# Thermodynamic Properties of Ni-S Melts Between 700° and 1100°C

M. NAGAMORI AND T. R. INGRAHAM

The vapor pressure of sulfur over Ni-S melts of various compositions was calculated from the equilibrium weight of the melt in gas streams of known H_2S-H_2 composition. The Gibbs-Duhem equation was used to calculate the activity of nickel and other thermodynamic properties. For the reaction:

$$3Ni(s) + S_2(g) \rightleftharpoons Ni_3S_2(l)$$
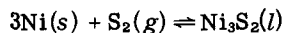
the suggested free energy relationship is: $\Delta G° = -57{,}910 + 15.89\,T$ (800° to 1100°C). The calculations were extrapolated to predict that for the reaction:

$$Ni(s) + 1/2\,S_2(g) \rightleftharpoons NiS(l), \quad \Delta G° = -26{,}730 + 10.5\,T \quad (1000° \text{ to } 1100°C)$$
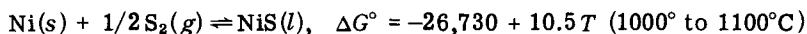
IN the process of recovering nickel from its sulfide ores, large tonnages of molten nickel sulfide mattes are processed annually. Sokolova[1] has reported that molten phases can exist in the Ni-S system at temperatures as low as 637°C. Sulfur has a negligible solubility in solid nickel.[2] Some thermodynamic measurements were made on the Ni-S system by Rosenqvist[3] but not enough measurements are available to evaluate the thermodynamic functions in the liquid region. The technique of using a continuous thermal balance method to determine the relationship between the composition of sulfide and the partial pressure of sulfur over it was used by Burgmann[4] and Turkdogan[5] in their studies of the Fe-S system. In this paper we report the results of using this method to study the Ni-S system.

EXPERIMENTAL

Materials

Nickel sheet of 99.96 pct purity and containing only 0.007 pct Co and 0.003 pct Fe was used in the experiments. The sheet was rolled to 0.2 mm thickness and treated in purified and dried hydrogen at 600°C for several hours prior to an experiment. Hydrogen sulfide (99.6 pct grade) was dried through fresh phosphorus pentoxide before use. The melt was contained in a 12-mm OD by 4-mm silica crucible which was suspended from the balance by a silica rod.

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The weight of the sample was continuously monitored with an R.G. model Cahn Electrobalance. The balance signal was read on a Philips Model PR 2210 U strip chart recorder. Corrosion of the balance mechanism was prevented by using a 150 cu cm per min back flush of dry nitrogen through the case. To prevent this flow of nitrogen from altering the com-

position of the H_2S-H_2 mixture over the sample, an outlet tube having three constrictions was designed to fit between the balance case and the furnace tubing. The sample and crucible were supported within a 20-mm ID silica tube mounted in a furnace equipped with Kanthal windings. The furnace temperature was controlled to within ±2°C with a pulse-pyrovane controller which was activated by a thermocouple placed adjacent to the furnace winding. The furnace temperature was monitored with a calibrated Pt-Pt 10 pct Rh thermocouple attached to a potentiometer.

Calibrated capillary flow meters containing dibutyl phthalate were used to monitor the flows of H_2S and H_2. Because the partial pressure of sulfur was to be
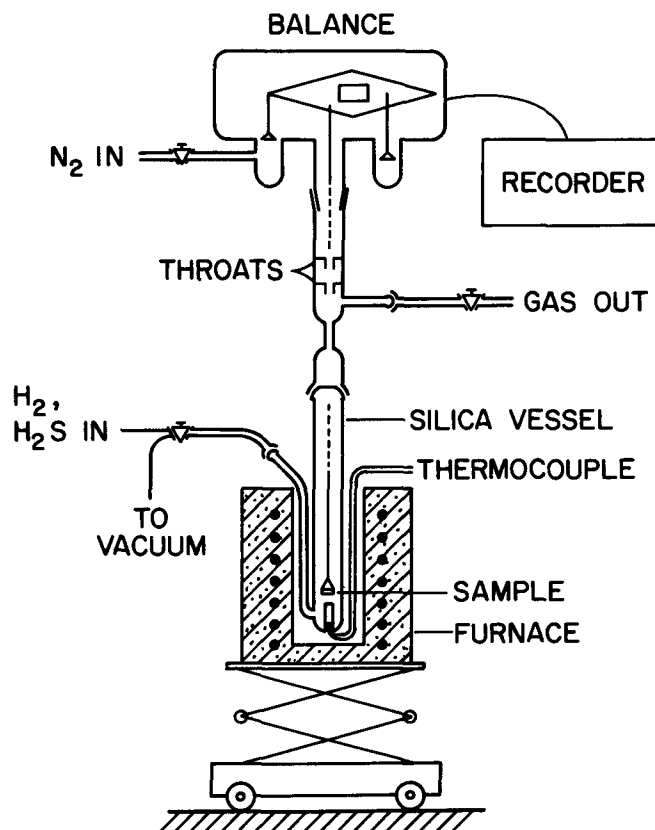

Fig. 1—Sketch of apparatus.

M. NAGAMORI is Post-Doctorate Fellow, National Research Council of Canada, Ottawa, Canada. T. R. INGRAHAM is Head, Extraction Metallurgy Research Section, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

varied over a wide range, the H_2S flowmeter was equipped with two capillaries, one for a small flow and the other for a large flow. Nitrogen flows were measured with a rotameter flowmeter. The flows were adjusted for room temperature, which was maintained within $\pm2°C$ during an experiment. The flow rate of the H_2S-H_2 mixture was maintained at 90 cu cm per min. A slight effect of thermal diffusion was noted when the flow rate was varied from 60 to 120 cu cm per min. Because the thermal effect could only cause a potential error of less than 0.03 pct S in the sample, it was considered negligible and therefore disregarded.

At each new experimental temperature, the balance mechanism was equilibrated to the new ambient temperature over the furnace for at least a day before measurements were made.

Procedure

The thermal balance was calibrated in air at room temperature. When the balance was mounted over the furnace there was a slight rise in temperature that caused a small drift in the balance readings until a steady-state temperature had been reached. No readings were made until the steady-state had been attained. It was found that the air calibration was valid, whatever the furnace temperature, as long as the balance was in thermal equilibrium with its surroundings.

A small piece of nickel sheet of known weight (0.6 to 1.0 g) was placed in the silica crucible (0.8 g). To add sulfur to the hot nickel, small amounts of H_2S were added to the H_2 gas stream. When about 10 mg of sulfur had been added, the gas composition was varied to determine the particular partial pressure of sulfur that was in equilibrium with the sample at a given temperature. Equilibration in the two-phase region of nickel metal and sulfide melt was a slow process. Near equilibrium, a period of about 20 hr was required before the direction of the drift in sample weight could be determined. The equilibrium position was taken as midway between that sulfur pressure which caused a detectable increase in sample weight in about 20 hr and

Table I. Experimental Results for the Homogeneous Ni-S Melts

Temperature, °C	$p_{S_2}^{1/2}$, Atm$^{1/2}$	$n^o{}_{H_2S}$	Composition	
			Wt Pct S	N_S
700	1.45×10^{-5}	2.67×10^{-3}	21.22	0.3302
	1.92×10^{-5}	3.54×10^{-3}	21.80	0.3379
800	5.36×10^{-5}	3.49×10^{-3}	21.01	0.3274
	1.00×10^{-4}	6.50×10^{-3}	22.45	0.3463
	1.00×10^{-3}	6.141×10^{-2}	25.98	0.3911
	5.00×10^{-3}	2.466×10^{-1}	27.97	0.4155
900	1.37×10^{-4}	3.77×10^{-3}	19.74	0.3104
	1.00×10^{-3}	2.686×10^{-2}	24.15	0.3682
	6.00×10^{-3}	1.421×10^{-1}	26.73	0.4004
	1.00×10^{-1}	7.542×10^{-1}	30.33	0.4435
1000	3.32×10^{-4}	4.41×10^{-3}	18.44	0.2927
	1.00×10^{-3}	1.317×10^{-2}	21.96	0.3399
	1.00×10^{-2}	1.179×10^{-1}	26.11	0.3927
	1.00×10^{-1}	5.918×10^{-1}	29.40	0.4325
1100	6.76×10^{-4}	4.82×10^{-3}	16.43	0.2646
	2.00×10^{-3}	1.421×10^{-2}	20.92	0.3262
	1.00×10^{-2}	6.743×10^{-2}	24.60	0.3739
	1.00×10^{-1}	4.401×10^{-1}	28.41	0.4207

Table II. Experimental Results for the Nickel-Saturated Melts

Temperature, °C	$p_{S_2}^{1/2}$ ($\times 10^5$) Atm$^{1/2}$	$n^o{}_{H_2S}$ ($\times 10^3$)	H_2S/H_2 ($\times 10^3$)	Composition		
				Wt Pct S	N_S	N_S, After Elliott[2]
700	1.02 ± 0.01	1.90 ± 0.01	1.90	20.6	0.322	0.329
800	4.11 ± 0.02	2.68 ± 0.01	2.69	20.28	0.3177	0.320
900	12.1 ± 0.1	3.33 ± 0.03	3.34	19.24	0.3036	0.306
900	12.2 ± 0.1	3.35 ± 0.03	3.36			
1000	29.9 ± 0.2	3.97 ± 0.02	3.99	17.94	0.2858	0.284
1100	61.6 ± 0.3	4.39 ± 0.02	4.41	15.76	0.2551	0.248

that which caused a detectable decrease in weight in the same period.

Equilibrium in the single phase region was attained within a few hours. Gas compositions were then altered, and the new equilibrium position was determined. The rate of volatilization of Ni_3S_2 and NiS is a function of both the sample temperature and their mole fraction in solution. At 1100°C the rate of evaporation of the sulfides becomes just detectable at the higher sulfur pressures used in the experiments. For this reason no high-sulfur-pressure experiment at 1100°C was continued for more than 3 days. At 1200°C the sulfides volatilized readily and deposited on the silica rod support. The technique is considered unreliable at that temperature.

It was observed that when rapid sulfur additions were made to the melt, uncontrolled spattering occurred. No spattering occurred when the maximum rate of addition was less than 20 mg of sulfur per hour.

RESULTS

Mixtures of H_2S and H_2 were made at room temperature and equilibrated in the apparatus at the sample temperature. Below 1050°C, the only significant species are H_2S, H_2, and S_2. The two-term equation suggested by Kubaschewski, Evans, and Alcock[6] was used to calculate the equilibrium constant for the formation of H_2S. At temperatures above 1050°C, it was necessary to make small corrections for the amount of HS formed. When the partial pressure of sulfur was known to be small, the pressure was calculated by dividing the H_2S/H_2 ratio by the equilibrium constant for the formation of H_2S. Larger partial pressures of sulfur were calculated by the method used by Nagamori and Kameda.[7] The results obtained from studies with homogeneous melts are shown in Table I for experiments done with various mole fractions of H_2S ($n^o{}_{H_2S}$) at temperatures from 700° to 1100°C. The compositions reported in the table are the average values obtained when the equilibrium was approached from both directions. In almost all cases, the measurements were identical when obtained from different directions.

In this paper, sulfur activities are reported in the form, $p_{S_2}^{1/2}$.

The weight percent of sulfur (wt pct S) and its mole fraction (N_S) were calculated directly from the equilibrium weight of the specimen.

The results obtained from experiments with nickel-saturated melts are shown in Table II. The partial pressure of sulfur over samples having a composition in the miscibility gap between Ni-S liquid and solid nickel was determined directly from the experimental
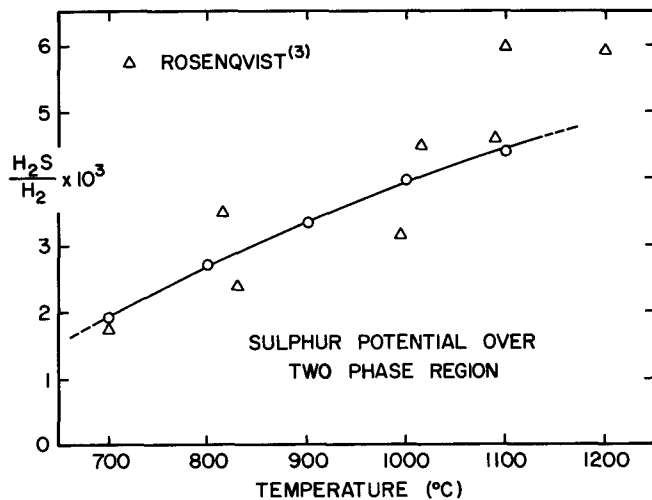
Fig. 2—Sulfur potential over two phase region.

nickel. The activities of nickel relative to solid nickel are then calculated by:

$$\log a_{\mathrm{Ni}} = - \int_{N_\mathrm{S}=N_\mathrm{S}^*}^{N_\mathrm{S}=N_\mathrm{S}} (N_\mathrm{S}/N_{\mathrm{Ni}})\, d \, \log p_{\mathrm{S}_2}^{1/2} \qquad [2]$$

where N_S^* designates the mole fraction of sulfur when the melt is saturated with nickel. Because the solid solubility of sulfur in solid nickel has been reported to be negligibly small,[2] the activity of nickel at the composition N_S^* can be assumed to be unity. To facilitate the above integration, the curve was divided into three parts and for each part the relation was approximated by the following quadratic equation:

Table III. Calculated Properties for Stoichiometric $Ni_3 S_2$ (l)

Temperature, °C	$p_{\mathrm{S}_2}^{1/2}$, Atm$^{1/2}$	a_{Ni}	K	ΔG_T°, cal/mole, ±200
800	1.81×10^{-3}	1.15×10^{-1}	2.03×10^8	−40,780
900	5.86×10^{-3}	1.11×10^{-1}	2.14×10^7	−39,340
1000	1.50×10^{-2}	1.13×10^{-1}	3.04×10^6	−37,760
1100	3.22×10^{-2}	1.21×10^{-1}	5.41×10^5	−36,010

results. Compositions of the liquidus were estimated by extrapolation from the homogeneous liquid range. The partial pressure vs composition relationship in the vicinity of the solubility limit was approximated at each temperature by a quadratic equation that was fitted to the data by regression analysis. The composition at any required temperature and at any required partial pressure of sulfur was obtained by solving the quadratic equation. Because the position of the liquidus boundary on the phase diagram changes only slightly with changes in temperature between 700° and 1100°C, the regression method is considered more reliable than the conventional thermal analysis method.

In Table II, the extreme right-hand column includes data taken from the work of Elliott[2] on the mole fraction of sulfur in the melts at various temperatures. The inherent accuracy of this method permits the establishment of a more reliable limit within which to make activity calculations by a Gibbs-Duhem integration.

Table II shows values of the H_2S/H_2 ratio over the two-phase region at the experimental temperatures. The data are used in Fig. 2 for comparison with the work of Rosenqvist.[3] It will be apparent from Fig. 2 that the scatter in the data obtained by this method is considerably less than for the data reported by Rosenqvist.[3]

The relationship between $p_{\mathrm{S}_2}^{1/2}$ and composition of the homogeneous solutions is shown in Fig. 3. The figure includes the data for experiments at 700°, 800°, 900°, 1000°, and 1100°C. The data are highly reproducible and the scatter about smooth curves is small. For comparison, the data of Rosenqvist, which were established by a different experimental method, are included.

Activity of Nickel

The Gibbs-Duhem equation for the homogeneous Ni-S solution can be expressed as follows:

$$N_\mathrm{S} d \, \log p_{\mathrm{S}_2}^{1/2} + N_{\mathrm{Ni}} d \, \log a_{\mathrm{Ni}} = 0 \qquad [1]$$

where N_S and N_{Ni} represent mole fraction of sulfur and nickel, respectively, and a_{Ni} is the activity of
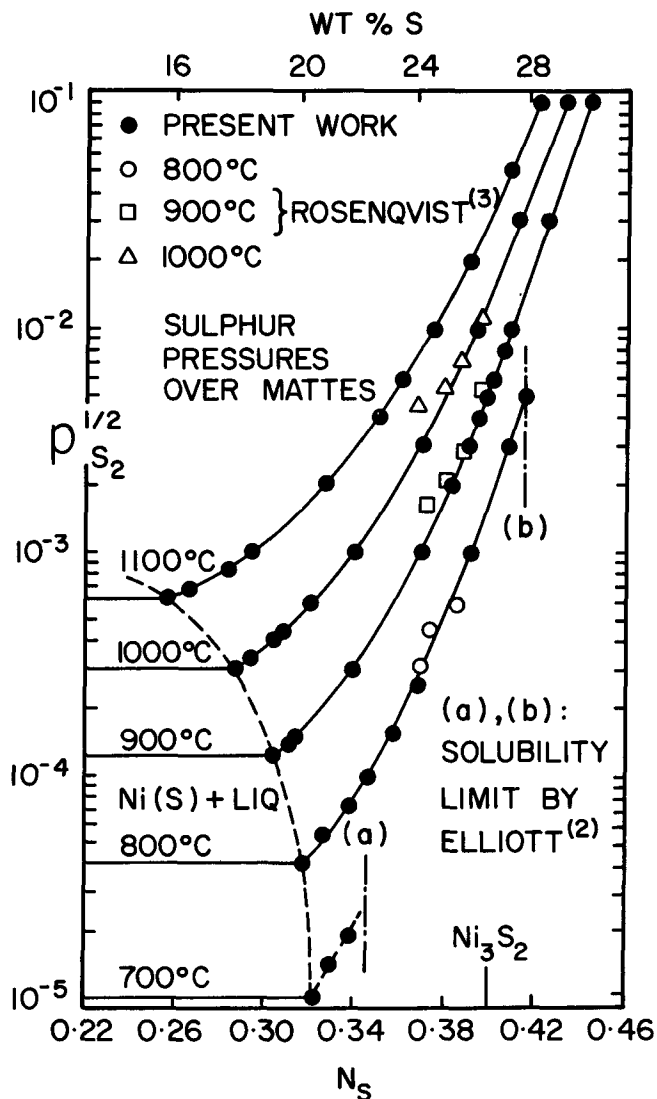

Fig. 3—Sulfur pressures over Ni-S mattes.

$$N_S/(1 - N_S) = a + bx + cx^2 \qquad [3]$$

where $x = \log p_{S_2}^{1/2}$. The activity of nickel can then be calculated by

$$\log a_{Ni} = -[ax + (b/2)x^2 + (c/3)x^3]_{x=x*}^{x=x} \qquad [4]$$

where $x*$ is the value of $\log p_{S_2}^{1/2}$ at compositions saturated with solid nickel. The nickel activities thus calculated were checked by the graphical integration method. The activities of nickel are shown in Fig. 4 as a function of composition at each temperature.

Stoichiometric Nickel Sulfides

From the preceding calculations, the activities of sulfur and nickel are known for the stoichiometric Ni_3S_2 at temperatures between 800° to 1100°C. Some selected values are shown in Table III. Equilibrium constants and the standard free energy change for the following reaction may be calculated from the data:

$$3Ni(s) + S_2(g) = Ni_3S_2(l) \qquad [5]$$

$$K = \frac{a_{Ni_3S_2}}{a_{Ni}^3 p_{S_2}} = \frac{1}{a_{Ni(at\ Ni_3S_2)}^3\ p_{S_2(at\ Ni_3S_2)}} \qquad [6]$$

Table IV. Estimated Properties for Stoichiometric NiS (*l*)

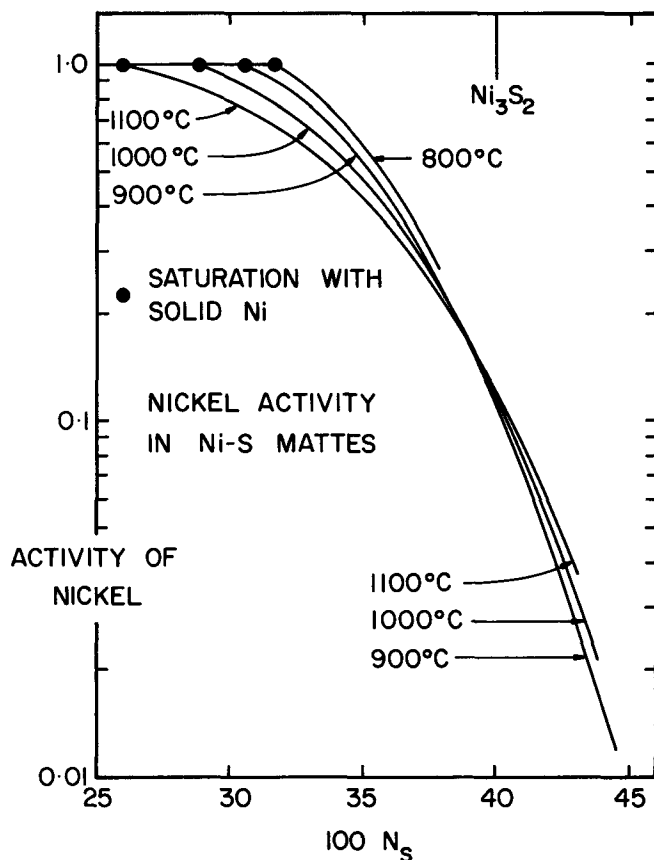| Temperature, °C	$p_{S_2}^{1/2}$, Atm$^{1/2}$	a_{Ni}	K	ΔG_T°, cal/mole, ±400
900*	5.7	3.7 X 10^{-4}	474	−14,400
1000	9.4	5.4 X 10^{-4}	198	−13,400
1100	16	6.8 X 10^{-4}	91.9	−12,300

*Assuming supercooled NiS (*l*).

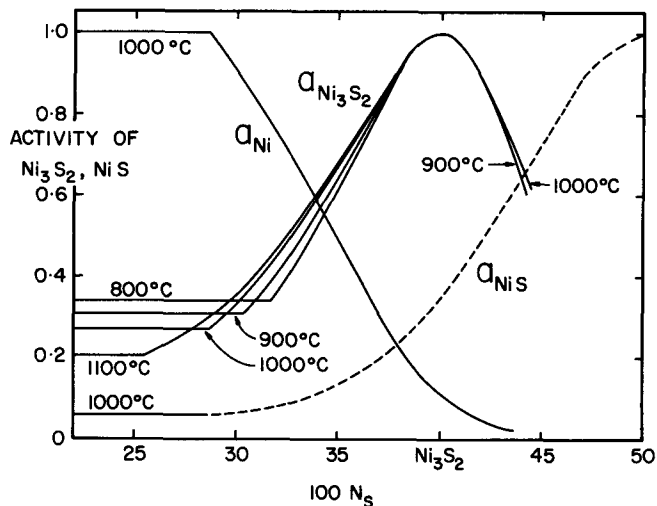Fig. 4—Nickel activity in Ni-S mattes.

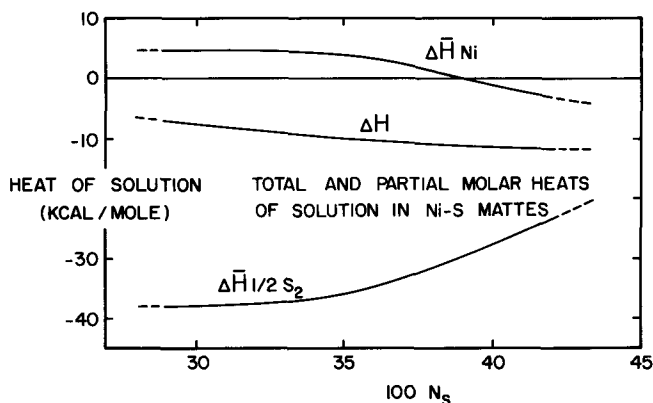Fig. 5—Activity of $Ni_3S_2(l)$ and $NiS(l)$.

Fig. 6—Total and partial molar heats of solution in Ni-S mattes at 900° to 1100°C.

$$\Delta G_T^\circ = -4.575\ T\ \log K \qquad [7]$$

The calculated values of K and ΔG_T° are also listed in Table III. From these, the activity of Ni_3S_2 can be calculated by the relationship: $a_{Ni_3S_2} = Ka_{Ni}^3 p_{S_2}$. The results are shown in Fig. 5. The values of ΔG_T° for Reaction [3] can be expressed by the equation:

$$\Delta G_T^\circ(Ni_3S_2) = -57,910 + 15.89\ T\ (\pm0.2\ kcal/mole)$$
$$(800° \text{ to } 1100°) \qquad [8]$$

The values of the uncertainty are based on a regression fit of the data, but the actual uncertainty may be somewhat larger because of the uncertainty in the equilibrium constant for the formation of H_2S. Stoichiometric $Ni_3S_2(s)$ melts incongruently between 770° and 790°C. If the melting point of Ni_3S_2 is assumed to be 790°C, the value for its free energy is 40.7 kcal per mole when the calculation is made from Rosenqvist's data[3] and 41.0 kcal per mole when it is calculated by extrapolation of Eq. [8] into the liquid region. The agreement is good. On the basis of calculations made for a temperature of 790°C, with the solid data of Rosenqvist[3] and the liquid data from this study, the estimated heat of fusion of $Ni_3S_2(s)$ is 11.3 kcal per mole.

The $p_{S_2}^{1/2}$-composition relations in the Ni-S melts may be extrapolated to the composition of NiS. The extrapolated values are summarized in Table IV. The
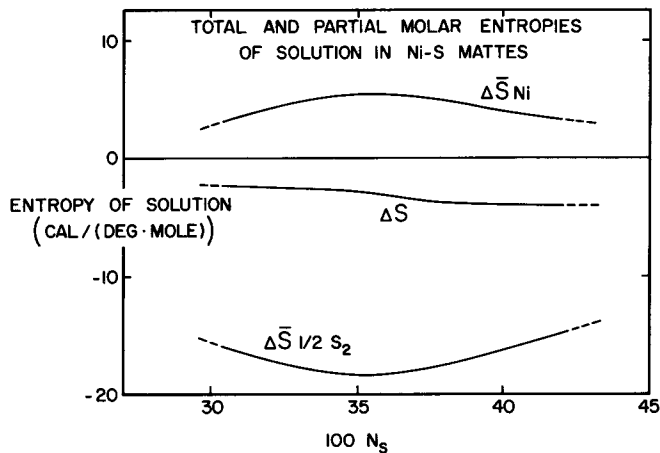
Fig. 7—Total and partial molar entropies of solution in Ni-S mattes at 900° to 1100°C.

Fig. 8—Free energy of Ni-S mattes at 1000°C.

partial pressure of sulfur over NiS(l) is more than 1 atm at temperatures between 900° and 1100°C, as seen from Table IV. According to the same procedures as used for $Ni_3S_2(l)$, the values of K and ΔG_T° can be calculated for the following reaction:

$$Ni(s) + 1/2 S_2(g) = NiS(l) \qquad [9]$$

$$K = \frac{a_{NiS}}{a_{Ni}p_{S_2}^{1/2}} = \frac{1}{a_{Ni(at\ NiS)}\ p_{S_2}^{1/2}(at\ NiS)} \qquad [10]$$

$$\Delta G_T^\circ = -4.575\,T \log K \qquad [7]$$

$$\Delta G_T^\circ = -26,730 + 10.5\,T \quad (1000° \text{ to } 1100°C)$$
$$(\pm 0.4 \text{ kcal/mole}) \qquad [11]$$

The calculated results are also shown in Table IV. The data were used to calculate the activity of NiS(l), which is shown in Fig. 5. When the ΔG_T° for NiS(s) by Rosenqvist[3] was extrapolated to 980°C, which is the liquidus temperature of the stoichiometric NiS, a value of 13.6 kcal per mole was found. The corresponding value obtained from this work, by interpolation, is 13.6 kcal per mole for NiS(l). The agreement is excellent. The estimated heat of fusion of NiS(s) is 7.4 kcal per mole.

Heat, Entropy, and Free-Energy Change of Solution for Ni-S Melts

The heat and entropy of solution, ΔH and ΔS, were calculated with the Gibbs-Helmholtz equations in the following form:

$$\Delta \bar{H}_{1/2S_2} = -4.575\,T^2 (d \log p_{S_2}^{1/2})/dT$$

$$\Delta \bar{H}_{Ni} = -4.575\,T^2 (d \log a_{Ni})/dT \qquad [12]$$

$$\Delta H = N_S \Delta \bar{H}_{1/2S_2} + N_{Ni} \Delta \bar{H}_{Ni}$$

and

$$\Delta \bar{S}_{1/2S_2} = -4.575 [T (d \log p_{S_2}^{1/2})/dT + \log p_{S_2}^{1/2}]$$

$$\Delta \bar{S}_{Ni} = -4.575 [T (d \log a_{Ni})/dT + \log a_{Ni}] \qquad [13]$$

$$\Delta S = N_S \Delta \bar{S}_{1/2S_2} + N_{Ni} \Delta \bar{S}_{Ni}$$

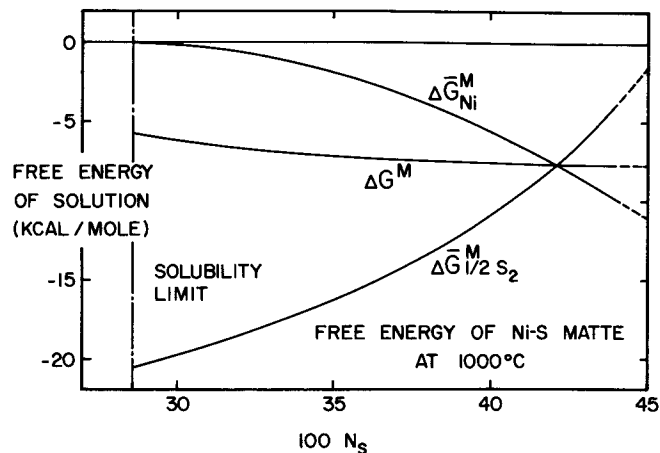where $^-$ indicates the partial molar quantities. The calculated values are shown in Fig. 6 and Fig. 7. The

free energy of solution, ΔG^M, can be calculated by:

$$\Delta \bar{G}_{1/2S_2}^M = 4.575\,T \log p_{S_2}^{1/2}$$

$$\Delta \bar{G}_{Ni}^M = 4.575\,T \log a_{Ni} \qquad [14]$$

$$\Delta G^M = 4.575\,T (N_S \log p_{S_2}^{1/2} + N_{Ni} \log a_{Ni}) = \Delta H - T\Delta S$$

The values at 1000°C are shown in Fig. 8.

The partial molar heat of nickel changes from positive to negative between 37 and 38 at. pct S; this is caused by the choice of solid nickel as the reference state. From published thermal data[6] the free energy of fusion of nickel can be calculated as:

$$Ni(s) = Ni(l), \quad \Delta G° = 3,920 - 2.27\,T, \quad (800° \text{ to } 1450°C) \qquad [15]$$

If the reference state for a_{Ni} were chosen to be supercooled-liquid nickel, the $\Delta \bar{H}_{Ni}$ curve would be displaced downwards by 3.92 kcal per mole, Fig. 6, and $\Delta \bar{H}_{Ni(l)}$ would become practically zero for $N_S < 0.33$. The choice of the liquid reference state for a_{Ni} would also change the $\Delta \bar{S}_{Ni}$ curve in Fig. 7 by -2.27 cal per mole·deg.

The partial molar entropies show a maximum or a minimum at about 35 at. pct S. It is interesting to note that the absolute Seebeck coefficient[8] changes its sign in the same range of composition. In addition, the electrical conductivity has a minimum value in the same compositional range.[9] In the liquid Ag-S,[10] Bi-S,[11] and Fe-S[12] systems, the partial molar functions also exhibit maxima or minima on the metal-rich side of the stoichiometric composition.

REFERENCES

1. M. A. Sokolova: *Proc. Acad. Sci. USSR, Chem. Sect.*, 1956, vol. 106, p. 59.
2. R. P. Elliott: *Constitution of Binary Alloys*, McGraw-Hill Book Co., New York, 1965.
3. T. Rosenqvist: *J. Iron Steel Inst.*, 1954, vol. 175, p. 37.
4. W. Burgmann: Dr. Eng. Thesis, Berlin Technical Univ., Berlin, 1967.
5. E. T. Turkdogan: *Trans. TMS-AIME*, 1968, vol. 242, p. 1665.
6. O. Kubaschewski, E. Ll. Evans, and C. B. Alcock: *Metallurgical Thermochemistry*, Pergamon Press, London, 1967.
7. M. Nagamori and M. Kameda: *Trans. Japan Inst. Metals*, 1968, vol. 9, p. 187.
8. E. A. Dancy, R. L. Pastorek, and G. Derge: *Trans. Met. Soc. AIME*, 1965, vol. 233, p. 1645.
9. E. A. Dancy and G. Derge: *Trans. Met. Soc. AIME*, 1963, vol. 227, p. 1034.
10. T. Rosenqvist: *AIME Trans.*, 1949, vol. 185, p. 451.
11. D. Cubicciotti: *J. Phys. Chem.*, 1963, vol. 67, p. 118.
12. M. Nagamori, T. Hatakeyama, and M. Kameda: *Nippon Kinzoku Gakkaishi (Japan)*, 1969, vol. 33, p. 366.