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

A.A. Gurov[1]   aleksgurow@yandex.ru
S.V. Kozhevnikova[2]
A.N. Ozhogina[2]
S.N. Solovyev[2]   snsol@muctr.ru

[1] Bauman Moscow State Technical University, Moscow, Russian Federation
[2] D. Mendeleev University of Chemical Technology of Russia,
Moscow, Russian Federation

Abstract

Calorimeter with an isothermal shell was used at a temperature of 298.15 K to measure the following parameters: enthalpy of $NiSO_{4(k)}$ dissolution in water followed by generation of two molar concentration solutions; enthalpy of four $NiSO_4$ 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 $NiSO_4$ 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 Ni^{2+} cation formation in an aqueous solution, which turned out to be equal to -52.3 ± 0.5 kJ/mol

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 Ni^{2+} 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 Ni^{2+} 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 thermo-chemical 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 $P_2O_{5(k)}$ 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, greening in the air due to their absorption of water. They were stored in closed containers in a dry chamber above the $P_2O_{5(k)}$ 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: $5 \cdot 10^{-5}$ 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 $KCl_{(k)}$ 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 $NiSO_{4(k)}$ dissolution enthalpy in water and the enthalpy of this salt solutions dilution, i.e., the electrolyte, are presented in Tables 1 and 2.

Table 1

**Values of the dissolution enthalpy ΔH_s $NiSO_{4(k)}$
in water at the temperature 298.15 K**

Initial temperature during the experiment t_0, Ω	Heat exchange correction δ, Ω	Corrected temperature raise during the experiment ΔR_c, Ω	Salt batch weight m_s $NiSO_{4(k)}$, mg	Quantity of heat generated during the experiment due to dissolution Q, J	Dissolution enthalpy ΔH_s, kJ/mol
$C_{m\,av} = 0.0018$ mol/kg; $\Delta H_{s.\,av} = -89.4 \pm 0.1$ kJ/mol					
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
$C_{m\,av} = 0.0030$ mol/kg; $\Delta H_{s.\,av} = -89.2 \pm 0.1$ kJ/mol					
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
Note. $C_{m\,av}$ is solution molal concentration average value; $\Delta H_{s.\,av}$ is dissolution enthalpy average value.					

Values of the dilution enthalpy ΔH_{dil} of NiSO$_4$ aqueous solutions at the temperature 298.15 K

Initial temperature during the experiment t_0, Ω	Heat exchange correction δ, Ω	Corrected temperature raise during the experiment ΔR_c, Ω	Quantity of heat generated during the experiment due to dissolution Q, J	Dilution enthalpy ΔH_{dil}, kJ/mol
$C_{m\,in} = 0.2780$ mol/kg; $C_{mf} = 0.0035$ mol/kg; $V_{dil} = 2.5$ ml; $\Delta H_{dil.\,av} = -1.38 \pm 0.02$ kJ/mol				
10020.18	0.105	−0.342	0.959	−1.38
10021.37	0.127	−0.352	0.987	−1.42
10022.44	0.134	−0.332	0.931	−1.34
10020.95	0.096	−0.340	0.952	−1.37
$C_{m\,in} = 0.1390$ mol/kg; $C_{mf} = 0.0035$ mol/kg; $V_{dil} = 5.0$ ml; $\Delta H_{dil.\,av} = -1.32 \pm 0.02$ 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
$C_{m\,in} = 0.0695$ mol/kg; $C_{mf} = 0.0035$ mol/kg; $V_{dil} = 10.0$ ml; $\Delta H_{dil.\,av} = -1.03 \pm 0.02$ 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
$C_{m\,in} = 0.0348$ mol/kg; $C_{mf} = 0.0035$ mol/kg; $V_{dil} = 20.0$ ml; $\Delta H_{dil.\,av} = -0.584 \pm 0.004$ 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

Note. $C_{m\,in}$ and $C_{m\,f}$ are molal concentrations of initial and final solutions; $\Delta H_{dil.\,av}$ are dilution enthalpy average values; V_{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 $NiSO_4$ aqueous solution were determined, which constituted the following:

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

Table 3

$NiSO_4$ solution dilution enthalpy at the temperature 298.15 K

Molar concentration in solutions, mol/kg		$NiSO_4$ solution dilution enthalpy, kJ/mol		Enthalpy difference: $\Delta H_{dil.\,exp} - \Delta H_{dil.\,D-H}$, kJ/mol
initial, $C_{m\,in}$	final, $C_{m\,f}$	experimentally determined $\Delta H_{dil.\,exp}$	calculated based on the Debye — Hückel theory [13], $\Delta H_{dil.\,D-H}$	
0.2780	0.0035	-1.380 ± 0.020	-3.05 ± 0.40	1.67 ± 0.40
0.1390	0.0035	-1.320 ± 0.020	-2.67 ± 0.35	1.35 ± 0.35
0.0695	0.0035	-1.030 ± 0.020	-2.07 ± 0.30	1.04 ± 0.30
0.0348	0.0035	-1.584 ± 0.004	-1.30 ± 0.20	0.72 ± 0.20

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 ΔH_s^0 $NiSO_{4(k)}$ standard dissolution enthalpy in water was calculated by the ratio [14]:

$$\Delta H_s^0 = \Delta H_{s.\,av} + (1 - \alpha)\Delta H_{dis} + \Delta H_{dil.\,D-H},$$

where $\Delta H_{s.\,av}$ is the dissolution enthalpy (average value) accompanied by generation of the $C_{m\,av}$ molar concentration solution; α is the degree of dissociation of ion pairs; ΔH_{dis} is the enthalpy of the ion pairs dissociation, while $\Delta H_{dis} = -\Delta H_{ass}$; $\Delta H_{dil.\,D-H}$ 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:

$$\Delta H_s^0 = (-89.4 \pm 0.1) + (1 - 0.998)\,(-5) + (-0.42 \pm 0.05) = -89.8 \pm 0.1 \text{ kJ/mol};$$

$$\Delta H_s^0 = (-89.2 \pm 0.1) + (1 - 0.997)\,(-5) + (-0.50 \pm 0.05) = -89.7 \pm 0.1 \text{ kJ/mol}.$$

In this case, the $\Delta H^0_{s.\,av}$ average value is equal to -89.75 ± 0.1 kJ/mol. Then, the $NiSO_4$ standard formation enthalpy in the aqueous solution is equal to:

$$\Delta_f H^0_{NiSO_4\,(s.\,st)} = \Delta_f H^0_{NiSO_4\,(k)} + \Delta H^0_{s.av} = (-873.5 \pm 0.5) + (-89.75 \pm 0.10) =$$

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

Value of the standard crystalline nickel sulfate formation enthalpy equal to -873.5 ± 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 ± 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:

$$\Delta_f H^0_{Ni^{2+}_{(s.\,st)}} = \Delta_f H^0_{NiSO_4\,(s.\,st)} - \Delta_f H^0_{SO_4^{2+}_{(s.\,st)}} =$$

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

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 ± 0.5 kJ/mol, and with an error that should be noted significantly lower than the current value used in this thermochemical characteristic.

REFERENCES

[1] Gorchakova E.A., Gurov A.A., Solov'yev S.N. Standard enthalpy of ion Cu^{2+} formation in aqueous solution. *Herald of the Bauman Moscow State Technical University, Series Natural Sciences*, 2018, no. 3, pp. 104–111 (in Russ.).
DOI: https://doi.org/10.18698/1812-3368-2018-3-104-111

[2] Gurov A.A., Slitikov P.V., Mednykh Zh.N. Metally i splavy [Metals and alloys]. Moscow, BMSTU Publ., 2018.

[3] Greenwood N.N., Earnshaw A. Chemistry of the elements. Butterworth-Heinemann, 1997.

[4] Glushko V.P., ed. Termicheskie konstanty veshchestv. Vyp. 6 [Thermal constants of materials. Iss. 6]. Moscow, VINITI Publ., 1972.

[5] Cox J.D., Wagman D.D., Medvedev V.A., eds. CODATA key values of chemical thermodynamics. Hemisphere Publ. Corp., 1989.

[6] Rossini F.D., Wagman D.D., Evans W.H., et al. Selected values of chemical thermodynamic properties. Government Printing Office, 1952.

[7] Karyakin Yu.V., Angelov I.I. Chistye khimicheskie veshchestva [Pure chemicals]. Moscow, Khimiya Publ., 1975.

[8] Zaytsev O.S. Issledovatel'skiy praktikum ob obshchey khimii [Research workshop on general chemistry]. Moscow, Izd-vo MGU Publ., 1994.

[9] Solov'ev S.N., Shatalov K.I., Dupal A.Ya. Standard enthalpy of formation of crystalline Ca[NiF$_6$]. *Russ. J. Phys. Chem.*, 2014, vol. 88, iss. 5, pp. 893–895.
DOI: https://doi.org/10.1134/S003602441405032X

[10] Glushko V.P., ed. Termicheskie konstanty veshchestv. Vyp. 10. Ch. 2 [Thermal constants of materials. Iss. 10. P. 2]. Moscow, VINITI Publ., 1981.

[11] Solovyev S.N., Khekalo T.V. Determination of electrolytes association thermodynamical properties in solution using hermochemistry measurements. *Trudy RKhTU im. D.I. Mendeleeva*, 1989, no. 158, pp. 129–138 (in Russ.).

[12] Marcus Y., Hefter G. Ion pairing. *Chem. Rev.*, 2006, vol. 106, iss. 11, pp. 4583–4611.
DOI: https://doi.org/10.1021/cr040087x

[13] Solovyev S.N., Privalova N.M., Vorobyev A.F. About application of Debye — Hückel theory for enthalpy calculation of non-aqueous solution dilution electrolytes. *Zhurnal fizicheskoy khimii*, 1976, vol. 50, no. 10, pp. 2719–2720 (in Russ.).

[14] Mishchenko K.P., Poltoratskiy G.M. Termodinamika i stroenie vodnykh i nevodnykh rastvorov elektrolitov [Thermodynamics and structure of aqueuos and non-aqueuos electrolytes solutions]. Leningrad, Khimiya Publ., 1976.

[15] Glushko V.P., ed. Termicheskie konstanty veshchestv. Vyp. 2 [Thermal constants of materials. Iss. 2]. Moscow, VINITI Publ., 1966.

Gurov A.A. — Cand. Sc. (Chem.), Assoc. Professor, Department of Chemistry, Bauman Moscow State Technical University (2-ya Baumanskaya ul. 5, str. 1, Moscow, 105005 Russian Federation).

Kozhevnikova S.V. — Cand. Sc. (Chem.), Assoc. Professor, Department of General and Inorganic Chemistry, D. Mendeleev University of Chemical Technology of Russia (Miusskaya ploshchad 9, Moscow, 125047 Russian Federation).

Ozhogina A.N. — Bachelor's Degree Student, Department of General and Inorganic Chemistry, D. Mendeleev University of Chemical Technology of Russia (Miusskaya ploshchad 9, Moscow, 125047 Russian Federation).

Solovyev S.N. — Dr. Sc. (Chem.), Professor, Head of the Department of General and Inorganic Chemistry, D. Mendeleev University of Chemical Technology of Russia (Miusskaya ploshchad 9, Moscow, 125047 Russian Federation).