Journal of Fluorine Chemistry, 5 (1975) 172 - 174

Short Communication

The standard heat of formation of arsenic trifluoride

A. A. WOOLF

School of Chemistry, Bath University, Bath BA2 7AY (Great Britain)

(Received April 18, 1974)

The enthalpy of formation of arsenic trifluoride has been needed in some recent work. For example, the As—F bond energy has been used as one of a series of energies which were extrapolated to find bond energies of noble gas fluorides. The energetics of fluoride ion transfer [1] in the gas phase

$$SF_6^- + AsF_x \rightarrow AsF_{x+1}^- + SF_5$$

has been suggested as a measure of the relative acidities of arsenic fluorides, uncomplicated by condensed phase interactions.

A heat of formation (-198.3 kcal mol^{-1}) was derived from the heat of hydrolysis of arsenic trifluoride in molar sodium hydroxide solution, together with the heat of solution of solid arsenious oxide and sodium fluoride in the same solution [2]. The value reported in N. B. S. Circular 500 from the same measurements is -226.8, and in the revised version [3] -228.55 kcal mol^{-1}. The original measurements have now been repeated and a value recalculated which takes into account recent changes in the auxiliary heats of reaction.

Experimental

The trifluoride was prepared and purified as described previously [4]. Samples were taken into thin-walled glass ampoules and broken under alkali solution in a Dewar-type calorimeter. The calorimeter was checked by measuring the heat of neutralisation of tris(hydroxymethyl)amino methane in 0.1 mol l^{-1} HCl [5]. A mean value 7.110 ± 0.015 kcal mol^{-1} was obtained. The purity of the trifluoride (99.9%) was confirmed by iodimetric analysis of the hydrolysates.

Subtracting the above heats for

$$2AsF_3(l) + 6NaOH(55H_2O) = [As_2O_3 + 6NaF](NaOH) + 3H_2O(l) + 2\Delta H_1$$

$$As_2O_3(s) + 6NaF(s) = [As_2O_3 + 6NaF](NaOH) + \Delta H_2$$

gives

$$2AsF_3(l) + 6NaOH(55H_2O) = As_2O_3(s) + 6NaF(s) + 3H_2O(l) + (2\Delta H_1 - \Delta H_2)$$

TABLE 1

Heat of hydrolysis of AsF_3 in NaOH solution

AsF_3 (g)	NaOH (g)	H_2O/AsF_3 (mole ratio)	Heat evolved/AsF_3 (kcal mol^{-1})		(kJ mol^{-1})
2.7481	259.0	664	59.05	$\Delta H'_1$	247.06
2.1924	258.9	865	59.04		247.02
1.7863	259.2	1023	59.19	ΔH_1	247.65
1.3924	258.9	1311	59.19		247.65
1.2618	259.4	1023	59.16		247.53

TABLE 2

Heat of solution of (As_2O_3 + 6NaF) in NaOH solution

[As_2O_3 + 6NaF] (g)	NaOH (g)	H_2O/As_2O_3 (mole ratio)	Heat evolved/[As_2O_3 + 6NaF] (kcal mol^{-1})		(kJ mol^{-1})
4.4003	259.0	1415	10.36	$\Delta H'_2$	43.35
2.1509	261.1	2926	10.58	ΔH_2	44.27

The mean value of this heat (107.76 kcal mol^{-1}) taken with $-\Delta H_f$[NaOH-($55H_2O$)] = 112.4 [6]; As_2O_3(s) = 160.30 [7]; NaF(s) = 137.85; and H_2O = 68.315 kcal mol^{-1}, yields $-\Delta H_f[AsF_3(l)]$ = 205.1 kcal mol^{-1} (858.14 kJ mol^{-1}). The value for NaF(s), derived from the heat of neutralisation of NaOH and HF (−79.93 kcal mol^{-1}) [8] at infinite dilution and the heat of solution of NaF (0.21 kcal mol^{-1}) [9], is close to the value of −137.91 kcal mol^{-1} given in a recent compilation [8].

Discussion

The measured heat of hydrolysis is less than that reported by Yost and Sherborne (64.5 ± 0.76 kcal mol^{-1}) [2] although the heats of solution agree within experimental error (10.7 ± 0.8 kcal mol^{-1}). A further check on the heat of solution is obtainable by subtracting the heat of solution of 6NaF (1.26 kcal mol^{-1}) from the value for the heat of solution of arsenious oxide in sodium hydroxide (12.03 ± 0.04 kcal mol^{-1} in 1.87 mol l^{-1} NaOH) [7], although it does assume that the former heat is the same in water as in alkaline solution. The new heat of formation of arsenic trifluoride of −205.1 kcal mol^{-1} (858.14 kJ mol^{-1}) is 23.4 kcal mol^{-1} less negative than the N. B. S. value and it is possible that the heat of solution had been inadvertently taken as endothermic.

The overall uncertainty in the new value is as much dependent on the uncertainties in the auxiliary heat of formation of As_2O_3, and especially HF, as on the above measured heats. A more direct method is needed and a determination of the heat of fluorination of AsF_3 to AsF_5 in a fluorine bomb or a medium-pressure glass calorimeter is suggested.

The As-F bond energy in the trifluoride (108.5 kcal mol^{-1}) is now closer to that in the pentafluoride (92.4 kcal mol^{-1}) than previously supposed [10]. The heat of formation of $AsF_4^-(g)$ calculated from the thermoneutrality of the ion-molecule reaction [1]

$$AsF_3 + SF, \rightarrow AsF_4^- + SF,$$

becomes even more divergent from the value calculated from the electron capture reaction

$$AsF_5 + e \rightarrow AsF_4^- + F^-$$

An independent value for $AsF_4^-(g)$ is needed. This could be obtained *via* a Born-Haber cycle on $KAsF_4$ if the heat of formation of this salt were determined.

1 T. C. Rhyne and J. G. Dillard, Inorg. Chem., 13 (1974) 322.
2 D. M. Yost and J. E. Sherborne, J. Amer. Chem. Soc., 77 (1935) 700.
3 N. B. S. Circular 500 and Technical Note 270-3, “Selected Values of Chemical Thermodynamic Properties”.
4 A. A. Woolf and N. N. Greenwood, J. Chem. Soc., (1950) 2200.
5 T. Wadso and R. J. Irving, Acta. Chem. Scand., 18 (1964) 195.
6 S. R. Gunn and L. G. Green, J. Amer. Chem. Soc., 80 (1958) 4782.
7 A. E. Beezer, C. T. Mortimer and E. G. Tyler, J. Chem. Soc., (1965) 4471.
8 J. D. Cox, Computer Analysis of Thermochemical Data, Halogen Compounds, 1972 (J. B. Pedley, Univ. of Sussex, Brighton BN1 9QJ, Gt. Britain).
9 L. G. Hepler, W. L. Jolly and W. M. Latimer, J. Amer. Chem. Soc., 75 (1953) 2809.
10 P. A. G. O’Hare and W. N. Hubbard, J. Phys. Chem., 69 (1965) 4385.