Heat of Formation of some Alkali Hexahalogenoniobates(IV) and Potassium Hexachlorotantalate(IV)

By **Dinsukh Lal** and **Alan D. Westland,*** Department of Chemistry, University of Ottawa, Ottawa K1N 6N5

Enthalpies of reaction are determined by solution calorimetry for the process $2AX(c) + MX_4(c) \longrightarrow A_2MX_6(c)$ where A_2MX_6 is K_2NbCl_6, Rb_2NbCl_6, Cs_2NbCl_6, Cs_2NbBr_6, and K_2TaCl_6. Heats of formation, ΔH°_{f298}, are determined for the chloro-complexes. The tantalum complex is more stable than K_2NbCl_6. There is no appreciable difference in the affinity exhibited by Nb^{IV} toward Cl^- and Br^- respectively.

THERE have been no reports of thermochemical measurements on ternary salts of niobium in reduced oxidation states, other than one by Safonov and Korshunov [1] who measured decomposition pressures of A_2NbCl_6 complexes. However, our work [2] has shown that the products of decomposition are of ill-determined composition. The heat of formation of K_2TaCl_6 has been measured calorimetrically.[3] It seemed desirable to pursue further calorimetric work in this area by measuring the heats of formation of the salts A_2NbX_6 and to redetermine the heat of formation of K_2TaCl_6.

RESULTS

When $NbCl_4$ is dissolved in concentrated hydrochloric acid, $NbCl_6^{2-}$ ion is formed in equilibrium with certain partially hydrolysed species.[4,5] We found that $NbCl_4$ and K_2NbCl_6 dissolved rapidly in hydrochloric acid to give blue solutions having identical absorption spectra. As expected, the spectra showed a dependence upon acid concentration. Likewise, $TaCl_4$ and K_2TaCl_6 dissolved in 1 : 1 HCl/H_2O to give solutions with identical spectra but, in this case, the colour was deep amber. We concluded that enthalpies of complexing for A_2NbCl_6 and A_2TaCl_6, *i.e.* enthalpies of reactions such as

$$2KCl(c) + NbCl_4(c) \longrightarrow K_2NbCl_6(c)$$

could be obtained by measuring the heats of solution in hydrochloric acid of the various substances appearing in the equation. The following partial reactions were used to calculate heats of complexing. The square brackets denote solution components.

$$\begin{aligned} &2KCl(c) + [H_2NbCl_6 + 580\ HCl] \\ &\qquad = [2KCl + H_2NbCl_6 + 580\ HCl] \quad \Delta H_1 \end{aligned}$$

$$\begin{aligned} &NbCl_4(c) + [2KCl + 582\ HCl] \\ &\qquad = [2KCl + H_2NbCl_6 + 580\ HCl] \quad \Delta H_2 \end{aligned}$$

$$\begin{aligned} &[2KCl + H_2NbCl_6 + 580\ HCl] \\ &\qquad = K_2NbCl_6(c) + [582\ HCl] \quad \Delta H_3 \end{aligned}$$

$$\begin{aligned} &[2KCl + H_2NbCl_6 + 1162\ HCl] \\ &\quad = [2KCl + 582\ HCl] + [H_2NbCl_6 + 580\ HCl] \quad \Delta H_4 \end{aligned}$$

$$\begin{aligned} &[2KCl + H_2NbCl_6 + 580\ HCl] + [582\ HCl] \\ &\qquad = [2KCl + H_2NbCl_6 + 1162\ HCl] \quad \Delta H_5 \end{aligned}$$

From these equations we obtain $\sum_{i=1}^{5}\Delta H_i = \Delta H_c$ for the heat of the complexing reaction. ΔH_4 and ΔH_5, Which represent heats of mixing of solutions, are assumed to be negligible with respect to ΔH_c because,

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[1] V. V. Safonov and B. G. Korshunov, *Izvest. Akad. Nauk. S.S.S.R., Neorg. Materialy*, 1965, **1**, 604.

[2] D. Lal, Doctoral Thesis, University of Ottawa, Ottawa, 1974.

[3] V. M. Tsintsius and E. K. Smirnova, *Russ. J. Inorg. Chem.*, 1969, **14**, 1729.

[4] I. S. Morozov and L. P. Lipitova, *Russ. J. Inorg. Chem.*, 1966, **11**, 550.

[5] D. P. Johnson and R. D. Bereman, *J. Inorg. Nuclear Chem.*, 1972, **34**, 679.

as is shown below, the solutes are close to infinite dilution. Moreover, ΔH_4 and ΔH_5 would be very nearly equal and of opposite signs. The quantities appearing in the equations for the partial processes are based on the typical example of 0·5 g of $NbCl_4$ being dissolved in 200 ml of 6·20M-hydrochloric acid.

As the tetrahalides and their complexes are somewhat air-sensitive, it was not convenient to weigh out samples of predetermined weight. Instead, approximate quantities were put into tared nitrogen-filled ampoules and the exact weight was found after sealing. There was no apparent dependence of the heat values on sample weight, therefore the solutes were essentially at infinite dilution. The heats of solution ΔH_1, ΔH_2, and ΔH_3 are recorded in Tables 1 to 3. The heats of complexing, ΔH_c, are given in Table 4. Heats of formation of the chloro-complexes, ΔH_{f298}, are also given. The heats of formation for the alkali chlorides were taken from Rossini's compilation.[6] The heats of formation of $NbCl_4$ and $TaCl_4$ have been reported,[7,8] but there is no value in the literature for $NbBr_4$.

Our value for the heat of complexing of K_2TaCl_6 differs from that (−25·9 kcal mol^{-1}) reported earlier.[3] In the previous work, 0·03% hydrogen peroxide was used as a calorimetric liquid which converted $TaCl_4$ and K_2TaCl_6 into gels. We found that there was a time lapse of some minutes between nucleation and flocculation of the hydrated oxide. It appears to us to be questionable whether a gel should be considered as a suitable product in a calorimetric process.

In order to test the validity of our measurements, we have sought to compare our results with independent estimates. To this end, we have calculated the heats of formation of Rb_2NbCl_6 and Cs_2NbCl_6 by the method of Tsintsius and Smirnova [3] for which we used the measured value for K_2NbCl_6 as a point of departure. The lattice energies were estimated by use of the expression given

$$U = \frac{287{\cdot}2\Sigma n z_c z_a}{r_c + r_a}\left(1 - \frac{0{\cdot}345}{r_c + r_a}\right) + 2{\cdot}5\Sigma n z_c z_a$$

by Yatsimirskii [9] where Σn is the number of ions forming a molecule of the salt and z_c and z_a are the charges on the cation and anion respectively.

TABLE 1

Heats of solution, $\Delta H_1/2$, for the alkali halides dissolved in 6·20M-hydrochloric acid

Compound	Weight of sample/g	$\Delta H_1/2$ / kcal mol^{-1}	Mean $\Delta H_1/2$ / kcal mol^{-1}
KCl	1·247	4·60	
	1·341	4·56	4·58
RbCl	1·419	3·64	
	1·458	3·64	3·64
CsCl	1·574	·85	
	1·657	2·74	2·80
CsBr	1·580	4·53	
	1·619	4·62	4·58

According to Yatsirmirskii, the sum of the ion radii $r_c + r_a$ is given by the quantity $11{\cdot}85 \times J^{-1/3}$ where J is the concentration of ions in the crystal in mol l^{-1}. This quantity was calculated by using the reported lattice constants [4,10,11] and recognizing that there are 12 ions in the unit cell of the complexes.

TABLE 2

Heats of solution of metal tetrahalides, ΔH_2, in 6·20M-hydrochloric acid

Compound	Weight of sample/g	ΔH_2 / kcal mol^{-1}	Mean ΔH_2 / kcal mol^{-1}
$NbCl_4$	0·3478	−29·1	
	0·3754	−29·5	
	0·5171	−29·6	
	0·5739	−29·7	−29·5
$NbBr_4$	0·7490	−34·1	
	0·8104	−34·4	
	1·0354	−34·2	−34·2
$TaCl_4$	0·2459	−52·8	
	0·2530	−52·7	
	0·2530	−52·6	−52·7

TABLE 3

Heats of solution of hexahalogenometallates, $-\Delta H_3$, in 6·20M-hydrochloric acid

Compound	Weight of sample/g	$-\Delta H_3$ / kcal mol^{-1}	Mean $-\Delta H_3$ / kcal mol^{-1}
K_2NbCl_6	0·2940	−13·9	
	0·5294	−14·3	
	0·5878	−14·3	−14·2
Rb_2NbCl_6	0·7689	−7·1	
	1·2196	−6·8	
	1·2698	−7·1	−7·0
Cs_2NbCl_6	1·0468	+1·4	
	1·1837	+1·4	
	1·3599	+1·3	+1·4
Cs_2NbCl_6 (aqueous preparation)	0·4046	+0·5	
	1·1760	+0·2	+0·3
Cs_2NbBr_6	1·5767	−1·6	
	1·6696	−1·6	
	1·8637	−1·3	−1·5
K_2TaCl_6	0·1260	−27·3	
	0·3446	−27·0	
	0·3001	−27·3	−27·2

TABLE 4

Heats of complexing ΔH_c and heats of formation ΔH°_f at 298 K for some hexahalogenometallates

Compound	ΔH_c / kcal mol^{-1}	ΔH°_f / kcal mol^{-1}
K_2NbCl_6	−6·1 ± 0·3	−381
Rb_2NbCl_6	−15·2 ± 0·3	=387
Cs_2NbCl_6	−25·3 ± 0·2	−398
Cs_2NbCl_6 (aqueous preparation)	−24·2 ± 0·2	−397
Cs_2NbBr_6	−23·6 ± 0·2	
K_2TaCl_6	−16·3 ± 0·2	−394

Admittedly, the lattice energy of a ternary complex salt is given only approximately by the above formula because the anion is treated as a point charge. The failure to take into account the distribution of charge within the $NbCl_6^{2-}$ unit introduced an error which is not encountered in calculations on binary salts. How-

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[6] F. D. Rossini, Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Standards, Circular 500, Washington, 1952.

[7] D. N. Tarasenkow and A. V. Komandin, *Zhur. obshchei Khim.*, 1940, **10**, 1319.

[8] H. Schäfer and F. Kahlenberg, *Z. anorg. Chem.*, 1960, **305**, 178.

[9] K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1961, **6**, 518.

[10] E. K. Smirnova and I. V. Vasilkova, *Russ. J. Inorg. Chem.*, 1967, **12**, 292.

[11] B. A. Torp, Doctoral Thesis, Iowa St te University, Ames, Iowa, 1964.

ever, we shall be concerned only with differences in lattice energies and we may assume that the error is eliminated when the difference is taken between values for the various alkali salts containing a common complex anion.

Using the equation $U_{M_2A} = -\Delta H_{M_2A} + 2\Delta H_{M^+} + \Delta H_{A^{2-}}$ transformed for two salts of the same type with a common anion, the following relationship is obtained for $\Delta H^\circ_{Rb_2NbCl_6}$:

$$\Delta H^\circ_{Rb_2NbCl_6} = \Delta H^\circ_{K_2NbCl_6} + 2(\Delta H^\circ_{Rb^+} - \Delta H^\circ_{K^+}) + U_{K_2NbCl_6} - U_{Rb_2NbCl_6}$$

The heats of formation of Rb_2TaCl_6 and Cs_2TaCl_6 were also estimated. The calculated thermochemical data are given in Table 5. The measured values are in satisfactory agreement with these.

By use of the experimental value for $TaCl_4$ and the other data above we obtain

$$NbCl_4(g) + 2Cl^- \longrightarrow NbCl_6^{2-}(g)$$
$$\Delta H_g = -375{\cdot}5 \text{ kcal} + U_{K_2NbCl_6}$$

and

$$TaCl_4(g) + 2Cl^- \longrightarrow TaCl_6^{2-}(g)$$
$$\Delta H_g = -384{\cdot}5 \text{ kcal} + U_{K_2TaCl_6}$$

If we assume $U_{K_2NbCl_6} = U_{K_2TaCl_6}$, the gas-phase enthalpy for the tantalum(IV) chloride reaction is 9·0 kcal more negative than the corresponding reaction for niobium(IV) chloride. The difference is to be found in the non-electrovalent features of the bonding. The valence orbitals of the third-row elements are more diffuse than those of second-row elements. Further, the effective nuclear charge of the tantalum atom should be somewhat greater than that of the niobium atom owing to somewhat imperfect shielding by the 4*f* electrons.

TABLE 5

Calculated heats of formation

Compound	Lattice constant Å	$r_c + r_a$ Å	$\Delta H_{M^+}^\circ$ kcal mol^{-1}	U kcal mol^{-1}	ΔH°_f kcal mol^{-1}
K_2NbCl_6	9·97	4·36	123·1	379	
Rb_2NbCl_6	10·10	4·42	118·3	375	−386
Cs_2NbCl_6	10·31	4·51	110·1	368	−396
K_2TaCl_6	9·96	4·36	123·1	379	
Rb_2TaCl_6	10·11	4·42	118·3	375	−399
Cs_2TaCl_6	10·32	4·51	110·1	368	−409

It is interesting to compare the gas phase reactions $MCl_4(g) + 2Cl^-(g) \longrightarrow MCl_6^{2-}(g)$ for M = Nb and Ta. The enthalpy of such a reaction is related to other reaction enthalpies by the following cycle:

$$\begin{tikzcd}
2K^+(g) + 2Cl^-(g) & + & MCl_4(g) \arrow[r, "\Delta H_a"] & 2K^+(g) + MCl_6^{2-}(g) \\
2KCl(c) \arrow[u, "U_{KCl}"] & + & MCl_4(c) \arrow[u, "\Delta H_{subl.}"] \arrow[r, "\Delta H_c"] & K_2MCl_6(c) \arrow[u, "U_{K_2MCl_6}"]
\end{tikzcd}$$

Again, the lattice energies of K_2MCl_6 cannot be calculated with good accuracy but the difference in lattice energies for M = Nb and Ta obtained by the use of Yatsimirskii's equation is zero and the true difference is probably close to zero also, provided that the polarities of the Nb–Cl and Ta–Cl bonds do not differ greatly. From a Born-Haber cycle we obtain 169·0 kcal mol^{-1} for the lattice energy of KCl. By means of vapour-pressure measurements, Schäfer and Bayer [12] obtained the value 31·4 kcal mol^{-1} as the enthalpy of sublimation of $NbCl_4$. The enthalpy of sublimation of $TaCl_4$ was estimated [13] on the basis of certain assumptions to be 32·5 kcal mol^{-1}. A subsequent measurement by Shchukarev and Kurbanov [14] provided the value 30·2 kcal mol^{-1} which agrees with the estimate sufficiently well so that we may assume these values to be correct to within about 2 kcal mol^{-1}.

It is interesting to make a similar comparison of gas-phase enthalpies for the reactions $NbX_4 + 2X^- \longrightarrow NbX_6^{2-}$ where X = Cl and Br. This cannot be done accurately as no published value of $\Delta H_{subl.}$ for $NbBr_4$ is available. Moreover, there is a greater uncertainty in comparing the lattice energies of Cs_2NbCl_6 and Cs_2NbBr_6. However, as the heat of sublimation of $ZrBr_4$ exceeds that of $ZrCl_4$ by only 2·5 kcal mol^{-1},[15,16] we assume that the heat of sublimation of $NbBr_4$ lies in the range 30—35 kcal mol^{-1}.

The lattice energies given by Yatsimirskii's equation are presumably in error but by an indeterminate amount. However, the difference in the lattice energies given by this equation for Cs_2NbCl_6 and Cs_2NbBr_6 can be estimated from the work of Hoppe [17] which gives the variation of the Madelung factor as a function of the lattice parameter which is the ratio of the Nb–X distance to the lattice constant a_0. From ionic radii of Cl^- and Br^- and an estimate of 0·69 Å for the radius of Nb^{4+}, we find lattice parameters of 0·243 and 0·247 respectively for Cs_2NbCl_6 and Cs_2NbBr_6. From Hoppe's plot of Madelung factor against lattice parameter, we arrive at a value of *ca.* 4 kcal mol^{-1} as the error in assuming that the Madelung factor is a constant as is implied by Yatsimirskii's equation.

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[12] H. Schäfer and L. Bayer, *Z. anorg. Chem.*, 1954, **277**, 140.

[13] H. Schäfer and F. Kahlenberg, *Z. anorg. Chem.*, 1960, **305**, 178.

[14] S. A. Shchukarev and A. R. Kurbanov, *Vestnik Leningrad. Univ.* (*Fiz. Khim.*), 1962, **17**, 144.

[15] S. S. Berdonosov, V. I. Tsirelnikov, and A. V. Lapitskii, *Vestnik Moskov Univ., Ser. II Khim.*, 1965, **20**, 26.

[16] A. A. Palko, A. D. Ryon, and D. W. Kuhn, *J. Phys. Chem.*, 1958, **62**, 319.

[17] R. Hoppe, *Z. anorg. Chem.*, 1956, 283, 196.

If we use values of lattice energy as given by Yatsimirskii's equation with no allowance for a difference in Madelung factor we obtain

$$\mathrm{NbCl_4(g) + 2Cl^-(g) \longrightarrow NbCl_6{}^{2-}(g)} \quad \Delta H_g = 0{\cdot}7 \text{ kcal}$$

and

$$\mathrm{NbBr_4(g) + 2Br^-(g) \longrightarrow NbBr_6{}^{2}\ (g)} \quad \Delta H_\mathrm{g} = -1 \text{ to } +4 \text{ kcal}$$

The correction due to change in Madelung factor would favour the bromide reaction relative to the chloride reaction by a further difference of 4 kcal. The difference in these energies is not great, although one might reasonably have expected the bromide ion to be rather less strongly co-ordinated than chloride. Niobium(IV) may be showing here an incipient class b [18] character. In a previous calorimetric study conducted in this laboratory,[19] $ZrCl_4$ was shown to form a slightly stronger complex with tetrahydrothiophen than with tetrahydrofuran in the gas phase.

We recognize that one should take into account the reorganization energies involved in going from sp^3 hybridization in the gaseous tetrahalides—assuming that the molecules are tetrahedral—to sp^3d^2 hybridization in the complexes. However, when one considers that *d*-orbital energies are lowered when the charge on the central atom is increased, it might be assumed that the sp^3d^2 hybrid would be at lower energy in the $NbCl_6{}^{2-}$ ion as a chlorine ligand should attract more negative charge than bromine. Moreover, steric considerations suggest that attainment of six-co-ordination should be readier in the case of the smaller chloro-ligand.

If allowance could be made quantitatively for these effects, it would likely be seen that bromide is bound preferentially by Nb^{IV}. We attempted a study of iodoniobate but NbI_4 dissolved only slowly in acid and the low heats of solution obtained suggested that an equilibrium position was not being attained in the dissolving process.

EXPERIMENTAL

Materials.—Niobium (99·95%) and tantalum (99·95%) were obtained in the form of thin sheets from Fansteel Metals, Baltimore, Maryland. Research grade chlorine (Matheson) was used after passing over P_4O_{10}. Bromine (J. T. Baker) was dried for several days over P_4O_{10} in a N_2-filled container and distilled immediately prior to use in a break-seal apparatus. The potassium halides were J. T. Baker A.R. material. Other alkali halides (99·9%) were supplied by K and K Laboratories, Hollywood, California. The alkali halides were heated under high vacuum immediately prior to use.

Preparation of $NbCl_4$ *and* $TaCl_4$.—The pentachlorides were prepared by heating the metals in an atmosphere of chlorine. The apparatus used was first flamed and well flushed with chlorine in order to keep production of oxochloride to a negligible level. The initial product of reaction between tantalum and chlorine was not pure white. The crude pentachloride was purified by heating with tantalum powder at 400° for four days. The material, when subsequently sublimed, was colourless.

The tetrachlorides were prepared according to established procedures [20,21] by reduction of the pentachlorides with Nb and Ta metal respectively in sealed evacuated tubes (Found: Nb, 39·5; Cl, 60·5. Calc. for $NbCl_4$: Nb, 39·5; Cl, 60·4. Found: Ta, 55·8; Cl, 43·6. Calc. for $TaCl_4$: Ta, 56·0; Cl, 44·0).

Preparation of $NbBr_4$.—The pentabromide was prepared by reaction of bromine vapour with niobium metal in a sealed tube. The end containing the metal was kept at 400 °C for several days, during which time the product sublimed to a cooler part of the tube. Some $NbOBr_3$ was invariably formed, but this did not interfere with the subsequent preparation of $NbBr_4$. The reduction to tetrabromide was carried out in the manner described by McCarley and Torp [22] (Found: Nb, 22·2; Br, 77·2. Calc. for $NbBr_4$: Nb, 22·5; Br, 77·5%).

Preparation of Complex Salts.—The complexes were prepared in evacuated quartz tubes essentially in the manner described by Torp,[11] *i.e.*, by heating stoicheiometric mixtures of the tetrahalides and the appropriate alkali halides for 1—3 h at the melting point of the latter. On cooling, dark coloured, sintered, solids were obtained. Completeness of reaction was indicated by *X*-ray diffraction patterns which were identical to those obtained by Torp.

The preparations were tested for complete solubility in 6·2M-HCl. A small quantity of black residue was always found. Several portions of the substance obtained from niobium complexes were combined and washed thoroughly. *X*-Ray diffraction showed that it was NbO. The quantity could be kept to <0·5% by careful attention to preparative technique, however.

Cs_2NbCl_6 Was also prepared from aqueous solution in the manner described by Morozov and Lipitova.[4] The product was separated by pressure filtration in an atmosphere of HCl and dried in a desiccator filled with HCl gas and which contained P_4O_{10} (Found: Nb, 17·0; Cl, 37·1. Calc. for Cs_2NbCl_6: Nb, 16·3; Cl, 37·2%).

Calorimeter.—The calorimeter, constructed of Pyrex, was contained in a thermostat bath which was maintained at 25·0 ± 0·1 °C. The calorimeter was provided with a silvered jacket which could be evacuated after the interior had been brought close to thermal equilibrium with the thermostat. The solid sample was contained in a thin-walled bulb of *ca.* 3 ml capacity. There was provision for breaking two sample bulbs under the calorimeter liquid. Thrusting rods for this purpose passed through mercury seals. The calorimeter contained 180—200 ml of 6·20M-hydrochloric acid which served as the solvent. Two considerations governed the choice of concentration of the acid. (*a*) When the tetrahalides and their complexes are dissolved in hydrochloric acid, some hydrolysis, which is a highly exothermic process, takes place.[5] In the interest of achieving good reproducibility, we wished to keep the extent of hydrolysis to a minimum. A high acid concentration was therefore required. (*b*) While concentrated hydrochloric acid would cause little hydrolysis, its composition could be difficult to maintain constant; however, the composition of 6·2M-acid is hardly affected if evapor-

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[18] S. Arhland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[19] F. M. Chung and A. D. Westland, *Canad. J. Chem.*, 1969, **47**, 195.

[20] H. Schäfer, C. Göser, and L. Bayer, *Z. anorg. Chem.*, 1951, **265**, 258.

[21] H. Schäfer and K. D. Dohman, *Z. anorg. Chem.*, 1961, **311**, 139.

[22] R. E. McCarley and B. A. Torp, *Inorg. Chem.*, 1963, **2**, 540.

ation occurs. The titre against standard base of a large supply of this acid remained unchanged throughout the entire period of this work. The sensing element was a thermistor (Sargent-Welch, model S81620) immersed in silicone oil contained in a thin-walled glass well. It was connected through a thermistor bridge (Sargent-Welch model S81601) to a 10 mV recorder which was used as a null indicating device. The calibration heater, also immersed in silicone oil contained in a second thin-walled well, was a coil of No. 30 Constantan wire with a resistance of 5 Ω. Current for this heater was drawn from a large 2 V accumulator. In order to achieve a current constant to within ±0·5%, it was passed through a 5 Ω dummy heater for at least 1 h before a measurement. The current was measured with a potentiometer connected across a bank of five 1 Ω standard resistors connected in parallel. The duration of the heating period was measured by means of a synchronized electrical timer. A glass stirrer for the calorimeter liquid passed through a ground ball and socket bearing.

Calorimetric Measurement.—Very finely powdered samples were sealed under nitrogen into thin-walled bulbs. During sealing, the bulbs were kept cool by wrapping them in wet filter paper. Two such sample bulbs were crushed in the calorimeter in the course of each run. The first bulb to be broken contained $NbCl_4$ which served as a getter to remove any dissolved oxygen. The use of the getter may have been an unnecessary refinement, as essentially identical results were obtained with and without the getter. However, in all of the measurements reported above, a getter was used. Before commencing a measurement, the calorimeter was assembled with the joints lightly greased and argon was passed through for 1 h. After breaking the getter bulb, the calorimeter was allowed to attain an appropriate temperature and the jacket was evacuated. The calorimeter constant was determined, after which the sample bulb was broken. Dissolution of the sample was complete in 2—4 min in most cases. After the sample measurement, the calorimeter constant was re-determined and the mean of the two determinations was used.

The heat of solution of KCl in water was determined as a check on the accuracy of the equipment. The value obtained was 4·22 kcal mol^{-1}, which is in good agreement with published values, *viz.* 4·20[6] and 4·21[23] kcal mol^{-1}.

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[23] N. N. Greenwood and P. G. Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.