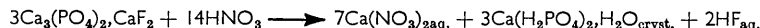


711. The Heats of Formation of Fluorapatite and Hydroxyapatite.

By J. K. JACQUES.

Heats of solution of samples of the apatites, $3\text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$ and $3\text{Ca}_3(\text{PO}_4)_2, \text{Ca}(\text{OH})_2$, obtained from natural sources, and of stoichiometric mixtures of their component oxides, fluorides, hydroxides, and phosphates, in 31% aqueous nitric acid have been compared. From these results the enthalpies of formation (ΔH_f°) at 25° have been deduced to be: fluorapatite -3296 ± 5 and hydroxyapatite -3229 ± 5 kcal. mole⁻¹. While these heats of solution agree fairly well with measurements by other workers who used artificial samples, the calculated enthalpy of formation for fluorapatite is higher than recorded values; possible reasons for this are discussed.

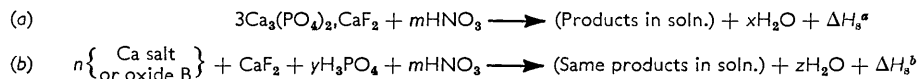
AN accurate knowledge of the enthalpies of formation of apatite minerals, particularly fluorapatite, $3\text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$, is of importance since these materials provide the principal natural sources from which phosphorus and its oxyacids are derived. Gottschal¹ obtained the enthalpies of formation of artificial apatites indirectly, from measurements of their heats of solution in 20% and 30% aqueous nitric acid solution. Well-defined products were claimed for these solution processes, e.g.:



There are three reasons for doubting the accuracy of values calculated for fluorapatite on the basis of the above equation and assumed heats of formation for the reaction products: (a) at least in 30% nitric acid solution, no precipitated product such as $\text{Ca}(\text{H}_2\text{PO}_4)_2, \text{H}_2\text{O}$ was found in repetitions of the experiments; (b) although $\text{Ca}(\text{H}_2\text{PO}_4)_2, \text{H}_2\text{O}$ was isolated on evaporation, there was no evidence that other calcium phosphates and fluorophosphates were absent from the calorimetric solutions; and (c) no allowance has been made for likely interactions between calcium nitrate, hydrogen fluoride, and calcium phosphates in solution.

In the present work, an attempt was made to remove the ambiguities about the nature of the products of the solution reaction. The method involves comparing heats of solution of the apatites with the heats of solution of stoichiometrically identical mixtures of calcium phosphate with calcium fluoride and of calcium oxide or hydroxide with calcium fluoride in phosphoric-nitric acid mixtures.

Thus if we have the reactions:



where ΔH_s is in kcal. mole⁻¹ at 25°, and if the product activities are common to reactions (a) and (b), then we may write:

$$\Delta H_f^\circ(\text{apatite}) \doteq -[n\Delta H_f(\text{B}) + y\Delta H_f(\text{H}_3\text{PO}_4 \text{ in } 31\% \text{ HNO}_3) + \Delta H_s^b] + \Delta H_s^a + (z - x)\Delta H_f(\text{H}_2\text{O})$$

Thus, when B = $\text{Ca}_3(\text{PO}_4)_2$, $n = 3$, $y = 0$, and $z = x$;
 when B = $\text{Ca}(\text{OH})_2$, $n = 9$, $y = 6$, and $z - x = 18$;
 when B = CaO , $n = 9$, $y = 6$, and $z - x = 9$.

In this manner we eliminate the need for a detailed knowledge of the products of solution if the relative activities of Ca^{2+} , F^- , HPO_4^{2-} , NO_3^- , and H_2O are kept constant in all experiments.

¹ Gottschal, *J. South Africa Chem. Inst.*, 1958, **11**, 45.

EXPERIMENTAL

Materials.—"AnalaR" calcium fluoride, calcium carbonate, calcium nitrate, and nitric acid, and B.P. grade phosphoric acid ($H_3PO_4 : H_2O = 1 : 0.87$ molar) were used. β -Tricalcium phosphate, $Ca_3(PO_4)_2$, was obtained by heating laboratory-prepared hydrated calcium phosphate at 850° for 12 hr. Calcium hydroxide was prepared by precipitation from air-free solutions of "AnalaR" calcium nitrate by carbonate-free 10% sodium hydroxide solution. The precipitate was washed with water, dried at 180° and stored in a desiccator. Calcium oxide was prepared by heating the calcium hydroxide (as prepared above) at 900° to constant weight.

Fluorapatite. A high-quality mineral sample from a Canadian mine was crushed and ground to pass a 200 mesh BSS sieve. The principal impurities (Found: P_2O_5 , 40.9; CaO, 54.8; F, 2.20; Cl, 0.08; Al_2O_3 , 0.86; Fe_2O_3 , 0.41; MgO, 0.19. Calc. for $3Ca_3(PO_4)_2 \cdot CaF_2 \cdot P_2O_5$, 42.3; CaO, 55.5; F, 2.20%) formed $<1.7\%$ of the sample weight, and because they were not expected to influence notably the observed heats of solution in nitric acid, they were accounted as "dead" weight in the final calculations.

Hydroxyapatite. It was not practicable to prepare good artificial samples by calcination of calcium hydrogen phosphates to 800 – 900° since large amounts of free tricalcium phosphate were always present in the product. An excellent source of hydroxyapatite proved to be the roots of human teeth freed from organic matter and calcined at 900 – 950° for 12 hr. X-Ray powder analysis of this material indicated a very pure apatite structure with only traces of free tricalcium phosphate or calcium fluoride. The presence of 0.15% w/w of fluoride was therefore accounted as fluorapatite and allowance was made for this in the final estimation of heat of solution in nitric acid.

Heats of Solution.—The procedure for measurement of heats of solution was that of Gottschal.¹ The solutions were examined after each run for the presence of precipitates or undissolved sample; apart from traces of alumina and silica from the fluorapatite, no solid was found.

RESULTS

Table 1 summarises the mixtures studied. The experimental heats of solution are the mean of at least three determinations and, for fluorapatite and hydroxyapatite, have been corrected for impurities as far as possible. From these results, and the accepted heats of formation of β - $Ca_3(PO_4)_2$, CaF_2 , CaO, $Ca(OH)_2$ (Rossini),² and aqueous H_3PO_4 (Egan and Luff³) the

TABLE I.
Summary of results.

No.	Compound or mixture, and molar proportions	Masses (g.) dissolved (average values)	Aqueous acid to which mixture is added	ΔH (kcal. mole ⁻¹ or per molar unit of compound or mixture dissolved in acid)
1	$[3Ca_3(PO_4)_2, CaF_2]$ (fluorapatite)	4.17	31% aq. HNO_3 250 ml.	$-49.6 \pm 0.84^*$
2	$3Ca_3(PO_4)_2 + 1CaF_2$	4.17	" "	$-90.0_7 \pm 0.54$
3	$6H_3PO_4$ (d 1.75)	7.14	" "	$(-2.92 \pm 0.03) \times 6$
4	$1CaF_2 + 9Ca(OH)_2$	2.65	Acid mixture from expt. 3	-310.8 ± 1.5
5	$1CaF_2 + 9CaO$	2.40	" "	-451.6 ± 2.5
6	$1Ca_3(PO_4)_2$ (β)	3.78	31% aq. HNO_3 250 ml.	$-31.55 \pm 0.7_4$
7	$[3Ca_3(PO_4)_2, Ca(OH)_2]$ (hydroxyapatite)	3.5	" "	$-98.6 \pm 1.1_2^*$
8	$3Ca_3(PO_4)_2 + Ca(OH)_2$	3.5	" "	-125.3 ± 1.38
9	$10Ca(OH)_2$	2.85	Acid mixture from expt. 3	-349.6 ± 1.7
10	$10CaO$	2.02	" "	-505.1 ± 2.8

* These values have been corrected for impurities found on analysis.

heats for formation of the apatites can be derived, using the general expression: $\Delta H_f^\circ(\text{apatite}) = +\Delta H_a - \Delta H_b - \Delta H_f^\circ$ (summed for all reactants in comparison with reaction b), where ΔH_a = heat of solution of the apatite in nitric acid and ΔH_b = heat of solution of an equivalent weight

² Rossini, *U.S. Nat. Bur. Stand.*, Circular 500, 1952.

³ Egan and Luff, *J. Phys. Chem.*, 1961, **65**, 523.

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of calcium oxides, hydroxides, phosphates, and fluorides in the correct stoichiometric proportion.

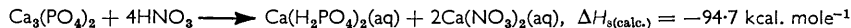
The results of substituting the appropriate combination of values from Table 1 into this expression are given in Table 2.

TABLE 2.
Derived results.

Compound	Expts. used	ΔH_f° (kcal. mole ⁻¹)	Compound	Expts. used	ΔH_f° (kcal. mole ⁻¹)
Fluorapatite	1 and 2	-3297.9 ± 1.4	Hydroxyapatite	7 and 8	-3229.2 ± 2.5
	1, 3, and 4	-3294.4 ± 2.5		3, 7, and 9	-3229.3 ± 2.8
	1, 3, and 5	-3294.9 ± 3.5		3, 7, and 10	-3228 ± 3.9
β -Tricalcium phosphate	6 and 9	-987.5 ± 1.2			
	6 and 10	-987.4 ± 1.4			

DISCUSSION

Substantial agreement is found between heats of formation of the apatite [and of β -Ca₃(PO₄)₂] obtained by various thermochemical routes. The values derived for hydroxyapatite and β -tricalcium phosphate agree well with those given by recent authors.^{1,2} However, the mean value obtained for fluoroapatite is 28 kcal. mole⁻¹ higher than the previous figure¹ (-3264 kcal. mole⁻¹), which fails to account for strong interactions of hydrogen fluoride (formed on dissolution of fluoroapatite in nitric acid) and other calcium salts in solution, leading possibly to a variety of phosphate and fluorophosphate ions. Further evidence for the incorrectness of the assumption that tricalcium phosphate and calcium nitrate are the only salts in solution (whether or not hydrogen fluoride is present) is provided by examination of the expected heat of solution for β -tricalcium phosphate in nitric acid for the reaction:



This value is considerably higher than that observed (-31.55 kcal. mole⁻¹) and is clear evidence that other products must be included in the reaction scheme.

Farr and Elmore⁴ use a value of ΔH_f (-3267.2 kcal. per mole of fluorapatite) for an indirect calculation of the solubility product K_{FA} of apatite in water, and find a value of $\text{p}K_{\text{FA}}$ which is somewhat lower than that obtained from direct activity measurements. This suggests that a higher enthalpy of formation should be ascribed to fluorapatite.

Further, the heat and free-energy changes for the equilibrium reaction



at 25° are $\Delta H = -12$ kcal. mole⁻¹ and $\Delta G = -11.8$ kcal. mole⁻¹. These values suggest that replacement of hydroxyl by fluoride ions in the open columnar apatite lattice⁵ should occur easily. This exchange is well known in dental chemistry, but it is doubtful whether it occurs to the extent suggested by these results.

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⁴ Farr and Elmore, *J. Phys. Chem.*, 1962, **66**, 315.

⁵ Beevers and McIntyre, *Mineral. Mag.*, 1946, **27**, 254.