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SHORT COMMUNICATION

The Enthalpy of Formation of Manganese Tetrafluoride

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A value of -265 kcal mol^{-1} (-1109 kJ mol^{-1}) has been reported for the enthalpy of formation of solid manganese tetrafluoride, $\Delta H_f(MnF_4(s))$ [1]. This value was obtained from electron impact threshold measurements, and has an estimated error of $\pm$ 88 kJ mol^{-1}. Though it was claimed that much of the uncertainty and ambiguity in interpreting electron impact measurements had been eliminated in this determination, we felt that it would be worthwhile to determine $\Delta H_f(MnF_4)$ by solution calorimetry. We might thus at least obtain confirmation of this earlier estimate, and also hope to obtain a more precise value for $\Delta H_f(MnF_4)$.

Crystalline manganese tetrafluoride was prepared by heating manganese difluoride under a pressure of about 3000 atmospheres of fluorine, in the presence of small amounts of bromine pentafluoride and oxygen, for 5 to 6 days at about 400°C. The autoclave was then allowed to cool to room temperature very slowly, about 10°C per day. The manganese tetrafluoride was thus obtained in the form of dark blue needles; these had to be ground before use in the thermochemical experiments.

Portions of about 30 mg of manganese tetrafluoride, taken variously from three independent preparations of this material, were transferred to ampoules in a dry-box. These ampoules were broken under 100 cm^3 of potassium hydroxide solution (1.00 mol dm^{-3}) at 298.2K in an LKB 8700 calorimeter fitted with thermistor and detection arrangements as described earlier [2]. The mean value for the measured enthalpy of hydrolysis was -415 kJ mol^{-1}, from eight hydrolyses. The 90% confidence limits [3] of this mean were $\pm$ 10 kJ mol^{-1}; there was no significant difference between enthalpies of hydrolysis of the different samples of manganese tetrafluoride. The calorimeter's performance was checked by determination of the enthalpy of solution of potassium chloride in water [4].

Manganese tetrafluoride hydrolyses in aqueous alkali as follows:

$$MnF_4 + 4OH^- = MnO_2 + 4F^- + 2H_2O.$$

From the measured enthalpy of this reaction, and published enthalpies of formation of OH^-aq (-230.025 kJ mol^{-1}) [5], F^-aq (-335.35 kJ mol^{-1}) [6], MnO_2 (-502.3 kJ mol^{-1}) [7], and water (-285.83 kJ mol^{-1}) [5], we calculate $\Delta H_f(MnF_4(s))$ = -1080 kJ mol^{-1}. We estimate the uncertainty in this result to be approximately $\pm$ 15 kJ mol^{-1}; this includes the statistical error from the calorimetric measurements and an allowance for some slight uncertainty in $\Delta H_f(MnO_2(s))$ arising from small uncertainties in the exact degree of hydration of this material when precipitated under different conditions. Our value for $\Delta H_f(MnF_4(s))$ comes within the range of the previous estimate, and our uncertainty is considerably smaller. Using a value of 142 kJ mol^{-1} for the enthalpy of sublimation [1], we obtain $\Delta H_f(MnF_4(g))$ = -938 kJ mol^{-1}.

The enthalpy of formation of manganese tetrafluoride has already been discussed in relation to formation enthalpies of other manganese fluorides [1]; our result does not affect this discussion materially. The enthalpy of formation of manganese tetrafluoride may be compared with values for one or two other tetrafluorides, for example those of silicon ($\Delta H_f(SiF_4(g))$ =

-1615 kJ mol^{-1} [8]), and of titanium ($\Delta H_f(TiF_4(g))$ = -1551 kJ mol^{-1} [9]). The ΔH_f value for manganese tetrafluoride is, as one might expect, markedly less negative than those for the tetrafluorides of silicon and of titanium.

We hope to be able to use our value for $\Delta H_f(MnF_4)$ in conjunction with thermochemical data and lattice energies for hexafluoromanganates(IV) to obtain an estimate of the (two-)fluoride ion affinity of manganese tetrafluoride:

$$MnF_4 + 2F^- = MnF_6^{2-}$$

to augment slightly our present meagre data on halide affinities of metal halides [10].

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