THE HEATS OF FORMATION OF METAL HALIDES

ALUMINIUM FLUORIDE

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The heat of the reaction $\frac{3}{2}$ $PbF_2 + Al = AlF_3 + \frac{3}{2}$ Pb has been measured calorimetrically, the reactants being in powder form. The heat of reaction is − 117·9 ± 0·1 kcal/mole from which, with the value of − 158·5 kcal/mole for the heat of formation of lead fluoride, the value of − 355·7 kcal/mole for the heat of formation of aluminium fluoride is derived. The value is used to correct the heat of formation of aluminium monofluoride vapour, which is − 59·2 kcal/mole. Some measurements were also carried out on the reaction between lead fluoride and magnesium.

No experimental determination of the heat of formation of anhydrous aluminium fluoride has been published. The value of − 329 kcal/mole[1] commonly accepted is based upon an estimated value[2] of the heat of dehydration of the hydrate $AlF_3 . \frac{1}{2}H_2O$, although the basis of this estimate is unreliable. The usual method of determining the heat of formation of insoluble substances by measuring the heat of precipitation from an aqueous solution is not applicable to aluminium fluoride, since the product obtained is a hydrate; while the anhydrous substance cannot itself be readily hydrated. The heat of formation has therefore been determined by measuring the heat evolved in the reaction,

$$3\,PbF_2 + 2\,Al = 2\,AlF_3 + 3\,Pb, \qquad (1)$$

the reactants being in the form of a briquetted powder mixture. The reaction with lead fluoride was chosen because the heat of formation of lead fluoride is quite well known, and because no complications due to alloying between lead and aluminium are to be expected, the two elements being scarcely soluble in one another under standard conditions.

In the course of developing the method used, measurements were also made on the reaction between lead fluoride and magnesium.

EXPERIMENTAL

Apparatus.—The calorimeter used was of conventional design consisting of an inner water bath (containing about 2000 ml of water), separated by a 5-mm air gap from the outer bath, the temperature of which was kept constant to ± 0·001° C. Each bath contained two stirrers driven independently by two synchronous motors. The bath temperatures were measured by a Stantel thermistor (type F. 2311/300) which was calibrated at three fixed points (0°, 32·38° and 100° C), the resistance at each standard temperature being determined by extrapolation to zero current from measurements at various loads. Recalibration of the thermistor after a considerable interval indicated no change in the readings. To make the thermistor less sensitive to small temperature fluctuations in its immediate environment, it was surrounded by a small bead of mercury contained in a thin glass bulb. The bath temperature could be measured to within 0·0003° C.

The reaction was carried out in a small brass bomb fitted with the usual electrical contacts and a needle valve for filling with argon. The reaction mixture, in briquette form, was placed in an alumina crucible; the contents were prevented from being scattered during the reaction by an aluminium cover. The crucible fitted closely inside a thick copper cylinder connected to the walls of the bomb by copper strips.

MATERIALS.—The purity of the aluminium powder exceeded 99·96 %, apart from a slight oxide content, which is immaterial. Before use the powder was treated for some hours with thiophene-free benzene in a Soxhlet extractor to remove traces of hydrocarbons, and afterwards was heated in vacuum to 500° C, with a view to removing any water that might be adsorbed in the oxide film.

Lead fluoride was prepared by dissolving spectrographically pure lead in A.R. nitric acid and precipitating with A.R. hydrofluoric acid. When this precipitate was dried by heating in vacuum at 300° C the product gave values for the heat of reaction with aluminium which were much too high (173 to 177 kcal/mole) and also showed poor agreement with one another; the reaction with magnesium gave a similar high value (160 kcal/mole). Treatment in a stream of pure hydrogen fluoride at 600° C gave much lower and more consistent values for the heat of reaction (expt. 5, 6 and 8), but it was found that in order to obtain results of the highest reproducibility for the aluminium reaction, the lead fluoride must be heated to fusion in hydrogen fluoride. For this purpose the precipitate was contained in a platinum boat and heated in an alumina tube through which hydrogen fluoride of at least 99·9 % purity was passed; after the salt had melted, the hydrogen fluoride was displaced by purified argon, in which the salt was finally allowed to cool. This treatment introduced into the lead fluoride 0·7 % of aluminium fluoride which was allowed for in calculating the heat data, the lead fluoride being otherwise spectrographically pure.

The magnesium powder used was a spectrographically pure sample obtained from Johnson Matthey Ltd. Its magnesium metal content, as determined by evaporation in a high vacuum, was about 90 %, the remainder being magnesium oxide. The powder was extracted with benzene for some hours to remove hydrocarbons, and then heated in vacuum to 400° C. The particle size of the powders used was of the order 10^{-2} mm diameter. This was not sufficiently small for the surface energy to influence the observed heat of reaction significantly.

PROCEDURE.—Weighed quantities of the purified reactants, in the form of fine powders, were carefully mixed together and pressed into a briquette in which was embedded a short length of fine tungsten wire (resistance about 0·1 ohm); a small amount of mixture remaining in the briquette press was subsequently recovered, weighed and analyzed, so that the weight and composition of the briquette itself could be accurately determined. The briquette was placed in the alumina crucible inside the bomb, and the ends of the tungsten wire connected to the terminals of the bomb. Before reaction the bomb was filled with purified argon.

The reaction was started by connecting the tungsten wire momentarily with a 12-V battery; it was complete in a few seconds. The energy expended in igniting the mixture was deduced from the deflection of a ballistic galvanometer in circuit with the ignition wire, the deflection having previously been correlated (in blank experiments) with a directly measured quantity of heat. The uncertainty in this measurement did not usually exceed 2 or 3 cal, corresponding to a temperature change of about 0·001° C.

The quantity of substance reacting was calculated from the weight of that reactant not present in excess. In all cases it was assumed that the reaction went to completion. The quantities of unreacted material remaining were too small to be detected by X-rays, and no satisfactory analytical method could be found for their determination, since the reactions studied usually proceeded spontaneously in the presence of reagents. The high degree of consistency in the heat data obtained in the aluminium fluoride experiments, even when the briquette composition was varied, suggests that reaction was essentially complete.

CALIBRATION.—The heat capacity of the calorimeter, measured electrically in the usual way, by inserting a manganin spiral into the bomb, was found to be 2·294 ± 0·0015 kcal per °C. This agreed with the additively calculated value to within 10 cal.

RESULTS

The data obtained for the aluminium + lead fluoride reaction are summarized in table 1. Runs 5, 6 and 8 were carried out with lead fluoride heated in hydrogen fluoride to about 600° C; in the remainder the lead fluoride had been fused in hydrogen fluoride. The observed heats of reaction in the first three runs are significantly higher, and also less consistent, than those of the second group, and it would appear that adequate purification was achieved only by fusion of the lead fluoride. The heat of reaction adopted as most reliable is the mean of the values obtained from runs 17, and 23 to 27; this gives a value of − 117·9 ± 0·1 kcal/mole. Four values [3–6] for the heat of formation of lead fluoride, obtained by different methods, exist; they show a total spread of about 1 kcal/mole. With the value of − 158·5 kcal/mole given in *Selected Values of Chemical Thermodynamic Properties* [7] our measurements lead to − 355·7 kcal/mole for the heat of formation of aluminium fluoride.

TABLE 1

expt. no.	weight PbF_2 (g)	weight Al (g)	temp. corrections (°C)		corrected temp. rise (° C)	heat of reaction (kcal/mole)
			heat loss	ignition energy		
5	8·850	1·961	0·008	0·004$_5$	1·243	118·7
6	8·098	2·683	0·004$_5$	0·009	1·135	118·3
8	8·470	2·820	0·012	0·009	1·194$_5$	118·8
17	7·541	2·117	0·026	0·003	1·052	118·1
23	7·440	2·095	− 0·062	0·002	1·035	117·9
24	7·364	2·251	− 0·053$_5$	0·002	1·024$_5$	117·8
25	7·477	2·093	0·023	0·004	1·042	118·1
26	7·214	1·620	0·042$_5$	0·004	1·003$_5$	117·6
27	7·246	1·615	0·024	0·004	1·010	117·8

Four experiments on the magnesium + lead fluoride reaction, using an excess of magnesium, gave the following heats of reaction, allowance being made for the heat of formation of $PbMg_2$ (− 12·5 kcal/mole); [8] 109·7, 110·3, 109·9, 108·1 kcal/mole. When an excess of lead fluoride was used, the values were: 110·4, 109·3, 108·8 kcal/mole. While the two series of measurements on magnesium fluoride agree well with one another, and tend to confirm the heat of formation of $PbMg_2$, it is possible that this agreement is fortuitous, since the variation of the single values is significantly greater than that of the aluminium + lead fluoride measurements, and suggests that magnesium is less suitable than aluminium for use in these experiments. Again adopting − 158·5 kcal/mole for the heat of formation of lead fluoride, our data give − 268 ± 0·3 kcal/mole as the heat of formation of magnesium fluoride. Five values [3, 6, 9, 10, 11] from about − 261 to − 266 kcal/mole may be obtained from previously published data; a value of − 263·5 kcal/mole is adopted in *Selected Values of Chemical Thermodynamic Properties*; [7] the mean value of − 268 kcal/mole obtained is thus rather higher than previous values. This difference, and the variations, possibly arise from several causes—errors in determining the relatively high oxide content of the magnesium, small amounts of water adsorbed in it, an error in the heat of alloying, etc. Since measurements on magnesium fluoride were not the particular object of this investigation, the matter was not pursued further.

If the data on the magnesium + lead fluoride and the aluminium + lead fluoride reactions are combined, and the standard value for magnesium fluoride taken as − 263·5 kcal/mole, the value obtained for the heat of formation of aluminium fluoride is − 348·9 kcal/mole.

DISCUSSION

The standard heat of formation of − 355·7 kcal/mole for aluminium fluoride obtained from these measurements is about 27 kcal/mole higher than the previously recognized value [1] and 45 kcal/mole higher than the calculated value given in *Selected Values of Chemical Thermodynamic Properties.* [7] If, despite the high reproducibility of results, the reaction used did not go to completion, the true value of the heat of formation of aluminium fluoride would be still higher than that given here. There is an appreciable mutual solubility of lead and aluminium at the temperatures (above 1000° C) reached momentarily during the reaction. If supersaturated solutions of the metals in one another were present in the products, a correction for the heats of solution would be necessary, and would increase the heat of formation of aluminium fluoride by a maximum value of about 2·5 kcal/mole.

With the revised heat of formation of aluminium fluoride, the heat of formation of aluminium monofluoride vapour can be corrected. Data on the free energy of aluminium monofluoride have been obtained from measurements of the equilibrium,[12] $AlF_3(s) + 2\,Al\,(l) \rightarrow 3\,AlF(g)$. More recent measurements give 1·92 for the aluminium/lead ratio, from which the aluminium monofluoride pressure is derived, and which was originally reported as 1·49. Combining this with the new value for the heat of formation of aluminium fluoride, and with the other thermodynamic data previously given, the standard heat of formation of aluminium monofluoride vapour becomes − 59·2 kcal/mole. With a heat of evaporation of 77·4 kcal/mole for aluminium,[13] and a heat of dissociation of 37·9 ± 3·5 kcal/mole for fluorine,[14] this gives 6·72 eV for the energy of dissociation of AlF. This has to be compared with the lower limit of 6·51 eV and the most probable value of 7·2 ± 0·3 eV derived by Rowlinson and Barrow.[15] The value is decidedly above the lower limit determined spectrographically. The agreement between the thermochemical value and the value of 7·2 eV derived by graphical extrapolation is about as good [12] as with AlCl.

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