**Report of Investigations 8588**

# Electrochemical Determination of Gibbs Energies of Formation of Cobalt and Nickel Sulfides

By Seth C. Schaefer

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Bureau of Mines
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# ELECTROCHEMICAL DETERMINATION OF GIBBS ENERGIES OF FORMATION OF COBALT AND NICKEL SULFIDES

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## ERRATA

Page 7: Footnote 2 to table 2 should read as follows:

[2] Calculated from linear equation $E = 751.336 - 0.2084T \pm 1.04$.

Page 8: Equation 15 should read as follows:

$$\log pO_2 = -\frac{15,147}{T} + 2.25857.$$

Page 17: Thermodynamics is misspelled in the title of reference 2.

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## ILLUSTRATIONS

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# ELECTROCHEMICAL DETERMINATION OF GIBBS ENERGIES OF FORMATION OF COBALT AND NICKEL SULFIDES

by

Seth C. Schaefer [1]

## ABSTRACT

The Bureau of Mines has determined the standard Gibbs energies (ΔGf°) of $CoS_{1.035}$ (cobalt sulfide) and $Ni_{2.515}S_2$ (nickel sulfide) with high-temperature galvanic cells using stabilized $ZrO_2$ (zirconia) as the electrolyte. Potential measurements were obtained for the cell

$$Pt,\ CoS_{1.035},\ CoO,\ SO_2(g,\ 1\ atm)//ZrO_2//O_2(g,\ 0.0114\ atm),\ Pt,$$

with the overall cell reaction

$$CoS_{1.035}(c) + 1.535\ O_2(g,\ 0.0114\ atm) = CoO(c) + 1.035\ SO_2(g).$$

These results, combined with the best available data for ΔGf° of CoO and $SO_2$ from the literature, give the standard Gibbs energy of formation of $CoS_{1.035}$ for the reaction

$$Co(c) + 0\ 5175\ S_2(g) = CoS_{1.035}(c)$$

$$\Delta Gf° = -38.890 + 18.87 \times 10^{-3}T \pm 0.185\ kcal/mole$$

$$(866.0 - 1{,}104.9\ K),$$

where temperature (T) is expressed in kelvins.

Similar measurements were obtained for the cell

$$Pt,\ Ni_{2.515}S_2,\ NiO,\ SO_2(g,\ 1\ atm)//ZrO_2//O_2(g,\ 0.0122\ atm),\ Pt,$$

with the overall cell reaction

$$Ni_{2.515}S_2(c) + 3.2575\ O_2(g,\ 0.0122\ atm) = 2.515\ NiO(c) + 2\ SO_2(g).$$

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[1] Metallurgist, Albany Research Center, Bureau of Mines, Albany, Oreg.

Combination of these results with data for ΔGf° of NiO and $SO_2$ from the literature yields the standard Gibbs energy of formation of $Ni_{2.515}S_2$ for the reaction

$$2.515\ Ni(c) + S_2(g) = Ni_{2.515}S_2(c)$$

$$\Delta Gf^\circ = -65.377 + 24.67 \times 10^{-3}T \pm 0.541\ \text{kcal/mole}$$

$$(968.6 - 1{,}053.7\ \text{K}).$$

## INTRODUCTION

Thermodynamic properties of $CoS_{1.035}$ (cobalt sulfide) and $Ni_{2.515}S_2$ (nickel sulfide) were investigated by the Bureau of Mines as part of its program to expand the base of scientific information required to develop innovative technologies for mineral processing. These data were developed for application in research efforts to maximize recovery of important metals, with minimal energy requirements. Complex sulfide minerals are the primary source of cobalt and nickel. Consequently, a thorough understanding of thermodynamic properties of the cobalt-sulfur and nickel-sulfur systems is desirable.

Application of stabilized $ZrO_2$ (zirconia) as a selective solid anion electrolyte has been demonstrated in determining Gibbs energies for cell reactions involving metal-metal oxide systems at elevated temperatures (5).[2] Within the limitation of the ionic domain of stabilized $ZrO_2$ (18), any equilibrium involving oxygen may be investigated by this technique. The method is based on measurement of the difference in chemical potential between an electrode of unknown oxygen potential and a reference electrode of known oxygen potential. In this investigation, the difference was measured between the oxygen potential of a reference electrode containing approximately 1 mole-pct $O_2$ in nitrogen and the oxygen potential of an electrode consisting of a mixture of a sulfide and its coexisting oxide. The sulfide-oxide electrode was equilibrated in pure $SO_2$ at approximately 1 atm. The transport number of oxygen ion is essentially unity in the range of oxygen potential of this investigation (18). The relationship between the open-circuit potential of the cell and the Gibbs energy change for the actual cell reaction is

$$\Delta G(\text{reaction}) = -nFE, \tag{1}$$

where ΔG is the change in Gibbs energy for the cell reaction, n is the number of electrochemical equivalents involved in the cell reaction, F is the Faraday constant (23.061 cal/mv equivalent), and E is the emf (electromotive force) in millivolts.

Thermodynamic data for the nonstoichiometric cobalt monosulfide ($CoS_{1+x}$) are sparse and consist primarily of gas-equilibration studies (1, 12-13, 16). Phase diagram studies show that cobalt monosulfide is thermodynamically stable only at temperatures above 733 K and has a wide range of homogeneity (3). The

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

stoichiometric compound (CoS) is 50 at. pct S. The $CoS_{1+x}$ phases (the subscript 1+x designates the deviation from stoichiometric composition) range from approximately 51 at. pct S to 53 at. pct S (13).

Thermodynamic data for nickel sulfide ($Ni_{3\pm x}S_2$) are quite extensive, but considerable disagreement exists among investigators. Phase diagram studies done about 20 years ago (3, 6) and equilibration studies done in 1974 (13) reported that $Ni_{3\pm x}S_2$ is a single homogeneous phase that extends over a composition range of 36.6 to 44.3 at. pct S and includes the low-temperature stoichiometric compound heazlewoodite ($Ni_3S_2$). Heazlewoodite has a hexagonal crystal structure and is stable up to 838 K; above 838 K, it transforms to a nonstoichiometric, nonquenchable cubic structure. Its lattice constant diminishes with increasing sulfur content (7).

Recently, two gas-phase equilibrium studies (8, 17) have indicated that the previously reported $Ni_{3\pm x}S_2$ phase is actually two nonstoichiometric phases, which can be designated as $\beta_1$-$Ni_3S_2$ and $\beta_2$-$Ni_4S_3$, plus a low-temperature, stoichiometric heazlewoodite phase designated as $\beta'$-$Ni_3S_2$ (8). Data from a recent compilation (9) for the stoichiometric $\beta'$-$Ni_3S_2$ phase are included in the "Results and Discussion" section for $Ni_{2.515}S_2$.

In view of the lack of data for the Co-S system and the disagreement over the existing data for the Ni-S system, further investigation of the thermodynamic properties and behavior of both these important systems is needed.

## EXPERIMENTAL WORK

### Materials

High-purity reagents were obtained from commercial sources and used without further purification. Analyses of these reagents were confirmed, and the results are presented in table 1. Anhydrous-grade $SO_2$ and a certified standard mixture of 1 mole-pct $O_2$ in nitrogen were used. The 1-mole-pct-$O_2$ mixture was dried by passing through $Mg(ClO_4)_2$ (magnesium perchlorate), and the $SO_2$ was dried by passing through a column packed with $CaSO_4$ (calcium sulfate).

TABLE 1. - Impurities detected in reagents

| Reagent | Impurity element[1] | Wt-pct | Reagent | Impurity element[1] | Wt-pct |
|---|---|---|---|---|---|
| CoO.... | Aluminum... | 0.29 | CoS.... | Aluminum... | 0.34 |
| | Copper..... | .26 | | Calcium.... | .72 |
| | Iron....... | .33 | | Iron....... | .12 |
| | Lead....... | <.02 | | Lead....... | .07 |
| | Magnesium.. | .08 | | Magnesium.. | .05 |
| | Manganese.. | .04 | | Manganese.. | .03 |
| | Nickel..... | .39 | | Nickel..... | .02 |
| | Silicon.... | .18 | | Silicon.... | .36 |
| | Sodium..... | .62 | | | |
| | | | $Ni_3S_2$.. | Aluminum... | <.003 |
| NiO.... | None....... | NAp | | Cobalt..... | <.10 |
| | | | | Manganese.. | .03 |

NAp Not applicable.

[1] Impurities not detected by spectrochemical analyses except as noted in table were Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Pt, Sb, Si, Sn, Ta, Ti, V, Zn, Zr, and Y.

NOTE.--X-ray emission and chemical analyses were performed by members of the analytical and spectrochemistry groups at Albany Research Center, Bureau of Mines, Albany, Oreg.

## Apparatus and Procedure

Internal arrangement of the cell component is shown in figure 1.[3] The apparatus, potentiometer, standardized thermocouple, and procedure have been described in previous publications (14-15). Measurements were completed in 1 day, following a 12-hour stabilization period. Cell response to temperature change was rapid above 1,000 K, and potentials stabilized within 1 hour after a steady-state temperature was obtained. Experiments were repeated two or three times with each cell before electrodes were removed and analyzed for identification.

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[3] Reference in this figure to specific trade names does not imply endorsement by the Bureau of Mines.

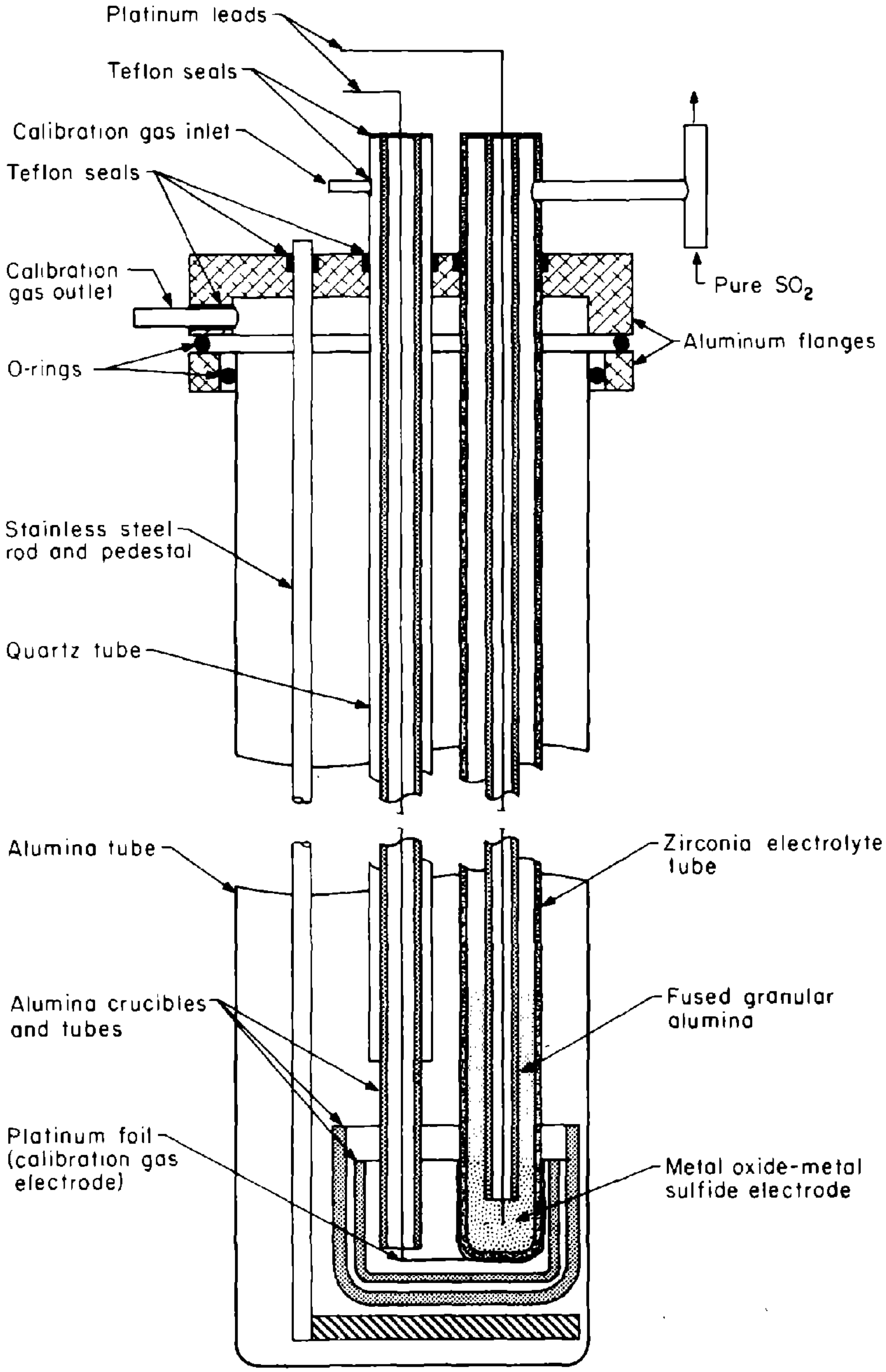

FIGURE 1. - High-temperature galvanic cell.

# RESULTS AND DISCUSSION

## $CoS_{1.035}$

The standard Gibbs energy of formation of $CoS_{1.035}$ was determined by measuring the Gibbs energy change for the reversible cell

$$\text{Pt, CoS}_{1.035}\text{, CoO, SO}_2\text{(g, 1 atm)//ZrO}_2\text{//O}_2\text{(g, 0.0114 atm), Pt.}$$

The overall cell reaction is

$$\text{CoS}_{1.035}\text{(c)} + 1.535\ \text{O}_2\ \text{(g, 0.0114 atm)} = \text{CoO(c)} + 1.035\ \text{SO}_2\text{(g)}. \qquad (2)$$

Potential measurements from three cells that were used for the $CoS_{1.035}$ determination are given in table 2. These results may be expressed as a function of temperature by the least-squares equation and standard error of estimate as follows:

$$E = 751.336 - 0.2084T \pm 1.04$$

$$(866.0 - 1{,}104.9\ \text{K}), \qquad (3)$$

where E is expressed in millivolts. The standard error of estimate is

$$S_{y.x} = \frac{1}{n}\left[n\Sigma y^2 - (\Sigma y)^2 - \frac{(n\Sigma xy - \Sigma x\Sigma y)^2}{n\Sigma x^2 - (\Sigma x)^2}\right]^{0.5}. \qquad (4)$$

Smooth emf data derived from equation 3 are given in column 4 of table 2. Representative emf-versus-temperature data are illustrated in figure 2.

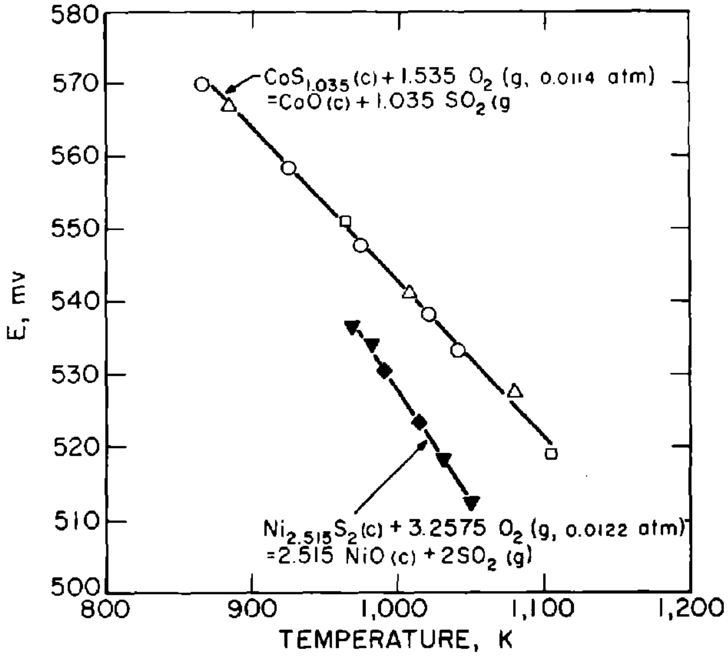

FIGURE 2. - Electromotive force (E) versus temperature for $CoS_{1.035}$ and $Ni_{2.515}S_2$ reactions. Open symbols represent measurements from three different $CoS_{1.035}$ cells. Closed symbols represent measurements from two $Ni_{2.515}S_2$ cells.

TABLE 2. - Electromotive force (E) of cell Pt, $CoS_{1.035}$, CoO, $SO_2$(g, 1 atm)//$ZrO_2$//$O_2$(g, 0.0114 atm), Pt

| Measurement | Temperature, K | E, mv | |
|---|---|---|---|
| | | Measured[1] | Calculated[2] |
| 1 | 866.0 | 569.96±0.005 | 570.86 |
| 2 | 875.7 | 567.46± .005 | 568.84 |
| 3 | 876.6 | 566.34± .005 | 568.65 |
| 4 | 884.7 | 567.46± .005 | 566.97 |
| 5 | 894.2 | 565.14± .005 | 564.99 |
| 6 | 916.2 | 561.92± .005 | 560.40 |
| 7 | 924.9 | 558.19± .005 | 558.59 |
| 8 | 927.0 | 557.95± .005 | 558.15 |
| 9 | 934.6 | 557.76± .005 | 556.57 |
| 10 | 943.2 | 555.73± .010 | 554.77 |
| 11 | 965.9 | 551.64± .010 | 550.04 |
| 12 | 973.5 | 547.82± .005 | 548.46 |
| 13 | 974.7 | 547.91± .005 | 548.21 |
| 14 | 982.2 | 547.17± .010 | 546.65 |
| 15 | 991.2 | 545.11± .010 | 544.77 |
| 16 | 1,008.1 | 541.35± .005 | 541.25 |
| 17 | 1,012.4 | 541.92± .005 | 540.35 |
| 18 | 1,019.6 | 537.78± .005 | 538.85 |
| 19 | 1,021.0 | 538.34± .005 | 538.56 |
| 20 | 1,033.4 | 536.96± .005 | 535.98 |
| 21 | 1,034.8 | 537.27± .005 | 535.68 |
| 22 | 1,036.6 | 535.68± .005 | 535.31 |
| 23 | 1,042.5 | 533.34± .005 | 534.08 |
| 24 | 1,043.3 | 533.67± .005 | 533.91 |
| 25 | 1,060.1 | 530.23± .005 | 530.41 |
| 26 | 1,078.2 | 527.50± .020 | 526.64 |
| 27 | 1,080.4 | 526.86± .005 | 526.18 |
| 28 | 1,086.9 | 523.14± .005 | 524.83 |
| 29 | 1,088.7 | 523.70± .005 | 524.45 |
| 30 | 1,104.9 | 519.18± .005 | 521.08 |

[1] Average of 2 measurements taken at 15-minute intervals and corrected for cell calibration.

[2] Calculated from linear equation E = 751.336 - 0.2084 ± 1.04.

The Gibbs energy change for reaction 2 is

$$\Delta G(\text{reaction 2}) = -nFE = \Delta Gf^\circ(CoO) + 1.035\ \Delta Gf^\circ(SO_2) - \Delta Gf^\circ(CoS_{1.035}) + 1.035\ RT\ \ln pSO_2 - 1.535\ RT\ \ln pO_2', \qquad (5)$$

where p is expressed in atmospheres.

The standard Gibbs energies of formation of $SO_2$ (10) and CoO (11) for the temperature range 800 to 1,100 K may be expressed by the equations

$$\Delta Gf°(CoO) = -55.673 + 16.63 \times 10^{-3}T \pm 0.100 \text{ kcal/mole} \quad (6)$$

and

$$\Delta Gf°(SO)_2 = -86.569 + 17.49 \times 10^{-3}T \pm 0.050 \text{ kcal/mole}. \quad (7)$$

The Gibbs energy change for reaction 2 is

$$\Delta G(\text{reaction 2}) = -nFE = -106.385 + 29.508 \times 10^{-3}T \pm 0.147 \text{ kcal}, \quad (8)$$

where $n = 6.14$ and E is from equation 3. The quantity 1.535 RT ln $pO_2'$ is the chemical potential at the reference electrode, which consists of a calibration gas containing 1.14 mole-pct $O_2$ in nitrogen.

Calculation of the quantity RT ln in $pSO_2$ in equation 5 requires resolution of the partial pressure of $SO_2$ at the reaction site, which involves evaluation of the following reaction equilibria:

$$SO_3(g) = SO_2(g) + 0.5\ O_2(g), \quad (9)$$

$$K_{p,9} = \frac{pSO_2(pO_2)^{0.5}}{pSO_3}, \quad (10)$$

$$SO_2 = 0.5\ S_2(g) + O_2(g), \quad (11)$$

$$K_{p,11} = \frac{(pS_2)^{0.5}pO_2}{pSO_2}, \quad (12)$$

and

$$P_{total} = pSO_3 + pSO_2 + pO_2 + pS_2, \quad (13)$$

where $P_{total}$ is the total pressure in atmospheres, and $pSO_3$, $pSO_2$, $pO_2$, and $pS_2$ are the partial pressures of the gaseous components. The oxygen partial pressure at the reaction site was determined from the potential measurements of the cell for reaction 2 and the relationship

$$\Delta G(\text{reaction 2}) = -nFE = RT \ln pO_2 - RT \ln pO_2', \quad (14)$$

where $pO_2'$ is the oxygen pressure at the reference electrode (containing the calibration gas) and $n = 4$. Rearranging equation 14 and inserting values of $pO_2'$ and E (from equation 3) yields

$$\log pO_2 = \frac{15,147}{T} + 2.25857. \quad (15)$$

Figure 3 illustrates the thermodynamic stability of the Co-S-O system, where CoO and $CoS_{1.035}$ coexist in the temperature range 866 to 1,104.9 K at a $SO_2$ pressure of approximately 1 atm. The $SO_2$ pressure at the interface of the CoS-CoO electrode with the electrolyte was calculated by combining equations 10, 12, and 13 and $pO_2$ from equation 15 to obtain

$$P_{total} = pSO_2 + \frac{pSO_2(pO_2)^{0.5}}{K_{p,9}} + \frac{(K_{p,11})^2(pSO_2)^2}{(pO_2)^2} + pO_2, \qquad (16)$$

where $K_{p,9}$ and $K_{p,11}$ are the equilibrium constants for reactions 9 and 11, respectively. The equilibrium constant, $K_{p,9}$, is derived from data in the literature (2, 4). This constant may be expressed as

$$\log K_{p,9} = 8.8557 - \frac{5,465}{T} - 1.21574 \log T. \qquad (17)$$

Similarly, $pS_2$ was calculated by rearranging equation 12 to obtain

$$pS_2 = \frac{(K_{p,11})^2(pSO_2)^2}{(pO_2)^2}, \qquad (18)$$

where $K_{p,11}$, the equilibrium constant for reaction 11, was obtained from the following relationship and data (10):

$$\Delta G°(\text{reaction 11}) = -RT \ln K_{p,11} = 86.545 - 17.47T. \qquad (19)$$

The average total pressure of the system for the $CoS_{1.035}$ measurements was 1.00074 atm. Calculations show that $pSO_2$ varies from 1.00056 atm at 866.0 K to 1.00054 atm at 1,104.9 K. Consequently, in the temperature range of this investigation, the Gibbs energy change for reaction 2 is not appreciably affected by the slight variation of $pSO_2$ from standard conditions.

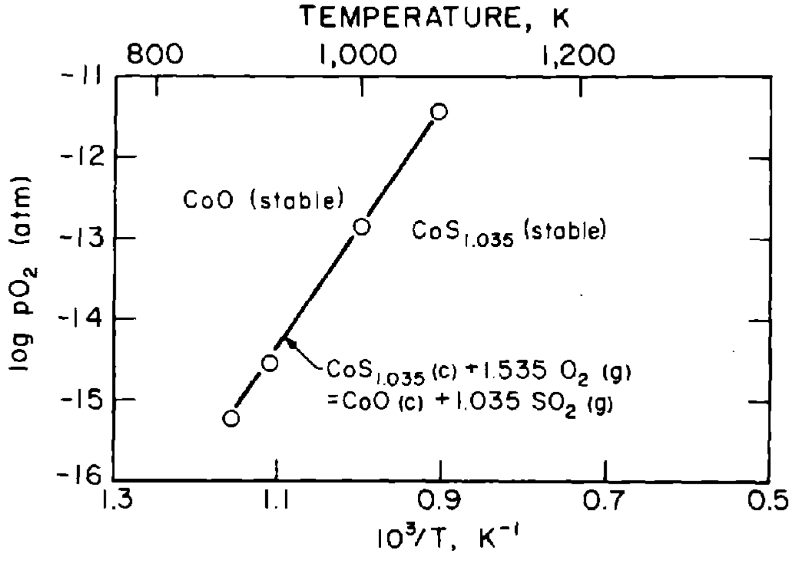

FIGURE 3. -. Equilibrium diagram for Co-S-O system.

X-ray diffraction analyses of the electrode products are given in table 3. The results showed no major change in lattice parameters between the reagents and the components in the equilibrated electrode mixtures. The lattice parameter of a solid solution generally changes with composition up to the saturation limit and then remains constant beyond that point. Consequently, the assumption of unit activity for the condensed phases of reaction 2 did not introduce any appreciable error in the standard Gibbs energy of formation of $CoS_{1.035}$.

TABLE 3. - X-ray diffraction analyses of samples for $CoS_{1.035}$ cell

| Sample | Crystal structure | Parametric measurements, A[1] | | Card[2] |
|---|---|---|---|---|
| | | $a_o$ | $c_o$ | |
| Reagents: | | | | |
| $Co_{1.035}$......... | Hexagonal | 3.384 | 5.196 | 25-1081 |
| CoO............. | Cubic.... | 4.260 | NAp | 9-402 |
| Electrode mixture: | | | | |
| $CoS_{1.035}$........ | Hexagonal | 3.37 ±0.01 | 5.18 ±0.001 | 25-1081 |
| CoO............. | Cubic.... | 4.261 | NAp | 9-402 |

NAp Not applicable.

[1] Parametric measurements for reagents were obtained from the literature.

[2] Numbers refer to data file cards of Joint Committee of Powder Diffraction Standards, International Centre for Diffraction Data.

NOTE.--X-ray diffraction analyses were performed by members of the analytical laboratory at the Albany Research Center, Bureau of Mines, Albany, Oreg.

The standard Gibbs energy of formation of $CoS_{1.035}$ for the reaction

$$Co(c) + 0.5175\ S_2(g) = CoS_{1.035}(c) \qquad (20)$$

was derived by rearranging equation 5 and substituting the proper values for the Gibbs energy change for reaction 2, as required by equation 8; the quantity 1.035 RT ln $pSO_2$ obtained from this investigation; the standard Gibbs energies of formation of CoO (11) and $SO_2$ (10), as given by equations 6 and 7; and the chemical potential at the reference electrode, 1.535 RT ln $pO_2'$. Combining these data yields a standard Gibbs energy of formation of $CoS_{1.035}$ for reaction 20, which may be expressed as

$$\Delta Gf°(CoS_{1.035}) = -38.890 + 18.87 \times 10^{-3}T \pm 0.185 \text{ kcal/mole}$$

$$(866.0 - 1,104.9 \text{ K}). \qquad (21)$$

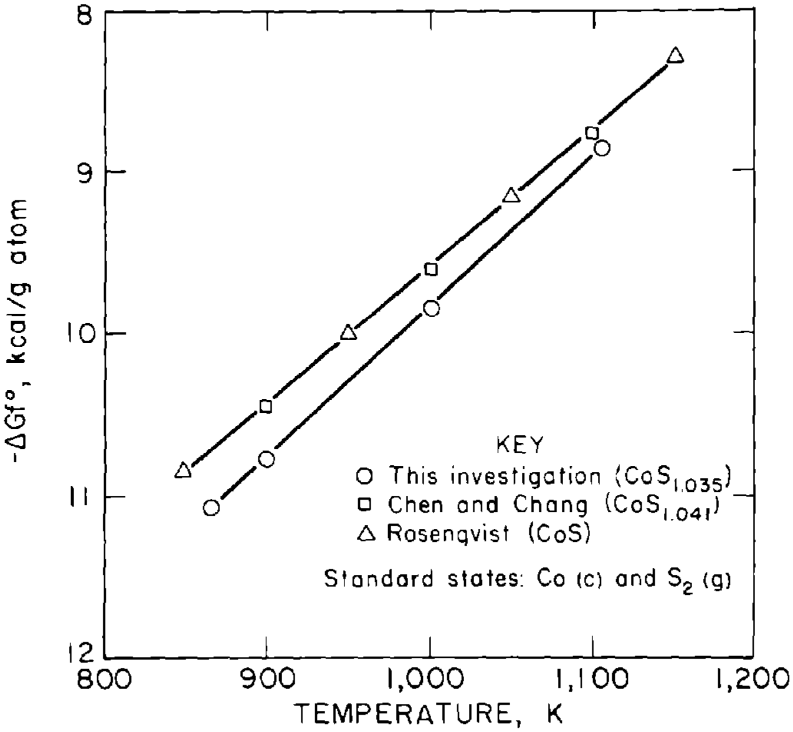

FIGURE 4. - Standard Gibbs energy of formation of $CoS_{1.035}$.

Figure 4 illustrates the general agreement of the Gibbs energy of formation of $CoS_{1.035}$ from this investigation with the results from two equilibrium studies (1, 13) for $CoS_{1+x}$. As noted in figure 4, the present results are approximately 0.21 kcal/g-atom more negative, and the slope or standard entropy change (-ΔS)° for the formation $CoS_{1.035}$ is slightly greater than that reported for the formation of $CoS_{1.041}$ (1) and the hypothetical compound CoS (13).

Because no experimental entropy and enthalpy data are available for $CoS_{1.035}$, a standard enthalpy of formation at 298 K cannot be derived by the third-law method. If ΔH° is assumed to be constant in the temperature range 866.0 to 1,104.9 K, the enthalpy of formation (ΔHf°) for $CoS_{1.035}$, according to the first constant in equation 21, is

$$\Delta Hf^\circ = -38.890 \pm 0.2 \text{ kcal/mole}$$

$$(866.0 - 1{,}104.9 \text{ K}). \qquad (22)$$

The standard states are pure crystalline cobalt, $CoS_{1.035}$, and gaseous sulfur at 1 atm.

## $Ni_{2.515}S_2$

A standard Gibbs energy of formation of $Ni_{2.515}S_2$ was determined by measuring the open-circuit potential for the cell

$$\text{Pt, } Ni_{2.515}S_2\text{, NiO, } SO_2(\text{g, 1 atm})//ZrO_2//O_2(\text{g, 0.0122 atm})\text{, Pt.}$$

The overall reaction for this cell is

$$Ni_{2.515}S_2(c) + 3.2575\ O_2(g,\ 0.0122\ atm) = 2.515\ NiO(c) + 2\ SO_2(g). \qquad (23)$$

Potential measurements obtained from two cells that were designed to determine the Gibbs energy of formation of $Ni_{2.515}S_2$ are given in table 4 and may be expressed by the linear equation and standard error of estimate as follows:

$$E = 829.517 - 0.3014T \pm 0.57$$

$$(968.6 - 1{,}053.7\ K), \tag{24}$$

where E is in millivolts. Potential measurements and their corresponding smooth values, derived from equation 24, are given in columns 3 and 4 of table 4. Representative emf-versus-temperature data are illustrated in figure 2. The Gibbs energy change for reaction 23 is therefore

$$\Delta G(\text{reaction } 23) = -nFE = -249.258 + 90.56 \times 10^{-3}T \pm 0.171\ \text{kcal/mole}, \tag{25}$$

where n = 13.03 and E is expressed by equation 24.

TABLE 4. - Electromotive force (E) of cell Pt, $Ni_{2.515}S_2$, NiO, $SO_2$(g, 1 atm)//$ZrO_2$//$O_2$(g, 0.0122 atm), Pt

| Measurement | Temperature, K | E, mv | |
|---|---|---|---|
| | | Measured[1] | Calculated[2] |
| 1.................. | 968.6 | 537.47±0.005 | 537.60 |
| 2.................. | 968.9 | 536.74± .005 | 537.51 |
| 3.................. | 982.6 | 534.53± .005 | 533.38 |
| 4.................. | 988.1 | 532.08± .005 | 531.72 |
| 5.................. | 991.5 | 530.38± .005 | 530.70 |
| 6.................. | 992.4 | 530.80± .005 | 530.43 |
| 7.................. | 1,009.0 | 525.46± .005 | 525.43 |
| 8.................. | 1,012.3 | 524.66± .005 | 524.43 |
| 9.................. | 1,015.7 | 523.39± .005 | 523.41 |
| 10................. | 1,015.8 | 522.45± .005 | 523.38 |
| 11................. | 1,031.3 | 518.57± .005 | 518.71 |
| 12................. | 1,038.5 | 516.35± .005 | 516.54 |
| 13................. | 1,052.0 | 512.13± .005 | 512.47 |
| 14................. | 1,053.7 | 512.64± .005 | 511.95 |

[1] Average of 2 measurements taken at 15-minute intervals and corrected for cell calibration.

[2] Calculated from linear equation E = 829.517 - 0.3014T ± 0.57.

A Gibbs energy of formation of $Ni_{2.515}S_2$ can be deduced from the relationship

$$\Delta G(\text{reaction } 23) = 2.515\ \Delta Gf°(NiO) + 2\ \Delta Gf°(SO_2) - \Delta Gf°(Ni_{2.515}S_2)$$

$$+ 2\ RT \ln pSO_2 - 3.2575\ RT \ln pO_2', \tag{26}$$

where ΔG for reaction 23 is expressed by equation 25, and $3.2575\ RT \ln pO_2'$ is the chemical potential at the reference electrode (which consists of a calibration gas containing 1.22 mole-pct $O_2$ in nitrogen). Auxiliary data obtained from the literature were the standard Gibbs energies of formation of $SO_2$ (10) and NiO (9). In the temperature range 800 to 1,100 K, the standard Gibbs energy of formation of $SO_2$ may be expressed by equation 7:

$$\Delta Gf°(SO_2) = -86.569 + 17.49 \times 10^{-3}T \pm 0.050 \text{ kcal/mole},$$

and that of NiO by the following linear equation:

$$\Delta Gf°(NiO) = -56.266 + 20.57 \times 10^{-3}T \pm 0.200 \text{ kcal/mole}. \qquad (27)$$

To calculate the Gibbs energy change for reaction 23, as given by equation 26, requires resolution of the partial pressure of $SO_2$ at the reaction site by the method previously described in equations 9 through 13. The oxygen pressure at the reaction site was deduced from the emf measurements of reaction 23 and equation 14. Rearranging equation 14 and inserting the value of $pO_2^{\prime}$, the the partial pressure of oxygen at the reference electrode, and E (from equation 24) yields

$$\log pO_2 = -\frac{16,723}{T} + 4.16216 \qquad (28)$$

Figure 5 illustrates the thermodynamic stability of the Ni-S-O system, where $Ni_{2.515}S_2$ coexists with NiO in the temperature range 968.6 to 1,053.7 K at a $SO_2$ pressure of approximately 1 atm. The condition of coexistence of a sulfide and oxide of nickel at equilibrium requires that the chemical potential of nickel is the same in both phases.

The average total pressure of the system for $Ni_{2.515}S_2$ measurements was 1.0019 atm, and the partial pressure of $SO_2$ at the reaction site was 1.0016 atm at 968.6 K and 1.0012 atm at 1,053.7 K.

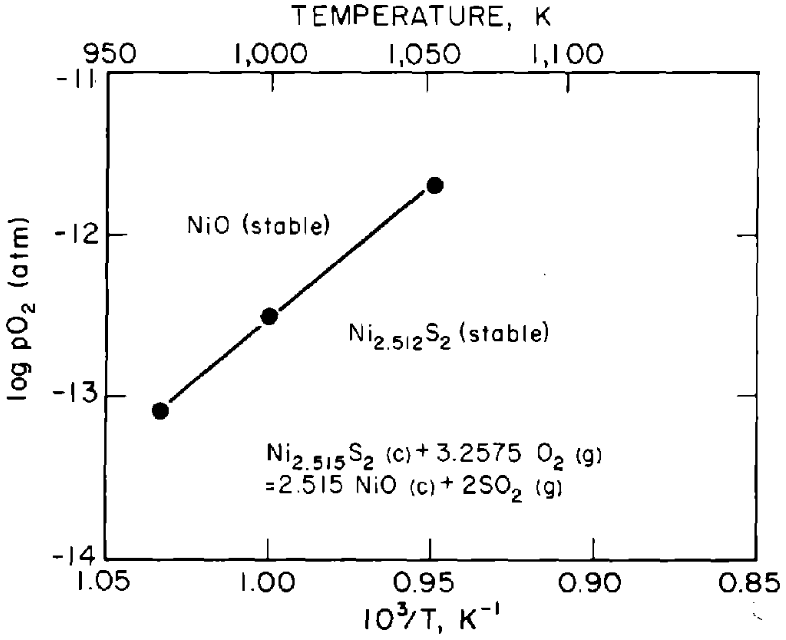

FIGURE 5. - Equilibrium diagram for Ni-S-O system.

The standard Gibbs energy of formation of $Ni_{2.515}S_2$ for the reaction

$$2.515\ Ni(c) + S_2(g) = Ni_{2.515}S_2 \qquad (29)$$

was deduced by rearranging equation 26 and substituting the proper values for the Gibbs energy change for reaction 23, as given by equation 25; the quantity RT ln $pSO_2$, the chemical potential, RT ln $pO_2^{\prime}$, at the reference electrode; and the standard Gibbs energies of formation of $SO_2$ (10) and NiO (9), as given by equations 7 and 27, respectively. By combining these data, a standard Gibbs energy of formation of $Ni_{2.515}S_2$ is obtained for reaction 29. These results may be expressed as

$$\Delta Gf^\circ(Ni_{2.515}S_2) = -65.377 + 24.67 \times 10^{-3}T \pm 0.541 \text{ kcal/mole}$$

$$(968.6 - 1{,}053.7 \text{ K}). \qquad (30)$$

X-ray diffraction analyses of the electrode components are given in table 5. As noted in column 1 of table 5, the X-ray diffraction analyses made at room temperature showed that an initial two-phase mixture consisting of $Ni_3S_2$ + NiO was converted to a three-phase mixture of $Ni_3S_2$ + $Ni_7S_6$ + NiO in the final equilibrated electrode sample. During equilibration in 1 atm of $SO_2$, a high-temperature phase $Ni_{3-x}S_2$, containing sulfur in excess of that in $Ni_3S_2$, was produced. As the sample cooled to room temperature, this high-temperature phase, which is not quenchable, disproportionated to yield $Ni_3S_2$ + $Ni_7S_6$ (6). Chemical analyses for total nickel, sulfur, and oxygen were obtained by standard analytical procedures. These analyses, in conjunction with X-ray diffraction analyses, confirmed the presence of excess sulfur in the high-temperature $Ni_{3-x}S_2$ phase. A composition of $Ni_{2.515}S_2$ was calculated from these chemical analyses, which agrees with the upper limit of sulfur content that has been reported in phase diagram and equilibrium studies (3, 6, 13).

TABLE 5. - X-ray diffraction analyses of samples for $Ni_{2.515}S_2$ cell

| Sample | Crystal structure | Parametric measurements, A | | Card[1] |
|---|---|---|---|---|
| | | $a_o$ | $c_o$ | |
| Reagents: | | | | |
| $Ni_3S_2$ | Hexagonal | 5.739±0.003 | 7.133±0.007 | 8-126 |
| NiO | Cubic | 4.176± .002 | NAp | 4-835 |
| Electrode mixture: | | | | |
| $Ni_3S_2$ | Hexagonal | 5.74 ± .001 | 7.14 ± .001 | 8-126 |
| $Ni_7S_6$ | Orthorhombic | NAp | NAp | NAp |
| NiO | Cubic | 4.177± .001 | NAp | 4-835 |

NAp Not applicable.

[1] Numbers refer to data file cards of Joint Committee of Powder Diffraction Standards, International Centre for Diffraction Data.

NOTE.--X-ray diffraction analyses were performed by members of the analytical laboratory at the Albany Research Center, Bureau of Mines, Albany, Oreg.

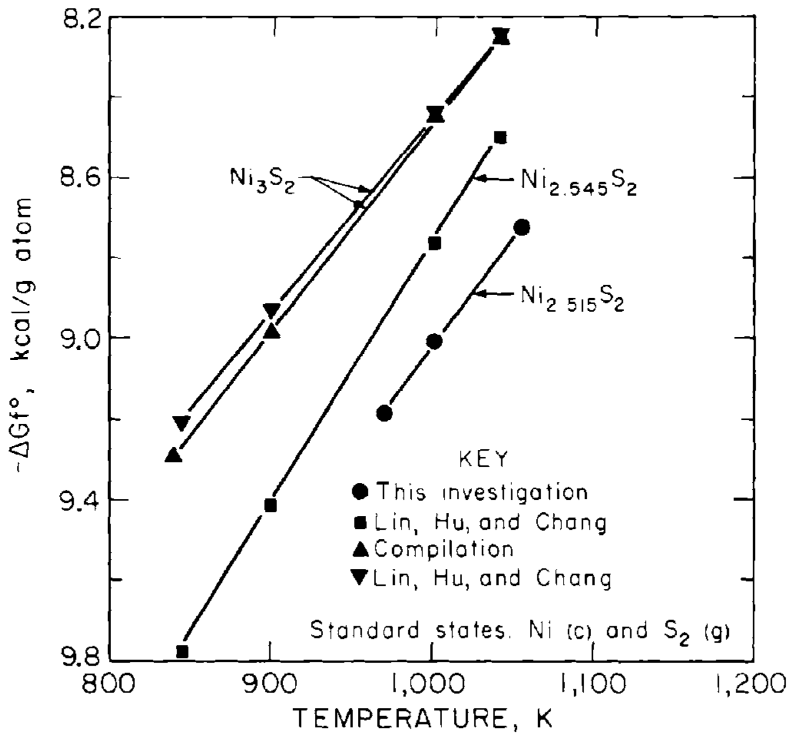

FIGURE 6. - Standard Gibbs energy of formation of $Ni_{2.515}S_2$.

In figure 6, the standard Gibbs energy of formation of $Ni_{2.515}S_2$ obtained from this investigation is compared with results of previous investigations (8) and data from a recent compilation (9). Direct comparison of the various results is not possible because the sulfur content is different in each of the nickel sulfides; however, figure 6 shows an increase in thermodynamic stability ($\Delta G$ becomes more negative) with an increase in sulfur content in the solid solution.

No experimental entropy and enthalpy data are available for $Ni_{2.515}S_2$; consequently, a standard enthalpy of formation at 298 K cannot be derived by the third-law method. Assuming that $\Delta H°$ is constant in the temperature range 968.6 to 1,053.7 K, the enthalpy of formation of $Ni_{2.515}S_2$, according to the first constant in equation 30, is

$$\Delta Hf° = -65.377 \pm 0.54 \text{ kcal/mole}$$

$$(968.6 - 1{,}053.7 \text{ K}). \tag{31}$$

The standard states are pure crystalline nickel, $Ni_{2.515}S_2$, and gaseous sulfur at 1 atm.

## SUMMARY AND CONCLUSIONS

Standard Gibbs energies of formation of $CoS_{1.035}$ and $Ni_{2.515}S_2$ were determined at elevated temperatures with galvanic cells employing stabilized $ZrO_2$ as the electrolyte. Because no enthalpy and entropy data are available for $CoS_{1.035}$ and $Ni_{2.515}S_2$, the standard enthalpies of formation at 298 K cannot be derived by the third-law method from experimental data. If $\Delta H°$ is assumed to be constant over the temperature range of the measurements used in this investigation, the enthalpies of formation are

$$\Delta Hf^\circ(CoS_{1.035}) = -38.890 \pm 0.20 \text{ kcal/mole}$$

$$(866.0 - 1.104.9 \text{ K})$$

and

$$\Delta Hf^\circ(Ni_{2.515}S_2) = -65.377 \pm 0.54 \text{ kcal/mole}$$

$$(968.6 - 1{,}053.7 \text{ K}).$$

Activity-composition data and high-temperature X-ray diffraction studies are needed to characterize the thermodynamic stability of the high-temperature nonstoichiometric $Ni_{3\pm x}S_2$ region, which has recently been reported to consist of two nonstoichiometric phases separated by a two-phase region.

In view of the disagreement over existing data, and the lack of enthalpy and entropy data, further thermodynamic investigation of both the Ni-S and Co-S systems is needed.

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