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Titel	The PSI/Nagra Chemical Thermodynamic Database 12/07 (update oft he Nagra/PSI TDB 01/01): Data Selection of Selenium	Ersetzt
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Abstract:

This report provides an update oft the Nagra/PSI Chemical Thermodynamic Data Base 01/01 (Hummel et al. 2002) with respect to selenium. Most information on compounds complexes and solid phases reported was taken from the NEA review of the „Chemical Thermodynamics of Selenium“ by Olin et al. (2005). More recent data were taken from corresponding publications (e.g. on barium selenates, Rai et al. 2014) when available, or from inhouse work (e.g. solubility of Se(0)).

The updated database will be called PSI/Nagra Chemical Thermodynamic Database 12/07. The numbering of paragraphs and equilibria in the present report was selected according to the summarising PSI database report.

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7 Selenium

7.1 Introduction

Intermediate updates of the Nagra/PSI thermodynamic database 01/01 (Hummel et al. (2002) concerning selenium had been performed mainly based on a comprehensive review of Séby et al. (2001), but was never reported as a separate TDB update report. In the meantime the OECD NEA Thermodynamic Database (TDB) project on selenium has finished (Olin et al. 2005). The present chapter provides and discusses the equilibria selected from Olin et al. (2005) for the PSI/Nagra Chemical Thermodynamic Database 12/07.

The compilation of Séby et al. (2001) and the NEA report Olin et al. (2005) list a large number of "solubility products" for metal selenates, -selenites and -selenides. However, selenates and selenites often have high solubilities and it is questionable, whether such solids will ever be solubility limiting phases in environmental systems or not. We therefore restricted our selection to solubility products for use in systems relevant to radioactive waste management. On the other hand, many metal selenides are reported to have extremely low solubility products (similar to the sulfides; the winner in this list is PtSe with a $\log_{10}K_{so}$ of -81.4!). In database applications these low solubility products have then to be "compensated" with rather high complex formation constants for the neutral complexes, in order to describe expected/measured solute concentrations. We do not think that such data should flow into the update in their present state, particularly when reliable solubility data for neutral complexes are missing (note that exceptions were made in the report for silver- and mercury selenides).

The NEA review volumes provide tables with selected SIT coefficients for the interaction of cations with Cl^-, ClO_4^-, and NO_3^-, and of anions with Li^+, Na^+, and K^+. Since numerous ion interaction coefficients of selenium species are not known, we used an estimation method based on charge correlations by Hummel (2009) to fill the gaps. The selected ion interaction coefficients are listed in Table 7.2.

7.2 Elemental selenium

Based on Gaur et al. (1981), Olin et al. (2005) recommend

$$S^\circ_m \text{ (Se, trigonal, 298.15 K)} = (42.09 \pm 0.33) \text{ J mol}^{-1} \text{ K}^{-1},$$

$$C^\circ_{p,m} \text{ (Se, trigonal, 298.15 K)} = (25.09 \pm 0.30) \text{ J mol}^{-1} \text{ K}^{-1}.$$

for the trigonal elemental selenium, also termed Se(cr). The unusual analytical heat capacity expression from the original source was re-evaluated to the standard form:

$$C^\circ_{p,m} \text{ (Se, trigonal, 298.15 – 500 K)} =$$

$$= (24.8014 + 1.2859\cdot10^{-3}\ T + 9.9273\cdot10^{-6}\ T^2 - 0.8713\cdot10^5\ T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Note that an earlier recommendation by Grenthe et al. (1992), based on the work of Grønvold et al. (1984), provided (42.27 ± 0.05) J K^{-1} mol^{-1} for S°_m(Se, trigonal, 298.15 K), the molal entropy of elemental selenium.

7.2.1 Solubility of elemental selenium

Earlier applications of the thermodynamic data for selenium (Berner 2002, 2002a) demonstrate a rather deep minimum of calculated selenium solubilities between the stability fields of Se(-II) and Se(IV) (Figure 7.1). Such behavior is chemically unreasonable and most likely indicates missing solution species. A reasonable candidate for such a missing species is $Se^0_x(aq)$. Indeed, Hummel (2013) found evidence in the literature that a few elements (metals) from the groups 11 to 16 (exhibiting a B-type character) may dissolve in aqueous solution as neutral species.

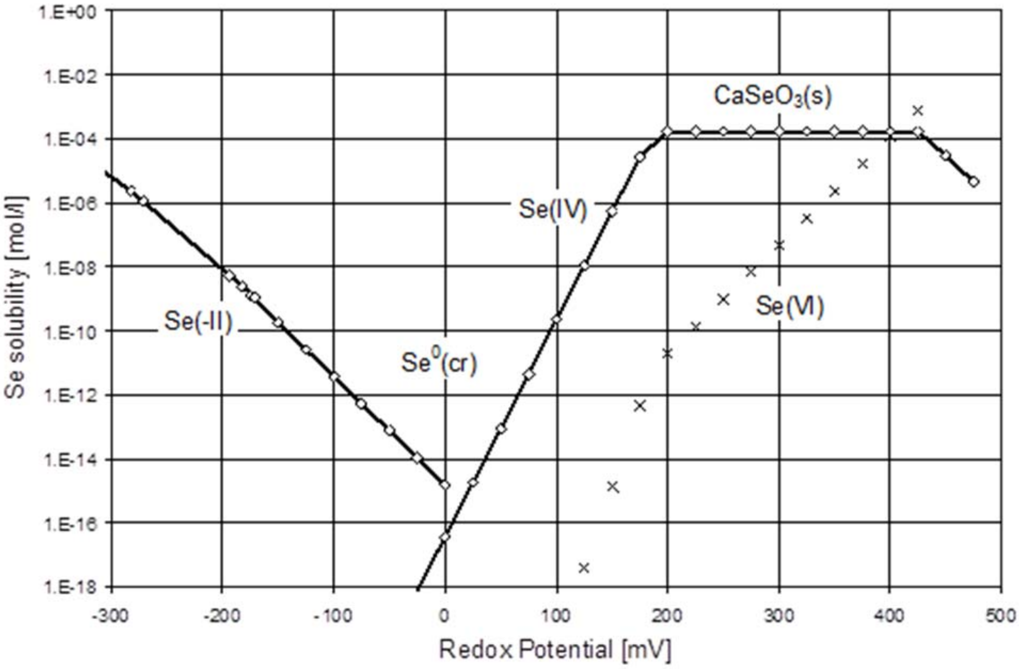

Figure 7.1: Solubility of Se in bentonite pore water at pH 7.3 as a function of system Eh, taken from Berner (2002). All solution parameters except Eh were kept constant.

Olin et al. (2005) debate on the formation of the polyselenides Se_2^{2-}, Se_3^{2-}, and Se_4^{2-} in equilibrium with Se(cr) and provide a model and thermodynamic data (see below). They do, however, not mention the potential formation of $Se_8^0(aq)$ in equilibrium with Se(cr).

In the chemically similar sulfur system the solubility of elemental sulfur is well established. In contact with solid sulfur $S_8(s)$ Boulegue (1978) and Kamishny Jr. (2009) measured $S_8^0(aq)$ solubilities of $(1.9 \pm 0.6)\cdot 10^{-8}$ and $(3.01 \pm 1.04)\cdot 10^{-8}$ $mol\cdot kg^{-1}$ in water. With $(2.63 \pm 0.04)\cdot 10^{-8}$ $mol\cdot l^{-1}$ Wang and Tessier (2009) reported a value between the former two solubilities. Taking the average of these values, the solubility of elemental sulfur may be estimated with a rather high precision ($(2.63 \pm 0.13)\cdot 10^{-8}$ $mol\cdot kg^{-1}$ of $S_8^0(aq)$).

For many processes the analogy among sulfur and selenium is well established. If this analogy is also applied to the solubility of selenium, one obtains

$$Se(s) \Leftrightarrow Se^0_8(aq) \qquad (7.1)$$

$$K_s°(7.1) = (2.63 \pm 0.13)\cdot 10^{-8}$$

Solid selenium forms a modification with a (distorted) structure similar to that of rhomboedric $S_8(\alpha)$.The formation of $Se_8(aq)$ is not confirmed by experimental studies but may be surmised from the polyselenide model accepted by Olin et al. (2005). It should be noted that the few experimental studies justifying the polyselenide model were conducted at millimolar solutions of selenide. This means that trace concentrations of neutral $Se_8(aq)$ would disappear as undetectable within the analytical error. However, if compared to the formerly calculated minimum of about 10^{-15} $mol\cdot kg^{-1}$ (Figure 7.1), trace concentrations of about 10^{-7} $mol\cdot kg^{-1}$ constitute an increase of about 8 orders of magnitude in the Eh range of ~0 mV. From a point of view of applying thermodynamic data to real systems the assumption of a species $Se_8(aq)$ would consistently meet the requirements of the missing species.

However, for practical use it's suggested to establish an equilibrium of the form

$$Se(cr) \Leftrightarrow Se^0(aq) \qquad (7.2)$$

with

$$K_s(7.2) = 2 \cdot 10^{-7}$$

The uncertainty of this value is unclear, from $K_s(7.1)$ one would calculate $(\pm\ 0.1) \cdot 10^{-7}$. The value of $K_s(7.2)$ is in the range from $\sim 10^{-9}$ mol·kg^{-1} to about $2 \cdot 10^{-7}$ mol·kg^{-1} and we propose using the upper end of this range for the solubility of elemental selenium.

From equilibrium (7.2), using $\Delta_f G°_m(Se(cr), 298.15\ K) = 0$, one derives

$$\Delta_f G°_m(Se^0(aq), 298.15\ K) = 38.24\ kJ \cdot mol^{-1},$$

or, similarly,

$$\Delta_f G°_m(Se_8(aq), 298.15\ K) = (43.27 \pm 0.12)\ kJ \cdot mol^{-1}.$$

The equilibrium (7.2) (as well as the corresponding $\Delta_f G°_m$-values) are not included in the TDB 12/07. It is, however, recommended to use equilibrium (7.2) to fill an obvious gap in the database when the calculation of selenium solubilities becomes an important task.

7.3 Redox equilibria in the selenium system

There are nearly no studies concerning the redox equilibria among the relevant oxidation states Se(IV)/Se(VI) and Se(IV)/Se(0), which seems to be a consequence of slow reaction rates. Additionally, it has been demonstrated by Runnels et al. (1987) that redox potentials measured by Pt electrodes are not affected by the ratio of Se(IV)/Se(VI) present in solution. Hence, one should not be astonished at the fact that Olin et al. (2005) were forced to base their evaluation on one single experimental investigation for each redox couple.

7.3.1 The Se(IV)/Se(0) couple

For the equilibrium

$$Se(s) + 2I_2(cr) + 3H_2O(l) \Leftrightarrow H_2SeO_3(aq) + 4I^- + 4H^+ \qquad (7.3)$$

Olin et al. (2005) evaluated $\log_{10}K°((7.3), 298.15\ K) = -(13.831 \pm 0.021)$**,** based on data from Schott et al. (1928), activity coefficients for hydroiodic acid taken from Pearce et al. (1923) and based on corrections for side reactions including the solubility of iodine, the formation of tri-iodide and the dissociation of $H_2SeO_{3(aq)}$. Olin et al. (2005) observed that improving the equilibria for the side reactions did not significantly change the resulting constant. They further noted an inconsistency with the state of solid selenium, which was probably not in its standard state. However, based on their assessment of the experimental procedure they concluded that "*the specimen was most likely close enough to the standard state activity*". Additional re-evaluations using activity data from Harned and Robinson (1941) and using an SIT approach ($\varepsilon(H^+, ClO_4^-) = 0.12$, $\varepsilon(H^+, I^-) = 0.18$ kg·mol^{-1} and $\varepsilon(H^+, ClO_4^-) = 0.014$ kg·mol^{-1}) gave similar results for $\log_{10}K°(7.3)$. Therefore, Olin et al (2005) selected

$$\log_{10}K°((7.3), 298.15\ K) = -(13.90 \pm 0.10).$$

For the reaction

$$H_2SeO_3(aq) + 2\ H_2(g) \Leftrightarrow Se(cr) + 3H_2O(l), \qquad (7.4)$$

Using the Gibbs energy of formation of -(51.734 ± 0.112) kJ·mol^{-1} for I^- one obtains

$$\Delta_rG°_m((7.4), 298.15\ K) = -(286.24 \pm 0.84)\ kJ\cdot mol^{-1}, \text{ or}$$

$$\log_{10}K°((7.4), 298.15\ K) = (50.15 \pm 0.15).$$

The standard electrode potential for the redox couple $H_2SeO_3(aq) + 4H^+ + 4e^- \Leftrightarrow Se(cr) + 3\ H_2O(l)$ is thus E°(298.15 K) = (0.742 ± 0.002) V, which agrees with the 0.740 V from Latimer (1956) and with (0.745 ± 0.004) V from Osman-Zade and Vagramyan (1966). Séby et al. (2001) reported an additional independent study (Nevskii et al. 1968) that seems to confirm the above results, but this last study was not considered in Olin et al. (2005).

Combining $\Delta_rG°_m$((7.4), 298.15 K) with $\Delta_fG°_m(H_2O(l)$, 298.15 K) = -(237.140 ± 0.041) kJ·mol^{-1} produces

$$\Delta_fG°_m(H_2SeO_3(aq), 298.15\ K) = -(425.18 \pm 0.85)\ kJ\cdot mol^{-1}.$$

7.3.2 The Se(VI)/Se(IV) couple

Sherill and Izard (1928) investigated the reactions

$$Cl_2(g) + H_2SeO_3(aq) + H_2O(l) \Leftrightarrow HSeO_4^- + 3H^+ + 2Cl^- \qquad (7.5)$$

and

$$Br_2(l) + H_2SeO_3(aq) + H_2O(l) \Leftrightarrow HSeO_4^- + 3H^+ + 2Br^- \qquad (7.6)$$

in 7 to 8 m HCl and 0.2 to 0.4 m HBr, respectively, and measured the equilibrium concentrations by chemical analysis. They made assumptions on the relative acidity constants of $H_2SeO_3(aq)$ and H_2SeO4^-, neglected the activity of uncharged species, took mean activity coefficients (based on HCl or HBr) for monovalent ions and used the water activity from vapour pressure data (which were later on confirmed by data from Harned et al. 1936 and Åkerlöf and Teare 1937). Obviously, Olin et al. (2005) accepted the results given by Sherill and Izard (1928) as were, because the reference is not further discussed in their chapter "Appendix A: discussion of selected references". For the further evaluation, Olin et al. (2005) used $\log_{10}K°$((7.5), 298.15 K) = -(9.148 ± 0.057) ($\Delta_rG°_m$= -52.217 ± 0.325 kJ·mol^{-1}) and $\log_{10}K°$((7.6), 298.15 K) = -(0.0560 ± 0.0256) ($\Delta_rG°_m$= 0.320 ± 0.146 kJ·mol^{-1}), respectively. With $\Delta_rG°_m(½Cl_2(g)/Cl^-$, 298.15 K) = -(131.22 ± 0.12) kJ·mol^{-1} and $\Delta_rG°_m(½Br_2(aq)/Br^-$, 298.15 K) = -(106.30 ± 0.53) kJ·mol^{-1} (Grenthe et al. 1992) one calculates $\Delta_rG°_m$((7.7), 298.15 K) = -(210.223 ± 0.404) kJ·mol^{-1} and $\Delta_rG°_m$((7.7), 298.15 K) = -(212.920 ± 1.070) kJ·mol^{-1}, respectively for reaction (7.7):

$$HSeO_4^- + 3\ H^+ + 2\ e^- \Leftrightarrow H_2SeO_3(aq) + H_2O(l) \qquad (7.7)$$

Based on more recent Raman measurements Olin et el. (2005) concluded that side reactions of the type $H_2SeO_3(aq) + H^+ + Cl^-/Br^- \Leftrightarrow H_2SeO_2Cl/Br(aq) + H_2O(l)$ cannot be ruled out at elevated halogenide ion concentrations above about 4 M, although the resulting complexes seem to be rather weak (i.e, $\log_{10}$K's are below 1.0). Hence, Olin et al. (2005) preferred selecting the results for reaction (7.6), because this experiment was performed at substantially lower halogenide ion concentrations than experiment (7.5) conducted in high chloride medium. It was thus expected that the reaction in the bromine/bromide system is potentially less affected by side reactions. The present assessment accepts this view and adopts

$$\Delta_rG°_m((7.7), 298.15\ K) = -(212.920 \pm 1.070)\ kJ\cdot mol^{-1}$$

$$\log_{10}K°((7.7), 298.15\ K) = (37.30 \pm 0.19)$$

$$E°((7.7), 298.15\ K) = (1.103 \pm 0.006)\ V$$

Note the small difference in $\Delta_rG°_m$((7.7), 298.15 K) given by Olin et al. (2005) (i.e. $\Delta_rG°_m$((7.7, Olin et al. (2005)), 298.15 K)= -(212.85 ± 1.00) $kJ\cdot mol^{-1}$), which is most likely a consequence of rounding errors: Calculating back from E°((7.7), 298.15 K) = (1.103 ± 0.006) V to $\Delta_rG°_m$((7.7), 298.15 K) indeed produces -212.85 $kJ\cdot mol^{-1}$, but it is not necessary to truncate the real value of E° (1.10338 V) to three digits. Although the very small difference is only relevant for consistency reasons, it will induce similar tiny differences in the Gibbs free energies of all species including the unit "$Se(VI)O_4^{2-}$" .

Using $\log_{10}K°$(7.49) = (1.75 ± 0.10) for the protonation of the selenate ion (see below) leads to

$$\Delta_fG°_m(HSeO_4^-, 298.15\ K) = -(449.4 \pm 1.4)\ kJ\cdot mol^{-1}$$

and

$$\Delta_fG°_m(SeO_4^{2-}, 298.15\ K) = -(439.4 \pm 1.5)\ kJ\cdot mol^{-1}$$

7.3.3 The Se(0)/Se(-II) couples

Lyons and Young (1986) reported on the formal redox equilibria and on UV-visible molar absorptivity of the equilibria (7.8) to (7.10)

$$1/2Se_2^{2-} + e^- \Leftrightarrow Se^{2-} \qquad (7.8)$$

$$1/3Se_3^{2-} + 4/3e^- \Leftrightarrow Se^{2-} \qquad (7.9)$$

$$1/4Se_4^{2-} + 3/2e^- \Leftrightarrow Se^{2-} \qquad (7.10)$$

at the non-standard conditions (1 M KOH, 304 K). Using $\log_{10}K_w$(I=1M, 304 K) = -13.79 and $\log_{10}K_1$($HSe^- \Leftrightarrow H^+ + Se^{2-}$, I=1M, 304 K) = 13.97, Olin et al. (2005) corrected these values to

$$\log_{10}K((7.8), 1M\ KOH, 304\ K) = -(11.97 \pm 0.10),$$

$$\log_{10}K((7.9), 1M\ KOH, 304\ K) = -(15.74 \pm 0.14),$$

$$\log_{10}K((7.10), 1M\ KOH, 304\ K) = -(17.24 \pm 0.15),$$

in good agreement with independent values reported by Licht and Forouzan (1995). The problem was now to connect these equilibria to Se(cr), i.e., to find a constant for the reaction

$$Se(cr) + 2e^- \Leftrightarrow Se^{2-} \qquad (7.11).$$

Based on the experimental observation of both, Lyons and Young (1986) and Licht and Forouzan (1995), that the resulting polyselenide solutions reached equilibrium with elemental Se(cr) at a ratio of $Se(0)_{tot}/Se(-II)_{tot}$ = (2.8 ± 0.05), Olin et al. (2005) performed a mass balance iteration with the equilibria (7.8) to (7.10) and found $\log_{10}K$((7.11), 1M KOH, 304 K) = -(21.08 ± 0.15).

Finally, the recalculation to I = 0 with the estimate $\varepsilon(Se_n^{2-}, K^+) \approx -0.06\ kg\cdot mol^{-1}$ produced $\Delta_rG°_m$((7.11), 298.15 K) (≡ $\Delta_fG°_m(Se^{2-}$, 298.15 K)) = (127.9 ± 1.9) $kJ\cdot mol^{-1}$, corresponding to $\log_{10}K$((7.11), 298.15 K) = -(22.4 ± 0.3). Note that the estimate $\varepsilon(Se_n^{2-}, K^+) \approx -0.06\ kg\cdot mol^{-1}$ is based on the average o f $\varepsilon(X^{2-}, K^+)$ data presented in Olin et al. (2005, Table B-5). The Gibbs free energy of Se^{2-} derived in this way is in good agreement with $\Delta_fG°_m(Se^{2-}$, 298.15 K) = (129.4 ± 2.3) $kJ\cdot mol^{-1}$ derived from the dissociation of H_2Se(aq) and based on the selected data of H_2Se(g) (see below). Olin et al. (2005) selected the average of the two values according to the rules of the NEA reviews, which is also accepted in this assessment.

$$\Delta_fG°_m(Se^{2-}, 298.15\ K) = (128.6 \pm 3.0)\ kJ\cdot mol^{-1}$$

$$\log_{10}K°((7.11), 298.15\ K) = -(22.5 \pm 0.5)$$

$$E°((7.11), 298.15) = -(0.666 \pm 0.010)\ V$$

For the polyselenide equilibria the finally selected constants are

$$E°((7.8), 298.15) = -(0.749 \pm 0.010)\ V$$

$$\log_{10}K°((7.8), 298.15\ K) = -(12.6 \pm 0.2)$$

$$E°((7.9), 298.15) = -(0.739 \pm 0.010)\ V$$

$$\log_{10}K°((7.9), 298.15\ K) = -(16.7 \pm 0.2)$$

$$E°((7.10), 298.15) = -(0.720 \pm 0.010)\ V$$

$$\log_{10}K°((7.10), 298.15\ K) = -(18.3 \pm 0.3)$$

and the corresponding Gibbs free energies of formation are

$$\Delta_fG°_m(Se_2^{2-}, 298.15\ K) = (112.7 \pm 6.3)\ kJ \cdot mol^{-1}$$

$$\Delta_fG°_m(Se_3^{2-}, 298.15\ K) = (100.6 \pm 9.2)\ kJ \cdot mol^{-1}$$

$$\Delta_fG°_m(Se_4^{2-}, 298.15\ K) = (97.6 \pm 12.1)\ kJ \cdot mol^{-1}$$

In their final Table III-2 (Olin et al. 2005, p.53) represent reactions (7.8) to (7.10) with integer numbers of stoichiometric reaction coefficients, i.e., multiples of the reactions (7.8) to (7.10) as presented above. The values for $\log_{10}K°$ and $\Delta_rG°_m$ are adjusted correctly, but the uncertainties for reactions (7.9) and (7.10) are not consistent with the uncertainties associated with the Gibbs free energies of the polymeric species. Hence, it is recommended to use

$$Se_2^{2-} + 2e^- \Leftrightarrow 2Se^{2-} \tag{7.8'}$$

$$\Delta_rG°_m(7.8') = (144.53 \pm 1.90)\ kJ \cdot mol^{-1}$$

$$\log_{10}K°(7.8') = -(25.32 \pm 0.33)$$

$$Se_3^{2-} + 4e^- \Leftrightarrow 3Se^{2-} \tag{7.9'}$$

$$\Delta_rG°_m(7.9') = (285.21 \pm 3.86)\ kJ \cdot mol^{-1}$$

$$\log_{10}K°(7.9') = -(49.97 \pm 0.68)$$

$$Se_4^{2-} + 6e^- \Leftrightarrow 4Se^{2-} \tag{7.10'}$$

$$\Delta_rG°_m(7.10') = (416.82 \pm 5.79)\ kJ \cdot mol^{-1}$$

$$\log_{10}K°(7.10') = -(73.02 \pm 1.01)$$

7.4 Selenide species and solids

7.4.1 Aqueous (and gaseous) selenide species

From molecular parameters in Lane et al. (1984), Olin et al. (2005) selected:

$$C°_{p,m}(H_2Se(g), 298.15\ K) = (34.7 \pm 0.1)\ J \cdot K^{-1} \cdot mol^{-1},$$

$$S°_m(H_2Se(g), 298.15\ K) = (219.0 \pm 0.1)\ J \cdot K^{-1} \cdot mol^{-1}, \text{ and}$$

$$\Delta_fS°_m(H_2Se(g), 298.15\ K) = (46.2 \pm 0.2)\ J \cdot K^{-1} \cdot mol^{-1}.$$

From several studies investigating the formation of $H_2Se(g)$ from $H_2(g)$ and elemental selenium Olin et al. (2005) selected:

$$\Delta_f H^\circ_m(H_2Se(g), 298.15\ K) = (29.0 \pm 2.0)\ kJ\cdot mol^{-1}$$

and calculated

$$\Delta_f G^\circ_m(H_2Se(g), 298.15\ K) = (15.2 \pm 2.0)\ kJ\cdot mol^{-1}.$$

The *Henry constant* for the solubility of $H_2Se(g)$, i.e. the equilibrium

$$H_2Se(g) \Leftrightarrow H_2Se(aq) \qquad (7.12)$$

was evaluated based on two studies(McAmis and Felsing 1925, Dubeau and Sisi 1971) at a partial pressure of 1 atm $H_2Se(g)$ under the assumption that the first dissociation constant of $H_2Se(aq)$ is $10^{-(3.85\pm0.05)}$. This assumption was necessary because both studies measured total dissolved selenium (i.e., the sum of $H_2Se(aq)$ and HSe^-) by precipitation with silver ($Ag_2Se(s)$). Olin et al. (2005) took the average of the two studies and selected

$$\log_{10}K^\circ((7.12), 298.15\ K) = -(1.10 \pm 0.01)$$

The enthalpy of reaction $\Delta_r H^\circ_m((7.112), 298.15) = -(14.7 \pm 0.3)\ kJ\cdot mol^{-1}$ was selected from Dubeau and Sisi (1971) with an increased uncertainty due to the fact that Dubeau and Sisi (1971) did not consider the dissociation of $H_2Se(aq)$ in their evaluation.

The first hydrolysis

$$H_2Se(aq) \Leftrightarrow H^+ + HSe^- \qquad (7.13)$$

was evaluated from two conductometric (Bruner-Krakau 1913, de Hlasko 1923) and one potentiometric study (Hagisawa 1941). However, the evaluation of the two conductance measurements depended on the "assumption" of a solubility value for $H_2Se(aq)$ at $\rho_{H2Se(g)} = 1$ atm and were re-evaluated by Olin et al. (2005) using the value for the *Henry constant* as given above. There is, however, some feedback from the assumption made for evaluating $\log_{10}K^\circ(7.12)$ to the hydrolysis reaction (7.13) and vice versa, but this is not further investigated here. The re-evaluated results from the two conductometric studies compared sufficiently well with the potentiometric study by Hagisawa (1941), and Olin et al. (2005) selected the average:

$$\log_{10}K^\circ((7.13), 298.15\ K) = -(3.85 \pm 0.05).$$

For the second hydrolysis reaction

$$HSe^- \Leftrightarrow H^+ + Se^{2-} \qquad (7.14)$$

Olin et al. (2005) in principle accepted $\log_{10}K^\circ((7.14), 298.15\ K) = -(15.05 \pm 0.20)$ as "*by far the most reliable value of* $\log_{10}K^\circ(7.14)$". This value can be traced back to UV-spectrometric studies in concentrated KOH solutions by Lyons and Young (1986) and Levy and Myers (1990), where hydroxide concentrations were systematically varied. From the constants (7.13), (7.14) and from the selected value of $\Delta_f G^\circ_m(H_2Se(g), 298.15\ K) = (15.2 \pm 2.0)\ kJ\cdot mol^{-1}$ (see above), Olin et al. (2005) selected

$$\Delta_f H^\circ_m(H_2Se(aq), 298.15\ K) = (14.3 \pm 2.0)\ kJ\cdot mol^{-1},$$

$$\Delta_f S^\circ_m(H_2Se(aq), 298.15\ K) = -(24.1 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1},$$

$$\Delta_f G^\circ_m(H_2Se(aq), 298.15\ K) = (21.5 \pm 2.0)\ kJ\cdot mol^{-1} \text{ and}$$

$$\Delta_f G^\circ_m(HSe^-, 298.15\ K) = (43.5 \pm 2.0)\ kJ\cdot mol^{-1}.$$

From $\Delta_f S^\circ_m(H_2Se(aq), 298.15\ K) = -(24.1 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1}$, the present work calculates

$$S^\circ_m(H_2Se(aq), 298.15\ K) = (148.7 \pm 9.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Note that the corresponding value for $\Delta_fG°_m(Se^{2-}, 298.15\ K)$ of (129.4 ± 2.3) $kJ\cdot mol^{-1}$ was not selected. Instead, Olin et al. (2005) selected the mean of this value and that independently evaluated from the redox studies in the poly-selenide systems (i.e., (127.9 ± 1.9) $kJ\cdot mol^{-1}$ see above) to obtain

$$\Delta_fG°_m(Se^{2-}, 298.15\ K) = (128.6 \pm 3.0)\ kJ\cdot mol^{-1}.$$

This selected Gibbs free energy of formation for Se^{2-} in turn corresponds to

$$\log_{10}K°((7.14), 298.15\ K) = -(14.91 \pm 0.20).$$

The present review prefers selecting this somewhat larger $\log_{10}K°(7.14)$, because this value is consistent with the selected $\Delta_fG°_m(Se^{2-}, 298.15\ K)$ and with the free energies of the species as given above.

7.4.2 Solid selenide species

Mercury selenides

Mercury is not included in the TDB update but is one of the cases where low solubility products seem to be compensated with moderate to strong complex formation, finally leading to noticeable concentrations of neutral complexes in solution. That is why the section of mercury selenide solubility/complex formation is added here anyway.

$$HgSe(s) + 2H^+ \Leftrightarrow Hg^{2+} + H_2Se(aq) \qquad (7.15)$$

Olin et al. (2005) combined solubility measurements according to reaction (7.15) from Mehra (1968), performed below pH 3 ($\log_{10}K((7.15), 1\ M\ NaClO_4, 298.15\ K) = -(41.65 \pm 04.5)$), with various high temperature measurements on HgSe(s,α) to obtain a selected free energy of formation of

$$\Delta_fG°_m(HgSe, \alpha, 298.15\ K) = -(51.2 \pm 4.0)\ kJ\cdot mol^{-1}$$

and a standard enthalpy of formation of

$$\Delta_fH°_m(HgSe, \alpha, 298.15\ K) = -(57.0 \pm 4.1)\ kJ\cdot mol^{-1}$$

based on

$$\Delta S°_m(HgSe, \alpha, 298.15\ K) = (98.5 \pm 3.0)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Olin et al. (2005) did not explicitly select an equilibrium constant for reaction (7.15), but they recalculated $\log_{10}K°_{s,0}(HgSe, s, 298.15\ K) = -(60.7 \pm 0.5)$, obviously using $\varepsilon(Hg^{2+}, ClO_4^-) = 0.34\ kg\cdot mol^{-1}$. This value is sufficiently close to the value which is obtained from the selected $\Delta_fG°_m(HgSe, \alpha, 298.15\ K)$ and the present assessment decides to neglect a potential inconsistency in the nature of the solid (i.e., between HgSe(s) and HgSe(α)). Hence,

$$\log_{10}K°_{s,0}(HgSe, s, 298.15\ K) \approx \log_{10}K°_{s,0}(HgSe, \alpha, 298.15\ K) = -(60.35 \pm 0.70).$$

Mehra and Gübeli (1971) interpreted their solubility measurements with the formation of the complexes $Hg(HSe)(OH)(aq)$ (pH 0 to 3), $Hg(HSe)_2(OH)^-$ (pH 4 to 5.5) and $Hg(HSe)_2(OH)_2^{2-}$ (pH > 7). Olin et al. (2005) preferred a different notation without the OH^--ion. Using $\Delta\varepsilon = 0.04\ kg\cdot mol^{-1}$ they recalculated for reaction

$$HgSe(s) + HSe^- \Leftrightarrow HgSe_2^{2-} + H^+ \qquad (7.16)$$

$$\log_{10}K°((7.16), 298.15\ K) = -(12.8 \pm 0.6),$$

which corresponds to

$$\Delta_fG°_m(HgSe_2^{2-}, 298.15 \text{ K}) = -(65.3 \pm 5.6) \text{ kJ·mol}^{-1}.$$

For the solubility of the neutral species

$$HgSe(s) \Leftrightarrow HgSe(aq) \qquad (7.17)$$

Olin et al. (2005) provide the constant $\log_{10}K((7.17), 1 \text{ M } NaClO_4, 298.15 \text{ K}) = -(7.84 \pm 0.44)$, but they claim that this constant is "*most likely too large due to the rather simple method used for the separation of the solid from the aqueous phase. It is tentatively included due to its potential importance in connection with the mobility of mercury from repositories*".

Since no charge is involved, reaction (7.17) is not subject to ionic strength corrections in the presently valid implementation of the SIT framework. Hence, and following the arguments of Olin et al. (2005), in the present assessment the constant (7.17) is selected with a somewhat increased uncertainty (as in the case of reaction (7.16)):

$$\log_{10}K°((7.17), 298.15 \text{ K}) = -(7.8 \pm 0.6),$$

Note that $\Delta_fG°_m(Hg^{2+}, 298.15 \text{ K}) = -(164.667 \pm 0.313) \text{ kJ·mol}^{-1}$ should be used for all calculations involving the Hg^{2+}-cation.

Silver selenides

A similar problem as in the case of mercury is observed in the case of silver: Several high temperature data are available for $Ag_2Se(s,\alpha)$, but there are only two relevant studies that performed solubility measurements with not further specified solids termed $Ag_2Se(s)$. The solubility product is very low, but noticeable concentrations of neutral complexes may exist in aqueous solution. Since silver may be of some relevance in radioactive waste systems it was decided to report available data (as well as a recommendation for practical use) anyway. From the Mehra (1968) and Mehra and Gübeli (1971) data measured in different pH ranges, Olin et al. (2005) finally "accepted" for the reaction

$$Ag_2Se(s) \Leftrightarrow 2Ag^+ + Se^{2-} \qquad (7.18)$$

$\Delta_fG°_m(Ag_2Se, s, 298.15 \text{ K}) = -(46.3 \pm 4.1) \text{ kJ·mol}^{-1}$ or $\log_{10}K°_{s,0}((7.18), 298.15 \text{ K}) = -(57.65 \pm 0.50)$, based on $\varepsilon(H^+,ClO_4^-) = (0.14 \pm 0.02) \text{ kg·mol}^{-1}$ and $\varepsilon(Ag^+,ClO_4^-) = (0.00 \pm 0.01) \text{ kg·mol}^{-1}$. However, they also selected

$$\Delta_fG°_m(Ag_2Se, \alpha, 298.15 \text{ K}) = -(46.9 \pm 1.3) \text{ kJ·mol}^{-1}$$

$$\Delta_fH°_m(Ag_2Se, \alpha, 298.15 \text{ K}) = -(40.1 \pm 1.3) \text{ kJ·mol}^{-1},$$

$$S°_m(Ag_2Se, \alpha, 298.15 \text{ K}) = (149.9 \pm 0.5) \text{ J·K}^{-1}\text{·mol}^{-1}.$$

which, by neglecting a certain inconsistency in the nature of the solid and by associating a somewhat increased uncertainty, gives the solubility product recommended by this assessment:

$$\log_{10}K°_{s,0}(Ag_2Se, s, 298.15 \text{ K}) \approx \log_{10}K°_{s,0}(Ag_2Se, \alpha, 298.15 \text{ K}) = -(57.8 \pm 0.6).$$

Note that this solubility product is consistent with both, the free energy of formation of $Ag_2Se(s,\alpha)$ and the measured solubility of $Ag_2Se(s)$. Note further that $\Delta_fG°_m(Ag^+, 298.15 \text{ K}) = -(77.096 \pm 0.156) \text{ kJ·mol}^{-1}$ should be used for applications involving equilibrium (7.18).

Olin at al. (2005) discussed the formation of aqueous silver (I) selenide complexes based on the measurements of Mehra and Gübeli (1971). These authors found "*constant dissolved*" silver selenide concentrations in the range $6·10^{-8}$ to $8·10^{-9}$ mol·L^{-1} at pH > 10, independent of the total Se(-II) concentration in the test solution. Mehra and Gübeli (1971) interpreted their finding with a species having the formula $Ag_2(HSe)(OH)(aq)$, which is formally equivalent to $Ag_2Se(aq)$.

Olin et al. (2005) did not accept Mehra and Gübeli's (1971) interpretation and did not select the proposed species. From the data of Mehra (1968) Olin et al. (2005) re-evaluated the equilibrium

$$Ag_2Se(s) \Leftrightarrow Ag_2Se(aq) \qquad (7.19)$$

and obtained $\log_{10}K°(7.19, 1\ M\ NaClO_4, 298.15\ K) = -(7.66 \pm 0.48)$. Combining the equilibria (7.18) and (7.19) and neglecting the fact that equilibrium (7.19) is valid in 1 M $NaClO_4$ formally leads to a formation constant for the equilibrium $2Ag^+ + Se^{2-} \Leftrightarrow Ag_2Se(aq)$ (7.19a) of $\log_{10}K(7.19a, 298.15\ K) = (50.14 \pm 0.77)$. By using equilibrium (7.14) one further may calculate $\log_{10}K(7.19b, 298.15\ K) = (35.1 \pm 0.8)$ for the equilibrium $2Ag^+ + HSe^- \Leftrightarrow Ag_2Se(aq) + H^+$ (7.19b). The formal constant (7.19b) is very high and means that the dissociation of $Ag_2Se(aq)$ into Ag^+ and HSe^- actually does not take place. At pH = 8 and measured $Ag_2Se(aq)$ concentrations of $\sim 6 \cdot 10^{-8}\ mol \cdot L^{-1}$ the free HSe^- concentration is calculated to be less than $\sim 1 \cdot 10^{-17}\ mol \cdot L^{-1}$. The present evaluation does not recommend using the equilibria (7.18), (7.19a), and (7.19b) as selected data, but for practical use and for estimating silver/selenium solubilities it is recommended to use equilibrium (7.19).

Manganese selenides

From experimental data of Mehra and Gübeli (1970) and Mehra (1968) using radioactively labelled Mn Olin et al. (2005) calculated

$$\log_{10}K(7.20, 1\ M\ NaClO_4, 298.15\ K) = -(0.52 \pm 0.70)$$

for the equilibrium

$$MnSe(s) + H^+ \Leftrightarrow Mn^{2+} + HSe^-. \qquad (7.20)$$

This corresponds to

$$\Delta_f G°_m(MnSe, s, 298.15\ K) = -(190.8 \pm 6.8)\ kJ \cdot mol^{-1}$$

when using $\Delta_f G°_m(Mn^{2+}, 298.15\ K) = -228.1\ kJ \cdot mol^{-1}$ from Wagman et al. (1982). From equilibra (7.20, using $\Delta\varepsilon = 0.25\ kg \cdot mol^{-1}$) and (7.14) Olin et al. (2005) evaluated $\log_{10}K°_{s,0}(MnSe, s, 298.15\ K) = -(16.0 \pm 0.8)$. The solubility of MnSe(s) is not included in the TDB 20/07, but for estimates/scoping calculations, particularly at elevated pH, $\log_{10}K(7.20)$ may be used to estimate maximum HSe^- concetrations in the presence of manganese.

Olin et al. (2005) do not provide/select data for any other metal selenide solids related to aqueous solutions.

7.5 Selenite species and solids

7.5.1 Aqueous selenious acid

Olin et al. (2005) discussed a series of studies proposing the formation of several polymeric species of the type $H_x(SeO_3)_2^y$ with variable charge, but based on converse studies not indicating the polymers, they did not accept the formation of polymeric species in their assessment. Note, however, that Walrafen (1962) confirmed the presence of polymers by Raman spectroscopy in extremely concentrated aqueous solutions of H_2SeO_3.

For the protonation constants

$$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^- \quad (7.21)$$

$$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq) \quad (7.22)$$

they accepted studies from Kawassiades et al. (1967), Sekine et al. (1969), Salomaa et al. (1969), Vesala and Koskinen (1975), Fowless and Stranks (1977), Ozeki et al. (1988), and Dasgupta and Nara (1990) and found

$$\log_{10}K°_1((7.21), 298.15\ K) = (8.36 \pm 0.23)$$

$$\log_{10}K°_{2,1}((7.22), 298.15\ K) = (2.64 \pm 0.14).$$

With $\Delta_fG°_m(H_2SeO_3(aq), 298.15\ K) = -(425.18 \pm 0.85)\ kJ\cdot mol^{-1}$ (see above) the formation constants (7.21) and (7.22) yield

$$\Delta_fG°_m(HSeO_3^-, 298.15\ K) = -(410.1 \pm 1.7)\ kJ\cdot mol^{-1}.$$

$$\Delta_fG°_m(SeO_3^{2-}, 298.15\ K) = -(362.39 \pm 1.76)\ kJ\cdot mol^{-1}.$$

Using the above selected protolysis constants, Olin et al. (2005) calculated the enthalpy change of the dissolution of $H_2SeO_3(cr)$ from measurements of Selivanova and Pakhorukov (1961) to finally obtain

$$\Delta_fH°_m(H_2SeO_3(aq), 298.15\ K) = -(505.32 \pm 0.65)\ kJ\cdot mol^{-1},$$

and, consequently,

$$\Delta_fH°_m(HSeO_3^-, 298.15\ K) = -(512.3 \pm 1.0)\ kJ\cdot mol^{-1},$$

$$\Delta_fH°_m(SeO_3^{2-}, 298.15\ K) = -(507.2 \pm 1.1)\ kJ\cdot mol^{-1},$$

$$S°_m(SeO_3^{2-}, 298.15\ K) = (5.2 \pm 7.1)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Corresponding entropies of formation can be calculated from $\Delta_fG°_m = \Delta_fH°_m - T\Delta_fS°_m$ to yield $\Delta_fS°_m(H_2SeO_3(aq), 298.15\ K) = -(268.79 \pm 3.59)\ J\cdot K^{-1}\cdot mol^{-1}$, $\Delta_fS°_m(HSeO_3^-, 298.15\ K) = -(342.78 \pm 6.62)\ J\cdot K^{-1}\cdot mol^{-1}$ and $\Delta_fS°_m(SeO_3^{2-}, 298.15\ K) = -(485.66 \pm 7.08)\ J\cdot K^{-1}\cdot mol^{-1}$. The molal entropies $S°_m(i, 298.15\ K)$ should then be calculated from consistent elemental entropies according to $\Delta_fS°_m(i, 298.15\ K) = S°_m(i, 298.15\ K) - \Sigma\ S°(element, 298.15\ K) + Z/2\cdot S°(H_2)$ (where Z = 0, ±1, ±2…). From Cox et al. (1989) the present work used $S°_m(O_2(g), 298.15\ K) = (205.152 \pm 0.005)\ J\cdot K^{-1}\cdot mol^{-1}$, and $S°_m(H_2(g), 298.15\ K) = (130.68 \pm 0.003)\ J\cdot K^{-1}\cdot mol^{-1}$.

It is interesting to note that Olin et al. (2005) did not consider the evaluation of Séby et al. (2001) based on poly selenite equilibria from Barcza and Sillén (1971), nor did they consider these data.

7.5.2 Solid selenite species

Solid selenite species are known for many aqueous cations, but the present work primarily concentrates on elements relevant for geochemical radioactive waste systems and on elements included in the PSI/Nagra TDB. Therefore, only a subset of selenite solids is discussed here.

Magnesium selenites

A number of studies measured the solubility product of solids denoted with $MgSeO_3(s)$. Olin et al. (2005) assume that the various determinations pertain to the hexadydrate and formulate the equilibrium as

$$MgSeO_3 \cdot 6H_2O(cr) \Leftrightarrow Mg^{2+} + SeO_3^{2-} + 6H_2O(l) \qquad (7.23)$$

Based on the measurements of Savenko (1995) (which was considered by Olin et al. 2005 to be the most reliable determination), neglecting hydrolysis of Mg^{2+} and using the equilibria (7.21, 7.22) Olin et al. (2005) estimated

$$\log_{10}K^{\circ}_{s,0}((7.23), 298.15\ K) = -(5.82 \pm 0.25),$$

the uncertainty estimated by Olin et al. (2005).

From enthalpy changes in reactions between Na_2SeO_3(cr), magnesium sulfate solutions and $MgSeO_3 \cdot 6H_2O$(cr) performed by Leshchinskaya and Selivanova (1966) Olin et al. (2005) derived

$$\Delta_f H^{\circ}_m(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = -(2707.21 \pm 1.30)\ kJ \cdot mol^{-1},$$

and, consequently,

$$\Delta_f G^{\circ}_m(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = -(2273.83 \pm 2.60)\ kJ \cdot mol^{-1}$$

$$S^{\circ}_m(MgSeO_3 \cdot 6H_2O,\ cr,\ 298.15\ K) = (328.5 \pm 9.8)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Calcium selenites

From studies in the system $CaSeO_3$-SeO_2-H_2O (Dumm and Brown 1997, Ebert and Havlicek 1981) Olin et al. (2005) concluded that the solid phase studied in solubility experiments has the composition $CaSeO_3 \cdot H_2O$ and wrote the equilibrium

$$CaSeO_3 \cdot H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} + H_2O(l). \qquad (7.24)$$

Due to shortcomings in the paper of Sharmasarkar et al. (1996) Olin et al. (2005) gave no weight to that evaluation but considered the work of Savenko (1995) to be the most “satisfactory”. They selected

$$\log_{10}K^{\circ}_{s,0}((7.24), 298.15\ K) = -(6.40 \pm 0.25).$$

From calorimetric measurements of Leshchinskaya and Selivanova (1963) and in good agreement with Wagman et al. (1982) Olin et al. (2005) adopted

$$\Delta_f H^{\circ}_m(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = -(1324.83 \pm 2.81)\ kJ \cdot mol^{-1},$$

and, consequently,

$$\Delta_f G^{\circ}_m(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = -(1188.90 \pm 2.50)\ kJ \cdot mol^{-1}$$

$$S^{\circ}_m(CaSeO_3 \cdot H_2O,\ cr,\ 298.15\ K) = (168.8 \pm 12.6)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Note that the above values of $\Delta_f H^{\circ}_m(CaSeO_3 \cdot H_2O$, cr, 298.15 K) and $S^{\circ}_m(CaSeO_3 \cdot H_2O$, cr, 298.15 K) are not selected values but considered as “*best values currently available*”. Particularly, the value for S°_m is considered to be “*somewhat too large*” in the opinion of Olin et.al (2005) and the authors recommend performing additional measurements with better control of the solid phase composition.

Strontium selenites

From chemical analyses performed by Selivanova and Leshchinskaya (1963) and Leshchinskaya et al. (1965) Olin et al. (2005) concluded that the solid phase in aquesous solubility studies is best represented by $SrSeO_3$(cr), in contrast to the composition

$SrSeO_3 \cdot 6H_2O(cr)$ reported by Ebert and Havlicek (1982). Olin et al. (2005) adopt the equilibrium

$$SrSeO_3(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} \qquad (7.25)$$

and evaluated

$$\log_{10}K^{\circ}_{s,0}((7.25), 298.15\ K) = -(6.30 \pm 0.50)$$

from experimental data measured by Chukhlantsev (1956). From enthalpy changes during the formation of $SrSeO_3(cr)$ in aqueous $SrCl_2 \cdot 6H_2O$-Na_2SeO_3 mixtures investigated by Selivanova and Leshchinskaya (1963) Olin et al. (2005) evaluated

$$\Delta_fH^{\circ}_m(SrSeO_3, cr, 298.15\ K) = -(1051.9 \pm 2.7)\ kJ \cdot mol^{-1}.$$

Wagman et al. (1982) reported -1047.7 $kJ \cdot mol^{-1}$ for this $\Delta_fH^{\circ}_m$-value. The difference could be ascribed to changes in the strontium data made by Grenthe et al. (1992). Consequently, Olin et al. (2005) calculated

$$\Delta_fG^{\circ}_m(SrSeO_3, cr, 298.15\ K) = -(962.2 \pm 3.40)\ kJ \cdot mol^{-1}$$

$$S^{\circ}_m(SrSeO_3, cr, 298.15\ K) = (104.7 \pm 14.6)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Barium selenites

From the phase diagram of the system $BaSeO_3$-SeO_2-H_2O at 298.15 K Neall and McCrosky (1938) concluded $BaSeO_3$ and $BaSe_2O_5$ to be the solids formed.

Ripan and Vericeanu (1968) studied the solubility of $BaSeO_3(s)$ in pure water at 291 K and found a mean solubility value of $7.92 \cdot 10^{-4}\ mol \cdot L^{-1}$. For the equilibrium

$$BaSeO_3(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} \qquad (7.26)$$

Olin et al. (2005) evaluated $\log_{10}K^{\circ}_{s,0}((7.26), 291\ K) = -(6.43 \pm 0.10)$. Leshchinskaya et al. (1965) prepared crystalline barium selenite and measured the solubility at 298.15, leading to $\log_{10}K^{\circ}_{s,0}((7.26), 291\ K) = -6.58$ at I = 0 (no uncertainties, only one single experiment). From these experiments Olin et al. (2005) selected

$$\log_{10}K^{\circ}_{s,0}((7.26), 298.15\ K) = -(6.50 \pm 0.25).$$

Leshchinskaya et al. (1963) measured the enthalpy change of the the reaction between equimolar quantities of $BaCl_2 \cdot 2H_2O(cr)$ and $Na_2SeO_3(aq)$ with the formation of crystalline $BaSeO_3$. From these data Olin et al. (2005) calculated

$$\Delta_fH^{\circ}_m(BaSeO_3, cr, 298.15\ K) = -(1036.7 \pm 2.9)\ kJ \cdot mol^{-1}.$$

Wagman et al. (1982) reported -1040.6 $kJ \cdot mol^{-1}$ for this $\Delta_fH^{\circ}_m$-value. As in the case of strontium, the difference could partly be ascribed to changes in the barium data made by Grenthe et al. (1992). Consequently, Olin et al. (2005) calculated

$$\Delta_fG^{\circ}_m(BaSeO_3, cr, 298.15\ K) = -(957.2 \pm 3.40)\ kJ \cdot mol^{-1}$$

$$S^{\circ}_m(BaSeO_3, cr, 298.15\ K) = (145.6 \pm 15.0)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Manganese selenites

A phase diagram for the system $MnSeO_3$-SeO_2-H_2O does not seem to exist. There is actually only one experimental study that was accepted by Olin et al. (2005). Chukhlantsev and Tomashevsky (1957) precipitated ampophous $MnSeO_3$ and aged the mixture for a long time to obtain a crystalline product. No X-ray diffraction was performed but chemical analysis confirmed the 1:1 ratio between Mn(II) and Se(IV). Based on an independent preparative study by Leshchinskaya and Selivanova (1966a) Olin et al. (2995) concluded that the composition of the solid was $MnSeO_3\cdot 2H_2O$.

$$MnSeO_3\cdot 2H_2Ocr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} + 2H_2O \qquad (7.27)$$

From the data of Chukhlantsev and Tomashevsky (1957) at 293.15 K Olin et al. (2005) evaluated $\log_{10}K^\circ_{s,0}((7.27), 293.15\ K) = -(7.64 \pm 0.08)$. From the more recent study of Sharmasarkar et al. (1996) they obtained $\log_{10}K^\circ_{s,0}((7.27), 298.15\ K) = -7.11$, but as in the case of calcium they gave no weight to this determination. Olin et al. (2005) selected

$$\log_{10}K^\circ_{s,0}((7.27), 293.15\ K) = -(7.6 \pm 1.0),$$

and, recalculated from Leshchinskaya and Selivanova (1966a)

$$\Delta_f H^\circ_m(MnSeO_3\cdot 2H_2O, cr, 298.15\ K) = -(1280.7 \pm 2.6)\ kJ\cdot mol^{-1}.$$

Consequently,

$$\Delta_f G^\circ_m(MnSeO_3\cdot 2H_2O, cr, 298.15\ K) = -(1108.2 \pm 7.7)\ kJ\cdot mol^{-1}$$

$$S^\circ_m(SrSeO_3\cdot H_2O, cr, 298.15\ K) = (269.3 \pm 24.1)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Iron selenites

Complexes and solids of iron was not subject of the present TDB update. Iron is foreseen to be updated later on, when the next issue from the NEA review series on iron is completed. Note that volume 13a of this series (Lemire et al. 2013) does not yet include selenium complexes and solids. Hovever, an exception was made for aqueous complexes with iron(III). Rai et al. (1995) studied the solubility of $Fe_2(SeO_3)\cdot 6H_2O(cr)$ (the stable phase in aqueous solution at pH < 4). Note that above this pH-value the selenie starts transforming into another phase of not yet known composition. Rai et al. (1995) used two equilibria (the solubility constant and the 1:1 complex) to explain measured data. From this work Olin et al. (2005) selected the solubility constant and the formation constant

$$Fe^{3+} + SeO_3^{2-} \Leftrightarrow FeSeO_3^{+} \qquad (7.28)$$

$$\log_{10}\beta^\circ_1((7.28), 296\ K) = (11.15 \pm 0.11)$$

The present review adopts equilibrium 7.28, the solubility constant (see equilibrium 7.31) is noted below.

Nickel selenites

Ebert et al. (1982) established the phase diagram in the system $NiSeO_3$-SeO_2-H_2O at 298.15 K and found the solid phases $NiSeO_3\cdot 2H_2O$, $Ni(HeSO_3)_2\cdot 2H_2O$ and H_2SeO_3. From the chemical analysis of Chukhlantsev and Tomashevsky (1957) (no X-ray data but 1:1 ratio between Ni(II) and Se(IV)) Olin et al. (2005) assumed the solid phase to be $NiSeO_3\cdot 2H_2O$.

$$NiSeO_3 \cdot 2H_2O(cr) \Leftrightarrow Ni^{2+} + SeO_3^{2-} + 2H_2O(l) \qquad (7.29)$$

Chukhlantsev (1956), Chukhlantsev and Tomashevsky (1957) and Ripan and Vericeanu (1968) measured the solubiliy of $NiSeO_3$ at 293 and 291 K (about 2.25 $mol \cdot L^{-1}$). Olin et al. (2005) argued that under these conditions Ni(II) is partly hydrolysed and re-evaluated the experimental data accordingly. Their rather large associated uncertainty reflects the variance from the solubility measurements:

$$\log_{10}K°_{s,0}((7.29), 298.15\ K) = -(5.80 \pm 1.0).$$

The enthalpy $\Delta_f H°_m(NiSeO_3 \cdot 2H_2O, cr, 298.15\ K)$ was derived from measurements of Selivanova et al. (1963) and Olin et al. (2005) selected

$$\Delta_f H°_m(NiSeO_3 \cdot 2H_2O, cr, 298.15\ K) = -(1109.33 \pm 2.83)\ kJ \cdot mol^{-1}.$$

Wagman et al. (1982) provide -1134.32 $kJ \cdot mol^{-1}$ for the same entity. However, Olin et al. (2005) do not further discuss this large difference but just say that they do not accept the Wagman et al. (1981) - value. They refer to their "*Appendix A*", but this cross reference seems to be rather empty. Nevertheless, Olin et al. (2005) selected:

$$\Delta_f G°_m(NiSeO_3 \cdot 2H_2O, cr, 298.15\ K) = -(915.56 \pm 6.02)\ kJ \cdot mol^{-1}$$

$$S°_m(SrSeO_3 \cdot H_2O, cr, 298.15\ K) = (169.3 \pm 22.3)\ J \cdot K^{-1} \cdot mol^{-1}.$$

The PSI/Nagra Chemical Thermodynamic Database 12/07 is compiled in Thoenen (2012) and selected relevant data for elements not considered in this update are provided in Thoenen (2012a). Olin et al. (2005) list a variety of selenite solid solubilities for elements that were not subject of the PSI/Nagra database update. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These selenite equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have "noted" or "selected" the equilibrium.

Other selenite equilibria

Aluminium:

$$Al_2(SeO_3)_3 \cdot 6H_2O(cr) \Leftrightarrow 2Al^{3+} + 3SeO_3^{2-} + 6H_2O(l) \qquad (7.30)$$

$$\log_{10}K°_{s,0}((7.30), 298.15\ K) = -3.11 \qquad \text{(noted)}$$

Iron:

$$Fe_2(SeO_3)_3 \cdot 6H_2O(cr) \Leftrightarrow 2Fe^{3+} + 3SeO_3^{2-} + 6H_2O(l) \qquad (7.31)$$

$$\log_{10}K°_{s,0}((7.31), 296\ K) = -(41.58 \pm 0.11) \qquad \text{(selected)}$$

Cobalt:

$$CoSeO_3 \cdot 2H_2O(cr) \Leftrightarrow Co^{2+} + SeO_3^{2-} + 2H_2O(l) \qquad (7.32)$$

$$\log_{10}K°_{s,0}((7.32), 298.15\ K) = -(7.9 \pm 0.4) \qquad \text{(selected)}$$

Copper:

$$CuSeO_3 \cdot 2H_2O(s) \Leftrightarrow Cu^{2+} + SeO_3^{2-} + 2H_2O(l) \qquad (7.33)$$

$$\log_{10}K°_{s,0}((7.33), 298.15\ K) = -(9.5 \pm 1.5) \qquad \text{(noted)}$$

Zinc:

$$ZnSeO_3\cdot[H_2O](cr) \Leftrightarrow Zn^{2+} + SeO_3^{2-} + [H_2O(l)] \qquad (7.34)$$

$\log_{10}K°_{s,0}((7.34), 298.15\ K) = \leq -7.25$ (noted)

Gallium:

$$Ga_2(SeO_3)_3\cdot 6H_2O(cr) \Leftrightarrow 2Ga^{3+} + 3SeO_3^{2-} + 6H_2O(l) \qquad (7.35)$$

$\log_{10}K°_{s,0}((7.35), 298.15\ K) = -(37.0 \pm 2.0)$ (selected)

Silver:

$$Ag_2SeO_3(cr) \Leftrightarrow 2Ag^{+} + SeO_3^{2-} \qquad (7.36)$$

$\log_{10}K°_{s,0}((7.36), 298.15\ K) = -(15.8 \pm 0.3)$ (selected)

Cadmium:

$$CdSeO_3(cr) \Leftrightarrow Cd^{2+} + SeO_3^{2-} \qquad (7.37)$$

$\log_{10}K°_{s,0}((7.37), 298.15\ K) = -(9.3 \pm 1.2)$ (selected)

Indium:

$$In_2(SeO_3)_3\cdot 6H_2O(cr) \Leftrightarrow 2In^{3+} + 3SeO_3^{2-} + 6H_2O(l) \qquad (7.38)$$

$\log_{10}K°_{s,0}((7.38), 298.15\ K) = -(39.0 \pm 2.0)$ (selected)

Lanthanum:

$$La_2(SeO_3)_3(s) \Leftrightarrow 2La^{3+} + 3SeO_3^{2-} \qquad (7.39)$$

$\log_{10}K°_{s,0}((7.39), 298.15\ K) = -(31.0 \pm 2.0)$ (noted)

Cerium:

$$Ce_2(SeO_3)_3(s) \Leftrightarrow 2Ce^{3+} + 3SeO_3^{2-} \qquad (7.40)$$

$\log_{10}K°_{s,0}((7.40), 298.15\ K) = -(31.17 \pm 0.30)$ (noted)

Praesodymium:

$$Pr_2(SeO_3)_3(s) \Leftrightarrow 2Pr^{3+} + 3SeO_3^{2-} \qquad (7.41)$$

$\log_{10}K°_{s,0}((7.41), 298.15\ K) = -(34.0 \pm 2.0)$ (noted)

Neodymium:

$$Nd_2(SeO_3)_3(s) \Leftrightarrow 2Nd^{3+} + 3SeO_3^{2-} \qquad (7.42)$$

$\log_{10}K°_{s,0}((7.42), 298.15\ K) = -(30.0 \pm 2.0)$ (noted)

Samarium:

$$Sm_2(SeO_3)_3(s) \Leftrightarrow 2Sm^{3+} + 3SeO_3^{2-} \qquad (7.43)$$

$\log_{10}K°_{s,0}((7.43), 298.15\ K) = -(35.0 \pm 2.0)$ (noted)

Mercury(I):

$$Hg_2SeO_3(cr) \Leftrightarrow Hg_2^{2+} + SeO_3^{2-} \qquad (7.44)$$

$\log_{10}K°_{s,0}((7.44), 298.15\ K) = -(15.2 \pm 1.0)$ (selected)

Mercury(II):

$$HgSeO_3(cr) \Leftrightarrow Hg^{2+} + SeO_3^{2-} \qquad (7.45)$$

$\log_{10}K°_{s,0}((7.45), 298.15\ K) = -(15.98 \pm 0.30)$ (noted)

$$HgSeO_3(cr) + SeO_3^{2-} \Leftrightarrow Hg(SeO_3)_2^{2-} \qquad (7.46)$$

$\log_{10}K°_{s,0}((7.46), 298.15\ K) = -(1.35 \pm 0.15)$ (selected)

Lead:

$$PbSeO_3(cr) \Leftrightarrow Pb^{2+} + SeO_3^{2-} \qquad (7.47)$$

$\log_{10}K°_{s,0}((7.47), 298.15\ K) = -(12.5 \pm 1.0)$ (selected)

Uranium:

$$UO_2SeO_3(s) \Leftrightarrow UO_2^{2+} + SeO_3^{2-} \qquad (7.48)$$

$\log_{10}K°_{s,0}((7.48), 298.15\ K) = -(12.5 \pm 1.0)$ (noted)

7.6 Selenate species and solids

7.6.1 Aqueous selenic acid

Selenic acid H_2SeO_4 is a strong acid, comparable with sulfuric acid (H_2SO_4). The species $H_2SeO_4(aq)$ needs not being considered below total aqueous concentrations of 11 to 12 mol·L^{-1}. Hence, only the equilibrium

$$SeO_4^{2-} + H+ \Leftrightarrow HSeO_4^{2-} \qquad (7.49)$$

is relevant in aqueous solution. Several authors (Nair 1964, Covington and Dobson 1965, Ghosh and Nair 1970, Baes and Mesmer 1976) found $\log_{10}$K-values in the narrow range 1.66 to 1.78, depending on the esitmates for the activity coefficients. Olin et al. (2005) based their selected value of

$$\log_{10}K°((7.49), 298.15\ K) = (1.75 \pm 0.10).$$

solely on the work of Nair (1964 and Ghosh and Nair (1970). This value differs slightly from the value selected by Grenthe et al. (1992) $\log_{10}K°((7.49), 298.15\ K$, Genthe et al. 1992) = (1.80 ± 0.14). For the SIT calculation Olin et al. (2005) introduced the approximations $\varepsilon(H^+, HSeO_4^-) = \varepsilon(H^+, Cl^-) = 0.12$ kg·mol^{-1}, $\varepsilon(Na^+, HSeO_4^-) = \varepsilon(Na^+, HSO_4^-) = -(0.01 \pm 0.02)$ kg·mol^{-1}, and $\varepsilon(Na^+, SeO_4^{2-}) = \varepsilon(Na^+, SO_4^{2-}) = -(0.12 \pm 0.06)$ kg·mol^{-1} and took the numerical values from Grenthe et al. (1992).

From nine experiments between 273 and 318 K of Nair (1964), Olin et al. (2005) evaluated $\Delta_rH°_m((7.49), 298.15\ K) = 24.2$ kJ·mol^{-1} using $\log_{10}K^0_1(7.49, T) = a + bT^{-1} + C \ln T$ and Ghosh and Nair (1970) obtained $\Delta_rH°_m((7.49), 298.15\ K) = (24.0 \pm 1.5)$ kJ·mol^{-1} from seven experiments between 273 and 318 K. From an analogous investigation of the protonation of the sulfate ion Nair and Nancollas (1958) obtained $\Delta_rH°_m$ of 23.4 kJ·mol^{-1}, similar to the value of 22.4 kJ·mol^{-1} selected by Cox et al. (1989). For $\Delta_rH°_m((7.49), 298.15\ K)$ Wagman et al. (1982) indicate a value of only 17.5 kJ·mol^{-1} based on measurements of Thomsen (1882). It is not fully obvious why Olin et al. (2005) gave the high weight to the measurements of Thomsen (1882), but they finally selected the mean of Ghosh and Nair (1970) and Thomsen (1882) to obtain

$$\Delta_rH°_m((7.49), 298.15\ K) = (20.80 \pm 3.20)\ kJ·mol^{-1}.$$

Olin et al. (2005) finally recommended

$$\Delta_f G^\circ_m(\mathrm{HSeO_4^-}, 298.15\ \mathrm{K}) = -(449.5 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}}\ \text{and}$$

$$\Delta_f H^\circ_m(\mathrm{HSeO_4^-}, 298.15\ \mathrm{K}) = -(582.7 \pm 4.7)\ \mathrm{kJ\cdot mol^{-1}},$$

$$S^\circ_m(\mathrm{HSeO_4^-}, 298.15\ \mathrm{K}) = (136.2 \pm 16.4)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},$$

and,

$$\Delta_f G^\circ_m(\mathrm{SeO_4^{2-}}, 298.15\ \mathrm{K}) = -(439.5 \pm 1.4)\ \mathrm{kJ\cdot mol^{-1}}\ \text{and}$$

$$\Delta_f H^\circ_m(\mathrm{SeO_4^{2-}}, 298.15\ \mathrm{K}) = -(603.5 \pm 3.5)\ \mathrm{kJ\cdot mol^{-1}},$$

$$S^\circ_m(\mathrm{SeO_4^{2-}}, 298.15\ \mathrm{K}) = (33.0 \pm 12.7)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

7.6.2 Solid and aqueous selenate species

Like in the case of selenite species this section starts with equilibria that were considered to be subject of the database update 12/07. Many other equilibra, also assessed by Olin et al. (2005), will be summarized under the heading “other selenite equilibra”.

Magnesium selenates

Phase diagrams of the type $MgSeO_4$-(M(I),M(II)SeO_4-H_2O were investigated by at least ten different authors over the last seventy years. Isopiestic data from Ojkova and Staneva (1989) at 298.15 K have independently been evaluated by Kumov and Batyreva (1990) and Christov (1997). For the equilibrium

$$\mathrm{MgSeO_4\cdot 6H_2O(cr)} \Leftrightarrow \mathrm{Mg^{2+}} + \mathrm{SeO_4^{2-}} + \mathrm{6H_2O(l)} \qquad (7.50)$$

selected

$$\log_{10}K^\circ_{s,0}((7.50), 298.15\ \mathrm{K}) = (1.133 \pm 0.044).$$

Parker et al. (1997) cited the value of the equilibrium constant

$$\mathrm{Mg^{2+}} + \mathrm{SeO_4^{2-}} \Leftrightarrow \mathrm{MgSeO_4(aq)} \qquad (7.51)$$

$$\log_{10}\beta^\circ_1((7.51), 298.15\ \mathrm{K}) = (2.2 \pm 0.2)$$

based on a “thesis by Quinn” that was not available to Olin et al. (2005). This value was selected by Olin et al. (2005) since it is consistent with the corresponding sulfate complex. The present update accepts the selection but puts the value into “supplemental data”.

From Selivanova et al. (1961) Olin et al. (2005) evaluated and selected (in agreement with Wagman et al. 1982)

$$\Delta_f H^\circ_m(\mathrm{MgSeO_4\cdot 6H_2O, cr}, 298.15\ \mathrm{K}) = -(2781.4 \pm 2.4)\ \mathrm{kJ\cdot mol^{-1}},$$

and, consequently,

$$\Delta_f G^\circ_m(\mathrm{MgSeO_4\cdot 6H_2O, cr}, 298.15\ \mathrm{K}) = -(2324.20 \pm 2.00)\ \mathrm{kJ\cdot mol^{-1}}$$

$$S^\circ_m(\mathrm{MgSeO_4\cdot 6H_2O, cr}, 298.15\ \mathrm{K}) = (351.1 \pm 10.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Calcium selenates

From solubility data of Meyer and Aulich (1928) and Welton and King (1939) Olin et al. (2005) selected the mean solubility m($CaSeO4\cdot 2H_2O$(cr), aq sat, 298.15) = (0.380 ± 0.025) $mol\cdot kg^{-1}$, and from this value the solubility product

$$CaSeO_4\cdot 2H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_4^{2-} + 2H_2O(l) \qquad (7.52)$$

$$\log_{10}K°_{s,0}((7.52), 298.15\ K) = -(2.68 \pm 0.25).$$

Olin et al. (2005) based the extrapolation of $\log_{10}K(7.52)$ to $I = 0$ on the mean activity coefficient of $MgSO_4$, $\gamma_\pm = 0.12$, and on only moderate variations of mean activity coefficients observed by Ojkova and Staneva (1989) for aqueous selenates.

Parker et al. (1997) investigated the equilibrium

$$Ca^{2+} + SeO_4^{2-} \Leftrightarrow CaSeO_4(aq), \qquad (7.53)$$

with

$$\log_{10}\beta°_1((7.53), 298.15\ K) = (2.00 \pm 0.10).$$

Olin et al. (2005) accepted and selected this value based on the fact that the similarly determined value for the sulfate complex agreed with literature data. From Selivanova and Shneider (1959) Olin et al. (2005) evaluated and selected

$$\Delta_fH°_m(CaSeO_4\cdot 6H_2O, cr, 298.15\ K) = -(1709.0 \pm 2.6)\ kJ\cdot mol^{-1},$$

and, consequently

$$\Delta_fG°_m(CaSeO_4\cdot 6H_2O, cr, 298.15\ K) = -(1481.9 \pm 2.3)\ kJ\cdot mol^{-1},$$

$$S°_m(CaSeO_4\cdot 6H_2O, cr, 298.15\ K) = (198.8 \pm 11.7)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Barium selenates

For the equilibrium

$$BaSeO_4(cr) \Leftrightarrow Ba^{2+} + SeO_4^{2-} + 2H_2O(l) \qquad (7.54)$$

Olin et al. (2005) selected $\log_{10}K°_{s,0}(298.15\ K) = -(7.56 \pm 0.10)$ for this equilibrium, based on data from Selivanova and Shneider (1958). However, very recently Rai et al. (2014) in a very careful study investigated the solubility of $BaSO_4$(cr) from under- and oversaturation in Na_2SeO_4 solutions from 0.04 up to 4.1 $mol\cdot kg^{-1}$. The solids formed were investigated by XRD to be $BaSeO_4$(cr) and β-Na_2SeO_4 (above 1.0 $mol\cdot kg^{-1}$ of Na_2SeO_4). Rai et al. (2014) used both, a Pitzer- as well as a SIT-model to evaluate the experimental data and obtained

$$\log_{10}K°_{s,0}((7.54), 298.15\ K) = -(7.25 \pm 0.11)$$

for the SIT model. This study prefers using the Rai et al. (2014) value, based on the very careful and comprehensive thermodynamic analysis provided in the paper. This preference is further corroborated by the fact that Rai et al.'s (2014) model is also capable to describe independent solubility data of $BaSeO_4$(cr) in a wide range from pH 1.4 to 13.8 described by Hata et al. (2004).

Consequently,

$$\Delta_fG°_m(BaSeO_4, cr, 298.15\ K) = -(1038.54 \pm 0.64)\ kJ\cdot mol^{-1},$$

compared to -(1040.3 ± 3.0) $kJ\cdot mol^{-1}$ provided by Olin et al. (2005).

The model of Rai et al. (2014) requires the species $Ba(SeO_4)_2^{2-}$ when applying an SIT approach to the experimental data (the species is not necessary in the Pitzer-approach) above Na_2SeO_4 concentrations of ~0.1 $mol\cdot kg^{-1}$. For the equilibrium

$$Ba^{2+} + 2SeO_4^{2-} \Leftrightarrow Ba(SeO_4)_2^{2-} \qquad (7.55)$$

Rai et al. (2014) provide

$$\log_{10}\beta^\circ_2((7.55), 298.15\ K) = (3.44 \pm 0.12).$$

The species $BaSeO_4(aq)$ has no region of dominance in the experiments of Rai et al. (2014) and the authors adopt a maximum value of $\log_{10}\beta_1 < 2.15$ for the stability of $BaSeO_4(aq)$, in accordance with the corresponding stabilities for Mg ($\log_{10}\beta^\circ_1(298.15\ K) = (2.2 \pm 0.2)$) and Ca ($\log_{10}\beta^\circ_1(298.15\ K) = (2.00 \pm 0.10)$).

A relevant parameter in the experiments and the modelling of Rai et al. (2014) is the SIT interaction parameter $\varepsilon(Na^+, SeO_4^{2-})$. Rai et al. (2014) performed a comprehensive sensitivity analysis for this parameter, whose range must fall into the range $0.00 > \varepsilon(Na^+, SeO_4^{2-}) > -0.26$, when following the arguments of the authors (the lower border has been reported by Philipini et al. (2009). Rai et al. (2014) conclude that $\varepsilon(Na^+, SeO_4^{2-}) = -0.12\ kg\cdot mol^{-1}$ (the value provided by Olin et al. 2005, see above) best fits the experimental data.

From Selinova et al. (1959) Olin et al. (2005) adopted

$$\Delta_f H^\circ_m(BaSeO_4, cr, 298.15\ K) = -(1144.0 \pm 5.0)\ kJ\cdot mol^{-1},$$

which leads to $\Delta_f S^\circ_m = (\Delta_f G^\circ_m - \Delta_f H^\circ_m)/(-298.15) = -(353.71 \pm 16.9)\ J\cdot K^{-1}\cdot mol^{-1}$, and, consequently to the selection of

$$S^\circ_m(BaSeO_4, cr, 298.15\ K) = (161.1 \pm 16.9)\ J\cdot K^{-1}\cdot mol^{-1}.$$

Note that Olin et al. (2005) gave $S^\circ_m(BaSeO_4, cr, 298.15\ K) = (167.0 \pm 19.6)\ J\cdot K^{-1}\cdot mol^{-1}$.

Manganese selenates

The stable selenate solid in aqueous solution is the pentahydrate $MnSeO_4\cdot 5H_2O(cr)$, which is not stable against oxidation. The solubility of the salt is high. From several references Olin et al. (2005) selected the mean solubility $m(MnSeO_4\cdot 5H_2O(cr), aq\ sat, 298.15) = (2.86 \pm 0.08)\ mol\cdot kg^{-1}$, and from Kumov and Batyreva (1990) they adopted the equilibrium

$$MnSeO_4\cdot 5H_2O(cr) \Leftrightarrow Mn^{2+} + SeO_4^{2-} + 5H_2O(l) \qquad (7.56)$$

$$\log_{10}K^\circ_{s,0}((7.56), 298.15\ K) = -(2.05 \pm 0.03),$$

which was not selected by Olin et al. (2005) nor by this review due to the high resulting concentrations.

For the equilibrium

$$Mn^{2+} + SeO_4^{2-} \Leftrightarrow MnSeO_4(aq), \qquad (7.57)$$

determined by Ghosh and Nair (1970) using potentiometric measurements, Olin et al. (2005) accepted and selected

$$\log_{10}\beta^\circ_1((7.57), 298.15\ K) = (2.43 \pm 0.05).$$

Nickel selenates

Below 355 K $NiSeO_4\cdot 6H_2O$ is the stable phase. From Ojkova et al. (1998) Olin et al. (2005) selected a solubility of $m(NiSeO_2\cdot 6H_2O(cr), aq\ sat, 298.15) = (1.92 \pm 0.05)\ mol\cdot kg^{-1}$, and for the equilibrium

$$NiSeO_4\cdot 6H_2O(cr) \Leftrightarrow Ni^{2+} + SeO_4^{2-} + 6H_2O(l), \qquad (7.58)$$

based on the isopiestic measurements of Ojkova and Stanev (1989) they selected

$$\log_{10}K^{\circ}_{s,0}((7.58), 298.15\ K) = -(1.381 \pm 0.045).$$

Due to very high resulting concentrations equilibrium 7.58 is not included in the update.

For the equilibrium

$$Ni^{2+} + SeO_4^{2-} \Leftrightarrow NiSeO_4(aq), \qquad (7.59)$$

determined by Ghosh and Nair (1970) using potentiometric measurements at various temperatures, Olin et al. (2005) accepted and selected

$$\log_{10}\beta^{\circ}_1((7.59), 298.15\ K) = (2.67 \pm 0.05).$$

They did, however, not accept $\Delta_rH^{\circ}_m((7.59)\ 298.15\ K) = (14.7 \pm 1.3)\ kJ\cdot mol^{-1}$, which may be used as an indication.

Uranium selenates

With $m(UO_2SeO_4\cdot 4H_2O(cr), aq\ sat, 298.15) = 5.31\ mol\cdot kg^{-1}$ the solubility of uranium selenate is very high. The solubility product $UO_2SeO_4\cdot 4H_2O(cr) \Leftrightarrow UO_2^{2+} + SeO_4^{2-} + 4H_2O(l)$, $\log_{10}K^{\circ}_{s,0}(298.15\ K) = -(2.25 \pm 0.04)$, reported by Kumov and Batyreva (1990) was not accepted by Olin et al. (2005), but is noted here if for specific reasons there is a need to assess the solubility of UO_2SeO_4.

For the enthalpy of formation Olin et al. (2005) adopted and selected the value from Grenthe at al. (1992):

$$\Delta_fH^{\circ}_m(UO_2SeO_4, cr, 298.15\ K) = -(1539.3 \pm 3.3)\ kJ\cdot mol^{-1},$$

but no standard enthalpy of formation was available for $UO_2SeO_4\cdot 4H_2O(cr)$.

From spectrophotometric/potentiometric studies of in 3 M $Na^+(ClO_4^-, SeO_4^{2-})$ solutions at (298.2 ± 0.5) K by Lubal and Havel (1997) and from a voltammetric study of the same system at (296 ± 2) K by Djogic et al. (1999) Olin et al. (2005) concluded a convincing evidence for the existence of the aqueous species $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$.

From these studies and by using $\varepsilon(UO_2^{2+}, SeO_4^{2-}) = -(0.34 \pm 0.07)\ kg\cdot mol^{-1}$ Olin et al. (2005) derived and selected a mean of

$$\log_{10}\beta^{\circ}_1((7.60), 298.15\ K) = (2.74 \pm 0.25)$$

for the equilibrium

$$UO_2^{2+} + SeO_4^{2-} \Leftrightarrow UO_2SeO_4(aq), \qquad (7.60)$$

and,

$$\Delta_fG^{\circ}_m(UO_2SeO_4, aq, 298.15\ K) = -(1407.7 \pm 2.7)\ kJ\cdot mol^{-1}.$$

For the equilibrium

$$UO_2^{2+} + 2SeO_4^{2-} \Leftrightarrow UO_2(SeO_4)_2^{2-} \qquad (7.60a)$$

Olin et al. (2005) derived

$$\log_{10}\beta^{\circ}_2(7.60a) = (3.10 \pm 0.50),$$

but did not select the value because they ascertained a lack of supporting data in the long extrapolation procedure. From Lubal and Havel (1997) they indicate that $\log_{10}\beta^{\circ}_2$ does not exceed 3.4. The present update accepts equilibrium 7.60a as supplemental data.

Olin et al. (2005) list a variety of selenate solid solubilities (and complexes) for elements that are not contained in the PSI/Nagra TDB 12/07. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These selenate equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have "noted" or "selected" the equilibrium.

Other selenate equilibria

Beryllium:

$$BeSeO_4\cdot 4H_2O(cr) \Leftrightarrow Be^{2+} + SeO_4^{2-} + 4H_2O(l) \qquad (7.61)$$

$\log_{10}K^{\circ}_{s,0}((7.61), 298.15\ K) = -(2.94 \pm 0.06)$ (noted)

Ammonium:

$$(NH_4)_2SeO_4(cr) \Leftrightarrow 2NH_4^{+} + SeO_4^{2-} \qquad (7.62)$$

$\log_{10}K^{\circ}_{s,0}((7.62), 298.15\ K) = (0.911 \pm 0.065)$ (seleced)

Lithium:

$$Li_2SeO_4\cdot H_2O(cr) \Leftrightarrow 2Li^{+} + SeO_4^{2-} + H_2O(l) \qquad (7.63)$$

$\log_{10}K^{\circ}_{s,0}((7.63), 298.15\ K) = (1.762 \pm 0.087)$ (seleced)

Sodium:

$$Na_2SeO_4\cdot 10H_2O(cr) \Leftrightarrow 2Na^{+} + SeO_4^{2-} + 10H_2O(l) \qquad (7.64)$$

$\log_{10}K^{\circ}_{s,0}((7.64), 298.15\ K) = -(0.681 \pm 0.087)$ (seleced)

Potasium:

$$K_2SeO_4(cr) \Leftrightarrow 2K^{+} + SeO_4^{2-} \qquad (7.65)$$

$\log_{10}K^{\circ}_{s,0}((7.65), 298.15\ K) = (0.904 \pm 0.065)$ (seleced)

Scandium:

$$Sc^{3+} + SeO_4^{2-} \Leftrightarrow ScSeO_4^{+} \qquad (7.66)$$

$\log_{10}\beta^{\circ}_1((7.66), 0.5\ M\ NaClO_4, 298.15\ K) = (1.65 \pm 0.20)$ (noted)

Cobalt:

$$CoSeO_4\cdot 6H_2O(cr) \Leftrightarrow Co^{2+} + SeO_4^{2-} + 6H_2O(l) \qquad (7.67)$$

$\log_{10}K^{\circ}_{s,0}((7.67), 298.15\ K) = -(1.759 \pm 0.043)$ (selected)

$$Co^{2+} + SeO_4^{2-} \Leftrightarrow CoSeO_4(aq) \qquad (7.68)$$

$\log_{10}\beta°_1((7.68), 298.15\ K) = (2.70 \pm 0.05)$ (selected)

Copper:

$$CuSeO_4\cdot 5H_2O(cr) \Leftrightarrow Cu^{2+} + SeO_4^{2-} + 5H_2O(l) \qquad (7.69)$$

$\log_{10}K°_{s,0}((7.69), 298.15\ K) = -(2.44 \pm 0.20)$ (selected)

$$Co^{2+} + SeO_4^{2-} \Leftrightarrow CoSeO_4(aq) \qquad (7.70)$$

$\log_{10}\beta°_1((7.70), 298.15\ K) < 2.2$ (noted)

Zinc:

$$ZnSeO_4\cdot 6H_2O(cr) \Leftrightarrow Zn^{2+} + SeO_4^{2-} + 6H_2O(l) \qquad (7.71)$$

$\log_{10}K°_{s,0}((7.71), 298.15\ K) = -(1.538 \pm 0.064)$ (selected)

$$Zn^{2+} + SeO_4^{2-} \Leftrightarrow ZnSeO_4(aq) \qquad (7.72)$$

$\log_{10}\beta°_1((7.72), 298.15\ K) = (2.19 \pm 0.06)$ (selected)

$$Zn^{2+} + 2SeO_4^{2-} \Leftrightarrow Zn(SeO_4)_2^{2-} \qquad (7.73)$$

$\log_{10}\beta°_2((7.73), 298.15\ K) = (2.76 \pm 0.12)$ (noted)

For the neutral complex $ZnSeO_4(aq)$ Olin et al. (2005) further selected

$$\Delta_fG°_m(ZnSeO_4(aq), 298.15\ K) = -(599.0 \pm 1.5)\ kJ\cdot mol^{-1},$$

$$\Delta_fH°_m(ZnSeO_4(aq), 298.15\ K) = -(752.3 \pm 5.3)\ kJ\cdot mol^{-1}, \text{ and}$$

$$S°_m(ZnSeO_4(aq), 298.15\ K) = -(20.1 \pm 18.5)\ kJ\cdot mol^{-1}.$$

Rubidium:

$$Rb_2SeO_4(cr) \Leftrightarrow 2Rb^{+} + SeO_4^{2-} \qquad (7.74)$$

$\log_{10}K°_{s,0}((7.74), 298.15\ K) = (0.430 \pm 0.065)$ (seleced)

Strontium:

$$SrSeO_4 \Leftrightarrow Sr^{2+} + SeO_4^{2-} \qquad (7.75)$$

$\log_{10}K°_{s,0}((7.75), 298.15\ K) = -(4.35 \pm 0.15)$ (noted)

Cesium:

$$Cs_2SeO_4(cr) \Leftrightarrow 2Cs^{+} + SeO_4^{2-} \qquad (7.76)$$

$\log_{10}K°_{s,0}((7.76), 298.15\ K) = (0.636 \pm 0.065)$ (seleced)

Thallium(I):

$$Tl_2SeO_4(cr) \Leftrightarrow 2Tl^{+} + SeO_4^{2-} \qquad (7.77)$$

$\log_{10}K°_{s,0}((7.77), 298.15\ K) = -(3.90 \pm 0.15)$ (seleced)

Lead:

$$PbSeO_4(cr) \Leftrightarrow Pb^{2+} + SeO_4^{2-} \qquad (7.78)$$

$\log_{10}K°_{s,0}((7.78), 298.15\ K) = -(6.90 \pm 0.25)$ (selected)

$$Pb^{2+} + SeO_4^{2-} \Leftrightarrow PbSeO_4(aq) \qquad (7.79)$$

$\log_{10}\beta°_1((7.79), 298.15\ K) < 2.2$ (noted)

7.7 Selenocyanate species

Due to their potential importance in radioactive waste systems the database update includes species for Ni-selenocyanate complexes. Further, specific types of radioactive wastes may include cyanide complexes (Prussian blue), leading to the formation of cyanoselenate ligands. Hence, this section first explains, how thermodynamic data for the selenocyanate ion $SeCN^-$ is extracted from Olin et al. (2005). The selenocyanate ion $SeCN^-$ is an ambidentate complexing agent which may coordinate to metal ions via either the nitrogen atom (to "hard" metal ions) or the selenium atom (to "soft" metal ions).

Olin et al. (2005) "partly" selected the thermodynamic values provided by Hamada (1961) (particulary they disagreed with $S^\circ_m(SeCN^-, 298.15\ K) = 8.3\ kJ\cdot mol^{-1}$ because it is inconsistent with corresponding values for OCN^- and SCN^- provided by Wagman et al. (1982)).

For the equilibrium

$$SeCN^- + H^+ \Leftrightarrow Se(monoclinic) + HCN(aq) \qquad (7.80)$$

Olin et al. (2005) accepted

$$\log_{10}K^\circ_{s,0}((7.80), 298.15\ K) = (3.6 \pm 0.5)$$

and derived

$$\Delta_f G^\circ_m(SeCN^-, 298.15\ K) = (136.1 \pm 3.8)\ kJ\cdot mol^{-1}.$$

From Wunderlich and Chu (1980) and Gaur et al. (1981) Olin et al. (2005) evaluated and selected

$$\Delta_f H^\circ_m(Se, monoclinic, 298.15\ K) = (2.4 \pm 1.10)\ kJ\cdot mol^{-1},$$

$$S^\circ_m(Se, monoclinic, 298.15\ K) = (44.97 \pm 0.40)\ J\cdot K^{-1}\cdot mol^{-1},$$

and, consequently derived

$$\Delta_f G^\circ_m(Se, monoclinic, 298.15\ K) = (1.28 \pm 0.18)\ kJ\cdot mol^{-1},$$

which, with $\Delta_f G^\circ_m(Se, cr, 298.15\ K) = (0.00 \pm 0.00)\ kJ\cdot mol^{-1}$, may be reformulated as

$$Se(cr) \Leftrightarrow Se(monoclinic) \qquad (7.81)$$

$$\log_{10}K^\circ_{s,0}((7.81), 298.15\ K) = -(0.224 \pm 0.032).$$

We express the formation of $SeCN^-$ as a reaction in homogenous aqueous solution by an appropriate combination of the equilibria 7.4, 7.21, 7.22, 7.80, 7.81 and $4H^+ + 4e^- \Leftrightarrow 2H_2(g)$:

$H_2SeO_3(aq) + 2\ H_2(g) \Leftrightarrow Se(cr) + 3H_2O(l)$ (7.4, $\log_{10}K^\circ_{s,0} = (50.15 \pm 0.15)$)
$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^-$ (7.21, $\log_{10}K^\circ_{s,0} = (8.36 \pm 0.23)$)
$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq)$ (7.22, $\log_{10}K^\circ_{s,0} = (2.64 \pm 0.14)$)
$Se(monoclinic) + HCN(aq) \Leftrightarrow SeCN^- + H^+$ (inv. 7.80, $\log_{10}K^\circ_{s,0} = -(3.6 \pm 0.5)$)
$Se(cr) \Leftrightarrow Se(monoclinic)$ (7.81, $\log_{10}K^\circ_{s,0} = -(0.224 \pm 0.032)$)
$4H^+ + 4e^- \Leftrightarrow 2H_2(g)$ (base definition, $\log_{10}K^\circ_{s,0} = (0.0 \pm 0.0)$).

By adding these equilibria we obtain

$$SeO_3^{2-} + HCN(aq) + 5H^+ + 4e^- \Leftrightarrow SeCN^- + 3H_2O(l) \qquad (7.82)$$

$$\log_{10}K^\circ((7.82), 298.15\ K) = (57.3 \pm 0.6).$$

Note that equilibrium (7.82) strongly favours the formation of $SeCN^-$ from SeO_3^{2-} and CN^- under conditions relevant for radioactive waste systems (i.e. pH 7.5, Eh -200 mV). On the other hand, SeCN- rapidly decomposes to Se(monoclinic) and HCN when acidified with HCl (Boughton and Keller 1966). This observation conversely supports the arguments provided in section 7.2.1 on the solubility of elemental selenium.

For SIT evaluations and based on Ciavatta (1980) Olin et al. (2005) propose to use the interaction coefficient $\varepsilon(SeCN^-, Na^+) \approx \varepsilon(SCN^-, Na^+) = (0.05 \pm 0.01)\ kg \cdot mol^{-1}$, in analogy to the interaction of the thiocyanate ion SCN^- with sodium.

Nickel selenocyanates

Kulberg (1974) and Satyanarayana et al. (1975) studied the formation of Ni-SeCN complexes. Olin et al. (2005) did not fully agree with the evaluation of Satyanarayana et al. (1975), but selected from Kulberg (1974):

$$Ni^{2+} + SeCN^- \Leftrightarrow NiSeCN^+ \qquad (7.83)$$

$$\log_{10}\beta^\circ_1((7.83), 298.15\ K) = (1.77 \pm 0.06)$$

and

$$Ni^{2+} + 2SeCN^- \Leftrightarrow Ni(SeCN)_2(aq) \qquad (7.84)$$

$$\log_{10}\beta^\circ_2((7.84), 298.15\ K) = (2.24 \pm 0.14).$$

Note that Kulberg (1974) did not give sufficient evidence to establish the complex $Ni(SeCN)_3^-$. Equilibrium data were extrapolated from I = 1M $NaClO_4$ to I = 0 using $\Delta\varepsilon$ values of cadmium thiocaynate complexes provided by Bahta et al. (1997).

Kulberg (1974) provided his calorimetric measurements for 1 M $NaClO_4$ solutions. Olin et al. (2005) assumed that these data are also valid at I = 0, but accounted for this assumption by doubling the associated uncertainties. They selected

$$\Delta_r H^\circ_m((7.83), 298.15\ K) = -(12.8 \pm 0.4)\ kJ \cdot mol^{-1}, \text{ and}$$

$$\Delta_r H^\circ_m((7.84), 298.15\ K) = -(25 \pm 4)\ kJ \cdot mol^{-1}.$$

For the Gibbs energy of Ni^{2+} Olin et al. (2005) used $\Delta_f G^\circ_m(Ni^{2+}, 298.15\ K) = -(45.773 \pm 0.771)\ kJ \cdot mol^{-1}$ as taken from Gamsjäger et al. (2005) and calculated

$$\Delta_f G^\circ_m(NiSeCN^-, 298.15\ K) = (80.2 \pm 3.9)\ kJ \cdot mol^{-1}, \text{ and,}$$

$$\Delta_f G^\circ_m(Ni(SeCN)_2, aq, 298.15\ K) = (213.5 \pm 7.7)\ kJ \cdot mol^{-1}.$$

Other selenocyanates equilibria

Olin et al. (2005) list a variety of cyanoselenate equilbria for elements that are not contained in the PSI/Nagra TDB. However, some of these equilibria may be useful for specific purposes and/or may be relevant for a subsequent database update. These cyanoselenate equilibria are assembled in the following subsection, following the atomic number of elements. An indication is given of whether Olin et al. (2005) have “noted” or “selected” the equilibrium.

Cobalt:

$Co^{2+} + SeCN^{-} \Leftrightarrow CoSeCN^{+}$ (7.85)

$\log_{10}\beta^{\circ}_{1}((7.85), 298.15\ K) = (1.5 \pm 0.3)$ (noted)

Copper(I):

CuSeCN(s, cr) solids seems to be sparingly soluble in aqueous solution, but complexes disproportionate to Se(0) and Cu(I) cyanide complexes.

Zinc:

$Zn^{2+} + SeCN^{-} \Leftrightarrow ZnSeCN^{+}$ (7.86)

$\log_{10}\beta^{\circ}_{1}((7.86), 298.15\ K) = (1.21 \pm 0.06)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.026 \pm 0.058)$

$Zn^{2+} + 2SeCN^{-} \Leftrightarrow Zn(SeCN)_2(aq)$ (7.87)

$\log_{10}\beta^{\circ}_{2}((7.87), 298.15\ K) = (1.68 \pm 0.11)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.145 \pm 0.094)\ kg \cdot mol^{-1}$.

Silver:

$Ag^{+} + 3SeCN^{-} \Leftrightarrow Ag(SeCN)_3^{-}$ (7.88)

$\log_{10}\beta^{\circ}_{3}((7.88), 298.15\ K) = (13.85 \pm 0.30)$ (selected)

$Ag(SeCN)(cr) \Leftrightarrow Ag^{+} + SeCN^{-}$ (7.89)

$\log_{10}K^{\circ}_{s,0}((7.89), 298.15\ K) = -(14.0 \pm 0.5)$ (selected)

Cadmium:

$Cd^{2+} + SeCN^{-} \Leftrightarrow CdSeCN^{+}$ (7.90)

$\log_{10}\beta^{\circ}_{1}((7.90), 298.15\ K) = (2.24 \pm 0.06)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.026 \pm 0.058)\ kg \cdot mol^{-1}$.

$Cd^{2+} + 2SeCN^{-} \Leftrightarrow Cd(SeCN)_2$ (7.91)

$\log_{10}\beta^{\circ}_{2}((7.91), 298.15\ K) = (3.34 \pm 0.12)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.145 \pm 0.094)\ kg \cdot mol^{-1}$.

$Cd^{2+} + 3SeCN^{-} \Leftrightarrow Cd(SeCN)_3^{-}$ (7.92)

$\log_{10}\beta^{\circ}_{3}((7.92), 298.15\ K) = (3.81 \pm 0.21)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.202 \pm 0.134)\ kg \cdot mol^{-1}$.

$Cd^{2+} + 4SeCN^{-} \Leftrightarrow Cd(SeCN)_4^{2-}$ (7.93)

$\log_{10}\beta^{\circ}_{4}((7.93), 298.15\ K) = (4.60 \pm 0.11)$ (selected)

Extrapolated from 1 M $NaClO_4$, using $\Delta\varepsilon = -(0.173 \pm 0.099)\ kg \cdot mol^{-1}$.

$Cd(SeCN)_2(cr) \Leftrightarrow Ag^{+} + 2SeCN^{-}$ (7.94)

$\log_{10}K^{\circ}_{s,0}((7.94), 298.15\ K) = -(5.7 \pm 0.5)$ (selected)

Mercury:

$$Hg^{2+} + 2SeCN^- \Leftrightarrow Hg(SeCN)_2 \quad (7.95)$$

$\log_{10}\beta^\circ_2((7.95), 298.15\ K) = (22.3 \pm 1.0)$ (noted)

$$Hg^{2+} + 3SeCN^- \Leftrightarrow Hg(SeCN)_3^- \quad (7.96)$$

$\log_{10}\beta^\circ_3((7.96), 298.15\ K) = (26.8 \pm 1.0)$ (noted)

$$Hg^{2+} + 4SeCN^- \Leftrightarrow Hg(SeCN)_4^{2-} \quad (7.97)$$

$\log_{10}\beta^\circ_4((7.97), 298.15\ K) = (29.3 \pm 0.5)$ (noted)

Thallium:

$$Tl^+ + SeCN^- \Leftrightarrow TlSeCN(aq) \quad (7.98)$$

$\log_{10}\beta^\circ_1((7.98), 298.15\ K) = (1.75 \pm 0.2)$ (noted)

Table 7.1: Selected selenium data. All data included in TDB Version 12/07 are taken from Olin et al. (2005), except where marked with an asterisk (*). 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**	$\Delta_f G_m°$ [kJ·mol^{-1}]	$\Delta_f H_m°$ [kJ·mol^{-1}]	$S_m°$ [J·K^{-1}·mol^{-1}]	$C_{p,m}°$ [J·K^{-1}·mol^{-1}]	$\Delta_f G_m°$ [kJ·mol^{-1}]	$\Delta_f H_m°$ ε[kJ·mol^{-1}]	$S_m°$ [J·K^{-1}·mol^{-1}]	$C_{p,m}°$ [J·K^{-1}·mol^{-1}]	**Species**
HSeO4-	VI	-	-	-	-	-449.5 ± 1.3	-582.7 ± 4.7	136.2 ± 16.4	-	$HSeO_4^-$
SeO3-2	IV	-361.60 ± 1.47	-	-	-	-362.4 ± 1.8	-507.2 ± 1.1	5.2 ± 7.1	-	SeO_3^{2-}
Se(cr)	0	0.0	0.0	42.27 ± 0.05	25.03 ± 0.05	0.0	0.0	42.09 ± 0.33	25.09 ± 0.30	Se(cr)
H2Se	-II	-	-	-	-	21.5 ± 2.0	14.3 ± 2.0	148.7 ± 9.5	-	$H_2Se(aq)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	$\log_{10}\beta°$ $\log_{10}K°$	$\Delta_r H_m°$ [kJ·mol^{-1}]	**Reaction**
HSeO4-	IV/VI	-25.58	-	-26.3 ± 0.3[a]	-	$SeO_3^{2-} + H_2O(l) \Leftrightarrow HSeO_4^- + H^+ + 2\ e^-$
H2Se	IV/-II	57.39	-	57.4 ± 0.6[b]	-	$SeO_3^{2-} + 8\ H^+ + 6\ e^- \Leftrightarrow H_2Se(aq) + 3\ H_2O(l)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$** **$\log_{10}K°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
SeO4-2	VI	-1.80 ± 0.14	-23.8 ± 5.0	-1.75 ± 0.10	-20.80 ± 3.20	$HSeO_4^- \Leftrightarrow SeO_4^{2-} + H^+$
NiSeO4	VI	-	-	2.67 ± 0.05	-	$Ni^{2+} + SeO_4^{2-} \Leftrightarrow NiSeO_4(aq)$
MnSeO4	VI	-	-	2.43 ± 0.05	-	$Mn^{2+} + SeO_4^{2-} \Leftrightarrow MnSeO_4(aq)$
UO2SeO4	VI	-	-	2.74 ± 0.25	-	$UO_2^{2+} + SeO_4^{2-} \Leftrightarrow UO_2SeO_4(aq)$
UO2(SeO4)2-2	VI	-	-	*(3.10 ± 0.50)*[c]	-	$UO_2^{2+} + 2\ SeO_4^{2-} \Leftrightarrow UO_2(SeO_4)_2^{2-}$
MgSeO4	VI	-	-	*2.2 ± 0.2*	-	$Mg^{2+} + SeO_4^{2-} \Leftrightarrow MgSeO_4(aq)$
CaSeO4	VI	-	-	2.00 ± 0.10	-	$Ca^{2+} + SeO_4^{2-} \Leftrightarrow CaSeO_4(aq)$
(HSeO3-)[d]	IV	8.4 ± 0.1	5.02 ± 0.50	8.36 ± 0.23	-	$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^-$
(H2SeO3)[e]	IV	2.8 ± 0.2	7.07 ± 0.5	2.64 ± 0.14	-	$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3(aq)$
FeSeO3+	IV	-	-	11.15 ± 0.11	-	$Fe^{3+} + SeO_3^{2-} \Leftrightarrow FeSeO_3^+$
SeCN-	0	-	-	57.3 ± 0.6	-	$HCN(aq) + SeO_3^{2-} + 5\ H^+ + 4\ e^- \Leftrightarrow SeCN^- + 3\ H_2O(l)$

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}\beta°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**$\log_{10}\beta°$** **$\log_{10}K°$**	**$\Delta_r H_m°$** [kJ·mol^{-1}]	**Reaction**
NiSeCN+	0	-	-	1.77 ± 0.06	-12.8 ± 0.4	$Ni^{2+} + SeCN^- \Leftrightarrow NiSeCN^+$
Ni(SeCN)2	0	-	-	2.24 ± 0.14	-25 ± 4	$Ni^{2+} + 2\ SeCN^- \Leftrightarrow Ni(SeCN)_2(aq)$
Se2-2	0|-II	-	-	25.32 ± 0.33	-	$2\ Se^{2-} \Leftrightarrow Se_2^{2-} + 2\ e^-$
Se3-2	0|-II	-	-	(49.97 ± 0.68)[f]	-	$3\ Se^{2-} \Leftrightarrow Se_3^{2-} + 4\ e^-$
Se4-2	0|-II	-	-	(73.02 ± 1.01)[f]	-	$4\ Se^{2-} \Leftrightarrow Se_4^{2-} + 6\ e^-$
HSe-	-II	-3.8 ± 0.3	-	-3.85 ± 0.05	-	$H_2Se(aq) \Leftrightarrow HSe^- + H^+$
Se-2	-II	-	-	(-14.91 ± 0.20)*	-	$HSe^- \Leftrightarrow Se^{2-} + H^+$

[a] $\log_{10}K°$ and reaction derived from combining equilibria 7.7, 7.21 and 7.22.

[b] $\log_{10}K°$ and reaction derived from combining equilibria 7.4, 7.21, 7.22, 7.11, (-714), (-713) and $4H^+ + 4e^- \Leftrightarrow 2H_2(g)$.

[c] Value reported but not selected by Olin et al. (2005)

[d] Note that in TDB Version 01/01 the formation reaction was formulated the other way round (formation of SeO_3^{2-} in terms of $HSeO_3^-$)

[e] Note that in TDB Version 01/01 the formation reaction was formulated the other way round (formation of $HSeO_3^-$ in terms of $H_2SeO_3(aq)$)

[f] Note that that the uncertainty differs from that given by Olin et al. (2005)

		TDB Version 01/01		**TDB Version 12/07**		
Name	**Redox**	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**$\log_{10}K_{s,0}°$** **$\log_{10}K°$**	**$\Delta_f H_m°$** [kJ·mol^{-1}]	**Reaction**
Se(cr)	0/IV	-61.29	-	-61.15 ± 0.31	-	$Se(cr) + 3 H_2O(l) \Leftrightarrow SeO_3^{2-} + 6 H^+ + 4 e^-$
BaSeO4(cr)	VI	-	-	-7.56 ± 0.10 -7.25 ± 0.11[g]	-1144.0 ± 5.0 -	$BaSeO_4(cr) \Leftrightarrow Ba^{2+} + SeO_4^{2-}$
NiSeO3:2H2O(cr)	IV	-	-	-5.80 ± 1.0	-	$NiSeO3\cdot 2H_2O(cr) \Leftrightarrow Ni^{2+} + SeO_3^{2-} + 2 H_2O(l)$
MnSeO3:2H2O(cr)	IV	-	-	-7.6 ± 1.0	-	$MnSeO3\cdot 2H_2O(cr) \Leftrightarrow Mn^{2+} + SeO_3^{2-} + 2 H_2O(l)$
MgSeO3:6H2O(cr)	IV	-	-	-5.82 ± 0.25	-2707.21 ± 1.30	$MgSeO3\cdot 6H_2O(cr) \Leftrightarrow Mg^{2+} + SeO_3^{2-} + 6 H_2O(l)$
CaSeO3:H2O(cr)	IV	-	-	-6.40 ± 0.25	-	$CaSeO3\cdot H_2O(cr) \Leftrightarrow Ca^{2+} + SeO_3^{2-} + H_2O(l)$
SrSeO3(cr)	IV	-	-	-6.30 ± 0.50	-1051.9 ± 2.7	$SrSeO3(cr) \Leftrightarrow Sr^{2+} + SeO_3^{2-}$
BaSeO3(cr)	IV	-	-	-6.50 ± 0.25	-1036.7 ± 2.9	$BaSeO3(cr) \Leftrightarrow Ba^{2+} + SeO_3^{2-}$
H2Se(g)	-II	-	-	-1.10 ± 0.01	-14.7 ± 0.3	$H_2Se(g) \Leftrightarrow H_2Se(aq)$

[g] This improved (and preferred) solubility product of Rai et al. (2014) was discovered not till a very late stage of the reporting process. It should replace the value of Olin et al. (2005) in practical applications. Note that Rai et al. (2014) did not provide values for $\Delta_f H°$.

Table 7.2: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg·mol^{-1}] for selenium species. All data included in TDB Version 12/07 are taken from Olin et al. (2005). Own data estimates based on charge correlations (Hummel 2009) are shaded. Supplemental data are in italics.

j k→	**Cl^-**	**ClO_4^-**	**NO_3^-**	**Li^+**	**Na^+**	**K^+**
↓	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$	$\varepsilon_{j,k}$
H2Se	0	0	0	0	0	0
HSeO4-	0	0	0	-	-0.01 ± 0.02	-
SeO4-2	0	0	0	-	-0.12 ± 0.06	-
NiSeO4	0	0	0	0	0	0
MnSeO4	0	0	0	0	0	0
UO2SeO4	0	0	0	0	0	0
UO2(SeO4)2-2	*0*	*0*	*0*	-	*-0.10 ± 0.1*	-
MgSeO4	*0*	*0*	*0*	*0*	*0*	*0*
CaSeO4	0	0	0	0	0	0
H2SeO3	0	0	0	0	0	0
HSeO3-	0	0	0	-	-0.05 ± 0.1	-
SeO3-2	0	0	0	-	-0.10 ± 0.1	-
FeSeO3+	0.05 ± 0.1	0.2 ± 0.1	-	0	0	0
SeCN-	0	0	0	-	0.05 ± 0.01	-
NiSeCN+	0.05 ± 0.1	0.2 ± 0.1	-	0	0	0
Ni(SeCN)2	0	0	0	0	0	0
Se2-2	0	0	0	-	-0.10 ± 0.1	-0.06[a]
Se3-2	0	0	0	-	-0.10 ± 0.1	--0.06[a]
Se4-2	0	0	0	-	-0.10 ± 0.1	-0.06[a]
HSe-	0	0	0	-	-0.05 ± 0.1	-
Se-2	0	0	0	-	-0.10 ± 0.1	-

[a] Data given by Olin et al. (2005) in text but not in Tables B.3 of selected ion interaction coefficients.

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