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CHEMICAL ENGINEERING DIVISION

THERMOCHEMICAL STUDIES

SEMIANNUAL REPORT

July-December 1972

W. N. Hubbard, P. A. G. O'Hare,

G. K. Johnson, M. Ader,

and R. C. Vogel

CONFIDENTIAL NATIONAL BUREAU OF STANDARDS, ALCOHOL, F. HANCOCK

REPORT FOR THE U.S. NATIONAL BUREAU OF STANDARDS

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ABSTRACT

Standard enthalpies of formation at 298°K have been determined (most values are of a preliminary nature) as follows. Values for cesium and rubidium molybdate were determined by solution calorimetry to be $\Delta H_f^\circ(\text{Cs}_2\text{MoO}_4, c) = -362.00 \pm 0.11$, and $\Delta H_f^\circ(\text{Rb}_2\text{MoO}_4, c) = \sim -356 \text{ kcal mol}^{-1}$. These compounds are important in studies of the interactions between oxide fuels and their fission products. Similar determinations made for $\alpha\text{-Na}_2\text{UO}_4$ and NaUO_3 , both of which compounds are of interest in LMFBR fuel-coolant studies, gave $\Delta H_f^\circ(\text{Na}_2\text{UO}_4, \alpha) = \sim -445.5 \pm 0.9$ and $\Delta H_f^\circ(\text{NaUO}_3, c) = \sim -374 \text{ kcal mol}^{-1}$. Selected enthalpies of formation were determined for the molybdenum and vanadium carbide systems by fluorine bomb calorimetry. These studies have yielded $\Delta H_f^\circ(\text{MoC}_{0.496}, \alpha) = \sim -5.53$ and $\Delta H_f^\circ(\text{MoC}_{0.642}, \alpha) = \sim -3.66 \text{ kcal mol}^{-1}$. Preparatory to making measurements on several carbides of vanadium, the enthalpy of formation of VF_5 was determined; it was found to be $\Delta H_f^\circ(\text{VF}_5, g) = \sim -343.50 \pm 0.21 \text{ kcal mol}^{-1}$. Preparations are being made for fluorine bomb calorimetric measurements on U_3Si , a compound of general interest, and Li_2Se , of interest in the lithium-chalcogen cell development program. Total Hartree-Fock energies of AsF and AsF^+ , computed at the experimental internuclear separation of the parent species, lead to 11.8 eV for the vertical ionization potential of AsF .

SUMMARY

Cs_2MoO_4 and Rb_2MoO_4

Electron microprobe analyses of irradiated urania-plutonia fuel pins have indicated a large concentration of both fission-product cesium and molybdenum in the oxide-cladding interface region of the fuel pin. To make predictions concerning the possible formation of cesium molybdate, it is necessary to have data on the Gibbs energy of formation. As a first step in this direction, the standard enthalpy of formation, $\Delta H_f^\circ(\text{Cs}_2\text{MoO}_4, c)$, has been determined by solution calorimetry to be $-362.00 \pm 0.11 \text{ kcal mol}^{-1}$.

Although rubidium is a less abundant fission product, we have also determined the enthalpy of formation of rubidium molybdate. A preliminary value of $-356 \text{ kcal mol}^{-1}$ was obtained for $\Delta H_f^\circ(\text{Rb}_2\text{MoO}_4, c)$.

α -Na₂UO₄ and NaUO₃

Because of the significant disagreements between published ΔH_f° data for α -Na₂UO₄ and NaUO₃, we have undertaken a study of these compounds. Our preliminary ΔH_f° values are -445.5 ± 0.9 and -374 kcal mol⁻¹ for α -Na₂UO₄ and NaUO₃, respectively.

Refractory Carbides

The thermodynamic properties of refractory carbides are basic data needed for understanding the chemistry of carbide fuel-fission product systems. A collaborative effort has been undertaken with E. K. Storms of Los Alamos Scientific Laboratory to determine the enthalpies of formation of the carbides of molybdenum and vanadium. The experimental work on the determination of the enthalpies of formation of Mo₂C and MoC_{1-x} by fluorine bomb calorimetry has been completed. Preparatory to work on the vanadium carbides, it was necessary to determine the enthalpy of formation of VF₅(g), which is needed to derive the enthalpies of formation of the vanadium carbides. The experimental work on the determination of ΔH_f° (VF₅, g) has been completed.

U₃Si

A cooperative venture has been undertaken between I. J. Hastings of Atomic Energy of Canada and this laboratory to prepare and characterize specimens of U₃Si at Chalk River for thermodynamic studies at Argonne. Specimens have been received for measurements of high-temperature enthalpy increments and heat of combustion in fluorine. The enthalpy increment measurements are complete and preparations are being made for the combustion studies. Specimens for low-temperature measurements of heat capacity and entropy have not been received.

Li₂Se

Calorimetric measurement of the standard enthalpy of formation of Li₂Se has been undertaken because of the current ANL interest in lithium-chalcogen couples for high-energy batteries, as well as the intrinsic scientific value of this datum. The technique selected is fluorine bomb calorimetry. Numerous noncalorimetric experiments have been run to find optimal conditions for the reaction $\text{Li}_2\text{Se}(\text{c}) + 4\text{F}_2(\text{g}) \rightarrow 2\text{LiF}(\text{c}) + \text{SeF}_6(\text{g})$. Successful results have been obtained by adding auxiliary combustion aids to powdered Li₂Se and carrying out the combustions at fluorine pressures greater than 20 atm in a two-compartment bomb. Of several combustion aids tested, graphite felt has proved most suitable.

AsF and AsF⁺

The total Hartree-Fock energies of AsF and AsF⁺, computed at the experimental internuclear separation of the parent molecule, lead to a value of 11.8 eV for the vertical ionization potential of AsF.

I. MOLYBDATES OF CESIUM AND RUBIDIUM (Cs_2MoO_4 and Rb_2MoO_4)
(P. A. G. O'Hare)

Electron microprobe analyses of irradiated urania-plutonia fuel pins have indicated a large concentration of both fission-product cesium and molybdenum in the oxide-cladding interface region of the fuel pin.¹ To make predictions concerning the possible formation of cesium molybdate, it is necessary to have data on the Gibbs energy of formation. As a first step in this direction, the standard enthalpy of formation, $\Delta H_f^\circ(\text{Cs}_2\text{MoO}_4, \text{c})$, has been determined by solution calorimetry. Although rubidium is a less abundant fission product, we have also determined $\Delta H_f^\circ(\text{Rb}_2\text{MoO}_4, \text{c})$. Thus, thermochemical data are now available for all the known solid alkali metal molybdates with the exception of Li_2MoO_4 .

The component reactions of the thermochemical cycle from which we have derived $\Delta H_f^\circ(\text{Cs}_2\text{MoO}_4)$ are as follows:

In Reactions 1 to 6, the species are in the aqueous phase except as otherwise designated.

In our experiments, we measured the enthalpy of solution (ΔH_1) of MoO_3 in aqueous CsOH to be $-18.646 \pm 0.032 \text{ kcal mol}^{-1}$, and the enthalpy of solution of $\text{Cs}_2\text{MoO}_4(\text{c})$ in aqueous CsOH , $-\Delta H_2$, to be $0.530 \pm 0.015 \text{ kcal mol}^{-1}$ (Tables 1 and 2). These data were obtained in an LKB-8700 solution calorimeter. Thermochemical values for Reactions 3 to 6 were obtained from the literature. Thus, $\Delta H_3 = 0.028 \pm 0.015$,^{2,3} $\Delta H_4 = -96.458 \pm 0.022$,² $\Delta H_5 = -68.315 \pm 0.010$,⁴ and $\Delta H_6 = -178.08 \pm 0.15 \text{ kcal mol}^{-1}$. Summation of ΔH_1 through ΔH_6 yields $-362.00 \pm 0.11 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ(\text{Cs}_2\text{MoO}_4, \text{c})$.

Heat capacity measurements on Cs_2MoO_4 are also planned at both high and low temperatures. In this way, the Gibbs energy of formation and, thus, the thermodynamic stability of Cs_2MoO_4 will be known over a wide temperature range.

Similar solution calorimetric measurements on Rb_2MoO_4 have yielded a preliminary value of approximately $-356 \text{ kcal mol}^{-1}$ for ΔH_f° .

Table 1. Calorimetric Data for the Reaction between $\text{MoO}_3(\text{c})$ and $\text{CsOH}(\text{aq})^{\text{a}}$

Expt. No.	1	2	3 ^b	4	5	6	7	8
$m(\text{MoO}_3)$, g	0.29523	0.30015	0.31531	0.30054	0.31470	0.30954	0.30683	0.30198
$\Delta\theta_{\text{c}}$, °K	0.36179	0.36886	0.39183	0.37326	0.38982	0.38461	0.37995	0.37597
$\bar{e}(\text{calor})$, J °K ⁻¹	441.400	440.949	436.573	436.852	436.504	436.552	436.018	436.699
$\bar{e}(\text{calor}) \times (-\Delta\theta_{\text{c}})$, J	-159.694	-162.648	-171.062	-163.059	-170.158	-167.902	-165.665	-164.186
ΔH_{vap} , J	-0.053	-0.053	-0.052	-0.053	-0.052	-0.052	-0.052	-0.053
$\Delta H/\text{M}$, J g ⁻¹	-541.09	-542.07	-542.68	-542.73	-540.86	-542.59	-540.09	-543.87
Mean $\Delta H/\text{M} = -542.00 \pm 0.44^{\text{c}}$ J g ⁻¹ ($-129.54 \pm 0.11^{\text{c}}$ cal g ⁻¹)								
$\Delta H_1 = -18,645.8 \pm 31.6^{\text{d}}$ cal mol ⁻¹								

^aThe symbols used in this table have the following significance: $\Delta\theta_{\text{c}}$ is the corrected temperature rise; $\bar{e}(\text{calor})$ is the mean energy equivalent of the calorimetric system based on electrical calibrations before and after each experiment; ΔH_{vap} is the correction for evaporation of water into the free space of the ampoule and is based on values of 10,519 cal mol⁻¹ and 4.709 g ml⁻¹ for the enthalpy of vaporization of water and density of MoO_3 , respectively; $\Delta H/\text{M}$ is the enthalpy of reaction per gram of MoO_3 ; ΔH_1 is based on a molecular weight of 143.9382 for MoO_3 .

^bA new calorimeter vessel was used for the experiments after Experiment No. 2.

^cStandard deviation of the mean.

^dTwice the standard deviation of the mean.

Table 2. Calorimetric Data for Reaction between $\text{Cs}_2\text{MoO}_4(\text{c})$ and $\text{CsOH}(\text{aq})^{\text{a}}$

Expt. No.	1	2	4	5	6	7
$m(\text{Cs}_2\text{MoO}_4)$, g	0.92537	0.92157	0.92462	0.92397	0.92349	0.92370
$\Delta\theta_{\text{c}}$, $^{\circ}\text{K}$	0.00320	-0.00124	0.00045	-0.00007	-0.00048	0.00018
$\bar{E}(\text{calor})$, $\text{J}^{\circ}\text{K}^{-1}$	431.45	431.99	434.96	437.34	438.14	432.22
$\bar{E}(\text{calor}) \times (-\Delta\theta_{\text{c}})$, J	-1.381	0.536	-0.196	0.031	0.210	-0.078
$\Delta H(\text{electrical})$, J	6.403	4.402	4.802	4.802	4.802	4.802
ΔH_{vap} , J	-0.045	-0.045	-0.045	-0.045	-0.045	-0.045
$\Delta H/M$, J g^{-1}	5.378	5.309	4.933	5.182	5.379	5.065

$$\text{Mean } \Delta H/M = 5.208 \pm 0.074^{\text{b}} \text{ J g}^{-1} (1.245 \pm 0.018^{\text{b}} \text{ cal g}^{-1})$$

$$\Delta H_2 = 530.1 \pm 15.3^{\text{c}} \text{ cal mol}^{-1}$$

^aThe symbols have the same significance as those in Table 1; $\Delta H(\text{electrical})$ denotes the electrical energy input to the system during the (endothermal) reaction between Cs_2MoO_4 and $\text{CsOH}(\text{aq})$, and ΔH_{vap} is based on an estimated density of 4.7 g ml^{-1} for Cs_2MoO_4 . Our calculation of ΔH_2 from $\Delta H/M$ is based on a molecular weight of 425.7484 for Cs_2MoO_4 .

^bStandard deviation of the mean.

^cTwice the standard deviation of the mean.

II. SODIUM URANATES ($\alpha\text{-Na}_2\text{UO}_4$ and NaUO_3) (P. A. G. O'Hare)

A recent series of papers⁶⁻⁹ from this laboratory described an extensive investigation of the thermodynamic properties of trisodium uranium (V) oxide, Na_3UO_4 . One of the papers,⁹ based on a mass spectrometric study, reported, in addition to the data for Na_3UO_4 , values for the standard enthalpies of formation, ΔH_f° , of a number of other uranates. Those data did not agree very well with the values reported by Cordfunke and Loopstra,¹⁰ Ippolitova et al.,¹¹ and King et al.¹² from solution calorimetric studies. The various enthalpies of formation for the uranates are collected together in Table 3. Apart from Na_3UO_4 , for which the ΔH_f° values agree rather well, there are significant discrepancies between the various results. Each compound will be discussed separately.

$\alpha\text{-Na}_2\text{UO}_4$. This is the most common sodium uranate. The three results reported for its ΔH_f° differ by rather large amounts. If the error in the value determined by Battles et al.⁹ is doubled, i.e., if the uncertainty is changed to reflect a 95% confidence level (since this data had to be extrapolated over a large temperature range), the mass spectrometric result will almost, but not quite, overlap that of Cordfunke and Loopstra. Ippolitova's value, on the other hand, is in serious disagreement with the other data.

We have obtained a sample of α - Na_2UO_4 from Dr. H. Hoekstra (ANL Chemistry Division). This material, prepared by heating a mixture of Na_2CO_3 and UO_3 , is of acceptable purity for calorimetric experiments. However, the complete analytical data are not yet available.

We have measured calorimetrically the enthalpies of the reactions between (a) Na_2UO_4 and 0.1M-HCl , (b) NaCl and 0.1M-HCl , and (c) $\text{UO}_2\text{Cl}_2(\text{c})$ and the mixture formed in (b). Based on these experiments and the overall reaction

we have obtained a preliminary value of $-445.5 \pm 0.9 \text{ kcal mol}^{-1}$ for $\Delta\text{Hf}^\circ(\text{Na}_2\text{UO}_4)$. This result is in satisfactory agreement with that of Cordfunke and Loopstra, but does not overlap that of Battles et al. The ΔHf° reported by Ippolitova et al. is evidently erroneous since our measured ΔH° for the reaction of the uranate with HCl was about $-42 \text{ kcal mol}^{-1}$, while, for the same reaction, Ippolitova et al. reported $\Delta\text{H}^\circ = -23 \text{ kcal mol}^{-1}$. We suspect that perhaps the material used by the latter authors was not pure $\alpha\text{-Na}_2\text{UO}_4$ or that there was a systematic error in their calorimetry.

NaUO_3 . Inspection of Table 3 reveals that the data for NaUO_3 are even more discrepant than those for $\alpha\text{-Na}_2\text{UO}_4$. We believe that because of the presence of large amounts ($\sim 25\%$) of UO_2 as an impurity phase, the result of King et al. would have to be regarded as being uncertain by several kilocalories. Again, if one chooses to double the uncertainty given by Battles et al., reasonable agreement is obtained with the ΔHf° reported by King et al. We are inclined to believe that the result of Cordfunke and Loopstra for NaUO_3 is badly in error, since preliminary results of our study on NaUO_3 indicate a ΔHf° of approximately $-374 \text{ kcal mol}^{-1}$. Work is continuing on this project.

$\text{Na}_2\text{U}_2\text{O}_7$ and Na_4UO_5 . We do not plan to study these materials at the present time. However, straightforward dissolution of the compounds in dilute HCl would probably yield reliable ΔHf° values.

III. CARBIDES OF MOLYBDENUM AND VANADIUM (G. K. Johnson)

As has been previously discussed,¹³ a collaborative program has been undertaken between E. K. Storms of Los Alamos Scientific Laboratory and this laboratory to determine the enthalpies of formation of the carbides of molybdenum and vanadium.

Carbides of Molybdenum

The molybdenum-carbon phase diagram^{14,15} shows two compounds, Mo_2C and MoC_{1-x} , in this system. Mo_2C , which is stable at room temperature, has two crystal modifications--a low-temperature ordered form, designated α , and a high-temperature disordered form, designated β . Similarly, the MoC_{1-x} phase, which is stable only at elevated temperatures, has two

Table 3. Enthalpies of Formation of Sodium Uranates (kcal mol⁻¹)

Compound	Battles et al. ⁹	Cordfunke & Loopstra ¹⁰	Ippolitova et al. ¹¹	King et al. ¹²	Present Investigation
Na ₃ UO ₄	-479.0 ± 2.5				-477.7 ± 0.9
α-Na ₂ UO ₄	-430.9 ± 12.6	-448 ± 2.2	-478		-445.5 ± 0.9 ^a
NaUO ₃	-344.2 ± 4.2	-273.4 ± 1		-357	-374 ^a
Na ₂ U ₂ O ₇	-734.8 ± 15.0	-760 ± 4			
Na ₄ UO ₅	-554.9 ± 19.0	-577 ± 3			

^aPreliminary result, subject to revision.

crystal forms, a low-temperature form and a high-temperature form which have been designated as α and β, respectively, by Storms.¹⁴ In the present investigation, a sample of α-Mo₂C and a sample of α-MoC_{1-x} were reacted with fluorine in a bomb calorimeter to form MoF₆(g) and CF₄(g).

The samples of α-Mo₂C and α-MoC_{1-x} used in the calorimetric study were prepared at Los Alamos Scientific Laboratory by arc-melting molybdenum and graphite, followed by appropriate heat treatments to insure homogeneity and composition. The Mo₂C sample is single-phase α-Mo₂C having an analyzed composition of MoC_{0.496±0.005} and containing less than 5 ppm oxygen. Additional analyses to determine the presence of other impurities are being performed at Los Alamos. The MoC_{1-x} sample contains 890 ppm free carbon, <5 ppm oxygen, no detectable Mo₂C phase, and a combined carbon content of MoC_{0.650±0.002}. Correcting for the free carbon gives a composition of MoC_{0.642} for the MoC_{1-x} phase.

Trial combustions established that the molybdenum carbide combustions would have to be conducted in a two-chambered bomb because the samples were attacked by fluorine. The trial combustions also established that stringent conditions would be necessary to prevent the formation of lower molybdenum fluorides, MoF₅ and MoF₃, as well as to minimize the formation of lower carbon fluorides. These conditions were achieved by the use of high fluorine pressures (√28 atm in the tank, which reduces to √12 atm after expansion into the bomb), a small nickel crucible of low heat capacity to support the sample, and an auxiliary combustion aid (Se) to promote the reaction. The selenium also served as a fuse to initiate the reaction.

All operations which involved handling the sample or opening the bomb were conducted in a helium-atmosphere glovebox. Following the combustion, the bomb gases were condensed with liquid nitrogen, the excess fluorine was removed by pumping, and a portion of the residual gas was submitted for gas-chromatographic analysis to determine the amounts of C₂F₆(g) and C₃F₈(g) in the combustion product. The nickel support crucible was weighed following the combustion. The crucible always exhibited a weight increase of 0.4 to 1.8 mg which was attributed to fluorination of the crucible.

The results of the combustions of $\text{MoC}_{0.496}$ and $\text{MoC}_{0.642}$ in fluorine are presented in Tables 4 and 5, respectively. The symbols $n^f\text{C}_2\text{F}_6$ and $n^f\text{C}_3\text{F}_8$ are the moles of C_2F_6 and C_3F_8 produced in the combustions. ΔE_{blank} is the correction for the energy of expansion of fluorine from the tank into the bomb and subsequent reaction of fluorine with the bomb surfaces. This quantity was determined by a series of calorimetric experiments in which fluorine was expanded into the bomb. The mean and standard deviation of eight such experiments was 3.98 ± 0.34 cal. $\Delta E_{\text{C}_2\text{F}_6}$ and $\Delta E_{\text{C}_3\text{F}_8}$ are the corrections for the fluorination of the C_2F_6 and C_3F_8 produced in the combustion to CF_4 . The energies of reaction of C_2F_6 and C_3F_8 to form CF_4 were taken to be -128^{16} and -250^{16} kcal mol $^{-1}$, respectively. ΔE_{Se} is the correction for the energy of combustion of the selenium auxiliary. The selenium sample was the same as that previously used to determine $\Delta H_f^\circ(\text{SeF}_6, \text{g})$, and its energy of combustion has been determined¹⁷ to be -3364.9 cal g $^{-1}$.

Table 4. Calorimetric Data for the Combustion of $\text{MoC}_{0.496}(\text{c})$ in Fluorine

Expt. No.	1	2	3	4	5	6	7	8
$m'(\text{MoC}_{0.496}), \text{g}$	0.89801	0.90582	0.88838	0.45050	0.44699	0.67722	0.68026	0.68620
$m''(\text{Se}), \text{g}$	0.30033	0.29740	0.30079	0.30467	0.29372	0.30026	0.31155	0.29876
$n^f_{\text{C}_2\text{F}_6}, \mu\text{mole}$	21.04	12.02	20.18	12.44	12.58	9.10	7.64	9.22
$n^f_{\text{C}_3\text{F}_8}, \mu\text{mole}$	6.11	3.75	6.82	3.65	2.42	2.43	1.05	2.69
$\Delta T_c, ^\circ\text{K}$	1.53585	1.54622	1.52380	0.92495	0.90740	1.23094	1.24804	1.24246
$\epsilon(\text{calor})(-\Delta T_c), \text{cal}$	-5190.42	-5225.47	-5149.70	-3125.88	-3066.57	-4159.97	-4217.76	-4198.91
$\Delta E_{\text{cont}}, \text{cal}$	-9.01	-9.08	-8.94	-5.40	-5.30	-7.19	-7.27	-7.22
$\Delta E_{\text{gas}}, \text{cal}$	0.47	0.47	0.46	0.25	0.24	0.34	0.34	0.35
$\Delta E_{\text{blank}}, \text{cal}$	-3.98	-3.98	-3.98	-3.98	-3.98	-3.98	-3.98	-3.98
$\Delta E_{\text{C}_2\text{F}_6}, \text{cal}$	-2.63	-1.50	-2.52	-1.55	-1.57	-1.14	-0.95	-1.15
$\Delta E_{\text{C}_3\text{F}_8}, \text{cal}$	-1.53	-0.94	-1.71	-0.91	-0.61	-0.61	-0.26	-0.67
$\Delta E_{\text{Ni}}, \text{cal}$	2.51	4.78	4.45	7.54	2.80	1.77	2.80	1.90
$\Delta E_{\text{Se}}, \text{cal}$	1010.58	1000.72	1012.13	1025.18	988.34	1010.34	1048.33	1005.30
$\Delta E_c^\circ/M, \text{cal g}^{-1}$	-4670.34	-4675.32	-4671.21	-4672.03	-4668.23	-4666.78	-4672.85	-4669.75

$$\text{Average } \Delta E_c^\circ/M = -4670.81 \pm 0.95 \text{ cal g}^{-1}$$

$$\Delta E_c^\circ(\text{MoC}_{0.496}) = -475.94 \text{ kcal mol}^{-1}$$

$$\Delta H_c^\circ(\text{MoC}_{0.496}) = -477.41 \text{ kcal mol}^{-1}$$

$$\Delta H_f^\circ(\text{MoC}_{0.496}) = -5.53 \text{ kcal mol}^{-1}$$

Table 5. Calorimetric Data for the Combustion of $\text{MoC}_{0.642}(\text{c})$ in Fluorine

Expt. No.	1	2	3	4	6	7
$m'(\text{MoC}_{0.642})$, g	0.85305	0.85337	0.84570	0.60098	0.61920	0.41887
$m''(\text{Se})$, g	0.29635	0.29475	0.29436	0.29668	0.30201	0.30253
$n_{\text{C}_2\text{F}_6}^f$, μmol	23.03	17.53	13.71	13.23	7.90	9.62
$n_{\text{C}_3\text{F}_8}^f$, μmol	7.58	5.39	3.36	3.78	1.87	2.21
ΔT_c , $^\circ\text{K}$	1.53689	1.53620	1.52547	1.17043	1.20300	0.91074
$\epsilon(\text{calor})(-\Delta T_c)$, cal	-5193.94	-5191.60	-5155.34	-3955.48	-4065.55	-3077.85
ΔE_{cont} , cal	-8.87	-9.01	-8.95	-6.85	-7.04	-5.32
ΔE_{gas} , cal	0.39	0.43	0.42	0.30	0.31	0.22
ΔE_{blank} , cal	-3.98	-3.98	-3.98	-3.98	-3.98	-3.98
$\Delta E_{\text{C}_2\text{F}_6}$, cal	-2.88	-2.19	-1.71	-1.65	-0.99	-1.20
$\Delta E_{\text{C}_3\text{F}_8}$, cal	-1.89	-1.35	-0.84	-0.95	-0.47	-0.55
ΔE_{Ni} , cal	4.00	3.67	7.13	2.31	7.13	3.79
ΔE_{Se} , cal	997.19	991.80	990.49	998.30	1016.23	1017.98
$\Delta E_c^\circ/M$, cal g^{-1}	-4935.21	-4935.99	-4934.11	-4938.60	-4932.75	-4934.49

$$\text{Average } \Delta E_c^\circ/M = -4935.19 \pm 0.81 \text{ cal g}^{-1}$$

$$\text{Correction for free carbon} = 12.09 \text{ cal g}^{-1}$$

$$\Delta E_c^\circ/M(\text{MoC}_{0.642}) = -4923.10 \text{ cal g}^{-1}$$

$$\Delta E_c^\circ(\text{MoC}_{0.642}) = -510.28 \text{ kcal mol}^{-1}$$

$$\Delta H_c^\circ(\text{MoC}_{0.642}) = -511.84 \text{ kcal mol}^{-1}$$

$$\Delta H_f^\circ(\text{MoC}_{0.642}) = -3.66 \text{ kcal mol}^{-1}$$

The enthalpies of formation for $\text{MoC}_{0.496}$ and $\text{MoC}_{0.642}$ were derived using values for $\Delta H_f^\circ(\text{CF}_4, \text{g})^{16}$ and $\Delta H_f^\circ(\text{MoF}_6, \text{g})^{18}$ of -223.04 ± 0.18 kcal mol^{-1} and -372.31 ± 0.22 kcal mol^{-1} , respectively. The derived ΔH_f° values are subject to change when the complete analytical results for the samples have been obtained. For this reason we have not attempted to calculate the uncertainty. It is anticipated that each ΔH_f° result will be good to ± 0.5 kcal mol^{-1} .

The tentative results obtained in this work are $\Delta H_f^\circ(\text{MoC}_{0.496}, \alpha) = -5.53$ kcal mol^{-1} and $\Delta H_f^\circ(\text{MoC}_{0.642}, \alpha) = -3.66$ kcal mol^{-1} . Previous results were based on the oxygen bomb calorimetric study of Mah,¹⁹ who reports $\Delta H_f^\circ(\text{Mo}_2\text{C}) = -11.0 \pm 0.7$ kcal mol^{-1} and $\Delta H_f^\circ(\text{MoC}) = -2.4 \pm 1.0$ kcal mol^{-1} . The result for Mo_2C [$\Delta H_f^\circ(\text{MoC}_{0.5}) = -5.50 \pm 0.35$ kcal mol^{-1}] is in excellent agreement with our result. The result for "MoC", however, must be considered to be erroneous. The sample of "MoC" for which analysis gave $\text{MoC}_{0.86}$ was considered to be a mixture of 73.73% MoC and 26.27% Mo_2C . Since the high carbon boundary of the MoC_{1-x} phase is $\text{MoC}_{0.67}$,¹⁴ the sample was probably a mixture of $\text{MoC}_{0.67}$ and free carbon. If the measured

data are treated based on the above assumption, one derives $\Delta H_f^\circ(\text{MoC}_{0.67}) = -1.94 \text{ kcal mol}^{-1}$, which is in poor agreement with our result. The sample of "MoC" used in the oxygen bomb study is too poorly characterized to derive any meaningful ΔH_f° result. Thus the result obtained herein for MoC_{1-x} is the only definitive value available.

Carbides of Vanadium

The determination of the enthalpy of formation of a number of vanadium carbide samples covering the composition ranges of the V_2C and VC phases are planned. These samples are being prepared at Los Alamos Scientific Laboratory. Preparatory to studying the carbides, it will be necessary to determine the enthalpy of formation of $\text{VF}_5(\text{g})$ according to

A sample of vanadium foil, having a stated purity of >99.9%, was purchased from Materials Research Corp. The sample is being analyzed for impurities, but the results are not yet available. A number of preliminary experiments established that it would be necessary to use a two-chambered reaction vessel since the vanadium was attacked by fluorine, that high fluorine pressures would be required to prevent the formation of a VF_3 residue, and that a nickel combustion support could be used provided the contact between the nickel and vanadium was minimal. The latter condition was met by bending the four corners of the vanadium foil so that only the points of the foil rested on the nickel support. Small residues ($\sim 0.2 \text{ mg}$) of vanadium, generally in the form of a bead on the nickel support, were found after the combustions. Microscopic examination of these beads indicated that the residue was entirely metal and did not contain any VF_3 .

The mass of vanadium metal used in each combustion ($\sim 0.19 \text{ g}$) was chosen so that the entire VF_5 product would be gaseous rather than a mixture of gas and liquid. The vapor pressure of $\text{VF}_5(\text{g})$ is 230 Torr²⁰ at 26°C, the final temperature of the experiments.

The results of seven combustions of vanadium in fluorine are given in Table 6. The symbols $m''(\text{s})$ and ΔE_{S} are the mass and correction for the energy of combustion of a small amount of sulfur which was used to initiate the combustions. The other entries have the usual significance. The correction for the impurities in the sample is based on the manufacturer's analysis. For this reason the derived $\Delta H_f^\circ(\text{VF}_5, \text{g})$ of $-343.50 \pm 0.21 \text{ kcal mol}^{-1}$ must be considered to be a tentative value.

The only previous value for the enthalpy of formation of VF_5 is based on a solution calorimetric study by Cavell and Clark.²¹ They obtained $\Delta H_f^\circ(\text{VF}_5, \ell) = -352 \pm 4 \text{ kcal mol}^{-1}$. Combination of this result with $\Delta H_v^\circ(\text{VF}_5, \ell) = 10.60 \text{ kcal mol}^{-1}$ ²⁰ yields $\Delta H_f^\circ(\text{VF}_5, \text{g}) = -341.4 \pm 4 \text{ kcal mol}^{-1}$. This result within its large uncertainty would be in agreement with the value derived herein.

Table 6. Calorimetric Data for the Combustion of Vanadium in Fluorine

$m^i(V)$, g	0.19259	0.19072	0.19129	0.19341	0.19428	0.18853	0.19237
$m^f(V)$, g	0.00014	0.00023	0.00013	0.00019	0.00018	0.00019	0.00052
$m'(V)$, g	0.19245	0.19049	0.19116	0.19322	0.19410	0.18834	0.19185
$m''(S)$, g	0.00575	0.00694	0.00782	0.00669	0.00602	0.00572	0.00595
ΔT_c , °K	0.39680	0.39620	0.39964	0.40085	0.40176	0.38866	0.39610
$\epsilon(\text{calor})(-\Delta T_c)$,	-1341.41	-1339.38	-1351.01	-1355.10	-1358.17	-1313.89	-1339.04
$\Delta E_{\text{cont}}^{\text{cal}}$, cal	-1.07	-1.06	-1.08	-1.08	-1.04	-1.00	-1.02
ΔE_{gas} , cal	-0.22	-0.22	-0.23	-0.23	-0.23	-0.22	-0.22
ΔE_S , cal	52.11	62.89	70.87	60.63	54.56	51.84	53.92
ΔE_{blank} , cal	-3.70	-3.70	-3.70	-3.70	-0.88	-3.70	-3.70
ΔE_{Ni} , cal	---	0.37	---	0.25	---	---	---
$\Delta E_c^{\circ}/M(\text{sample})$, cal g^{-1}	-6725.33	-6825.29	-6722.90	-6724.10	-6727.25	-6727.04	-6724.32

$$\text{Average } \Delta E_c^{\circ}/M(\text{sample}) = -6725.18 \pm 0.60^a \text{ cal g}^{-1}$$

$$\text{Impurity correction}^b = -0.65 \pm 0.25^a \text{ cal g}^{-1}$$

$$\Delta E_c^{\circ}/M(V,c) = -6725.8 \pm 4.2^c \text{ cal g}^{-1}$$

$$\Delta E_c^{\circ}(V,c) = \Delta E_f^{\circ}(\text{VF}_5, \text{g}) = -342.62 \pm 0.21^c \text{ kcal mol}^{-1}$$

$$\Delta H_c^{\circ}(V,c) = \Delta H_f^{\circ}(\text{VF}_5, \text{g}) = -343.50 \pm 0.21^c \text{ kcal mol}^{-1}$$

^aStandard deviation of the mean.

^bBased on manufacturers analysis.

^cUncertainty interval.

IV. TRIURANIUM SILICIDE (U₃Si) (W. N. Hubbard)

As was mentioned in the previous report,²² a cooperative venture has been undertaken between I. J. Hastings of Atomic Energy of Canada and this laboratory to prepare and characterize a good sample of U₃Si at Chalk River and to measure its thermodynamic properties at Argonne. The following determinations are to be made: heat capacities and entropies at low temperatures by D. W. Osborne and H. E. Flotow of the Argonne Chemistry Division; enthalpy increments to 1200°K by drop calorimetry by D. R. Fredrickson of the Argonne Chemical Engineering Division; and standard enthalpy of formation by fluorine bomb calorimetry in this laboratory. The sample requirements for the three different measurements were found to be somewhat different and several different specimens had to be prepared.

The high-temperature enthalpy increment measurements have been completed on one specimen and preliminary results reported.²³ Specimens for low-temperature measurements have not been received. Preparations are being made to proceed with fluorine calorimetric studies on a specimen already received.

Because some spontaneous fluorination occurs on exposure of U_3Si to fluorine, the combustion studies will be made with a two-compartment bomb, in which it is possible to prevent fluorination of the sample until intentional ignition. Work is being done toward preparing the high-pressure, two-chamber bomb Ni-8 for combustions with U_3Si in fluorine. This is the bomb which had been plated internally with gold for measurements of the enthalpy of formation of HF by the reaction between hydrogen and fluorine. The bomb was completely disassembled and all corrosion and internal plating removed. The sealing surfaces of the bomb were resurfaced and all the Teflon O-rings, gaskets, and valve packings were replaced.

Several calibration experiments will be carried out with benzoic acid before calorimetric combustions with U_3Si are made.

V. LITHIUM MONOSELENIDE, Li_2Se (M. Ader)

Thermodynamic properties of lithium-chalcogen systems have been investigated at ANL for several years in support of an ongoing program to develop high-temperature electrical secondary cells.²⁴ Thermodynamic data based on calorimetric measurements can be extremely valuable for comparing ideal versus actual performances of electrochemical cells. For example, in a cell of the type $Li/Li \text{ halide}/Se$, which may be operated at about $400^\circ C$, the driving force is the reaction $2Li + xSe \rightarrow Li_2Se_x$. Calorimetric measurement of the standard enthalpy of formation (ΔH_f°) of Li_2Se at $25^\circ C$ and of the enthalpy increments to $400^\circ C$ would permit calculation of theoretical emf's and comparison with experimental data. In addition, determination of the enthalpy increments, and therefore of the term $T\Delta S^\circ$, would provide practical information regarding absorption and rejection of heat during charge-discharge cycles. Calorimetric study of Li_2Se (and analogous compounds such as Li_2S and Li_2Te) also adds to our basic knowledge concerning the interactions and binding forces of elements of widely different electronegativities.

The only previous measurements of $\Delta H_f^\circ(Li_2Se)$ were made by solution calorimetry 60 to 85 years ago, from which the National Bureau of Standards selected the value $\Delta H_f^\circ(Li_2Se, c, 298^\circ K) = -91.1 \text{ kcal mol}^{-1}$.²⁵ Cairns et al.,^{24b,c} using emf measurements on $Li/LiBr-RbBr/Li$ in Se cells, calculated the standard free energy of formation (ΔG_f°) of Li_2Se to be $-94.0 \text{ kcal mol}^{-1}$ at $360^\circ C$.

Recently, a high-purity specimen* of Li_2Se was provided us for

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*Prepared by P. T. Cunningham and S. A. Johnson, ANL Chemical Engineering Division, by the reaction of selenium vapor with molten lithium contained in a Nb-1%Zr crucible.

calorimetric determination of its enthalpy of formation. The experimental technique of fluorine bomb calorimetry has been chosen, employing the reaction

$\Delta\text{Hf}^\circ(\text{Li}_2\text{Se}, \text{c}, 298^\circ\text{K})$ will be derived from the sum $\Delta\text{Hf}^\circ(\text{SeF}_6, \text{g}) + 2\text{Hf}^\circ(\text{LiF}, \text{c}) - \Delta\text{H}(9)$. The auxiliary enthalpies are (in kcal mol⁻¹ at 25°C): $\Delta\text{Hf}^\circ(\text{SeF}_6, \text{g}) = -(266.95 \pm 0.14)$; ¹⁷ and $\Delta\text{Hf}^\circ(\text{LiF}, \text{c}) = -(147.90 \pm 0.08)$, which may be calculated by a cycle involving $\Delta\text{Hf}^\circ(\text{Li}^+, \text{aq}) = -(66.555 \pm 0.039)$, ² $\Delta\text{Hf}^\circ(\text{F}^-, \text{aq}) = -(87.22 \pm 0.07)$, ²⁶ and $\Delta\text{H}_{\text{soln}}^\circ(\text{LiF}, \text{c}) = -(1.130 \pm 0.025)$. ³

Numerous noncalorimetric combustion experiments have been run to find conditions for complete fluorination of Li_2Se according to Reaction 9. These trials have led to the following conclusions: (1) Li_2Se , which is hygroscopic and must be handled in an inert atmosphere, ignites spontaneously in fluorine and thus requires use of a two-compartment bomb for the calorimetric measurements. (2) When Li_2Se alone is burned in fluorine, combustion is incomplete, presumably because the LiF product melts (m.p. 842°C) and covers unreacted Li_2Se , thus quenching the reaction. (3) Nickel supports or crucibles holding the Li_2Se are generally attacked and, if thin enough (~ 20 mil), are ignited, even under moderate (~ 5 atm) fluorine pressures. Thus the Li_2Se must not contact the support. Massive nickel crucibles, though less subject to attack, tend to cool and quench the combustion reaction. The same effect occurs if Li_2Se is burned on top of a LiF bed. (4) Complete fluorination is promoted by using Li_2Se as a powder rather than as granules. However, the powder should be kept covered initially so that the turbulence created by intruding fluorine and by the reaction itself does not blow or spatter material onto cold surfaces. (5) Complete fluorinations are obtained using high fluorine pressures (~ 20 atm) and an auxiliary combustible material that yields about three times the heat provided by combustion of the Li_2Se . Under such conditions, an appreciable fraction of the LiF is vaporized, and the fused residue remaining in the crucible is white (pure LiF) rather than some shade of red (unburned selenium in LiF).

Auxiliary combustion aids for Li_2Se were sought which would burn in fluorine to an unreactive product. In practice, this meant choosing substances that burned to gaseous (at 25°C) fluorides unreactive to $\text{SeF}_6(\text{g})$, since condensed fluorides were too likely to react with LiF , giving unknown, undesirable heat effects. Fluorine bomb combustions of Li_2Se were tried with the following auxiliaries: elemental selenium powder, tungsten foil, Teflon powder (pelletized with Li_2Se), graphite cloth, and graphite felt. The amount of auxiliary added was such as to yield 65 to 75% of an estimated total heat evolution of 6500 to 8000 cal. Examination of the postcombustion residues indicated that all the auxiliaries except selenium powder effected complete fluorination of the Li_2Se . Failure of the selenium powder is attributed to its partial vaporization to $\text{Se}(\text{g})$ at the onset of the reaction, thereby causing heat from the subsequent fluorination of $\text{Se}(\text{g})$ to be dissipated in the gas phase, away from the reacting Li_2Se .

Graphite felt has been selected as the auxiliary to be used in the calorimetric measurements. The decision was based on its (a) availability (National Carbon Grade WDF, 0.206 in. thick, 99.9% graphite), (b) ease of cutting and fabricating into suitable shapes (tungsten foil is too brittle), (c) ease of handling and weighing (weighing, mixing, and pelletizing Teflon plus Li_2Se powders is difficult and time consuming in an inert-atmosphere box), and (d) almost negligible residue after combustion (less than with Teflon or graphite cloth).

Experiments are now in progress to calibrate the two-compartment bomb Ni-7^{27} by combustions of benzoic acid in oxygen. These will be followed by calorimetric fluorine bomb combustions of graphite felt alone and graphite felt plus Li_2Se , in conjunction with necessary analytical work.

VI. MOLECULAR ORBITAL STUDIES: THE VERTICAL IONIZATION POTENTIAL OF AsF (P. A. G. O'Hare)

We have computed the total Hartree-Fock energy of $\text{AsF}(^3\Sigma^-)$ at its experimental internuclear separation to be -2333.72006 hartrees;* at the same internuclear separation, the total energy for $\text{AsF}^+(^2\Pi)$ was computed as -2333.28789 hartrees and, thus, the vertical ionization potential of AsF is calculated to be 0.43217 hartrees or 11.8 eV. Since the correlation energy change for ionization of the group VA diatomic fluorides appears to be quite small,²⁸ we believe that the computed ionization potential is accurate to within 0.2 eV.

The dissociation enthalpies (D_0°) of the ion and parent molecule are related by

$$D_0^\circ(\text{AsF}^+) - D_0^\circ(\text{AsF}) = \underline{I}(\text{As}) - \underline{I}(\text{AsF}) \quad (10)$$

Now, since $\underline{I}(\text{As}) = 9.81$ eV, it follows that $D_0^\circ(\text{AsF}^+)$ is less than $D_0^\circ(\text{AsF})$. This might indicate that, whereas both NF and PF are ionized by removal of an antibonding electron,²⁸ AsF appears to ionize by removal of a bonding electron. This would be quite unexpected.

However, we have computed the total energy of AsF at one internuclear separation only and, in order to arrive at a reliable conclusion regarding the ionization process, it is highly desirable that the total energy be computed at other internuclear separations. These computations will be performed, it is hoped, when the Laboratory's new IBM 360-195 computer system becomes operational.

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*1 hartree = 27.20974 eV.

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