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CHEMICAL ENGINEERING DIVISION
THERMOCHEMICAL STUDIES
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July 1973—June 1974

by

P. A. G. O'Hare, G. K. Johnson,
M. Ader, W. N. Hubbard,
F. A. Cafasso, and L. Burris

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ABSTRACT

Measurements of the enthalpy of reaction of $\text{MoO}_3(\text{c})$ with $\text{LiOH}(\text{aq})$ and of the enthalpy of solution of $\text{Li}_2\text{MoO}_4(\text{c})$ in $\text{LiOH}(\text{aq})$ yielded $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4, \text{c}, 298.15 \text{ K}) = -363.26 \pm 0.12 \text{ kcal mol}^{-1}$. A value of $-200.0 \pm 0.3 \text{ kcal mol}^{-1}$ has been deduced for $\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ based on the solubility products and thermochemical data for several sparingly soluble molybdates. The enthalpy of reaction of $\text{Cs}_2\text{Mo}_2\text{O}_7$ with $\text{CsOH}(\text{aq})$ yielded $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -550.3 \pm 0.2 \text{ kcal mol}^{-1}$. Calorimetric measurements of the enthalpy of reaction of NaUO_3 with an aqueous mixture of HCl and XeO_3 yielded $\Delta H_f^\circ(\text{NaUO}_3, \text{c}, 298.15 \text{ K}) = -357.5 \pm 0.8 \text{ kcal mol}^{-1}$; and the enthalpies of reaction of $\alpha\text{-Li}_2\text{UO}_4$, K_2UO_4 , and Rb_2UO_4 with $\text{HCl}(\text{aq})$ gave ΔH_f° values of -463.31 ± 0.84 , -451.39 ± 0.83 , and $-452.00 \pm 0.85 \text{ kcal mol}^{-1}$ respectively. Measurements of the enthalpies of reaction of Li_3N with both acid and water and of Li_2O with water yielded $\Delta H_f^\circ(\text{Li}_3\text{N}, \text{c}, 298.15 \text{ K}) = -39.42 \pm 0.26 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{Li}_2\text{O}, \text{c}, 298.15 \text{ K}) = -142.903 \pm 0.067 \text{ kcal mol}^{-1}$. Based on fluorine bomb combustion experiments, $\Delta H_f^\circ(\text{VC}_{0.787}, \text{c}, 298.15 \text{ K}) \approx -26 \text{ kcal mol}^{-1}$ and $\Delta H_f^\circ(\text{Li}_2\text{Se}, \text{c}, 298.15 \text{ K}) = -101.8 \pm 2.0 \text{ kcal mol}^{-1}$. Some preliminary data are given for combustions of U_3Si in fluorine. Exploratory combustions of WS_2 , MoSe_2 , MoTe_2 , FeS_2 , and Al_2SiO_5 were run to learn if fluorine bomb calorimetry could be readily applied to the determination of their enthalpies of formation. Molecular orbital calculations on the selenium-fluorine system yielded the following properties for $\text{SeF}(\text{g})$: $\Delta H_f^\circ = -0.8 \pm 2 \text{ kcal mol}^{-1}$; standard entropy, $S^\circ = 57.2 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$; ionization potential, $I = 9.4 \pm 0.4 \text{ eV}$; electron affinity, $E_a = 1.8 \text{ eV}$; and dipole moment, $\mu = 2.05 \text{ debye}$. Except for $\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq}, 298.15 \text{ K})$ and $\Delta H_f^\circ(\text{Li}_2\text{Se}, \text{c}, 298.15 \text{ K})$, values quoted in this abstract are to be considered preliminary, and should not be used without prior consultation with the authors.

SUMMARY

Li_2MoO_4 , $\text{MoO}_4^{2-}(\text{aq})$, and $\text{Cs}_2\text{Mo}_2\text{O}_7$

In order that well-established values would be available for the enthalpies of formation, ΔH_f° , of all the alkali-metal molybdates, a solution calorimetric study of lithium molybdate, Li_2MoO_4 , has been performed. The result obtained is $-363.26 \pm 0.12 \text{ kcal mol}^{-1}$. Based on literature data for several sparingly soluble metal molybdates, a

value of $-200.0 \pm 0.3 \text{ kcal mol}^{-1}$ is recommended for $\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq}, 298.15 \text{ K})$. Based on the measured enthalpy of reaction of cesium dimolybdate, $\text{Cs}_2\text{Mo}_2\text{O}_7$, with $\text{CsOH}(\text{aq})$, $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7, \text{c}, 298.15 \text{ K})$ was found to be $-550.3 \pm 0.2 \text{ kcal mol}^{-1}$.

NaUO_3 , M_2UO_4 ($\text{M} = \text{Li, K, Rb}$), and $\text{Cs}_2\text{U}_2\text{O}_7$

Existing literature data for $\Delta H_f^\circ(\text{NaUO}_3)$ were discordant; our determination, based on dissolution of NaUO_3 in an aqueous $\text{XeO}_3 + \text{HCl}$ mixture, gave a value of $-357.5 \pm 0.8 \text{ kcal mol}^{-1}$. Similarly, because a previous determination of ΔH_f° for alkali metal uranates was suspect, the enthalpies of reaction with $\text{HCl}(\text{aq})$, ΔH_r , were determined for $\alpha\text{-Li}_2\text{UO}_4$, K_2UO_4 , and Rb_2UO_4 and new values for ΔH_f° were deduced. The results are as follows:

	<u>ΔH_r, kcal mol^{-1}</u>	<u>$\Delta H_f^\circ(\text{c}, 298.15 \text{ K})$, kcal mol^{-1}</u>
$\alpha\text{-Li}_2\text{UO}_4$	-41.77 ± 0.02	-463.31 ± 0.84
K_2UO_4	-42.07 ± 0.05	-451.39 ± 0.83
Rb_2UO_4	-41.30 ± 0.05	-452.00 ± 0.85

A study of $\text{Cs}_2\text{U}_2\text{O}_7$ is in progress.

Li_3N and Li_2O

Because of the interest in lithium in connection with the Controlled Thermonuclear Research (CTR) program, the enthalpies of formation of two of the most common contaminants of lithium, *i.e.*, the nitride, Li_3N , and the oxide, Li_2O have been determined by solution calorimetry. The results obtained (kcal mol^{-1}) were: $\Delta H_f^\circ(\text{Li}_3\text{N}, \text{c}, 298.15 \text{ K}) = -39.42 \pm 0.26$ and $\Delta H_f^\circ(\text{Li}_2\text{O}, \text{c}, 298.15 \text{ K}) = -142.903 \pm 0.067$.

Li_2Se

Final calculations for the combustion of Li_2Se in fluorine yielded $\Delta H_f^\circ(\text{Li}_2\text{Se}, \text{c}, 298.15 \text{ K}) = -101.8 \pm 2.0 \text{ kcal mol}^{-1}$. A description of this work appears in J. Chem. Thermodyn. 6, 587 (1974).

U_3Si

Triuranium silicide, U_3Si , which has a number of attractive features as a nuclear fuel, has been included in that part of our program which deals with the thermodynamic properties of uranium compounds. A sample was prepared and characterized at the Chalk River, Ontario, laboratories of Atomic Energy of Canada, Ltd. Calorimetric measurements of the enthalpy of reaction of this sample with fluorine have been completed. Derivation of $\Delta H_f^\circ(\text{U}_3\text{Si})$ awaits analytical results on the combustion residues.

$\text{VC}_{0.787}$

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. In this report, results of the combustion of a sample of $\text{VC}_{0.787}$ in fluorine are given. A preliminary result for $\Delta H_f^\circ(\text{VC}_{0.787}, \text{c.})$ of $\sim -26 \text{ kcal mol}^{-1}$ was obtained.

Exploratory Experiments in Fluorine Bomb Calorimetry

Exploratory combustions of WS_2 , MoSe_2 , MoTe_2 , FeS_2 , and Al_2SiO_5 were run to learn if fluorine bomb calorimetry could be readily applied to the determination of their enthalpies of formation. The results were quite satisfactory for WS_2 , MoSe_2 , and MoTe_2 . For FeS_2 and Al_2SiO_5 , success is much more dependent on analysis of reaction products.

SeF

Molecular orbital studies of the Hartree-Fock-Roothaan type have been carried out for the selenium-fluorine system. Based on these calculations, the spectroscopic constants (r_e , ω_e , $\omega_e x_e$, B_e , and α_e) and the following properties for SeF(g) have been obtained: $\Delta H_f^\circ = -0.8 \pm 2 \text{ kcal mol}^{-1}$; $S^\circ = 57.26 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$; ionization potential = $9.4 \pm 0.4 \text{ eV}$; electron affinity = 1.8 eV , and dipole moment (Se^+F^-) = 2.05 debye .

I. MOLYBDATES
(P. A. G. O'Hare)

A. Lithium Molybdate (Li_2MoO_4)

Accurate and precise thermochemical data for the molybdates of sodium,¹ potassium,² rubidium,³ and cesium⁴ are now available. As we have previously indicated,⁵ the present investigation was undertaken to provide data of similar quality for lithium molybdate. When this work was commenced, it was not known to us that a value for the standard enthalpy of formation, $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4)$, had already been reported several years ago by Tkhin' and Zharkova.⁶ However, because the results obtained by the latter authors are inconsistent with a substantial body of other experimental data, the present investigation would have been carried out even if we had been aware of the earlier study. It now appears that the measurements of Tkhin' and Zharkova are indeed erroneous.

Lithium molybdate was prepared from reagent-grade lithium carbonate and molybdenum trioxide; both of these compounds were dried at 773 K prior to use. The calculated quantities of the reactants, 50 mmol of each, were weighed into a gold crucible and heated slowly to 1023 K over a 6 hr period. The fused product was then cooled and ground to a fine powder in an agate mortar.

Thermal analysis of the preparation showed no phase transformation below the melting point at 983 K. The X-ray diffraction pattern agreed with that given in the literature by Swanson *et al.*⁷ for hexagonal lithium molybdate. Chemical analyses of the preparation were as follows: Li, 7.98 ± 0.01 mass percent (theoretical, 7.99 mass percent); Mo, 55.08 ± 0.06 mass percent (theoretical, 55.20 mass percent). The observed molar ratio of Li to Mo is 2.003 ± 0.001 . No significant metallic contaminants were detected by emission spectroscopy. Thus, the analytical evidence indicated that the lithium molybdate preparation was of high purity and, as such, was suitable for calorimetric study.

The calorimetric phase of the investigation consisted of careful measurements of the enthalpies of the following processes:

These measurements were carried out in an LKB-8700 Precision Calorimetric System, and the results obtained are to be found in Tables 1 and 2. Symbols in those tables have the following significance: m is the mass of compound reacted or dissolved, $\Delta\theta_c$ is the temperature increase of the calorimeter corrected for heat exchange with the environment; $\langle \epsilon(\text{calor}) \rangle$ is the mean energy equivalent of the calorimetric system; ΔH_{vap} is the correction for saturating the gas in the free volume of the ampoules with water vapor; and $\Delta H_r/M$ is either the enthalpy of reaction or solution.

TABLE 1. Calorimetric Results for the Reaction
of MoO_3 with LiOH(aq)^a

(cal = 4.184 J)

Expt. No.	m(MoO_3), g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J g^{-1}	$\Delta H_r/M$, J g^{-1}
3	0.30626	0.37687	438.75	-0.052	-540.08
6	0.31299	0.38500	439.03	-0.052	-540.21
7	0.31080	0.38115	438.94	-0.052	-538.46
8	0.30635	0.37539	438.80	-0.052	-537.86
9	0.31423	0.38404	439.14	-0.052	-536.86
10	0.31091	0.38258	438.65	-0.052	-539.93

$$\text{Mean } \Delta H_r/M = -538.90 \pm 0.57 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = -18539 \pm 39 \text{ cal mol}^{-1} \text{ }^{c,d}$$

^aConcentration of the LiOH was 0.20 mol dm^{-3} ; in each experiment, 99.41 cm^3 of aqueous LiOH was used. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^bUncertainty is the standard deviation of the mean.

^cMolar mass of MoO_3 was taken to be $143.94 \text{ g mol}^{-1}$.

^dUncertainty is *twice* the standard deviation of the mean.

TABLE 2. Calorimetric Results for Solution
of Li_2MoO_4 in LiOH(aq)^a

Expt. No.	m(Li_2MoO_4), g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J g^{-1}	$\Delta H_r/M$, J g^{-1}
1	0.37071	0.15473	438.83	-0.049	-183.29
2	0.37572	0.15693	438.42	-0.049	-183.25
3	0.37554	0.15619	438.79	-0.049	-182.63
4	0.37410	0.15623	438.97	-0.049	-183.45
5	0.37350	0.15572	439.34	-0.049	-183.30
6	0.36828	0.15386	438.06	-0.049	-183.15

$$\text{Mean } \Delta H_r/M = -183.18 \pm 0.12 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = -7610 \pm 10 \text{ cal mol}^{-1} \text{ }^{c,d}$$

^aConcentration of the LiOH was 0.16 mol dm^{-3} ; in each experiment, 99.41 cm^3 of aqueous LiOH was used. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^bUncertainty is the standard deviation of the mean.

^cMolar mass of Li_2MoO_4 was taken to be $173.82 \text{ g mol}^{-1}$.

^dUncertainty is *twice* the standard deviation of the mean.

The overall reaction scheme and the thermochemical data on which $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4)$ is based are given in Table 3. Summation of the enthalpies for reactions 1 through 6 in that table yields $-\Delta H_f^\circ(\text{Li}_2\text{MoO}_4)$. Values for

TABLE 3. Reaction Scheme and Thermochemical Data for Derivation of $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4, \text{c}, 298.15 \text{ K})^a$

1.	$\text{MoO}_3(\text{c}) + 9.307(\text{LiOH} \cdot 273.78\text{H}_2\text{O}) = \text{Li}_2\text{MoO}_4 \cdot 7.307\text{LiOH} \cdot 2549.04\text{H}_2\text{O}, \Delta H_1$ $= -18.539 \pm 0.039 \text{ kcal}$
2.	$\text{Li}_2\text{MoO}_4 \cdot 7.307\text{LiOH} \cdot 2549.04\text{H}_2\text{O} = \text{Li}_2\text{MoO}_4(\text{c}) + 7.307(\text{LiOH} \cdot 348.86\text{H}_2\text{O}), \Delta H_2$ $= 7.610 \pm 0.010 \text{ kcal}$
3.	$9.307(\text{LiOH} \cdot 348.86\text{H}_2\text{O}) = 9.307(\text{LiOH} \cdot 273.78\text{H}_2\text{O}) + 698.77\text{H}_2\text{O}(\text{l}), \Delta H_3$ $= 0.158 \pm 0.028 \text{ kcal}$
4.	$2\text{Li}(\text{c}) + 699.77\text{H}_2\text{O}(\text{l}) = 2(\text{LiOH} \cdot 348.86\text{H}_2\text{O}) + \text{H}_2(\text{g}), \Delta H_4$ $= -106.092 \pm 0.078 \text{ kcal}$
5.	$\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l}), \Delta H_5 = -68.315 \pm 0.010 \text{ kcal}$
6.	$\text{Mo}(\text{c}) + 3/2\text{O}_2(\text{g}) = \text{MoO}_3(\text{c}), \Delta H_6 = -178.08 \pm 0.08 \text{ kcal}$

^aAll species are in the aqueous phase except where denoted otherwise.

ΔH_1 and ΔH_2 are taken directly from Tables 1 and 2. The concentration term, ΔH_3 , has been taken from Parker's⁸ dilution data for $\text{LiOH}(\text{aq})$. Combination of the standard enthalpy of reaction of $\text{Li}(\text{c})$ with water, $-53.210 \pm 0.039 \text{ kcal mol}^{-1}$,⁹ with the dilution data⁸ yielded ΔH_4 . Finally, ΔH_5 and ΔH_6 are simply the standard enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ ¹⁰ and $\text{MoO}_3(\text{c})$,¹¹ respectively. The uncertainty in $\Delta H_f^\circ(\text{MoO}_3)$ is that quoted by Nuttall *et al.*¹²

Thus, $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4, \text{c}, 298.15 \text{ K})$ is calculated to be $-363.26 \pm 0.12 \text{ kcal mol}^{-1}$, and refers to the reaction

The uncertainty is the square root of the sum of the squares of the uncertainties in ΔH_1 through ΔH_6 .

Only one previous determination of $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4, \text{c})$ has been reported, namely that by Tkhin' and Zharkova.⁶ They measured the enthalpy of reaction of MoO_3 with $\text{LiOH}(\text{aq}, 0.5 \text{ mol dm}^{-3})$ and the enthalpy of solution of Li_2MoO_4 in $\text{LiOH}(\text{aq}, 0.5 \text{ mol dm}^{-3})$. Thus, their determination was similar to that reported by us except that the LiOH solution was 2.5 times more concentrated. For ΔH_1 , they obtained $-22.34 \pm 0.09 \text{ kcal mol}^{-1}$, and for ΔH_2 , $9.20 \pm 0.10 \text{ kcal mol}^{-1}$ (see Tables 1 and 2), from which they derived $\Delta H_f^\circ(\text{Li}_2\text{MoO}_4, \text{c}, 298.15 \text{ K}) = -365.25 \pm 0.19 \text{ kcal mol}^{-1}$.

Apart from relatively minor dilution effects, the enthalpy of reaction of MoO_3 with completely ionized alkali metal hydroxide, $\text{MOH}(\text{aq})$, should be essentially independent of M. Thus, for reaction with $\text{NaOH}(\text{aq})$, Graham and Hepler obtained -18.85 ± 0.2 ;^{1a} Koehler *et al.*, -18.45 ± 0.03 ;^{1b} Nuttall *et al.*, -18.65 ± 0.08 ;¹² and Shchukarev *et al.*, $-18.60 \pm 0.28 \text{ kcal mol}^{-1}$.¹³

For reaction with RbOH(aq) and CsOH(aq) , the present authors have reported -18.61 ± 0.01^3 and $-18.65 \pm 0.03 \text{ kcal mol}^{-1},^4$ respectively. On the basis of the above evidence, we are led to conclude that Tkhin' and Zharkova's result for ΔH_1 is about twenty percent too exothermic. By comparison with the other studies, our result of $-18.54 \pm 0.04 \text{ kcal mol}^{-1}$ appears to be reasonable.

It is also significant, we believe, that the earlier result for the enthalpy of solution is also about twenty percent more negative than our determination. Although the twenty percent offset in the two sets of results could be considered to be coincidental, we believe, rather, that it points to a systematic calorimetric bias.

B. Thermodynamic Data for Formation of the Alkali Metal Molybdates

Since the enthalpies of formation of all the solid alkali metal molybdates are now known, together with a limited number of the standard entropies, we have collected together, in Table 4, all the ΔH° , ΔS° , and ΔG° data for formation of these compounds both from the elements and from the component oxides. These values indicate that, with respect to the component elements, Li_2MoO_4 is marginally the most stable compound. With respect to formation from the component oxides, the Gibbs energies (as well as the enthalpies) increase monotonically from lithium through cesium, being very largely influenced by ΔH_f° of the corresponding oxides.

TABLE 4. Thermodynamic Data for Formation of the Alkali Metal Molybdates at 298.15 K

Reaction	$\Delta H^\circ,^a$ kcal mol^{-1}	$\Delta S^\circ,^b$ $\text{cal K}^{-1} \text{ mol}^{-1}$	$\Delta G^\circ,$ kcal mol^{-1}
(a) Formation from the elements.			
$2\text{Li(c)} + \text{Mo(c)} + 2\text{O}_2(\text{g}) = \text{Li}_2\text{MoO}_4(\text{c})$	-363.26 ± 0.12	-87.7 ± 2.1	-337.11 ± 0.64
$2\text{Na(c)} + \text{Mo(c)} + 2\text{O}_2(\text{g}) = \text{Na}_2\text{MoO}_4(\text{c})$	-350.68 ± 0.11	-91.34 ± 0.32	-323.45 ± 0.15
$2\text{K(c)} + \text{Mo(c)} + 2\text{O}_2(\text{g}) = \text{K}_2\text{MoO}_4(\text{c})$	-357.99 ± 0.22	-90.42 ± 2.1	-331.03 ± 0.66
$2\text{Rb(c)} + \text{Mo(c)} + 2\text{O}_2(\text{g}) = \text{Rb}_2\text{MoO}_4(\text{c})$	-357.04 ± 0.09	-85.55 ± 2.0	-331.53 ± 0.60
$2\text{Cs(c)} + \text{Mo(c)} + 2\text{O}_2(\text{g}) = \text{Cs}_2\text{MoO}_4(\text{c})$	-362.00 ± 0.11	-86.19 ± 0.10	-336.30 ± 0.11
(b) Formation from the solid oxides.			
$\text{Li}_2\text{O(c)} + \text{MoO}_3(\text{c}) = \text{Li}_2\text{MoO}_4(\text{c})$	-42.28 ± 0.16	3.4 ± 2.0	-43.29 ± 0.62
$\text{Na}_2\text{O(c)} + \text{MoO}_3(\text{c}) = \text{Na}_2\text{MoO}_4(\text{c})$	-73.46 ± 0.15	1.57 ± 0.32	-73.93 ± 0.18
$\text{K}_2\text{O(c)} + \text{MoO}_3(\text{c}) = \text{K}_2\text{MoO}_4(\text{c})$	-93.11 ± 0.55	4.0 ± 2.5	-94.31 ± 0.93
$\text{Rb}_2\text{O(c)} + \text{MoO}_3(\text{c}) = \text{Rb}_2\text{MoO}_4(\text{c})$	-96.16 ± 1.01	5.7 ± 2.8	-97.9 ± 1.3
$\text{Cs}_2\text{O(c)} + \text{MoO}_3(\text{c}) = \text{Cs}_2\text{MoO}_4(\text{c})$	-101.11 ± 0.31	5.68 ± 0.14	-102.80 ± 0.31

^aStandard enthalpies of formation of Na_2MoO_4 and K_2MoO_4 were recalculated from data in Refs. 1 and 2, respectively; standard enthalpies of formation of Rb_2O and Rb_2MoO_4 are in Ref. 3 and of Cs_2O and Cs_2MoO_4 in Ref. 4. Standard enthalpies of formation (kcal mol^{-1}) of Li_2O , -142.90 ± 0.07 , Na_2O , -99.14 ± 0.07 , and K_2O , -86.8 ± 0.5 are taken from this report and from Refs. 14 and 15, respectively.

^bStandard entropies, $S^\circ(298 \text{ K})$, of Rb_2MoO_4 , Cs_2MoO_4 , and the component elements and oxides are to be found in Refs. 3 and 4. For Na_2MoO_4 , Li , Na , K , Li_2O , Na_2O , and K_2O we have taken $S^\circ(298 \text{ K})$ values ($\text{cal K}^{-1} \text{ mol}^{-1}$) of 38.1 (Ref. 16), 6.95 (Ref. 17), 12.30 (Ref. 17), 15.34 (Ref. 18), 9.06 (Ref. 19), 17.94 (Ref. 20), and 22.5 (Ref. 15), respectively. The entropies of Li_2MoO_4 and K_2MoO_4 were estimated to be ($\text{cal K}^{-1} \text{ mol}^{-1}$) 30.5 ± 2 , and 45.1 ± 2 , respectively.

C. Gibbs Energy of Formation of the Aqueous Molybdate Ion

The Gibbs energy of formation and the solubility product, K_{sp} , are both well enough known for a few sparingly soluble molybdates to enable one to derive a consistent value for the Gibbs energy of formation of the aqueous molybdate ion, $\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq}, 298.15 \text{ K})$. Since these molybdates dissociate as follows:

then,

$$\begin{aligned} \Delta G^\circ(298.15 \text{ K}) = -RT \ln K_{sp} = n \Delta G_f^\circ(M^{+2/n}, \text{aq}) + \Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq}) \\ - \Delta G_f^\circ(M_n\text{MoO}_4, c) \end{aligned} \quad (\text{V})$$

The requisite thermodynamic and solubility data for the molybdates of barium, strontium, calcium, and silver, all of which are rather well established, are detailed in Table 5, together with the literature references. For ferrous molybdate, K_{sp} is based upon the observations of Zelikman and Prosenkova²⁸ that the solubility of FeMoO_4 is about half that of CaMoO_4 .

TABLE 5. Solubility and Thermodynamic Data at 298.15 K for Selected Molybdates

Equilibrium	K_{sp}	ΔG° , kcal mol ⁻¹	$\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq})$, kcal mol ⁻¹
1. $\text{BaMoO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{MoO}_4^{2-}$ ^a	3.8×10^{-8}	10.1 ± 0.3	-199.8 ± 0.7
2. $\text{SrMoO}_4 \rightleftharpoons \text{Sr}^{2+} + \text{MoO}_4^{2-}$ ^b	2.58×10^{-7}	8.99 ± 0.2	-201.5 ± 1
3. $\text{CaMoO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{MoO}_4^{2-}$ ^c	3.16×10^{-9}	11.6 ± 0.3	-200.1 ± 0.4
4. $\text{Ag}_2\text{MoO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{MoO}_4^{2-}$ ^d	1.7×10^{-12}	16.06 ± 0.2	-199.6 ± 0.5
5. $\text{FeMoO}_4 \rightleftharpoons \text{Fe}^{2+} + \text{MoO}_4^{2-}$ ^e	7.8×10^{-10}	12.4 ± 1.0	-200.7 ± 5.1
Weighted Mean:			-200.0 ± 0.3

^aGibbs energy of formation and solubility product for BaMoO_4 from Ref. 21; Gibbs energy of formation of $\text{Ba}^{2+}(\text{aq})$ from Ref. 22.

^bSolubility product from Ref. 23; Gibbs energies of formation of SrMoO_4 and $\text{Sr}^{2+}(\text{aq})$ from Ref. 22.

^cSolubility product from Ref. 24; Gibbs energy of formation of CaMoO_4 from Ref. 25; Gibbs energy of formation of $\text{Ca}^{2+}(\text{aq})$ from Ref. 22.

^dSolubility product from Ref. 26; Gibbs energies of formation of $\text{Ag}^+(\text{aq})$ and Ag_2MoO_4 from Refs. 18 and 11, respectively.

^eGibbs energies of formation of FeMoO_4 and $\text{Fe}^{2+}(\text{aq})$ calculated from Refs. 11 and 27; for discussion of solubility data, see text.

As can be seen from Table 5, the derived values for $\Delta G_f^\circ(\text{MoO}_4^{2-}, \text{aq})$ form a satisfactorily consistent set, and the weighted mean is very close to that selected by the National Bureau of Standards.¹¹

Similar calculations were carried out for PbMoO_4 ; the results obtained, however, suggest that $\Delta H_f^\circ(\text{PbMoO}_4, \text{c})$ may be erroneous. The determination of $\Delta H_f^\circ(\text{PbMoO}_4, \text{c})$ is based on calorimetric studies²⁹ of enthalpies of precipitation from aqueous lead nitrate solutions, according to

and

We have taken ΔH_f° values for $\text{NO}_3^-(\text{aq})$, $\text{Pb}^{2+}(\text{aq})$, and $\text{Na}^+(\text{aq})$ from Ref. 18, for $\text{MoO}_4^{2-}(\text{aq})$ from Ref. 3, for $\text{Pb}(\text{NO}_3)_2(\text{c})$ from Ref. 30, and for $\text{Na}_2\text{MoO}_4(\text{c})$ from Table 4. Based on Equations VI and VII respectively, we obtain -248.8 and -249.8 kcal mol⁻¹ for $\Delta H_f^\circ(\text{PbMoO}_4)$. The mean value is -249.3 ± 0.9 kcal mol⁻¹, where the uncertainty is the same as that given in the original investigation.²⁹ We calculate ΔS_f° to be $-80.64 \text{ cal K}^{-1} \text{ mol}^{-1}$ from the standard entropies in Refs. 18 and 11 and, thus, $\Delta G_f^\circ(\text{PbMoO}_4, \text{c}, 298.15 \text{ K}) = -225.3 \pm 0.9 \text{ kcal mol}^{-1}$. This result, in combination with the appropriate ΔG_f° values for $\text{Pb}^{2+}(\text{aq})$ and $\text{MoO}_4^{2-}(\text{aq})$, leads to $\Delta G^\circ(298 \text{ K}) = 19.5 \pm 0.4 \text{ kcal mol}^{-1}$ for the solution equilibrium

For K_{sp} , a value of 3.3×10^{-12} has been reported by Skobets *et al.*³¹ and, thus, $\Delta G^\circ(298 \text{ K})$ based on the solubility data is $15.7 \pm 0.2 \text{ kcal mol}^{-1}$. There is, therefore, a discrepancy of about 4 kcal mol⁻¹ between the two results for $\Delta G^\circ(298 \text{ K})$. It could be argued that the solubility product is in error. However, an earlier determination quoted by Busev³² gave 2.5×10^{-11} , which tends to lend credence to the K_{sp} used above. Indeed, for the $\Delta G^\circ(298 \text{ K})$ values to be in agreement, K_{sp} would have to be about 1×10^{-15} , which seems unlikely.

We are therefore inclined to conclude that $\Delta G_f^\circ(\text{PbMoO}_4, \text{c})$ is erroneous and, since $S^\circ(\text{PbMoO}_4, \text{c})$ seems to be satisfactory,²⁷ it appears that $\Delta H_f^\circ(\text{PbMoO}_4, \text{c})$ may be faulty. Since Reactions VI and VII were carried out in acidic media, it is quite probable that unaccounted-for polymolybdate species were formed and, for that reason, the derived $\Delta H_f^\circ(\text{PbMoO}_4)$ would have to be viewed with suspicion. A value of about $-245 \text{ kcal mol}^{-1}$ for ΔH_f° would reconcile the solubility and thermodynamic data. Kubaschewski's²⁷ estimate of $-10.0 \pm 3.5 \text{ kcal mol}^{-1}$ for $\Delta H^\circ(298 \text{ K})$ of the process

gives $\Delta H_f^\circ(\text{PbMoO}_4) = -240.5 \pm 3.5 \text{ kcal mol}^{-1}$, which would tend to support our suggested value.

Thus, in conclusion, well-established values for the basic thermodynamic properties of $\text{MoO}_4^{2-}(\text{aq})$, namely, ΔH_f° ,³ S° ,³³ and ΔG_f° (this work), are now available.

D. Cesium Dimolybdate ($\text{Cs}_2\text{Mo}_2\text{O}_7$)

Substantial quantities of fission-product cesium and molybdenum have been found in the region of the interface between the oxide fuel and the cladding in irradiated fuel pins.³⁴ These elements are thought to be combined in part as cesium orthomolybdate, Cs_2MoO_4 . For this reason, the thermodynamic properties of Cs_2MoO_4 have been determined over a wide temperature range.^{4, 35, 36}

Our current interest in cesium dimolybdate ($\text{Cs}_2\text{Mo}_2\text{O}_7$) stems from the observation³⁷ that at higher (~ 1200 K) temperatures, Cs_2MoO_4 evidently disproportionates to form the dimolybdate and gaseous Cs_2O . The latter decomposes to Cs(g) and $\text{O}_2\text{(g)}$ very rapidly and, so, the overall reaction can be depicted as

A knowledge of ΔG° as a function of temperature for this process would enable the equilibrium constant to be calculated, which in turn would yield the pressures of the gaseous species. The partial pressure of Cs(g) is of particular interest in connection with the distribution of fission products in the fuel pins.

The complete chemical thermodynamic properties are known for all the species in Reaction X with the exception of the dimolybdate. This investigation, regarded as a first step toward providing a similar range of data for $\text{Cs}_2\text{Mo}_2\text{O}_7$, was directed to the determination of the standard enthalpy of formation, ΔH_f° .

It is well known that isopolyanions of molybdenum form readily from the alkali metal molybdates in acid solution. The isopolyanions revert to MoO_4^{2-} in alkaline solution. Accordingly, our determination is based on measurements of the enthalpy of the reaction

In this way, since ΔH_f° values are already available for $\text{Cs}_2\text{MoO}_4\text{(aq)}$, CsOH(aq) , and $\text{H}_2\text{O(l)}$, $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7)$ can be readily deduced.

Cesium dimolybdate was prepared by the reaction of equimolar quantities of cesium orthomolybdate and molybdenum trioxide. The Cs_2MoO_4 was a portion of the sample that had been prepared earlier for low-temperature heat-capacity measurements;³⁵ the MoO_3 was a Merck reagent-grade powder which had been air-dried at 773 K. The two powders were mixed and heated to 823 K in a gold crucible over a 4-hr period. The clear melt was maintained at that temperature for 1 hr before it was cooled slowly to 623 K for approximately 3 hr to crystallize the dimolybdate. The product was annealed at that temperature for 18 hr before cooling to room temperature. It was then crushed to a powder and dried at 573 K before analysis. Chemical and X-ray diffraction analyses of this material showed it to be $\text{Cs}_2\text{Mo}_2\text{O}_7$ of satisfactory purity for calorimetric studies. Minor amounts of Na, K, and Rb were detected by emission spectrography.

Calorimetric specimens were encapsulated, weighed, and introduced into the LKB-8700 solution calorimeter as previously described.^{3,4} Reaction between the $\text{Cs}_2\text{Mo}_2\text{O}_7$ and CsOH was rather slow. Even though dissolution took place quite rapidly, the conversion to MoO_4^{2-} was complete only after a period of about 0.7 hr. No solid residue was ever observed after any of the experiments.

Detailed calorimetric results for the reaction of $\text{Cs}_2\text{Mo}_2\text{O}_7$ with CsOH(aq) are given in Table 6. For the calculation of the impurity correction, Na, K, and Rb were taken to be present as dimolybdates. The enthalpy of formation of $\text{Na}_2\text{Mo}_2\text{O}_7$, $-536.38 \pm 0.33 \text{ kcal mol}^{-1}$, has been reported by Koehler, Pankratz, and Barany,^{1b} and we have estimated ΔH_f° values of -545 ± 2 and $-544 \pm 2 \text{ kcal mol}^{-1}$ for $\text{K}_2\text{Mo}_2\text{O}_7$ and $\text{Rb}_2\text{Mo}_2\text{O}_7$, respectively. Corrections for the other impurities were negligible.

TABLE 6. Calorimetric Results for the Reaction of $\text{Cs}_2\text{Mo}_2\text{O}_7$ with CsOH(aq) ^a

Expt. No. ^b	$m(\text{Cs}_2\text{Mo}_2\text{O}_7)$, g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
1	0.61506	0.08175	434.243	-0.048	-57.79
2	0.61406	0.08020	433.704	-0.048	-56.72
3	0.61505	0.08056	433.372	-0.048	-56.84
4	0.61537	0.08284	434.258	-0.048	-58.54
5	0.61555	0.08281	434.420	-0.048	-58.52
6	0.61480	0.08164	434.075	-0.048	-57.72
8	0.61704	0.08307	434.393	-0.048	-58.56
9	0.61444	0.08209	433.201	-0.048	-57.95

$$\text{Mean } \Delta H_r/M(\text{sample}) = -57.83 \pm 0.26 \text{ J g}^{-1} \text{ }^c$$

$$\text{Impurity correction} = 0.67 \pm 0.19 \text{ J g}^{-1} \text{ }^c$$

$$\Delta H_r/M = -57.16 \pm 0.32 \text{ J g}^{-1} \text{ }^c$$

$$\Delta H_r = -7783 \pm 87 \text{ cal mol}^{-1} \text{ }^{d,e,f}$$

^aIn each experiment, 99.41 cm^3 of CsOH solution was used. The concentration of the solution was $0.218 \text{ mol dm}^{-3}$. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^bExperiment No. 7 was rejected because it deviated excessively from the value for the mean enthalpy of reaction.

^cUncertainty is the standard deviation of the mean.

^dFor conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of $\text{Cs}_2\text{Mo}_2\text{O}_7$ was taken to be $569.69 \text{ g mol}^{-1}$.

^e ΔH_r is for reaction 1 in Table 7.

^fUncertainty is *twice* the standard deviation of the mean.

The thermochemical cycle and enthalpy values on which $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7)$ is based are given in Table 7. The enthalpy of reaction 1, ΔH_1 , is just ΔH_r in Table 6; ΔH_2 is based on a previous determination;⁴ ΔH_3 and ΔH_4 are from Gunn's measurements⁹ of the enthalpy of reaction of cesium with water and the enthalpy of dilution of CsOH(aq) , estimated by analogy with KOH(aq) ;⁸

TABLE 7. Reaction Scheme and Enthalpy Values for Calculation of $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7)^a$

Reaction	ΔH , kcal
1. $\text{Cs}_2\text{Mo}_2\text{O}_7(\text{c}) + 20.128(\text{CsOH} \cdot 253.67 \text{ H}_2\text{O}) = 2(\text{Cs}_2\text{MoO}_4 \cdot 9.064 \text{ CsOH} \cdot 2553.48 \text{ H}_2\text{O})$	-7.78 ± 0.09
2. $2(\text{Cs}_2\text{MoO}_4 \cdot 9.064 \text{ CsOH} \cdot 2553.48 \text{ H}_2\text{O}) = 2 \text{ MoO}_3(\text{c}) + 22.128(\text{CsOH} \cdot 230.70 \text{ H}_2\text{O})$	37.29 ± 0.06
3. $2(\text{CsOH} \cdot 253.67 \text{ H}_2\text{O}) + \text{H}_2(\text{g}) = 2 \text{ Cs}(\text{c}) + 509.34 \text{ H}_2\text{O}(\text{l})$	96.42 ± 0.02
4. $22.128(\text{CsOH} \cdot 230.70 \text{ H}_2\text{O}) + 508.28 \text{ H}_2\text{O}(\text{l}) = 22.128(\text{CsOH} \cdot 253.67 \text{ H}_2\text{O})$	-0.09 ± 0.01
5. $\text{H}_2\text{O}(\text{l}) = \text{H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g})$	68.32 ± 0.01
6. $2 \text{ MoO}_3(\text{c}) = 2 \text{ Mo}(\text{c}) + 3 \text{ O}_2(\text{g})$	356.16 ± 0.16
7. $\text{Cs}_2\text{Mo}_2\text{O}_7(\text{c}) = 2 \text{ Cs}(\text{c}) + 2 \text{ Mo}(\text{c}) = 7/2 \text{ O}_2(\text{g})$	550.32 ± 0.19

^aAll species are in the aqueous phase except where denoted otherwise.

ΔH_5 and ΔH_6 involve the standard enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ ¹⁰ and $\text{MoO}_3(\text{c})$.¹² Addition of ΔH_1 through ΔH_6 gives ΔH_7 , which is simply equal to $-\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7)$. Thus, $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -550.3 \pm 0.2 \text{ kcal mol}^{-1}$. The uncertainty is the square root of the sum of the squares of the uncertainties in Table 7.

There have been no previous experimental values for $\Delta H_f^\circ(\text{Cs}_2\text{Mo}_2\text{O}_7)$. The only other alkali-metal dimolybdate for which there are thermodynamic data is $\text{Na}_2\text{Mo}_2\text{O}_7$; Koehler *et al.*^{1b} determined ΔH_f° based on solution calorimetry, and Weller and Kelley³⁸ reported the heat capacity and entropy from a low-temperature calorimetric study.

In Table 8, ΔH° , ΔS° , and ΔG° are given for several processes involving $\text{Cs}_2\text{Mo}_2\text{O}_7$. Reactions A, B, and C in that table are for the formation of the dimolybdate from its elements and component oxides. However, it is Reaction D that holds most interest for us.

TABLE 8. Thermodynamic Data at 298.15 K for Reactions that Involve $\text{Cs}_2\text{Mo}_2\text{O}_7$

Reaction	$\Delta H^\circ,^a$ kcal mol ⁻¹	$\Delta S^\circ,^b$ cal K ⁻¹ mol ⁻¹	$\Delta G^\circ,$ kcal mol ⁻¹
A. $2 \text{ Cs}(\text{c}) + 2 \text{ Mo}(\text{c}) + 7/2 \text{ O}_2(\text{g}) = \text{Cs}_2\text{Mo}_2\text{O}_7(\text{c})$	-550.3 ± 0.2	-144.7 ± 1.0	-507.2 ± 0.4
B. $\text{Cs}_2\text{O}(\text{c}) + 2 \text{ MoO}_3(\text{c}) = \text{Cs}_2\text{Mo}_2\text{O}_7(\text{c})$	-111.5 ± 0.4	8.9 ± 1.0	-114.2 ± 0.5
C. $\text{Cs}_2\text{MoO}_4(\text{c}) + \text{MoO}_3(\text{c}) = \text{Cs}_2\text{Mo}_2\text{O}_7(\text{c})$	-10.2 ± 0.2	3.2 ± 1.0	-11.2 ± 0.4
D. $2 \text{ Cs}_2\text{MoO}_4 = \text{Cs}_2\text{Mo}_2\text{O}_7 + 2 \text{ Cs}(\text{g}) + 1/2 \text{ O}_2(\text{g})$	210.1 ± 0.3	70.7 ± 1.0	189.0 ± 0.4

^aStandard enthalpies of formation (kcal mol⁻¹) are given in the text or were taken to be as follows: -82.69 ± 0.28 for Cs_2O , Ref. 39; -362.00 ± 0.10 for Cs_2MoO_4 , Ref. 4; and 18.18 ± 0.05 for $\text{Cs}(\text{g})$, Ref. 40(a).

^bStandard entropies (cal K⁻¹ mol⁻¹) were taken to be as follows: 20.33 ± 0.1 and 41.94 ± 0.05 for $\text{Cs}(\text{c})$ and $\text{Cs}(\text{g})$, respectively, Ref. 40(a); 6.85 ± 0.05 for $\text{Mo}(\text{c})$, Ref. 40(b); 49.00 ± 0.01 for $\text{O}_2(\text{g})$, Ref. 41(a); 81.2 ± 1.0 for $\text{Cs}_2\text{Mo}_2\text{O}_7$, estimated; 35.1 ± 0.1 for Cs_2O , Ref. 42; 18.59 ± 0.15 for MoO_3 , Ref. 41(b); and 59.4 ± 0.1 for Cs_2MoO_4 , Ref. 35.

As we indicated earlier, one of the main reasons for the present study was to derive a value for the partial pressure of Cs(g) in Reaction X. If it is assumed that both ΔH° and ΔS° for that reaction are independent of temperature, T, then we may write

$$\Delta G^\circ(T) = 210,100 - 70.7 T \text{ cal mol}^{-1} \quad (\text{XII})$$

Thus, at reactor temperatures, with T estimated to be 1300 K, $\Delta G^\circ(1300 \text{ K}) = 118 \text{ kcal mol}^{-1}$ and $K = 1.5 \times 10^{-20}$, where K is the equilibrium constant. If it is assumed that the partial pressure of Cs(g), p_{Cs} , is four times that of $\text{O}_2(\text{g})$, then it follows that $p_{\text{Cs}}^{5/2} = 3.0 \times 10^{-20} \text{ atm}$ and thus $p_{\text{Cs}} = 1.2 \times 10^{-5} \text{ Torr}$.

In writing Reaction X, we imply that the activities of both Cs_2MoO_4 and $\text{Cs}_2\text{Mo}_2\text{O}_7$ are unity. This is almost certainly not so. However, even with non-unity values for the activities, the partial pressure of Cs(g) would still be rather low--probably of the order of $1 \times 10^{-3} \text{ Torr}$.

II. COMPOUNDS OF THE ALKALI METALS AND URANIUM (P. A. G. O'Hare)

A. Sodium Uranium (V) Trioxide (NaUO_3)

In the $\text{Na} + \text{U} + \text{O}$ system, sodium uranium (V) trioxide (NaUO_3) can coexist in equilibrium with trisodium uranium (V) tetroxide (Na_3UO_4) under certain conditions.⁴³ Reliable thermodynamic data have been reported⁴³⁻⁴⁶ for Na_3UO_4 , which is of interest because it is analogous to the (U, Pu) compound that would form⁴⁷ if sodium coolant in the liquid metal fast breeder reactor (LMFBR) were inadvertently to come into contact with the oxide fuel. Although NaUO_3 apparently would not form in the reactor under the conditions that lead to the formation of Na_3UO_4 , nevertheless, because of its close relationship with Na_3UO_4 , we decided to determine the standard enthalpy of formation, $\Delta H_f^\circ(\text{NaUO}_3)$. For the same reason, we have recently⁴⁸ carried out a similar study of the normal uranate, $\alpha\text{-Na}_2\text{UO}_4$.

There are three values in the literature for $\Delta H_f^\circ(\text{NaUO}_3)$. The first of these⁴⁹ is for a sample that contained about twenty mole percent UO_2 and is stated by the authors to be uncertain by several kcal mol^{-1} . The second value,⁴³ based on a high-temperature mass-spectrometric study, also has a large associated uncertainty. The third value⁵⁰ is about 80 kcal mol^{-1} less negative than the other results. Most of the discrepancy in the latter value has been traced to an arithmetical error.

Thus, there was a necessity for a clear-cut, precise calorimetric study on a pure, well-characterized specimen of NaUO_3 . A significant portion of the present work was devoted to the synthesis and analysis of such a specimen.

Sodium uranium (V) trioxide was synthesized by the reaction of $\alpha\text{-Na}_2\text{UO}_4$ with UO_2 , as reported by Rüdorff and Leutner.⁵¹ The α -sodium uranate was prepared by heating reagent-grade Na_2CO_3 with α -uranyl hydroxide,⁴⁸ and the uranium dioxide by reducing U_3O_8 with hydrogen at 1073 K. The uranium-bearing starting materials were shown by spectroscopic analyses to contain less than 100 ppm of any other metallic impurities.

Subsequent steps in the preparation of NaUO_3 were performed in a dry nitrogen atmosphere. The $\alpha\text{-Na}_2\text{UO}_4$ and UO_2 were mixed and thoroughly ground in an agate mortar, then loaded into a platinum boat which was placed in a Vycor tube and heated for 24 hr at 1023 K. The product was reground and reheated twice to insure complete reaction.

An X-ray diffraction powder pattern of the final product showed no detectable unreacted UO_2 , and the infrared spectrum gave no evidence for the presence of either Na_2UO_4 or $\text{Na}_2\text{U}_2\text{O}_7$.⁵²

The preparation was analyzed for total sodium and uranium. Sodium was determined by precipitation with magnesium uranyl acetate, and the uranium was determined by conversion to U(IV) in a lead reductor, followed by titration with standardized ceric sulfate. The results obtained, 7.40 mass percent for sodium (theoretical, 7.44 mass percent), and 76.57 mass percent for uranium (theoretical, 77.03 mass percent), correspond to a Na-to-U molar ratio of (1.001 ± 0.003) . A total of (300 ± 150) ppm by mass of miscellaneous metallic impurities was detected by emission spectroscopic examination.

On the basis of the X-ray diffraction, infrared spectroscopic, and analytical evidence, the NaUO_3 preparation was deemed to be sufficiently pure for calorimetric study.

Magnetic measurements⁵³ have shown the presence of U(V) ions in NaUO_3 . It is well known that U(V) readily disproportionates in aqueous media to U(IV) and U(VI); the U(IV) can be easily oxidized to U(VI). On that basis, for the calorimetric phase of the present work, it was decided to react NaUO_3 with an aqueous mixture of HCl (solvent) and XeO_3 (oxidant), both of which were in large stoichiometric excess. As pointed out previously,⁴⁴ XeO_3 has a pragmatic advantage as oxidant inasmuch as it yields xenon gas as the sole reaction by-product. In our study, the overall calorimetric process can be represented as

The completeness of the reaction as written was verified by iodometric titration of the XeO_3 remaining after the experiments. No unreacted NaUO_3 was ever observed after the calorimetric measurements.

Auxiliary determinations of the enthalpies of solution of NaCl, UO_2Cl_2 , and $\text{XeO}_3(\text{aq})$ in the acid medium were also required.

The calorimetric phase of the experimental procedure involved measurements of the energy released or absorbed after ampoules containing either NaUO_3 , NaCl, UO_2Cl_2 , or $\text{XeO}_3(\text{aq})$ were broken in the reaction vessel and their contents had reacted with or dissolved in the appropriate solution. Detailed calorimetric data for the three sets of measurements performed in the present study are in Tables 9, 10, and 11, and the overall reaction scheme (including the appropriate enthalpy values) on which $\Delta H_f^\circ(\text{NaUO}_3)$ is based, is given in Table 12.

Because of the low level of metallic contaminants in the NaUO_3 and NaCl, no impurity corrections were required. The considerations that led to the assignment of the impurity correction for UO_2Cl_2 (Table 11) have been discussed elsewhere.⁴⁴

By addition of the enthalpies of reaction (or solution) for items 1 through 10 in Table 12, one obtains $-\Delta H_f^\circ(\text{NaUO}_3)$. Enthalpy values for processes 1, 3, and 4 have been taken directly from Tables 9, 10, and 11. We found that ΔH for the mixing process depicted in reaction 2 was indistinguishable from the enthalpy of dilution that one would calculate if the XeO_3 moiety were omitted entirely; thus, ΔH for 2 has been based on Parker's dilution data⁸ for HCl. Similarly, ΔH for 5 has been computed as if only dilution of HCl were involved. Finally, the enthalpies of processes 6 through 10 are based on the ΔH_f° values for $\text{HCl}(\text{aq})$,¹⁸ $\text{XeO}_3(\text{aq})$,⁵⁴ $\text{H}_2\text{O}(\text{l})$,¹⁰ NaCl, and UO_2Cl_2 .⁴⁴ For NaCl, ΔH_f° has been calculated by combining (kcal mol^{-1}) $\Delta H_f^\circ(\text{Na}^+, \text{aq}) = -57.39 \pm 0.02$ ¹⁸ and $\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = -39.95 \pm 0.02$ ¹⁸ (uncertainties have been estimated) together with Parker's⁸ value, $0.93 \pm 0.01 \text{ kcal mol}^{-1}$, for the enthalpy of solution of NaCl. Thus, $\Delta H_f^\circ(\text{NaUO}_3, \text{c}, 298.15 \text{ K}) = -357.5 \pm 0.8 \text{ kcal mol}^{-1}$.

TABLE 9. Calorimetric Results for the Reaction Between NaUO_3 and an Aqueous Mixture of HCl and XeO_3 ^a

Expt. No.	m(NaUO_3), g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
1	0.09913	0.17330	428.01	-0.055	-748.80
2	0.10103	0.17688	428.07	-0.055	-750.00
3	0.10030	0.17625	428.00	-0.055	-752.64
4	0.10072	0.17640	427.68	-0.055	-749.58
5	0.10075	0.17664	427.89	-0.055	-750.74
6	0.09995	0.17447	427.96	-0.055	-747.58
7	0.10022	0.17438	430.39	-0.055	-749.41
8	0.10007	0.17463	428.60	-0.055	-748.49

$$\text{Mean } \Delta H_r/M(\text{sample}) = -749.65 \pm 0.55 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = -55367 \pm 80 \text{ cal mol}^{-1} \text{ }^{c,d}$$

^aIn each experiment, 99.41 cm³ of the aqueous mixture was used of which 20 cm³ was 0.02 mol dm⁻³ $\text{XeO}_3(\text{aq})$. The mean temperature of each experiment was 298.15 ± 0.01 K.

^bUncertainty is the standard deviation of the mean.

^cFor conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of NaUO_3 was taken to be 309.017 g mol⁻¹.

^dUncertainty is *twice* the standard deviation of the mean.

TABLE 10. Calorimetric Results for the Solution of NaCl in Aqueous ($\text{HCl} + \text{XeO}_3$)^a

Expt. No.	m(NaCl), g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
1	0.01907	-0.00424	423.00	-0.056	91.14
2	0.01911	-0.00421	421.84	-0.056	90.01
3	0.01910	-0.00408	438.00	-0.056	90.63
4	0.01892	-0.00412	432.41	-0.056	91.23
5	0.02625	-0.00563	429.45	-0.056	89.98

$$\text{Mean } \Delta H_r/M(\text{sample}) = 90.60 \pm 0.27 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = 1265 \pm 7 \text{ cal mol}^{-1} \text{ }^{c,d}$$

^aIn each experiment, 99.41 cm³ of the aqueous mixture (Soln B in Table 12) was used, and the mean temperature of the experiments was 298.15 ± 0.01 K.

^bUncertainty is the standard deviation of the mean.

^cFor the conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of NaCl was taken to be 58.443.

^dUncertainty is *twice* the standard deviation of the mean.

TABLE 11. Calorimetric Results for the Solution of UO_2Cl_2 in Aqueous ($\text{HCl} + \text{XeO}_3 + \text{NaCl}$)^a

Expt. No.	m(UO_2Cl_2), g	$\Delta\theta_c$, K	$\langle\varepsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
1	0.10619	0.06738	422.77	-0.055	-268.77
2	0.10804	0.06880	423.41	-0.055	-270.14
3	0.10799	0.06698	431.55	-0.055	-268.17
4	0.10885	0.06818	431.45	-0.055	-270.75
5	0.11019	0.06954	431.74	-0.055	-272.96

$$\text{Mean } \Delta H_r/M(\text{sample}) = -270.16 \pm 0.84 \text{ J g}^{-1} \text{ }^b$$

$$\text{Impurity correction} = -8.03 \pm 0.19 \text{ J g}^{-1} \text{ }^{b,c}$$

$$\Delta H_r/M(\text{UO}_2\text{Cl}_2) = -278.19 \pm 0.86 \text{ J g}^{-1} \text{ }^{d,e}$$

$$\Delta H_r = -22668 \pm 140 \text{ cal mol}^{-1}$$

^aIn each experiment, 99.41 cm³ of mixture was used, and the mean temperature of the experiments was 298.15 ± 0.01 K.

^bUncertainty is the standard deviation of the mean.

^cFor the calculation of the impurity correction, see Ref. 44.

^dFor the conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of UO_2Cl_2 was taken to be 340.934 g mol⁻¹.

^eUncertainty is *twice* the standard deviation of the mean.

TABLE 12. Reaction Scheme for Calculation of $\Delta H_f^\circ(\text{NaUO}_3)$ ^a

Reaction	ΔH , kcal
1. $\text{NaUO}_3(\text{c}) + 12.07(\text{XeO}_3 \cdot 2746.70 \text{ H}_2\text{O}) + 349.78(\text{HCl} \cdot 37.85 \text{ H}_2\text{O})$ = $(\text{Na}^+ + \text{UO}_2^{2+} + 3\text{Cl}^-) \cdot \text{Soln A} + 0.17\text{Xe}(\text{g})$	-55.37 ± 0.08
2. $\text{Soln B} = 11.90(\text{XeO}_3 \cdot 2746.70 \text{ H}_2\text{O}) + 346.78(\text{HCl} \cdot 37.85 \text{ H}_2\text{O})$	0.10 ± 0.02
3. $(\text{Na}^+ + \text{Cl}^-) \cdot \text{Soln B} = \text{NaCl}(\text{c}) + \text{Soln B}$	-1.26 ± 0.01
4. $(\text{Na}^+ + \text{UO}_2^{2+} + 3\text{Cl}^-) \cdot \text{Soln B} = \text{UO}_2\text{Cl}_2(\text{c}) + (\text{Na}^+ + \text{Cl}^-) \cdot \text{Soln B}$	22.67 ± 0.14
5. $(\text{Na}^+ + \text{UO}_2^{2+} + 3\text{Cl}^-) \cdot \text{Soln A} = (\text{Na}^+ + \text{UO}_2^{2+} + 3\text{Cl}^-) \cdot \text{Soln B} + 581.99 \text{ H}_2\text{O}(\text{l})$	0.54 ± 0.05
6. $3/2 \text{ H}_2(\text{g}) + 3/2 \text{ Cl}_2(\text{g}) + 113.55 \text{ H}_2\text{O}(\text{l}) = 3(\text{HCl} \cdot 37.85 \text{ H}_2\text{O})$	-118.31 ± 0.06
7. $0.17\text{Xe}(\text{g}) + 0.26 \text{ O}_2(\text{g}) + 466.94 \text{ H}_2\text{O}(\text{l}) = 0.17(\text{XeO}_3 \cdot 2746.70 \text{ H}_2\text{O})$	16.99 ± 0.04
8. $3/2 \text{ H}_2\text{O}(\text{l}) = 3/2 \text{ H}_2(\text{g}) + 3/4 \text{ O}_2(\text{g})$	102.47 ± 0.02
9. $\text{NaCl}(\text{c}) = \text{Na}(\text{c}) + 1/2 \text{ Cl}_2(\text{g})$	98.27 ± 0.03
10. $\text{UO}_2\text{Cl}_2(\text{c}) = \text{U}(\text{c}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g})$	291.37 ± 0.81
11. $\text{NaUO}_3(\text{c}) = \text{Na}(\text{c}) + \text{U}(\text{c}) + 3/2 \text{ O}_2(\text{g})$	357.47 ± 0.83

^aAll species are in the aqueous phase except where denoted otherwise.

As we have mentioned earlier, there have been three previous determinations of the enthalpy of formation of NaUO_3 . King, Siemens, and Richardson⁴⁹ used a solution calorimetric technique in which the reaction medium consisted of a mixture of HClO_4 and $\text{Ce}(\text{ClO}_4)_4$. Two preparations of NaUO_3 were studied, and each one contained about 20 mole percent of UO_2 . Based on experiments with each sample, values of -355.5 and $-356.6 \text{ kcal mol}^{-1}$ were obtained for $\Delta H_f^\circ(\text{NaUO}_3)$. A tentative result, $-357 \text{ kcal mol}^{-1}$, was selected; it is stated to be uncertain by several kcal mol^{-1} because of the compositional problems. Nevertheless, the agreement with the present determination is satisfactory.

Cordfunke and Loopstra⁵⁰ also reported $\Delta H_f^\circ(\text{NaUO}_3)$ based on solution calorimetry. They used $\text{H}_2\text{SO}_4 + \text{Ce}(\text{SO}_4)_2$ as a reaction medium and deduced $\Delta H_f^\circ(\text{NaUO}_3) = -273.4 \text{ kcal mol}^{-1}$. We rechecked their calculations and found an error (confirmed by Dr. Cordfunke) in the summation of the enthalpies of the following reactions:

Upon combination of the above equations with ΔH_f° values for U_3O_8 ,⁵⁵ H_2O ,¹⁰ $\text{Na}^+(\text{aq})$,¹⁸ and $\beta\text{-UO}_3$,⁵⁶ one derives $\Delta H_f^\circ(\text{NaUO}_3) = -356.7 \pm 1.9 \text{ kcal mol}^{-1}$, in good agreement with the present determination.

Battles, Shinn, and Blackburn⁴³ carried out a mass-spectrometric investigation of the $\text{Na} + \text{U} + \text{O}$ system and reported $\Delta H_f^\circ(\text{NaUO}_3)$ to be $-344.2 \pm 4.2 \text{ kcal mol}^{-1}$ at 1000 K; this result is not expected to change appreciably when referred to 298.15 K. For strict comparison with the calorimetric values, the uncertainty for the 1000 K value should be doubled. In view of the approximations that had to be made by Battles *et al.*, the disagreement with the calorimetric determinations is surprisingly small.

In Table 13, we have given thermodynamic data at 298.15 K for some reactions that involve NaUO_3 . Unfortunately, we do not have the enthalpy increments to convert the values to the higher temperatures at which these processes are of most interest. Nevertheless, the Gibbs energies in Table 13 indicate that NaUO_3 is a rather stable compound. Indeed, Cordfunke and Loopstra⁵⁰ found that, even at 1273 K in an inert atmosphere, NaUO_3 decomposed only slowly. They also reported that air oxidation to $\text{Na}_2\text{U}_2\text{O}_7$ took place only at temperatures above 600 K. However, the thermodynamic data suggest that NaUO_3 should oxidize even at room temperature. Evidently, at this temperature, the rate of oxidation is exceedingly low.

TABLE 13. Thermodynamic Data at 298.15 K for Reactions Involving NaUO₃

REACTION	$\Delta H^\circ,^a$ kcal mol ⁻¹	$\Delta S^\circ,^b$ cal K ⁻¹ mol ⁻¹	$\Delta G^\circ,$ kcal mol ⁻¹
Na(c) + U(c) + 3/2 O ₂ (g) = NaUO ₃ (c)	-357.5 ± 0.8	-67.6 ± 3.0	-337.3 ± 1.2
1/2 Na ₂ O(c) + 1/2 UO ₂ (c) + 1/2 γ-UO ₃ (c) = NaUO ₃ (c)	-31.6 ± 0.9	0.1 ± 3.0	-31.6 ± 1.3
NaUO ₃ (c) + Na ₂ O(c) = Na ₃ UO ₄ (c)	-21.1 ± 1.2	-0.6 ± 3.0	-20.9 ± 1.5
1/2 Na ₂ UO ₄ (c) + 1/2 UO ₂ (c) = NaUO ₃ (c)	-5.1 ± 0.9	0.9 ± 3.0	-5.4 ± 1.3
2NaUO ₃ (c) + 1/2 O ₂ (g) = Na ₂ U ₂ O ₇ (c)	-45.0 ± 4.1	-22.3 ± 6.7	-38.4 ± 4.6

^aStandard enthalpies of formation (kcal mol⁻¹) and their sources are as follows: Na₂O, -99.14 ± 0.07, Ref. 14; UO₂, -259.3 ± 0.2, Ref. 55; γ-UO₃, -293.5 ± 1.0, Ref. 57; Na₃UO₄, -477.7 ± 0.9, Ref. 44; Na₂UO₄, -445 ± 0.9, Ref. 48; Na₂U₂O₇, -760 ± 3.8, Ref. 50.

^bStandard entropies (cal K⁻¹ mol⁻¹) and their sources are as follows: Na, 12.24 ± 0.1, Ref. 18; U, 12.0 ± 0.1, Ref. 58; O₂, 49.00 ± 0.01, Ref. 18; Na₂O, 17.9 ± 0.1, Ref. 59; UO₂, 18.6 ± 0.1, Ref. 58; γ-UO₃, 23.6 ± 0.1, Ref. 58; Na₃UO₄, 47.4 ± 0.1, Ref. 45; Na₂UO₄, 39.68 ± 0.04, Ref. 60. In addition, S°(298 K) values of 30.1 ± 3 and 62.4 ± 3 cal K⁻¹ mol⁻¹ have been estimated for NaUO₃ and Na₂U₂O₇, respectively.

B. Uranates of Lithium, Potassium, and Rubidium

About twelve years ago, Ippolitova, Faustova, and Spitsyn⁶¹ described a thermochemical study of the five alkali metal monouranates, M₂UO₄. They determined the standard enthalpies of formation from calorimetric measurements of the enthalpies of reaction with aqueous hydrochloric acid. Recently, however, results obtained by Cordfunke and Loopstra and the present authors for both α-Na₂UO₄^{48,50} and Cs₂UO₄⁶² have disagreed with those obtained by Ippolitova *et al.* There was reason to believe, therefore, that the data for the other uranates might also be suspect, and it was decided to redetermine ΔH_f° not only for Rb₂UO₄, which was of immediate interest to us, but also for α-Li₂UO₄ and K₂UO₄. Toward this end, the enthalpies of reaction with aqueous hydrochloric acid of carefully prepared and characterized specimens of the uranates were measured in a solution calorimeter. Auxiliary enthalpies of solution in acid of the corresponding alkali metal chlorides and of uranyl chloride were also determined.

Our interest in Rb₂UO₄ stems from the likelihood that, by analogy with Cs₂UO₄,⁶² it could be formed as a result of the interaction between fission-product rubidium⁶³ and the uranium-plutonium oxide in nuclear reactor fuel pins. Thus, a reliable determination of ΔH_f° (Rb₂UO₄) would be of value in helping to unravel the complex chemistry of irradiated fuels. Although neither Li₂UO₄ nor K₂UO₄ plays a role in reactor-fuel chemistry, nevertheless we decided to determine their enthalpies of formation in order to complete a careful, systematic study of the alkali metal uranates.

Lithium and potassium uranate were prepared by reaction of the alkali-metal carbonates with U₃O₈, while rubidium uranate was prepared from the nitrate. The uranates obtained by these methods were subjected to careful chemical analyses for both total uranium and total alkali-metal content. Emission spectrochemical examinations were also performed. The results obtained are given in Table 14. Lithium and rubidium in Li₂UO₄ and Rb₂UO₄ were determined as the sulfates, and uranium as U₃O₈, by the procedures given in Refs. 62 and 3. For K₂UO₄, potassium was determined by precipitation as the chloroplatinate and uranium by titration with ceric sulfate after reduction to U(IV).

TABLE 14. Analytical Results for the Uranates (M_2UO_4)

M	U, mass percent		M, mass percent		Trace metals, mass percent ^b	Molar ratio M/U
	Found ^a	Calculated	Found ^a	Calculated		
Li	75.35	75.35	4.39	4.39	0.012	1.997 ± 0.005
K	62.70	62.60	20.59	20.57	0.048	1.999 ± 0.005
Rb	50.38	50.33	36.16	36.14	0.043	1.999 ± 0.005

^aAverage of duplicate analyses run in tandem with blanks and standard mixtures containing U and M. Analytical uncertainty is ±0.1 percent.

^bDetermined by emission spectroscopy. Results are estimated to be accurate to within an order of magnitude. The predominant metallic impurities are other alkali metals.

The only significant (≥ 100 ppm by mass) impurity, apart from other alkali metals revealed by emission spectrographic analysis was Si, 300 ppm by mass, in the K_2UO_4 . Extraneous alkali metals totalled (ppm by mass) 50 in Li_2UO_4 , 110 in K_2UO_4 , and 350 in Rb_2UO_4 .

Reactions of the uranates with hydrochloric acid proceed as follows in the calorimeter:

The measured enthalpies of Reaction XVII are given in Table 15. In addition, the enthalpies of solution of UO_2Cl_2 in acid and of MCl in the ($HCl + UO_2Cl_2$) mixture had also to be determined; these results are also to be found in Table 15 (processes 2 and 3, respectively). All the other auxiliary data for processes 4 through 10 have been taken from the literature. Uncertainties in the individual values for $\Delta H_f^\circ(M_2UO_4)$, process 11, were calculated by taking the square root of the sum of the squares of the uncertainties of each of the component enthalpies of reaction and solution.

Ippolitova, Faustova, and Spitsyn⁶¹ reported the enthalpies of reaction of the alkali-metal uranates with approximately 1 mol dm^{-3} HCl ; for Li_2UO_4 they obtained -47.27 ± 0.12 ; for K_2UO_4 , -33.72 ± 0.10 ; and for Rb_2UO_4 , -33.42 ± 0.05 kcal mol⁻¹. The values deviate significantly from those given in Table 15. Similar discrepancies were found recently for α - Na_2UO_4 ⁴⁸ and Cs_2UO_4 ,⁶² for which the above authors obtained enthalpies of reaction of -23.05 ± 0.09 and -45.40 ± 0.17 kcal mol⁻¹, respectively.

One would expect the enthalpies of reaction of all five uranates to be within a few kcal mol⁻¹ of each other, as we have found. The results of Ippolitova *et al.*, on the other hand, show a spread of about 24 kcal mol⁻¹. Their analytical data appear to be satisfactory, although the Li-to-U ratio for Li_2UO_4 is disturbingly high at 2.05. However, we are unable to give a comprehensive reassessment of this work because of the paucity of experimental data and other details. We are led to the tentative conclusion that the samples were probably inadequate for reliable calorimetric studies. This conclusion is buttressed by the recent findings of Osborne *et al.*⁶⁰ that the heat capacity of a specimen of α - Na_2UO_4 prepared⁶⁵ by a technique identical to that used by Ippolitova *et al.* was about 20 percent in error.

TABLE 15. Reaction Scheme and Enthalpy Values for Calculation of $\Delta H_f^\circ(\text{M}_2\text{UO}_4)$ ^a

Reaction	ΔH , kcal M		
	Li	K	Rb
1. $(2\text{M}^+ \cdot \text{UO}_2^{2+} \cdot 4\text{Cl}^-) \cdot 183.80$ (HCl $\cdot$ 55.572 H ₂ O) = $\text{M}_2\text{UO}_4(\text{c}) + 187.80$ (HCl $\cdot$ 54.378 H ₂ O)	41.77 ± 0.02^b	42.07 ± 0.05^b	41.30 ± 0.05^b
2. $\text{UO}_2\text{Cl}_2(\text{c}) + 183.80$ (HCl $\cdot$ 55.572 H ₂ O) = $(\text{UO}_2^{2+} \cdot 2\text{Cl}^-) \cdot 183.80$ (HCl $\cdot$ 55.572 H ₂ O)	-22.49 ± 0.13^b	-22.49 ± 0.13^b	-22.49 ± 0.13^b
3. $2\text{MCl}(\text{c}) + (\text{UO}_2^{2+} \cdot 2\text{Cl}^-) \cdot 183.80$ (HCl $\cdot$ 55.572 H ₂ O) = $(2\text{M}^+ \cdot \text{UO}_2^{2+} \cdot 4\text{Cl}^-) \cdot 183.80$ (HCl $\cdot$ 55.572 H ₂ O)	-16.38 ± 0.03^b	8.61 ± 0.03^b	8.30 ± 0.02^b
4. 4 (HCl $\cdot$ 55.572 H ₂ O) = $2 \text{H}_2(\text{g}) + 2\text{Cl}_2(\text{g}) + 222.288 \text{H}_2\text{O}(1)$	158.11 ± 0.09^c	158.11 ± 0.09^c	158.11 ± 0.09^c
5. 187.80 (HCl $\cdot$ 54.378 H ₂ O) + $224.233 \text{H}_2\text{O}(1)$ = 187.80 (HCl $\cdot$ 55.572 H ₂ O)	-1.05 ± 0.05^d	-1.05 ± 0.05^d	-1.05 ± 0.05^d
6. $\text{U}(\text{c}) + \text{O}_2(\text{g}) + \text{Cl}_2(\text{g}) = \text{UO}_2\text{Cl}_2(\text{c})$	-291.37 ± 0.81^e	-291.37 ± 0.81^e	-291.37 ± 0.81^e
7. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{H}_2\text{O}(1)$	-136.63 ± 0.02^f	-136.63 ± 0.02^f	-136.63 ± 0.02^f
8. $2\text{M}^+(\text{aq}, \underline{m} = 1) + 2\text{Cl}^-(\text{aq}, \underline{m} = 1) = 2\text{MCl}(\text{c})$	17.70 ± 0.10^g	-8.23 ± 0.02^g	-8.26 ± 0.15^g
9. $2\text{M}(\text{c}) = 2\text{M}^+(\text{aq}, \underline{m} = 1)$	-133.10 ± 0.04^h	-120.54 ± 0.05^h	-120.04 ± 0.06^h
10. $\text{Cl}_2(\text{g}) = 2\text{Cl}^-(\text{aq}, \underline{m} = 1)$	-79.87 ± 0.04^i	-79.87 ± 0.04^i	-79.87 ± 0.04^i
11. $2\text{M}(\text{c}) + \text{U}(\text{c}) + 2\text{O}_2(\text{g}) = \text{M}_2\text{UO}_4(\text{c})$	-463.31 ± 0.84	-451.39 ± 0.83	-452.00 ± 0.85

^aAll species are in the aqueous phase except where denoted otherwise.

^bMeasured in present investigation.

^cCalculated from $\Delta H_f^\circ(\text{Cl}^-, \text{aq}, \underline{m} = 1)$, Ref. 10, and dilution data from Ref. 8.

^dDilution data from Ref. 8.

^e $\Delta H_f^\circ(\text{UO}_2\text{Cl}_2, \text{c})$ from Ref. 44.

^f $\Delta H_f^\circ(\text{H}_2\text{O}, 1)$ from Ref. 10.

^gEnthalpies of solution from Ref. 8.

^h $\Delta H_f^\circ(\text{M}^+, \text{aq}, \underline{m} = 1)$ from Ref. 64.

ⁱ $\Delta H_f^\circ(\text{Cl}^-, \text{aq}, \underline{m} = 1)$ from Ref. 10.

C. Thermodynamic Data for Formation of the Alkali-Metal Uranates

In Table 16, we have collected together values of ΔH° , ΔS° , and ΔG° for formation of the alkali-metal uranates from the elements and component oxides at 298.15 K. The values in Table 16 indicate that Li_2UO_4 is the most stable member of the series. The data in this table are qualitatively in harmony with the findings of Efremova *et al.*,⁶⁶ who studied the thermal decomposition of the uranates at elevated temperatures. The trend in the thermodynamic stabilities of the uranates parallels very closely that for the alkali-metal molybdates (see Section IB of this report) but does not appear to be influenced by the size of the cations as suggested by Efremova *et al.*

D. Thermochemical Studies on Cesium Diuranate ($\text{Cs}_2\text{U}_2\text{O}_7$)

As a first step toward establishing reliable thermodynamic data for the high-temperature decomposition of cesium monouranate according to the reaction:

the standard enthalpy of formation of cesium diuranate, $\text{Cs}_2\text{U}_2\text{O}_7$, is being determined by solution calorimetry.

TABLE 16. Enthalpies (kcal mol^{-1}), Entropies ($\text{cal K}^{-1} \text{mol}^{-1}$), and Gibbs Energies (kcal mol^{-1}) for Formation of the Alkali-Metal Uranates at 298.15 K

M	$2\text{M}(\text{c}) + \text{U}(\text{c}) + 2\text{O}_2(\text{g}) = \text{M}_2\text{UO}_4(\text{c})$			$\text{M}_2\text{O}(\text{c}) + \gamma\text{-UO}_3(\text{c}) = \text{M}_2\text{UO}_4(\text{c})$		
	$\Delta H^\circ{}^a$	$\Delta S^\circ{}^b$	ΔG°	$\Delta H^\circ{}^a$	$\Delta S^\circ{}^b$	ΔG°
Li	-463.31 ± 0.84	-92.3 ± 1.7	-435.8 ± 1.0	-26.7 ± 1.4	-1.0 ± 1.5	-26.4 ± 1.5
Na	-445.56 ± 0.85	-94.8 ± 0.1	-417.3 ± 0.9	-52.9 ± 1.3	-1.9 ± 0.1	-52.3 ± 1.3
K	-451.39 ± 0.83	-97.8 ± 1.5	-422.2 ± 0.9	-71.1 ± 1.4	-5.9 ± 1.8	-69.3 ± 1.5
Rb	-452.00 ± 0.85	-98.2 ± 1.5	-422.7 ± 1.0	-75.7 ± 1.6	-6.3 ± 1.8	-73.8 ± 1.7
Cs	-453.46 ± 0.85	-98.8 ± 1.5	-424.0 ± 1.0	-77.3 ± 1.3	-6.8 ± 1.5	-75.3 ± 1.4

^a ΔH_f° for Li_2UO_4 , K_2UO_4 , and Rb_2UO_4 from present research and for $\alpha\text{-Na}_2\text{UO}_4$ and Cs_2UO_4 from Refs. 48 and 62, respectively. For Li_2O , Na_2O , K_2O , Rb_2O , and Cs_2O , ΔH_f° values have been taken from the sources given in footnote a of Table 4, and $\Delta H_f^\circ(\gamma\text{-UO}_3)$ is from Ref. 57.

^b S° values for the alkali metals, their oxides, and O_2 have been taken from the sources given in footnote b of Table 4; and $S^\circ(\text{U})$ and $S^\circ(\gamma\text{-UO}_3)$ are from Ref. 58. In addition, S° ($\text{cal K}^{-1} \text{mol}^{-1}$), has been estimated for the following compounds: Li_2UO_4 , 31.7 ± 1.5 ; K_2UO_4 , 43.1 ± 1.5 ; Rb_2UO_4 , 48.5 ± 1.5 ; Cs_2UO_4 , 51.9 ± 1.5 ; K_2O , 25.4 ± 1.0 ; and Rb_2O , 31.2 ± 1.0 .

III. LITHIUM NITRIDE AND LITHIUM OXIDE (G. K. Johnson and P. A. G. O'Hare)

Lithium metal has potential use as a blanket material in fusion reactors.⁶⁷ In this connection, information concerning the effect of dissolved impurities on the compatibility of liquid lithium with likely materials of construction is important. Lithium nitride, Li_3N , and lithium oxide, Li_2O , which form by spontaneous combination of the elements, are common contaminants in lithium and have a significant deleterious effect on alloys and ceramics⁶⁸ that are being considered in the design of fusion reactors. Accordingly, reliable thermodynamic data for Li_3N and Li_2O would be helpful for the prediction and interpretation of their interactions with other materials.

A. Lithium Nitride (Li_3N)

Although two values for the standard enthalpy of formation of Li_3N , $\Delta H_f^\circ(\text{Li}_3\text{N}, c, 298.15 \text{ K})$, ostensibly in agreement with each other, were available, we decided that this property needed redetermination. This decision was based on the probability that one of the earlier studies⁶⁹ had been carried out on samples of questionable purity, and that the other study,⁷⁰ which yielded incorrect ΔH_f° values for other metallic nitrides, might likewise have yielded an erroneous value for Li_3N .

Our result for $\Delta H_f^\circ(\text{Li}_3\text{N})$ is derived from two different thermochemical cycles based on measurements of the enthalpies of reaction of Li_3N with HCl(aq) and H_2O according to

and

Measurements of the enthalpies of solution of LiCl(c) and $\text{NH}_4\text{Cl(c)}$ in both HCl(aq) and LiOH(aq) were also performed.

It is difficult to prepare and maintain lithium nitride in a high-purity form because it reacts readily with air and moisture and is easily oxidized. The method of synthesis chosen was the direct combination of high-purity lithium and nitrogen at about 9 atm pressure, in a closed system.⁷¹ The lithium (Foote Mineral Co., Exton, Pa.) was shown by mass-spectrometric examination to have a Li^6/Li^7 ratio of 0.0815 ± 0.0007 and, therefore, its atomic weight was 6.934 ± 0.001 .

Spherules of lithium were placed in a stainless steel cup which was then inserted in a furnace tube, and a second cup containing freshly poured sodium to act as an oxygen getter was placed above the lithium. The lid was then bolted to the furnace tube. All of the preceding operations were carried out in a glovebox filled with dry, high-purity recirculating helium.

Next, the furnace-tube assembly was removed from the glovebox, attached to a manifold, evacuated, and charged with nitrogen (Liquid Air Inc., "Ultra High Purity" grade) to a pressure of 8.8 atm. The nitrogen and lithium

combined spontaneously, and reaction had virtually ceased after about 4 hr. However, to ensure complete reaction, the nitrogen pressure was maintained at its original value for a further 24 hr. Based on the total charge of lithium and the mass of product formed, the Li-to-N ratio was calculated to be 3.006. The product was then ground in a stainless steel apparatus in the glovebox.

Analytical determinations of the lithium and nitrogen contents of the preparation were based on the spontaneous hydrolysis of Li_3N to LiOH and NH_3 . A weighed sample was placed in a distillation apparatus in a glovebox, the apparatus was removed from the box, and a stream of dry argon was passed through the system while distilled water was added dropwise. The ammonia was collected in boric acid. After cessation of hydrolysis, the solution was boiled to ensure the complete removal of dissolved ammonia. The collected ammonia and the lithium hydroxide in the distillation flask were then determined by titration. The analytical results were as follows: Li, 59.84 ± 0.11 mass percent; N, 39.76 ± 0.10 mass percent.

Based on fast-neutron activation analysis, the oxygen content was found to be 0.59 ± 0.05 mass percent. Gas-chromatographic analyses indicated a carbon (as carbonate) level below 5 ppm, and the only significant trace metals found by emission and mass-spectrographic analyses were (in ppm): Na(3), Mg(14), Si(25), Ca(10), and K(3). The calorimetric specimen thus contained 98.72 ± 0.11 mole percent Li_3N and 1.28 ± 0.11 mole percent Li_2O , based on the assumption that the oxygen was present solely as Li_2O . This composition agrees satisfactorily with the analyses for Li and N.

Calorimetric measurements were carried out as described in the preceding section of this report. The results of the reactions of Li_3N with HCl(aq) and with LiOH(aq) are given in Tables 17 and 18, respectively.

TABLE 17. Calorimetric Results for Reaction of Li_3N with HCl(aq) ^a

Expt. No.	m, g	$\Delta\theta_c$, K	$\langle \epsilon(\text{calor}) \rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
Li_3N - 1	0.02417	1.26283	438.620	-0.056	-22919.2
- 2	0.02457	1.28409	438.730	-0.056	-22931.4
- 3	0.02462	1.28609	438.447	-0.056	-22905.7
- 4	0.02521	1.31998	438.497	-0.056	-22961.6
- 5	0.02509	1.30996	438.375	-0.056	-22890.0
- 6	0.02514	1.31241	438.475	-0.056	-22892.4

$$\text{Mean } \Delta H_r/M(\text{sample}) = -22916.7 \pm 11.0 \text{ J g}^{-1} \text{ }^b$$

$$\text{Impurity correction} = -166.1 \pm 14.0 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r/M(\text{Li}_3\text{N}) = -23082.8 \pm 17.8 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = -192.04 \pm 0.30 \text{ kcal mol}^{-1} \text{ }^{c,d}$$

^aIn each experiment, 99.41 cm³ of 0.1M HCl was used.

^bStandard deviation of the mean.

^cTo convert $\Delta H_r/M(\text{Li}_3\text{N})$ to ΔH_r , the molar mass of Li_3N was taken to be 34.809.

^dUncertainty interval.

TABLE 18. Calorimetric Results for Reaction of Li_3N with LiOH(aq) ^a

Expt. No.	m, g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle$, J K^{-1}	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
Li_3N - 1	0.02493	0.94387	438.940	-0.056	-16620.9
- 2	0.02524	0.95263	438.927	-0.056	-16568.6
- 3	0.02510	0.94448	438.888	-0.056	-16517.0
- 4	0.02504	0.94459	438.902	-0.056	-16559.0
- 5	0.02487	0.94254	439.129	-0.056	-16644.7
- 6	0.02490	0.93879	438.965	-0.056	-16552.3
- 7	0.02489	0.93768	438.972	-0.056	-16539.6

$$\text{Mean } \Delta H_r/M(\text{sample}) = -16571.7 \pm 17.1 \text{ J g}^{-1} \text{ }^b$$

$$\text{Impurity correction} = -137.1 \pm 11.5 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r/M(\text{Li}_3\text{N}) = -16708.8 \pm 20.6 \text{ J g}^{-1} \text{ }^b$$

$$\Delta H_r = -139.01 \pm 0.34 \text{ kcal mol}^{-1} \text{ }^{c,d}$$

^aIn each experiment, 99.41 cm³ of a solution 0.1M in LiOH and $\sim 0.007M$ in LiCl was used.

^bStandard deviation of the mean.

^cThe molar mass of Li_3N was taken to be 34.809.

^dUncertainty interval.

The impurity corrections were based on the assumption that oxygen was present as Li_2O , silicon as SiO_2 , magnesium, strontium, and calcium as the nitrides, and sodium and potassium as the uncombined elements. These impurity compounds were assumed to have undergone their normal chemical reactions in basic and acidic media during the course of the calorimetric experiments. The correction for oxygen, which comprises almost 99 percent of the total correction, was based on $\Delta H_f^\circ(\text{Li}_2\text{O}, c, 298.15 \text{ K})$, as given in the next section of this report. The other requisite enthalpies of formation were taken from current compilations of thermochemical data.

The overall reaction schemes that lead to $\Delta H_f^\circ(\text{Li}_3\text{N})$ are detailed in Tables 19 and 20. Summation of the ΔH values in each of those tables gives $\Delta H_f^\circ(\text{Li}_3\text{N})$.

In Table 19, the enthalpy of reaction 1 was taken from Table 17 and the enthalpies of reactions 2 and 3 were measured in this study. The data for HCl(aq) in reactions 4 and 5 have been taken from the CODATA selection¹⁰ and Parker's compilation.⁸ The standard enthalpy of formation of NH_4Cl , reaction 6, was obtained by combining ΔH_f° of $\text{NH}_4^+(\text{aq})$ ⁷¹ and $\text{Cl}^-(\text{aq})$,¹⁰ together with the enthalpy of solution of NH_4Cl .⁷² Similarly, for reaction 7, the standard enthalpy of formation of LiCl was obtained by combining ΔH_f° of $\text{Li}^+(\text{aq})$ ⁶⁴ and $\text{Cl}^-(\text{aq})$ ¹⁰ together with the enthalpy of solution of LiCl .⁸

TABLE 19. Cycle Used to Calculate $\Delta H_f^\circ(\text{Li}_3\text{N}, \text{c})$ from $\text{HCl}(\text{aq})$ Experiments^a

Reaction	ΔH , kcal
1. $3 \text{ LiCl} \cdot \text{NH}_4\text{Cl} \cdot 9.962 \text{ HCl} \cdot 7750.31 \text{ H}_2\text{O} = \text{Li}_3\text{N}(\text{c}) + 13.962 (\text{HCl} \cdot 555.1 \text{ H}_2\text{O})$	192.04 ± 0.30
2. $\text{NH}_4\text{Cl}(\text{c}) + 9.962 (\text{HCl} \cdot 777.99 \text{ H}_2\text{O}) = \text{NH}_4\text{Cl} \cdot 9.962 \text{ HCl} \cdot 7750.31 \text{ H}_2\text{O}$	3.672 ± 0.020
3. $3 \text{ LiCl}(\text{c}) + \text{NH}_4\text{Cl} \cdot 9.962 \text{ HCl} \cdot 7750.31 \text{ H}_2\text{O} = 3 \text{ LiCl} \cdot \text{NH}_4\text{Cl} \cdot 9.962 \text{ HCl} \cdot 7750.31 \text{ H}_2\text{O}$	-25.905 ± 0.024
4. $9.962 (\text{HCl} \cdot 555.1 \text{ H}_2\text{O}) + 2220.43 \text{ H}_2\text{O}(\text{l}) = 9.962 (\text{HCl} \cdot 777.99 \text{ H}_2\text{O})$	-0.184 ± 0.010
5. $4 (\text{HCl} \cdot 555.1 \text{ H}_2\text{O}) = 2 \text{ H}_2(\text{g}) + 2 \text{ Cl}_2(\text{g}) + 2220.43 \text{ H}_2\text{O}(\text{l})$	159.20 ± 0.08
6. $1/2 \text{ N}_2(\text{g}) + 1/2 \text{ Cl}_2(\text{g}) + 2 \text{ H}_2(\text{g}) = \text{NH}_4\text{Cl}(\text{c})$	-75.295 ± 0.05
7. $3 \text{ Li}(\text{c}) + 3/2 \text{ Cl}_2(\text{g}) = 3 \text{ LiCl}(\text{c})$	-292.91 ± 0.18
8. $3 \text{ Li}(\text{c}) + 1/2 \text{ N}_2(\text{g}) = \text{Li}_3\text{N}(\text{c})$	-39.38 ± 0.36

^aAll species are in the aqueous phase except where denoted otherwise.TABLE 20. Cycle Used to Calculate $\Delta H_f^\circ(\text{Li}_3\text{N}, \text{c})$ from $\text{LiOH}(\text{aq})$ Experiments^a

Reaction	ΔH , kcal
1. $16.845 \text{ LiOH} \cdot \text{LiCl} \cdot \text{NH}_3 \cdot 7682.36 \text{ H}_2\text{O} = \text{Li}_3\text{N}(\text{c}) + 13.845 (\text{LiOH} \cdot 555.1 \text{ H}_2\text{O}) \cdot \text{LiCl}$	139.01 ± 0.34
2. $\text{LiCl} \cdot 13.845 (\text{LiOH} \cdot 555.1 \text{ H}_2\text{O}) = \text{LiCl}(\text{c}) + 13.845 (\text{LiOH} \cdot 555.1 \text{ H}_2\text{O})$	8.632 ± 0.017
3. $\text{NH}_4\text{Cl}(\text{c}) + 17.845 (\text{LiOH} \cdot 430.45 \text{ H}_2\text{O}) = \text{NH}_3 \cdot \text{LiCl} \cdot 16.845 \text{ LiOH} \cdot 7682.36 \text{ H}_2\text{O}$	2.572 ± 0.014
4. $13.845 (\text{LiOH} \cdot 555.1 \text{ H}_2\text{O}) = 13.845 (\text{LiOH} \cdot 430.45 \text{ H}_2\text{O}) + 1725.78 \text{ H}_2\text{O}(\text{l})$	0.233 ± 0.010
5. $4 \text{ Li}(\text{c}) + 1725.78 \text{ H}_2\text{O}(\text{l}) = 4 (\text{LiOH} \cdot 430.45 \text{ H}_2\text{O}) + 2 \text{ H}_2(\text{g})$	-212.26 ± 0.11
6. $1/2 \text{ N}_2(\text{g}) + 2 \text{ H}_2(\text{g}) + 1/2 \text{ Cl}_2(\text{g}) = \text{NH}_4\text{Cl}(\text{c})$	-75.295 ± 0.05
7. $\text{LiCl}(\text{c}) = \text{Li}(\text{c}) + 1/2 \text{ Cl}_2(\text{g})$	97.635 ± 0.058
8. $3 \text{ Li}(\text{c}) + 1/2 \text{ N}_2(\text{g}) = \text{Li}_3\text{N}(\text{c})$	-39.47 ± 0.37

^aAll species are in the aqueous phase except where denoted otherwise.

In Table 20, the enthalpy of reaction 1 was taken from Table 18 and the enthalpies of reactions 2 and 3 were measured in this study. Data for $\text{LiOH}(\text{aq})$, reactions 4 and 5, have been deduced from the CODATA selection for $\Delta H_f^\circ(\text{Li}^+, \text{aq})$,⁶⁴ $\Delta H_f^\circ(\text{OH}^-, \text{aq})$ ¹⁰ and $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l})$ ¹⁰ and Parker's selected enthalpies of dilution.⁸ The enthalpies of reactions 6 and 7 are simply $\Delta H_f^\circ(\text{NH}_4\text{Cl})$ and $-\Delta H_f^\circ(\text{LiCl})$, respectively.

Thus, from the experiments in acid, $\Delta H_f^\circ(\text{Li}_3\text{N}) = -39.38 \pm 0.36 \text{ kcal mol}^{-1}$, and from the experiments in base, $\Delta H_f^\circ(\text{Li}_3\text{N}) = -39.47 \pm 0.37 \text{ kcal mol}^{-1}$. These results are in excellent agreement with each other and we take the weighted mean, $-39.42 \pm 0.26 \text{ kcal mol}^{-1}$, as the best value for $\Delta H_f^\circ(\text{Li}_3\text{N}, \text{c}, 298.15 \text{ K})$.

There have been two previous determinations of $\Delta H_f^\circ(\text{Li}_3\text{N})$, one based on solution calorimetry, the other on direct combination of the elements.

Guntz⁶⁹ reported the enthalpy of Reaction XX to be $-131.1 \text{ kcal mol}^{-1}$ at 291.15 K. The final concentration of the LiOH was not specified. However, even when reasonable assumptions are made concerning the concentration, and the enthalpy of reaction is corrected to 298.15 K, the result of Guntz still differs by about 8 kcal mol^{-1} from our determination, $-139.01 \pm 0.34 \text{ kcal mol}^{-1}$. A discrepancy of this magnitude could have been caused, for instance, by unaccounted-for LiOH or Li_2O in the lithium nitride used by Guntz.

Neumann, Kröger, and Haebler⁷⁰ measured the enthalpy of reaction of lithium with nitrogen at 5 atm pressure by heating at 893 K for one minute. They obtained $\Delta H_f^\circ(\text{Li}_3\text{N}) = -47.2 \pm 1 \text{ kcal mol}^{-1}$. As part of the same investigation, ΔH_f° values were reported for AlN , Mg_3N_2 , and Be_3N_2 . Each of these results has been superseded by more modern determinations, which have shown the data of Neumann *et al.* to be in error by as much as 10 kcal mol^{-1} . The discrepancy of about 7 kcal mol^{-1} between our ΔH_f° result and that of Neumann *et al.* is, therefore, in harmony with the findings of several other investigators.

The agreement between the present ΔH_f° values, obtained by two essentially independent routes, and the careful synthesis, characterization, and manipulation of the lithium nitride used are substantive reasons for preferring our determination over those of Guntz and Neumann *et al.*

B. Lithium Oxide (Li_2O)

Three previous thermochemical studies of Li_2O by solution calorimetric methods have been reported.^{73,74,75} These results were reviewed by the compilers of the JANAF Thermochemical Tables⁷⁶ when selecting the standard enthalpy of formation of Li_2O , $\Delta H_f^\circ(\text{Li}_2\text{O}, \text{c}, 298.15 \text{ K})$, and an uncertainty of $\pm 0.5 \text{ kcal mol}^{-1}$ was assigned to the selected value. In our opinion, because Li_2O is a basic compound in the chemistry of lithium, such a large uncertainty assigned to its enthalpy of formation is unacceptable. Consequently, we have redetermined $\Delta H_f^\circ(\text{Li}_2\text{O})$.

Our result for $\Delta H_f^\circ(\text{Li}_2\text{O})$ is based on measurements of the enthalpy of reaction of Li_2O with H_2O according to

Combination of the enthalpy of Reaction XXI with the enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{LiOH}(\text{aq})$, both of which are well known, yields $\Delta H_f^\circ(\text{Li}_2\text{O})$.

The sample of Li_2O was prepared by thermal decomposition of Li_2CO_3 (Cerac/Pure, 99.99%) at temperatures between 970 and 1100 K. Heating with frequent grinding for approximately one month did not completely decompose all the carbonate. Duplicate analyses for carbonate in the sample yielded results of 0.186 and 0.182 mass percent CO_3^{2-} . Spark-source mass-spectrometric analysis revealed the following impurities (in ppm): Na, 1000; Mg, 20; Al, 10; S, 30; K, 10; Ca, 50; and Ba, 50. Since Na_2CO_3 and BaCO_3 do not decompose below 1100 K, the sodium and barium impurities were assumed to be

present as carbonates; the sulfur impurity was assumed to be present as Li_2SO_4 , and the remaining metallic impurities as oxides. The excess CO_3^{2-} over that combined as Na_2CO_3 , was assumed to be present as Li_2CO_3 . On this basis, the Li_2O content of the preparation was 99.67₅ mass percent.

The results of six measurements of the enthalpy of reaction of Li_2O with water are given in Table 21. The impurity correction is based on the previously stated assumptions concerning the states of combination of the impurities. The impurities were assumed to have undergone their normal chemical reactions during the course of the calorimetric experiments.

TABLE 21. Results of the Reaction of Li_2O with H_2O ^a

Expt. No.	1	2	4	5	6	7
m, g	0.09902	0.09739	0.09710	0.09736	0.10072	0.09904
$\Delta\theta_c$, K	0.99218	0.97400	0.97203	0.97338	1.00918	0.99093
$\langle\epsilon(\text{calor})\rangle$, cal K^{-1}	104.861	105.021	104.950	104.996	104.878	104.973
$-\Delta\theta_c \times \langle\epsilon(\text{calor})\rangle$, cal	-104.041	-102.290	-102.015	-102.201	-105.841	-104.021
ΔH_{vap} , cal	-0.013	-0.013	-0.013	-0.013	-0.013	-0.013
$\Delta H_r/M(\text{sample})$, cal g^{-1}	-1050.83	-1050.45	-1050.75	-1049.86	-1050.97	-1050.42

$$\text{Mean } \Delta H_r/M(\text{sample}) = -1050.55 \pm 0.16 \text{ cal g}^{-1} \text{ }^b$$

$$\text{Impurity correction} = -3.23 \pm 0.32 \text{ cal g}^{-1} \text{ }^b$$

$$\Delta H_r/M(\text{Li}_2\text{O}) = -1053.78 \pm 0.36 \text{ cal g}^{-1} \text{ }^b$$

$$\Delta H_r = -31.488 \pm 0.022 \text{ kcal mol}^{-1} \text{ }^c, \text{ }^d$$

^aThe reaction vessel contained 99.41 cm³ of 0.05M LiOH for each experiment.

^bStandard deviation of the mean.

^cUncertainty interval.

^dThe molar mass of Li_2O was taken to be 29.881.

The overall reaction scheme which leads to $\Delta H_f^\circ(\text{Li}_2\text{O})$ is detailed in Table 22. The enthalpy of reaction 1 was taken from Table 21. The data for $\text{LiOH}(\text{aq})$ in reactions 2 and 3 were taken from the CODATA selection^{6,4} and from Parker's compilation.⁸ Reaction 4 is simply $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l})$.¹⁰ The standard

TABLE 22. Cycle Used to Calculate $\Delta H_f^\circ(\text{Li}_2\text{O})$ ^a

Reaction	ΔH , kcal
1. $3.505 (\text{LiOH} \cdot 475.84 \text{ H}_2\text{O}) \rightarrow \text{Li}_2\text{O}(\text{c}) + 1.505 (\text{LiOH} \cdot 1108.84 \text{ H}_2\text{O})$	31.488 ± 0.022
2. $1.505 (\text{LiOH} \cdot 1108.84 \text{ H}_2\text{O}) \rightarrow 1.505 (\text{LiOH} \cdot 475.84 \text{ H}_2\text{O}) + 952.68 \text{ H}_2\text{O}(\text{l})$	0.068 ± 0.007
3. $2 \text{ Li}(\text{c}) + 953.68 \text{ H}_2\text{O}(\text{l}) \rightarrow 2 (\text{LiOH} \cdot 475.84 \text{ H}_2\text{O}) + \text{H}_2(\text{g})$	-106.144 ± 0.062
4. $\text{H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-68.315 ± 0.010
5. $2 \text{ Li}(\text{c}) + 1/2 \text{ O}_2(\text{g}) \rightarrow \text{Li}_2\text{O}(\text{c})$	-142.903 ± 0.067

^aAll species are in the aqueous phase except where denoted otherwise.

enthalpy of formation of Li_2O as given by reaction 5 is the sum of the enthalpies of the four preceding reactions.

The enthalpy of formation of $\text{Li}_2\text{O}(\text{c})$ obtained in this research is $-142.903 \pm 0.067 \text{ kcal mol}^{-1}$. This may be compared with the JANAF⁷⁶ selected value of $-143.1 \pm 0.5 \text{ kcal mol}^{-1}$. The JANAF value is based on the measurements by Kolesov *et al.*,⁷⁵ who reported $\Delta H_f^\circ = -31.74 \pm 0.08 \text{ kcal mol}^{-1}$ for the reaction

By comparison, our value for this reaction would be $-31.84 \pm 0.02 \text{ kcal mol}^{-1}$. The agreement between our result and that of Kolesov *et al.* indicates that JANAF was much too conservative in assigning the uncertainty to the selected $\Delta H_f^\circ(\text{Li}_2\text{O})$.

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IV. LITHIUM MONOSELENIDE, Li_2Se (M. Ader)

Experimental results obtained in the determination of $\Delta H_f^\circ(\text{Li}_2\text{Se})$ by fluorine bomb calorimetry were given in the preceding report⁵¹ in this series. At that time, analysis of the Li_2Se sample for oxygen and hydrogen had not been accomplished. Appreciable concentrations of both oxygen (2.56 ± 0.13 wt %) and hydrogen (0.248 ± 0.037 wt %) were subsequently found. From this and other evidence, the molar composition of the sample was deduced to be $0.9284 \text{ Li}_2\text{Se(c)} + 0.0714 \text{ LiOH} \cdot \text{H}_2\text{O(c)} + 0.0002$ impurities. With all corrections taken into account, the standard enthalpy of formation, $\Delta H_f^\circ(\text{Li}_2\text{Se, c, 298.15 K}) = -101.8 \pm 2.0 \text{ kcal mol}^{-1}$ was derived. A complete description of this work has been published.⁷⁷

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 ml^{-1}), high uranium content (approximately 96.2%), and high thermal conductivity ($0.036 \text{ cal sec}^{-1}\text{cm}^{-1} \text{ K}^{-1}$ at room temperature). It has potential application as a fuel in water-cooled nuclear reactors.⁷⁸ Recently, considerable research on the irradiation behavior and other properties has been and still is being carried out at Atomic Energy of Canada Ltd. (AECL), Chalk River, Ontario.^{79,80,81}

U_3Si has been included as part of our program to elucidate the thermochemistry of uranium compounds. This mutual interest has led to a cooperative effort to prepare and characterize a good sample of U_3Si at AECL (I. J. Hastings) and to measure its thermodynamic properties at Argonne National Laboratory (ANL). High-temperature enthalpy measurements on one specimen have already been reported;⁸² preliminary results for measurements of the enthalpy of combustion in fluorine at 298.15 K are given in this report; and D. W. Osborne and H. E. Flotow of the ANL Chemistry Division plan to start measurements of low-temperature heat capacities soon.

The experimental method chosen for the determination of the enthalpy of formation of U_3Si in this study was based on measurements of the enthalpy of combustion of U_3Si in fluorine in a rotating bomb calorimeter. A two-compartment bomb⁸³ with modified interconnecting valve⁸⁴ was used because U_3Si reacts spontaneously with fluorine at room temperature.

Calorimetric temperatures were measured to within $1 \times 10^{-4} \text{ K}$ by means of a quartz crystal thermometer (Hewlett-Packard Model 2801 A) as described by Johnson, Van Deventer, Kruger, and Hubbard.⁸⁵ Calibration of the calorimetric system was carried out by combustion in oxygen of National Bureau of Standards benzoic acid (sample 39i). The average value of the energy equivalent of the calorimetric system was found to be $\epsilon(\text{calor}) = 3244.93 \pm 0.38 \text{ cal K}^{-1}$ for nine calibrations, four of which were completed prior to the combustions of U_3Si .

The sample of U_3Si was prepared at AECL by a peritectoid reaction between U and U_3Si_2 at 1200 K, following which it was annealed for 5 days at 1070 K under vacuum to ensure completion of the peritectoid reaction. A summary of the impurities in the sample as detected by AECL is given in Table 23. Additional analyses have been carried out at ANL, the results of which are not available at this time. Three to 10 mg of rhombic sulfur (USBM-p-1b) was used to initiate rapid spontaneous combustion of U_3Si in fluorine. The sulfur, a secondary standard for sulfur compounds, was obtained from the Bureau of Mines. Its energy of combustion in fluorine was $9,062 \text{ cal g}^{-1}$.⁸⁶ High-purity (99.99 mol %) fluorine was prepared by distillation of commercial fluorine in a low-temperature still.⁸⁷

The sample was prepared for the experiment by cutting the U_3Si into small ($\sim 0.02 \text{ g}$) chunks, which were arranged as a layer in the center of a crucible so that the pieces were touching each other. The rhombic sulfur ignition aid was placed in the center of the arrangement. In this way, all the sample was ignited but not fused.

TABLE 23. Concentration (ppm) of Impurities in U_3Si

C	140	V	10	Mo	<2
Fe	120	Zn	<10	Sn	<2
P	<100	Ca	5	Bi	<2
Al	50	Pb	5	Cu	<1
Ni	25	Mg	4	B	0.3
Cr	10	Mn	2		

The crucible, whose construction was critical, was a flat, 50-g nickel disk (1/8-in. thick) with a machined 1/8-in.-high wall at its outer edge. It stood on three legs (1/4 in. high, 1/16-in. dia). It was 1/16 in. smaller than the inner compartment of the bomb. This heavy crucible, which had minimal contact with the bomb, prevented rapid heat conduction away from the reaction zone and subsequent incomplete combustion of the sample.

The crucible and its contents were loaded into the bomb in a helium-atmosphere glovebox to prevent contact of the bomb walls with atmospheric moisture. The helium was pumped from both compartments, the interconnecting valve was closed, and the storage compartment was charged with fluorine to a pressure of 5.37 atm. The bomb was placed in the calorimeter and initial rating-period measurements were taken. Ignition of the sample was initiated by opening the interconnecting valve. Main period and final rating-period measurements completed the calorimetric part of the experiment.

The bomb was then evacuated overnight to remove the products of combustion, which were SiF_4 , UF_6 (both solid and gaseous), and SF_6 . Subsequently, the bomb was opened in the glovebox. Between 20 and 40 mg of nonvolatile residues were found in the bomb. These residues were weighed and submitted for various analyses.

The use of the two-compartment bomb necessitated the performance of blank experiments, which were identical with combustion experiments except that the crucible and sample were omitted. The blank determinations measured the combination of two thermal effects: (1) the endothermic expansion of fluorine from the storage compartment into the evacuated combustion compartment, and (2) the exothermic reaction of fluorine with the walls of the bomb and/or reaction with any adsorbed moisture. Five blank experiments interspersed among the combustion experiments gave an average value of $\Delta U_{\text{blank}} = 4.72 \pm 0.54$ cal per experiment.

The preliminary results of six satisfactory combustions are presented in Table 24. The entries in the table have the same significance as given previously,⁸⁸ except that the masses m' and m'' refer to the U_3Si sample and the sulfur ignitor, respectively, and ΔU_s is the energy due to combustion of the sulfur ignitor. It is also pointed out that $\Delta U_c/M$ (sample) does not refer to standard state conditions, as certain corrections have not yet been made. The data, which are presented to show the nature and precision of the experimental work, are considered to be preliminary, and no enthalpy-of-formation value should be derived therefrom.

TABLE 24. Results for Combustions of U_3Si in Fluorine

Expt. No. ^a	2	3	4	5	6	8
$m'(U_3Si)$, g	1.55574	1.56540	1.50180	1.51029	1.51273	1.53061
$m''(S)$, g	0.00300	0.00989	0.00351	0.00993	0.00840	0.00712
$\Delta\theta_c$, K	1.24268	1.26902	1.20099	1.22248	1.22374	1.23625
$\epsilon(\text{calor})(-\Delta\theta_c)$, cal	-4032.41	-4117.89	-3897.14	-3966.87	-3970.97	-4011.55
ΔU_{cont} , cal	-8.35	-8.38	-8.23	-8.11	-8.14	-8.34
ΔU_s , cal	27.19	89.63	31.81	89.99	76.72	64.52
ΔU_{gas} , cal	-0.19	-0.19	-0.18	-0.18	-0.18	-0.18
ΔU_{blank} , cal	4.72 ± 1.20					
$\Delta U_c/M(\text{sample})$, cal g^{-1}	-2576.93	-2575.77	-2576.25	-2569.34	-2576.70	-2581.21
Mean $\Delta U_c/M = -2576.03 \pm 1.56$ cal g^{-1} (std. dev.)						

^aExperiment No. 1 was discarded due to a leak in the calorimeter can. Experiment No. 7 was discarded because a significant portion of the U_3Si did not react with the fluorine.

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VI. VANADIUM CARBIDE (G. K. Johnson)

The thermodynamic properties of refractory carbides are basic data needed for understanding the chemistry of carbide fuel-fission product systems. The work reported here is part of a continuing collaborative program with E. K. Storms of Los Alamos Scientific Laboratory to determine the enthalpies of formation of the carbides of molybdenum and vanadium. Results for the enthalpies of formation of $\text{MoC}_{0.502}$, $\text{MoC}_{0.651}$, and $\text{VC}_{0.847}$ were presented previously.⁵ In this report, the results of the combustion of a sample of vanadium monocarbide, $\text{VC}_{0.787}$, in fluorine according to

are presented.

The sample of $\text{VC}_{0.787}$ was prepared at Los Alamos Scientific Laboratory by arc-melting vanadium and graphite. The arc-melted button was pulverized and annealed at 1720 K for 63 hr to obtain compositional homogeneity. X-ray diffraction analysis of the sample gave the lattice parameter as 4.149 ± 0.001 Å. The X-ray pattern also indicated some compositional inhomogeneity which apparently had not been removed by the annealing process. The oxygen content of the sample was determined to be less than 10 ppm. Analyses for other impurities are still pending.

The combustion procedure was identical to that used previously for $\text{VC}_{0.847}$.⁵ The method consisted of using small sample sizes and selenium as an auxiliary combustion aid. The small sample sizes (~ 0.21 g) assured that all the VF_5 produced in the reaction was gaseous. By the use of the auxiliary combustion aid, we were able to achieve complete reaction of the vanadium monocarbide without the formation of VF_3 . The combustions were conducted in a two-chambered reaction vessel using high fluorine pressure (~ 24 atm in the tank) and a nickel saucer to support the samples. Following each combustion, a portion of the product gas was analyzed for C_2F_6 by gas chromatography. Although C_2F_6 was detected in all the product gases, it was not present in a large enough concentration to require a thermal correction. The nickel saucer was weighed following each combustion; an increase in mass, which was attributed to the formation of NiF_2 , was found for each experiment.

The results of seven combustions of $\text{VC}_{0.787}$ are given in Table 25. The energy equivalent of the calorimetric system, $\epsilon(\text{calor})$, was determined by combustion of benzoic acid to be $3378.72 \pm 0.14 \text{ cal K}^{-1}$. The correction for the combined effects of expansion of the fluorine from the tank into the combustion chamber and its subsequent reaction with the bomb surfaces, ΔU_{blank} , was determined in separate experiments to be $-3.42 \pm 0.38 \text{ cal}$. The energy of combustion of the selenium was taken to be $-3364.9 \pm 0.6 \text{ cal g}^{-1}$.⁸⁶

The result for $\Delta U_{\text{c}}^{\circ}/M$ (sample) can be used to calculate $\Delta H_{\text{f}}^{\circ}(\text{VC}_{0.787}) = -25.59 \text{ kcal mol}^{-1}$, which must be considered tentative owing to the incomplete impurity analysis. We had previously⁵ obtained a tentative value for $\Delta H_{\text{f}}^{\circ}(\text{VC}_{0.847})$ of $-25.56 \text{ kcal mol}^{-1}$. These results, which appear to be the same, are likely to change when corrections for impurities are applied.

[illegible]

VII. EXPLORATORY EXPERIMENTS IN FLUORINE BOMB CALORIMETRY (M. Ader)

Exploratory experiments were run on a variety of compounds to learn if fluorine bomb calorimetry could be readily applied to the determination of their standard enthalpies of formation. The compounds investigated, FeS_2 , Al_2SiO_5 , WS_2 , MoSe_2 , and MoTe_2 , were combusted in a two-chambered nickel bomb,⁸³ with samples supported on nickel dishes. Brief descriptions of the work and conclusions drawn are given below.

FeS_2 : ANL's Chemical Engineering Division is currently developing high-temperature Li/S batteries that employ iron pyrite, FeS_2 , as a cathode component. The literature data for $\Delta H_f^\circ(\text{FeS}_2)$ appear to be questionable and in need of redetermination. On the basis of oxygen bomb calorimetry performed in 1942⁸⁹ and 1939,⁹⁰ the National Bureau of Standards has selected¹¹ $\Delta H_f^\circ(\text{FeS}_2) = -42.6 \text{ kcal mol}^{-1}$. However, a calorimetric measurement of the reaction between FeS_2 and Zn was reported⁹¹ to yield $\Delta H_f^\circ(\text{FeS}_2) = -39.0 \pm 0.5 \text{ kcal mol}^{-1}$.

In our experiments, powdered technical-grade FeS_2 did not react spontaneously with F_2 at 10 atm; when elemental sulfur was added as an ignitor, reaction did occur. Examination of the products indicated that most of the FeS_2 had reacted, forming $\text{FeF}_3(\text{c})$ and $\text{SF}_6(\text{g})$ as the major products and a minor amount of $\text{FeF}_2(\text{c})$. It was concluded that analytical methods for assaying FeF_2 , FeF_3 , and unreacted FeS_2 in the solid products would have to be developed before proceeding with calorimetric measurements. Furthermore, two auxiliary values needed to derive $\Delta H_f^\circ(\text{FeS}_2)$, namely, $\Delta H_f^\circ(\text{FeF}_3)$ and $\Delta H_f^\circ(\text{FeF}_2)$, are not known precisely and therefore require determination. The investigation of $\Delta H_f^\circ(\text{FeS}_2)$ has been temporarily set aside.

Al_2SiO_5 : The objective of this work was to learn if fluorine bomb calorimetry could be used for alumina- and silica-containing compounds that are insoluble in aqueous reagents and thus not amenable to solution calorimetry. Compounds of this type may be produced in coal-fired MHD generators and their thermodynamic properties are of interest. The naturally occurring Al_2SiO_5 polymorphs kyanite, sillimanite, and andalusite typify such compounds. Because of their geological importance, extensive thermodynamic data have been obtained for them, including apparently well-established ΔH_f° values. For example, JANAF gives $\Delta H_f^\circ(\text{kyanite}) = -620.06 \pm 0.5 \text{ kcal mol}^{-1}$,⁹² which is based on the reaction $\text{Al}_2\text{O}_3(\alpha) + \text{SiO}_2(\text{quartz}) = \text{Al}_2\text{SiO}_5(\text{kyanite})$. The enthalpy change of this reaction at 968 K was obtained by dissolutions of the kyanite and the component oxides in an oxide melt ($9\text{PbO} \cdot 3\text{CdO} \cdot 4\text{B}_2\text{O}_3$), and the result was reduced to 298 K by means of auxiliary Cp and ΔH_f° data. Nevertheless, we were advised that an independent check of $\Delta H_f^\circ(\text{Al}_2\text{SiO}_5)$ would be of value. Because of this, as well as the availability of calorimetric-grade samples and our own interest in testing the applicability of fluorine bomb calorimetry, we undertook exploratory combustions of kyanite.

The initial experiments showed that the reaction $\text{Al}_2\text{SiO}_5(\text{c}) + 5 \text{F}_2(\text{g}) = 2 \text{AlF}_3(\text{c}) + \text{SiF}_4(\text{g}) + 2.5 \text{O}_2(\text{g})$ did not proceed appreciably unless the kyanite was powdered. But even with finely divided samples, additional heat was needed to prevent sintering, which quenched the reaction. It was found possible to burn ~95% of the kyanite by inclusion of graphite felt

as an auxiliary combustant. With the combustion of graphite to $\text{CF}_4(\text{g})$ providing a threefold excess of energy, most of the AlF_3 vaporized and subsequently condensed on surfaces within the combustion chamber. Post-combustion analyses revealed several difficult analytical problems concerning the composition of the reaction products. For example, several unidentified infrared bands, possibly due to oxyfluorides, were detected in the gaseous products. Also, unburned sample could not be assumed to be kyanite, since X-ray evidence indicated the presence of AlF_3 , $\alpha\text{-Al}_2\text{O}_3$, and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite) in what appeared to be unreacted, sintered sample.

Rather than engage in an extensive analytical and calorimetric effort, which at best would yield a value for $\Delta H_f^\circ(\text{kyanite})$ uncertain by about 2 to 3 kcal mol^{-1} , this research was discontinued. As to the applicability of fluorine bomb calorimetry to refractory alumina- and silica-containing compounds, no general conclusion is warranted. Obviously, in the present instance, fluorine bomb calorimetry would have been quite promising in the absence of analytical complications.

WS_2 , MoSe_2 , MoTe_2 : The Calorimetry Group within ANL's Chemical Engineering Division has for many years been engaged in determining thermodynamic data for materials of interest in high-temperature science and technology. The compounds WS_2 , MoSe_2 , and MoTe_2 fit this category by virtue of their low frictional coefficients and high stabilities at elevated temperatures. They have been used or proposed⁹³ for use as lubricants or components in self-lubricating bearings, bushings, gears, etc. An additional reason for interest in WS_2 is the occasional use of tungsten metal as a current collector in the Li/S batteries being developed at ANL.

Values of $\Delta H_f^\circ(\text{WS}_2)$ ranging between -46 and -59 kcal mol^{-1} appear in the literature or can be estimated from high-temperature equilibrium data. Information on MoSe_2 and MoTe_2 is too scarce to enable similar estimation. An effort to derive $\Delta H_f^\circ(\text{WS}_2)$ by oxygen bomb calorimetry was made in this laboratory about 15 years ago, but was unsuccessful because of the complex chemistry of the bomb process. Fluorine bomb calorimetry offers an improved approach to thermochemical study of these compounds via the reaction $\text{MCh}_2(\text{c}) + 9\text{F}_2(\text{g}) = \text{MF}_6(\text{g}) + 2\text{ChF}_6(\text{g})$, where $\text{M} = \text{W}$ or Mo , and $\text{Ch} = \text{S}$, Se , or Te . All the auxiliary data needed to derive $\Delta H_f^\circ(\text{MCh}_2)$ are available, and the technique has already been demonstrated with MoS_2 .⁹⁴ Recently, commercial specimens of WS_2 , MoSe_2 , and MoTe_2 powders were acquired, and calorimetric combustions were tried. The preliminary results given below, show that fluorine bomb calorimetry will be quite satisfactory for all three compounds.

The WS_2 , specified as being 99.99% pure, was burned in ~ 12 atm F_2 with the aid of a small amount of sulfur ignitor. Post-combustion examination revealed that the sample had burned completely, leaving no visible residue. Although duplicate measurements of the energy of combustion gave good precision, the value derived for $\Delta H_f^\circ(\text{WS}_2)$ was about three times greater than expected. The purity of the WS_2 was suspected and therefore the sample was re-examined. Spark-source mass-spectrographic analysis indicated a very low impurity content. However, an X-ray diffraction pattern showed the presence of elemental tungsten which, by other analyses, was subsequently estimated at ~ 15 wt %. In addition, ~ 0.8 wt % O was found. The

presence of these impurities, particularly W which has a lower energy of combustion than expected for WS_2 , accounts very nicely for the high enthalpy of formation obtained. Attempts to purify the WS_2 specimen by treatment with $H_2S(g)$ are now in progress.

The $MoSe_2$ and $MoTe_2$ specimens were analyzed by emission spectrography. Impurity levels were higher than desirable for calorimetric-grade specimens, but tolerable. For example, the $MoSe_2$ contained (in ppm) Fe(100), Si(700), Al(500), and W(150); the $MoTe_2$ contained Fe(100), Si(300), Zr(200), Al(300), and W(500). A more serious problem was uncertainty concerning the stoichiometry of the specimens. X-ray analyses indicated Mo_3Se_4 in the $MoSe_2$, and Te in the $MoTe_2$. It was concluded that these specimens were unsuitable for a thorough calorimetric investigation. However, duplicate calorimetric combustions were run with both specimens to observe combustion behavior and obtain preliminary ΔH_f° values. Samples were burned in ~ 11 atm F_2 with the aid of a small amount of selenium ignitor. The $MoSe_2$ samples burned cleanly, leaving a very small amount of white residue, which is probably attributable to formation of impurity fluorides (e.g., AlF_3). The $MoTe_2$ samples behaved similarly, except that 0.1 to 0.2 wt % of the sample remained unburned. The calorimetric measurements in each set were in good agreement. Rough thermal corrections were applied to the calorimetric data, from which the following values were derived: $\Delta H_f^\circ(MoSe_2) = -55$ kcal mol^{-1} , and $\Delta H_f^\circ(MoTe_2) = -43$ kcal mol^{-1} . The trend of decreasing $\Delta H_f^\circ(MoCh_2)$ with increasing size of chalcogen is expected and in accord with $\Delta H_f^\circ(MoO_2) = -140.76$ kcal mol^{-1} ¹¹ and $\Delta H_f^\circ(MoS_2) = -65.8 \pm 1.2$ kcal mol^{-1} .⁹⁴

VIII. MOLECULAR ORBITAL STUDIES: THE SELENIUM-FLUORINE SYSTEM
(P. A. G. O'Hare)

Molecular orbital calculations on selected diatomic fluorides have continued. The most recent system studied was selenium monofluoride. Wavefunctions were computed for SeF at six internuclear separations via the Hartree-Fock matrix expansion procedure described by Roothaan.⁹⁵ Details of the computer system BISON have been given by Wahl *et al.*,⁹⁶ and the IBM-360-195 machine at Argonne National Laboratory was used for the calculations. Slater-type-orbital basis function sets and the electronic configuration of SeF were identical to those used in our earlier study.⁹⁷ Total, potential, and kinetic energies for SeF at internuclear separations of 2.9, 3.1, 3.29, 3.5, and 3.7 bohrs were calculated initially and are given in Table 26. The total energies were fitted to an analytical expression from which a Dunham analysis yielded the spectroscopic constants in Table 27. This analysis also indicated the Hartree-Fock minimum to be at 3.24 bohr, and additional wavefunctions were computed at this distance for SeF, SeF⁺, and SeF⁻. The energies obtained are to be found in Table 26 along with the electric dipole and quadrupole moments as a function of internuclear separation.

TABLE 26. Total (E), Potential (V), and Kinetic (T) Energies, Dipole (μ) and Quadrupole (Q) Moments of SeF, SeF⁺, and SeF⁻ as a Function of Internuclear Separation (R)^a

R	E	V	T	-V/T	μ^b	Q ^c
SeF (² Π)						
2.90	-2499.29411	-4999.17573	2499.88162	1.99976	-0.91	0.08
3.10	-2499.31725	-4998.86222	2499.54497	1.99991	-1.60	-0.49
3.24 ^d	-2499.32095	-4998.69667	2499.37571	1.99998	-2.05	-0.89
3.29 ^e	-2499.32053	-4998.64430	2499.32337	2.00000	-2.21	-1.04
3.50	-2499.31217	-4998.47046	2499.15829	2.00006	-2.83	-1.65
3.70	-2499.29774	-4998.34547	2499.04773	2.00010	-3.38	-2.25
SeF ⁺ (³ Σ)						
3.24 ^d	-2498.98640	-4997.87425	2498.88786	2.00004	-5.39	-0.44
SeF ⁻ (¹ Σ)						
3.24 ^d	-2499.36240	-4999.05509	2499.69269	1.99987	1.51	-0.84

^aEnergies are in hartrees (hartree = 27.20974 eV), dipole moments in debyes, quadrupole moments in units of 10^{-26} esu cm², and internuclear separations in bohrs (bohr = 0.52917Å).

^bNegative sign for μ denotes Se⁺-F⁻ polarity.

^cQuadrupole moments measured from center of mass.

^dHartree-Fock minimum of SeF (² Π).

^eExperimental internuclear separation.

TABLE 27. Comparison of the Computed and Literature Spectroscopic Constants for SeF

	Computed	Literature
r_e (Å)	1.715	1.742 ^a
ω_e (cm ⁻¹)	757	735 ^b
$\omega_e x_e$ (cm ⁻¹)	4.9	
B_e (cm ⁻¹)	0.372	0.3625 ^a
α_e (cm ⁻¹)	0.0026	

^a Experimental results, from Ref. 105, are for r_0 and B_0 , respectively.

^b Estimate (Ref. 102) based on Guggenheimer's formulae.

In our earlier paper on SeF,⁹⁷ we estimated the dissociation enthalpy to be 4.2 ± 0.2 eV. The present results, supplemented by a recent⁹⁸ experimental determination of $D_0^\circ(\text{SF})$, enables us to make a more reliable estimate for $D_0^\circ(\text{SeF})$.

By combining the Hartree-Fock energies of Se,⁹⁶ F,⁹⁶ and SeF (Table 26), the Hartree-Fock binding energy of SeF is calculated to be 0.0454 hartree. This result, when added to the molecular extra correlation energy (MECE) correction⁹⁹ yields $D_0^\circ(\text{SeF})$. In a homologous series such as the monofluorides of the chalcogens, the MECE correction decreases with increasing atomic number of the chalcogen. Thus, for oxygen monofluoride, MECE (OF) is 0.1046 hartree.¹⁰⁰ For sulfur monofluoride, MECE (SF) is calculated to be 0.0756 hartree, based on the Hartree-Fock dissociation energy of SF^{101} and Hildebrand's experimental result, 3.51 eV,⁹⁸ for $D_0^\circ(\text{SF})$. For selenium monofluoride, therefore, MECE (SeF) will be less than 0.0756 hartree and, consequently, $D_0^\circ(\text{SeF}) < 3.29$ eV.

The latter value can be refined somewhat. From thermochemical data,¹⁰² the mean bond enthalpy $\bar{D}_0^\circ$ in SF_6 is calculated to be 3.36 eV, somewhat lower than $D_0^\circ(\text{SF})$. Similarly, $\bar{D}_0^\circ$ in SeF_6 was deduced to be 3.10 eV.¹⁰³ By analogy with SF, one would therefore predict $D_0^\circ(\text{SeF}) > 3.10$ eV, and thus $D_0^\circ(\text{SeF})$ is estimated to be 3.2 ± 0.1 eV or 74 ± 2 kcal mol⁻¹. This value supercedes our earlier D_0° which is too large because the correlation energy of SeF was overestimated. If it is assumed that $D_0^\circ(\text{SeF}) = D_{298}^\circ(\text{SeF})$, it then follows that

$$\begin{aligned} \Delta H_f^\circ(\text{SeF}, g, 298.15 \text{ K}) &= \Delta H_f^\circ(\text{Se}, g, 298.15 \text{ K}) \\ &+ \Delta H_f^\circ(\text{F}, g, 298.15 \text{ K}) - (74 \pm 2) \end{aligned} \quad (\text{XXIV})$$

The values are well established¹⁸ for both Se(g) and F(g); thus, $\Delta H_f^\circ(\text{SeF}, g, 298.15 \text{ K}) = -0.8 \pm 2$ kcal mol⁻¹.

Sufficient data are also available to enable us to calculate the standard entropy, $S^\circ(\text{SeF}, \text{g}, 298.15 \text{ K})$, based on the formulas of statistical mechanics.¹⁰⁴ For the present purpose, we have taken $r_e = 1.742 \text{ \AA}$,¹⁰⁵ $\omega_e = 757 \text{ cm}^{-1}$, $\omega_e x_e = 4.9 \text{ cm}^{-1}$, and σ (the symmetry number) = 1. We have assumed ω_e to be uncertain by $\pm 50 \text{ cm}^{-1}$. Thus, we calculate $S^\circ(\text{SeF}, \text{g}, 298.15 \text{ K}) = 57.26 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$. Furthermore, with S° values for $\text{Se}(\text{c})$ and $\text{F}_2(\text{g})$ from the literature,¹⁸ we deduce $\Delta G_f^\circ(\text{SeF}, \text{g}, 298.15 \text{ K}) = 7.6 \pm 2.0 \text{ kcal mol}^{-1}$.

The Hartree-Fock energy for the $\text{SeF} \rightarrow \text{SeF}^+$ process is 9.1 eV; this value, combined with our previous estimate,⁹⁷ $0.3 \pm 0.2 \text{ eV}$, for the difference in correlation energy between the ion and parent species, yields $9.4 \pm 0.4 \text{ eV}$ for the ionization potential, $I(\text{SeF})$. This result is within 0.1 eV of our previous value and is slightly lower, as expected, than the ionization potential of Se, 9.75 eV.¹⁰⁶ The ionization potential is for the overall process

Thus, $\Delta H_f^\circ(\text{SeF}^+) = 216 \pm 9 \text{ kcal mol}^{-1}$.

The dissociation enthalpy of SeF^+ is given by

$$D_0^\circ(\text{SeF}^+) = D_0^\circ(\text{SeF}) + I(\text{Se}) - I(\text{SeF}) \quad (\text{XXVI})$$

where the ionization potentials are 9.75 ± 0.005 and $9.4 \pm 0.4 \text{ eV}$, respectively, for Se and SeF . Thus, $D_0^\circ(\text{SeF}^+) = 82 \pm 9 \text{ kcal mol}^{-1}$. The bond in SeF^+ may therefore be marginally stronger than that in SeF and this is due, apparently, to ionization of an electron from a bonding orbital in SeF .

Since we are unable to reliably estimate MECE for the $\text{SeF}^- \rightarrow \text{SeF}$ process, we use Koopmans'¹⁰⁷ theorem to deduce the electron affinity, E_a . The least stable orbital in SeF^- has an energy of -0.0666 hartree, which corresponds to $E_a(\text{SeF}) = 1.8 \text{ eV}$. Thus, the electron affinity is rather close to that for Se, 2.0201 eV ,¹⁰⁸ which is not surprising since the electron added to SeF to form SeF^- goes almost exclusively into a pure Se 4p orbital. A similar situation prevails for SF for which we deduced $E_a = 1.7 \text{ eV}$; this may be compared with $E_a(\text{S}) = 2.0772 \text{ eV}$.¹⁰⁹ The electron affinities of SF and SeF are rather close, as is the case with SH and SeH.¹¹⁰ However, the large uncertainties in the values for the fluorides precludes any further meaningful comparison with the hydrides. Our result suggests that there is no thermodynamic reason why SeF^- , for which we calculate $D_0^\circ = 36 \text{ kcal mol}^{-1}$, should not be stable toward dissociation at ordinary temperatures.

Carrington *et al.*¹⁰⁵ determined r_0 and B_0 for SeF based on electron resonance studies; our results for r_e and B_e are, as would be expected, slightly smaller than the data for the zeroeth vibrational level.

The dipole moment, 2.05 D, differs significantly from the experimental result, $1.52 \pm 0.05 \text{ D}$, obtained by Byfleet, Carrington, and Russell.¹¹¹ Disagreements of this magnitude are common for calculations of the type described in the present paper. To date, the quadrupole moment of SeF has not been determined experimentally.

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