822. *The Heats of Formation of Cuspidine,* $3CaO,2SiO_2,CaF_2$, *and the Mineral Phase,* $3CaO,3Al_2O_3,CaF_2$.

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A double-walled, copper calorimeter has been used to measure the heats of solution of cuspidine, $3CaO,2SiO_2,CaF_2$, and the mineral phase, $3CaO,3Al_2O_3,CaF_2$, in 40% aqueous hydrofluoric acid at 25°. These values have been combined with the heats of solution of calcium silicate–calcium fluoride and calcium aluminate–calcium fluoride mixtures of correct stoicheiometry (and known heats of formation) to yield reliable estimates for the heats of formation ($\Delta H_f°$) of the three-component phases at 25°, as follows: $3CaO,2SiO_2,CaF_2$ $-1219{\cdot}9$ ($\pm 4{\cdot}5$) and $3CaO,3Al_2O_3,CaF_2$ $-1845{\cdot}3$ ($\pm 5{\cdot}5$) kcal. mole^{-1}.

CUSPIDINE, $3CaO,2SiO_2,CaF_2$, is present to approximately 30% by weight in most silicate slags obtained from present phosphorus-furnace operation.[1] The aluminous phase, $3CaO,3Al_2O_3,CaF_2$, has similarly been identified in small quantities in aluminous slags but has only recently been described in detail.[2] For convenience, this material will be referred to as " Calfidine." *

While heats of formation and some high-temperature specific-heat data are available for all the common binary calcium silicates and aluminates,[3-5] no data are available for the tertiary phases involving calcium fluoride.

In the present work, heats of formation of cuspidine and calfidine at 25° have been obtained by a method of comparison, in which the heats of solution of the phases in concentrated hydrofluoric acid are compared directly with those of stoicheiometrically correct mixtures of their component oxide, silicate, or aluminate phases with calcium fluoride.

EXPERIMENTAL

Materials.—" AnalaR " calcium carbonate, calcium fluoride, alumina, and silica were the starting materials for all the silicate and aluminate preparations. Temperature and approximate times of firing the mixtures in order to achieve conversion are listed in Table 1. Completion of conversion was tested by *X*-ray powder diffraction analysis and optical examination of thin sections.

TABLE 1.

Phase	Temperature	Time
$2CaO,SiO_2$	1300°	24 Hr., followed by repeated cooling, crushing, and re-heating
$3CaO,2SiO_2$ (Rankinite)	1420° ± 10° (very critical)	48 hr., followed by crushing and re-heating
$3CaO,2SiO_2,CaF_2$ (Cuspidine)	>1410° (fused)	½ hr.
CaO,Al_2O_3	>1600° (fused)	½ hr.
$3CaO,3Al_2O_3,CaF_2$ (Calfidine)	>1510° (fused)	½ hr.

" AnalaR " 40% aqueous hydrofluoric acid was employed, undiluted as the solution reagent, and the calorimetric liquid in the outer jacket of the calorimeter was reagent-grade chlorobenzene (specific heat 0·273 cal. g.$^{-1}$ degree^{-1}).

Apparatus.—The calorimeter employed is shown in cross-section in the Figure. Principal features of the experimental design are: (1) Aqueous hydrofluoric acid is separated from the

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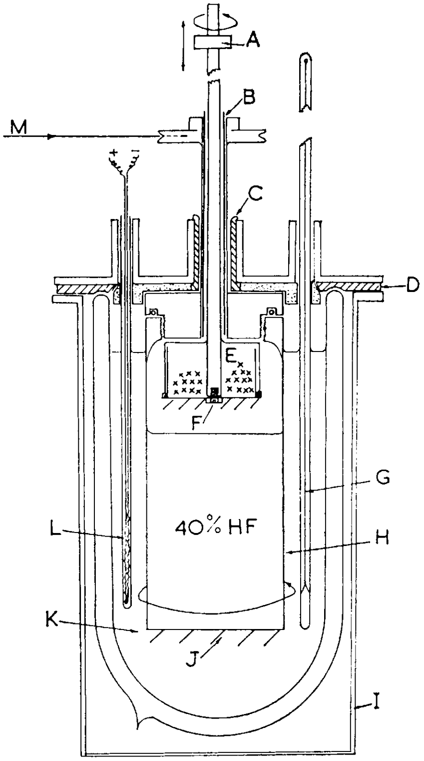
* The analogy with cuspidine is incomplete, from the viewpoint of both stoicheiometry and crystal structure; however, the similarity of origin of the two slag phases and the descriptive nature of the chosen title may be sufficient justification for an unconventional name in this field.

[1] Wilson and Leary, *Amer. Min.*, 1961, **46**, 759.
[2] Leary, *Nature*, 1962, **194**, 79.
[3] Rossini, U.S. Bureau Stand., Circular 500, 1952.
[4] Kelly, *U.S. Bureau of Mines Bull.*, 1949, **194**, 476.
[5] Petrossian and Babushkin, *Silikat Tech.*, 1958, **9**, 209.

thermometer and calibration heater by means of a copper, rotating, reaction vessel. (2) The silicate sample is held above the surface of the acid solution, during the fore-period of the experiment, in a Teflon-lined piston-and-cylinder device. The latter is constructed from copper and is in good contact with the rest of the calorimeter; hydrogen fluoride vapour cannot come into contact with the sample in the raised piston. When the piston assembly is depressed, the solid is forced down and mixed with the aqueous acid. (3) The bulk of the calorimetric liquid, between the rotating reaction vessel, and a standard Dewar flask of 4″ diameter consists of chlorobenzene (500 c.c.), and in it are immersed a Beckmann thermometer and an electrical calibration heater. The total energy equivalent is less than 400 cal. degree^{-1} (c). (4) Stirring of the chlorobenzene is provided by rotation of the copper reaction vessel. This also provides stirring within the reaction vessel when the piston sample-holder is depressed at the commencement of reaction and the plunger-rod clamped externally. Thus, reaction mixture and calorimetric liquid are stirred by a single mechanical system. Evolution of heat from the stirrer system accounted for a steady rate of temperature rise of 0·005° min.$^{-1}$ in the calorimeter; this was readily accounted for in the usual Regnault–Pfaundler cooling corrections. (5) Copper components which came into contact with hydrofluoric acid were treated with 40% hydrofluoric acid before the experiments and were thus coated with an inert layer of cupric fluoride.



Calorimeter. A, Clamping bush. B, Friction-fit Teflon bearing. C, Outer Teflon bearing. D, " Rubazote " water seal. E, Sample. F, Screw-fit sample-holder. G, Beckmann thermometer. H, Rotating copper calorimeter body. I, Can, immersed in water-bath at 25°. J, Propellor. K, Calorimetric liquid (chlorobenzene). L, Oil-immersed calibration heater. M, Motor drive to pulley.

Results.—Reactions of the silicate phases with hydrofluoric acid were usually complete within 8—10 min. of addition of the sample. In Table 2 are examples of the silicate–fluoride and aluminate–fluoride compositions that were caused to react with the acid, and the mean values of the determined heats of reaction.

Since all the products except calcium fluoride remain in solution, and since similar masses of calcium fluoride are precipitated at a given stoicheiometric composition in each case, the assumption that reactions (1)—(3) lead to the same products and the same activities of various ions (such as SiF_6^{2-}) in solution is justifiable. In the same way, the products of reactions (5) and (6) must be identical.

TABLE 2.

	Compound or mixture and molar propns.	Masses (g.) dissolved in 200 ml. of 40% HF (average)	ΔH (kcal. per mole or mole unit of compound or mixture dissolved in acid)	Solid products
(1)	$3CaO,2SiO_2,CaF_2$ (Cuspidine)	1·073	−193·9 ± 0·8	CaF_2 only
(2)	$[3CaO,2SiO_2]$, (Rankinite) ± CaF_2	1·0718	−206·3 ± 0·9	CaF_2 only
(3)	$\frac{3}{2}(2CaO,SiO_2) + \frac{1}{2}SiO_2 + 1CaF_2$	1·0798	−217·0 ± 0·8	CaF_2 only
(4)	$3CaO + 2SiO_2 + CaF_2$	1·072	Incomplete reaction (CaO coated by CaF_2)	
(5)	$3CaO,3Al_2O_3,CaF_2$ (Calfidine)	1·114	−227·7 ± 1·7	CaF_2 only
(6)	$3[CaO,Al_2O_3] + CaF_2$	1·104	−147·7 ± 0·9	CaF_2 only

Individual results (Table 3) for the molar heats of solution of various amounts of cuspidine illustrate how the molar heat quantities are not particularly sensitive to concentration in the dilution range studied (this would, of course, cease to be true if the solubility of $CaSiF_6$ or some similar phase were exceeded at any stage).

TABLE 3.

Cuspidine (g.) dissolved in 40% HF (200 ml.)	1·0096	1·0731	2·8354	3·2030
Molar heat of solution (kcal.)	194·7	193·2	193·4	194·2

The only available criteria for the completeness of reaction and for the equivalence of products are: (1) The close similarity between the masses of calcium fluoride ejected from solution, per weight of starting material in the various thermochemical routes. This suggested similar total activities of (Ca), (Si), and (F) in solution in reactions (1)—(3), and of (Ca), (Al), and (F) in reactions (5) and (6). (2) The rapid completion of the heat evolution on mixing; this was achieved in all cases where calcium silicate and calcium aluminate phases were involved. When free calcium oxide or hydroxide was used (*e.g.*, in the primary mixture $3CaO + 2SiO_2 + CaF_2$) reaction with 40% hydrofluoric acid was exceedingly slow, and heat was still being evolved 45 min. after mixing, probably owing to rapid coating of calcium oxide particles by insoluble fluoride. No similar difficulty was, however, experienced with free silica in mixture (3) and complete dissolution of finely powdered silica was readily achieved.

We may therefore compare the heats of solution of cuspidine (ΔH_a) and of the correct stoicheiometric mixture of its component silica and fluoride phases (ΔH_b), in order to obtain values for the heat of formation of the tertiary phase ($\Delta H^{\circ}_{f(a)}$) according to a general relation:

$$\Delta H_{f(a)}{}^{\circ} = +\Delta H_a{}^{soln.} - \Delta H_b{}^{soln.} - \sum \Delta H_{f(b)} \text{ [summed for all reactants in comparison reaction b].}$$

Values of $\Delta H_f{}^{\circ}$ for CaF_2, SiO_2, $[2CaO,SiO_2]$, and CaO,Al_2O_3 are taken from Rossini's work and for $3CaO,SiO_2$ from Petrossian and Babushkin's.[5] The results are presented in Table 4.

TABLE 4.

Derived results.

Compound	Exptl. obsns. used to calculate heats of formation	ΔH_f (kcal. mole^{-1})
Cuspidine	(1 and 2)	−1216·7 ± 1·7
	(1 and 3)	−1223·1 ± 1·6
Calfidine	(5 and 6)	−1845·3 ± 2·6

From these results we conclude $\Delta H_f{}^{\circ}$ (cuspidine) = −1219 ± 4·5 kcal. mole^{-1} in which the probable error gives equal weight to both the experimental results. For calfidine, where only one experimental route proved convenient, it is more difficult to assess the probable error, but, by analogy with the cuspidine result, we may conclude $\Delta H_f{}^{\circ}$ (calfidine) = −1845·3 ± 5·5 kcal. mole^{-1}.

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