PAUL SCHERRER INSTITUT

Registrierung
TM-44-14-05

Titel
The PSI/Nagra Chemical Thermodynamic Database 12/07 (Update of the Nagra/PSI TDB 01/01): Data Selection for Nickel

Ersetzt
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Erstellt
4. Juni 2014

Abstract:

This report provides an update of the Nagra/PSI thermochemical Data Base 01/01 (HUMMEL et al. 2002) with respect to nickel. Most information on compounds and complexes of nickel reported here was taken from the NEA review of the “Chemical Thermodynamics of Nickel” by GAMSJÄGER et al. (2005). Data for nickel sulphide complexes were selected by an in-house review. Data for nickel amine complexes were taken from the work of BJERRUM (1941). The updated database will be called PSI/Nagra Chemical Thermodynamic Database 12/07.

This is the 11th and last of a continuing series of reports concerning the PSI/Nagra Chemical Thermodynamic Database 12/07.

Verteiler

Abt.	Empfänger / Empfängerinnen	Expl.	Abt.	Empfänger / Empfängerinnen	Expl.
44	B. Baeyens	1	Nagra	V. Cloet	1
	U. Berner	1		L. Johnson	1
	S. Churakov	1		J. Mibus	1
	E. Curti	1		J. Schneider	1
	R. Dähn	1		B. Schwyn	1
	T. Gimmi	1		P. Zuidema	1
	M. Glaus	1			
	W. Hummel	1	New Bern	F.J. Pearson	1
	G. Kosakowski	1			
	D. Kulik	1			
	M. Marques	1			
	W. Pfingsten	1			
	T. Thoenen	1			
	J. Tits	1			
	L. Van Loon	1			
	E. Wieland	1			

	Expl.
Bibliothek	2
Reserve	4
Total	29
Seiten	35
Beilagen	-

Informationsliste

D	1	2	3	4	5	8	9	A

Visum ~~Abt./Laborleitung~~:

5 Nickel

Almost all information on inorganic compounds and complexes of nickel reported here was taken from the NEA review of the "Chemical Thermodynamics of Nickel" by GAMSJÄGER et al. (2005). Data for nickel sulphide complexes were selected by an in-house review. Data for nickel amine complexes were taken from the work of BJERRUM (1941).

However, not all values recommended by GAMSJÄGER et al. (2005) are included in our database since the NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. Ni data selected by NEA but not included in our database are summarised in Table 5.4. The data selected for the database update are listed in Table 5.5.

5.1 Elemental nickel

Pure Ni metal is defined as the nickel reference phase. As such, its Gibbs energy of formation and enthalpy of formation are zero by definition at 298.15 K and 0.1 MPa. The absolute entropy and heat capacity of Ni(cr) are well established. The entropy value selected by NEA

$$S_m^\circ\,(\text{Ni, cr, 298.15 K}) \quad = \quad (29.87 \pm 0.20)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is essentially the same as the value given in the NIST-JANAF Thermochemical Tables (CHASE 1998), (29.87 ± 0.21) $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and qualifies as core data value.

The heat capacity selected by NEA

$$C_{p,m}^\circ\,(\text{Ni, cr, 298.15 K}) \quad = \quad (26.07 \pm 0.10)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is also included in our database.

The melting point of Ni(cr) at (1726 ± 4) K indicates that nickel liquid, Ni(l), and nickel gas, Ni(g), are not relevant under environmental conditions. Although GAMSJÄGER et al. (2005) selected thermochemical data for both, none of these phases is included in our database (Table 5.4).

5.2 Simple nickel aqua ion

In aqueous media, the nickel aqua ion exists only in the divalent oxidation state Ni(II). Although the trivalent state of Ni can be stabilised by certain arrangement of donor ligands, no stable aqua ion of Ni(III) appears to exist in dilute aqueous solutions at ambient conditions.

The standard Gibbs energy of formation of Ni^{2+} can be obtained directly from potentiometric data, most accurately from measuring the standard electrode potential of $Ni^{2+} \mid Ni$ in a cell without liquid junction, such as $Ni \mid NiSO_4 \mid Hg_2SO_4 \mid Hg$. The NEA selected value is

$$\Delta_f G_m^\circ\,(\text{Ni}^{2+}, \text{298.15 K}) \quad = \quad -(45.77 \pm 0.77)\ \text{kJ} \cdot \text{mol}^{-1}$$

The partial molar entropy of Ni^{2+} has been derived from experimental data about the solubility, the standard enthalpy of the dissolution reaction and low temperature calorimetry of $NiSO_4 \cdot 7H_2O(cr)$:

$$S_m^\circ\,(\text{Ni}^{2+}, \text{298.15 K}) \quad = \quad -(131.8 \pm 1.4)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The enthalpy of formation of Ni^{2+} has been calculated from the above selected values as

$$\Delta_f H_m^\circ\,(\text{Ni}^{2+}, \text{298.15 K}) \quad = \quad -(55.01 \pm 0.88)\ \text{kJ} \cdot \text{mol}^{-1}$$

The heat capacity of Ni^{2+} was derived from reported apparent molar heat capacity values for several nickel salts in aqueous solution. An unweighted average of the values discussed by GAMSJÄGER et al. (2005) was selected:

$$C_{p,m}° (Ni^{2+}, 298.15\ K) \quad = \quad -(46.1 \pm 7.5)\ J \cdot K^{-1} \cdot mol^{-1}$$

All these NEA selected values were included in our database.

The SIT ion interaction coefficient for Ni^{2+} in ClO_4^- media has been evaluated by GAMSJÄGER et al. (2005). They selected the mean value of entirely independent measurements (emf measurements and isopiestic measurements)

$$\varepsilon(Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)\ kg \cdot mol^{-1}.$$

The ion interaction coefficient $\varepsilon(Ni^{2+}, NO_3^-)$ has also been derived by GAMSJÄGER et al. (2005) from the osmotic and mean activity coefficients of $Ni(NO_3)_2$ solutions. From a fit to experimental data up to an ionic strength of 15 $kg \cdot mol^{-1}$ they selected

$$\varepsilon(Ni^{2+}, NO_3^-) = (0.182 \pm 0.010)\ kg \cdot mol^{-1}.$$

The ion interaction coefficient $\varepsilon(Ni^{2+}, Cl^-)$ has been taken from GRENTHE et al. (1992):

$$\varepsilon(Ni^{2+}, Cl^-) = (0.17 \pm 0.02)\ kg \cdot mol^{-1}.$$

It is also based on osmotic and mean activity coefficients of $NiCl_2$ solutions.

5.3 (Hydr)oxide compounds and complexes

5.3.1 Aqueous nickel hydroxo complexes

The hydrolysis of Ni(II) has mainly been studied by potentiometric titrations, although some solubility, kinetic and calorimetric studies have also been reported. According to these studies, the formation of five water soluble hydroxo complexes of Ni(II) is generally recognised: $NiOH^+$, $Ni(OH)_2(aq)$, $Ni(OH)_3^-$, Ni_2OH^{3+} and $Ni_4(OH)_4^{4+}$.

In acidic or near neutral solutions, hydrolysis of Ni^{2+} is weak, and in publications before 1965, the experimental data were interpreted only in terms of formation of the mononuclear $NiOH^+$ complex. However, at Ni(II) concentrations higher than 0.005 M, the $Ni_4(OH)_4^{4+}$ complex is dominant in the acidic pH region. The dinuclear Ni_2OH^{3+} species is always a minor component, and its formation is considered to account for small deviations between the observed and calculated titration curves. A re-analysis of all reliable experimental data lead to the following NEA data selection:

$$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^+ + H^+$$

$$\log_{10}{}^*\beta_1° (298.15\ K) \quad = \quad -9.54 \pm 0.14$$

$$\Delta_r H_m° (298.15\ K) = 53.8 \pm 1.7\ kJ \cdot mol^{-1}$$

$$2\ Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+} + H^+$$

$$\log_{10}{}^*\beta_{21}° (298.15\ K) = -10.6 \pm 1.0$$

$$\Delta_r H_m° (298.15\ K) = 45.9 \pm 6.0\ kJ \cdot mol^{-1}$$

$$4\ Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\ H^+$$

$$\log_{10}{}^*\beta_{44}° (298.15\ K) \quad = \quad -27.52 \pm 0.15$$

$$\Delta_r H_m^\circ \text{ (298.15 K)} = 190 \pm 10 \text{ kJ} \cdot \text{mol}^{-1}$$

The SIT ion interaction coefficient for Ni^{2+} in ClO_4^- and Cl^- has been evaluated by GAMSJÄGER et al. (2005) from their SIT analyses of experimental data in $NaClO_4$ and NaCl media:

$$\varepsilon(NiOH^+, ClO_4^-) = (0.14 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}$$

and

$$\varepsilon(NiOH^+, Cl^-) = -(0.01 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}.$$

No value was selected by GAMSJÄGER et al. (2005) for $\varepsilon(NiOH^+, NO_3^-)$.

The SIT ion interaction coefficient for $Ni_4(OH)_4^{4+}$ in ClO_4^- and Cl^- has been evaluated by GAMSJÄGER et al. (2005) from their SIT analyses of experimental data in perchlorate and NaCl:

$$\varepsilon(Ni_4(OH)_4^{4+}, ClO_4^-) = (1.08 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$$

and

$$\varepsilon(Ni_4(OH)_4^{4+}, Cl^-) = (0.43 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}.$$

In the case of Ni_2OH^{3+} GAMSJÄGER et al. (2005) did extrapolations to $I = 0$ by assuming

$$\varepsilon(Ni_2OH^{3+}, ClO_4^-) = (0.50 \pm 0.15) \text{ kg} \cdot \text{mol}^{-1}$$

based on the estimated value for $\varepsilon(Be_2OH^{3+}, ClO_4^-) = (0.50 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$.

Three further complexes have been reported to form in Ni(II) solutions above pH = 9, $Ni(OH)_2(aq)$, $Ni(OH)_3^-$ and $Ni(OH)_4^{2-}$, based on the increasing solubility of $Ni(OH)_2(cr)$ in alkaline solutions. Values of the respective hydrolysis constants selected by previous reviews are based on a few experimental points of a single paper by GAYER & GARRETT (1949). The data situation has not improved, but these experimental points can be equally well described when only $Ni(OH)_3^-$ is assumed to be present. The numerical value of this third hydrolysis constant remains within its error limits whether $Ni(OH)_2(aq)$ is taken into account or not, and the NEA reviewers did not find any convincing evidence for formation of $Ni(OH)_4^{2-}$. A re-evaluation of the data reported by GAYER & GARRETT (1949) resulted in the following NEA selected value:

$$Ni^{2+} + 3\,H_2O(l) \Leftrightarrow Ni(OH)_3^- + 3\,H^+$$

$$\log_{10} {}^*\beta_3^\circ \text{ (298.15 K)} = -29.2 \pm 1.7$$

No thermodynamic quantities for the species $Ni(OH)_2(aq)$ are selected in the NEA review, though the reviewers state that for the reaction $Ni(OH)_2(cr) \Leftrightarrow Ni(OH)_2(aq)$ $\log_{10}K \leq -7$ can be tentatively assigned as its upper limit. Together with the solubility product selected for $Ni(OH)_2(cr)$ (see 5.3.2) this results in the following supplemental data:

$$\mathit{Ni^{2+} + 2\,H_2O(l) \Leftrightarrow Ni(OH)_2(aq) + 2\,H^+}$$

$$\mathit{\log_{10} {}^*\beta_2^\circ (298.15\ K) \leq -18}$$

From the temperature dependence of $\log_{10} {}^*\beta_2^\circ$ and $\log_{10} {}^*\beta_3^\circ$ measured between 150 and 300°C, rough estimates for their standard reaction enthalpies can be derived as $\Delta_r H_m^\circ$ (298.15 K) ≈ *90* and *121.2 ± 6.5* kJ · mol^{-1}, respectively.

5.3.2 Solid nickel oxides and hydroxides

5.3.2.1 Ni(II) oxide

Bunsenite (NiO) is an extremely rare mineral. It has been discovered as early as 1868 in Johanngeorgenstadt, Erzgebirge, Saxony, Germany in a hydrothermal Ni-U vein.

A very accurate technique for the determination of the standard entropy of a solid crystalline compound is the integration of low-temperature heat capacity data between 0 and 298.15 K. In the case of nickel oxide several publications dealing with heat capacity measurements in the temperature range 3.2 – 477.8 K are available. Based on a simultaneous evaluation of five independent experimental studies of comparable accuracy GAMSJÄGER et al. (2005) selected the standard entropy of NiO as

$$S_m^\circ \text{ (NiO, cr, 298.15 K)} = (38.4 \pm 0.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Based on these studies and two high-temperature heat capacity studies GAMSJÄGER et al. (2005) selected

$$C_{p,m}^\circ \text{ (NiO, cr, 298.15 K)} = (44.4 \pm 0.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The enthalpy of formation of nickel oxide was determined directly by means of combustion calorimetry as

$$\Delta_f H_m^\circ \text{ (NiO, cr, 298.15 K)} = -(239.7 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

GAMSJÄGER et al. (2005) state: “When the selected data for Ni(cr), the calorimetric value for the standard enthalpy of formation of NiO, … the heat capacity function and the standard entropy of NiO (selected above) are used, the predicted temperature dependence of the Gibbs energy of formation agrees remarkably well with experimental data obtained from various high-temperature electrochemical measurements.” Thus, the NEA reviewer selected the standard enthalpy of formation from combustion calorimetry and calculated a value for the Gibbs energy of formation from the above selected values as

$$\Delta_f G_m^\circ \text{ (NiO, cr, 298.15 K)} = -(211.66 \pm 0.42) \text{ kJ} \cdot \text{mol}^{-1}$$

GAMSJÄGER et al. (2005) further state: “Due to the kinetically inert nature of nickel oxide with respect to its dissolution in aqueous media the solubility of NiO has been studied only at elevated temperatures so far. These studies are not suitable for the calculation of any thermodynamic properties of NiO because of the high uncertainty of the measured solubilities compared to the high-temperature emf data and the low-temperature heat capacity data discussed above. Moreover, the evaluation of the solubility experiments performed at hydrothermal conditions may cause an additional uncertainty for the solubility constant of NiO owing to the lack of heat capacity functions for the ionic species including the hydroxo species. Thus, the calculated value for the solubility constant pf NiO at 298.15 K, according to the reaction:

$$\text{NiO(cr)} + 2\text{H}^+ \Leftrightarrow \text{Ni}^{2+} + \text{H}_2\text{O(l)}$$

derived from the thermodynamic data accepted in the present assessment, is :

$$\log_{10}{}^*K_{s,0}^\circ \text{ (NiO, cr, 298.15 K)} = 12.48 \pm 0.15.\text{“}$$

The values selected for $\log_{10}{}^*K_{s,0}^\circ$, S_m° and $C_{p,m}^\circ$ by GAMSJÄGER et al. (2005) are included in our database.

5.3.2.2 Ni(II) hydroxides, $Ni(OH)_2$

Theophrastite, β-$Ni(OH)_2$, is a gangue mineral in ore consisting of magnetite (Fe_3O_4), chromite ($FeCr_2O_4$) and Ni-sulphide as minor component. Theophrastite is formed from Ni-bearing solutions between $80 \leq T(°C) \leq 115$ in alkaline moderately oxidising media.

Other varieties of crystallised divalent nickel hydroxide, α-$Ni(OH)_2$ and α^*-$Ni(OH)_2$, differ from the thermodynamically stable β-form by the presence of a layer of water in the van der Waals gap. Proposed formulae are α-$3Ni(OH)_2 \cdot 2H_2O$ and α^*-$Ni(OH)_2 \cdot 0.75H_2O$. Although the α-form plays an important role in the charge/discharge cycle of nickel batteries (see below) no thermodynamic data can definitely be assigned to it. The natural occurrence of α-$Ni(OH)_2$ has never been reported as it is probably too unstable to persist under ambient conditions.

The heat capacity of $Ni(OH)_2$(cr) has been measured at low temperatures and these data have been used to determine the standard entropy $S_m°$(298.15 K) and $C_{p,m}°$(298.15 K). GAMSJÄGER et al. (2005) selected

$$S_m° \,(Ni(OH)_2, \beta, 298.15\text{ K}) \quad = \quad (80.0 \pm 0.8)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}° \,(Ni(OH)_2, \beta, 298.15\text{ K}) \quad = \quad (82.0 \pm 0.3)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Both values are included in our database.

GAMSJÄGER et al. (2005) state that actually most solubility data of $Ni(OH)_2$(cr) reported so far suffer from an uncertainty in the physical state of the solid investigated. They continue “apart from the well defined β-$Ni(OH)_2$, a number of basic salts of changing composition exist. When nickel hydroxide is precipitated from aqueous $NiCl_2$, $Ni(NO_3)_2$, or $NiSO_4$ with NaOH or KOH solutions it is always contaminated with basic salts. The solubility of the latter varies depending on the anion and the molar ration OH/Ni. This means that solubility studies on poorly defined nickel hydroxide or the representative basic salts are useless as an experimental basis to derive accurate thermodynamic functions of nickel hydroxide. They may, however, serve to find out relevant information concerning removal of Ni^{2+} from radioactive effluents.”

The value selected by GAMSJÄGER et al. (2005) for the reaction

$$\beta\text{-}Ni(OH)_2 \ + \ 2\,H^+ \ \Leftrightarrow \ Ni^{2+} \ + \ 2\,H_2O(l)$$

$$\log_{10}{}^*K_{s,0}° \,(Ni(OH)_2, \beta, 298.15\text{ K}) \ = \ 11.02 \ \pm 0.20$$

is based on the new experimental study of GAMSJÄGER et al. (2002). This value is included in our database.

According to the present thermodynamic model the equilibrium temperature for

$$\beta\text{-}Ni(OH)_2 \ \Leftrightarrow \ NiO(cr) \ + \ H_2O(l)$$

amounts to $T = (503 \pm 31)$ K.

5.3.2.3 Ni(III,IV) hydroxides

Nickel hydroxides of oxidation state two and higher have been used as the active material in the positive electrodes of several alkaline batteries for more than a hundred years:

$$\begin{tikzcd}
\text{charge} \rightarrow & \leftarrow \text{discharge} \\
\beta\text{-Ni(OH)}_2 \arrow[r, Leftrightarrow] & \beta\text{-NiOOH} \arrow[d, "\text{overcharge}"] \\
\alpha\text{-Ni(OH)}_2 \arrow[u, "\text{dehydration}"] \arrow[r, Leftrightarrow] & \gamma\text{-NiOOH}
\end{tikzcd}$$

The charge and discharge cycles of nickel batteries involve two different pairs of solid phases. Oxidation of β-$Ni(OH)_2$ produces β-NiOOH, oxidation of α-$Ni(OH)_2$ produces γ-NiOOH. The end-products of these cycles are interconnected by dehydration and overcharge. In order to complicate things further, the so-called "α-$Ni(OH)_2$ | γ-NiOOH" system forms regular solid solutions of Ni(II) and Ni(IV) compounds in the whole range of compositions between α-$Ni(OH)_2$ and $NiO_2 \cdot xH_2O$, without any participation of Ni(III) oxide hydroxides.

No thermodynamic data for any of these compounds are recommended by Gamsjäger et al. (2005).

5.4 Halogen compounds and complexes

5.4.1 Nickel halide compounds

The solubility and the thermochemical properties of nickel halide compounds have been studied extensively since the end of the 19th century, and the relevant literature was reviewed in detail by Gamsjäger et al. (2005).

The anhydrous forms NiF_2(cr), $NiCl_2$(cr), $NiBr_2$(cr) and NiI_2(cr) are unstable in aqueous systems. They are sold with the label "hygroscopic" on the bottle, implying hydration and instantaneous dissolution in contact with water.

A number of hydrated $NiCl_2$ solids have been studied. In contact with saturated aqueous solutions at ambient pressure, the hexahydrate $NiCl_2 \cdot 6H_2O$(cr) was reported to be the stable form to approximately 36°C, with a solubility of 4.9 $mol \cdot kg^{-1}$, and the dehydration of the tetrahydrate $NiCl_2 \cdot 4H_2O$(cr) to the dihydrate $NiCl_2 \cdot 2H_2O$(cr) occurs above 60°C.

Anhydrous nickel iodate, β-$Ni(IO_3)_2$, is unstable in aqueous systems, and the most stable form near room temperature, the hydrated compound $Ni(IO_3)_2 \cdot 2H_2O$(cr), is highly soluble in water.

In summary, all these nickel halide solids are either unstable in aqueous systems or they are highly soluble salts. None of them is included in our database (Table 5.3).

5.4.2 Aqueous nickel halide complexes

Halide ions, with the exception of fluoride, form rather unstable complexes with Ni(II) in aqueous solution. This is mostly due to the strong hydration of Ni(II). Thus, water can efficiently compete with the essentially electrostatic Ni(II)-halide interaction. Consequently, high and varying excesses of ligand anions over Ni(II) have been used to assess the stability of the complexes formed. As it is almost impossible to distinguish between a medium effect and the formation of higher complexes, for lack of solid evidence, only NiX^+ species were accepted by Gamsjäger et al. (2005).

A considerable number of stability constants have been reported for the reaction

$$Ni^{2+} + F^- \Leftrightarrow NiF^+$$

The majority of data were obtained in $NaClO_4$ solutions using a fluoride selective electrode, but some pH-metric, kinetic and polarographic data were published, too. Gamsjäger et al. (2005) did a weighted linear regression using 11 data points and obtained the selected value of

$$\log_{10}\beta_1° \text{ (298.15 K)} = 1.43 \pm 0.08.$$

The resulting Δε value is -(0.049 ± 0.060) kg·mol^{-1}. Using the selected values for ε(Ni^{2+}, ClO_4^-) and ε(Na^+, F^-) leads to a value of

$$\varepsilon(NiF^+, ClO_4^-) = (0.34 \pm 0.08) \text{ kg·mol}^{-1}.$$

In the absence of an experimental value for ε(NiF^+, Cl^-) an estimate based on charge correlations (HUMMEL 2009) is included in our database:

$$\varepsilon(NiF^+, Cl^-) = (0.05 \pm 0.15) \text{ kg·mol}^{-1}.$$

Published reaction enthalpy values for the formation of the NiF^+ complex were evaluated by GAMSJÄGER et al. (2005) and they selected a value of

$$\Delta_r H_m°\text{(298.15 K)} = 9.5 \pm 3.0 \text{ kJ · mol}^{-1}.$$

All these values are included in our database.

The formation of higher complexes (NiF_n^{2-n}, $n > 1$) is not reported in the literature, not even in the presence of more than a thousand-fold excess of fluoride over Ni(II).

The derivation of a stability constant for the reaction

$$Ni^{2+} + Cl^- \Leftrightarrow NiCl^+$$

proved to be a bumpy road as described by GAMSJÄGER et al. (2005).

GAMSJÄGER et al. (2005) did not consider a number of reported data for reasons discussed in their Appendix A and stated further: "Most of the accepted data are, however, also subject to substantial experimental errors, due to the medium effect, and in such cases we assigned significantly higher uncertainty to the selected constants than reported in the original literature."

GAMSJÄGER et al. (2005) then started their analysis by stating: "The data in LIBUS & TIALOWSKA (1975) are free of significant medium effects, and this is the only data set where the systematic errors can be assumed identical for each point. Therefore, these data were used to determine the ion interaction coefficient between $NiCl^+$ and ClO_4^-, in spite of the fact that the applied ionic strength (I_m = 3 – 9 m) is well above of the recommended range for the SIT analysis." The results of the linear regression are: $\log_{10}\beta_1°$ (298.15 K) = -(0.37 ± 0.27) and Δε = -(0.073 ± 0.040) kg·mol^{-1}. However, deriving a value for ε($NiCl^+$, ClO_4^-) is difficult as $Ni(ClO_4)_2$ was used as a constant ionic medium (with a chloride content of ≈0.01 m) and Δε has to be calculated as Δε = ε($NiCl^+$, ClO_4^-) - ε(Ni^{2+}, Cl^-) - ε(Ni^{2+}, ClO_4^-). Using the selected value ε(Ni^{2+}, ClO_4^-) = (0.37 ± 0.03) kg·mol^{-1} is no problem, but what value should be used for ε(Ni^{2+}, Cl^-)? The NEA selected value ε(Ni^{2+}, Cl^-) = (0.17 ± 0.02) kg·mol^{-1} was derived from isopiestic measurements and thus already implicitly includes the effects of nickel chloride complexation. It should be replaced by ε(Ni^{2+}, ClO_4^-) in all calculations when chloride is part of the ionic medium. Doing so, a value ε($NiCl^+$, ClO_4^-) = (0.67 ± 0.06) kg·mol^{-1} can be calculated. GAMSJÄGER et al. (2005) discussed this but concluded: "This value of ε($NiCl^+$, ClO_4^-) is too high, taking into account the relatively accurate value for ε(NiF^+, ClO_4^-)." They decided to use ε(Ni^{2+}, Cl^-) = (0.17 ± 0.02) kg·mol^{-1} which leads to a value of:

$$\varepsilon(NiCl^+, ClO_4^-) = (0.47 \pm 0.06) \text{ kg·mol}^{-1}.$$

GAMSJÄGER et al. (2005) then used the remaining (accepted) experimental values for $NaClO_4$ media for a second SIT analysis. As a result only Δε = (0.11 ± 0.06) kg·mol^{-1} is given in the text. The stability constant extrapolated to $I = 0$ is nowhere mentioned in the text and can only guessed as $\log_{10}\beta_1°$ (298.15 K) ≈ (0.92 ± 0.22) from Figure V-23 in GAMSJÄGER et al. (2005). In this case $\Delta\varepsilon$ has to be calculated as $\Delta\varepsilon = \varepsilon(\mathrm{NiCl^+, ClO_4^-}) - \varepsilon(\mathrm{Na^+, Cl^-}) - \varepsilon(\mathrm{Ni^{2+}, ClO_4^-})$. Using the selected values for $\varepsilon(\mathrm{Ni^{2+}, ClO_4^-})$ and $\varepsilon(\mathrm{Na^+, Cl^-})$ results in $\varepsilon(\mathrm{NiCl^+, ClO_4^-}) = 0.51$ kg·mol^{-1}. GAMSJÄGER et al. (2005) stated: “This may support the value calculated using $\varepsilon(\mathrm{Ni^{2+}, Cl^-})$ from the data in LIBUS & TIALOWSKA (1975), however, this is not particularly convincing because most of the remaining data in the other papers have relatively low accuracy, due to substantial medium effects.” Consequently, $\log_{10}\beta_1°$ (298.15 K) ≈ (0.92 ± 0.22) is not considered by GAMSJÄGER et al. (2005).

Instead, GAMSJÄGER et al. (2005) used their selected $\varepsilon(\mathrm{NiCl^+, ClO_4^-}) = (0.47 \pm 0.06)$ kg·mol^{-1} to extrapolate the remaining accepted data in (H/Li/Na)$\mathrm{ClO_4}$ and KCl media to $I = 0$ with the caveat that due to medium effects, most of the constants derived by this extrapolation represent only the upper limits of the true values. The average of these data is reported as $\log_{10}\beta_1°$ (298.15 K) = (0.52 ± 0.38).

Finally, GAMSJÄGER et al. (2005) took the average of the two values $\log_{10}\beta_1°$ (298.15 K) = -(0.37 ± 0.27) and $\log_{10}\beta_1°$ (298.15 K) = (0.52 ± 0.38) as their selected value

$$\log_{10}\beta_1° \text{ (298.15 K)} = 0.08 \pm 0.60.$$

Despite some doubts about the validity of the NEA selection procedure we included the selected values for $\log_{10}\beta_1°$ and $\varepsilon(\mathrm{NiCl^+, ClO_4^-})$ in our database. Note that $\varepsilon(\mathrm{NiCl^+, Cl^-}) = \varepsilon(\mathrm{NiCl^+, ClO_4^-})$, although the derivation of $\varepsilon(\mathrm{NiCl^+, ClO_4^-})$ itself is inconsistent as discussed above.

Several authors reported equilibrium constants K_2 for the reaction $\mathrm{NiCl^+ + Cl^- \Leftrightarrow NiCl_2(aq)}$. However, GAMSJÄGER et al. (2005) did not find it justified to select a recommended value for K_2.

Only a few studies have reported reaction enthalpies for the formation of $\mathrm{NiCl^+}$ species, but no value was selected by GAMSJÄGER et al. (2005).

Only a few studies are available concerning the complex formation between Ni(II) and bromide ions. GAMSJÄGER et al. (2005) evaluated data for the reaction $\mathrm{Ni^{2+} + Br^- \Leftrightarrow NiBr^+}$ and reported a value $\log_{10}\beta_1°$ (298.15 K) = -(0.03 ± 1.30) but stated: “Taking into account this large uncertainty, the above value cannot be recommended, but can be used as the most probable value, until more precise data are published.” This value is not included in our database.

Finally, no quantitative data are available for the formation of NiI_n^{2-n} complexes.

5.5 Chalcogen compounds and complexes

5.5.1 Nickel sulphides

5.5.1.1 Nickel sulphide compounds

The known pure Ni-sulfide minerals are NiS(cr) (millerite), $\mathrm{NiS_2}$(cr) (vaesite), $\mathrm{Ni_3S_2}$(cr) (heazlewoodite), $\mathrm{Ni_3S_4}$(cr) (polydymite), and $\mathrm{Ni_7S_6}$(cr) (godlevskite). For a discussion of their natural formation environments see THOENEN (1999).

Millerite, NiS(cr), is a low temperature hydrothermal mineral found in cavities in carbonate rocks and as an alteration product of other nickel minerals. Furthermore, it should be mentioned that millerite is the only nickel sulphide identified so far in natural low-temperature anoxic sulphidic environments according to THOENEN (1999).

The only solubility studies available are for NiS(s), e.g. THIEL & GESSNER (1914) (for a detailed discussion see 5.5.1.3), all of which are unreliable and no data can be recommended for inclusion in our database.

Furthermore, thermochemical data selected by GAMSJÄGER et al. (2005) for α-NiS, β-NiS, NiS_2(cr), Ni_3S_2(cr) and Ni_9S_8(cr), which are all based on calorimetric data, e.g. ROSENQVIST (1954) (for a detailed discussion see 5.5.1.3), were not included in our database (Table 5.4).

5.5.1.2 Aqueous nickel sulphide complexes

Complexation data are available for $NiHS^+$, $Ni(HS)_2$(aq), $Ni_2(HS)^{3+}$, $Ni_3(HS)^{5+}$, NiS(aq), and $NiS(HS)^-$ (see Table below), but only data for $NiHS^+$ and $Ni(HS)_2$(aq) are included in our database.

Complex	**References**
$Ni(HS)^+$	DYRSSEN (1988) LUTHER et al. (1996) ZHANG & MILLERO (1994) AL-FARAWATI & VAN DEN BERG (1999)
$Ni_2(HS)^{3+}$	LUTHER et al. (1996)
$Ni_3(HS)^{5+}$	LUTHER et al. (1996)
$NiS(HS)^-$	DYRSSEN & WEDBORG (1980) DYRSSEN (1985) DYRSSEN & KREMLING (1990)
NiS(aq)	DYRSSEN (1988) DYRSSEN (1989)
$Ni(HS)_2$(aq)	DYRSSEN & WEDBORG (1980) DYRSSEN (1985) DYRSSEN (1988) AL-FARAWATI & VAN DEN BERG (1999)

Apart from theoretical estimations of the stability constants of aqueous nickel sulphide complexes by DYRSSEN & WEDBORG (1980), DYRSSEN (1985; 1988; 1989) and DYRSSEN & KREMLING (1990), conditional stability constants of Ni-bisulfide complexes have been experimentally determined by ZHANG & MILLERO (1994), LUTHER et al. (1996), and AL-FARAWATI & VAN DEN BERG (1999) in seawater and diluted seawater at pH = 8 (see 5.5.1.3 for a short description of the experiments). We used the conditional stability constants of all three experimental sets for the determination of the stability constant for

$$Ni^{2+} + HS^- \rightleftharpoons NiHS^+ \quad (5.1)$$

by extrapolating the data to $I = 0$ using SIT. Note that AL-FARAWATI & VAN DEN BERG (1999) corrected their logarithmic conditional stability constants by adding a term accounting for the side reaction of Ni with the major anions of seawater. However, they reported only the values of the side-reaction coefficients (different for each salinity), without specifying which additional Ni-complexes they considered. We also added such corrections to the data by Zhang & Millero (1994) and Luther et al. (1996). As the dilution of seawater does not change the relative amounts of dissolved salts, the concentration of one component (e.g. the molality of Cl^-) is sufficient to characterize the total composition of the diluted seawater and the SIT regression can be performed in terms of the molality of Cl^- (see Section 5.5.1.4 for details). A weighted linear regression to the data corrected for side-reactions (see Table 5.1 for the data and Fig. 5.1 for the regression) results in our recommended value

$$\log_{10}\beta_1^\circ(5.1,\ 298.15\ \text{K}) = (5.5 \pm 0.2)$$

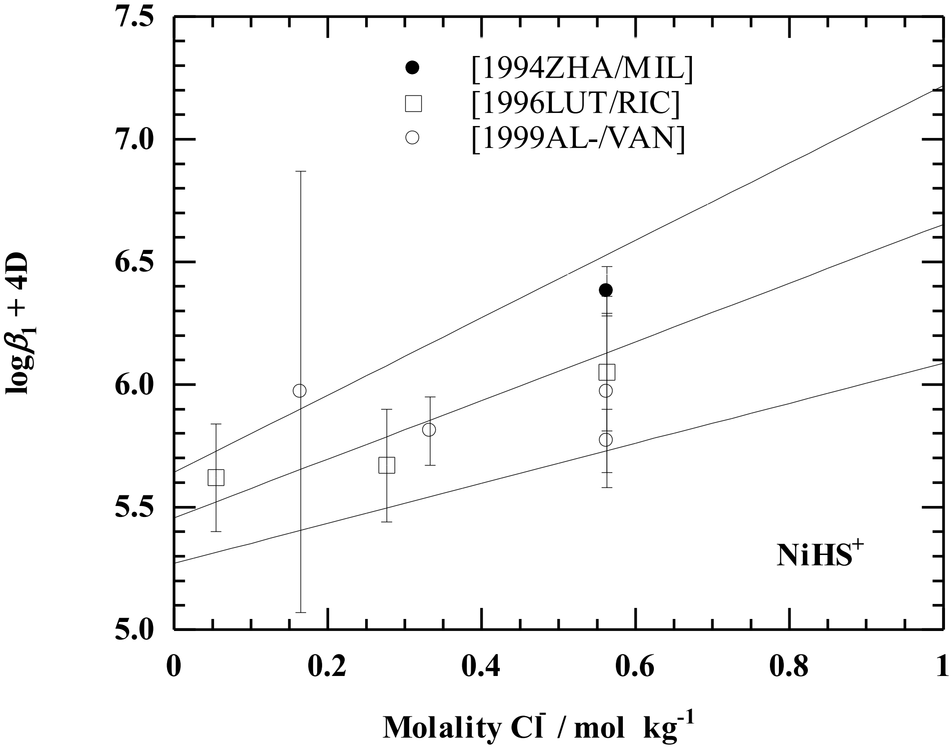
with

$$\Delta\varepsilon(5.1,\ \text{seawater}) = -\ (1.2 \pm 0.4)\ \text{kg}\cdot\text{mol}^{-1}$$

A discussion of this $\Delta\varepsilon$ is given in Section 5.5.1.4.

Table 5.1: Values for conditional stability constants of $NiHS^+$ used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.1). $\log_{10}\beta_1'$ refers to the stability constant without consideration of side-reactions and $\log_{10}\alpha_{Ni}$ to the side-reaction coefficient. Original data in boldface type. See Section 5.5.1.4 for the calculation of the ionic strength and the molality of Cl^- from the salinity, and for the conversion of the stability constants from molar to molal units. [1994ZHA/MIL]: Zhang & Millero (1994), [1996LUT/RIC]: Luther et al. (1996), [1999AL-/VAN]: Al-Farawati & van den Berg (1999).

Source	**Salinity** [‰]	**Cl^-** molal units	**I** molal units	**$\log_{10}\beta_1'$** molar units	**$\log_{10}\alpha_{Ni}$** molar units	**$\log_{10}\beta_1$** molar units	**$\log_{10}\beta_1$** molal units
[1994ZHA/MIL]	35	0.563	0.72	**5.30 ± 0.10**	0.33	5.63 ± 0.10	5.62 ± 0.10
[1996LUT/RIC]	3.5	0.055	0.07	**4.94 ± 0.22**	0.30	5.24 ± 0.22	5.23 ± 0.22
[1996LUT/RIC]	17.5	0.276	0.35	**4.73 ± 0.23**	0.31	5.04 ± 0.23	5.03 ± 0.23
[1996LUT/RIC]	35	0.563	0.72	**4.97 ± 0.24**	0.33	5.30 ± 0.24	5.29 ± 0.24
[1999AL-/VAN]	**10.5**	0.165	0.21	**5.12 ± 0.90**	**0.30**	**5.42 ± 0.90**	5.42 ± 0.90
[1999AL-/VAN]	**21**	0.333	0.43	**4.83 ± 0.14**	**0.31**	**5.14 ± 0.14**	5.14 ± 0.14
[1999AL-/VAN]	**35**	0.563	0.72	**4.89 ± 0.39**	**0.33**	**5.22 ± 0.39**	5.21 ± 0.39
[1999AL-/VAN]	**35**	0.563	0.72	**4.69 ± 0.13**	**0.33**	**5.02 ± 0.13**	5.01 ± 0.13



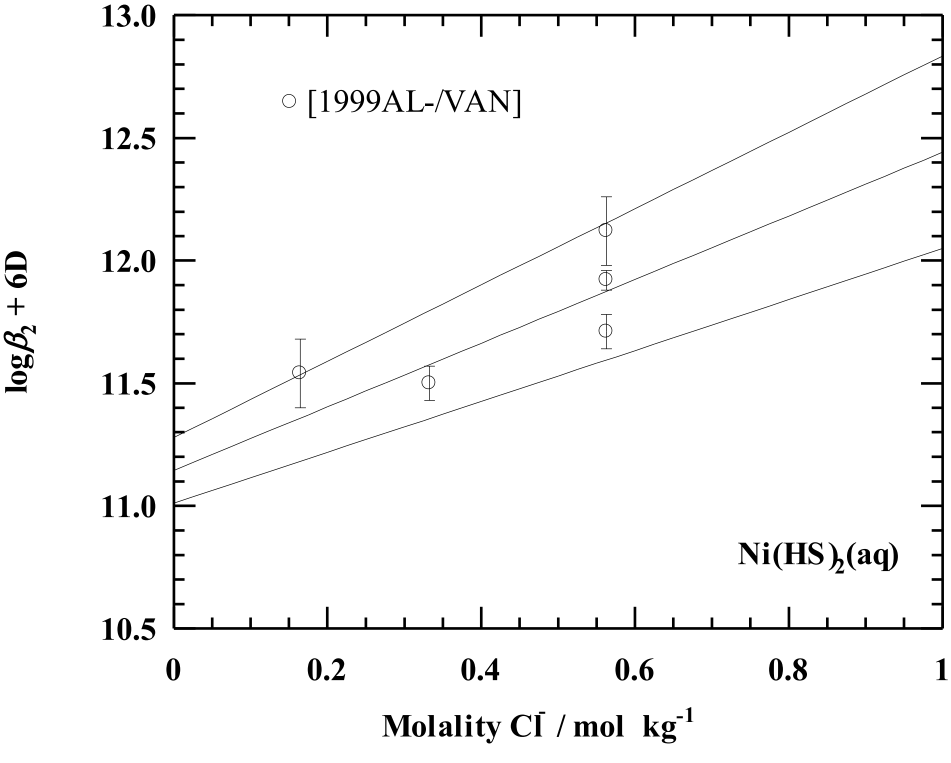


Fig. 5.1: Weighted linear regressions for the extrapolation to $I = 0$ of conditional stability constants determined in seawater for $NiHS^+$ (above) and $Ni(HS)_2(aq)$ (below). Experimental data by ZHANG & MILLERO (1994) [1994ZHA/MIL], LUTHER et al. (1996) [1996LUT/RIC], and AL-FARAWATI & VAN DEN BERG (1999) [1999AL/VAN].

Only AL-FARAWATI & VAN DEN BERG (1999) provided conditional stability constants (corrected for side-reactions) for the reaction

$$\mathrm{Ni^{2+} + 2HS^- \rightleftharpoons Ni(HS)_2(aq)} \qquad (5.2)$$

A weighted linear regression to these data (see Table 5.2 for the data and Fig. 5.1 for the regression) results in our recommended value

$$\log_{10}\beta_2°(5.2, 298.15\ \mathrm{K}) = (11.1 \pm 0.1)$$

with

$$\Delta\varepsilon(5.2, \text{seawater}) = -\ (1.3 \pm 0.3)\ \mathrm{kg \cdot mol^{-1}}$$

A discussion of this $\Delta\varepsilon$ is given in Section 5.5.1.4.

Table 5.2: Values for conditional stability constants of $\mathrm{Ni(HS)_2(aq)}$ used for extrapolation of the stability constants to $I = 0$ (see Fig. 5.1). $\log_{10}\beta_2'$ refers to the stability constant without consideration of side-reactions and $\log_{10}\alpha_{\mathrm{Ni}}$ to the side-reaction coefficient. Original data in boldface type. See Section 5.5.1.4 for the calculation of the ionic strength and the molality of $\mathrm{Cl^-}$ from the salinity, and for the conversion of the stability constants from molar to molal units. [1999AL-/VAN]: AL-FARAWATI & VAN DEN BERG (1999).

Source	**Salinity [‰]**	**$\mathrm{Cl^-}$ molal units**	**I molal units**	**$\log_{10}\beta_2'$ molar units**	**$\log_{10}\alpha_{\mathrm{Ni}}$ molar units**	**$\log_{10}\beta_2$ molar units**	**$\log_{10}\beta_2$ molal units**
[1999AL-/VAN]	**10.5**	0.165	0.21	**10.41 ± 0.14**	**0.30**	**10.71 ± 0.14**	10.71 ± 0.14
[1999AL-/VAN]	**21**	0.333	0.43	**10.19 ± 0.07**	**0.31**	**10.50 ± 0.07**	10.49 ± 0.07
[1999AL-/VAN]	**35**	0.563	0.72	**10.25 ± 0.07**	**0.33**	**10.58 ± 0.07**	10.57 ± 0.07
[1999AL-/VAN]	**35**	0.563	0.72	**10.66 ± 0.14**	**0.33**	**10.99 ± 0.14**	10.98 ± 0.14
[1999AL-/VAN]	**35**	0.563	0.72	**10.46 ± 0.04**	**0.33**	**10.79 ± 0.04**	10.78 ± 0.04

Note that GAMSJÄGER et al. (2005) missed the publication of AL-FARAWATI & VAN DEN BERG (1999) in their review, and thus based their data evaluation only on ZHANG & MILLERO (1994) and LUTHER et al. (1996). They did SIT regression analyses for the reactions

$$\mathrm{Ni^{2+} + HS^- \rightleftharpoons NiHS^+} \qquad \log_{10}\beta_1° = (5.18 \pm 0.20) \qquad \Delta\varepsilon = -(0.97 \pm 0.39)\ \mathrm{kg \cdot mol^{-1}}$$

$$\mathrm{2Ni^{2+} + HS^- \rightleftharpoons Ni_2HS^{3+}} \qquad \log_{10}\beta_2° = (9.92 \pm 0.10) \qquad \Delta\varepsilon = -(0.05 \pm 0.22)\ \mathrm{kg \cdot mol^{-1}}$$

$$\mathrm{3Ni^{2+} + HS^- \rightleftharpoons Ni_3HS^{5+}} \qquad \log_{10}\beta_3° = (14.01 \pm 0.10) \qquad \Delta\varepsilon = (0.59 \pm 0.22)\ \mathrm{kg \cdot mol^{-1}}$$

It is unclear how GAMSJÄGER et al. (2005) did their SIT analyses for data in seawater. The only information given is found in the caption of Figure A-39 of GAMSJÄGER et al. (2005), “logarithm of solubility constants of nickel bisulphide complexes in seawater (NaCl solutions) plus the Debye-Hückel term for ionic strength correction plotted as a function of ionic strength."

Nevertheless, the results reported by GAMSJÄGER et al. (2005) for the first reaction, based on ZHANG & MILLERO (1994) and LUTHER et al. (1996) only, are consistent with our recommended values within their associated uncertainties.

The SIT analyses for the second and third reaction were solely based on the data reported by LUTHER et al. (1996). GAMSJÄGER et al. (2005) calculated the distribution of nickel sulphide complexes as a function of total molality of nickel(II) in aqueous solutions and found that "the uncommon complexes Ni_2HS^{3+} and Ni_3HS^{5+} become the most dominant species in aqueous solution. As this situation seems to be unrealistic and no studies on the structure of these complexes are reported in the literature, we select thermodynamic data only for the aqueous species $NiHS^+$."

We agree with this judgment not to consider the uncommon complexes Ni_2HS^{3+} and Ni_3HS^{5+}. However, we prefer $\log_{10}\beta_1°(5.1, 298.15\ K) = (5.5 \pm 0.2)$ evaluated in this review because this value is based on more experimental data and a clearly defined procedure for extrapolation to $I = 0$.

GAMSJÄGER et al. (2005) reported a value $\varepsilon(NiHS^+, ClO_4^-) = (0.85 \pm 0.39)\ kg\cdot mol^{-1}$ in their Table B-4 with the footnote "see details in Section V.5.1.1.2". However, there are no details in Section V.5.1.1.2 of GAMSJÄGER et al. (2005) except the value $\Delta\varepsilon = -(0.97 \pm 0.39)\ kg\cdot mol^{-1}$ given in Table V-22. We do not include this coefficient $\varepsilon(NiHS^+, ClO_4^-)$ in our database. Furthermore, $\Delta\varepsilon(5.1, \text{seawater}) = -\ (1.2 \pm 0.4)\ kg\cdot mol^{-1}$ cannot be deconvoluted because of the lack of necessary SIT interaction coefficients (see Eq. (5.21) in Section 5.5.1.4). As substitutes, estimate values based on charge correlations (HUMMEL 2009) are included in our database.

5.5.1.3 Discussion of selected references

THIEL & GESSNER (1914) studied the solubility of freshly precipitated NiS in order to explain why some NiS-precipitates are much more soluble in dilute acids than others. They concluded that there must exist three modifications of NiS which they named NiS(α), NiS(β), and NiS(γ). The evidence was circumstantial as the structural properties of these modifications could not be investigated at that time. THIEL & GESSNER (1914) measured the solubility (unreversed, from undersaturation) of NiS(α), NiS(β), and NiS(γ) at room temperature in HCl-solutions saturated with $H_2S(g)$ under atmospheric pressure, and determined values for K_{so} of 3×10^{-21}, 10^{-26}, and 2×10^{-28}, respectively. In their calculations, THIEL (1914) used a value of 0.91×10^{-7} for K_{1,H_2S} ($\log K_{1,H_2S} = -7.04$) and a value of 1.2×10^{-15} for K_{2,H_2S} ($\log K_{2,H_2S} = -14.92$).

THIEL & GESSNER (1914) explicitly stated that their solubility product constants were crude estimates that were only meant to give some idea of their order of magnitude: "Es kommt hier gar nicht darauf an, eine recht grosse Genauigkeit der Löslichkeitsbestimmung zu erzielen, sondern nur darauf, einen Anhalt für die Grössenordnung der Löslichkeit der drei Formen zu gewinnen. Wir kommen daher mit einer gröberen Schätzung aus; mehr ist auch bei der zum Teil noch recht erheblichen Unsicherheit der Grundlage vorläufig nicht möglich."

Ironically, these dubious constants were included in the "Critical Stability Constants" by SMITH & MARTELL (1976). Any solubility product for NiS(α), NiS(β), or NiS(γ) found in compilations is ultimately based on THIEL & GESSNER (1914).

ROSENQVIST (1954) performed an experimental study of the phase relations in the Ni-S system at temperatures between 400 and 1200˚C. A temperature dependent free energy of reaction for

$$2Ni(s) + S_2(g) \rightleftharpoons 2NiS(s) \qquad (a)$$

was calculated from free energies of reaction for

$$3/2Ni(s) + H_2S(g) \rightleftharpoons 1/2Ni_3S_2(s) + H_2(g),$$

$$2Ni_3S_2 + H_2S(g) \rightleftharpoons Ni_6S_5(s) + H_2(g), \text{ and}$$

$$Ni_6S_5(s) + H_2S(g) \rightleftharpoons 6NiS + H_2(g),$$

which were calculated from experimentally determined reaction properties at temperatures between 400 and 560˚C. The Gibbs free energy of reaction for equation (a) was then extrapolated down to 25˚C by using an assumed value for the integrated $\Delta_r C_p$ between 400˚C and 25˚C, and by using an estimated heat of transformation for the NiS(s) to millerite transformation. Combining this result with the Gibbs free energy of $S_2(g) \rightleftharpoons 2S(s,rhomb)$, ROSENQVIST (1954) finally obtained $\Delta_f G_m°$(NiS, s, 298.15 K) = -20.6 kcal·mol^{-1} and $\Delta_f H_m°$(NiS, s, 298.15 K) = -20.2 kcal·mol^{-1} (without explaining how he derived the latter).

These data, relying on estimates and a very long extrapolation from high temperature experiments cannot be recommended.

ZHANG & MILLERO (1994) used voltammetric methods to determine conditional stability constants of metal bisulfide complexes for Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} in seawater at a pH of 8 (we assume that this seawater corresponds to a salinity of 35‰). For this purpose, seawater with an added metal (at concentrations between 0.5 and 1.5 μM) was titrated with sulfide (in concentrations from 0.25 to 0.5 μM that were low enough to prevent precipitation of sulfide minerals) and the concentration of free sulfide was measured with cathodic stripping square wave voltammetry. The decrease in free sulfide was attributed to the formation of metal bisulfide complexes and it was assumed that 1:1 and 1:2 complexes with HS^- were formed. Values of the stability constants were then determined by regression of the titration data. In the case of Ni^{2+}, titration results could be fitted by assuming that only the 1:1 complex, $NiHS^+$, had formed. We assume that the reported conditional stability constants refer to molar units.

LUTHER et al. (1996) determined the stability constants of sulfide complexes of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} in seawater and diluted seawater (ionic strengths of 0.7, 0.35, and 0.07 M) with sulfide concentrations between 1 to 10 μM. They titrated the solutions with metal (in concentrations between 1 to 10 μM) and monitored the concentration of free sulfide by square wave voltammetry. Acid-base titrations were used to determine the proton stoichiometry of the complexes in order to distinguish between the ligands S^{2-} and HS^{-}. In the case of Ni^{2+}, titrations could be fitted by assuming that $NiHS^{+}$, Ni_2HS^{3+}, and Ni_3HS^{5+} had formed. Note that the authors did not discuss the plausibility of such peculiar Ni-clusters with bisulfide centers. We assume that the reported conditional stability constants refer to molar units.

AL-FARAWATI & VAN DEN BERG (1999) determined the conditional stability constants in seawater of pH 8 at various salinities by flow-analysis with detection by cathodic stripping voltammetry (FA-CSV). Two methods were employed. The first method consists in titration of the sulfide by adding metals (Ag^{+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Al^{3+}) and detection of the remaining free sulfide by FA-CSV.

The second method was used for the detection of the bisulfide complexes of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. It depends on the ligand competition between sulfide and oxine (8-hydroxyquinoline) for free metal ions. Metal oxine complexes are electroactive and are therefore detected by FA-CSV. After addition of sulfide, the signal of the metal oxine complex decreases as a result of the complexation of the metal by sulfide.

In the experiments with Ni, metal concentrations of 100 or 150 nM were used, and the maximum amount of added sulfide was about 10 μM. Curve fitting of the titration data resulted in conditional stability constants for $NiHS^{+}$ and $Ni(HS)_2(aq)$ at salinities of 10.5, 21, and 35 ‰. AL-FARAWATI & VAN DEN BERG (1999) corrected the conditional stability constants with a side-reaction coefficient to account for complexation of Ni with the major anions of seawater. However, they gave only the values of the side-reaction coefficients (different for each salinity), without specifying which additional Ni-complexes they considered. We assume that the reported conditional stability constants refer to molar units.

5.5.1.4 SIT in Seawater

Calculation of ionic strength and molality of Cl^{-} from the salinity of seawater

Complexation experiments are often made in seawater diluted with various amounts of pure water. As the dilution of seawater does not change the relative amounts of dissolved salts, one parameter is sufficient to characterize the total composition of the diluted seawater. For the purpose of SIT regressions, it is useful to characterize the composition of seawater with the molality of Cl^{-}.

If the composition of seawater is given in terms of the salinity, $S(‰)$, the corresponding chlorinity, $Cl(‰)$, can be calculated according to

$$Cl(‰) = S(‰)/1.8154 \quad (5.3)$$

(see MILLERO 1996 for this equation and for a definition of salinity and chlorinity). From the chlorinity follows the ionic strength

$$I = 0.035989\ Cl(‰) \tag{5.4}$$

and the molinity (number of moles per kg of seawater) of Cl^-

$$n_{Cl^-} = 0.028176\ Cl(‰) \tag{5.5}$$

see MILLERO (1996).

In these equations, S(‰), Cl(‰), I, and n_{Cl^-} all refer to 1 kg of seawater. Thus, the ionic strength given by equation (5.4) and the concentration of Cl^- given by equation (5.5) have to be converted from molinity to molality which is done by dividing the molinity by the weight fraction of pure H_2O in seawater, W_{H_2O},

$$\text{molality} = \frac{\text{molinity}}{W_{H_2O}} \tag{5.6}$$

where

$$W_{H_2O} = 1\text{-S(‰)}/1000 \tag{5.7}$$

Conversion of conditional stability constants from molarity to molality for seawater

Conditional stability constants are usually given in molar units. The conversion to molal units is done as follows: Noting that the molarity is calculated from the molinity by multiplying with the density of seawater, ρ,

Table 5.3: Various compositional parameters of seawater as calculated from the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.1 and 5.2 were performed. Seawater is abbreviated by sw.

S(‰) $\left[\frac{\text{g}}{\text{kg sw}}\right]$	Cl(‰) $\left[\frac{\text{g}}{\text{kg sw}}\right]$	$[Cl^-]$ $\left[\frac{\text{mol}}{\text{kg sw}}\right]$	I $\left[\frac{\text{mol}}{\text{kg sw}}\right]$	W_{H_2O} $\left[\frac{\text{kg}}{\text{kg sw}}\right]$	ρ(25°C, 1 bar) $\left[\frac{\text{kg}}{\text{l}}\right]$	$\log_{10} f$
3.5	1.928	0.054	0.07	0.9965	1.000	0.0016
10.5	5.784	0.333	0.21	0.9895	1.005	0.0024
17.5	9.640	0.163	0.35	0.9825	1.010	0.0033
21	11.57	0.326	0.42	0.9790	1.013	0.0037
35	19.28	0.543	0.69	0.9650	1.023	0.0054

$$\text{molarity} = \text{molinity} \cdot \rho \tag{5.8}$$

and combining this with equation (5.6), one obtains

$$\text{molality} = f \text{ molarity} \tag{5.9}$$

with

$$f = \frac{1}{\rho W_{\mathrm{H_2O}}} \tag{5.10}$$

The density of seawater as a function of salinity, temperature, and pressure can be calculated from the international equation of state for seawater (MILLERO et al. 1980 and MILLERO & POISSON 1981).

With equations (5.9) and (5.10) and data from Table 5.3, the molar conditional stability constants for the nickel bisulfide complexes listed in Tables 5.1 and 5.2 can be converted into molal constants according to

$$\log_{10}\beta_1(5.1, \text{molal units}) = \log_{10}\beta_1(5.1, \text{molar units}) - \log_{10}f \tag{5.11}$$

and

$$\log_{10}\beta_2(5.2, \text{molal units}) = \log_{10}\beta_2(5.2, \text{molar units}) - 2\log_{10}f \tag{5.12}$$

Table 5.3 lists values for Cl(‰), I, $n_{\mathrm{Cl^-}}$, $W_{\mathrm{H_2O}}$, ρ(25˚C, 1 bar), and $\log_{10}f$ calculated from the above equations for the salinities at which the nickel bisulfide complexation experiments reported in Tables 5.1 and 5.2 were performed.

Determination of SIT interaction coefficients for seawater

The composition of seawater is dominated by $\mathrm{Na^+}$, $\mathrm{Mg^{2+}}$, $\mathrm{Cl^-}$, and $\mathrm{SO_4^{2-}}$. Therefore, activity coefficients for $\mathrm{Ni^{2+}}$, $\mathrm{NiHS^+}$, $\mathrm{Ni(HS)_2(aq)}$, and $\mathrm{HS^-}$ can be expressed according to SIT as

$$\log_{10}\gamma_{\mathrm{Ni^{2+}}} = -4D + \varepsilon(\mathrm{Ni^{2+}},\mathrm{Cl^-})m_{\mathrm{Cl^-}} + \varepsilon(\mathrm{Ni^{2+}},\mathrm{SO_4^{2-}})m_{\mathrm{SO_4^{2-}}} \tag{5.13}$$

$$\log_{10}\gamma_{\mathrm{NiHS^+}} = -D + \varepsilon(\mathrm{NiHS^+},\mathrm{Cl^-})m_{\mathrm{Cl^-}} + \varepsilon(\mathrm{NiHS^+},\mathrm{SO_4^{2-}})m_{\mathrm{SO_4^{2-}}} \tag{5.14}$$

$$\begin{aligned}\log_{10}\gamma_{\mathrm{Ni(HS)_2(aq)}} = {} & \varepsilon(\mathrm{Ni(HS)_2(aq)},\mathrm{Na^+})m_{\mathrm{Na^+}} + \varepsilon(\mathrm{Ni(HS)_2(aq)},\mathrm{Mg^{2+}})m_{\mathrm{Mg^{2+}}} \\ & + \varepsilon(\mathrm{Ni(HS)_2(aq)},\mathrm{Cl^-})m_{\mathrm{Cl^-}} + \varepsilon(\mathrm{Ni(HS)_2(aq)},\mathrm{SO_4^{2-}})m_{\mathrm{SO_4^{2-}}}\end{aligned} \tag{5.15}$$

$$\log_{10}\gamma_{\mathrm{HS^-}} = -D + \varepsilon(\mathrm{HS^-},\mathrm{Na^+})m_{\mathrm{Na^+}} + \varepsilon(\mathrm{HS^-},\mathrm{Mg^{2+}})m_{\mathrm{Mg^{2+}}} \tag{5.16}$$

The following ratios hold for seawater (see Table 2.5 in MILLERO 1996)

$$\mathrm{a} \equiv \frac{m_{\mathrm{SO_4^{2-}}}}{m_{\mathrm{Cl^-}}} = 0.05173 \tag{5.17}$$

$$\mathrm{b} \equiv \frac{m_{\mathrm{Na^+}}}{m_{\mathrm{Cl^-}}} = 0.85929 \tag{5.18}$$

$$\mathrm{c} \equiv \frac{m_{\mathrm{Mg^{2+}}}}{m_{\mathrm{Cl^-}}} = 0.09676 \tag{5.19}$$

With equations (5.13), (5.14), (5.16), and (5.17)-(5.19), the equilibrium relation for

$$Ni^{2+} + HS^{-} \Leftrightarrow NiHS^{+} \tag{5.1}$$

can be written as

$$\log_{10}\beta_1(5.1) + 4D = \log_{10}\beta_1°(5.1) - \Delta\varepsilon(5.1)m_{Cl^-} \tag{5.20}$$

where

$$\begin{aligned}\Delta\varepsilon(5.1) = &+\varepsilon(NiHS^{+},Cl^{-}) + \varepsilon(NiHS^{+},SO_4^{2-})\cdot a\\ &- \varepsilon(Ni^{2+},Cl^{-}) - \varepsilon(Ni^{2+},SO_4^{2-})\cdot a\\ &- \varepsilon(HS^{-},Na^{+})\cdot b - \varepsilon(HS^{-},Mg^{2+})\cdot c\end{aligned} \tag{5.21}$$

In a similar manner, the equilibrium relation for

$$Ni^{2+} + 2HS^{-} \Leftrightarrow Ni(HS)_2(aq) \tag{5.2}$$

can be written as

$$\log_{10}\beta_2(5.2) + 6D = \log_{10}\beta_2°(5.2) - \Delta\varepsilon(5.2)m_{Cl^-} \tag{5.22}$$

where

$$\begin{aligned}\Delta\varepsilon(5.2) = &+\varepsilon(Ni(HS)_2(aq),Na^{+})\cdot b + \varepsilon(Ni(HS)_2(aq),Mg^{2+})\cdot c\\ &+ \varepsilon(Ni(HS)_2(aq),Cl^{-}) + \varepsilon(Ni(HS)_2(aq),SO_4^{2-})\cdot a\\ &- \varepsilon(Ni^{2+},Cl^{-}) - \varepsilon(Ni^{2+},SO_4^{2-})\cdot a\\ &- 2\varepsilon(HS^{-},Na^{+})\cdot b - 2\varepsilon(HS^{-},Mg^{2+})\cdot c\end{aligned} \tag{5.23}$$

5.5.2 Nickel sulphates

5.5.2.1 Nickel sulphate compounds

Several hydrated nickel sulphate solids from $NiSO_4\cdot7H_2O$ to $NiSO_4\cdot H_2O$, including two forms of $NiSO_4\cdot6H_2O$, a tetrahydrate, and a dihydrate have been reported.

The heptahydrate, $NiSO_4\cdot7H_2O$, is the stable nickel sulphate hydrate at 298.15 K. Its solubility at 25°C is m(sat) = (2.62 ± 0.05) $mol\cdot kg^{-1}$ $NiSO_4\cdot7H_2O(cr)$.

In contact with saturated solutions, the α-hexahydrate becomes the stable nickel sulphate near 302 K, and is transformed to the β-hexahydrate at approximately 327 K. Solubility data indicate that β-$NiSO_4\cdot6H_2O$ is the stable solid in contact with saturated solutions of nickel sulphate in water for temperatures between 327 and 358 K. There is evidence for the decomposition of the β-hexahydrate to a tetrahydrate at temperatures near 400 K and to the monohydrate near 440 K. The monohydrate does not readily lose water below 500 K.

All these nickel sulphate hydrates are highly soluble salts. $NiSO_4(cr)$ is unstable in water. They are not relevant under environmental conditions and thus, thermodynamic data selected by GAMSJÄGER et al. (2005) are not included in our database (Table 5.4).

5.5.2.2 Aqueous nickel sulphate complexes

The complexation reactions of Ni^{2+} with SO_4^{2-} have been the subject of a large number of investigations. For the reaction

$$Ni^{2+} + SO_4^{2-} \Leftrightarrow NiSO_4(aq)$$

GAMSJÄGER et al. (2005) re-analysed conductance and emf data and selected a weighted average of these two data sets:

$$\log_{10}K^\circ\ (298.15\ \mathrm{K}) = 2.35 \pm 0.03.$$

GAMSJÄGER et al. (2005) stated further: “At high sulphate concentrations, there is some evidence for formation of $Ni(SO_4)_2^{2-}$ in several studies. However, the evidence is reasonably ambiguous, and may only reflect systematic errors in the experiment. No value is selected for K_2° in the present review.”

There have been several studies of the temperature dependence of the formation constant of the complex $NiSO_4(aq)$, as well as a determination of the enthalpy of reaction at 25°C by a titration calorimetric method. GAMSJÄGER et al. (2005) accepted the weighted average of the results from the calorimetric study and two determinations of the temperature dependence of $\log_{10}K^\circ$:

$$\Delta_r H_m^\circ(298.15\ \mathrm{K}) = 5.66 \pm 0.81\ \mathrm{kJ \cdot mol^{-1}}.$$

We included both values, $\log_{10}K^\circ$ and $\Delta_r H_m^\circ$, in our database.

5.6 Group 15 compounds and complexes

5.6.1 Nitrogen compounds and complexes

5.6.1.1 Nickel nitrate compounds

The hydrated nickel nitrate solids have been the subject of sporadic thermodynamic studies over the last 150 years, but the basic thermodynamic quantities for these materials are not well defined.

The stable hydrate in equilibrium with a solution saturated in nickel nitrate at 298.15 K is $Ni(NO_3)_2 \cdot 6H_2O(cr)$. The solid can easily lose water on exposure to dry air, but has also been reported to be slightly deliquescent in moist air. In a closed system, the hydrate begins to melt (or partially dissolve in its water of hydration) at 328K.

Dehydration of the hexahydrate leads to several lower hydrates, but the hydrate formed seems to depend markedly on the method used to carry out the dehydration. In few of the experiments were the dehydrated solids thoroughly characterised, nor was it established that the solids were stable over long periods.

All these nickel nitrate hydrates are highly soluble salts. They are not relevant under environmental conditions and thus, thermodynamic data selected by GAMSJÄGER et al. (2005) are not included in our database (Table 5.4).

5.6.1.2 Aqueous nickel nitrate complexes

For the reaction

$$Ni^{2+} + NO_3^- \Leftrightarrow NiNO_3^+$$

GAMSJÄGER et al. (2005) re-evaluated a data set measured in 1 – 4 M $Li(ClO_4, NO_3)$ taking into account only the formation of the $NiNO_3^+$ species. To minimise the medium effect, only half of the experimental data, for which $[NO_3^-] \leq [ClO_4^-]$, were taken into account. A weighted linear SIT regression resulted in the values $\log_{10}\beta_1^\circ(298.15\ \mathrm{K}) = (0.49 \pm 0.45)$ and $\Delta\varepsilon(LiClO_4) = -(0.08 \pm 0.14)\ \mathrm{kg \cdot mol^{-1}}$. GAMSJÄGER et al. (2005) stated, without any further explanation, that from the latter value $\varepsilon(NiNO_3^+, ClO_4^-) = (0.44 \pm 0.14)\ \mathrm{kg \cdot mol^{-1}}$ can be derived. How this derivation was done remains unclear. For the system analysed $\Delta\varepsilon$ has to be calculated as $\Delta\varepsilon = \varepsilon(NiNO_3^+, ClO_4^-) - \varepsilon(Li^+, NO_3^-) -$

$\varepsilon(Ni^{2+}, ClO_4^-)$. Using the selected values $\varepsilon(Ni^{2+}, ClO_4^-) = (0.37 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Li^+, NO_3^-) = (0.08 \pm 0.01)$ kg·mol^{-1} the correct result is

$$\varepsilon(NiNO_3^+, ClO_4^-) = (0.37 \pm 0.14)\ \text{kg·mol}^{-1}.$$

This value is included in our database, together with an estimate $\varepsilon(NiNO_3^+, Cl^-) = (0.05 \pm 0.10)$ kg·mol^{-1} based on charge correlations (HUMMEL 2009).

For $\log_{10}\beta_1°$ GAMSJÄGER et al. (2005) selected the result of their SIT analysis with an increased uncertainty :

$$\log_{10}\beta_1°(298.15\ \text{K}) = 0.5 \pm 1.0.$$

This value is also included in our database.

5.6.1.3 Aqueous nickel ammine complexes

Aqueous nickel amine complexes can be relevant for modelling work concerning the degradation products of anion exchange resins in a repository (VAN LOON & HUMMEL 1999). The stability constants for nickel amine complexes are taken from the seminal work of BJERRUM (1941).

We assumed that the ionic strength dependence of the isocoulombic reactions

$$Ni^{2+} + nNH_3(aq) \Leftrightarrow Ni(NH_3)_n^{2+} \qquad (n = 1 - 6)$$

can be neglected and thus, $\log_{10}\beta_n \approx \log_{10}\beta_n°$. We included the values of BJERRUM (1941) as supplemental data in our database.

In the absence of experimental data at varying ionic strength we used $\varepsilon(Ni(NH_3)_n^{2+}, Cl^-) = 0.15 \pm 0.10$ and $\varepsilon(Ni(NH_3)_n^{2+}, ClO_4^-) = 0.4 \pm 0.1$ as estimates based on charge correlations (HUMMEL 2009) and included them as supplemental data in our database.

5.6.2 Phosphorous compounds and complexes

5.6.2.1 Nickel phosphate compounds

A number of nickel phosphate solids have been reported, such as $Ni_3(PO_4)_2·8H_2O$, $Ni_3(PO_4)_2·7H_2O$, $Ni_3(PO_4)_2·1.25H_2O$, $NiHPO_4·3H_2O$, $(NiHPO_4)_2·3H_2O$, $Ni(H_2PO_4)_2·2H_2O$ and $Ni_3(PO_4)_2$. Nevertheless, chemical thermodynamic data for these solids are almost non-existent.

The most thoroughly studied solid is $Ni_3(PO_4)_2·8H_2O$.

However, GAMSJÄGER et al. (2005) concluded: “Though solubility measurements have been reported for $Ni_3(PO_4)_2·8H_2O$, $Ni_3(PO_4)_2·7H_2O$ and $NiHPO_4$, none are of adequate quality to allow chemical thermodynamic quantities to be calculated for these solids.”

5.6.2.2 Aqueous nickel phosphate complexes

The literature on complex formation between phosphate and Ni(II) ions in solution is not extensive. Under most conditions the complexes are weak, and difficult to identify unambiguously because of protonation equilibria involving both the ligand and the complexes.

Most of the studies were inspired by the possible parallels between phosphate complexation and biochemical interactions between phosphate esters and metal ions. These studies have been carried out over a fairly limited pH range (usually between 4 and 6) at low ionic strength (≤ 0.2 M). Most authors interpreted their results in terms of a single complex, $NiHPO_4(aq)$,

$$Ni^{2+} + HPO_4^{2-} \Leftrightarrow NiHPO_3(aq).$$

GAMSJÄGER et al. (2005) corrected these values to $I = 0$, and selected a weighted average of three results at 25°C:

$$\log_{10}K^\circ(298.15\ \mathrm{K}) = 3.05 \pm 0.09.$$

This value is included in our database.

As in the NEA-TDB uranium review (GRENTHE et al. 1992), the only polyphosphate(V) species considered by GAMSJÄGER et al. (2005) are the pyrophosphates (diphosphato complexes). Other polyphosphoric acid species have negligible equilibrium concentrations at total phosphate concentrations < 0.045 $\mathrm{mol \cdot dm^{-3}}$ and at temperatures below 200°C.

The complexes of the highly charged pyrophosphate ion with nickel are generally stronger than the phosphate complexes, but interpretation of the experiments is beset by the same difficulties as the interpretation of the phosphate studies with respect to unambiguous identification of the species.

GAMSJÄGER et al. (2005) selected the following values:

$$\mathrm{Ni^{2+} + P_2O_7^{4-} \Leftrightarrow NiP_2O_7^{2-}}$$

$$\log_{10}K^\circ(298.15\ \mathrm{K}) = 8.73 \pm 0.25$$

$$\Delta_r H_m^\circ(298.15\ \mathrm{K}) = 30.6 \pm 10.0\ \mathrm{kJ \cdot mol^{-1}}$$

$$\mathrm{Ni^{2+} + HP_2O_7^{3-} \Leftrightarrow NiHP_2O_7^{-}}$$

$$\log_{10}K^\circ(298.15\ \mathrm{K}) = 5.14 \pm 0.25$$

$$\Delta_r H_m^\circ(298.15\ \mathrm{K}) = 47.9 \pm 15.0\ \mathrm{kJ \cdot mol^{-1}}$$

The $\log_{10}K^\circ$ values were derived from a single reliable study at 25°C in 0.1 M $\mathrm{(CH_3)_4NCl}$ medium. The values for the enthalpies of reactions were derived from a single reliable study by analysing the temperature dependence of formation constants between 5 to 35°C in 0.1 M $\mathrm{KNO_3}$. GAMSJÄGER et al. (2005) accepted $\Delta_r H_m$ to be the same as $\Delta_r H_m^\circ$ at $I = 0$ without correction for either ionic strength or association of $\mathrm{K^+}$ with pyrophosphate and estimated their uncertainties.

All these values are included in our database, together with the estimates $\varepsilon(\mathrm{NiP_2O_7^{2-},Na^+}) = -(0.10 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$ and $\varepsilon(\mathrm{NiHP_2O_7^{-},Na^+}) = -(0.05 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$ based on charge correlations (HUMMEL 2009).

GAMSJÄGER et al. (2005) further stated: "It must be emphasised that the values selected in this review for formation for $\mathrm{NiHP_2O_7^-}$ and $\mathrm{NiP_2O_7^{2-}}$ should not be used for solutions more than 0.01 M in alkali metal ions unless explicit values are introduced for the pyrophosphate-alkali metal ion association constants."

5.6.3 Arsenic compounds and complexes

5.6.3.1 Nickel arsenide compounds

GAMSJÄGER et al. (2005) selected enthalpy of formation values for NiAs(cr), $\mathrm{NiAs_2}$(cr), $\mathrm{Ni_5As_2}$(cr), $\mathrm{Ni_{11}As_8}$(cr), as well as entropy values for NiAs(cr), $\mathrm{Ni_5As_2}$(cr), $\mathrm{Ni_{11}As_8}$(cr), and heat capacity functions for NiAs(cr) and $\mathrm{Ni_{11}As_8}$(cr). No information is available about the behaviour of these compounds in aqueous systems under environmental conditions and hence, the thermochemical data selected by GAMSJÄGER et al. (2005) are not included in our database (Table 5.4).

5.6.3.2 Nickel arsenate compounds

GAMSJÄGER et al. (2005) evaluated published values for the solubility of $Ni_3(AsO_4)_2·8H_2O(cr)$ (annabergite) for:

$$Ni_3(AsO_4)_2·8H_2O(cr) \Leftrightarrow 3\ Ni^{2+} + 2\ AsO_4^{3-} + 8\ H_2O(l)$$

using their selected auxiliary data and considering the effect of formation of the complex $NiHAsO_4(aq)$ (see Section 5.6.3.3) and selected:

$$\log_{10}K°(298.15\ K) = -(28.1 \pm 0.5).$$

This value is included in our database.

5.6.3.3 Aqueous nickel arsenate complexes

LANGMUIR et al. (1999) reported an estimated value of $\log_{10}K = 2.90$ for

$$Ni^{2+} + HAsO_4^{2-} \Leftrightarrow NiHAsO_3(aq).$$

GAMSJÄGER et al. (2005) argued that this value is similar to the value (3.05 ± 0.09) for the corresponding phosphate complex (see Section 5.6.2.2), and is an acceptable analogue value. They selected the value from LANGMUIR et al. (1999), but because of the unavailability of experimental values for comparison they assigned an uncertainty of ± 0.3,

$$\log_{10}K°(298.15\ K) = 2.9 \pm 0.3.$$

Usually, estimated values are included in our database as supplemental data. However, as GAMSJÄGER et al. (2005) used the above estimated value in their evaluation of the solubility product of $Ni_3(AsO_4)_2·8H_2O(cr)$ (annabergite) (see Section 5.6.3.2), these values should be used together in geochemical modelling and hence, both values are included as recommended values in our database.

5.6.3.4 Nickel arsenite compounds

GAMSJÄGER et al. (2005) used reported nickel concentrations, obtained from dissolution experiments of samples of nickel orthoarsenite in dilute nitric acid solutions at 20°C over 12 hours, assumed that the dissolution of the solid corresponds to the reaction:

$$Ni_3(AsO_3)_2·xH_2O(cr, hydr.) + 6\ H^+ \Leftrightarrow 3\ Ni^{2+} + 2\ HAsO_2(aq) + (2 + x)\ H_2O(l)$$

and calculated an equilibrium constant:

$$\log_{10}K°(298.15\ K) = 28.7 \pm 0.7.$$

Considering the limited data available, the assumptions made by the reviewers, and the lack of a corresponding nickel arsenite complex, this value is included in our database as supplemental data.

5.7 Group 14 compounds and complexes

5.7.1 Carbon compounds and complexes

5.7.1.1 Nickel carbonate compounds

$NiCO_3(cr)$, gaspéite, is the nickel end member of the solid solution $(Ni,Mg)CO_3(cr)$. GAMSJÄGER et al. (2005) analysed solubility data of synthetic $NiCO_3(cr)$ for the reaction:

$$NiCO_3(cr) + 2\ H^+ \Leftrightarrow Ni^{2+} + CO_2(g) + H_2O(l)$$

and selected

$$\log_{10}{}^*K°(298.15\ K) = 7.16 \pm 0.18.$$

They stated that this value obtained from solubility measurements of pure synthetic $NiCO_3$(cr) falls well within the error limits of values re-evaluated from decomposition studies, $NiCO_3(s) \Leftrightarrow NiO(s) + CO_2(g)$, but clearly is more precise.

Recalculation of this value for the reaction

$$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$$

using the selected values for the carbonic acid system results in

$$\log_{10}K°(298.15\ K) = -(11.00 \pm 0.18).$$

It seems that there is only one low temperature heat capacity study of $NiCO_3$(cr), and GAMSJÄGER et al. (2005) selected from this source

$$S_m° (NiCO_3, cr, 298.15\ K) = (85.4 \pm 2.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}° (NiCO_3, cr, 298.15\ K) = (90.3 \pm 4.1)\ J \cdot K^{-1} \cdot mol^{-1}$$

All these values are included in our database.

$NiCO_3 \cdot 5.5H_2O$(cr), hellyerite, has been prepared by a new method, and solubility measurements were carried out at different temperatures at $I = 1.0$ m (Na)ClO_4, as well as solubility data have been determined at 25°C and different ionic strengths. In either case the pH variation method was used to study the dissolution reaction according to:

$$NiCO_3 \cdot 5.5H_2O(cr) + 2\ H^+ \Leftrightarrow Ni^{2+} + CO_2(g) + 6.5\ H_2O(l)$$

GAMSJÄGER et al. (2005) selected

$$\log_{10}{}^*K°(298.15\ K) = 10.63 \pm 0.10$$

from these new studies. A re-evaluation of two very old experimental data sets by GAMSJÄGER et al. (2005) resulted in $\log_{10}{}^*K° = 10.56 \pm 0.10$, which compares favourably with the new data.

Recalculation of this value for the reaction

$$NiCO_3 \cdot 5.5H_2O(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-} + 5.5\ H_2O(l)$$

using the selected values for the carbonic acid system results in

$$\log_{10}K°(298.15\ K) = -(7.53 \pm 0.10).$$

From the weak temperature dependence of the solubility constant GAMSJÄGER et al. (2005) calculated the enthalpy of reaction and the entropy of $NiCO_3 \cdot 5.5H_2O$(cr) using a non-linear least squares optimisation routine. They selected:

$$S_m° (NiCO_3 \cdot 5.5H_2O, cr, 298.15\ K) = (311.1 \pm 10.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

Apparently no experimental low-temperature heat capacity data of $NiCO_3 \cdot 5.5H_2O$(cr) have been reported so far. GAMSJÄGER et al. (2005) obtained a crude estimate by analogy to magnesium carbonate and its hydrates:

$$C_{p,m}° (NiCO_3 \cdot 5.5H_2O, cr, 298.15\ K) = (405.4 \pm 50.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

All these values are included in our database.

5.7.1.2 Aqueous nickel carbonate complexes

GAMSJÄGER et al. (2005) start this section with:

"The formation of carbonato complexes in the system Ni^{2+} – H_2O – CO_2 has been critically discussed and re-evaluated in a seminal review by HUMMEL & CURTI (2003).

So far only one paper has been published (EMARA et al. 1987) describing an attempt to experimentally determine the equilibrium constant, β_1, of the reaction

$$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$$

EMARA et al. (1987) clearly misinterpreted their data and did not provide enough information to allow recalculation. Consequently, the stability constant of $NiHCO_3^+$ reported in EMARA et al. (1987) cannot be included in this review."

Values of equilibrium constants for the above reaction estimated by various procedures differ considerably: $0.96 \le \log_{10}\beta_1° \le 3.08$.

The stability constant of the carbonato complex according to reaction

$$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq)$$

has also been estimated leading to an even larger discrepancy: $2.56 \le \log_{10}K_1° \le 6.87$.

For the reaction

$$NiCO_3(aq) + CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$$

one estimate exists for its equilibrium constant ($\log_{10}K_2° = 3.24$).

As the basis of the individual estimation procedures is rather dubious, variations of up to more than four log-units in these stability constants are to be expected (HUMMEL & CURTI 2003). Again neither of these values appeared GAMSJÄGER et al. (2005) suitable to be included in their review.

HUMMEL & CURTI (2003) proposed estimating K_1 using either the good correlation between the equilibrium constants of Ni(II) and Co(II) complexes and the poor data available for K_1 of $CoCO_3(aq)$ or the rather poor correlation between Ni(II) and Zn(II) complexes and the excellent data for K_1 of $ZnCO_3(aq)$. Both methods result in similar lower and upper bounds: $4 < \log_{10}K_1° < 5.5$.

A comparison of the stabilities of transition metal hydrogen carbonato as well as carbonato complexes led to $1 < \log_{10}\beta_1° < 2$ and $\log_{10}K_2° < (\log_{10}K_1° - 2)$ (HUMMEL & CURTI 2003). GAMSJÄGER et al. (2005) then concluded that "even the careful and competent guesswork of HUMMEL & CURTI (2003) resulted in rough estimates only."

GAMSJÄGER et al. (2005) continued: "Fortunately, in a recent paper, BAEYENS et al. (2003) investigated Ni-carbonato and -oxalato complexes by an ion exchange method. Ni-carbonato complexes were investigated at constant ionic strength $I = 0.5$ M $NaClO_4$ / $NaHCO_3$ and (22 ± 1)°C. The experimentally obtained complexation constant, $\log_{10}K_1(295.12\ K) = 2.9 \pm 0.3$, was extrapolated to $I = 0$ with the SIT approach to give

$$\log_{10}K_1°(298.15\ K) = 4.2 \pm 0.4.$$

This result was finally selected for the present review. The somewhat higher uncertainty was assigned, because BAEYENS et al. (2003) carried out their measurements at 22°C instead of 25°C, and used a relatively simple approximation to extrapolate $\log_{10}K_1°$ to $I = 0$."

This value is included in our database.

GAMSJÄGER et al. (2005) further stated: “Only upper bounds can be given for the stabilities of $NiHCO_3^+$ and $Ni(CO_3)_2^{2-}$: $\log_{10}\beta_1°(298.15\ K) < 1.4$ and $\log_{10}K_2°(298.15\ K) < 2$ (BAEYENS et al. 2003). Both upper bounds compare well with the lower limits of the range predicted by HUMMEL & CURTI (2003), but do not qualify for being included in the list of selected values in this review.”

We included in our database the values $\log_{10}\beta_1°(298.15\ K) \approx 1$ and $\log_{10}\beta_2°(298.15\ K) < 6$ as supplemental data.

In the absence of experimentally determined SIT interaction coefficients, we included the estimates $\varepsilon(NiHCO_3^+, Cl^-) = (0.05 \pm 0.10)$ kg·mol^{-1}, $\varepsilon(NiHCO_3^+, ClO_4^-) = (0.2 \pm 0.1)$ kg·mol^{-1} and $\varepsilon(Ni(CO_3)_2^{2-}, Na^+) = -(0.10 \pm 0.10)$ kg·mol^{-1} based on charge correlations (HUMMEL 2009).

5.7.1.3 Aqueous nickel cyanide complexes

Most authors have agreed that the formation of $NiCN^+$, $Ni(CN)_2(aq)$ and $Ni(CN)_3^-$ cannot be detected in the equilibrated solutions. Reliable values were reported for the equilibrium

$$Ni^{2+} + 4\ CN^- \Leftrightarrow Ni(CN)_4^{2-}$$

GAMSJÄGER et al. (2005) found that although only a limited number of data are available in $NaClO_4$ media, the precision of the constants is assumed to be good enough to perform an SIT analysis. The weighted linear regression using five data points yielded the selected value of:

$$\log_{10}\beta_4°(298.15\ K) = 30.20 \pm 0.12.$$

From the slope of the SIT regression line, $\Delta\varepsilon(NaClO_4) = -(0.465 \pm 0.045)$ kg·mol^{-1} can be calculated. Using the selected value for $\varepsilon(Ni^{2+}, ClO_4^-)$ and $\varepsilon(Na^+, CN^-) = (0.07 \pm 0.03)$ kg·mol^{-1} leads to a value of

$$\varepsilon(Na^+, Ni(CN)_4^{2-}) = (0.185 \pm 0.081)\ kg\cdot mol^{-1}.$$

The reaction enthalpy of the formation of the tetracyano complex has been studied calorimetrically. GAMSJÄGER et al. (2005) selected:

$$\Delta_r H_m°(298.15\ K) = -(180.7 \pm 4.0)\ kJ \cdot mol^{-1}.$$

Since the pentacyano complex is rather unstable, high cyanide concentrations were used to achieve its formation, which resulted in considerable replacement of the original background electrolyte by NaCN. Due to this medium effect, GAMSJÄGER et al. (2005) assigned considerably higher uncertainties to the equilibrium constants than originally reported. The SIT analysis of the constants determined in $NaClO_4$ media for the reaction:

$$Ni(CN)_4^{2-} + CN^- \Leftrightarrow Ni(CN)_5^{3-}$$

resulted in

$$\log_{10}K_5°(298.15\ K) = -(1.70 \pm 0.36)$$

and $\Delta\varepsilon(NaClO_4) = (0.00 \pm 0.11)$ kg·mol^{-1}. From the latter value,

$$\varepsilon(Na^+, Ni(CN)_5^{3-}) = (0.25 \pm 0.14)\ kg\cdot mol^{-1}$$

can be derived. Using the equilibrium constant $\log_{10}\beta_4°$ from above, the overall formation constant of the $Ni(CN)_5^{3-}$ species is

$$Ni^{2+} + 5\ CN^- \Leftrightarrow Ni(CO)_5^{3-}$$

$$\log_{10}\beta_5°(298.15\ K) = 28.5 \pm 0.5.$$

Neglecting the ionic strength dependence, $\Delta_r H_m°(298.15\ K) = -(10.4 \pm 4.0)\ kJ \cdot mol^{-1}$ can be estimated from the temperature variation of $\log_{10}K_5$. The combination of the above two enthalpy values yielded for the overall formation reaction:

$$\Delta_r H_m°(298.15\ K) = -(191.1 \pm 8.0)\ kJ \cdot mol^{-1}.$$

These values have been included in our database.

5.7.1.4 Aqueous nickel thiocyanide complexes

In the aqueous nickel thiocyanide system, depending on the ligand-to-metal ratio, the formation of four species is generally recognised:

$$Ni^{2+} + q\ SCN^{-} \Leftrightarrow Ni(SCN)_q^{2-q}$$

with $q = 1 – 4$. A majority of the experimental data accepted by GAMSJÄGER et al. (2005) refers to the formation of the $NiSCN^{+}$ species in perchlorate media. SIT analysis of these data showed acceptable consistency, and the weighted linear regression using 12 data points yielded the selected value of:

$$\log_{10}\beta_1°(q = 1, 298.15\ K) = 1.81 \pm 0.04.$$

From the slope of the SIT regression line, $\Delta\varepsilon(q = 1, ClO_4^-) = -(0.109 \pm 0.025)\ kg\cdot mol^{-1}$ can be calculated. Since no experimental data are available $\varepsilon(H^+, CN^-)$ and $\varepsilon(Li^+, CN^-)$ were assumed to be equal to $\varepsilon(Na^+, CN^-)$. Using the selected values for $\varepsilon(Ni^{2+}, ClO_4^-)$ and $\varepsilon(Na^+, CN^-)$, $\Delta\varepsilon(q = 1, ClO_4^-)$ leads to a value of

$$\varepsilon(NiSCN^+, ClO_4^-) = (0.31 \pm 0.03)\ kg\cdot mol^{-1}.$$

Less data are available for the formation of the $Ni(SCN)_2(aq)$ and $Ni(SCN)_3^-$ species. The SIT treatment of the data accepted by GAMSJÄGER et al. (2005) resulted in the following selected thermodynamic formation constants:

$$\log_{10}\beta_2°(q = 2, 298.15\ K) = 2.69 \pm 0.07,$$

$$\log_{10}\beta_3°(q = 3, 298.15\ K) = 3.02 \pm 0.18.$$

From the slopes, $\Delta\varepsilon(q = 2, ClO_4^-) = -(0.091 \pm 0.043)\ kg\cdot mol^{-1}$ and $\Delta\varepsilon(q = 3, ClO_4^-) = -(0.14 \pm 0.12)\ kg\cdot mol^{-1}$ can be derived. These parameters lead to the values:

$$\varepsilon(Ni(SCN)_2(aq), Na^+ + ClO_4^-) = (0.38 \pm 0.06)\ kg\cdot mol^{-1},$$

$$\varepsilon(Na^+, Ni(SCN)_3^-) = (0.66 \pm 0.13)\ kg\cdot mol^{-1}.$$

Several experimental values are published for $\log_{10}\beta_4$ or $\log_{10}K_4$. However, GAMSJÄGER et al. (2005) concluded that, although there is good evidence for the existence of $Ni(SCN)_4^{2-}$, the available data cannot be used to derive a selected value.

GAMSJÄGER et al. (2005) found five reliable reports for the reaction enthalpies of the formation of $Ni(SCN)_q^{2-q}$ ($q = 1 – 3$) complexes. These data do not allow a correct evaluation of the ionic strength dependence, therefore it ws assumed that the reaction enthapies are independent of the ionic strength. GAMSJÄGER et al. (2005) selected the following weighted averages:

$$\Delta_r H_m°(q = 1, 298.15\ K) = -(11.8 \pm 5.0)\ kJ \cdot mol^{-1},$$

$$\Delta_r H_m°(q = 2, 298.15\ K) = -(21\pm 8)\ kJ \cdot mol^{-1},$$

$$\Delta_r H_m°(q = 3, 298.15\ K) = -(29 \pm 10)\ kJ \cdot mol^{-1}.$$

All these values have been included in our database.

5.7.2 Silicate compounds and complexes

Nickel silicate compounds and complexes are discussed in a separate report on silica and silicates.

Table 5.4: Ni data selected by NEA (Gamsjäger et al. 2005) but not included in TDB 12/07. For explanation see text.

Gas	Ni(g)
Liquid	Ni(l)
Solids	NiF_2(cr), $NiCl_2$(cr), $NiCl_2\cdot2H_2O$(cr), $NiCl_2\cdot4H_2O$(cr), $NiCl_2\cdot6H_2O$(cr), $NiBr_2$(cr), NiI_2(cr), β-$Ni(IO_3)_2$, $Ni(IO_3)_2\cdot2H_2O$(cr), α-NiS, β-NiS, NiS_2(cr), Ni_3S_2(cr), Ni_9S_8(cr), $NiSO_4$(cr), α-$NiSO_4\cdot6H_2O$, β-$NiSO_4\cdot6H_2O$, $NiSO_4\cdot7H_2O$(cr), $Ni(NO_3)_2\cdot2H_2O$(cr), $Ni(NO_3)_2\cdot4H_2O$(cr), $Ni(NO_3)_2\cdot6H_2O$(cr), NiAs(cr), $NiAs_2$(cr), Ni_5As_2(cr), $Ni_{11}As_8$(cr).

Table 5.5: Selected nickel data. All data included in TDB Version 12/07 are taken from GAMSJÄGER et al. (2005) with the exception of those marked with an asterisk (*). Core data are bold and supplemental data are in italics. New or changed data with respect to TDB Version 01/01 (HUMMEL et al., 2002) are shaded.

		TDB Version 01/01				TDB Version 12/07				
Name	**Redox**	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	S_{m}° [J · K^{-1} · mol^{-1}]	$C_{p,\mathrm{m}}^{\circ}$ [J · K^{-1} · mol^{-1}]	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	S_{m}° [J · K^{-1} · mol^{-1}]	$C_{p,\mathrm{m}}^{\circ}$ [J · K^{-1} · mol^{-1}]	**Species**
Ni(cr)	0	0.0	0.0	**29.87 ± 0.21**	-	0.0	0.0	**29.87 ± 0.20**	26.07 ± 0.10	Ni(cr)
Ni+2	II	-45.5 ± 3.4	-54.1 ± 2.5	-130 ± 3	-	-45.77 ± 0.77	-55.01 ± 0.88	-131.8 ± 1.4	-46.1 ± 7.5	Ni^{2+}

		TDB Version 01/01		TDB Version 12/07		
Name	**Redox**	$\log_{10}\beta^{\circ}$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\log_{10}\beta^{\circ}$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	**Reaction**
NiOH+	II	-9.50 ± 0.36	50 ± 21	-9.54 ± 0.14	53.8 ± 1.7	$Ni^{2+} + H_2O(l) \Leftrightarrow NiOH^{+} + H^{+}$
Ni(OH)2	II	-18.0 ± 1.0	86 ± 13	*(≤ -18)*[a]	*(≈ 90)*[a]	*$Ni^{2+} + 2\ H_2O(l) \Leftrightarrow Ni(OH)_2(aq) + 2\ H^{+}$*
Ni(OH)3-	II	-29.7 ± 1.5	121 ± 18	-29.2 ± 1.7	*(121.2 ± 6.5)*[a]	$Ni^{2+} + 3\ H_2O(l) \Leftrightarrow Ni(OH)_3^{-} + 3\ H^{+}$
Ni(OH)4-2	II	-44.9 ± 0.6	-	-	-	$Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni(OH)_4^{2-} + 4\ H^{+}$
Ni2OH+3	II	-9.8 ± 1.2	35 ± 17	-10.6 ± 1.0	45.9 ± 6.0	$2\ Ni^{2+} + H_2O(l) \Leftrightarrow Ni_2OH^{3+} + H^{+}$
Ni4(OH)4+4	II	-27.9 ± 1.0	170 ± 17	-27.52 ± 0.15	190 ± 10	$4\ Ni^{2+} + 4\ H_2O(l) \Leftrightarrow Ni_4(OH)_4^{4+} + 4\ H^{+}$
NiF+	II	1.3	-	1.43 ± 0.08	9.5 ± 3.0	$Ni^{2+} + F^{-} \Leftrightarrow NiF^{+}$
NiCl+	II	0.40	-	0.08 ± 0.60	-	$Ni^{2+} + Cl^{-} \Leftrightarrow NiCl^{+}$
NiCl2	II	0.96	-	-	-	$Ni^{2+} + 2\ Cl^{-} \Leftrightarrow NiCl_2(aq)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ · mol^{-1}]	$\log_{10}\beta^\circ$	$\Delta_r H_m^\circ$ [kJ · mol^{-1}]	**Reaction**
NiHS+	II	5.5 ± 0.2	-	(5.5 ± 0.2)*	-	$Ni^{2+} + HS^- \Leftrightarrow NiHS^+$
Ni(HS)2	II	11.1 ± 0.1	-	(11.1 ± 0.1)*	-	$Ni^{2+} + 2\ HS^- \Leftrightarrow Ni(HS)_2(aq)$
NiSO4	II	2.31	13.975	2.35 ± 0.03	5.66 ± 0.81	$Ni^{2+} + SO_4^{2-} \Leftrightarrow NiSO_4(aq)$
Ni(SO4)2-2	II	3.2	-	-	-	$Ni^{2+} + 2\ SO_4^{2-} \Leftrightarrow Ni(SO_4)_2^{2-}$
NiNO3+	II	0.4	-	0.5 ± 1.0	-	$Ni^{2+} + NO_3^- \Leftrightarrow NiNO_3^+$
Ni(NO3)2	II	-0.6	-	-	-	$Ni^{2+} + 2\ NO_3^- \Leftrightarrow Ni(NO_3)_2(aq)$
NiNH3+2	II	2.7	-	(2.7)*	-	$Ni^{2+} + NH_3(aq) \Leftrightarrow NiNH_3^{2+}$
Ni(NH3)2+2	II	4.9	-	(4.9)*	-	$Ni^{2+} + 2\ NH_3(aq) \Leftrightarrow Ni(NH_3)_2^{2+}$
Ni(NH3)3+2	II	6.5	-	(6.5)*	-	$Ni^{2+} + 3\ NH_3(aq) \Leftrightarrow Ni(NH_3)_3^{2+}$
Ni(NH3)4+2	II	7.6	-	(7.6)*		$Ni^{2+} + 4\ NH_3(aq) \Leftrightarrow Ni(NH_3)_4^{2+}$
Ni(NH3)5+2	II	8.3	-	(8.3)*	-	$Ni^{2+} + 5\ NH_3(aq) \Leftrightarrow Ni(NH_3)_5^{2+}$
Ni(NH3)6+2	II	8.2	-	(8.2)*	-	$Ni^{2+} + 6\ NH_3(aq) \Leftrightarrow Ni(NH_3)_6^{2+}$
NiH2PO4+	II	1.544	-	-	-	$Ni^{2+} + H_2PO_4^- \Leftrightarrow NiH_2PO_4^+$
NiHPO4	II	2.934	-	3.05 ± 0.09	-	$Ni^{2+} + HPO_4^{2-} \Leftrightarrow NiHPO_4(aq)$
NiPO4-	II	8.374	-	-	-	$Ni^{2+} + PO_4^{3-} \Leftrightarrow NiPO_4^-$
NiHP2O7-	II	9.258	-	-	-	$Ni^{2+} + 2\ HPO_4^{2-} + H^+ \Leftrightarrow NiHP_2O_7^- + H_2O(l)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ · mol^{-1}]	**Reaction**
NiHP2O7-	II	-	-	5.14 ± 0.25	47.9 ± 15.0	$Ni^{2+} + HP_2O_7^{3-} \Leftrightarrow NiHP_2O_7^-$
NIP2O7-2	II	3.088	9.917	-	-	$Ni^{2+} + 2\ HPO_4^{2-} \Leftrightarrow NiP_2O_7^{2-} + H_2O(l)$
NiP2O7-2	II	-	-	8.73 ± 0.25	30.6 ± 10.0	$Ni^{2+} + P_2O_7^{4-} \Leftrightarrow NiP_2O_7^{2-}$
NiHAsO4	II	-	-	2.9 ± 0.3	-	$Ni^{2+} + HAsO_4^{2-} \Leftrightarrow NiHAsO_4(aq)$
NiCO3	II	4.0 ± 0.3	-	4.2 ± 0.4	-	$Ni^{2+} + CO_3^{2-} \Leftrightarrow NiCO_3(aq)$
Ni(CO3)2-2	II	< 6	-	*(< 6)**	-	$Ni^{2+} + 2\ CO_3^{2-} \Leftrightarrow Ni(CO_3)_2^{2-}$
NiHCO3+	II	≈ 1	-	*(≈ 1)**	-	$Ni^{2+} + HCO_3^- \Leftrightarrow NiHCO_3^+$
Ni(CN)4-2	II	-	-	30.2 ± 0.12	-180.7 ± 4.0	$Ni^{2+} + 4\ CN^- \Leftrightarrow Ni(CN)_4^{2-}$
Ni(CN)5-3	II	-	-	28.5 ± 0.5	-191.1 ± 8.0	$Ni^{2+} + 5\ CN^- \Leftrightarrow Ni(CN)_5^{3-}$
NiSCN+	II	-	-	1.81 ± 0.04	-11.8 ± 5.0	$Ni^{2+} + SCN^- \Leftrightarrow NiSCN^+$
Ni(SCN)2	II	-	-	2.69 ± 0.07	-21 ± 8	$Ni^{2+} + 2\ SCN^- \Leftrightarrow Ni(SCN)_2(aq)$
Ni(SCN)3-	II	-	-	3.02 ± 0.18	-29 ± 10	$Ni^{2+} + 3\ SCN^- \Leftrightarrow Ni(SCN)_3^-$

[a] Derived from data reported but not selected by GAMSJÄGER et al. (2005)

		TDB Version 01/01		**TDB Version 12/07**			
Name	**Redox**	**$\log_{10}K_{s,0}°$**	**$\Delta_rH_m°$** [kJ · mol^{-1}]	**$\log_{10}K_{s,0}°$**	**$S_m°$** [J · K^{-1} · mol^{-1}]	**$C_{p,m}°$** [J · K^{-1} · mol^{-1}]	**Reaction**
Ni(OH)2(cr, β)[a]	II	10.5 ± 0.5	73 ± 10	11.02 ± 0.20	80.0 ± 0.8	82.0 ± 0.3	$Ni(OH)_2(cr, \beta) + 2 H^+ \Leftrightarrow Ni^{2+} + 2 H_2O(l)$
NiO(cr)	II	-	-	12.48 ± 0.15	38.4 ± 0.4	44.4 ± 0.1	$NiO(cr) + 2 H^+ \Leftrightarrow Ni^{2+} + H_2O(l)$
NiCO3(cr)	II	-11.2 ± 0.3	-	-11.00 ± 0.18	85.4 ± 2.0	90.3 ± 4.1	$NiCO_3(cr) \Leftrightarrow Ni^{2+} + CO_3^{2-}$
NiCO3:5.5H2O(s)	II	-	-	-7.53 ± 0.10	311.1 ± 10	405.4 ± 50	$NiCO_3 \cdot 5.5H_2O(s) \Leftrightarrow Ni^{2+} + CO_3^{2-} + 5.5 H_2O(l)$
Ni3(AsO4)2:8H2O(s)	II	-	-	-28.1 ± 0.5	540.8 ± 73.3	-	$Ni_3(AsO_4)_2 \cdot 8H_2O(s) \Leftrightarrow 3 Ni^{2+} + 2 AsO_4^{3-} + 8 H_2O(l)$
Ni3(AsO3)2:xH2O(s)	II	-	-	*28.7 ± 0.7*	-	-	*$Ni_3(AsO_3)_2 \cdot xH_2O(s) + 6H^+ \Leftrightarrow 3 Ni^{2+} + 2As(OH)_3(aq) + x H_2O(l)$*

[a] TDB Version 01/01: Theophrastite

Table 5.6: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg · mol^{-1}] for updated auxiliary data. The data included in TDB Version 12/07 are taken from GAMSJÄGER et al. (2005). Data estimated according to HUMMEL (2009) are shaded.

j ***k*** → ↓	**Cl^-**	**ClO_4^-**	**NO_3^-**	**$Na^+ + ClO_4^-$**	**Na^+**	**K^+**
	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
Ni+2	0.17 ± 0.02	0.37 ± 0.03	0.182 ± 0.010	0	0	0
NiOH+	-0.01 ± 0.07	0.14 ± 0.07	-	0	0	0
Ni(OH)2	0	0	0	0	0	0
Ni(OH)3-	0	0	0	0	-0.05 ± 0.20	-
Ni2OH+3	0.25 ± 0.10	0.59 ± 0.15	-	0	0	0
Ni4(OH)4+4	0.43 ± 0.08	1.08 ± 0.08	-	0	0	0
NiF+	0.05 ± 0.10	0.34 ± 0.08	-	0	0	0
NiCl+	(0.47 ± 0.06)[a]	(0.47 ± 0.06)[a]	-	0	0	0
NiHS+	0.05 ± 0.10	0.2 ± 0.1	-	0	0	0
Ni(HS)2	0	0	0	0	0	0
NiSO4	0	0	0	0	0	0
NiNO3+	0.05 ± 0.10	0.37 ± 0.14	-	0	0	0
NiNH3+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)2+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)3+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)4+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)5+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
Ni(NH3)6+2	*0.15 ± 0.10*	*0.4 ± 0.1*	-	0	0	0
NiHPO4	0	0	0	0	0	0
NiHP2O7-	0	0	0	0	*-0.05 ± 0.10*	-
NiP2O7-2	0	0	0	0	*-0.10 ± 0.10*	-
NiHAsO4	0	0	0	0	0	0
NiCO3	0	0	0	0	0	0
Ni(CO3)2-2	0	0	0	0	*-0.10 ± 0.10*	-
NiHCO3+	*0.05 ± 0.10*	*0.2 ± 0.1*	-	0	0	0
Ni(CN)4-2	0	0	0	0	0.185 ± 0.081	-
Ni(CN)5-3	0	0	0	0	0.25 ± 0.14	-
NiSCN+	*0.05 ± 0.10*	0.31 ± 0.04	-	0	0	0
Ni(SCN)2	0	0	0	0.38 ± 0.08	0	0
Ni(SCN)3-	0	0	0	0	0.66 ± 0.13	-

[a] In combination with $\varepsilon(Ni^{2+}, Cl^-) = (Ni^{2+}, ClO_4^-) = 0.37 \pm 0.03$

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