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SOME THERMODYNAMIC PROPERTIES OF FLUORAPATITE, FLUORPARGASITE, AND FLUORPHLOGOPITE

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ABSTRACT. The enthalpies of formation for fluorapatite, fluorpargasite, and fluorphlogopite from the oxides at 985 K were determined by oxide melt solution calorimetry to be -73.09 ± 6.86, -349.36 ± 9.46, and -199.20 ± 5.94 kJmol^{-1}, respectively. Using tabulated values of heat content and entropy, the Gibbs energy of formation from the elements for fluorapatite and fluorphlogopite were found to be $\Delta G^{\circ}_{f,298.15} = -6495.31 \pm 8.08$ and -6013.93 ± 7.03 kJmol^{-1}, respectively. The heat content of fluorpargasite was experimentally determined to be $(H_{985}\text{-}H_{298.15}) = 621.55 = 0.85$ kJmol^{-1}. Combined with an estimated entropy, one obtains $\Delta G^{\circ}_{f,298.15} = -12117.80 \pm 11.88$ kJmol^{-1}. These results demonstrate that reliable thermodynamic data for well characterized fluorosilicate and fluorophosphate compounds can be obtained by high temperature solution calorimetry. Some differences between these data and those of early investigators can be attributed to differences in the fluorine content and crystallinity of the samples.

INTRODUCTION

Fluorine occurs in hydrous minerals from a variety of geologic environments, ranging from phosphates (for example, apatite) in oceanic sediments (McConnell, 1973) to micas, amphiboles, and topaz in the higher pressure and temperature regimes of igneous and metamorphic rocks (Bailey, 1977; Ekstrom, 1972; Nash, 1976). Substitution of fluoride for hydroxyl has been found to have a significant effect upon the stability limits of several hydrous minerals (Comeforo and Kohn, 1954; Holloway and Ford, 1975; Kelley and others, 1959). Subsequently, fluorine may seriously affect the fractionation trends of trace elements as well as the composition of primary melts from source rocks containing hydrous minerals (Wyllie and Tuttle, 1961; Holloway and Ford, 1975).

Calculations of mineral equilibria involving fluorine-bearing phases are feasible if the proper thermodynamic data are available. Typically, thermochemical data for hydrous minerals are obtained by room temperature HF calorimetry or by analyzing ion exchange reactions and dehydration equilibria. Unfortunately, these methods are often less suited for detailed examination of fluorine-bearing minerals because of additional experimental difficulties. In this paper we demonstrate that high temperature solution calorimetry is both a simple and useful technique to acquire new thermodynamic data for a variety of fluorminerals. In particular, we have measured the enthalpies of solution at 985 K for fluorapatite, fluorpargasite, and fluorphlogopite and have calculated their Gibbs energies of formation.

EXPERIMENTAL PROCEDURE

Sample preparation.—Reagent grade chemicals with total impurities amounting to less than 0.2 percent were used for this study. These reagents

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were initially annealed in platinum crucibles prior to calorimetric measurements so as to ensure homogeneity and dryness. Table 1 lists the reagents and their annealing temperatures. After heating, all samples except NaF and KF were crushed and sieved to less than 44 μm. Because NaF and KF dissolve readily in the calorimetric solvent and also to preclude water absorption, they were crushed only to 150 μm. All samples were then stored in a desiccator with "Drierite" prior to calorimetric measurement.

Synthetic fluorapatite was prepared by mixing stoichiometric proportions of finely ground CaF_2 and $Ca_3(PO_4)_2$ in a platinum crucible. This crucible was then inserted within another slightly larger platinum crucible containing CaF_2. A platinum lid was then crimped over the outer crucible both to prevent contamination and also to retain an atmosphere enriched in fluorine. The double crucible was then heated at 1273 K for 24 hrs, after which the fluorapatite mixture was ground and reheated for an additional 12 hrs.

Fluorpargasite and fluorphlogopite were also synthesized by solid state reaction; however, they were prepared from gels using the procedure of Hamilton and Henderson (1968). Initial gels were made without fluorine and with a deficiency of either Ca or Mg. After firing the gel, the appropriate composition was attained by adding CaF_2 for fluorpargasite or MgF_2 for fluorphlogopite. Then both mixtures were ground finely in an agate ball mill. The double platinum crucible technique was again employed for solid state crystallization of the fluorpargasite and fluorphlogopite "gel" mixtures. In the case of fluorpargasite, the larger outer crucible contained CaF_2, whereas MgF_2 was used for fluorphlogopite. Both mixtures were heated at 1273 K for 24 hrs after which they were ground finely and stored in a desiccator.

Unit cell parameters for the synthetic fluor-minerals were calculated from powder diffraction patterns using Si metal ($a_0 = 5.4309$ Å) as an internal standard. These parameters as well as X-ray fluorescence analyses are listed in table 2. Petrographic examination of these synthetic minerals was limited because of their fine-grained nature. The characteristic grain

TABLE 1

Preparation of reagents used in calorimetry

Compound	Temperature (K)	Time (hrs)	Manufacturer
βAlF_3	1173	24	Matheson, Coleman, and Bell
αAl_2O_3	1673	16	Baker
CaF_2	1273	26	Alfa Inorganics
$\beta Ca_3(PO_4)_2$	1873 1323	2 24	Matheson, Coleman, and Bell
KF	773	24	Baker
MgF_2	1273	24	Alfa Inorganics
NaF	773	24	Mallinckrodt

size of fluorapatite and fluorpargasite averaged less than 5 μm prior to grinding, whereas the fluorphlogopite was considerably smaller, averaging less than 2 μm. Optical studies did indicate however, that impurities in the form of other oxide phases were 1 to 2 percent for fluorapatite and fluorpargasite, whereas the impurities found in the fluorphlogopite appeared to be slightly lower (< 1 percent).

Calorimetry.—A Calvet-type twin microcalorimeter was used to measure the heats of solution of all the fluor-minerals and their constituent fluorides, phosphates, and oxides. This technique has been previously described by Navrotsky and Kleppa (1968) and Navrotsky (1977). However, several of the fluoride compounds, including MgF_2, CaF_2, and fluorapatite were exceedingly difficult to dissolve in the lead borate flux ($2PbO \cdot B_2O_3$) using standard methods. Therefore, to enhance the rate of solution, a second compound, which readily dissolves in the solvent, was mixed in a 1:1 or a 2:1 molar ratio with the fluoride sample. The heat of solution for the second compound was determined previously and its contribution to the total heat of solution could be calculated. Several compounds were tried, including AlF_3, NaF, and SiO_2. These additives served primarily to prevent local supersaturation of the flux by the fluoride and to decrease the sintering of the solid sample.

Two samples containing fluorapatite were prepared for calorimetry by combining two moles of AlF_3 or SiO_2 with one mole of fluorapatite. In addition, $Ca_3(PO_4)_2$ was mixed with AlF_3 and SiO_2 in a 1:2 molar ratio, even though it readily dissolves in the lead borate flux. This was done in order to facilitate comparison of the heats of solution for

TABLE 2

Chemical compositions* and unit cell dimensions** of the fluorminerals used in calorimetry

			Fluorapatite		Fluorpargasite		Fluorphlogopite	
			Ideal	XRF	Ideal	XRF	Ideal	XRF
SiO_2			—	—	42.93	43.3	42.79	43.9
Al_2O_3			—	—	18.21	18.2	12.10	12.3
MgO			—	—	19.20	19.9	18.71	28.8
CaO			55.60	54.7	13.35	13.7	—	—
Na_2O			—	—	3.69	3.69***	—	—
K_2P			—	—	—	—	11.18	11.5
P_2O_5			42.22	40.3	—	—	—	—
F†			3.77	3.84	4.52	4.63	9.02	8.67
	a	(Å)	9.330 ± 0.004		9.858 ± 0.005		5.319 ± 0.006	
Cell	b	(Å)	—		17.922 ± 0.009		9.189 ± 0.005	
Parameters	c	(Å)	6.849 ± 0.004		5.284 ± 0.003		10.172 ± 0.007	
	β		120.00		105.73 ± 0.08		100.14 ± 0.07	
Cell Volume		(Å^3)	516.340 ± 0.394		898.681 ± 0.613		489.295 ± 0.471	

* Analyzed by H. Westrich.

** Refined from Guinier powder diffraction patterns using least-squares refinement program of Appleman and Evans (1973); uncertainties refer to one estimated standard deviation.

*** Not analyzed; assumed to be stoichiometric.

† Fluorine determined by steam distillation/specific ion electrode (Ingram, 1970; Huang and Jackson, 1967).

$Ca_3(PO_4)_2$ with fluorapatite. Sample mixtures containing CaF_2 or MgF_2 were mixed in equimolar proportions with AlF_3 as a diluent. Additional mixtures containing CaF_2 or MgF_2 were prepared in a 2:1 molar ratio using NaF and SiO_2 as diluents. The heat of solution for the compound of interest was subsequently obtained by subtracting the heat effect of the added component.

RESULTS AND DISCUSSION

Enthalpies of solution.—The experimentally measured heats of solution are given in table 3 along with their associated uncertainties (1 esd) and the number of experimental runs. Most of the data have experimental uncertainties of less than 5 percent relative. The heats of solution for CaO, MgO, and SiO_2 were taken from Navrotsky and Coons (1976) and were not repeated. To ensure that our results were consistent with previous studies, the heat of solution was determined for Al_2O_3 and was found to agree with the earlier results of Charlu, Newton, and Kleppa (1975).

As previously mentioned, CaF_2, MgF_2, and fluorapatite were difficult to dissolve in the lead borate flux, thereby requiring addition of another

TABLE 3

Heats of solution of fluorides, oxides, and silicates at 985 K in $2PbO \cdot B_2O_3$

Compound	$\Delta H^\circ_{sol,\,985}$ ($kJmol^{-1}$)*	Number of Experiments
AlF_3	+15.73 ± 0.75	7
Al_2O_3	+32.46 ± 1.21	8
CaF_2/AlF_3**	+92.69 ± 5.23	9
CaF_2/Al_2O_3**	+94.81 ± 6.32	5
$CaF_2/2NaF$**	+91.84 ± 7.24	6
$CaF_2/2SiO_2$**	+82.13 ± 3.09	8
CaF_2**	+93.01 ± 6.26	20
CaO†	−54.52 ± 0.92	6
$Ca_3(PO_4)_2$	+105.81 ± 5.86	9
$Ca_3(PO_4)_2/2AlF_3$**	+108.37 ± 5.27	4
$Ca_3(PO_4)_2/2SiO_2$**	+96.23 ± 2.80	7
KF	+33.26 ± 0.59	8
MgF_2/AlF_3**	+77.32 ± 1.88	4
$MgF_2/2NaF$**	+86.99 ± 13.01	7
$MgF_2/2SiO_2$**	+74.06 ± 1.72	7
MgF_2***	+82.16 ± 7.45	11
MgO†	+4.81 ± 0.59	5
NaF	+56.02 ± 1.09	9
NaF/SiO_2**	+54.64 ± 1.80	5
SiO_2†	−3.18 ± 0.42	6
Fluorapatite/$2AlF_3$**	+282.96 ± 3.47	4
Fluorapatite/$2SiO_2$**	+257.19 ± 2.13	7
Fluorpargasite	+345.01 ± 1.84	7
Fluorphlogopite	+253.38 ± 1.92	7

* Uncertainties refer to one estimated standard deviation.

** Enthalpy measurements obtained using a mixture containing another reagent (for example, CaF_2/AlF_3 indicates that an equimolar mixture of CaF_2 and AlF_3 was used to determine the enthalpy of solution for CaF_2).

*** Average value of mixture, with AlF_3, Al_2O_3, and NaF as diluents.

† Values taken from Navrotsky and Coons (1976).

compound to facilitate dissolution. Providing that no reaction occurs between the two compounds, the measured heat of solution should equal the sum of the individual components. However, in cases where SiO_2 was added as the diluent, the resulting heat of solution was consistently more exothermic than those mixtures containing AlF_3, Al_2O_3, or NaF.

These data suggest that SiF_4 is evolved either before or after dissolution of the fluoride/quartz mixture in the lead borate flux, or that a fluorosilicate complex is formed in the melt. Therefore, a portion of the MgF_2/SiO_2 mixture was heated at 1073 K for 24 hrs after which its X-ray diffraction pattern was examined. If MgF_2 or another fluoride-bearing compound had undergone a solid state reaction with SiO_2 such as,

$$2MgF_{2(s)} + SiO_{2(s)} = 2MgO_{(s)} + SiF_{4(v)} \tag{1}$$

in which silicon tetrafluoride is evolved, then MgO would have been observed in the X-ray diffraction pattern. However, this was not found to be the case.

To test whether some fluorosilicate complex was formed and/or released during dissolution, the following experiment was tried. The heat of solution of NaF was determined using a lead borate flux which also contained an equimolar amount of dissolved SiO_2. The resulting heat of solution for this experiment was 55.15 ± 1.67 $kJmol^{-1}$ for five measurements. This value is well within the experimental uncertainties of that value for NaF using a "clean" flux, which suggests that such a reaction is not significant. Thus the above experiments do not explain satisfactorily the differences in the enthalpies of solution for several fluoride/quartz mixtures compared to mixtures using other diluents.

We have chosen to use the heats of solution using AlF_3, Al_2O_3, and NaF as diluents to obtain preferred values for CaF_2, MgF_2, and fluorapatite. Weighted averages for these compounds are also listed in table 3. The internal consistency of these preferred values was checked in two ways. First, the preferred values of MgF_2 and CaF_2 may be compared to those enthalpies listed in Robie, Hemingway, and Fisher (1978). The following reactions may be written:

$$\tfrac{1}{2}\,Al_2O_3 + 1\tfrac{1}{2}\,CaF_2 = AlF_3 + 1\tfrac{1}{2}\,CaO \tag{2}$$

$$\tfrac{1}{2}\,Al_2O_3 + 1\tfrac{1}{2}\,MgF_2 = AlF_3 + 1\tfrac{1}{2}\,MgO \tag{3}$$

$$CaF_2 + MgO = CaO + MgF_2. \tag{4}$$

The enthalpies for the above reactions using the results of this study and the data from Robie, Hemingway, and Fisher (1978) are listed in table 4. These comparisons indicate that the preferred heats of solution for CaF_2 and MgF_2 yield reaction enthalpies consistent with the literature values within experimental error (2 esd).

Second, the heat of solution for another phosphate compound, $Ca_3(PO_4)_2$ (whitlockite), which dissolves well in the lead borate flux, was redetermined using AlF_3 as a diluent. The two enthalpies were in good agreement with each other (105.81 ± 5.86 versus 108.37 ± 5.27 $kJmol^{-1}$).

These results suggest that AlF_3 effectively acts as an inert compound during dissolution of the sample and would prove useful as a diluent for other fluoride compounds.

Enthalpy and Gibbs energy of fluorapatite.—The enthalpy of formation of fluorapatite was calculated from the heats of solution measurements (table 3) using both AlF_3 and SiO_2 as diluents. The following reaction was written for fluorapatite

$$\tfrac{1}{2}\,CaF_2 + 1\tfrac{1}{2}\,Ca_3(PO_4)_2 = \underset{\text{Fluorapatite}}{Ca_5(PO_4)_3F} \qquad (5)$$

$$H^\circ_{985} = -73.09 \pm 6.86\ \text{kJmol}^{-1}\ (\text{from } SiO_2 \text{ diluent})$$

$$H^\circ_{985} = -74.27 \pm 17.90\ \text{kJmol}^{-1}\ (\text{from } AlF_3 \text{ diluent})$$

These are identical within experimental limits (2 esd), indicating the internal consistency of both methods. Because of its smaller standard deviation, the first value was used for calculation of the Gibbs energy of formation for fluorapatite.

The heat contents tabulated in Robie, Hemingway, and Fisher (1978) were employed to correct our data to 298.15 K. These are listed in table 5. We calculate $\Delta H^\circ_{f,298.15} = -6859.39 \pm 8.06$ kJmol^{-1}. The enthalpy of formation for fluorapatite listed in Robie, Hemingway, and Fisher (1978), -6872.200 ± 5.000 kJmol^{-1}, is slightly more exothermic than our value. However, the enthalpy they listed was derived from previous investigations including both HNO_3 and HCl calorimetric studies (Gottschal, 1958; Jacques, 1963) and solubility measurements (Farr and Elmore, 1962) of fluorapatite. From these experiments, the enthalpy of formation of fluorapatite was found to range from -6824 to -6895 kJmol^{-1}, within which range our value is found. More recently, a more endothermic enthalpy (-6741 kJmol^{-1}) was calculated from a

TABLE 4

A comparison of the enthalpies of solution for CaF_2 and MgF_2 at 985 K

Reaction	ΔH°_{985}, kJmol^{-1}* A	B	C	D
$\tfrac{1}{2}\,Al_2O_3 + 1\tfrac{1}{2}\,CaF_2 = AlF_3 + 1\tfrac{1}{2}\,CaO$	−221.36 ±2.09	−221.80 ±19.08	−221.30 ±16.04	−205.48 ±9.84
$\tfrac{1}{2}\,Al_2O_3 + 1\tfrac{1}{2}\,MgF_2 = AlF_3 + 1\tfrac{1}{2}\,MgO$	−112.13 ±2.40	−116.52 ±22.50	−109.26 ±6.22	−104.37 ±5.79
$CaF_2 + MgO = CaO + MgF_2$	−72.82 ±1.61	−70.18 ±19.58	−74.69 ±11.32	−67.40 ±7.40

* Uncertainties refer to two estimated standard deviations.

Sources for calculation of ΔH°_{985}:

A. Robie, Hemingway, and Fisher (1978); includes correction for heat content from 298.15 to 985 K.

B. This study; average value of CaF_2 or MgF_2.

C. This study; using AlF_3 as a diluent for CaF_2 or MgF_2.

D. This study; using SiO_2 as a diluent for CaF_2 or MgF_2.

series of transformation reactions involving several phosphate minerals in aqueous KF solutions (Duff, 1971).

These discrepancies in enthalpy values may be partly attributed to deviations of the samples from ideal fluorapatite stoichiometry or to variations in the crystallinity of the fluorapatite samples used in these studies, both of which have significant effects upon the heat of solution obtained in calorimetric studies. For example, Jacques (1963) used a natural "fluorapatite" for his calorimetric measurements. The sample he used was well crystalline, but unfortunately, it was not stoichiometric fluorapatite; that is, this sample contained 2.20 wt percent fluorine as compared to 3.77 percent F for the pure endmember. Other minor impurities were also identified in that sample.

Those investigations in which the thermodynamic parameters of synthetic fluorapatite were calculated from solubility measurements required equilibration in aqueous solutions near room temperatures (Farr and Elmore, 1962; Duff, 1971). A problem may arise because apatites synthesized from aqueous solutions at low temperatures are extremely fine-grained and generally lack good crystallinity (McConnell, 1973; Van Wazer, 1958). Finally, there is yet another source of error often underestimated in the calculation of solubility products from experimental studies. The use of concentrations in place of activities for the aqueous species may result in significant errors.

Because our value of ΔH°_f refers to a fluorapatite of well-characterized composition and crystallinity, we use it for calculation of the Gibbs energy of formation. Using the tabulated value for the entrophy of fluorapatite, $S^\circ_{f298.15} = -1221.75 \pm 1.67$ $JK^{-1}mol^{-1}$ (Robie, Hemingway, and Fisher, 1978), the Gibbs energy is $\Delta G^\circ_{f,298.15} = -6495.31$

TABLE 5

Heat content and enthalpy of formation for minerals and compounds used in calorimetry measurements*

Compound	$H^\circ_{985} - H^\circ_{298.15}$ (kJmol^{-1})	$\Delta H^\circ_{f,ox,298.15}$ (kJmol^{-1})	$\Delta H^\circ_{f,298.15}$ (kJmol^{-1})
αAl_2O_3	76.01 ± 0.38**	—	−1675.70 ± 1.30**
βAlF_3	65.81 ± 0.13**	—	−1510.40 ± 1.30**
CaF_2	54.71 ± 0.16**	—	−1229.26 ± 0.42**
CaO	34.41 ± 0.10**	—	−635.09 ± 0.88**
$\beta Ca_3(PO_4)_2$	206.38 ± 0.83**	—	−4120.82 ± 2.10**
KF	37.73 ± 0.11***	—	−568.61 ± 0.42***
MgF_2	51.13 ± 0.10**	—	−1124.20 ± 1.20**
MgO	32.19 ± 0.26**	—	−601.49 ± 0.29**
NaF	36.60 ± 0.11**	—	−576.55 ± 0.67**
SiO_2	43.91 ± 0.04**	—	−910.70 ± 1.00**
Fluorapatite	327.36 ± 0.65**	−63.53 ± 7.42†	−6859.39 ± 8.06†
Fluorpargasite	621.55 ± 1.70†	−350.46 ± 9.68†	−12799.50 ± 11.74†
Fluorphlogopite	300.25 ± 0.90**	−186.14 ± 6.20†	−6353.35 ± 7.01†

* The uncertainties reported are two estimated standard deviations.

References:

** Robie, Hemingway, and Fisher (1978).

*** JANAF (1970).

† This paper, see text.

± 8.08 kJmol^{-1}, which is only slightly different from the tabulated value.

Enthalpy and Gibbs energy of fluorpargasite.—Using the results from table 3, several reactions may be written to calculate the heat of formation from the oxides for fluorpargasite. The following reaction was used

$$NaF + 2\,CaO + 4\,MgO + 1/3\,AlF_3 + 1\,1/3\,Al_2O_3 + 6\,SiO_2 = \underset{\text{Fluorpargasite}}{NaCa_2Mg_4AlAl_2Si_6O_{22}F_2} \qquad (6)$$

$$\Delta H^\circ_{985} = -349.36 \pm 9.46\ kJmol^{-1}.$$

In order to correct our data to 298.15 K, the heat contents for all the compounds used in reaction (6) were needed. Except for fluorpargasite, these values have been measured and are listed in table 5.

The heat content of fluorpargasite was experimentally measured by transposed temperature drop calorimetry (see Holm, Kleppa, and Westrum, 1967). This method measures the amount of heat absorbed as a sample is allowed to fall from T_1 near the top of the calorimeter to T_2 (985 K) at the bottom with $T_1 < T_2$. A total of 10 drops were made at several initial temperatures. The samples were contained in crimped platinum capsules, and the total heat effect measured was corrected for the contribution of the platinum. The results of these measurements are shown in figure 1, where $H_{985}-H_{T_1}$ is plotted against the difference in temperature (T_2-T_1). These data fit a linear equation with a slope of 904 JK^{-1}mol^{-1} and an r-square value of 0.99.

Using these data, the enthalpy of formation from the oxides of fluorpargasite at 298.15 K was calculated, $\Delta H^\circ_{f,ox,298.15} = -350.46 \pm 9.68$ kJmol^{-1}. The tabulated values of enthalpy for the constituent oxides and fluorides (table 5) were then used to calculate the enthalpy of formation from the elements of fluorpargasite, $\Delta H^\circ_{f,298.15} = -12799.50 \pm 11.74$ kJmol^{-1}. This value is more exothermic than the enthalpy of

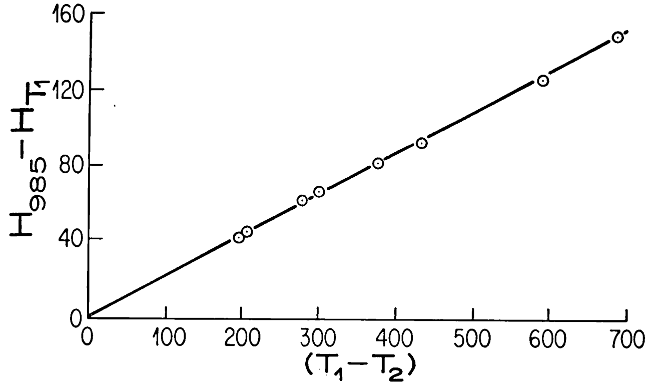

Fig. 1. Heat content of fluorpargasite as measured by transposed temperature drop calorimetry.

formation of hydroxypargasite, $\Delta H^\circ_{f,298.15} = -12678.11 \pm 18.73$ kJmol^{-1} (Westrich and Holloway, 1981), as is expected.

Two reactions analogous to (6) may also be written which employ the preferred values of CaF_2 and MgF_3 in the calculation of the enthalpy of formation for fluorpargasite,

$$NaF + 2\,CaO + \tfrac{1}{2}\,MgF_2 + 3\tfrac{1}{2}\,MgO + 1\tfrac{1}{2}\,Al_2O_3 + 6\,SiO_2 = NaCa_2Mg_4AlAl_2Si_6O_{22}F_2 \qquad (7)$$

$$\Delta H^\circ_{985} = -310.51 \pm 10.92 \text{ kJmol}^{-1}$$

$$\Delta H^\circ_{f,298.15} = -12802.74 \pm 13.38 \text{ kJmol}^{-1}$$

and

$$NaF + \tfrac{1}{2}\,CaF_2 + 1\tfrac{1}{2}\,CaO + 4\,MgO + 1\tfrac{1}{2}\,Al_2O_3 + 6\,SiO_2 = NaCa_2Mg_4AlAl_2Si_6O_{22}F_2 \qquad (8)$$

$$\Delta H^\circ_{985} = -275.42 \pm 10.60 \text{ kJmol}^{-1}$$

$$\Delta H^\circ_{f,298.15} = -12802.69 \pm 13.18 \text{ kJmol}^{-1}.$$

The close agreement amongst the three values when using reactions (6), (7), or (8) further demonstrates the internal consistency of our data.

To date, there are no experimental data for the entropy of fluorpargasite. Therefore, the third law entropy of fluorpargasite was estimated using the volume-corrected algorithm described by Helgeson and others (1978, eq 62)

$$S^\circ_{FParg} = S^\circ_s(V^\circ_s + V^\circ_{FParg})/2V^\circ_s \qquad (9)$$

where

$$S^\circ_s = S^\circ_{FParg} + \Delta S^\circ_R \text{ and } V^\circ_s = V^\circ_{FParg} + \Delta V^\circ_R.$$

For this method, an exchange reaction with assumed zero entropy change was written. The reaction chosen should contain fluorpargasite as well as other structurally similar minerals with well known molar entropies. We used the following reaction

$$\underset{\text{Fluorpargasite}}{NaCa_2Mg_4Al(Al_2Si_6)O_{22}F_2} + \underset{\text{Brucite}}{Mg(OH)_2} + \underset{\text{Quartz}}{2\,SiO_2} =$$

$$\underset{\text{Tremolite}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \underset{\text{Corundum}}{1\ 1/3\ Al_2O_3} + 1/2\ AlF_3 + NaF \qquad (10)$$

where the molar volumes and entropies are listed in table 6. However, aluminum is octahedrally coordinated in corundum and occurs in two tetrahedral and only one octahedral site in fluorpargasite. Therefore, the estimated entropy calculated from reaction (10) must be adjusted to reflect the entropy difference between tetrahedrally and octahedrally coordinated aluminum. This difference can be estimated from the sillimanite (Al^{IV})-kyanite (Al^{VI}) transformation, where $\Delta S(Al^{IV}\text{-}Al^{VI})$

amounts to an increase of about 24.7 $JK^{-1}mol^{-1}$ for the estimated entropy of fluorpargasite. In addition, Westrich and Holloway (1981) have determined that the entropy of hydroxypargasite, as calculated from phase equilibrium studies, includes a configurational entropy term amounting to 55.9 $JK^{-1}mol^{-1}$. This entropy term results from mixing of Al on both octahedral and tetrahedral sites in the pargasite structure and positional disorder of Na around the A site. Combining both configurational and site transformation contributions with the entropy calculated from eqs (9) and (10) yields an estimated entropy for fluorpargasite, $S° = 635.0 \pm 1.4$ $JK^{-1}mol^{-1}$. However, the relatively small uncertainty for $S°_{FParg}$ is somewhat misleading as it is derived solely from the sums of the uncertainties in reaction (10). A more conservative estimate of uncertainty was chosen for the estimated entropy of formation of fluorpargasite, $S°_{f,298.15} = -2287.6 \pm 3.0$ $JK^{-1}mol^{-1}$. From these data, the Gibbs energy of formation may be obtained, $\Delta G°_{f,298.15} = -12117.80 \pm 11.75$ $kJmol^{-1}$.

Enthalpy and Gibbs energy of fluorphlogopite.—From the calorimetric data, the following reaction may be written,

$$KF + 3\ MgO + 1/3\ AlF_3 + 1/3\ Al_2O_3 + 3\ SiO_2 = \underset{\text{Fluorphlogopite}}{KMg_3AlSi_3O_{10}F_2} \quad (11)$$

$$\Delta H°_{985} = -199.20 \pm 5.94\ kJmol^{-1}.$$

The heat contents of the compounds in reaction (11) were used to correct our calorimetric values (see table 5) to 298.15 K, $\Delta H°_{298.15} = -186.14 \pm 6.20$ $kJmol^{-1}$. Furthermore, the enthalpy of formation of the constituent oxides and fluorides were combined with our data to yield the enthalpy of formation from the elements $\Delta H°_{f,298.15} = -6353.35 \pm 7.01$ $kJmol^{-1}$.

The heat capacity and the enthalpy of formation of fluorphlogopite have been previously determined by HF solution calorimetry (Kelley and others, 1959). They reported an enthalpy of formation for fluorphlogopite from its constituent oxides and fluorides using reaction (11), $\Delta H°_{298.15} = -173.22 \pm 4.60$ $kJmol^{-1}$, which is only slightly more endothermic than

TABLE 6

Molar volumes and entropies used in the estimation of entropy for fluorpargasite

Compound	V° ($Jbar^{-1}$)	S° ($JK^{-0}mol^{-1}$)
AlF_3*	2.615 ± 0.010	66.48 ± 0.42
Al_2O_3*	2.5575 ± 0.0007	50.92 ± 0.10
$Mg(OH)_2$	2.463 ± 0.007	63.18 ± 0.13
NaF*	1.4984 ± 0.0005	51.30 ± 0.08
SiO_2	2.2688 ± 0.0001	41.46 ± 0.20
$Ca_2Mg_5Si_8O_{22}(OH)_2$*	27.292 ± 0.073	548.90 ± 1.25
$NaCaMg_4AlAl_2Si_6O_{22}F_2$**	27.060 ± 0.019	554.43 ± 1.34

References:

* Robie and others (1978).

** Estimated from eqs (9) and (10), see text; does not include configurational entropy or (Al^{IV} - Al^{VI}) entropy contributions.

our result. However, recent HF calorimetric measurements of several aluminous compounds have permitted Hemingway and Robie (1977) to revise the thermodynamic data for fluorphlogopite where they report that $\Delta H^{\circ}_{f,298.15} = -6392.885 \pm 3.660$ kJmol^{-1}. This value is approx 40 KJmol^{-1} more exothermic than the results of this study. If these revisions are correct, this discrepancy might be caused by compositional differences between our fluorphlogopite and that sample used by Kelley and others (1959) or by uncertainties in the tabulated heat contents. Finally, there may still be uncertainties in the enthalpies of solution for aluminous compounds used in HF calorimetry (Hemingway and Robie, 1977) as was suggested by Helgeson and others (1978). The Gibbs energy of formation was calculated using our calorimetric value for the enthalpy and the tabulated entropy for fluorphlogopite, $\Delta S^{\circ}_{f,298.15} = -1140.31 \pm 2.10$ JK^{-1}mol^{-1}, found in Robie and others (1978). From these data, we calculate $\Delta G^{\circ}_{f,298.15} = -6013.93 \pm 7.03$ kJmol^{-1}.

CONCLUSIONS

Although several fluoride compounds were troublesome to dissolve, our results demonstrate that such difficulties can be overcome and that reliable thermodynamic data for fluorosilicate and fluorophosphate minerals can be acquired by high temperature solution calorimetry. This method is especially useful for relatively refractory materials, for which few thermochemical measurements have been attempted because of the difficulties associated with these samples in HF. Our results allow calculation of the enthalpies of formation for fluorapatite, fluorpargasite, and fluorphlogopite which may then be combined with standard thermochemical data in order to yield the Gibbs energies of formation for these minerals. In the case of fluorpargasite where heat capacity data are lacking, the entropy was estimated from the mathematical algorithms of Helgeson and others (1978) and the experimental dehydration equilibria of Westrich and Holloway (1981), while the heat content (H_{985}-$H_{298.15}$) was measured with a high temperature calorimeter by transposed temperature drop calorimetry (Holm, Kleppa, and Westrum, 1967).

Several discrepancies exist between the published enthalpies of formation for fluorapatite and fluorphlogopite and those values presented in this paper. These discrepancies may be because of interlaboratory variability in sample stoichiometry and crystallinity. Our data also suggest that the controversy surrounding the validity of the enthalpies for various aluminous compounds may not have been completely resolved as reported by Hemingway and Robie (1977). It is also hoped that our investigation will encourage additional calorimetric studies on fluorosilicate minerals, especially when one considers the paucity of thermochemical data for the many compositional varieties of fluormicas and fluoramphiboles. These studies should include both high temperature heat of solution and low temperature heat capacity measurements.

Finally, these results have special application to anion exchange equilibria, such as fluoride-hydroxyl partitioning between a hydrous mineral and a coexisting aqueous fluid or between coexisting hydrous phases. Complementary to the early experimental F-OH exchange studies (Munoz and Eugster, 1969; Munoz and Ludington, 1974, 1977), one could calculate the same equilibria (see Stormer and Carmichael, 1971) using the thermodynamic parameters obtained from both high temperature stolution calorimetry and dehydration equilibria (Fisher and Zen, 1971; Zen, 1972). A comparison between several calculated and experimental exchange reactions will be reported in a later article.

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