \Delta r_2)$
$\text{U}^{18}\text{O}_2(\nu_3)$	737.10	737.0	$0.2529(\Delta r_1 - \Delta r_2)$
(ν_1)		721.5	$0.2357(\Delta r_1 + \Delta r_2)$
$\text{U}^{16}\text{O}^{18}\text{O}(\nu_3)$	771.60	771.7	$0.1491(\Delta r_1 + \Delta r_2) + 0.2135(\Delta r_1 - \Delta r_2)$
(ν_1)	728.40	728.3	$0.1918(\Delta r_1 + \Delta r_2) - 0.1479(\Delta r_1 - \Delta r_2)$
2. Krypton			
$\text{U}^{16}\text{O}_2(\nu_3)$	767.95	768.0	$0.2663(\Delta r_1 - \Delta r_2)$
(ν_1)		758.6	$0.2500(\Delta r_1 + \Delta r_2)$
$\text{U}^{18}\text{O}_2(\nu_3)$	729.40	729.3	$0.2529(\Delta r_1 - \Delta r_2)$
(ν_1)		715.2	$0.2357(\Delta r_1 + \Delta r_2)$
$\text{U}^{16}\text{O}^{18}\text{O}(\nu_3)$	764.05	764.1	$0.1517(\Delta r_1 + \Delta r_2) + 0.2115(\Delta r_1 - \Delta r_2)$
(ν_1)	721.50	721.5	$0.1898(\Delta r_1 + \Delta r_2) + 0.1507(\Delta r_1 - \Delta r_2)$

mode analysis for the stretching frequencies are shown in Table 4. Differences between the observed and calculated frequencies are within the experimental uncertainty of $\pm 0.05 \text{ cm}^{-1}$. Uncertainties related to corrections for anharmonicity have not been considered.

The calculated eigenvectors indicate that the normal coordinates for $\text{U}^{16}\text{O}^{18}\text{O}$ involve a high degree of mixing of the symmetric stretch ($\Delta r_1 + \Delta r_2$) and the antisymmetric stretch ($\Delta r_1 - \Delta r_2$). The " ν_3 " coordinate corresponds to nearly a pure U^{16}O (Δr_1) stretch and the " ν_1 " coordinate to a U^{18}O (Δr_2) stretch, whereas the normal coordinates for the homonuclear isotopes correspond to pure antisymmetric (ν_3) and symmetric (ν_1) stretches. This high degree of decoupling of the two bond vibrations in $^{16}\text{O}-\text{U}-^{18}\text{O}$ is reasonable to expect because of the very large relative mass of the central uranium atom and is also observed in the HDO molecule. The unusually high relative intensity of " ν_1 " ($\text{U}^{16}\text{O}^{18}\text{O}$) may also be explained by this high degree of mixing of ν_1 and ν_3 characteristics, although for the homonuclear isotopes the ν_1 transition is forbidden for symmetry reasons. The infrared selection rules require a change in dipole moment with change in normal coordinate for a transition to be active. If one assumes fixed nuclear charges on the uranium and oxygen atoms, then the change in dipole moment is proportional to the change in the antisymmetric stretching coordinate. The intensity depends on the square of the coefficients for the ($\Delta r_1 - \Delta r_2$) terms, since the ($\Delta r_1 + \Delta r_2$) term does not contribute to the intensity for linear symmetric molecules.¹⁰ In this manner the calculated intensity ratio $I(\nu_3)/I(\nu_1)$ is found to be 1.9 from the krypton analysis and 2.1 from the argon analysis. The fact that this is in excellent agreement with the observed ratio of 1.85 (see Fig. 1) is further corroboration of the frequency assignments.

III. THEORETICAL EXTRAPOLATION OF MEASURED PHYSICAL PROPERTY DATA TO HIGHER TEMPERATURES (M. G. Chasanov)

The high-temperature experimental studies reported in the preceding sections can provide physical-property data for fuel materials, cladding, coolant, and structural materials at temperatures that are extremely high from our experimental point of view ($\sim 3300^\circ\text{K}$), but are still markedly less than temperatures of interest in reactor safety analyses. To satisfactorily correlate and extrapolate experimental data for utilization at these significantly higher temperatures ($\sim 6000^\circ\text{K}$), recourse to existing theory, such as corresponding states, scaled particle, and significant structures, is necessary. Our program involves calculational studies, based on theory, to assess consistency and validity of such extrapolation and correlation of available data.

A. Fuel and Fission-Product Vapor Pressures (S. D. Gabelnick, M. G. Chasanov)

The vapor pressure above fuel/fission-product systems at high temperatures is of importance in several phases of liquid-metal-fast-breeder-reactor accident analysis. A method of calculation, vapor pressures up to 6000°K based on that method, and available thermodynamic data have been previously described.^{11,12} In these calculations, the Pu/(U+Pu) ratio was considered to affect the oxygen potential, but for the purpose of calculating the pressures of the fuel-bearing species, the uranium and plutonium were treated together as MO_{2+x} , and the thermodynamic functions of the condensed and vapor-phase uranium oxides were employed. In the presently reported calculations, the partial pressures of the uranium and plutonium species have first been evaluated separately on the basis of currently available thermodynamic information obtained from vibrational spectra of matrix-isolated uranium oxides⁹ and available plutonium oxide data. In addition, a revised model by P. E. Blackburn¹³ of the oxygen pressure above plutonium-uranium-oxygen systems has been used. Values of the total pressure, as well as pressures of the alkali metals, noble gases, and fuel species, together with oxygen pressures and post-burnup oxygen-to-fuel-metal ratios, are presented in Tables 5-11 as a function of burnup, smear fuel density, and initial fuel composition.

B. Equation of State of Sodium (S. D. Gabelnick, M. G. Chasanov)

To meet the needs of those Reactor Analysis and Safety Division (RAS) groups at ANL working in the areas of fuel-coolant interaction, fuel-element failure propagation, and post-accident heat removal, a program has been undertaken to provide the best values for various thermophysical properties of liquid- and vapor-phase sodium systems from 600 to 3300°K . In addition to the critical constants, properties such as the saturation pressure, liquid and vapor-phase densities, heat capacity, enthalpies, and coefficients of thermal expansion, compressibility, and thermal pressure are needed as a function of temperature.

Work, to date, has centered on modification of the NAPROP computer code originally written by D. Miller and subsequently modified by N. McNeal and A. Padilla, all of RAS. The program was designed to calculate thermodynamic and physical properties of subcooled, saturated, and superheated sodium systems from 400°K to above the critical temperature ($\sim 2730^\circ\text{K}$). The

Table 5. Calculated Pressures (Atmospheres) for Initial Fuel Composition
 $(U_{0.8}Pu_{0.2})O_{1.98}$ and Fuel Density of 5 g/cm^3

Burnup, %	Post-Burnup O/M	$p(O_2)$	$p(\text{Total})$	$p(\text{AlkaliMetals})$	$p(\text{NobleGases})$	$p(\text{FuelSpecies})$
<u>2500°K</u>						
1	1.9829	9.37×10^{-6}	31.3	11.2	17.3	2.25×10^{-3}
3	1.9893	2.30×10^{-5}	79.8	21.5	51.9	3.25×10^{-3}
5	1.9951	4.69×10^{-5}	122	26.2	86.5	4.39×10^{-3}
8	2.0029	1.05×10^{-4}	182	29.9	138	6.21×10^{-3}
10	2.0078	1.60×10^{-4}	220	31.4	173	7.45×10^{-3}
<u>3000°K</u>						
1	1.9818	1.35×10^{-3}	41.2	14.9	21.7	0.120
3	1.9869	1.82×10^{-3}	105	30.1	65.1	0.131
5	1.9924	2.45×10^{-3}	160	37.4	108	0.144
8	2.0003	3.65×10^{-3}	237	43.2	173	0.164
10	2.0053	4.60×10^{-3}	287	45.5	217	0.177
<u>4000°K</u>						
1	1.9796	0.284	80.3	22.0	37	4.92
3	1.9812	0.293	194	46.7	113	4.87
5	1.9840	0.308	292	59.1	188	4.83
8	1.9894	0.341	428	68.7	301	4.80
10	1.9935	0.366	515	72.4	377	4.79
<u>5000°K</u>						
1	1.9746	6.25	239	12.0	56	34.3
3	1.9708	5.99	454	32.8	168	33.6
5	1.9691	5.89	628	48.4	281	32.9
8	1.9691	5.89	868	64.5	449	32.0
10	1.9702	5.96	1020	71.9	561	31.5
<u>6000°K</u>						
1	1.9671	56.5	662	3.04	83	106
3	1.9578	52.9	1280	9.6	250	104
5	1.9501	50.0	1820	16.5	417	102
8	1.9407	46.8	2520	27.0	667	99
10	1.9360	45.3	2920	33.7	834	97

Table 6. Calculated Pressures (Atmospheres) for Initial Fuel Composition $(U_{0.8}Pu_{0.2})O_{1.95}$ and Fuel Density of 5 g/cm^3

Burnup, %	Post-Burnup O/M	$p(O_2)$	$p(\text{Total})$	$p(\text{AlkaliMetals})$	$p(\text{NobleGases})$	$p(\text{FuelSpecies})$
<u>2500°K</u>						
1	1.9562	1.85×10^{-7}	30.4	10.5	17.3	6.68×10^{-4}
3	1.9681	1.03×10^{-6}	77.4	19.3	51.9	1.01×10^{-3}
5	1.9772	4.06×10^{-6}	119	23.6	86.5	1.58×10^{-3}
8	1.9864	1.55×10^{-5}	180	27.7	138	2.64×10^{-3}
10	1.9911	2.90×10^{-5}	219	29.5	173	3.41×10^{-3}
<u>3000°K</u>						
1	1.9533	1.81×10^{-4}	40.7	14.6	21.7	6.65×10^{-2}
3	1.9619	3.50×10^{-4}	103	28.6	65.1	7.74×10^{-2}
5	1.9698	6.17×10^{-4}	158	35.4	108	8.99×10^{-2}
8	1.9799	1.19×10^{-3}	235	41.0	173	1.09×10^{-1}
10	1.9858	1.70×10^{-3}	284	43.4	217	1.21×10^{-1}
<u>4000°K</u>						
1	1.9499	0.158	81.3	23.5	37.7	4.45
3	1.9522	0.165	195	48.3	113	4.41
5	1.9559	0.179	292	59.9	188	4.39
8	1.9627	0.205	427	68.4	301	4.38
10	1.9676	0.226	513	71.7	377	4.38
<u>5000°K</u>						
1	1.9452	4.50	237	14.7	56.1	33.4
3	1.9421	4.34	455	38.7	168	32.7
5	1.9411	4.29	632	55.3	281	32.1
8	1.9421	4.35	874	70.8	449	31.3
10	1.9439	4.43	1030	77.4	561	30.8
<u>6000°K</u>						
1	1.9381	45.9	639	3.6	83.4	105
3	1.9288	43.0	1260	11.3	250	103
5	1.9211	40.7	1800	19.4	417	101
8	1.9121	38.2	2490	31.4	667	98.0
10	1.9078	37.0	2900	38.9	834	96.1

Table 7. Calculated Pressures (Atmospheres) for Initial Fuel Composition
 $(U_{0.85}Pu_{0.15})O_{1.98}$ and Fuel Density of 5 g/cm^3

Burnup, %	Post-Burnup O/M	$p(O_2)$	$p(\text{Total})$	$p(\text{AlkaliMetals})$	$p(\text{NobleGases})$	$p(\text{FuelSpecies})$
<u>2500°K</u>						
1	1.9836	3.80×10^{-6}	31.1	11.1	17.3	1.68×10^{-3}
3	1.9908	1.33×10^{-5}	79.4	21.2	51.9	2.72×10^{-3}
5	1.9967	3.18×10^{-5}	122	26.0	86.5	3.92×10^{-3}
8	2.0045	7.99×10^{-5}	182	29.8	138	5.81×10^{-3}
10	2.0094	1.27×10^{-4}	220	31.3	173	7.10×10^{-3}
<u>3000°K</u>						
1	1.9823	6.64×10^{-4}	41.1	14.8	21.7	0.100
3	1.9885	1.05×10^{-3}	105	29.8	65.1	0.115
5	1.9947	1.58×10^{-3}	160	36.9	108	0.130
8	2.0033	2.61×10^{-3}	237	42.7	173	0.153
10	2.0086	3.45×10^{-3}	286	45.0	217	0.168
<u>4000°K</u>						
1	1.9802	0.163	81.5	23.4	37.7	4.73
3	1.9830	0.173	195	48.3	113	4.70
5	1.9871	0.189	292	59.9	188	4.68
8	1.9944	0.221	427	68.6	301	4.69
10	1.9996	0.245	514	71.9	377	4.70
<u>5000°K</u>						
1	1.9760	3.94	239	16.0	56.1	34.9
3	1.9738	3.85	458	41.0	168	34.2
5	1.9740	3.85	635	57.5	281	33.6
8	1.9765	3.97	877	72.4	449	32.8
10	1.9792	4.09	1030	78.7	561	32.3
<u>6000°K</u>						
1	1.9690	41.9	636	3.9	83.4	110
3	1.9606	39.6	1260	12.1	250	108
5	1.9538	37.8	1800	20.6	417	106
8	1.9461	35.9	2490	32.9	667	103
10	1.9427	35.1	2900	40.4	834	101

Table 8. Calculated Pressures (Atmospheres) for Initial Fuel Composition
 $(U_{0.8}Pu_{0.2})O_{1.98}$ and Burnup of 1%

Fuel Smear Density, g/cm ³	Post-Burnup O/M	p(O ₂)	p(Total)	p(Alkali Metals)	p(Noble Gases)	p(Fuel Species)
<u>2500°K</u>						
3	1.9828	9.34 x 10 ⁻⁶	14.6	5.7	7.5	2.25 x 10 ⁻³
4	1.9829	9.35 x 10 ⁻⁶	21.9	8.2	11.6	2.25 x 10 ⁻³
5	1.9829	9.37 x 10 ⁻⁶	31.3	11.2	17.3	2.25 x 10 ⁻³
6	1.9829	9.38 x 10 ⁻⁶	44.2	14.7	25.8	2.25 x 10 ⁻³
7	1.9829	9.40 x 10 ⁻⁶	63.7	18.9	39.7	2.26 x 10 ⁻³
<u>3000°K</u>						
3	1.9818	1.35 x 10 ⁻³	18.8	7.2	9.1	0.120
4	1.9818	1.35 x 10 ⁻³	28.4	10.6	14.3	0.120
5	1.9818	1.35 x 10 ⁻³	41.2	14.9	21.7	0.120
6	1.9819	1.35 x 10 ⁻³	59.4	20.2	33.0	0.120
7	1.9819	1.35 x 10 ⁻³	88.3	27.0	52.8	0.120
<u>4000°K</u>						
3	1.9796	0.285	38.5	10.1	13.5	4.92
4	1.9796	0.285	55.1	15.2	22.5	4.92
5	1.9796	0.284	80.3	22.0	37.7	4.92
6	1.9794	0.283	125	31.1	68.2	4.92
7	1.9791	0.282	244	43.8	162	4.91
<u>5000°K</u>						
3	1.9727	6.12	138	8.0	17.9	34.3
4	1.9740	6.21	180	10.1	31.2	34.3
5	1.9746	6.25	239	12.0	56.1	34.3
6	1.9750	6.28	344	13.5	120	34.3
7						
<u>6000°K</u>						
3	1.9506	50.2	407	3.0	22.9	106
4	1.9608	54.0	496	3.0	41.9	106
5	1.9671	56.5	662	3.0	83.4	106
6	1.9714	58.3	1190	3.0	246	106

Table 9. Calculated Pressures (Atmospheres) for Initial Fuel Composition
 $(U_{0.8}Pu_{0.2})O_{1.98}$ and Burnup of 3%

Fuel Smear Density, g/cm ³	Post-Burnup O/M	p(O ₂)	p(Total)	p(Alkali Metals)	p(Noble Gases)	p(Fuel Species)
<u>2500°K</u>						
3	1.9892	2.27 x 10 ⁻⁵	39.2	13.4	22.4	3.23 x 10 ⁻³
4	1.9893	2.29 x 10 ⁻⁵	57.0	17.6	34.8	3.24 x 10 ⁻³
5	1.9893	2.30 x 10 ⁻⁵	79.8	21.5	51.9	3.25 x 10 ⁻³
6	1.9894	2.31 x 10 ⁻⁵	111	25.1	77.4	3.25 x 10 ⁻³
7	1.9894	2.32 x 10 ⁻⁵	159	28.4	119	3.26 x 10 ⁻³
<u>3000°K</u>						
3	1.9868	1.81 x 10 ⁻³	50.5	17.7	27.4	0.131
4	1.9869	1.81 x 10 ⁻³	74.3	23.9	42.9	0.131
5	1.9869	1.82 x 10 ⁻³	105	30.1	65.1	0.131
6	1.9870	1.82 x 10 ⁻³	149	36.3	99.1	0.131
7	1.9870	1.82 x 10 ⁻³	219	42.2	158	0.131
<u>4000°K</u>						
3	1.9814	0.294	89.0	25.7	40.5	4.87
4	1.9813	0.294	131	35.9	67.6	4.87
5	1.9812	0.293	194	46.7	113	4.87
6	1.9810	0.292	308	58.1	205	4.86
7	1.9809	0.291	628	69.7	486	4.86
<u>5000°K</u>						
3	1.9700	5.94	260	23.1	53.7	33.6
4	1.9707	5.99	341	28.4	93.5	33.6
5	1.9708	5.99	454	32.8	168	33.6
6	1.9706	5.98	691	36.3	361	33.5
7	1.9703	5.96	2470	39.2	1990	33.5
<u>6000°K</u>						
3	1.9435	47.7	618	9.4	68.7	104
4	1.9523	50.8	851	9.5	126	104
5	1.9578	52.9	1280	9.6	250	104
6	1.9619	54.5	2540	9.5	739	104

Table 10. Calculated Pressures (Atmospheres) for Initial Fuel Composition
($U_{0.8}Pu_{0.2}O_{1.98}$) and Burnup of 5%

Fuel Smear Density, g/cm ³	Post-Burnup O/M	p(O ₂)	p(Total)	p(Alkali Metals)	p(Noble Gases)	p(Fuel Species)
<u>2500°K</u>						
3	1.9950	4.63×10^{-5}	60.7	18.4	37.4	4.37×10^{-3}
4	1.9951	4.66×10^{-5}	87.5	22.7	57.9	4.38×10^{-3}
5	1.9951	4.69×10^{-5}	122	26.2	86.5	4.39×10^{-3}
6	1.9952	4.71×10^{-5}	171	29.2	129	4.40×10^{-3}
7	1.9952	4.73×10^{-5}	248	31.6	199	4.41×10^{-3}
<u>3000°K</u>						
3	1.9922	2.42×10^{-3}	78.3	24.8	45.7	0.144
4	1.9923	2.44×10^{-3}	114	31.5	71.5	0.144
5	1.9924	2.45×10^{-3}	160	37.4	108	0.144
6	1.9924	2.46×10^{-3}	227	42.6	165	0.144
7	1.9925	2.47×10^{-3}	339	47.1	264	0.145
<u>4000°K</u>						
3	1.9841	0.309	133	36.9	67.5	4.83
4	1.9841	0.309	196	48.4	113	4.83
5	1.9840	0.308	292	59.1	188	4.83
6	1.9839	0.308	470	68.9	341	4.83
7	1.9838	0.308	987	77.6	810	4.83
<u>5000°K</u>						
3	1.9692	5.89	352	35.8	89.5	33.0
4	1.9695	5.91	462	42.9	15.6	33.0
5	1.9691	5.89	628	48.4	281	32.9
6	1.9686	5.85	1010	52.8	602	32.8
7	1.9680	5.81	3940	56.2	3310	32.8
<u>6000°K</u>						
3	1.9368	45.5	820	16.1	114	102
4	1.9448	48.2	1180	16.4	209	102
5	1.9501	50.0	1820	16.5	417	102
6	1.9545	51.6	3580	16.2	1230	101

Table 11. Calculated Pressures (Atmospheres) for Initial Fuel Composition
 $(U_{0.8}Pu_{0.2})O_{1.98}$ and Burnup of 8%

Fuel Smear Density, g/cm ³	Post-Burnup O/M	p(O ₂)	p(Total)	p(Alkali Metals)	p(Noble Gases)	p(Fuel Species)
<u>2500°K</u>						
3	2.0029	1.04 x 10 ⁻⁴	90.0	23.1	59.8	6.18 x 10 ⁻³
4	2.0029	1.04 x 10 ⁻⁴	130	27.0	92.7	6.20 x 10 ⁻³
5	2.0029	1.05 x 10 ⁻⁴	182	29.9	138	6.21 x 10 ⁻³
6	2.0030	1.05 x 10 ⁻⁴	257	32.2	206	6.22 x 10 ⁻³
7	2.0030	1.05 x 10 ⁻⁴	377	33.9	318	6.23 x 10 ⁻³
<u>3000°K</u>						
3	2.0000	3.60 x 10 ⁻³	116	31.8	73.1	0.164
4	2.0001	3.63 x 10 ⁻³	168	38.2	114	0.164
5	2.0003	3.65 x 10 ⁻³	237	43.2	173	0.164
6	2.0003	3.67 x 10 ⁻³	339	47.1	264	0.165
7	2.0004	3.68 x 10 ⁻³	512	50.3	422	0.165
<u>4000°K</u>						
3	1.9893	0.340	192	48.3	108	4.80
4	1.9893	0.340	285	59.5	180	4.80
5	1.9894	0.341	428	68.7	301	4.80
6	1.9894	0.341	702	76.1	546	4.80
7	1.9895	0.341	1510	82.1	1300	4.80
<u>5000°K</u>						
3	1.9700	5.94	465	50.6	143	32.2
4	1.9698	5.93	620	58.6	249	32.1
5	1.9691	5.89	868	64.5	449	32.0
6	1.9683	5.83	1450	69.0	964	31.9
7	1.9676	5.79	6100	72.2	5300	31.8
<u>6000°K</u>						
3	1.9283	42.9	1110	26.6	183	98.8
4	1.9355	45.1	1620	27.1	335	98.7
5	1.9407	46.8	2520	27.0	667	98.5
6	1.9458	48.5	4870	26.1	1970	98.2

basis of the computer code has been documented by D. Miller.¹⁴ Improvements in the P-V-T relations in the superheated vapor and subcooled liquid regions have been obtained by refitting the thermal pressure coefficients (γ) to available data. The pressure in these regions is given by

$$P_T = P_{\text{sat}} + (T - T_{\text{sat}}) \gamma \text{ for } T_{\text{sat}} < T < T_{\text{critical}}$$

where γ equals $(\partial P / \partial T)_V$ for saturated sodium vapor in the superheated vapor region ($V > V_{\text{critical}}$) and for the saturated liquid in the subcooled liquid region ($V < V_{\text{critical}}$). A polynomial fit of the form

$$\frac{1}{\gamma_{\text{vapor}}} = -0.1803 + 0.2038 V + 0.2142 \times 10^{-8} V^2$$

was obtained by utilizing γ 's from an adaption of a virial equation of state determined by Ewing *et al.*¹⁵ in the region of its close fit to the available experimental data (1300-1650°K) and those predicted by the Himpan equation of state¹⁶ above 1650°K, where V is the specific volume (cm^3/mol) and γ is in units of $\text{bar}/^\circ\text{K}$.

The values of γ for the saturated liquid region are obtained from the ratio of the thermal-expansion coefficient to the isothermal compressibility. Based on a fit of data of Pochapsky¹⁷ and Stone *et al.*,¹⁸ the following equation was obtained

$$\frac{1}{\gamma_{\text{liquid}}} = -0.6011 + 1.0611 V - 0.5157 V^2 + 0.09918 V^3$$

This equation is being reevaluated in the light of more recent data of Leibowitz *et al.*¹⁹ and Chasanov *et al.*²⁰ The resulting P-V-T diagram, which uses the Himpan equation above T_{critical} , is shown in Fig. 2.

Fig. 2. P-V-T Diagram for Sodium

IV. THERMAL DIFFUSIVITY OF REACTOR MATERIALS (M. G. Chasanov)

Values of the thermal diffusivity of reactor materials in the liquid state are needed for the reactor safety program to evaluate means of safely cooling the core of an LMFBR in the event of hypothetical meltdown. The thermal diffusivity can be used in conjunction with heat-capacity and density data to provide thermal conductivity data for oxide fuel, which are needed to help in determining temperature distribution in fuel, cooling rates, and heat dissipation and in establishing suitable containment measures for molten fuel in a hypothetical reactor meltdown accident.

A. Liquid UO_2 (J. Fischer, J. Haley, R. Land)

An experimental method is being developed for the determination of thermal diffusivity of liquid materials at high temperatures. The method is being applied initially to UO_2 and then may be extended to mixed oxides. Thermal diffusivity values that we have obtained for solid UO_2 and tungsten, using this method, agree with the results of other investigators who have used similar and other methods. Our next goal is to obtain thermal diffusivity values for liquid UO_2 . This determination requires that the UO_2 be encapsulated in tungsten. Therefore, the method and analysis of data differ considerably from those used previously by other investigators. The analysis entails special mathematical development and computer programming.

As described previously, the thermal diffusivity is determined from the phase change in a thermal wave which has passed through a sample. Successive heat waves are produced by heating one surface of a disk-shaped sample with a sinusoidally modulated electron beam. The other surface of the disk is heated with a second unmodulated electron beam. A second beam is required to prevent too large a temperature differential between the surfaces and to provide the additional power needed to attain the high temperatures. Sinusoidally fluctuating temperatures are monitored on each surface of the sample disk with a pair of pyrometers. The voltage outputs of the pyrometers, which are proportional to the temperatures, are fed as inputs into an x-y recorder. This results in the display of a Lissajous figure from which the phase shift is calculated. Initial testing, temperature determination, measurement of temperature profiles, factors leading to choice of disk and cell dimensions, and the theoretical basis for the experimental method were described earlier.²²

Thermal diffusivity data for tungsten have now been obtained from 1870 to 3300°C. The measured phase shifts were used in a computer program to calculate the thermal diffusivity of tungsten. The computations were based on a two-dimensional heat-transfer model developed with the aid of Professor E. M. Sparrow.* These results are compared with those in the literature in Fig. 3; details of the literature studies are given in Table 12. Thermal diffusivity values for UO_2 , determined in a similar manner at 1600°C, are presented in Table 13, along with literature values.

Above 2000°C, the electron beam rapidly damages and erodes the surface of UO_2 . Therefore, it is necessary to enclose the UO_2 , and tungsten was chosen because it is the only metal that will contain liquid UO_2 up to a

*Consultant from the University of Minnesota.

Fig. 3. Thermal Diffusivity of Tungsten

TABLE 12. Literature Values for Tungsten Thermal Diffusivity

Author and Publication	Symbol in Fig. 3	Temperature Range, $^{\circ}\text{K}$	Sample Description	Stated Precision
C. Sheer et al., WADC-TR-58-142, pp. 75-96 (1958)	∇ $\square$ $\blacktriangledown$	407-1298 868-1543 828-1793	Cylindrical: 1.0 cm dia, 4.5 cm length	$\pm 30\%$
O. Kraev and A. Stel'makh, High Temp. <u>1</u> , 5 (1963)	$\diamond$	1873-3223	Disk cut from polished plate 0.7-0.8 cm dia, 0.02 cm thick	$\pm 5\%$
R. Taylor and M. Nakata, WADD-TR-60-581 (Pt. IV) (1963)	$\triangle$	1728-2743		
M. Wheeler, Brit. J. Appl. Phys. <u>16</u> , 365 (1965)	$\circ$	1300-2900	Disks cut from swaged rod 0.15 cm thick	$\pm 5\%$

TABLE 13. Thermal Diffusivity and Conductivity of UO_2 at 1600°C

Experimenters, Laboratory and Literature Reference	Method Used	Diffusivity, cm^2/sec	Conductivity, $\text{W}/\text{cm-deg}$	Material Description	Precision Stated
J. B. Ainscough and M. J. Wheeler, United Kingdom Atomic Energy Authority Brit. J. Appl. Phys. <u>1</u> (Ser. 2), 859 (1968)	Modulated electron beam		0.026 (0.02-0.03) ^a (0.02277+3.38) ⁻¹⁺ $6.6 \times 10^{-13}T^3$ (970-2020K)	1.45-cm dia 0.05 cm thick O/U = 2.000-2.003 96-97% density	95% Confidence Limit - $\pm 14\%$
J. L. Bates, Battelle Northwest High Temperature Fuels Meeting, Dec. 1969	Flash	0.0057	0.020	0.625-cm dia 0.076 cm thick O/U = 2.003 98% density	$\pm 5\%$
J. A. Christensen et al., WAPD (Hanford) Trans. Amer. Nucl. Soc. <u>7</u> , 390 (1964)	Radial flow		0.027 (0.020-0.021) ^a	5.08-cm dia 2.54 cm thick O/U = 2.01-1.99 94% density	
J. B. Conway and A. D. Feith, GE-NSP-GEMP-715	Radial flow		0.023 (0.021-0.035) ^a	5.04-cm dia 1.27 cm thick O/U = 2.003 98% density	$\pm 6\%$
M. Serizawa et al., in Proc. 8th Conf., Thermal Conduc- tivity, C. Ho and R. Taylor, Eds., Plenum Press, New York (1969)	Modulated electron beam	0.0073	0.022	1.0-cm dia 0.14-0.20 cm thick O/U = 1.99-1.95 96% density	$\pm 10\%$ accuracy
ANL results	Modulated electron beam	0.0048 ^b 0.0058 ^c	0.022	1.55-cm dia 0.051-0.102 cm thick O/U = 1.97 95% density	

^aRange of literature values discussed in article.^bSample thickness 0.051 cm.^cSample thickness 0.102 cm.

temperature of approximately 3300°C. Because the radiation heat losses are large and the electron beams do not fall on the edge of the sample, it is necessary to heat a disk-shaped tungsten cell* containing UO_2 to approximately 3200°C at the center of its upper surface to assure that all of the UO_2 is melted.† It had been demonstrated²² twice that an empty welded cell could be heated at these temperatures without distortion of the upper or lower surfaces of the cell. A cell that contains UO_2 undergoes some surface buckling when heated in the same manner as the empty cell above 2500°C. This is probably due to the desorption of gas from the UO_2 , which produces some pressure in the container while the outside of the container is at about 10^{-5} Torr. Experiments are now being performed to determine a means of eliminating or releasing this pressure.

The phase shift of a signal which has passed through a container and sample is a function of the total diffusivity of the container. Proceeding from the upper surface, whose temperature is modulated by the electron beam, to the lower surface of a tungsten container holding molten UO_2 , the signal passes through a layer of tungsten, a void space (in the event that the liquid does not fill the space between the upper and lower layers of tungsten), a layer of molten UO_2 , and the bottom layer of tungsten. The total phase shift is not simply the sum of the phase shifts one would calculate for the individual layers, but the resultant of complex interactions through the various layers and the radiation emissions from all the radiating surfaces. In addition, the total phase shift is a function of the radial heat transfer. All of these complex interactions must be accounted for in the differential equations describing the heat flow and boundary conditions of the container and sample. A mathematical description of heat flow has been written with the thermal diffusivities of UO_2 and tungsten as functions of the total phase shift of the system and with the heat-flow and energy-conservation equations in central-difference form. The equations are being programmed in order that a numerical solution can be obtained with the use of the IBM 360 computer.

*The cell has an outside diameter of 0.75 in.

†A gradient of about 350° occurs between the center and outer edge of the cell.

V. REACTOR MATERIALS--FUEL PHASE STUDIES AT HIGH TEMPERATURES (M. G. Chasanov)

Knowledge of the distribution of fission products to the phases produced in the event of a hypothetical LMFBR core meltdown is required to predict the fission-product heat distribution after an incident and to assure that means are available for cooling the products of the meltdown. In the type of hypothetical incident being considered, simultaneous failure of multiple safeguards and loss of effective cooling could lead to melting of the oxide fuel, the stainless steel cladding, the core-support steel, and the concrete container. To properly evaluate the capabilities of heat removal after a hypothetical meltdown incident, it is necessary to know the physical distribution of the phases, the quantitative distribution of fission-product heat among the phases, and the physical properties of any interaction products. This program seeks to provide this information.

A. Distribution of Fission Products Among Molten-Fuel and Reactor-Material Phases (J. Fischer, F. Mrazek)

The objective of these studies is to investigate the phase interactions that result when molten-fuel materials are in contact with cladding, structural materials, coolant, and containment materials. The determination of the nature of immiscible phases and the distribution of important decay-heat-generating fission products between the metallic and oxide phases possible in a hypothetical meltdown situation will be included in these studies. A study of the composition of the liquidus and the melting points of equilibrium phases for important components of cladding, structural material, and containment materials with oxide fuel will be determined in those cases where information is insufficient. Studies of the distribution of inactive fission products between molten iron and molten UO_2 have been completed and a final report has been published.²³

Some consideration has been given to the use of basalt as a diluent for molten reactor fuel in the unlikely event that the primary steel container of a reactor is breached. The basalt would melt and the UO_2 - PuO_2 fuel would dissolve in the melt. It is necessary to know the distribution of fission products among the resultant phases. Work has been in progress to determine the solubility of UO_2 in molten basalt and to determine the distribution of fission products between molten iron and a molten UO_2 -basalt mixture.

The ordinary methods of determining solubility are not practical for use with UO_2 in molten basalt. Because the temperatures of interest are above 1500°C , the materials one can use are severely limited. It would be extremely difficult to sample phases, and thermal methods would be of questionable value for such a complex silicate mixture.

It was determined in preliminary experiments with simulated molten concrete that sintered microspheres of UO_2 dissolve in molten concrete. When the quantity of UO_2 present exceeds that required for saturation, the microspheres become porous and retain their shape after partial dissolution. Also, if the UO_2 microspheres are equilibrated with molten concrete at approximately 2200°C in a tungsten crucible, the partially dissolved microspheres, which are more dense than the silicate melt, are

readily discerned on the bottom of the crucible, after solidification, by metallographic examination. It was therefore concluded that if gram amounts of the UO_2 microspheres are equilibrated with molten basalt for several hours at 2200°C with occasional mixing by heating, cooling, and inversion, the presence of microspheres after equilibration will signify that the liquid basalt is saturated with the UO_2 .

Accordingly, experiments were performed to determine the solubility of UO_2 in basalt at 2200°C . The UO_2 was obtained from Nuclear Materials and Equipment Corporation, Appollo, Pennsylvania, and analysis was provided by the vendor. The analysis and physical condition of the microspheres are shown in Table 14. The basalt was supplied by J. McCormack of WADCO. The analysis of the basalt is given in Table 15, along with the analysis for the simulated concrete we used. The similarity between the basalt and concrete would lead one to believe that the solubility behavior of UO_2 in molten concrete and basalt would be similar.

Table 14. UO_2 Microspheres--Analysis and Description

Element	Analysis ppm	Description	
Cd	<0.5	Density (% theoretical)	91
B	<0.5	Mesh	-60+140
Mn	<10	U, wt %	88.11
Mg	<10	O/U	2.01
Pb	2		
Si	<50	12,600 microspheres/gram	
Fe	<20		
Cr	<10		
Ni	<10		
Al	100		
Mo	35		
Sn	2		
V	<1		
Cu	<6		
Ti	<10		
Co	<5		
W	<25		
Be	<10		
Zr	<50		
Na	<20		
Li	<0.1		

Table 15. Chemical Composition of Concrete and Basalt

	Concrete ^a	Simulated Concrete, ^b wt %	Basalt ^c	
			ANL ^d	WADCO ^e
SiO ₂	50.3	54.0	52.4	50.0
TiO ₂	-	-	-	1.7
Al ₂ O ₃	11.6	12.5	15.8	13.4
Fe ₂ O ₃	9.7	10.4	11.2	11.7
MgO	1.8	1.9	6.7	7.0
CaO	19.8	21.3	9.9	10.3
Na ₂ O	0.2	-	2.7	2.3
K ₂ O	0.1	-	-	0.5
Volatiles	5.6	-	1.0	1.0

^aTypical concrete for FFTF (BNWL-CC-2369).^bSimulated mixture used in preliminary experiments.^cSupplied by WADCO.^dANL analysis.^eWADCO analysis.Table 16. Dissolution of UO₂^a in Basalt at 2200°C^b

UO ₂ , wt %	UO ₂ , g	Basalt, g	Metallographic Observation ^c
23.9	1.98	6.31	No UO ₂ microspheres
36.8	3.94	6.77	No UO ₂ microspheres
44.9	3.80	4.66	No UO ₂ microspheres
50.0	4.46	4.46	No UO ₂ microspheres
54.9	8.35	6.87	Residual microspheres

^aSintered microspheres; see Table 13 for analysis and description.^bThe tungsten crucible and contents were heated for 3 hr at 2200°C, cooled to room temperature, and inverted. The cycle was repeated four more times.^cExamined, ground and polished, and reexamined at several depths.

Cylindrical tungsten crucibles, 2 in. high, 0.5-in. ID, 0.02-in. wall thickness, were used to contain the UO_2 basalt mixture. The crucibles were loaded with UO_2 and basalt using the quantities shown in Table 16. A tungsten cover was placed on a crucible and it was welded closed under vacuum by electron-beam welding. Each crucible was then placed in a tungsten-element, resistance-heated furnace and heated for 3 hr at 2200°C . It was then cooled to room temperature and inverted. The cycle was repeated four more times. A crucible was then cut longitudinally, mounted, and examined metallographically for the presence of undissolved UO_2 microspheres. The surface was ground several times to expose different surfaces and reexamined for the presence of microspheres.

Various concentrations of UO_2 were used as shown in Table 16. In all cases the typical fine reticulate precipitate of UO_2 was observed in the solidified silicate. No microspheres of UO_2 were found up to and including the case where the initial UO_2 concentration in the unmelted mixture was 50.0 wt %. It was deduced that all of the UO_2 had dissolved at 2200°C . In the case where the UO_2 concentration in the unmelted basalt mixture was 54.7 wt %, residual microspheres were evident on the bottom of the crucible. The reticulate UO_2 precipitate was more dense and not nearly as fine as observed in the cases of lower UO_2 concentration. It is therefore deduced that the solubility of UO_2 in basalt is a value between 50.0 and 54.7 wt % at 2200°C .

Additional observations were made on the section that had been examined metallographically from the crucible that contained 36.8 wt % UO_2 . Microprobe analysis was made on areas of the basalt matrix which were shown by metallography to be free of precipitated UO_2 . Twenty such areas were analyzed with a finely focussed beam which scanned an area 16 by 16 μm at an accelerating potential of 15 kV. The net count rate, obtained by monitoring the uranium $\text{M}\alpha$ emission line, was compared with the net counts obtained from a standard sample of uranium dioxide under identical excitation conditions. A value of 2.32 ± 0.49 wt % UO_2 was found. In addition, a random sampling of the precipitated UO_2 at eight different locations showed it to be 100.1 ± 0.9 wt % UO_2 . Thus, if there were no incongruent transformations, UO_2 can be considered to be the solid in equilibrium with molten basalt. The value of 2.32 % UO_2 in the basalt matrix most likely represents the UO_2 concentration in the eutectic composition for this region. The temperature of complete solidification, inferred from work at WADCO, is close to 1100°C .

Experimental work on the distribution of fission products between UO_2 -basalt and iron is in progress, and involves the fission products Mo, Nb, Ce, and Ru. Preliminary results indicate that molybdenum is distributed to the iron phase. Analysis has not been obtained for the other elements.

B. Physical Properties of Interaction Products

1. Viscosity of Molten Basalt-Urania Solutions (L. Leibowitz, C. Williams)

An experiment is under way to measure the viscosity of molten basalt and basalt-uranium solutions in the temperature range 1500 – 2000°C . This physical property, along with other experimental data, can be used

to help predict the behavior of basalt as a sacrificial material in the unlikely event that the primary container of a reactor is breached.

A Brookfield Synchro-Lectric Viscometer (Brookfield Engineering Laboratories, Stoughton, Massachusetts) has been purchased for these high-temperature viscosity measurements. It is a rotational viscometer that measures viscous drag or retarding force as a function of speed for a cylinder or spindle that is immersed in the experimental solution. A tungsten spindle has been designed by the Brookfield Engineering Laboratories and is being fabricated by Ultramet, Inc., Pacoima, California.

The experiment will be performed in a high-vacuum, tungsten-mesh furnace on which the viscometer will be mounted. Preliminary tests of the equipment have been performed. Sample temperatures will be measured using W-5% Re/W-26% Re thermocouple spot-welded directly to a tungsten crucible holding the molten material under investigation.

High-temperature testing of the entire experimental procedure will be performed using a viscosity standard glass obtained from NBS and also with B_2O_3 glass which was recommended to us by NBS. Great care must be taken in the preparation of the B_2O_3 glass to avoid the presence of water. A small amount of the B_2O_3 glass is being prepared to test procedures for its formation.

2. Density of Molten Basalt-Urania Solutions (L. E. Ross, P. D. Hunt)

Determination of the density of molten basalt and molten urania-basalt mixtures will provide information to be used in the calculation of the thermal-expansion coefficients of basalt and urania-basalt mixtures.

The method employed is that of Archimedes in which the weight of a bob is determined in air and when immersed in the liquid. The density of the liquid is then calculated from the difference in these weights. The method lends itself to the determination of the density of liquid at various temperatures.

A Varian vacuum furnace with a W-Mo furnace tube is used to heat the samples. A Cahn RH electrobalance is used to determine the weight of the bob and is mounted over the furnace tube. The balance and the open end of the furnace tube are covered with a bell jar, which allows either an inert atmosphere or a vacuum to be maintained. An argon atmosphere was used in this work.

A rod that can be extended inside the bell jar was installed with a vacuum seal. This rod is used to displace the suspension wire to raise the bob out of the melt. Care must be exercised in raising the bob from the melt so that the bob does not contact the crucible wall above the melt and stick to it.

The temperature of the melt was first measured with an optical pyrometer. There was some doubt as to the accuracy of this measurement since the density values for potassium chloride varied by a constant percentage from the reported values. The optical pyrometer was recalibrated and a Pt/Pt-10% Rh thermocouple was used in subsequent tests. The thermocouple was

placed in the annulus between the crucible and the furnace tube and gave consistently higher readings than the pyrometer. This difference was real, since the surface of the melt was cooler than the bottom of the melt. This was probably due to the length of the crucible, the upper end of which extended out of the hot zone, although the melt was within the hot zone.

The system is evacuated and filled with argon twice to remove traces of oxygen from the system and to degas the sample. A slight positive pressure of argon is maintained.

The apparatus was tested with potassium chloride and barium chloride over the temperature ranges 860 to 940°C and 1020 to 1350°C, respectively. The salt was contained in a nickel crucible 15-mm ID by 150 mm long. A platinum bob, 6 by 12.5 mm, with cone-shaped ends was suspended from the balance arm with 0.150-mm platinum wire. The output of the electrobalance was recorded on a strip chart.

The values for the density of potassium chloride were within 0.1% of those reported by Peake and Bothwell²⁴ and within 0.6% of those reported by Van Artsdalen and Yaffee.²⁵ Some difficulty was experienced with condensation of the salt on the suspension wire. A correction was made based on the increase of weight at temperature and the final weight of salt on the suspension wire.

The values for the density of barium chloride were within 0.5% of those reported by Yaffee and Van Artsdalen.²⁶

The density of the molten basalt and the molten urania-basalt mixtures will be determined using a tungsten crucible, a tungsten bob, and a tantalum suspension wire. Temperature will be measured with a calibrated W-5% Re/W-26% Re thermocouple attached to the side of the crucible. Heat shields will be installed above the crucible to maintain a constant temperature throughout the melt. The density will be determined over the temperature range 1200 to ~1900°C.

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