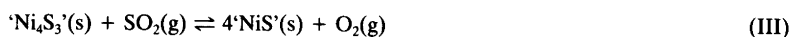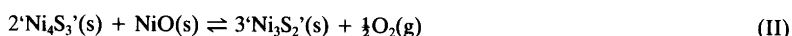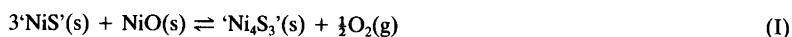# Equilibrium Studies of the System Ni–S–O using the Solid Electrolyte Galvanic Cell Technique

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Equilibria (I)–(III) were studied in the temperature interval 850–1050 K by measuring the equilibrium oxygen pressures using galvanic cells incorporating calcia-stabilized zirconia as solid electrolyte.

$$3\text{'NiS'(s)} + \text{NiO(s)} \rightleftharpoons \text{'Ni}_4\text{S}_3\text{'(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \qquad (I)$$

$$2\text{'Ni}_4\text{S}_3\text{'(s)} + \text{NiO(s)} \rightleftharpoons 3\text{'Ni}_3\text{S}_2\text{'(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \qquad (II)$$

$$\text{'Ni}_4\text{S}_3\text{'(s)} + \text{SO}_2\text{(g)} \rightleftharpoons 4\text{'NiS'(s)} + \text{O}_2\text{(g)} \qquad (III)$$

A controlled SO_2 pressure was maintained by a continuously flowing SO_2–Ar gas mixture of known composition. The Gibbs free energy values obtained for these equilibria were used together with literature data to calculate $\Delta_f G^\circ$ values for the Ni-sulfides 'Ni$_4$S$_3$' and 'Ni$_3$S$_2$', the phases of which have variable compositions.

The ternary system Ni–S–O is of great geological and metallurgical interest. Reliable thermodynamic data on existing phases in this system, as well as sulfur and oxygen pressures under various conditions, would be useful in the process development of Ni-extraction and to gain a better understanding of the formation of Ni-sulfide minerals.

In the Ni–S binary system, nine intermediate phases have been reported.[1,2] Some of these sulfides, viz. heazlewoodite (Ni_3S_2), godlevskite (Ni_7S_6), millerite(NiS), polydymite (Ni_3S_4) and vacsite (NiS_2), are typical minerals of sulfide copper–nickel deposits of a magmatic genesis. Their formation occurs at the final stage of crystallization of the depleted iron sulfide melt.

At higher temperatures there exist four stable Ni-sulfides which are designated β_1-Ni_3S_2, β_2-Ni_4S_3, δ-NiS and η-NiS_2.[1] The first three phases mentioned have variable compositions within the ranges $0.37 \lesssim X_S \lesssim 0.41$, $0.42 \lesssim X_S \lesssim 0.44$ and $0.50 \lesssim X_S \lesssim 0.52$, respectively, where X_S is the atomic fraction of sulfur. These nonstoichiometric phases will here be designated 'Ni$_3$S$_2$', 'Ni$_4$S$_3$' and 'NiS'. Although many thermochemical and equilibrium investigations have been carried out on the binary system Ni–S,[1,3–9] there are still discrepancies in the thermodynamic data.

The present study was undertaken to establish reliable phase relations in the system Ni–S–O by studying redox equilibria containing two of the solid Ni-sulfides 'Ni$_3$S$_2$', 'Ni$_4$S$_3$', 'NiS' and NiO(s) or SO_2(g). The generated equilibrium oxygen pressures were measured using the solid-state EMF method.

Experimental

Equilibria considered. The stability regions for the various Ni phases at 1000 K are visualized in Fig. 1, which is a stability diagram with $\log p(SO_2)$ and $\log p(O_2)$ as axes. The phase boundary lines are constructed by applying the law of mass action to various equilibria, each containing two solid phases and the gaseous species SO_2 and O_2. At the univariant points 1 and 2 in the diagram, the equilibrium reactions (I) and (II) can be written.
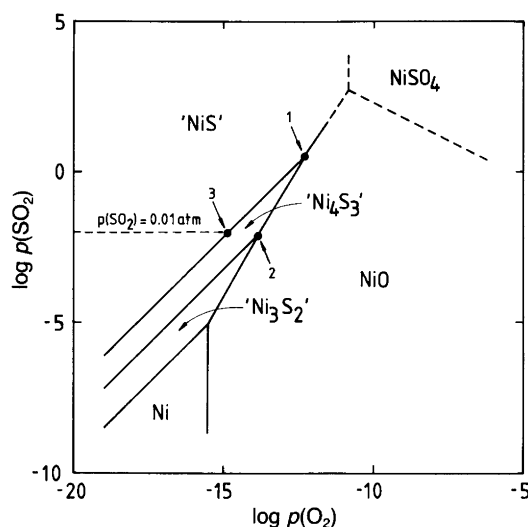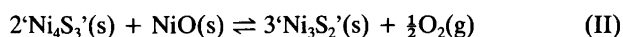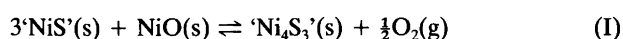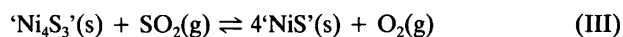

Fig. 1. Stability diagram for the Ni–S–O system at 1000 K.

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$$3\text{'NiS'(s)} + \text{NiO(s)} \rightleftharpoons \text{'Ni}_4\text{S}_3\text{'(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \qquad \text{(I)}$$

$$2\text{'Ni}_4\text{S}_3\text{'(s)} + \text{NiO(s)} \rightleftharpoons 3\text{'Ni}_3\text{S}_2\text{'(s)} + \tfrac{1}{2}\text{O}_2\text{(g)} \qquad \text{(II)}$$
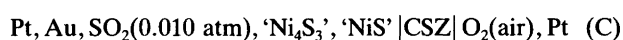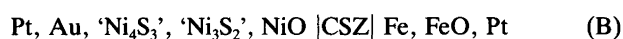
These three-solid phase equilibria will result in fixed oxygen pressures. For point 3, which lies on a boundary line, the equilibrium conditions are controlled by reaction (III).

$$\text{'Ni}_4\text{S}_3\text{'(s)} + \text{SO}_2\text{(g)} \rightleftharpoons 4\text{'NiS'(s)} + \text{O}_2\text{(g)} \qquad \text{(III)}$$

By equilibrating the solid phases 'Ni$_4$S$_3$' and 'NiS' with an SO$_2$–Ar mixture of constant (and known) composition, a stable O$_2$ pressure will be attained.

The oxygen pressures, $p(\text{O}_2)$, generated in accordance with equilibria (I)–(III) have been determined by solid-state EMF measurements.

Galvanic cells used. To study equilibria (I)–(III), the following galvanic cells, incorporating calcia-stabilized zirconia (CSZ) as the solid electrolyte, were arranged.

Pt, Au, 'NiS', 'Ni$_4$S$_3$', NiO |CSZ| Fe, FeO, Pt   (A)

Pt, Au, 'Ni$_4$S$_3$', 'Ni$_3$S$_2$', NiO |CSZ| Fe, FeO, Pt   (B)

Pt, Au, SO$_2$(0.010 atm), 'Ni$_4$S$_3$', 'NiS' |CSZ| O$_2$(air), Pt   (C)

As a Pt wire, normally used as the electrode material, would be corroded by sulfide phases, the terminal in contact with the sample mixture was made of Au. The construction of the galvanic cells and cell operation has been described in detail by Pejryd.[10]

Chemicals. The Ni sulfides used in the present study were prepared by reacting starting materials in evacuated silica glass tubes kept at 775 K for about 24 h. In addition to the initial chemicals, a solid silica glass rod was inserted into the ampoule to reduce the free volume. At first, stoichiometric Ni$_3$S$_2$ was synthesized from Ni powder (Merck p.a.) and sulfur (Spec pure, Johnson Matthey Chemicals). The initial mixture was loosely packed to avoid violent reactions. The stoichiometric Ni$_3$S$_2$ thus prepared was then used, together with appropriate amounts of sulfur, in producing the stoichiometric phases Ni$_4$S$_3$ and NiS. It should be mentioned that, despite fast quenching in an ice–water bath, Ni$_4$S$_3$ was converted into the phases Ni$_3$S$_2$ and γ-Ni$_7$S$_6$ in accordance with the equilibrium phase diagram.[2] The oxide phase NiO was synthesized by decomposing NiCO$_3$ (BDH Chemicals) at 850 K. All synthesized phases were identified by X-ray powder diffraction. The gas mixture was analysed and delivered by Alfax AB, Sweden, and consisted of 0.997 ± 0.030 vol% SO$_2$ in Ar.

Results and calculations

EMF values obtained. The EMF values obtained at various temperatures (E_{exp}/mV, T/K) from cells A, B and C are given in Tables 1, 2 and 3, respectively. The measured values were smoothed by a least-squares treatment to yield the $E(T)$ relationships of eqns. (1)–(3) (E in mV, T in K).

$$E(\text{A}) = 11110.7 - 11.075T + 1.3809T \ln T$$
$$844 < T/\text{K} < 965 \qquad (1)$$

$$E(\text{B}) = 499.0 - 5.1658T + 0.62321T \ln T$$
$$841 < T/\text{K} < 1053 \qquad (2)$$

$$E(\text{C}) = 203.77 + 2.5767T - 0.29978T \ln T$$
$$923 < T/\text{K} < 1059 \qquad (3)$$

Eqns. (1)–(3) correspond to the assumption of a constant (but non-zero) value of ΔC_p for the equilibrium reactions considered. The residuals, calculated as $\Delta E = E_{exp} - E$, are also given in Tables 1–3, the mean errors being $\sigma E(\text{A}) = \pm 0.98$ mV, $\sigma E(\text{B}) = \pm 0.92$ mV, $\sigma E(\text{C}) = \pm 0.34$ mV.

Calculation of oxygen pressures. The equilibrium oxygen pressures [$p(\text{O}_2)$/atm] for the equilibria studied are related to the EMF (E/mV) and temperature (T/K) values and the reference oxygen pressures $p^*(\text{O}_2)$, by eqn. (4), in which

$$\log p(\text{O}_2) = \log p^*(\text{O}_2) - \frac{4F}{R\ln 10}\frac{10^{-3}E}{T} \qquad (4)$$

$R = 8.31441$ J K^{-1} mol^{-1} is the gas constant and $F = 96484.56$ C mol^{-1} is the Faraday constant.

For cell (C) air was used as the reference system, in which case $p^*(\text{O}_2) = 0.2096$ atm (1 atm = 101.325 kPa). For cells (A) and (B), Fe, FeO was used to generate the reference oxygen pressures, which can be expressed by eqn. (5) according to Fredriksson and Rosén.[11]

Table 1. The experimental data, T/K and E_{exp}/mV, and residuals $\Delta E = E_{exp} - E$, obtained for cell (A).

T/K	E_{exp}/mV	ΔE/mV
844.9	−384.1	−0.4
855.1	−387.6	0.0
870.3	−392.7	0.3
881.0	−396.4	0.2
896.3	−401.5	0.0
901.5	−402.6	0.5
905.0	−403.4	0.7
905.5	−403.7	0.5
915.2	−406.8	0.2
915.0	−407.9	−0.9
922.4	−409.2	−0.2
930.5	−412.6	−1.5
935.5	−413.3	−1.0
943.5	−412.8	1.5
946.3	−414.2	0.7
950.4	−416.7	−0.8
961.2	−419.7	−1.5
964.4	−417.1	1.8

Table 2. The experimental data, T/K and E_{exp}/mV, and residuals $\Delta E = E_{exp} - E$, obtained for cell (B).

T/K	E_{exp}/mV	$\Delta E/mV$
841.3	−315.5	0.3
851.5	−319.5	−0.2
861.9	−323.8	−1.0
872.1	−327.3	−1.2
882.2	−330.3	−1.0
888.3	−329.7	1.6
897.9	−335.2	−1.0
898.6	−333.1	1.3
909.0	−336.4	1.1
909.2	−336.3	1.3
918.5	−340.9	−0.6
929.7	−342.5	1.1
929.9	−342.2	1.4
939.2	−346.9	−0.7
950.3	−349.8	−0.5
959.7	−352.3	−0.5
970.9	−355.4	−0.7
980.4	−357.3	−0.2
991.5	−360.5	−0.7
1000.7	−362.4	−0.4
1012.1	−365.2	−0.5
1021.5	−366.6	0.2
1032.7	−369.4	−0.1
1042.9	−371.1	0.3
1053.2	−372.8	0.8

$$\log p^*(O_2) = -0.8839 - 26506/T + 2.2012 \log T$$
$$862 < T/K < 1405, \, \delta \log p^*(O_2) = \pm 0.004 \tag{5}$$

By introducing the E-relationships, eqns. (1)–(3), and the relevant equation for $\log p^*(O_2)$ into eqn. (4), eqns. (6)–(8) can be derived.

$$\log p(O_2, I) = 222.38 - 48897/T = 61.898 \log T$$
$$844 < T/K < 965, \, \delta \log p(O_2) = \pm 0.02 \tag{6}$$

$$\log p(O_2, II) = 103.25 - 36565/T - 26.727 \log T$$
$$841 < T/K < 1053, \, \delta \log p(O_2) = \pm 0.02 \tag{7}$$

Table 3. The experimental data, T/K and E_{exp}/mV, and residuals $\Delta E = E_{exp} - E$, obtained for cell (C).

T/K	E_{exp}/mV	$\Delta E/mV$
923.0	692.5	−0.4
944.6	698.0	0.2
964.4	702.6	0.4
974.6	704.7	0.4
985.1	706.4	−0.1
995.2	708.5	−0.1
1006.0	710.7	−0.2
1016.1	712.8	−0.2
1027.1	714.9	−0.2
1037.6	716.8	−0.4
1047.9	719.5	0.3
1058.3	721.5	0.3

$$\log p(O_2, III) = -52.42 - 4107.8/T + 13.915 \log T$$
$$923 < T/K < 1059, \, \delta \log p(O_2) = \pm 0.007 \tag{8}$$

Calculation of $\Delta G°$ values. The Gibbs energies $(\Delta G°)$ for the various equilibria can be evaluated from the general expression given by eqn. (9) where the equilibrium constant K can be replaced by the appropriate form, eqns. (10), (11) or (12).

$$\Delta G° = -R \ln 10 \cdot T \log K \tag{9}$$

$$\log K(I) = 0.5 \log p(O_2, I) \tag{10}$$

$$\log K(II) = 0.5 \log p(O_2, II) \tag{11}$$

$$\log K(III) = \log p(O_2, III) - \log p(SO_2) \tag{12}$$

Accordingly, the ensuing relationships given in eqns. (13)–(15) were derived (in J mol^{-1}).

$$\Delta G°(I) = 468058 - 2128.7T + 592.51T \log T$$
$$844 < T/K < 965 \tag{13}$$

$$\Delta G°(II) = 350012 - 988.34T + 255.84T \log T$$
$$841 < T/K < 1053 \tag{14}$$

$$\Delta G°(III) = 78642 + 965.27T - 266.40T \log T$$
$$923 < T/K < 1059 \tag{15}$$

The estimated uncertainties are ± 200 J for all reactions.

Calculation of $\Delta_f G°$ values. As has been discussed above, the Ni sulfides 'Ni$_3$S$_2$' and 'Ni$_4$S$_3$' are nonstoichiometric phases. The free energy of formation $(\Delta_f G°)$ for these phases will therefore be dependent on their compositions. To calculate the $\Delta_f G°$ values of stoichiometric Ni$_3$S$_2$ and Ni$_4$S$_3$, it is necessary to consider the corrections given in eqns. (16)–(18) (Fig. 2).

$$\Delta_1 = \Delta_f G°(Ni_4S_3) - \Delta_f G°(Ni_4S_{3+x}) \tag{16}$$

$$\Delta_2 = \Delta_f G°(Ni_4S_{3-x}) - \Delta_f G°(Ni_4S_{3+x}) \tag{17}$$

$$\Delta_3 = \Delta_f G°(Ni_3S_2) - \Delta_f G°(Ni_3S_{2+x}) \tag{18}$$

These corrections can be evaluated using the ΔG composition relationships given by Lin et al.[1] We derived eqns. (19)–(21).

$$\Delta_1 = 10408 - 9.1667T \tag{19}$$

$$\Delta_2 = 209160 - 1530.6T + 440.94T \log T \tag{20}$$

$$\Delta_3 = 221550 - 1947.5T + 577.46T \log T \tag{21}$$

The uncertainties in the Δ values are estimated to be of the order ± 1000 J for Δ_1 and Δ_2 and ± 2000 J for Δ_3.
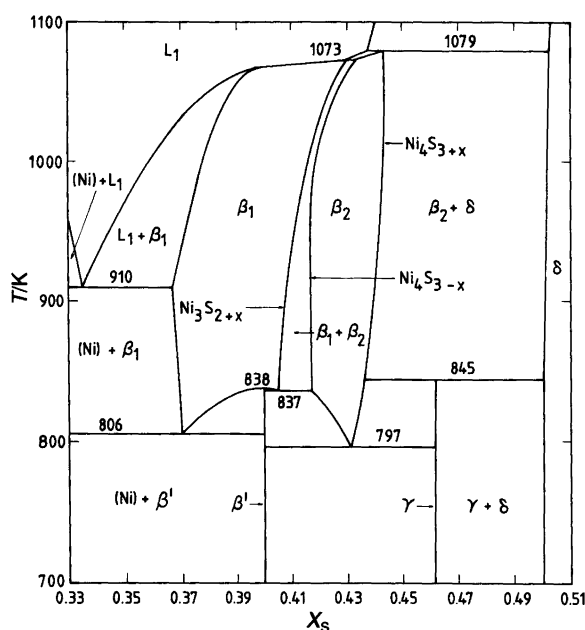
Fig. 2. Part of the T–X_S phase diagram for the Ni–S system according to Ref. 9. The variable X_S is the atomic fraction of sulfur.

In the calculations discussed above, literature values of $\Delta_f G°$ (in J mol^{-1}) for NiS,[9] NiO,[12] and SO$_2$[13] have been used [eqns. (25)–(27)].

$$\Delta_f G°(\text{'NiS'}) = -147800 + 73.3T \tag{25}$$

$$\Delta_f G°(\text{NiO}) = -232358 + 77.105T + 2.1688T \log T \tag{26}$$

$$\Delta_f G°(\text{SO}_2) = -363097 + 80.980T - 2.2884T \log T \tag{27}$$

Estimated uncertainties are $\pm$ 2500, $\pm$ 200 and $\pm$ 100 J mol^{-1}, respectively.

Values of $\Delta_f G°(\text{Ni}_4\text{S}_{3+x})$ and $\Delta_f G°(\text{Ni}_4\text{S}_3)$ have been calculated from eqn. (24) and eqns. (24), (16) and (19), respectively. These values, as well as calculated data from earlier studies,[1,8] are presented in Table 4. The estimated uncertainty in $\Delta_f G°(\text{Ni}_4\text{S}_{3+x})$ is $\pm$ 8000 J mol^{-1}, which is largely attributable to the aforementioned uncertainty in the 'NiS' data. Consequently, consideration of eqn. (16) indicates that the error term for the calculated $\Delta_f G°(\text{Ni}_4\text{S}_3)$ value will be somewhat larger, $\pm$ 9000 J mol^{-1}.

Corresponding calculations have been carried out concerning the 'Ni$_3$S$_2$' phase. Using the equilibrium reaction (II) and the phase diagram (Fig. 2) again, we obtain eqn. (25).

Considering the phase diagram (Fig. 2) and equilibrium (I), we obtain eqn. (22).

$$\Delta_f G°(\text{Ni}_4\text{S}_{3+x}) = \Delta G°(\text{I}) + 3\Delta_f G°(\text{'NiS'}) + \Delta_f G°(\text{NiO}) \tag{22}$$

Analogously, from equilibrium (III) we obtain eqn. (23).

$$\Delta_f G°(\text{Ni}_4\text{S}_{3+x}) = -\Delta G°(\text{III}) + 4\Delta_f G°(\text{'NiS'}) - \Delta_f G°(\text{SO}_2) \tag{23}$$

By taking into account the $\Delta_f G°(\text{Ni}_4\text{S}_{3+x})$ values from eqn. (22), valid in the temperature range 845–965 K, and extrapolating to 1050 K using the temperature dependence obtained from eqn. (23), eqn. (24) was derived (in J mol^{-1}).

$$\Delta_f G°(\text{Ni}_4\text{S}_{3+x}) = -439889 + 183.48T$$
$$850 < T/\text{K} < 1050 \tag{24}$$

$$\Delta_f G°(\text{Ni}_3\text{S}_{2+x}) = \tfrac{1}{3}\Delta G°(\text{II}) + \tfrac{2}{3}\Delta_f G°(\text{Ni}_4\text{S}_{3+x}) + \tfrac{1}{3}\Delta_f G°(\text{NiO}) \tag{28}$$

Utilizing eqns. (14), (17), (20), (24) and (28), it is then possible to calculate $\Delta_f G°$ values for stoichiometric Ni$_3$S$_2$. Values thus calculated for $\Delta_f G°(\text{Ni}_3\text{S}_{2+x})$ and $\Delta_f G°(\text{Ni}_3\text{S}_2)$ are given in Table 5 as well as corresponding values from the literature.[1] The uncertainties in $\Delta_f G°(\text{Ni}_3\text{S}_{2+x})$ and $\Delta_f G°(\text{Ni}_3\text{S}_2)$ are estimated to be $\pm$ 6000 and $\pm$ 8000 J mol^{-1}, respectively.

Discussion

The present investigation has successfully demonstrated the applicability of the solid electrolyte EMF method for studying equilibria involving Ni sulfides. Thus the equilibrium reactions (I)–(III) could be determined very accu-

Table 4. Gibbs free energy of formation values for Ni$_4$S$_{3+x}$ and for stoichiometric Ni$_4$S$_3$, from the present study and from data given in the literature.

T/K	$\Delta_f G°(\text{Ni}_4\text{S}_{3+x})$/J mol^{-1}			$\Delta_f G°(\text{Ni}_4\text{S}_3)$/J mol^{-1}	
	Present study	Ref. 1	Ref. 8	Present study	Ref. 1
850	−283930	−285310	−284290	−281310	−282600
900	−274750	−275760	−275970	−272600	−273590
950	−265580	−266200	−267650	−263880	−264580
1000	−256410	−256640	−259330	−255160	−255570
1050	−247230	−247090	−250970	−246450	−246560

Table 5. Gibbs free energy of formation values for Ni_3S_{2+x} and for stoichiometric Ni_3S_2, from the present study and from data given in the literature.

T/K	$\Delta_fG°(Ni_3S_{2+x})$/J mol^{-1}	$\Delta_fG°(Ni_3S_2)$/J mol^{-1}	
	Present study	Present study	Ref. 1
850	−190040	−186040	−192090
950	−185990	−181890	−186950
950	−181480	−176580	−181810
1000	−176540	−170170	−176670
1050	−171180	−162730	−171530

rately with uncertainties of only about ± 200 J. This means that stability diagrams, such as that shown in Fig. 1, can be constructed in the temperature range 850–1050 K with high precision. Even if the uncertainties in the 'Ni$_4$S$_3$' and 'Ni$_3$S$_2$' data caused by their composition variations are considered, the phase boundary lines at a certain temperature permit reading off the pressure values for SO$_2$ and O$_2$ to better than ± 0.1 log units.

The calculated $\Delta_fG°$ values for Ni_4S_{3+x} and stoichiometric Ni_4S_3 have turned out to be of rather poor precision (± 8000 J mol^{-1}), largely because of the uncertainty of the 'NiS' data, which is stated to be ± 2500 J mol^{-1}.[9] Otherwise, the astonishingly good agreement between the present $\Delta_fG°$ values and corresponding literature values (Table 4) can be taken as confirmation of the applicability of the solid electrolyte EMF method for equilibrium studies in the

Ni–S–O system. It is, however, apparent that there is an urgent requirement for more precise $\Delta_fG°(NiS)$ values to reduce the uncertainties in derived thermodynamic data.

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