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CHEMICAL ENGINEERING DIVISION
THERMOCHEMICAL STUDIES SEMIANNUAL REPORT
January-June 1972

by

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J. L. Settle, P. A. G. O'Hare,
A. D. Tevebaugh, and R. C. Vogel

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ABSTRACT

Final values for $\Delta H_f^\circ(\text{Na}_2\text{C}_2, c, 298^\circ\text{K})$ and $\Delta H_f^\circ(\text{NaHC}_2, c, 298^\circ\text{K})$ have been determined to be $+4.80 \pm 0.40$ and $+23.10 \pm 0.27$ kcal mol⁻¹, respectively. Combination of the value for Na_2C_2 with measurements of the heat capacity and solubility in sodium of Na_2C_2 indicate that Na_2C_2 is an important species formed when graphite is dissolved in liquid sodium. Determination of the enthalpy of formation of monocationic acetylide by solution calorimetry in a similar study yielded the value $\Delta H_f^\circ(\text{CsHC}_2, c, 298^\circ\text{K}) = +18.84 \pm 0.27$ kcal mol⁻¹. Measurements of the enthalpies of solution of Cs_2O , ThS , and BrO_3F yielded values of the standard enthalpies of formation at 298°K for these compounds, in kcal mol⁻¹, as follows: $\Delta H_f^\circ(\text{Cs}_2\text{O}, c) = -82.52 \pm 0.18$, $\Delta H_f^\circ(\text{ThS}_{1.029 \pm 0.019}, c) = -96.9 \pm 0.9$, and $\Delta H_f^\circ(\text{BrO}_3\text{F}, l) = +26.78 \pm 0.25$. Measurements of the energies of reaction of XeF_6 , XeF_4 , and XeF_2 with PF_3 yielded values of the standard energies of formation at 298°K for these compounds, in kcal mol⁻¹, as follows: $\Delta H_f^\circ(\text{XeF}_6, c, l) = -80.82 \pm 0.53$, $\Delta H_f^\circ(\text{XeF}_4, c) = -63.84 \pm 0.21$, and $\Delta H_f^\circ(\text{XeF}_2, c) = -38.90 \pm 0.21$. I. J. Hastings (Atomic Energy of Canada) has prepared a sample of U_3Si , and E. K. Storms (Los Alamos Scientific Laboratory) is preparing molybdenum and vanadium carbide samples, all for enthalpy of formation studies to be performed in our laboratory by fluorine bomb calorimetry.

SUMMARY

Na_2C_2 and NaHC_2

The thermodynamic properties of disodium acetylide, Na_2C_2 , are of interest in connection with the use of liquid sodium as a coolant in the Liquid Metal Fast Breeder Reactor Program. Na_2C_2 has been postulated as a species causing the transport of carbon between steel structures in coolant loops. In cooperation with D. W. Osborne and H. E. Flotow of the Chemistry Division, the thermodynamic properties of Na_2C_2 up to 1100°K were evaluated. The results of this study show that the formation of a solution of Na_2C_2 by the reaction of liquid sodium and graphite is thermodynamically possible and can result in the introduction of significant concentrations of carbon in liquid sodium. Therefore, models based on dissolved Na_2C_2 for the transport of carbon in liquid-sodium-cooled reactors should be considered. In connection with this work, the enthalpy of formation of NaHC_2 was also determined.

CsHC₂

Determination of the enthalpy of formation of monocationic acetylide was undertaken as a byproduct of our interest in fission-product carbides, which, in turn, stems from the long-range potential of carbide-fueled fast breeder reactors. Initially it was planned to study both the cesium acetylides, Cs₂C₂ and CsHC₂, as had previously been done for the analogous sodium acetylides (see above). However, the vendor was unable to prepare Cs₂C₂. The standard enthalpy of formation of CsHC₂ was determined to be $+18.84 \pm 0.27$ kcal mol⁻¹.

Cs₂O

Postirradiation studies of urania-plutonia fuel pins have revealed high concentrations of fission-product cesium and molybdenum in the region of the oxide fuel adjacent to the fuel-cladding interface. These observations suggest the formation of oxides of these fission products. The first step in making reasonably accurate predications of the influence of these oxides in irradiated-fuel-cladding interactions is the accumulation of accurate data for the oxides. During this period, the enthalpy of formation of Cs₂O was determined by solution calorimetry.

ThS

As part of our effort to obtain basic thermodynamic information on actinide compounds, the enthalpy of solution of a sample of ThS_{1.029} in 6M HCl was measured in a cooperative study with the Chemistry Division of the thermodynamic properties of ThS. Metallographic analyses revealed the presence of at least two minor phases in the thorium monosulfide calorimetric specimen. The electron microprobe indicated that the S/Th atomic ratios approximated 1.5, i.e., the composition of Th₂S₃. The concentration of these impurity phases, considered as a composite Th₂S₃ phase, was estimated by areal analyses to be 3.77 ± 0.46 wt %. Computations based on this and other specimen analyses, on the calorimetrically measured reaction with 6M HCl, and on auxiliary thermochemical data yielded the value $\Delta H_f^\circ(\text{ThS}_{1.029 \pm 0.019}, c, 298.15^\circ\text{K}) = -96.9 \pm 0.9$ kcal mol⁻¹.

U₃Si

Triuranium silicide, U₃Si, is a binary uranium compound that has been on the program of our group for some time. However, early attempts to prepare a calorimetric-grade sample did not succeed. A sample has now been prepared by I. J. Hastings of Atomic Energy of Canada Ltd., Chalk River, where U₃Si is being investigated as a reactor fuel. Exploratory combustions on a preliminary sample sent here by Hastings indicate that satisfactory combustions of U₃Si in fluorine can be obtained with 2-g samples (in the form of small pieces of 1/16 by 1/16-in. rod) supported on a piece (~0.5 g) of corrugated molybdenum foil (0.003-in. thick) in 10 atm of fluorine pressure.

BrO₃F

Because the perbromates had been thought to be nonexistent, the recent syntheses of perbromic acid, the alkali perbromates, and perbromyl fluoride caused much interest in the thermodynamic properties of these compounds. A paper describing the determination of $\Delta H_f^\circ(\text{BrO}_3\text{F}, \ell)$ from measurements of its enthalpy of reaction with water has been accepted for publication.

XeF₆, XeF₄, XeF₂

The determination of the enthalpies of formation of XeF₆(c), XeF₄(c), and XeF₂(c) from measurements of their energies of reaction with PF₃(g) has been completed. A paper describing this work has been submitted for publication.

Refractory Carbides

The thermodynamic properties of refractory carbides are basic data needed for understanding the chemistry of carbide fuel-fission product systems. The determination of some needed enthalpy-of-formation data was begun in this laboratory within the last few years with measurements of the enthalpies of formation of PuC and Pu₂C₃. Our interest in carbides is also manifested in the studies of the sodium and cesium acetylides (see Sections I and II of this report). Recently, a collaborative effort has been undertaken with Los Alamos to determine the enthalpies of formation of several carbides in the molybdenum-carbon and vanadium-carbon systems. The samples will be prepared at Los Alamos and our group will measure the energy of combustion.

I. DISODIUM ACETYLIDE (Na₂C₂) AND MONOSODIUM ACETYLIDE (NaHC₂)
(G. K. Johnson, E. H. Van Deventer)

The thermodynamic properties of disodium acetylide, Na₂C₂, are of interest in connection with the use of liquid sodium as a coolant in the Liquid Metal Fast Breeder Reactor program of the U. S. Atomic Energy Commission. Disodium acetylide has been postulated as a species causing the transport of carbon between steel structures in simulated reactor coolant loops.^{1,2} The subsequent degradation of the steel structures could be important to reactor safety. The postulate that Na₂C₂ is involved in carbon transport is based on the observation that when liquid sodium that has been equilibrated at elevated temperatures with ferritic steel containing labeled carbon is subsequently hydrolyzed, detectable amounts of acetylene gas containing the labeled carbon are formed.¹ Because only acetylide salts are known to react with water to form acetylene, it is inferred that Na₂C₂ is the likely precursor of the acetylene.

It has been argued³ that Na₂C₂ cannot be responsible for the transport of carbon because the available thermodynamic data indicate that Na₂C₂ is thermodynamically unstable. However, it is clear that if the standard Gibbs energy of formation is positive but not too large, thermodynamics allows the formation of significant concentrations of Na₂C₂ in liquid sodium by

the reaction of liquid sodium and graphite, even though the formation of solid Na_2C_2 by this reaction is impossible.

The determination of the enthalpies of formation of $\text{Na}_2\text{C}_2(\text{c})$ and $\text{NaHC}_2(\text{c})$ from measurements of their enthalpies of reaction with water were reported previously.⁴ The final revised values for the enthalpies of formation are $\Delta H_f^\circ(\text{Na}_2\text{C}_2, \text{c}) = 4.80 \pm 0.40 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{NaHC}_2, \text{c}) = 23.10 \pm 0.27 \text{ kcal mol}^{-1}$. Subsequent to these measurements, D. W. Osborne and H. E. Flotow of the Chemistry Division measured the low-temperature heat capacity of Na_2C_2 between 5 and 350°K. The heat-capacity curve was then extrapolated up to 1100°K so that the thermodynamic properties of Na_2C_2 in the region of interest to reactor technology could be evaluated. The results for the Gibbs energy of formation, ΔG_f° , of Na_2C_2 are given in Table 1.

The positive values of ΔG_f° for all temperatures between 370.98°K and the normal boiling point of sodium, 1176.9°K, mean that solid Na_2C_2 cannot be formed by the reaction of liquid sodium and graphite in this temperature range. However, it is thermodynamically possible to form a solution of Na_2C_2 in liquid sodium, where the activity of Na_2C_2 is less than unity. The equilibrium constant, K_f , for the reaction is given by

$$K_f = \frac{a_{\text{Na}_2\text{C}_2}}{a_{\text{Na}}^2 \cdot a_{\text{C}}^2}$$

and

$$-RT \ln K_f = \Delta G_f^\circ$$

when all the activities are relative to $a = 1$ for each pure substance in its standard state at temperature T . The uncertainties in ΔG_f° cause K_f to be uncertain by a factor of 1.9 at 400°K and by a factor of 1.7 at 1100°K.

The activity of Na_2C_2 in dilute solutions can be evaluated from the solubility of Na_2C_2 in liquid sodium. Although $\text{Na}_2\text{C}_2(\text{c})$ is thermodynamically unstable relative to liquid sodium and graphite, below 800°K the rate of decomposition is so low that the solubility can be measured. Between 624 and 786°K, the experimental results of Ackerman, Allen, and Cafasso⁷ can be expressed by the equation

$$\log_{10} X_{\text{sat}} = 0.326 - 4289/T$$

where X_{sat} is the mole fraction of Na_2C_2 in the saturated solution. For dilute solutions in liquid sodium

$$a_{\text{Na}_2\text{C}_2} = kX$$

where X is the mole fraction of Na_2C_2 and k is a constant, and therefore

$$a_{\text{Na}_2\text{C}_2} = X/X_{\text{sat}}$$

TABLE 1. Gibbs Energy of Na_2C_2 and the Concentration of Na_2C_2 in Liquid Sodium in Equilibrium with Graphite

T, °K	ΔG_f° , kcal mol ⁻¹	c, ^a ppm	C ₀ , ppm	
			LT ^b	AI ^c
500	5.40 ± 0.5	2.6×10^{-5}	1.9×10^{-4}	4.0×10^{-5}
600	5.43 ± 0.6	1.7×10^{-3}	1.2×10^{-2}	2.6×10^{-3}
700	5.35 ± 0.7	3.5×10^{-2}	0.25	5.2×10^{-2}
800	5.20 ± 0.8	0.37	2.3	0.49
900	4.96 ± 0.9	2.4	13	2.8
1000	4.62 ± 1.0	11	54	11
1100	4.21 ± 1.1	41	171	35

^aConcentration of Na_2C_2 in liquid sodium in equilibrium with graphite, expressed in parts of carbon per million parts of sodium.

^bTotal concentration of dissolved carbon according to equation of Longson and Thorley (Ref. 5).

^cTotal concentration of dissolved carbon according to equation reported by Atomics International (Ref. 6).

Since the solution is very dilute, $a_{\text{Na}} = 1$. The equilibrium mole fraction of Na_2C_2 in liquid sodium in equilibrium with graphite was calculated from K_f , the equation for X^{sat} (extrapolated down to 500°K and up to the normal boiling point of liquid sodium), and the equation relating the activity of Na_2C_2 to X and X^{sat} . For convenience, the concentration of Na_2C_2 was converted from mole fraction to grams of carbon per 10^6 grams of sodium, denoted by c . The values of c calculated from thermodynamic data are given in Table 1. These values are uncertain by a factor of about 2, if the equation for the solubility of Na_2C_2 is valid from 500 to 1100°K. They are adequately represented (within 16%) by the following equation:

$$\log_{10} c(\text{ppm}) = 6.71 - 5679/T$$

For comparison, the results of two recent studies^{5,6} of the solubility of graphite in liquid sodium, denoted by c_0 (ppm), are given in Table 1. From an inspection of Table 1, it can be seen that the values of c calculated from the thermodynamic data on Na_2C_2 agree remarkably well with the solubility of graphite in liquid sodium obtained by Atomics International⁶ between 500 and 1100°K. The results of Longson and Thorley⁵ are higher by a factor of approximately 5, but the temperature dependence of $\log_{10} c_0$ is nearly the same. It is evident that dissolved Na_2C_2 can be an important species, and is possibly the only species formed when graphite is dissolved in liquid sodium. The results obtained in this work show that the formation of a solution of Na_2C_2 by the reaction of liquid sodium and graphite is thermodynamically possible and can result in the introduction of significant concentrations of carbon in liquid sodium. Likewise dissolved Na_2C_2 at different concentrations can be a product of the equilibration of steels, where the activity of carbon is not 1, with liquid sodium. Therefore, models based on dissolved Na_2C_2 for the transport of carbon in liquid-sodium-cooled reactors should be considered.

A paper⁸ describing this work, prepared jointly by the Chemical Engineering and Chemistry Divisions, includes the following abstract:

The enthalpies of reaction of Na_2C_2 and of NaHC_2 with water were measured, and the standard enthalpies of formation at 298.15 K were determined to be (4.80 ± 0.40) and (23.10 ± 0.27) kcal mol⁻¹, respectively. The heat capacity of Na_2C_2 was measured from 5 to 350 K. The following values were obtained for $\text{Na}_2\text{C}_2(c)$ at 298.15 K: heat capacity at constant pressure: $C_p^\circ(298.15 \text{ K}) = (90.98 \pm 0.27)$ J K⁻¹ mol⁻¹; entropy: $S^\circ(298.15 \text{ K}) = (111.24 \pm 0.33)$ J K⁻¹ mol⁻¹; enthalpy: $[H^\circ(298.15 \text{ K}) - H^\circ(0)] = (17389 \pm 52)$ J mol⁻¹; Gibbs energy divided by temperature: $[G^\circ(298.15 \text{ K}) - H^\circ(0)]/298.15 \text{ K} = -(52.92 \pm 0.16)$ J K⁻¹ mol⁻¹. The standard Gibbs energy of formation, ΔG_f° , of Na_2C_2 at 298.15 K is (5.02 ± 0.41) kcal mol⁻¹. The standard Gibbs energy of formation at higher temperatures was estimated from an extrapolation of the heat capacity curve. The concentration of Na_2C_2 in liquid sodium in equilibrium with graphite was calculated from ΔG_f° and the solubility of Na_2C_2 in liquid sodium, and a comparison was made with experimental values for the solubility of graphite in liquid sodium. The comparison indicates that dissolved Na_2C_2 can be an important species, and is possibly the only species formed when graphite is dissolved in liquid sodium. It is concluded that models

based on dissolved Na_2C_2 for the transport of carbon in liquid-sodium-cooled reactors are thermodynamically possible.

II. MONOCESIUM ACETYLIDE, CsHC_2 (M. Ader)

Determination of the enthalpy of formation of monocationic acetylide, $\Delta H_f^\circ(\text{CsHC}_2, c, 298^\circ\text{K})$, was undertaken as a byproduct of our interest in fission-product carbides, which, in turn, stems from the long-range potential of carbide-fueled fast breeder reactors. Initially, it was hoped that the enthalpies of formation of CsHC_2 and Cs_2C_2 could both be determined as had previously been done for the analogous sodium compounds NaHC_2 and Na_2C_2 (see previous section, this report). However, the vendor supplying us with these acetylides was unable to prepare Cs_2C_2 . A preliminary discussion of the determination of the enthalpy of formation of monocationic acetylide was presented earlier (ANL-7821, p. 8). The final report⁹ has been prepared and contains the following abstract:

Calorimetric measurements of the enthalpy of reaction of monocationic acetylide with water were combined with auxiliary thermochemical data to derive the standard enthalpy of formation $\Delta H_f^\circ(\text{CsHC}_2, c, 298.15 \text{ K}) = (18.84 \pm 0.27) \text{ kcal mol}^{-1}$.

III. DICESIUM MONOXIDE (J. L. Settle, G. K. Johnson)

Postirradiation studies of urania-plutonia fuel pins have revealed high concentrations of fission-product cesium and molybdenum in the region of the oxide fuel adjacent to the fuel-cladding interface.¹⁰ These observations suggest that the formation of cesium and molybdenum oxides and of cesium molybdate (and presumably of rubidium oxides and rubidium molybdate) are important factors in the determination of the oxygen chemical potential in the interface region. Therefore, these fission-product oxides can be expected to play a significant role in the chemical interactions between the irradiated fuel and its cladding. To make reasonably accurate predictions of the influence these fission product oxides have on fuel properties, it is necessary to have data on their thermodynamic properties.

No thermodynamic data have been reported for Cs_2MoO_4 or Rb_2MoO_4 . Standard enthalpies of formation have been reported for Cs_2O ,^{11,12} Cs_2O_2 ,¹³ CsO_2 ,^{13,14} Rb_2O ,¹¹ Rb_2O_2 ,^{13,14} and RbO_2 .^{13,14} Coughlin¹⁵ has estimated the uncertainties in the enthalpies of formation of these alkali metal oxides to be 5, 15, 10, 4, 10, and 15 kcal mol^{-1} , respectively. The enthalpies of formation of Cs_2O reported by Rengade¹¹ and Beketoff¹² differ by more than 10 kcal mol^{-1} . Also, recent work by Morris¹⁷ on the enthalpies of dissociation of Cs_2O_2 and CsO_2 and by Petrocelli¹⁸ on the enthalpies of dissociation of Rb_2O_2 and RbO_2 has indicated that there are large systematic errors in the results of Tzentvershver and Blumenthal¹³ (which were also on the enthalpies of dissociation of the peroxides and superoxides). De Forcrand¹⁴ derived the enthalpy of formation of CsO_2 from his measurement of its enthalpy of solution in aqueous H_2SO_4 . Combination of the

enthalpy of formation of Cs_2O ^{11,12} with the enthalpies of dissociation of Cs_2O_2 and CsO_2 ^{13,17} also yields the enthalpy of formation of CsO_2 . However, the values so obtained are not compatible with de Forcrand's value.

The first effort we made to improve the reliability of the thermodynamic properties of these systems was to prepare and characterize a sample of Cs_2O and to measure its enthalpy of solution in water.

The Cs_2O was prepared by incomplete oxidation of high-purity cesium followed by vacuum distillation at temperatures up to 320°C to remove the excess cesium. It was necessary to handle the sample in a helium-atmosphere (H_2O , 1-2 ppm; O_2 , 1 ppm) glovebox; previous experiments have shown that Cs_2O acts as a getter for water and oxygen, even when they are present in helium at these low concentration levels. Accordingly, the length of time of exposure of the sample to the glovebox atmosphere was recorded, and chemical analyses were performed at various times to determine the rate of formation of CsOH and Cs_2O_2 impurities. The results of the chemical analyses are given in Table 2 as a function of time. The cesium content is taken by difference. Because, within the limits of experimental error, the initial oxygen content, 5.7%, is equal to the expected 5.677% for Cs_2O , and because the preparation initially had no detectable peroxide oxygen or hydroxide oxygen, it is assumed that its composition, when exposed to the glovebox atmosphere, was >99.9% Cs_2O . It has previously been demonstrated that the rate of increase of hydroxide content was linear with respect to time, and it was assumed that the increase of peroxide content was also linear. Therefore, the hydroxide and peroxide contents of the bulk sample could be estimated at any time between the two sets of analyses. The X-ray diffraction pattern of the sample was in excellent agreement with the pattern for Cs_2O reported by Tsai, Harris, and Lassettre.¹⁹

The results of the measurements of the enthalpy of solution of Cs_2O in water are given in Table 3. The measurements were done in an LKB Model 8700 Precision Calorimetric System. The Pyrex reaction vessel of the calorimeter has been modified by the addition of a re-entrant well to accommodate the probe of a quartz-crystal thermometer used to measure temperature changes in the calorimeter.

The Cs_2O samples were contained in thin-walled Pyrex bulbs. The filling holes of the bulbs were sealed with silicone rubber stoppers over which was painted a thin layer of wax. The solvent was ~0.01M CsOH solution instead of pure water, so that any CO_2 dissolved in the solution was neutralized before the enthalpy of solution of Cs_2O was measured. The energy equivalent of the calorimeter, $c(\text{calor})$, was determined electrically before and after each enthalpy-of-solution measurement. In Table 3, ΔT^c is the temperature change of the calorimeter corrected for energy exchanged between the calorimeter and its surroundings; ΔH_{vap} is the enthalpy of vaporization of sufficient water to saturate the volume of the ampoule not occupied by the Cs_2O before its dissolution (about 0.9 ml); ΔH_{dil} is the sum of the enthalpy of dilution of the initial solution from $\text{CsOH} \cdot 1500 \text{ H}_2\text{O}$ to $\text{CsOH} \cdot 5560 \text{ H}_2\text{O}$ and the enthalpy of dilution of the final solution to $\text{CsOH} \cdot 1500 \text{ H}_2\text{O}$; ²⁰ $\Delta H_{\text{Cs}_2\text{O}_2}$ is the enthalpy of solution

TABLE 2. Chemical Analysis of Cs_2O Sample^a

CO_3^{2-} content:	negligibly small, $<<0.01\%$
Free Cs:	negligibly small, $<0.01\%$
Total O:	initially 5.7%, increasing to 5.8% in 10 hr
Hydroxide H:	initially none, increasing to 0.00126% in 10 hr
Trace impurities:	17 ppm total, of which the largest were Al (6 ppm), Na (3 ppm), Si (2 ppm), and Rb (2 ppm)
Oxygen as peroxide:	initially none, increasing to 0.16% in 10 hr
Total Cs (by difference):	initially 94.3%, decreasing to 94.2% after 10 hr

Tentative Composition of Sample, %

	<u>Initial</u>	<u>After 10 hr</u>
Cs_2O	>99.9	98.2 ₈
Cs_2O_2	<0.1	1.5 ₃
CsOH	$<<0.1$	0.1 ₉

^aValues given in weight percent and weight parts per million.

TABLE 3. Enthalpy of Solution of Cs_2O in Water^a

m sample, g	0.35321	0.37631	0.38279	0.41090	0.36679	0.37191
m ⁱ Cs_2O_2 , g	0.00118	0.00166	0.00189	0.00374	0.00339	0.00378
m ⁱ CsOH , g	0.00012	0.00019	0.00021	0.00044	0.00039	0.00044
m ⁱ Cs_2O , g	0.35191	0.37446	0.38069	0.40672	0.36301	0.36769
nCs in sample, mol	0.002506	0.002670	0.002716	0.002915	0.002601	0.002638
n ⁱ Cs^+ in soln, mol	0.000998	0.000998	0.000998	0.000998	0.000998	0.000998
n ⁱ H_2O , mol	5.55091	5.55091	5.55091	5.55091	5.55091	5.55091
n ^f Cs^+ in soln, mol	0.003505	0.003668	0.003714	0.003913	0.003600	0.003636
n ^f H_2O , mol	5.54955	5.54947	5.54945	5.54934	5.54959	5.54948
n in $\text{CsOH} \cdot n\text{H}_2\text{O}$ (final soln)	1583.6	1512.8	1494.1	1418.2	1541.5	1526.1
ϵ^{ave} (calor), cal deg ⁻¹	106.598	106.632	106.674	106.744	106.695	106.616
ΔT , deg	0.96624	1.02676	1.04141	1.12401	0.99289	1.00860
ϵ^{ave} (calor)($-\Delta T_c$), cal	-102.999	-109.485	-111.091	-118.981	-105.936	-107.533
ΔH_{vap} , cal	-0.012	-0.012	-0.012	-0.012	-0.012	-0.012
ΔH_{dil} , cal	-0.015	-0.023	-0.026	-0.038	-0.020	-0.022
$\Delta H_{\text{Cs}_2\text{O}_2}$, cal	+0.199	+0.281	+0.319	+0.632	+0.573	+0.639
ΔH_{CsOH} , cal	+0.014	+0.022	+0.024	+0.050	+0.044	+0.050
n ⁱ ΔH , cal	-102.813	-109.217	-110.786	-118.349	-105.351	-106.878
n ⁱ $\Delta H/m^i$, cal g ⁻¹	-292.16	-291.67	-291.01	-290.98	-290.22	-290.67

Mean = -291.12 cal g⁻¹Standard deviation of the mean = ± 0.28 cal g⁻¹

^a m and n denote mass and moles, respectively. Superscripts ⁱ, ^f, and ^{ave} denote Cs_2O , Cs_2O_2 , and CsOH , respectively. Superscripts i and f denote the initial and final solutions, respectively.

of the Cs_2O_2 impurity in the samples; and ΔH_{CsOH} is the enthalpy of solution of the CsOH impurity in the samples. The enthalpy of solution of Cs_2O , $-(82.04 \pm 0.08) \text{ kcal mol}^{-1}$, refers to the idealized reaction

The enthalpy of formation of Cs_2O is obtained by combining Reaction 1 with

where $\Delta H_f^\circ(\text{Cs}_2\text{O}, \text{c}) = \Delta H(4) = \Delta H(2) + \Delta H(3) - \Delta H(1) = 2(-48.309 \pm 0.01)^{20} - (68.315 \pm 0.010)^{21} + (82.041 \pm 0.18) = -(82.52 \pm 0.18) \text{ kcal mol}^{-1}$. The uncertainty attached to $\Delta H(4)$ is the uncertainty interval equal to twice the combined errors from all known sources.

The value of $\Delta H_f^\circ(\text{Cs}_2\text{O}, \text{c}) = -(82.52 \pm 0.18) \text{ kcal mol}^{-1}$ derived in this investigation is in excellent agreement with Rengade's¹¹ value of $-82.7 \text{ kcal mol}^{-1}$. We estimate the uncertainty in Rengade's investigation to be 1 kcal mol^{-1} .

Combination of $\Delta H_f^\circ(\text{Cs}_2\text{O}, \text{c})$ with

for which Morris¹⁷ derived $\Delta H(5) = 9.16 \text{ kcal mol}^{-1}$ at 320°C , yields $\Delta H_f^\circ(\text{Cs}_2\text{O}_2, \text{c}) = -91.7 \text{ kcal mol}^{-1}$. Similarly, combination of $\Delta H_f^\circ(\text{Cs}_2\text{O}_2, \text{c}) = -91.7 \text{ kcal mol}^{-1}$ with

for which Morris¹⁷ derived $\Delta H(6) = 9.591 \text{ kcal mol}^{-1}$ at 320°C , yields $\Delta H_f^\circ(\text{CsO}_2, \text{c}) = -55.4 \text{ kcal mol}^{-1}$. In calculating the enthalpies of formation of Cs_2O_2 and CsO_2 , ΔC_p for Reactions 5 and 6 were assumed to be the same at 25°C as they are at 320°C .

Table 4 compares the available values for the enthalpies of formation of Cs_2O , Cs_2O_2 , and CsO_2 . It is apparent that Cs_2O is the only one of these compounds for which a reliable enthalpy of formation is available. Additional, preferably calorimetric, experiments need to be performed in order to obtain reliable enthalpy-of-formation values for Cs_2O_2 and CsO_2 .

A portion of the Cs_2O sample was given to H. Flotow and D. Osborne (both of the ANL Chemistry Division) so that its low-temperature heat capacity and absolute entropy can be determined.

TABLE 4. Comparison of Available Values of ΔH_f° (in kcal mol⁻¹) for Cs₂O, Cs₂O₂, and CsO₂

Source	Cs ₂ O	Cs ₂ O ₂	CsO ₂
Rengade ^a	-82.7	-	-
Beketoff ^b	-92.6	-	-
de Forcrand ^c	-	-	-81.8
Tzentvershver and Blumenthal ^d	-	-120.5	-70.5
Coughlin ^e	-76 ± 5	-96 ± 15	-62 ± 10
Morris	-	-91.7 ^f	-55.4 ^f
This work	-82.52 ± 0.18	-	-

^aFrom Ref. 11.

^bFrom Ref. 12.

^cFrom Ref. 14.

^dFrom Ref. 13.

^eFrom Ref. 16.

^fEstimated by combining the data in Ref. 17 with $\Delta H_f^\circ(\text{Cs}_2\text{O}, \text{c}) = -(82.52 \pm 0.18) \text{ kcal mol}^{-1}$.

IV. THORIUM MONOSULFIDE, ThS (M. Ader)

As part of our effort to obtain basic thermodynamic information on actinide compounds, we determined the standard enthalpy of formation of thorium monosulfide by solution calorimetry. A preliminary value was given in the preceding report (ANL-7876, p. 21).

The overall scheme to derive ΔH_f° involved measurement of the enthalpy of reaction of the monosulfide powder specimen with 6M HCl, and combination of this enthalpy with auxiliary thermochemical data. After examining the pertinent thermochemical and analytical data, it became evident that the reliability of the derived ΔH_f° would be largely limited by the uncertainty surrounding the composition of the specimen, particularly with respect to the presence of minor phases containing thorium and sulfur.

Additional experimentation on this matter has now been completed. This was part of a cooperative study with the Chemistry Division of the thermodynamic properties of ThS. The sample was prepared by R. R. Walters, low-temperature C° and S° measurements were made by D. W. Osborne and H. E. Flotow, and high-temperature vaporization measurements are planned by R. J. Thorn (Walters, Osborne, Flotow, and Thorn are of the ANL Chemistry Div.).

Identification of thorium sesquisulfide as an impurity in the calorimetric specimen was reported by Flotow and coworkers,²² who had used the same specimen for low-temperature heat-capacity studies. By microscopy (ANL-7876), we had learned that the major phase, cubic thorium monosulfide, contained anisotropic inclusions, presumably orthorhombic Th_2S_3 , at a concentration roughly estimated by areal analysis to be 4 vol %. All these pieces of information, however, needed verification. Our observations had been made with a crudely prepared Polylite mount lacking in detail; the mount had been hand polished in a helium-atmosphere glovebox to avoid exposure to moisture. Subsequently, it was found that specimen mounts could be mechanically polished in air, even under water, with no apparent effect on the microstructure. Metallographic inspection of such mounts revealed further interesting details about the specimen.

Polylite mounts of the powdered specimen, highly polished with diamond paste (to 1 μm), were rinsed clean, air-dried, and examined without further treatment. The anisotropic inclusions, which were seen with difficulty in the earlier examination, were clearly visible at all magnifications as brown areas enveloped by the lustrous gold matrix of the monosulfide phase. The rounded edges of the brown inclusions indicated formation from the liquid state. At magnifications of 391 $\times$ to 984 $\times$, light-blue prisms occupying roughly 10% of the brown area were visible. Also, at 984 $\times$, tiny needles (possibly the 1.47 wt % ThOS previously found by chemical analysis) could be discriminated against the gold background of the monosulfide phase.

Electron-microprobe analysis of the various phases gave the following S/Th ratios: gold (monosulfide) = 1.06; brown (sesquisulfide) = 1.49, 1.44, 1.41; blue prisms (?) = 1.66. The accuracy of these ratios is probably about ± 0.1 . These results confirm the earlier assumption that the anisotropic (brown) inclusions were thorium sesquisulfide. The blue prisms within the sesquisulfide have a significantly higher S/Th ratio but are not identified. A stable compound, Th_7S_{12} , with S/Th = 1.71 is known.

To calculate the S/Th ratio of the monosulfide phase* and to make thermal corrections, the brown phase and blue prisms within it were considered to be a composite phase with an average S/Th ratio of 1.5 and with the properties of Th_2S_3 . The concentration of this composite phase was computed by estimating monosulfide and sesquisulfide areas of 325 particles of the specimen. The areal percent, which is proportional²³ to volume percent, was $4.55 \pm 0.50^\dagger$ or slightly higher than the earlier estimate. This was converted to $3.77 \pm 0.46^\dagger$ wt % Th_2S_3 , using the X-ray densities²⁴ $\text{Th}_2\text{S}_3 = 7.87 \text{ g ml}^{-1}$ and $\text{ThS} = 9.56 \text{ g ml}^{-1}$. The S/Th ratio of the thorium monosulfide phase was computed by adjusting the chemical analysis²² of the specimen, S/Th = 1.043 ± 0.005 ,[†] for the presence of (a) 3.77 wt % Th_2S_3 and 1.47 wt % ThOS , as separate phases, and (b) 88 ppm carbon²² and 15 ppm nitrogen²² as replacements for sulfur in the monosulfide lattice. The composition thus derived was $\text{ThS}_{1.029 \pm 0.019}$,[§] or on a gram-atomic basis, $\text{Th}_{0.493 \pm 0.005}\text{S}_{0.507 \pm 0.005}$. Corrections for the presence of metallic impurities were judged to be negligible from the results of a spark-source mass spectrographic analysis of the specimen.

The enthalpy of the calorimetrically measured reaction, $\text{ThS}_{1.029}(\text{c}) + (1200 \text{ HCl} \cdot 9776 \text{ H}_2\text{O}) = (\text{ThCl}_4 \cdot 1196 \text{ HCl} \cdot 9776 \text{ H}_2\text{O} \cdot 1.029 \text{ H}_2\text{S}) + 0.971 \text{ H}_2(\text{g})$, with all corrections applied is $-94.2 \pm 0.4^\S \text{ kcal mol}^{-1}$. By combining this result with auxiliary data, including ΔH_{soln} of thorium in 6M HCl and $\Delta H_f(\text{H}_2\text{S}, \text{aq})$, we obtain $\Delta H_f^\circ(\text{ThS}_{1.029 \pm 0.019}, \text{c}, 298.15^\circ\text{K}) = -96.9 \pm 0.9^\S \text{ kcal mol}^{-1}$. This value, on the gram-atomic basis, $\Delta H_f^\circ(\text{Th}_{0.493}\text{S}_{0.507}) = -47.7 \text{ kcal mol}^{-1}$, can be compared with the similarly expressed value for Th_2S_3 , $\Delta H_f^\circ(\text{Th}_{0.4}\text{S}_{0.6}) = -51.7 \text{ kcal mol}^{-1}$,²⁵

V. TRIURANIUM SILICIDE, U_3Si (W. N. Hubbard)

U_3Si has a number of attractive features as a nuclear fuel among which are high density (15.58 g cm^{-3}), high uranium content (approximately 96.2%), and high thermal conductivity ($0.036 \text{ cal sec}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$ at room temperature). Considerable research on U_3Si has been and still is being carried out at Atomic Energy of Canada, Chalk River, Ontario. For some time, U_3Si has also been included in our program to elucidate the thermochemistry of uranium compounds. This mutual interest has led to a cooperative effort between I. J. Hastings of Atomic Energy of Canada and our laboratory to prepare and characterize a good sample of U_3Si at Chalk River and to measure its thermodynamic properties at Argonne. D. W. Osborne and H. E. Flotow of the Argonne Chemistry Division will determine heat capacities and entropies by low-temperature calorimetry. Enthalpy of formation determination by fluorine bomb combustion calorimetry and determination of high-temperature thermodynamic functions by drop calorimetry will be carried out in this laboratory.

*The supposition that thorium monosulfide exists over a range of composition is consistent with its variation in lattice parameter, depending on whether it is in equilibrium with Th or Th_2S_3 .

[†]Standard deviation.

[§]Uncertainty interval.

Several years ago, attempts here to prepare a sample of U_3Si for enthalpy-of-formation measurements were not successful. Consequently, the cooperation and experience of Atomic Energy of Canada were most welcome. A specimen of U_3Si was chosen by Hastings for exploratory combustion studies. Nine 2-in.-long rods were cut from this specimen and sent to us for study; three rods were cut from each of three cross sections, 1/8 by 1/8, 1/16 by 1/16, and 1/32 by 1/32 in.

Exploratory combustions were carried out with variations in (1) the mass of sample (1.5 to 3.2 grams), (2) the physical condition of the rod (a solid piece, several pieces of rod, many fragments, etc.), (3) use or not of an auxiliary substance, molybdenum foil, to promote completeness of fluorination of uranium to UF_6 , and (4) fluorine pressure (5 to 10 atm). The tentative conclusions reached were that satisfactory combustions could be obtained with (1) a mass of 2 g of U_3Si , (2) pieces of fractured 1/16 by 1/16-in. rod (of the order of 0.1 g each), (3) with ~0.5 g of 3-mil corrugated sheet molybdenum as an auxiliary substance, and (4) 10-atm fluorine pressure. Possibly larger samples can be burned if the pieces are adequately dispersed. When the sample was in the form of one or several solid pieces of rod, apparently there resulted too much concentration of heat with subsequent melting of the support crucible. When the auxiliary material, molybdenum sheet, was not used, lower fluorides of uranium were formed where the sample was in contact with the crucible. When lower pressures of fluorine were used, there was evidence of incomplete fluorination of both the molybdenum fuse wire and of the uranium.

Fluorination tests indicated that some spontaneous fluorination occurs on exposure of the sample to fluorine. Consequently, for the calorimetric studies, it will be necessary to use a two-compartment calorimetric bomb, in which it is possible to prevent fluorination of the sample until ignition is desired.

VI. PERBROMYL FLUORIDE, BrO_3F (G. K. Johnson, P. A. G. O'Hare)

The synthesis of perbromic acid and the alkali perbromates^{26,27} led to the preparation of perbromyl fluoride, BrO_3F ,²⁸ which is the acid fluoride of perbromic acid. Inasmuch as the perbromates were thought until quite recently to be nonexistent, the thermodynamic properties of these compounds and their derivatives are of fundamental interest. A preliminary discussion of the calorimetric study of BrO_3F was given in the preceding report in this series. Since then, a paper describing the work has been published.²⁹ The abstract of the paper is as follows:

Calorimetric measurements of the enthalpy of hydrolysis of BrO_3F to HF and $HBrO_4$ are reported. From these experiments the enthalpy of formation ($\Delta H_f^\circ_{298.15}$) of $BrO_3F(l)$ was deduced to be 26.78 ± 0.25 kcal mol⁻¹. Between 188 and 292°K, the vapor pressure of BrO_3F is given by $\ln p = 17.6986 - 3048.45 T^{-1}$, where p is in Torr. This equation leads to an enthalpy of vaporization, ΔH°_{vap} , of 6.06 ± 0.06 kcal mol⁻¹. Thus, $\Delta H_f^\circ_{298.15}(BrO_3F, g) = 32.84 \pm 0.26$ kcal mol⁻¹. By means of statistical mechanics, the

standard entropy of the ideal gas, $S^\circ_{298.15}(\text{BrO}_3\text{F}, \text{g})$, has been calculated as $71.4 \pm 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$.

VII. THE XENON FLUORIDES, XeF_6 , XeF_4 , and XeF_2 (G. K. Johnson)

The details of the determinations of the enthalpies of formation of XeF_6 , XeF_4 , and XeF_2 , from measurements of their energies of reaction with PF_3 , have been given in previous semiannual reports.^{30,31} A paper describing this work has been prepared for publication.³² The abstract of the paper is as follows:

The energies of reaction of $\text{XeF}_6(\text{c})$, $\text{XeF}_4(\text{c})$, and $\text{XeF}_2(\text{c})$ with $\text{PF}_3(\text{g})$ were measured in a bomb calorimeter. These results were combined with the enthalpy of fluorination of $\text{PF}_3(\text{g})$, which was redetermined to be $-(151.98 \pm 0.07) \text{ kcal mol}^{-1}$, to derive (at 298.15 K) $\Delta H^\circ_f(\text{XeF}_6, \text{c}, \text{I}) = -(80.82 \pm 0.53) \text{ kcal mol}^{-1}$, $\Delta H^\circ_f(\text{XeF}_4, \text{c}) = -(63.84 \pm 0.21) \text{ kcal mol}^{-1}$, and $\Delta H^\circ_f(\text{XeF}_2, \text{c}) = -(38.90 \pm 0.21) \text{ kcal mol}^{-1}$. The enthalpies of formation of the solid xenon fluorides were combined with reported enthalpies of sublimation to derive (at 298.15 K) $\Delta H^\circ_f(\text{XeF}_6, \text{g}) = -(66.69 \pm 0.61) \text{ kcal mol}^{-1}$, $\Delta H^\circ_f(\text{XeF}_4, \text{g}) = -(49.28 \pm 0.22) \text{ kcal mol}^{-1}$, and $\Delta H^\circ_f(\text{XeF}_2, \text{g}) = -(25.58 \pm 0.21) \text{ kcal mol}^{-1}$. The average bond dissociation enthalpies, $\bar{D}^\circ(\text{Xe-F}, 298.15 \text{ K})$, are (29.94 ± 0.16) , (31.15 ± 0.13) , and $31.62 \pm 0.16) \text{ kcal mol}^{-1}$ in $\text{XeF}_6(\text{g})$, $\text{XeF}_4(\text{g})$, and $\text{XeF}_2(\text{g})$, respectively. The enthalpy of formation of $\text{PF}_3(\text{g})$ was determined to be $-(228.8 \pm 0.3) \text{ kcal mol}^{-1}$.

VIII. REFRACTORY CARBIDES (W. N. Hubbard, G. K. Johnson)

Just as the thermodynamic properties of refractory oxides are basic data needed for the understanding of the chemistry of oxide fuel-fission product systems, so are the thermodynamic properties of refractory carbides for carbide fuel-fission product systems. The determination of some needed enthalpy-of-formation data was begun in this laboratory within the past few years with measurements of the enthalpies of formation of PuC^{33} and Pu_2C_3 .³⁴ Our interest in carbides was also manifested in the studies of the sodium and cesium acetylides (see Sections I and II, this report). Because a large amount of work has been done on the carbides at Los Alamos Scientific Laboratory, our studies were coordinated with their efforts. For example, the sample of Pu_2C_3 which we used for enthalpy-of-formation measurements (ANL-7775, p. 79) was prepared at Los Alamos. E. J. Huber and C. E. Holley at Los Alamos have long been involved in enthalpy of formation measurements of carbides. They have made extensive measurements in the uranium-carbon system. They have measured the enthalpy of formation of NpC and plan to study Np_2C_3 . They plan to measure the enthalpies of formation for any rare earth carbides for which they can obtain samples. They have already worked on CeC_2 and Ce_2C_3 , are working on Gd_3C , Gd_2C_3 , and GdC_2 , and have done some work on the carbides of holmium. E. K. Storms of Los Alamos has exhaustively studied the

vaporization behavior of the transition metal carbides of groups 4, 5, and 6 and is author of the authoritative book "The Refractory Carbides."³⁵ He has cooperated with Huber and Holley in preparing pure samples for their study in the zirconium-carbon and niobium-carbon systems. Enthalpy-of-formation data are still needed for the molybdenum-carbon system. Because Huber and Holley are not able to work such measurements into their schedule and because of our interest in the fission-product carbides, a collaborative effort has been undertaken between Storms and ourselves to obtain the required data. The effort will also include needed enthalpy-of-formation data for about four compounds in the vanadium-carbon system.

A. Carbides of Molybdenum

The only literature data for carbides of molybdenum were determined by oxygen bomb calorimetry by A. D. Mah³⁶ in 1963 for Mo_2C and "MoC." Storms, in his book,³⁵ has this to say concerning the uncertainty in the data:

"However, the 'MoC' sample, for which analysis gave $\text{MoC}_{0.66}$, was assumed to be a mixture of MoC and Mo_2C . Since the high-carbon carbide actually has a stoichiometry of $\text{MoC}_{0.67}$, the material was no doubt a mixture of mainly MoC_{1-x} and free carbon. Whatever Mo_2C was present must have resulted from the decomposition of MoC_{1-x} into Mo_2C and carbon upon cooling. Therefore, the uncertainty for this value is a good deal larger than indicated."

Samples of two carbides of molybdenum, one of the high-carbon carbide $\text{MoC}_{0.663}$ and the other $\text{MoC}_{0.586}$ (a mixture of Mo_2C and Mo_3C_2), were prepared by Storms and sent to us for exploratory combustions in fluorine. In the exploratory combustions, conditions were found in which no lower fluorides of molybdenum were observed except an occasional blue dot at the point of contact of the molybdenum ignition wire with one of its electrical terminals.

Combustions carried out previously in fluorine of several forms of both carbon and silicon carbide always yielded small amounts of C_2F_6 and C_3F_8 for which thermal corrections had to be made to refer the reaction to CF_4 , the main product. The analyses of the products were carried out commercially. However, for the present investigation it may be possible to use gas chromatographic analysis equipment available here. The results of some exploratory work indicate that the retention times of CF_4 , C_2F_6 , and C_3F_8 on the column can be resolved in the existing equipment and that molybdenum hexafluoride does not interfere. Calibration runs indicate that the amounts of the heavier fluorocarbons formed are of the order of magnitude of 0.1% of the amount of CF_4 , and consequently only of borderline significance.

Two samples of carbides of molybdenum have already been prepared by Storms at Los Alamos. One has been received here and measurements should be started on it in the near future. This sample is single-phase $\alpha\text{-Mo}_2\text{C}$ and contains less than 5 ppm oxygen, the limit of detection. More complete analysis is being obtained. The other is a sample of Mo_3C_2 .

B. Carbides of Vanadium

Accurate oxygen bomb calorimetric measurements on vanadium compounds are especially difficult to make. Not only has incomplete combustion been frequent, but the form of the resulting oxides is uncertain. Literature values vary about 20 kcal mol⁻¹. Fluorine bomb calorimetry has not been used to date, although an isolated experiment or two with vanadium metal was carried out very early in the development of the technique. Because of the need for enthalpy-of-formation data for the carbides of vanadium and the experience of this laboratory in fluorine bomb calorimetry, some exploratory experiments were initiated.

Samples of two carbides of vanadium, one of VC_{0.79} and the other of VC_{0.726}, remaining from high temperature vaporization behavior studies, were sent to use for exploratory combustions in fluorine. Initial combustions have been very encouraging. The vanadium product of combustion is VF₅, a hygroscopic, volatile, and corrosive liquid. However, after pumping out the bomb no lower fluorides were found. Lower fluorides would be nonvolatile.

An auxiliary measurement for the fluorine bomb calorimetry of vanadium carbides is the combustion of vanadium itself in fluorine. A trial combustion of vanadium foil also led to volatile products with only a trace--two very thin spots--of a white powder being formed. It appears as though the determination of the enthalpy of formation of the carbides of vanadium by fluorine bomb calorimetry will not be unusually complicated.

A sample of high-purity vanadium metal and several carbides of vanadium are being prepared by Storms.

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