J. Chem. Thermodynamics 1983, 15, 279–285

Enthalpies of formation of strontium dichloride and of the strontium ion (Sr^{2+}) in water and in 1 mol \cdot dm⁻³ HCl, and an assessment of enthalpies of formation of alkaline-earth dichlorides"

LESTER R. MORSS and CLAYTON W. WILLIAMS

Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, U.S.A.

(Received 1 July 1982; in revised form 30 September 1982)

Measurements of the enthalpy of solution of SrCl₂ in water and in 1 mol·dm⁻³ HCl solution lead to $\Delta H_{\rm f}^{\circ}({\rm SrCl}_2, c, 298.15 \text{ K}) = -(832.7 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$, and to $\Delta H_{\rm f}^{\circ}({\rm SrC}^{2+}, aq, 298.15 \text{ K})$ $= -(549.7 \pm 0.9) \text{ kJ} \cdot \text{mol}^{-1}$. Literature data have been assessed to calculate corresponding enthalpies of formation for the other alkaline-earth ions as well as the enthalpies of formation of the alkaline-earth dichlorides in 1 mol·dm⁻³ HCl.

1. Introduction

Many of the assessed properties⁽¹⁾ of common elements such as the alkaline earths are based upon measurements conducted in the last century. There have been recent research problems that have needed auxiliary thermodynamic data on these elements. For example, in studying the thermochemistry of alkaline-earth uranates MUO_4 (M = Mg, Ca, Sr, Ba) O'Hare and co-workers^(2,3) needed to measure thermochemical properties of Ca(NO₃)₂ and BaCl₂. We have undertaken a series of thermochemical measurements of perovskite oxides (MM'O₃, M₃M'O₆, *etc.*) in which M is one or more alkaline earths.⁽⁴⁾ Since hydrochloric acid is often the most convenient calorimetric solvent for such compounds, and since the formation of these perovskites from the binary oxides depends on small energy differences, it is important to know the thermal properties of the alkaline-earth ions in water and in dilute hydrochloric acid.

An assessment of literature data revealed solution-calorimetric studies of $MgCl_2$,⁽⁵⁻⁷⁾ Mg and MgO,^(8,9) SrO,⁽¹⁰⁾ BaO,⁽¹¹⁾ SrCl₂,⁽¹²⁾ and BaCl₂,^(3,12) that have been conducted during the past few years (since publication of Technical Note 270–6).⁽¹⁾ These data, combined with earlier literature data on calcium, magnesium, and

^a This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

O-10

barium compounds,^(1,13-16) provide an experimental base for enthalpies of formation of M^{2+} and MCl₂ with the exception of M = Sr. For these reasons it was decided to carry out the needed measurements: the enthalpy of solution of SrCl₂ in water and in 1 mol \cdot dm⁻³ HCl.

2. Experimental

PREPARATION OF SrCl₂

A sample of about 20 g of SrCl₂ \cdot 6H₂O (Mallinckrodt reagent grade) was dehydrated under high vacuum (0.01 Pa) at 298 K for 18 h and then heated slowly to 873 K, where it was maintained under high vacuum for 24 h. The product (Sample A) was cooled and handled only in a dry box (less than 1×10^{-5} mass fraction of water). A sample of 0.6 g was observed to dissolve completely in distilled water, yielding a solution of pH = 6. Absence of hydrolysis thus indicated the purity of the product with respect to SrO, Sr(OH)₂, or oxychloride. The only elemental impurity detected by emission and atomic absorption spectrophotometry was 0.21 mass per cent of calcium. Volumetric analysis showed 44.55 mass per cent of chlorine (theoretical 44.73 per cent).

A second sample (Sample B) of about 5 g of anhydrous $SrCl_2$ (Johnson Matthey Puratronic, only impurities 2×10^{-6} mass fraction of calcium, 1×10^{-6} mass fraction of barium) was handled under conditions similar to those used for Sample A. Volumetric analysis showed 44.64 mass per cent of chlorine.

CALORIMETRIC PROCEDURES

Samples of SrCl₂ were weighed and sealed in Pyrex ampoules in a dry box with less than 5×10^{-6} mass fraction of water. Three or four samples were made to react sequentially in 880 cm³ of 1.00 mol·dm⁻³ HCl in an isoperibol Dewar-flask calorimeter that has been described previously.⁽¹⁷⁻¹⁹⁾ Additional groups of samples were made to react sequentially in 880 cm³ of water. Each calorimetric experiment was preceded and followed by electrical calibrations accurate to ± 0.02 per cent. The apparatus has been checked several times by dissolution of U.S. National Bureau of Standards (SRM724) tris(hydroxymethyl)aminomethane (THAM) in 0.1 mol·dm⁻³ HCl; the most recent set of three THAM dissolutions yielded $\Delta h = -245.66$, -245.50, and $-245.45 \text{ J} \cdot \text{g}^{-1}$. The certified value⁽²⁰⁾ is $-(245.76\pm 0.26) \text{ J} \cdot \text{g}^{-1}$. Results of SrCl₂ dissolution experiments are shown in tables 1 and 2. The column headings of table 2 parallel those of reference 19, table 1.

3. Results and discussion

Mg²⁺(aq) AND MgCl₂

Shomate and Huffman⁽¹³⁾ measured the enthalpy of reaction of very pure magnesium metal with 1 mol·dm⁻³ HCl. This measurement at 298.15 K has been accepted as a standard for metal-dissolution calorimetry, and has been reproduced many times.⁽²¹⁻²⁸⁾ Using the currently accepted (1981) molar mass of Mg, 24.305 g·mol⁻¹,

280

Sample	$\frac{m(\mathrm{SrCl}_2)}{g}$	<u>ΔΗ</u> " J	$\frac{\Delta H_{\rm sol}}{\rm kJ\cdot mol^{-1}}^{b}$	Sample	$\frac{m(\mathrm{SrCl}_2)}{\mathrm{g}}$	<u>ΔΗ</u> " J	$\frac{\Delta H_{\rm sol}}{\rm kJ\cdot mol^{-1}}^{b}$
A	0.07726	- 22.84	-46.53	В	0.15744	- 46.11	-46.43
Α	0.19442	- 57.63	-46.65	В	0.16384	- 48.49	-47.40
Α	0.49667	-147.26	- 46.65	В	0.07380	- 21.41	-46.00
В	0.05797	- 16.55	-45.26	В	0.11092	- 32.42	- 46.34
В	0.09537	- 27.80	-45.23	В	0.13096	- 38.39	- 46.48
В	0.07909	- 23.04	46 .18	В	0.04964	-14.37	-45.90
						Avera	ge: $-46.25 \pm 0.38^{\circ}$

TABLE 1. Enthalpy of solution of $SrCl_2(c)$ in 880 cm³ of 100 mol·dm⁻³ HCl at (298.15±0.05) K

^a Corrected for evaporation of water into dry gas escaping from ampoule.

^b Sample A results corrected for 0.82 mole per cent of CaCl₂ (corresponding to 0.21 mass per cent of calcium).

^e 95 per cent confidence.

Sample	$m(SrCl_2)$	$\sum n_i$	ΔH "	I,	$L'_{\phi,i}$	$\Delta H_{\rm sol}(\text{corr})^{b}$
	mg	mmol	J	mmol · kg ⁻¹	$kJ \cdot mol^{-1}$	kJ · mol ⁻¹
A	0.05449	0.3437	-17.64	1.172	0.196	-51.14
Α	0.09806	0.9623	- 31.60	3.281	0.324	-51.10
Α	0.19854	2.2147	- 64.06	7.55	0.483	- 51.38
Α	0.48920	5.3006	-156.68	18.07	0.728	- 51.30
В	0.16361	1.0320	- 53.59	3.518	0.335	-52.26°
В	0.11056	1.7294	- 35.19	5.90	0.429	- 51.02
В	0.15158	2.6856	- 48.24	9.16	0.530	- 51.16
В	0.13092	0.8258	- 42.05	2.815	0.301	- 51.22
В	0.12614	1.6215	-40.32	5.53	0.416	-51.21
В	0.17596	2.7315	55.94	9.31	0.534	-51.10
				ΔΗ,	ol(corr)/(kJ⋅mo	l^{-1}) = -51.12 ± 0.13

TABLE 2. Enthalpy of solution of $SrCl_2(c)$ in 880 cm³ of water at (298.15±0.05) K

" Corrected for evaporation of water into dry gas escaping from ampoule.

^b Sample A results corrected for presence of CaCl₂ (as in table 1).

^c Rejected statistically by use of Q test: Youmans, H. L. Statistics for Chemistry. Charles E. Merrill: Columbus, Ohio. 1973.

⁴ Twice the standard deviation.

we combine their results with the partial molar enthalpy of formation of $HCl^{(29, 30)}$ in 1 mol \cdot dm⁻³ aqueous solution to yield the partial molar enthalpy of formation of MgCl₂ in 1 mol \cdot dm⁻³ HCl (all data at 298.15 K):

$$\begin{split} \text{Mg(c)} + 2\text{HCl}(1 \ \text{mol} \cdot \text{dm}^{-3}) &= \text{MgCl}_2(\text{in} \ 1 \ \text{mol} \cdot \text{dm}^{-3} \ \text{HCl}) + \text{H}_2(\text{g});\\ \Delta H_1 &= -(465.48 \pm 0.17) \ \text{kJ} \cdot \text{mol}^{-1},\\ \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) &= 2\text{HCl}(1 \ \text{mol} \cdot \text{dm}^{-3});\\ \underline{\Delta H_2} &= 2 \times (-164.36 \pm 0.10) \ \text{kJ} \cdot \text{mol}^{-1},\\ \overline{Mg(c)} + \text{Cl}_2(\text{g}) &= \text{MgCl}_2(\text{in} \ 1 \ \text{mol} \cdot \text{dm}^{-3} \ \text{HCl});\\ \Delta H_3 &= \Delta H_f(\text{MgCl}_2 \ \text{in} \ 1 \ \text{mol} \cdot \text{dm}^{-3} \ \text{HCl})\\ &= \Delta H_1 + \Delta H_2 = -(794.20 \pm 0.26) \ \text{kJ} \cdot \text{mol}^{-1}. \end{split}$$

One can also formulate a set of equations leading to ΔH_3 from $\Delta H_f^\circ(MgO, c)$ and the enthalpy of reaction of MgO with HCl(aq). So as to use values independent of Shomate and Huffman's ΔH_1 , we use only $\Delta H_f^\circ(MgO, c)$ derived from the enthalpy of combustion of Mg⁽³¹⁾ in the following scheme.

$$\begin{split} Mg(c) + \frac{1}{2}O_2(g) &= MgO(c); & \Delta H_4 &= -(600.9 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1} \cdot \overset{(31)}{,} \\ MgO(c) + 2HCl(1 \text{ mol} \cdot \text{dm}^{-3}) &= MgCl_2(\text{in 1 mol} \cdot \text{dm}^{-3} \text{ HCl}) \\ &+ H_2O(\text{in 1 mol} \cdot \text{dm}^{-3} \text{ HCl}); \\ \Delta H_5 &= -(149.69 \pm 0.09) \text{ kJ} \cdot \text{mol}^{-1} \cdot \overset{(13)}{,} \\ H_2(g) + \frac{1}{2}O_2(g) &= H_2O(\text{in 1 mol} \cdot \text{dm}^{-3} \text{ HCl}); \\ &\Delta H_6 &= -(285.85 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}, \\ \hline Mg(c) + Cl_2(g) &= MgCl_2(\text{in 1 mol} \cdot \text{dm}^{-3} \text{ HCl}); \\ &\Delta H_3 &= \Delta H_4 + \Delta H_5 - \Delta H_6 + \Delta H_2 \\ &= -(793.5 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}. \end{split}$$

A weighted mean of these two results for $MgCl_2$ has been entered into table 3. It is consistent with the NBS value:⁽⁴⁾ - 794.2 kJ·mol⁻¹.

Shin and Criss⁽⁶⁾ measured the enthalpy of solution of $MgCl_2(c)$ in both water and 1 mol·dm⁻³ HCl. Their results are preferable to those of Shomate and Huffman for $MgCl_2(c)$ because of the higher purity of Shin and Criss's samples of $MgCl_2$. Their results for the enthalpy of solution in H₂O match those of Greyson and Snell⁽¹⁶⁾ when corrected to infinite dilution⁽¹⁾ but the corrected ΔH_{sol} of Vorob'ev *et al.*⁽⁷⁾ is significantly more negative (-157.5 kJ·mol⁻¹). From Shomate and Huffman's values for Mg(c), and Shin and Criss's values for MgCl₂, we accept Shin and Criss's $\Delta H_f^{\circ}(Mg^{2+}, aq) = -(465.96 \pm 0.33) kJ \cdot mol^{-1}$. (We have propagated the errors randomly rather than additively and enter the results in table 3.)

The last value agrees with the NBS value,⁽¹⁾ $-466.85 \text{ kJ} \cdot \text{mol}^{-1}$, and with that obtained by Coffey and Olefsson in dilute perchloric acid, $-(466.80 \pm 1.25) \text{ kJ} \cdot \text{mol}^{-1}$. It does not agree with the results of Monaenkova *et al.*,⁽⁸⁾ who obtained an average $\Delta H_f^{\circ}(Mg^{2+}, aq) = -(468.06 \pm 0.63) \text{ kJ} \cdot \text{mol}^{-1}$ from enthalpies of solution of Mg and MgO in perchloric acid and enthalpies of dilution of perchloric acid. It also does not agree with empirical extrapolations to infinite dilution of enthalpies of solution of Mg and MgO by Vasil'ev *et al.*,⁽⁹⁾ who obtained $-(467.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$. Vasil'ev *et al.* appeared to use an open calorimeter⁽³²⁾ but explicitly neglected the enthalpy of vaporization of water into evolved H₂; this correction would make their value even more negative.

Ca²⁺(aq) AND CaCl₂

In 1924 Bäckström^(14,15) reported enthalpies of solution of calcite, aragonite, and calcium oxide in 1 mol \cdot dm⁻³ HCl saturated with CO₂. We have corrected his results for CaCO₃ by -1.37 kJ \cdot mol⁻¹ for the enthalpy of evaporation of water into evolved CO₂.

$$CaCO_{3}(aragonitc) + 2HCl(1 \text{ mol} \cdot dm^{-3}) = CaCl_{2}(\text{in } 1 \text{ mol} \cdot dm^{-3} \text{ HCl}) + CO_{2}(g) + H_{2}O(\text{in } 1 \text{ mol} \cdot dm^{-3} \text{ HCl}); \qquad \Delta H_{7} = -(14.8 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1},$$

282

 $\begin{aligned} & \text{CaCO}_{3}(\text{calcite}) + 2\text{HCl}(1 \text{ mol} \cdot \text{dm}^{-3}) = \text{CaCl}_{2}(\text{in } 1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}) \\ & + \text{CO}_{2}(\text{g}) + \text{H}_{2}\text{O}(\text{in } 1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}); \qquad \Delta H_{8} = -(14.9 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}, \\ & \text{CaO}(\text{c}) + 2\text{HCl}(1 \text{ mol} \cdot \text{dm}^{-3}) = \text{CaCl}_{2}(\text{in } 1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}) \\ & + \text{H}_{2}\text{O}(\text{in } 1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}); \qquad \Delta H_{9} = -(193.2 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned}$

Using these corrected results, as well as $\Delta H_{f}^{\circ}(\text{CaCO}_{3}, \text{ aragonite}) = -1207.13$ kJ·mol⁻¹; $\Delta H_{f}^{\circ}(\text{CaCO}_{3}, \text{ calcite}) = -1206.92$ kJ·mol⁻¹; $\Delta H_{f}^{\circ}(\text{CaO}, \text{c}) = -(635.09 \pm 0.90)$ kJ·mol⁻¹; and $\Delta H_{f}^{\circ}(\text{CO}_{2}, \text{g}) = -(393.51 \pm 0.13)$ kJ·mol⁻¹,^(1,29,33) we calculate three values for $\Delta H_{f}(\text{CaCl}_{2}$ in 1 mol·dm⁻³ HCl): $\Delta H_{f}^{\circ}(\text{CaCO}_{3}, \text{ aragonite}) + \Delta H_{7} + \Delta H_{2} - \Delta H_{6} - \Delta H_{f}^{\circ}(\text{CO}_{2}, \text{g}) = -871.29$ kJ·mol⁻¹; $\Delta H_{f}^{\circ}(\text{CaCO}_{3}, \text{ calcite}) + \Delta H_{8} + \Delta H_{2} - \Delta H_{6} - \Delta H_{f}^{\circ}(\text{CO}_{2}, \text{g}) = -871.18$ kJ·mol⁻¹; and $\Delta H_{f}^{\circ}(\text{CaO}, \text{c}) + \Delta H_{9} + \Delta H_{2} - \Delta H_{6} = -(871.16 \pm 1.21)$ kJ·mol⁻¹. Since the CaO was handled in air, and since both CaCO₃ isomorphs yield more precise results, we accept $\Delta H_{f}(\text{CaCl}_{2}$ in 1 mol·dm⁻³ HCl) = -(871.2 \pm 1.0) kJ·mol⁻¹. (The error limit is estimated since Bäckström did not state the purity of his calcium compounds.)

Given $\Delta H_{f}^{\circ}(\operatorname{Ca}^{2+}, \operatorname{aq}) = -(543.10 \pm 0.80) \text{ kJ} \cdot \operatorname{mol}^{-1},^{(33)}$ and $\Delta H_{sol}^{\circ}(\operatorname{CaCl}_{2}) = -81.3 \text{ kJ} \cdot \operatorname{mol}^{-1},^{(1)}$ we calculate $\Delta H_{f}^{\circ}(\operatorname{CaCl}_{2}, \operatorname{aq}) = \Delta H_{f}^{\circ}(\operatorname{Ca}^{2+}, \operatorname{aq}) + 2\Delta H_{f}^{\circ}(\operatorname{HCl}, \operatorname{aq}) = -877.3 \text{ kJ} \cdot \operatorname{mol}^{-1}$; and $\Delta H_{f}^{\circ}(\operatorname{CaCl}_{2}, \operatorname{c}) = \Delta H_{f}^{\circ}(\operatorname{Ca}^{2+}, \operatorname{aq}) - 2\Delta H_{f}^{\circ}(\operatorname{HCl}, \operatorname{aq}) - \Delta H_{sol}^{\circ}(\operatorname{CaCl}_{2}, \operatorname{c}) = -796.0 \text{ kJ} \cdot \operatorname{mol}^{-1}$, values in good agreement with Parker *et al.*⁽¹⁾

Sr²⁺(aq) AND SrCl₂

Brink and Holley⁽¹⁰⁾ dissolved pure Sr in 1 mol·dm⁻³ HCl:

$$Sr(c) + 2HCl(1 \text{ mol} \cdot dm^{-3}) = SrCl_{2}(\text{in } 1 \text{ mol} \cdot dm^{-3} HCl) + H_{2}(g);$$

$$\Delta H_{10} = -(550.24 \pm 0.79) \text{ kJ} \cdot \text{mol}^{-1}.$$

We calculate $\Delta H_{\rm f}({\rm SrCl}_2 \text{ in } 1 \text{ mol} \cdot {\rm dm}^{-3} \text{ HCl}) = \Delta H_{10} + \Delta H_2 = -(878.96 \pm 0.80) \text{ kJ} \cdot \text{mol}^{-1}$. The experimental results of the present research are represented by those in tables 1 and 2. The enthalpies of solution of ${\rm SrCl}_2$ in 1.00 mol \cdot dm⁻³ HCl were averaged since there is negligible change in ionic strength throughout the experiments:

$$SrCl_2(c) = SrCl_2(in \ 1 \ mol \cdot dm^{-3} \ HCl);$$
 $\Delta H_{11} = -(46.25 \pm 0.38) \ kJ \cdot mol^{-1}.$

The values in table 2 were treated by the method of Silvester and Pitzer⁽³⁴⁾ to correct them to infinite dilution. Since the four samples were made to react sequentially in the same run, the dilution corrections were calculated by the method of Bernarducci *et al.*⁽¹⁹⁾ The symbols of table 2 and the equations used in the calculation parallel those of reference 19, table 1. The results were corrected to infinite dilution by extrapolation of $\Delta H_{sol}(corr)$ to infinite dilution as a function of the molality of SrCl₂ using the equation:

$$\Delta H_{i}(\text{soln, corr}) = (\Delta H_{i} + L'_{\phi, i-1} \sum_{i} n_{i-1} - L'_{\phi, i} \sum_{i} n_{i})/n_{i}.$$
(12)

Thus we obtain

$$SrCl_2(c) = SrCl_2(aq); \quad \Delta H_{13} = -(51.12 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1},$$

in agreement with the result of Greyson and Snell⁽¹⁶⁾ extrapolated to infinite dilution,⁽¹⁾ (-51.17 ± 0.12) kJ·mol⁻¹, and nearly in agreement with that of Dadgar and Taherian,⁽¹²⁾ -50.7 kJ·mol⁻¹. Thus $\Delta H_{\rm f}^{\circ}({\rm SrCl}_2, c) = \Delta H_{10} + \Delta H_2 - \Delta H_{11} = -(832.7\pm0.9)$ kJ·mol⁻¹ and $\Delta H_{\rm f}^{\circ}({\rm Sr}^{2+}, aq) = \Delta H_{10} + \Delta H_2 - \Delta H_{11} + \Delta H_{13} - \Delta H_9 = -(549.7\pm0.9)$ kJ·mol⁻¹, as shown in table 3.

Ba²⁺(aq) AND BaCl₂

Fitzgibbon, Huber, and Holley⁽⁷⁾ dissolved pure Ba in 1 mol·dm⁻³ HCl:

 $Ba(c) + 2HCl(1 \text{ mol} \cdot dm^{-3}) = BaCl_2(\text{in } 1 \text{ mol} \cdot dm^{-3} \text{ HCl}) + H_2(g);$ $\Delta H_{14} = -(535.34 \pm 1.72) \text{ kJ} \cdot \text{mol}^{-1}.$

Thus we recommend $\Delta H_{\rm f}(\text{BaCl}_2 \text{ in } 1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}) = \Delta H_{14} + \Delta H_2 = -(864.06 \pm 1.72) \text{ kJ} \cdot \text{mol}^{-1}$. O'Hare, Boerio, and Hoekstra⁽³⁾ dissolved BaCl₂ in 1 mol $\cdot \text{dm}^{-3}$ HCl:

BaCl₂(c) = BaCl₂(in 1 mol \cdot dm⁻³ HCl); $\Delta H_{15} = -(9.9 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$.

Thus $\Delta H_{f}^{\circ}(\text{BaCl}_{2}, c) = \Delta H_{14} + \Delta H_{2} - \Delta H_{20} = -(854.16 \pm 1.73) \text{ kJ} \cdot \text{mol}^{-1}$. These values are preferable to those of Parker *et al.*⁽¹⁾ since they were published more recently and represent work of high quality. Criss and Cobble⁽³⁵⁾ dissolved BaCl₂ in water and extrapolated the enthalpies to infinite dilution:

BaCl₂(c) = BaCl₂(aq);
$$\Delta H_{16} = -(13.51 \pm 0.03) \text{ kJ} \cdot \text{mol}^{-1}$$

This value is essentially that adopted by Parker *et al.*⁽¹⁾ Other comparable results are⁽¹⁶⁾ – (13.35±0.08) and⁽¹²⁾ – 12.61 kJ·mol⁻¹. Thus $\Delta H_{\rm f}^{\circ}({\rm Ba}^{2+},{\rm aq}) = \Delta H_{19} + \Delta H_2 - \Delta H_{20} + \Delta H_{21} - \Delta H_6 = -(533.51 \pm 1.73) kJ\cdotmol^{-1}$.

A summary of these thermochemical properties is presented as recommended values in table 3.⁺

М	$\frac{\Delta H_{\rm f}^{\circ}({\rm M}^{2+},{\rm aq})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta H_{f}^{\cup}(\mathrm{MCl}_{2}, \mathbf{c})}{\mathrm{k}\mathbf{J}\cdot\mathrm{mol}^{-1}}$	$\frac{\Delta H_{f}^{\circ}(\mathrm{MCl}_{2},\mathrm{aq})}{\mathrm{kJ}\cdot\mathrm{mol}^{-1}}$	$\frac{\Delta H_{\rm f}(\rm MCl_2~in~l~mol \cdot dm^{-3}~HCl)}{\rm kJ \cdot mol^{-1}}$
Mg	-465.96 ± 0.33	-644.28 ± 0.27	-800.1 ± 0.4	-794.0+0.3
Ca	-543.1 ± 0.8	- 796.0	-877.3 ± 0.8	-871.2 ± 1.0
Sr	-549.7 ± 0.9	-832.7 ± 0.9	-883.5 ± 1.0	-878.96 ± 0.80
Ba	-533.5 ± 1.7	-854.2 ± 1.7	-867.7 ± 1.7	-864.1 ± 1.7

TABLE 3. Recommended values of M²⁺(aq) and MCl₂ enthalpies of formation at 298.15 K

† Dr V. B. Parker pointed out to us that Samoilov (*Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk* 1952, 627; *Chem. Abstr.* 1953, 47, 437e) found that the enthalpy of solution of alkaline-earth chlorides becomes less negative in increasingly concentrated hydrochloric acid; however, all differences in the two right-hand columns of table 3 exceed Samoilov's $\Delta L/\Delta m$ values.

284

The authors thank P. A. G. O'Hare and G. K. Johnson (Argonne National Laboratory) and V. B. Parker (U.S. National Bureau of Standards) for helpful discussions.

REFERENCES

- 1. Parker, V. B.; Wagman, D. D.; Evans, W. H. U.S. Natl Bur. Stand. Tech. Note 270-6. 1971.
- O'Hare, P. A. G.; Boerio, J.; Frederickson, D. R.; Hoekstra, H. R. J. Chem. Thermodynamics 1977, 9, 963.
- 3. O'Hare, P. A. G.; Boerio, J.; Hoekstra, H. R. J. Chem. Thermodynamics 1976, 8, 845.
- 4. Morss, L. R.; Fuger, J.; Jenkins, H. D. B. J. Chem. Thermodynamics 1982, 14, 377.
- 5. Coffy, G.; Olofsson, G. J. Chem. Thermodynamics 1979, 11, 141.
- 6. Shin, C.; Criss, C. M. J. Chem. Thermodynamics 1979, 11, 663.
- 7. Vorob'ev, A. F.; Umyarova, R. S.; Urusov, V. S. Zh. Obsh. Khim. 1974, 44, 979.
- 8. Monaenkova, A. S.; Pashlova, E. B.; Vorob'ev, A. F. Dokl. Akad. Nauk SSSR 1971, 199, 1332.
- 9. Vasil'ev, V. P.; Vasil'eva, V. N.; Dmitrieva, N. G.; Kokurin, N. I. Zh. Neorg. Khim. 1981, 26, 30.
- 10. Brink, I. J.; Holley, C. E. Jr. J. Chem. Thermodynamics 1978, 10, 259.
- 11. Fitzgibbon, G. C.; Huber, E. J. Jr.; Holley, C. E. Jr. J. Chem. Thermodynamics 1973, 5, 577.
- 12. Dadgar, A.; Taherian, M. R. J. Chem. Thermodynamics 1977, 9, 711.
- 13. Shomate, C. H.; Huffman, E. H. J. Am. Chem. Soc. 1943, 65, 1625.
- 14. Bäckström, H. L. J. J. Am. Chem. Soc. 1925, 47, 2432.
- 15. Bäckström, H. L. J. J. Am. Chem. Soc. 1925, 47, 2443.
- 16. Greyson, J.; Snell, H. J. Phys. Chem. 1969, 73, 3208.
- 17. Morss, L. R. J. Chem. Thermodynamics 1975, 7, 709.
- 18. Nocera, D. G.; Morss, L. R.; Fahey, J. A. J. Inorg. Nucl. Chem. 1980, 42, 55.
- 19. Bernarducci, E. E.; Morss, L. R.; Miksztal, A. R. J. Solution Chem. 1979, 8, 717.
- 20. Prosen, E. J.; Kilday, M. V. J. Res. Natl Bur. Stand. Sect. A 1973, 77, 581.
- 21. Lohr, H. R.; Cunningham, B. B. J. Am. Chem. Soc. 1951, 73, 2025.
- Gunn, S. R.; Cunningham, B. B. J. Am. Chem. Soc. 1957, 79, 1563.
 Argue, G. R.; Mercer, E. E.; Cobble, J. W. J. Phys. Chem. 1961, 65, 2041.
- 24. Fuger, J. J.; Cunningham, B. B. J. Inorg. Nucl. Chem. 1963, 25, 1423.
- 25. Fitzgibbon, G. C.; Pavone, D.; Huber, E. J. Jr.; Holley, C. E. Jr. Los Alamos Sci. Lab. Rep. LA-3031. 1964.
- 26. Morss, L. R. J. Phys. Chem. 1971, 75, 392.
- 27. Fuger, J.; Peterson, J. R.; Stevenson, J. N.; Noé, M.; Haire, R. G. J. Inorg. Nucl. Chem. 1975, 37, 1725.
- 28. Raschella, D. L.; Fellows, R. L.; Peterson, J. R. J. Chem. Thermodynamics 1981, 13, 303.
- Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. Natl Bur. Stand. Tech. Note 270-3. 1968.
- 30. Parker, V. B. Thermal Properties of Aqueous Uni-univalent Electrolytes. NSRDS-NBS 2. U.S. Government Printing Office: Washington, D.C. 1965.
- 31. Holley, C. E. Jr.; Huber, E. J. Jr. J. Am. Chem. Soc. 1951, 73, 5577.
- 32. Vasil'ev, V. P.; Lobanov, G. A. Zh. Neorg. Khim. 1966, 11, 699.
- CODATA Recommended Key Values for Thermodynamics, 1977. J. Chem. Thermodynamics 1978, 10, 903.
- 34. Silvester, L. F.; Pitzer, K. S. J. Phys. Chem. 1977, 81, 1822.
- 35. Criss, C. M.; Cobble, J. W. J. Am. Chem. Soc. 1961, 83, 3223.