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Enthalpies of the hydrolysis reaction of Al^{3+} ion between 25 and 150°C

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Abstract

The heat produced when NaOH is added to Al^{3+} ($m^0_{Al} \simeq 0.03$ mol kg^{-1}) in water has been measured in the range 25–150°C. These calorimetric data are consistent with the chemical model proposed by Mesmer and Baes which considers two polynuclear and one polymeric hydrolytic species of aluminium ion. Other models which consider, in addition, the presence of mononuclear species might be valid as well, while models involving these latter species alone should be ruled out, at least in the experimental conditions adopted in this work. A simple equation is proposed for calculating the enthalpy of formation of hydrolytic species of aluminium from the measured value of the average enthalpy for addition to aqueous Al^{3+} of one mole of hydroxy groups.

INTRODUCTION

The chemistry of aqueous aluminium is relevant to many fields, ranging from soil chemistry to corrosion phenomena and to water–rock interactions. Particularly in the latter field the correct knowledge not only of the solubility of aluminium minerals but also of the equilibria among different hydrolytic species of aluminium ion is mandatory for the understanding of the formation of hydrothermal natural waters. The study of the hydrolysis of Al^{3+} ion has therefore attracted the attention of many researchers. In spite of this, owing to the inherent complexity of the equilibria involved and to complications of a kinetic nature, an unequivocal complete scheme of the hydrolytic species of this ion has not so far been identified.

An extensive collection of data as well as a detailed presentation of the proposed chemical models has recently been made available [2, 3]. The sole certain conclusion which can be drawn by examination of the pertinent literature, is that the thermodynamic behaviour of aqueous solutions of Al^{3+} at ambient temperature can be interpreted in terms of

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mononuclear complexes of the type $Al(OH)_y^{(3-y)+}$ only in dilute acidic solution ($m_{Al}^0 < 0.01$). The formation of small polynuclear species, such as $Al_2(OH)_2^{4+}$ [4], and of polymeric species of the general formula $Al_x(OH)_y^{(3x-y)+}$ with a y/x ratio ranging from 1 to about 2.5, has to be instead necessarily invoked for solutions more concentrated and/or more hydrolyzed after the addition of alkali metal hydroxide. In very alkaline solutions (pH > 10) the $Al(OH)_4^-$ ion is stable. The thermodynamic properties of formation of this ion were recently reported up to 350°C [5].

Unfortunately, besides the lack of a satisfactory chemical model able to explain the behaviour of the homogeneous aqueous solutions of aluminium ion in the whole pH-concentration field of their existence, there is also disagreement as to the actual stoichiometry of the polymeric species formed. In effect, the latter range from species such as $Al_{13}(OH)_{32}^{7+}$, supported by NMR [6], Raman [7] and e.m.f. [8] studies, to $Al_{14}(OH)_{34}^{8+}$ which best explained potentiometric data [1, 9], or to $Al_{13}O_4(OH)_{28}^{3+}$ whose existence was demonstrated with both NMR and potentiometric data [10]. The problem becomes even more complicated when one examines the hydrolysis of Al^{3+} ion at higher temperatures, since there are not many direct data collected over 25°C. To our knowledge, the only accurate study over a large temperature range is that by Mesmer and Baes [1] who made direct e.m.f. measurements on cells containing $AlCl_3$ and NaOH in 1 m KCl between 25 and 150°C.

No calorimetric determination has so far been made of the heats involved in the hydrolysis of Al^{3+}. The enthalpies of formation of the hydrolytic species have been generally derived from the temperature dependence of the equilibrium constants [1, 11]. Incidentally, we should like to observe that this indirect approach, apart from its intrinsic limited precision, is highly suspect when applied to unverified chemical models, particularly when the relative free energy data are obtained by indirect combination of data collected by different authors. In the specific case we have been able to demonstrate that the formation constants of mononuclear hydrolytic species according to reaction (2), proved consistent with either an endothermic or exothermic process; for example, we have calculated a formation enthalpy for $Al(OH)_2^+$ at 25°C of 7.3 and −4.6 kJ mol^{-1} using the data of Reed and Spycher [12] and Michard [11], respectively.

After a previous study on the specific heats of aqueous aluminium solutions [13], we aim with this work to provide some further contributions to the thermodynamic frame of the hydrolysis of Al^{3+} ion by direct calorimetric determination of the enthalpies of formation of its hydrolytic products, and to see whether these data might be utilized as a check of the validity of the adopted chemical model. For this purpose, we have measured the heat associated with the addition of NaOH to aqueous solutions of $AlCl_3$ ($\approx 0.03\,m$), for values of the ratio $R =$

m^0_{OH}/m^0_{Al} ranging from 0 to 2.5, in the temperature range 25–150°C, and the experimental data have been interpreted in terms of some of the chemical models so far proposed.

THE CHEMICAL MODELS

The reaction of hydrolysis of Al^{3+} may be sketched as

$$xAl^{3+} + yH_2O \rightarrow Al_x(OH)_y^{(3x-y)+} + yH^+ \quad (1a)$$

and the thermodynamic formation constant, $\beta_{x,y}$, of the species $Al_x(OH)_y^{(3x-y)+}$ is given by

$$\beta_{x,y} = \frac{[Al_x(OH)_y^{(3x-y)+}][H^+]^y}{[Al^{3+}]^x} \quad (1b)$$

The experimental conditions of concentration and pH used in the present work are consistent with the formation mainly of polynuclear ($x > 1$) and polymeric species [3].

As an example of polynuclear model we chose the data given by Mesmer and Baes [1] based on a careful potentiometric study of $AlCl_3$ aqueous solutions in 1 M KCl extended up to 150°C. Of the polynuclear species invoked by these authors, the 2-2 species had been also supported by NMR [6] and Raman-laser [7] investigations. The 3-4 and 14-34 species were instead identified as those species which best fit the experimental data. This model was also confirmed by Macdonald et al. [9] in their pH study of $AlCl_3$ hydrolysis induced by heating its aqueous solutions up to 200°C.

We deemed it reasonable to choose also a model which considers monomeric and polymeric species at the same time, since this would allow us to interpret the Al^{3+} hydrolysis throughout the whole range of concentration and pH. We chose the model proposed by Bottero et al. [10], which is based on both pH data and NMR data on ^{27}Al. Since these authors did provide data only at 25°C, we calculated the formation constants of the various species at the higher temperatures by integration of the van't Hoff equation using the ΔH values given by Michard [11] for the monomeric species and those obtained in this work for the polynuclear and polymeric species.

We finally used a chemical model which takes into consideration the formation of sole simple mononuclear species ($x = 1$) in order to verify the ability of our treatment to discriminate models which are very probably not in agreement with experimental conditions. Only a few authors [11, 12, 14] report the equilibrium constants for mononuclear hydrolytic species of Al^{3+} over a large temperature range. We chose the data given by Michard [11], because the data reported by Kuyunko et al. [14] are confined to 100°C and those reported by Reed and Spycher [12] reveal a

TABLE 1

Formation constants for hydrolytic species of Al^{3+}, according to different chemical models [a]

Model	Species (x, y)	$\lg \beta_{x,y}$			
		25°C	50°C	100°C	150°C
Mono-nuclear [b]	1, 1	−5.01	−4.33	−3.31	−2.60
	1, 2	−10.46	−9.22	−7.32	−5.95
	1, 3	−16.58	−14.58	−11.27	−8.74
	1, 4	−22.20	−19.85	−16.34	−13.92
Poly-nuclear [c]	2, 2	−7.45	−6.40	−4.81	−3.40
	3, 4	−13.36	−11.45	−8.20	−5.95
	14, 34	−110.45	−93.50	−67.89	−46.50
Mixed [d]	1, 1	−5.02	−4.34	−3.32	−2.61
	1, 2	−8.71	−7.47	−5.57	−4.20
	1, 3	−16.58	−14.58	−11.27	−8.74
	2, 2	−6.27	−5.22	−3.49	−2.26
	13, 36 [e]	−105.00	−86.08	−55.03	−32.75

[a] Listed values are thermodynamic ($I = 0$) formation constants, $\lg \beta_{x,y}$, defined by eqn. (1b). In the case of the polynuclear model, the data are concentration quotients, $\lg Q_{xy}$ valid in 1 *m* KCl. Throughout the paper, all equilibrium constants are defined in terms of molalities.

[b] Data at 25°C taken from Michard [11] except for the 1-3 complex, taken from Kuyunko et al. [14].

[c] Taken from Mesmer and Baes [1]. Values at 50°C and 150°C were calculated from van't Hoff equation from the data reported therein.

[d] Data at 25°C taken from Bottero et al. [10]. For calculation of the data above 25°C see text.

[e] The hydrolytic compound is written for convenience as $Al_{13}(OH)_{36}^{3+}$, i.e. the formula which, according to reaction (1), justifies the same number of charges as the proposed $AlO_4Al_{12}(OH)_{28}^{3+}$.

temperature dependence which is inconsistent with the sign of the heat effects determined by us. The equilibrium constants for the neutral species $Al(OH)_3^0$, not reported by Michard [11], were taken from Kuyunko et al. [14] and extrapolated to 150°C using a ΔH value interpolated among those given by Michard [11] in the series $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$.

The chosen chemical models and the formation constants of the respective hydrolytic species at the examined temperatures are summarized in Table 1.

DATA TREATMENT

The experimental data collected in this work consist of heat effects (q_{obs}) associated with consecutive additions of NaOH to $AlCl_3$ aqueous solutions. It was found convenient to interpret them in terms of the enthalpy of addition of an OH^- group to the aqueous Al^{3+} ion with reference to the reaction

$$\frac{x}{y}\,Al^{3+} + OH^- = \frac{1}{y}\,Al_x(OH)_y^{(3x-y)+} \qquad (2)$$

Indicating the thermodynamic equilibrium constant of reaction (2) by $K_{OH,x,y}$ we obtain

$$\lg K_{OH,x,y} = \frac{1}{y}\lg \beta_{x,y} + pK_w \qquad (3)$$

and analogously

$$\Delta H_{(OH),x,y} = \frac{1}{y}\Delta H_{x,y} - \Delta H_w \qquad (4)$$

where K_w and ΔH_w are the equilibrium constant and enthalpy of ionic dissociation of water, respectively. For simplicity, the symbol $\Delta H_{(OH),i}$ will be used for $\Delta H_{(OH),x,y}$. The heat observed, after correcting for dilution of the titrant and for water formation

$$q_{exp} = q_{obs} - q_{dil} - q_w \qquad (5)$$

($q_w = \delta n_H \cdot \Delta H_w$, where the variation of the number of moles of free H^+ following the titrant addition, δn_H, can be measured by direct pH determination or calculated by the species distribution) can be expressed by

$$q_{exp} = \sum y_i\,\delta n_i\,\Delta H_{(OH),i} \qquad (6)$$

where the index refers to the ith complex formed and δn_i is the variation of its number of moles. If we now define an average experimental enthalpy per mole of hydroxy group bonded to aluminium as

$$\Delta H_{exp} = \frac{q_{exp}}{n_{OH} + \delta n_H} \qquad (7)$$

where the number of bonded hydroxy groups is given by the added OH^- groups, n_{OH}, plus those derived by the dissociation of water, and then we consider that

$$n_{OH} + \delta n_H = \sum y_i\,\delta n_i \qquad (8)$$

we finally obtain

$$\Delta H_{exp} = \sum X_i\,\Delta H_{(OH),i} \qquad (9)$$

with

$$X_i = \frac{y_i\,\delta n_i}{\sum_i y_i\,\delta n_i}$$

By making available a series of experimental data collected in different pH conditions, i.e. in different conditions of the ratio R of the stoichiometric concentration of alkali with respect to aluminium ($R = m^0_{OH}/m^0_{Al}$), eqn. (9) can be in principle solved into the unknowns $\Delta H_{(OH),i}$, inside a specifically chosen chemical model. Furthermore, in favourable conditions, one might also identify the more probable chemical model as that which best reproduces the ΔH_{exp} values throughout the whole set of calorimetric titrations considered.

The knowledge of the quantities X_i of eqn. (9), as well as of δn_H of eqns. (5) and (7), requires a calculation of the species distribution from known values of the formation constants of the single hydrolytic species, pertinent to a specific chemical model. We therefore converted the equilibrium constants given by the chosen authors (see Table 1) to the values ($Q_{x,y}$) valid in our experimental conditions (ionic strength $I \approx 0.2$). The calculation of the activity coefficients has been accomplished following the procedure devised by Helgeson et al. [15], treating the polymeric species as hypothetical species characterized by a charge equal to the average charge per aluminium atom. Details of the procedure, as well as the values of the calculated activity coefficients for all species considered and the relative values of the formation quotients $Q_{x,y}$ may be obtained from the authors upon request.

It is worthwhile to note that the actual values of the activity coefficients, and of the derived equilibrium quotients, are critically dependent on the model chosen for their description. Nevertheless, this critical aspect is not reflected in the final enthalpy values calculated in this work for the following reasons: (i) our final choice of defining an average enthalpy value per OH group does not require knowledge of the exact concentration of the single complexes; (ii) the correction term q_w relative to the heat of water formation, calculated through the species distribution, is a significant fraction of the measured quantity q_{obs} only at the higher temperatures investigated. We should finally observe that a possible uncertainty in the values of activity coefficients would have a particularly small effect in the case of the polymeric model, because the two media involved in the conversion procedure ($I = 1 \rightarrow I = 0.2$) fall near the minimum usually displayed by activity coefficients of all electrolytes.

EXPERIMENTAL

Materials

All solutions were prepared by weighing, and their concentrations were expressed in mol per kilogram of solvent, m. A stock solution of 1 m $AlCl_3$ was prepared using $AlCl_3 \cdot 6H_2O$ from Merck, whose purity, determined periodically as Al_2O_3 by calcination in a platinum crucible, was about 99.9%. Water used was deionized, filtered, deaerated and maintained under vacuum. NaOH and HCl solutions were prepared using Normex vials (Carlo Erba): their titres were determined with potassium hydrogen phthalate. Samples used in the experiments were obtained by diluting amounts of $AlCl_3$ stock solution either with water and/or with NaOH or HCl solutions.

Measurements by isoperibolic calorimeter

Enthalpic titrations of aqueous $AlCl_3$ with NaOH were performed at 25°C by means of a computerized, conventional isoperibolic calorimeter built in our laboratory. The 400 cm^3 glass cell, besides usual calorimetric devices such as temperature probe (thermistor, 2000 Ω at 20°C), stirrer and calibration heater, was equipped with a combined glass electrode for continuous monitoring and measuring of pH (Radiometer PHM88 precision pHmeter, readings to 0.001 pH units). About 350 g of solution (about 0.01 *m* in $AlCl_3$ and approximately 3.5×10^{-3} *m* in HCl) were put into the cell for each experiment, and titrant (1 *m* NaOH) added stepwise through a digital automatic burette (Radiometer AUBU80). Before each addition (1 or 2 cm^3), the titrant solution was allowed to standby in a loop made of PTFE small tube (5 cm^3 total volume heat exchanger) placed close to the cell in a bath maintained at $25 \pm (5 \times 10^{-3})$°C. Stirring efficiency was such as to ensure a homogeneous solution 1–2 s after each addition, thus minimizing the possible formation of species favoured by large local concentrations of the titrant.

In a single titration, 10 to 15 NaOH additions were carried out up to the value 2.5–2.8 of the R ratio. Heat evolved in each step was calculated in the usual way from the cell heat capacity together with the observed changes in temperature obtained from the temperature–time data, collected and elaborated in real time by the computer. The heat capacity of the calorimetric cell was periodically measured during titrations by means of electrical calibration experiments. Some tests on the apparatus performance carried out using the $HCl_{aq} + NaOH_{aq}$ reaction, showed an accuracy of ±0.5% and a resolution of ±0.05 J in the measured heats.

The pH value was continuously monitored and recorded up to 10–15 min after titrant addition. This variable, however, kept displaying a slow continuous drift; stable data, collected in some cases after 12 h, were lower by 0.1 units. No particular care was devoted to pH measurements because H^+ concentrations were used only to calculate slight corrections for the heat due to the competitive water formation from H^+ and OH^- ions. Glass electrode calibration was performed using National Bureau of Standards (NBS) buffer solutions and the H^+ activity coefficient, γ_{H^+} was evaluated from pH measurements on solutions containing known amounts of HCl and KCl at proper ionic strength.

Measurements by liquid flow calorimeter

At 50, 100 and 150°C, measurements of heat evolved for the OH^- addition to the Al^{3+} ion were made by means of a differential liquid flow calorimeter already described [16]. Some important modifications were introduced [17] in order to improve the sensitivity and the precision of the apparatus particularly for the ΔH determinations. All "316" stainless steel tubings were substituted by a high nickel content alloy (Inconel 600) and the copper calorimetric block was replaced with an analogous lighter aluminium device. The arrangement and geometry of the cells were substantially revised (different shape of the temperature platinum probes and of the heaters) in order to achieve a quicker response of temperature signals. Finally the old built-in temperature regulator was replaced with the ASL system composed of the F16 resistance bridge and the automatic model 300 power supply, able to keep a constant temperature of the calorimetric block to within $\pm 5 \times 10^{-4}$°C.

The power P_r of a process taking place in the calorimeter can be obtained from the relation

$$P_r = F\Delta P \tag{10}$$

ΔP being the calorimetric signal resulting from the difference in the power applied to the measuring cell necessary to compensate for the power developed by the reaction. The empirical factor F, which accounts for heat losses, has been determined by chemical calibrations using the $HCl_{aq} + NaOH_{aq}$ reaction and resulted in values of 0.935, 0.867 and 0.907 at 50, 100 and 150°C, respectively. Enthalpy changes ΔH_r of the studied process can be calculated from measured power values P_r by means of the equation

$$\Delta H_r = P_r(1000 + mM)/(md\varphi) \tag{11}$$

where m, d and φ are molality, density and volumetric flow, respectively, of the solution containing the totally reacting component of molecular weight M.

Repeated experiments using as reagents 0.01 m HCl and 0.05 m NaOH solutions, each flowing at 0.017 $cm^3\,s^{-1}$, showed a reproducibility of measured ΔH_r better than 0.3%, 0.5% and 1% at 50, 100 and 150°C respectively. Observed sensitivity of the apparatus was $\pm 2 \times 10^{-5}$ W.

Two 0.03 m $AlCl_3$ solutions containing NaOH with initial formal R ratios of 0.2 and 1.3 (solutions I and II, respectively) were mixed alternately in the calorimeter with a 0.03 m NaOH solution also containing about 0.16 m NaCl. Sodium chloride was added in order to achieve the same ionic strength of Al^{3+} solution and depress the heat effects due to mutual dilution according to the Young rule [18]. Different R values, ranging from 0.5 to 2.0, were obtained for the final systems by mixing solutions I or II with NaOH in the calorimeter using different flow ratios and maintaining a constant value, equal to 0.034 cm s^{-1}, of the total flow rate. Reaction enthalpies ΔH_r were then calculated using eqn. (11) where m, d and φ are referred to NaOH solution. Densities were obtained at 25°C by means of an Anton Paar densimeter (model DMA60, equipped with DMA602 measuring cell) having a resolution of $\pm 2 \times 10^{-6}$ g cm^{-3}. Direct gravimetric determination of the weight flow φ^* showed consistency with the product $\varphi \cdot d$ within 0.5%. The total pressure over the solutions never exceeded 1.0 MPa. Its effect on reaction enthalpies was neglected.

Measurements by heat flow calorimeter

In a Calvet-type calorimeter (model BT 200 Setaram) approximately 500 mg of a 0.1 m NaOH aqueous solution were added to about 8 g of a 0.01 m $AlCl_3$ aqueous solution also containing NaOH ($R \approx 0.25$). The reaction was followed for 24 h. The calorimeter is characterized by a time constant such as to reach the baseline 45 min after any instantaneous heat effect, thus allowing slow processes to be revealed which release heat beyond that time. The minimum detectable power in the configuration of our apparatus is 10^{-5} W. No measurable heat effect was observed after the initial fast reaction.

RESULTS

The trend of the experimental temperature versus time, relative to each single step of a calorimetric titration at 25°C, clearly indicates that the evolution of reaction heat is instantaneous compared to the rate of response of the calorimeter. In other words, no appreciable evolution of heat is observed during the slow attainment of a stable pH value. This would indicate that the slow rearrangement of the hydrolytic species which follows the initial reaction, as reflected by the slow pH change with time (see Experimental part), is not associated with a measurable heat effect.

Table 2 reports the data collected in a typical calorimetric titration run at 25°C. In Fig. 1 is represented the overall experimental reaction heat against the average number of OH groups bonded per aluminium atom ($\bar{n}$). It can be noticed that the reaction heat is linearly dependent on the number of bonded OH groups clearly indicating that the heat of addition of OH groups is actually independent of the species distribution in solution. This suggested the possibility of assigning an average constant enthalpy ($\Delta H_{(OH)}$) to the binding of a single OH group independently of the actual stoichiometry of the complex being formed. The value of $\Delta H_{(OH)}$ was calculated by regression analysis of the function

$$q_{exp} = \Delta H_{(OH)}(n_{OH} + \delta n_H) - n_H^0 \cdot \Delta H_w \qquad (12)$$

TABLE 2

Calorimetric titration with 1 *m* NaOH of an aqueous solution (345.9 g) containing 0.0102 *m* $AlCl_3$ and 0.00346 *m* HCl at 25°C

$n_{OH} \times 10^3$ [a]	pH [b]	$\bar{n}$ [c]	$-q_{obs}$ [d,f] (J)	$-q_w$ [e,f] (J)
0	2.630	0.002		
1.191	3.822	0.017	58.32	52.85
2.073	4.225	0.256	15.05	2.20
2.954	4.271	0.505	15.48	0.15
3.835	4.317	0.755	15.28	0.13
4.720	4.323	1.006	15.43	0.02
5.620	4.379	1.261	15.41	0.14
6.524	4.434	1.517	15.90	0.12
7.429	4.503	1.773	16.85	0.13
8.331	4.601	2.028	17.08	0.15
9.287	4.783	2.299	17.78	0.20
9.997	5.341	2.499	13.87	0.29
10.898	6.114	2.754	16.37	0.09

[a] Total number of moles of NaOH added.

[b] Measured about 15 min after addition (see Experimental section).

[c] $\bar{n} = (m^0_{OH} - m^0_H + m_H)/m^0_{Al}$ where m^0_i indicates stoichiometric molality (i = OH, H, Al for NaOH, HCl and $AlCl_3$, respectively) and m_H is the molality of free H^+ ion, calculated using the activity coefficient $\gamma_{H^+} = 0.850$.

[d] Heat observed at each step. Owing to the nearly equal values of the apparent molal relative enthalpy of aqueous NaOH [19], at the initial and final ionic strength, no correction for the dilution of the titrant was necessary.

[e] Heat due to water formation, calculated using the enthalpy of water dissociation given by Olofsson and Olofsson [20].

[f] Throughout this paper negative heat values correspond to exothermic effects.

where n^0_H is the number of moles of HCl initially added. The procedure was applied to a total of 45 experimental points belonging to five calorimetric titrations in the range $2.5 < pH < 5$. Choice of this range eliminated points characterized by $\bar{n} < 0.2$, for which the corrections for water formation were large, and points with $\bar{n} > 2.5$ where $Al(OH)^0_3$ begins to precipitate. This procedure yielded a value $\Delta H_{(OH)} = -18.65 + 0.40$ kJ mol^{-1}.

Table 3 summarizes the experimental data collected by means of the differential flow calorimeter at 50, 100 and 150°C. The experiments starting from the more alkaline solutions ($R \approx 1.3$) and reaching final R values ranging from 1.7 to 2.5 have not been included. In these experiments, particularly at high temperature, the output signal of the instrument showed a much larger noise level and the final ΔH values which resulted were generally much lower than those observed in less

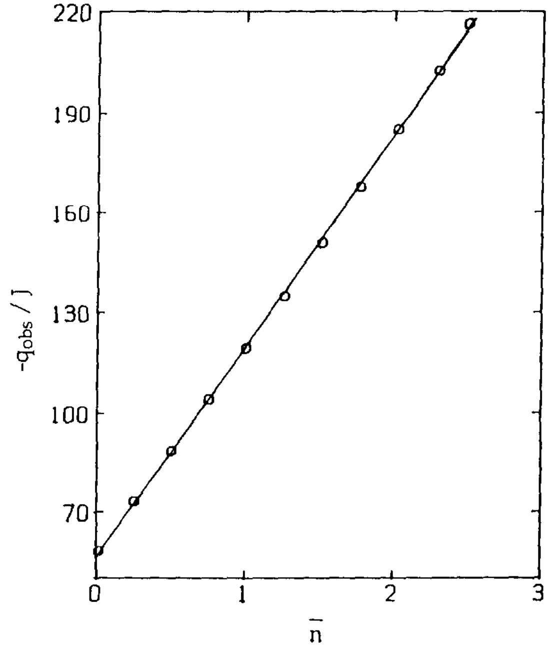

Fig. 1. Overall heat observed in a typical titration of Al^{3+} with NaOH at 25°C.

alkaline solution. The possible precipitation of $Al(OH)_3^0$ in these conditions led us to neglect these data.

Inspection of the ΔH_{obs} values of Table 3 suggests that also the high temperature data could be interpreted in terms of a constant binding enthalpy of OH^- to Al^{3+} in analogy to what observed at 25°C. In fact, the slight dependence of ΔH_{obs} on the R value of the final mixture is of the order of magnitude of the experimental errors. The justification for interpreting these data as if they were equilibrium values will be discussed in the next section.

Calorimetric data of Tables 2 and 3 were analyzed in order to test their consistency with the chemical models reported in Table 1. For this purpose for each model and for each hydrolytic species we calculated the equilibrium quotients valid in our experimental conditions ($I = 0.2$) and used these data for calculating the species distribution and pH before and after each calorimetric experiment. The calculated pH change was used to calculate the number of moles of water formed and the relative heat correction q_w. No correction for the dilution of the titrant was made at temperatures other than 25°C. At these temperatures the experiments with the flow calorimeter were performed at constant ionic strength and we assumed a Young's rule behaviour to be valid [16]. By applying eqn. (7) to the data so corrected we obtained ΔH_{exp} values which have to be analysed in terms of the formation enthalpies of the single species.

TABLE 3

Determination by flow calorimetry of the heats of the reaction $(x/y)\mathrm{Al}^{3+} + \mathrm{OH}^- \rightarrow (1/y)\mathrm{Al}_x(\mathrm{OH})_y^{(3x-y)+}$

T (°C)	φ_1^{*}[a] (g s^{-1})	φ_2^{*}[b] (g s^{-1})	R[c]	P_r[d] (mW)	ΔH_{obs}[e] (kJ mol^{-1})
50	0.02511	0.00865	0.55	−3.220	−12.41
	0.02185	0.01215	0.76	−4.252	−11.67
	0.01848	0.01562	1.05	−5.436	−11.60
100	0.02511	0.00865	0.55	−1.051	−4.05
	0.02185	0.01215	0.76	−1.871	−5.13
	0.01848	0.01562	1.05	−2.574	−5.49
150	0.02526	0.00864[f]	0.53	0.876	3.44
	0.02198	0.01204[f]	0.74	0.271	0.76

[a] Flow of solution 1 (0.03 m $\mathrm{AlCl_3}$ + 0.006 m NaOH).

[b] Flow of solution 2 (0.03031 m NaOH + 0.1544 m NaCl).

[c] $R = m^0_{\mathrm{OH}}/m^0_{\mathrm{Al}}$ after mixing; for the starting solution (1) $R \approx 0.2$.

[d] Reaction power calculated through eqn. (10) using $F = 0.935$, 0.867 and 0.907 at 50, 100 and 150°C respectively; each datum is the average of two or three experiments.

[e] Calculated through eqn. (11).

[f] Solution 2 = 0.02978 m NaOH + 0.1557 m NaCl.

DISCUSSION

It is rather well established [3,21,22] that the hydrolysis of Al^{3+} is characterized in general by a fast formation of mononuclear species, a less rapid formation of small polynuclear species and a much slower formation of polymeric species. Furthermore, the formation of polymeric species and also of microcrystalline aluminium trihydroxide, possible in non-acidic solutions, is reported [3] to be strongly dependent on the mixing conditions of the reagents, particularly as to the occurrence of a local excess of base.

In order to check whether our experimental ΔH values might be different from those which would have been observed in the case where the final equilibrium species had formed instantaneously, we made a few measurements of the heat evolved with time when NaOH is added to an $\mathrm{AlCl_3}$ solution inside a differential heat flow calorimeter. No slow release of heat was observed. However, under our experimental conditions (see Experimental) and the simplifying hypothesis of a first order reaction, we would be able to reveal processes characterized by a minimum enthalpy change given by $\Delta H_{\min}$ (kJ mol^{-1}) $\approx 0.5\ \tau_{1/2}$(h) which means that we can exclude enthalpies of rearrangement of the initially formed hydrolytic species, compatible with a safe estimate of the uncertainty (±2 kJ mol^{-1}) of our ΔH values, only for processes whose half-life times ($\tau_{1/2}$) do not exceed 4 h. A reasonable estimate of the rate of these processes, based on the careful kinetic study conducted by Brosset [23] under experimental conditions very similar to ours, leads to $\tau_{1/2}$ values lower than about 10 h. (Brosset's data, collected at 40°C, indicated that the slow reaction is completed within about 20 h. Even considering that after such time there is about 1% of unreacted material, this would correspond to 6–7 half-life times leading to $\tau_{1/2} \simeq 3$ h. This value, when converted to 25°C on the basis of an average activation energy of 55 kJ mol^{-1}, yields $\tau_{1/2} \simeq 9$ h.) Thus, in the worst case, our experiment would not have revealed rearrangement enthalpies lower than about 5 kJ mol^{-1}.

In order to find evidence for the possible slow release of molar heats of such magnitude, we tried to measure the heat of hydrolysis through a different experiment. Addition of an aqueous solution of $AlCl_3$ plus NaOH ($R \approx 1$) to aqueous excess NaOH to form the species $Al(OH)_4^-$, led to measurement of an enthalpy of reaction of -31.8 kJ mol^{-1}. This value was found to be significantly constant (± 1.0 kJ mol^{-1}), independently of the ageing period (1–10 days) of the titrant solution, thus indicating negligible thermic effects associated with the slower hydrolytic processes. Moreover, the latter ΔH value, when combined with the ΔH of formation of $Al(OH)_4^-$ starting from Al^{3+} and OH^- ($\Delta H = -49.8$ kJ mol^{-1} [24]) allowed us to calculate $\Delta H \approx -18$ kJ mol^{-1} for the binding to aqueous Al^{3+} of a single OH group, a value which compares fairly with the direct value of -18.65 kJ mol^{-1}. We can thus also deduce that the enthalpy values measured in our titrations with NaOH do not depend on the actual mixing conditions.

As far as the experiments at higher temperatures are concerned, in a parallel study on the heat capacity of these solutions [13], to which a significant contribution is given by the chemical heat capacity associated with the hydrolysis reaction, the recalculation of the experimental data at 100 and 150°C supported the assumption that at these temperatures equilibrium should have been reached. Kinetic data collected by Mesmer and Baes [1] in this temperature range actually show that equilibrium is reached after several minutes and thus it is very likely that in our experiment equilibrium is not fully attained and the possible missed heat effect is of the order of magnitude of the dispersion among the data.

In conclusion, there is sufficient experimental evidence to suggest that even in those cases in which equilibrium conditions are not fully reached, the heats experimentally determined in this work may be safely associated with the formation of thermodynamically stable species.

Application of the procedure described by eqns. (5–9) under the hypothesis of the validity of Mesmer polymeric model [1] leads to the results summarized in Table 4. This table shows that at all temperatures the majority of OH groups added react to form species 3; in addition, at 150°C, a fixed fraction of species 1 and 2 is destroyed in favour of the latter polymeric species. Analogous but more marked situations are found

TABLE 4

Analysis of the data collected with the flow calorimeter, following the polymeric model

T (°C)	R [a]	n_{OH} [b] (mol s^{-1} × 10^{+7})	δn_{H^+} [c] (mol s^{-1} × 10^{+9})	X_1 [d]	X_2 [d]	X_3 [d]	ΔH_{exp} (kJ mol^{-1})
50	0.55	2.595	0.658	0.030	0.229	0.741	−12.05
	0.76	3.645	0.864	−0.003	0.089	0.914	−11.47
	1.05	4.686	0.870	−0.023	0.008	1.015	−11.48
100	0.55	2.595	3.128	0.005	0.306	0.689	−2.20
	0.76	3.645	4.377	−0.010	0.094	0.916	−4.16
	1.05	4.686	4.273	−0.019	−0.030	1.049	−4.91
150	0.53	2.547	18.80	−0.117	−0.165	1.282	+0.98
	0.74	3.549	20.04	−0.119	−0.172	1.291	−1.18

[a] $R = m^0_{OH}/m^0_{Al}$ in the final solution (after mixing); in the starting solution $R \approx 0.2$.

[b] Flow of NaOH.

[c] Change in the flow of H^+ ions following the NaOH addition.

[d] Change in the fraction of OH^- bonded, calculated according to eqn. (9), for species 2-2, 3-4 and 14-34 respectively.

when treating the data under the hypothesis of the mononuclear and mixed modes. According to these latter models, at a specified temperature, fixed fractions of the added OH groups are consumed to form the single complexes independently of the actual ratio m^0_{OH}/m^0_{Al}; in the case of the mixed model, furthermore, $Al_{13}(OH)^{3+}_{36}$ is practically the sole species formed. Figure 2 reports, as an example, the species distribution predicted by the monomeric model at 100°C. It can be seen that inside the range $0.3 < R < 1$ the fractions of the various species exhibit a nearly linear dependence on R. As a consequence, the heat effects associated with different additions of NaOH to a fixed Al^{3+} solution, inside this range, depend on a linear combination of the formation enthalpies of the single species. This leads to the practical impossibility of distinguishing the heat associated with the OH bonded in the various complexes, at least under our experimental conditions, thus preventing us calculating the single $\Delta H_{(OH),i}$ values according to eqn. (9). Unfortunately, the conditions which would prove appropriate for this discrimination could not be adopted for the following reasons: at $R < 0.3$ due to the very large incidence of the heat correction for water formation, and at large R values due to the possible solid precipitation which cannot be controlled with our flow apparatus.

Nonetheless there are several observations which actually suggest that the possibility of attributing a constant enthalpy change to the binding of each OH group is a reasonable hypothesis. These include, (i) the trend of the function $q_{exp} = f(\bar{n})$, observed at 25°C up to $\bar{n} = 2.5$ (see Fig. 1); (ii) the feeble dependence of ΔH_{exp} on R at the other temperatures (see Table

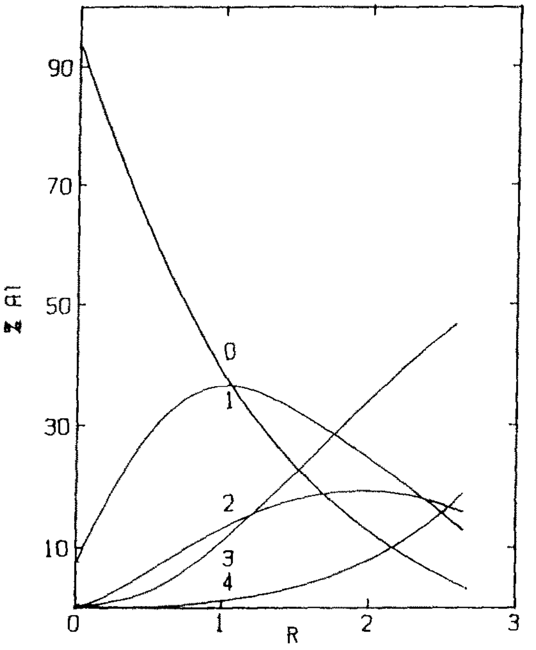

Fig. 2. Species distribution for aqueous solutions of $AlCl_3$ at 100°C, according to the mononuclear model. The numbers near each curve represent the OH groups bonded to Al^{3+}.

4); (iii) the zero thermal effect associated with the slow rearrangement reactions. In particular the third point allows us to associate a zero thermal effect directly with reactions of simple transfer of OH groups from one compound to another if one considers that under our experimental conditions (see Table 2) the number of free OH^- ions which bind aluminium through the slow process is actually a negligible fraction (always less than 1.5%, calculated for observed $\Delta pH \leqslant 0.1$ units) of the total moles of added OH^+. Incidentally, we recall that other authors [2] have already made the assumption of a common temperature dependence of the formation constants of the first three mononuclear hydroxy compounds of Al^{3+}. It would not be unrealistic to attribute a similar temperature dependence to other species (though polymeric) characterized by the same octahedral coordination around the aluminium atom (for example, the species $Al_{13}OH_{32}^{7+}$ displays only one tetrahedrally coordinated central atom surrounded by twelve aluminium atoms with octahedral coordination [3]). Only the tetrahedrally coordinated species $AlOH_4^-$ is instead characterized by a clearly different temperature dependence ($\Delta H = -12.5$ kJ (mol OH)$^{-1}$ [24]).

For the above reasons, all the calorimetric data collected in this work were analysed under the hypothesis of a constant reaction enthalpy per mole of OH^- ($\Delta H_{(OH)}$) for the formation of any hydroxy species of Al^{3+}, which is equivalent to reducing eqn. (9) to the simple equality

$$\Delta H_{(\mathrm{OH})} = \Delta H_{\mathrm{exp}} \tag{13}$$

Application of the polymeric model under the assumption of a constant $\Delta H_{(\mathrm{OH})}$ led to the enthalpy values given in the first column of Table 5. These values at the various temperatures were utilized in order to recalculate the formation constants of the various species, starting from those at 25°C, through the equation

$$\lg(Q)_T = \lg(Q)_{298} + \frac{1}{2.303R}\int_{298}^{T}\frac{\Delta H(T)}{T^2}\,\mathrm{d}T \tag{14}$$

For this comparison reference was made to the hydrolysis constants (Q_{OH}) given following eqn. (2), which are more sensitive to the basic effect of OH^- addition to Al^{3+}. The trend with temperature of the calculated formation constants (a trend which is common to all complexes as a consequence of the definition of a single $\Delta H_{(\mathrm{OH})}$) is compared in Fig. 3 with that of the original constants at $I = 0.2$. The agreement appears acceptable.

In order to check the thermodynamic consistency of our data and see whether the procedure adopted for calculating activity coefficients might bias, to some extent, the above agreement, we applied eqn. (14) also in conditions of $I = 1$ in order to obtain calculated hydrolysis constants which may be directly compared with those experimentally determined by Mesmer and Baes [1]. The $\Delta H_{(\mathrm{OH})}$ values at this different ionic strength, for the various temperatures, were calculated according to the reaction

$$(x/y)\mathrm{AlCl}_3 + \mathrm{NaOH} \rightarrow (1/y)\mathrm{Al}_x(\mathrm{OH})_y\mathrm{Cl}_{3x-y} + \mathrm{NaCl} \tag{15}$$

by means of the general equation

$$\Delta H^{I}_{\mathrm{OH}} = \Delta H^{I_{\mathrm{R}}}_{\mathrm{OH}} - \frac{1}{y}\left(x\,\Delta L^{I_{\mathrm{R}}\rightarrow I}_{\phi,\mathrm{AlCl}_3} - \Delta L^{I_{\mathrm{R}}\rightarrow I}_{\phi,i}\right) + \Delta L^{I_{\mathrm{R}}\rightarrow I}_{\phi,\mathrm{NaCl}} - \Delta L^{I_{\mathrm{R}}\rightarrow I}_{\phi,\mathrm{NaOH}} \tag{16}$$

TABLE 5

Average enthalpies for reaction (2) ($\Delta H_{(\mathrm{OH})}$ (kJ mol^{-1})) calculated following different chemical models

	Polynuclear		Mononuclear	Mixed
T (°C)	$I = 0.2$	$I = 1$	$I = 0.2$	$I = 0.2$
25	−18.9[a]	−19.4	−18.9[a]	−18.9[a]
50	−11.7	−13.4	−11.8	−12.2
100	−3.8	−6.6	−4.2	−6.6
150	−0.1	−4.6	+4.1	−3.0

[a] Values obtained from the experimental datum collected at $I \approx 0.1$ using eqn. (16).

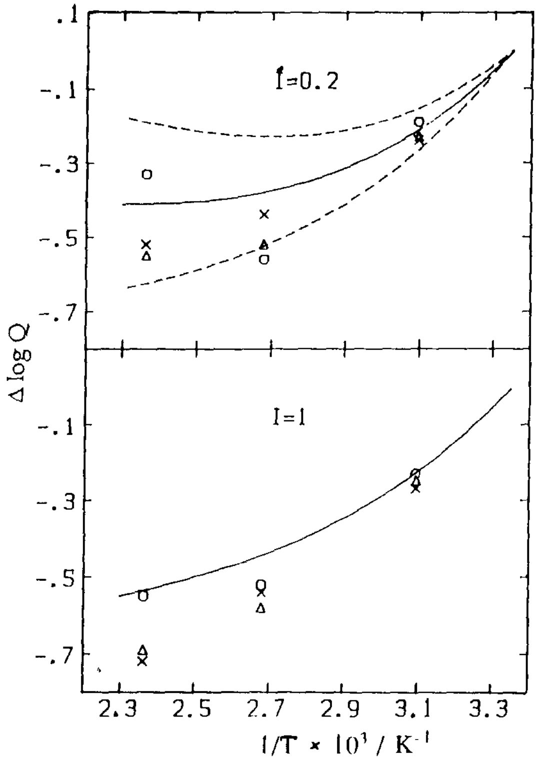

Fig. 3. Trend with temperature of the equilibrium constants ($\Delta \lg Q = \lg Q^{T}_{\mathrm{OH}} - \lg Q^{298}_{\mathrm{OH}}$) of complexes involved in the polynuclear model. ———, Calculated values. Experimental values refer to $\mathrm{Al_2(OH)_2^{4+}}$(O), $\mathrm{Al_3(OH)_4^{5+}}$(×) and $\mathrm{Al_{14}(OH)_{34}^{8+}}$(Δ). Broken lines show the effect of ±1 kcal $\mathrm{mol^{-1}}$ in $\Delta H_{(\mathrm{OH})}$.

where I_{R} is the reference ionic strength (here $I_{\mathrm{R}} = 0.2$), L_{Φ} terms are the apparent molar relative enthalpies and the index i indicates the ith complex. L_{Φ} values for NaOH were taken from Parker [19] at 25°C and from Conti et al. [16] at other temperatures; those for NaCl were taken from Silvester and Pitzer [25]. L_{Φ} values relative to $\mathrm{AlCl_3}$ and to the hydroxo complexes $\mathrm{Al}_x\mathrm{(OH)}_y\mathrm{Cl}_{3x-y}$ were calculated by us through the procedure proposed by Helgeson et al. [15], under the same assumption used above for activity coefficients. The slightly different enthalpy values yielded by eqn. (16), at constant temperature, for different complexes, were averaged to give a single $\Delta H_{(\mathrm{OH})}$ value. Values of $\Delta H_{(\mathrm{OH})}$ at $I = 1$ thus calculated, are reported in Table 5. Introduction into eqn. (14) of the function $\Delta H^{I=1}_{(\mathrm{OH})} = f(\mathrm{T})$ together with the values $(Q^{I=1}_{(\mathrm{OH})})_{298}$ allowed us to calculate the analogous constants between 25°C and 150°C. The comparison calculated versus experimental (see Fig. 3) shows that experimental points deviate from the calculated function at most by 0.15 pK units. Therefore, we can safely state that the enthalpy values $\Delta H_{(\mathrm{OH})}$ measured in this work are compatible with the polymeric model proposed by Mesmer and Baes [1].

The procedure described for the polymeric model, involving the proper correction of the experimental heats and calculation of $\Delta H_{(\mathrm{OH})}$ at $I = 0.2$, was then applied to the mononuclear model. Values of $\Delta H_{(\mathrm{OH})}$ thus obtained (see Table 4) were converted to zero ionic strength by means of eqn. (16) (in this case $\Delta L_{\Phi}^{I_R \to I} \equiv L_{\Phi}^{I}$) and then used in eqn. (14) in order to recalculate high temperature equilibrium constants. The comparison between calculated and experimental data assumed the aspect shown in Fig. 4, where the Reed and Spycher [12] data are also reported. Except for the species $Al(OH)_4^-$, there appears to be an inconsistency between original equilibrium data and those calculated through our direct calorimetric measurements. Moreover, if one tries to reproduce our experimental values of $\Delta H_{(\mathrm{OH})}$ by means of eqn. (9), introducing the species distribution and the enthalpy values given by Michard [11], values larger by more than 7 kJ at all temperatures are obtained. Because other sets of $\lg \beta_{x,y}$ values available in the literature for $x = 1$ do not differ substantially from those given by Michard [11], and here taken into consideration, this result was

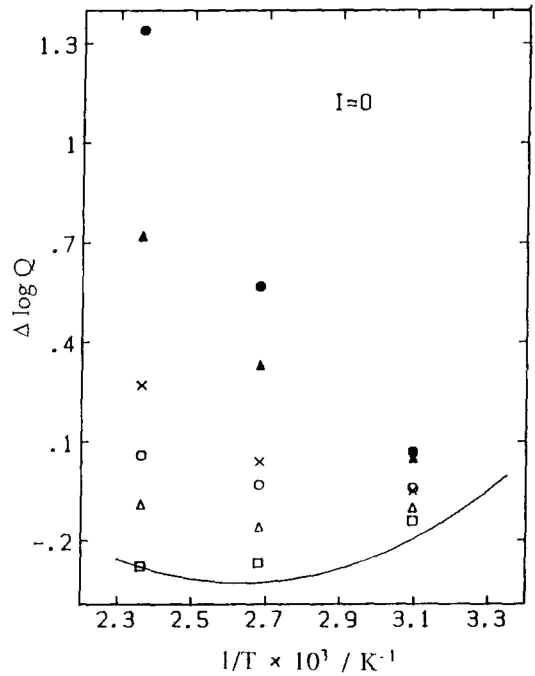

Fig. 4. Trend with temperature of the equilibrium constants ($\Delta \lg Q = \lg Q_{\mathrm{OH}}^{T} - \lg Q_{\mathrm{OH}}^{298}$) of complexes involved in the mononuclear model. ———, Calculated values. Experimental values: $Al(OH)^{2+}$ (○, ●), $Al(OH)_2^+$ (△, ▲), $Al(OH)_3$ (×), $Al(OH)_4^-$ (□). Filled symbols are data from Reed and Spycher [12].

considered a sufficient indication that a chemical model which involves only simple mononuclear complexes does not explain satisfactorily the thermodynamic behaviour of aqueous solutions of Al^{3+} ion, at least under our experimental conditions.

Our calorimetric data were finally processed in an analogous way under the assumption of validity of the chosen mixed model, which includes both mononuclear as well as polynuclear hydroxo species of Al^{3+}. Application of eqn. (13) leads to $\Delta H_{(OH)}$ values listed in the last column of Table 5. These values appear to be reasonable and do not differ significantly from those obtained with the polymeric model. The lack of directly measured data of equilibrium constants at high temperatures unfortunately deprives us of the common reliability criterion for these enthalpy values. However, integration of the van't Hoff equation starting from the 25°C data of Bottero et al. [10] produced formation constants which are fairly similar to those given in Table 1 and calculated by us. This test only allows us to deduce that the mixed model cannot be ruled out on the basis of our data.

Our analysis of calorimetric data on the hydrolysis of aluminium ion permits us therefore to define an average enthalpy value for the addition of a single OH group to Al^{3+} ($\Delta H_{(OH)}$) and indicates the chemical hydrolytic model proposed by Mesmer and Baes [1] as the most probable. An immediate advantage of the identification of $\Delta H_{(OH)}$ values is the possibility of calculating the molar enthalpy of formation of any hydrolytic species $Al_x(OH)_y^{(3x-y)+}$ from Al^{3+} and OH^- through the simple relationship

$$\Delta H_i = y_i \cdot \Delta H_{(OH),i} = y \cdot \Delta H_{(OH)} \qquad (17)$$

Combination of standard free energy data with standard enthalpy data obtainable through eqn. (17), allows us to complete the thermodynamic information on the formation of hydroxy species of aqueous Al^{3+}.

The standard thermodynamic functions for the formation of these species according to eqn. (2) exhibit a common trend with temperature which is exemplified in Fig. 5 for the species $Al_{14}(OH)_{34}^{8+}$. It may be observed that these hydroxy species at low temperatures are stabilized by both entropy and enthalpy factors. The increase with temperature of the formation enthalpy is more than compensated for by the entropy term, thus providing for the larger thermodynamic stability of the hydrolytic species and the consequent larger hydrolysis degree which is observed at the higher temperatures. This proves consistent with the fact that the destruction of the solvation shell of the free ions produces bulk water which has a larger entropy the higher the temperature, i.e. the more disordered the solvent structure.

Equation (17) certainly represents an approximation to the real situation. Yet, we believe that ΔH values given by this equation should provide a better route to the calculation of high temperature hydrolysis

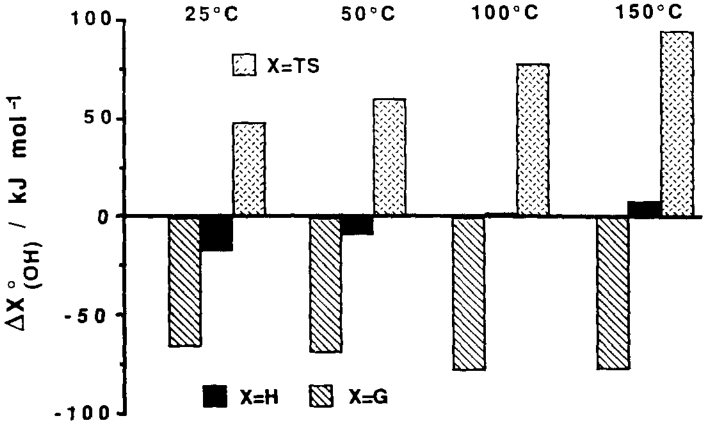

Fig. 5. Standard thermodynamic functions of formation of species $Al_{14}(OH)_4^{8+}$ according to reaction (2).

constants than so far accepted. This procedure appears to be particularly useful in the case of Al^{3+}, in which there is present disagreement on the exact stoichiometry of the hydrolytic species formed, since it allows us to calculate high temperature equilibrium constants whatever chemical model is assumed to be valid. The use of generalized $\Delta H_{(OH)}$ values for high temperature data might be profitably introduced, for instance, into those computer programs that simulate the genesis of hot natural waters.

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