NICKEL SULFATE AQUEOUS SOLUTIONS THERMAL CHEMISTRY AND ENTHALPY OF Ni²⁺ CATION FORMATION AT THE TEMPERATURE 298.15 K

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Abstract

Calorimeter with an isothermal shell was used at a temperature of 298.15 K to measure the following parameters: enthalpy of NiSO₄₉₀ dissolution in water followed by generation of two molar concentration solutions; enthalpy of four NiSO₄ aqueous solutions dilution having various molar concentrations followed by generation of solutions with approximately the same concentration values. Based on the data obtained, enthalpy and ion association constant in the NiSO₄ aqueous solution, as well as standard enthalpy of the aqueous solution formation, were determined for the indicated compound. The latter value made it possible to establish a more accurate value of standard enthalpy in the Ni²⁺ cation formation in an aqueous solution, which turned out to be equal to −52.3 ± 0.5 kJ/mol

Keywords

Dissolution enthalpy, dilution enthalpy, thermochemical characteristics, ion association, standard compound/ion formation enthalpies, aqueous solutions

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Introduction. Department of General and Inorganic Chemistry of the D. Mendeleev University of Chemical Technology of Russia and the Department of Chemistry of the Bauman Moscow State Technical University are carrying out scientific and research work to redefine and specify thermo-chemical characteristics of compositions and ions formation [1]. As part of this work, the task was set to clarify the value of standard enthalpy in the Ni²⁺ nickel cation formation in the aqueous solution.

Nickel metal is not only the basis of such important alloys as nichrome, Monel, Hastelloy, etc., but also being an alloying constituent is a part of other materials widely used in engineering and technology [2]. Its compositions, salts in particular, which provide Ni²⁺ cation in solutions, are extensively employed
both in chemistry and in technology [2, 3], and are also of certain interest for biologists [3].

Standard enthalpy value of the Ni$^{2+}$ cation formation provided in the most authoritative domestic [4] and foreign [5, 6] reference books possesses a relative error of about 5 %, which appears to be absolutely unsatisfactory. NiSO$_4$(k) nickel sulfate was selected as a reference electrolyte to find the value of this thermodynamic characteristic, since its enthalpy generation in the group of similar compositions was determined with the lowest relative error.

**Experimental part.** To obtain reliable results when conducting thermochemical measurements, two samples of crystalline nickel sulfate were used.

The first sample was synthesized from the NiCl$_2$(k) anhydrous salt, which was treated with the concentrated solution of sulfuric acid. At the end of the chemical reaction and after cessation of the HCl evolution, the solution was evaporated to dryness. Dry residue after calcination on a sand bath was dissolved in a small amount of distilled water accompanied by heating. The resulting solution was filtered. The filtrate was evaporated at the temperature of 70–80 °C before the crystal haze. Then, the contents were cooled to room temperature. Hazed crystals of nickel sulfate appearing during this procedure were separated using the Buchner funnel. After preliminary drying between the filter paper sheets, crystals were placed in a desiccator above the open surface of P$_2$O$_5$(k) for further dehydration and storage.

The second sample of nickel sulfate was obtained from its crystalline hydrate by carefully heating the latter under reduced pressure for 2 hours [7, 8]. Chemical reagents used in the synthesis of samples had purity characteristics not lower than the chemically pure class.

Residual water content in the obtained samples of anhydrous NiSO$_4$(k) determined by titration according to the Fisher method did not exceed 0.05 % (mass.) with the method accuracy of ± 0.01 % (mass.). Both anhydrous samples appeared to be light yellow crystals, greenish in the air due to their absorption of water. They were stored in closed containers in a dry chamber above the P$_2$O$_5$(k) open surface. When measuring the dissolution enthalpy in water and the enthalpy of aqueous solutions dilution, no differences in behavior were observed between them.

Thermochemical measurements were performed in a calorimeter with an isothermal shell [9], which had the following characteristics:

- thermometric sensitivity: 5·10$^{-5}$ K;
- calorimetric sensitivity: 0.05 J;
thermometer (thermistor) resistance at the temperature 298.15 K: 10020 Ω; thermometer resistance temperature coefficient: 350 Ω/K; accuracy of maintaining constant temperature of the isothermal shell: ± 0.005 K.

Calorimetric liquid mixing was carried out using a magnetic mixer. Calorimeter thermal value was determined by electrical technique with a systemic error of not more than 0.1 %. Reliability of the calorimetric installation was checked by measuring the KClₙₜ dissolution enthalpy in water accompanied by generation of a molar concentration solution equal to 0.02 mol/kg. The obtained value of this characteristic, i.e., 17.45 ± 0.08 kJ/mol, coincided within the error with the most reliable literature data [10].

Results of measuring the NiSO₄ₙₜ dissolution enthalpy in water and the enthalpy of this salt solutions dilution, i.e., the electrolyte, are presented in Tables 1 and 2.

\textit{Table 1}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Initial temperature during the experiment $t₀$, Ω & Heat exchange correction $δ$, Ω & Corrected temperature raise during the experiment $ΔR$, Ω & Salt batch weight $m$, NiSO₄ₙₜ, mg & Quantity of heat generated during the experiment due to dissolution $Q$, J & Dissolution enthalpy $ΔH$, kJ/mol \\
\hline
10032.18 & -0.52 & -10.36 & 50.24 & 29.02 & -89.4 \\
10027.37 & 0.44 & -9.48 & 45.81 & 26.55 & -89.7 \\
10020.56 & 0.68 & -10.10 & 49.16 & 28.30 & -89.1 \\
10027.49 & -0.05 & -11.21 & 54.29 & 31.40 & -89.5 \\
10039.11 & 0.27 & -11.34 & 55.07 & 31.77 & -89.3 \\
\hline
\end{tabular}
\end{table}

$C_m = 0.0018 \text{ mol/kg}; ΔH_{mₜ} = -89.4 ± 0.1 \text{ kJ/mol}$

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Initial temperature during the experiment $t₀$, Ω & Heat exchange correction $δ$, Ω & Corrected temperature raise during the experiment $ΔR$, Ω & Salt batch weight $m$, NiSO₄ₙₜ, mg & Quantity of heat generated during the experiment due to dissolution $Q$, J & Dissolution enthalpy $ΔH$, kJ/mol \\
\hline
10045.91 & 0.68 & 16.49 & 80.27 & 46.20 & -89.1 \\
10031.82 & -0.16 & 16.78 & 81.56 & 47.01 & -89.2 \\
10037.13 & -0.08 & 17.49 & 85.21 & 48.99 & -89.0 \\
10029.69 & -0.08 & 17.62 & 85.94 & 49.37 & -88.9 \\
10018.23 & -0.55 & 16.34 & 79.13 & 45.76 & -89.5 \\
\hline
\end{tabular}
\end{table}

$C_m = 0.0030 \text{ mol/kg}; ΔH_{mₜ} = -89.2 ± 0.1 \text{ kJ/mol}$

\textit{Note.} $C_m$ is solution molal concentration average value; $ΔH_{mₜ}$ is dissolution enthalpy average value.
### Table 2

Values of the dilution enthalpy $\Delta H_{\text{dil}}$ of NiSO$_4$ aqueous solutions at the temperature 298.15 K

<table>
<thead>
<tr>
<th>Initial temperature during the experiment $t_0$, $\Omega$</th>
<th>Heat exchange correction $\delta$, $\Omega$</th>
<th>Corrected temperature raise during the experiment $\Delta R_0$, $\Omega$</th>
<th>Quantity of heat generated during the experiment due to dissolution $Q$, J</th>
<th>Dilution enthalpy $\Delta H_{\text{dil}}$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>10020.18</td>
<td>0.105</td>
<td>-0.342</td>
<td>0.959</td>
<td>-1.38</td>
</tr>
<tr>
<td>10021.37</td>
<td>0.127</td>
<td>-0.352</td>
<td>0.987</td>
<td>-1.42</td>
</tr>
<tr>
<td>10022.44</td>
<td>0.134</td>
<td>-0.332</td>
<td>0.931</td>
<td>-1.34</td>
</tr>
<tr>
<td>10020.95</td>
<td>0.096</td>
<td>-0.340</td>
<td>0.952</td>
<td>-1.37</td>
</tr>
</tbody>
</table>

$C_{m_{\text{in}}} = 0.2780$ mol/kg; $C_{m_{f}} = 0.0035$ mol/kg; $V_{\text{dil}} = 2.5$ ml; $\Delta H_{\text{dil, av}} = -1.38 \pm 0.02$ kJ/mol

| 10018.21                                              | -0.056                          | -0.328                 | 0.917                           | -1.32               |
| 10020.76                                              | -0.078                          | -0.337                 | 0.945                           | -1.36               |
| 10020.36                                              | -0.094                          | -0.318                 | 0.890                           | -1.28               |
| 10015.18                                              | -0.102                          | -0.330                 | 0.924                           | -1.33               |

$C_{m_{\text{in}}} = 0.1390$ mol/kg; $C_{m_{f}} = 0.0035$ mol/kg; $V_{\text{dil}} = 5.0$ ml; $\Delta H_{\text{dil, av}} = -1.32 \pm 0.02$ kJ/mol

| 10027.29                                              | 0.094                           | -0.256                 | 0.716                           | -1.03               |
| 10029.42                                              | 0.083                           | -0.261                 | 0.730                           | -1.05               |
| 10015.87                                              | -0.075                          | -0.251                 | 0.702                           | -1.01               |
| 10011.61                                              | -0.066                          | -0.253                 | 0.709                           | -1.02               |

$C_{m_{\text{in}}} = 0.0695$ mol/kg; $C_{m_{f}} = 0.0035$ mol/kg; $V_{\text{dil}} = 10.0$ ml; $\Delta H_{\text{dil, av}} = -1.03 \pm 0.02$ kJ/mol

| 10017.00                                              | -0.047                          | 0.145                  | 0.407                           | -0.585              |
| 10018.14                                              | -0.064                          | 0.148                  | 0.414                           | -0.595              |
| 10030.92                                              | 0.028                           | 0.143                  | 0.400                           | -0.574              |
| 10028.81                                              | 0.036                           | 0.145                  | 0.406                           | -0.583              |

$C_{m_{\text{in}}} = 0.0348$ mol/kg; $C_{m_{f}} = 0.0035$ mol/kg; $V_{\text{dil}} = 20.0$ ml; $\Delta H_{\text{dil, av}} = -0.584 \pm 0.004$ kJ/mol

Note. $C_{m_{\text{in}}}$ and $C_{m_{f}}$ are molal concentrations of initial and final solutions; $\Delta H_{\text{dil, av}}$ are dilution enthalpy average values; $V_{\text{dil}}$ is diluted solution volume.

Experimental data processing, results and discussion. Thermochemical data on dilution enthalpies were processed within the framework of the existing concept on a present equilibrium in solution between ions and an ion pair of the
same type [11, 12] in cases of describing a solution of totally ionized electrolyte of any concentration using the Debye — Hückel theory. Source data for such processing are given in Table 3. As a result of processing the obtained data, enthalpy and ion association constant in the NiSO₄ aqueous solution were determined, which constituted the following:

\[ \Delta H_{\text{ass}} = 5 \pm 1 \text{ kJ/mole}; \ K_{\text{ass}} = 500 \pm 10. \]

Table 3

<table>
<thead>
<tr>
<th>Molar concentration</th>
<th>NiSO₄ solution dilution enthalpy, kJ/mol</th>
<th>Enthalpy difference: [ \Delta H_{\text{dil, eq}} - \Delta H_{\text{dil, D-} - \text{H}} \text{ kJ/mol} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial, C_{m in}</td>
<td>final, C_{m f}</td>
<td>[ \text{experimentally determined } \Delta H_{\text{dil, eq}} ]</td>
</tr>
<tr>
<td>0.2780</td>
<td>0.0035</td>
<td>[ -1.380 \pm 0.020 ]</td>
</tr>
<tr>
<td>0.1390</td>
<td>0.0035</td>
<td>[ -1.320 \pm 0.020 ]</td>
</tr>
<tr>
<td>0.0695</td>
<td>0.0035</td>
<td>[ -1.030 \pm 0.020 ]</td>
</tr>
<tr>
<td>0.0348</td>
<td>0.0035</td>
<td>[ -1.584 \pm 0.004 ]</td>
</tr>
</tbody>
</table>

Calculations demonstrate that in the studied solutions of a molar concentration equal to 0.0018 and 0.0030 mol/kg, degree of dissociation of ion pairs is close to 1, i.e., 0.998 and 0.997, respectively.

The \( \Delta H^0 \text{NiSO}_4(\text{k}) \) standard dissolution enthalpy in water was calculated by the ratio [14]:

\[ \Delta H^0_s = \Delta H_s \text{ av} + (1 - \alpha) \Delta H_{\text{dis}} + \Delta H_{\text{dil, D-} - \text{H}}, \]

where \( \Delta H_s \text{ av} \) is the dissolution enthalpy (average value) accompanied by generation of the \( C_m \text{ av} \) molar concentration solution; \( \alpha \) is the degree of dissociation of ion pairs; \( \Delta H_{\text{dis}} \) is the enthalpy of the ion pairs dissociation, while \( \Delta H_{\text{dil}} = -\Delta H_{\text{ass}} \); \( \Delta H_{\text{dil, D-} - \text{H}} \) is the enthalpy of diluting the \( C_m \) molar concentration solution accompanied by generation of an infinitely diluted solution calculated on the basis of the Debye — Hückel theory in the second approximation.

In regard to the two mentioned above solutions, this characteristic value would be as follows:

\[ \Delta H^0_s = (-89.4 \pm 0.1) + (1 - 0.998)(-5) + (-0.42 \pm 0.05) = -89.8 \pm 0.1 \text{ kJ/mol}; \]

\[ \Delta H^0_s = (-89.2 \pm 0.1) + (1 - 0.997)(-5) + (-0.50 \pm 0.05) = -89.7 \pm 0.1 \text{ kJ/mol}. \]
In this case, the $\Delta H^0_{\text{av}}$ average value is equal to $-89.75 \pm 0.1$ kJ/mol. Then, the NiSO$_4$ standard formation enthalpy in the aqueous solution is equal to:

$$\Delta_f H^0_{\text{NiSO}_4(s,\text{st})} = \Delta_f H^0_{\text{NiSO}_4(k)} + \Delta H^0_{s,\text{av}} = (-873.5 \pm 0.5) + (-89.75 \pm 0.10) =$$

$$= -963.3 \pm 0.5 \text{ kJ/mol}.$$

Value of the standard crystalline nickel sulfate formation enthalpy equal to $-873.5 \pm 0.5$ kJ/mol was taken from paper [4].

It is known that the NiSO$_4$ standard formation enthalpy solution is the total of standard enthalpies of Ni$^{2+}$ and SO$_4^{2-}$ ions formation. For the last particle, the value of this characteristic constitutes $-911.0 \pm 0.2$ kJ/mol, according to the reference book [15]. Hence, taking into account the above, the Ni$^{2+}$ ion standard formation enthalpy in an aqueous solution is equal to:

$$\Delta_f H^0_{\text{Ni}^{2+}(s,\text{st})} = \Delta_f H^0_{\text{NiSO}_4(s,\text{st})} - \Delta_f H^0_{\text{SO}_4^{2-}(s,\text{st})} =$$

$$= (-963.3 \pm 0.5) - (-911.0 \pm 0.2) = -52.3 \pm 0.5 \text{ kJ/mol}.$$

**Conclusion.** Based on thermochemical measurements, a reliable value of the Ni$^{2+}$ nickel cation standard enthalpy formation in an aqueous solution was obtained equal to $-52.3 \pm 0.5$ kJ/mol, and with an error that should be noted significantly lower than the current value used in this thermochemical characteristic.

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Nickel Sulfate Aqueous Solutions Thermal Chemistry...


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