CHEMICAL ENGINEERING DIVISION

THERMOCHEMICAL STUDIES

ANNUAL REPORT

July 1974—June 1975

by

P. A. G. O'Hare, G. K. Johnson, M. Ader,

W. N. Hubbard, D. R. Fredrickson,

F. A. Cafasso, and L. Burris

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. ENERGY RESEARCH

AND DEVELOPMENT ADMINISTRATION

under Contract W-31-109-Eng-38

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$5.45; Microfiche \$2.25

ANL-75-47

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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September 1975

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ANL-8121 July 1973—June 1974

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ABSTRACT

Standard enthalpies of formation have been determined for the following compounds: $\text{Cs}_2\text{U}_2\text{O}_7(\text{c})$, $\beta\text{-Na}_2\text{UO}_4(\text{c})$, $\text{BaUO}_4(\text{c})$, $\text{HI}(\text{aq})$, $\text{CsNO}_3(\text{c})$, $\text{Cs}_2\text{CO}_3(\text{c})$, $\text{CsCl}(\text{c})$, $\text{RbCl}(\text{c})$, $\text{Cs}_2\text{CrO}_4(\text{c})$, and $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{c})$. Preliminary reaction calorimetric studies of WS_2 and Li-Al alloys are described. High-temperature enthalpies and other thermodynamic properties are reported for α - and $\beta\text{-Na}_2\text{UO}_4(\text{c})$, $\text{Cs}_2\text{UO}_4(\text{c})$, and $\text{Al}_2\text{O}_3(\text{c})$.

SUMMARY

$\text{Cs}_2\text{U}_2\text{O}_7$, $\alpha\text{-Na}_2\text{UO}_4$, $\beta\text{-Na}_2\text{UO}_4$, BaUO_4

In connection with continuing studies of the thermodynamics of chemical reactions in nuclear reactors, ΔH_f° values have been obtained for $\text{Cs}_2\text{U}_2\text{O}_7$, α - and $\beta\text{-Na}_2\text{UO}_4$, and BaUO_4 . A thermodynamic analysis indicates that Cs_2UO_4 is likely to be the dominant species formed in oxide fuel + Cs reactions. The enthalpy of the α - to $\beta\text{-Na}_2\text{UO}_4$ transition at 298.15 K has been determined.

$\text{I}^-(\text{aq})$

In a variety of thermochemical cycles, $\Delta H_f^\circ(\text{I}^-, \text{aq})$ is a key component. Current critical compilations assign the rather large uncertainty of ± 0.2 kcal mol⁻¹ to this value. The present study has reduced the uncertainty to ± 0.02 kcal mol⁻¹.

CsNO_3

Previous determinations of the enthalpy of solution and, hence, of the enthalpy of formation, of CsNO_3 were rather uncertain. Current studies have yielded a new precise value for $\Delta H_f^\circ(\text{CsNO}_3)$. By combining solubility and enthalpy of solution data, the standard entropy, $S^\circ(\text{CsNO}_3)$, has been deduced.

Cs_2CO_3

The thermodynamic properties of Cs_2CO_3 are of interest in connection with seed loss in the coal-fired MHD process. The enthalpy of solution of Cs_2CO_3 in 0.5M CsOH was measured, and the standard enthalpy of formation, $\Delta H_f^\circ(\text{Cs}_2\text{CO}_3, \text{c}, 298.15 \text{ K})$, was derived.

CsCl and RbCl

Standard enthalpies of solution of CsCl and RbCl have been measured. The result for CsCl differs somewhat from the selected value, whereas the result for RbCl is essentially in agreement with several earlier determinations.

Cs₂CrO₄ and Cs₂Cr₂O₇

Interactions of fission-product cesium with chromium in the presence of oxygen is of interest in connection with the intergranular attack of the stainless steel cladding in irradiated fuel pins. Because of this interest, ΔH_f° values have been determined for Cs₂CrO₄ and Cs₂Cr₂O₇.

ScF₃, YF₃, LaF₃, and the Rare Earth Trifluorides

An earlier interest in the thermochemistry of the rare earth fluorides has been revived. Studies of PrF₃ and NdF₃ are planned.

WS₂

Bomb calorimetric measurements of the energy of reaction of WS₂(c) and F₂(g) yielded a value for ΔH_f° (WS₂, c, 298.15 K) that was in agreement with literature data. However, the WS₂ contained an undesirably high oxygen content, necessitating a large, uncertain calorimetric correction. The measurements will be repeated with a purer specimen.

Li-Al Compounds

Determination of the enthalpies of formation of various compounds in the Li-Al system by solution-reaction calorimetry has been undertaken. Preliminary experiments have revealed several problems and limitations having to do with mass, flotation, inhomogeneity, and reaction rates of the alloy samples. Some of the problems have been solved, others are still being investigated.

High Temperature Enthalpy Measurements

The resistance-heated drop-calorimetric system has been used to obtain physical property data for various materials of interest in reactor technology. Enthalpy measurements were made on both α - and β -Na₂UO₄, and the enthalpy of the α - β transition at 1193 K was determined. In addition, enthalpy data are reported for Cs₂UO₄ and sapphire, a high temperature reference material.

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

A. Cesium Diuranate ($\text{Cs}_2\text{U}_2\text{O}_7$)

The study of cesium diuranate is part of an ongoing effort at this Laboratory to obtain reliable thermodynamic data for compounds that may be involved in chemical reactions in liquid metal fast breeder reactors (LMFBR). Such compounds, for example, include those that may form between fuel and coolant (Na_3UO_4), between fission products and fuel (Cs_2UO_4 , Rb_2UO_4), between the fission products themselves (Cs_2MoO_4 , Rb_2MoO_4 , BaMoO_4), and between fission products and the stainless steel fuel cladding ($\text{Cs}_2\text{Cr}_2\text{O}_7$, Cs_3CrO_4). A typical study includes the synthesis and characterization of a particular compound, and measurements of the standard enthalpy of formation, ΔH_f° , at 298.15 K and the low-temperature (to 360 K) and high-temperature (to 1500 K) thermodynamic properties. These properties are then used in conjunction with other thermodynamic data to deduce whether the compound can form or undergo a specific reaction, given a particular set of conditions. The application of thermodynamics to the elucidation of processes in irradiated fuels is especially advantageous because, at the present time, analysis of such fuels by conventional techniques is either hazardous or impossible.

One of our recent investigations¹ dealt with cesium uranate, Cs_2UO_4 , which is believed to form in the cooler regions of the fuel and in the vicinity of the insulator pellets by reaction of fission product cesium and urania. There is evidence² that this compound can cause swelling and, ultimately, rupture of the fuel cladding. In a reactor environment, the temperature at the fuel-cladding interface is likely to be about 1000 K. At that temperature, one has to consider not only the formation of Cs_2UO_4 but also the formation of other uranates as decomposition products.³ Among the latter is cesium diuranate, $\text{Cs}_2\text{U}_2\text{O}_7$, which can form from the monouranate as follows:

A knowledge of ΔG for Reaction I would allow the equilibrium constant to be calculated and, since typical values for the oxygen pressure in the region of interest in the fuel pin are known, the equilibrium cesium pressure and the activity of diuranate could then be deduced. There are sufficient data in the literature to enable one to deduce ΔG_f° for all components of Reaction I except $\text{Cs}_2\text{U}_2\text{O}_7$. A value for ΔH_f° combined with the standard entropy and high-temperature data would yield $\Delta G_f^\circ(\text{Cs}_2\text{U}_2\text{O}_7)$ as a function of temperature.

This investigation is the first step toward the determination of the complete thermodynamic properties of $\text{Cs}_2\text{U}_2\text{O}_7$. We have deduced $\Delta H_f^\circ(\text{Cs}_2\text{U}_2\text{O}_7)$ from measurements of the enthalpy of the reaction

Auxiliary measurements were also made of the enthalpy of solution of CsCl in a HCl solution containing $\text{UO}_2^{2+}(\text{aq})$ ions.

Based on ΔH° and ΔS° for Reaction I, equilibrium cesium pressures have been calculated corresponding to typical oxygen pressures in a fuel pin. The formation of $\text{Cs}_2\text{U}_2\text{O}_7$, Rb_2UO_4 , and $\text{Rb}_2\text{U}_2\text{O}_7$ is also discussed.

The reactants used in the preparation of $\text{Cs}_2\text{U}_2\text{O}_7$ were CsNO_3 and U_3O_8 . Spectrographic analysis of the cesium salt revealed a total of less than 0.1 mass percent of other alkali metals; the uranium oxide contained less than 0.1 mass percent of other metals. Before use, the cesium nitrate and U_3O_8 were dried at 573 and 873 K, respectively. The calculated quantities of the two reactants were mixed, thoroughly ground, and heated slowly in a covered gold crucible to 1003 K over an 8-hr period. This temperature was maintained for three days. The product was carefully ground under an atmosphere of dry nitrogen and was reheated in air at 1003 K for an additional two days.

The X-ray power pattern⁴ and infrared spectrum⁵ of the product agreed in all details with the published data for $\text{Cs}_2\text{U}_2\text{O}_7$. Emission spectrographic and mass-spectrometric isotope dilution analyses revealed the following metallic impurities (ppm by mass): Na, 200; K, 200; Rb, 220. The total alkali metal content, determined gravimetrically as sulfate, was 31.11 ± 0.06 mass percent. On the assumption that the Na, K, and Rb were present as the diuranates, the Cs content was deduced to be 31.05 mass percent. The uranium content of the preparation, 55.81 ± 0.11 mass percent, was determined gravimetrically as U_3O_8 . This value was also adjusted for the U combined with the Na, K, and Rb impurities, leaving 55.42 mass percent U bound to Cs. Thus, the Cs-to-U ratio was 1.003 ± 0.008 , and the preparation contained a total of 0.54 ± 0.13 mass percent of $\text{Na}_2\text{U}_2\text{O}_7$, $\text{K}_2\text{U}_2\text{O}_7$, and $\text{Rb}_2\text{U}_2\text{O}_7$, together with 99.46 ± 0.13 mass percent of $\text{Cs}_2\text{U}_2\text{O}_7$.

Other calorimetric reagents were required, namely, cesium chloride, uranyl chloride, and hydrochloric acid. The CsCl and UO_2Cl_2 were from the same batches that had been used in previous work,^{1,6} and the hydrochloric acid was standardized against Na_2CO_3 .

An LKB-8700 Precision Calorimetric System was used in this study. The reaction vessel was made of glass and had a volume of 100 cm³. To prevent the diuranate from settling out at the bottom of the reaction vessel, the highest setting of the calorimeter stirrer speed was used. Temperatures were measured by means of a quartz-crystal thermometer (Hewlett-Packard Model 2801 A), and the thermometer output was recorded as a function of time on punched paper tape. This tape was processed by computer to give the corrected temperature change of the calorimeter.

Calorimetric experiments consisted of measurements of the enthalpy of reaction of $\text{Cs}_2\text{U}_2\text{O}_7$ with approximately 1 mol dm⁻³ HCl and of the enthalpy of solution of CsCl in HCl containing UO_2^{2+} ions.

Both $\text{Cs}_2\text{U}_2\text{O}_7$ and CsCl are hygroscopic and, accordingly, were handled exclusively in a glovebox filled with pure, dry ($\text{H}_2\text{O} \sim 1$ ppm by volume) recirculating helium. Calorimetric samples were weighed into predried glass ampoules, which were then stoppered with silicone rubber, sealed with wax, and placed in the stirrer-ampoule holder assembly of the calorimeter. The ampoules had very thin end windows that could be readily punctured to initiate the reaction between a sample and a calorimetric reagent.

The reaction of $\text{Cs}_2\text{U}_2\text{O}_7$ with HCl was rapid and went to completion in a few minutes. Electrical calibrations of the system were performed before and after each experiment. Not surprisingly, CsCl dissolved rapidly and completely in the $\text{UO}_2^{2+} + \text{HCl}$ solution. Because the dissolution was

endothermal, it was decided to supply a measured quantity of electrical energy to the system so that the corrected temperature change would be small. For these experiments, therefore, the energy equivalent of the calorimeter did not have to be known accurately, and it was based on just a few electrical calibrations.

TABLE 1. Calorimetric Results for Reaction of $\text{Cs}_2\text{U}_2\text{O}_7$ with HCl(aq)^a (1 cal = 4.184 J)

Expt. No.	m(sample), 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	0.22043	0.11768	421.12	-0.054	-225.06
2	0.22281	0.11908	421.08	-0.054	-225.29
3	0.22226	0.11885	420.58	-0.054	-225.14
4	0.22303	0.11981	420.57	-0.054	-226.17
5	0.22197	0.11840	420.79	-0.054	-224.70
6	0.22237	0.11953	420.58	-0.054	-226.32
7	0.22196	0.11916	420.71	-0.054	-226.10

$$\text{Mean } \Delta H_r/M(\text{sample}) = -225.54 \pm 0.24 \text{ J g}^{-1b}$$

$$\text{Impurity correction} = -0.29 \pm 0.05 \text{ J g}^{-1b}$$

$$\Delta H_r/M(\text{Cs}_2\text{U}_2\text{O}_7) = -225.83 \pm 0.50 \text{ J g}^{-1c}$$

$$\Delta H = -46087 \pm 102 \text{ cal mol}^{-1c,d}$$

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

^bUncertainty is the standard deviation of the mean.

^cUncertainty is twice the standard deviation.

^dThe molar mass of $\text{Cs}_2\text{U}_2\text{O}_7$ was taken to be 853.865 g mol⁻¹.

Detailed results for the two sets of measurements are in Tables 1 and 2. The symbols used in these tables have the following significance: m is the mass of sample reacted or dissolved; $\Delta\theta_c$ is the corrected temperature rise; $\langle\epsilon(\text{calor})\rangle$ is the mean energy equivalent of the calorimetric system; ΔH_{elec} is the electrical energy input; ΔH_{vap} is a correction for saturating the helium gas in the ampoules with water vapor; and $\Delta H_r/M$ is the specific enthalpy of reaction or solution. For the calculation of ΔH_{vap} , the enthalpy of vaporization of water was taken to be 44 kJ mol⁻¹,⁷ the densities of $\text{Cs}_2\text{U}_2\text{O}_7$,⁴ and CsCl ⁸ were taken to be 6.53 and 3.988 g cm⁻³, respectively, and the ampoules were assumed to be 1 cm³ in volume. No impurity correction was required for CsCl . The impurity correction for $\text{Cs}_2\text{U}_2\text{O}_7$ was based on the previously mentioned assumption that Na, K, and Rb were present as the di-uranates. The corresponding ΔH_f° values are to be found in Table 3, together with other auxiliary thermodynamic quantities.

TABLE 2. Calorimetric Results for Solution of CsCl^a

Expt. No.	m(CsCl), g	$\Delta\theta_c$, K	$\bar{\epsilon}$ (calor), J K ⁻¹	ΔH_{vap} , J	ΔH_{elec} , J	$\Delta H_r/M(CsCl)$, J g ⁻¹
1	0.08762	0.00053	420.6	-0.055	9.005	99.60
2	0.08713	0.00056	420.6	-0.055	9.004	100.00
3	0.08753	0.00049	420.6	-0.055	9.004	99.89
4	0.08877	0.00006	420.6	-0.055	9.004	100.53
5	0.08887	0.00021	420.6	-0.055	9.004	99.71
6	0.08830	0.00039	420.6	-0.055	9.004	99.49

$$\text{Mean } \Delta H_r/M(CsCl) = 99.87 \pm 0.15 \text{ J g}^{-1b}$$

$$\Delta H = 4019 \pm 12 \text{ cal mol}^{-1c,d}$$

^aIn each experiment, 99.41 cm³ of solution was used, and the mean temperature of the experiments was 298.15 $\pm$ 0.01 K.

^bUncertainty is the standard deviation of the mean.

^cThe molar mass of CsCl was taken to be 168.358 g mol⁻¹.

^dUncertainty is twice the standard deviation of the mean.

For the derivation of $\Delta H_f^\circ(Cs_2U_2O_7)$, the thermochemical cycle outlined in Table 4 was used. Values of ΔH for Reactions 1 and 3 are based on the data from Tables 1 and 2, and for Reaction 2 on a previous study.¹⁰ For Reactions 4 and 5, the dilution data have been taken from Parker's¹¹ compilation, and ΔH_f° for Cl⁻(aq) and H₂O(l) (Reactions 7 and 8) are Bureau of Standards selections.¹² Values for ΔH_f° and UO₂Cl₂⁶ and CsCl are to be found in Table 3; $\Delta H_f^\circ(CsCl)$ is based on the standard enthalpy of solution, 4100 $\pm$ 10 cal mol⁻¹,¹³ and the auxiliary data for Cs⁺(aq) and Cl⁻(aq). Summation of the ΔH values for Reactions 1 through 8 yielded $\Delta H_f^\circ(Cs_2U_2O_7, c, 298.15 \text{ K}) = -754.3 \pm 1.6 \text{ kcal mol}^{-1}$, where the uncertainty is the square root of the sum of the squares of the uncertainties of the ΔH values.

In an irradiated fuel pin, cesium monouranate is believed to form in the unrestructured region of the oxide fuel by combination of the oxide, fission-product cesium, and the oxygen resulting from fuel burnup. A similar reaction can take place with the urania insulator pellets. For a fuel composed of 80 mass per cent UO₂ and 20 mass per cent PuO₂, the formation of uranate can be depicted as follows:

*Throughout this report, 1 cal = 4.184 J; atm = 101.325 kPa.

TABLE 3. Auxiliary Thermochemical Data (298.15 K)

	ΔH_f° , kcal mol ⁻¹		ΔH_f° , kcal mol ⁻¹	S° , cal K ⁻¹ mol ⁻¹
Na ₂ U ₂ O ₇ (c)	-760 ± 4 ⁹	Cs ₂ UO ₄ (c)	-453.5 ± 0.9 ¹	52.5 ± 0.1 ¹⁷
K ₂ U ₂ O ₇ (c)	-754 ± 5 ^a	Cs(g)	18.18 ± 0.05 ¹⁵	41.9 ± 0.1 ¹⁵
Rb ₂ U ₂ O ₇ (c)	-750 ± 6 ^a	UO ₂ (c)	-259.3 ± 0.2 ¹⁶	18.41 ± 0.05 ¹⁸
HCl • 54.671				
H ₂ O(aq)	-39.543 ± 0.005 ¹¹	Cs ₂ U ₂ O ₇ (c)	-754.3 ± 1.6 ^b	76 ± 2 ^a
H ₂ O(l)	-68.315 ± 0.010 ¹²	O ₂ (g)	0	49.01 ± 0.01 ¹⁵
Cs ⁺ (aq)	-61.673 ± 0.030 ¹⁴	Rb(g)	19.33 ± 0.05 ¹⁵	40.6 ± 0.1 ¹⁵
Cl ⁻ (aq)	-39.952 ± 0.021 ¹⁴	Rb ₂ UO ₄ (c)	-452.00 ± 0.85 ¹⁰	48.5 ± 1.5 ¹⁰
CsCl(c)	-105.725 ± 0.038 ^c			
UO ₂ Cl ₂ (c)	-291.37 ± 0.81 ⁵			

^aEstimated value.^bThis work.^cDerivation of this value discussed in text.

TABLE 4. Reaction Scheme and Enthalpy Values for $\text{Cs}_2\text{U}_2\text{O}_7$ Experiments

Reaction	ΔH , kcal mol ⁻¹
1. $(2 \text{ Cs}^+ \cdot 2 \text{ UO}_2^{2+} \cdot 6 \text{ Cl}^-) \cdot 367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O)}$ = $\text{Cs}_2\text{U}_2\text{O}_7(\text{c}) + 373.60 \text{ (HCl} \cdot 54.671 \text{ H}_2\text{O)}$	46.09 ± 0.10
2. $2 \text{ UO}_2\text{Cl}_2(\text{c}) + 367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O)}$ = $(2 \text{ UO}_2^{2+} \cdot 4 \text{ Cl}^-) \cdot 367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O)}$	-44.98 ± 0.26
3. $(2 \text{ UO}_2^{2+} \cdot 4 \text{ Cl}^-) \cdot 367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O}) + 2 \text{ CsCl}(\text{c})$ = $(2 \text{ Cs}^+ \cdot 2 \text{ UO}_2^{2+} \cdot 6 \text{ Cl}^-) \cdot 367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O)}$	8.04 ± 0.02
4. $367.60 \text{ (HCl} \cdot 54.671 \text{ H}_2\text{O}) + 330.84 \text{ H}_2\text{O}(\text{l})$ = $367.60 \text{ (HCl} \cdot 55.571 \text{ H}_2\text{O)}$	-1.53 ± 0.07
5. $6 \text{ (HCl} \cdot 54.671 \text{ H}_2\text{O}) = 3 \text{ H}_2(\text{g}) + 3 \text{ Cl}_2(\text{g}) + 328.03 \text{ H}_2\text{O}(\text{l})$	237.26 ± 0.03
6. $2 \text{ U}(\text{c}) + 2 \text{ O}_2(\text{g}) + 2 \text{ Cl}_2(\text{g}) = 2 \text{ UO}_2\text{Cl}_2(\text{c})$	-582.74 ± 1.62
7. $2 \text{ Cs}(\text{c}) + \text{Cl}_2(\text{g}) = 2 \text{ CsCl}(\text{c})$	-211.45 ± 0.08
8. $3 \text{ H}_2(\text{g}) + 3/2 \text{ O}_2(\text{g}) = 3 \text{ H}_2\text{O}(\text{l})$	-204.96 ± 0.03
9. $2 \text{ Cs}(\text{c}) + 2 \text{ U}(\text{c}) + 3 \text{ 1/2 O}_2(\text{g}) = \text{Cs}_2\text{U}_2\text{O}_7(\text{c})$	-754.3 ± 1.6

At the temperatures of interest for Reaction III, *i.e.*, in the vicinity of 1000 K, the monouranate can be expected to decompose to diuranate;

The present results for $\text{Cs}_2\text{U}_2\text{O}_7$, together with other thermodynamic data from the literature, have been used to calculate the equilibrium cesium pressures for Reactions III and IV and, thence, to predict whether significant amounts of diuranate are likely to form.

In the absence of high-temperature enthalpy data for Cs_2UO_4 and $\text{Cs}_2\text{U}_2\text{O}_7$, it has been assumed that ΔH and ΔS for Reactions III and IV are both independent of temperature, and the following expressions have been deduced from the thermodynamic data in Table 3:

$$\Delta G(\text{III})_T = -230600 + 98.7 T \text{ cal mol}^{-1} \quad (\text{V})$$

$$\Delta G(\text{IV})_T = 189100 - 79.3 T \text{ cal mol}^{-1} \quad (\text{VI})$$

At $T = 1000 \text{ K}$, Equation V simplifies to

$$\log_{10} P_{\text{Cs}}(\text{III}) = -14.3622 - (1.093 \times 10^{-4}) \Delta \bar{G}(\text{O}_2) \quad (\text{VII})$$

where $P_{\text{Cs}}(\text{III})$ is the equilibrium cesium vapor pressure (atm) for Reaction III and $\Delta \bar{G}(\text{O}_2) = RT \ln P_{\text{O}_2}$ is the oxygen potential, P_{O_2} being the equilibrium oxygen pressure (atm). Similarly, Equation VI becomes

$$\log_{10} P_{\text{Cs}}(\text{IV}) = -11.9962 - (5.46 \times 10^{-5}) \Delta \bar{G}(\text{O}_2) \quad (\text{VIII})$$

TABLE 5. Cesium Partial Pressures for the $\text{Cs} + \text{U} + \text{O}$ System at 1000 K^a

$\Delta \bar{G}(\text{O}_2)$, cal mol ⁻¹	$P_{\text{Cs}}(\text{III})$, atm	$P_{\text{Cs}}(\text{IV})$, atm
-90,000	2.96×10^{-5}	8.28×10^{-8}
-95,000	1.04×10^{-4}	1.55×10^{-7}
-100,000	3.66×10^{-4}	2.91×10^{-7}
-105,000	1.29×10^{-3}	5.46×10^{-7}
-110,000	4.53×10^{-3}	1.02×10^{-6}

In Table 5, the equilibrium cesium vapor pressures are given as a function of $\Delta\bar{G}(O_2)$. The values for $\Delta\bar{G}(O_2)$ embrace those typical of oxide fuel systems in the region contiguous with the fuel-cladding interface. It is evident from the data in Table 5 that formation of Cs_2UO_4 requires cesium pressures of the order of 1×10^{-4} atm, whereas decomposition of Cs_2UO_4 to $Cs_2U_2O_7$ proceeds at pressures of the order of 1×10^{-7} atm. Thus, as Cs_2UO_4 forms, the equilibrium pressure will be significantly in excess of that required to form $Cs_2U_2O_7$. Similar calculations for the formation of $Cs_2U_2O_7$ from the elements and also from $Cs(g)$, $O_2(g)$, and $UO_2(c)$ show the cesium pressures to be significantly greater than are required for formation of Cs_2UO_4 according to Equation III. Thus, it is concluded that $Cs_2U_2O_7$ can form in irradiated fuel pins only by decomposition of Cs_2UO_4 . If the activity of Cs_2UO_4 is taken to be unity, then the activity of $Cs_2U_2O_7$ turns out to be of the order of 1×10^{-6} . It is expected, therefore, that the diuranate will be present at insignificant levels.

Similar calculations have been made for the $Rb + U + O$ system. For Rb_2UO_4 to form, the required pressures of $Rb(g)$ range from 3.2×10^{-5} atm at $\Delta\bar{G}(O_2) = -90,000$ cal mol $^{-1}$ to 4.9×10^{-3} atm at $\Delta\bar{G}(O_2) = -110,000$ cal mol $^{-1}$. These pressures are close to the values for P_{Cs} (III) in Table 5. Since the ratio of the fast fission yield of Rb to Cs is about 1:5,¹⁹ one can estimate that the ratio of the equilibrium vapor pressures will be similar. Bearing in mind that the uncertainties in our calculated pressures are of the order of about ± 30 per cent, it appears likely that Rb_2UO_4 will form in fuel pins, together with a minute quantity of $Rb_2U_2O_7$ as decomposition product.

B. α - and β -Sodium Uranates

In connection with drop calorimetric studies of α - and β - Na_2UO_4 (see Sections X.B and X.C), the enthalpy of the hypothetical $\alpha \rightarrow \beta$ transition at 298.15 K was required. Based on measurements of the enthalpies of reaction with $HCl(aq)$, this enthalpy of transition was found to be 3.3 kcal mol $^{-1}$.

C. Alkaline Earth Uranates

Of the alkaline earth uranates, only the strontium compounds have been subjected to in-depth calorimetric studies. Cordfunke and Loopstra²⁰ measured the enthalpies of reaction with 6*N* HNO_3 from which they derived the corresponding ΔH_f° values. Ippolitova *et al.*²¹ have reported $\Delta H_f^\circ(CaUO_4)$ based on reaction with HCl .

In connection with our studies on compounds that may form as a result of fission product-fuel interactions, we have recently determined $\Delta H_f^\circ(BaUO_4)$. This result is based on the reaction:

Additional studies on $MgUO_4$ and $CaUO_4$ are in progress.

II. THE AQUEOUS IODIDE ION (G. K. Johnson)

The standard enthalpy of formation of the aqueous iodide ion, $\Delta H_f^\circ(\text{I}^-, \text{aq}, 298.15 \text{ K})$, is an important basic thermodynamic datum that enters into the calculation of the enthalpies of formation of many metallic and nonmetallic iodides. Furthermore, a number of oxidizing substances have their enthalpies of formation based on $\Delta H_f^\circ(\text{I}^-, \text{aq})$. Therefore, it is surprising that, in spite of its fundamental importance, $\Delta H_f^\circ(\text{I}^-, \text{aq})$ is not known with high precision. For example, the CODATA selection¹⁴ gives an uncertainty of $\pm 0.20 \text{ kcal mol}^{-1}$ for $\Delta H_f^\circ(\text{I}^-, \text{aq})$, whereas the uncertainties for $\Delta H_f^\circ(\text{Cl}^-, \text{aq})$ and $\Delta H_f^\circ(\text{Br}^-, \text{aq})$ are only ± 0.021 and $\pm 0.035 \text{ kcal mol}^{-1}$, respectively. It was decided to redetermine $\Delta H_f^\circ(\text{I}^-, \text{aq})$ by measurement of the enthalpy of reaction of $\text{KBrO}_3(\text{c})$ with $\text{HI}(\text{aq})$ according to

Measurements were also performed on the enthalpy of solution of $\text{I}_2(\text{c})$ and $\text{KBr}(\text{c})$ in $\text{HI}(\text{aq})$ to complete the cycle.

The sample of KBrO_3 was Merck Reagent Grade material that had been twice recrystallized from distilled water. The recrystallized preparation was dried for five days at 400 K and stored thereafter in a helium-atmosphere glovebox. The oxidizing power of this material was equivalent to an assay of $100.0 \pm 0.5 \text{ mol per cent KBrO}_3$. Spectrographic analysis indicated less than 10 ppm of metallic impurities.

A sample of KBr was purchased from Alfa-Ventron (Beverly, Mass.). This material was dried for three days at 400 K and transferred to a helium-atmosphere glovebox. Metallic impurities in the sample totaled less than 15 ppm.

The iodine sample was part of a batch of high-purity crystalline material previously used at this laboratory for determining the enthalpies of formation of IF_5 and IF_7 ,²² as well as the enthalpy of solution of $\text{I}_2(\text{c})$ in $\text{HI}(\text{aq})$.²³ A total of 75 ppm of impurities had been previously found in this specimen.²² This material was stored in the glovebox.

Stock solutions of concentrated hydriodic acid were obtained from two different sources. One stock solution was prepared by distillation under argon of a commercial HI solution that contained $\sim 1\%$ H_3PO_3 as preservative. The other stock solution was prepared by dissolving gaseous HI in distilled H_2O . The resulting brown solution was treated with red phosphorus and distilled under argon. The stock solutions were stored in brown bottles under argon. For the calorimetric experiments, these solutions were diluted with distilled water to concentrations of 0.20 mol dm^{-3} and 0.15 mol dm^{-3} . These solutions could be used for approximately three days before decomposition of HI to I_2 became significant.

The calorimetric measurements were carried out in the LKB-8700 Precision Calorimetric System. The gold stirrer-ampoule holder assembly was replaced with one constructed of Kel-F plastic. Previous experience had shown that the gold stirrer is readily attacked by aqueous iodine.

Electrical calibration experiments were performed before and after each KBrO_3 experiment, and the mean value was used for the energy equivalent of the calorimetric system. For the endothermal experiments with KBr and I_2 , electrical energy was added to the calorimeter to offset the cooling effect of dissolution. Thus, the temperature change for the experiments was very small.

The samples of KBrO_3 , KBr , and I_2 were loaded in the glovebox into 1 cm³ glass ampoules that were equipped with glass filling stems. The ampoule stems were stoppered, and the ampoules were removed from the glovebox and promptly sealed with a flame.

The KBrO_3 -HI reactions were moderately fast, requiring approximately 30 min from the time the ampoule was broken until a final drift rate was established. The I_2 -HI experiments had reaction times that varied between 30 and 60 min.

Calorimetric data for the reaction of $\text{KBrO}_3(\text{c})$ with $\text{HI}(\text{aq})$ and for the dissolution of $\text{KBr}(\text{c})$ and $\text{I}_2(\text{c})$ in $\text{HI}(\text{aq})$ are given in Tables 6, 7, and 8, respectively.

Thermal effects of impurities in the samples were deemed to be insignificant. For conversion to molar quantities, the molecular weights of KBrO_3 , KBr and I_2 were taken to be 167.0002, 119.002, and 253.809 g mol⁻¹, respectively.

The thermochemical cycle used to derive $\Delta H_f^\circ(\text{HI}, \text{aq}, 298.15 \text{ K}) \equiv \Delta H_f^\circ(\text{I}^-, \text{aq}, 298.15 \text{ K})$ is given in Table 9. The enthalpies of reactions A, B, and C were based on the results in Tables 6, 7, and 8, respectively. The enthalpies of dilution of $\text{HI}(\text{aq})$ required for reactions D and G were taken from the data of Vanderzee and Gier.²⁴ The enthalpy of decomposition of KBrO_3 , reaction E, was previously determined at this laboratory.²⁵ For reaction F, $\Delta H_f^\circ(\text{H}_2\text{O}, \text{l})$ was taken to be $-68.315 \pm 0.010 \text{ kcal mol}^{-1}$.¹⁴ The standard enthalpy of formation of $\text{HI}(\text{aq})$ is one-sixth of reaction H or $-13.571 \pm 0.018 \text{ kcal mol}^{-1}$.

The value reported here for $\Delta H_f^\circ(\text{I}^-, \text{aq})$ is, therefore, in good agreement with, but much more precise than, the CODATA selected value of $-13.60 \pm 0.20 \text{ kcal mol}^{-1}$.

TABLE 6. Results for the Reaction of $\text{KBrO}_3(\text{c})$ with $\text{HI}(\text{aq})$

$m(\text{KBrO}_3),$ g	$\langle \epsilon(\text{calor}) \rangle,$ cal K^{-1}	$\Delta\theta_{\text{c}},$ K	$(-\Delta\theta_{\text{c}}) \langle \epsilon(\text{calor}) \rangle,$ cal	$\Delta H_{\text{vap}},$ cal	$\Delta H/M,$ cal g^{-1}
0.14017	104.979	0.98896	-103.820	-0.013	-740.76
0.13981	105.066	0.98633	-103.630	-0.013	-741.31
0.13967	105.012	0.98642	-103.586	-0.013	-741.74
0.13994	104.952	0.98813	-103.706	-0.013	-741.17
0.14124	105.053	0.99604	-104.637	-0.013	-740.94
0.14026	105.003	0.98940	-103.890	-0.013	-740.79
0.14009	105.022	0.98698	-103.655	-0.013	-740.01
0.14000	104.942	0.98853	-103.738	-0.013	-741.08

Mean $\Delta H/M = -740.98 \pm 0.18 \text{ cal g}^{-1}$

$\Delta H = -123.744 \pm 0.067 \text{ kcal mol}^{-1}$

TABLE 7. Results for the Dissolution of $\text{KBr}(\text{c})$ in $\text{HI}(\text{aq})$

$m(\text{KBr}),$ g	$\Delta\theta_{\text{c}},$ K	$(-\Delta\theta) \langle \epsilon(\text{calor}) \rangle,$ cal	$\Delta H_{\text{elec}},$ cal	$\Delta H_{\text{vap}},$ cal	$\Delta H/M,$ cal g^{-1}
0.09963	-0.00038	0.040	4.069	-0.013	41.11
0.09854	0.00006	-0.006	4.069	-0.013	41.10
0.09961	-0.00042	0.044	4.069	-0.013	41.16
0.09960	-0.00020	0.021	4.069	-0.013	40.93
0.09970	-0.00022	0.023	4.069	-0.013	40.91

Mean $\Delta H/M = 41.04 \pm 0.05 \text{ cal g}^{-1}$

$\Delta H = 4884 \pm 15 \text{ cal mol}^{-1}$

TABLE 8. Results for the Reaction of $I_2(c)$ with $HI(aq)$

$m(I_2),$ g	$\Delta\theta_c,$ K	$(-\Delta\theta_c) < \epsilon(\text{calor}) >, \Delta H_{elec},$ cal	$\Delta H_{elec},$ cal	$\Delta H_{vap},$ cal	$\Delta H/M,$ cal g^{-1}
0.63474	-0.00038	0.040	3.351	-0.012	5.323
0.63355	-0.00050	0.052	3.351	-0.012	5.352
0.63317	0.00039	-0.041	3.351	-0.012	5.209
0.64013	0.00009	-0.009	3.351	-0.012	5.202
0.63589	-0.00021	0.022	3.351	-0.012	5.286
0.63794	-0.00036	0.038	3.351	-0.012	5.294
0.63673	0.00005	-0.005	3.351	-0.012	5.236
0.63697	-0.00029	0.030	3.351	-0.012	5.289

Mean $\Delta H/M = 5.274 \pm 0.019$ cal g^{-1}

$\Delta H = 1339 \pm 10$ cal mol^{-1}

TABLE 9. Reaction Scheme for the Derivation of $\Delta H_f^\circ(HI, aq)$

A.	$3 I_2 \cdot KBr \cdot 17.692 HI \cdot 6519.485 H_2O = KBrO_3(c) + 23.692(HI \cdot 275.05 H_2O)$ $\Delta H = 123.744 \pm 0.067$ kcal mol^{-1}
B.	$KBr(c) + 17.692(HI \cdot 368.50 H_2O) = KBr \cdot 17.692 HI \cdot 6519.485 H_2O$ $\Delta H = 4.884 \pm 0.015$ kcal mol^{-1}
C.	$3 I_2(c) + KBr \cdot 17.692 HI \cdot 6519.485 H_2O = 3 I_2 \cdot KBr \cdot 17.692 HI \cdot 6519.485 H_2O$ $\Delta H = 4.017 \pm 0.030$ kcal mol^{-1}
D.	$17.692(HI \cdot 275.05 H_2O) + 1653.317 H_2O(c) = 17.692(HI \cdot 368.50 H_2O)$ $\Delta H = -0.212 \pm 0.031$ kcal mol^{-1}
E.	$KBrO_3(c) = KBr(c) + 3/2 O_2(g)$ $\Delta H = -8.098 \pm 0.060$ kcal mol^{-1}
F.	$3 H_2(g) + 3/2 O_2(g) = 3 H_2O(l)$ $\Delta H = -204.945 \pm 0.030$ kcal mol^{-1}
G.	$6(HI \cdot 275.05 H_2O) + \infty H_2O(l) = 6(HI \cdot \infty H_2O)$ $\Delta H = -0.816 \pm 0.008$ kcal mol^{-1}
H.	$3 H_2(g) + 3 I_2(c) + \infty H_2O(l) = 6(HI \cdot \infty H_2O)$ $\Delta H = -81.426 \pm 0.106$ kcal mol^{-1}

III. CESIUM NITRATE: STANDARD ENTHALPIES OF SOLUTION AND
FORMATION AND THE STANDARD ENTROPY AT 298.15 K
(P. A. G. O'Hare and Juliana Boerio*)

In the course of recent thermochemical studies of the cesium chromates, a reliable value for the standard enthalpy of solution of cesium nitrate, $\Delta H_{\text{soln}}^{\circ}(\text{CsNO}_3)$, was required. A literature search indicated that at least four previous determinations of $\Delta H_{\text{soln}}^{\circ}(\text{CsNO}_3)$ had been published. The results, however, spanned a range of about $0.25 \text{ kcal mol}^{-1}$ with uncertainties as large as $0.19 \text{ kcal mol}^{-1}$ and thus were not satisfactory for our purposes. Accordingly, we decided to redetermine $\Delta H_{\text{soln}}^{\circ}(\text{CsNO}_3)$. This result, in combination with the standard enthalpies of formation, ΔH_f° , of $\text{Cs}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$, gave $\Delta H_f^{\circ}(\text{CsNO}_3, \text{c}, 298.15 \text{ K})$.

The literature search also revealed that the standard entropy, $S^{\circ}(\text{CsNO}_3, \text{c}, 298.15 \text{ K})$, had not been determined experimentally. Combination of the measured enthalpy of solution with published solubility and activity coefficient data gave the standard Gibbs energy of solution, $\Delta G_{\text{soln}}^{\circ}$, and, ultimately, the standard entropy of CsNO_3 .

Single-crystal CsNO_3 was purchased from Gallard-Schlesinger Corp., Carle Place, N.Y. The X-ray diffraction powder pattern was in excellent agreement with the standard pattern for the trigonal modification.²⁶ Emission spectrochemical and mass-spectrometric isotope dilution analyses revealed only the following significant impurities (ppm by mass): Al, 80; Fe, 150; Rb, 317. The carbonate content was negligible. The specimen was dried by heating under vacuum for five days at 410 K; subsequently, it was not exposed to the atmosphere.

Enthalpies of solution of CsNO_3 in water were measured in our LKB-8700 Precision Calorimetric System. Two series of dissolutions in freshly boiled distilled water were carried out, using either 0.1- or 1-g samples. The cooling effect of the dissolution was offset by supplying a predetermined quantity of electrical energy to the calorimeter during the experiments. In this way, the temperature change was small. Calorimetric results are to be found in Table 10. For calculation of $\Delta H_{\text{vap}}^{\circ}$, the density of CsNO_3 was taken to be 3.69 g mol^{-1} .²⁶ The correction for impurities was negligible.

For series A, the average overall reaction was:

This result, along with the enthalpy of dilution given by Parker,¹¹ $-17 \pm 10 \text{ cal mol}^{-1}$, yields:

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TABLE 10. Calorimetric Results for the Solution of CsNO_3 in Water^a

Expt. No. ^b	m(CsNO_3), g	$\Delta\theta_c$, K	$\epsilon(\text{calor}) \times$ $-(\Delta\theta_c)$, ^c J	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M$, J g ⁻¹
A-2	0.10070	-0.00210	0.927	20.027	-0.055	207.54
-3	0.10009	0.00074	-0.327	21.029	-0.055	206.28
-4	0.09971	0.00001	-0.004	20.528	-0.055	205.29
-5	0.10043	-0.00073	0.322	20.528	-0.055	207.06
6	0.09953	-0.00032	0.141	20.528	-0.055	207.11
-7	0.09986	-0.00082	0.362	20.528	-0.055	208.64
-8	0.10056	0.00045	0.199	20.528	-0.055	205.57
Mean $\Delta H_r/M = 206.78 \pm 0.44 \text{ J g}^{-1}$ ^d						
$\Delta H_r = 9633 \pm 41 \text{ cal mol}^{-1}$ ^{e,f}						
B-10	0.98945	0.00224	-0.988	205.279	-0.041	206.43
-12	0.98586	0.00396	-1.746	205.281	-0.041	206.41
-13	0.97119	0.01084	-4.779	205.279	-0.041	206.41
-14	0.99345	0.00049	-0.216	205.281	-0.041	206.38
-15	0.98768	0.00331	-1.459	205.301	-0.041	206.34
-16	0.99012	0.00193	-0.851	205.298	-0.041	206.45
Mean $\Delta H_r/M = 206.40 \pm 0.02 \text{ J g}^{-1}$ ^d						
$\Delta H_r = 9615 \pm 2 \text{ cal mol}^{-1}$ ^{e,f}						

^aIn each experiment, 99.345 g of H_2O was used. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^bExperiment B-11 was excluded because the ampoule leaked.

^c $\epsilon(\text{calor})$ was 441.4 J K^{-1} for the A series, and 440.9 J K^{-1} for the B series.

^dUncertainty is the standard deviation of the mean.

^eFor conversion of $\Delta H/M$ to ΔH_r , the molar mass of CsNO_3 was taken to be $194.9103 \text{ g mol}^{-1}$.

^fUncertainty is equal to twice the standard deviation of the mean.

For series B, the average overall reaction was:

Again, this result along with the appropriate enthalpy of dilution, $24 \pm 10 \text{ cal mol}^{-1}$,¹¹ gives:

The enthalpies of dilution were arbitrarily assumed to be uncertain by $\pm 10 \text{ cal mol}^{-1}$. This assumption was made because Parker's selection was based on a series of measurements that was limited to the range between $m = 0.93$ and $m = 0.14$. The ΔH° values from the two series are in agreement. However, because of the superior precision of the measurements in series B (due, we believe, to the greater mass of CsNO_3 used), we select $9639 \pm 10 \text{ cal mol}^{-1}$ as the best result for $\Delta H_{\text{soln}}^\circ(\text{CsNO}_3)$.

From Reaction XIV and with ΔH_f° values of -61.67 ± 0.03 ¹⁴ and $-49.57 \pm 0.12 \text{ kcal mol}^{-1}$ ²⁷ for $\text{Cs}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$, respectively, we obtain $\Delta H_f^\circ(\text{CsNO}_3, \text{c}, 298.15 \text{ K}) = -120.88 \pm 0.12 \text{ kcal mol}^{-1}$.

The results for the four previous determinations reported for the enthalpy of solution of CsNO_3 are given in chronological order in Table 11. Haigh²⁸ in 1912 measured the enthalpy of solution at 293–295 K for a dilution of 400 H_2O . His results have been recalculated by Parker.¹¹ In 1964, Nosova and Samoilov²⁹ gave values for the enthalpies of solution of several chlorides and nitrates of the alkali and alkaline earth metals in aqueous MgCl_2 and $\text{Ca}(\text{NO}_3)_2$. They also gave the enthalpy of solution of CsNO_3 in water as $9.64 \text{ kcal mol}^{-1}$. However, they did not specify the exact concentration of the solution formed, but stated that it did not exceed 0.07 m. On that basis, the maximum correction to infinite dilution would be 44 cal mol^{-1} ,¹¹ as reflected by the results in Table 11. The uncertainty is based on a statement in the paper that the precision of the measurements was about 2 per cent.

TABLE 11. Enthalpy of Solution of CsNO_3 at 298.15 K

Investigator	$\Delta H_{\text{soln}}^\circ, \text{cal mol}^{-1}$
Haigh, ²⁸ recalculated by Parker ¹¹	9560 ± 50
Nosova and Samoilov ²⁹	$\leq 9684 \pm 190$
Krestov and Egorova ³⁰	9466 ± 28
Oyari ³³	9429 ± 140
This work	9639 ± 10

Krestov and Egorova³⁰ in 1967 reported $\Delta H_{\text{soln}}^{\circ}(\text{CsNO}_3) = 9466 \pm 28 \text{ cal mol}^{-1}$. This paper also gave similar data for various other nitrates; these data disagree with other determinations and accepted values for RbNO_3 ,³¹ $\text{Ca}(\text{NO}_3)_2$,³² and $\text{Sr}(\text{NO}_3)_2$.³² In 1971, Oyari³³ gave $\Delta H_{\text{soln}}^{\circ}(\text{CsNO}_3) = 9400 \pm 140 \text{ cal mol}^{-1}$ for a dilution of 1000 H_2O . The accuracy of the measurements was stated to be about 1.5 per cent. Thus our result agrees with, but is far more precise than, the value of Nosova and Samoilov. We are unable to explain the discrepancies in the other studies.

We have combined our results with data from the literature to derive a value for the standard entropy, $S^{\circ}(\text{CsNO}_3, \text{c}, 298.15 \text{ K})$, which, to date, has not been determined experimentally.

A saturated aqueous solution of CsNO_3 at 298.15 K contains 21.53 g of solute in 100 g of solution;³⁴ thus, the molality is 1.408. The activity coefficient, $\gamma_{\pm}(\text{CsNO}_3, \text{aq}, m = 1.408)$, is taken to be 0.368 from the tables of Robinson and Stokes,³⁵ and the activity, $a_{\pm}^{\pm} = m_{\pm}^2 \gamma_{\pm}^2 = 0.2685$. We now consider the following reactions:

Summation of Reactions XV, XVI, and XVII gives:

From our calorimetric studies, $\Delta H_{\text{soln}}^{\circ}$ for Reaction XVIII is $9639 \pm 10 \text{ cal mol}^{-1}$ and thus $\Delta S_{\text{soln}}^{\circ} = 29.72 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$. We take S° values of 31.75 ± 0.10 ¹⁴ and $35.12 \pm 0.20 \text{ cal K}^{-1} \text{ mol}^{-1}$ ¹⁴ for $\text{Cs}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$, respectively, and deduce $S^{\circ}(\text{CsNO}_3, \text{c}, 298.15 \text{ K}) = 37.1 \pm 0.2 \text{ cal K}^{-1} \text{ mol}^{-1}$. This result is in fair agreement with (1) the $36.5 \text{ cal K}^{-1} \text{ mol}^{-1}$ reported by Fermor and Kjekshus³⁶ based on lattice energy calculations, and (2) other recent estimates.

IV. THE ENTHALPY OF FORMATION OF Cs_2CO_3 (G. K. Johnson and K. H. Gayer*)

The thermodynamic properties of Cs_2CO_3 are of interest in connection with seed loss in the coal-fired MHD process. A previous determination of the enthalpy of formation of Cs_2CO_3 has been reported,³⁷ based on measurements of the enthalpy of solution of Cs_2CO_3 in water. This technique has a disadvantage, inasmuch as dissolution of Cs_2CO_3 in water is accompanied by the hydrolysis of CO_3^{2-} according to

The thermal correction required for this reaction is very concentration-dependent and can easily amount to 10 per cent of the measured enthalpy change.

Our determination, on the other hand, was based on measurements of the enthalpy of solution of Cs_2CO_3 in 0.5M CsOH . The use of CsOH for the solvent almost completely eliminated the hydrolysis correction.

The sample of Cs_2CO_3 was purchased from Alfa Inorganics. The material was dried to constant weight by heating at 543 K, under vacuum, for several days. Because the material is very hygroscopic, it was handled only in a helium atmosphere glovebox or in sealed containers. Spectrochemical analysis of the material revealed less than 40 ppm total of metallic contaminants, principally rubidium. The sample also contained 45 ppm hydrogen. It is not certain whether this hydrogen was present as H_2O or CsHCO_3 . Titration of weighed samples with standardized HCl required 99.82 per cent of the theoretical amount of acid. If the hydrogen had been present as H_2O , 99.96 per cent of the theoretical amount of acid should have been required, and if it had been present as CsHCO_3 , 99.86 per cent of the theoretical amount of acid should have been required. Since the latter value is in good agreement with the experimental result, we have tentatively assumed that the sample contained a bicarbonate impurity.

The results of six experimental measurements of the enthalpy of dissolution of Cs_2CO_3 in 0.5M CsOH are given in Table 12. Except for ΔH_{hyd} , which is the correction for the hydrolysis of CO_3^{2-} according to equation XIX, the entries in the table have the usual significance. For this reaction, the equilibrium constant is 1.8×10^{-11} , and ΔH_r is 9.8 kcal mol⁻¹.³⁸

The thermochemical cycle used to derive $\Delta H_f^\circ(\text{Cs}_2\text{CO}_3, \text{c}, 298.15 \text{ K})$ is given in Table 13. The first four reactions in that table yield the standard enthalpy of solution of $\text{Cs}_2\text{CO}_3(\text{c})$ according to

Reactions 5 and 6 in Table 13 correspond to the standard enthalpies of formation of the carbonate and cesium ions. The auxiliary thermochemical data for Reactions 3, 5, and 6 were taken from references 11, 12, and 14, respectively. Combination of Reactions 1 through 6 yields $\Delta H_f^\circ(\text{Cs}_2\text{CO}_3, \text{c}, 298.15 \text{ K})$ according to Reaction 7.

*Faculty Participant, Wayne State University, Detroit, Michigan.

TABLE 12. Results for the Dissolution of Cs_2CO_3 in 0.5M CsOH^a

Experiment No.	1	2	3	4	5	6
$m(\text{Cs}_2\text{CO}_3)$, g	0.74795	0.75082	0.75324	0.75199	0.74882	0.74920
$\langle \epsilon(\text{calor}) \rangle$, cal K^{-1}	103.094	103.388	103.317	103.339	103.332	103.294
$\Delta\theta_c$, K	0.29191	0.29209	0.29330	0.29313	0.29124	0.29162
$\langle \epsilon(\text{calor}) \rangle (-\Delta\theta_c)$, cal	-30.094	-30.199	-30.303	-30.292	-30.094	-30.123
ΔH_{vap} , cal	-0.011	-0.011	-0.011	-0.011	-0.011	-0.011
ΔH_{hyd} , cal	-0.008	-0.008	-0.008	-0.008	-0.008	-0.008
$\Delta H/M$, cal g^{-1}	-40.261	-40.247	-40.255	-40.308	-40.214	-40.232
Mean $\Delta H/M = -40.253 \pm 0.013$ cal g^{-1b}						
Impurity corr. = -0.12 ± 0.10 cal g^{-1b}						
$\Delta H/M(\text{Cs}_2\text{CO}_3) = -40.37 \pm 0.10$ cal g^{-1b}						
$\Delta H_r = -13.15 \pm 0.07$ kcal $\text{mol}^{-1c,d}$						

^aFor each experiment, the reaction vessel contained 99.41 cm^3 of 0.5M CsOH .

^bStandard deviation of the mean.

^cUncertainty interval.

^dThe molar mass of Cs_2CO_3 was taken to be 325.820 g.

TABLE 13. Reaction Scheme for Derivation of $\Delta H_f^\circ(\text{Cs}_2\text{CO}_3, \text{c})^a$

-
1. $\text{Cs}_2\text{CO}_3 \cdot 21.592 \text{ CsOH} \cdot 2397 \text{ H}_2\text{O} = \text{Cs}_2\text{CO}_3(\text{c}) + 21.592 (\text{CsOH} \cdot 111 \text{ H}_2\text{O}),$
 $\Delta H = 13.15 \pm 0.07 \text{ kcal mol}^{-1};$
 2. $\text{Cs}_2\text{CO}_3 \cdot 106.09 \text{ H}_2\text{O} + 21.592 (\text{CsOH} \cdot 106.09 \text{ H}_2\text{O})$
 $= \text{Cs}_2\text{CO}_3 \cdot 21.592 \text{ CsOH} \cdot 2397 \text{ H}_2\text{O},$
 $\Delta H = 0 \text{ kcal mol}^{-1};$
 3. $21.592 (\text{CsOH} \cdot 111 \text{ H}_2\text{O})$
 $= 21.592 (\text{CsOH} \cdot 106.09 \text{ H}_2\text{O}) + 106.09 \text{ H}_2\text{O}(\text{l}),$
 $\Delta H = 0.039 \pm 0.004 \text{ kcal mol}^{-1};$
 4. $\text{Cs}_2\text{CO}_3 \cdot \infty \text{H}_2\text{O} = \text{Cs}_2\text{CO}_3 \cdot 106.09 \text{ H}_2\text{O} + (\infty - 106.09) \text{ H}_2\text{O}(\text{l}),$
 $\Delta H = -0.25 \pm 0.20 \text{ kcal mol}^{-1};$
 5. $\text{C}(\text{graph}) + 3/2 \text{ O}_2(\text{g}) + \infty \text{H}_2\text{O}(\text{l}) = \text{CO}_3^{2-} \cdot \infty \text{H}_2\text{O},$
 $\Delta H = -161.84 \pm 0.05 \text{ kcal mol}^{-1};$
 6. $2 \text{ Cs}(\text{c}) + \infty \text{H}_2\text{O}(\text{l}) = 2 \text{ Cs}^+ \cdot \infty \text{H}_2\text{O},$
 $\Delta H = -123.35 \pm 0.06 \text{ kcal mol}^{-1};$
 7. $2 \text{ Cs}(\text{c}) + \text{C}(\text{graph}) + 3/2 \text{ O}_2(\text{g}) = \text{Cs}_2\text{CO}_3(\text{c}),$
 $\Delta H = -272.25 \pm 0.23 \text{ kcal mol}^{-1}.$
-

^aAll species in aqueous phase, except where designated otherwise.

Reaction 4, which involves the enthalpy of dilution of cesium carbonate, carries the dominant uncertainty in the cycle. This is because there are no dilution data for Cs_2CO_3 and the value for ΔH_4 was estimated from data for Cs_2SO_4 . C. E. Vanderzee (U. of Nebraska) is currently measuring the enthalpy of dilution of Na_2CO_3 . When these data become available, we should be able to better estimate ΔH_4 and thereby lower the uncertainty.

The results obtained in this work for the standard enthalpies of solution and formation of Cs_2CO_3 are -12.94 ± 0.21 and $-272.25 \pm 0.23 \text{ kcal mol}^{-1}$, which may be compared to the values of Raffelini and LeVan³⁷ who obtained -11.18 ± 0.61 and $-270.5 \pm 1.0 \text{ kcal mol}^{-1}$, respectively. The almost complete absence of experimental detail in the Raffelini and LeVan paper makes it impossible to evaluate their work. Since they measured the enthalpy of solution in water, it is possible that hydrolysis effects were not properly accounted for. The difference between their enthalpy of solution and ours would be approximately correct if, indeed, they had made no correction for hydrolysis.

V. ENTHALPIES OF SOLUTION OF THE CHLORIDES OF CESIUM AND RUBIDIUM
(G. K. Johnson and K. H. Gayer*)

The standard enthalpies of formation, ΔH_f° , of cesium chloride (CsCl) and rubidium chloride (RbCl) are of basic importance because they have frequently been used as auxiliary data in determinations of the enthalpies of formation of cesium and rubidium compounds (*e.g.* Cs_2UO_4 , Rb_2UO_4 , $\text{Cs}_2\text{U}_2\text{O}_7$). The standard enthalpies of solution in water, $\Delta H_{\text{soln}}^\circ$, are related to ΔH_f° as follows:

$$\Delta H_f^\circ(\text{MCl}, c) = \Delta H_f^\circ(\text{M}^+, \text{aq}) + \Delta H_f^\circ(\text{Cl}^-, \text{aq}) - \Delta H_{\text{soln}}^\circ(\text{MCl}) \quad (\text{XXI})$$

Since ΔH_f° of $\text{M}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ are already well known, an accurate determination of $\Delta H_{\text{soln}}^\circ$ is sufficient to establish $\Delta H_f^\circ(\text{MCl}, c)$.

In the course of a recent exploratory calorimetric investigation of Cs_2CO_3 , we found that our measured enthalpy of solution of CsCl in $\text{HCl}(\text{aq})$ differed significantly from the result that can be deduced from the selected value for $\Delta H_{\text{soln}}^\circ(\text{CsCl})$. This disagreement led us to believe that the selected value might be in error and, accordingly, we decided to redetermine $\Delta H_{\text{soln}}^\circ(\text{CsCl})$. As part of the same study, we carried out measurements on RbCl because we suspected that the selected value for its enthalpy of solution might be similarly erroneous.

Two specimens of CsCl were used: one was a high-purity crystalline material (Alfa Inorganics, Beverly, Mass.), and the other was a single-crystal material (Harshaw Chemical Co., Cleveland, Ohio). Both samples were dried at 823 K in a muffle furnace and subsequently handled only in a helium-atmosphere glovebox. Impurities in the Alfa CsCl were determined to be (in ppm): Mg, 12; Rb, 10; Na, 5; K, 5; and Cs_2CO_3 , 56. The single-crystal material was ground before use and was not analyzed,

The rubidium chloride was purchased from the National Bureau of Standards and carried the designation SRM-984. Impurities in this material were (in ppm): K, 420; Cs, 24; and Na, 2.3.

The calorimetric measurements, which are detailed in Tables XIV and XV, consisted of determinations of the enthalpies of the following reactions:

and

Enthalpies of dilution of $\text{CsCl} \cdot 600 \text{H}_2\text{O}$ and $\text{RbCl} \cdot 1700 \text{H}_2\text{O}$ to infinite dilution were taken from Parker's compilation.¹¹ We determined $\Delta H_{\text{soln}}^\circ(\text{CsCl})$ to be $4108 \pm 7 \text{ cal mol}^{-1}$ based on the measurements with the Alfa sample, and $4097 \pm 5 \text{ cal mol}^{-1}$ based on the measurements with the Harshaw material. Similarly, $\Delta H_{\text{soln}}^\circ(\text{RbCl})$ was determined to be $4036 \pm 6 \text{ cal mol}^{-1}$.

*Faculty participant, Wayne State University, Detroit, Michigan.

TABLE 14. Calorimetric Results for the Enthalpy of Solution of CsCl

m(CsCl), g	ϵ (calor), cal K ⁻¹	$\Delta\theta_c$, K	ϵ (calor)($-\Delta\theta_c$), cal	ΔH_{elec} , cal	ΔH_{vap} , cal	$\Delta H/M$, cal g ⁻¹
<u>"Alfa Inorganics" CsCl</u>						
1.55241	105.5	-0.00501	0.529	37.813	-0.008	24.693
1.55215	105.5	-0.00388	0.409	37.932	-0.008	24.697
1.55018	105.534	-0.36292	38.300	-	-0.008	24.702
1.55079	105.502	-0.36381	38.383	-	-0.008	24.745
1.54993	105.535	-0.36309	38.319	-	-0.008	24.718
1.55001	105.5	-0.00052	0.055	38.291	-0.008	24.734
1.54918	105.5	0.00022	-0.023	38.291	-0.008	24.697
Mean $\Delta H/M$ (sample) = 24.712 ± 0.008 cal g ⁻¹ ^a						
Impurity corr. = 0.023 ± 0.012 cal g ⁻¹ ^a						
$\Delta H/M(\text{CsCl}) = 24.735 \pm 0.014$ cal g ⁻¹ ^a						
$\Delta H_{soln}(\text{in } 600 \text{ H}_2\text{O}) = 4164.3 \pm 4.8$ cal mol ⁻¹ ^b						
$\Delta H_{soln}^\circ(\infty \text{ H}_2\text{O}) = 4108 \pm 7$ cal mol ⁻¹ ^b						
<u>"Harshaw Single-Crystal" CsCl</u>						
1.55193	105.5	-0.00028	0.030	38.291	-0.008	24.687
1.55119	105.5	0.00029	-0.031	38.291	-0.008	24.660
1.55174	105.5	0.00021	-0.022	38.291	-0.008	24.657
1.55728	105.5	0.00014	-0.015	38.411	-0.008	24.651
1.55042	105.5	0.00008	-0.008	38.291	-0.008	24.687
1.55300	105.5	-0.00025	0.026	38.291	-0.008	24.668
Mean $\Delta H/M$ (sample) = 24.668 ± 0.006 cal g ⁻¹ ^a						
$\Delta H_{soln}(\text{in } 600 \text{ H}_2\text{O}) = 4153.1 \pm 2.0$ cal mol ⁻¹ ^b						
$\Delta H_{soln}^\circ(\infty \text{ H}_2\text{O}) = 4097 \pm 5$ cal mol ⁻¹ ^b						

^aStandard deviation of the mean.^bUncertainty interval.

TABLE 15. Calorimetric Results for the Enthalpy of Solution of RbCl

m(RbCl), g	$\epsilon(\text{calor}),$ cal K ⁻¹	$\Delta\theta_c,$ K	$\epsilon(\text{calor})(-\Delta\theta_c),$ cal	$\Delta H_{\text{elec}},$ cal	$\Delta H_{\text{vap}},$ cal	$\Delta H/M,$ cal g ⁻¹
0.38732	105.5	0.00076	-0.080	13.282	-0.012	34.055
0.39720	105.5	-0.00027	0.029	13.522	-0.012	34.084
0.39334	105.5	0.00090	-0.095	13.522	-0.012	34.105
0.39112	105.5	0.00043	-0.045	13.402	-0.012	34.120
0.37733	105.5	0.00056	-0.059	12.923	-0.012	34.060

$$\text{Mean } \Delta H/M (\text{sample}) = 34.085 \pm 0.013 \text{ cal g}^{-1}{}^a$$

$$\text{Impurity corr.} = -0.018 \pm 0.010 \text{ cal g}^{-1}{}^a$$

$$\Delta H/M(\text{RbCl}) = 34.067 \pm 0.016 \text{ cal g}^{-1}{}^a$$

$$\Delta H_{\text{soln}} (\text{in } 1700 \text{ H}_2\text{O}) = 4091 \pm 4 \text{ cal mol}^{-1}{}^b$$

$$\Delta H_{\text{soln}}^{\circ} (\infty \text{ H}_2\text{O}) = 4036 \pm 6 \text{ cal mol}^{-1}{}^b$$

^aStandard deviation of the mean.

^bUncertainty interval.

TABLE 16. Comparison of the Enthalpies of Solution of CsCl and RbCl at 298.15 K

$\Delta H_{\text{soln}}^{\circ} (\text{CsCl}, c),$ cal mol ⁻¹		$\Delta H_{\text{soln}}^{\circ} (\text{RbCl}, c),$ cal mol ⁻¹	
4300	deForcrand ^a	4028	deForcrand ^a
4320	deForcrand ^a	4100	deForcrand ^a
4077 ± 50	Haigh ^a	4127	Zemczuzny et al. ^a
4254	Samoilov ^a	4000 ± 50	Haigh ^a
4180 ± 100	Rodnikova ^a	4112 ± 50	Samoilov ^a
4180 ± 100	Samoilov et al. ^a	4151 ± 75	Samoilov et al. ^a
4200 ± 40	Vorob'ev et al. ³⁹	4050 ± 30	Vorob'ev et al. ³⁹
4106	Sergeeva et al. ⁴⁰	4136	Sergeeva et al. ⁴⁰
4280	Oyari and Samoilov ⁴¹	4036 ± 6	This work
4092 ± 8	Melaugh and Rossini ⁴²		
4097 ± 5	This work		
4108 ± 7	This work		

^aThese values formed the basis of Parker's assessment.

In Table 16, our results are compared with previous determinations. Parker's assessment of the earlier work led her to select $\Delta H_{\text{soln}}^{\circ} = 4250 \pm 100 \text{ cal mol}^{-1}$ for CsCl and $4130 \pm 75 \text{ cal mol}^{-1}$ for RbCl. Our results clearly do not agree with this assessment and tend to be lower than many of the earlier values. Accordingly, several additional steps were taken to check the reliability of our data.

To ensure against the possibility of a calorimetric bias, the enthalpy of solution of KCl in water was measured. This reaction was chosen because it is endothermal and therefore comparable with the solution of CsCl and RbCl. In addition, KCl has traditionally been used as a test substance for solution calorimeters, and its enthalpy of solution is well established. Our $\Delta H_{\text{soln}}^{\circ}(\text{KCl}, c)$ was found to be $4119 \pm 5 \text{ cal mol}^{-1}$, in excellent agreement with the $4115 \pm 5 \text{ cal mol}^{-1}$ selected by Parker¹¹ from about seventy different determinations. As an additional check on our calorimetric system, a portion of the Alfa CsCl sample was sent to R. A. Melaugh and F. D. Rossini at Rice University. They performed a series of dissolutions of this material and determined the standard enthalpy of solution to be $4092 \pm 8 \text{ cal mol}^{-1}$ ⁴² in good accord with our result. These checks convince us that our calorimeter is functioning properly. Therefore, we conclude that the correct enthalpy of solution of CsCl lies within the range $4100 \pm 10 \text{ cal mol}^{-1}$ and not $4250 \pm 100 \text{ cal mol}^{-1}$ as selected by Parker.¹¹

Some of the results in Table 16 are in agreement with those obtained in the present investigation; however, the majority of the values are more positive. This disagreement could be due to unsuspected impurities in the earlier samples; however, in order to reconcile the data, large amounts of impurities would have had to be present, and this seems unlikely. Another possibility is that the high density of RbCl and CsCl caused these materials to settle to the bottom of the calorimeter for a significant amount of time prior to dissolution. This would create cold spots in the calorimeter and cause errors in calculating the corrected temperature change of the system. We were careful to avoid this problem in the present work.

Although the results obtained by us for the enthalpies of solution of RbCl and CsCl tend to be less positive than those obtained in many previous determinations, the use of well-characterized samples and the precautions taken in checking the calorimetry convince us that our results are to be preferred over much of the earlier data.

VI. CHROMATES

(P. A. G. O'Hare and Juliana Boerio*)

As we pointed out earlier in this report, the reactions of fission-product cesium with the stainless steel cladding in oxide fuel pins can lead to the formation of cesium chromates and thence to deterioration of the cladding. In this connection, we have chosen four chromates for thermochemical study. They are Cs_2CrO_4 , $\text{Cs}_2\text{Cr}_2\text{O}_7$, Cs_3CrO_4 , and Cs_4CrO_4 . The work on Cs_2CrO_4 and $\text{Cs}_2\text{Cr}_2\text{O}_7$ has been completed and is described.

A. Cesium Chromate (Cs_2CrO_4)

A literature search revealed that only one thermodynamic study of Cs_2CrO_4 had been reported to date. It was a determination of the enthalpy of solution by Shidlovskii, Balakireva, and Voskresenskii.⁴³ The final concentration in their experiments was $\text{Cs}_2\text{CrO}_4 \cdot 800 \text{ H}_2\text{O}$, and the conversion to infinite dilution required a long extrapolation of rather sparse and uncertain enthalpies of dilution. Since our ongoing studies of $\text{Cs} + \text{Cr} + \text{O}$ compounds will require a precise and unequivocal value for the enthalpy of formation, $\Delta H_f^\circ(\text{Cs}_2\text{CrO}_4, \text{c}, 298.15 \text{ K})$, we decided to redetermine the enthalpy of solution but with a final concentration close to $\text{Cs}_2\text{CrO}_4 \cdot 21000 \text{ H}_2\text{O}$. In our experiments, therefore, a long extrapolation to infinite dilution was obviated.

Calorimetric experiments consisted of measurements of the enthalpy of solution of Cs_2CrO_4 in water. The cesium chromate was part of the same batch as that used in the heat capacity studies.⁴⁴ It was dried in vacuo at 433 K and subsequently stored in a helium-filled glovebox. Distilled water was boiled immediately before use. Specimens of Cs_2CrO_4 were weighed into predried glass ampoules, which were then sealed with silicone rubber stoppers and wax. These operations were carried out in the glovebox. Calorimetric measurements were made in the LKB-8700 Precision Calorimetric System, whose energy equivalent was determined by electrical calibration.

Detailed calorimetric results are given in Table 17. For the calculation of ΔH_{vap} , the enthalpy of vaporization of water at 298.15 K and the density of Cs_2CrO_4 were taken to be 44 kJ mol^{-1} ⁷ and 4.24 g cm^{-3} ,⁴⁵ respectively, and the ampoules were each assumed to have an internal volume of 1 cm^{-3} .

The impurity correction arose solely from a sulfur contaminant that was assumed to be present as Cs_2SO_4 with an enthalpy of solution of 17.2 kJ mol^{-1} .³¹ Corrections for K and Rb as the chromates amounted to less than 0.01 J g^{-1} and were ignored.

In Table 17, $\Delta H_{\text{soln}}^\circ$ is for the average reaction:

For conversion to infinite dilution, the enthalpy has been estimated as $-110 \pm 20 \text{ cal mol}^{-1}$. This estimate lies between the limiting Debye-Hückel enthalpy of dilution, $-130 \text{ cal mol}^{-1}$, and that for the same dilution of Cs_2SO_4 , -89 cal mol^{-1} .⁴⁶ We have observed within the limited data at our disposal,⁴⁶ that the enthalpies of dilution of alkali metal chromates tend

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TABLE 17. Calorimetric Results for the Solution of Cs_2CrO_4 in H_2O ^a

Experiment ^b No.	m(sample), g	$\Delta\theta_c$, K	$\langle \epsilon(\text{calor}) \rangle^c$ $\times (-\Delta\theta_c)$, J	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g ⁻¹
1	0.09940	-0.00072	0.317	8.011	-0.055	83.23
2	0.09994	-0.00087	0.383	8.011	-0.055	83.44
3	0.10017	-0.00110	0.485	8.011	-0.055	84.27
5	0.10015	-0.01908	8.405	-	-0.055	83.37
6	0.09971	-0.01897	8.356	-	-0.055	83.25
7	0.09766	-0.01863	8.207	-	-0.055	83.47
9	0.10028	-0.00096	0.423	8.011	-0.055	83.56

$$\text{Mean } \Delta H_r/M(\text{sample}) = 83.51 \pm 0.13 \text{ J g}^{-1}\text{d}$$

$$\text{Impurity correction} = 0.02 \pm 0.01 \text{ J g}^{-1}$$

$$\Delta H_r/M(\text{Cs}_2\text{CrO}_4) = 83.53 \pm 0.13 \text{ J g}^{-1}\text{d}$$

$$\Delta H_r = \Delta H_{\text{soln}} = 7622 \pm 24 \text{ cal}_{\text{th}} \text{ mol}^{-1}\text{e}$$

^aIn experiments 1 through 7, 99.345g H_2O was used. The mean temperature in each of the experiments was $(298.15 \pm 0.01) \text{ K}$.

^bThe solution medium for experiment No. 9 was 99.41 cm³ of $1 \times 10^{-3} \text{ mol dm}^{-1} \text{ CsOH}$.

^c $\langle \epsilon(\text{calor}) \rangle$, a pooled average, was 440.5 J K^{-1} .

^dUncertainty is the standard deviation of the mean.

^eFor conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of Cs_2CrO_4 was taken to be $381.804 \text{ g mol}^{-1}$. Uncertainty is twice the standard deviation of the mean.

to be somewhat greater than those for the analogous sulfates. Combination of Equation XXIV and the enthalpy of dilution gives:

This result, along with the selected ΔH_f° values (kcal mol^{-1}) for $\text{Cs}^+(\text{aq})$ and $\text{CrO}_4^{2-}(\text{aq})$, -61.67 ± 0.03^{14} and -210.93 ± 0.45^{47} respectively, gives $\Delta H_f^\circ(\text{Cs}_2\text{CrO}_4, \text{c}, 298.15 \text{ K}) = -341.78 \pm 0.46 \text{ kcal mol}^{-1}$. The uncertainty is the square root of the sum of the squares of the uncertainties in ΔH° and the auxiliary ΔH_f° values.

Our standard enthalpy of solution, $7512 \pm 31 \text{ cal mol}^{-1}$, overlaps the value of $7400 \pm 100 \text{ cal mol}^{-1}$ reported by Shidlovskii *et al.*,⁴³ but is regarded as being somewhat more reliable because of the smaller extrapolation to infinite dilution and the likelihood that we employed a purer calorimetric specimen. Consequently, we feel that a reliable $\Delta H_f^\circ(\text{Cs}_2\text{CrO}_4)$ has been established that can be used with confidence as a basic datum in future studies involving other cesium chromates.

B. Cesium Dichromate ($\text{Cs}_2\text{Cr}_2\text{O}_7$)

Much of the earlier calorimetric work on alkali metal dichromates is suspect because corrections for the hydrolysis of the dichromate ion were neglected. The necessity for such a correction was avoided in the present work. Our result for $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7)$, the first to be reported in the literature, is a mean of two determinations. One is based on the reaction of $\text{Cs}_2\text{Cr}_2\text{O}_7$ with aqueous CsOH and the other on the reaction of Cs_2CrO_4 with aqueous HNO_3 .

The $\text{Cs}_2\text{Cr}_2\text{O}_7$ purchased from Electronic Space Products, Inc., Los Angeles, California, required purification. It was dissolved in distilled water at room temperature, and the solution was centrifuged and filtered. The filtrate was reduced to one-half its volume by slow evaporation and allowed to cool overnight. The resultant orange crystals were removed by filtration and recrystallized from distilled water. This material was then air-dried at 393 K, ground in an agate mortar, dried once more in vacuo at 413 K for 65 hr, and analyzed as follows.

Part of the preparation was dissolved in very pure NH_4OH , and the resulting chromate solution was passed through an anion-exchange column to adsorb the CrO_4^{2-} ions. The column was then washed with NH_4OH to remove trapped cesium ions, and the eluate was evaporated to dryness in a platinum beaker. The resulting CsOH was converted to Cs_2SO_4 by acidification with H_2SO_4 and careful evaporation to dryness. The Cs_2SO_4 was then dried at 873 K and weighed. Based on the mass of Cs_2SO_4 , the Cs content was calculated to be 55.25 ± 0.10 mass per cent (theoretical: 55.17 mass per cent).

Chromium was determined by dissolving part of the preparation in an excess of $\text{Fe}^{2+} + \text{H}_2\text{SO}_4$ solution. Some of the Fe^{2+} was thus oxidized to Fe^{3+} , and the unreacted Fe^{2+} was determined by titration with a Ce^{4+} solution. The standardization of the Fe^{2+} and Ce^{4+} solution was based on a certified National Bureau of Standards sample of $\text{K}_2\text{Cr}_2\text{O}_7$. The chromium content was found to be 21.47 ± 0.07 mass per cent (theoretical: 21.58 mass per cent). The Cs-to-Cr ratio was calculated to be 1.007 ± 0.009 .

Emission spectrochemical analysis indicated a Rb content of 300 ± 150 ppm, with other trace metals present in negligible amounts. Differential thermal analysis showed the material to be a pure compound with a transition at 632 K and a melting point of 651 ± 2 K. The X-ray diffraction powder pattern was in agreement with that given by Arkhipov *et al.*⁴⁸

The Cs_2CrO_4 used in the second determination was part of the high-purity batch described in the previous section of this report. Samples of CsNO_3 were purchased from Cerac/Pure, Inc., Butler, Wis., and Gallard-Schlesinger Corp., Carle Place, N.Y., and were dried at 390 K. The nitric acid solutions, prepared by diluting reagent-grade HNO_3 with distilled water, were standardized against sodium carbonate. Cesium hydroxide was purchased from Cerac/Pure, Inc. Solutions of the hydroxide were made with freshly boiled distilled water, standardized against hydrochloric acid, and protected as much as possible from exposure to the atmosphere.

Calorimetric specimens were weighed into predried glass ampoules in a glovebox filled with dry, recirculating helium. The ampoules were closed by means of silicone rubber stoppers which were then sealed over with wax. Calorimetric experiments consisted of measurements of the enthalpies of solution or reaction of the specimens with the appropriate calorimetric liquid.

Prior to the first set of experiments, the overall performance of the calorimetric system was checked by performing several measurements of the enthalpy of reaction of "TRIS" [tris(hydroxymethyl) amino methane, U. S. National Bureau of Standards Reference Material 724] with excess 0.1 mol dm^{-3} HCl. The mean enthalpy of reaction, $-7111 \pm 4 \text{ cal mol}^{-1}$, was well within the range of the certificate value, $-7115 \pm 7.5 \text{ cal mol}^{-1}$.

Results of the calorimetric measurements are in Tables 18 through 22. For the calculation of ΔH_{vap} , the densities of Cs_2CrO_4 , CsNO_3 , and $\text{Cs}_2\text{Cr}_2\text{O}_7$ were taken to be 4.26 ,⁴⁵ 3.69 ,²⁶ and 3.72 ⁴⁸ g cm^{-3} , respectively. Impurity levels in the CsNO_3 and $\text{Cs}_2\text{Cr}_2\text{O}_7$ were low enough that no thermochemical correction was required; for Cs_2CrO_4 , the impurity correction was for 0.0045 mass per cent S, assumed to be present as Cs_2SO_4 . The enthalpy of solution of Cs_2SO_4 in dilute acid and base was taken to be the same, $17.20 \text{ kJ mol}^{-1}$,³¹ as that in water.

The reaction scheme on which one of our determinations of $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7)$ is based is given in Table 23. Nitric acid was chosen as the reaction medium because Haight, Richardson, and Coburn⁴⁹ have shown that in such a solution the only mononuclear species of Cr(VI) present are H_2CrO_4 and HCrO_4^- . For the sake of simplicity, the reaction scheme indicates the formation of bichromate ion, HCrO_4^- , only. It should be pointed out that the strict matching and maintenance of the stoichiometries of the product solutions obviates the necessity to know the exact chemical composition of the reaction products.

Enthalpies of Reactions 1, 2, and 3 in Table 23 are taken directly from Tables 18, 19, and 20, respectively. Thermochemical data for dilution and formation of HNO_3 , Reactions 4 and 5, are taken from refs. 11 and 12; ΔH for Reactions 6, 7, and 8 are based on ΔH_f° values for $\text{H}_2\text{O}(l)$,¹⁴ $\text{CsNO}_3(c)$ (this report), and Cs_2CrO_4 (this report) respectively. Summation of ΔH_1 through ΔH_8 and multiplication by 2 gives $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7, c, 298.15 \text{ K}) = -499.58 \pm 1.00 \text{ kcal mol}^{-1}$. The uncertainty is twice the square root of the sum of the squares of the uncertainties of items 1 through 8.

TABLE 18. Calorimetric Results for the Reaction
of Cs_2CrO_4 with Aqueous HNO_3 ^a

Expt. No.	m(sample), 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}
2	0.98863	-0.14669	435.78	-0.043	64.62
3	0.98346	-0.14912	435.88	-0.043	66.05
4	0.98830	-0.14921	436.24	-0.043	65.82
6	0.98924	-0.14754	435.79	-0.043	64.95
7	0.99180	-0.14887	436.40	-0.043	65.46
8	0.98964	-0.14954	436.32	-0.043	65.89
9	0.97654	-0.14832	435.55	-0.043	66.11
10	0.99144	-0.15009	436.06	-0.043	65.97

$$\text{Mean } \Delta H_r/M(\text{sample}) = 65.61 \pm 0.19 \text{ J g}^{-1}\text{ }^b$$

$$\Delta H_r(\text{sample}) = 5987 \pm 35 \text{ cal mol}^{-1}\text{ }^c, \text{ }^d$$

$$\text{Impurity correction} = 2 \pm 1 \text{ cal mol}^{-1}$$

$$\Delta H_r = 5989 \pm 35 \text{ cal mol}^{-1}$$

^aIn each experiment, 99.41 cm³ of 0.36 mol dm⁻³ HNO_3 was used. The mean temperature of the experiments was 298.15 ± 0.01 K.

^bUncertainty is the standard deviation of the mean.

^cUncertainty is twice the standard deviation of the mean.

^dThe molar mass of Cs_2CrO_4 was taken to be 381.804 g mol⁻¹.

TABLE 19. Calorimetric Results for Solution of CsNO_3 in Aqueous HNO_3 ^a

Expt. No.	$m(\text{CsNO}_3)$, g	$\langle \epsilon(\text{calor}) \rangle \times$				
		$\Delta\theta_c$, K	$(-\Delta\theta_c)^b$, J	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M(\text{CsNO}_3)$, J g ⁻¹
1	0.50320	0.00761	-3.316	103.137	-0.048	198.28
2	0.50401	0.00039	-0.170	100.138	-0.048	198.25
3	0.50485	0.00014	-0.061	100.150	-0.048	198.16
4	0.50446	0.00011	-0.052	100.136	-0.048	198.31
5	0.50286	0.00144	-0.627	100.135	-0.048	197.79
6	0.50567	-0.00064	0.279	100.140	-0.048	198.49
7	0.50382	0.00010	-0.044	100.138	-0.048	198.57
Mean $\Delta H_r/M(\text{CsNO}_3) = 198.26 \pm 0.19 \text{ J g}^{-1}$ ^c						
$\Delta H_r = 9236 \pm 9 \text{ cal mol}^{-1}$ ^d						

^aIn each experiment, 99.41 cm³ of 0.357 mol dm⁻³ HNO_3 was used and the mean temperature was $298.15 \pm 0.01 \text{ K}$.

^b $\langle \epsilon(\text{calor}) \rangle$, a pooled average of several determinations, was equal to 435.7 J K^{-1} .

^cUncertainty is twice the standard deviation of the mean.

^dFor conversion of $\Delta H_r/M$ to ΔH_r , the molar mass of CsNO_3 was taken to be $194.9103 \text{ g mol}^{-1}$.

TABLE 20. Calorimetric Results for the Solution of $\text{Cs}_2\text{Cr}_2\text{O}_7$ in Aqueous $\text{CsNO}_3 + \text{HNO}_3$ ^a

Expt. No.	$m(\text{Cs}_2\text{Cr}_2\text{O}_7)$, g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle \times (-\Delta\theta_c)^b$, J	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M(\text{Cs}_2\text{Cr}_2\text{O}_7)$, J g ⁻¹
2	0.62470	-0.05135	22.332	90.122	-0.047	179.94
3	0.62183	-0.00238	1.035	110.150	-0.047	178.73
6	0.62142	-0.00573	2.492	110.153	-0.047	181.19
7	0.62136	-0.00453	1.970	110.157	-0.047	180.38
8	0.62394	-0.00764	3.323	110.164	-0.047	181.81
9	0.62631	0.00800	-3.479	115.163	-0.047	178.25
Mean $\Delta H_r/M(\text{Cs}_2\text{Cr}_2\text{O}_7) = 180.05 \pm 1.13 \text{ J g}^{-1}$ ^c						
$\Delta H_r = 20,733 \pm 130 \text{ cal mol}^{-1}$ ^d						

^aIn each experiment, 99.41 cm³ of the solution resulting from reaction 2, Table 23, was used. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^b $\langle\epsilon(\text{calor})\rangle$ was an average value, 434.9 J K⁻¹, obtained from several calibrations.

^cUncertainty is twice the standard deviation of the mean.

^dFor conversion of $\Delta H_r/M(\text{sample})$ to ΔH_r , the molar mass of $\text{Cs}_2\text{Cr}_2\text{O}_7$ was taken to be 481.799 g mol⁻¹.

TABLE 21. Calorimetric Results for the Reaction of $\text{Cs}_2\text{Cr}_2\text{O}_7$ with Aqueous CsOH ^a

Expt. No.	$m(\text{Cs}_2\text{Cr}_2\text{O}_7)$, g	$\Delta\theta_c$, K	$\langle\epsilon(\text{calor})\rangle^b$, J K ⁻¹	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M(\text{Cs}_2\text{Cr}_2\text{O}_7)$, J g ⁻¹
1	0.69653	0.11880	440.00	30.543	-0.046	-31.12
2	0.69906	0.04926	438.22	-	-0.046	-30.95
3	0.69455	0.05016	439.82	-	-0.046	-31.83
4	0.70975	0.05057	439.82	-	-0.046	-31.40
5	0.68403	0.04850	442.16	-	-0.046	-31.42
6	0.61243	0.04302	440.00	-	-0.046	-30.98
Mean $\Delta H_r/M(\text{Cs}_2\text{Cr}_2\text{O}_7) = -31.28 \pm 0.27 \text{ J g}^{-1}$ ^c						
$\Delta H_r = -3602 \pm 31 \text{ cal mol}^{-1}$ ^d						

^aFor each experiment, 99.41 cm³ of 0.09 mol dm⁻³ CsOH was used. The mean temperature of the experiments was $298.15 \pm 0.01 \text{ K}$.

^b $\langle\epsilon(\text{calor})\rangle$ for experiments 1 and 6 is the average of the $\langle\epsilon(\text{calor})\rangle$ values from the other experiments.

^cUncertainty is twice the standard deviation of the mean.

^dFor conversion of $\Delta H_r/M(\text{sample})$ to ΔH_r , the molar mass of $\text{Cs}_2\text{Cr}_2\text{O}_7$ was taken to be 481.799 g mol⁻¹.

TABLE 22. Calorimetric Results for the Solution
of Cs_2CrO_4 in Aqueous CsOH^a

Expt. No.	m(sample), g	$\Delta\theta_c$, K	$\langle \epsilon(\text{calor}) \rangle_x$ $(-\Delta\theta_c)^b$ J $^\circ\text{C}^{-1}$	ΔH_{elec} , J	ΔH_{vap} , J	$\Delta H_r/M(\text{sample})$, J g^{-1}
1	1.07753	-0.00618	2.716	87.123	-0.043	83.34
2	1.08473	-0.00082	0.360	90.128	-0.043	83.38
3	1.08343	-0.00061	0.268	90.129	-0.043	83.40
4	1.08462	-0.00072	0.316	90.127	-0.043	83.35
5	1.08394	-0.00114	0.501	90.125	-0.043	83.57
6	1.08443	-0.00118	0.519	90.126	-0.043	83.55

$$\text{Mean } \Delta H_r/M(\text{sample}) = 83.43 \pm 0.04 \text{ J g}^{-1}{}^c$$

$$\Delta H_r(\text{sample}) = 7613 \pm 7 \text{ cal mol}^{-1}{}^{d,e}$$

$$\text{Impurity correction} = 2 \pm 1 \text{ cal mol}^{-1}$$

$$\Delta H_r(\text{Cs}_2\text{CrO}_4) = 7615 \pm 7 \text{ cal mol}^{-1}$$

^aIn each experiment, 99.41 cm³ of 0.06 mol dm⁻³ CsOH was used, and the mean temperature of the experiments was 298.15 $\pm$ 0.01 K.

^b $\langle \epsilon(\text{calor}) \rangle = 439.5 \text{ J K}^{-1}$ is the average of several calibrations.

^cUncertainty is the standard deviation of the mean.

^dUncertainty is twice the standard deviation of the mean.

^eFor conversion of $\Delta H_r/M(\text{sample})$ to ΔH_r , the molar mass of Cs_2CrO_4 was taken to be 381.804 g mol⁻¹.

TABLE 23. Thermochemical Scheme for Reaction of Cs_2CrO_4 with HNO_3 ^a

1. $\text{Cs}_2\text{CrO}_4(\text{c}) + 12.792(\text{HNO}_3 \cdot 165.09 \text{ H}_2\text{O})$ $= (2\text{Cs}^+ \cdot \text{HCrO}_4^- \cdot \text{NO}_3^-) \cdot 11.792(\text{HNO}_3 \cdot 179.09 \text{ H}_2\text{O})$	$\Delta H_1 = 5.99 \pm 0.04 \text{ kcal mol}^{-1}$
2. $(\text{Cs}^+ \cdot \text{NO}_3^-) \cdot 11.792(\text{HNO}_3 \cdot 179.13 \text{ H}_2\text{O}) = \text{CsNO}_3(\text{c})$ $+ 11.792(\text{HNO}_3 \cdot 179.13 \text{ H}_2\text{O})$	$\Delta H_2 = -9.24 \pm 0.01 \text{ kcal mol}^{-1}$
3. $(2\text{Cs}^+ \cdot \text{HCrO}_4^- \cdot \text{NO}_3^-) \cdot 11.792(\text{HNO}_3 \cdot 179.09 \text{ H}_2\text{O})$ $= 1/2\text{Cs}_2\text{Cr}_2\text{O}_7(\text{c}) + (\text{Cs}^+ \cdot \text{NO}_3^-) \cdot 11.792(\text{HNO}_3 \cdot 179.13 \text{ H}_2\text{O})$	$\Delta H_3 = -10.37 \pm 0.07 \text{ kcal mol}^{-1}$
4. $11.792(\text{HNO}_3 \cdot 179.13 \text{ H}_2\text{O}) = 11.792(\text{HNO}_3 \cdot 165.09 \text{ H}_2\text{O})$ $+ 165.56 \text{ H}_2\text{O}(1)$	$\Delta H_4 = 0.01 \pm 0.01 \text{ kcal mol}^{-1}$
5. $1/2\text{H}_2(\text{g}) + 3/2 \text{O}_2(\text{g}) + 1/2\text{N}_2(\text{g})$ $+ 165.09 \text{ H}_2\text{O}(1) = \text{HNO}_3 \cdot 165.09 \text{ H}_2\text{O}$	$\Delta H_5 = -49.44 \pm 0.12 \text{ kcal mol}^{-1}$
6. $1/2\text{H}_2\text{O}(1) = 1/2\text{H}_2(\text{g}) + 1/4\text{O}_2(\text{g})$	$\Delta H_6 = 34.16 \pm 0.01 \text{ kcal mol}^{-1}$
7. $\text{CsNO}_3(\text{c}) = \text{Cs}(\text{c}) + 1/2\text{N}_2(\text{g}) + 3/2 \text{O}_2(\text{g})$	$\Delta H_7 = 120.88 \pm 0.12 \text{ kcal mol}^{-1}$
8. $2\text{Cs}(\text{c}) + \text{Cr}(\text{c}) + 2\text{O}_2(\text{g}) = \text{Cs}_2\text{CrO}_4(\text{c})$	$\Delta H_8 = -341.73 \pm 0.46 \text{ kcal mol}^{-1}$
9. $\text{Cs}(\text{c}) + \text{Cr}(\text{c}) + 7/4 \text{O}_2(\text{g}) = 1/2\text{Cs}_2\text{Cr}_2\text{O}_7(\text{c})$	$\Delta H_9 = -249.79 \pm 0.50 \text{ kcal mol}^{-1}$

^aUnless otherwise specified, all species in the above reaction scheme are in the aqueous phase.

The thermochemical cycle for the reaction of $\text{Cs}_2\text{Cr}_2\text{O}_7$ with $\text{CsOH}(\text{aq})$ is given in Table 24. Values for ΔH_1 and ΔH_2 are taken from Tables 21 and 22, respectively. Enthalpies of dilution of CsOH , items 3 and 4, are estimated by analogy with KOH ,¹¹ and twice the enthalpy of reaction of Cs with H_2O , the reverse of item 4, is taken from Gunn's study.⁵⁰ Items 5 and 6 are based on ΔH_f° values for Cs_2CrO_4 (this report) and $\text{H}_2\text{O}(\text{l})$,¹⁴ respectively. Addition of ΔH_1 through ΔH_6 gives $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -499.98 \pm 0.92 \text{ kcal mol}^{-1}$, where the uncertainty is the sum of the squares of the uncertainties in items 1 through 6.

Thus, the two results for the standard enthalpy of formation are in excellent agreement. A weighted mean, $-499.79 \pm 0.68 \text{ kcal mol}^{-1}$, is taken to be the best value for $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K})$. A significant part of the uncertainty in the results for $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7)$ comes from the uncertainty, $\pm 0.45 \text{ kcal mol}^{-1}$, in $\Delta H_f^\circ(\text{CrO}_4^{2-}, \text{aq})$.

There have been no previous determinations of $\Delta H_f^\circ(\text{Cs}_2\text{Cr}_2\text{O}_7)$. However, two other alkali metal dichromates have been studied calorimetrically. Nelson, Moss, and Hepler⁵¹ reported $\Delta H^\circ = -21.37 \pm 0.18 \text{ kcal mol}^{-1}$ for the reaction:

For auxiliary data, we have taken ΔH_f° values (kcal mol^{-1}) of -54.98 ± 0.02 ,²⁷ -57.43 ± 0.02 ,¹² -210.93 ± 0.45 ,⁴⁷ and -68.32 ± 0.01 ¹² for $\text{OH}^-(\text{aq})$, $\text{Na}^+(\text{aq})$, $\text{CrO}_4^{2-}(\text{aq})$, and $\text{H}_2\text{O}(\text{l})$, and have derived $\Delta H_f^\circ(\text{Na}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -473.71 \pm 0.92 \text{ kcal mol}^{-1}$. A determination of the enthalpy of solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ in water was reported by Shidlovskii and Valkina;⁵² however, the results of those experiments are suspect because the formation of HCrO_4^- from hydrolysis of $\text{Cr}_2\text{O}_7^{2-}$ was not taken into account.

For the derivation of $\Delta H_f^\circ(\text{K}_2\text{Cr}_2\text{O}_7)$ from enthalpy of solution measurements, Hepler⁵³ took the formation of HCrO_4^- into account. Based on an analysis of earlier work, he deduced $\Delta H^\circ = 20.7 \text{ kcal mol}^{-1}$ for

With ΔH_f° values (kcal mol^{-1}) of -60.27 ± 0.03 ¹⁴ and -210.0 ± 0.07 ⁵⁴ for $\text{K}^+(\text{aq})$ and $\text{HCrO}_4^-(\text{aq})$, we calculate $\Delta H_f^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -492.9 \pm 1.4 \text{ kcal mol}^{-1}$. Muldrow and Hepler⁵⁵ gave $\Delta H^\circ = -7.3 \pm 0.1 \text{ kcal mol}^{-1}$ for

from which we deduce $\Delta H_f^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K}) = -493.5 \pm 0.9 \text{ kcal mol}^{-1}$ based on previously given auxiliary data. The weighted mean, $-493.3 \pm 0.8 \text{ kcal mol}^{-1}$, is regarded as the best result for $\Delta H_f^\circ(\text{K}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K})$.

Earlier enthalpy of solution measurements on $\text{K}_2\text{Cr}_2\text{O}_7$ were reported by Kolosovskii and Grishkun⁵⁶ at 318.95, 328.53, and 333.22 K, but not at 298.15 K. Because the enthalpy of solution varied drastically with temperature, we were unable to reliably estimate the value at 298.15 K.

TABLE 24. Thermochemical Scheme for Reaction of $\text{Cs}_2\text{Cr}_2\text{O}_7$ with CsOH^a

1. $(4\text{Cs}^+ \cdot 2\text{CrO}_4^{2-}) \cdot 4.296(\text{CsOH} \cdot 902.06\text{H}_2\text{O})$ $= \text{Cs}_2\text{Cr}_2\text{O}_7(\text{c}) + 6.296(\text{CsOH} \cdot 615.35\text{H}_2\text{O})$	$\Delta H_1 = 3.60 \pm 0.03 \text{ kcal mol}^{-1}$
2. $2\text{Cs}_2\text{CrO}_4(\text{c}) + 4.296(\text{CsOH} \cdot 902.06\text{H}_2\text{O})$ $= (4\text{Cs}^+ \cdot 2\text{CrO}_4^{2-}) \cdot 4.296(\text{CsOH} \cdot 902.06\text{H}_2\text{O})$	$\Delta H_2 = 15.23 \pm 0.01 \text{ kcal mol}^{-1}$
3. $6.296(\text{CsOH} \cdot 615.35\text{H}_2\text{O}) + 1805.12\text{H}_2\text{O}(\text{l})$ $= 6.296(\text{CsOH} \cdot 902.06\text{H}_2\text{O})$	$\Delta H_3 = -0.09 \pm 0.03 \text{ kcal mol}^{-1}$
4. $2(\text{CsOH} \cdot 902.06\text{H}_2\text{O}) + \text{H}_2(\text{g}) = 2\text{Cs}(\text{c})$ $+ 1806.12\text{H}_2\text{O}(\text{l})$	$\Delta H_4 = 96.52 \pm 0.02 \text{ kcal mol}^{-1}$
5. $4\text{Cs}(\text{c}) + 2\text{Cr}(\text{c}) + 4\text{O}_2(\text{g}) = 2\text{Cs}_2\text{CrO}_4(\text{c})$	$\Delta H_5 = -683.56 \pm 0.92 \text{ kcal mol}^{-1}$
6. $\text{H}_2\text{O}(\text{l}) = \text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g})$	$\Delta H_6 = 68.32 \pm 0.01 \text{ kcal mol}^{-1}$
7. $2\text{Cs}(\text{c}) + 2\text{Cr}(\text{c}) + 7/2 \text{O}_2(\text{g}) = \text{Cs}_2\text{Cr}_2\text{O}_7(\text{c})$	$\Delta H_7 = -499.98 \pm 0.92 \text{ kcal mol}^{-1}$

^aAll species in the above reaction scheme are in the aqueous phase unless otherwise noted.

Since the enthalpies of formation of the dichromates of Na, K, and Cs from CrO_3 and the corresponding chromates, M_2CrO_4 , lie within the range of $13.5 \pm 2.5 \text{ kcal mol}^{-1}$, we assume that this relationship also applies to rubidium dichromate. Thus, $\Delta H_f^\circ(\text{Rb}_2\text{Cr}_2\text{O}_7, \text{c}, 298.15 \text{ K})$ is estimated to be $-492.0 \pm 2.7 \text{ kcal mol}^{-1}$ based on ΔH_f° values (kcal mol^{-1}) of -141.7 ± 0.5^{47} and -336.9 ± 0.8^{54} for $\text{CrO}_3(\text{c})$ and $\text{Rb}_2\text{CrO}_4(\text{c})$.

VII. THE THERMOCHEMISTRY OF THE TRIFLUORIDES OF SCANDIUM,
YTTRIUM, LANTHANUM, AND THE RARE EARTHS
(W. N. Hubbard)

Approximately eight years ago, Rudzitis⁵⁷ of this Laboratory carried out fluorine bomb calorimetric combustions of scandium, yttrium, lanthanum, and four rare earth elements: neodymium, holmium, gadolinium, and europium. He made an effort to use the data obtained to estimate values of the enthalpies of formation for the rest of the rare earth trifluorides.

Third ionization potentials were available for lanthanum and yttrium. This allowed calculation of the lattice energies of LaF_3 and YF_3 in the usual manner. Next, lattice energies were estimated for the lanthanide trifluorides by correlation of their molecular volume and structure with those of LaF_3 and YF_3 . Following this, reversal of the Born-Haber cycle for NdF_3 , HoF_3 , GdF_3 , and EuF_3 yielded values of the ionization potentials of the metals. Similar calculations for the trichlorides and sesquioxides yielded additional values of the ionization potentials of the metals. With these data, enthalpies of vaporization of the trifluorides from the literature, and the estimated lattice energies, enthalpies of formation were calculated for all the trifluorides. The results of the calculations seemed to be in reasonable agreement with Rudzitis' measurements for all the heavier trifluorides that are isostructural with yttrium trifluoride. The only lighter trifluoride isostructural with lanthanum trifluoride for which Rudzitis had an experimental value was neodymium trifluoride. His value was $\Delta H_f^\circ(\text{NdF}_3, c) = -396 \text{ kcal mol}^{-1}$. The estimated value for NdF_3 , which was based on the value for lanthanum trifluoride, was $-418 \text{ kcal mol}^{-1}$. Because of this discrepancy, the calorimetric result was not published.

Several events have since transpired to reawaken interest in this project, the most important being the recent appearance of a publication by Rezhukhina, Sisoeva, Holokhonova, and Ippolitov⁵⁸ in which solid state emf measurements were described for the trifluorides of scandium, yttrium, and lanthanum. The values reported for the enthalpies of formation of the trifluorides are about 5 kcal mol^{-1} more negative than those of Rudzitis for scandium and yttrium, whereas the value for lanthanum trifluoride is about 5 kcal mol^{-1} less negative. These authors quote Rudzitis' value, although it is unpublished, and indicate that it seems to be too negative. The recent publication of some new values for the enthalpies of vaporization of the trifluorides, along with some additional experimental values of the ionization potentials of the metals, have also helped to revive our interest. Finally, the fact that rare earth samples of much higher purity are now available for study leads to the decision that the project should take the direction of more experimental measurements rather than better empirical correlations.

A cooperative agreement has been arranged with Drs. B. Beaudry and K. Gschneidner of the Rare Earth Information Center, Institute of Atomic Research, Iowa State University, Ames, Iowa, for the preparation of materials, fabrication into appropriate geometry, and analysis of the samples. The first samples to be fabricated under this agreement are praseodymium and neodymium, two of the lighter rare earths. In Table 25, the results of spark source mass spectrometric analyses of the praseodymium material before fabrication are given. This material is of much higher purity than any of Rudzitis' samples.

After the results of exploratory combustions on these samples are analyzed, the rest of the praseodymium specimen and a specimen of neodymium that has also been prepared at Ames will be fabricated to the shape and thickness desired.

In addition to the metallic samples, some high-purity praseodymium trifluoride disks have been prepared for use as sample supports during the combustion experiments.

TABLE 25. Praseodymium Sample PR-9374. Spark Source Mass Spectrometric Analysis (ppm atomic)

Li	<0.02	Cu	0.66	Sb	<0.09
Be	<0.04	Zn	<0.07	Te	<0.1
B	0.03	Ga	<0.08	I	<0.08
Na	0.2	Ge	<0.2	Cs	<0.009
Mg	<0.1	As	<0.03	Ba	<0.2
Al	0.06	Se	<0.07	Hf	<2.
Si	<0.6	Kr	<0.2	Ta	12.
P	<0.03	Rb	<0.02	W	<3.
S	0.06	Sr	<0.05	Re	<1.
Cl	2.	Zr	<0.05	Cs	<1.
K	<0.1	Nb	<1.	Ir	<0.6
Ca	<0.2	Mo	<1.	Pt	<0.9
Ti	0.6	Ru	<0.7	Au	0.3
V	<0.04	Rh	<0.2	Hg	<0.2
Cr	2.5	Pd	<0.4	Tl	<0.1
Mn	<0.03	Ag	<0.07	Pb	<0.4
Fe	10.	Cd	<0.1	Bi	<0.1
Co	<0.09	In	<0.07	Th	<2.
Ni	3.	Sn	<0.2	H	<0.6

Rare Earth Impurities					
Sc	0.2	Sm	<0.4	Ho	<0.5
Y	0.63	Eu	<0.4	Er	<1.
La	2.6	Gd	12.	Tm	<0.2
Ce	4.	Tb	<0.5	Yb	<0.6
Nd	4.	Dy	1.6	Lu	1.

VIII. COMBUSTION OF WS₂ IN FLUORINE
(M. Ader, D. Applegate,* H. R. Hoekstra**)

Interest in the determination of the standard enthalpy of formation of tungsten disulfide, $\Delta H_f^\circ(\text{WS}_2, \text{c}, 298.15 \text{ K})$, was mentioned in the preceding report.⁵⁹ Our preliminary calorimetric experiments had shown that the energy of the reaction

could be satisfactorily measured by means of a two-chambered nickel combustion bomb. Thus, $\Delta H_f^\circ(\text{WS}_2, \text{c}, 298.15 \text{ K})$ could be calculated from

$$\Delta H_f^\circ(\text{WS}_2, \text{c}) = \Delta H_f^\circ(\text{WF}_6, \text{g}) + 2\Delta H_f^\circ(\text{SF}_6, \text{g}) - \Delta H_c^\circ(\text{WS}_2) \quad (\text{XXX})$$

where ΔH_f° values are already available for SF₆⁶⁰ and WF₆.⁶¹ The WS₂ specimen, which originally contained ~15 wt % elemental tungsten and ~0.8 wt % oxygen, has since been purified by treatment with flowing H₂S(g) at ~1420 K for several hours. Subsequent analyses indicated complete conversion of the tungsten to WS₂, reduction of the oxygen level to 0.0365 wt %, and an anion/cation (S/W) atomic ratio of 2.001. The only other calorimetrically significant impurities were 0.0044 wt % C and 0.0020 wt % N.

A series of eight fluorine bomb combustions of good precision yielded an enthalpy change of -929.6 kcal mol⁻¹ for Reaction XXIX, from which $\Delta H_f^\circ(\text{WS}_2, \text{c}, 298.15 \text{ K}) = -65.4 \text{ kcal mol}^{-1}$ is calculated. The latter, however, differs considerably from previously reported values for $\Delta H_f^\circ(\text{WS}_2)$, namely, (a) -50 kcal mol⁻¹^{62,63} from high-temperature equilibrium studies of the reaction $1/2 \text{ WS}_2(\text{c}) + \text{H}_2(\text{g}) = 1/2 \text{ W}(\text{c}) + \text{H}_2\text{S}(\text{g})$, and (b) -48 kcal mol⁻¹,⁶⁴ from oxygen combustion of WS₂ in a high-temperature differential calorimeter. Reasons for the discrepancy were sought, and it was eventually discovered that the oxygen content of our WS₂ specimen had been misreported and was actually 0.365 wt %. The calorimetric correction for oxygen (based on $\text{WO}_2(\text{c}) + 3\text{F}_2(\text{g}) = \text{WF}_6(\text{g}) + \text{O}_2(\text{g})$, $\Delta H_{298}^\circ = -270.6 \text{ kcal mol}^{-1}$) now becomes quite appreciable, leading to $\Delta H_f^\circ(\text{WS}_2, \text{c}, 298.15 \text{ K}) = -51.4 \text{ kcal mol}^{-1}$, which agrees well with the previously reported studies.

Since oxygen in WS₂ may in fact exist as species other than WO₂(c), attempts to characterize the impurity were made but were unsuccessful. We intend, therefore, to repeat the calorimetric combustions with a purer WS₂ specimen so as to obviate the large, uncertain oxygen correction. Accordingly, the WS₂ will be treated again with H₂S(g), but under slightly modified conditions that are expected to reduce oxygen to an acceptable level.

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** ANL Chemistry Division

IX. ENTHALPIES OF FORMATION OF LITHIUM-ALUMINUM COMPOUNDS
(M. Ader, J. L. Settle*)

Thermodynamic information on the Li-Al system is of interest in connection with the Chemical Engineering Division's development of Li-Al/S batteries. Four compounds that are stable at room temperature have been identified in the Li-Al system: LiAl_3 , LiAl , Li_3Al_2 , and Li_9Al_4 . Thermodynamic data on the formation of three of these compounds is lacking; for LiAl , the Gibbs free energy, enthalpy, and entropy of formation have been determined⁶⁵ at 573 K by emf measurements. An effort is now under way to investigate these compounds by thermochemical methods. Calorimetric-grade samples will be synthesized for enthalpy of formation measurements (298 K), and for low- and high-temperature heat capacity studies.

The enthalpies of formation of the LiAl_x compounds will be determined by solution-reaction calorimetry, employing a reaction scheme illustrated by the following skeleton equations:

We intend to measure the enthalpies of Reactions A, B, and C; the enthalpies of Reactions D and E can be obtained from literature data. Summation of all of these enthalpies gives $\Delta H_f^\circ(\text{LiAl}_x)$.

Preliminary studies of Reaction C, the dissolution of LiAl_x alloys, revealed some of the problems and limitations of the thermochemical measurements. Alloys with the nominal compositions $\text{LiAl}_{0.96}$, $\text{LiAl}_{0.67}$, and $\text{LiAl}_{0.41}$ were treated with 99.41 cm³ of H_2 -saturated 4.366 molal HCl in the LKB-8700 Precision Calorimetry System. Initially, the reaction was very rapid, especially with $\text{LiAl}_{0.41}$, and vigorous H_2 evolution caused the samples to float to the liquid-gas interface. Under such conditions, some heat may be lost with the escaping gas as it leaves the open calorimeter. This possibility was circumvented by enveloping one of the two windows of the cylindrical glass sample container with cotton cloth. Breaking the cloth-wrapped window first and then allowing some time to elapse before breaking the second window restricted circulation of the solvent and movement of the sample. The reaction was slowed, and flotation minimized. Eventually, the very rapid initial reaction was followed by a very slow reaction, presumably the dissolution of the Al or Al-rich residue. To speed the latter reaction, a minute amount of H_2PtCl_6 "catalyst" was added to the initial solvent.

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High specific enthalpies of reaction of the alloys (-5500 to -6200 cal g⁻¹) and limitations on large temperature rises for the LKB-8700 calorimeter (1 to 1.5 K) require that the sample masses be small, 17 to 24 mg. This makes it imperative that the alloy specimens be homogeneous. Evidence of inhomogeneity in the trial specimens was inferred from differences observed in the enthalpies of reaction with particle size. Very rough values of the enthalpies of formation at 298 K were estimated from these preliminary trials, namely, -12, -10, and -8 kcal mol⁻¹, respectively, for LiAl_{0.96}, LiAl_{0.67}, and LiAl_{0.41}. The first value may be compared with $\Delta H_f^\circ(\text{LiAl}, c, 573 \text{ K}) = -10.40 \text{ kcal mol}^{-1}$,⁶⁵ derived from emf measurements.

Preliminary studies of Reaction A, the dissolution of ~15 mg Al in H₂-saturated 4.366 molal HCl, were made using Baker Reagent Grade (99.8%) 32-mil Al wire. As expected, reaction was slow, but by pretreating the wire with 8M HCl and adding H₂PtCl₆ to the calorimetric solvent, the rate could be speeded up to permit reliable measurements. However, when a very pure grade (99.995%) of Al wire or filings was substituted, the reaction became exceedingly slow and the reliability of the measurements became questionable. The problem with very slow reactions is that a relatively large exchange of heat occurs between the calorimeter and its surroundings. This is reflected by a relatively large and uncertain temperature correction. Experiments on calibration of the calorimeter by electrical heating are now in progress to determine how reproducibly the calorimeter behaves when the electrical energy is introduced over extended periods of time. If the LKB-8700 calorimeter proves to be unsuitable for measuring the enthalpy of Reaction A, a value will be calculated from Coughlin's study,⁶⁶ which was made under slightly different conditions of Al/acid ratio and temperature.

X. HIGH TEMPERATURE ENTHALPY MEASUREMENTS (D. R. Fredrickson)

The resistance-heated drop-calorimetric system has been used to obtain physical property data for materials of interest in reactor technology. Enthalpy measurements were made on both α - and β - Na_2UO_4 and the enthalpy of the α - β transition was determined. In addition, enthalpy data are reported for Cs_2UO_4 and sapphire (Al_2O_3), a reference material.

The resistance-heated drop-calorimetric system has been completely disassembled and the furnace rebuilt. Two sets of tantalum heater windings and seven platinum-platinum 10% rhodium thermocouples located in the core of the furnace were replaced. An extensive repair job of this type is to be expected from time to time. It was last done five years ago.

A. Sapphire

Immediately after the repairs mentioned above had been completed, the accuracy of the drop-calorimetric system was checked by making a series of measurements on an N.B.S. certified sample of synthetic sapphire (Al_2O_3). For this work, the (platinum + 10 mass % rhodium) capsule contained 12.3059 g of sapphire.

The experimentally measured enthalpies for sapphire above the reference temperature (298.15 K) are given in Table 26. Data are reported in this table for eleven drops covering the temperature range 587 to 1205 K. The following equation, with the constants determined by the method of least squares, represents the data over the temperature range 600-1200 K:

$$\begin{aligned} (H_T^\circ - H_{298}^\circ) = & 27.5275 T + 1.61008 \times 10^{-3} T^2 \\ & + 8.75433 \times 10^5 T^{-1} - 11,371.75 \text{ cal mol}^{-1} \end{aligned} \quad (\text{XXXI})$$

The enthalpies calculated from this equation are shown in column 4 of Table 26. The standard deviation for Equation XXXI is 16 cal mol⁻¹.

In Table 27, the present data are compared with our previously published data,⁶⁷ as well as with the NBS certified data. From these results, one concludes that the drop-calorimetric data are reproducible within the expected limits.

B. α - Na_2UO_4

High-temperature enthalpy measurements were made on α - Na_2UO_4 at 618 to 1165 K. The sample was a portion of the bright orange powder that had previously been used by Osborne *et al.*⁶⁸ for low-temperature heat capacity measurements. For the drop-calorimetric studies, a cylindrical (platinum-10% rhodium) capsule with a 0.015-in. wall thickness and 0.500-in. diameter was used to contain the sample. The capsule was filled with 9.6033 g of α - Na_2UO_4 ($M = 348.006 \text{ g mol}^{-1}$) and was welded closed under an atmosphere of helium.

The experimental results for α - Na_2UO_4 are given in Table 28. The twelve drops reported in this table cover a temperature range between 618 and 1165 K.

TABLE 26. Summary of Enthalpy Data
for N. B. S. Certified
Synthetic Sapphire (Al_2O_3)

Temp, K	$(H_T^\circ - H_{298}^\circ)$ observed, cal	$(H_T^\circ - H_{298}^\circ)$ observed, cal mol ⁻¹	$(H_T^\circ - H_{298}^\circ)$ calculated, ^a cal mol ⁻¹
587.4	825.89	6842.96	6843.79
587.8	826.78	6850.33	6854.54
714.8	1252.85	10380.56	10352.27
805.5	1558.54	12913.37	12933.12
805.7	1559.43	12920.74	12938.88
902.0	1899.42	15737.75	15738.55
902.2	1901.45	15754.57	15744.42
1002.9	2261.19	18735.21	18727.89
1077.4	2530.71	20968.33	20967.86
1205.0	3000.96	24864.61	24863.23
1205.3	3001.44	24868.59	24872.48

^aFrom Equation XXXI.

TABLE 27. Comparison of Enthalpy
Data for Sapphire

Temp, K	$(H_T^\circ - H_{298}^\circ)$, cal mol ⁻¹		
	This Work Eq. XXXI	Ref. 67	NBS
600	7183	7196	7194
700	9937	9936	9939
800	12775	12766	12773
900	15680	15666	15676
1000	18641	18625	18634
1100	21652	21637	21638
1200	24709	24695	24684

TABLE 28. Enthalpy of α -Na₂UO₄

Temp, K	Total Enthalpy Measured, cal	Enthalpy of Capsule, cal	(H _T ^o - H ₂₉₈ ^o) Observed, cal	(H _T ^o - H ₂₉₈ ^o) Observed, cal mol ⁻¹	(H _T ^o - H ₂₉₈ ^o) Calculated, ^a cal mol ⁻¹
617.8	586.77	243.63	343.14	12434.77	12444.73
702.9	753.66	310.54	443.12	16057.87	16012.09
740.2	823.62	340.06	483.56	17523.34	17593.15
796.6	937.82	384.90	552.92	20036.82	20004.03
847.4	1038.74	425.52	613.22	22221.98	22196.36
904.0	1151.87	471.01	680.66	24673.13	24662.24
942.6	1228.45	502.19	726.26	26318.35	26357.98
1010.4	1367.87	557.25	810.62	29375.40	29364.09
1066.5	1481.61	603.09	878.52	31835.97	31878.03
1106.1	1565.63	635.60	930.03	33702.60	33667.06
1165.0	1687.33	684.19	1003.14	36351.97	36350.22
1165.0	1687.22	684.19	1003.03	36347.99	36350.22

^aFrom Eq. XXXII.

The following equation, with the constants determined by the method of least squares, represents the data over the experimental range only:

$$(H_T^o - H_{298}^o) = 36.86849 T + 3.82458 \times 10^{-3} T^2 - 11,792.38 \text{ cal mol}^{-1} \quad (\text{XXXII})$$

The enthalpies calculated from this equation are shown in column 6 of Table 28.

To provide an equation applicable down to 298.15 K, the following constraints were applied in fitting the data: $(H_T^o - H_{298}^o) = 0$, $C_p^o = 35.055$,⁶⁸ and $S^o = 39.68 \text{ cal K}^{-1}$.⁶⁸ The derived equation (applicable over the range 298 to 1200 K) is:

$$(H_T^o - H_{298}^o) = 38.8476 T + 3.09342 \times 10^{-3} T^2 + 5.01109 \times 10^5 T^{-1} - 13,538.12 \text{ cal mol}^{-1} \quad (\text{XXXIII})$$

The heat capacity expression from Equation XXXIII is given by:

$$C_p^o = 38.8476 + 6.18684 \times 10^{-3} T - 5.01109 \times 10^5 T^{-2} \text{ cal K}^{-1} \text{ mol}^{-1} \quad (\text{XXXIV})$$

The smoothed enthalpies from Equation XXXIII, along with the derived high-temperature heat capacities, entropy increments, and Gibbs free energies, are given in Table 29 at 100 K intervals.

TABLE 29. Thermodynamic Functions of α -Na₂UO₄

Temp, K	(H _T [°] - H ₂₉₈ [°]), cal mol ⁻¹	C _P [°] , cal K ⁻¹ mol ⁻¹	S [°] , cal K ⁻¹ mol ⁻¹	-[(G [°] - H ₂₉₈ [°])]/T, cal K ⁻¹ mol ⁻¹
298.15	0	35.055	39.68	39.68
300	64.93	35.14	39.90	39.68
400	3748.63	38.19	50.47	41.10
500	7661.25	39.94	59.20	43.88
600	11719.24	41.17	66.59	47.06
700	15886.83	42.16	73.02	50.32
800	20146.12	43.01	78.70	53.52
900	24487.16	43.80	83.81	56.61
1000	28903.99	44.53	88.47	59.56
1100	33392.82	45.24	92.74	62.39
1193	37630.00	45.88	96.44	64.90

C. β -Na₂UO₄

β -Na₂UO₄ was prepared by heating α -Na₂UO₄ to 1245 K for 4 hr in the capsule used for the drop-calorimetry measurements. The experimental data for β -Na₂UO₄ are given in Table 30 and are shown graphically with those for α -Na₂UO₄ in Fig. 1. It is evident that a transition occurs in the system, as shown by the discontinuity of the curve. This transition from α - to β -Na₂UO₄ has been reported to occur at 1193 K.⁹

The drops reported in Table 30 cover a fairly narrow range (1198-1273 K) and were made primarily to establish an enthalpy value for β -Na₂UO₄ at the transition temperature. A straight line best represents the molar enthalpies over the experimental range as follows:

$$(H_T^\circ - H_{298}^\circ) = 53.69844 T - 23,824.88 \text{ cal mol}^{-1} \quad (\text{XXXV})$$

In order to evaluate the enthalpy of transition, $\Delta H_{tr}(1193 \text{ K})$, Equations XXXIII and XXXV were extrapolated to the transition temperature.

From Equation XXXI at 1193 K:

$$[H_{1193}^\circ(\alpha) - H_{298}^\circ(\alpha)] = 37,635 \text{ cal mol}^{-1} \quad (\text{XXXVI})$$

From Equation XXXV at 1193 K:

$$[H_{1193}^\circ(\beta) - H_{298}^\circ(\beta)] = 40,237 \text{ cal mol}^{-1} \quad (\text{XXXVII})$$

TABLE 30. Enthalpy of β -Na₂UO₄

Temp, K	Total Enthalpy Measured, cal	Enthalpy of Capsule, cal	(H _T [°] - H ₂₉₈ [°]) observed, cal	(H _T [°] - H ₂₉₈ [°]), cal mol ⁻¹	(H _T [°] - H ₂₉₈ [°]), Calculated, ^a cal mol ⁻¹
1197.8	1830.13	711.37	1118.76	40,541.83	40,495.12
1205.2	1844.33	717.52	1126.81	40,833.55	40,892.49
1224.4	1890.79	733.48	1157.31	41,938.82	41,923.50
1246.0	1940.11	751.48	1188.63	43,073.80	43,083.39
1273.2	2003.57	774.19	1229.38	44,550.50	44,543.99

^aFrom Eq. XXXV.

Fig. 1. Enthalpy of α and β - Na_2UO_4 relative to α - Na_2UO_4 at 298 K.

Combination of Equations XXXVI and XXXVII gives

$$[H_{193}^{\circ}(\alpha) - H_{193}^{\circ}(\beta)] = [H_{298}^{\circ}(\alpha) - H_{298}^{\circ}(\beta)] - 2.6 \text{ kcal mol}^{-1} \quad (\text{XXXVIII})$$

It follows from the above equations that $\Delta H_{\text{tr}}(1193 \text{ K}) = \Delta H_{\text{tr}}(298 \text{ K}) + 2.6 = 3.3 + 2.6 = 5.9 \text{ kcal mol}^{-1}$. The value for $\Delta H_{\text{tr}}(298 \text{ K})$ was given earlier in this report.

D. Cs₂UO₄

Enthalpy measurements were also made on Cs₂UO₄. The sample was a portion of the preparation described by O'Hare and Hoekstra.¹ The (platinum-10% rhodium) capsule was filled with 15.6897 g Cs₂UO₄ (M = 567.837 g mol⁻¹), crimped, and welded closed under vacuum.

The results for Cs₂UO₄ are given in Table 31. The experiments reported in this table cover a temperature range between 593 and 1061 K. The following equation, with the constants determined by the method of least squares, represents the data over the experimental range only.

$$(H_T^{\circ} - H_{298}^{\circ}) = 38.01220T + 2.54332 \times 10^{-3} T^2 - 11904.92 \text{ cal mol}^{-1} \quad (\text{XXXIX})$$

The enthalpies calculated from this equation are also shown in the table.

To provide an equation applicable down to 298.15 K, the following constraints at T = 298.15 K were applied when fitting the data: $(H_T^{\circ} - H_{298}^{\circ}) = 0$, $C_p^{\circ} = 36.511 \text{ cal K}^{-1} \text{ mol}^{-1}$, and $S^{\circ} = 52.50 \text{ cal K}^{-1} \text{ mol}^{-1}$.⁶⁹ The derived equation (applicable over the range 298-1100 K) is

$$\begin{aligned} (H_T^{\circ} - H_{298}^{\circ}) = & 39.4076 T + 2.03432 \times 10^{-3} T^2 \\ & + 3.65323 \times 10^5 T^{-1} - 13,155.51 \text{ cal mol}^{-1} \end{aligned} \quad (\text{XL})$$

The heat capacity derived from Equation XL is given by

$$C_p^{\circ} = 39.4076 + 4.06864 \times 10^{-3} T - 3.65323 \times 10^5 T^{-2} \text{ cal K}^{-1} \text{ mol}^{-1} \quad (\text{XLI})$$

The smoothed enthalpies from Equation XL, along with the derived high-temperature heat capacities, entropies, and Gibbs energy functions, are given in Table 32 at 100 K intervals.

TABLE 31. Enthalpy of Cs_2UO_4

Temp, K	Total Enthalpy Measured, cal	Enthalpy of Capsule, cal	$(H_T^\circ - H_{298}^\circ)$ Observed, cal	$(H_T^\circ - H_{298}^\circ)$, cal mol ⁻¹	$(H_T^\circ - H_{298}^\circ)$, calculated, ^a cal mol ⁻¹
593.5	542.02	223.11	318.91	11,541.75	11,551.18
677.0	703.46	288.15	415.31	15,030.58	14,995.01
745.8	834.82	342.16	492.66	17,829.97	17,859.21
807.2	955.45	390.69	564.76	20,439.36	20,435.68
842.4	1024.66	418.65	606.01	21,932.25	21,921.39
845.5	1030.10	421.12	608.98	22,039.74	22,052.53
890.0	1117.57	456.62	660.95	23,920.60	23,940.50
930.7	1198.58	489.23	709.25	25,668.63	25,676.06
971.9	1281.05	522.37	758.68	27,457.57	27,441.53
1001.3	1340.40	545.11	794.29	28,746.34	28,706.63
1060.6	1457.67	594.20	863.47	31,250.05	31,271.72
1060.7	1458.32	594.28	864.04	31,270.67	31,276.06

^aFrom Eq. XLI.

TABLE 32. Thermodynamic Functions of Cs_2UO_4

Temp, K	$(H_T^\circ - H_{298}^\circ),$ cal mol ⁻¹	$C_p^\circ,$ cal K ⁻¹ mol ⁻¹	$S^\circ,$ cal K ⁻¹ mol ⁻¹	$-[(G^\circ - H_{298}^\circ)]/T,$ cal K ⁻¹ mol ⁻¹
298.15	0	36.511	52.50	52.50
300	67.60	36.57	52.73	52.50
400	3846.33	38.75	63.58	53.97
500	7787.51	39.98	72.37	56.80
600	11830.28	40.83	79.74	60.02
700	15948.52	41.51	86.09	63.30
800	20129.19	42.09	91.67	66.51
900	24365.04	42.62	96.66	69.59
1000	28651.73	43.11	101.17	72.52
1100	32986.49	43.58	105.30	75.32

XI. CHEMICAL THERMODYNAMIC DATA ACCESSMENT,
EVALUATION, AND TABULATION
(W. N. Hubbard)

There is a continuing need to access, evaluate, and tabulate chemical thermodynamic data for use in solving chemical problems. In times of special need, additional funding has been allocated to increase the effort in the area of thermodynamic data evaluation. For example, the space program led various Army, Navy, Air Force, and NASA agencies to support tabulations in the field of chemical rocket propellants. These tabulations involved compounds of many of the lighter elements. As the support from the space program and other programs has been diverted from data compilation to more direct programmatic efforts, tabulations have been contributed by individual scientists in their own specialties.

A part-time program of that kind was begun at this Laboratory. The initial effort was in the area of thermodynamic data for uranium compounds. Because the U. S. National Bureau of Standards was about to embark on a selection of the data for uranium compounds at 298.15 K, the main thrust of our effort was connected with the thermal values as a function of temperature. Cooperation with the Bureau was manifested by their providing us with a microfilm copy of all their bibliographic cards on uranium compounds for the years prior to 1969, and a promise of magnetic tape documentation of all subsequent data.

About that time, a program was initiated by Dr. F. L. Oetting under the auspices of the International Atomic Energy Agency to evaluate thermodynamic data for all the actinides. The compilation is to comprise chapters on the elements, ions, halides, chalcogenides, pnictides, oxides, hydrides, miscellaneous compounds, alloys, and some ternary systems. The organization of the compilation thus cuts across the actinides, rather than taking each one separately as was the plan of the Bureau of Standards and ourselves. To avoid duplication of effort, and also because two members of this group were asked to be responsible for two separate chapters of the IAEA compilation, the independent compilation of data for uranium compounds was discontinued.

The cooperative effort between the Bureau of Standards and ANL was expanded to embrace the IAEA compilation. Computer programs have been written at ANL to search the NBS tapes and print out the desired files. To date, tapes for the years 1969 and 1970 have been received. These have been searched, and separate computer printouts have been made for most of the classes of compounds listed above. These printouts have been mailed to the appropriate IAEA authors.

Magnetic tapes of the data for the years subsequent to 1970 are expected to be shipped from the Bureau of Standards very soon.

ACKNOWLEDGMENTS

The research described in this report was very much aided by several people whom we would like to thank. H. R. Hoekstra prepared many of the samples, and analytical work was carried out by K. J. Jensen, Irene Fox, J. P. Faris, Alice Essling, and M. I. Homa. We have had the benefit of discussions with Irving Johnson, and R. H. Land helped with computer programing.

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