

The Enthalpy of Formation of $\text{MoF}_6(\ell)$ by Solution Calorimetry

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Enthalpies of reaction of $\text{MoF}_6(\ell)$ in NaOH solutions, of $\text{MoO}_3(\text{cr})$ in NaOH solutions, of $\text{NaF}(\text{cr})$ in MoO_3 -NaOH solutions, and of $\text{NaF}(\text{cr})$ in $\text{H}_2\text{O}(\ell)$ were measured to obtain the enthalpy of reaction of $\text{MoF}_6(\ell)$ in infinitely dilute NaOH solution:



$$\Delta H^\circ(298.15 \text{ K}) = (-641.23 + 1.8, -4.0) \text{ kJ mol}^{-1}$$

From this were calculated $\Delta H_f^\circ[\text{MoF}_6(\ell)] = (-1593.3 + 5.6, -4.3) \text{ kJ mol}^{-1}$, $\Delta H_f^\circ[\text{F}^-(\text{aq})] = (-334.05 + 0.34, -0.69) \text{ kJ mol}^{-1}$.

From the measurements of $\text{NaF}(\text{cr})$ in H_2O , values for apparent molal enthalpy, ϕ_L , were tabulated at concentrations from 0 to 0.2 $\text{mol} \cdot \text{kg}^{-1}$. $\Delta H^\circ_{\text{soln}}(298.15 \text{ K}) = (937 \pm 36) \text{ J} \cdot \text{mol}^{-1}$.

Keywords: $\text{F}^-(\text{aq})$, enthalpy of formation; $\text{MoF}_6(\ell)$, enthalpy of formation and enthalpy of reaction in NaOH soln.; $\text{MoO}_3(\text{cr})$, enthalpy of soln. in NaOH; $\text{NaF}(\text{cr})$, enthalpies of soln. and diln. in H_2O , and enthalpy of soln. in MoO_3 -NaOH; thermochemistry.

1. Introduction

An accurate value for the enthalpy of formation of $\text{MoF}_6(\ell)$ was needed as an element in a program to determine the enthalpies of formation of the lower fluorides of molybdenum. Myers and Brady [1]¹ have measured enthalpies of solution of $\text{MoF}_6(\ell)$ and $\text{MoO}_3(\text{cr})$ in 0.531 $\text{mol} \cdot \text{L}^{-12}$ sodium hydroxide, and of $\text{NaF}(\text{cr})$ in 0.531 $\text{mol} \cdot \text{L}^{-1}$ NaOH containing molybdate. Recalculation of their results using newer selected values [3] for the enthalpies of formation of $[\text{NaOH} \cdot 515 \text{H}_2\text{O}](\text{soln})$, $\text{MoO}_3(\text{cr})$, and $\text{NaF}(\text{cr})$, yields $-1645.1 \text{ kJ} \cdot \text{mol}^{-13}$ for the enthalpy of formation of $\text{MoF}_6(\ell)$.

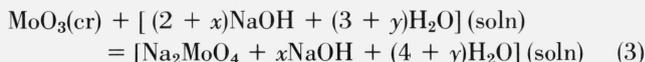
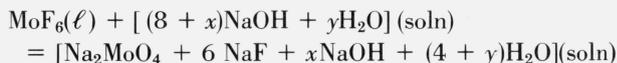
Settle et al. [4] measured the enthalpy of reaction of molybdenum sheet suspended on a nickel rod in about 1.5 MPa (15atm) of $\text{F}_2(\text{g})$ in a combustion bomb. Unambiguous and accurate corrections for unburned molybdenum were made. However, greater uncertainty existed in the other corrections which made relatively small contributions to the enthalpy of formation of $\text{MoF}_6(\text{g})$ (namely, enthalpy of formation of $\text{MoF}_5(\text{cr})$, 0.005%; of $\text{NiF}_2(\text{cr})$, 0.11%; and impurities in original sample, 0.026%). Recalculation of the latter two values using newer selected enthalpy of formation values [3] resulted in $\Delta H_f^\circ[\text{MoF}_6(\text{g})] = (-1557.66 \pm 0.92) \text{ kJ} \cdot \text{mol}^{-1}$ according to the reaction,



Values for the enthalpy of vaporization of MoF_6 have been reported by Ruff and Ascher [5], Cady and Hargreaves [6], and by Osborne, et al. [7]. Using the value of Osborne, et al. [7], 27.74 $\text{kJ} \cdot \text{mol}^{-1}$, for the enthalpy of vaporization of $\text{MoF}_6(\ell)$, one obtains $\Delta H_f^\circ[\text{MoF}_6(\ell)] = (-1585.40 \pm 0.92) \text{ kJ} \cdot \text{mol}^{-1}$. Thus, there is a discrepancy of 59.7 $\text{kJ} \cdot \text{mol}^{-1}$ between this value and that obtained from the solution calorimetry of Myers and Brady. The latter we considered to be more likely in error and therefore made the measurements reported here.

After our experiments were completed Burgess, et al. [8] reported four measurements of the enthalpy of hydrolysis of MoF_6 in 1 or 0.1 $\text{mol} \cdot \text{kg}^{-1}$ NaOH solutions; the mean value was $-732 \text{ kJ} \cdot \text{mol}^{-1}$ with a standard deviation of 4 $\text{kJ} \cdot \text{mol}^{-1}$. From this they derived $\Delta H_f^\circ[\text{MoF}_6(\text{g})] = -1564 \text{ kJ} \cdot \text{mol}^{-1}$. They do not give enough information to make a reasonable estimate of the accuracy of their result.

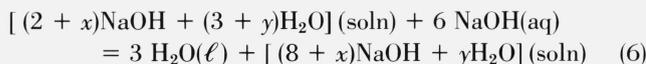
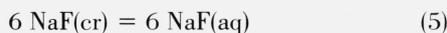
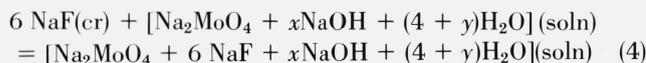
The following is an outline of the reaction scheme for the solution experiments to be reported in this work:



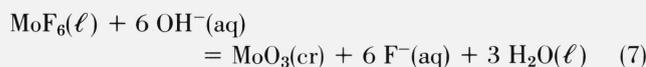
¹ Figures in brackets indicate the literature references at the end of this paper.

² The National Bureau of Standards (U.S.) has recently recommended the use of "L" as the symbol for liter, the metric unit commonly used to measure volume [2].

³ Throughout this paper 1 cal = 4.184 J.



By combining reactions: (2) - (3) - (4) + (5) + (6), one obtains:



Thus, the enthalpy of reaction (7) is

$$\Delta H_7 = \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6,$$

and

$$\Delta H_f^\circ[\text{MoF}_6(\ell)] = \Delta H_f^\circ[\text{MoO}_3(\text{cr})] + 3 \Delta H_f^\circ[\text{H}_2\text{O}(\ell)] \\ + 6 \Delta H_f^\circ[\text{F}^-(\text{aq})] - 6 \Delta H_f^\circ[\text{OH}^-(\text{aq})] - \Delta H_7 \quad (8)$$

The enthalpies of reactions (2) through (5) were measured; (4) and (5) were done to eliminate uncertainties in the state and impurities of the sample of NaF(cr). The uncertainty in the assumed value for $\Delta H_f^\circ[\text{F}^-(\text{aq})]$ is about equal to that estimated for ΔH_7 .

2. Experimental Procedures and Results

The experiments reported in this work were completed between June 1971 and March 1972 except seven experiments in December 1975 to resolve significant uncertainty existing in the values for reaction (4). NBS certified calibrations of the standards which are the basis for the energy and temperature measurements were made as follows: 0.1- Ω , 10- Ω , and 10-k Ω standard resistors in June 1969 and January 1973; saturated standard cells (Eppley Group No. 2625) in July 1969 and March 1973 based on the 1969 volt; and the capsule-type platinum resistance thermometer (No. 769892) in October 1961. The latter was checked at the ice point in January 1968. The quartz-oscillator thermometer system was calibrated in this laboratory in August 1975 by direct comparison with a calibrated platinum resistance thermometer. The 1969 atomic weights [9] were used in the calculations. Molecular weights, densities and buoyancy factors are given in table 1 for the materials in these experiments.

Table 1. Data used in calculations for various materials.

Material	Molar Mass [9]	Density [10]	Buoyancy Factor
	g/mol	g/cm ³	
MoF ₆ (ℓ)	209.9304	2.537 [7]	* *
MoO ₃ (cr)	143.9382	4.692	1.00011
NaF(cr)	41.9882	2.558	1.00032
H ₂ O(ℓ)	18.0154	0.9965	1.00104
NaOH	39.9972	-	-
[NaOH] 0.297 mol·L ⁻¹	-	1.0132	1.00102
.302	-	1.0133	1.00102
.304	-	1.0135	1.00102
.392	-	1.0173	1.00102
.545	-	1.0238	1.00101
.643	-	1.0280	1.00101
.653	-	1.0284	1.00101
.694	-	1.0301	1.00100
.706	-	1.0306	1.00100
.718	-	1.0311	1.00100
.798	-	1.0344	1.00100

** The buoyancy correction for the mass of MoF₆ was determined from the volume of the ampoule.

2.1 Materials

MoF₆, purchased from the Ozark-Mahoning Company⁴, was purified by trap-to-trap distillation in a Monel and stainless steel system. Calorimetric samples were transferred by distillation into Kel-F⁵ (poly(chlorotrifluoroethylene)) ampoules through a sidearm which was sealed off by pinching with a hot iron. Similar samples analyzed by Krause [11] using a freezing-temperature method indicated an impurity of 0.03 percent, but the impurity was not identified.

The molybdc anhydride, MoO₃, and sodium fluoride, NaF, were Fisher Certified Reagent Grade, Lots No. 753459 and 721170, respectively. The volatile matter determined from the mass lost on heating at 475 K was 0.02 percent and 0.12 percent, respectively. Spectroscopic examination for metals by the Analytical Chemistry Division of NBS detected magnesium and silicon in amounts in the range, 0.001 to 0.01 percent, in the MoO₃. Both of these materials were used

⁴ Certain commercial products are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products identified are necessarily the best available for the purpose.

⁵ Trademark of MMM Company.

without further purification, and the calorimetric samples were weighed directly in the sample holder.

The cylindrical ampoules for the MoF_6 calorimetric samples were made from 13-mm lengths of Kel-F tubing (9.5 mm i.d.) with a sidearm tube (3 mm o.d.). On each end of the cylinder was sealed a window of 0.1 mm Kel-F film. The internal volume of these ampoules was about 1 cm^3 , but the liquid MoF_6 occupied not more than one-half of this volume. The measured enthalpy of reaction was corrected for the heat evolved by condensing the $\text{MoF}_6(\text{g})$ in the remaining volume in the ampoule. Each empty ampoule was attached by means of a Swagelok compression fitting to the distillation line and tested for leakage with a helium leak detector. The thin windows were all permeable to the helium. A maximum leak rate of approximately $10 \text{ pmol} \cdot \text{s}^{-1}$ was arbitrarily chosen and the ampoules which exceeded this rate were rejected. Leak rates of other gases such as O_2 , H_2O , and MoF_6 were probably smaller than that of helium and such leakage would have affected the experimental results by less than 0.01 percent.

Some experiments were made to test the suitability of using Kel-F ampoules to contain liquid MoF_6 in a sodium hydroxide solution: (1) Samples of Kel-F, including finished ampoules (about 1.7 g), were soaked in NaOH solutions for periods of time up to several days; no change in mass larger than 0.1 mg was observed. (2) Ampoules were filled with $\text{MoF}_6(\ell)$, allowed to stand in air for up to 1 hour, and then the MoF_6 was pumped out; no change in mass greater than 0.2 mg was found. (3) Ampoules were filled with MoF_6 , then opened in NaOH or ammonia solutions; the empty ampoules each gained less than 1.0 mg. (See later discussion of calorimetric experiments where this gain in mass reached several milligrams.) (4) Ampoules filled with MoF_6 were exposed to air for long periods of time (days to weeks). After several days clear crystals formed above the liquid. These crystals were not positively identified but were believed to be MoOF_4 . One ampoule with thick (0.8 mm instead of the usual 0.1 mm) end windows also showed formation of the clear crystals after a period of three weeks. These ampoules, after opening in NaOH solutions, had gained up to several milligrams.

It was concluded from these preliminary tests that, although Kel-F ampoules are not suitable for long term storage of $\text{MoF}_6(\ell)$, they could be used for calorimetric experiments.

2.2. Calorimeter

The precision, platinum-lined, adiabatic, solution calorimeter and operating procedures have been previously described in detail [12]. The capacity of the reaction vessel

is $300 \pm 15 \text{ mL}$ of the calorimetric solution, and the energy equivalent when filled with water is approximately $1700 \text{ J} \cdot \text{K}^{-1}$.

The calorimeter temperature was measured with the platinum resistance thermometer system in all experiments reported in this paper except seven later measurements for reaction (4) where a quartz-oscillator thermometer system was used. Details of both these systems are given in [12] as well as a complete description of the platinum sample holder (0.5-mL capacity and opening energy, $0.00 \pm 0.02 \text{ J}$) used for the MoO_3 and NaF samples. This sample holder was replaced by a Monel frame which supported the Kel-F ampoule for the MoF_6 solution experiments and the windows were cut out by a cutter at the end of a Monel rod to initiate a reaction. The Monel frame did not change weight during prolonged soaking in NaOH solution. The average opening energy measured in four experiments was 0.44 J with an average deviation of 0.14 J; in a single experiment where the windows were cut with unusual difficulty, the opening energy was measured as 1.54 J.

Each experiment consisted of an electrical calibration of the initial system followed by the chemical reaction and then an electrical calibration of the final system. The mean of the two calibrations is used in computing the enthalpy of reaction referred to the mean temperature of reaction. Calculations and procedures have been described in detail [12].

2.3. Criteria for Rejection of Experiments for Reaction (2) and the Determination of the Amount of Reaction

The determination of the enthalpy of reaction of $\text{MoF}_6(\ell)$ in NaOH solutions, reaction (2), was complicated by a number of problems. First, the necessity of using plastic ampoules for the highly corrosive samples introduced the possibilities of prereaction with moisture and/or oxygen before installation in the calorimeter and with the NaOH solution prior to opening the ampoule if leakage through the windows or seals occurred. The prereaction referred to here and later in this section is larger than that due to diffusion through the windows. Second the mass of the empty ampoule was greater after the calorimetric experiment than before. These problems will be discussed in greater detail in this section.

The enthalpy of reaction (2) was measured in 19 experiments; 9 of these were rejected for reasons to be given in the following subsection. Pertinent data for the 19 experiments are given in table 2 where the experiments are divided into three sets. Division between the sets is primarily one of time (2 months in each case) although procedural techniques may have been refined, such as different tolerances in the helium leak rate for the sample ampoules.

Table 2. Data showing criteria for rejection of preliminary experiments for MoF₆ in NaOH, Reaction (2).

Set	Expt. No.	Reaction Period	[NaOH] mol/L	Stirring Rate rpm	Drift Rates for Rating Periods				Rejection Criteria ^a		MoF ₆ Mass		
					1	2	3	4	Drift	Visual	A	B	A-B
		min			μΩ/min						g	g	g
1	559*	40	0.706	350	17.4	22.0	16.9	8.9	P, I	P	0.5065	0.5055	0.0010
	560*	40	.643	"	19.2	21.4	10.1	8.3	P	P	.3404	.3385	.0019
	562*	40	.643	"	11.8	15.2	13.3	9.2	I?	P	.2011	.1987	.0024
	563*	40	.643	"	17.7	20.0	11.1	9.0	P	P	.2368	.2350	.0018
	564*	40	.643	"	22.8	29.0	16.2	8.6	P, I	P	.2526	.2503	.0023
2	583*	60	.694	350	67.6	74.0	22.8	19.9	P	P	.3750	.3514	.0056
	^c 584	55	.694	"	24.9	26.7	26.3	23.4	-	-	(.3721)	.3698	(.0023)
	585*	25	.694	"	48.8	49.3	23.4	24.3	P	-	.5539	.5521	.0018
	586	35	.694	"	24.1	22.5	19.6	18.7	-	-	.5123	.5109	.0014
	587*	30	.694	"	31.5	31.7	23.5	22.9	P	S	.8108	.8092	.0016
	588	55	.694	"	23.0	25.9	26.7	26.8	-	-	.2305	.2273	.0032
	589	45	.302	"	24.9	24.3	24.0	23.0	-	-	.2725	.2702	.0023
3	^b 611	55	.653	350	--	10.3	12.6	10.8	-	-	.4273	.4258	.0015
	612	35	.653	"	--	8.1	6.7	5.3	-	-	.3347	.3338	.0009
	628*	70	.718	550	40.9	40.2	34.7	32.5	P	-	.3626	.3594	.0032
	629	85	.718	"	36.1	35.0	34.5	32.0	-	-	.3969	.3956	.0013
	630	70	.718	350	14.0	13.0	14.3	12.9	-	-	.2361	.2344	.0017
	632	45	.718	"	14.6	13.9	14.3	13.1	-	-	.4016	.4014	.0002
	633	75	.718	"	14.0	13.7	10.9	9.9	-	-	.4107	.4096	.0011

* Rejected experiments.

^aRejection criteria: P = prereaction, I = incomplete reaction, S = spattering of products in vessel (see text).

^bNew stirrer bearings before this experiment.

^cIn Expt. No. 584 mass A could not be determined. It was estimated from mass B by adding 0.0023 g (the average value of A-B from Expt. Nos. 586, 588, 589). This experiment was used only to determine the temperature coefficient, ΔC_p, of the reaction.

2.3.1. Drift Rates as a Criterion for Rejection

In each experiment there were four rating periods consisting of five calorimeter-temperature measurements at 5-min intervals. The slope of a line derived from a least squares fit of these data to a linear equation (see [12]) will be referred to as the "drift rate" (DR).

Rating period 1 was followed by the electrical calibration of the initial system, then by rating period 2, the chemical reaction, rating period 3, the electrical calibration of the final system, and finally, rating period 4.

The drift rates can be influenced by many factors such as the temperature, vapor pressure (since the vessel was vented to the atmosphere), and viscosity of the calorimetric solution as well as the stirring speed and the condition of the bearing surfaces for the stirrer shaft. However, if these factors remain essentially constant in the course of a single experiment, the drift rates for the four rating periods should also remain constant. This can be seen in the drift rates for experiments not marked with an asterisk in table 2. Also, the effect of changing stirring speed can be observed in the drift rates for Expts. No. 629 and 630. New polytetrafluoroethylene bearings for the stirrer were installed before Expt. No. 611. This usually results in a period of somewhat erratic drift rates until the bearings have worn to proper alignment with the stirrer shaft.

In the measurements of reaction (2) where the possibility of prereaction exists, the drift rates for the first two rating periods would be expected to be significantly larger than the third if leakage were permitting slow prereaction with the NaOH solution. Also, if the chemical reaction were incomplete, the drift rate for the third period would be significantly larger than that of the fourth period. Based on previous experience with this calorimeter a difference in drift rates within a given experiment of 3 μΩ·min⁻¹ is considered evidence of a significant change. Therefore we have set the following criteria:

Prereaction (P) occurred if

$$DR(1) - DR(3) \geq 6 \mu\Omega \cdot \text{min}^{-1} \text{ or} \\ DR(2) - DR(3) \geq 3 \mu\Omega \cdot \text{min}^{-1}, \text{ and}$$

Incomplete reaction (I) if

$$DR(3) - DR(4) \geq 6 \mu\Omega \cdot \text{min}^{-1}.$$

Therefore, the nine experiments in table 2 marked with an asterisk have been rejected because of prereaction and/or incomplete reaction. In the earlier experiments, additional evidence of prereaction was provided when blue color on the windows of the ampoule was observed before it was placed in the calorimeter.

In Expt. No. 587, where the MoF_6 sample was considerably larger than any others, the reaction was so vigorous that when the calorimeter vessel was opened after the experiment, small droplets of blue solution from incomplete reaction were found above the solution level. This experiment was also rejected because of prereaction.

2.3.2. The Amount of Reaction

Precise analyses of the products of reaction (2) were not made, and it was necessary to base the enthalpy of reaction on the mass of $\text{MoF}_6(\ell)$; this is the largest uncertainty in these measurements. The method of preparing the calorimetric samples and the possibilities of prereactions contribute to this uncertainty.

The calorimetric sample of MoF_6 was distilled under vacuum at 195 K into a weighed Kel-F ampoule (previously tested for helium leak rate) and the sidearm was sealed off with a hot iron. The filled ampoule was warmed and dried with a jet of dry helium before weighing. An effort was made to minimize the time between transferring the MoF_6 into the ampoule and placing it in the calorimeter in order to reduce the amount of moisture, oxygen, and MoF_6 which diffused through the thin windows of the ampoule.

The mass of sample of MoF_6 in the ampoule was determined from three weights: The empty ampoule with sidearm ($W1$), typically 9 g (which includes the Swagelok fitting); the filled ampoule ($W2$); and, the sidearm fragment removed when the ampoule was sealed ($W3$). The mass of the empty ampoule, typically 1.7 g, is given by $W1-W3$ and the mass of sample, by $W2-(W1-W3)$. The mass of sample obtained here is designated mass A , and is shown in column 12 of table 2.

On the assumption that this mass A of the sample reacted during the main period of the experiment in accordance with eq (2), a value for ΔH_2 and then for ΔH_7 was calculated for each of the experiments in table 2. The values of ΔH_7 obtained in this way (Method A) are shown in table 8 and in figure 1.

In an attempt to verify the amount of $\text{MoF}_6(\ell)$ sample, the empty ampoule was recovered from the calorimeter after the experiment and weighed to give $W4$. In each case the ampoule had gained mass; $W4 > (W1-W3)$. These increases in mass are shown as $A-B$ in column 14 of table 2.

By making the unlikely assumptions that the gain in mass of the ampoule is equal to an amount of MoF_6 that does not participate in the reaction in the calorimeter, and that a mass $B = W2-W4$ reacting in accordance with eq (2) is the only process taking place in the main period of the experiment, values for ΔH_2 and then ΔH_7 were calculated (Method B). The mass B is shown in column 13 of table 2, and the value of ΔH_7 derived from it for each experiment in table 2 is shown in figure 1.

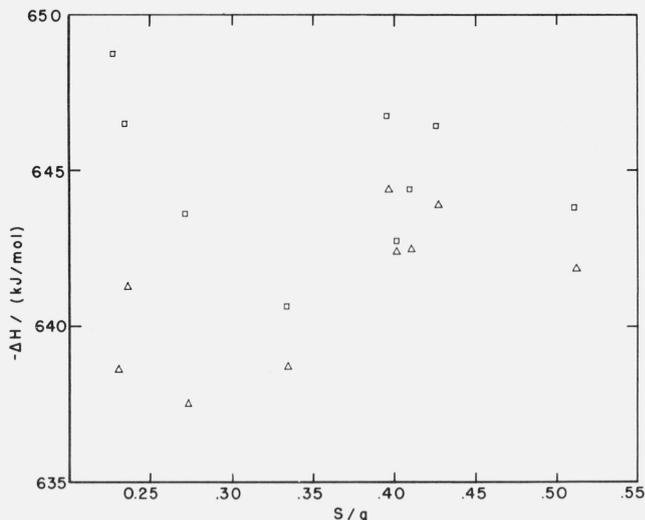


FIGURE 1. Plot of values for ΔH_7 versus sample mass calculated by method A (triangles) and by method B (squares).

Further discussion of the mass of $\text{MoF}_6(\ell)$ sample is given in section 3.

2.4 Enthalpy Measurements

The enthalpies of solution for reactions (2), (3), (4), and (5) were measured; the composition and calorimetric data are given in tables 3, 4, 5, and 6; and the experiments are discussed in 2.4.1. through 2.4.4.

2.4.1. Solution of MoF_6 in NaOH

Some of the difficulties encountered in the measurement of the enthalpy of the highly exothermic reaction of $\text{MoF}_6(\ell)$ in NaOH solutions, reaction (2), were discussed in 2.1 and 2.3. Data for the ten experiments which were not rejected are given in table 3; the experiments are arranged in order of the magnitude of the mol ratio, $[\text{H}_2\text{O}]/[\text{NaOH}]$. The following definitions apply to this and subsequent tables except as noted (for details of calculation methods, see [12]):

Expt. No. is a serial number for experiments with this calorimeter.

$[\text{NaOH}]$ is the concentration ($\text{mol} \cdot \text{L}^{-1}$) of the stock solution of NaOH determined by titration with standardized HCl solution. The calorimetric solution is a weighed amount (~ 300 g) of this stock solution.

EEE is the electrical energy equivalent which was measured for the initial (EEE_i) and final (EEE_f) systems in each experiment.

Table 3. Composition and calorimetric data for reactions of MoF₆(l) in sodium hydroxide solutions, Reaction (2).

Expt. No.	MoF ₆ ^a Mass	Initial Cal. Soln.		Mole Ratios for Initial System			EEE - 17,000 J·Ω ⁻¹		ΔR _c	q _v	Q ^c	-ΔH ₂ (T) ^d	T _{reaction}	Corr. to ^e 298.15 K	-ΔH ₂ (298.15 K)
		[NaOH]	Mass -312 g	[H ₂ O] [NaOH]	[NaOH] [MoF ₆] (8+x)	[H ₂ O] [MoF ₆] (y)	Initial ^b	Final							
	g	mol/L	g				J/Ω	Ω	J	J	J/g	K	J/g	kJ/mol	
633	0.4107	0.718	0.452	77.49	111.2	8,618	165.00	199.34	0.0823719	0.57	1414.32	344.3.7	298.095	0.2	722.90
629	.3969	.718	.462	77.49	115.1	8,918	180.57	196.00	.0797882	.57	1370.41	345.2.8	298.111	0.2	724.81
630	.2361	.718	.467	77.49	193.5	14,992	169.30	198.51	.0473086	.62	811.89	3438.8	297.908	1.0	721.70
632	.4016	.718	.417	77.49	113.7	8,813	161.87	147.25	.0806699	.57	1382.85	344.3.4	298.080	0.3	722.81
584	^f .3721	.694	.387	80.17	118.7	9,519	261.63	266.36	.0736483	.58	1269.38	3411.4	303.305	--	--
588	.2305	.694	.437	80.17	191.7	15,369	202.47	196.85	.0460077	.62	790.26	3428.5	297.143	4.1	718.89
586	.5123	.694	.322	80.17	86.2	6,913	179.33	218.27	.1025906	.54	1763.45	344.2.2	297.560	2.4	722.12
611	.4273	.653	.425	85.20	97.5	8,304	--	239.30	.0855510	.56	1473.84	3449.2	297.907	1.0	723.88
612	.3347	.653	.345	85.20	124.4	10,598	--	303.22	.0663013	.59	1146.19	3424.5	297.907	1.0	718.70
589	.2725	.302	.383	184.0	71.7	13,199	436.25	440.96	.0533690	.61	929.63	3411.5	298.055	0.4	716.09

^aSample mass calculated according to Method A (see 2.3 b).

^b0.80 J·Ω⁻¹ was added to correct for the change in heat capacity when the Monel rod was pushed down to initiate the reaction.

^cTo correct for the energy of opening the sample ampoule, q_o = 0.44 J (see 2.2) was subtracted from each experiment except Expt. No. 584 where an estimated value for q_o of 1.5 J was used because of unusual difficulty in breaking the windows of the ampoule.

^dT_{reaction} is the mean temperature of reaction except in Expts. No. 611 and 612 where it is the initial temperature of reaction because only the energy equivalent of the final system was measured.

^eΔC_p = 4.09 J·g⁻¹·K⁻¹.

^fSee note c in table 2.

ΔR_c is the corrected temperature rise for the chemical reaction period. It is obtained by extrapolation of the curves for the rating periods before (RP2) and after (RP3) the reaction period to the time of initiating the reaction. These are the initial and final temperatures of reaction, T_i and T_f, respectively. Since this calorimeter is adiabatic, no correction is made for energy transfer to the surroundings.

q_v is the correction for the enthalpy of vaporization of the MoF₆(g) in the ampoule.

Q, the heat of reaction, is the product of ΔR_c and the mean electrical energy equivalent, corrected for q_v and the ampoule opening energy q_o:

$$Q = [(\Delta R_c)(EEE_i + EEE_f)/2] - q_v - q_o$$

T_{reaction} is the temperature of reaction which is usually the mean temperature of reaction, (T_i + T_f)/2.

ΔH(T) is the enthalpy per gram of sample at the temperature of reaction or -Q/(mass of sample). When a correction, ΔC_p (T_{reaction} - 298.15 K), derived from the temperature coefficient for the reaction is added to this, ΔH(298.15 K) is obtained.

In Expts. No. 611 and 612 the electrical calibration of the initial system was eliminated in order to reduce the time of exposure of the sample ampoule to the solution prior to

initiating reaction and hopefully to reduce pre-reaction. Therefore, Q is derived from the energy equivalent of the final system and T_i is the temperature of reaction. In the equation for reaction (2), (8 + x) = [NaOH]/[MoF₆] and y = [H₂O]/[MoF₆] listed in table 3. The temperature coefficient for the reaction, ΔC_p = 4.09 J·g⁻¹·K⁻¹, was derived from Expt. No. 584 and the mean of Expts. No. 586 and 588. ΔC_p can also be estimated (with lower accuracy) from the difference, EEE_f - EEE_i. The mean of the values estimated is 3.98 J·g⁻¹·K⁻¹ with a standard deviation of 2.2 J·g⁻¹·K⁻¹.

The reactions were complete in times ranging from 35 to 85 min and the final solutions were clear and colorless with no evidence of undissolved products.

2.4.2. Solution of MoO₃ in NaOH

The reaction of MoO₃(cr) in NaOH solutions, reaction (3), was only slightly exothermic and required 1 to 3 h for complete reaction. Within the limits of these measurements (concentration of NaOH from 0.3 to 0.7 mol·kg⁻¹), the enthalpy change is independent of the concentration of the solution.

The enthalpy of this reaction was measured in five experiments and the data are given in table 4. The temperature coefficient, ΔC_p = 0.777 J·g⁻¹·K⁻¹, was derived from Expt. No. 636 and the mean of Expts. No. 556, 561, and 634. In the equation for reaction (3), (2 + x) = [NaOH]/[MoO₃] and (3 + y) = [H₂O]/[MoO₃] which are listed in table 4.

Table 4. Composition and calorimetric data for reactions of MoO₃(cr) in NaOH solutions, Reaction (3).

Expt. No.	MoO ₃ Mass	Mass of NaOH Soln. -312 g	[NaOH]	Mole Ratios for Initial System				EEE - 17,000 J·Ω ⁻¹		ΔR _c	Q	-ΔH ₃ (T)	T _{reaction}	Corr. to 298.15 K	-ΔH ₃ (298.15 K)
				[H ₂ O] [NaOH]	[NaOH] [MoO ₃] (2 + x)	[H ₂ O] [MoO ₃] (3 + y)	Initial	Final							
	g	g	mol/L					J/Ω		Ω	J	J/g	K	J/g	kJ/mol
556	0.606746	0.362	0.706	78.81	50.76	4,000	101.41	119.53	0.0192645	329.625	543.27	298.041	0.08	78.185	
557	.256515	.343	.304	182.8	52.6	9,612	361.04	365.63	.0079712	138.407	539.57	298.083	.05	77.657	
561	.226220	.400	.643	86.53	124.33	10,758	139.72	147.86	.0071694	122.911	543.32	298.029	.09	78.191	
634	.218738	.417	.694	80.17	138.51	11,104	117.89	122.31	.0068991	118.113	539.97	298.185	-.03	77.726	
636	.236132	.472	.694	80.17	128.33	10,288	223.61	219.18	.0073276	126.191	534.41	308.100	-7.73	78.035	
														Mean = 77.959	
														sdm = 0.114	

Table 5. Composition and calorimetric data for reactions of NaF(cr) in MoO₃-NaOH solutions, Reaction (4).
(a) Experiments where electrical energy was added during the chemical reaction, and temperatures were measured with a platinum resistance thermometer.

Expt. No.	NaF Mass	Mass of Cal. Soln. -311 g	Mole Ratios for Initial System				EEE - 17,000 J·Ω ⁻¹		ΔR _T	EIt	-Q	ΔH ₄ (T)/6	T _{reaction}	Corr. to 298.15 K	ΔH ₄ (298.15 K)/6
			[H ₂ O] [NaOH] (MR)	[MoO ₃] [6 NaF] (x)	[H ₂ O] [6 NaF] (4 + y)	[H ₂ O]	Initial	Final							
	g	g					J/Ω		Ω	J	J	J/g	K	J/g	J/mol
565(561)	0.386766	0.649	86.68	1.0196	126.66	10,979	102.29	109.84	0.0273441	476.26	8.51	22.00	298.172	0.01	924.2
635(634)	.379661	.671	80.17	1.0050	139.25	11,164	89.75	102.23	.0501280	863.66	6.67	17.56	298.206	0.03	738.6
637(636)	.383322	.786	80.16	1.0740	137.85	11,051	186.77	195.49	.0499182	861.99	3.84	10.02	308.118	5.95	670.6

(b) Experiments where electrical energy was not added during the chemical reaction and temperatures were measured with a quartz-oscillator.

Expt. No.	NaF Mass	Calorimetric Soln.		Mole Ratios for Initial System				EEE - 1700 J·K ⁻¹		-ΔR _c	-Q	ΔH ₄ (T)/6	T _{reaction}	Corr. to 298.15 K	ΔH ₄ (298.15 K)/6	
		Mass -300 g	MoO ₃	[H ₂ O] [NaOH] (MR)	[MoO ₃] [6 NaF] (x)	[NaOH] [6 NaF] (4 + y)	[H ₂ O]	Initial	Final							
	g	g	mass%	mol/L					J/K	K	J	J/g	K	J/g	J/mol	
1093	0.393866	12.357	0.0724	0.798	69.80	1.0043	153.93	10,741	22.855	22.752	0.0033870	5.835	14.815	298.0972	-0.026	621.0
1095	.375505	2.343	.0754	.392	141.76	1.0627	78.14	11,078	5.938	4.426	.0065103	11.101	29.564	297.9963	0.412	1258.6
1096	.371405	2.273	.0754	.392	141.76	1.0745	78.99	11,198	11.075	9.059	.0032387	5.538	14.913	309.0866	13.714	1202.0
1097	.402884	12.302	.0724	.798	69.78	0.9818	150.46	10,499	28.314	27.719	.0026503	4.580	11.368	309.1052	5.335	701.3
1098	.380860	2.310	.0764	.548	102.09	1.0570	106.34	10,856	-3.866	-4.899	.0056646	9.605	25.220	298.1056	-0.037	1057.4
1099	.375756	2.203	.0736	.297	186.89	1.0339	59.43	11,107	11.191	9.565	.0067654	11.571	30.796	298.0999	-0.087	1289.4
1100	.373229	2.483	.0736	.297	186.89	1.0456	59.89	11,193	15.274	13.776	.0027866	4.778	12.801	308.8025	18.493	1314.0

In these experiments there was no evidence of prereaction or incomplete reaction and the final solutions were clear.

2.4.3. Solution of NaF in MoO₃-NaOH

Data for the slightly endothermic reaction of NaF(cr) in solutions of MoO₃ and NaOH, reaction (4), are given in tables 5(a) and (b). In the first three experiments the NaF samples were dissolved in final solutions from experiments on reaction (3) in table 4; these Expt. Nos. are in parentheses following the Expt. No. in table 5(a). To prevent a drop in calorimeter temperature during the endothermic reaction, precisely measured electrical energy was added during the chemical reaction. Thus, ΔR_T is the corrected temperature rise resulting from the chemical reaction plus the electrical energy added, EIt, and Q = R_T(EEE) - EIt.

It was initially assumed that the enthalpy of this reaction would be small and unimportant in the scheme outlined. However, when the measured enthalpy was multiplied by the factor of six, ΔH₄ was nearly 1 percent of ΔH₇. Also the possible concentration dependence of the enthalpy was

disturbing. Therefore, several years later seven additional measurements were made; these data are given in table 5(b). At this time the calorimeter temperatures were measured with a quartz-oscillator thermometer system [12] with automatic digital print-out of the data. Since the chemical energy in the reactions was known to be around 10 J, no electrical energy was added during the reaction period; the stirring energy was sufficient to prevent a significant drop in calorimeter temperature. In these experiments, the calorimetric solutions were taken from stock solutions containing weighed amounts of MoO₃ dissolved in weighed amounts of the NaOH stock solutions. These experiments showed that both the enthalpy and ΔC_p of the reaction are dependent on the mole ratio (MR), [H₂O]/[NaOH]. Four values for ΔC_p obtained from Expts. No. 637-635, 1096-1095, 1097-1093, and 1100-1099 were fitted by least squares to a linear equation with the following result:

$$\Delta C_p = \{ [0.258 - 0.0107 (MR)] \pm 0.36 \} \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1} \\ 70 \leq MR \leq 190$$

The uncertainty is twice the standard error. The temperature coefficients derived from this equation were used to calculate the corrections to 298.15 K given in table 5. Figure 2 is a plot of the 10 values for the enthalpy of reaction showing the dependence on concentration of the NaOH solutions. The result of a least squares fit of these data is as follows:

$$[\Delta H_4(298.15 \text{ K})]/6 = \{[-13.6 + 0.521(MR) - 0.00152(MR)^2] \pm 3.0\} \text{J} \cdot \text{g}^{-1} \quad (9)$$

$$70 \leq MR \leq 190$$

The uncertainty is twice the standard error. The curve in figure 2 is a plot of eq (9).

These reactions required from 20 to 50 minutes for complete reaction and there was no evidence of prereaction or incomplete reaction.

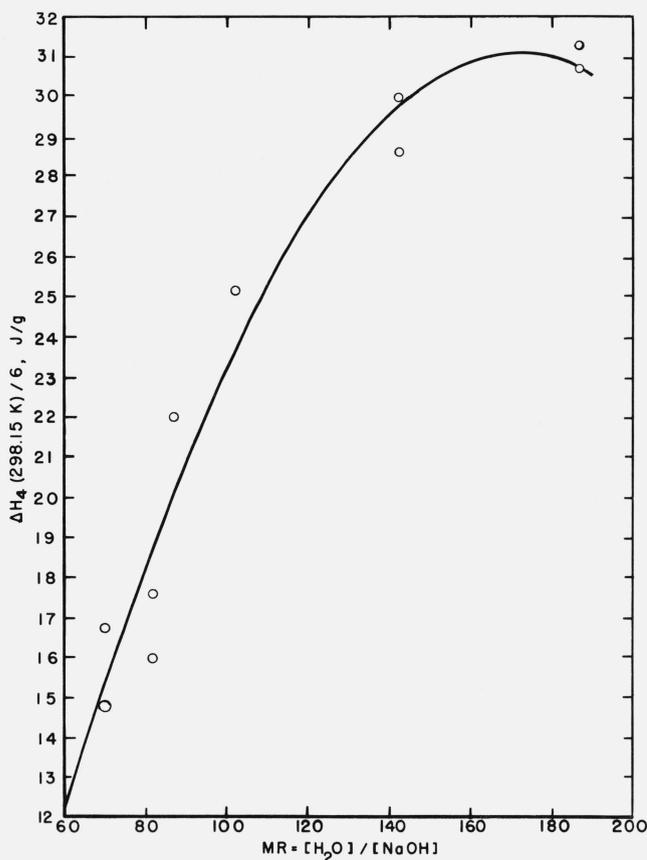


FIGURE 2. Plot showing dependence of the enthalpy of reaction of NaF(cr) in $\text{Mo}_{0.3}\text{-NaOH}$ solutions on the mole ratio of $[\text{H}_2\text{O}]/[\text{NaOH}]$.

2.4.4. Solution of NaF in H_2O

Parker's value for ΔH_∞° for NaF(cr) [13] is an estimate based on only four measurements at three concentrations.

We considered it worthwhile to check this value since the enthalpy of reaction (5) is about 1 percent of that of reaction (7). The enthalpy of solution of NaF(cr) in H_2O was measured in 10 experiments in the concentration range 0.016 to 0.132 $\text{mol} \cdot \text{kg}^{-1}$, and the data are given in table 6. $\Delta H'_5$ is the enthalpy at the final NaF concentration before correction to infinite dilution; the other terms are similar to those described for table 5a. The temperature coefficient for the reaction, $\Delta C_p = -2.4586 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ was derived from the mean of Expts. No. 642, and 647 and the mean of Expts. No. 641, 644, and 646.

Values for the apparent molal enthalpy, ϕ_L , and the enthalpy of solution at infinite dilution, ΔH_∞° , were computed from the NaF concentrations and $[\Delta H'_5(298.15 \text{ K})]/6$ by following a method described by Owen and Brinkley [15, 16]. The data were fitted to the equation

$$\Delta H'_5/6 - (2/3)A_H \sqrt{m} Y = \Delta H_\infty^\circ + b m$$

to determine $\Delta H_\infty^\circ = 0.9366 \text{ kJ} \cdot \text{mol}^{-1}$ and the empirical constant, $b = -0.2496 \text{ kJ} \cdot \text{mol}^{-1} (\text{mol} \cdot \text{kg}^{-1})^{-1}$; the standard deviations were 0.018 $\text{kJ} \cdot \text{mol}^{-1}$ and 0.21 $\text{kJ} \cdot \text{mol}^{-1} (\text{mol} \cdot \text{kg}^{-1})^{-1}$ respectively. ϕ_L is then calculated from the equation

$$\phi_L = (2/3)A_H \sqrt{m} Y + b m.$$

In these equations: A_H is the theoretical limiting slope with a value of 2.879 $\text{kJ} \cdot (\text{mol} \cdot \text{kg}^{-1})^{-1/2}$ in water at 298.15 K; m is the molality; Y is a function given by

$$Y = \frac{1 + h}{1 + B \sqrt{m}} - \sigma h$$

B is the (temperature dependent) ion-size parameter. We have used $B = 1.2 (\text{mol} \cdot \text{kg}^{-1})^{-1/2}$ for NaF in H_2O at 298.15 K [17].

$$h = -\frac{\alpha}{3} \left[\frac{\partial \ln D}{\partial T} + \frac{1}{T} + \frac{\alpha}{3} \right]^{-1}$$

where α is the expansion coefficient; D , the dielectric constant; and T , the temperature of the solvent. For water at 298.15 K, $\alpha = 257.05 \times 10^{-6} \text{ K}^{-1}$ [18].

$$\frac{\partial \ln D}{\partial T} = -4543 \times 10^{-6} \text{ K}^{-1} [19]$$

$$\text{and } h = 0.07766.$$

$$\sigma = \frac{3}{(B \sqrt{m})^3} [1 + B \sqrt{m} - 1/(1 + B \sqrt{m}) - 2 \ell_n(1 + B \sqrt{m})].$$

Values for h and σ are tabulated in reference [16]. Their value of h differs slightly from ours because a different

Table 6. Composition and calorimetric data for reactions of NaF(cr) in H₂O(l), Reaction (5).

Expt. No.	NaF Mass	H ₂ O Mass	$\frac{[H_2O]}{[NaF]}$	(EEE - 17,000) J \cdot g ⁻¹		ΔR_c	EIt	-Q	$\frac{\Delta H_5^{\circ}(T)}{6}$	T _{reaction}	Corr. to 298.15 K	$\frac{\Delta H_5^{\circ}(298.15 K)}{6}$	ϕ_L
				Initial	Final								
		g		J/g		Ω	J	J	J/g	K	J/g	kJ/mol	J/mol
641	0.383820	312.555	1898	588.39	581.82	0.0483542	861.23	10.92	28.441	298.197	0.116	1.1991	267.0
642	0.382465	312.530	1904	654.37	645.02	.0487644	862.12	1.44	3.773	308.396	25.191	1.2162	266.6
643	1.635803	312.525	445	610.02	568.68	.0460108	862.69	53.39	32.638	298.176	0.064	1.3731	451.2
644	0.997932	312.530	730	603.59	566.16	.0474028	863.36	29.79	29.849	298.675	1.291	1.3075	383.0
645	1.592899	312.475	457	653.68	631.80	.0486120	871.16	13.51	8.482	308.418	25.245	1.4161	447.5
646	1.600218	287.504	419	-432.74	-470.88	.0495350	872.95	53.24	33.268	298.239	0.219	1.4060	459.8
647	1.035612	287.479	647	-375.08	-401.31	.0516696	863.64	5.31	5.132	308.459	25.346	1.2797	399.3
648	0.633103	287.489	1058	-442.29	-454.84	.0509222	862.26	19.42	30.681	298.241	0.224	1.2977	334.9
649	0.797692	287.479	840	-441.16	-459.51	.0506911	863.70	24.78	31.064	298.250	0.246	1.3146	364.5
650	0.212330	312.530	3431	585.81	584.68	.0487202	862.49	5.73	27.002	298.198	0.118	1.1387	208.9

$$\frac{\Delta H_5^{\circ}(298.15 K)}{6} = 0.937 \text{ kJ/mol}$$

$$sd = 0.018 \text{ kJ/mol}$$

source of dielectric constant data was used. A similar method [with $B = 1 \text{ (mol} \cdot \text{kg}^{-1})^{-1/2}$, independent of temperature] described by Wagman and Kilday [20] gives nearly the same value of ϕ_L . Our results are tabulated in table 7 with those of Parker for comparison. Our value, $\Delta H_{\infty}^{\circ} = 936.6 \text{ J} \cdot \text{mol}^{-1}$ may be compared with those derived from other enthalpy of solution measurements combined with our ϕ_L values: Tsvetkov, $870 \text{ J} \cdot \text{mol}^{-1}$ [21]; Hepler, et al., $923 \text{ J} \cdot \text{mol}^{-1}$ [22]; and Latimer and Jolly, $955 \text{ J} \cdot \text{mol}^{-1}$ [23].

3. Enthalpy and Formation of MoF₆(ℓ)

The enthalpy of reaction of MoF₆(ℓ) with infinitely dilute base, reaction (7), can be calculated from the enthalpies for reactions (2) through (6). The data for these calculations are summarized in table 8 for the experiments for reaction (2) given in table 3. The value for ΔH_3 is from table 4. The enthalpy for reaction (4) is dependent on the NaOH concentration and was calculated using eq (9). Our value for ΔH_5 is discussed in 2.4.4. ΔH_6 is $6 \cdot L_2$ as described by Parker [13]; her values for ϕ_L of NaOH in table XIV A were used in the calculations. These values of $-\Delta H_7$, $-\Delta H_7(A)$, are based on the mass of MoF₆(ℓ) calculated from the mass of the empty capsule prior to reaction (2). They have a mean value of $-\Delta H_7(A) = 641.23 \text{ kJ} \cdot \text{mol}^{-1}$ and a sdm of $0.81 \text{ kJ} \cdot \text{mol}^{-1}$. There is a small trend for $-\Delta H_7(A)$ to increase as the mass of MoF₆(ℓ) increases. The values of $-\Delta H_7(B)$, calculated on the basis of the mass of the empty capsule after reaction (2), method B of section 2.3, have a mean of $-\Delta H_7(B) = 644.85 \text{ kJ} \cdot \text{mol}^{-1}$ and a sdm of $0.82 \text{ kJ} \cdot \text{mol}^{-1}$. Values of $-\Delta H_7(B)$ are shown, for comparison, in the last column of table 8. There is no significant trend with the mass of MoF₆(ℓ).

The discrepancy between $-\Delta H_7(A)$ and $-\Delta H_7(B)$ is due to the gain in mass of the empty capsule during reaction (2). This gain in mass suggests that all of the MoF₆(ℓ) does not react in accordance with eq (2) and that the correct value of

Table 7. Apparent molal heat content of NaF·n H₂O(aq) at 298.15 K

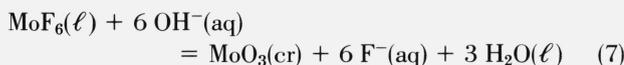
Molality	n	ϕ_L or $-\Delta H_{\text{dilln}}$	
		This work	Parker [13]
mol/kg	mol H ₂ O/mol NaF	J/mol	J/mol
0.01	5,551	169.6	176
.02	2,776	228.5	238
.03	1,850	269.7	280
.04	1,388	302.1	310
.05	1,110	328.9	339
.06	925	351.9	360
.07	793	372.0	377
.08	684	389.8	397
.09	617	405.8	414
.10	555	420.3	423
.11	505	433.6	435
.12	462	445.8	444
.13	427	457.1	452
.14	396	467.5	460
.15	370	477.3	464
.16	347	486.4	469
.17	326	494.9	473
.18	308	502.9	477
.19	292	510.4	481
.20	278	517.5	485

Table 8. Calculation of enthalpy of reaction of $\text{MoF}_6(\ell)$ in $\text{NaOH}(\text{aq})$ at 298.15 K, Reaction (7). $\Delta H_7 = \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6$.

Expt. No.	$\frac{[\text{H}_2\text{O}]}{[\text{NaOH}]}$	$-\Delta H_2$ (method A)	$-\Delta H_3$	kJ/mol				$-\Delta H_7$ (A)	$-\Delta H_7$ (B)
				$+\Delta H_4$	$+\Delta H_5$	$+\Delta H_6$			
633	77.49	722.90	77.96	4.45	5.62	1.29	642.48	644.41	
629	77.49	724.81	"	"	"	"	644.39	646.77	
630	77.49	721.70	"	"	"	"	641.28	646.50	
632	77.49	722.81	"	"	"	"	642.39	642.74	
588	80.17	718.89	"	4.64	"	1.33	638.62	648.74	
586	80.17	722.12	"	"	"	"	641.85	643.83	
611	85.20	723.88	"	4.98	"	1.40	643.88	646.43	
612	85.20	718.70	"	"	"	"	638.70	640.64	
589	184.0	716.09	"	7.76	"	2.76	637.51	643.61	
							mean =	641.23	644.85
							sdm =	0.81	0.82

$-\Delta H_7$ is greater than $-\Delta H_7(A)$. The trend in values of $-\Delta H_7(A)$ to increase as the $\text{MoF}_6(\ell)$ increases (apparently to a value near that of $-\Delta H_7(B)$) coupled with an absence in the trend in the values of $-\Delta H_7(B)$ suggests the selection of $-\Delta H_7(B)$ as the most probable value of $-\Delta H_7$. However, the assumptions upon which $-\Delta H_7(B)$ is based are unrealistic (see section 2.3). Consequently, we have adopted $-\Delta H_7(A)$ as the value for $-\Delta H_7$ and have used $-\Delta H_7(B) + \Delta H_7(A)$ as an estimate of the systematic error due to the uncertainty in the amount of reaction $\text{MoF}_6(\ell)$.

Thus, we obtain for the reaction



$$\begin{aligned} \Delta H^\circ(298.15 \text{ K}) \\ = (-641.23 + 1.8, -4.0) \text{kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The uncertainty interval assigned to the enthalpy of reaction of $+1.8, -4.0 \text{kJ} \cdot \text{mol}^{-1}$ was calculated as the square root of the sum of the squares of the following sources of imprecision and systematic error in ΔH_7 :

Experimental imprecision in	% of ΔH_7
ΔH_2	0.25
ΔH_3	0.04
ΔH_4	0.04
ΔH_5	0.04
ΔH_6	0.02

Systematic uncertainties in ΔH_2

Impurity in MoF_6	± 0.10
Ampoule opening energy	± 0.02
Amount of reaction	-0.56

The enthalpy of formation of $\text{MoF}_6(\ell)$ calculated according to eq (8) is $\Delta H_f^\circ(298.15 \text{ K}) [\text{MoF}_6(\ell)] = -1593.3 + 5.6, -4.3 \text{kJ} \cdot \text{mol}^{-1}$ using the following auxiliary data

$$-\Delta H_f^\circ(298.15 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$$

$\text{MoO}_3(\text{cr})$	745.09 ± 0.33	[3b]
$\text{H}_2\text{O}(\ell)$	285.830 ± 0.042	[14]
$\text{F}^-(\text{aq})$	335.35 ± 0.65	[14]
$\text{OH}^-(\text{aq})$	230.025 ± 0.045	[14]

The uncertainty interval of $+5.6, -4.3 \text{kJ} \cdot \text{mol}^{-1}$ in the enthalpy of formation for MoF_6 is the square root of the sum of the squares of the individual uncertainties.

The enthalpy of formation of $\text{MoF}_6(\ell)$ determined in this work differs from the recalculated value from Settle's work, $-1585.40 \pm 0.92 \text{kJ} \cdot \text{mol}^{-1}$, by slightly more than the combined uncertainty intervals.

4. Conclusions

We have measured the enthalpy of solution of $\text{MoF}_6(\ell)$ in sodium hydroxide solutions. In infinitely dilute solution according to eq (7), $\Delta H_{\text{soln}} = -641.23 \text{kJ} \cdot \text{mol}^{-1}$ with an uncertainty interval of $+1.8, -4.0 \text{kJ} \cdot \text{mol}^{-1}$. If this value is used with the best value of ΔH_f° for $\text{MoF}_6(\ell)$, that recalculated from Settle's work, and the values for ΔH_f° for $\text{MoO}_3(\text{cr})$, $\text{H}_2\text{O}(\ell)$, and $\text{OH}^-(\text{aq})$ given in section 3, a value of $-334.05 \text{kJ} \cdot \text{mol}^{-1}$ with an uncertainty interval of $+0.34, -0.69 \text{kJ} \cdot \text{mol}^{-1}$ is obtained for $\Delta H_f^\circ[\text{F}^-(\text{aq})]$ which agrees with the CODATA Recommended Key Value [14] within their combined uncertainty intervals.

The enthalpy of solution of $\text{NaF}(\text{cr})$ in water was measured and new values for the apparent molal enthalpy, ϕ_L , are tabulated from 0 to $0.2 \text{mol} \cdot \text{kg}^{-1}$. The enthalpy of solution at infinite dilution is $937 \pm 36 \text{J} \cdot \text{mol}^{-1}$. Parker's "Best" value of $912 \pm 42 \text{J} \cdot \text{mol}^{-1}$ based on very limited data is in good agreement with our result.

5. References

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