

Thermochemistry of some aqueous ions*

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Abstract: The enthalpies of formation of aqueous ions at infinitely dilution are key constants in thermochemistry of compounds of corresponding elements. New determinations of the enthalpies of formation of aqueous scandium(III), cobalt(II), and nickel(II) ions were carried out, because the literature data on these values were not quite reliable. To solve this task, corresponding methods were developed, and measurements of the enthalpies of solution of $\text{ScCl}_3(\text{cr})$, $\text{ScBr}_3(\text{cr})$, $\text{CoCl}_2(\text{cr})$, and $\text{NiCl}_2(\text{cr})$ in perchloric acid solutions of various concentrations were performed in an isoperibolic calorimeter LKB-8700. On the basis of the results obtained and corresponding literature data it was calculated:

$$\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -643.4 \pm 0.8 \text{ kJ/mol};$$

$$\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -59.0 \pm 0.6 \text{ kJ/mol};$$

$$\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -55.7 \pm 0.6 \text{ kJ/mol}.$$

These values were recommended as the most reliable at present. The standard entropy of the $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$ ion, $S^\circ(298.15 \text{ K}) = -270 \pm 12 \text{ J/K/mol}$, was calculated using Latimer-Powell equation. The standard Gibbs energy of formation of the aqueous Sc^{3+} ion ($-610.9 \pm 3.7 \text{ kJ/mol}$) was also calculated.

INTRODUCTION

Modern reference books on thermodynamics are based on key thermodynamic constants for corresponding elements and their compounds. By 'key' compounds we mean species whose thermochemical properties are of the strategic importance because many other compounds are dependent upon their thermochemical properties. The enthalpies of formation of aqueous ions at infinitely dilution are ones from the most important key values in thermochemistry of corresponding elements. They must be known with particularly high precision. However, analysis of the literature data has shown that reliable values of the enthalpies of formation of such ions as $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$, $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$, and $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ are absent. The present investigation is devoted to new experimental determinations of the enthalpies of formation of ions indicated by solution calorimetry method. To solve this task new thermochemical reaction cycles were devised, corresponding methods were developed, and measurements of enthalpies of solution of $\text{ScCl}_3(\text{cr})$, $\text{ScBr}_3(\text{cr})$, $\text{CoCl}_2(\text{cr})$, and $\text{NiCl}_2(\text{cr})$ in perchloric acid solutions of various concentrations were fulfilled. Moreover, the standard entropy of $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$ was calculated using Latimer-Powell equation. Taking into account selected values of $S^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ and $\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ the standard Gibbs energy of formation of this ion was also calculated.

SURVEY OF PRECEDING RESULTS

The value of $\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O})$ recommended in the reference book [1] is $-614.5 \pm 2.1 \text{ kJ/mol}$. The calculation of this value was based on the data of Bommer and Hohmann [2] and Huber *et al.* [3]. These

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authors measured the enthalpies of reactions of Sc(cr) with 4.02 mol/dm³ [2] and 5.09 mol/dm³ [3] HCl(aq). The calculation of corrections to these results for the transition to infinite dilution could not be carried out with a sufficient precision. It connected with the formation of some chloride complexes of scandium(III) at such considerable concentrations of HCl(aq). Therefore the $\Delta_f H^\circ(\text{Sc}^{3+}, \text{aq})$ value recommended in [1] is not quite reliable.

Recalculated literature data on enthalpies of formation of $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ and $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ are given in the Table 1 and Table 2, respectively. Recalculations were connected with the use of recent auxiliary values and taking into account the correction for transition to standard temperature. The data of the most old works [4,5] have only a historical interest because at that time experimental techniques, methods and materials were of a poor quality.

Table 1 Recalculated literature data on the enthalpy of formation of $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ at 298.15 K (in kJ/mol)

Authors	Method	$\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$
Thomsen [4]	Measuring enthalpies of reaction Co(cr) with HCl(aq) and some exchanged reactions with participation of CoHal ₂ (aq) (Hal = Cl, Br, I). Solution of CoCl ₂ (cr) in water	-62 to -65 -57
Fabre [5]	Measuring the enthalpy of reaction of Co(cr) with Br ₂ (sln)	-69
Katrin, Ferraro [6]	Measuring the enthalpy of solution of CoCl ₂ (cr) in water; concentration of CoCl ₂ (sln) is unknown	-58.5
Mischenko, Podgornaya [7]	Measuring of the enthalpy of solution of CoCl ₂ (cr), $\text{CoCl}_2(\text{cr}) + n\text{H}_2\text{O}(\text{l}) = \text{Co}^{2+}(\text{sln}) + 2\text{Cl}^-(\text{sln})$; $n = 2200$	-57.6 ± 1.0
Paoletti, Vacca [8]	The same; the n -value is unknown	-57.9
Vasilkova, Barvinok [9]	The same; $n = 50\,000 - 60\,000$	-58.8 ± 1.0
Brodale, Giauque [10]	Measuring the enthalpy of solution of CoSO ₄ ·6H ₂ O(cr) in water	-57.3 ± 1.6
Goldberg <i>et al.</i> [11]	Measuring the enthalpy of solution of CoSO ₄ (cr) in water ($n = 10\,000$)	-57.8 ± 1.8
Vasilev <i>et al.</i> [12]	Measuring the enthalpy of reaction $\text{Co}(\text{cr}) + 2\text{HClO}_4(\text{sln}) + \text{H}_2\text{O}_2(\text{sln}) = \text{Co}(\text{ClO}_4)_2(\text{sln}) + 2\text{H}_2\text{O}(\text{sln})$	-55.2 ± 0.7
Efimov, Furkaluk [13]	Measuring the enthalpies of solution of CoCl ₂ (cr) and CoBr ₂ (cr) in 0.001 mol/dm ³ HClO ₄ (aq)	-58.9 ± 0.4

There are some contradictions in the available data on the enthalpies of formation of ions $\text{Co}^{2+}(\text{aq})$ and $\text{Ni}^{2+}(\text{aq})$ (see Tables 1 and 2). So, the $\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$ value obtained in the [13] is close to the data on other works [7,9–11], but differs considerably from the result of Vasil'ev *et al.* [12]. The $\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$ value obtained in [13] is close to the result of work [14], but differs essentially from data of Vasil'ev *et al.* [15,16]. The reasons of these contradictions are not quite clear.

DETERMINATION OF THE ENTHALPY OF FORMATION OF $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$

The enthalpy of formation of aqueous scandium(III) ion was determined using two independent calorimetric methods. Thermochemical cycles used for the calculation of the $\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15\text{ K})$ values in first and second cases are given below:

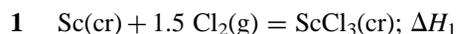
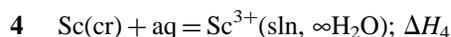
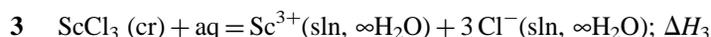
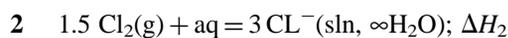
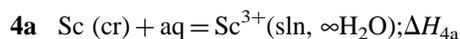
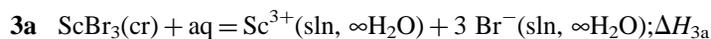
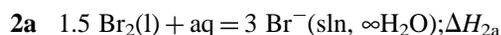
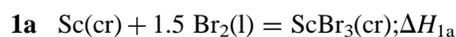


Table 2 Recalculated literature data on the enthalpy of formation of $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ at 298.15 K (in kJ/mol)

Authors	Method	$\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$
Thomsen [4]	Measuring enthalpies of reaction $\text{Ni}(\text{cr})$ with $\text{HCl}(\text{aq})$ and some exchanged reactions with participation of $\text{NiHal}_2(\text{aq})$ ($\text{Hal} = \text{Cl}, \text{Br}, \text{I}$). Solution of $\text{NiCl}_2(\text{cr})$ in water	-57.7 to -60.6
Fabre [5]	Measuring the enthalpy of reaction of $\text{Ni}(\text{cr})$ with $\text{Br}_2(\text{sln})$	-53.9
Ko, Hepler [14]	Measuring the enthalpy of solution of $\text{NiCl}_2(\text{cr})$ in water	-62.3
Vasil'ev <i>et al.</i> [15]	Measuring the enthalpies of reactions: $\text{Ni}(\text{cr}) + 2\text{HClO}_4(\text{sln}) + \text{H}_2\text{O}_2(\text{sln}) = \text{NiClO}_4(\text{sln}) + 2\text{H}_2\text{O}(\text{sln})$ and $\text{Ni}(\text{cr}) + 2\text{HCl}(\text{sln}) + \text{H}_2\text{O}_2(\text{sln}) = \text{NiCl}_2(\text{sln}) + \text{H}_2\text{O}(\text{sln})$	-55.0 ± 1.0
Vasil'ev <i>et al.</i> [16]	Measuring the enthalpies of reactions: $\text{Ni}(\text{cr}) + \text{Br}_2(\text{sln}) = \text{NiBr}_2(\text{sln})$ and $\text{NiBr}_2(\text{sln}, n\text{H}_2\text{O}, m\text{HClO}_4) + \text{Br}_2(\text{sln}) = \text{NiBr}_2(\text{sln})$	-52.2 ± 0.5
Efimov, Furkaluk [13]	Measuring the enthalpies of solution of $\text{NiCl}_2(\text{cr})$, $\text{NiBr}_2(\text{cr})$, and $\text{NiI}_2(\text{cr})$ in 0.001 mol/dm^3 $\text{HClO}_4(\text{aq})$	-51.8 ± 0.9
		-55.7 ± 0.3



$$\Delta H_4 = \Delta H_1 - \Delta H_2 + \Delta H_3 = \Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}).$$



$$\Delta H_{4a} = \Delta H_{1a} - \Delta H_{2a} + \Delta H_{3a} = \Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}).$$

The values of enthalpies of formation of $\text{ScCl}_3(\text{cr})$ ($\Delta H_1 = -944.8 \pm 0.6 \text{ kJ/mol}$) and $\text{ScBr}_3(\text{cr})$ ($\Delta H_{1a} = -781.5 \pm 1.3 \text{ kJ/mol}$) were determined in our works [17,18]. The values of enthalpies of formation of ions $\text{Cl}^-(\text{sln}, \infty\text{H}_2\text{O})$ ($\Delta H_{2/3} = -167.08 \pm 0.10 \text{ kJ/mol}$) and $\text{Br}^-(\text{sln}, \infty\text{H}_2\text{O})$ ($\Delta H_{2a/3} = -121.41 \pm 0.15 \text{ kJ/mol}$) are also known with a high precision [19]. Therefore the task consisted in the determination of the values of ΔH_3 and ΔH_{3a} only. To solve this task the enthalpies of solution of $\text{ScCl}_3(\text{cr})$ and $\text{ScBr}_3(\text{cr})$ in $\text{HClO}_4(\text{aq})$ were measured. All measurements were carried out in 0.1 dm^3 reaction vessel of an isoperibolic calorimeter LKB-8700. Electrical energy input was used to calibrate the calorimetric system. The salts were loaded into 0.001 dm^3 Pyrex ampoules in a glove box filled with dry argon. The ampoules were sealed off without a contact of the samples with air. The substances were weighed on a microbalance 'Mettler M5SA'. The masses of samples are judged to be accurate to 0.01%.

High purity scandium halide samples were used for this investigation. The scandium and chlorine contents in the ScCl_3 sample were found to be (mass per cent): 29.67 ± 0.10 and 70.29 ± 0.05 (calculated values are 29.71% and 70.29%). The purity of the ScBr_3 sample was also established by chemical

analyses which yielded the results (in mass per cent): Sc, 15.77 ± 0.07 ; Br, 84.14 ± 0.11 (calculated values are 15.79% and 84.21%). The X-ray powder diffraction analysis showed that no other crystalline phases (except ScCl_3 or ScBr_3 , respectively) were detected in the samples. The HClO_4 solvent was prepared from the 'Particularly pure grade' acid and analyzed by potentiometric titration with standard NaOH solution.

Results of the measurements are given in the Table 3. The ΔH_3 and ΔH_{3a} values obtained are given in the last column of the table. For their calculations corrections ΔH_{D-H} for a transition to infinite dilution were introduced to measured values of enthalpies of solution of scandium halides. These corrections were calculated using the Debye–Hückel relation [20]. The precision of the mean values in Table 3 was calculated as a product 't.σ', where σ is the standard deviation of the mean, and t the Student coefficient. The total uncertainties of the $\Delta_{\text{sol}}H^\circ_\infty$ values were found to be equal ± 0.7 kJ/mol and ± 0.6 kJ/mol for solution of $\text{ScCl}_3(\text{cr})$ and $\text{ScBr}_3(\text{cr})$, respectively, taking into account the reproducibility of results and uncertainty of the ΔH_{D-H} corrections estimated in ± 0.3 kJ/mol (or 10 relative per cent).

Table 3 Results of experiments on the determination of the enthalpies of solution of $\text{ScHal}_3(\text{cr})$ in $\text{HClO}_4(\text{aq})$ (Hal = Cl or Br)

Amount of $\text{ScHal}_3(\text{cr})$ (10^4 n/mol)	Concentration of the HClO_4 solution (mol/dm^3)	Enthalpy of solution of $\text{ScHal}_3(\text{cr})$ measured, ($\Delta_{\text{sol}}H^\circ$, kJ/mol)	Correction for the transition to infinite dilution, ($\Delta_{\text{sol}}H^\circ_{D-H}$, kJ/mol)	Enthalpy of solution of $\text{ScHal}_3(\text{cr})$ at infinite dilution, ($\Delta_{\text{sol}}H^\circ_\infty$, kJ/mol)
Solution $\text{ScCl}_3(\text{cr})$				
3.5156	0.099	-196.72	-2.85	-199.57
5.2273	0.099	-196.55	-2.93	-199.48
5.5285	0.099	-196.77	-2.94	-199.71
3.7244	0.010	-197.06	-1.73	-198.79
5.3128	0.010	-197.85	-1.91	-199.76
6.1116	0.010	-197.05	-2.00	-199.05
Mean: -199.39 ± 0.41				
Solution $\text{ScBr}_3(\text{cr})$				
2.6971	0.099	-224.68	-2.81	-227.49
3.0132	0.099	-224.16	-2.82	-226.98
3.2692	0.099	-224.49	-2.83	-227.32
2.9871	0.010	-224.84	-1.62	-226.46
3.5959	0.010	-225.01	-1.71	-226.72
4.1594	0.010	-225.18	-1.78	-226.98
4.1704	0.010	-224.75	-1.78	-226.53
Mean: -226.93 ± 0.35				

On the basis of the ΔH_3 and ΔH_{3a} values obtained and the of ΔH_1 , ΔH_2 , ΔH_{1a} and ΔH_{2a} values indicated above, two values of the standard enthalpy of formation of aqueous scandium(III) ion were calculated:

$$\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty \text{H}_2\text{O}, 298.15 \text{ K}) = -643.0 \pm 1.0 \text{ kJ/mol (cycle of reactions 1–3);}$$

$$\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty \text{H}_2\text{O}, 298.15 \text{ K}) = -644.2 \pm 1.5 \text{ kJ/mol (cycle of reactions 1a–3a).}$$

Both values are in a good agreement. It seems that the use of perchloric acid as solvent permitted to prevent side processes of hydrolysis and formation of complex compounds of scandium(III) ion (see also [21]). The weighted mean of two last values was recommended as the most reliable, at present, value of the enthalpy of formation of aqueous scandium(III) ion:

$$\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty \text{H}_2\text{O}, 298.15 \text{ K}) = -643.4 \pm 0.8 \text{ kJ/mol.}$$

THE EVALUATION OF THE STANDARD ENTROPY AND THE GIBBS ENERGY OF FORMATION OF THE $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$ ION

The reliable experimental data permitting to calculate the standard entropy of $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$ are absent. Therefore this value was calculated using Latimer–Powell equation [22,23]:

$$S^\circ(298.15 \text{ K}) - 1.5R \ln A = -1130z/(r+x)^2 + 155,$$

where $S^\circ(298.15 \text{ K})$ is the standard entropy of the aqueous ion (in J/K/mol), R is the gas constant, A the atomic mass of corresponding element, r -radius of ion in the crystalline substance (in Å) and x is a constant that is adopted to be 2 for positive ions and 1 for negative ions.

The following equation was obtained by the least squares method:

$$S^\circ(298.15 \text{ K}) - 1.5 \ln A = 135.4 - 3574.0(1/(r+2)).$$

It was calculated using the enough reliable $S^\circ(298.15 \text{ K})$ values for aqueous Ga^{3+} , In^{3+} , Ce^{3+} , Nd^{3+} , Dy^{3+} and Lu^{3+} ions [1] and the values of radius of these ions [24]. The last equation was used for practical calculation of the standard entropy of aqueous ion of scandium(III), found to be:

$$S^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -270 \pm 12 \text{ J/K/mol}.$$

The uncertainty of the entropy of the $\text{Sc}^{3+}(\text{aq})$ ion was calculated taking into account uncertainties of the entropy values of indicated six ions [1] and the values of radius of these ions [24].

The Gibbs energy of formation of aqueous scandium(III) ion was calculated using the reaction $\text{Sc}(\text{cr}) + 3\text{H}^+(\text{sln}, \infty\text{H}_2\text{O}) = \text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O}) + 1.5\text{H}_2(\text{g})$ and the relation $\Delta_r G^\circ(298.15 \text{ K}) = \Delta_r H^\circ(298.15 \text{ K}) - 298.15 \Delta_r S^\circ(298.15 \text{ K})$. It is obviously that $\Delta_r G^\circ(298.15 \text{ K}) = \Delta_f G^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ and $\Delta_r H^\circ(298.15 \text{ K}) = \Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$. Therefore it was found:

$$\begin{aligned} \Delta_f G^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) &= (-643.4 \pm 0.8) - 298.15(-109 \pm 12) \cdot 10^{-3} \\ &= -610.9 \pm 3.7 \text{ kJ/mol}. \end{aligned}$$

The $\Delta_r S^\circ(298.15 \text{ K})$ value was calculated using the $S^\circ(298.15 \text{ K})$ values (in J/K/mol) for $\text{Sc}^{3+}(\text{sln}, \infty\text{H}_2\text{O})$ (-270 ± 12), $\text{H}_2(\text{g})$ (130.52 ± 0.02) and $\text{Sc}(\text{cr})$ (34.79 ± 0.15).

It seems that the value of $\Delta_f G^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ obtained is more reliable than that based on electrochemical data of Noddack & Brukl [25].

DETERMINATION OF THE ENTHALPIES OF FORMATION OF THE AQUEOUS $\text{Co}(\text{II})$ AND $\text{Ni}(\text{II})$ IONS

New determinations of the enthalpies of formation of the $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ and $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ ions were carried out by solution calorimetry. They were based on precise measurements of enthalpies of solution of $\text{CoCl}_2(\text{cr})$ and $\text{NiCl}_2(\text{cr})$ in dilute $\text{HClO}_4(\text{aq})$ solutions of different concentrations.

The auxiliary values of the enthalpies of formation of $\text{CoCl}_2(\text{cr})$ and $\text{NiCl}_2(\text{cr})$ are known with a high precision. Therefore, combining these values with the enthalpies of solution of corresponding salts at infinite dilution allows to calculate the reliable values $\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$ and $\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O})$. The $\Delta_f H^\circ(\text{CoCl}_2, \text{cr}, 298.15 \text{ K})$ value was adopted to be equal to $-311.05 \pm 0.26 \text{ kJ/mol}$ (as the weighted mean of the results of works of [26,27]). The $\Delta_f H^\circ(\text{NiCl}_2, \text{cr}, 298.15 \text{ K})$ value was selected to be $-304.75 \pm 0.15 \text{ kJ/mol}$ (as the weighted mean of the results of works of [28,29]).

High purity cobalt and nickel chlorides were used for these measurements. The Co and Cl contents in the CoCl_2 sample were found to be 45.40 ± 0.15 mass per cent and 54.60 ± 0.10 mass per cent, respectively (calculated values are 45.39% and 54.61%). The purity of the NiCl_2 sample was also established by chemical analysis which yielded the results. Ni, 45.30 ± 0.15 mass per cent; Cl, 54.65 ± 0.10 mass per cent (calculated values are 45.30% and 54.70%). According to X-ray analysis the CoCl_2 and NiCl_2 samples were pure phases.

Methods of measurements were similar to the ones used for the solution of scandium halides. Results of these experiments are given in the Table 4. Data of last column of the table were used to calculate the values of enthalpies of solution of $\text{CoCl}_2(\text{cr})$ and $\text{NiCl}_2(\text{cr})$ at infinite dilution ($\Delta_{\text{sol}} H^\circ_\infty$). Two equations

Table 4 Results of measurements of the enthalpies of solutions of CoCl₂(cr) and NiCl₂(cr) in HClO₄(aq)

10 ⁴ n/mol	C (HClO ₄), mol/dm ³	μ	(Δ _{sol} H° + ΔH° _{D-H}), kJ/mol
Solution of CoCl ₂ (cr)			
4.6413	0.01	0.0239	-82.09
5.7968	0.01	0.0274	-82.27
7.0871	0.01	0.0313	-82.28
7.4100	0.01	0.0322	-82.25
7.9769	0.01	0.0339	-82.22
6.4697	0.10	0.119	-81.40
8.9663	0.10	0.126	-81.52
5.1922	0.20	0.213	-80.75
6.6132	0.20	0.218	-80.67
Solution of NiCl ₂ (cr)			
4.4104	0.001	0.0142	-84.96
4.4219	0.001	0.0143	-84.67
4.5840	0.001	0.0148	-84.85
5.2129	0.001	0.0166	-85.02
5.4946	0.001	0.0175	-84.84
7.8150	0.10	0.123	-84.11
8.1114	0.10	0.124	-84.03
6.0429	0.20	0.216	-83.26
7.4841	0.20	0.220	-83.19

Note: n = amount of salt (in mol); $C_{(\text{HClO}_4)}$ = concentration of aqueous HClO₄ solution; $\Delta_{\text{sol}}H^\circ$ = the measured enthalpy of solution of salt; μ = ion strength of a solution; $\Delta H^\circ_{\text{D-H}}$ = the Debye–Hückel [30] limiting law contribution in the enthalpy of dilution of the solute to infinite dilution. This contribution is caused by a change of electrostatic ion interaction under the dilution. The method of calculation of the $\Delta H^\circ_{\text{D-H}}$ -values was indicated earlier.

$(\Delta_{\text{sol}}H^\circ + \Delta H^\circ_{\text{D-H}}) = \Delta_{\text{sol}}H^\circ_\infty + b\mu$, where b , a constant, and μ the ion strength of solution, were obtained by the least squares method. It was found: $\Delta_{\text{sol}}H^\circ_\infty$ (CoCl₂, cr) = -82.4 ± 0.3 kJ/mol ($b = 8.11$); $\Delta_{\text{sol}}H^\circ_\infty$ (NiCl₂, cr) = -85.0 ± 0.3 kJ/mol ($b = 8.01$).

To verify the reliability of the method of determination of the $\Delta_{\text{sol}}H^\circ_\infty$ values, another way of a calculation of the enthalpy of solution of CoCl₂(cr) at infinite dilution was also used. It consists in a graphic extrapolation of the dependence $\Delta_{\text{sol}}H^\circ(\text{CoCl}_2, \text{cr}) = f(m^{1/2})$, where m is the molality of a solution, to infinite dilution ($m = 0$). The result obtained (-82.6 ± 0.4 kJ/mol) proves to be in an excellent agreement with the preceding $\Delta_{\text{sol}}H^\circ_\infty$ (CoCl₂, cr) value.

The values of $\Delta_{\text{sol}}H^\circ_\infty$ (CoCl₂, cr) and $\Delta_{\text{sol}}H^\circ_\infty$ (NiCl₂, cr) obtained were combined with enthalpies of formation of these salts and the Cl⁻(sln, ∞H₂O) ion to derive the $\Delta_f H^\circ(298.15 \text{ K})$ values for Co²⁺(sln, ∞H₂O) and Ni²⁺(sln, ∞H₂O) ions:

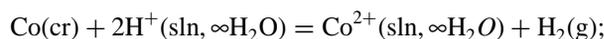
$$\begin{aligned} \Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) &= \\ &= \Delta_{\text{sol}}H^\circ_\infty(\text{CoCl}_2, \text{cr}) - 2\Delta_f H^\circ(\text{Cl}^-, \text{sln}, \infty\text{H}_2\text{O}) + \Delta_f H^\circ(\text{CoCl}_2, \text{cr}, 298.15 \text{ K}) = \\ &= (-82.4 \pm 0.3) - 2(-167.08 \pm 0.10) + (-311.08 \pm 0.26) = -59.3 \pm 0.4 \text{ kJ/mol.} \end{aligned}$$

$$\begin{aligned} \Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) &= \\ &= \Delta_{\text{sol}}H^\circ_\infty(\text{NiCl}_2, \text{cr}) - 2\Delta_f H^\circ(\text{Cl}^-, \text{sln}, \infty\text{H}_2\text{O}) + \Delta_f H^\circ(\text{NiCl}_2, \text{cr}, 298.15 \text{ K}) = \\ &= (-85.0 \pm 0.3) - 2(-167.08 \pm 0.10) + (-304.75 \pm 0.15) = -55.6 \pm 0.4 \text{ kJ/mol.} \end{aligned}$$

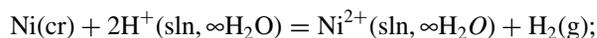
The results obtained are in a good agreement with the previous data [13], but differ considerably from the data of Vasil'ev *et al.* [12,15,16] (see Tables 1 and 2). As the analysis showed that Vasil'ev *et al.* used more complicated methods for the determination of enthalpies of formation of aqueous Co²⁺ and Ni²⁺

ions than ones used in given work; moreover authors [12,15,16] used a greater quantity of auxiliary values under calculations. Therefore it seems that our results are more reliable.

It is interesting that we carried out also the calculation of the enthalpies of formation of $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ and $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ ions using another way. This way was based on reactions indicated below and a relation $\Delta_f H^\circ(298.15 \text{ K}) = \Delta_r G^\circ(298.15 \text{ K}) + 298.15 \Delta_r S^\circ(298.15 \text{ K})$. It was found:



$$\begin{aligned} \Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) &= \Delta_r H^\circ(298.15 \text{ K}) = \\ &= \Delta_r G^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) + 298.15 \Delta_r S^\circ(298.15 \text{ K}) = \\ &= (-55.6 \pm 1.5) + 298.15(-10.5 \pm 4.0) \times 10^{-3} = -58.7 \pm 1.8 \text{ kJ/mol.} \end{aligned}$$



$$\begin{aligned} \Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) &= \Delta_r H^\circ(298.15 \text{ K}) = \\ &= \Delta_r G^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) + 298.15 \Delta_r S^\circ(298.15 \text{ K}) = \\ &= (-47.8 \pm 1.5) + 298.15(-29.75 \pm 2.8) \times 10^{-3} = -56.7 \pm 1.7 \text{ kJ/mol.} \end{aligned}$$

The selection of the $\Delta_r G^\circ(298.15 \text{ K})$ and $S^\circ(298.15 \text{ K})$ values for aqueous cobalt(II) and nickel(II) ions was grounded in the work [31]. Obtained values of the enthalpies of formation of aqueous Co^{2+} and Ni^{2+} ions at infinite dilution prove to be essentially nearer to the results of this investigation than to Vasil'ev *et al.* results. It proves that our data are more preferable than data of previous works [12,15,16].

Efimov & Furkaluk [13] found the following values of enthalpies of formation of aqueous cobalt(II) and Ni(II) ions at 298.15 K:

$$\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}) = -58.8 \pm 0.5 \text{ kJ/mol (from data on the } \Delta_{\text{sol}} H^\circ(\text{CoBr}_2, \text{cr});$$

$$\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}) = -55.3 \pm 0.6 \text{ kJ/mol (from data on the } \Delta_{\text{sol}} H^\circ(\text{NiBr}_2, \text{cr});$$

The uncertainty of these values were slightly increased by us taking into account the inaccuracy of extrapolation of their results to infinite dilution.

As the most reliable values of the enthalpies of formation of aqueous Co^{2+} and Ni^{2+} ions we recommend the weighted means from results of this investigation and the reference [13]:

$$\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -59.1 \pm 0.3 \text{ kJ/mol;}$$

$$\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -55.7 \pm 0.3 \text{ kJ/mol.}$$

Two values of the enthalpy of formation of $\text{Co}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ and three values of the enthalpy of formation of $\text{Ni}^{2+}(\text{sln}, \infty\text{H}_2\text{O})$ were used in these calculations.

CONCLUSIONS

For the first time a precise experimental determination was carried out for the enthalpy of formation of the aqueous scandium(III) ion at infinite dilution.

The value $-643.4 \pm 0.8 \text{ kJ/mol}$ is recommended as the most reliable at present $\Delta_f H^\circ(\text{Sc}^{3+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K})$ value.

The values of standard entropy ($-270 \pm 12 \text{ J/K/mol}$) and Gibbs energy of formation at 298.15 K ($-610.9 \pm 3.7 \text{ kJ/mol}$) for this ion were also calculated.

All three thermodynamic constants for aqueous Sc^{3+} ion are in the mutual agreement.

New experimental determinations of the enthalpies of formation of aqueous cobalt(II) and nickel(II) ions were carried out taking into account some contradictions in available data on these thermochemical parameters. On the basis of results obtained and the following literature data, values of these parameters are recommended as the most reliable at present:

$$\Delta_f H^\circ(\text{Co}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -59.1 \pm 0.3 \text{ kJ/mol};$$

$$\Delta_f H^\circ(\text{Ni}^{2+}, \text{sln}, \infty\text{H}_2\text{O}, 298.15 \text{ K}) = -55.7 \pm 0.3 \text{ kJ/mol sln}.$$

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