A Thermodynamic Study of the Systems Ni-S and Co-S by CaF₂ Solid Electrolyte Galvanic Cell Technique*

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Electromotive force measurements of the following galvanic cells were carried out using CaF₂ solid electrolyte:

From the emf and the standard free energy of formation of reference electrode, the sulfur pressure of the system Ni-S in the range of 20–47 mol% S and 801–1372 K and of the system Co-S at 35 mol% S and 995–1322 K was calculated. The results were compared with those by other investigators.

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I. Introduction

Since the pioneering work of Kiukkola and Wagner⁽¹⁾ in 1957, the electrochemical cells incorporating oxide solid electrolytes have proved to be applicable to many thermodynamic and kinetic investigations of oxide systems. On the other hand, the measurements of sulfide systems are still insufficient as compared with oxide systems.

In 1957, Ure⁽²⁾ measured transport numbers and diffusion coefficients of Ca in pure CaF₂ as well as in NaF and YF₃ doped CaF₂, and concluded that CaF₂ is predominantly an ionic conductor, namely F⁻ ion conductor. Thereafter, the galvanic cells with CaF₂ solid electrolyte have been used in the thermodynamic study of

fluorides⁽³⁾, carbides^{(4)–(8)}, borides, phosphides, sulfides, oxides and alloy systems^{(8)–(11)}.

So far, the following studies of sulfide systems have been made using solid electrolytes. Larson and Elliott⁽¹²⁾ used ZrO₂(CaO) solid electrolyte to obtain the standard free energies of formation of ZnS, MnS, MoS₂, NbS, TaS, PtS and Rh_xS. The same kind of cell constitution was applied to determination of the standard free energies of formation of FeS by Armanyanova *et al.*⁽¹³⁾, and Cu₂S and MnS by Sadakane *et al.*⁽¹⁴⁾. Further, Nagata *et al.*⁽¹⁵⁾ used CaS solid electrolyte in the measurement of the standard free energies of formation of MoS₂, Cu₂S, PbS and FeS. One of the authors and his co-workers⁽¹⁶⁾, and Gu and Tang⁽¹⁷⁾ measured sulfur potentials in carbon saturated liquid iron using CaS(TiS₂), and three of the authors⁽¹⁸⁾ used CaS(ZrS₂) for measuring the sulfur partial pressure of the systems Cu-S, Fe-S, Ni-S, Co-S and Cr-S.

Aronson⁽¹⁹⁾ carried out the thermodynamic study of thorium sulfides making use of CaF₂, but his cell arrangement was different from that of the authors. Three of the authors and their co-workers have measured the standard free energies of formation of Cu₂S and FeS⁽²⁰⁾, and MnS and FeS again⁽²¹⁾ by the CaF₂ solid

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electrolyte. Jacob *et al.*⁽²²⁾ measured sulfur potentials in Ar+H₂S+H₂ gas using CaF₂. Worrell and Ramanarayanan⁽¹¹⁾ used similar cells for measuring free energies of FeS, Ag₂S, MnS and CrS.

In this study, electromotive force measurements were made using CaF₂ solid electrolyte, in order to elucidate the thermodynamic properties of the systems Ni-S and Co-S.

II. CaF₂ Solid Electrolyte

Ure⁽²⁾ measured transport numbers and diffusion coefficients of Ca in pure CaF₂ and in NaF or YF₃ doped CaF₂. He came to the conclusion that CaF₂ is ion conductive and the transport number of Ca²⁺ ion is negligibly small as compared with that of F⁻ ion. Earlier Zintl *et al.*⁽²³⁾ showed that YF₃ doped CaF₂ leads to the formation of interstitial F⁻ ion structures. Similar to the oxide solid electrolytes, the CaF₂ exhibits substantial electronic or positive hole conduction under a certain condition of fluorine potential and temperature. Hinze and Patterson⁽²⁴⁾ measured the electric conductivity of single crystal CaF₂ by the ac bridge method. They controlled the fluorine potential using metal-metal fluoride electrodes. They concluded that the low limit of ionic conductive range exists at a little higher potential than Ca-CaF₂ equilibrium at 823–1023 K. Two of the authors and their co-workers⁽²⁵⁾ carried out similar measurements and obtained the same results, as shown in Fig. 1. No detailed information is available on the high limit of P_{F_2} . However, Heus and Egan⁽²⁶⁾ and others have measured Ni-NiF₂ equilibrium fluorine pressure and obtained $\log P_{F_2}(\text{Pa}) = -26.7$ at 873 K. Furthermore, Patterson⁽²⁷⁾ has proposed that in view of the extreme electronegativity difference between Ca²⁺ and F⁻ ions and the correspondingly large forbidden bandgap for CaF₂, it would not be surprising if this boundary were found to be located for about 10⁵ Pa fluorine pressure.

The lowest temperature measured using CaF₂ solid electrolyte was reported to be 773 K by Worrell and Ramanarayanan⁽¹¹⁾. Though the highest temperature was reported to be about 1273 K by many investigators the

Fig. 1 Total conductivity of CaF₂ as a function of $\log P_{F_2}$.

authors measured emfs at temperatures up to 1372 K in this study.

III. Experimental Principle

Wagner⁽²⁸⁾ has derived a general formula for the emf of the following cell, $\mu'(M), \mu'(X)/MX/\mu''(M), \mu''(X)$.

$$E = -\frac{1}{Z(X)F} \int_{\mu'(X)}^{\mu''(X)} t_{\text{ion}} d\mu(X) \\ = -\frac{1}{Z(M)F} \int_{\mu''(M)}^{\mu'(M)} t_{\text{ion}} d\mu(M), \quad (1)$$

where F is the Faraday constant, $\mu(X)$ and $\mu(M)$ the chemical potential of X and M , respectively, and Z is the valence of ion.

Applying eq. (1) to the CaF₂ cell, one obtains

$$E = -\frac{1}{2F} \int_{\mu'(F_2)}^{\mu''(F_2)} t_{\text{ion}} d\mu(F_2) \\ = -\frac{1}{2F} \int_{\mu''(Ca)}^{\mu'(Ca)} t_{\text{ion}} d\mu(Ca). \quad (2)$$

In the simple case where $t_{\text{ion}}=1$ throughout range of integration, eq. (2) is reduced to

$$2EF = RT \ln (P'_{F_2}/P''_{F_2}) = RT \ln (a''_{Ca}/a'_{Ca}). \quad (3)$$

The present experiments were carried out on the following galvanic cells:

Au/Ag, Ag₂S, CaS/CaF₂/CaS, Ni_xS_y,
Ni/Au.

(I)

Pt/Cr, CrS, CaS/CaF₂/CaS, Ni-S(1),
Ni/Pt.

(II)

Pt/Cr, CrS, CaS/CaF₂/CaS, Co_xS_y,
Co/Pt.

(III)

In the cell (I), for instance, the equilibrium sulfur pressure at the left-hand electrode, $P'_{S_2}(\text{Ag-Ag}_2\text{S})$, is constant at a constant temperature. When the mutual solubility of Ag and Ag₂S is ignored,

$$\Delta G^0(\text{Ag}_2\text{S}) = RT \ln P_{S_2}'^{1/2}(\text{Ag-Ag}_2\text{S}), \quad (4)$$

where $\Delta G^0(\text{Ag}_2\text{S})$ is the standard free energy of formation of Ag₂S. When CaS is regarded as a stoichiometric compound,

$$\Delta G^0(\text{CaS}) = RT \ln [a'_{\text{Ca}}(\text{in CaS}) P_{S_2}'^{1/2}(\text{in CaS})]. \quad (5)$$

From eqs. (4) and (5), $\Delta G^0(\text{CaS})$ is given by eq. (6).

$$\Delta G^0(\text{CaS}) = RT \ln [a'_{\text{Ca}}(\text{in CaS}) P_{S_2}'^{1/2}(\text{Ag-Ag}_2\text{S})]. \quad (6)$$

where $\Delta G^0(\text{CaS})$, $a'_{\text{Ca}}(\text{in CaS})$ and P_{S_2}' are, respectively, the standard free energy of formation of CaS, the calcium activity and the sulfur pressure in CaS.

At the interface between the CaF₂ electrolyte and the left-hand electrode of the cell (I),

$$\Delta G^0(\text{CaF}_2) = RT \ln [a'_{\text{Ca}}(i) P_{F_2}'(i)], \quad (7)$$

where $\Delta G^0(\text{CaF}_2)$ is the standard free energy of formation of CaF₂ and $P_{F_2}'(i)$ and $a'_{\text{Ca}}(i)$ are, respectively, the fluorine pressure and the calcium activity at the interface between the electrolyte and the Ag-Ag₂S electrode. When CaF₂ is regarded as a stoichiometric compound, $a'_{\text{Ca}}(\text{in CaS})$ is equal to $a_{\text{Ca}}(i)$. Combining eqs. (4), (6) and (7),

$$RT \ln P_{F_2}'(i) = \Delta G^0(\text{CaF}_2) - \Delta G^0(\text{CaS}) + \Delta G^0(\text{Ag}_2\text{S}). \quad (8)$$

A similar equation may be written at the right-hand electrode in the cell (I),

$$RT \ln P_{F_2}''(i) = \Delta G^0(\text{CaF}_2) - \Delta G^0(\text{CaS})$$

$$+ RT \ln P_{S_2}''^{1/2}(\text{Ni-Ni}_x\text{S}_y), \quad (9)$$

where $P_{S_2}''(\text{Ni-Ni}_x\text{S}_y)$ is the equilibrium sulfur pressure at the right-hand electrode. From eqs. (3), (8) and (9) one then obtains

$$2EF = \Delta G^0(\text{Ag}_2\text{S}) - RT \ln P_{S_2}''^{1/2}(\text{Ni-Ni}_x\text{S}_y). \quad (10)$$

IV. Experimental

1. Preparation of electrodes

(1) Ag, Ag₂S and CaS reference electrode

The Ag + Ag₂S + CaS pellets were prepared by mixing commercial high purity silver, silver sulfide and calcium sulfide powders in about 1:1.2:1.2 molar ratio, pressing into discs 8 mm in diameter and 4 mm thick at 2.5×10^8 Pa and sintering for about 86 ks in argon at 823 K.

The X-ray analysis of the resulting mixture indicated the existence of Ag, Ag₂S and CaS only.

(2) Cr, CrS, CaS reference electrode

The Cr + CrS + CaS pellets were prepared by mixing commercial high purity chromium, sulfur and calcium sulfide powders in about 2:1:1 molar ratio, pressing into discs 8 mm in diameter and 4 mm thick at 3×10^8 Pa, enclosing in silica tube under vacuum and sintering for about 170 ks at 1073 K.

In the preliminary experiments, the mixtures with the ratio mentioned above were enclosed in silica tubes in vacuum and heated for 260 ks at 773, 873 and 1073 K and quenched into water. After these treatments, X-ray analysis of the three resulting mixtures indicated the existence of only Cr, CrS and CaS.

(3) Ni, Ni_xS_y, CaS electrode

Commercial carbonil nickel powder was reduced in hydrogen for 11 ks at 573 K to eliminate oxide. Ni + Ni_xS_y powder was prepared by mixing the reduced nickel and commercial high purity nickel mono-sulfide in various ratios, pressing, sintering for 86 ks in argon at 973 K and grinding. The nickel content of this powder was analyzed. The Ni + Ni_xS_y + CaS pellets were prepared by mixing

this powder and calcium sulfide powder in about 2:1 molar ratio and pressing.

The X-ray analysis of the resulting mixtures indicated the existence of three-phase equilibria, $\text{Ni} + \text{Ni}_3\text{S}_2 + \text{CaS}$, $\text{Ni}_3\text{S}_2 + \text{Ni}_7\text{S}_6 + \text{CaS}$ and $\text{Ni}_7\text{S}_6 + \text{NiS} + \text{CaS}$ depending on the Ni/S ratio.

(4) Co, Co_xS_y , CaS electrode

Commercial carbonil cobalt powder was reduced in hydrogen for 11 ks at 573 K to eliminate oxide. $\text{Co} + \text{Co}_x\text{S}_y$ powder was prepared by mixing the reduced cobalt and commercial high purity sulfur in 2:1 molar ratio, pressing, enclosing in silica tube under vacuum, sintering for 170 ks at 1123 K and gridding. The $\text{Co} + \text{Co}_x\text{S}_y + \text{CaS}$ pellets were prepared by mixing this powder and calcium sulfide powder in about 2:1 molar ratio and pressing. The X-ray analysis of the resulting mixture indicated the coexistence of Co and Co_9S_8 .

2. Experimental apparatus and procedure

The schematic diagram of the cell assembly is shown in Fig. 2. The CaF_2 solid electrolyte is a polished single crystal 12 mm in diameter and 4 mm thick. As conducting leads, gold wires were used for cell (I) and platinum wires for cells (II) and (III). The spiral ends of lead wires were pushed to the electrode in order to increase the contact area between lead and electrode. The Ag, Ag_2S and CaS reference electrodes were used mainly below the eutectic temperature of Ag– Ag_2S . The surface of each electrode was made flat with emery paper to ensure good contact with the electrolyte. These electrodes and electrolyte were pressed by a silica holder and springs, as seen in the figure. In order to separate two electrodes into two

compartments, CaF_2 solid electrolyte was fixed to one end of an alumina tube 12 mm in inner diameter and 100 mm long with heat resistance alumina seal cement.

The cell was placed in a transparent quartz reaction tube 36 mm in diameter and 450 mm long, closed at the bottom and fitted at the top with a vacuum-tight water cooled glass head.

The cell was evacuated to 1 Pa and then heated to 473 K and maintained for a while under vacuum. After the cell temperature was slowly raised to 973 K, purified argon was introduced to reach 10^5 Pa at temperatures 50 K higher than the highest measuring temperatures.

A zirconia crucible containing sponge titanium was placed at the inner bottom of the quartz tube (not shown in the figure) to prevent electrodes and electrolyte from oxidation.

A horizontal Nichrom-wound or SiC resistance furnace was used for the experiments, and pick up of stray currents was avoided by surrounding the quartz tube by a grounded stainless steel tube.

The furnace temperature was held to within ± 1 K using a temperature controller. The emf of the cell was measured using a potentiometer below 973 K, or a digital voltmeter with input impedance higher than $10^9 \Omega$ and reading accuracy of 10^{-4} V.

V. Experimental Results

The variations of observed emf with temperature and the Ni/S ratios of the cell (I) and (II) are shown in Figs. 3 and 4.

If the case of cell (I), the real cell constitutions are expressed as follows, according to the Ni/S ratios and temperatures;

Fig. 2 Cell assembly.

Fig. 3 Temperature dependence of the emfs for the cell (I).

Fig. 4 Temperature dependence of the emfs for the cell (II).

According to Hansen⁽²⁹⁾, the eutectic temperature of Ag–Ag₂S is 1077 ± 2 K. Some of the cells were measured up to temperatures a little higher than this eutectic temperature, but the electrode disk remained solid shape because of the existence of CaS. This phenomenon was also observed in the case of Ni–S electrode of the cell(Ic).

The variation of emf with temperature of the cell(III) is shown in Fig. 5. In this case the real cell constitutions are expressed as follows;

The average standard deviations of emf were 1.5, 1.0 and 1.3 mV for the cell (I), (II) and (III), respectively.

The initial equilibrium emfs of cell(I), (II) and (III) were attained within 4–7, 43–86 and 130 ks, respectively, after reaching a desired temperature. When emf remained steady within ± 0.1 mV for a period of 3.6 ks at a given temperature, it was considered to be equilibrium. A new stable emf was obtained in 3.6–11 ks, after the cell temperature became stable at 1073 K and more at lower temperatures for any cells. The subsequent readings were made with both ascending and descen-

Fig. 5 Temperature dependence of the emfs for the cell (III).

Fig. 6 $\log P_{S_2}$ vs $1/T$ plot for the Ni-S system.
 $P_{S_2} = P(\text{Pa})/1.013 \times 10^5 \text{ Pa}$.

ding temperatures to eliminate systematic errors in emf measurements. In the case of cell(I), the equilibrium emf was obtained so rapidly and so stably that the composition changes of Ni/S in electrodes were considered to be negligible during the emf measurements.

Sulfur pressure of each cell was calculated from emf, temperature and the standard free energy of formation of sulfide for the reference electrode according to eq. (10), as shown in Figs. 6 and 7. As the standard free energy of formations of Ag₂S and CrS, values of Thompson and Flengas⁽³⁰⁾ and the authors⁽³¹⁾ are adopted. Both of them were measured by the

Fig. 7 $\log P_{S_2}$ vs $1/T$ plot for the Co-S system.
 $P_{S_2} = P(\text{Pa})/1.013 \times 10^5 \text{ Pa}$.

electrochemical techniques.

$$\Delta G^0(\text{Ag}_2\text{S}) = -87900 + 37.0 \text{ T J/mol.} \quad (11)$$

$$\Delta G^0(\text{CrS}) = -201200 + 57.20 \text{ T J/mol.} \quad (12)$$

The equations for the lines in Figs. 3-7 were determined as shown in Tables 1, 2 by the least

Table 1 Emf and sulfur pressure of cells (I) and (II).
 $\text{EMF(mV)} = A + B \cdot T \cdot \log T + C \cdot T \quad \log P_{S_2} = D/T + E \cdot \log T + F$

Cell	Phase	Temp.(K)	A	B	C	D	E	F
Ia	Ni + Ni ₃ S _{2-x}	849-920	340.3		-0.1498	-16040		6.89
Ib	Ni + Ni-S(1)	933-1071	593.4	-3.0491	-0.8854	-18620	-13.991	51.32
II	Ni + Ni-S(1)	1033-1372	-224.7	0.4765	-1.4922			
Id	Ni ₃ S _{2+x} + Ni-S(1)	968-1083	11132.4	-28.8722	97.890	215270	582.115	-1969.77
Ih	Ni ₇ S ₆ + NiS _{1+x}	801-840	365.5		-0.4219	-16550		12.38
Ii	Ni ₃ S _{2+x} + NiS _{1+x}	849-1080	403.0		-0.4659	-17300		13.26

Table 2 Emf and sulfur pressure of the cell (III).
 $\text{EMF(mV)} = A + C \cdot T \quad \log P_{S_2} = D/T + F$

Cell	Phase	Temp.(K)	A	C	D	F
IIIa	Co + Co ₉ S ₈	995-1064	9.0	-0.3247	-21200	12.52
IIIb	Co + Co ₄ S _{3-x}	1075-1154	-382.7	0.0414	-13310	5.14
IIIc	Co + Co-S(1)	1161-1322	-503.9	0.1462	-10860	3.03

square or multiple regression method. Both of the measuring points of emfs for the cell (If) and (Ig) were too few to be expressed by precise equations for curved lines. The linear equation of emf for the cell (Ih) was determined by the calculated emf for the cell (Ii) at the decomposition temperature of Ni_7S_6 (845 K) and three measuring emfs of the cell (Ih). The equation of sulfur pressure for the cell (Ib) and (II) could be smoothly combined by one curved line as shown in Table 1 and Fig. 6 in spite of different reference electrodes.

These results are in good agreement with the data of Rosenqvist⁽³²⁾ and Lin *et al.*⁽³³⁾ within the error range of mixed gas equilibrium method, as shown in Figs. 6 and 7. The whole errors of these measurements are within ± 0.1 in $\log P_{\text{S}_2}$, which is quite less than that of mixed gas method.

The isobar lines of P_{S_2} on Ni-S and Co-S phase diagram⁽³³⁾⁽³⁴⁾ are shown in Figs. 8 and 9, respectively. The liquidus and solidus temperatures of $\text{Ni}_3\text{S}_{2+x}$ and the decomposition temperature of stoichiometric Ni_3S_2 were a little higher than those of Elliott's diagram⁽³⁴⁾ and agreed with those by Lin *et al.*⁽³³⁾, as shown in Fig. 8. The existence of β_1 and β_2 phases in non-stoichiometric $\text{Ni}_3\text{S}_{2+x}$ proposed by Lin *et*

Fig. 8 Iso-bar lines of S_2 on phase diagram for Ni-S system. $P_{\text{S}_2} = P(\text{Pa})/1.013 \times 10^5 \text{ Pa}$.

Fig. 9 iso-bar lines of S_2 on phase diagram for Co-S system. $P_{\text{S}_2} = P(\text{Pa})/1.013 \times 10^5 \text{ Pa}$.

al.⁽³³⁾, drawn in dotted lines in Fig. 8 was not obvious by emf technique of this study. Sulfur pressures in the liquid phase are connected smoothly with the results of Nagamori and Ingraham⁽³⁵⁾ and Takewaki *et al.*⁽³⁶⁾, both of which were obtained by $\text{H}_2 + \text{H}_2\text{S}$ mixed gas equilibrium method.

VI. Conclusion

The electromotive force measurements of the following cells were carried out using CaF_2 solid electrolyte:

From the emf and the standard free energy of formation of reference electrode, the sulfur pressure of the system Ni-S in the range of 20–

47 mol% S and 801–1372 K and that of the system Co-S at 35 mol% S and 995–1322 K were calculated. These results are in good agreement with the data of other investigators within the error range of mixed gas equilibrium method.

REFERENCES

- (1) K. Kiukkola and C. Wagner: J. Electrochem. Soc., **104** (1957), 379.
- (2) R. W. Ure, Jr.: J. Chem. Phys., **26** (1957), 1363.
- (3) H. Tanaka, A. Yamaguchi and J. Moriyama: J. Japan Inst. Metals, **35** (1971), 1161 (in Japanese).
- (4) H. Tanaka, Y. Kishida, A. Yamaguchi and J. Moriyama: J. Japan Inst. Metals, **35** (1971) 523, 997 (in Japanese).
- (5) H. Tanaka, Y. Kishida and J. Moriyama: J. Japan Inst. Metals, **37** (1973), 564 (in Japanese).
- (6) H. Tanaka, Y. Kishida, T. Kotani and J. Moriyama: J. Japan Inst. Metals, **37** (1973), 568 (in Japanese).
- (7) K. Koyama and Y. Hashimoto: J. Japan Inst. Metals, **37** (1973), 406 (in Japanese).
- (8) R. Benz: Met. Trans., **5** (1974), 2217.
- (9) W. H. Skelton, N. J. Magnami and J. F. Smith: Met. Trans., **1** (1970), 1833; **2** (1971), 473; **4** (1973), 917.
- (10) Y. D. Tretyakov and A. R. Kaul: *Physics of Electrolytes*, Ed by J. Hladik, Academic Press, vol. 2 (1972), p. 623.
- (11) W. L. Worrell and T. A. Ramanarayanan: *Proc. Int. Conf. Advances in Chemical Metallurgy*, vol. 2 (1979), p. 1.
- (12) H. R. Larson and J. F. Elliott: Trans. Met. Soc. AIME, **239** (1967) 1713.
- (13) L. I. Armyanova and S. I. Filippov: Izv. Vuzov. Cher. Met., No. 9 (1972), 8.
- (14) K. Sadakane, M. Kawakami and K. S. Goto: Tetsu to Hagané, **63** (1977), 44.
- (15) K. Nagata and K. S. Goto: Met. Trans., **5** (1974), 899.
- (16) A. Egami, T. Onoye and K. Narita: Solid State Ionics, **3/4** (1981), 617.
- (17) L. Gu and Z. Tang: Iron and Steel China, **19** No. 5 (1984), 13.
- (18) K. Ono, T. Oishi and J. Moriyama: J. Japan Inst. Metals, **45** (1981), 1022 (in Japanese).
- (19) S. Aronson: J. Inorg. Nucl. Chem., **29** (1967), 1611.
- (20) J. Moriyama, T. Oishi, K. Ogino and A. Egami: *Thermal Analysis* (Proc. IVth ICTA Budapest 1974), vol. 3, p. 867.
- (21) T. Oishi, T. Fujimura, K. Ogura and J. Moriyama: J. Japan Inst. Metals **40** (1976), 969 (in Japanese).
- (22) K. T. Jacob, D. B. Rao and H. G. Nelson: J. Electrochem. Soc., **125** (1975), 758.
- (23) E. Zintl and A. Udgard: Z. Anorg. Allg. Chem., **240** (1939), 150.
- (24) J. W. Hinze and J. W. Patterson: J. Electrochem. Soc., **120** (1973), 96.
- (25) T. Ono, T. Fujimura and J. Moriyama: J. Japan Inst. Metals, **42** (1978), 469 (in Japanese), Trans. JIM, **20** (1979), 543.
- (26) R. W. Heus and J. J. Egan: Z. Phys. Chem., **21** (1933), 25.
- (27) J. W. Patterson: J. Electrochem. Soc., **118** (1971), 1033.
- (28) C. Wagner: Z. Phys. Chem., **21** (1933), 25.
- (29) M. Hansen and K. Anderko: *Constitution of Binary Alloys*, 2nd ed., McGraw-Hill, New York, (1958), p. 1034.
- (30) W. T. Thompson and S. N. Flengas: J. Electrochem. Soc., **118** (1971), 419.
- (31) J. Moriyama, T. Oishi, K. Ogura and T. Nagakawa: Abs. Vth Int. Conf. Chem. Thermody., Ronneby (1977), p. 84.
- (32) T. Rosenqvist: J. Iron Steel Inst., **176** (1954), 37.
- (33) R. Y. Lin, D. C. Hu and Y. A. Chang: Met. Trans., **9B** (1978), 531.
- (34) R. P. Elliott: *Constitution of Binary Alloys*, 1st Supplement, McGraw-Hill, New York, (1965), p. 668.
- (35) M. Nagamori and T. R. Ingraham: Met. Trans., **1** (1970), 1821.
- (36) M. Takewaki, T. Azakami and M. Kameda: Senken Ihou, Tohoku Univ., **28** (1972), 114.